MONTANA STATE UNIVERSITY

Preparation and reactions of platina(IV) cyclobutanes and the first platinum(IV)-bound olefin from bicyclo[n.1.0]hydrocarbons

by Edith Jane Parsons

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

Montana State University

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Abstract:
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The platinacyclobutane from bicyclononene formed as a dimeric platinum(II)-platinum(IV) species wherein the platinum(IV) was incorporated into a 2,4-disubstituted platinacyclobutane. This complex also contained the first reported platinum (IV)-olefin bond and was characterized by X-ray crystallography. The reactivity of the complex was dominated by reductive elimination of the original cyclopropane, although the nucleophiles H- and EtO- were induced to attack the platinum (IV)-bound olefin.

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A thesis submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

December 1986

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Edith Jane Parsons

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ABSTRACT

Platina(IV)cyclobutanes were prepared by the reaction of platinum(II) in the form of Zeise's dimer with bicyclo-[4.1.0]heptane, bicyclo[6.1.0]nonane, and bicyclo[6.1.0]non-4-ene. The bicycloalkanes formed insoluble polymeric platinacyclobutanes which were solubilized upon conversion to monomeric species with pyridine or bipyridine ligands. The bicycloheptane complex was much less stable than the corresponding bicyclononane complex. Reaction of these platinacyclobutanes with soft ligands KCN, $P\phi_3$, DMSO, and THF reproduced the original cyclopropanes or yielded olefinic products. The platinacycles also rearranged thermally to one or more olefinic compounds.

The platinacyclobutane from bicyclononene formed as a dimeric platinum(II)-platinum(IV) species wherein the platinum(IV) was incorporated into a 2,4-disubstituted platinacyclobutane. This complex also contained the first reported platinum(IV)-olefin bond and was characterized by X-ray crystallography. The reactivity of the complex was dominated by reductive elimination of the original cyclopropane, although the nucleophiles H^- and EtO^- were induced to attack the platinum(IV)-bound olefin.

INTRODUCTION

Platinum(II)-Olefin Complexes

The first metal π-complex to be recognized was Zeise's salt, $K[C_2H_4PtCl_3]:H_2O$[1]. This complex was made by W.C. Zeise and was published (in Latin) in 1830. Since then, a tremendous variety of olefin complexes of Pt(II) have been prepared and identified.

Mono-olefin complexes of Pt(II) can be separated into two main classes. The first group is comprised of four general forms[2], where X can be a halogen, an alkoxide, or a hydride and L is a neutral ligand:

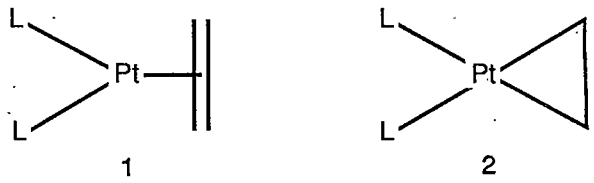
a) Dimeric, bridged complexes $[Pt(olefin)X_2]_2$;

b) Salts of an olefin-containing anion $M^+[Pt(olefin)X_3]^-$

c) Salts of an olefin-containing cation $[Pt(olefin)XL_2]^+A^-$

d) Neutral mononuclear complexes, $[Pt(olefin)X_2L]$, where L can be an olefin $[Pt(olefin)_2X_2]$.

The second class, illustrated by complexes 1 and 2, may be regarded as Pt(0) or as Pt(II). In the latter case, the Pt(II) and olefin carbons are connected by σ bonds and form a platinacyclopropane ring. The two possibilities represent bonding extremes.

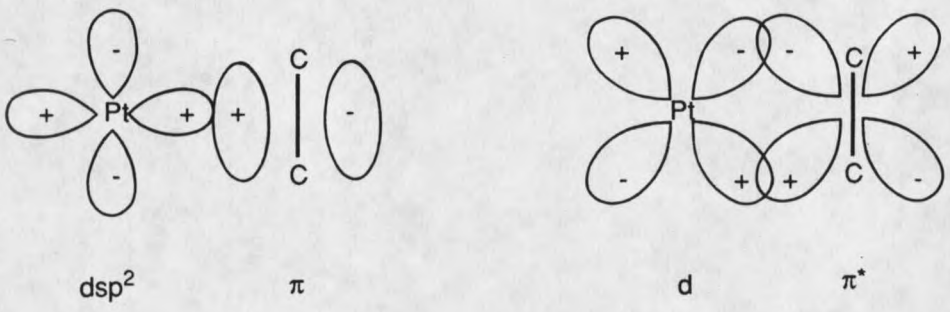


1 2

Bonding between Pt(II) and an olefin consists of one σ- and one π-bond. The σ-bond is formed when the olefin's filled π-orbital donates electron density to an empty dsp^2 orbital on the platinum. The π bond then results from back donation of electron density from a filled platinum d orbital to the vacant olefin π* orbital[3]. As shown in Figure 1, these bonds act synergistically. A platinacyclopropane ring is formed when back bonding from the platinum to the olefin becomes greatly enhanced.

X-ray analyses of Zeise's salt[4] and other Pt-olefin complexes[5] have shown that platinum and its non-olefin ligands define a plane coincident with the platinum dsp^2 plane. The olefin lies perpendicular to this plane, as shown in Figure 2. The olefinic hydrogen atoms probably form a plane which is displaced slightly from co-planarity with the carbon atoms but is parallel to the ClZCl plane. The carbon-carbon bond length in the olefin is about 1.4 Å[6], which is slightly elongated from that of uncomplexed olefins (≈1.3 Å).

Figure 1. Bonding Between Platinum(II) and an Olefin.



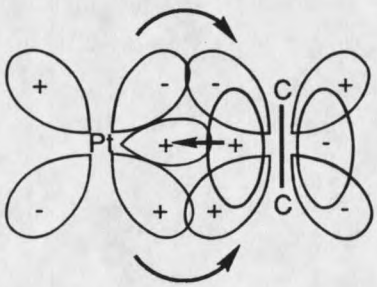
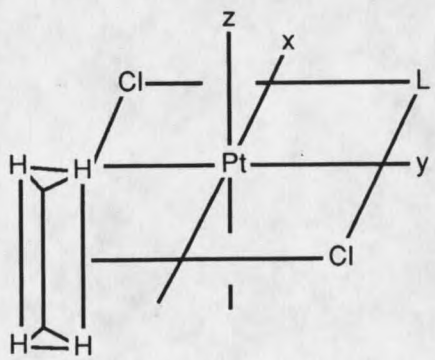


Figure 2. Situation of a Platinum-Bound Olefin with Respect to the Ligand Plane.



I

Infrared and Raman spectroscopies provide a useful qualitative picture of Pt-olefin π-bonding[7-9]. Generally, the C-C stretching frequency moves to lower wave numbers with increasing Metal-olefin bond strength. Some examples are shown in Table 1. As a quantitative tool for determining Pt-olefin bond strength, however, this frequency must be used with caution. The C-C stretching frequency can couple with other modes to lead to complex results. A better diagnostic tool for bond strength is the Pt-olefin stretching frequency. This vibration normally comes between 410 and 380 cm^{-1}, as illustrated in Table 2.

Table 1. Representative Platinum(II)-Olefin Infrared Carbon-Carbon Stretching Frequencies.

	cm^{-1}
$H_2C=CHCH_2$	1647
$H_2C=CH_2$ (gas)	1623 (Raman)
$[Pt(C_2H_4)Cl_2]_2$	1506
$[Pt(C_3H_6)Cl_2]_2$	1504
$K_2[Pt(C_4H_6)Cl_3]_2$	1413
$K[Pt(C_2H_4)Cl_3]$	1516
$t-[Pt(C_2H_4)(NH_3)Cl_2]$	1521
$t-[Pt(C_2H_4)(NH_3)Br_2]$	1517
$K[Pt(C_3H_6)Cl_3]H_2O$	1504

Table 2. Representative Platinum(II)-Olefin Infrared Metal-Carbon Stretching Frequencies.

	cm^{-1}
$K[Pt(C_2H_4)Cl_3]H_2O$	407
$K[Pt(C_2H_4)Br_3]H_2O$	395
$K[Pt(C_3H_6)Cl_3]$	393
$K[Pt(t\text{-}C_4H_8)Cl_3]$	387
$K[Pt(c\text{-}C_4H_8)Cl_3]$	405
$t\text{-}[Pt(C_2H_4)(NH_3)Cl_2]$	383

Platinum is particularly useful as an NMR marker. Its 195 isotope (33.8% natural abundance) is NMR active with spin ½ and receptivity 19.1 (relative to carbon). This allows platinum coupling to the ^1H and ^{13}C nuclei to be observed[10]. By ^{13}C NMR spectroscopy, Pt-bound olefinic carbons always appear upfield relative to the free olefins. Resonances have been reported from δ7 to δ130, as listed in Table 3, with <u>trans</u>-$Pt(C_2H_4)pyCl_2$ appearing at about midrange[11].

Table 3. Range of Platinum(II)-Olefin ^{13}C NMR Resonances.

		ppm
$Pt(C^1H_2{=}C^2HCN)Me(HBpz_3)$	C^2	= 7.4
$Pt(t\text{-}NCCH{=}CHCN)Me(HBpz_3)$	C_{olef}	= 7.8
$[Pt(cod)(C_8H_{13})]^+$	C_{olef}	= 126.9
$t\text{-}Pt(C_2H_4)pyCl_2$	C_{olef}	= 75.0

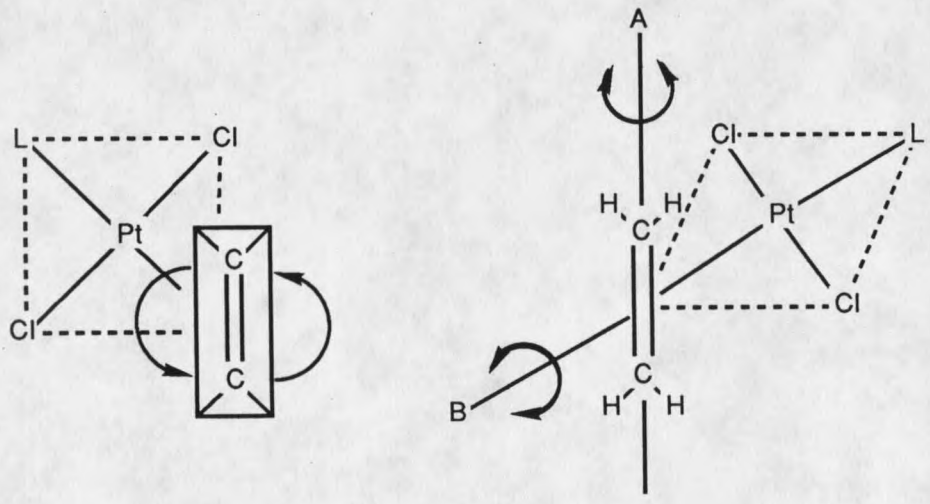
Although $^{1}J_{Pt,C}$ depends mainly on carbon hybridization, Pregosin has observed that platinum coupling to the directly bound olefinic carbons indicates the strength of the platinum-olefin bond[12]. This coupling ranges from 40 to 400 Hz, and generally decreases with increasing <u>trans influence</u> in the ligand <u>trans</u> to the olefin. However, olefin geometry, at least for non-strained olefins, does not appear to affect the constant.

Proton NMR shifts are dependent on complicated shielding effects, making it difficult to predict changes upon binding to the platinum. Generally platinum is thought to shield the protons. However, ligand effects and various other incompletely characterized effects may move the resonance downfield. Platinum bonding to other remote functionality in the olefinic molecule may also result in a change in the chemical shift of the olefinic protons.

Platinum to olefinic proton couplings in the range of 10 to 83 Hz have been observed, however this coupling is not always indicative of bond strength. Often, Pt-H coupling is not observed at all; instead broad olefinic resonances are obtained. This may be due to the platinum-bound olefin exchanging with free olefin in the solution. In most cases the exchange is very rapid, but can be halted at low temperatures. Alternately, broadening may be the result of a propeller-like rotation of the coordinated olefin, shown in Figure 3. This internal, hindered rotation ranges from 10-20

kcal/mole and increases with decreasing platinum-olefin bond strength and lower steric hinderance. In a non-symmetrical complex the motion makes the protons equivalent, but can be halted at low temperatures. Rotation about axis A also appears to occur, but does not affect the solution NMR spectrum[13].

Figure 3. Rotation of a Platinum Coordinated Olefin.



Nucleophilic Attack on Pt(II)-Olefin Complexes

Platinum(II) bound olefins are known to undergo nucleophilic attack[14-25]. The two mechanisms illustrated in Figure 4 have been postulated for this attack. The olefin and nucleophile may both coordinate to platinum, followed by

cis attack of the nucleophile on the olefin. Alternatively, the olefin may bond to the platinum followed by external nucleophilic attack, or trans-addition. In either case, the olefin is probably activated by a slippage of the platinum[26], as shown in Figure 5.

Figure 4. Mechanisms for Nucleophilic Attack on Platinum(II) Bound Olefins.

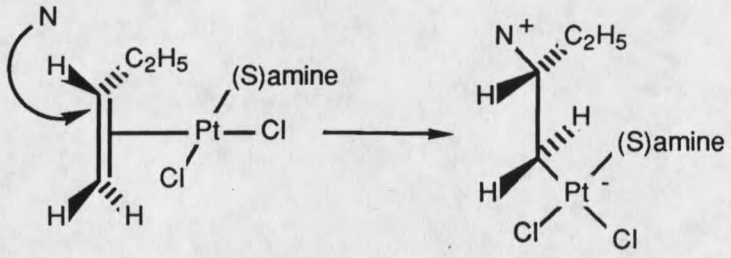


Figure 5. Activation of Platinum(II)-Olefins.



Monoolefins bound to other platinum-group metals appear to react via prior nucleophile coordination and cis-attack. However, in 1970, Panunzi[14] reported a stereochemical study of amine attack on (+)-cis-dichloro[(S)-1-butene][(S)-α-methylbenzylamine] platinum(II). The results, shown in Figure 6, clearly demonstrated that the nucleophile did not coordinate to the platinum. In other studies involving Pt(II)-monoolefin complexes, no attempt was made to determine stereochemistry[15-18].

Figure 6. Stereochemistry of Amine Attack on a Platinum(II)-Olefin.



A variety of platinum-bound monoolefins undergo nucleophilic attack. These include ethylene, propene, 1-butene, cis-2-butene, 3-methyl-1-butene, cyanoethylene, methylvinylester, and styrene. Reaction completeness depends on the olefin's steric bulk, but not on electronic factors. Electron withdrawing groups do cause anti-Markovnikoff addition, however. For instance, when pyridine is the attacking amine, propene yields 90% of the Markovnikoff product (pyridine added to the substituted carbon), while cyanoethylene produces 95% of the anti-Markovnikoff product.

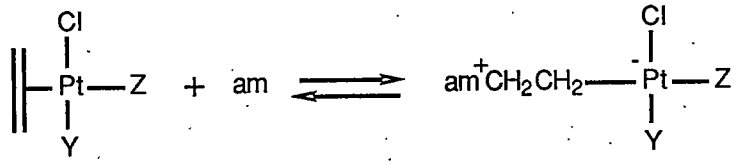
Platinum-diene complexes, typically involving norbornadiene, 1,5-cyclooctadiene, dicyclopentadiene, and dipentene, have been more extensively studied. These complexes usually undergo trans attack[27], and yield isolatable products.

Steric factors, and to a lesser degree, nucleophile basicities determine whether a platinum bound olefin will be attacked. Soft nucleophiles, such as phosphines, dimethylsulfoxide, dimethylsulfide, and pyridine N-oxide,

preferentially coordinate to platinum. Amines, alkoxides, and a thio compound have been successfully added to the olefin. Of the amines studied[14-17,19], 1° and 2° amines possessing high basicity and low steric hinderance add directly to the olefin. Pyridines add to either the platinum or the olefin, and all other amines attack the platinum, or fail to react.

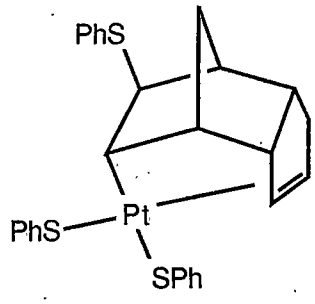
Most of the amine complexes were studied by low temperature NMR spectroscopy. However, stable complexes represented in Figure 7, were isolated when Y-Z = acac, am = morph and when Y = Cl, Z = am = morph, 4-NMe_2py, NH_2Pr^i, or NH_2Bu^t. Compounds containing two different amines were observed only for Z = py, and am = morph or NH_2Bu^t.

Figure 7. Reaction of Amines with Platinum-Ethylene.



Many complexes resulting from alkoxide attack have been reported[19-25]. The alkoxide ion could be generated by adding base to an alcohol, however ethanol also displaced methoxide from a complex when a small amount of acid was present[21]. Boiling the complexes in concentrated HCl regenerated the Pt-bound olefin[22].

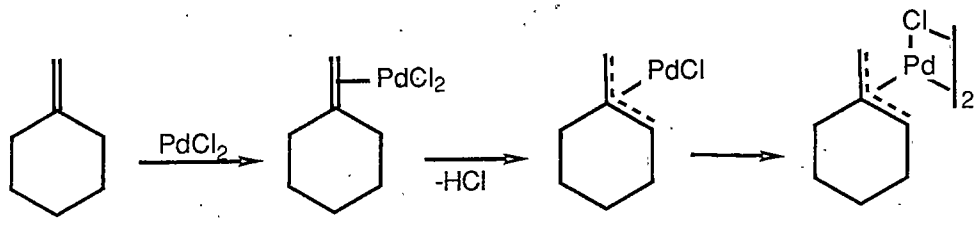
Only one thio nucleophile, thiophenol, was reported to attack a platinum bound olefin[19], resulting in compound 3.



3

π-Allyl Formation From Pt(II)-Olefin Complexes

Insight into the mechanism of π-allyl formation from platinum bound olefins may be obtained by examining an analagous reaction with palladium[28] (equation 1). Insertion of the palladium into the allylic C-H bond can occur by one of three mechanisms shown in Figure 8. Each pathway involves a different non-linear transition state, and so can be differentiated by the magnitude of the hydrogen isotope effect[29]. Hydrogen removal was found to occur by external or



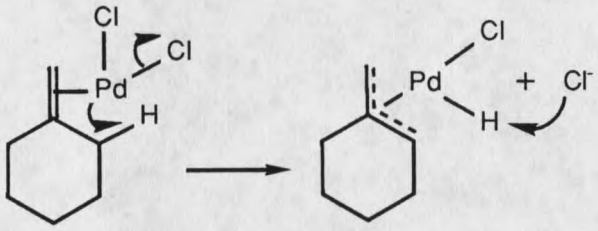
(1)

complexed base attack (paths (b) or (c)), and not, as was previously supposed, by palladium insertion.

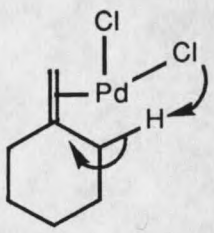
Similarly, in platinum insertions into the C-H bond of an alkane, three transition states are possible, and are depicted in Figure 9. A kinetic study by Rudakov showed that platinum(II) probably attacks the C-H bond by an inner

Figure 8. Mechanism for Palladium Insertion into an Allylic Carbon-Hydrogen Bond.

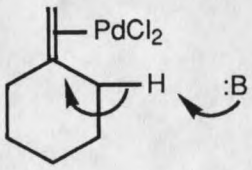
a) Pd insertion into C-H bond



b) Cl removal of H^+

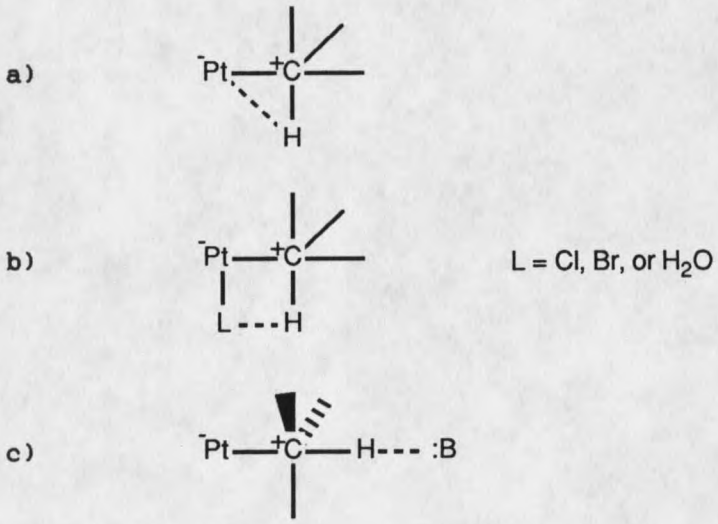


c) External base removal of H^+



sphere mechanism (paths (a) or (b))[30]. In the same reaction, palladium was found to proceed via an outer-sphere attack (path (c)).

Figure 9. Possible Transition States in Platinum Insertion into an Alkane Carbon-Hydrogen Bond.



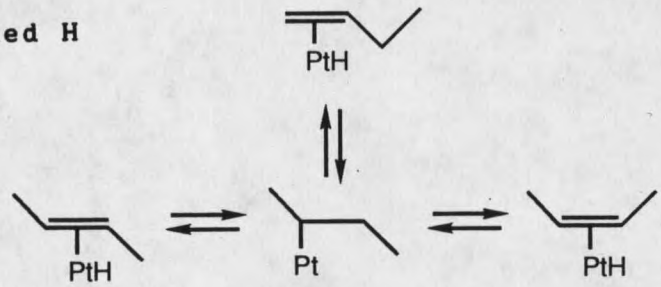
Platinum Catalyzed Rearrangement of Olefins

Olefin isomerization is heterogeneously catalyzed by platinum metal[31], and by platinum supported on carbon, silica, or alumina[32,33]. Homogenous platinum catalysts, however, are generally inferior to other transition metal catalysts[34]. Most platinum catalysts include another metal, usually tin, as a cocatalyst[35,36]. Sodium tetrachloroplatinate[37], platinum(II)-olefins[38-41], π-allyl complexes[42], and certain preformed platinum(II) hydrides[43] are also known to isomerize double bonds.

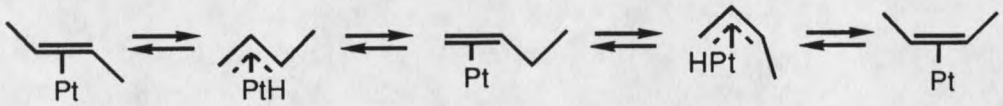
Some species require the addition of a hydrogen source, while others react autocatalytically. These mechanisms are shown in Figure 10[31]. In (a) H^+ is added to the platinum to form a platinum-hydride. This then transfers the hydride to the olefin, forming an alkyl complex. Abstraction of hydrogen from a different beta carbon leads to isomerization. In pathway (b), the platinum abstracts a hydrogen from the olefin, producing a π-allyl complex. Returning the hydrogen to a different carbon results in isomerization.

Figure 10. Platinum Catalyzed Olefin Isomerization Mechanisms.

a) added H



b) autocatalytic



Several platinum hydride generating reactions are possible[39], and are depicted in Figure 11. These are initiation reactions only; the hydride is regenerated from the solvent or olefin. Sodium tetrachloroplatinate(II) appears to abstract a hydrogen from the olefin[37], and the π-allyl

Figure 11. Possible Platinum Hydride-Generating Reactions and Their Analogues.

a) Oxidation of a carbon compound

$$CH_3CH_2OH + OH^- + ClPt(II) \rightarrow CH_3CHO + HPt(II) + Cl^- + H_2O$$

b) H_2 disproportionation

$$H_2 + ClPt(II) \rightarrow HPt(II) + Cl^- + H^+$$

c) Platinum oxidized by H_2

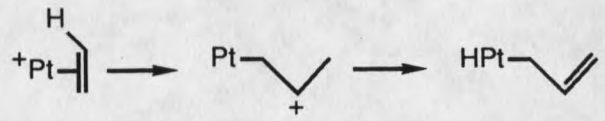
$$H_2 + Pt(II) \rightarrow H_2Pt(IV)$$

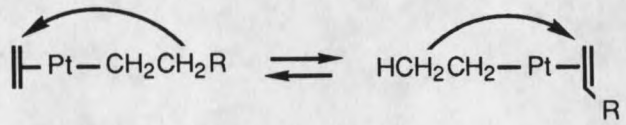
d) Platinum oxidized by H^+

$$HCl + Pt(II) \rightarrow HPt(IV)Cl$$

e) Displacement of H from an olefin







complexes also react by intramolecular hydrogen abstraction[42]. These are analogous to initiation by reaction (e). When Zeise's dimer is the catalyst, alcohols, acid, and H_2 are effective hydrogen sources, but water and base are not. Hydrogen probably reacts by initiation reaction (b) or (c), while acid initiation proceeds by reaction (d).

The rate of isomerization by any process depends on the source of the hydride and the olefin exchange rate. With Zeise's dimer, the rate decreases such that H_2 > EtOH > Pr^iOH > Bu^tOH ≈ CH_3CO_2H[38,39]. If exchange is faster than isomerization, the products will be formed in a stepwise manner, with the initial ratio favoring the more stable olefin complex[38].

Platinum(IV)-Olefin Complexes

No Pt(IV)-olefin complexes were reported, as of 1985[44,45].

Bridged, Binuclear Platinum Complexes

Bridged diplatinum complexes having both platinums in the same oxidation state are known for states I, II, III, and IV[24,25,44,46-48]. Mixed-valence bridged complexes of platinum are also well known, however most of these exist as extended linear chains[49,50].

Of the molecular species known, two are Pt(0)-Pt(II) complexes[51], and are displayed in Figure 12. Binuclear Pt(II)-Pt(IV) complexes are also relatively rare[52,53], but are represented by those shown in Figure 13. Of these, complex 4 was the first reported neutral Pt(II)-Pt(IV) bridged dimer.

Platinum Carbonyl Complexes

While platinum(IV) carbonyls are relatively rare, the addition of carbon monoxide to platinum(II) to form monomeric complexes proceeds readily[54]. Several addition routes are available. For example, a chlorine ligand can be replaced with carbon monoxide, providing a counterion is supplied (equation 2). Carbon monoxide can also cleave a halogen-bridged complex (equation 3), or displace an olefin (equation 4).

$$L_2PtCl_2 + CO + NaClO_4 \rightarrow [L_2Pt(CO)Cl]+ClO_4^- + NaCl \quad (2)$$

$$[L_2PtCl]_2 + CO \rightarrow L_2Pt(CO)Cl \quad (3)$$

$$[Pt(C_2H_4)LCl_2] + CO \rightarrow [Pt(CO)LCl_2] + CH_2=CH_2 \quad (4)$$

Figure 12. Binuclear Platinum(0)-Platinum(II) Complexes.

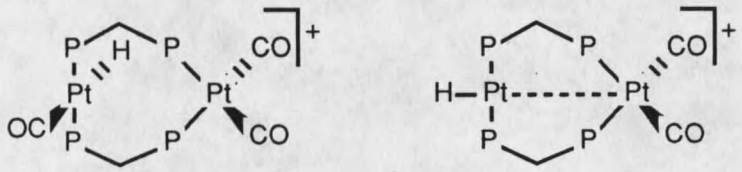
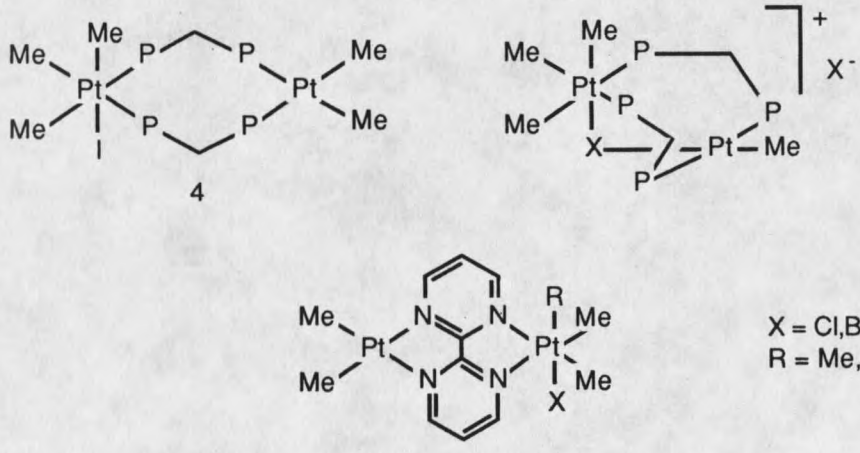


Figure 13. Binuclear Platinum(II)-Platinum(IV) Complexes.



Carbon NMR spectroscopy is a convenient technique for detecting platinum carbonyls, although no good empirical rules exist for predicting the carbon shift. Ligands opposite the carbonyl influence the platinum-carbon coupling constant such that $^{1}J_{Pt,C}$ ranges from 960-999 Hz for ligands of high <u>trans</u>-influence and 1658-1817 Hz for ligands of low <u>trans</u>-influence.

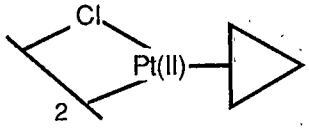
Platina(IV)cyclobutane Complexes

Platinacyclobutane Structure and Bonding

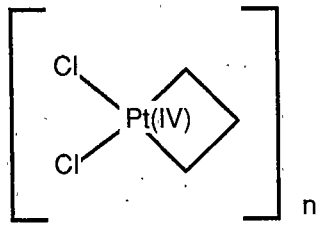
In this thesis, platinacyclobutane means platina(IV)-cyclobutane.

In 1949, Walsh[55] suggested that cyclopropane was more analagous to olefins than it was to alkanes, with carbon hybridizations of approximately sp^2 and orbitals as shown in Figure 14.

This prompted Tipper[56], in 1955, to attempt formation of platinum cyclopropane complexes analagous to platinum olefin complexes. He succeeded in forming a complex containing platinum and cyclopropane, but believed it was complex 5: a platinum(II) with the cyclopropane edge-bound, as an olefin would be. It was later shown that the cyclopropane had opened and chelated to platinum in the +4 oxidation state[57,58]. The complex was further determined to be the polymer 6 because of its general insolubility.

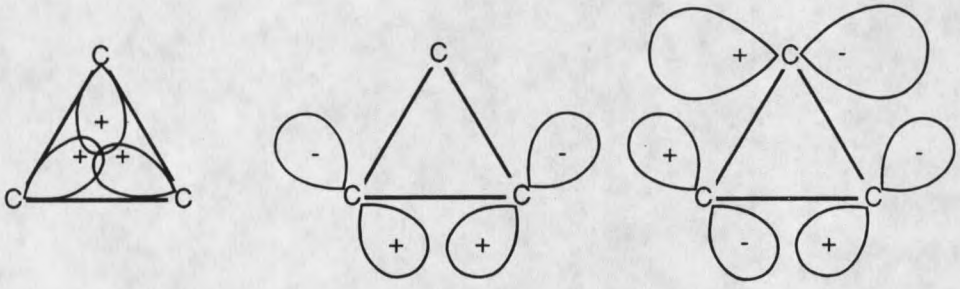


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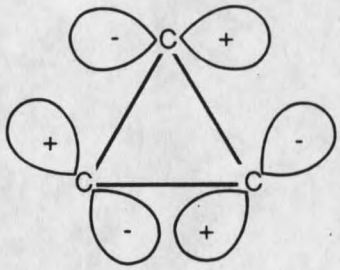


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Figure 14. Walsh Cyclopropane Orbitals.

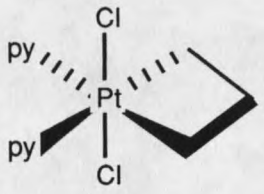


bonding, filled



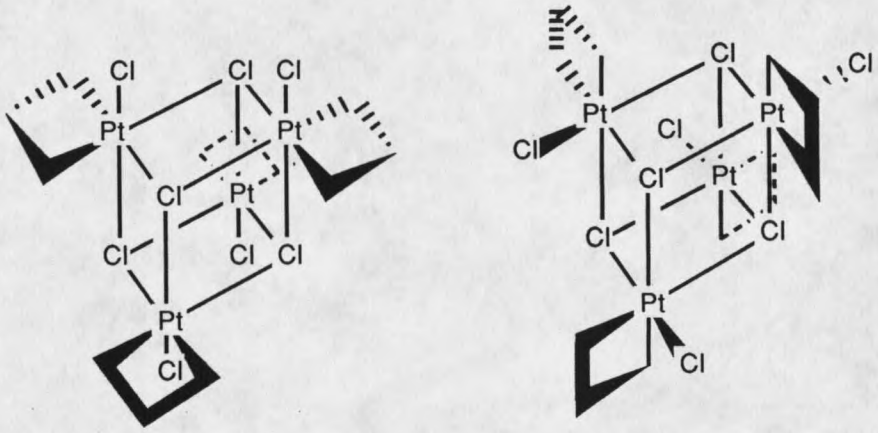
antibonding, empty

Reaction of the diamagnetic polymer with neutral ligands produced only one compound, which suggested that all the platinum atoms in the polymer were equivalent and 6-coordinate[59]. X-ray powder diffraction studies showed the solid was ordered, while MS and molecular weight determinations indicated it was a tetramer. Based on this evidence, two possible structures were proposed and are shown in Figure 15. Although complex 7 has D_{2d} symmetry, while the other structure has S_4 symmetry, it was difficult to distinguish between these possibilities. Reaction of the tetramer with 1,4-dioxane probably produced a dioxane bridged dimer, however. Presuming the dioxane attacked <u>trans</u> to the methylene groups, the tetramer with S_4 symmetry could not form a dimer. This suggested that 7 was the correct structure. After reacting the tetramer, the resulting monomers had the structure shown by compound 8[57,60,61]. This was confirmed by IR, NMR, and X-ray crystallography.



8

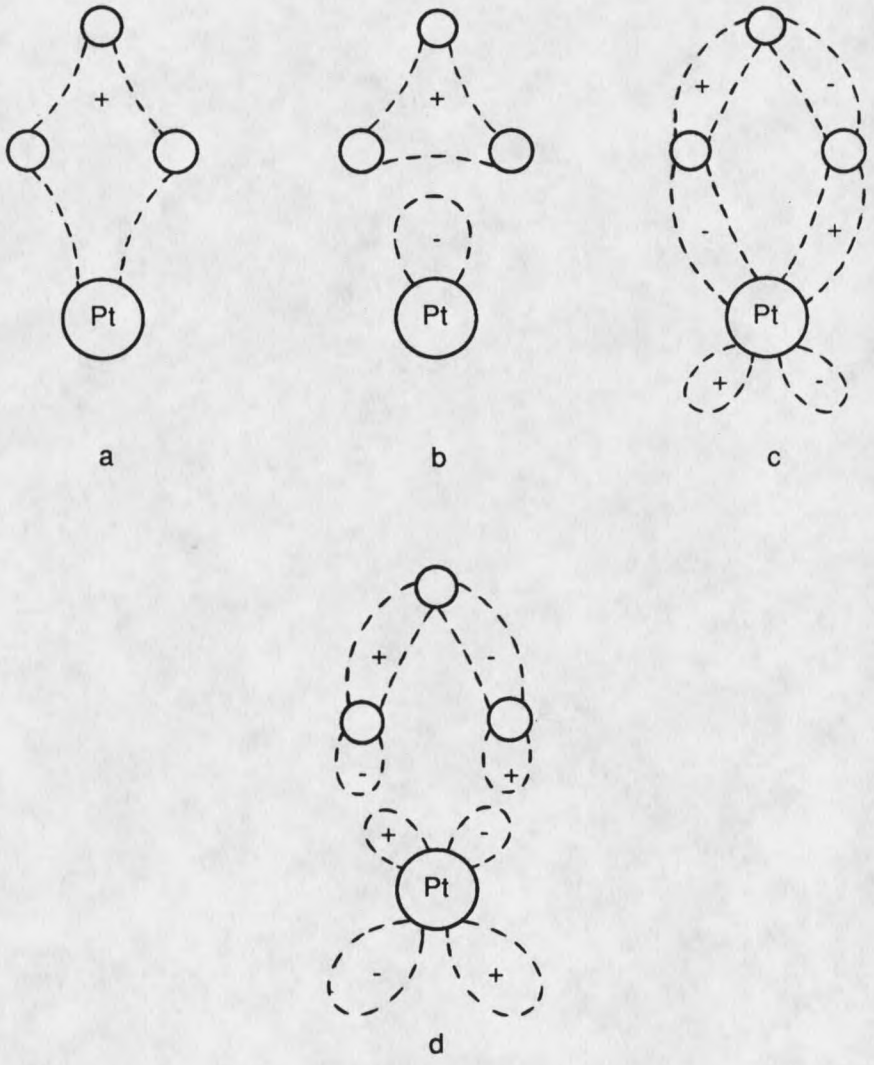
Figure 15. Proposed Tetrameric Platinacyclobutane Structures.



7

The bonding scheme in platinacyclobutanes is far from certain. One approach, proposed by McGinnety[60], consists of the linear combination of Walsh cyclopropane orbitals with dsp^3 and d orbitals on the platinum, and is illustrated in Figure 16. There are eight bonding electrons filling these orbitals. Orbitals (a) and (b) are comprised of the σ-orbitals on cyclopropane and platinum dsp^3 orbitals, while (c) and (d) are constructed from cyclopropane p-orbitals and the metal d-orbital. This clearly shows the possibility of bent bonds in platinacyclobutanes, but is otherwise not useful, as no net bonding interaction between the platinum and the cyclopropane is pictured.

Figure 16. McGinnety Platinacyclobutane Orbitals.



Analysis of Platinacyclobutanes

Several X-ray crystal structures of platinacyclobutanes have been reported. The first was of $Pt(C_3H_6)Cl_2py_2$ and appeared in 1971[61]. Unfortunately, the data set for this structure was of limited accuracy. McGinnety[60] then analyzed trans-$Pt(CH\phi CH\phi CH_2)Cl_2py_2$ and found the C-C bond distances to be elongated, with no bond existing between the two chelating carbons. Furthermore, the platinacyclobutane ring was not planar. This puckering was observed in other platinacyclobutanes as well, and ranged from 0-30°. It appeared to increase as the ring became more substituted[62,63]. The pucker may be due to crystal packing effects, and probably differs in solution.

The C_3H_6 unit of the platinacyclobutane can be identified by IR. This is illustrated for two simple complexes in Table 4. The local symmetry of cyclopropane is not retained, which also clearly shows that the ring has opened[57].

As with platinum-olefins, the ^1H NMR spectra of platinacyclobutanes can be difficult to interpret. Coupling between the platinum and protons ranges from 70-110 Hz for $^2J_{Pt,H}$, 0-50 Hz for $^3J_{Pt,H}$, and 0-10 Hz for $^4J_{Pt,H}$[64-67]. In complicated molecules, these couplings may be obscured.

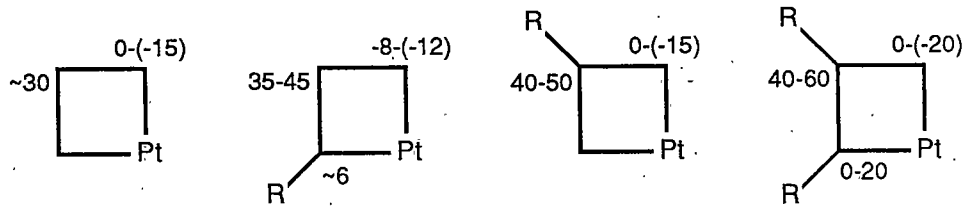
Conversely, carbon-13 NMR spectroscopy is a very useful tool for the identification of platinacyclobutanes[68,69]. The monomeric complexes exhibit distinctive resonances for

Table 4. Infrared Bands of Cyclopropane and its Platinacyclobutanes.

bands due to the C_3H_6 unit	$[Pt(C_3H_6)Cl_2]_4$	$Pt(C_3H_6)Cl_2py_2$	C_3H_6
C-H	3025	2992	3103
	2954	2938	
	2948	2917	
CH_2 deformation	1414	1437	1442
CH_2 wag	1255	1238	
	1237		
CH_2 twist	1165	1217	
ring deformation	1149	1134	
	1125	1087	
CH_2 rock	1087	1038	1029
	1022		
ring deformation	981	980	
CH_2 rock	948	976	869
	890	892	
	663		
ring deformation (mainly Pt-C)	563		

the platinacyclobutane carbons. These appear in the approximate ranges shown in Figure 17. In the solid state these resonances appear as broad lines, while in solution the lines are sharp and exhibit platinum coupling.

Figure 17. Platinacyclobutane ^{13}C NMR Reasonance Ranges With all Values in ppm.



Solid State ^{13}C NMR spectra of the tetrameric IPCs also exhibit broad lines. The resonances for the carbons bound to platinum are shifted downfield with respect to the monomers. This is probably due to the greater <u>trans influence</u> of chlorines which are <u>trans</u> to the platinum bound carbons in the tetramer.

Within the platinacyclobutane, platinum-carbon coupling has been reported in the ranges $^{1}J_{Pt,C}$ 335-460 Hz and $^{2}J_{Pt,C}$ 80-130Hz. Coupling to substituent carbons is approximately $^{2}J_{Pt,C}$ 0-25 Hz and $^{3}J_{Pt,C}$ 20-65 Hz[64,65,69-71].

A Karplus type relationship was determined for pyridine complexes of substituted platinacyclobutanes, in which the alkane fragment was held rigid[63]. Dihedral angles were determined from X-ray crystallographic studies, and $^{3}J_{Pt,C}$

constants were obtained by ^{13}C NMR spectroscopy. When no additive coupling contributions were included, the equation $^{3}J_{Pt,C} = 15.7 - 6.8\cos\phi + 16.1\cos 2\phi$ (ϕ = dihedral angle) was obtained. Including additive coupling contributions led to $^{3}J_{Pt,C} = 15.4 - 5.8\cos\phi + 17.0\cos 2\phi$. This relationship was developed without consideration of the Puddephatt rearrangement or ligand effects, however, and consequently fails to model a number of complexes.

Platinum-195 spectroscopy can be a useful technique in identifying platinacyclobutanes. Platinum-195 is an NMR active isotope, and so can be directly observed. Platinum shifts cover a range of approximately 13000 ppm[72], with platinum(II) complexes appearing at higher field than platinum(IV) complexes. Changing solvent generally results in a large shift in the platinum resonance of a compound, while temperature causes about a 0.1 ppm/°K shift. A variation in ligand can effect a major shift. Generally, as one moves down a group, there is an upfield shift. The group N, P, As, and Sb is an exception to this rule. Changing remote substituents has a relatively small effect on the chemical shift, providing there is no major change in steric bulk. For example, analogous compounds having different phosphine ligands, PR_3, where R = Me, Et, Pr^n, or Ph, have similar chemical shifts.

The usual standard against which platinum shifts are measured is $[PtCl_6]^{2-}$, however this is not a very good

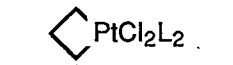
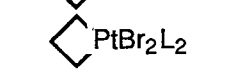
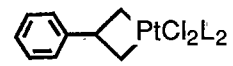
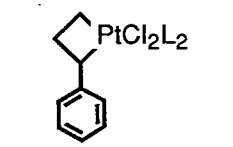
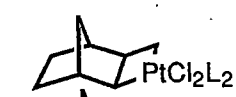
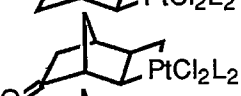
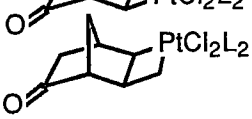
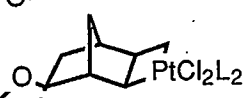
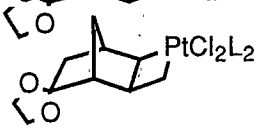
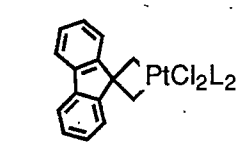
standard[10]. Its chemical shift exhibits high temperature and solvent dependence, and it decomposes with time. Also, nearly all other compounds' shifts are negative relative to it. Sodium tetracyanoplatinate(II) has been used as a standard, and is less sensitive to solvent and temperature[73]. Sodium tetracyanoplatinate(II) also appears at higher field than most other platinum complexes.

Platinacyclobutanes possessing two chloride ligands and neutral ligands of the type bipy, py, or THF, resonate between about δ3000 and δ3600. Several examples are displayed in Table 5. Olefin complexes of the same type appear between δ1700 to δ2500. This, then can provide a useful indication of platinacyclobutane formation.

Formation of Platinacyclobutanes

The first reported platinacyclobutane was made from cyclopropane and chloroplatinic acid in acetic anhydride[56]. This method failed with substituted cyclopropanes, however. The now-generally used method involves addition of the cyclopropane to a solution containing Zeise's dimer[74]. Several different solvents have been tried, although diethylether is the most popular. Instead of displacing ethylene from platinum, a cyclopropane can also exchange with a different platinum-bound cyclopropane[75]. Another method suggested to form platinacyclobutanes is the addition of 1,3-di-Grignards to platinum[76,77].

Table 5. ^{195}Pt NMR Resonances of Monomeric Platinacyclobutanes, With Respct to 1.0M $Na_2Pt(CN)_4$ in D_2O.

	L	solvent	shift (ppm)
	py	$CDCl_3$	3317, 3126
	py	$CDCl_3$	2611
	THF	THF	3387
	py	$CDCl_3$	3308
	THF	THF	3591
	py	$CDCl_3$	3417
	THF	THF	3365
	THF	THF	3278
	py	$CDCl_3$	3350
	py	$CDCl_3$	3368
	py	$CDCl_3$	3390
	py	$CDCl_3$	3333
	py	$CDCl_3$	3322
	py	$CDCl_3$	3350

Not all cyclopropanes react with platinum(II) to form platinacyclobutanes. Those which do include simple cyclopropanes having up to three aryl or alkyl substituents, and are listed in Table 6. If the cyclopropane bears two substituents, they are either geminal or trans to each. A tri-substituted cyclopropane, 1,1,2-trimethylcyclopropane, has also been reported to form a stable platinacyclobutane.

As of 1972, cis-1,2-dialkylcyclopropanes were thought not to form platinacyclobutanes. For example, McQuillin[66] reported that norcarane reacted with Zeise's dimer to yield two π-allyl complexes (inferred only), which then decomposed to a mixture of olefins (equation 5). Aryl compounds appeared to be exceptions as cis-1,2-diphenylcyclopropane lead to a stable platinacycle. In 1982, however, Jennings[69] reported stable platinacyclobutanes obtained from norbornylcyclopropanes. Since then, several norbornyl complexes have been made and characterized[70] from the cyclopropanes listed in Table 7.

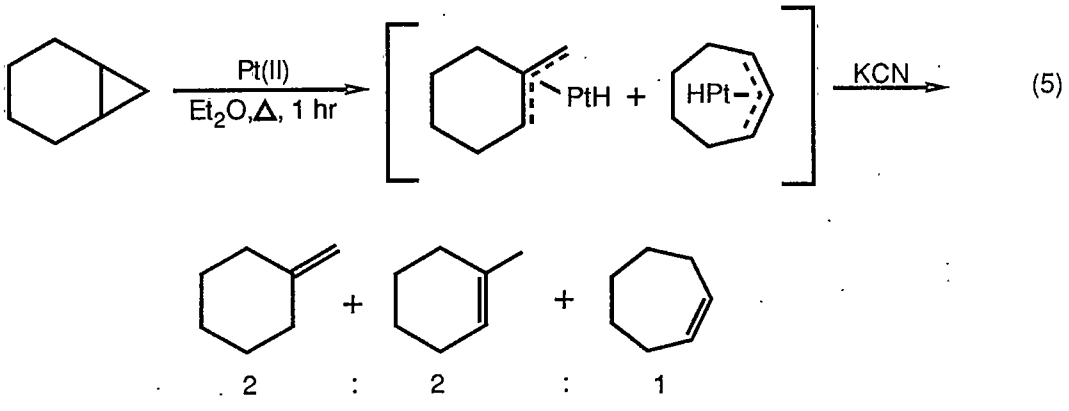


Table 6. Cyclopropanes Which Form Platinacyclobutanes.

cyclopropane	methylcyclopropane
ethylcyclopropane	isopropylcyclopropane
butylcyclopropane	n-hexylcyclopropane
phenylcyclopropane	benzylcyclopropane
p-toluylcyclopropane	o-toluylcyclopropane
spiro[2,2]pentane	spiro[2,4]heptane
spiro[2,5]octane	
o-nitrophenylcyclopropane	
p-methoxyphenylcyclopropane	
p-ethoxyphenylcyclopropane	
trans-1,2-diphenylcyclopropane	
cis-1,2-diphenylcyclopropane	
trans-1,2-ditoluylcyclopropane	
trans-1-methyl-2-phenylcyclopropane	
trans-1,2-dimethylcyclopropane	
trans-1-(n-butyl)-2-methylcyclopropane	
1,1-dimethylcyclopropane	
1,1-diethylcyclopropane	
1,2-dicyclopropylethane	
1,1,2-trimethylcyclopropane	
cyclopropylmethylmesylate	
1-(cyclopropyl)-1-ethylmesylate	
2-(cyclopropyl)-2-propylmesylate	
(1-methyl-1-cyclopropyl)methylmesylate	

Table 7. Norbornylcyclopropanes Which Form Platinacyclobutanes.

exo-tricyclo[3.2.1.$0^{2,4}$]octane

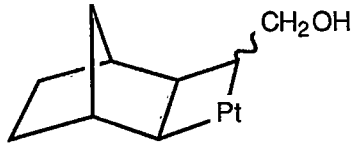
exo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene

exo, exo-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane

exo-tricyclo[3.2.1.$0^{2,4}$]-6-octanone

exo-tricyclo[3.2.1.$0^{2,4}$]-6-octanone, ketal with ethylene glycol

More recently, a 1,2,3-trisubstituted norbornyl cyclopropane was shown to form the stable platinacyclobutane 9[78].



9

Cyclopropanes directly bearing electron withdrawing groups, including those listed in Table 8, fail to react with platinum(II). A few other exceptions, such as 1,1-diphenylcyclopropane and trans-1,2-di(4-methoxyphenyl)cyclopropane react to give non-platinacyclopropane products.

Table 8. Cyclopropanes Which Do Not Form Platinacyclobutanes.

1,1-diphenylcyclopropane

cis-1-(n-butyl)2-methylcyclopropane

cis-bicyclo[4.1.0]heptane

trans-1,2-di(p-methoxyphenyl)cyclopropane

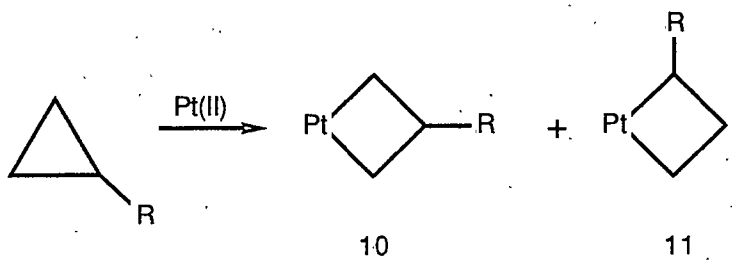
cyclopropylmethylester

cyclopropylcyanide

1,1,2,2-tetramethylcyclopropane

Platinacyclobutane Rearrangement

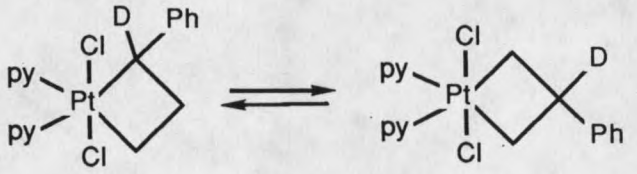
Cyclopropanes having unique bonds can yield different platinacyclobutane isomers (equation 6). Puddephatt discovered that isomer 11 was the kinetic product from phenylcyclopropane, but with time an equilibrium between 10 and 11 was established[79,80]. It was later shown that this isomerization was general for platinacyclobutanes[81].



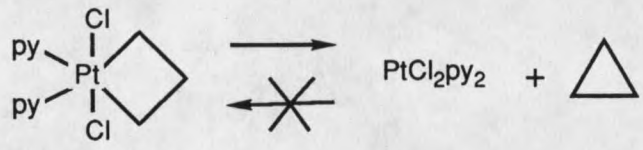
10 11 (6)

Isomerization was deterred by chelating ligands, or excess free ligand. This indicated that isomerization proceeds by an initial ligand loss, which was verified by kinetic studies.

Substituent migration was ruled out since the isomerization of 1-deuterio-1-phenylplatinacyclobutane proceeded with no scrambling of the deuterium and phenyl groups onto different carbons[80] (equation 7). Reversible elimination of the cyclopropane was also disproved, because cylopropanes won't react with $PtCl_2py_2$, and free cyclopropane in the isomerization mixture was not incorporated into a platinacyclobutane[82] (equation 8).



(7)



(8)

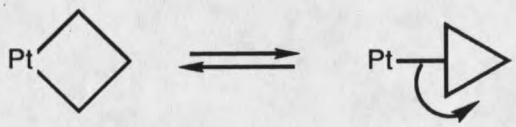
Four major mechanisms, shown in Figure 18 have therefore been proposed for the Puddephatt rearrangement. Mechanism (a) is attractive because of the ongoing interest in olefin metathesis, however, it is incorrect. The olefin-carbene intermediate would be expected to produce thermal decomposition products representing fragmentation of the

Figure 18. Proposed Puddephatt Rearrangement Mechanisms.

a. Methasis with rotation



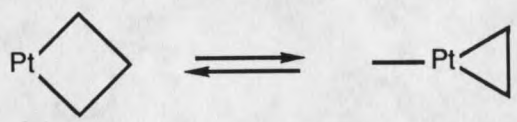
b. Edge migration



c. Concerted



d. Cyclobutylcation analogy



cyclopropane. These products are not observed. Also, olefin metathesis often results in cis-trans isomerization, and the same result would be expected from mechanism (a). Only if the number of olefin rotations differed from the number of carbene rotations by an odd number would the cyclopropane stereochemistry be retained. However, the rearrangement of cis-2-phenyl-4-deuterioplatinacyclobutane yielded the 3-phenyl isomer with no loss of stereochemistry. Reductive elimination of phenylcyclopropane also retained the cis configuration. (Using deuterium in the study eliminated any thermodynamic or steric stereochemical preference[82].)

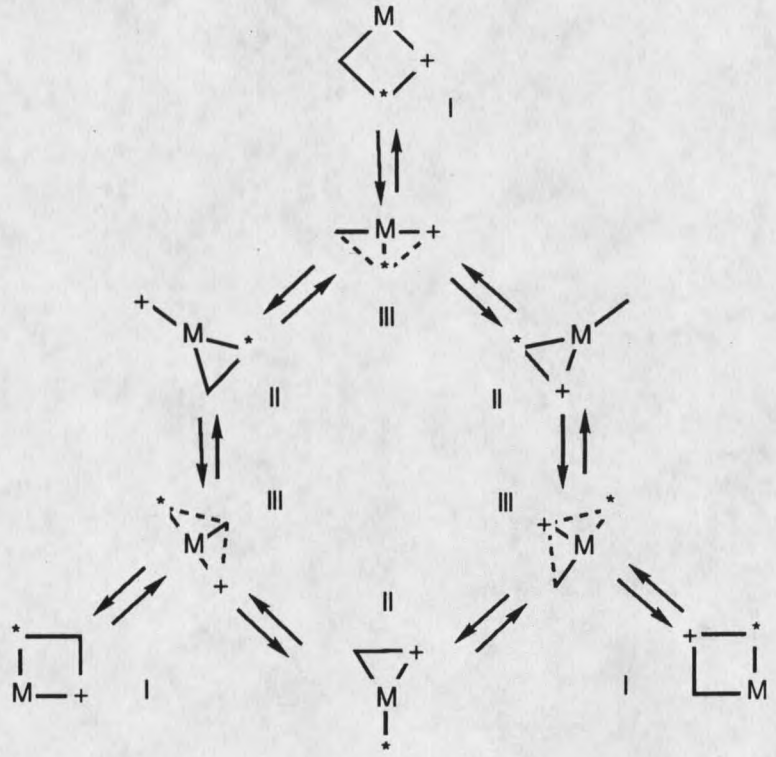
Further evidence against mechanism (a) was obtained from a crossover experiment in which 1-phenylplatinacyclopropane was isomerized in the presence of p-methylstyrene. No p-tolylplatinacyclobutane was produced.

Of the three remaining mechanisms, (b) is the least likely, although it can't at present be disproved. The crossover experiment with cyclopropane, mentioned earlier, indicates that the cyclopropane, though intact, must still be strongly bound to the platinum. This situation is thermodynamically unfeasable and has no precedent[83].

The fourth mechanism arises from theoretical extended Huckel studies, assuming that the initial loss of a ligand leaves the platinum as a 5-coordinate fragment with square-pyramidal geometry. The platinacyclobutane is then isolobal to a cyclobutyl cation. Rearrangement proceeds as shown in

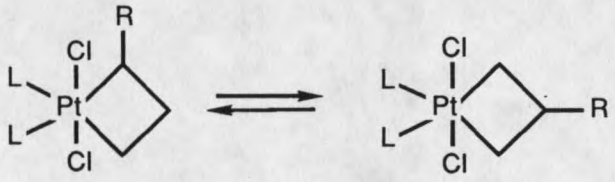
Figure 19. The analysis predicted II to represent minima; however, to fit the experimental data, III must be the intermediates and II the transition states. This discrepancy was dismissed as a failure of the extended Huckel calculation to properly predict the relative energies.

Figure 19. Mechanism Proposed for the Puddephatt Rearrangement by Analogy to the Cyclobutyl Cation.



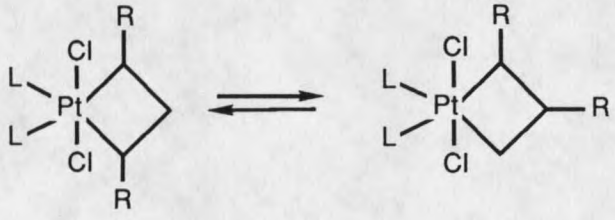
Currently, mechanisms (c) and (d) explain all the available data, but cannot be distinguished experimentally, if they are indeed different.

Although the Puddephatt rearrangement occurs with most or all platinacyclobutanes, the position of equilibrium varies. Generally, large ligands on platinum or large substituents on the cyclopropane favor isomer 13, in which the substituent is remote from the platinum (equation 9). Also, electron donating substituents favor isomer 13, while electron withdrawing substituents are expected to favor isomer 12[80]. Steric concerns appear to be the overriding factor, however.



12 13 (9)

The instability of some cis-1,2-disubstituted cyclopropane platinacycles may be due to steric interactions between platinum and the substituents in isomer 14. Placing the substituents trans partially relieves this interaction (equation 10).



14 (10)

The Puddephatt rearrangemant makes it impossible in most cases to determine where platinum inserted into the cyclopropane ring. Methylcyclopropane leads to both possible isomers, but with other alkylcyclopropanes only isomer 13 is observed[64]. From this it could be assumed that insertion occured into the least substituted bond. Steric factors, however, may disfavor one isomer such that it is not observed. This is supported by the observation that alkylplatinacyclobutanes rearrange rapidly, and many reactions appear to proceed from isomer 12[81].

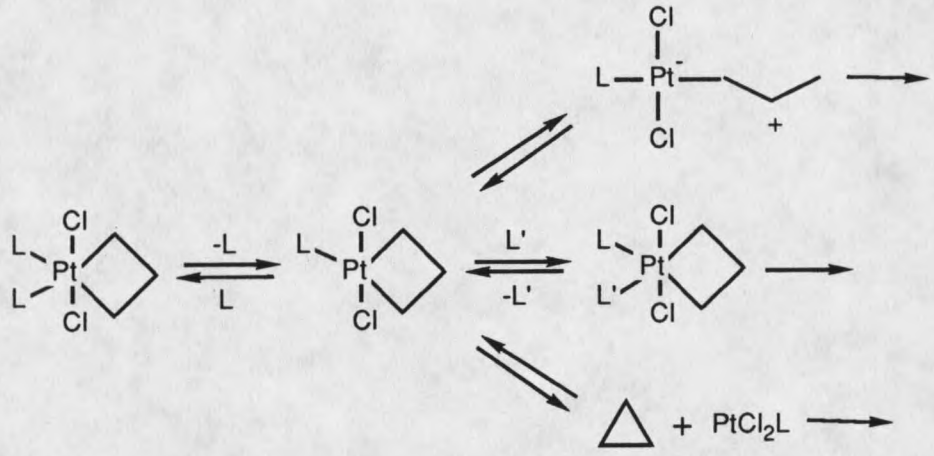
Arylcyclopropanes generally exist as two observable isomers. With some arylcyclopropanes an equilibrium mixture is immediately obtained. Phenylcyclopropane, 4-substituted-phenylcyclopropanes, and trans-1,2-di(4-tolyl)cyclopropane produce one initial isomer, however. In these complexes insertion is thought to occur into the most substituted bond of the cyclopropane. This preference may be due to increased electron density in that bond, as electron-donating substituents are known to increase cyclopropane reactivity with platinum(II)[75].

Chemistry of Platinacyclobutanes

Reactions of monomeric platinacyclobutane complexes generally proceed by initial dissociation of a neutral ligand, as illustrated in Figure 20. This can be halted by

ligand saturation or chelating ligands, such that the ligand cannot dissociate[84,85]. Photolysis carried out in polar solvents, such as DMSO, can cause loss of a chlorine instead of a neutral ligand[86].

Figure 20. Initial Ligand Dissociation From a Platinacyclobutane.



Platinacyclobutane Decomposition

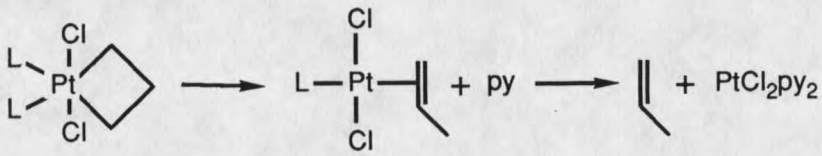
Platinacyclobutanes decompose by three major pathways: reductive elimination of the parent cyclopropane; rearrangement to form an ylide; or rearrangement to form an olefin.

Reductive elimination of cyclopropane can occur from either a tetrameric or monomeric platinacyclobutane complex. The elimination appears to be concerted and proceeds with retention of stereochemistry about the cyclopropane ring[64]. Generally, elimination is induced by photolysis[87], thermolysis or reaction with soft ligands. These ligands include

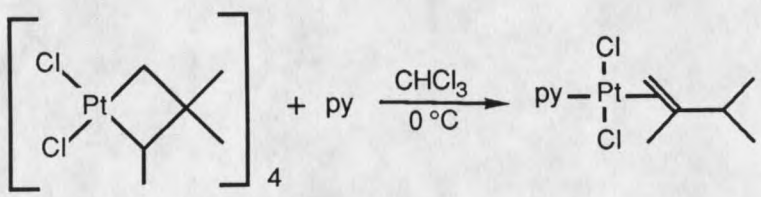
alkenes, CO, PPh_3, KCN, and DMSO[61,67,84,88,89]. A soft ligand added to a monomeric complex must successfully compete with the previous ligand for a coordination site.

In one report, cyclopropane was eliminated from a platinacyclobutane bearing the bipyridine ligand. The bipyridine completely dissociated from the platinum before the elimination occured[90].

Olefin forming decomposition of a platinacyclobutane preferentially produces the least-substituted olefin possible. If <u>cis</u> and <u>trans</u> isomers can be formed, the <u>cis</u> isomer is favored. The reaction is initiated by dissociation of a neutral ligand, followed by hydrogen abstraction. This probably forms a platinum-bound olefin from which the free olefin is displaced (equation 11). Only a few such intermediates have been observed, however. The first was reported by Brown in 1978[85] (equation 12).



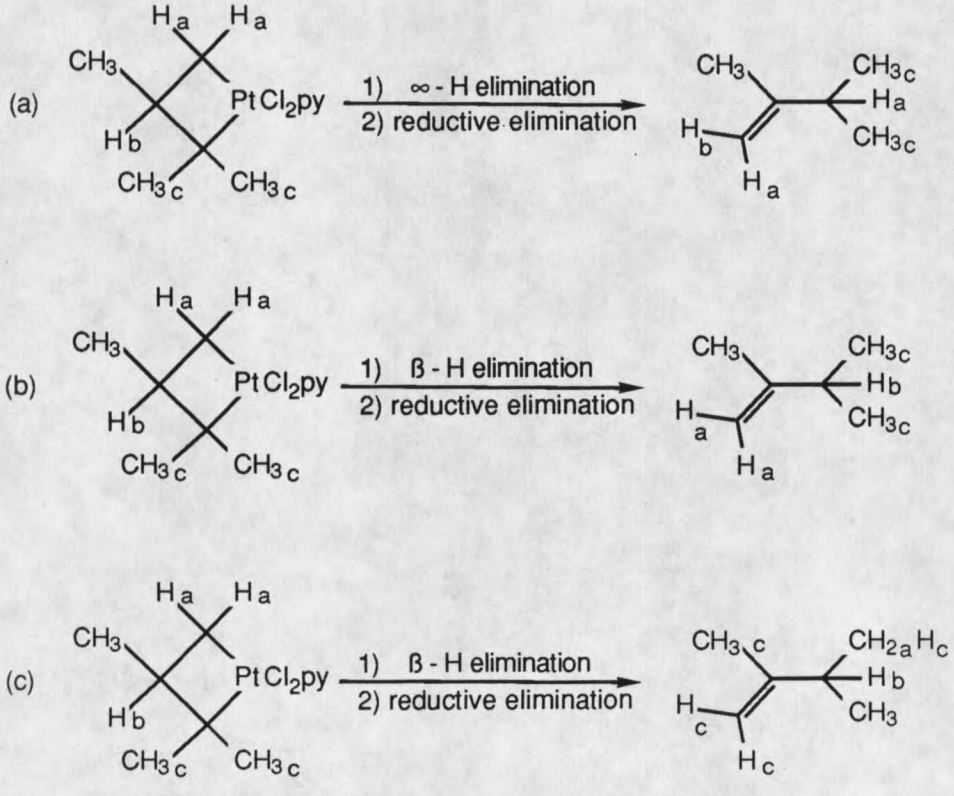
(11)

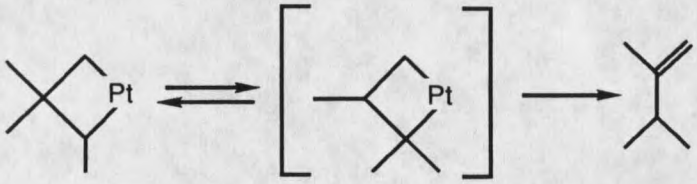


(12)

Three mechanisms for olefin formation have been proposed, and are shown in Figure 21. The first route involves α-hydrogen elimination, while the second and third proceed by ß-hydrogen elimination from the ring or a methyl substituent, respectively. In each case, the platinacyclobutane undergoes the Puddephatt rearrangement rapidly compared to the hydride shift. This frequently results in the alkene having a different carbon skeleton from that of the observed platinacyclobutane (equation 13).

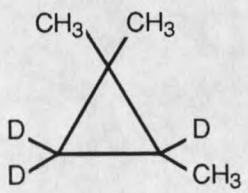
Figure 21. Mechanisms Proposed for the Rearrangement of Platinacyclobutanes to Olefins.



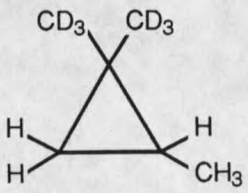


(13)

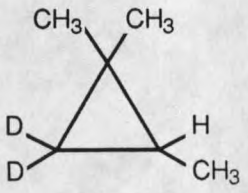
To differentiate between these pathways, Johnson[91] examined the deuterium labeled cyclopropanes **15**, **16** and **17**. Only cyclopropane **17** could differentiate between an α- and a ß-hydrogen abstraction. In each case, a major olefin resulted which could be derived by pathway (b), while a minor olefin resulting from pathway (c) was also obtained. This indicated the olefins were produced by the ß-hydrogen elimination mechanism. The labeling also showed, via cyclopropane **16**, that no methyl migration was involved in the rearrangement.



15

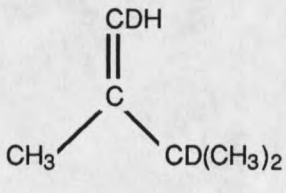


16

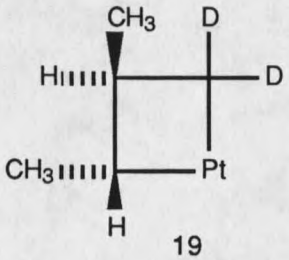


17

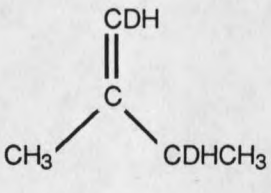
This reaction was reexamined by Puddephatt[92], who found that cyclopropane 17 produced compound 18 as the major product. This indicated (a) was the pathway followed. Further confirmation was obtained by the decomposition of complex 19 which yielded 20 as the major product. However, since Puddephatt's and Johnson's experiments were carried out under different reaction conditions, different mechanisms may actually have been in effect.



18



19

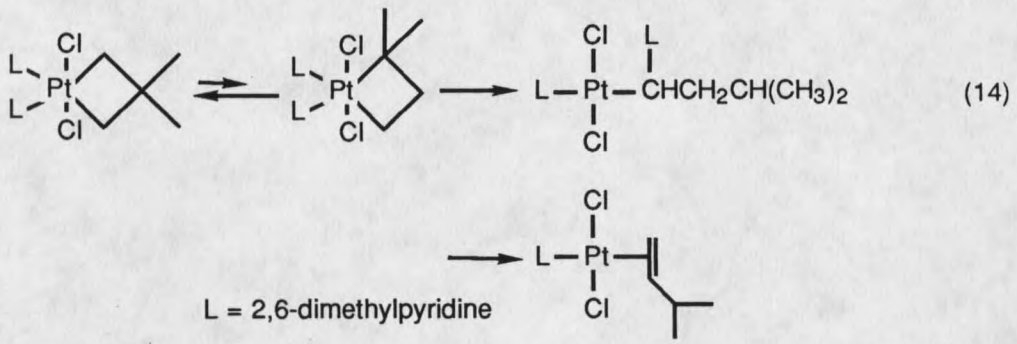


20

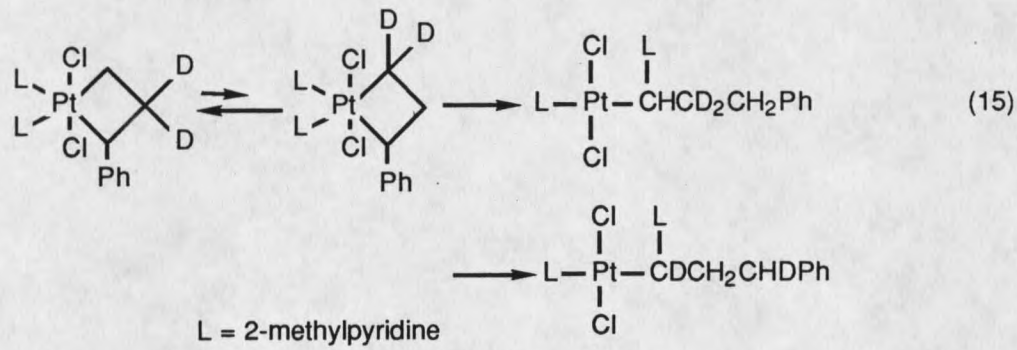
Although many platinacyclobutane reactions are known to yield ylides, only those mechanisms which also pertain to olefin formation will be considered here.

Puddephatt[93] reported production of an alkene by the decomposition of a platinacyclobutane, which proceeded via an intermediate ylide complex (equation 14). Labelling studies showed that the ylide was formed by an α-hydrogen elimination, and 1,3-H shift (equation 15). The 1,3-H shift formed a platinum-carbene which then proceeded to either the ylide or the olefin. Three conditions were necessary to form the ylide: the carbene carbon ß to the

platinum had to be primary; the attacking ligand had to be compact; and it had to be a strong base. Schrock type platinum(II) carbenes, however, have never been observed and are a matter of speculation only.

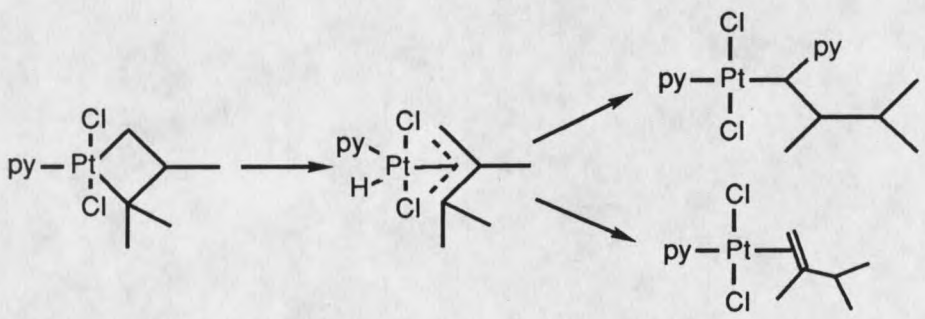


(14)



(15)

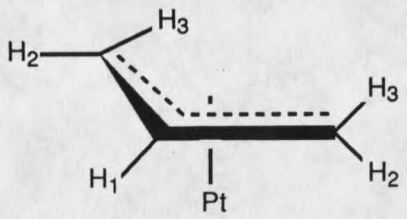
Brown[74], reported that both ylide and olefin formation proceeded via ß-hydrogen abstraction to a common π-allyl intermediate, although no hard evidence exists for this mechanism (equation 16). With weakly coordinating ligands, all the platinacycles investigated yielded olefin complexes, while with pyridine, platinayclobutanes substituted at only one carbon yielded ylides, and those substituted at two carbons yielded olefins.



(16)

Pi-allyls are most easily identified by ^{1}H and ^{13}C NMR spectroscopies. In general, π-allyl protons can be divided into three types, shown in Figure 22, with shifts[95] ranging from δ2-δ9. Carbon resonances usually appear between δ50 and δ124. Platinum-carbon coupling to the central carbon (0-80Hz) is less than to the end carbons (42-250 Hz)[42,96].

Figure 22. Pi-allyl ^{1}H NMR Resonance Ranges.



$H_1 : H_2 : H_3 = 1 : 2 : 2$

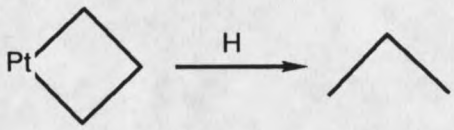
H_1 4-9 ppm

H_2 3.4-4.4 ppm

H_3 2-3 ppm

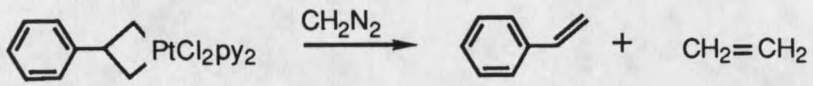
Additions to Platinacyclobutanes

Platinacyclobutanes can be hydrogenated to alkanes by reaction with lithium aluminum hydride, hydrogen in alcohol solution[88,97], or hydrochloric acid in water[98] (equation 17). The mechanism of this hydrogenolysis is not known.

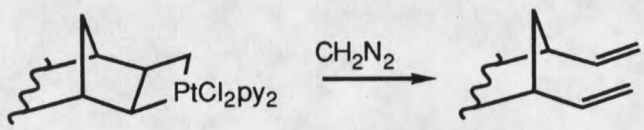


(17)

Diazomethane adds CH_2 to platinacyclobutane hydrocarbons, yielding two olefins (equations 18 and 19). A mechanism involving a platinacyclopentane intermediate has been proposed[99], and is illustrated in Figure 23.



(18)

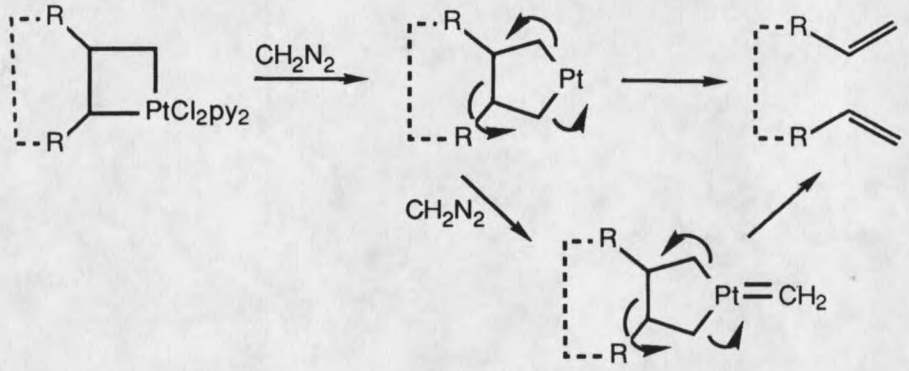


(19)

Reactions of Norbornyl Platinacyclobutanes

Norbornyl platinacyclobutanes occasionally react differently than other known platinacyclobutanes. For instance, typical platinacyclobutanes react with DMSO or CO

Figure 23. Mechanism Proposed for the Reaction of Diazomethane with Platinacyclobutanes.



to reductively eliminate cyclopropane. Reaction of norbornyl platinacycles with DMSO yields both cyclopropane and ring homologation with respect to the parent olefin, as shown in Figure 24. The double bond or cyclopropane across the ring from the platinacyclobutane probably assists in the ring expansion, as the saturated case carries out this process poorly[99,100].

When reacted with carbon monoxide, as illustrated in Figure 25, the norbornyl systems yield olefinic and cation capture products as well as cyclopropanes. Mechanistic studies showed that several products resulted from cationic pathways involving skeletal isomerization and capture of HCl and/or ROH[101] shown in Figure 26.

Likewise, thermolysis of some norbornyl cyclopropanes yields diolefins, which require a formal cleavage of the platinacyclobutane ring. These reactions and their proposed mechanisms are displayed in Figures 27 and 28. Once again,

assistance may come from the cyclopropane or double bond across the ring, as the saturated system does not produce a diolefin[102].

Figure 24. Reactions of Norbornyl Platinacyclobutanes with DMSO.

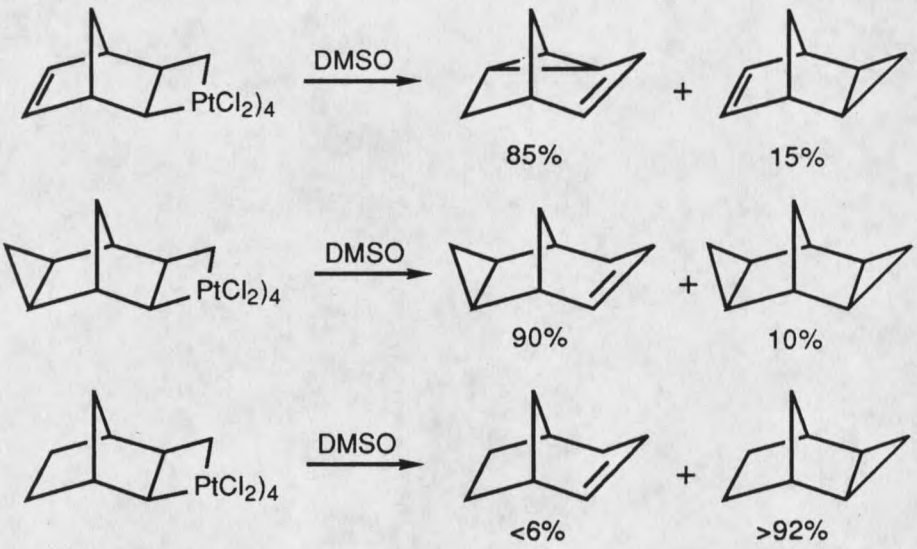


Figure 25. Reactions of Norbornyl Platinacyclobutanes with CO.

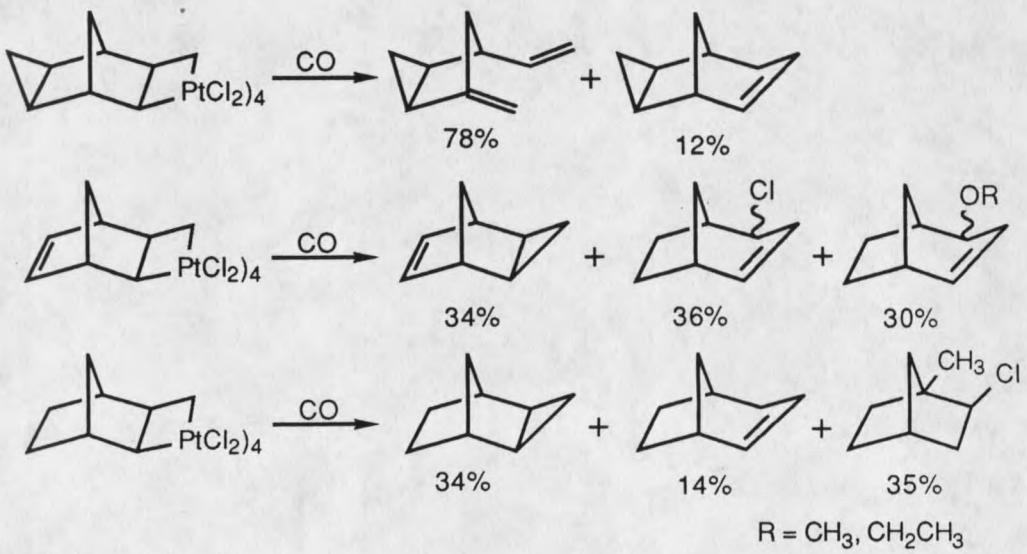


Figure 26. Cationic Mechanisms Proposed for the Reactions of Norbornyl Platinacyclobutanes with CO.

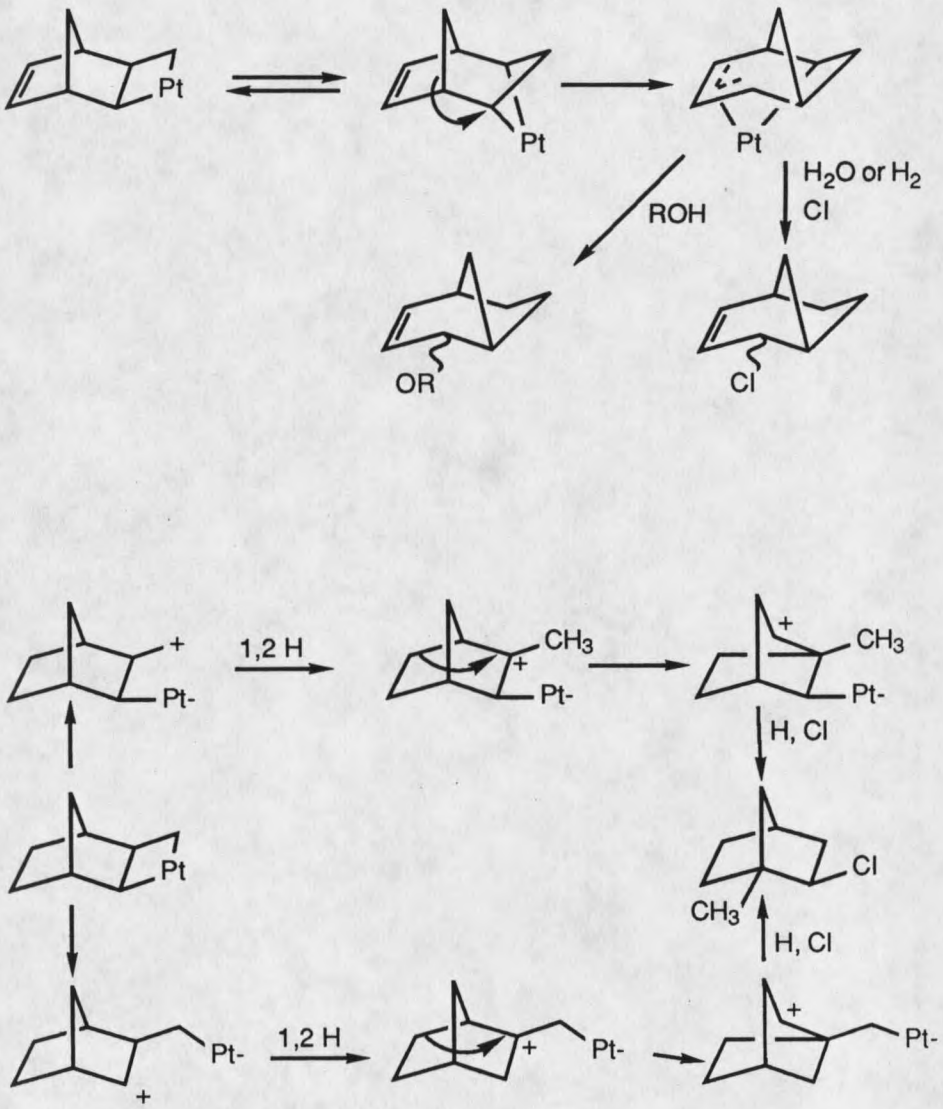


Figure 27. Thermolysis of Norbornyl Platinacyclobutanes.

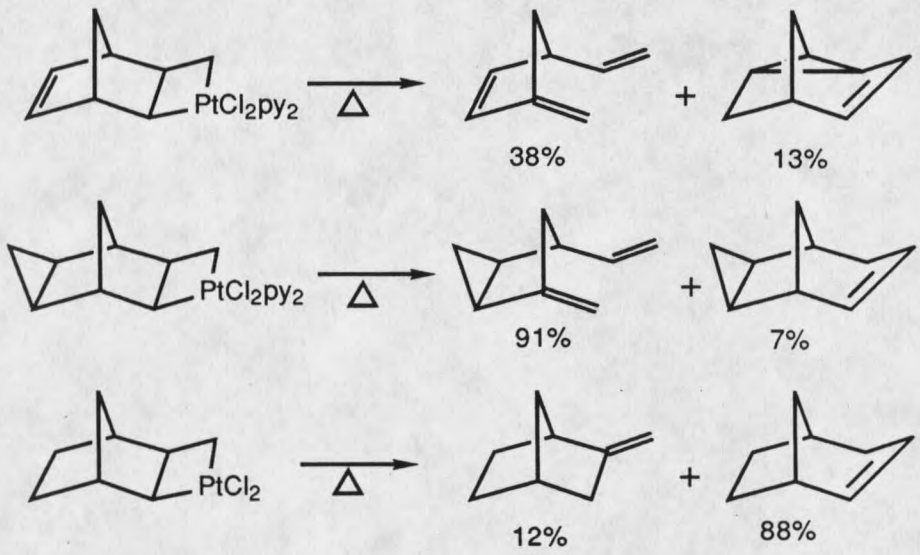
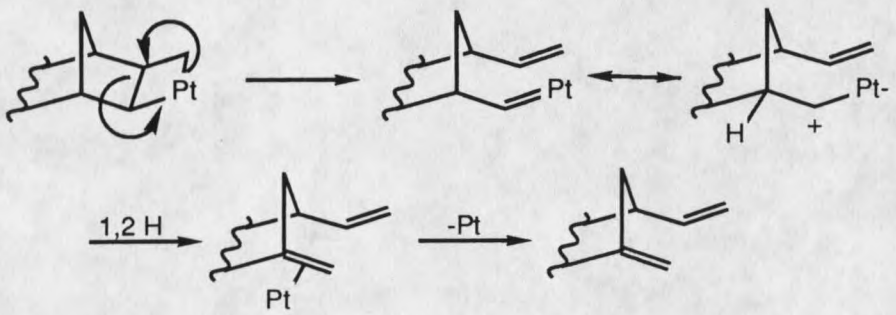


Figure 28. Proposed Mechanism for Formation of Diolefins from Norbornyl Platinacyclobutane Thermolysis.



RESULTS AND DISCUSSION

Statement of Problem

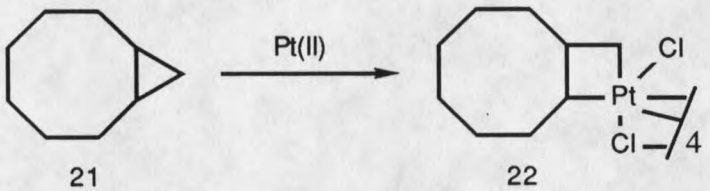
Platinum(II) forms platinacyclobutanes by inserting into a variety of simple cyclopropanes containing aryl and alkyl substituents[64]. However, cis-1,2-dialkyl substituted cyclopropanes were reported not to form platinacyclobutanes[66]. This was maintained until 1982, when stable platinacyclobutanes from norbornyl cyclopropanes were reported[69]. The stability of the norbornyl systems may be due to their rigidity, which could minimize steric interactions between the cyclopropane substituents and platinum's ligands.

We wished to examine other cis-1,2-dialkyl substituted cyclopropanes having steric considerations intermediate to those of the rigid norbornyl cyclopropanes and the relatively unconstrained simple cyclopropanes. The bicyclo[n.1.0]alkanes, or bicyclic cyclopropanes, met this requirement and were chosen for study. Furthermore, transformations of the resulting platinacyclobutanes could be of synthetic interest, as cyclic molecules are ubiquitous in nature.

Formation of Platinacyclobutanes

Complexes from Cyclopropane 21

The reaction of bicyclo[6.1.0]nonane (**21**) with Zeise's dimer proceeded at room temperature to yield a yellow IPC (Initially Precipitated Complex) (equation 20). Characterization of the complex by its solid state ^{13}C NMR spectrum, which is reproduced in Figure 29, showed platinacyclobutane carbon resonances at δ51 (C2) and δ6.9 (C1). A third resonance at about δ30 (C3) was expected, but overlapped with resonances for the substituent ring carbons. Good correlation existed between the spectrum of **22**, and those observed for the norbornyl IPCs, as reported by Waddington[68]. Data for these complexes are listed in Table 9. The elemental analysis was reasonable for the proposed compound as well, indicating that complex **22** was the desired platinacyclobutane.



21 22 (20)

Generally, platinacyclobutanes do not melt but thermally decompose instead. This was true of complex **22**, which decomposed between 136° and 139°C.

Figure 29. Solid State ^{13}C NMR Spectrum of 22.

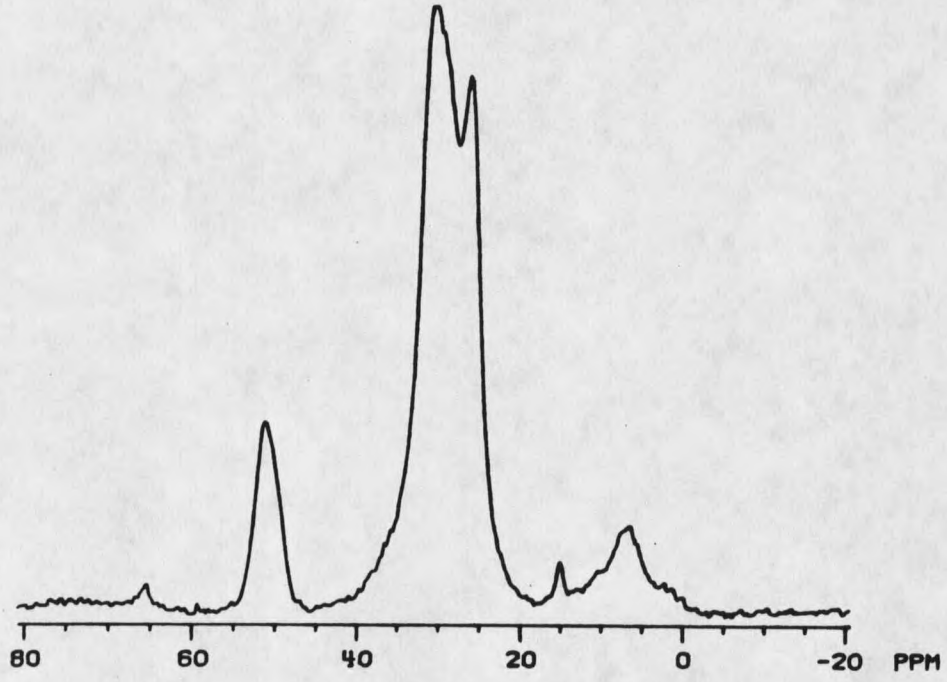
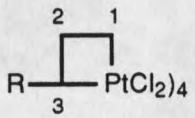


Table 9. Platinacyclobutane 22 Solid State ^{13}C NMR Resonances.



22

33 34 35

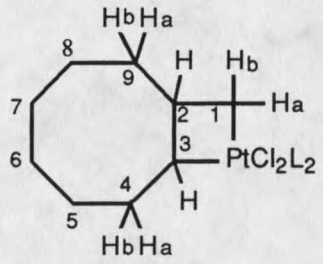


R= H Ph

atom #	22*	33	34	35	R=H	R=Ph
1	6.9**	4	15	4	2.4	1.9
2	51.0	58	54	56	34	38
3	obsc.	33	32	33	25	

*3-9: 30.6; 30.4; 29.6; 26.0.
**all shifts are in ppm

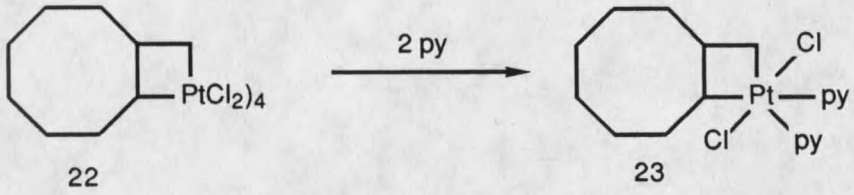
Table 10. NMR Resonances for Compounds 23 (L = py) and 24 (L = bipy).



	L =	py	py	1/2bipy
	solvent =	$CDCl_3$	py-d_5	$CDCl_3$
^{13}C NMR****				
C#	1	-7.2 t (351)**	-7.6 t (357)	-6.7 t (364)
	2	48.6 d (85)	49.2 d (100)	47.4 d (85)
	3	14.2 d (348)	12.9 d (354)	13.3 d (342)
	4*	31.2 t	31.9 t	31.6 t
	5*	30.0 t	30.8 t	30.5 t
	6*	25.9 t	26.3 t	26.1 t
	7*	25.6 t	26.0 t	26.0 t
	8*	29.5 t	30.0 t	29.8 t
	9*	30.8 t	31.5 t	30.8 t
^{1}H NMR				
H#	1a	2.6 dd	3.0 dd (88)	2.6 dd (91)
	1b	2.5 dd	2.8 dd	2.4 dd
	2	2.7 m	3.0 m	2.9 m
	3	3.6 dd (96)	3.9 dd (95)	3.5 dd (98)
	4a	2.2 m	2.5 m	2.2 ddd
	4b-8	1.3 m	1.1 m	1.6 m
	9a	2.2 m	2.3 m	2.0 ddd
	9b	0.7 d	1.1 m	1.3 d
^{195}Pt NMR				
		3263***	3300	3076

* not rigorously assigned
** platinum coupling in Hz
*** relative to 1.0M $Na_2Pt(CN)_4$ in D_2O at 25°C
**** all shifts in ppm

Reaction of IPC 22 with two equivalents of pyridine yielded the monomeric complex 23 (equation 21). The platinacyclobutane ring protons could be distinguished by proton NMR spectroscopy, as shown in Table 10. Most of the peaks overlapped and platinum coupling was obscured, with the exception of the resonance for the proton at carbon 3 which came at δ3.6. This peak was in a clear region of the spectrum and exhibited platinum coupling of 96 Hz. Its utility in platinacyclobutane identification and kinetic studies will be discussed later.



22 23 (21)

The carbon-13 NMR spectrum of complex 23 showed characteristic platinacyclobutane resonances at δ-7.2 (C1), δ14.2 (C3), and δ48.6 (C2). The assignment of these peaks to a 2,3-dialkylplatinacyclobutane was established with the norbornyl platinacyclobutanes[69]. The complex was non-symmetrical as manifested by the lack of magnetic equivalence between the carbons. Platinum couplings of 351 Hz and 348 Hz to C1 and C3, respectively, indicated the presence of platinum-carbon sigma bonds. Platinum coupling was also observed to C2 (85 Hz), but was too large to be $^{2}J_{Pt,C}$

except within the platinacyclobutane. A platinum-195 resonance was observed at δ3263, which was also consistent with a platina(IV)cyclobutane bearing pyridine and chlorine ligands.

Complex 23 could be isolated as a yellow solid by precipitation from pentane, but was relatively unstable and decomposed at 245°C. In solution 23 decomposed within six hours at room temperature. Similar platinacyclobutane decompositions have been shown to require an open coordination site on the platinum formed by an initial pyridine ligand loss[85]. This process could be halted by maintaining complex 23 in pyridine solution or by replacing the pyridines with the chelating 2,2'-bipyridine (bipy) ligand.

In pyridine, the ^{13}C and ^{1}H NMR spectra of complex 23 were similar to those obtained in chloroform solution and are also listed in Table 10. A slight downfield shift of the proton resonances was noted and is typical of complexes in pyridine solution. The platinum NMR resonance showed a greater shift, to δ3300, due to platinum's NMR sensitivity to solvent.

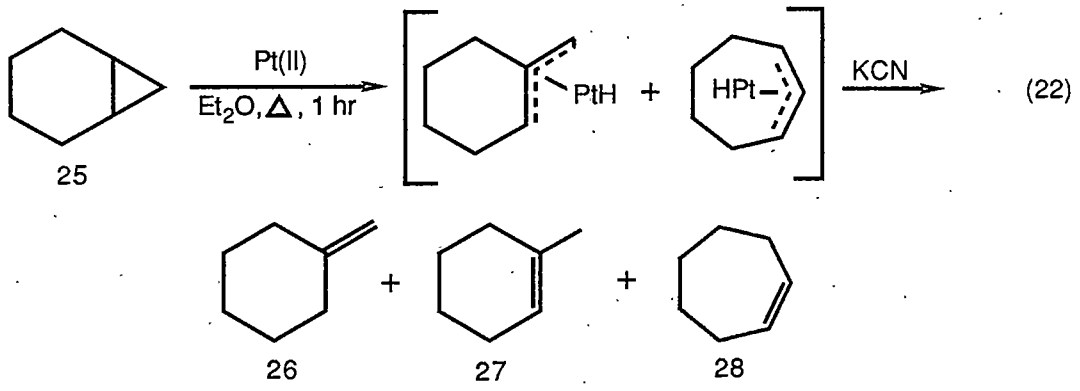
Stabilization of the platinacyclobutane with the bipy ligand permitted isolation of 24 as a pale yellow solid, which was thermally stable up to 300°C. The structure of this compound was confirmed by elemental analysis and NMR spectroscopies (Table 10). The sensitivity of platinum NMR to ligand changes caused the platinum resonance to shift to

δ3076. The ^{1}H and ^{13}C NMR spectra remained relatively unchanged from those of complex **23**, however.

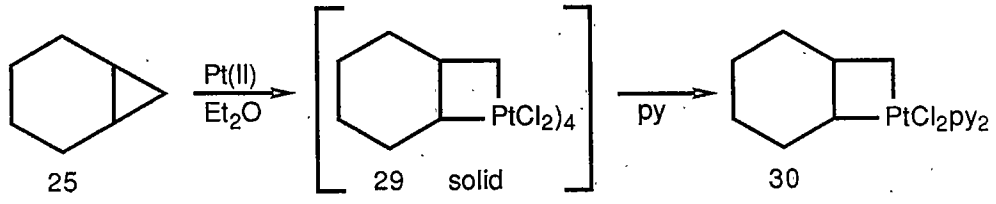
Complexes from Cyclopropane **25**

Although reaction of cyclopropane **21** with platinum showed that a platinacyclobutane could be made from a bicyclo[n.1.0]alkane, the reaction of cyclopropane **25** had been specifically reported not to yield this product. The reaction of cyclopropane **25** with platinum was therefore reexamined.

According to McQuillin[66], cyclopropane **25** produced π-allyl complexes when refluxed with platinum in diethyl-ether (equation 22). These complexes were not directly observed, but their decomposition with potassium cyanide yielded a mixture of olefins, while a platinacyclobutane would have reproduced the original cyclopropane.



Cyclopropane 25 contained more ring strain than 21, so both 25 and its resulting platinacyclobutanes were thought to be more reactive than 21 and its complexes. Therefore, when the reflux of 25 with Zeise's dimer in diethylether yielded olefinic products as reported, it was hypothesized that if the platinacycle had formed, it had subsequently rearranged. The reaction was therefore repeated at 23°C, 0°C, and -10°C. At 0°C and -10°C a yellow solid was obtained, but darkened almost immediately upon isolation. Likewise, when the solid was placed in chloroform and two equivalents of pyridine were added, the solution darkened rapidly and did not exhibit any evidence of a platinacyclobutane. However, when the solid was solvated in pyridine, the platinacyclobutane 30 was observed and remained intact for over a year (equation 23).



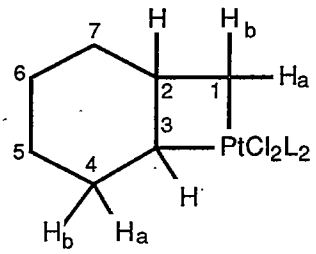
(23)

Optimization of the reaction required balancing time and temperature to yield a maximum amount of IPC 29 before its rearrangement products could accumulate. The reaction of three equivalents of 25 with platinum for 36 hours at -10°C appeared optimal, but yields greater than 32% were not obtained.

Spectroscopically, the identification of **30** was very similar to that of **23**. As listed in Table 11, the ^{1}H NMR peak for the proton at carbon 3 was again easily identifiable at δ3.66 and showed platinum coupling of 93 Hz. A platinum-195 resonance appeared at δ3315 and correlated well with the δ3300 peak obtained for complex **23** in pyridine solution. Likewise, the platinacyclobutane carbons appeared at δ44.6 (C2), δ5.8 (C3) and δ-8.6 (C1) in the ^{13}C NMR spectrum. These were coupled to platinum by 98 Hz, 369 Hz, and 354 Hz, respectively. The carbon-13 spectrum was also examined for evidence of π-allyl complex formation. Excess pyridine should decompose π-allyl compounds to their respective olefin analogues as does potassium cyanide. These olefins exhibit sp^2 carbon resonances between δ105 and δ150, however no such peaks were observed in the spectrum of **30**. Furthermore, all the sp^3 carbon resonances in the spectrum could be assigned to either complex **30** or to residual cyclopropane **25**. Therefore, under the mild reaction conditions used, platinacyclobutane **30** was the major organoplatinum species formed.

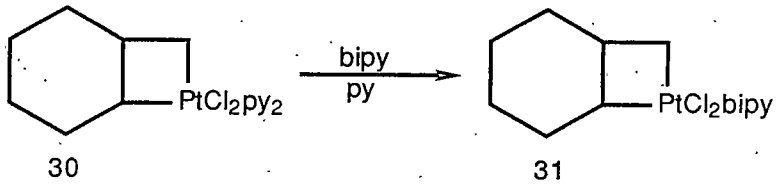
Attempts to isolate **30** as a solid proved futile, so it was converted to the bipy adduct, **31** (equation 24). Because of the instability of IPC **29**, the bipy ligand was added by direct displacement of the pyridines in complex **30**. The reaction was carried out in pyridine solution to stabilize the complex prior to complete bipy chelation.

Table 11. NMR Resonances for Compounds 30 (L = py) and 31 (L = bipy).



		L = py	1/2 bipy
		Solvent = py	$CDCl_3$
^{13}C NMR****			
C#	1	-8.6 t (354)**	-7.7 t (342)
	2	44.6 d (98)	42.8 d (92)
	3	5.8 d (369)	5.2 d (366)
	4*	27.2 t	27.5 t (24)
	5*	20.4 t	20.3 t (43)
	6*	19.9 t	19.4 t (49)
	7*	25.7 t	24.7 t (15)
^{1}H NMR			
H#	1a	3.0 d	2.7 dd (85)
	1b	2.8 dd	2.4 dd (80)
	2	3.0 m	3.1 m
	3	3.7 ddd (93)	3.3 ddd (92)
	4a	2.2 m	2.0 m
	4b-7a	1.5 m	1.6 m
	7b	2.0 m	1.6 m
^{195}Pt NMR			
		3315***	3095

* not rigorously assigned
** platinum coupling in Hz
*** relative to 1.0M $Na_2Pt(CN)_4$ in D_2O at 25°C
**** all shifts in ppm



30 31 (24)

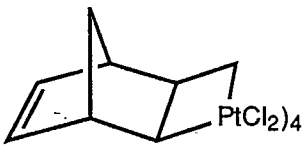
After purification on a silica gel column, complex **31** was obtained as a pale yellow solid which was stable at room temperature for several days. The solid decomposed thermally at 213°C, confirming that **31** was much less stable than the analagous complex **24**. This increased instability led to difficulties in obtaining an elemental analysis, and the final analysis was off by 0.62% in carbon.

Analysis of **31** by proton, carbon-13, and platinum-195 NMR spectroscopies verified that **31** was structurally analogous to **24**. The respective resonances for **31** are shown in Table 11. The proton resonances for **31** were well separated and permitted observation of 85 and 80 Hz platinum couplings to H1a and H1b, respectively.

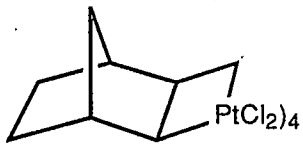
Complexes from Cyclopropane 32

The reactions of cyclopropanes **21** and **25** with platinum(II) clearly showed that platinacyclobutanes can be made from cis-bicyclo[n.1.0]alkanes. This research was therefore extended to examine olefin-containing bicyclic cyclopropanes as well. Platinum(II) bonds strongly to unhindered olefins,

usually to the exclusion of cyclopropane insertion, so the development of a method for forming platinacyclobutanes in the presence of these olefins was desirable. Furthermore, transformations of platinacycle **34** produced some unusual products not obtained from the reactions of **35**. This reactivity difference might occur with the bicyclic platinacyclobutanes as well.



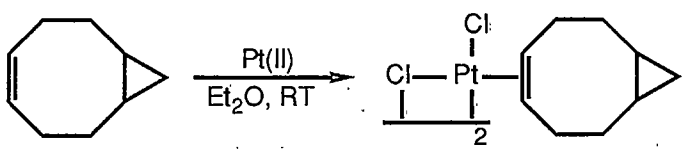
34



35

Bicyclo[6.1.0]non-4-ene, **32**, was chosen for this study. By analogy to **21**, this platinacyclobutane might be reasonably stable once formed.

Initially, reaction of **32** with platinum(II) made the platinum-bound olefin complex, **36** (equation 25). No insertion into the cyclopropane was observed. A second equivalent of platinum was expected to insert into complex **36**, however, since the first platinum protected the olefin from further complexation. This did not occur, indicating the insertion was energetically unfavorable.

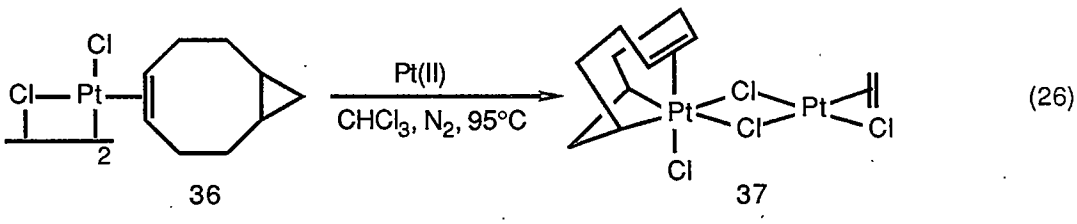


(25)

32

36

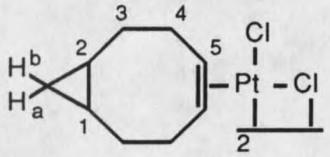
The reaction mixture was heated to 60°C, but still no insertion occurred. Above 60°C platinacyclobutanes have been reported to decompose[64], so attempting to form one above this temperature appeared counterproductive. However, removal of oxygen from the reaction environment was found to halt the decomposition. Complex 36 and a second equivalent of platinum were therefore placed in a deoxygenated chloroform solution and sealed in an evacuated tube. After heating to 95°C for 15 minutes a most unusual platinacyclobutane was obtained (equation 26).



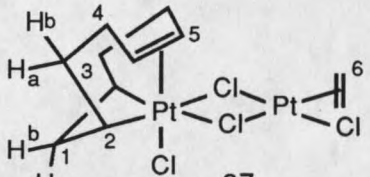
36 37 (26)

Complex 37 was not an IPC, and was soluble in chloroform. Its analysis by ^{13}C NMR spectroscopy showed five carbon resonances, indicating a symmetric complex. These resonances are listed in Table 12. Olefinic carbons appeared at δ120.4 and were coupled to platinum by 94 Hz. This resonance was upfield of the platinum(II)-bound olefinic carbon resonance in 36 (δ89.9, $^{1}J_{Pt,C}$ 162 Hz) and was close to the resonance of the free olefin 32 (δ130.3). The coupling of 94 Hz was larger than expected for secondary coupling to platinum elsewhere in the molecule, but was too small

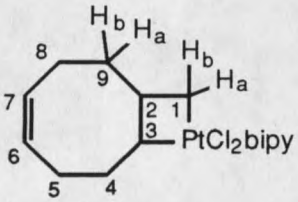
Table 12. NMR Resonances for Compounds 36, 37, and 48.



36



37



48

^{13}C NMR****

C#				
	1	16.3 t	36.8 t (100)**	-6.1 t (361)
	2	30.3 d	29.6 d (338)	47.8 d (82)
	3	19.9 t *	44.4 t *	12.5 d (345)
	4	28.5 t *	22.7 t *	34.0 t *
	5	89.9 d (162)	120.4 d (94)	25.3 t *
	6		71.0 t (205)	131.8 d *
	7			130.4 d *
	8			24.9 t *
	9			32.2 t *

^{1}H NMR

H#				
	1a	0.02 dd	2.97 ddd (92) *	2.6 dd (91)
	1b	0.78 ddd	2.6-2.2 m *	2.5-1.8 m
	2	1.05 m	1.26 d (108)	3.15 m
	3a	2.44 dd *	3.73 ddd (82) *	3.6 ddd (95)
	3b	2.44 dd *	2.6-2.2 m *	3.6 ddd (95)
	4	2.59 m	2.6-2.2 m *	2.5-1.8 m
	5	5.57 m (66)	7.40 dd (60)	2.5-1.8 m
	6		4.70 s (69)	5.73 m
	7			5.73 m
	8-9a			2.5-1.8 m
	9b			1.6 m

^{195}Pt NMR

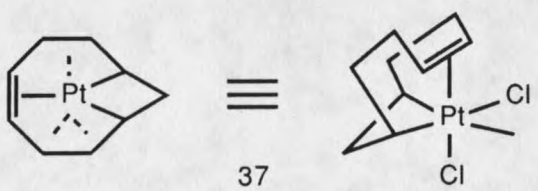
2338 ***	2796	3072
	2184	

* not rigorously assigned
** platinum coupling in Hz
*** relative to 1.0M $Na_2Pt(CN)_4$ in D_2O at 25°C
**** all shifts in ppm, solvent was $CDCl_3$

to be due to a platinum(II)-olefin bond. In the proton NMR spectrum, the olefin resonance appeared at δ7.4, which indicated an olefin bearing an electron withdrawing group. This peak was coupled to platinum by 60 Hz.

The platinacyclobutane carbons appeared at δ29.6 (C2) and δ36.8 (C1) and were coupled to platinum by 338 Hz and 100 Hz, respectively. These peaks were downfield of those observed for platinacyclobutanes **23** and **30**, and are indicative of carbons <u>trans</u> to chlorines on platinum. This relationship was established by Waddington[68] for the norbornyl platinacyclobutanes.

The proton and carbon NMR data were consistent with the platinum(IV) portion of complex **37**, where the unusual olefin resonances and platinum couplings were due to the presence of a platinum(IV)-olefin bond. The backbonding contribution to this bond was expected to be much less than in a platinum(II) bond. Therefore, donation of electron density from the olefin to the platinum might have deshielded the olefinic protons and carbons relative to those in a platinum(II) bound olefin. Decreased backbonding may have also caused the reduced platinum-carbon coupling constant, but this is uncertain.



37

The platinum-195 NMR spectrum, however, showed two platinum resonances at δ2796 and δ2184. The upfield peak (δ2184) was indicative of a platinum(II) species. An X-ray crystallographic analysis was therefore undertaken to elucidate the inorganic portion of the molecule, and the resulting data is listed in Appendix B. The structure obtained was that of 37, and contained two different platinum atoms: a four-coordinate, square planar platinum(II) and a six-coordinate, octahedral platinum(IV). These geometries and coordination numbers, together with a distance of 3.66 Å between the two platinums, indicated a mixed valence complex rather than a platinum(III) dimer.

The platinums were bridged by two chlorines and the resulting dichlorodiplatinum ring was puckered by 28°. The platinum(IV) to bridging chlorine bond distance was 2.6 Å, while the platinum(II) to bridging chlorine bond distance was 2.3 Å. This difference may have reflected the enlarged coordination sphere of the platinum(IV), but was more likely due to the high <u>trans influence</u> of the carbons <u>trans</u> to the chlorines on the platinum(IV).

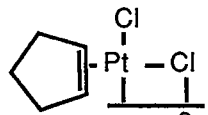
The platinum(II) portion of the molecule resembled half of the reactant Zeise's dimer, while the platinum(IV) portion contained the platinacyclobutane. The platinacycle consisted of platinum inserted into the most substituted bond of the cyclopropane, and the resulting ring was puckered by 11°. Platinacyclobutane rings are frequently

puckered[62], but this was the first report of platinum residing in the most substituted bond of a 1,2-dialkyl-substituted cyclopropane. Only once has platinum even been observed in the most substituted bond of a monoalkylcyclopropane[64]. It has been suggested, however, that platinum may insert into the most substituted bond initially, due to the increased electron density in this bond, but rapidly rearranges to a less substituted bond because of unfavorable steric interactions[61]. Rearrangement of platinum into the most substituted bond has also been invoked to explain the carbon linkages found in some platinacyclobutane reaction products.

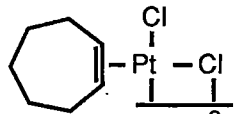
The platinum(IV) in compound 37 was trapped and prohibited from undergoing the Puddephatt rearrangement by chelation of the olefin. Whether the platinum inserted directly into the most substituted bond and was immediately trapped, or whether it inserted into a less substituted bond and was trapped upon rearranging into the proper bond is not known. Breaking the platinum bond to the olefin moiety, however, caused the platinum to rearrange to a less substituted bond, as will be discussed later.

The platinum(IV) bound olefin was of particular significance, as it was the first ever reported. It had a bond distance of 2.13 Å, while the platinum(II)-olefin bond distance in the same molecule was 1.97 Å. This change in bond length probably reflected the change in olefin

character rather than the change in platinum oxidation state, as bond distances of 2.09 Å and 2.00 Å have been reported for the platinum(II)-olefin species **38** and **39**, respectively[5]. The platinum(IV)-olefin in **37** was not fluxional, as evidenced by its sharp NMR lines.

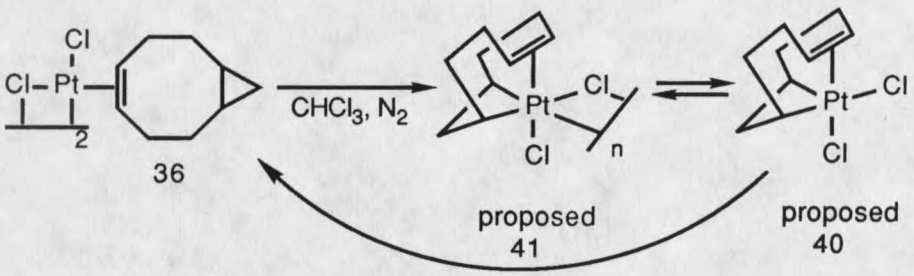


38



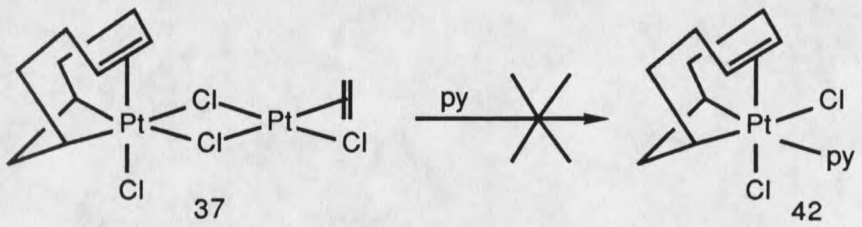
39

Since **37** contained a platinum which was still bound to the olefin and also inserted into the cyclopropane, it might not be necessary to react **36** with extra platinum. The reaction was therefore repeated without a second equivalent of platinum, and produced a complex similar to **37** but in low yield (equation 27). This product was identified by ^{1}H NMR, and may be dimeric. It was not stable, however, and reductively eliminated cyclopropane. This suggested that the complex was readily converted to a species containing an open coordination site, **40**, from whence reductive elimination could occur. If the complex was **41**, then the chlorines were only weakly bridging, either because of the <u>trans influence</u> of the platinum bound carbons, or steric interactions between the two halves of the molecule. Addition of a stoichiometric amount of THF or pyridine to either the reaction mixture or product failed to stabilize the complex, however.



(27)

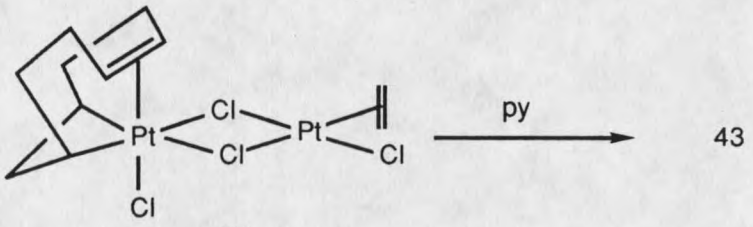
Isolation of the platinum(IV) portion of **37** as a monomer would facilitate the study of both the platinum(IV)-olefin and the platinacyclobutane without interference from the platinum(II). Complex **37** was therefore placed in pyridine solution, on the premise that the pyridine monomer would be formed and then stabilized by the excess pyridine. The product was stable in pyridine solution, but could not be isolated as a solid, and was not the desired complex **42** (equation 28).



(28)

The ^{13}C and ^{195}Pt NMR spectra of the product were obtained and are shown in Table 13. Carbon resonances at δ35.7 (t, $J_{Pt,C}$ 116), δ10.4 (d, $J_{Pt,C}$ 494), and δ-9.7 (d, $J_{Pt,C}$ 473) suggested a 2,4-dialkylplatinacyclobutane, however platinum coupling between 450 and 550 Hz generally indicates

Table 13. ^{195}Pt and ^{13}C NMR Resonances for Compound 43.



37

^{13}C NMR*	ppm	mult.	$J_{Pt,C}$ (Hz)
	74.5	d	
	37.6	t	
	35.7	t	(116)
	34.1	d	(797?)
	32.8	t	
	25.4	t	
	10.4	d	(494)
	-9.7	d	(473)

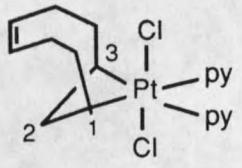
^{195}Pt NMR

2891**

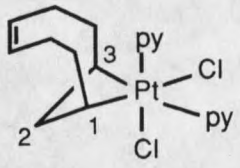
* in py-d_5 solvent
** relative to 1.0M $Na_2Pt(CN)_4$ in D_2O at 25°C

a platinacyclopentane[103]. The platinum peak at δ2891, although it was close to the platinum(IV) resonance for complex **37**, might also have indicated a platinacyclopentane. Furthermore, platinum may have been coupled to the carbon peak at δ34.1 by 797 Hz, which if true, indicated an ylide complex.

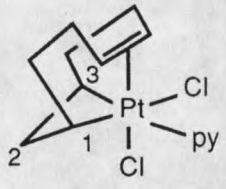
One structure proposed to fit this data was **44**, assuming that the olefinic carbon resonances were obscurred by pyridine and the peak at δ74.5 was due to an impurity. However, C1 and C3 of **44**, should be magnetically equivalent, which they were not in the complex obtained. In **45**, an isomer of **44**, the bridgehead carbons are made nonequivalent by the different <u>trans influences</u> of chlorine and pyridine. Unfortunately, the shifts of these carbons are predicted to be about δ10 and δ40, by analogy to complexes **23** and **37**. In fact, the resonances appeared at δ10 and δ-10. The same arguments ruled out **42** as the reaction product.



44



45

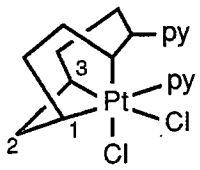


42

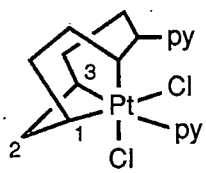
Attempts to determine whether a free olefin existed in the complex were unsuccessful. As previously mentioned, the olefin region in the ^{13}C NMR spectrum was obscured by pyridine. Likewise, the olefin C-C stretch region in the IR

spectrum was obscured by pyridine, while C-Cl stretch prevented model C-C bend frequencies from being determined, and the C-C bend band was not assigned. Complexation of the olefin by $CpFe(CO)_2$ was attempted, but pyridine replaced the CO ligands and thwarted the reaction. Reaction of 37 with morpholine, a non-aromatic, nitrogen ligand similar in steric bulk to pyridine, yielded a different product altogether, which was not characterized further.

Isomeric complexes 46 and 47, which each contain platinacyclobutane and pentane rings and an ylide, but have no olefin, were proposed as alternatives to structures 42, 44 and 45. They are derived from nucleophilic attack by pyridine on the platinum bound olefin in 42, giving a pyridine substituted carbon (assigned to δ74.5) and a platinum bound carbon (δ34.1, $J_{Pt,C}$797). However, the upfield shift of C1 to δ-10 was still unexplained. Attempts to replace the proposed carbon-coordinated pyridine with morpholine or n-butylamine were unsuccessful.



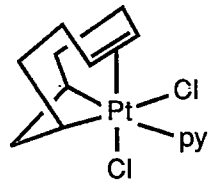
46



47

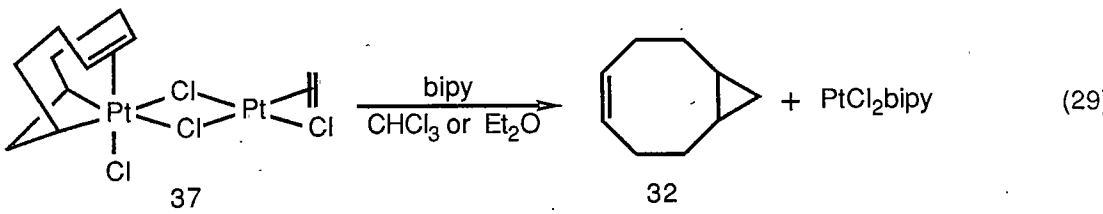
The product obtained from 37 in pyridine should be completely reexamined, as our inability to elucidate its structure may have been due to insufficient or misleading

data. For instance, the carbon-13 NMR resonances at δ37.6, δ32.8, and δ25.4 were broad, which suggested the complex may have actually been fluxional. However, since it was apparent that **42**, the desired complex, wasn't formed the reaction was abandoned (see equation 28).

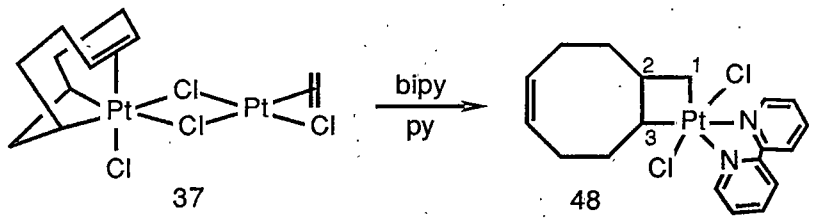


42
(not formed)

In a further attempt to isolate the platinum(IV) portion of **37** as a monomer, the complex was reacted with bipy. This was expected to cleave the platinum(IV)-olefin bond, but leave the platinacyclobutane intact. However, in diethylether and chloroform the reaction led to decomposition of the complex (equation 29). By analogy to the formation of the bicycloheptane platinacycle **31**, the reaction was therefore carried out in pyridine solution (equation 30). This produced complex **48**, which could be isolated as a white solid.



37 32 (29)



37 48 (30)

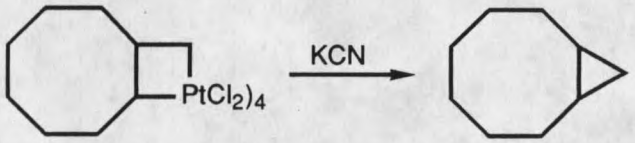
Complex **48** was intermediate in stability to analagous platinacyclobutanes **24** and **31**, and as a solid decomposed thermally at 243°C. It's NMR data, listed in Table 12, also correlated well with that of **24** and **31**. A proton resonance for H3 was observed at δ3.6 and was coupled to platinum by 95 Hz. The carbons in the platinacyclobutane ring resonated at δ47.8 (C2), δ12.5 (C3) and δ-6.1 (C1) and were coupled by 82, 345, and 361 Hz, respectively. The platinum resonance appeared at δ3072 in the ^{195}Pt NMR spectrum.

Chemistry of the Platinacyclobutanes

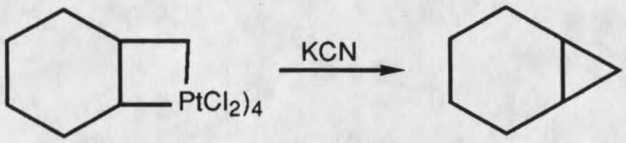
Reactions with KCN, DMSO, and Pφ$_3$

Platinacyclobutanes have been reported to reductively eliminate cyclopropane when reacted with soft ligands[89] such as potassium cyanide (KCN), dimethylsulfoxide (DMSO), and triphenylphosphine (Pφ$_3$). These reactions therefore can be used as standards against which the reactivity of new platinacyclobutanes can be compared. If cyclopropane is produced, they also confirm the prior existence of a platinacyclobutane.

Complexes **22** and **29** were reacted with KCN and the hydrocarbon products were examined by proton NMR spectroscopy (equations 31 and 32). As expected, cyclopropanes **21** and **25** were obtained, respectively.

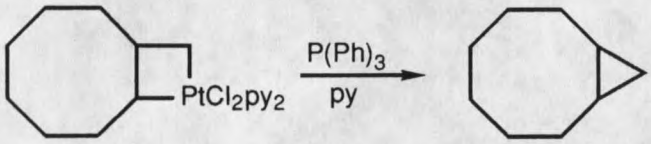


22 21 (31)

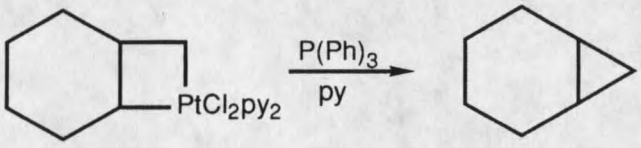


29 25 (32)

The pyridine monomers **23** and **30** were also examined by reaction with a soft ligand (equations 33 and 34). In each case, five equivalents of $P\phi_3$ were added to the complex in pyridine solution. Again, cyclopropanes **21** and **25** were the



23 21 (33)

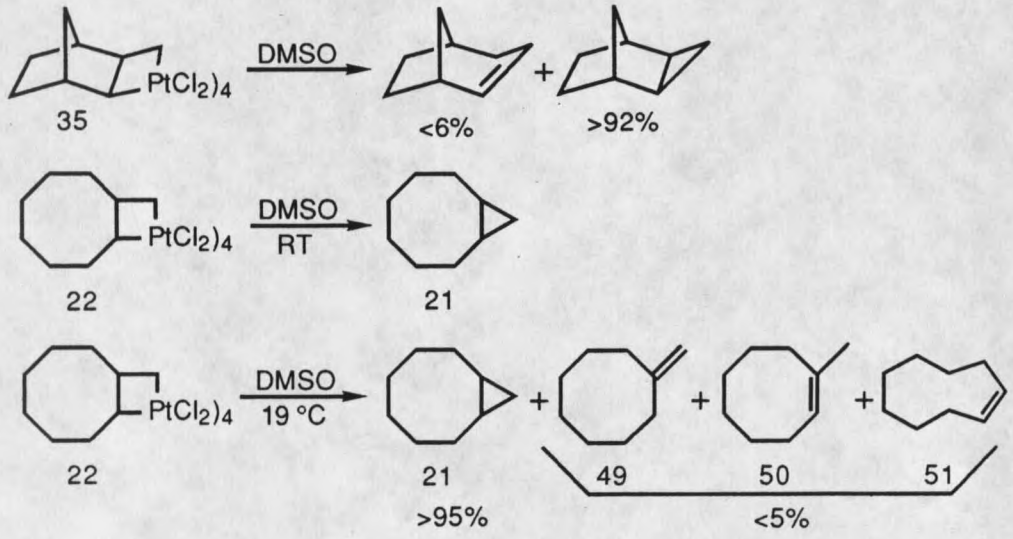


30 25 (34)

only hydrocarbon products observed by proton NMR spectroscopy. These results indicated that the platinacyclobutanes of **21** and **25** were formed and reacted with soft ligands similarly to the simple platinacyclobutanes previously reported.

The reaction of IPC **22** with DMSO was not so straightforward, however, as shown in Figure 30. At room temperature, reductive elimination proceeded as expected, but at 19°C a small amount of olefin products was obtained as well. Three olefins, **49**, **50**, and **51**, were formed and

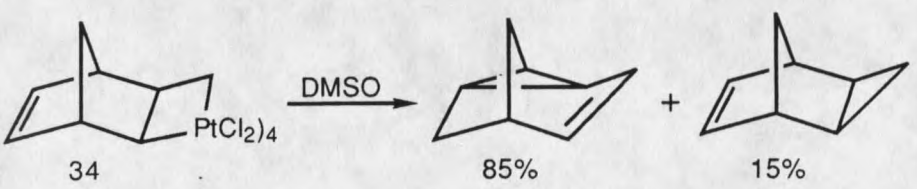
Figure 30. Reactions of Platinacyclobutanes **22** and **35** With DMSO.



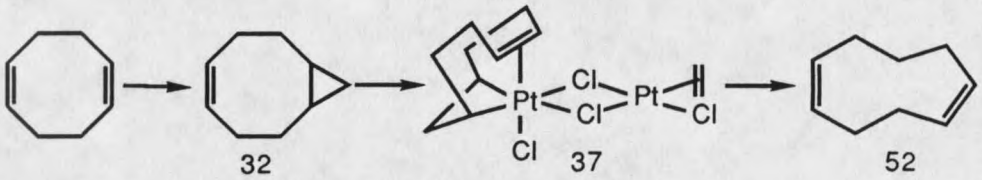
together constituted less than 5% of the product mixture. This reactivity is interesting, as it is more like that observed for norbornyl platinacycle 35[99], than for the simple cyclopropanes.

In an attempt to increase the yield of the olefins, the reaction was run at an even lower temperature. The DMSO was mixed with a two-fold excess of chloroform to keep it from freezing, and was cooled to -10°C. The reaction again produced olefins, but in smaller yield than was obtained at 19°C. This may have been the result of decreased DMSO concentration, rather than the lower temperature.

If complex 37 also reacted like its norbornyl counterpart[99] (equation 35), it would produce 1,5-cyclonondiene, 52, in good yield. This constitutes ring homologation with respect to the diolefin from which cyclopropane 32 was made (equation 36). Although ring expansion can be facilitated by conventional organic chemistry, it is not applicable to all systems. Platinacyclobutane rearrangements, therefore, might provide an alternative synthetic route to these products. Complex 37, in particular, appeared likely to undergo this reaction, as platinum had already disrupted the bridging bond.



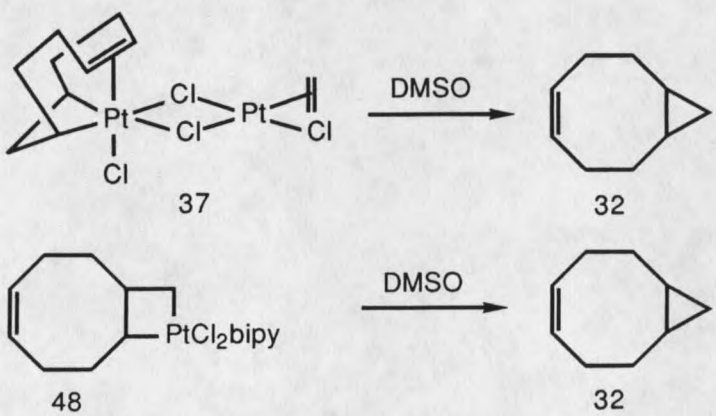
34 85% 15% (35)



32 37 52 (36)

Unfortunately, as illustrated in Figure 31, reaction of 37 with DMSO yielded only cyclopropane 32. This may have been a consequence of the dimeric nature of 37, however, since cleavage of the dimer by DMSO might have instigated immediate reductive elimination. The bipy monomer 48 was therefore reacted with DMSO, as shown in Figure 31. This reaction was very slow, indicating that it required prior dissociation of the bipy ligand. However, no products other than cyclopropane 32 were obtained from this reaction, either. These results suggested that the norbornyl complex 35 was receiving assistance from its olefin bond which was not available to the platinacyclobutanes of 32.

Figure 31. Reactions of Platinacyclobutanes 37 and 48 With DMSO.



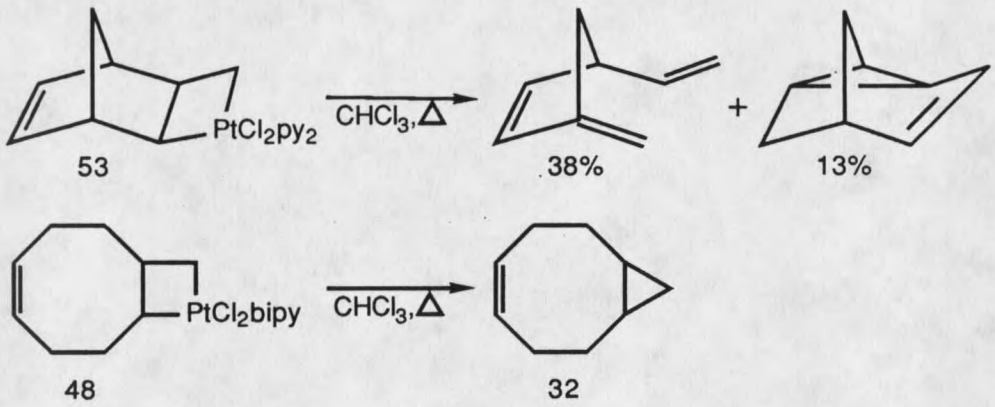
37 32

48 32

Thermal Decomposition of 23 and 48.

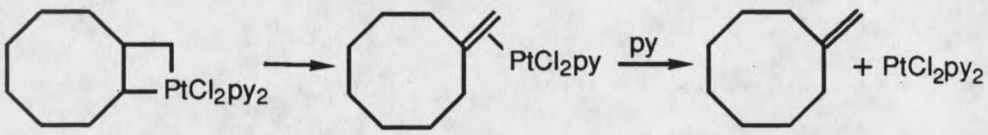
The thermal decomposition of **48**, shown in Figure 32, confirmed that **48** and the norbornyl complex **53** react differently. Again, a long reaction time was required, presumedly due to the presence of the chelating ligand, bipy. Upon completion, however, the volatiles contained only cyclopropane **32**.

Figure 32. Thermal Reactions of Platinacyclobutanes **48** and **53**.



Complex **23** decomposed much more rapidly, but its moderate stability allowed the process to be followed by ^{1}H and ^{13}C NMR. In chloroform or benzene at room temperature, the decomposition occurred over a period of six hours, and proceeded to the free olefin, **49** (equation 37). An intermediate platinum-bound olefin, **54**, was observed in a small, steady-state concentration by ^{13}C NMR spectroscopy. The

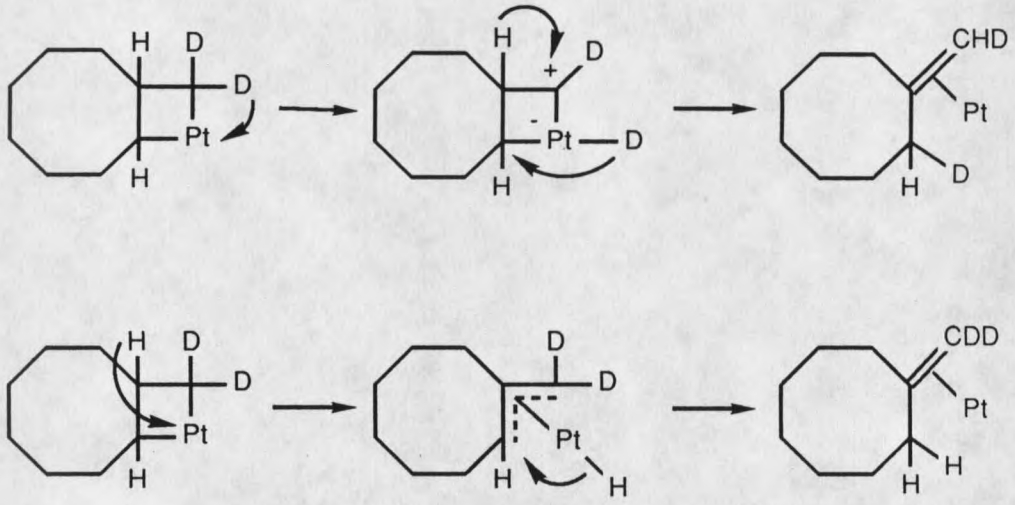
reaction was also monitored at -40°C and at 37°C, which showed the concentration of **54** to be proportional to the temperature, however no other intermediates were observed. The temperature dependence of **54** suggested that the rate of formation of **54** was more sensitive to temperature than was its decomposition rate, which allowed **54** to accumulate at higher temperatures.



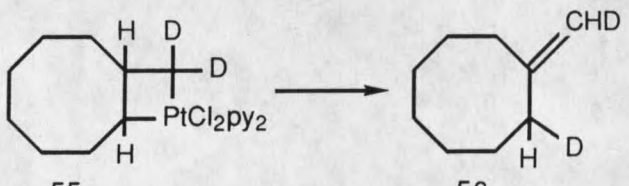
23 54 49 (37)

Two mechanisms have been described in the literature to account for the isomerization of platinacyclobutanes to olefins. These differ in whether the isomerization is initiated by an α-[92] or a ß-hydride[91] abstraction. The two mechanisms can therefore be distinguished by deuterium labelling as shown in Figure 33. Both mechanisms propose the formation of a platinum-hydride species, which should be visible in the ^{1}H NMR spectrum between δ-7 and δ-24. No such species was observed between -40°C to 25°C, however, nor has it been observed in other reported platinacyclobutane decompositions. Therefore, the platinum-hydride either never existed, or it was high in energy and existed too transiently to be observed.

Figure 33. Platinacyclobutane Decomposition Mechanisms as Differentiated by Deuterium Labelling.



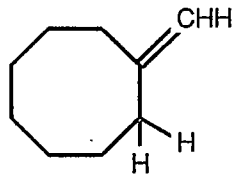
The product from the decomposition of the deuterated platinacyclobutane 55 was made and examined by proton and deuterium NMR spectroscopy (equation 38). An attempt to run the decomposition reaction in carbon tetrachloride, which contains neither protons nor deuteriums to interfere with the spectroscopy, proceeded very slowly and required more than 24 hours to complete. The rate difference was probably due to the change in solvent polarity and its effects on the charge separated transition state. The deuterium NMR



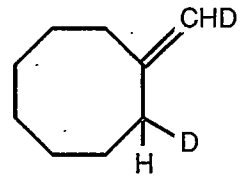
55 56 (38)

spectrum contained two peaks: one at δ4.77 and one at δ2.17, which are listed in Table 14. Integration of the proton NMR spectrum likewise showed the absence of one proton at δ4.74 and one at δ2.18. This data indicated that the product was formed via the α-hydride abstraction mechanism.

Table 14. ^{1}H and ^{2}H NMR Resonances for Olefins **49** and **56**.



49



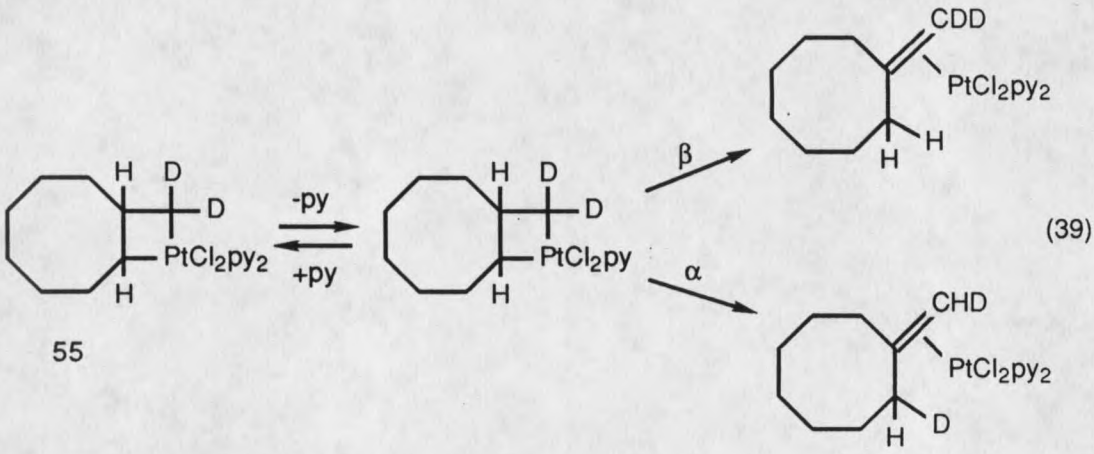
56

^{1}H NMR*	ppm	intg.	ppm	intg.
	4.74	2	4.74	1
	2.18	4	2.18	3
	1.63	4	1.63	4
	1.49	6	1.49	6
^{2}H NMR**			4.77	
			2.17	

* in $CDCl_3$ solvent
** in CCl_4 solvent

The integrations, however, were not consistent with exclusive formation of **56**. By ^{1}H NMR spectroscopy, the peak at δ4.74 actually contained less than one proton, compared to the peaks at δ1.63 and δ1.49. The δ2.18 peak overlapped with an impurity, and could not be integrated as accurately. Cyclopropane **57** contained 13% hydrogen at each deuterium position and after correcting for this, the integrations

indicated a product mixture of 80% 56 and 20% 58, where 58 was produced by the ß-hydrogen abstraction mechanism (equation 39). Twenty percent was a maximum, since the most probable integration error would have occurred if an impurity were coincident with the δ1.63 and δ1.49 peaks. This would have caused the olefin to appear low in hydrogen. It is interesting, however, that both α- and ß-hydrogen abstraction mechanisms appeared to be occurring, as it has been traditionally assumed that the reaction proceeds by only one mechanism.



55

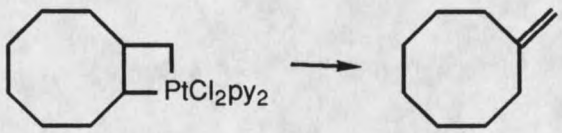
(39)

The kinetics of the reaction also indicated that other pathways were competing with the α-abstraction. Decomposition of 23 and 55 was monitored by integrating the platinacyclobutane H(3) peak at δ3.6 in the ^{1}H NMR spectrum. This peak appeared in an uncomplicated region of the spectrum and was unaffected by conversion to the deuterated compound. Scans were obtained every 1-10 minutes for five half lives,

and each point was obtained in one pulse. Loss of the reactant platinacyclobutane could be obtained in this manner. However, growth of the initial product **54** could not be adequately determined, as its resonances overlapped with those of the final product, **49**.

Reaction of non-deuterated **23** was monitored at 37°, 47° and 57°C and appeared to obey first order kinetics at all temperatures. Varying concentrations of 20, 30 and 40 mg/ml were monitored at 37°C and exhibited no significant rate differences. Three repetitions of each experiment were examined and the average rates from these are reported in Table 15. The decomposition of 30 mg/ml of **23** at 47° and 57°C confirmed an increase in rate with increasing temperature. Good correlations were obtained for all analyses.

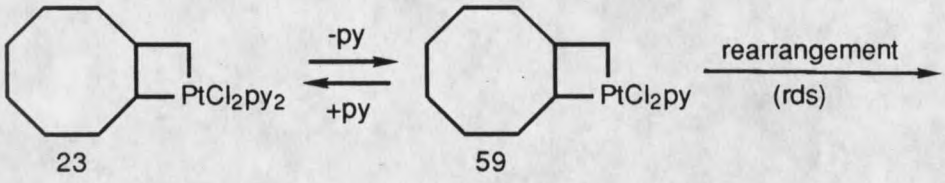
Table 15. Average Rate Constants for the Decomposition of Complex **23**.



23 49

Temperature (°C)	Concentration (mg/ml)	k (10^4 s^{-1})
37	20	8.6 ± 0.6
37	30	7.3 ± 0.8
37	40	6.9 ± 1.1
47	30	22 ± 2

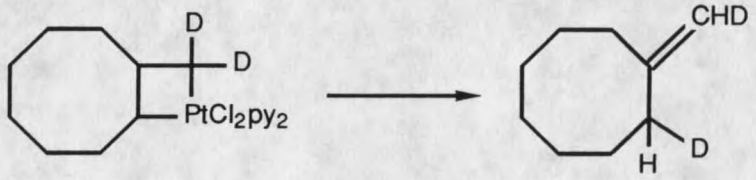
A plot of ln k vs. T^{-1} yielded activation parameters of $\triangle H^{\ddagger}$ = 19.4 ± 0.02 kcal mol^{-1} and $\triangle S^{\ddagger}$ = -6.2 ± 0.06 cal K^{-1} mol^{-1}. The entropy of activation was of little assistance in elucidating the reaction mechanism, since it fell in the $-10 < \triangle S^{\ddagger} < +10$ range where the contribution from solvent reordering is a complicating factor[104]. Furthermore, neither the entropy nor enthalpy of activation appeared to reflect the preequilibrium dissociation of pyridine known to occur prior to platinacyclobutane decomposition (equation 40). This reversible first step was probably very rapid compared to the rate determining step, since first-order kinetics were observed[105].



(40)

The kinetics of the deuterated compound, **55**, were also measured at 37°, 47° and 57°C for platinacycle concentrations of 30 mg/ml. The reactions again appeared to obey first order kinetics and the rates, which are displayed in Table 16, increased with increasing temperature. Comparison of the respective rates for **23** and **55** gave kinetic isotope effects (KIEs) of 2.5 at 57°C, 2.0 at 47°C, and 1.8 at 37°C. Extrapolation of the rates to 25°C yielded a KIE of 1.4.

Table 16. Average Rate Constants for the Decomposition of Complex 55.

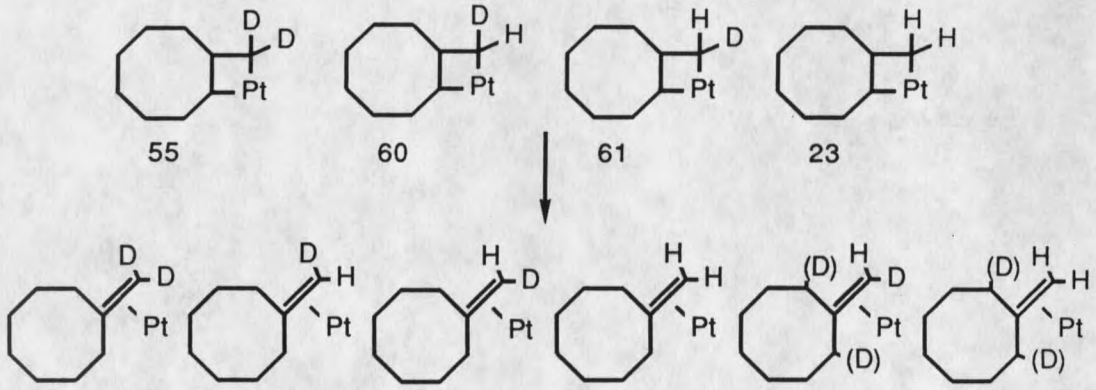


55 56

Temperature (°C)	Concentration (mg/ml)	k (10^3 s^{-1})
37	30	.43 ± 0.01
47	30	1.1 ± 0.1
57	30	2.3 ± 0.2

Obtaining KIEs in this manner is generally invalid unless the substrates are isotopically pure[106]. However, isotopic competition determinations were also deemed insufficient because the reaction began with four isotopomers, and produced up to six others, as shown in Figure 34. Mass spectral determination of the isotope positions can not distinguish between these isomers so, until a better method for deuterium incorporation is developed, the KIEs will be correspondingly inaccurate. The rate comparison method presented a useful qualitative KIE picture, however.

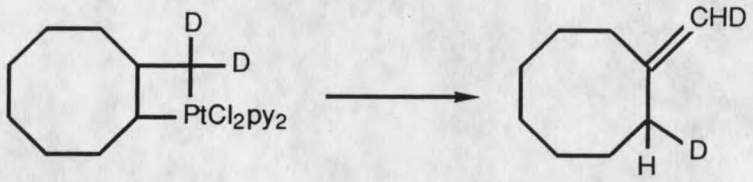
Figure 34. Possible Isotopomers in the Decomposition of 55.



A rough correction for hydrogen impurities was applied to the observed deuterium rate constants in the following manner. The reactant mixture was assumed to contain only 23 and 55 of which 13% was 55 as determined by proton NMR spectroscopy. This 55 reacted faster than 23 and was probably completely consumed during the monitoring of the reaction. A correction factor was therefore applied assuming $k_D obs = (.87)k_D + (.13)k_H$, and gave corrected deuterium rate constants as shown in Table 17. In fact, isomers 60 and 61 probably showed KIEs intermediate to those of 23 and 55, and the situation was further complicated by the concurrent α- and ß-abstraction mechanisms. The ß-mechanism should exhibit varying secondary isotope effects (SIEs) depending on the reactant.

Comparing the corrected deuterium rate constants to the observed hydrogen rate constants yielded KIEs of 3.6 at

Table 17. Corrected Rate Constants for the Decomposition of Complex 55.



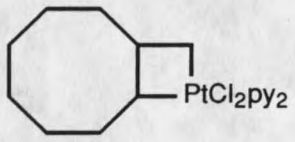
55 56

Temperature (°C)	Concentration (mg/ml)	k_{corr} (10^4 s^{-1})
37	30	3.3 ± 0.1
47	30	8.1 ± 0.1
57	30	16 ± 2

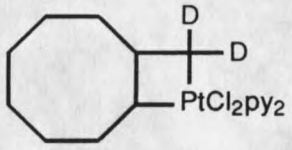
57°C, 2.7 at 47°C, and 2.3 at 37°C, with extrapolation to 1.7 at 25°C, as listed in Table 18. These KIEs obviously diverged at higher temperatures, as did the uncorrected KIEs. Therefore, the observed rates must have included contributions from two or more isotopically dependant processes. One possibility was that the pyridine preequilibrium may have been affected by deuterium α to the platinum. This could have been a <u>trans</u> effect whereby the deuterium changed the <u>trans</u> <u>influence</u> of the carbon, or a steric effect on the pyridine reassociation. Although possible, this effect is expected to be small compared to the partial occurance of the ß-mechanism.

As previously discussed, up to 20% of the reaction proceeded by the ß-hydrogen abstraction mechanism. This process should follow first order kinetics and show a SIE,

Table 18. Kinetic Isotope Effects for the Decomposition of Complexes 23 and 55.



23



55

Temperature (°C)	k_H/k_D observed	k_H/k_D corrected
57	2.5	3.6
47	2.0	2.7
37	1.8	2.3
25*	1.4	1.7

* obtained by extrapolation

which could be either normal if hyperconjugation effects dominate, or inverse if inductive effects dominate[106]. Some possible magnitudes of the rate constant for ß-abstraction were obtained by assuming it affected only the decomposition of 23 such that $k_H$obs = (.80)$k_H\alpha$ + (.20)$k_H\beta$. This yielded a $k_H\beta$ range of approximately $5*10^{-4}$ s^{-1} to $4*10^{-11}$ s^{-1} at room temperature. Furthermore, this model suggested a maximum KIE at 25°C of $k_H\alpha/k_D\alpha$ = 2. More precise modelling was prohibited by the complexity of the reaction and the lack of additional data.

Tunnelling was deemed insignificant in this reaction, because of the small KIE value obtained at 37°C and extrapolated to room temperature[108,109]. Comparison of the preexponential constants was useless, due to the rate divergence observed at high temperature.

Values of 1.4-2 are relatively small for a primary KIE at room temperature. This was probably due in part to the SIE component, but otherwise suggested the reaction proceeded through a bent transition state[29]. For a hydride transfer with an angle θ between the bonds to hydrogen in the transition state, a bend of $60° < \theta < 120°$ was probable. Of course the KIE magnitude also depends on the order of the bond being broken. Even for an angle of $\theta = 180°$, the KIE approaches unity as the bond order approaches one or zero in the transition state. Reported measurements of KIEs for intramolecular 1,2-hydride shifts in other systems generally fell between 1.5 and 3.3.

In summary, only qualitative KIE values for the decomposition of 23 and 55 were determined. A KIE of 1.4-2 at 25°C was suggested, and indicated a bent transition state geometry. Furthermore, the observed KIE increased at high temperatures which could be attributed to a rate contribution by the ß-hydrogen abstraction process.

As has been discussed, the rearrangement of platinacyclobutane 23 proceeded after loss of one pyridine ligand, however 23 was initially formed by adding two pyridine

ligands to IPC 22. Therefore, it was hypothesized that the reactive species could be obtained by adding only one pyridine ligand to IPC 22 in the first place. This was indeed the case, and the two reactions are compared in Figure 35. Both reactions formed olefin complex **54**, which rapidly released olefin **49** when reacted with a second equivalent of pyridine. However, in the reaction of IPC 22 with only one ligand, no second pyridine was available and complex **54** slowly isomerized to complex **62**.

This reaction of **22** with one pyridine suggested that multiple olefins produced from a platinacyclobutane rearrangement could be the result of a secondary olefin isomerization process, as illustrated in Figure 36, pathway (b). In the past, the formation of olefin mixtures from such reactions was thought to substantiate a π-allyl intermediate such as shown in pathway (a) (or see equation 22).

A mixture of olefins, shown in Figure 37, reaction (a) was obtained from the decomposition of platinacyclobutane **23** in refluxing chloroform. Formation of this mixture may have been due to isomerization of the intermediate olefin complex **54** as illustrated in reaction (c). At room temperature, the isomerization of olefin complex **54** to olefin complex **62** was shown to be slower than release of the olefin **49** by reaction of complex **54** with another equivalent of pyridine (reaction (b)). However, at elevated temperatures the rate of

Figure 35. Decomposition of Platinacyclobutane 22 with one or two Pyridines.

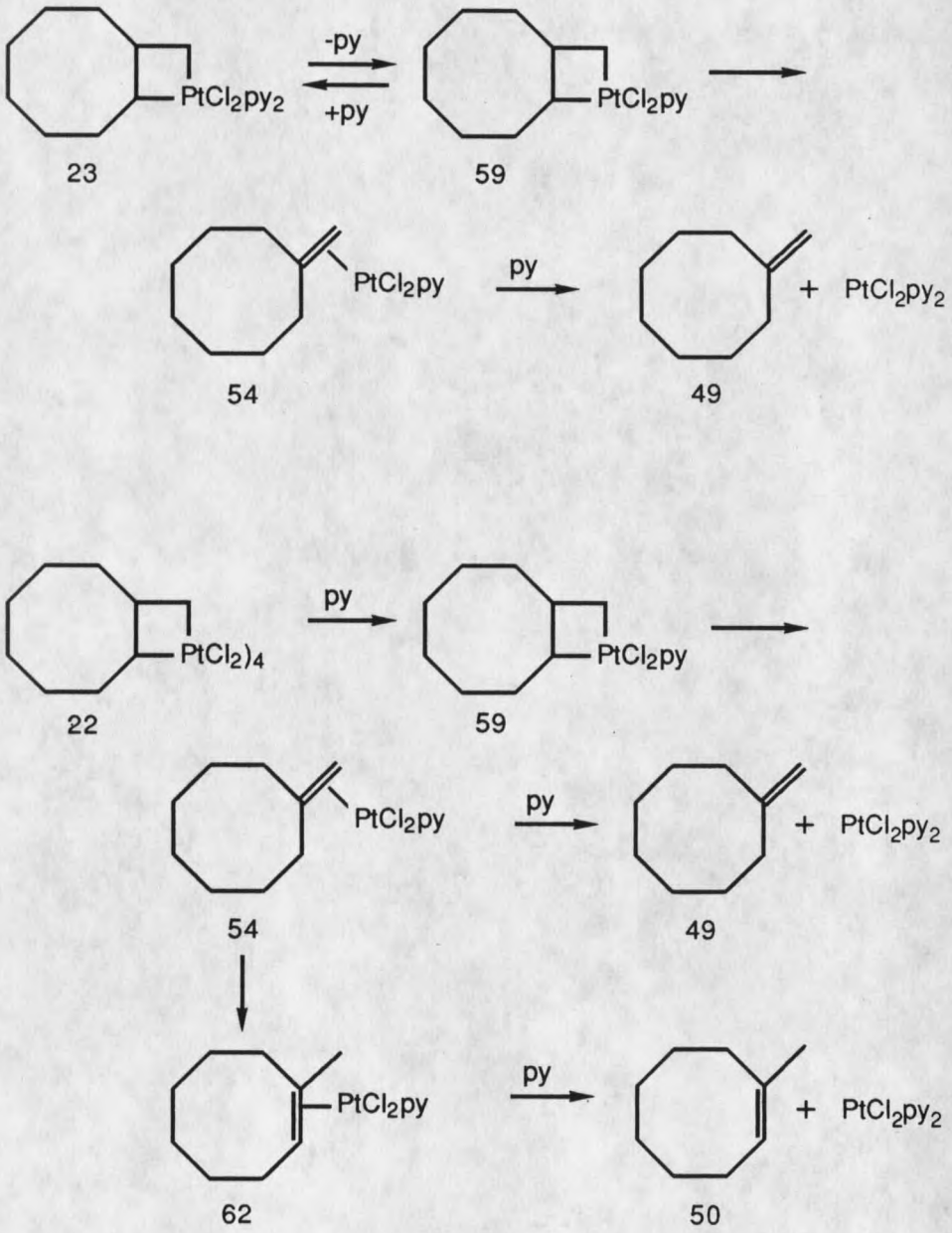


Figure 36. Possible Mechanisms for Producing Olefin Mixtures From Platinacyclobutanes.

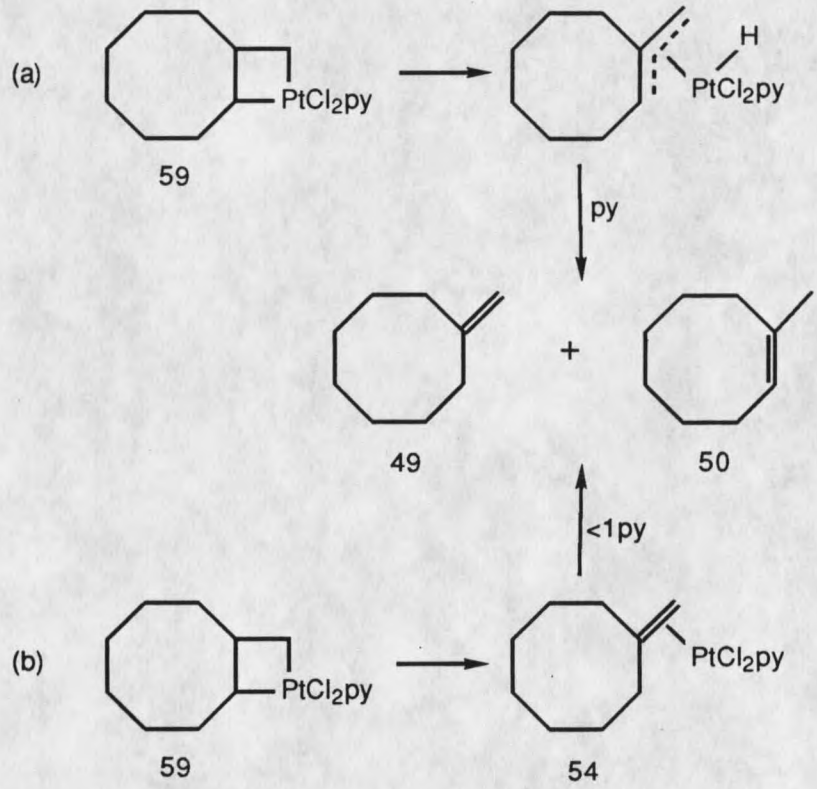
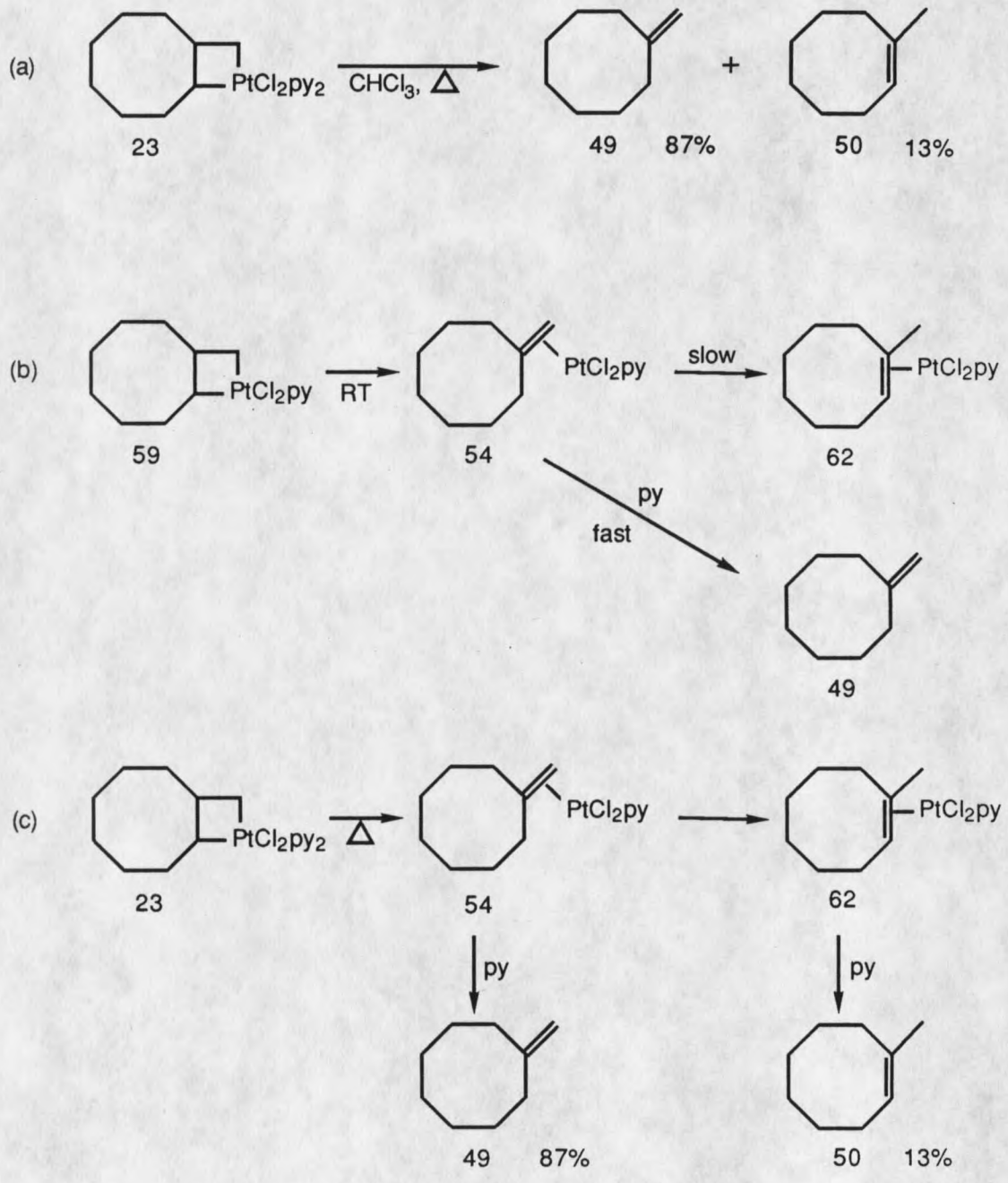


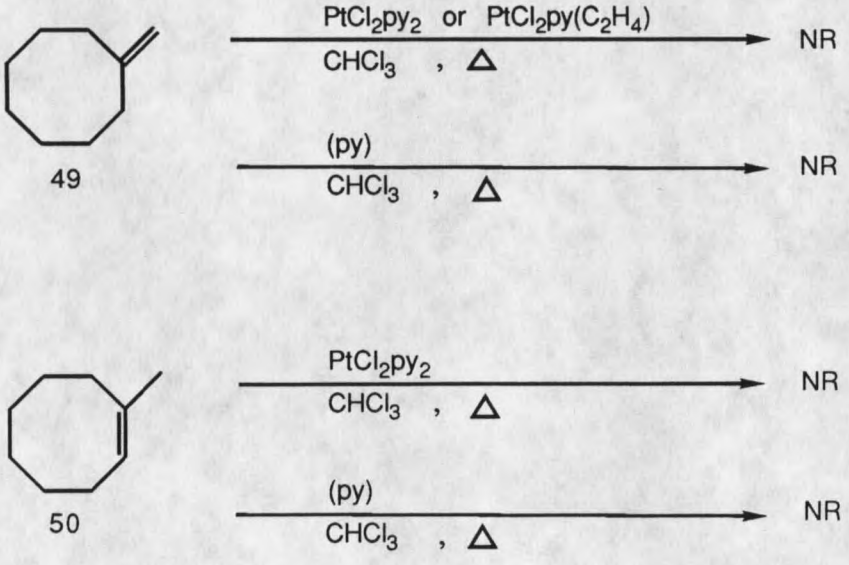
Figure 37. Thermal Decompositions of 23 Involving Isomerization of Olefin 54.



isomerization may have been competitive with the olefin release rate, allowing some formation of olefin **50**.

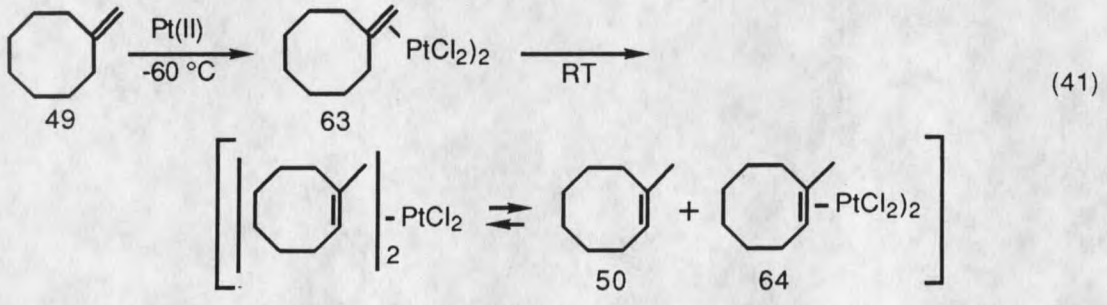
The species causing the olefins to isomerize is not known, but some possibilities have been ruled out and are displayed in Figure 38. From these it appeared that the reaction was not producing free olefin which then isomerized by reacting with a catalyst in the solution. For instance, bis(pyridine)platinum dichloride and Zeise's pyridine monomer could not cause the isomerization, as they did not react at all with standards of the olefins. Likewise, pyridine did not catalyze the rearrangement of the olefin standards, nor did the olefins undergo autoisomerization.

Figure 38. Species Not Responsible for the Isomerization of Olefins **49** and **50**.



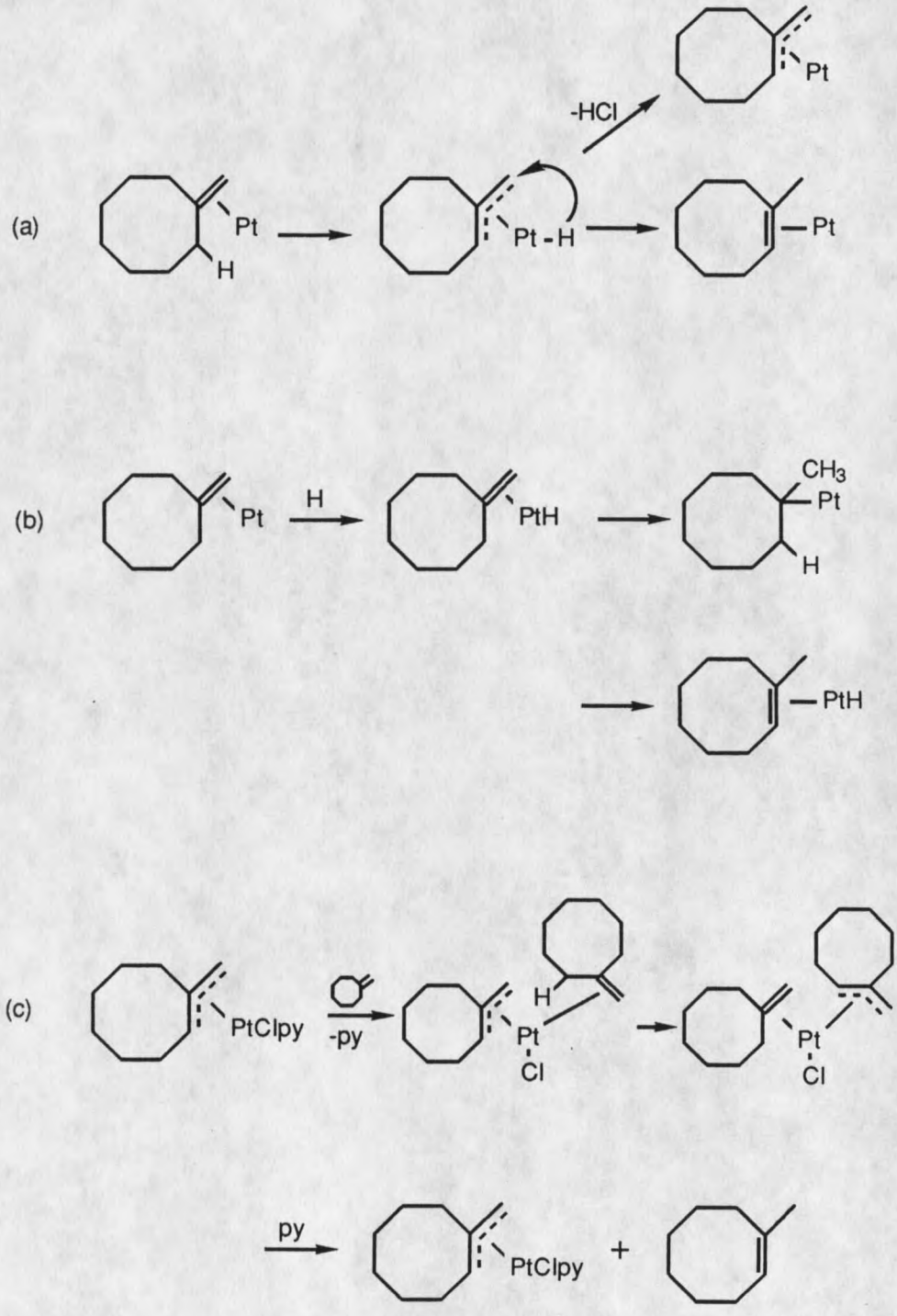
As shown in Figure 39, the platinum-bound olefin complex may have isomerized directly, either autocatalytically (mechanism (a)), or with the aid of an external hydrogen cocatalyst such as ethanol or HCl[38-41] (mechanism (b)). A small amount of a π-allyl complex was formed during the reaction, and may have been a side product from the autocatalytic isomerization. Alternatively, it may actually have been the isomerization catalyst, a possibility which is shown in mechanism (c) of Figure 39[42].

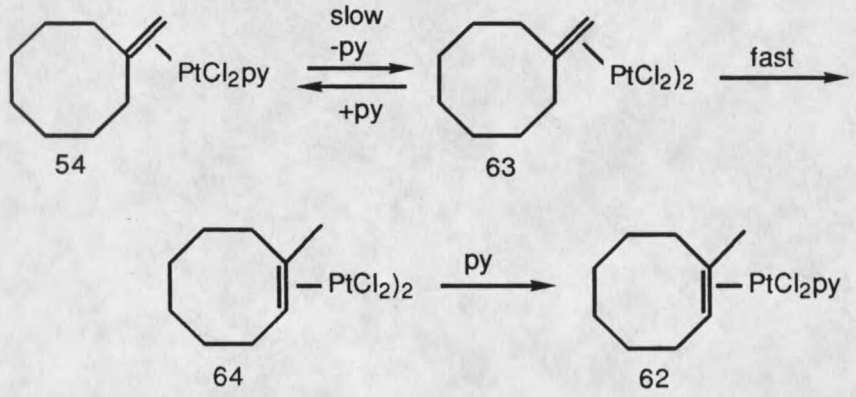
The isomerization of the platinum-bound olefins was studied independant of any complications from the platinacyclobutane rearrangement, by reacting the olefins directly with Zeise's dimer. In either chloroform or methylene chloride, olefin **49** rapidly formed an equilibrium mixture consisting of olefin **50** and its platinum complexes (equation 41). The intermediate platinum-bound olefin **63** could be observed by NMR spectroscopy at -60°C. Isomerization of **63** was very fast compared to that of its pyridine analogue, **54**, which suggested that **54** dissociated pyridine in a slow step prior to isomerizing (equation 42).



(41)

Figure 39. Possible Mechanisms for the Isomerization of Olefin **49**.





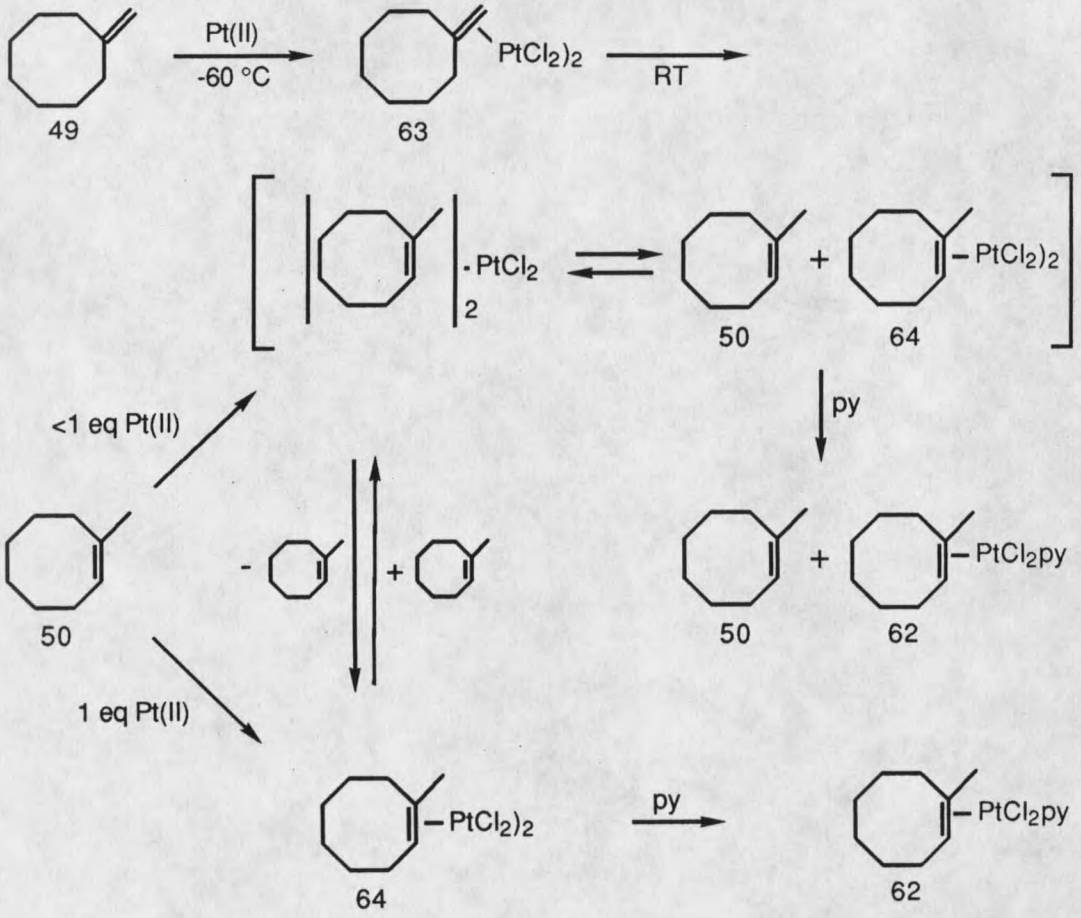
54 63 (42)

64 62

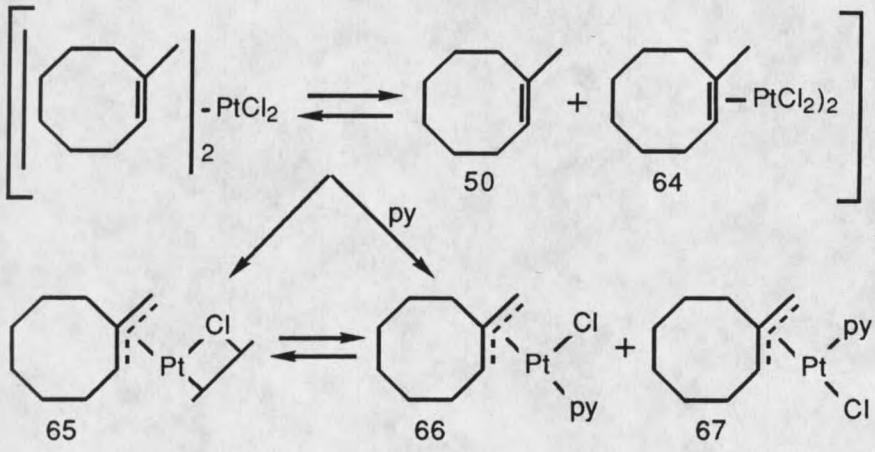
Addition of one equivalent of platinum to olefin **50** simply produced complex **64**, as shown in Figure 40. However, the addition of an excess of olefin **50** to the platinum yielded the same equilibrium mixture of **50** and its complexes as was obtained from the reaction of olefin **49**. This equilibrium was fast on the NMR time scale, but could be frozen out at -60°C. Excess **50** could also be removed from the mixture to generate complex **64**. Addition of pyridine to the mixture yielded olefin **50** and pyridine complex **62**. No formation of olefin **49** was observed at any point, indicating that the isomerization of **49** to **50** was preferred over that of **50** to **49**. These reactions are summarized in Figure 40.

As was mentioned previously, the isomerization of olefin **49** produced a small amount of a π-allyl complex. In fact, any process which proceeded through the equilibrium

Figure 40. Reactions of Olefins **49** and **50** With Platinum(II).

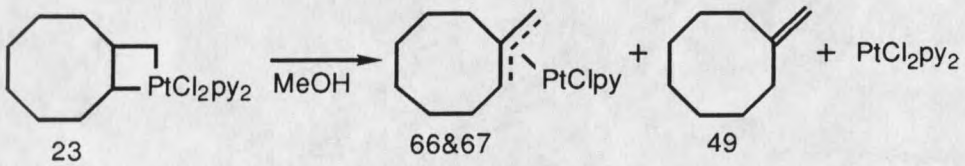


mixture of olefin **50** and its platinum complexes also produced a small amount of the π-allyl (equation 43). In the absence of pyridine, the π-allyl complex existed as a chlorine bridged dimer, **65**. With the addition of pyridine, however, two isomeric π-allyl complexes, **66** and **67**, were produced.



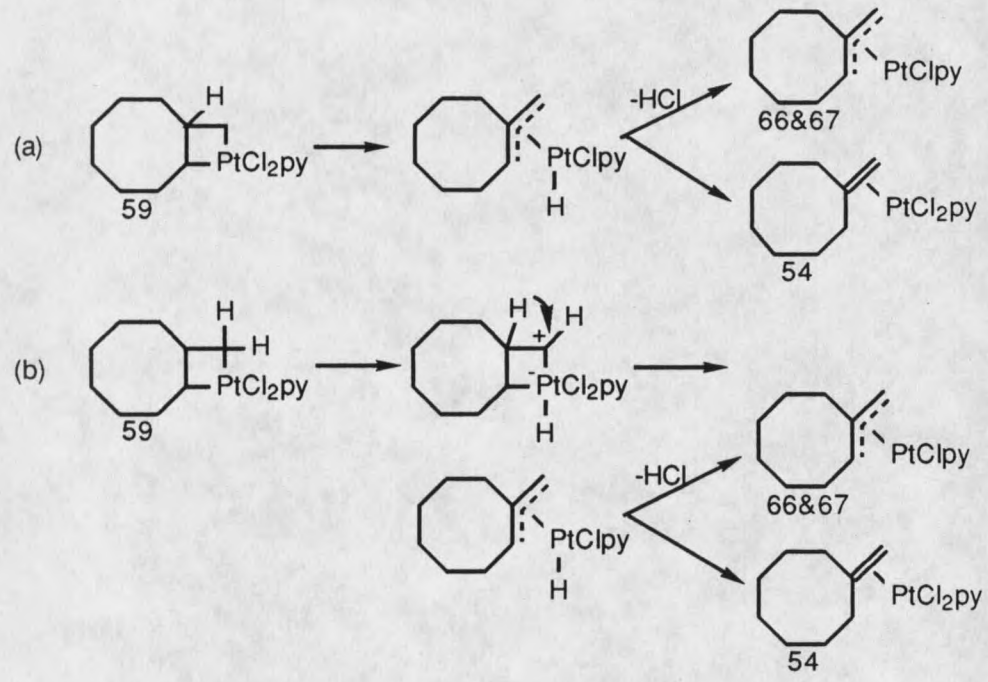
(43)

The rearrangment of platinacyclobutane 23 also produced the π-allyl isomers 66 and 67, in about 60% yield, when the reaction was run in methanol (equation 44). Since these products differed greatly from those obtained when the same rearrangement was run in chloroform, the change in mechanism was probably due to the increase in solvent polarity. As illustrated in Figure 41, a more polar solvent might have favored the ß-hydride abstraction mechanism (a), which could yield the π-allyl directly. Or it might have stabilized a charged intermediate in the α-hydride abstraction pathway (b), allowing the intermediate to form a π-allyl.

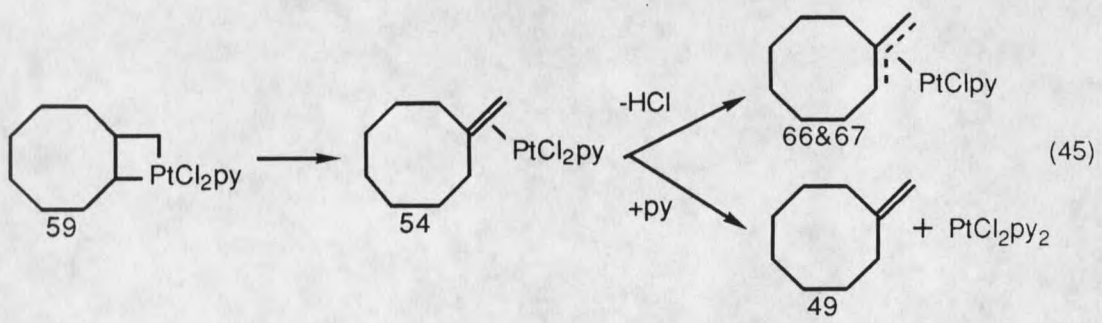


(44)

Figure 41. Formation of Pi-Allyls 66 and 67 From Decomposition of 23 in Methanol.

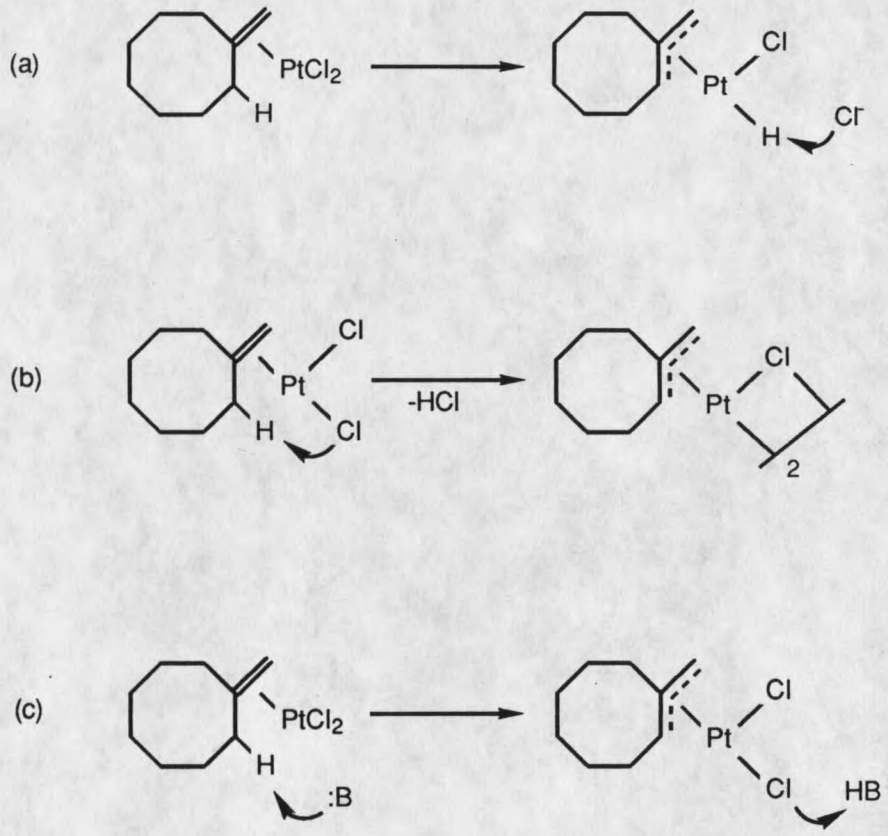


Another possibility is that methanol promoted π-allyl formation from the olefin complex **54** (equation 45). To accomplish this, a proton α to the olefin must have been removed by one of the three mechanisms[28] shown in Figure 42. Pathway (c) in particular might be promoted by a highly polar solvent.

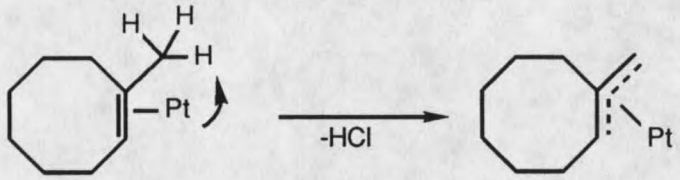


(45)

Figure 42. Possible Mechanisms For the Formation of a Pi-Allyl From Olefin Complex 54 Following Loss of a Pyridine Ligand.



The same processes are possibilities for π-allyl formation from both olefins **49** and **50**. The mechanisms involving olefin **50** are analagous to those in Figure 42, except that a proton from the methyl group is removed (equation 46).



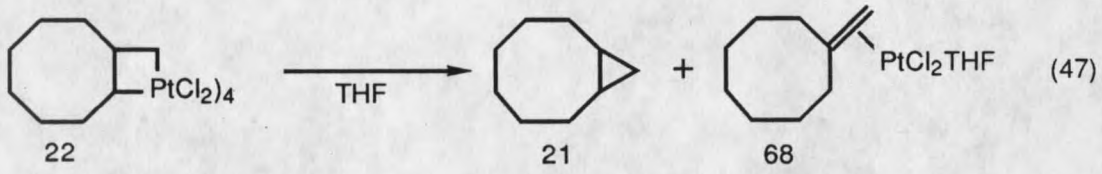
(46)

A closer examination of the π-allyl formation from platinacyclobutane **23** was undertaken by NMR spectroscopy. Complex **54** was observed prior to the appearance of the π-allyl complexes **66** and **67**, indicating it might have been their precursor. However, the difference in time between the complexes' respective appearances was slight, and given the spectroscopic sensitivity limits, may have been nonexistent. Therefore, it could not be determined whether **54** produced **66** and **67** or whether they were formed by concurrent pathways.

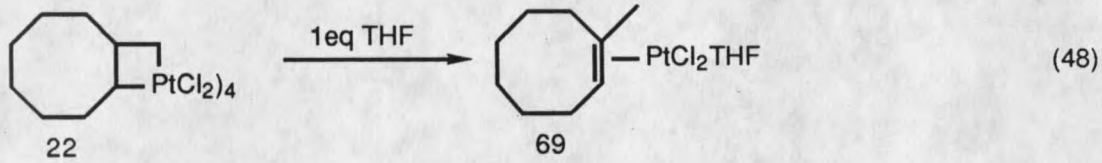
Reactions of **22** and **37** with THF and CO.

Secondary olefin rearrangement has been observed in other reactions of **22** as well. For instance, in excess THF,

a complex analagous to the pyridine complex **54** was observed and did not isomerize (equation 47). However, when **22** was reacted with only one equivalent of THF, it rearranged as observed previously for the reaction of **22** with one equivalent of pyridine (equation 48). This suggested that ligand deficiency instigated the olefin isomerization, while excess ligand inhibited the process.

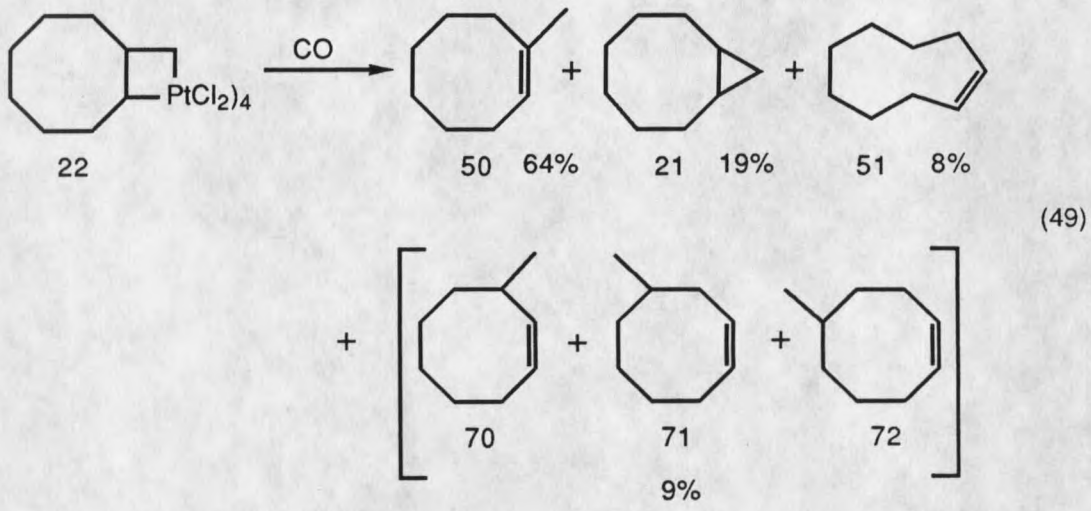


22 21 68 (47)



22 69 (48)

Reaction of **22** with carbon monoxide also involved a secondary isomerization of **49** to **50**. Simple platinacyclobutanes reportedly react with CO to form cyclopropanes[64], however **22** produced only 19% of **21** (equation 49). Specifically, placement of complex **22** under 80 psi of carbon monoxide for 36 hours produced a product mixture containing 64% **50**, 19% **21**, 8% **51**, and 9% minor methylcyclooctene isomers.

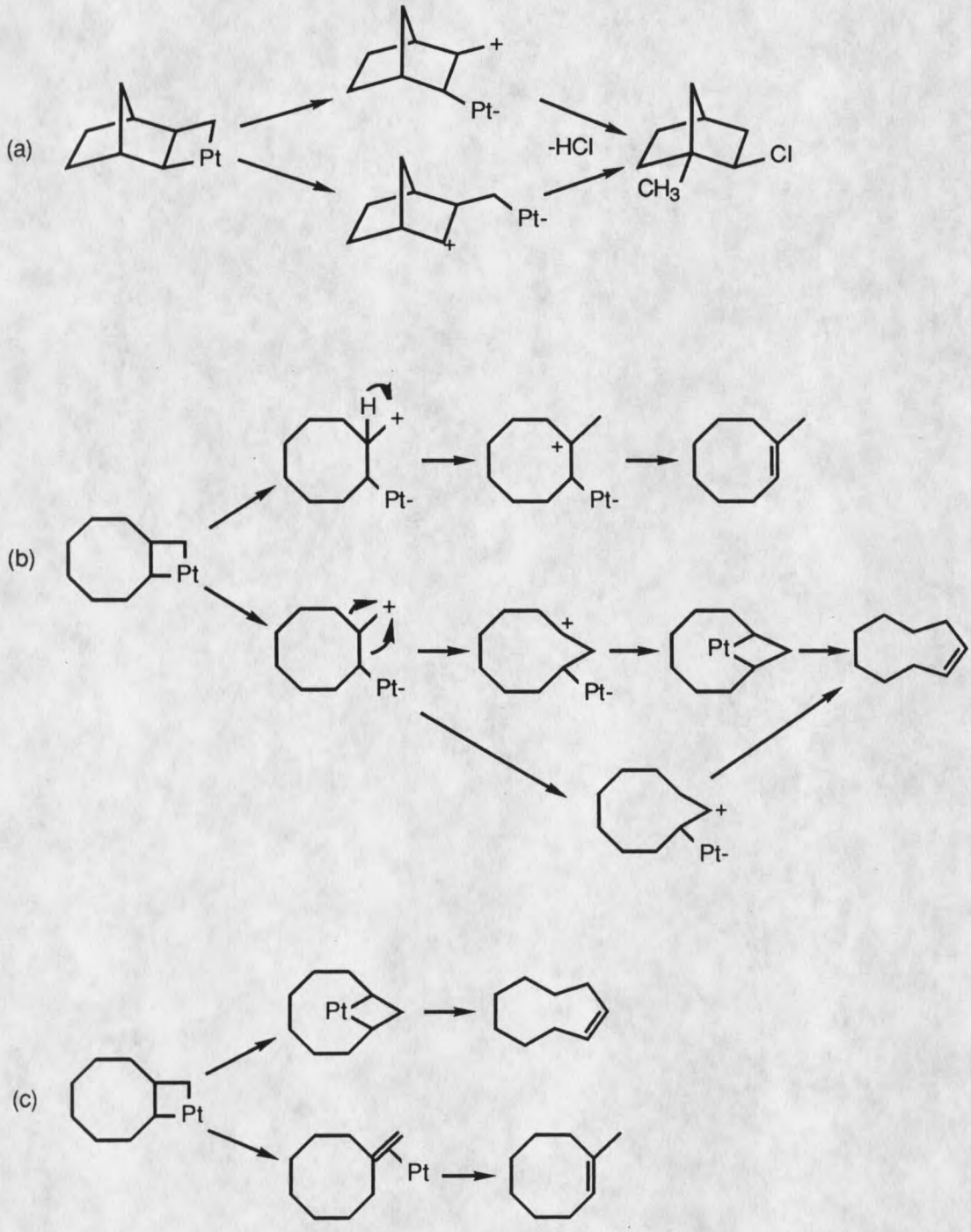


(49)

Olefins **70**, **71**, and **72** were probably products from further isomerization of **50**, but might also have been formed by reaction of cyclopropane **21** with acid in the solution[110]. However, under the reaction conditions, **21** was not observed to produce any methylcyclooctene products. A standard of **70** was made, and by comparison the product mixture was about 1% in **70**. Proton NMR data for **70** is listed in Appendix A. Olefins **71** and **72** exhibited similar proton NMR spectra, but were not rigorously differentiated.

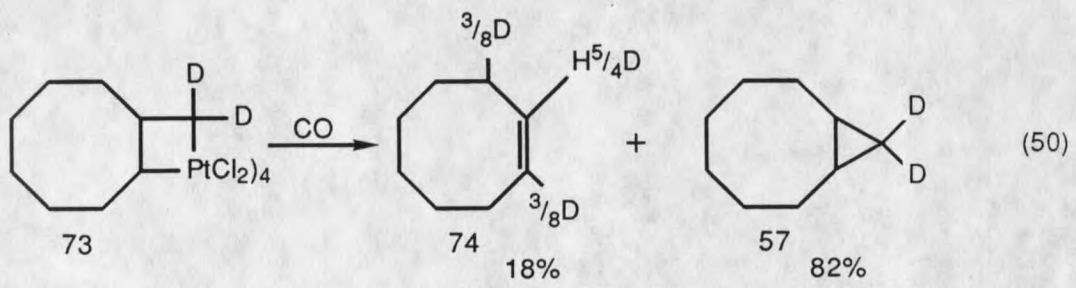
Since **22** did not mimic the simple platinacyclobutanes' reactivity, it might have undergone cationic rearrangement, illustrated in mechanism (b) of Figure 43, as did the norbornyl platinacycles[101] (mechanism (a)). Alternatively, as shown in mechanism (c), **51** may have arisen from a Puddephatt rearrangement of the platinacyclobutane, followed by either an α- or a ß-hydrogen abstraction process, and

Figure 43. Possible Mechanisms for the Reaction of Platinacyclobutanes with CO.



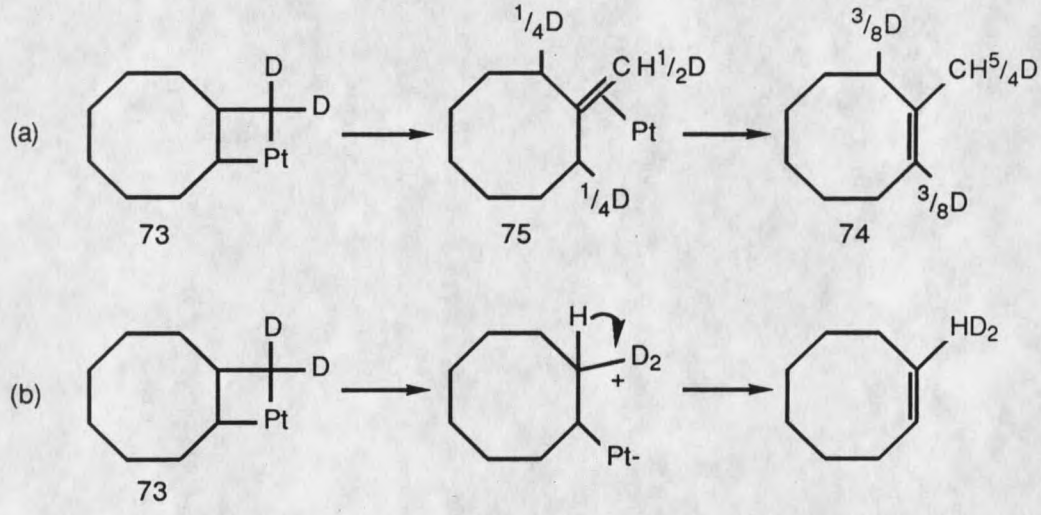
olefin **50** may have been formed by isomerization of **49** as has been discussed previously.

These mechanistic possibilities can be distinguished by determining the positions at which deuterium labelling is incorporated into **50**, as illustrated in Figure 44. The reaction was therefore run with deuterated **57** (equation 50), followed by ^{1}H and ^{2}H NMR product analysis. The ^{2}H NMR spectrum contained peaks at $\delta 5.33$, $\delta 2.09$, and $\delta 1.64$ which were assigned to compound **74**, and at $\delta 0.50$, and $\delta -0.32$ for **57**. Evidence for deuterium on the olefin indicated that the reaction proceeded through the exomethylene complex. This was supported by a substantial deuterium isotope effect which altered the product ratios. Cyclopropane became the major product from the deuterated substrate, while only 18% of **74** and none of the other olefins were observed. This suggested that the reaction proceeded through **75** in pathway (a) of Figure 44, since the deuterium isotope effect would disfavor **75**, and therefore **74** relative to **57**. Pathway (b) in Figure 44 should have exhibited a much smaller isotope effect.

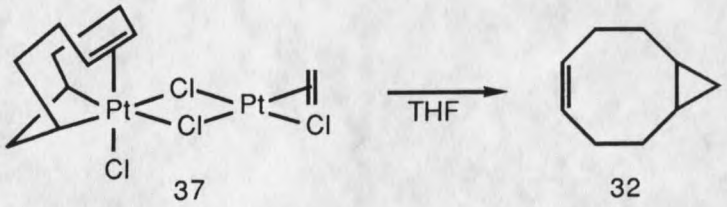


(50)

Figure 44. Deuterium Labelling to Distinguish Between the Possible Mechanisms in the Reaction of 22 with CO.

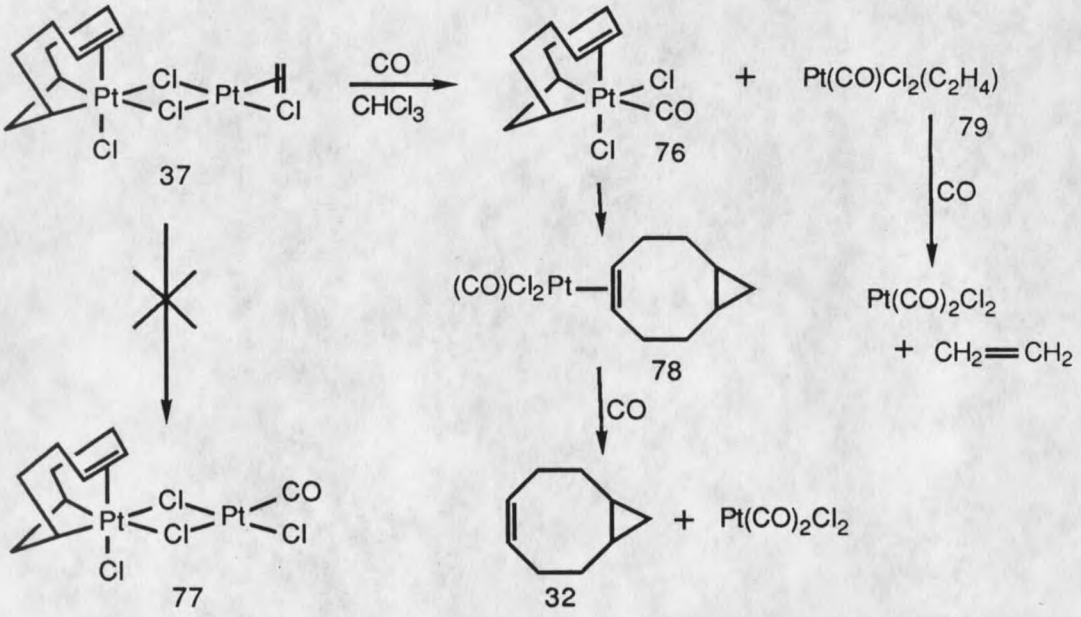


Complex 37 was also reacted with THF and CO. In THF solution, 37 yielded only cyclopropane 32 (equation 51). Once again, this may have been an artifact of splitting the dichlorodiplatinum ring. In fact, ligand induced cleavage of the dichlorodiplatinum ring followed by reductive elimination of cyclopropane 32 was directly observed in the reaction of 37 with carbon monoxide, as shown in Figure 45. In this case the decomposition was slower and could be followed by NMR spectroscopy.



(51)

Figure 45. Reaction of Complex 37 with CO.



Initially, carbon monoxide which was bubbled through a chloroform solution divided 37 into two monomers. These monomers could not be isolated, but were identified in solution by ^{1}H, ^{13}C and ^{195}Pt NMR, and IR spectroscopies. The infrared spectrum of 76 showed a terminally bound carbonyl resonance at 2070 cm^{-1}. Typically[111], terminally bound carbonyls resonate between 2140 and 1800 cm^{-1}, while bridging carbonyls appear at 1850-1700 cm^{-1}, and free carbon monoxide shows a band at 2143 cm^{-1}. A resonance ascribed to the platinum bound carbonyl was also observed in the ^{13}C NMR spectrum at δ151.6 with platinum coupling of 1557 Hz. Although no data for platinum(IV)-carbonyl model compounds was found, platinum(II)carbonyl couplings range from 960 to 1817 Hz[54], which correlates with the observed coupling.

Little change was seen in the rest of the carbon-13 NMR spectrum, except for broadening of the platinacyclobutane carbon peak at δ30. The ^{195}Pt NMR spectrum of complex **76** showed a resonance at δ1276. This was very different from the platinum(IV) resonance observed for complex **37** (δ2796) which suggested that the carbonyl was bound to the platinum(IV) as shown in **76**, and not to the platinum(II) as in complex **77**.

Platinum(IV) carbonyl complexes are rare and are usually halide or hydride complexes which exist as salts[54]. This made the observation of **76** both interesting and unexpected, but suggested that it should not be a stable complex. In fact, the reductive elimination of cyclopropane from **76** formed **78** and occurred in less than a week. Complex **78** then released free hydrocarbon **32** within three hours, while **79** released ethylene within two days. Bis(carbonyl)-platinum dichloride is proposed as the final platinum species formed, but was not actually identified. Resonances for **78** and **79** appeared in the ^{195}Pt NMR spectrum at δ1107 and δ778, respectively, and were identified by comparison to standards.

Thermal Rearrangement of IPCs 22 and 29

Thermal platinacyclobutane rearrangement occurred with the IPCs as well as with the monomeric species. The IPC

rearrangements were carried out in chloroform or diethyl-ether, after which the products were treated with potassium cyanide to release the hydrocarbons from their platinum complexes. The products were generally olefins, although cyclopropanes were obtained from any unreacted starting material. Examination of the products from the decomposition of **22**, previous to treatment with KCN, showed them to be the platinum-olefin complexes **63**, **64**, and **80**, shown in Figure 46. These were identified by comparison to standards, except in the case of **63**, and their NMR data is compiled in Appendix A.

The rearrangement of **22** proceeded slowly in refluxing chloroform, and was only 42% complete after 46 hours, as shown in Table 19. The disappearance of **22** was linear with

Figure 46. Thermal Decomposition of **22** Followed by Treatment with KCN.

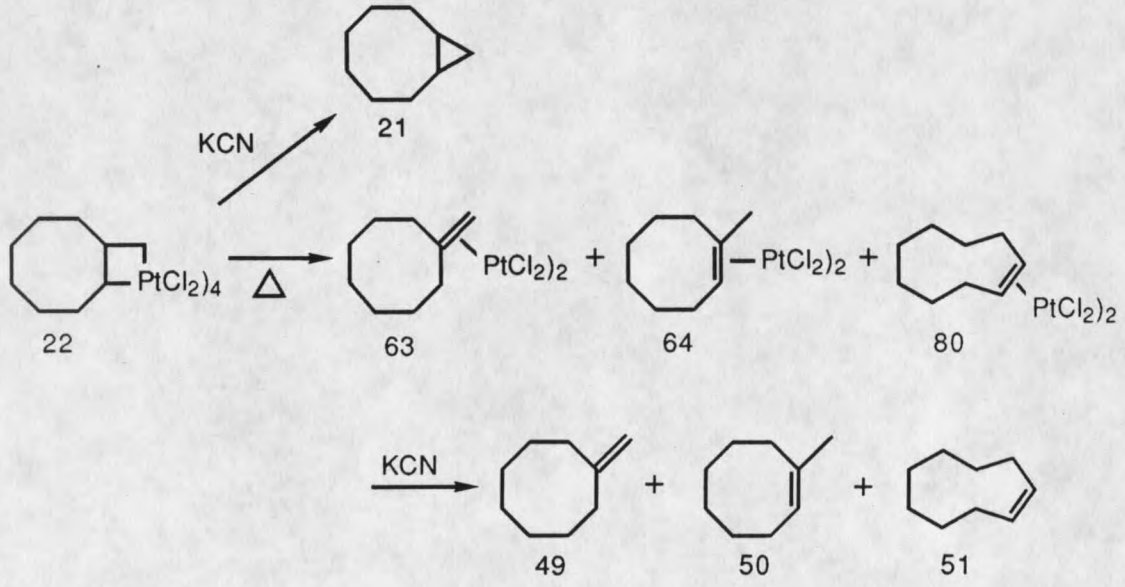
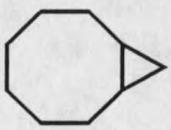
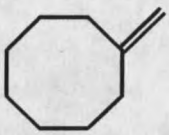


Table 19. Product Yields From the Decomposition of 22 With Time.

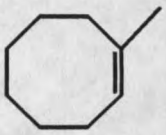
Absolute Yields



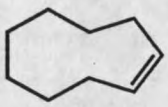
21



49



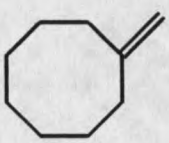
50



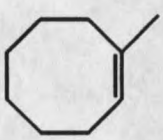
51

Time (hrs)				
1	100			
10	93.4	3.6	2.4	0.6
34	72.8	14.9	11.2	1.1
46	58.4	16.0	20.6	4.9

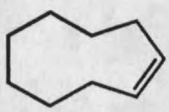
Relative Yields



49



50



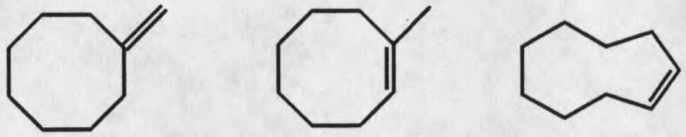
51

Time (hrs)			
10	54.5	36.3	9.1
34	54.9	41.1	4.0
46	38.5	49.6	11.9

time, but the relative yields of the olefin products were unpredictable. These variations may have been the result of integration errors, however, as signal-to-noise limited the proton integration accuracies below about 5%. Therefore, the only conclusion which could be drawn from this data was that **50** appeared to increase relative to **49** with time. In light of the previous olefin isomerizaton studies, this trend suggested that **50** was formed by isomerization of **49**, and that this rearrangement occurred faster that the formation of **49** by decomposition of **22**.

The interrelationships of the olefin yields, shown in Table 20, were examined without any platinacyclobutane decomposition contribution by isolating the products from the partial reaction of **22** in refluxing diethylether. These complexes were then refluxed in chloroform and aliquots were

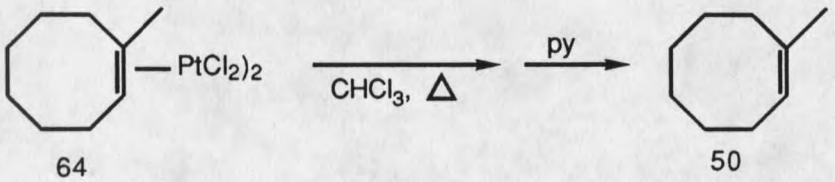
Table 20. Variation in Relative Concentrations of Olefins **49-51** Upon Heating With Platinum.



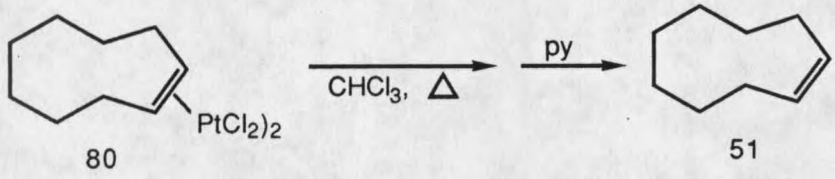
49 50 51

Time (hrs)			
0	45.4	27.1	27.4
6	56.4	24.3	19.3
12	67.0	21.0	12.0

removed after 0, 6, and 12 hours. The aliquots were treated with KCN, and the relative olefin yields were determined by proton NMR spectroscopy. In previous experiments, complexes **64** and **80** produced only olefins **50** and **51**, respectively, after being refluxed in chloroform and decomposed with pyridine (equations 52 and 53). The present experiment, however, suggested that **64** and **80** were rearranging to produce olefin **49**. This may have been due to the influence of cyanide ligand on the isomerization of the platinum-olefin complexes, and will be discussed in more detail for the analagous reaction of a different substrate.



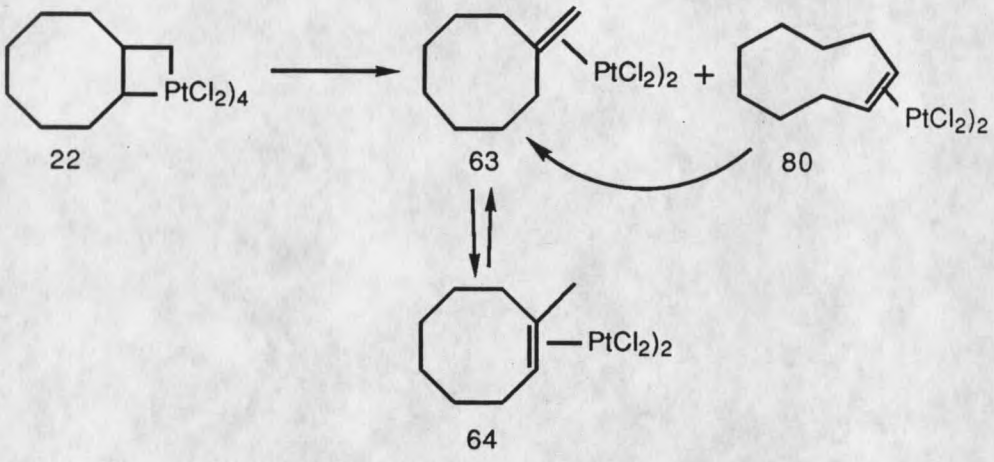
64 50 (52)



80 51 (53)

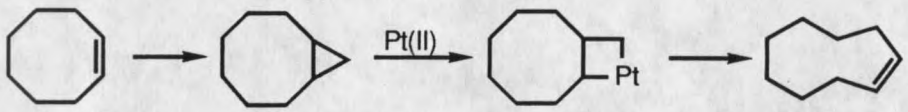
Although neither experiment was continued to equilibrium, the trends suggested that complex isomerization processes were occurring between the platinum-olefin species. At the very least the situation was probably similar to that depicted in Figure 47.

Figure 47. Possible Relationships Affecting the Relative Product Yields in the Thermal Decomposition of **22**.

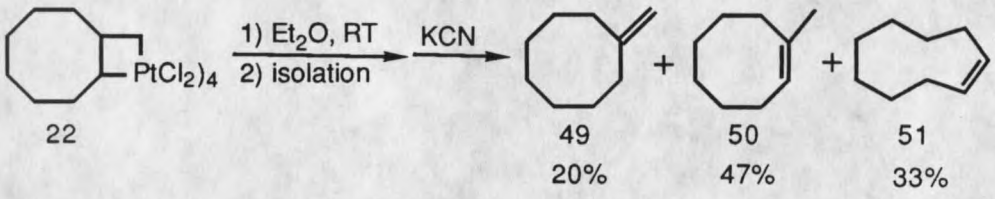


The production of olefin **51** was of synthetic interest, as it represented ring homologation with respect to cyclooctene, from which **21** was made (equation 54). Although formation of **51** was not unique to the thermal decomposition of **22**, it was this process which provided **51** in the highest relative yields. The highest yield observed was 33% relative to **50** and **49**, and was obtained from the room temperature decomposition of **22** in diethylether (equation 55). Since the application of heat to the platinum-olefin complexes appeared to decrease the relative yield of **51**, it was

hypothesized that lowering the reaction temperature might have the opposite effect.



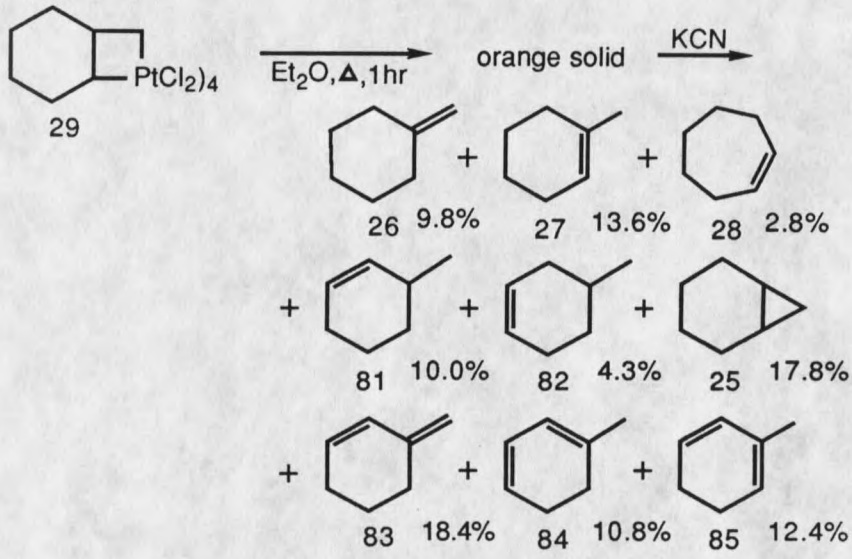
(54)



(55)

The decomposition of **22** in diethylether was therefore attempted at -5°C. After six months, the reaction had barely progressed, but the products consisted of a plethora of olefinic species. This suggested that the low temperature greatly decreased the rate of IPC decomposition, while the long reaction time permitted isomerization of any olefin products formed. Therefore, if the yield of **51** is to be maximized at low temperatures, a means of simultaneously decreasing the reaction time must be employed.

The decomposition of IPC **29** was much more rapid, and was complete after one hour in refluxing ether (equation 56). Treatment of the products with KCN yielded a mixture of olefins, which included **78**, **79**, and **80** (the three analogues of **49**, **50**, and **51**) and the two other methylolefin isomers, **81** and **82**. Most surprising, however, was the formation of three dienes, **83**, **84**, and **85**. All the olefins, with the

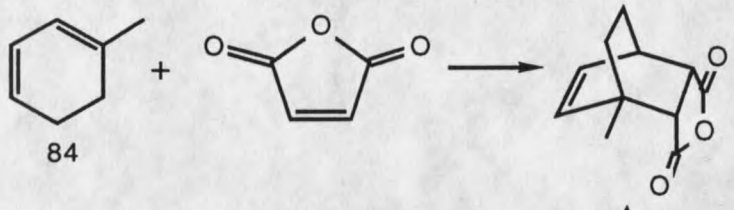


(56)

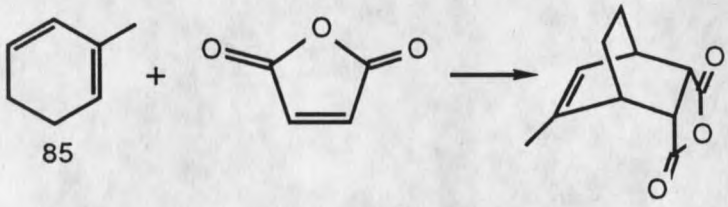
exception of **85**, were identified by comparison to standards. The NMR and GC-MS data for these olefins can be found in Appendix A. Relative yields were determined by capillary GC with mass spectral detection, and are reported as averages of several experiments. Olefins **81** and **82** appeared as one GC peak, so their relative yields were determined by ^{1}H NMR spectroscopy. Some polymeric material was also obtained, but was not examined.

Olefin **85** was identified by comparing its ^{1}H NMR and MS data, which is compiled in Appendix A, to those reported in the literature[112]. However, **85** was isolated as a mixture with **84**, and its ^{1}H NMR data was accordingly imprecise. Further confirmation of the identity of **85** was therefore obtained by reacting the entire product mixture with maleic anhydride. After refluxing in chloroform for 5 minutes, a dramatic decrease in the GC-MS total ion current peaks

assigned to **84** and **85** was observed. Therefore, **84** and **85** were shown to be dienes capable of forming Diels Alder products with maleic anhydride (equations 57 and 58), while none of the other olefins were.



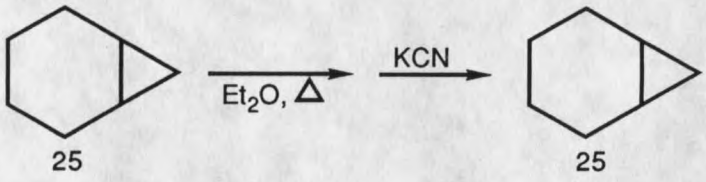
84 (57)



85 (58)

The solubilities of the intermediate complexes were such that removal of the initially precipitated orange solid (see equation 56) yielded mostly **84** and **85**, after treatment with KCN. Slow evaporation of the filtrate yielded more precipitate which, upon KCN treatment, produced increasing amounts of **85** relative to **84**. Finally upon complete solvent removal, the entire olefin mixture was obtained. For this reason all the solid product was normally collected and examined at once.

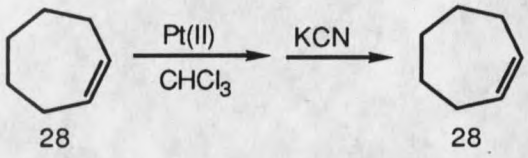
Several reactions were undertaken in an attempt to determine the origins of the various olefin products. The presence of platinum was shown to be crucial, as a blank run with only cyclopropane **25** also produced **25** (equation 59).



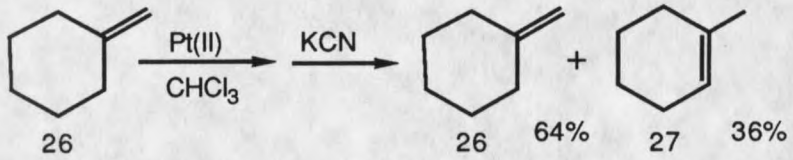
(59)

Isomerization processes could produce some of the olefins, however, as has been previously reported and discussed for the reaction of platinacycle **22**. To explore this possibility, standards of the olefins with the exception of **85** and **82** were individually reacted with platinum under conditions similar to those used in the decomposition reaction. Only trends were observed, as the isomerizations were not continued to equilibrium.

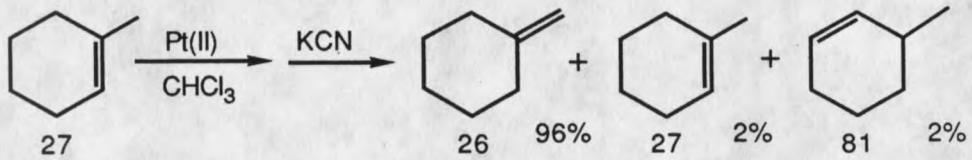
Cycloheptene did not isomerize, except possibly to other cycloheptenes, which were indistinguishable without a marker in the molecule (equation 60). Olefins **78** amd **79** appeared interconvertible, while **48** also partially rearranged to another methyl olefin isomer, **52** (equations 61 and 62). A similar isomerization of 1-methylcycloalkene to n-methylcycloalkenes was proposed to account for the product mixture obtained from the reaction of IPC **22** with CO. Interestingly, in similar experiments where the products were treated with pyridine instead of KCN, **79** was not oberved to rearrange at all, and the isomerization of **78** was curtailed (equations 63 and 64). This suggested that the ligand properties of ^-CN, which is softer and a better <u>trans</u> director than pyridine, caused it to promote platinum


Pt(II)
CHCl3
KCN
28
28

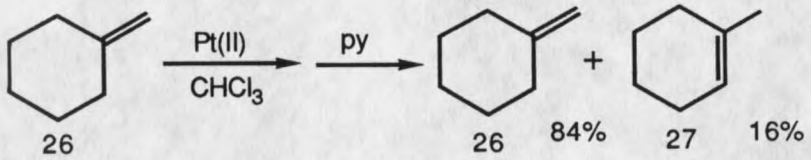
(60)


Pt(II)
CHCl3
KCN
26
26
64%
27
36%

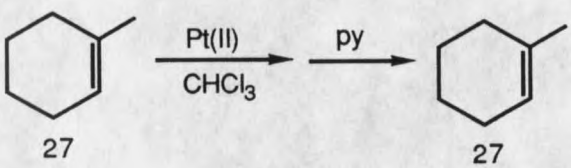
(61)


Pt(II)
CHCl3
KCN
27
26
96%
27
2%
81
2%

(62)

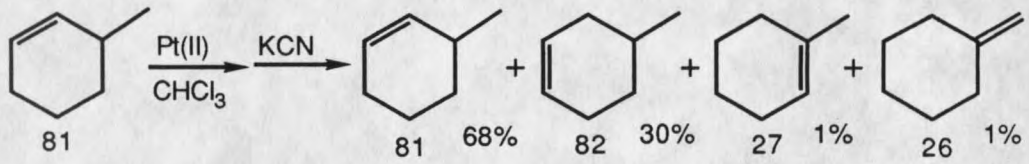

Pt(II)
CHCl3
py
26
26
84%
27
16%

(63)


Pt(II)
CHCl3
py
27
27

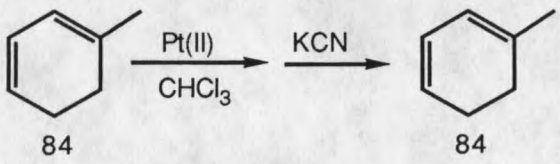
(64)

induced olefin rearrangements. This possibility was also observed for the analagous decomposition of **22**. The isomerization of **81** (equation 65) illustrated the complexity of the rearrangement contribution to the relative olefin yields.

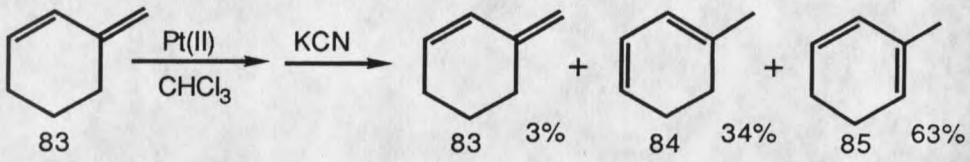


(65)

Dienes **83** and **84** were reacted in a similar manner, and were expected to yield the more thermodynamically stable **83**. However, **84** did not appear to isomerize (equation 66), while **83** rearranged almost completely to **84** and **85** (equation 67). This suggested that the products were controlled by the stability of their bonds to platinum, with <u>cis</u>-dienes bonding more strongly than <u>trans</u>-dienes, and not by the inherent stability of the dienes. Furthermore, it indicated that of the diolefins in equation 56, only diene **83** needed to be formed initially, while its subsequent isomerization could have produced the other dienes, **84** and **85**.



(66)

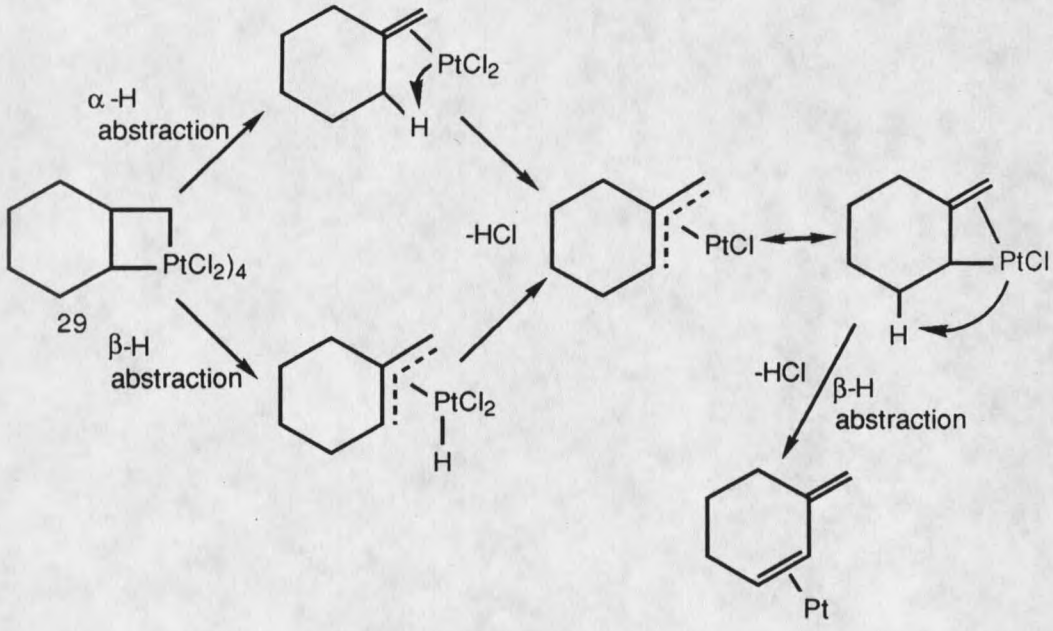


(67)

One possible mechanism to explain the formation of **83** is illustrated in Figure 48, and involves a π-allyl type intermediate which could arise from either the IPC **29** or the olefin complex **86**. The IPC could proceed by a ß-hydrogen abstraction mechanism to form a π-allyl, from which loss of HCl would produce a platinum(II) species. The same complex could also arise by abstraction of a hydrogen α to the olefin in complex **86**, again followed by loss of HCl. A second hydrogen abstraction and HCl loss from the platinum-(II) species could then produce **83** complexed to a platinum(0). Further isomerization might be induced by platinum(0), or reaction with HCl could regenerate platinum(II). Although purely speculation, this mechanism illustrates that rationalization of the diene products observed from decomposition of IPC **29** is possible.

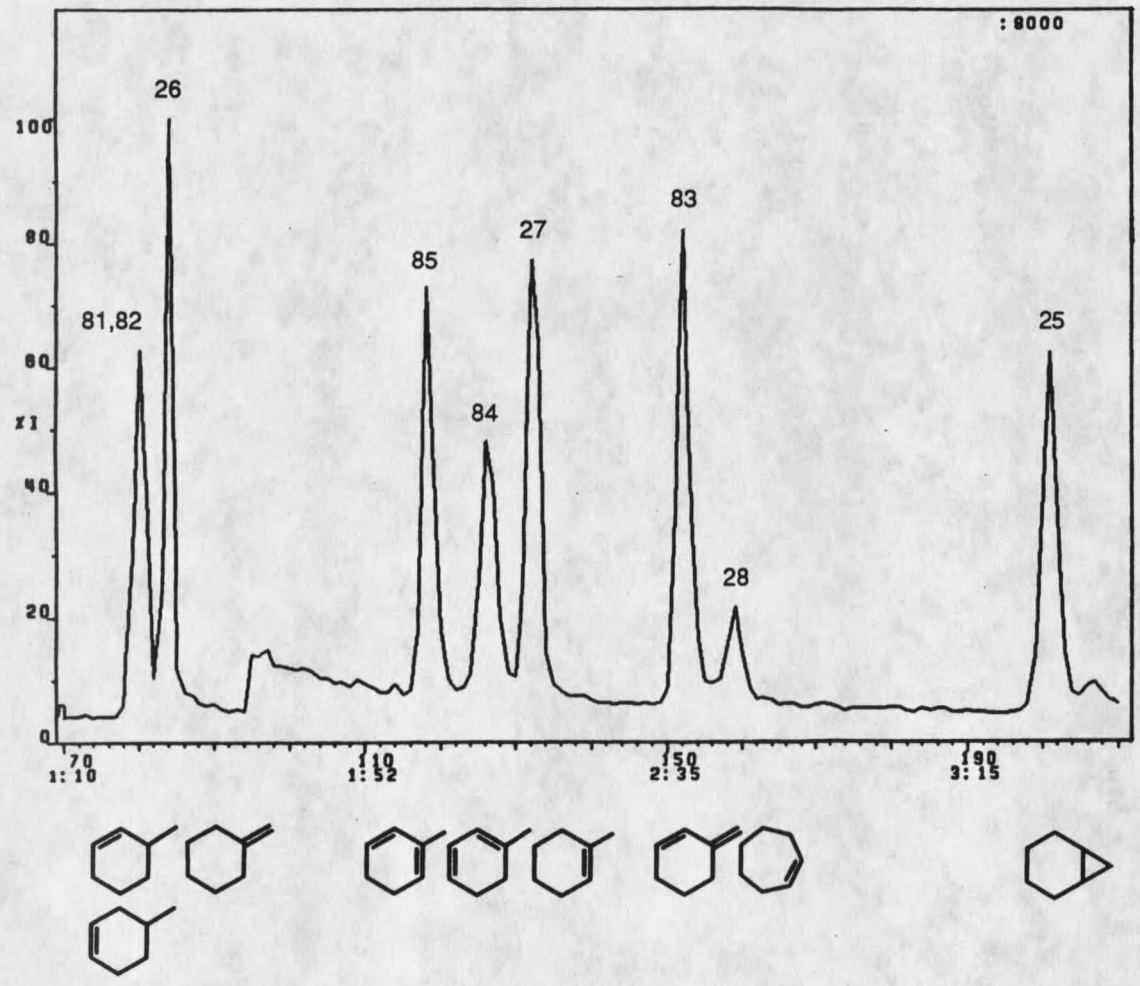
Although the decomposition of IPC **29** led to the described olefin mixture, McQuillin[66] previously reported that the reaction of cyclopropane **25** with platinum under identical conditions produced only **26**, **27** and **28** in 2:2:1 relative yields. Therefore, McQuillin's reaction was repeated to determine if it did in fact yield different product ratios. In our hands the two reactions were

Figure 48. A Possible Mechanism for the Formation of Diolefin 83 by Thermal Decomposition of 29.



identical, with no change other than a decrease in rate on going from 34°C to -10°C. There is still the possibility that McQuillin's actual reaction conditions were sufficiently different from ours as to give different results. However, McQuillin's product analysis was done by GC, and the products may have been missassigned. The capillary GC used in our analysis resolved all the products except 81 and 82, but the peaks were clustered in three groups. This pattern is displayed in Figure 49. Each group contained one of McQuillin's reported products as well as one or two other products. Assuming that McQuillin was only able to resolve the clusters, and not their individual constituents, only three peaks would have been detected. The relative yields of

Figure 49. GC Peaks for Compounds 25-28, and 81-85.



the clusters corresponded to 1.2 (78) : 1.9 (79) : 1 (80), while McQuillin reported 2 (78) : 2 (79) : 1 (80). This difference may reflect the response variation between a mass spectrometer detector and a conventional GC detector.

Reaction of 23 and 37 with CH_2N_2.

The reactions of platinacyclobutanes thus far discussed have involved isomerization of the basic hydrocarbon skeletons, with no overall change in atoms or functional groups. The next two sections will therefore present reactions of this latter type.

Diazomethane is a reagent which, when reacted with platinacyclobutanes, results in the addition or removal of a CH_2 unit, as shown in Figure 50. The mechanism may involve fragmentation of an intermediate platinacyclopentane, and could produce olefins 87 - 91 from complexes 22 and 37, as illustrated in Figure 51. Although the symmetric platinacyclopentane has been previously proposed as the intermediate, an assymetric isomer, also shown in Figure 51, is possible[99].

The reaction of 22 with diazomethane produced a 21% relative yielded of 88 (equation 68), possibly via the assymetric platinacyclopentane. Other products included the reductively eliminated cyclopropane 21, and olefins 49 and

Figure 50. Precedence for Possible Products from the Reactions of 22 and 37 with CH_2N_2.

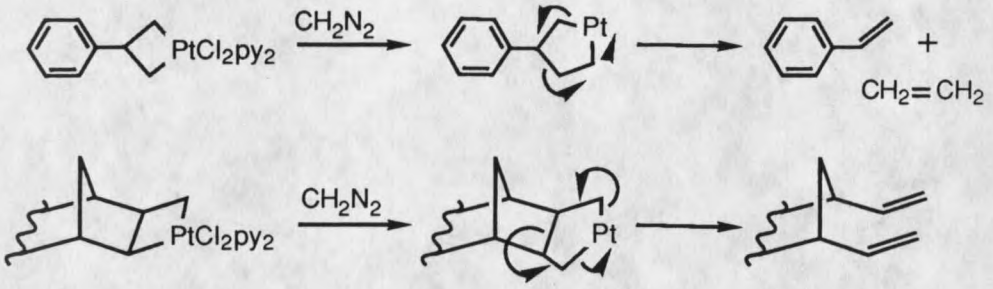
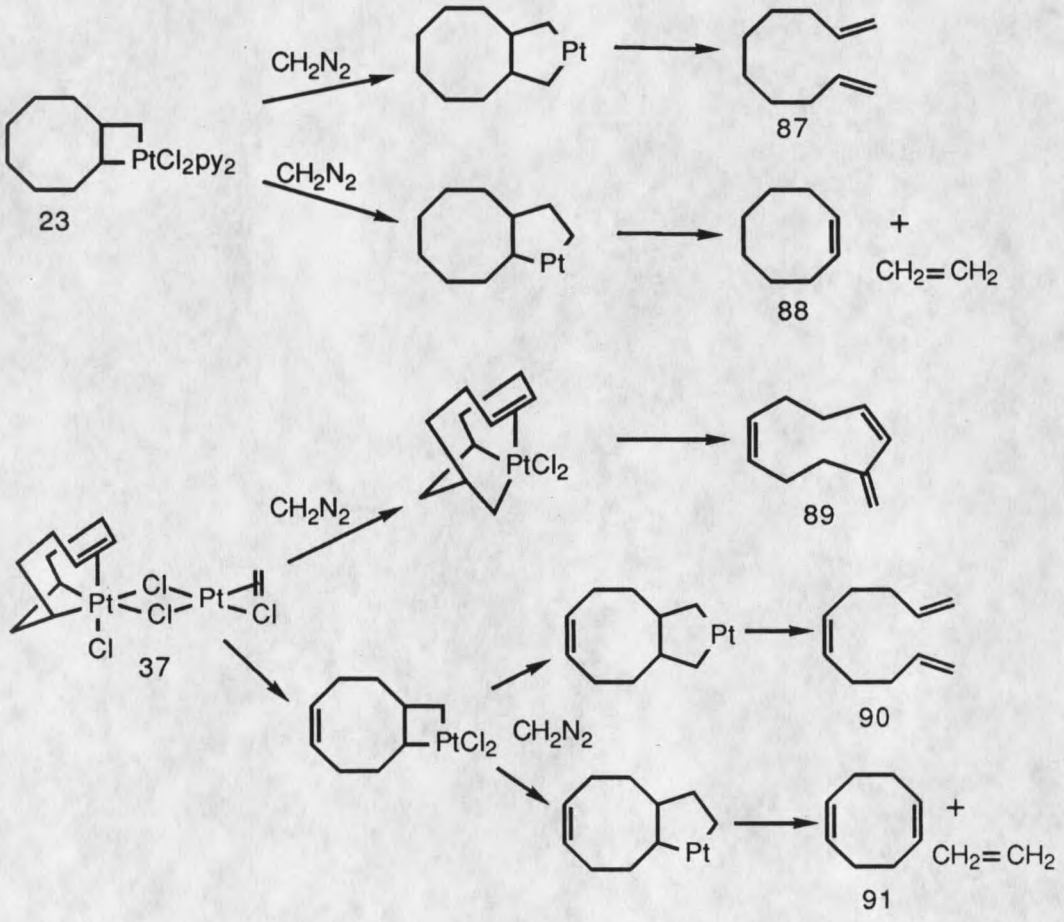
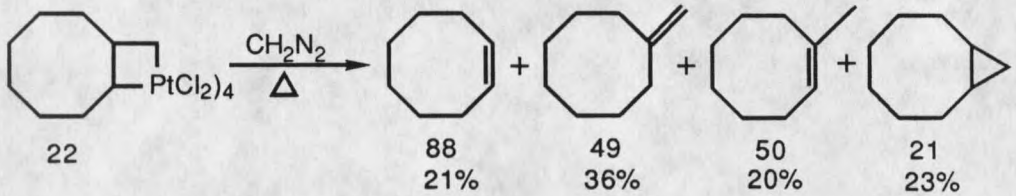


Figure 51. Possible Products and Mechanisms for the Reactions of 22 and 37 with CH_2N_2.

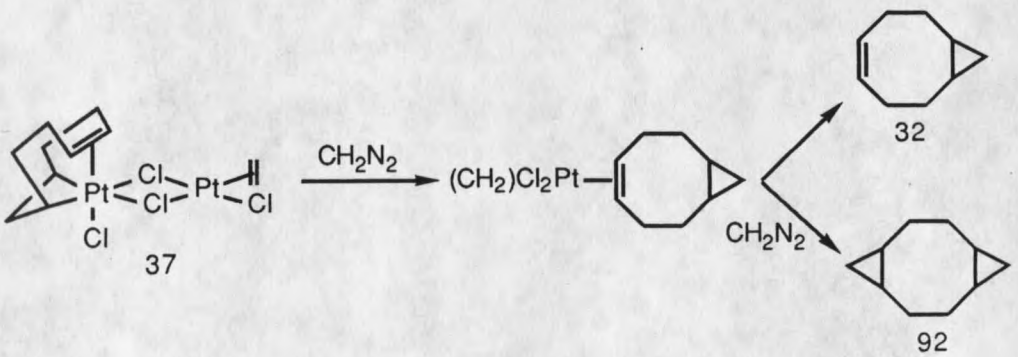


50. The olefins presumedly arose from pathways previously discussed: that is, decomposition of the platinacyclobutane to form a complex of olefin **49**, followed by isomerization of this complex to ultimately form olefin **50**. Either pyridine or CH_2 could be the active ligand on platinum. Heating was essential to the formation of **88**, while at room temperature only **21**, **49**, and **50** were observed. Regardless of the temperature, some cyclopropanation of the olefin products **49** and **50** occurred.



22 — **88** 21% — **49** 36% — **50** 20% — **21** 23% (68)

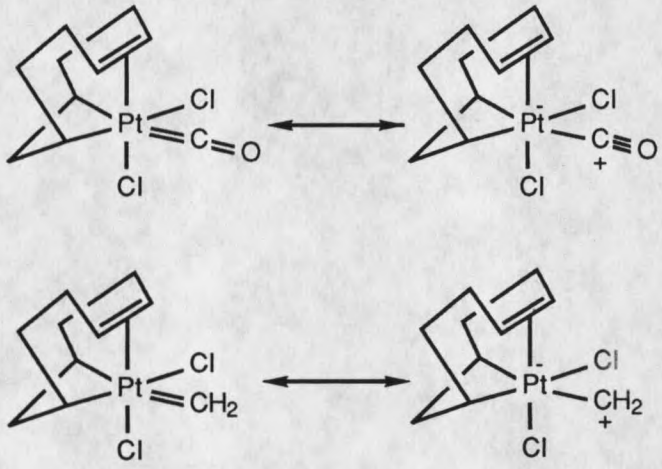
Complex **37** did not produce any of the predicted olefin products upon reaction with diazomethane (equation 69). Instead, only **32** and its cyclopropanation product, **92**, were observed. Since CO and CH_2 are potentially very similar



37 — **32** — **92** (69)

ligands, as indicated in Figure 52, the same mechanistic arguments presented for the reaction of 37 with CO may be applicable to the reaction of 37 with CH_2N_2.

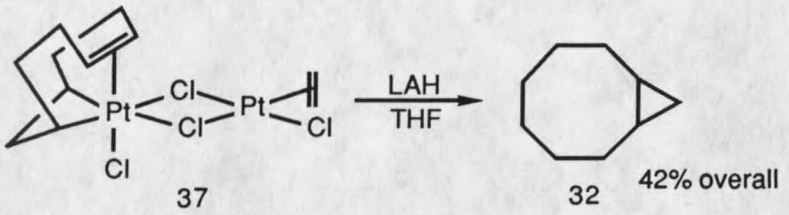
Figure 52. Illustration of the Similarity of CO and CH_2 as Ligands.



Reaction of 37 with nucleophiles.

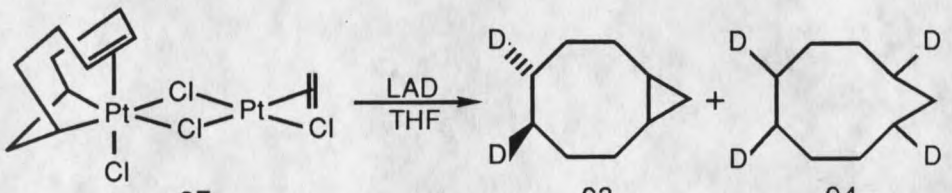
Complex 37 contained the only reported platinum(IV)-olefin moiety, and therefore provided a unique opportunity to examine the chemistry of such a system. The susceptibility of the olefin to nucleophilic attack was studied, as the platinum(IV) was expected to withdraw electron density from the olefin. This reactivity has been previously observed with platinum(II)-bound olefins[14-25].

Complex 37 was reacted with the simplest of nucleophiles, the hydride ion, from lithium aluminum hydride in THF (equation 70). It produced cyclopropane 21 which



37 32 (70)

suggested that the olefin was reduced followed by reductive elimination of the cyclopropane. Platinum(II) olefins undergo trans nucleophilic attack, however cis-attack could also occur by migration of a platinum-bound nucleophile to the olefin. Therefore, the stereochemistry of the platinum(IV) reaction was studied by replacing the hydride ion with deuteride ion from lithium aluminum deuteride (equation 71). This reaction produced the deuterated analogue of 21, as expected, along with tetradeuterated cyclononane. Although the deuterium positions in the cyclononane were never determined, the product probably arose from hydrogenation of both the olefin and the platinacyclobutane carbons[88].



37 93 >95% 94 <5% (71)

The deuterium positions in 93, however, were analyzed by ^{1}H and ^{2}H NMR spectroscopy. Many peaks in the proton NMR

spectrum were obscured due to overlap, but a comparison of the integrations and multiplicities to those of 21 indicated an absence of one proton at δ1.3 and one at δ1.65. This was confirmed by deuterium NMR resonances at δ1.68 and δ1.34 which were assigned to 93. A peak at δ1.49 was assigned to 94. The peak at δ1.49 might have been due to a water impurity, but persisted when the sample was carefully dried and when the shift reagent Resolv-al was added. The assignment of the proton resonances to their respective protons is shown in Figure 53 and was accomplished by proton-proton decoupling experiments performed on nondeuterated 21. These assignments therefore suggested that the deuteriums in 93 were <u>trans</u> to each other on adjacent carbons. If so, one hydride ion probably attacked the olefin <u>trans</u> to the platinum, while the other hydride was platinum bound and reductively eliminated with the resulting σ-bound carbon. This possibility is illustrated in Figure 54.

Figure 53. Proton NMR Resonance Assignments for 21 and 93.

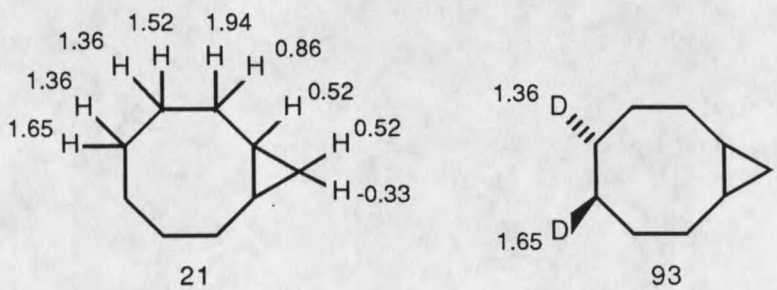
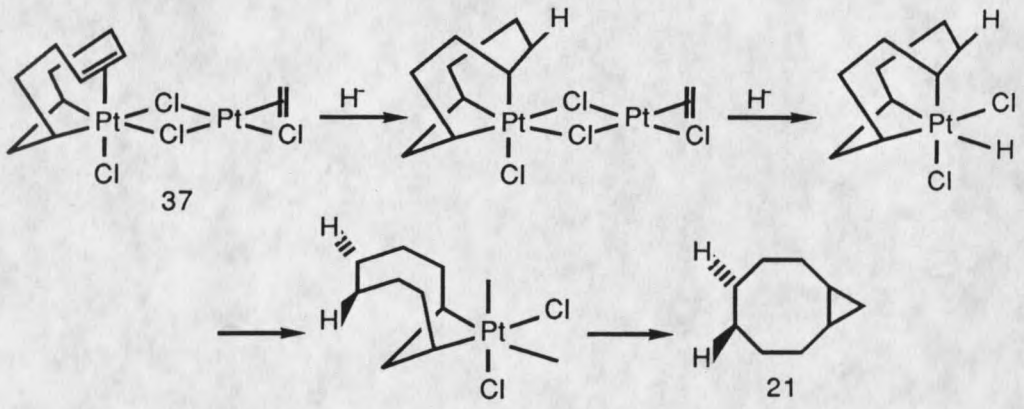
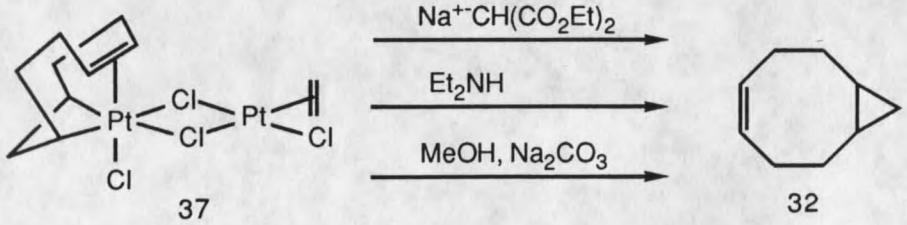


Figure 54. Proposed Mechanism for the Reaction of 37 With H^-.

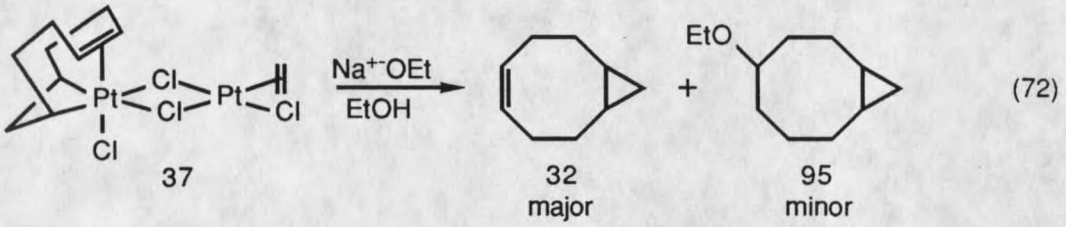


Other nucleophiles were also expected to attack the platinum(IV)-olefin, however most simply caused reductive elimination of the cyclopropane, as shown in Figure 55. Many nucleophiles attack platinum as well as platinum bound olefins, and may have caused reductive elimination in 37 by splitting the dichlorodiplatinum ring. This mechanism has been proposed for the reaction of other ligands with complex 37, as well.

Figure 55. Reaction of 37 with Nucleophiles.



Evidence of a nucloephilic addition was observed when 37 was reacted with sodium ethoxide (equation 72). Cyclopropane 32 was the major product, but a small amount of the addition product 95 was identified by GC-MS. An additional proton was required to form this product, and probably came from the ethanol solvent.



37 32 major 95 minor (72)

EXPERIMENTAL

General

Instrumentation. Proton, ^{13}C, and ^{195}Pt NMR spectra were collected on a Bruker WM 250 spectrometer. MAS/CP spectra were obtained at 37.7 MHz for ^{13}C. Mass spectral data were collected on a VG-16 spectrometer. Infrared spectra were obtained on a Nicolet 5DX FT-IR spectrometer. X-ray data was collected on a Nicolet R3ME automated diffractometer and structure determinations and refinement calculations were carried out with SHELXTL software on a Nicolet R3mE crystallographic system. Preparative GLC collections were made with an Aerograph Autoprep chromatograph series 2700 equipped with a 10' x 3/8" column packed with SE 30 on Chromsorb W. Analyses were done by Galbraith Laboratories. High pressure reactions were run in a Parr Instrumental bomb no. 4501 with glass insert.

Chemicals. Pyridine-d_5, DMSO-d_6, THF-d_8, benzene-d_6, CD_2Cl_2, and $CDCl_3$ were obtained from Stohler/KOR Stable Isotopes and Norell, Inc. Diethylether was distilled from CaH_2 prior to use. Diazomethane was prepared from Aldrich Diazald, and Zeise's dimer was prepared from K_2PtCl_4 on loan

from Johnson-Matthey Corp. Olefins 26-28, 81 and 82 were purchased from Aldrich and were distilled prior to use as standards.

Synthesis of Substrates and Standards

Methylenecyclooctane 49 and 3-Methylenecyclohexene 83. Olefins 49 and 83 were prepared by the method of Wittig and Schoellkopf[113]:

(a) 49: ^{1}H NMR ($CDCl_3$) δ4.74 (s,2H), δ2.18 (dd,4H), δ1.63 (m,4H), δ1.49 (m,6H);
^{13}C NMR[114];
MS[115].

(b) 83: ^{1}H NMR[116];
MS[116].

1-Methyl-1,3-cyclohexadiene 84. Olefin 84 was prepared by the method of Birch and Subba Rao[117]:
^{1}H NMR[118],
MS[119].

Methylcyclooctene 50. Olefin 50 was prepared by addition of methyl Grignard to cyclooctanone with strong acid work-up:
^{1}H NMR ($CDCl_3$) δ5.32 (dd,1H), δ2.11 (dd,2H), δ2.04 (ddd,2H), δ1.66 (s,3H), δ1.44 (m,8H);

^{13}C NMR ($CDCl_3$) δ137.0 (s), δ124.1 (d), δ30.3 (t), δ30.2 (t), δ28.0 (t), δ26.6 (t), δ26.5 (t), δ26.2 (t), δ23.5 (q);

MS, m/e (%) 124 (M^+, 41.5), 109 (15.9), 96 (90.7), 81 (100), 67 (86.8), 55 (52.2), 42 (69.4).

Cyclononene 51. Olefin 51 was prepared by LAH reduction of cyclononanone followed by P_2O_5 dehydration:

^1H NMR ($CDCl_3$) δ5.50 (m, 2H), δ2.12 (m, 4H), δ1.46 (m, 8H);

^{13}C NMR ($CDCl_3$) δ130.1 (d), δ25.9 (t), δ25.7 (t), δ25.3 (t), δ25.2 (t);

MS[120].

3-Methylcyclooctene 70. Olefin 70 was prepared by the method of Cope and Woo[121]:

^1H NMR ($CDCl_3$) δ5.56 (ddd, 1H), δ5.24 (dd, 1H), δ2.57 (m, 1H), δ2.24 (m, 1H), δ2.02 (m, 1H), δ1.64 (m, 2H), δ1.52 (m, 4H), δ1.37 (m, 1H), δ1.14 (m, 1H), δ1.00 (d, 3H);

^{13}C NMR ($CDCl_3$) δ136.6 (d), δ128.2 (d), δ38.5 (t), δ30.4 (d), δ29.5 (t), δ26.6 (t), δ26.4 (t), δ26.0 (t), δ22.0 (q);

MS, m/e (%) 124 (M^+, 21.2), 109 (15.9), 96 (42.7), 81 (82.1), 67 (100), 55 (60.3), 41 (78.8).

Cyclopropanes 21, 25 and 32. Cyclopropanes 21, 25, and 32 were prepared from cyclooctene, cyclohexene, and

1,5-cyclooctadiene, respectively, by the method of Rawson and Harrison[122].

(a) 21: ^{1}H NMR[123];

^{13}C NMR ($CDCl_3$) δ30.0 (t), δ27.3 (t), δ26.7 (t), δ15.5 (d), δ9.82 (t);

MS[120].

(b) 25: ^{1}H NMR[66];

^{13}C NMR[124];

MS[125].

(c) 16: ^{1}H NMR[126];

^{13}C NMR ($CDCl_3$) δ130.3 (d), δ29.8 (t), δ27.2 (t), δ16.5 (d), δ12.2 (t);

MS, m/e (%) 122 (M^+, 3.6), 107 (8.0), 93 (26.3), 80 (100), 67 (68.2), 54 (60.2), 41 (32.8).

Cyclopropane 57. Cyclooctene was reacted with CD_2N_2 in dry ether in the presence of a catalytic amount of $Rh_2(OAc)_6$. The CD_2N_2 was generated by addition of Aldrich Diazald to 30% NaOD in D_2O with 2-(2-ethoxyethoxy)ethan-(ol-d) as a solvent. Cyclopropane 57 showed 87% deuterium per proton at C(1):

^{1}H NMR ($CDCl_3$) δ1.94 (2H), δ1.65 (2H), δ1.52 (2H), δ1.30 (4H), δ1.86 (2H), δ0.52 (1H);

^{2}H NMR (CCl_4) δ0.5, δ0.3;

^{13}C NMR ($CDCl_3$) deuterium coupling to the resonance at δ9.82 was evident.

Formation of Platinacyclobutanes

Reaction of 21 and 57 with Pt(II). In a 5 dram vial was placed 483 µl of 21 or 57 (0.422g, 3.40mmole) and 3 ml of dry ether. Zeise's dimer (0.100g, 0.34mmole) was added and the reaction was stirred at room temperature until the ether turned yellow. The mixture was then further diluted with 10 ml of dry ether, and stirring was continued until all the ether had evaporated. The light orange residue was washed with chloroform until the washings were colorless, then was washed once with 10 ml of pentane. The resulting yellow solid was dried under vacuum, and yielded 0.120g of the IPC in 90% yield.

22: mp 136-139 °C dec.;

MAS/CP NMR δ51.019, δ30.625, δ30.352, δ29.563, δ26.052, δ6.940.

Reaction of 25 with Pt(II). Forty-five µl of 25 (0.033g, 0.34mmole) and 2 ml of dry ether were placed in a 5 dram vial. The suspension was cooled to -10°C and Zeise's dimer (0.050g, 0.17mmole) was added. The mixture was maintained at -10°C with stirring for 36 hours then was rapidly evaporated to dryness at 0°C. The solid IPC was not stable and was immediately reacted with pyridine.

Reaction of 22, 73 and 25 with Pyridine. The pyridine adducts of the IPCs were obtained by adding 2 equiv. of pyridine to a stirred suspension of the platinum compound in $CHCl_3$. In chloroform the adducts were unstable and decomposed with time. As solids the pyridine adducts decomposed rapidly. Alternatively, the pyridine adducts could be obtained by placing the IPC directly in pyridine, and were stable if kept in pyridine solution.

(a) 23: mp 245 °C dec.;

^1H NMR (py-d_5) δ3.93 (dd, 1H, $J_{Pt,H}$95), δ3.00 (m, 1H), δ3.00 (dd, 1H, $J_{Pt,H}$88), δ2.78 (dd, 1H), δ2.50 (m, 1H), δ2.33 (m, 1H), δ1.33-0.99 (m, 10H);

^{13}C NMR (py-d_5) δ49.2 (d, $J_{Pt,C}$100), δ31.9 (t), δ31.5 (t), δ30.8 (t), δ30.0 (t), δ26.3 (t), δ26.0 (t), δ12.9 (d, $J_{Pt,C}$354), δ-7.6 (t, $J_{Pt,C}$357);

^{195}Pt NMR (py-d_5) δ3300;

^1H NMR ($CDCl_3$) δ3.59 (dd, 1H, $J_{Pt,H}$96), δ2.72 (m, 1H), δ2.65 (dd, 1H), δ2.47 (dd, 1H), δ2.15 (m, 2H), δ1.36 (m, 9H), δ0.74 (d, 1H);

^{13}C NMR ($CDCl_3$) δ48.6 (d, $J_{Pt,C}$85), δ31.2 (t), δ30.8 (t), δ30.0 (t), δ29.5 (t), δ25.9 (t), δ25.6 (t), δ14.2 (d, $J_{Pt,C}$348), δ-7.2 (t, $J_{Pt,C}$351);

^{195}Pt NMR ($CDCl_3$) δ3263.

(b) 55: ^{1}H NMR ($CDCl_3$) δ3.59 (1H), δ2.72 (1H), δ2.15 (2H), δ1.36 (9H), δ0.74 (1H);

2H NMR (CCl_4) δ2.85, δ2.63;

^{13}C NMR ($CDCl_3$) deuterium coupling appeared to the resonance at δ-7.2.

(c) 30: The adduct was unstable, and could not be isolated.

^{1}H NMR (py-d_5) δ3.66 (ddd, 1H, $J_{Pt,H}$93), δ3.04 (m, 1H), δ3.01 (dd, 1H), δ2.76 (dd, 1H), δ2.14 (m, 2H), δ1.5-1.0 (m, 6H);

^{13}C NMR (py-d_5) δ44.6 (d, $J_{Pt,C}$98), δ27.2 (t), δ25.7 (t), δ20.4 (t), δ19.9 (t), δ5.8 (d, $J_{Pt,C}$369), δ-8.6 (t, $J_{Pt,C}$354);

^{195}Pt NMR (py-d_5) δ3315.

Complex 36. To a stirred solution of 32 (0.151g, 1.24mmole) in 10 ml of ether was added Zeise's dimer (0.366mg, 1.24 mmole). The reaction was allowed to stir for 1 hour, during which time a yellow precipitate formed. Filtration yielded 0.202g of 36 (41.6% yield):

^{1}H NMR ($CDCl_3$) δ5.57 (dd, 2H, $J_{Pt,H}$66), δ2.44 (dd, 4H), δ1.94 (m, 2H), δ1.05 (m, 2H), δ0.78 (m, 3H), δ0.02 (dd, 1H);

^{13}C NMR ($CDCl_3$) δ89.9 (d, $J_{Pt,C}$162), δ30.3 (d), δ28.5 (t), δ19.9 (t), δ16.33 (t);

^{195}Pt NMR ($CDCl_3$) δ2338.

Platinacyclobutane 37. A mixture of 36 (0.047g, 0.12mmole) and Zeise's dimer (0.035g, 0.12mmole) in 1.5 ml of chloroform was purged with N_2 for 20-30 minutes. The mixture was then subjected to three freeze-thaw cycles and flame sealed in a thick walled tube under vacuum. The sealed tube was heated to 95°C for 15 minutes, with frequent agitation. Extraction with chloroform followed by centrifugation and removal of the solvent by rotoevaporation yielded 0.124g of 13 as an orange solid:

mp 168-172°C dec;

^{1}H NMR ($CDCl_3$) δ7.40 (dd, 2H, $J_{Pt,H}$60), δ4.70 (s, 4H, $J_{Pt,H}$69), δ3.73 (ddd, 2H, $J_{Pt,H}$82), δ2.97 (ddd, 1H, $J_{Pt,H}$92), δ2.6-2.2 (m, 7H), δ1.26 (d, 2H, $J_{Pt,H}$108);

^{13}C NMR ($CDCl_3$) δ120.4 (d, $J_{Pt,C}$94), δ71.0 (t, $J_{Pt,C}$205), δ44.4 (t), δ36.8 (t, $J_{Pt,C}$100), δ29.6 (d, $J_{Pt,C}$338), δ22.7 (t);

^{195}Pt NMR ($CDCl_3$) δ2184, δ2796.

Formation of 43 from 37. Platinacyclobutane 37 rapidly formed 43 when placed in pyridine solution. As a solid complex 43 was unstable and could not be isolated.

^{13}C NMR (py-d_5) δ74.5 (d), δ37.6 (t), δ35.7 (t, $J_{Pt,C}$116), δ34.1 (d, $J_{Pt,C}$797?), δ32.8 (t), δ25.4 (t), δ10.4 (d, $J_{Pt,C}$494), δ-9.7 (d, $J_{Pt,C}$473);

^{195}Pt NMR (py-d_5) δ2891.

Reaction of 22, 30 and 37 with 2,2'-Bipyridine. Three to four equivalents of bipy were added to a stirred suspension of 22 in chloroform, while 30 and 37 were reacted in pyridine. Rotoevaporation of the solution yielded a pink or yellow solid which was chromatographed on SiO_2 with $CHCl_3$ solvent to give the bipy adduct (87% average yield):

(a) 24: mp >300 °C dec.;

Anal. Calcd for $C_{19}H_{24}N_2Cl_2Pt$: C 41.76; H 4.43; Found: C 41.63; H 4.42;

^1H NMR ($CDCl_3$) δ3.5 (dd, 1H, $J_{Pt,H}$98), δ2.9 (dddd, 1H), δ2.6 (dd, 1H, $J_{Pt,H}$91), δ2.4 (dd, 1H), δ2.2 (m, 1H), δ2.0 (m, 1H), δ1.7-1.5 (m, 9H), δ1.3 (d, 1H);

^{13}C NMR ($CDCl_3$) δ47.4 (d, $J_{Pt,C}$84), δ31.6 (t, $J_{Pt,C}$≈38), δ30.8 (t), δ30.5 (t), δ29.8 (t), δ26.1 (t), δ26.0 (t), δ13.3 (d, $J_{Pt,C}$341), δ-6.6 (t, $J_{Pt,C}$364);

^{195}Pt NMR ($CDCl_3$) δ3076.

(b) 31: mp 213 °C dec.;

Anal. Calcd. for $C_{17}H_{20}N_2Cl_2Pt$: C 39.39; H 3.89; Found: C 38.80; H 3.84;

^1H NMR ($CDCl_3$) δ3.28 (ddd, 1H, $J_{Pt,H}$92), δ3.06 (m, 1H), δ2.68 (dd, 1H, $J_{Pt,H}$84), δ2.46 (dd, 1H, $J_{Pt,H}$80), δ2.05 (m, 1H), δ1.8-1.3 (m, 7H);

^{13}C NMR ($CDCl_3$) δ42.8 (d, $J_{Pt,C}$91), δ27.4 (t, $J_{Pt,C}$24), δ24.6 (t, $J_{Pt,C}$15), δ20.3 (t,

$J_{Pt,C}$42), δ19.4 (t, $J_{Pt,C}$48) δ5.2 (d, $J_{Pt,C}$366), δ-7.7 (t, $J_{Pt,C}$341);

^{195}Pt NMR ($CDCl_3$) δ3095.

(c) 48: mp 243 °C dec.;

^{1}H NMR ($CDCl_3$) δ5.73 (m, 2H), δ3.57 (dddd, 1H, $J_{Pt,H}$95), δ3.15 (m, 1H), δ2.59 (dd, 1H, $J_{Pt,H}$91), δ2.54-1.82 (m, 8H), δ1.56 (m, 1H);

^{13}C NMR ($CDCl_3$) δ131.8 (d), δ130.4 (d), δ47.8 (d, $J_{Pt,C}$82), δ34.1 (t), δ32.2 (t), δ25.3 (t), δ24.9 (t), δ12.5 (d, $J_{Pt,C}$345), δ-6.1 (t, $J_{Pt,C}$361);

^{195}Pt NMR ($CDCl_3$) δ3072.

X-ray Diffractometry on Platinacyclobutane 37

Suitable yellow-orange crystals of 37 were grown by slowly allowing heptane to diffuse into a chloroform solution. A crystal, 0.16 x 0.22 x 0.33 mm, suitable for X-ray analysis was mounted on a glass fiber, and data collection was carried out using θ/2θ scans and graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Absorption corrections were made by the Gaussian integration method using crystal dimensions between indexed crystal faces. Carbon positions were refined with isotropic thermal parameters.

Space group pbca

a = 10.963 (3)

b = 13.606 (3)

c = 21.170 (7)

D_{calc} = 2.88 g/cm^3

R = 0.080

2θ range = 3-50°

reflections with I≥3σ(I) = 1174

Reactions of Platinacyclobutanes

Reaction of 22 and 29 with KCN. IPCs 22 and 29 (0.025g, 0.08 and 0.07mmole, respectively) were each added to stirred solutions of KCN (0.021g, 0.32mmole) in 2 ml H_2O. (IPC 29 had to be reacted immediately upon its isolation, as it was extremely unstable.) Once the IPCs were solubalized, the solutions were extracted with chloroform. These extracts contained only 21 and 25, respectively.

Reaction of 23 and 30 with $P\phi_3$. To a stirred solution of 23 or 30 (0.050g, 0.09 and 0.10mmole, respectively) in pyridine was added $P\phi_3$ (0.116g, 0.46mmole). After 2 hours a white precipitate dropped out of solution. The volatiles were then collected by rapid vacuum distillation and contained only 21 or 25, respectively.

Reaction of 22 with DMSO. IPC 22 (0.100g, 0.26mmole) was placed in 2 ml of DMSO at 23°C and at 19°C. Green solutions were formed which were left standing for 12 hours. After this time, the only hydrocarbon species in the 23°C solution was 21. The 19°C solution contained a mixture of hydrocarbons in relative yields of >95% 21 and <5% 49, 50 and 51 combined. The reaction was also run at -10°C in a 2:1 $CHCl_3$:DMSO mixture, and produced >>95% 21 and <<5% 49, 50 and 51 (relative yields).

Reaction of 48 with DMSO. Bipyridine complex 48 (0.100g, 0.18mmole) was placed in 2 ml of DMSO at 23°C. After one week the IPC was completely consumed, at which time the only hydrocarbon species in solution was cyclopropane 32.

Thermal Decomposition of 48 in $CHCl_3$. Platinacyclobutane 48 (0.021g, 0.05mmole) in 5 ml $CHCl_3$ was refluxed with stirring for 3 weeks. The volatiles were collected by rapid vacuum distillation and contained >99% cyclopropane 32.

Decomposition of 23 and 55 in $CHCl_3$. Platinacyclobutanes 23 and 55 (0.050g, 0.09mmole) were placed in 2 ml chloroform, and after six hours had decomposed to a mixture of $PtCl_2py_2$ and 49 or 56, respectively. The reaction of 55

was also attempted in CCl_4, but had not visibly progressed after one week. Complex 23 reacted similarly in both chloroform and benzene, however. Decomposition of 23 was also carried out at temperatures ranging from -40°C to 37°C and was monitored by ^1H and ^{13}C NMR spectroscopies. At the higher temperatures, intermediate 54 was observed. When 23 was refluxed with stirring in chloroform for 24 hours followed by rapid distillation under vacuum, the volatiles contained 87% 49 and 13% 50, while the solids again contained $PtCl_2py_2$.

(a) 56: ^1H NMR ($CDCl_3$) δ4.74 (s,1H), δ2.18 (m,3H), δ1.63 (m,4H), δ1.49 (m,6H);

^2H NMR (CCl_4) δ4.77, δ2.17.

(b) 54: ^1H NMR ($CDCl_3$) δ4.93 (s,2H, $J_{Pt,H}$64), δ2.6 (m4H), δ2.1 (m,4H), δ1.6 (m,6H);

^{13}C NMR ($CDCl_3$) δ146.7 (s, $J_{Pt,C}$131), δ67.2 (t, $J_{Pt,C}$159), δ38.2 (t, $J_{Pt,C}$23), δ27.2 (t), δ27.1 (t), δ25.5 (t);

^{195}Pt NMR ($CDCl_3$) δ2107.

Decomposition of 23 in MeOH. Platinacyclobutane 23 (0.050g, 0.09mmole) was placed in 2 ml methanol and after 8 hours had decomposed to a mixture containing isomers 66 and 67 in 60% yield, along with 40% 49 and $PtCl_2py_2$. Although 66 and 67 could not be separated from each other, they were isolated from the other products on a SiO_2 column with $CHCl_3$

solvent. However this treatment partially converted the isomeric complexes to 65.

(a) 66 and 67: mp 147°C (dec);

^{1}H NMR ($CDCl_3$) δ3.4 (s, 1H, $J_{Pt,H}$22), δ3.3 (s, 1H, $J_{Pt,H}$36), δ2.8 (m, 2H), δ2.6 (m, 2H), δ2.3-1.9 (m, 4H), δ1.9-1.3 (m, 20H);

^{13}C NMR ($CDCl_3$) δ116.3 (s, $J_{Pt,C}$107), δ115.5 (s, $J_{Pt,C}$110), δ61.6 (d, $J_{Pt,C}$264), δ57.5 (d, $J_{Pt,C}$218), δ44.3 (t, $J_{Pt,C}$304), δ38.6 (t, $J_{Pt,C}$250), δ31.3 (t), δ31.0 (t), δ28.5 (t), δ28.2 (t), δ27.5 (t), δ26.2 (t), δ25.9 (t);

^{195}Pt NMR ($CDCl_3$) δ2977, δ2818.

(b) 65: mp 176°C (dec);

^{1}H NMR ($CDCl_3$) δ3.44 (s, 1H, $J_{Pt,H}$38), δ2.63 (s, 2H, $J_{Pt,H}$90), δ2.08 (m, 1H), δ1.9-1.2 (m, 11H);

^{13}C NMR ($CDCl_3$) δ111.0 (s, $J_{Pt,C}$182), δ63.1 (d, $J_{Pt,C}$265), δ42.2 (t, $J_{Pt,C}$250), δ30.7 (t), δ30.6 (t), δ29.6 (t), δ28.3 (t), δ28.1 (t), δ26.2 (t), δ25.9 (t).

Reaction of 22 with one Equivalent of Pyridine. IPC 22 was placed in chloroform and one equivalent of pyridine was added. After 6 hours the solution was observed by ^{13}C NMR spectroscopy to contain 54. After an additional three days the solution was again examined by ^{13}C NMR spectroscopy and contained a mixture of 12.5% 49, 25% 50, 25% 62 and 37.5%

$PtCl_2py_2$. No further monitoring was undertaken to determine the equilibrium composition.

Reaction of 22 and 37 in THF. IPCs 22 and 37 (0.100g, 0.26 and 0.15mmole, respectively) were placed in THF solution and left in the dark for several days. Examination of the solutions by ^1H NMR spectroscopy showed cyclopropanes 21 and 32 were the only free hydrocarbons produced in the respective reactions. The reaction of 22 also produced platinum- olefin 68, but a relative yield was not obtained. IPC 22 was then placed in $CHCl_3$ and one equivalent of THF was added. After several days only the platinum-olefin complex 69 was observed in the solution.

Reaction of 22 and 73 with CO. A suspension of the IPC 22 or 73 (0.100g, 0.26mmole) in 5 ml chloroform was placed in a pressure reaction bomb under 80 psi of CO. After 36 hours the reaction mixture was removed from the bomb and the volatiles were collected by rapid vacuum distillation. The volatiles from 22 contained 19% 21, 64% 50, 8% 51, and 9% of a mixture of 70, 71 and 72, while the volatiles from 73 contained 82% 57 and 18% 74.

Reaction of 37 with CO. IPC 37 was placed in chloroform and a stream of CO was bubbled through until the solution turned clear. This solution was then promptly analyzed. The

reaction was repeated with Zeise's dimer and platinum-olefin 36 to obtain standards for comparison to the products from 37. Three main products, 76, 78 and 79, were obtained but decomposed within one week, two days, and three hours, respectively. These could not be isolated as solids due to their instability.

(a) 76: IR ν_{max} ($CDCl_3$) 2810, 2070, 1755, 1615, 1450, 1363, 1085 cm^{-1};

^1H NMR ($CDCl_3$) δ7.40 (dd, 2H, $J_{Pt,H}$57), δ3.76 (ddd, 2H, $J_{Pt,H}$80), δ2.95 (ddd, 1H, $J_{Pt,H}$95), δ2.7-2.2 (m, 7H), δ1.26 (d, 2H, $J_{Pt,H}$111);

^{13}C NMR ($CDCl_3$) δ151.6 (s, $J_{Pt,C}$1557) δ120.2 (d, $J_{Pt,C}$96), δ44.3 (t), δ36.4 (t, $J_{Pt,C}$98), δ31.4 (bd, $J_{Pt,C}$338), δ22.7 (t);

^{195}Pt NMR ($CDCl_3$) δ1276.

(b) 78: partial data only

IR ν_{max} ($CDCl_3$) 2120 cm^{-1};

^{195}Pt NMR ($CDCl_3$) δ1107.

(c) 79: partial data only

IR ν_{max} ($CDCl_3$) 2185, 2145 cm^{-1};

^{195}Pt NMR ($CDCl_3$) δ778.

Thermal Decomposition of 22 in Et_2O. IPC 22 (0.100g, 0.26mmole) in 10 ml diethylether was refluxed with stirring for 46 hours. Aliquots were removed at 10 and 34 hours. The solid products were rotoevaporated, then were each added to

stirred solutions of KCN (0.064g, 1.00mmole) in 2 ml H_2O. Stirring was continued until the solids dissolved, then the solutions were extracted with chloroform. The extracts contained **21**, **49**, **50**, and **51** in the following ratioes:

10 hrs: 93.4% **21**, 2.4% **49**, 3.6% **50**, and 0.6% **51**;

34 hrs: 72.8% **21**, 11.2% **49**, 14.9% **50**, and 1.1% **51**;

46 hrs: 58.4% **21**, 20.6% **49**, 16.0% **50**, and 4.9% **51**.

In a separate experiment, **22** was refluxed for one hour in diethylether, and after KCN workup yielded **21** in essentially quantitative yield.

IPC **22** was also stirred in diethylether at room temperature until it went into solution and the solution turned orange. An orange solid was isolated upon filtering off any remaining IPC and evaporating the filtrate. By ^{13}C NMR spectroscopy this solid was shown to be a mixture of the platinum-bound olefins **63**, **64**, and **80**. Treatment of these olefins with KCN produced 20% **49**, 47% **50**, and 33% **51**.

(a) **63**: unstable, observed only briefly in the product mixture. Partial ^{13}C NMR ($CDCl_3$) δ145.0, δ65.2, δ43.8.

(b) **64**: ^{1}H NMR ($CDCl_3$) δ5.51 (dd, 1H, $J_{Pt,H}$69), δ2.43 (m, 1H), δ2.21 (m, 1H), δ2.00 (m, 2H), δ1.74 (overlapping s and m, 6H), δ1.38 (m, 3H), δ1.21 (m, 2H), all peaks very broad;

^{13}C NMR ($CDCl_3$) δ115.8 (s), δ88.8 (d), δ34.4 (t), δ30.1 (t), δ29.9 (t), δ28.1 (t), δ26.3

(t,q), δ25.4 (t);

^{195}Pt NMR ($CDCl_3$) 2410.

(c) **80**: ^{1}H NMR ($CDCl_3$) δ5.48 (dd,2H), δ2.19 (bm), δ1.66 (bm), δ1.35 (bs);

^{13}C NMR ($CDCl_3$) δ91.0 (d, $J_{Pt,C}$≈209), δ27.4 (t), δ24.4 (t), δ23.6 (t), δ22.7 (t);

^{195}Pt NMR ($CDCl_3$) δ2351.

The complexes **63**, **64**, and **80** from a room temperature experiment identical to the one above, were placed in chloroform and refluxed for 12 hours. Aliquots were withdrawn initially and after 6 hours. Treatment of these samples with KCN yielded:

0 hrs: 45.4% **49**, 27.1% **50**, and 27.3% **51**;

6 hrs: 56.4% **49**, 24.3% **50**, and 19.3% **51**;

12 hrs: 67.0% **49**, 21.0% **50**, and 12.0% **51**.

IPC **22** was placed in diethylether and stored at -5°C for six months. A light orange solid was then isolated by rotoevaporation of the mixture at 0°C, followed by treatment with KCN, also at 0°C. Analysis of the chloroform extract by ^{1}H NMR spectroscopy showed >90% **21** and a plethora of minor olefin-bearing compounds which were not further characterized.

Thermal Decomposition of **30** in Et_2O. IPC **30** (estimated 0.020g, 0.06mmole) was isolated and immediately placed in diethylether and refluxed for 1 hour. The solid products

were obtained by rotoevaporation of the product mixture, then were added to stirred solutions of KCN (0.021g, 0.32mmole) in H_2O. The solids dissolved very rapidly, after which the solution was extracted with chloroform. The extract was examined by ^1H NMR spectroscopy and GC-MS and contained cyclopropane 25 and olefins 26-28, 81-85. All products were identified by comparison to standards except for 85, which was identified by comparison to literature data.

85: ^1H NMR[112]; MS[112].

Reaction of 25 with Pt in Et_2O. Zeise's dimer (0.038g, 0.13mmole) and 25 (0.049g, 0.51mmole) were placed in diethylether and stirred until an orange solid began to drop out of solution. The reaction was run at -10°C, 0°C, 23°C, and 34°C and the reaction rate was proportional to the temperature. For example, at -10°C the reaction required 3 days, while at 34°C it was complete in 1 hour. The orange solid from each reaction was isolated by rotoevaporating off the solvent and any unreacted 25 at low temperature. These solids were then placed in stirred solutions of KCN (0.17g, 0.052mmole) in 2ml H_2O. Upon solvation of the solid the mixture was extracted with chloroform. Analysis of the extracts showed they were identical in composition to the product mixture obtained from the decomposition of 29 in Et_2O. Relative yields of the products were obtained by

integrating the capillary CG peaks from GC-MS analyses of three randomly chosen reactions. The integrations were accomplished by weighing cutouts of the peaks. Olefins **81** and **82** appeared as one GC peak, so their relative yields were obtained by integrating their ^{1}H NMR olefin resonances relative to each other. For this reason their total relative yield is fairly certain, but their individual yields may be inaccurate.

reaction 1: 12.2% **81&82**, 13.7% **26**, 14.0% **85**, 10.1% **84**, 16.2% **27**, 16.2% **83**, 2.7% **28**, 14.9% **25**;

reaction 2: 10.9% **81&82**, 11.8% **26**, 15.6% **85**, 15.0% **84**, 7.0% **27**, 34.8% **83**, 2.3% **28**, 2.6% **25**;

reaction 3: 20.0% **81&82**, 3.8% **26**, 7.6% **85**, 7.4% **84**, 17.6% **27**, 4.3% **83**, 3.5% **28**, 36.0% **25**;

average: 14.4% **81&82**, 9.8% **26**, 12.4% **85**, 10.8% **84**, 13.6% **27**, 18.4% **83**, 2.8% **28**, 17.8% **25**;

81&82: by ^{1}H NMR: 69.6% **81** vs. 30.4% **82**;

average relative yields: 10.0% **81**, 4.3% **82**.

When the orange solids were left in diethylether solution, an initial precipitate dropped out and could be collected. Treatment of this solid with KCN produced diolefins **84** and **85**. Slow evaporation of the remaining diethylether solution yielded a second precipitate, which in turn produced a decreased amount of **84** and an increased amount of **85**. Finally evaporating the solution to dryness

yielded a third solid which contained the complete product mixture seen previously.

The complete product mixture (25-28, 81-85) in chloroform was sealed in a 1ml screw cap vial along with excess maleic anhydride. This was dropped in a boiling H_2O bath for 15 minutes. Reanalysis of the mixture by GC-MS showed a decrease in the intensity of the TIC peaks attributed to 84 and 85.

Reaction of 22 and 37 with CH_2N_2. A large excess of CH_2N_2 was added to a solution of 22 or 37 in chloroform, via a stream of dry N_2. Following completion of the reaction, the mixture was distilled under full vacuum to obtain any volatile products. GC/MS and NMR analyses of these products revealed only 32 and its cyclopropanation product, 92 from the reaction with 37. The reaction of 22 yielded 15% 21, 75% 49, and 10% 50, along with the cyclopropanes of the product olefins. When the reaction with 22 was preformed at ≈40°C the product mixture contained 21% 88, 20% 21, 36% 49, and 23% 50. Some polymeric material was also obtained from each of the reactions.

Reaction of 37 with $LiAlH_4$ and $LiAlD_4$. Platinacyclobutane 37 (0.050g, 0.08mmole) was placed in 1.5 ml dry THF at 0°C and $LiAlH_4$ or $LiAlD_4$ (0.003g, 0.07mmmole) was added with stirring. A black precipitate dropped out of

solution, after which the volatiles were obtained by rapid vacuum distillation. The $LiAlH_4$ reaction yielded 21 in 42% overall yield. No other significant hydrocarbons were obtained. The $LiAlD_4$ reaction produced >95% 93 relative to <5% 94.

(a) 93: ^{1}H NMR (THF) δ1.94 (dd, 2H), δ1.65 (m, 1H, overlaps with THF), δ1.52 (m, 2H), δ1.36 (m, 3H, shows loss of coupling relative to 21), δ0.86 (m, 2H, shows loss of coupling relative to 21), δ0.52 (m, 3H), δ-0.33 (dd, 1H).

^{2}H NMR (THF) δ1.68, δ1.34.

(b) 94: ^{1}H and ^{2}H NMR (THF) δ1.49.

Reaction of 37 with $Na^+{}^-CH(CO_2Et)_2$. Sodium (0.004g, 0.17mmole) was added slowly to 4ml ethanol at 0°C with stirring. The mixture was refluxed until all the Na dissolved, then $CH_2(CO_2Et)_2$ (1.055g, 6.59mmole) was added over a 10 minute period. Finally 37 (0.100g, 0.15mmole) was added, and the mixture was stirred at reflux for 2 hours. The volatile products, obtained by rapid vacuum distillation, were analyzed by GC-MS and showed mostly 32 with a minor amount of 95.

Reaction of 37 with Et_2NH. Platinacyclobutane 37 (0.050g, 0.08mmole) was placed in 1.1 ml dry THF in a dry-ice/chloroform bath. Diethylamine (0.027g, 0.37mmole) was

added dropwise after which the reaction was stirred for 40 minutes, and $LiAlH_4$ (0.003g, 0.08mmole) was added. The reaction was warmed to room temperature and the volatile products were isolated by rapid vacuum distillation. Analysis by ^1H NMR spectroscopy showed these contained 32 and unreacted amine.

Reaction of 37 with MeOH. The reaction of 37 with methanol was catalyzed by Na_2CO_3, following the method of Chatt[22]. The only volatile product observed after rapid vacuum distillation of the product mixture, besides unreacted MeOH, was 32.

Reaction of 37 with $Na^+{}^-OEt$. This reaction was run identically to the reaction of 37 with $Na^+{}^-CH(CO_2Et)_2$, except that no $CH_2(CO_2Et)_2$ was added. Analysis of the volatile products by GC-MS showed 32 was the major product, along with a minor amount of 94.

Kinetic Measurements

General Kinetic Method. All reactions were measured by ^1H NMR spectroscopy. In a typical experiment, 10-20mg IPC 22 or 73 was added to 0.5ml $CDCl_3$ in an NMR tube, and the tube was brought to thermal equilibrium in a thermostated water bath. Two equivalents of pyridine were then added to the

tube which was shaken until all the solid IPC went into solution. The tube was then returned to the bath for 15 seconds to return to temperature, after which it was wiped dry and lowered into the probe on a string. This was necessary to reduce temperature vacillations in the probe, which was thermostated to the same temperature as the bath. The sample was then quickly locked on and the first data point acquired. All spectra were obtained without spinning. The decomposition of 23 and 55 were monitored by integrating the platinacyclobutane peak at δ3.6. Data points were obtained every 1-10 minutes for five half lives, and each point was obtained in one pulse. Each spectrum contained 8K of data and was line broadened by 3 Hz of Lorentzian broadening before Fourier transforming.

All slopes from the acquired data were determined by the method of least squares, and showed good correlation (coefficients >0.99, except for three experiments with coefficients >0.98). All experiments appeared to obey first order kinetics, and each rate constant was determined as the average of three experiments.

Kinetic isotope effects were determined by direct comparison of the rate constants from the reactions of 23 and 55. The KIE at 23°C was obtained by extrapolating the rates to this temperature, then comparing those rates. Activation parameters were obtained from plots of ln k vs. T^{-1}, where the slope = $-E_a/R$ and the intercept = ln A

vs. T^{-1}, where the slope = $-E_a/R$ and the intercept = ln A according to the equation ln k = ln A - E_a/RT, where R =1.987 cal K^{-1} mol^{-1}. Again, the method of least squares was used, and correlation coefficients of >0.99 were obtained.

Kinetics of the Decomposition of 23. The kinetics of 23 were determined for concentrations of 20, 30, and 40 mg/ml at 37°C, and 30 mg/ml for 47°, and 57°C. Varying the concentration led to no significant rate differences, and all rates increased with increasing temperature. All rates are listed in Table 15. Errors of 5-16% were observed in the various rate constants.

Activation parameters of $\triangle H^{\ddagger}$ =19.4 ± 0.02 kcal mol^{-1} and $\triangle S^{\ddagger}$ = -6.2 ± 0.06 cal K^{-1} mol^{-1} were obtained.

Kinetics of the Decompositon of 55. The kinetics of 55 were determined for concentrations of 30 mg/ml at 37°, 47°, and 57°C. All rates increased at increasing temperature and are listed in Table 16. Errors of 2-9% were observed in the various rate constants.

Olefin Isomerizations Catalyzed by Platinum

Isomerizations of 26-28, 81, 83 and 84 Followed by Treatment with KCN. Each of the olefins 26-28, 81, 83 and 84 (0.003g, 0.03mmole) was placed in 1ml chloroform containing

at reflux for 2 hours, then at room temperature overnight. The product mixtures were each added to 1ml H_2O containing KCN and were stirred until any solids went into solution. The chloroform layers were then removed and analyzed by ^1H NMR spectroscopy.

(a) The reaction of 28 produced only 28.

(b) The reaction of 26 yielded 64% 26 and 36% 27.

(c) The reaction of 27 yielded 96% 26, 2% 27, and 2% 81.

(d) The reaction of 81 produced 68% 81, 30% 82, 1% 27, and 1% 26.

(e) The reaction of 83 yielded 3% 83, 34% 84 and 63% 85.

(f) The reaction of 84 produced only 84.

Isomerizations of 26, 27, 50 and 51 Followed by Treatment with pyridine. Olefins 26, 27, 50 and 51 (0.040g, 0.42mmole 26 and 27; 0.044g, 0.35mmole 50 and 51) were each placed in chloroform and Zeise's dimer (0.103g, 0.35mmole and 0.123g, 0.42mmole, respectively) was added. These solutions were stirred with gentle heating for 1-2 hours, then 1 equivalent of pyridine was added. Olefin 27 was not observed to form a platinum complex, and yielded only 27 with time. Olefin 26 formed a platinum-olefin complex which after 5 days decomposed to 83.9% 26 and 16.1% 27. Olefins 50 and 51 each formed platinum-olefin complexes. The complex

from 51 decomposed very rapidly and reproduced only 51. Decomposition of the complex of 50 was slower, but also produced only 50.

Isomerizations of 49 and 50. Isomerizations of olefins 49 and 50 were attempted by heating chloroform solutions of the olefins containing either excess pyridine, 1 equivalent of $PtCl_2py_2$, or no additional catalyst. These produced no reaction. A chloroform solution of 49 was also heated with 1 equivalent of $Pt(C_2H_4)Cl_2py$, but again produced no reaction after 48 hours. Olefin 49 (0.016g, 0.13mmole) was added to Zeise's dimer (0.035g, 0.12mmole) in chloroform, however a small amount of the Zeise's dimer appeared not to react. Analysis of the product by NMR spectroscopies showed a species which did not appear to contain an olefin. The reaction was rerun in methylenechloride, with the same result. Olefin 50 (0.088g, 0.71mmole) was also added to Zeise's dimer (0.200g, 0.68mmole) in chloroform, and again only part of the Zeise's dimer appeared to react. Analysis of the unreacted platinum showed that one platinum reacted with two olefin molecules. The product was the same as observed from the reaction of 49. Excess 50 was removed from the product through repeated crystallizations, and left platinum-olefin complex 64. Addition of 1 equivalent of 50 to 64 regenerated the observed reaction product. At room temperature the solution was a dark orange, while at -60°C

it lightened perceptibly. Carbon-13 NMR analysis of the product at -60°C showed olefin **50** and platinum-olefin complex **64**. From this data it appears that the product from both the reactions of **49** and **50** is an equilibrium mixture of two molecules of **50** bound to platinum in equilibrium with **50** and **64**.

equilibrium mixture (room temperature): ^{1}H NMR ($CDCl_3$) δ5.38 (dd, 1H), δ2.1 (m, 4H), δ1.6 (s, 3H), δ1.5 (m, 4H), δ1.37 (m, 4H), all peaks very broad; ^{13}C NMR ($CDCl_3$) δ30.1 (t), δ27.9 (t), δ26.4 (t), δ25.8 (t).

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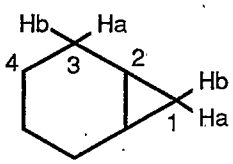
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APPENDICES

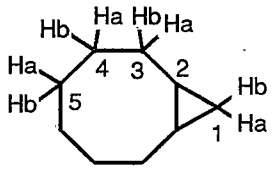
APPENDIX A

NMR and Mass Spectral Data for Cyclopropanes, Olefins, and Platinum-Olefin Complexes

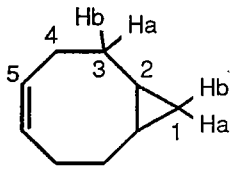
Table 21. NMR and MS Data for Cyclopropanes 21, 25 and 32.



25



21



32

^{1}H NMR**

H#				
	1a	-0.03 dd	-0.33 dd	-0.19 dd
	1b	0.50 m	0.52 m	0.64 ddd
	2	0.82 m	0.52 m	0.81 m
	3a	1.55 m *	0.86 m	1.24 m *
	3b	1.85 m *	1.94 dd	2.19 m *
	4a	1.18 m *	1.52 m	2.08 m *
	4b	1.18 m *	1.36 m	2.08 m *
	5a		1.36 m	5.62 dd
	5b		1.65 m	

^{13}C NMR**

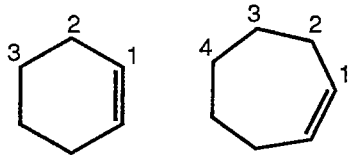
C#				
	1	10.0 t	9.8 t	12.2 t
	2	9.2 d	15.5 d	16.5 d
	3	23.8 t *	30.0 t *	27.2 t *
	4	21.3 t *	27.3 t *	29.8 t *
	5		26.7 t *	130.3 d

MS***

M^+	96 (46.9)	124 (18.7)	122 (3.6)
	81 (71.7)	109 (5.7)	107 (8.0)
	67 (100)	96 (70.4)	93 (26.3)
	54 (79.5)	81 (76.8)	80 (100)
	42 (35.9)	67 (100)	67 (68.2)
		54 (82.2)	54 (60.2)
		42 (79.8)	41 (32.8)

* not rigorously determined.
** shifts in ppm, $CDCl_3$ solvent
*** m/e (%)

Table 22. NMR and MS Data for Olefins 28, 51, 88, 91 and 96.



96 28 88 51 91

^{1}H NMR**

H#					
	1	5.64 s	5.77 dd	5.60 m	5.48 m	5.58 bs
	2	1.99 bs	2.10 m	2.12 bm	2.10 bm	2.36 bs
	3	1.61 bs	1.49 m	1.47 bs	1.44 bs	
	4		1.70 m	1.47 bs	1.44 bs	
	5				1.44 bs	

^{13}C NMR**

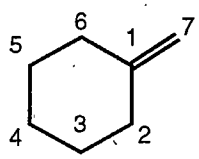
C#					
	1	127.3 d	132.3 d	129.9 d	130.1 d	128.6 d
	2	24.5 t *	29.4 t *	29.4 t *	25.9 t *	28.5 t
	3	22.1 t *	27.7 t *	26.4 t *	25.7 t *	
	4		32.6 t	25.6 t *	25.2 t *	
	5				25.3 t *	

MS***

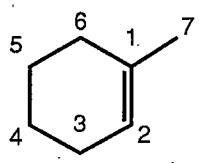
M^+	82(37.5)	96(53.4)	110(41.4)	124(32.4)	108(6.9)
	67(100)	81(71.2)	95(20.3)	109(11.1)	93(11.9)
	54(87.2)	67(100)	82(73.5)	96(70.0)	80(34.5)
	39(50.0)	54(91.6)	67(100)	81(65.0)	79(30.2)
		42(33.7)	54(84.4)	67(100)	67(84.5)
			42(74.2)	54(93.0)	54(100)
				42(81.3)	41(19.3)

* not rigorously determined
** shifts in ppm, $CDCl_3$ solvent
*** m/e (%)

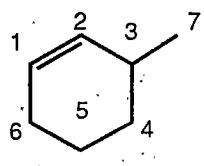
Table 23. NMR and MS Data for Olefins 26, 27, 81 and 82.



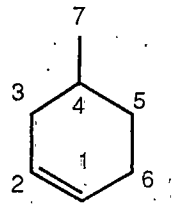
26



27



81



82

^{1}H NMR**

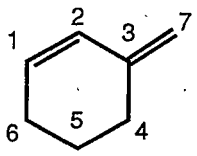
H#					
	1			5.63 ddd	5.64 d
	2	2.10 bs *	5.36 dd	5.50 dd	5.64 d
	3	1.51 bs *	1.91 m *	2.15 m	1.63 m *
	4a	1.51 bs *	1.56 m *	1.50 m *	1.19 m *
	4b	1.51 bs *	1.56 m *	1.15 m *	1.19 m *
	5	1.51 bs *	1.56 m *	1.73 m *	1.63 m *
	6	2.10 bs *	1.91 m *	1.94 m *	2.03 m *
	7	4.55 s	1.61 bs	0.94 d	0.94 d

MS***

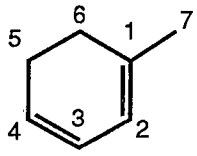
M^+	96	(46.6)	(35.4)	(24.4)	(34.1)
	81	(100)	(100)	(100)	(100)
	67	(81.5)	(42.4)	(38.2)	(32.5)
	55	(43.5)	(29.7)	(33.0)	(69.2)
	42	(28.0)	(18.2)	(25.9)	(22.2)

* not rigorously determined
** shifts in ppm, $CDCl_3$ solvent
*** m/e (%)

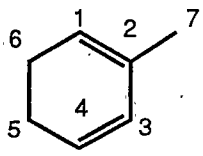
Table 24. NMR and MS Data for Dienes 83, 84 and 85.



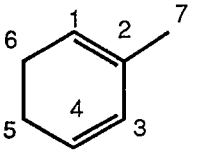
83



84



85

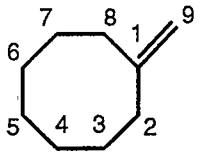


85

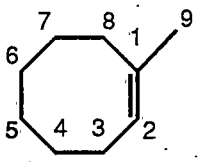
			observed	literature
^{1}H NMR**				
1	5.82 ddd		5.46 dd *	5.45 m
2	6.13 ddd	5.63 m		
3		5.83 m	5.79 m *	5.78 m
4	2.10 bdd	5.63 m	5.46 m *	5.45 m
5	1.70 ddd	2.14 m	2.1 m *	2.08 m
6	2.33 ddd	2.07 bd	2.1 m *	2.08 m
7	4.73 2bs	1.76 bs	1.7 bs	1.7 bs
MS***				
M^+	94 (34.0)	94 (41.8)	94 (37.8)	94 (42)
	93 (12.3)	93 (16.6)	93 (14.5)	93 (16)
	91 (16.2)	92 (31.1)	92 (8.4)	91 (30)
	79 (100)	91 (58.2)	91 (28.0)	80 (8)
	77 (33.7)	79 (100)	79 (100)	79 (100)
	66 (14.5)	77 (45.0)	77 (44.9)	77 (49)
	65 (10.8)	65 (14.1)	65 (12.1)	
	53 (12.7)	51 (13.9)	48 (14.7)	
	51 (10.4)			

* not rigorously determined
** shifts in ppm, $CDCl_3$ solvent
*** m/e (%)

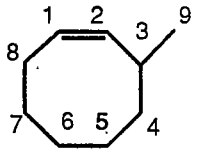
Table 25. NMR and MS Data for Olefins 49, 50 and 70.



49



50



70

^{1}H NMR**

H#			
1			5.24 dd
2	2.18 dd	5.32 dd	5.56 ddd
3	1.63 m	2.04 bm	2.57 m *
4	1.49 m	1.44 bs	1.8-1.1 m *
5	1.49 m	1.44 bs	1.8-1.1 m *
6	1.49 m	1.44 bs	1.8-1.1 m *
7	1.63 m	1.44 bs	1.8-1.1 m *
8a	2.18 dd	2.11 dd	2.02 m *
8b	2.18 dd	2.11 dd	2.24 m *
9	4.74 s	1.66 s	1.00 d

^{13}C NMR**

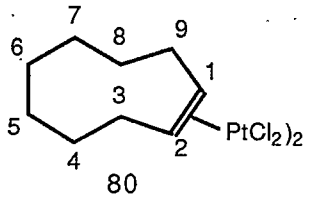
C#			
1	152.3 s	137.0 s	136.6 d
2	35.2 t *	124.1 d	128.2 d
3	27.4 t *	30.2 t *	30.4 d
4	26.7 t *	26.5 t *	26.6 t *
5	25.8 t	26.2 t *	26.0 t *
6	26.7 t *	26.6 t *	26.4 t *
7	27.4 t *	28.0 t *	29.5 t *
8	35.2 t *	30.3 t *	38.5 t *
9	110.7 t	23.5 q	22.0 q

MS***

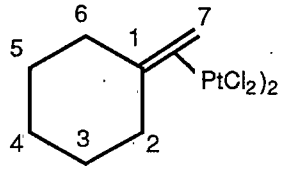
M^+ 124	(9.0)	(41.5)	(21.2)
109	(10.3)	(15.9)	(15.9)
96	(76.8)	(90.7)	(42.7)
81	(100)	(100)	(82.1)
67	(57.7)	(86.8)	(100)
55	(41.1)	(52.2)	(60.3)
42	(65.7)	(69.4)	(78.8)

* not rigorously determined
** shifts in ppm, $CDCl_3$ solvent
*** m/e (%)

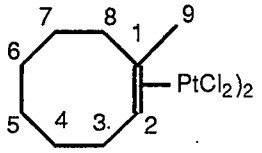
Table 26. NMR Data for Platinum-Olefin Complexes 64, 80 and 86.



80



86



64

^{1}H NMR**

H#				
	1	5.48 dd		
	2	5.48 dd	2.25 m *	5.51 m (≈69)***
	3	2.19 m *	1.92-1.38 m *	2.00 m *
	4	1.66 m *	1.92-1.38 m *	1.74 m *
	5	1.35 m *	1.92-1.38 m *	1.38 m *
	6	1.35 m *	2.25 m *	1.21 m *
	7a	1.35 m *	4.74 s (82)	1.74 m *
	7b	1.35 m *	4.74 s (82)	1.38 m *
	8a	1.66 m *		2.43 m *
	8b	1.66 m *		2.21 m *
	9	2.19 m *		1.74 s

^{13}C NMR**

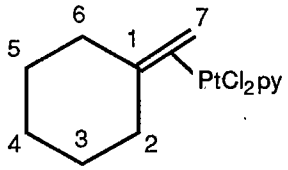
C#				
	1	91.0 d	131.0 s (216)	115.8 s
	2	91.0 d	39.0 t *	88.8 d
	3	27.4 t *	27.9 t *	34.4 t *
	4	24.4 t *	25.6 t	29.9 t *
	5	23.6 t *	27.9 t *	26.3 t *
	6	22.6 t	39.0 t *	25.4 t *
	7	23.6 t *	63.6 t (211)	28.1 t *
	8	24.4 t *		30.1 t *
	9	27.4 t *		26.3 q

^{195}Pt NMR****

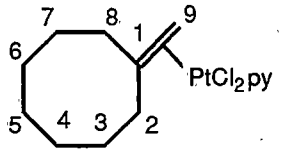
2351	≈2390	2410

* not rigorously determined
** shifts in ppm, $CDCl_3$ solvent
*** platinum coupling in Hz
**** relative to 1.0M $Na_2Pt(CN)_4$ in D_2O at 25°C

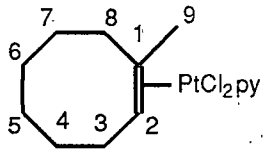
Table 27. NMR Data for Platinum-Olefin Complexes 54, 62 and 97.



97



54



62

^{1}H NMR**

H#	1		
2a	2.66 m *	2.63 *	5.63 dd (66)***
2b	2.20 m *	2.63 *	5.63 dd (66)
3a	1.97 m *	2.1 *	2.34 m *
3b	1.57 m *	2.1 *	2.11 m *
4	1.73 m *	1.6 *	1.70 m *
5a	1.97 m *	1.6 *	1.44 m *
5b	1.57 m *	1.6 *	1.44 m *
6a	2.66 m *	1.6 *	1.25 m *
6b	2.20 m *	1.6 *	1.25 m *
7a	4.76 s (64)	2.1 *	1.70 m *
7b	4.76 s (64)	2.1 *	1.44 m *
8a		2.6 *	2.98 m *
8b		2.6 *	2.46 m *
9		4.93 s (64)	2.06 s

^{13}C NMR**

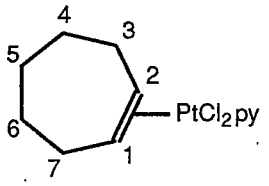
C#	1	138.0 s (143)	146.7 s (131)	120.4 s (138)
	2	38.6 t (21) *	38.2 t (23)	90.7 d (158)
	3	28.4 t (25) *	27.2 t *	34.1 t (≈10) *
	4	25.8 t	27.1 t *	30.7 t (42) *
	5	28.4 t (25) *	25.5 t	25.4 t *
	6	38.6 t (21) *	27.1 t *	26.4 t *
	7	64.5 t (159)	27.2 t *	28.6 t (36) *
	8		38.2 t (23)	30.1 t (≈10) *
	9		67.2 t (159)	26.0 q

^{195}Pt NMR****

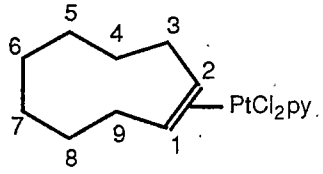
1999	2107	2036

* not rigorously determined
** shifts in ppm, $CDCl_3$ solvent
*** platinum coupling in Hz
**** relative to 1.0M $Na_2Pt(CN)_4$ in D_2O at 25°C

Table 28. NMR Data for Platinum-Olefin Complexes 98 and 99.



98



99

^{1}H NMR**

H#			
	1	5.86 dd (71)***	5.49 bdd (69)
	2	5.86 dd (71)	5.49 bdd (69)
	3a	2.80 ddd *	2.12 bm
	3b	2.34 m *	2.12 bm
	4	1.93 m *	1.45 bs
	5a	1.68 m *	1.45 bs
	5b	1.28 dd *	1.45 bs
	6a	1.68 m *	1.45 bs
	6b	1.28 dd *	1.45 bs
	7a	2.80 ddd *	1.45 bs
	7b	2.34 m *	1.45 bs
	8		1.45 bs
	9		2.12 bm

^{13}C NMR**

C#			
	1	95.9 d (162)	94.0 d (161)
	2	95.9 d (162)	94.0 d (161)
	3	28.1 t *	27.5 t *
	4	24.4 t (39) *	24.8 t *
	5	32.8 t (≈24)	23.7 t *
	6	24.4 t (39) *	22.6 t
	7	28.1 t *	23.7 t *
	8		24.8 t *
	9		27.5 t *

^{195}Pt NMR****

1869	1924

* not rigorously determined
** shifts in ppm, $CDCl_3$ solvent
*** platinum coupling in Hz
**** relative to 1.0M $Na_2Pt(CN)_4$ in D_2O at 25°C

APPENDIX B

X-ray Data for Complex 37

Table 29. Atomic Coordinates ($x10^4$) and Isotropic Thermal Parameters ($Å^2 x10^3$).

	x	y	z	U
Pt(1)	1152(2)	5311(1)	6446(1)	42(1)*
Pt(2)	-1270(2)	6910(1)	5847(1)	44(1)*
Cl(1)	-1246(12)	5330(9)	6259(6)	63(4)*
Cl(2)	786(11)	6701(9)	5622(7)	57(4)*
Cl(3)	768(15)	6457(12)	7217(8)	85(6)*
Cl(4)	-1243(14)	8436(10)	5407(8)	80(5)*
C(1)	1071(35)	3994(26)	5860(19)	44(11)
C(2)	1994(27)	4501(32)	5604(23)	54(13)
C(3)	3377(29)	4441(29)	5694(19)	44(12)
C(4)	3951(40)	5211(36)	6136(20)	74(16)
C(5)	2910(37)	5252(28)	6623(18)	40(11)
C(6)	2802(35)	4394(33)	7094(23)	66(16)
C(7)	1407(35)	4324(32)	7168(23)	62(13)
C(8)	858(59)	3337(35)	6954(24)	94(21)
C(9)	1101(68)	3058(30)	6261(21)	96(20)
C(10)	-3092(47)	6932(30)	5849(18)	50(8)
C(11)	-2822(44)	7337(32)	6409(18)	50(8)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 30. Bond lengths (Å).

Pt(1)-Cl(1)	2.659(16)	Pt(1)-Cl(2)	2.604(15)
Pt(1)-Cl(3)	2.296(18)	Pt(1)-C(1)	2.180(38)
Pt(1)-C(2)	2.290(45)	Pt(1)-C(5)	1.965(41)
Pt(1)-C(6)	2.592(43)	Pt(1)-C(7)	2.054(47)
Pt(2)-Cl(1)	2.321(14)	Pt(2)-Cl(2)	2.321(14)
Pt(2)-Cl(4)	2.276(16)	Pt(2)-C(10)	1.997(51)
Pt(2)-C(11)	2.155(45)	C(1)-C(2)	1.340(53)
C(1)-C(9)	1.530(56)	C(2)-C(3)	1.530(45)
C(3)-C(4)	1.540(60)	C(4)-C(5)	1.540(59)
C(5)-C(6)	1.540(60)	C(6)-C(7)	1.540(54)
C(7)-C(8)	1.540(67)	C(8)-C(9)	1.540(68)
C(10)-C(11)	1.340(55)		

Table 31. Bond Angles (°).

Cl(1)-Pt(1)-Cl(2)	75.0(4)	Cl(1)-Pt(1)-Cl(3)	85.3(5)
Cl(2)-Pt(1)-Cl(3)	87.4(5)	Cl(1)-Pt(1)-C(1)	83.3(10)
Cl(2)-Pt(1)-C(1)	102.1(11)	Cl(3)-Pt(1)-C(1)	162.6(11)
Cl(1)-Pt(1)-C(2)	106.7(9)	Cl(2)-Pt(1)-C(2)	83.7(11)
Cl(3)-Pt(1)-C(2)	162.6(10)	C(1)-Pt(1)-C(2)	34.8(14)
Cl(1)-Pt(1)-C(5)	176.9(12)	Cl(2)-Pt(1)-C(5)	108.0(12)
Cl(3)-Pt(1)-C(5)	94.1(12)	C(1)-Pt(1)-C(5)	96.6(15)
C(2)-Pt(1)-C(5)	74.6(14)	Cl(1)-Pt(1)-C(6)	140.7(10)
Cl(2)-Pt(1)-C(6)	144.3(10)	Cl(3)-Pt(1)-C(6)	94.5(11)
C(1)-Pt(1)-C(6)	86.2(14)	C(2)-Pt(1)-C(6)	84.2(14)
C(5)-Pt(1)-C(6)	36.3(15)	Cl(1)-Pt(1)-C(7)	104.6(11)
Cl(2)-Pt(1)-C(7)	173.9(14)	Cl(3)-Pt(1)-C(7)	86.5(14)
C(1)-Pt(1)-C(7)	83.8(16)	C(2)-Pt(1)-C(7)	102.1(17)
C(5)-Pt(1)-C(7)	72.4(16)	C(6)-Pt(1)-C(7)	36.4(14)
Cl(1)-Pt(2)-Cl(2)	87.3(5)	Cl(1)-Pt(2)-Cl(4)	177.5(5)
Cl(2)-Pt(2)-Cl(4)	90.9(5)	Cl(1)-Pt(2)-C(10)	91.4(12)
Cl(2)-Pt(2)-C(10)	166.7(12)	Cl(4)-Pt(2)-C(10)	90.0(12)
Cl(1)-Pt(2)-C(11)	92.9(12)	Cl(2)-Pt(2)-C(11)	155.9(12)
Cl(4)-Pt(2)-C(11)	89.5(12)	C(10)-Pt(2)-C(11)	37.4(16)
Pt(1)-Cl(1)-Pt(2)	94.4(5)	Pt(1)-Cl(2)-Pt(2)	95.8(5)
Pt(1)-C(1)-C(2)	77.1(25)	Pt(1)-C(1)-C(9)	111.6(27)
C(2)-C(1)-C(9)	129.5(42)	Pt(1)-C(2)-C(1)	68.1(24)
Pt(1)-C(2)-C(3)	109.2(28)	C(1)-C(2)-C(3)	132.1(39)
C(2)-C(3)-C(4)	116.4(34)	C(3)-C(4)-C(5)	97.4(32)
Pt(1)-C(5)-C(4)	126.9(28)	Pt(1)-C(5)-C(6)	94.6(24)
C(4)-C(5)-C(6)	117.6(35)	Pt(1)-H(5b)-C(5)	143.7(19)
Pt(1)-C(6)-C(5)	49.1(19)	Pt(1)-C(6)-C(7)	52.4(22)
C(5)-C(6)-C(7)	100.9(33)	Pt(1)-C(7)-C(6)	91.1(28)
Pt(1)-C(7)-C(8)	107.4(32)	C(6)-C(7)-C(8)	114.4(39)
Pt(1)-H(7a)-C(7)	143.7(19)	C(7)-C(8)-C(9)	115.3(44)
C(1)-C(9)-C(8)	108.6(34)	Pt(2)-C(10)-C(11)	77.7(30)
Pt(2)-H(10a)-C(10)	111.0(16)	Pt(2)-C(11)-C(10)	64.9(27)
Pt(2)-H(11a)-C(11)	98.8(15)		

Table 32. Anisotropic Thermal Parameters ($Å^2 x 10^3$).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	45(1)	32(1)	48(1)	-6(1)	-5(1)	6(1)
Pt(2)	35(1)	48(1)	47(1)	6(1)	-2(1)	3(1)
Cl(1)	45(7)	56(7)	88(9)	25(6)	12(8)	-6(8)
Cl(2)	37(7)	51(7)	84(9)	23(7)	4(6)	4(6)
Cl(3)	88(11)	86(11)	80(10)	-46(9)	-16(9)	22(10)
Cl(4)	49(8)	61(8)	128(12)	36(8)	-18(10)	5(9)

The anisotropic temperature factor exponent takes the form:
$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Figure 56. Computer-Generated View of the Non-Hydrogen Atoms For Complex 37.

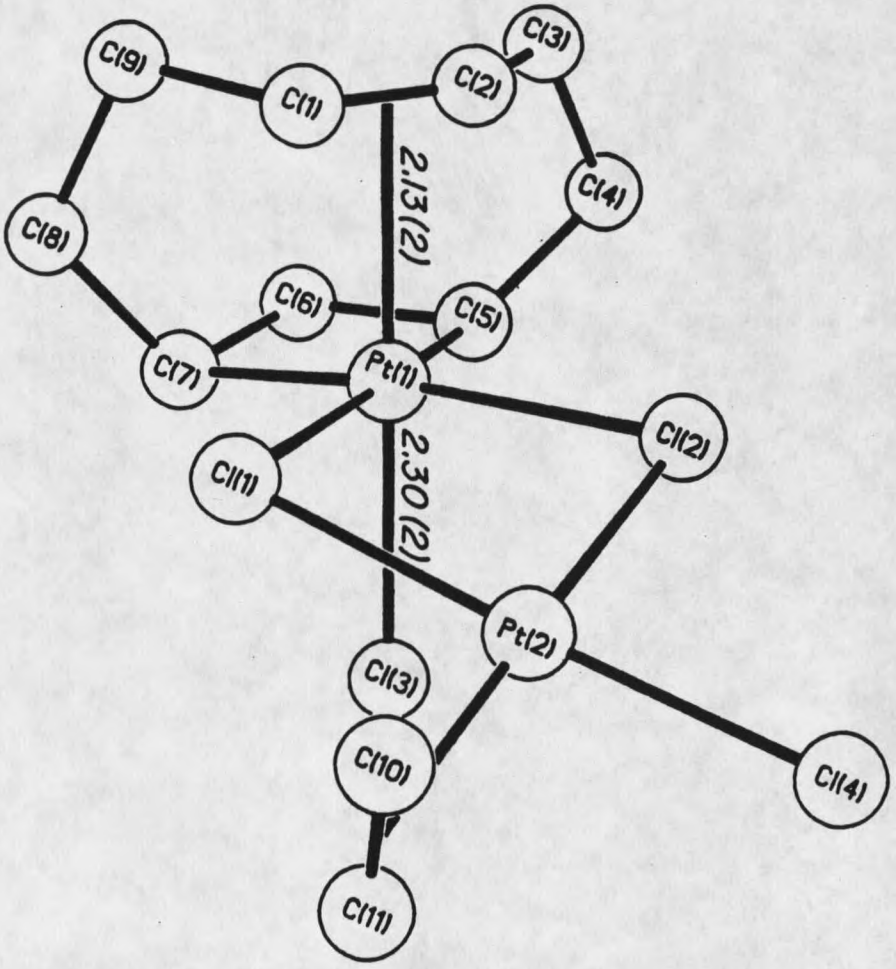
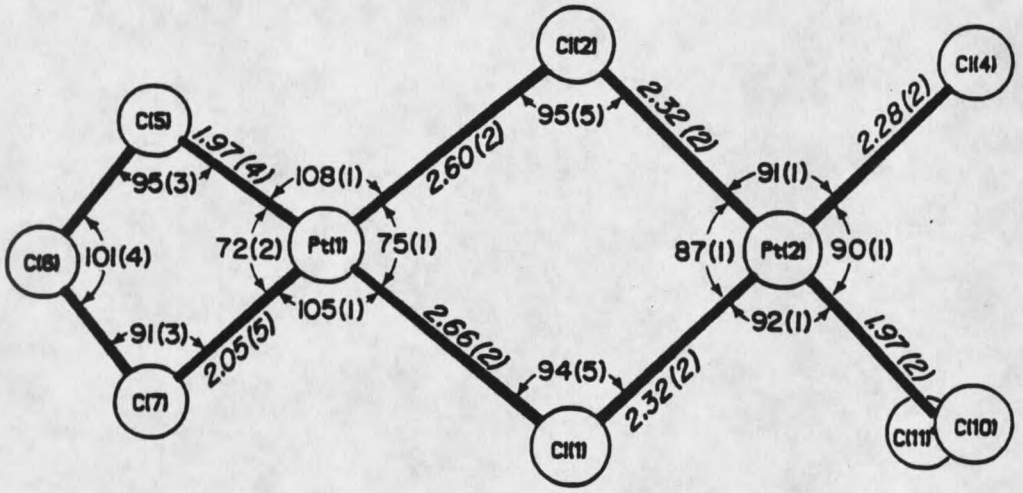
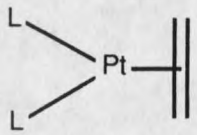


Figure 57. Computer-Generated View of the Platinacyclobutane Ring and Dichlorodiplatinum Ring System with Corresponding Bond Lengths for Complex 37.

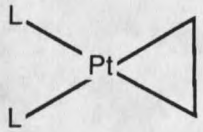


APPENDIX C

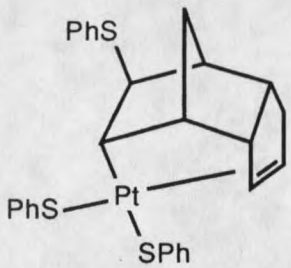
Structures


L
Pt
L

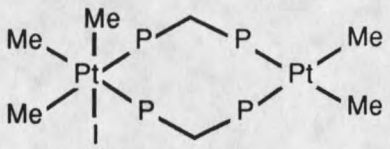
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L
Pt
L

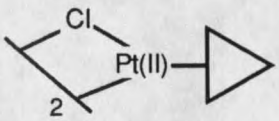
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PhS
PhS
Pt
SPh

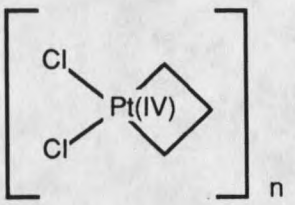
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Me
Me
P
P
Pt
Me
Pt
Me
P
P
Me

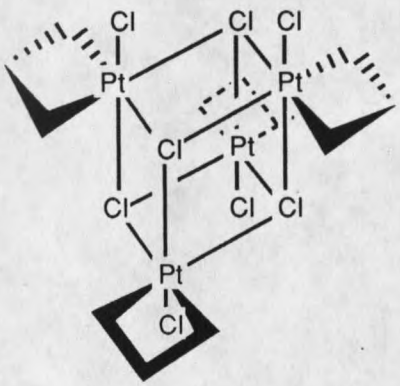
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Cl
Pt(II)
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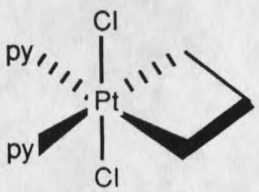
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Cl
Pt(IV)
Cl
n

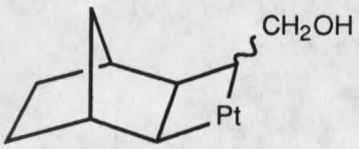
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Cl
Cl
Cl
Pt
Pt
Cl
Pt
Cl
Cl
Cl
Pt
Cl

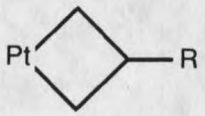
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Cl
py
Pt
py
Cl

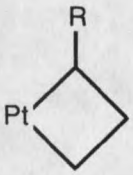
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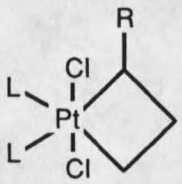
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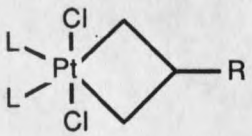
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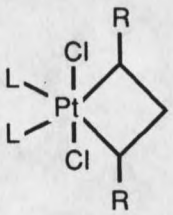
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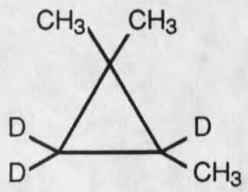
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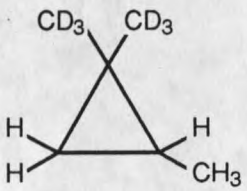
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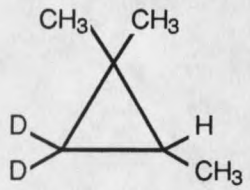
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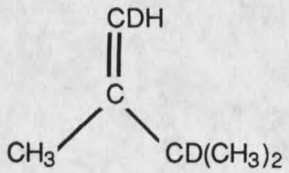
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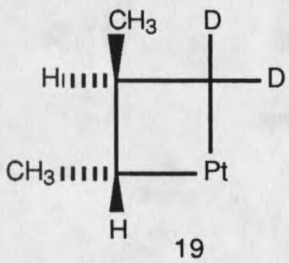
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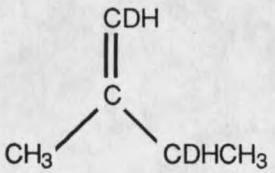
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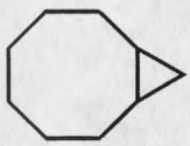
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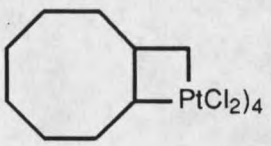
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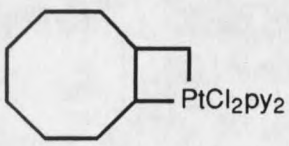
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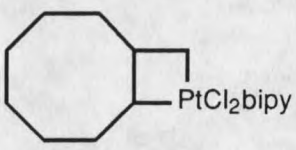
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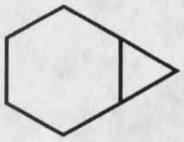
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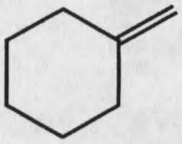
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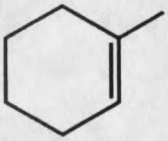
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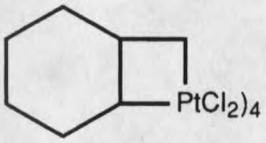
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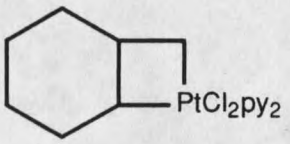
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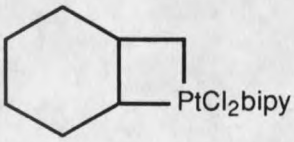
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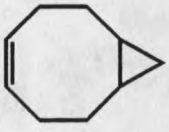
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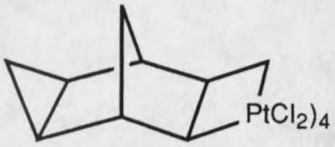
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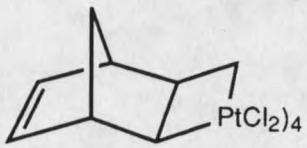
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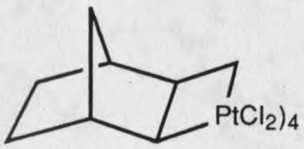
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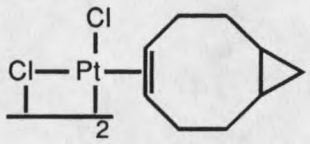
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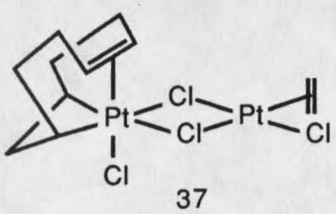
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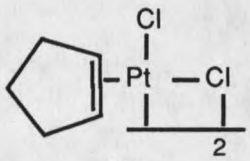
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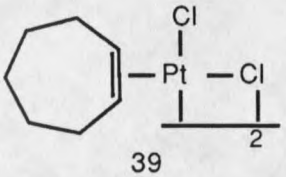
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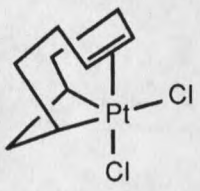
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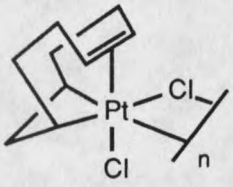
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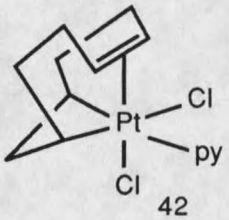
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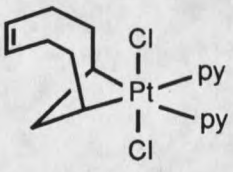


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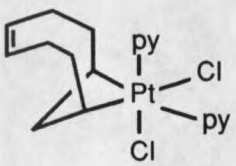


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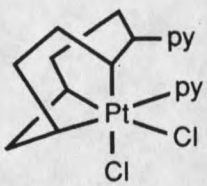
43 = Complex 37 in pyridine, structure not known



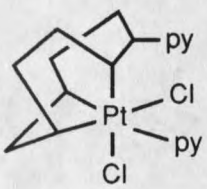
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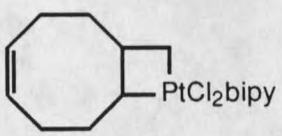
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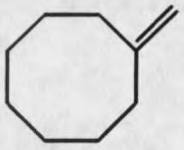
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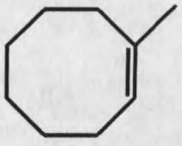
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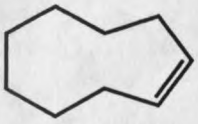
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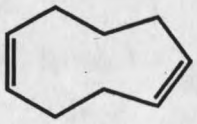
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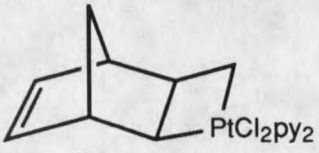
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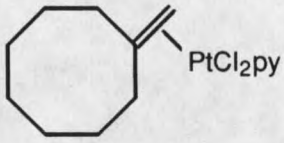
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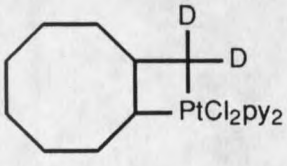
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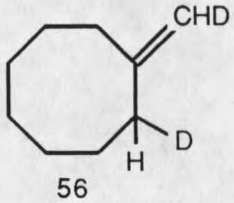
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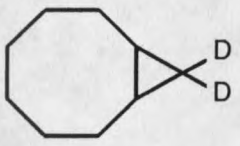
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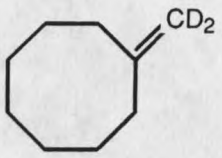
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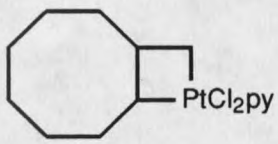
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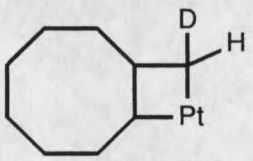
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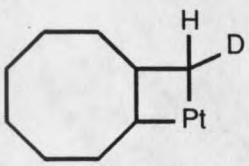
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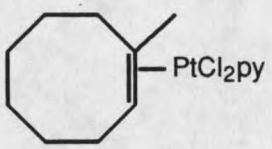
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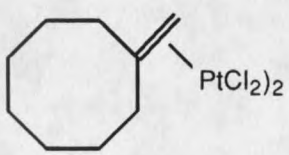
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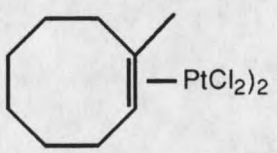
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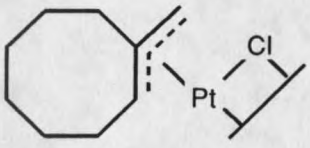
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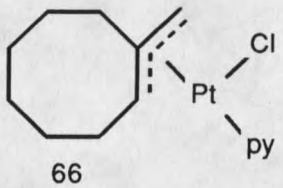
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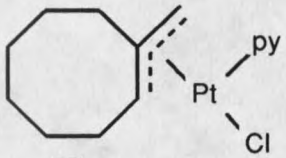
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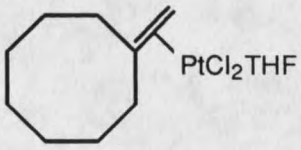
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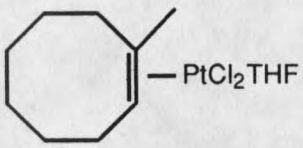
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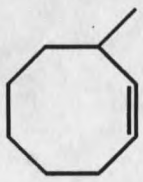
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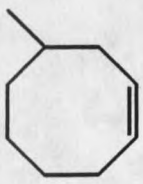
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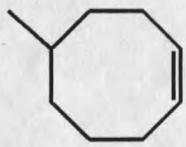
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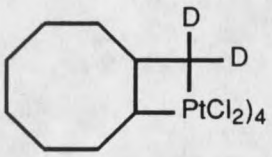
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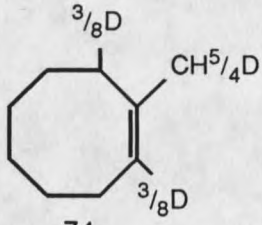
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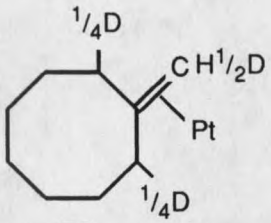
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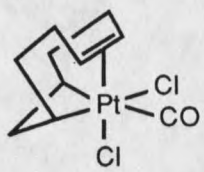
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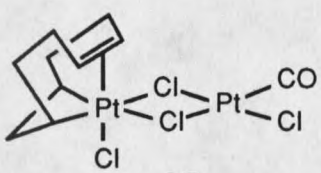
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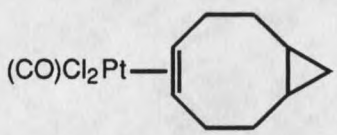
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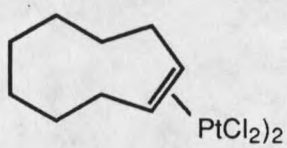
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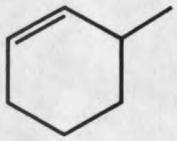
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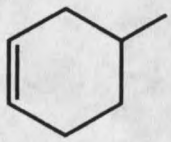
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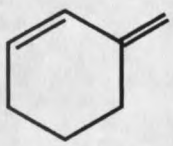
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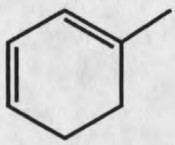
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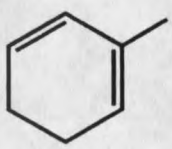
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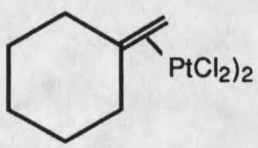
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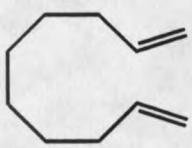
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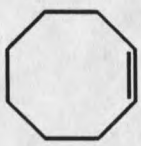
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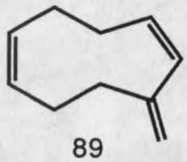
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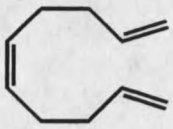
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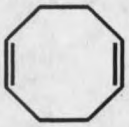
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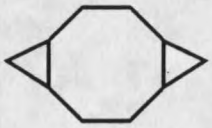
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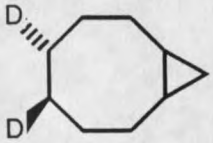
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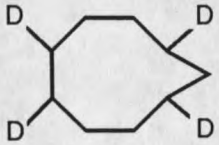
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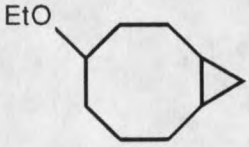
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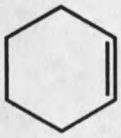
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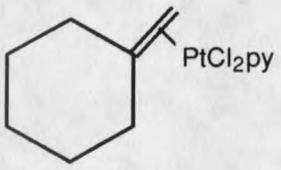
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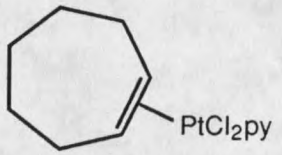
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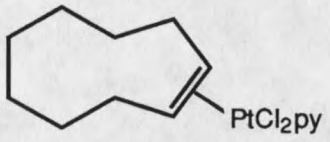
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