

Investigation of the dimerization of norbornadiene using photolysis of nickel and pseudo-nickel carbonyls
by Gerald Elery Voecks

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:
Dimers of norbornadiene are known to form when norbornadiene solutions of various metal carbonyls are thermally excited. Of the numerous stereoisomeric dimers which norbornadiene will form various mixtures of them are generated by different metal carbonyls. In order to obtain needed information regarding factors contributing to the path-way responsible for the stereospecificity of the dimers formed a series of isostructural and isoelectronic transition metal carbonyls—-nickel and the pseudo-nickel carbonyl series—were investigated® In this series of compounds triphenylphosphine derivatives of the nickel, cobalt, and iron species were included® Photochemistry was used as the mode of excitation because of the ability to specifically excite the carbonyl complex independently of the norbornadiene. With the exception of nickel tetracarbonyl the series of compounds produced a specific dimer isomer—--exo-trans-exo. Nickel tetracarbonyl produced two 2 + 2 + 2 or pseudo-Diels-Alder dimers of norbornadiene photochemically. Since this complex was unique in its dimer product formation and since it provided an opportunity to observe ligand participation by comparison to the bistriphenyl-phosphinedicarbonylnickel complex the reaction was studied in detail. A norbornadiene complex as well as dimer complexes were isolated and their participation in the dimer formation process thermally and photochemically was studied resulting in a proposed mechanism for dimerization by nickel tetracarbonyl. The major 2+2+2 dimer also afforded the opportunity to study the effect of a cyclopropyl ring on neighboring protons in proton nmr experiments®

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by

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A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree

of

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in

Chemistry

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ABSTRACT

Dimers of norbornadiene are known to form when norbornadiene solutions of various metal carbonyls are thermally excited. Of the numerous stereoisomeric dimers which norbornadiene will form various mixtures of them are generated by different metal carbonyls. In order to obtain needed information regarding factors contributing to the pathway responsible for the stereospecificity of the dimers formed a series of isostructural and isoelectronic transition metal carbonyls——nickel and the pseudo-nickel carbonyl series——were investigated. In this series of compounds triphenylphosphine derivatives of the nickel, cobalt, and iron species were included. Photochemistry was used as the mode of excitation because of the ability to specifically excite the carbonyl complex independently of the norbornadiene. With the exception of nickel tetracarbonyl the series of compounds produced a specific dimer isomer—— exo-trans-exo. Nickel tetracarbonyl produced two 2 + 2 + 2 or pseudo-Diels-Alder dimers of norbornadiene photochemically. Since this complex was unique in its dimer product formation and since it provided an opportunity to observe ligand participation by comparison to the bistriphenylphosphinedicarbonylnickel complex the reaction was studied in detail. A norbornadiene complex as well as dimer complexes were isolated and their participation in the dimer formation process thermally and photochemically was studied resulting in a proposed mechanism for dimerization by nickel tetracarbonyl. The major 2 + 2 + 2 dimer also afforded the opportunity to study the effect of a cyclopropyl ring on neighboring protons in proton nmr experiments.

INTRODUCTION

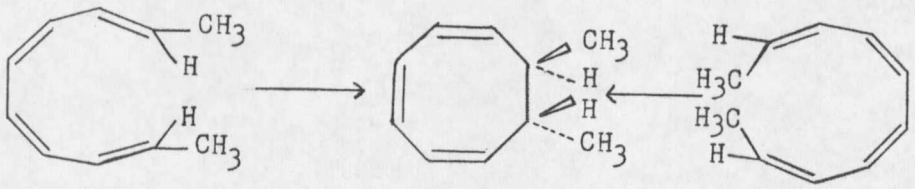
During the past ten to fifteen years norbornadiene (bicyclo-2,2,1-hepta-2,5-diene) has been shown to dimerize and trimerize when in the presence of various transition metals and excited thermally or photochemically. Some examples of the transition metal systems investigated with norbornadiene thermally are rhodium on carbon,[1] "bare" metals by reduction of nickel, cobalt, and iron acetylacetonates by triethyl aluminum,[2] nickel bisacrylonitrile,[3] zinc bistetracarbonylcobaltate,[4] dicobaltoctacarbonyl,[5] iron pentacarbonyl,[6] nickel tetracarbonyl,[7] cobalt tricarbonylnitrosyl,[8] and phosphine-substituted derivatives of the metal carbonyls. Fewer investigations have been pursued using photochemically excited metal systems in norbornadiene. Examples of these are chromium hexacarbonyl,[9] iron pentacarbonyl (or di-iron nonacarbonyl),[10] and subustituted and unsubstituted-butadiene iron tricarbonyls.[11] The norbornadiene products obtained vary in type and amount depending on the transition metal used to catalyze the reaction.

Various intermediates have been postulated to explain the stereochemistry of the organic products. These intermediates have been based in part on isolated complexes of norbornadiene and in part on the stereochemistry necessary to coincide with that of the products. However, few attempts have been made to work out the details involved in determining what parameters are important to reach these postulated intermediates and from them to reach the products.

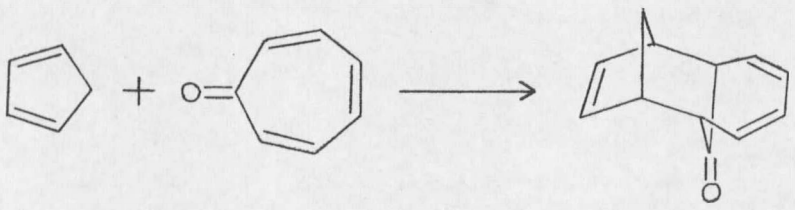
The isolation and characterization of intermediates is extremely helpful in determining reaction pathways of certain known reactants to form certain known products. Unfortunately, as in many reactions involving one or more fast steps the intermediates may be extremely unstable and cannot be isolated intact. Recently, some success has been obtained in isolating intermediates involved in hydrogenation of olefins. In one case, the complex $Ir(CO)Cl[P(C_6H_5)_3]_2$[12] was known to be square planar with the $P(C_6H_5)_3$ group trans.[13] When hydrogen was added to a benzene solution of this complex a different complex was formed which when isolated was found to be $Ir(CO)Cl[P(C_6H_5)_3]_2H_2$.[14] Its structure was found to be octahedral.[15] The subsequent reaction of $Ir(CO)Cl[P(C_6H_5)_3]_2H_2$ with an olefin in solution resulted in the same hydrogenated hydrocarbon as obtained in the original experiment.[16] Thus, one step was verified in this reaction. Although this type of intermediate yields much information about homogeneous catalysis very little of it can be directly applied to the cycloaddition reactions encountered with norbornadiene.

However, two important orbital symmetry theories have been reported, one by Woodward-Hoffmann[17] and the other by Mango,[18] which relate to specificity in stereochemistry in concerted organic and organometallic reactions. These theories neither answer the question of how to obtain an intermediate nor contribute to the kinetics but they do produce a basis on which intermediates could be reasonably postulated based on the conservation of orbital symmetry.

The first ideas to be presented in the literature regarding orbital symmetry restrictions on a generalized level were those of Woodward and Hoffmann. These ideas were first introduced in relation to electrocyclic reactions.[19] Electrocyclic reactions are defined as those reactions (forward or reverse) in which two π systems on the ends of a linear molecule combine to form a single σ bond. Many times in these reactions there is also either a double bond formed or double bonds rearranged within the molecule. An example of this type of reaction is the ring closure of decatetraenes thermally by conrotatory motion but photochemically by a disrotatory motion. The stereochemistry of the thermal reaction products is shown below.[20]



Orbital symmetry relationships were then incorporated into concerted intermolecular cycloaddition reactions which rationalized the stereochemistry maintained in these reactions.[21] An example of this type of reaction is the thermally excited reaction of cyclopentadiene and tropone to produce the tricyclic system as shown.[22]



The orbital symmetry relationships between reactants and products involved constructing "orbital correlation diagrams" whenever possible. The reacting orbitals were correlated with the newly formed bonding orbitals of the products but in a manner which portrayed a reasonable reaction approach. This meant first assuming a geometrical approach of only the reacting orbitals of the reactants and constructing molecular orbitals of the resulting arrangement (bonding and antibonding) based on all the symmetry elements which were available and pertinent. The same was done with the orbitals that were consequently formed in the resulting product; again with respect to the same symmetry elements present in the reactants. Now by comparing the molecular orbitals of the reactants to those of the products with approximate alignment based on presumed relative energies, lines could be drawn to connect molecular orbitals which corresponded in geometry. The resulting diagram would show changes in respective energy levels as the reaction passed through the transition state.

There are two examples commonly used to illustrate the interaction of orbitals in cycloaddition reactions. One is a 2 + 2 reaction

and the other is a 2 + 4 reaction. The 2 + 2 cycloaddition reaction is represented by the cyclobutanation of two ethylene molecules whereas the Diels-Alder reaction of butadiene and ethylene represents the 2 + 4 reaction. Assuming the geometries shown in Figures 1 and 2 depict the approach of the reacting species corresponding orbital correlation diagrams can then be constructed as in Figures 3 and 4.[23]

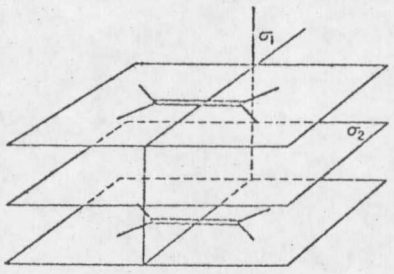


Figure 1

Assumed Geometry of Approach for Two Ethylene Molecules to Produce Cyclobutane

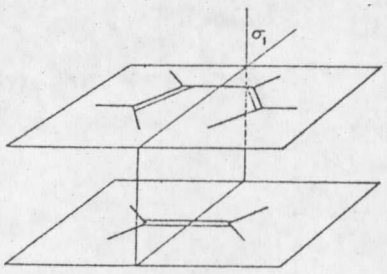


Figure 2

Assumed Geometry of Approach for Butadiene and Ethylene to Produce Cyclohexene

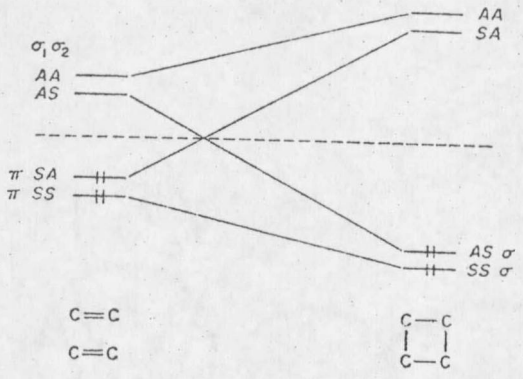


Figure 3

Correlation Diagram for the Combination of Two Ethylene Molecules to Form Cyclobutane

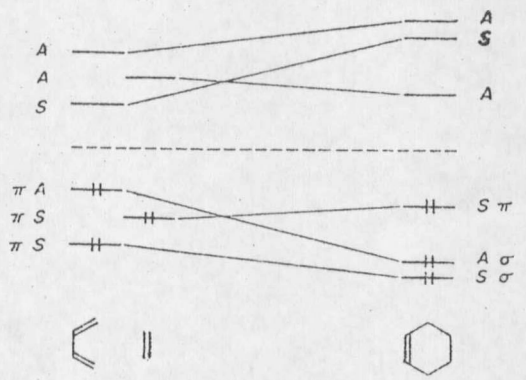


Figure 4

Correlation Diagram for the Combination of Butadiene and Ethylene to Form Cyclohexene

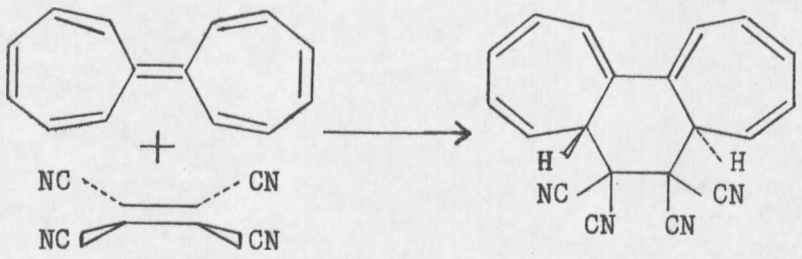
Symmetry planes are drawn in the transition state diagrams to show the relationship of symmetry of the interacting orbitals. (In the figures S = symmetric; A = antisymmetric with respect to symmetry in the planes 1 and 2.) One can see that in the 2 + 2 reaction a bonding and antibonding orbital of the reacting ethylene species must cross during the ensuing reaction in order to correlate their symmetry with that required of the antibonding and bonding orbitals of cyclobutane. However, in the Diels-Alder reaction (2 + 4) the symmetry of the interacting bonding orbitals of butadiene and ethylene correlate with the symmetry of the bonding orbitals of the product cyclohexene; likewise, the antibonding orbitals on either side of the reaction coordinate also correlate. Woodward and Hoffmann[24] refer to the reaction in the first case (2 + 2)

as being symmetry forbidden in the ground state. Symmetry forbiddance is due to the high energy that would be needed to take the electrons from the symmetry orbital (SA) and place them into the symmetry orbital (AS) which corresponds to the symmetry of the highest occupied orbital of cyclobutane in the 2 + 2 reaction. No such energy requirement is needed in the 2 + 4 reaction and is, therefore, a symmetry allowed reaction in the ground state.

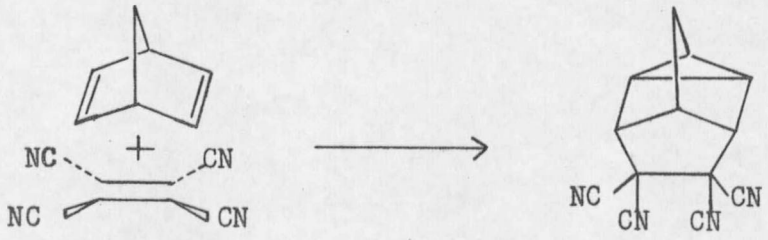
On the other hand Woodward and Hoffmann have pointed out that photochemically the excited state may be reached where an electron in the highest occupied π orbital is excited to the lowest unoccupied π^* orbital. If the cyclobutanation reaction now proceeded the net change in energy of the two excited states would be very small and the reaction could easily proceed insofar as symmetry is concerned. Applying the same sequence of events to the 2 + 4 reaction would result in the occupation of two orbitals which would have positive overlap similar to the other symmetry forbidden examples. Therefore, the 2 + 2 reaction would be classified as symmetry allowed photochemically and the 2 + 4 reaction would be photochemically forbidden.

The outline of orbital symmetry correlation in cycloaddition reactions just presented is only a simple one. For example, there are various ways in which molecules can approach one another prior to reaction, resulting in a variety of correlation diagrams. However, the principle of conservation of orbital symmetry is maintained even if a correlation diagram cannot be constructed due to the complexity of the

reacting molecules. There are also many variations and combinations of reactions that can take place; cycloreversions (the opposite of cycloadditions), σ and/or π bond participation and multicomponent combinations, for example:



$\pi 14_a + \pi 2_s$



$\pi 2_s + \pi 2_s + \pi 2_s$

Thus, the 2 + 2 reaction mentioned previously is more specifically labeled $\pi 2_s + \pi 2_s$ meaning the interaction of two π bonds, both bonding suprafacially. (Suprafacial processes refer to cis geometry while antarafacial processes refer to trans geometry in respect to bond breakage or formation.) In Figure 5[27] are the orientations of two ethylene molecules whose interaction in each case would correspond to the reaction processes $(\pi 2_s + \pi 2_s)$, $(\pi 2_s + \pi 2_a)$, and $(\pi 2_a + \pi 2_a)$.

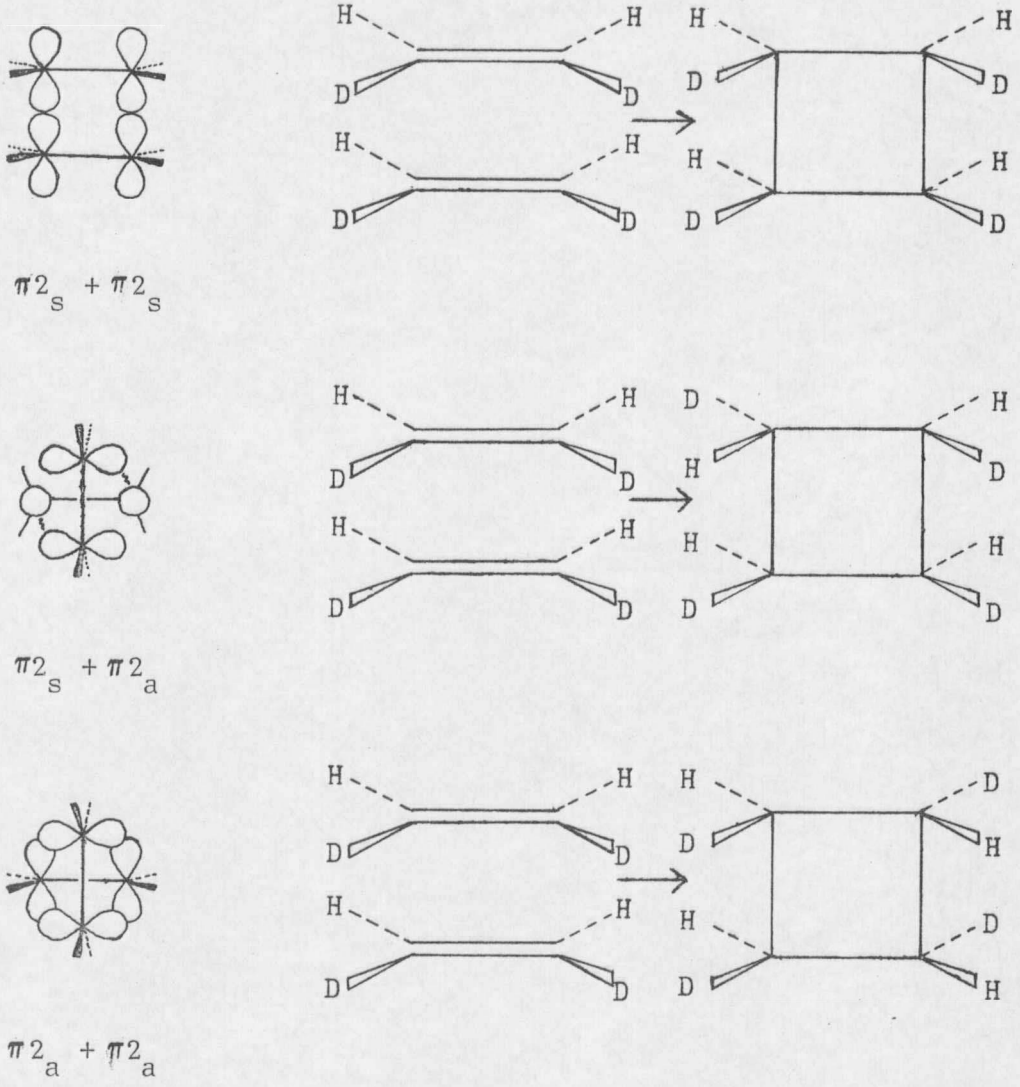


Figure 5

The Various $\pi 2 + \pi 2$ Reactions Using Interacting Ethylene Molecules as Examples

Some reactions which yield products that do not conform to the orbital symmetry predictions are either assumed not to be concerted (for example, go through an intermediate) or go through two reactions, each reaction conforming to orbital symmetry control. When the symmetry of the molecule is changed such that it is no longer symmetrical but the local reaction site is still basically the same the effects of the changes in its ability to react are hard to predict by this method. This can be seen in the $\pi 2_s + \pi 2_s$ reactions of two ethylene molecules compared to an ethylene molecule and a propylene molecule. In the latter case the symmetry of the σ plane through the two interacting double bonds in the transition state is destroyed because of the methyl group. Thus, all levels would appear to be reduced to the same symmetry making the reaction thermally allowed. Actually, the bonding sites have changed very little from those of two reacting ethylenes and the reaction is still thermally forbidden. These cases as well as the cases where no correlation diagrams can be constructed due to the complexity of the molecular structure do occasionally provide some skepticism about this method.

It should be pointed out that electronic state diagrams have been constructed for some of the reactions referred to above. This supplement to the Woodward-Hoffmann rules was reported by Longuet-Higgins and Abrahamson[28] as a means to follow a reaction and make qualitative conclusions such as the variation of energy of the system during the course of the reaction without involved calculations. These state

symmetry diagrams are based on the same symmetry elements as the orbital symmetry diagrams of Woodward and Hoffmann. However, the orbital correlation diagrams are most frequently used due to their relative ease of construction and their pictorial quality. Figure 6 shows the electronic state diagrams for the reaction of the ethylenes to give cyclobutane and Figure 7 shows the diagram corresponding to the Diels-Alder reaction of ethylene and butadiene.[29]

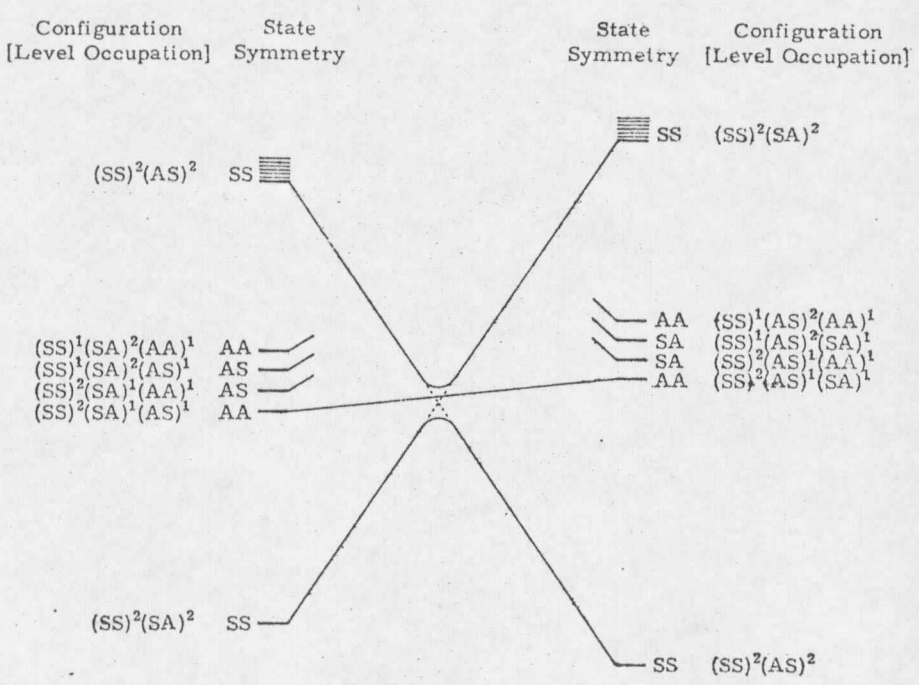


Figure 6

State Correlation Diagram for the Cycloaddition Reaction of Two Ethylene Molecules

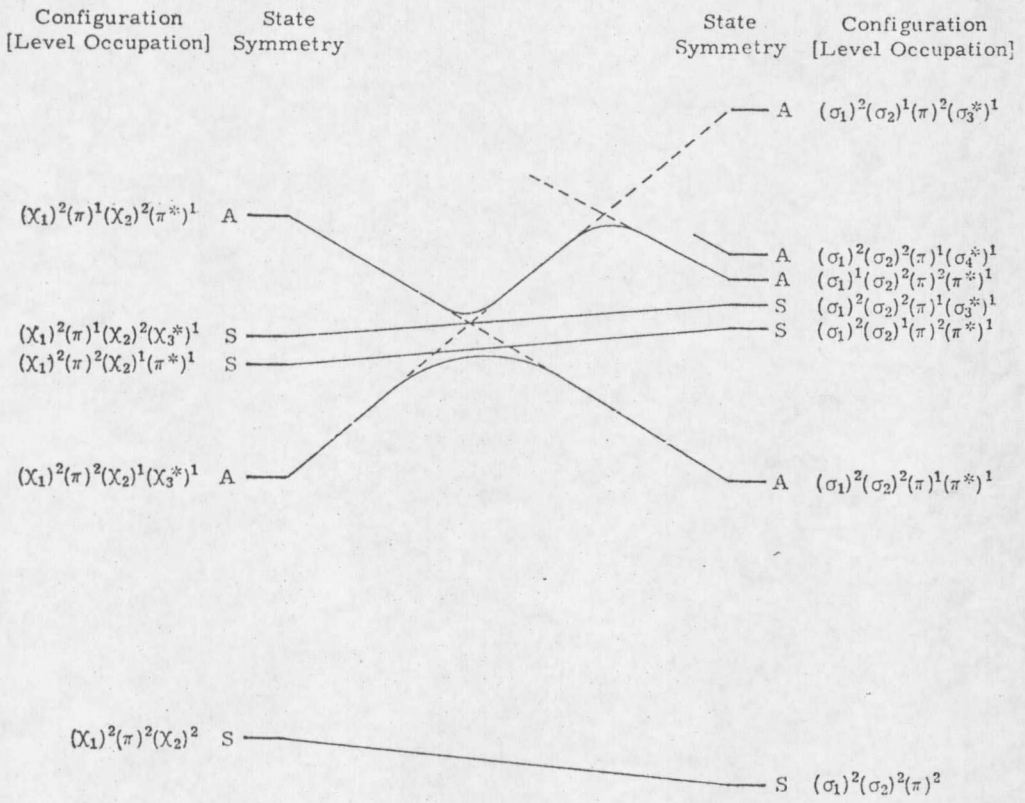


Figure 7

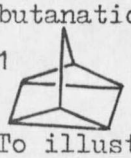
State Correlation Diagram for the Cycloaddition Reaction of 1,3-Butadiene and Ethylene

By and large, the forbiddenness or allowedness of numerous cycloaddition reactions have been shown to adhere quite well to the idea of the conservation of orbital symmetry.

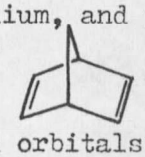
With the use of transition metals as catalysts for organic reactions it became apparent that metals were capable of allowing some

reactions to take place thermally (see Page 1) that according to orbital symmetry were forbidden. Such is the case of norbornadiene. This leads to the second application of orbital symmetry conservation which helps describe the feasibility of a transition state incorporating the metal with the organic molecules for a given reaction.

Mango and Schachtschneider[30] were the first to correlate metal orbitals with olefin orbitals in a symmetrical manner such that the resultant interaction allowed reactions that were forbidden sans metal. One example of this forbidden-to-allowed reaction is the thermal conversion of quadricyclene to norbornadiene or, in other words, the reverse of cyclobutanation by use of rhodium, palladium, and platinum complexes.[31]



+ $Rh(norbornadiene)_2Cl_2 \xrightarrow{-26^\circ}$



To illustrate how transition metal d orbitals may participate in the suprafacial cycloaddition of ethylene recall the geometry of the transition state arrangement of the two olefins (Figure 1). The d orbitals must participate in this transition state such that the highest occupied (bonding) and lowest unoccupied (antibonding) orbitals of the reactants can cross by a symmetry allowed pathway in order to help facilitate the reaction progress. If, for example, one assumed that the lowest bonding orbital (SS) of the transition state could bond to a metal p ordz^2 orbital and the highest antibonding orbital (AA) may or may not participate in backbonding the remaining orbitals to consider (SA and AS) are the important ones, the so-called "frontier orbitals." Now the geometry of these "frontier orbitals" corresponds to that of two d

orbitals at right angles to one another, the dyz and dxz, for example. The correlation of the geometrical orbital symmetry arrangement is illustrated in Figure 8.[32]

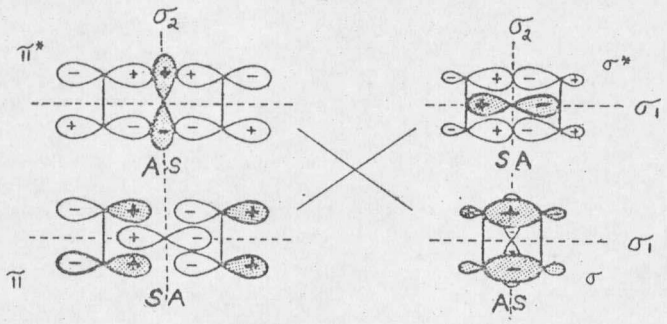


Figure 8

Correlation Diagram Involving the AS and SA Orbitals of the Olefins and the Metal d Orbitals

If the dyz orbital were oriented in the same plane as σ_1 and was empty, whereas the dxz orbital was at right angles in the plane of σ_2 and filled, this would create a bonding and backbonding arrangement typically ascribed to that which takes place in olefin-transition metal complexes.

This convenient combination of orbitals, which by no means is meant to imply a complete localization of electrons, could conceivably permit a flow of a pair of electrons from the olefin AS orbital into the metal dyz orbital and, likewise, a flow of a pair of electrons from the metal dxz orbital into the olefin SA antibonding orbital (Figure 9).[33]

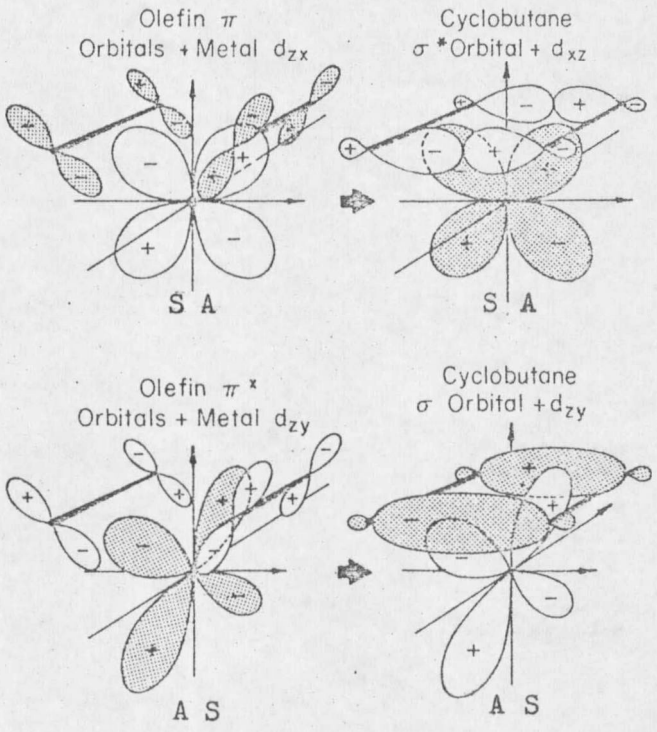


Figure 9

Illustration of Electron Pair Exchange between Metal d_{xz} , d_{yz} Orbitals and Interacting Olefin Orbitals

If the electrons are free to move simultaneously this total exchange would be called a concerted reaction. The result of this electron exchange would be creating a σ bond between the two ethylene entities without going through a high energy transition and leaving the metal essentially unchanged.

Of course, this simple description is merely used to depict a possible pathway for orbital symmetry conservation to be maintained and

at the same time show how electron transfer could take place. There are, however, other parameters that could determine whether such a geometric or energetic arrangement of orbitals would be feasible. For example, the orbital overlap must permit a measurable transfer of electrons from organic orbitals to metal orbitals. Specifically, unfavorable overlap between dyz and the filled olefin orbital could hamper the reaction. A complex may form but cycloaddition may not occur, perhaps due to unfavorable overlap between dxz and the antibonding olefin orbital. This could imply a large difference between the bonding and antibonding levels resulting in poor metal-organic orbital mixing. There is also the problem of the correct geometrical arrangement for the chain of events to occur. The effect of other ligands on the metal in regard to ease of stabilizing the reacting specie could contribute to this problem as well.

Thus, it can be seen that the role of the metal in these reactions is not just to change symmetry forbidden reactions to allowed reactions. It appears that transition metals can, in general, allow reactions to take place if the symmetry of the d orbitals can be utilized to permit electron transfer to take place. Reactions may proceed if the effects of ligands, geometry, steric interference, structural behavior, and electronic interactions are favorable.

The degree of bonding which must be formed between the organic molecules and the metal before dimerization may take place is unknown. This step in the reaction sequence of bonding to the metal followed by

dimerization may be the step which determines whether electron transfer will take place allowing the reaction to proceed. The reaction may be more feasible when the organic molecules are not tightly bound to the metal whereby electrons are less rigidly held in space and less feasible when a stable complex can form. It is a parameter of this type which is presently being investigated by various workers that may give a more accurate picture of the intermediate involved.

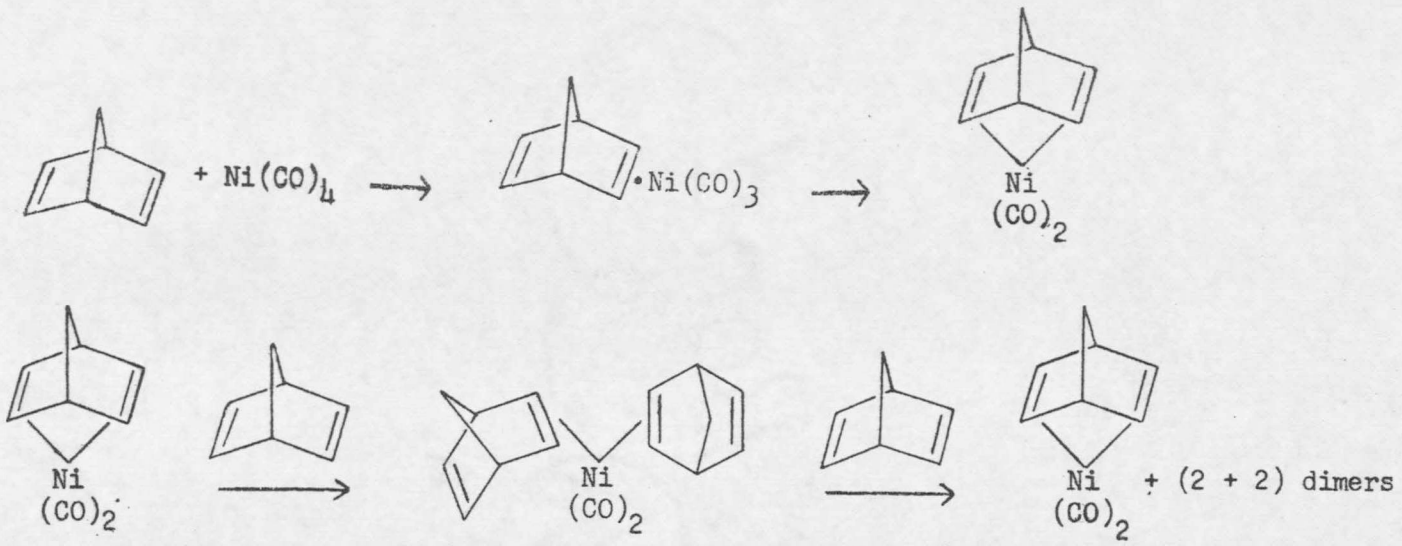
The work reported in this thesis has applied the orbital symmetry conservation idea to help explain a plausible pathway of metal mediated norbornadiene dimerization and trimerization under photochemical and thermal conditions. Incorporated into the overall reaction picture are some useful implications regarding the effects of metals, ligands, and geometry as well as photochemical and thermal excitation. In general the results of such investigations are aimed at an eventual understanding of the importance of various parameters in metal catalyzed reactions.

DISCUSSION

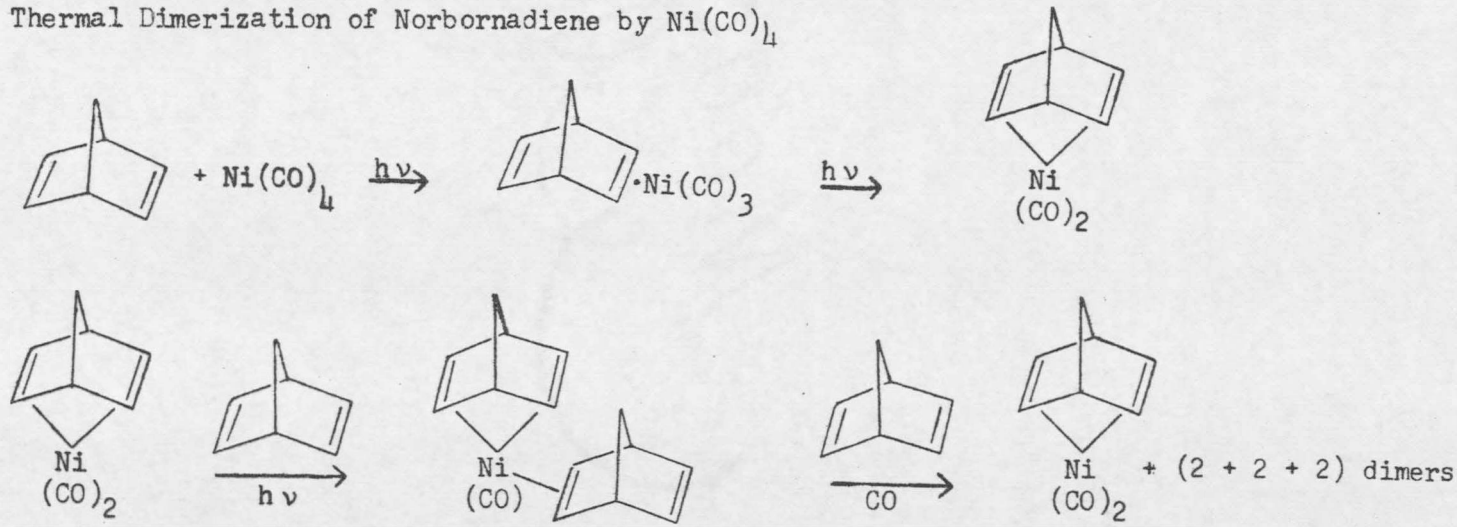
The work reported in this thesis is aimed primarily at helping to elucidate the mechanism by which transition metal carbonyls participate in the dimerization of norbornadiene. The various dimers formed by such reactions according to the literature are shown in Figure 10. The photochemical reactions of one specific group of metal carbonyl complexes——nickel and pseudo-nickel carbonyls and some of their triphenylphosphine derivatives——have been investigated. However, all of the intermediates which have been postulated for this dimerization reaction are those involved in the nickel tetracarbonyl mediated case. A hypothetical mechanism has been deduced based on the data combined with an existing theory of transition metal orbital participation in cycloaddition reactions. The outline on the following page is the mechanism which will be discussed in more detail after various parts of the data have been presented.

Determination of Molecular Structures

Structures of various compounds were determined during the course of this research to provide necessary information on the stereochemistry at different steps in the reaction sequence. The structures of the three known $\pi 2_s + \pi 2_s$ dimers of norbornadiene have been assigned in the literature[34] and were based on proton nmr spectra. However, structures of some of the other products and most of the metal reactants have not specifically been assigned. Although electron density structure



Thermal Dimerization of Norbornadiene by $Ni(CO)_4$



Photochemical Dimerization of Norbornadiene by $Ni(CO)_4$

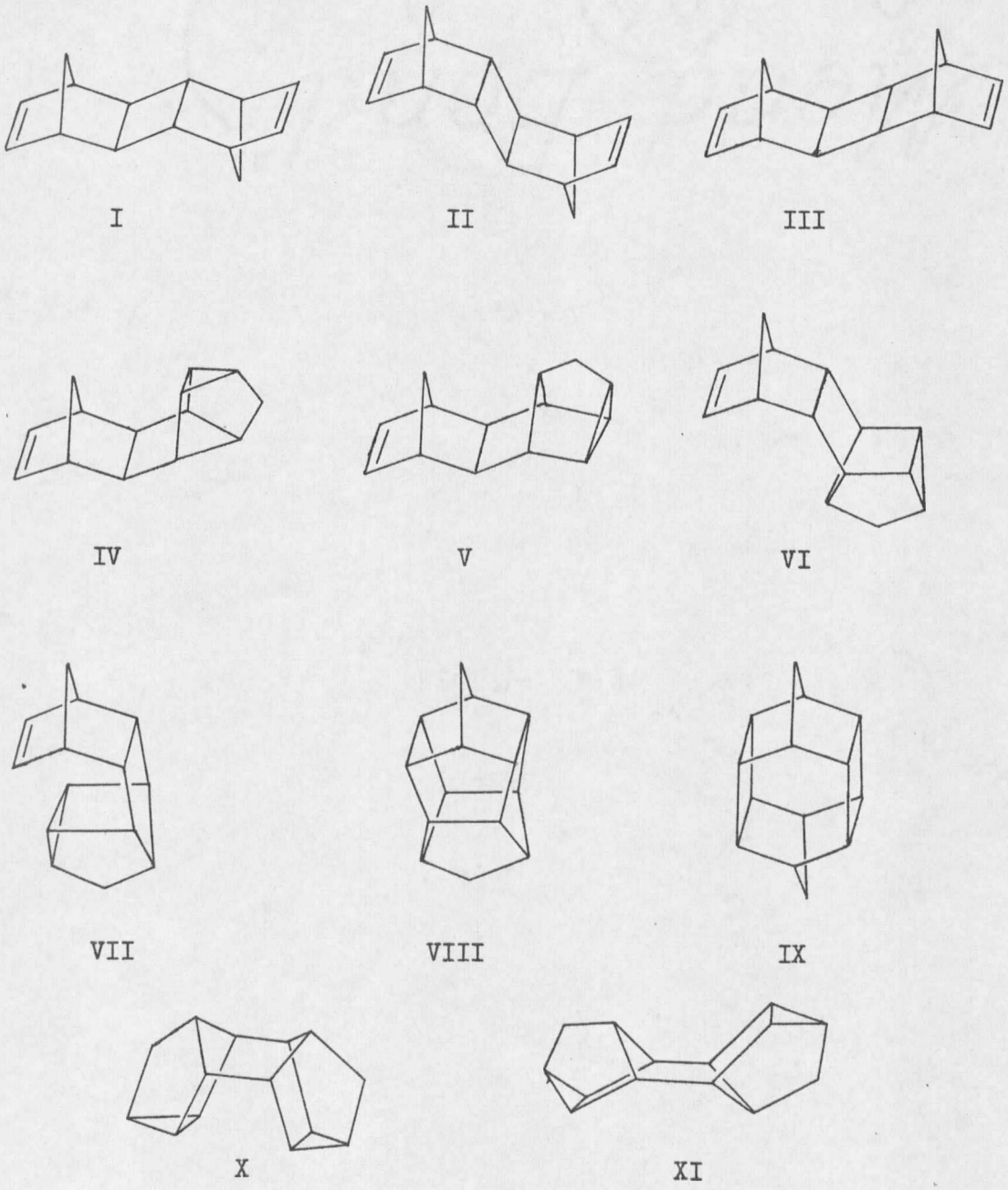


Figure 10

Norbornadiene Dimer Stereoisomers

determinations[35] have been done on $Ni(CO)_4$, $Co(CO)_3(NO)$, and $Fe(CO)_2(NO)_2$ there are no structure proofs for any of their derivatives. The choice of this group of carbonyls for study was based on the isostructural and isoelectronic properties of the central metal atoms. An X-ray structure determination was carried out on $Co(CO)_2(NO)[P(C_6H_5)_3]$ to verify the presumed near-tetrahedral arrangement of ligands around the central atom in these derivatives.

The crystal structure was done by D. L. Ward[36] on a single crystal of $Co(CO)_2(NO)[P(C_6H_5)_3]$. A G.E. XRD-5 diffractometer was used with MoK_α radiation. The crystal was found to be triclinic (space group $P\bar{1}$) with $\underline{a}$ = 11.055(2)Å, $\underline{b}$ = 11.024(4)Å, $\underline{c}$ = 10.260(2)Å, α = 121.07(2)°, β = 101.01(2)°, γ = 105.14(2)°, Z = 2, Dm = 1.39 g/cm^3, Dx = 1.42 g/cm^{-3}. The 2006 observed intensities were collected and refined to an R of 0.033. The average angle between carbonyl and nitrosyl groups was about 113.4° whereas the average angle between the phosphorous and the nitrosyl and carbonyl groups was about 105.0°. Thus, it appears that the arrangement of ligands are quite close to a tetrahedral arrangement about the cobalt atom. Listed in Tables 1 and 2 are the bond lengths and bond angles of the complex. The structure in perspective is illustrated with the numbering scheme in Figure 11.[37] It is interesting to note that the phenyl rings are within approximately 6° of eclipsing the carbonyl and nitrosyl groups and the phenyl rings are all canted the same direction giving it a "propeller" appearance. The carbonyl and nitrosyl groups are all nearly linear (average angle is about 178.68°).

Table 1

Bond Distances of the Crystalline Molecular Structure of Dicarbonylnitrosyltriphenylphosphinecobalt(0)

Bond	Distance	Bond	Distance
Co----P	2.224(1)Å	C(24)-C(25)	1.367(8)Å
Co----N(1)	1.727(15)	C(25)-C(26)	1.379(8)
Co----C(1)	1.709(9)	C(26)-C(21)	1.385(6)
Co----N(2)	1.744(18)	C(31)-C(32)	1.381(7)
Co----C(2)	1.748(8)	C(32)-C(33)	1.378(7)
Co----N(3)	1.760(10)	C(33)-C(34)	1.383(7)
Co----C(3)	1.709(9)	C(34)-C(35)	1.373(8)
O(1)--N(1)	1.139(16)	C(35)-C(36)	1.374(7)
O(1)--C(1)	1.157(10)	C(36)-C(31)	1.408(6)
O(2)--N(2)	1.145(18)	C(12)-H(12)	1.00 (3)
O(2)--C(2)	1.142(9)	C(13)-H(13)	1.01 (5)
O(3)--N(3)	1.104(11)	C(14)-H(14)	0.99 (5)
O(3)--C(3)	1.155(9)	C(15)-H(15)	1.02 (4)
P-----C(11)	1.824(4)	C(16)-H(16)	1.01 (4)
P-----C(21)	1.820(4)	C(22)-H(22)	1.01 (4)
P-----C(31)	1.817(4)	C(23)-H(23)	1.01 (5)
C(11)-C(12)	1.385(7)	C(24)-H(24)	0.95 (4)
C(12)-C(13)	1.378(7)	C(25)-H(25)	1.04 (4)
C(13)-C(14)	1.365(7)	C(26)-H(26)	1.01 (4)
C(14)-C(15)	1.373(8)	C(32)-H(32)	0.96 (4)
C(15)-C(16)	1.388(7)	C(33)-H(33)	0.93 (4)
C(16)-C(11)	1.376(5)	C(34)-H(34)	0.97 (4)
C(21)-C(22)	1.386(6)	C(35)-H(35)	0.98 (4)
C(22)-C(23)	1.380(7)	C(36)-H(36)	1.02 (4)
C(23)-C(24)	1.365(9)	C(36)-H(36)	1.02 (4)

Table 2

Bond Angles of the Crystalline Molecular Structure of Dicarbonylnitrosyltriphenylphosphinecobalt(0)

Atoms	Angle	Atoms	Angle	Atoms	Angle
P-----Co----N(1)	103.98(43)	C(11)-C(12)-C(13)	120.57(41)	C(13)-C(14)-H(14)	120.2(28)
P-----Co----C(1)	104.26(25)	C(12)-C(13)-C(14)	120.39(47)	C(15)-C(14)-H(14)	119.7(28)
P-----Co----N(2)	106.81(56)	C(13)-C(14)-C(15)	120.11(50)	C(14)-C(15)-H(15)	120.6(27)
P-----Co----C(2)	106.00(24)	C(14)-C(15)-C(16)	119.45(46)	C(16)-C(15)-H(15)	119.8(27)
P-----Co----N(3)	104.85(37)	C(15)-C(16)-C(11)	121.09(42)	C(15)-C(16)-H(16)	116.0(22)
P-----Co----C(3)	104.74(33)	C(16)-C(11)-C(12)	118.40(39)	C(11)-C(16)-H(16)	123.0(22)
Co----N(1)-O(1)	178.24(108)	P-----C(21)-C(22)	117.66(32)	C(21)-C(22)-H(22)	118.0(22)
Co----C(1)-O(1)	179.20(64)	P-----C(21)-C(26)	123.52(32)	C(23)-C(22)-H(22)	121.7(22)
Co----N(2)-O(2)	178.99(143)	C(21)-C(22)-C(23)	120.29(43)	C(22)-C(23)-H(23)	116.1(27)
Co----C(2)-O(2)	178.10(65)	C(22)-C(23)-C(24)	119.97(49)	C(24)-C(23)-H(23)	123.9(27)
Co----N(3)-O(3)	178.35(98)	C(23)-C(24)-C(25)	120.64(53)	C(23)-C(24)-H(24)	121.2(26)
Co----C(3)-O(3)	179.20(85)	C(24)-C(25)-C(26)	119.85(51)	C(25)-C(24)-H(24)	118.0(26)
N(1)-Co----N(2)	111.85(70)	C(25)-C(26)-C(21)	120.43(44)	C(24)-C(25)-H(25)	125.8(25)
C(1)-Co----C(2)	111.14(35)	C(26)-C(21)-C(22)	118.82(40)	C(26)-C(25)-H(25)	114.3(25)
N(1)-Co----N(3)	116.20(56)	P-----C(31)-C(32)	123.45(33)	C(25)-C(26)-H(26)	120.2(23)
C(1)-Co----C(3)	116.25(41)	P-----C(31)-C(36)	118.29(33)	C(21)-C(26)-H(26)	119.2(23)
N(2)-Co----N(3)	112.09(67)	C(31)-C(32)-C(33)	121.28(43)	C(31)-C(32)-H(32)	118.4(23)
C(2)-Co----C(3)	113.26(41)	C(32)-C(33)-C(34)	119.77(47)	C(33)-C(32)-H(32)	120.3(24)
Co----P-----C(11)	116.44(14)	C(33)-C(34)-C(35)	119.79(49)	C(32)-C(33)-H(33)	117.9(23)
Co----P-----C(21)	113.93(14)	C(34)-C(35)-C(36)	120.87(49)	C(34)-C(33)-H(33)	122.3(23)
Co----P-----C(31)	115.02(14)	C(35)-C(36)-C(31)	119.98(44)	C(33)-C(34)-H(34)	117.2(26)
C(11)-P-----C(21)	102.93(19)	C(36)-C(31)-C(32)	118.26(40)	C(35)-C(34)-H(34)	123.0(27)
C(11)-P-----C(31)	103.55(19)	C(11)-C(12)-H(12)	117.00(22)	C(34)-C(35)-H(35)	125.1(24)
C(21)-P-----C(31)	103.29(19)	C(13)-C(13)-H(12)	122.3 (22)	C(36)-C(35)-H(35)	114.0(24)
P-----C(11)-C(12)	119.29(31)	C(12)-C(13)-H(13)	119.4 (23)	C(35)-C(36)-H(36)	124.2(22)
P-----C(11)-C(16)	122.30(32)	C(14)-C(13)-H(13)	120.3 (23)	C(31)-C(36)-H(36)	115.8(22)

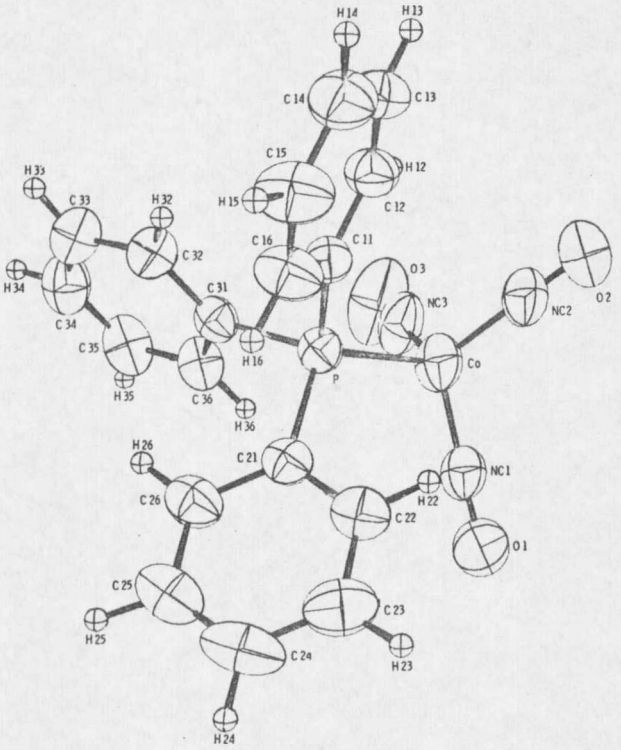


Figure 11

Perspective View of the Dicarbonylnitrosyltriphenylphosphinecobalt(0)

Two dimers (IV and V in Figure 10) of norbornadiene which were obtained in the photochemical reaction with nickel tetracarbonyl had not been previously assigned exact stereospecific structures in the literature due to the complexity of the proton nmr spectra.[38] Even though it seemed apparent what the structures were it was not apparent which structure should be assigned to which nmr. However, it was of interest to know which of the stereochemical products was the major product.

Also, it would be of interest to know what the effect the cyclopropyl ring had on the protons on the bridge carbon of the norbornene fragment in dimer IV where this proximity would allow interaction. In order to obtain all of this information both proton nmr spin-decoupling experiments and a crystal structure determination were conducted.

In Figures 12 and 13 the proton nmr spectra of the two dimers are shown, and in Figure 14 are structures of the two dimers.

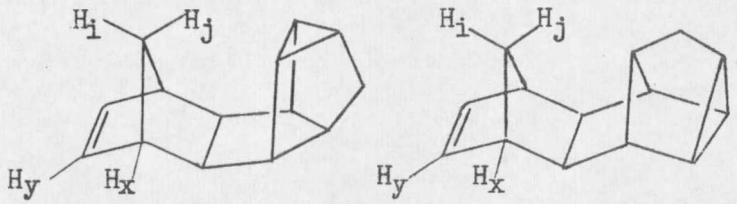


Figure 14

Dimers IV and V

The general peak assignments that have been made for Dimers IV and V in the nmr are the olefin protons (H_y) at 6.17 and 6.08 ppm, the bridgehead protons (H_x) at 2.61 and 2.58 ppm, and the two equivalent protons of the cyclopropyl ring at 0.82 and 0.85 ppm, respectively. In addition to coupling with the bridgehead protons (H_x), the bridge proton anti to the double bond (H_j) couples with the olefin protons (H_y). Consequently, by decoupling the bridge protons from the olefin protons it was found that

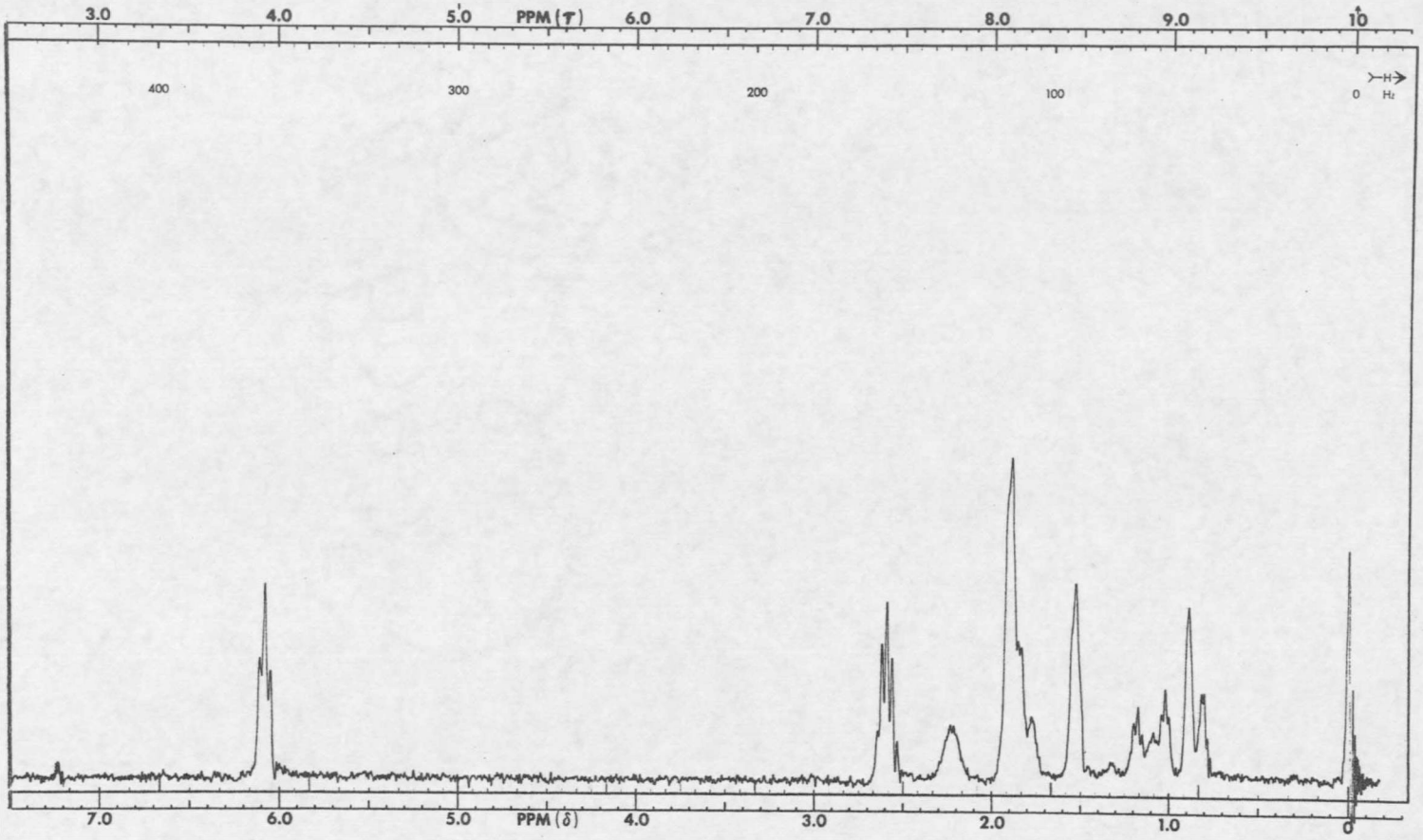


Figure 12

Proton NMR Spectrum of the Minor Dimer Formed in the Photolysis of $Ni(CO)_4$ in Norbornadiene - Dimer V

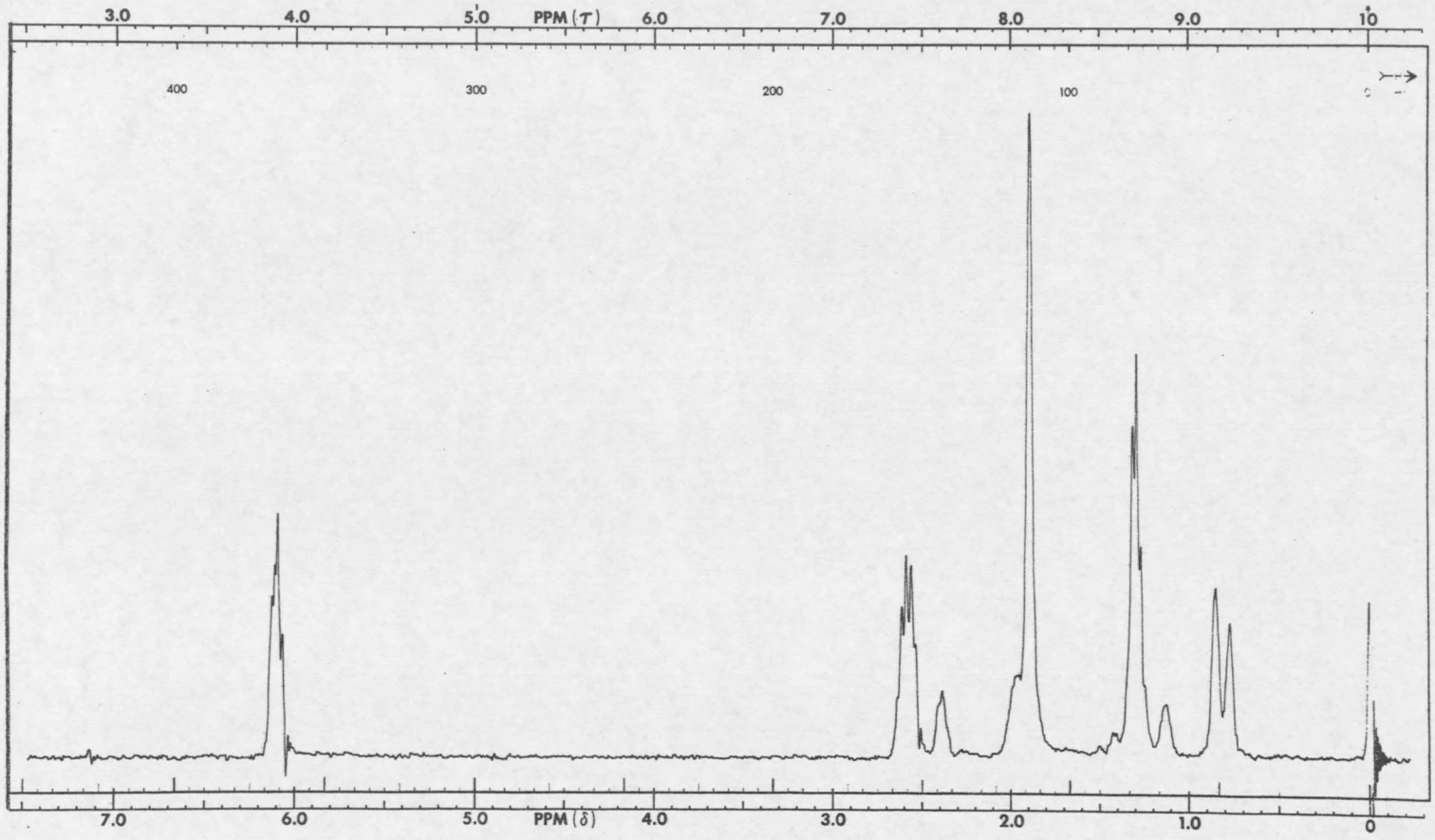


Figure 13

Proton NMR Spectrum of the Major Dimer Formed in the Photolysis of $Ni(CO)_4$ in Norbornadiene - Dimer IV

the proton anti to the double bond was located at 2.43 ppm in Dimer IV (Figure 15) and at 1.80 ppm in Dimer V (Figure16). The shift position of the bridge proton syn to the double bond in each dimer was then located by irradiating the bridgehead protons (H_x) in Dimer IV (Figure 15) and by irradiating the other bridge proton (H_j) in Dimer V (Figure 16). The coupling constant of the bridge protons is J_{ij} = 10 cps whereas the shift positions are as shown in Table 3.

Table 3

Proton NMR Peak Assignments for H_j and H_i in Structures A and B

	H_j ppm	H_i ppm	Difference
Dimer IV	2.43	1.15	1.28
Dimer V	1.80	1.17	0.63

A crystal structure determination was done by Dr. G. D. Smith[39] on the silver nitrate complex of Dimer IV whose spectrum is shown in Figure 13. The same diffractometer was used as before but the MoK_α radiation was zirconium filtered. Cell dimensions for the monoclinic crystals (point group $P\ 2_{1/c}$) were $\underline{a}$ = 17.554(9)Å, $\underline{b}$ = 6.908(4)Å, $\underline{c}$ = 11.031(5)Å, and β = 103.10°. Two crystals were used to collect 841 observed pieces of data. The structure was solved by the heavy atom method and the hydrogen positions were found by use of a difference map. The data was refined to an R of 0.033. Figure 17 illustrates the dimer

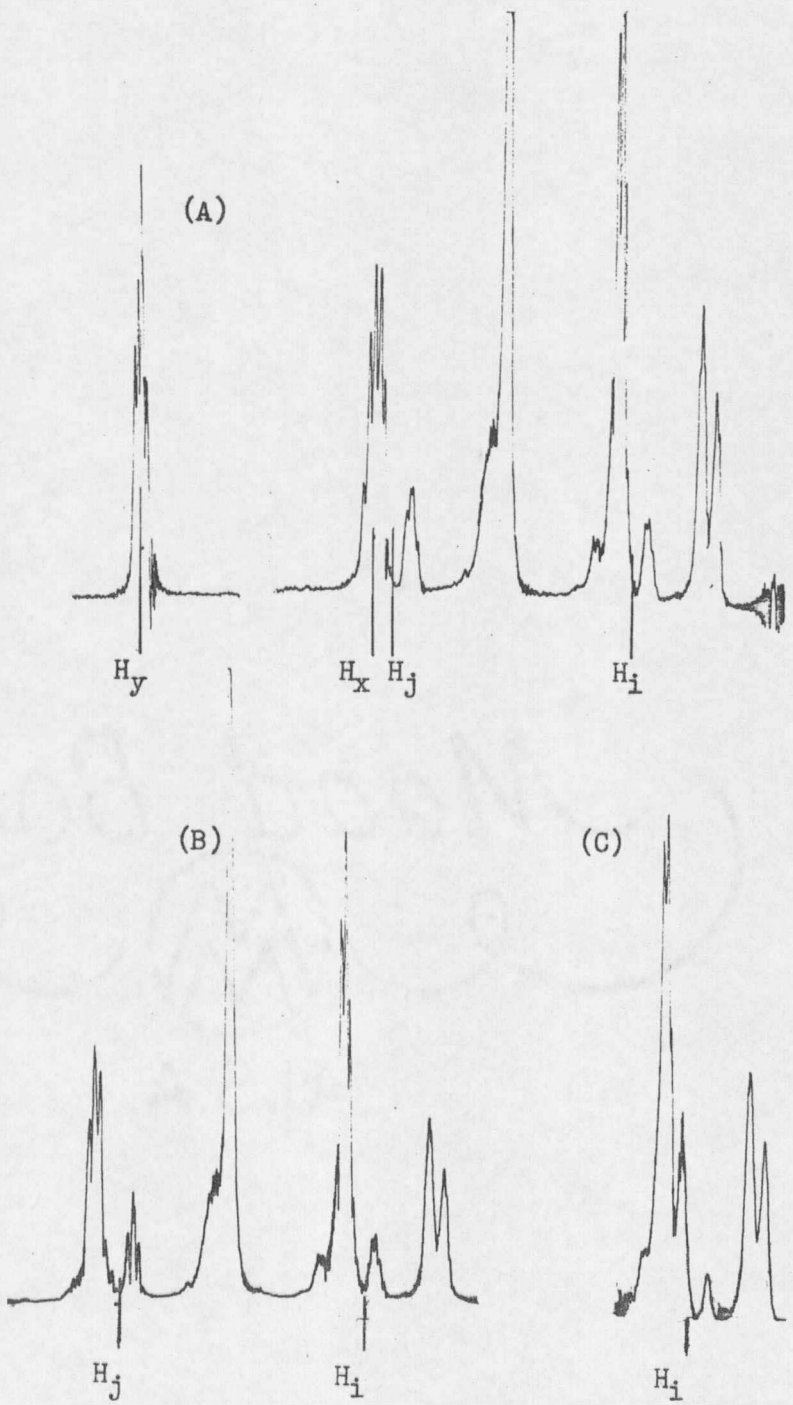


Figure 15

Proton NMR Decoupling Experiments on Dimer IV
(A) Proton NMR Spectrum Showing Position of Protons before Decoupling Experiments
(B) Protons H_y Decoupled from Proton H_j, Proton H_i Unchanged
(C) Proton H_j Decoupled from Proton H_i

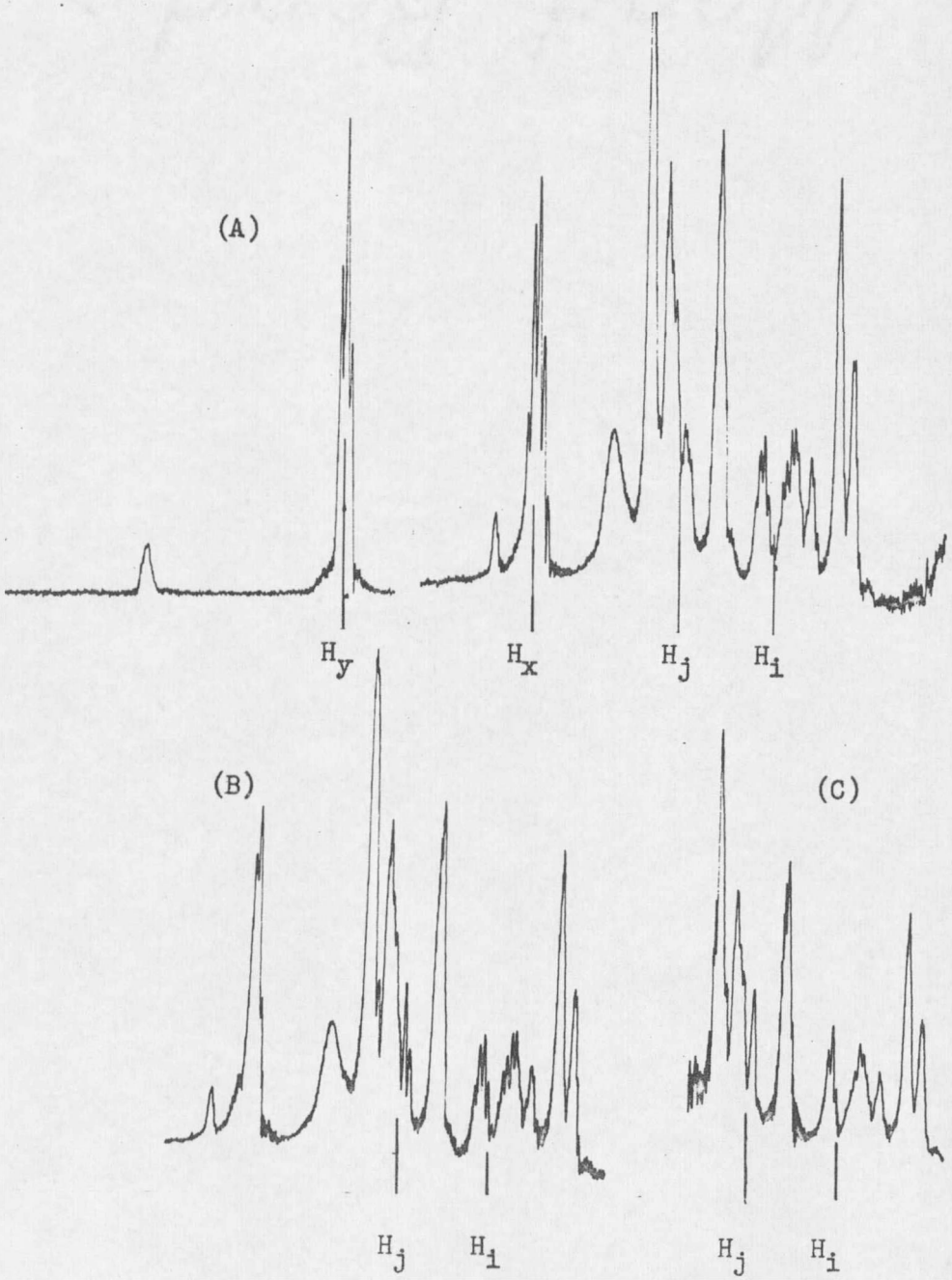


Figure 16

Proton NMR Decoupling Experiments on Dimer V
(A) Proton NMR Spectrum Showing Position of Protons before Decoupling Experiment
(B) Protons H_y Decoupled from H_j, Proton H_i Unchanged
(C) Protons H_x Decoupled from Proton H_j and H_i

complex and the carbon-carbon bond lengths. Bond angles are recorded in Table 4.

When the plane of the cyclopropane ring is projected out to the bridge carbon of the norbornene fragment (Figure 18) it can be seen that the bridge proton anti to the double bond is 0.61Å (approximately 15°) above this plane and 2.34Å away from the nearest carbon-carbon bond of the ring. From the shift positions of the bridge protons in Table 3 the position of the two protons (H_i) are nearly the same whereas the other bridge proton (H_j) of the dimer in the crystal structure is shifted further downfield than the corresponding proton in the other dimer. This is as would be predicted from the hypothesis of ring current in cyclopropyl rings.[40] A proton in the plane of the ring would be deshielded. In this dimer the distance that the proton (H_j) is from the cyclopropane ring together with its closeness to being in the plane of the ring are presumed to be responsible for a deshielding of 0.63 ppm.

There are other interesting features in the crystal as well. The angles that the silver ion and the olefin protons make with respect to the four carbon plane adjoining is shown in Figure 19. Assuming little effect from crystal packing, the position of the protons could indicate a change in hybridization at the olefin carbon atoms.

It is also of interest to note that the bridge carbon is not symmetrical with respect to the two planes below it (Figure 19). However, the effect of packing is not known so the relative effects of the silver ion on one side and the cyclopropane ring on the other cannot be

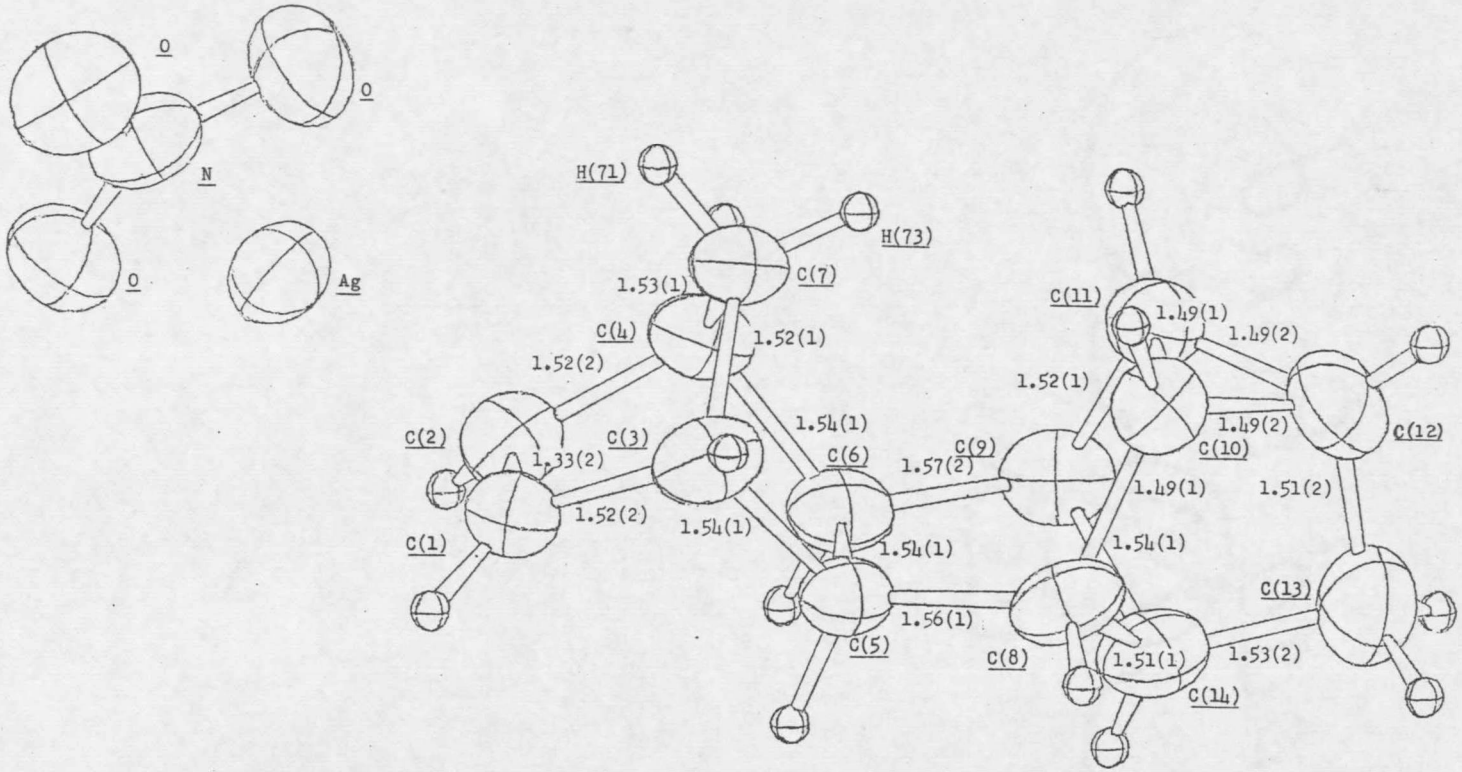


Figure 17

Carbon-Carbon Bond Distances in the 2 + 2 + 2 Dimer
Silver Nitrate Structure

Table 4

Bond Angles for the Silver Nitrate Complex of the Major Pseudo-Diels-Alder Dimer Product

Atoms	Angle
C(1)--Ag----H(13)	33.3(4)
C(2)--C(1)-H(1)	120.4(51)
C(3)--C(2)-H(1)	124.1(51)
C(5)--C(6)-C(9)	102.2(7)
C(4)--C(6)-C(9)	122.0(8)
C(10)--C(7)-H(73)	37.4(38)
C(11)--C(7)-H(73)	42.5(38)
H(73)--C(7)-H(71)	105.2(62)
C(3)--C(7)-C(4)	95.2(8)
C(12)--C(10)-H(73)	132.5(16)
C(12)--C(11)-H(73)	128.1(16)
C(9)--C(11)-H(11)	117.1(34)
C(8)--C(10)-H(10)	113.8(48)
C(13)--C(12)-H(12)	119.6(56)
H(31)--C(13)-H(32)	110.8(70)
H(10)--H(73)-H(11)	73.3(31)
H(10)--H(73)-C(7)	138.6(54)
H(10)--C(7)-H(73)	29.8(41)
H(11)--C(7)-H(73)	39.5(40)
C(1)--C(3)-H(3)	123.8(34)
C(2)--C(4)-H(4)	124.6(56)
C(5)--C(3)-H(3)	111.8(34)
C(6)--C(4)-H(4)	114.4(56)

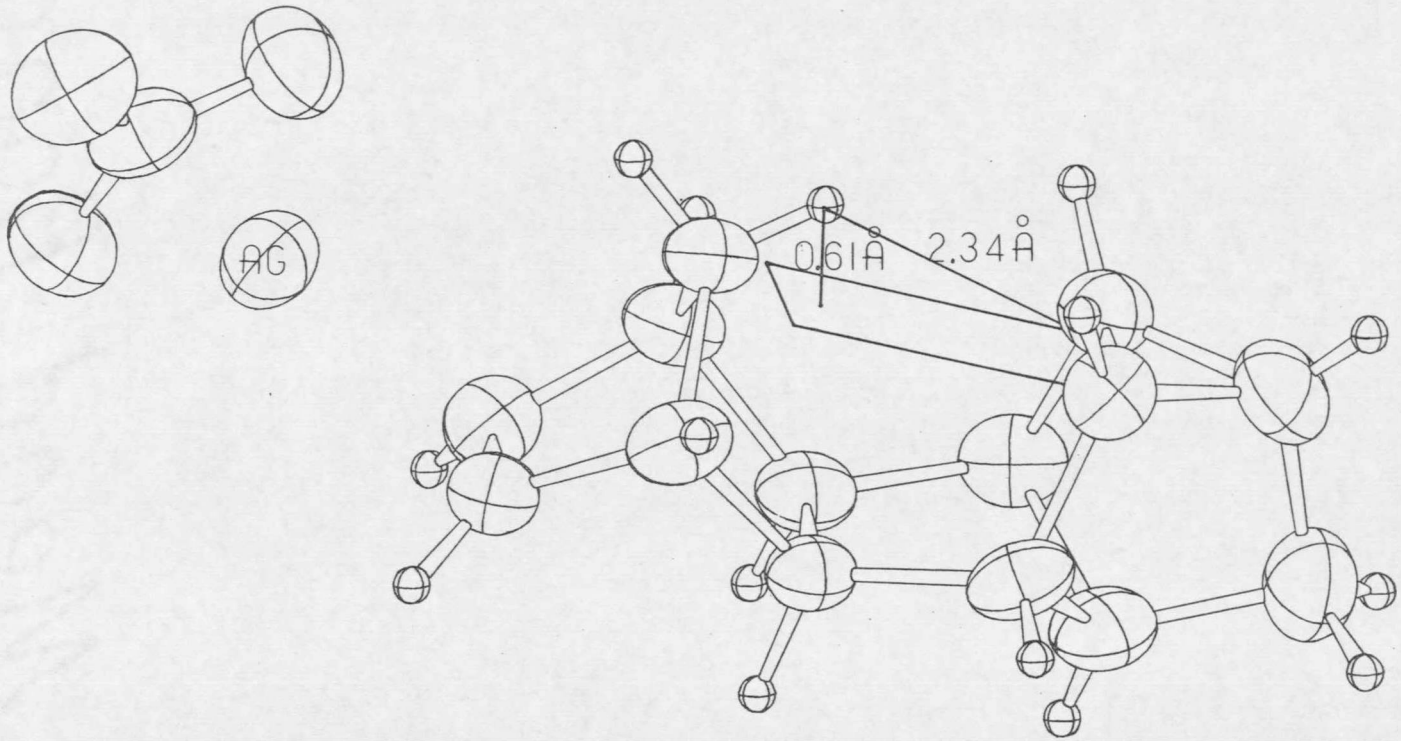


Figure 18

Diagram Showing the Bridge Carbon Proton with Respect to the Plane of the Cyclopropyl Ring in the 2 + 2 + 2 Dimer Silver Nitrate Structure

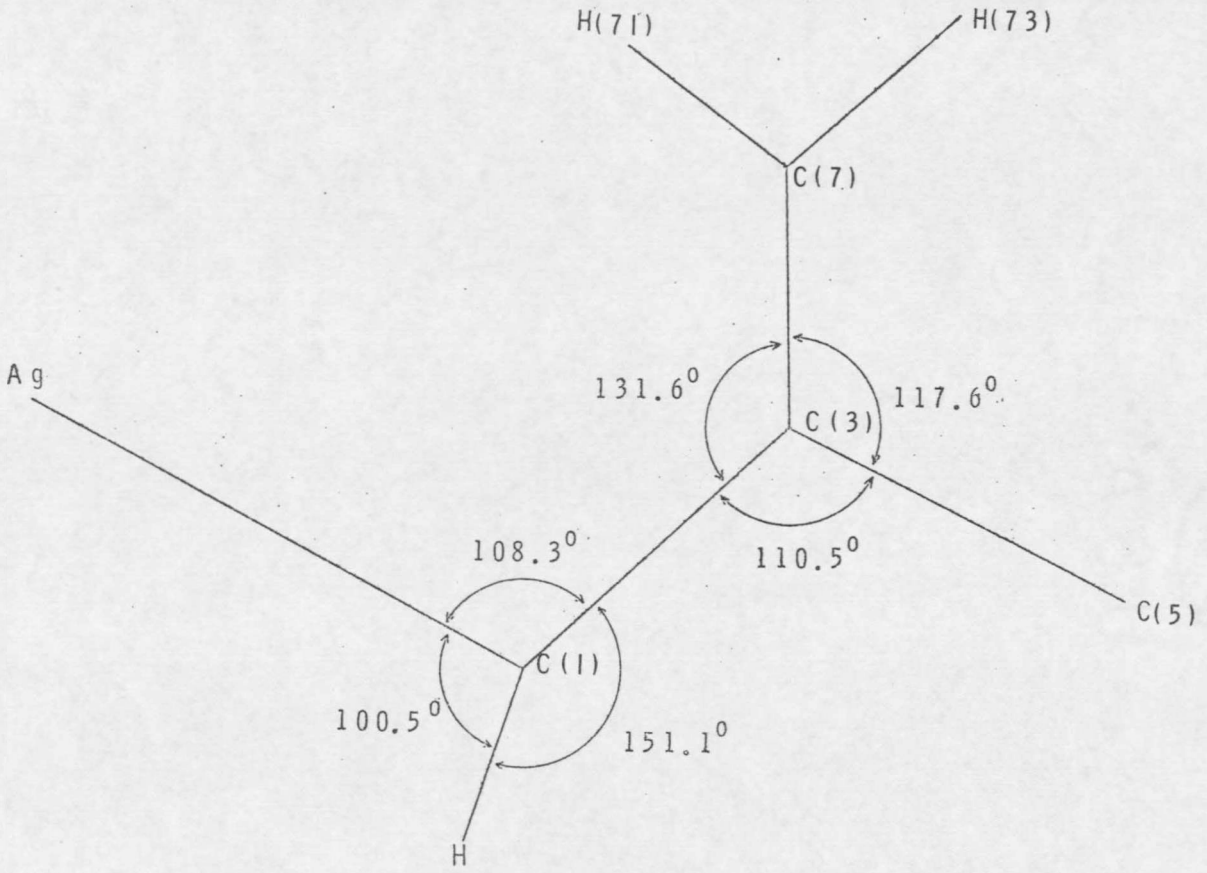


Figure 19

Diagram Showing Relative Angles of the Planes Containing Carbon Rings in the Norbornene Fragment of the 2 + 2 + 2 Dimer Silver Nitrate Structure

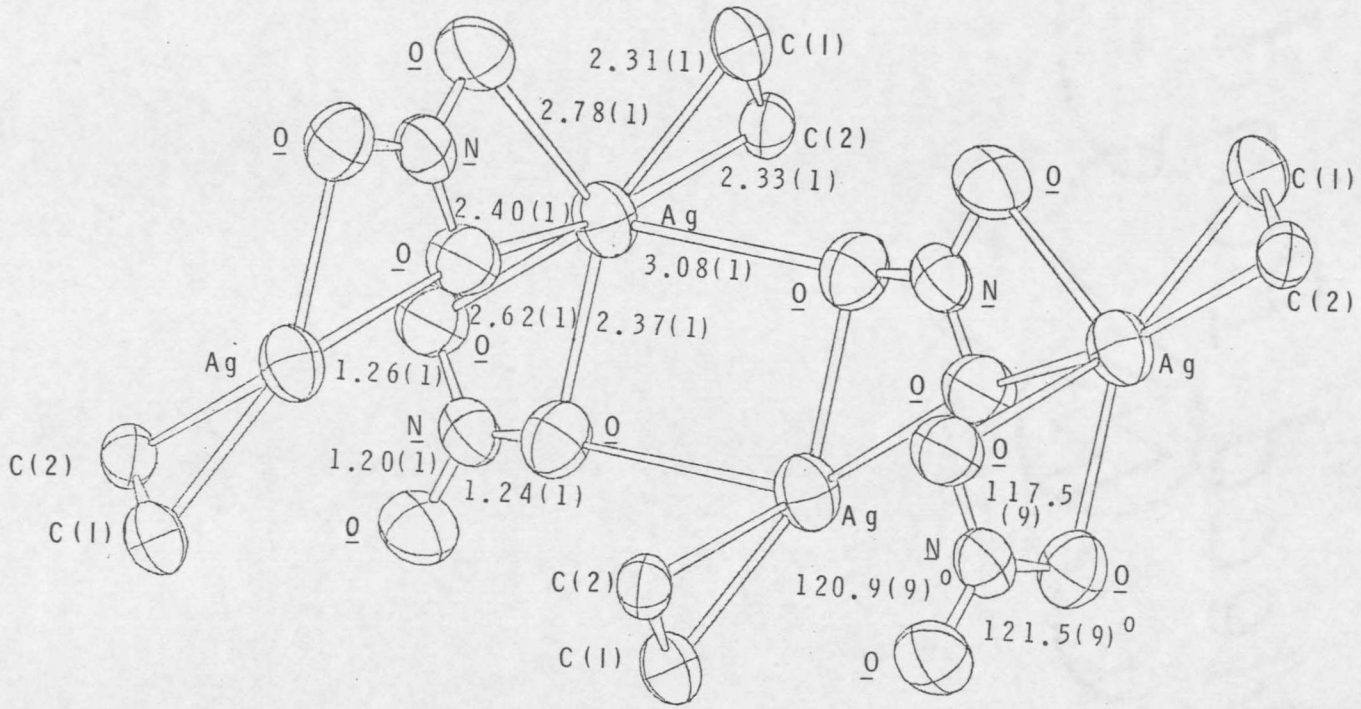
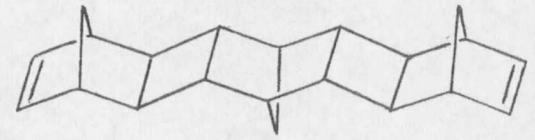


Figure 20

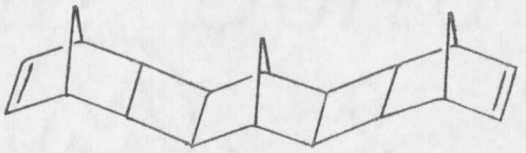
Packing and Bond Distances of the Silver and Nitrate Ions
Shown with the Olefin Carbons of the 2 + 2 + 2 Dimer

measured. Figure 20 shows the bonding around the silver ions including the relative nitrate anion positions.

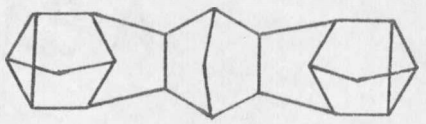
Structures of two trimers were assigned and a gross assignment was made for a mixture of trimers (Figure 21) based on proton nmr spectra by comparison to the nmr spectra of known dimers. All three were assumed to be trimers from their retention time on gas-liquid phase chromatography and mass spectra which in every case had a parent peak at m/e of 276.



I



II



III

Figure 21

Proposed Structures of Trimers

One trimer to which stereochemistry was assigned (Figure 21, I) was formed in the photochemical reaction of dicarbonylbistriphenylphosphinenickel in norbornadiene. The proton nmr spectrum (Figure 22) was a very simple one made up of only one triplet at 5.86 ppm(4) assigned to olefin protons, a broad multiplet at 2.56 ppm(4) assigned to bridgehead protons and other peaks at 1.88 ppm(2.5H), 1.71 ppm(3.5H), 1.33 ppm(8H), 1.18 ppm(1.5H) and 1.03 ppm(0.5H) which were unassigned. The simplicity of the spectrum implied a symmetric molecule and integration of four olefin and four bridgehead protons indicated a 2 + 2 bonded trimer since the 2 + 2 + 2 trimers have no olefin protons. When the exo-trans-exo dimer of norbornadiene was put into the norbornadiene solution of dicarbonylbistriphenylphosphinenickel and the solution photolyzed, four times as much trimer was formed as in the photolysis with no addition of dimer. This indicated at least part of the trimer structure was that of the exo-trans-exo dimer. Since only one peak in the bridgehead proton region was observed and the olefin proton shift position coincided with that of the exo-trans-exo dimer olefin protons (5.97 ppm), it seemed logical to assume that both of the norbornene fragments of the trimer contained exo-trans cyclobutane junctures. A less symmetrical trimer would have two different bridgehead protons and two different olefin protons. Changes in solvent for spectra shifted peak positions and showed there was only one AB quartet resulting from the bridge protons of the norbornene fragments as was shown in the published 2 + 2 dimer nmr spectra (Figure 23). This reinforced the assumption that the trimer was composed

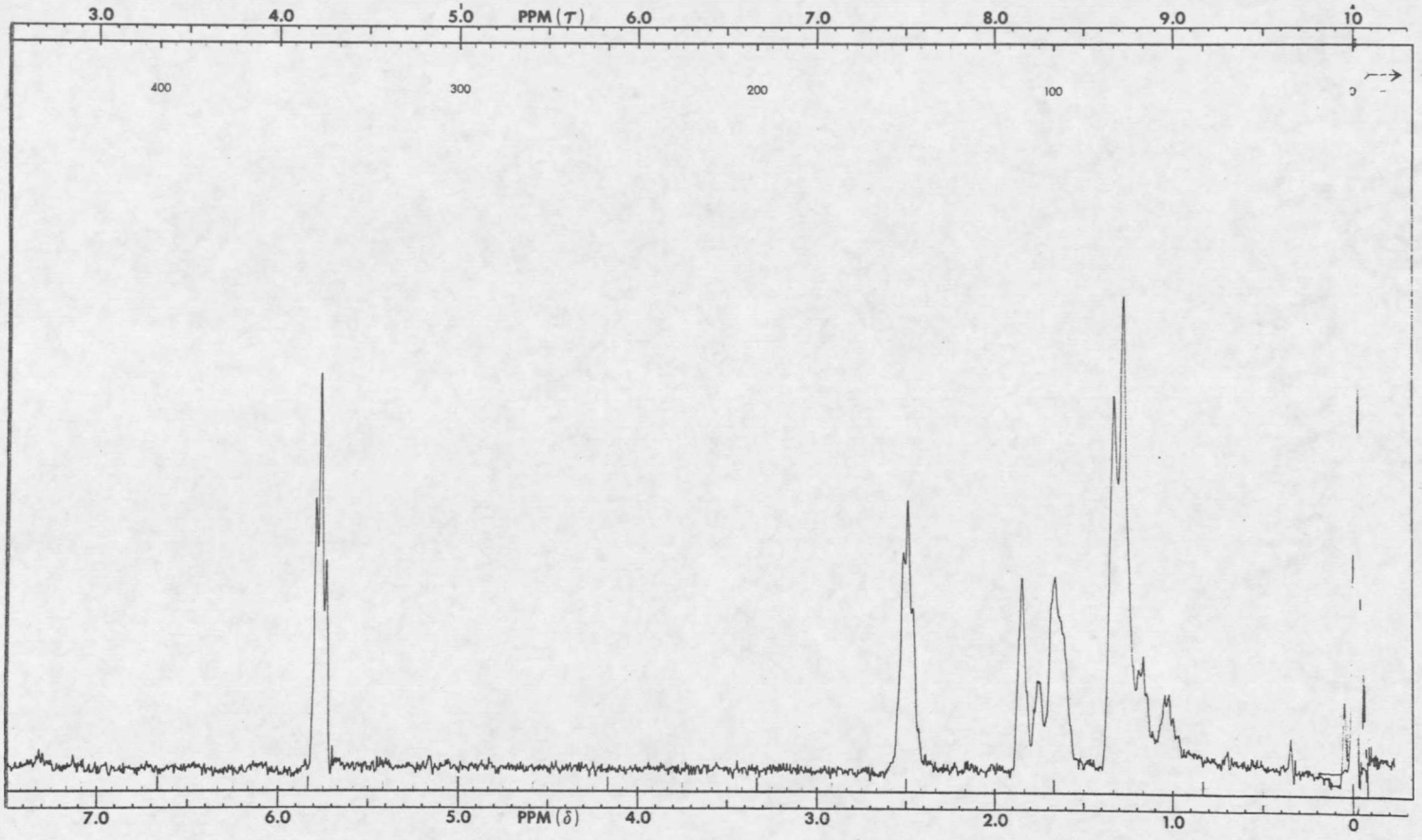


Figure 22

Proton NMR Spectrum of the Trimer Isolated from the Photolysis of $Ni(CO)_2[P(C_6H_5)_3]_2$ in Norbornadiene Silanor C Solvent

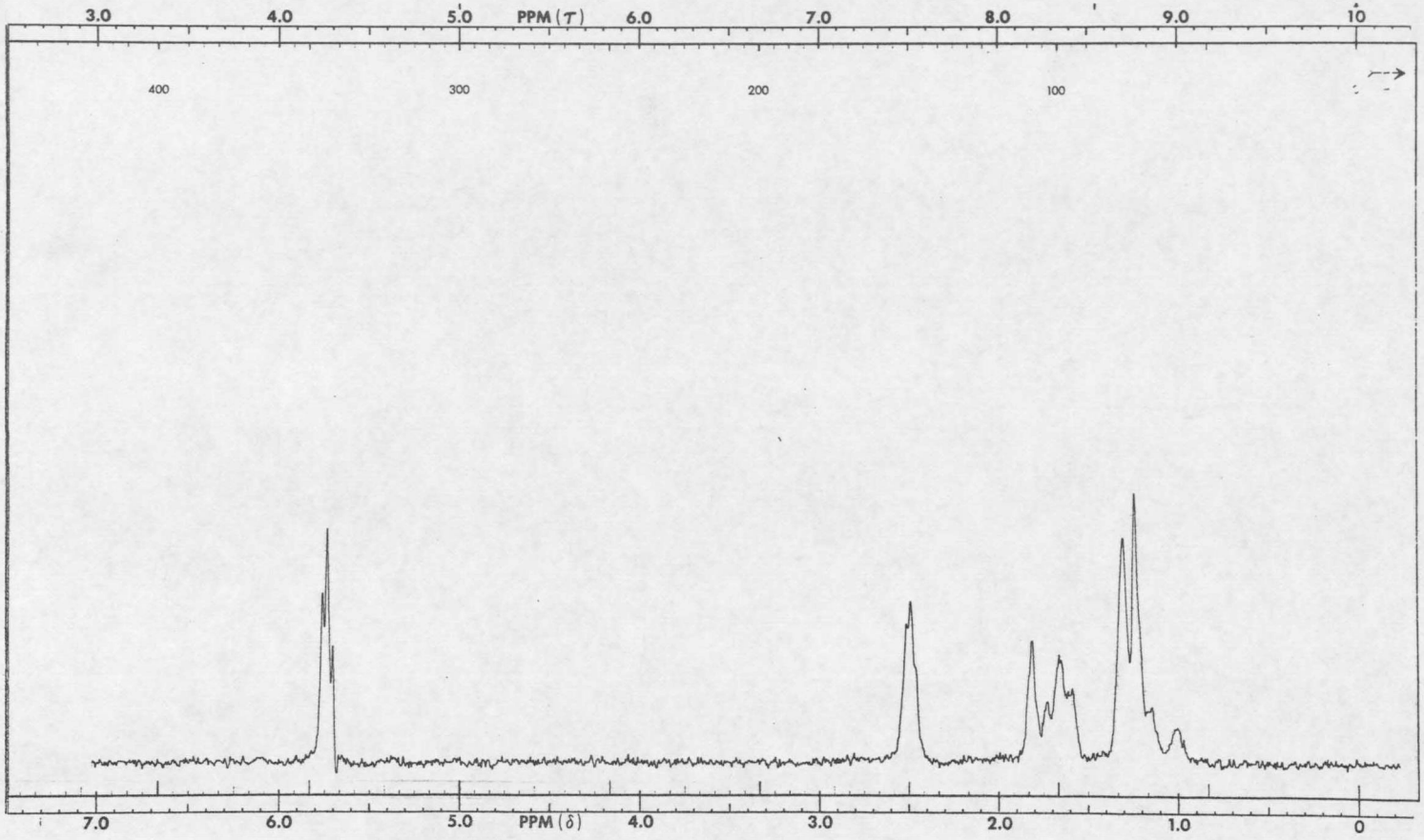


Figure 23

Proton NMR Spectrum of the Trimer Isolated from the Photolysis of $Ni(CO)_2[P(C_6H_5)_3]_2$ in Norbornadiene CS_2 Solvent

of symmetrically bonded norbornene fragments. Because the trimer from the exo-trans-exo incorporation experiment was the same as in the normal reaction of norbornadiene the central norbornene fragment must be bonded exo as well. The structure, therefore, is presumed to be that shown in Figure 21.

The second trimer (Figure 21, II) to which a structure was assigned from proton nmr spectral data was obtained from the thermal reaction of nickel tetracarbonyl in a solution of exo-trans-endo and endo-trans-endo dimers (3:1 respectively) and norbornadiene. Although the trimer was not isolated from the other three minor trimer constituents ($<20\%$) the peaks in the spectrum were easily discernible (Figure 24). Again, the number and symmetry of the peaks indicate the trimer may be reasonably symmetrical. There was only one olefin proton peak (6.22 ppm) and one bridgehead proton peak (2.78 ppm) implying that only one type of ring juncture exists on the norbornene fragments. It also appeared as if only one AB quartet was present, therefore, indicating one type of bridge carbon on the norbornene. The shift position of the olefin proton peak is very similar to that of the peak for olefin protons on the endo-bonded fragment of the exo-trans-endo dimer (6.20 ppm). Since the two dimers added and the dimers that form in this reaction are the same and do not include exo-trans-exo dimer to any extent it appears that the major trimer resulting from the symmetrical combination of the exo-trans-endo dimer and norbornadiene. Thus, the structure assigned is shown in Figure 21.

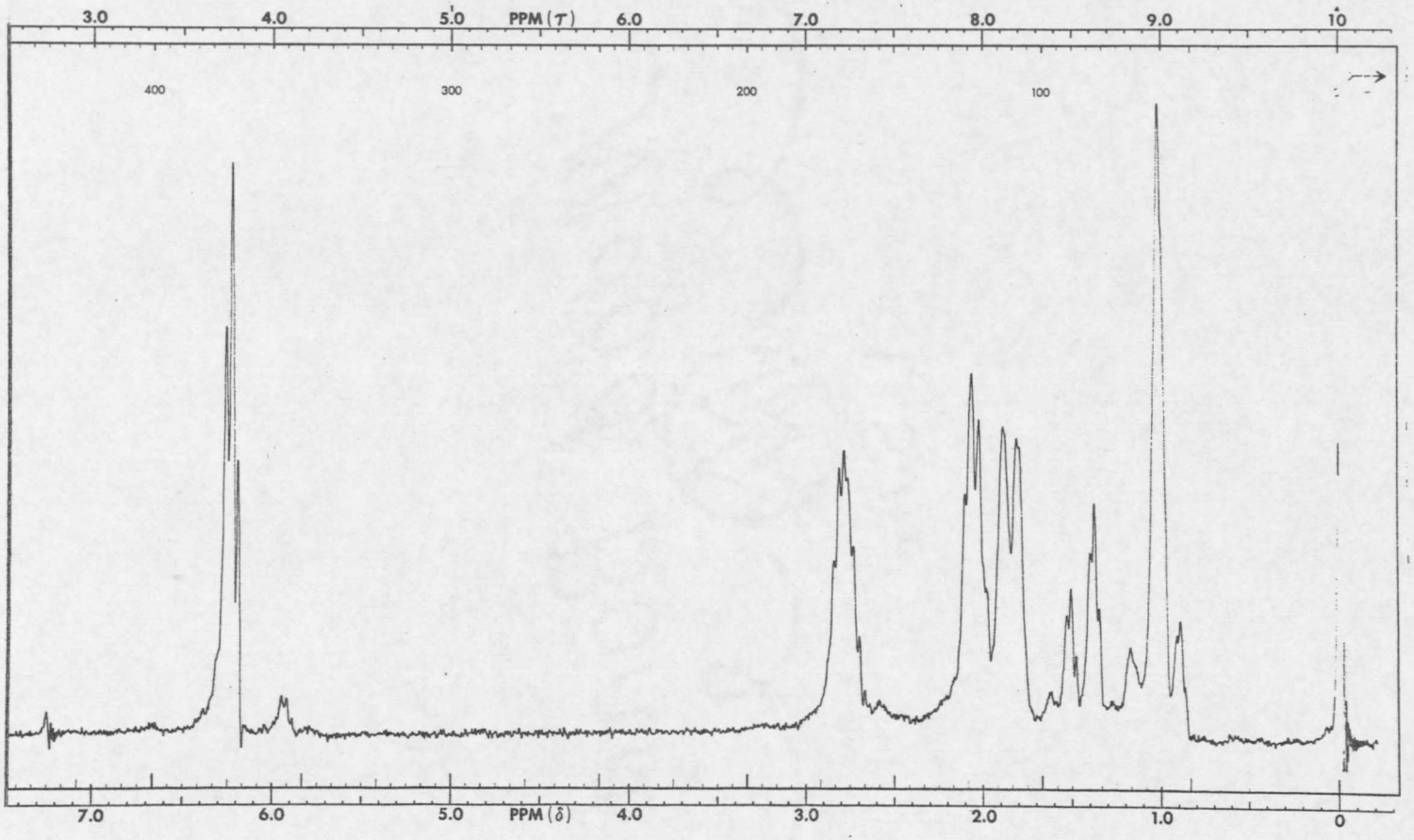


Figure 24

Proton NMR Spectrum of the Trimer Isolated from the Photolysis of $Ni(CO)_4$ in Norbornadiene Containing Added Exo-trans-endo and Endo-trans-endo Dimers

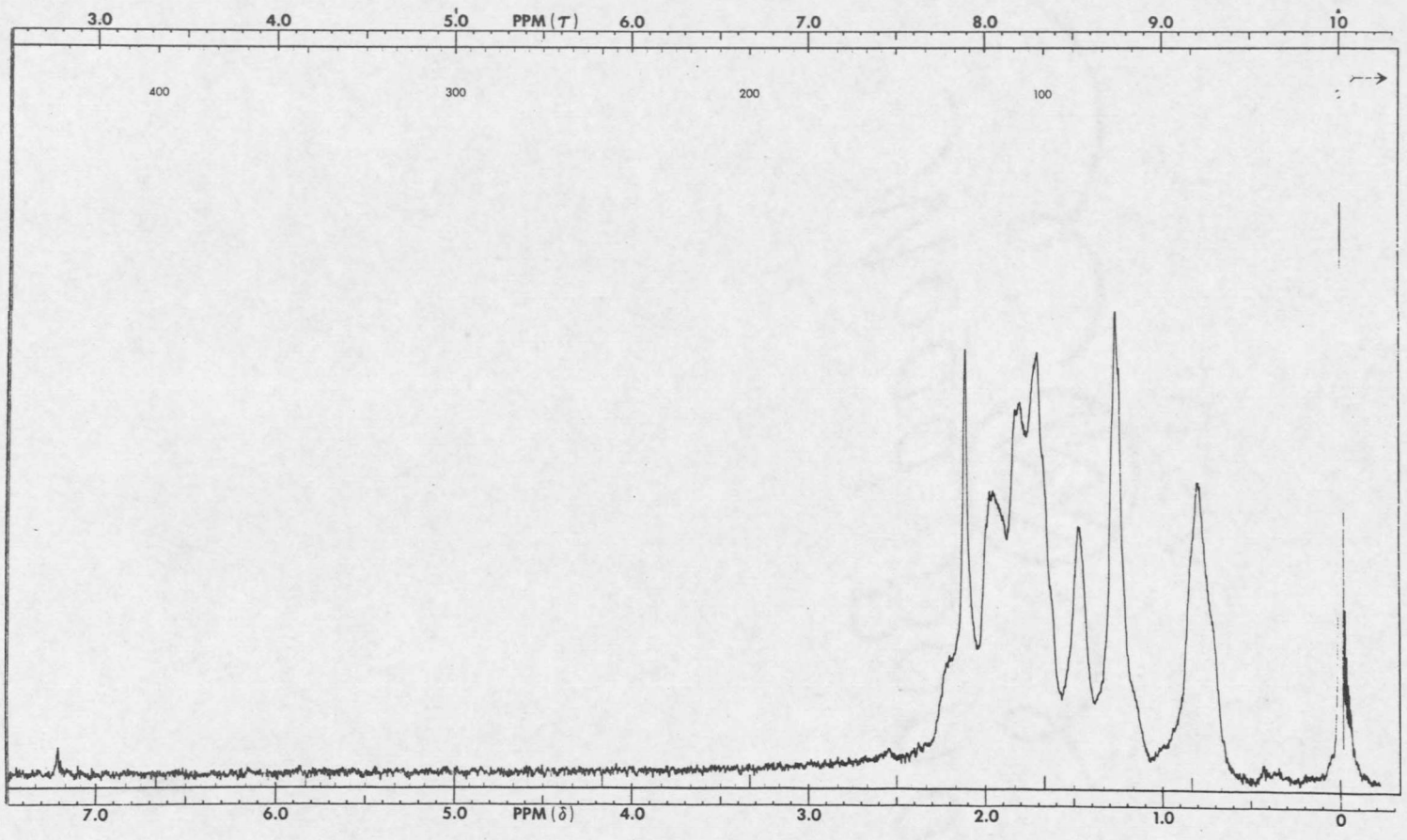


Figure 25

Proton NMR Spectrum of the Trimer Mixture formed in the Photolysis of $Ni(CO)_4$ in Norbornadiene

The mixture of trimers (Figure 21, III) was formed in the photochemical reaction of nickel tetracarbonyl and norbornadiene. The proton nmr spectrum (Figure 25) revealed no peaks in the olefin proton region and a poorly defined doublet above 1.0 ppm. Some of the peaks coincided with the trimer spectrum published by Katz.[41] The structure assignment from this data could be no more definitive than that the mixture of trimers apparently have two nortricyclene systems that could result from the 2 + 2 cycloaddition reaction between a pseudo-Diels-Alder dimer and norbornadiene. A nonstereochemical configuration is shown in Figure 21.

Review of the Dimerization of Norbornadiene

As was mentioned previously dimers and trimers of norbornadiene are produced when norbornadiene solutions of transition metal carbonyl complexes are excited. Speculation on the active complexes involved in the dimerization of norbornadiene have been made at various times in the literature. G. N. Schrauzer[42] suggested the possibilities that are generally accepted for transition metal carbonyl complexes of norbornadiene that could conceivably be responsible for the stereochemistry of the dimers produced in various experiments. Basically, the assumption was accepted that the norbornadiene molecules to be bonded to one another were bound to the metal first. This meant that at least two carbon monoxide ligands must be replaced by norbornadiene molecules in order to activate them and generate the dimer. Upon dimerization a metallic specie was left having two sites available for bonding to two more norbornadiene molecules and the process could continue. This, however, did not

explain how the actual dimerization took place on the metal nor did it explain the various stereoisomers that were found when different complexes were used. Many workers[43] have contributed to the long list of transition metal carbonyl complex-catalyzed dimerization of norbornadiene, most of whom carried out the reaction thermally. The structures of the dimer stereoisomers which have been isolated are shown in Figure 10, Page 20, and examples of proposed intermediates are illustrated in Figure 26.[44]

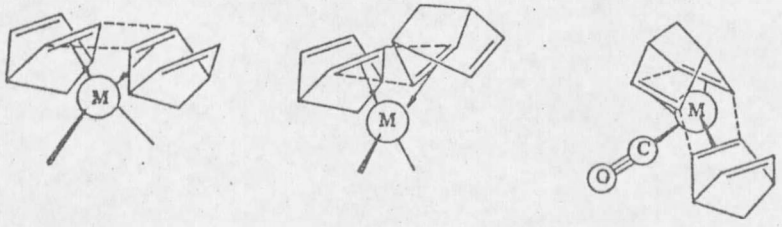


Figure 26

Possible Intermediates for Norbornadiene Dimerization on Metals Proposed by Schrauzer

Some examples of the major dimer products obtained from various thermally excited carbonyl complexes in norbornadiene are listed in Table 5.

No apparent trend or similarities exist between the stereoisomers of the dimers formed and the transition metal complex responsible for the reaction. The ratio of the amounts of dimers formed from each catalyst varied when reported.

Table 5

Norbornadiene Dimers Formed by Various Thermal Experiments with Transition Metal Carbonyl Catalysts with Approximate Ratios of Amounts When Known (Dimers Refer to Figure 10, Page 20)

Catalyst	Dimers	Reference
$Ni(CO)_4$	II, III (3:1)	45
$Co(CO)_3(NO)$	I, Mixture of dimers (IV - VII) (1:1)	46
$Fe(CO)_2(NO)_2$	I, III (6:1)	47
$Co_2(CO)_8$	I, III, (IV or V), VII (6:4:7:7)	48
$Fe(CO)_5$	I, Two of the dimers (IV - VII) VIII or IX	49
$Fe(CO)_2[P(C_6H_5)_3]_2$	No reaction	50
$Co_2(CO)_6[P(C_6H_5)_3]_2$	I, III (10:1)	51
$Ni(CO)_2[P(C_6H_5)_3]_2$	I, III (1:2)	

One question about the product variations seems evident: What is responsible for the stereoselectivity of the isomers which are formed? Assuming that the metal provides the reaction site, is the metal or the geometry of the ligands around the metal responsible for these products? It was these initial questions which prompted the research discussed here.

Effect on Dimerization of Norbornadiene with Nickel and Pseudo-Nickel Carbonyls

The family of complexes——nickel and pseudo-nickel carbonyls—— which were investigated with respect to their participation in the norbornadiene dimerization were chosen because of both the similarities and differences within the group. Listed below are the complexes which were used in this research.

A) $Ni(CO)_4$

B) $Ni(CO)_2[P(C_6H_5)_3]_2$

C) $Co(CO)_3(NO)$

D) $Co(CO)_2(NO)[P(C_6H_5)_3]$

E) $Co(CO)(NO)[P(C_6H_5)_3]_2$

F) $Fe(CO)_2(NO)_2$

G) $Fe(CO)(NO)_2[P(C_6H_5)_3]$

H) $Fe(NO)_2[P(C_6H_5)_3]_2$

Electron diffraction studies[52] and bond angle calculations from ir spectra[53] have shown that the three parent carbonyls——$Ni(CO)_4$, $Co(CO)_3(NO)$ and $Fe(CO)_2(NO)_2$——are isostructural. For example, the ligands are tetrahedrally arranged or nearly so with respect to the central atom. They are also considered to be isoelectronic based on their diamagnetic properties and the assumption that the nitric oxide is a three electron donor deduced from the position of the N-O stretching frequency in the ir spectra.[54] Therefore, these complexes allow the study of three different transition metals which have the same geometry. The crystal structure of the monosubstituted derivative of $Co(CO)_3(NO)$, $Co(CO)_2(NO)[P(C_6H_5)_3]$, also shows a geometry of ligands very nearly that of tetrahedral. From this data it was assumed, then that the general

arrangement of ligands for these complexes and their derivative would be tetrahedral or as close as steric hindrances would allow.

These complexes were chosen for study for other reasons in addition to their isostructural and isoelectronic properties. As can be seen in the list of complexes investigated there are eight which were available for studying so that a comparison between the parent carbonyl complex and at least one derivative could be made in every case. Also, the fact that all these complexes are soluble in norbornadiene meant the reactions investigated would all be homogeneous.

An additional factor which made these complexes ideal for investigation was that they have a range in number of carbon monoxide ligands which could be replaced. Thus, information regarding the carbon monoxide replacement could be collected.

With few exceptions,[55, 56, 57] all the work on catalytic dimerization of norbornadiene with transition metal catalysts had been done thermally. Thermal excitation provided not only an excitation of the active catalyst but also of all the other species in solution. It also resulted in a rapid collision rate. On the other hand photochemistry can be used to excite a particular specie or species with the exception of others in the solution. Furthermore, it has been shown that various transition metal complexes will undergo ligand displacement photochemically that would not occur thermally. An example of this was the photochemical displacement of a carbon monoxide ligand on $(\pi C_5H_5)Mn(CO)_3$ by an olefin as compared to no reaction thermally.[58] However, in

photochemical reactions a specie may be destroyed if too high energy is absorbed so conditions must be adjusted to the experiment. In consideration of these factors photochemical excitation appeared to be the best method of exciting these complexes. Since some of the complexes chosen for this research had previously been used in thermal experiments with norbornadiene this provided a chance to compare the results of stereoselectivity of dimers formed from photochemical excitation.

Shown in Table 6 are the results of the major dimer(s) formed when the nickel and pseudo-nickel carbonyls and their derivatives were excited photochemically compared to reported results from thermal excitation. It is apparent that when the complexes are photochemically excited the stereochemistry of the dimers becomes quite specific and very uniform from metal to metal except for nickel tetracarbonyl. In general, it appears that the "tetrahedral" geometry could be responsible for the formation of the exo-trans-exo dimer, $\pi 2_s + \pi 2_s$ cycloaddition, and that the metal itself does not dictate the stereochemistry of the dimer to be formed. For the time being the results from nickel tetracarbonyl will be ignored and referred to later. One important point to make here is that all reactions were clear solutions throughout irradiation. Therefore, no free metal on the glass surface or decomposition particles were apparent and were ruled out as possible reaction sites for heterogeneous reactions.

More specifically, however, it can also be seen that the number of carbon monoxide ligands on the transition metal seems to make no

Table 6

Peak Height Ratios of Dimer Products
from Gas Chromatography Analysis

Catalyst	Peak Height Ratio of Dimers	Irradiation Time of Solution
$Ni(CO)_4$	2:1	6 days
$Ni(CO)_2[P(C_6H_5)_3]_2$	95:6:1	3 days
$Co(CO)_3(NO)$	47: 5:4:1 3: 1:5:3	30 hours 3 days
$Co(CO)_2(NO)[P(C_6H_5)_3]$	16: 1:1:1 118:13:7:1 21: 3:3:1	1 day 3 days 9 days
$Co(CO)(NO)[P(C_6H_5)_3]_2$	96:15:8:1 83:12:6:1 8: 1:2:1	1 day 3 days 9 days
$Fe(CO)_2(NO)_2$	9:1	1 hour
$Fe(CO)(NO)_2[P(C_6H_5)_3]$	9:1 8:1	1 day 3 days
$Fe(NO)_2[P(C_6H_5)_3]_2$	Trace of exo-trans-exo	1 day 3 days

Except for $Ni(CO)_4$, the first value in the peak height ratio of dimers corresponds to that of exo-trans-exo.

no difference in the major type of stereoisomer of the dimer formed. For comparison the cobalt complexes range from three carbon monoxide ligands in the parent compound to one in the disubstituted derivative. Yet, all three produce the same stereoisomer as the major product. Thermal substitution reactions on $Co(CO)_3(NO)$ reported in the literature[59] show that when σ-donor complexes such as triphenylphosphine are used only two carbon monoxide ligands can be replaced. It is not known, however, if the third carbon monoxide can be replaced when photochemically excited. In looking at complexes of $Fe(CO)_2(NO)_2$, Complex G has only one carbon monoxide ligand which is replaceable since Complex H can be formed. The fact that it produces the same stereoisomer as the other complexes indicates one of three possible reactions takes place: only one carbon monoxide needs to be replaced, triphenylphosphine can be replaced as well as carbon monoxide or a nitric oxide ligand can be replaced. $Fe(NO)_2[P(C_6H_5)_3]_2$ produced a small amount of dimer, however, the formation of the exo-trans-exo dimer in this case could conceivably be due to a small amount of Complex G and may, therefore, not be conclusive enough to show that carbon monoxide need not be present as a ligand. The formation of dimer from Complex G and Complex E indicates the loss of triphenylphosphine as a possibility.

The replacement of a nitric oxide ligand would not be expected to take place due to its strong bonding to the metal and also its donation of three electrons to the metal. There are no other molecules in the system capable of donating three electrons as nitric oxide so if a

metal lost a nitric oxide ligand a bi-metallic specie would have to be formed to make up the odd electron (such as in the case of $Co_2(CO)_8$). If this would happen the cobalt and iron species would be different than the nickel specie and each other; and they would not be expected to produce the same stereoisomer of the dimers which they do. Thus, the replacement of nitric oxide has been deemed improbable.

However, the loss of triphenylphosphine from the complex appears to be a good possibility. It is a two electron donor as are carbon monoxide and carbon-carbon double bond systems. This would explain the results in the iron complexes: $Fe(CO)_2(NO)_2$ would have two carbon monoxide ligands replaced, $Fe(CO)(NO)_2[P(C_6H_5)_3]$ would have one carbon monoxide and one triphenylphosphine ligand replaced, and $Fe(NO)_2[P(C_6H_5)_3]_2$ would have two triphenylphosphine ligands replaced. Thus, the active specie in each case is a norbornadiene bound $Fe(NO)_2$.

In the case of the cobalt complexes and $Ni(CO)_2[P(C_6H_5)_3]_2$ there are possibilities of both carbon monoxide and triphenylphosphine ligands being displaced. Since $Ni(CO)_4$ and $Ni(CO)_2[P(C_6H_5)_3]_2$ do not give the same products photochemically it appears as though the active specie in the second case would probably be $Ni(CO)[P(C_6H_5)_3]$ resulting from a displacement of one carbon monoxide and one triphenylphosphine ligand by norbornadiene or $Ni[P(C_6H_5)_3]_2$, the result from the loss of two carbon monoxide ligands.

The cobalt complexes also have two possible active species in the substituted complexes, either $Co(NO)[P(C_6H_5)_3]$ or $Co(NO)(CO)$. The

first of these two possibilities resembles one of the suggested active specie of bistriphenylphosphinenickeldicarbonyl but the second would be the same specie as would be expected from the parent cobalt complex $Co(CO)_3(NO)$ after two carbon monoxide ligands had been replaced. It has been found that when $Co(CO)_3(NO)$ was irradiated for one week decomposition and a variety of dimers was found to result. In comparison, the two triphenylphosphine derivatives of cobalt did not behave in like fashion under the same conditions. Therefore, it appears as if the active specie is Co(CO)(NO) from the parent cobalt complex but $Co(NO)\ P(C_6H_5)_3$ from the other two cobalt complexes. Since there are some other dimers formed in the reaction Co(CO)(NO) may be present in a small amount.

Concentration of Efforts for Mechanism of Dimerization on $Ni(CO)_4$

The anomaly in the results from this entire series of complexes is that $Ni(CO)_4$ does not give the same stereoisomer for the major dimer formed. In fact, two dimers are formed in a ratio of 2:1 and these dimers are not even 2 + 2 type dimers but pseudo-Diels-Alder dimers (IV and V respectively in Figure 10, Page 20). It would appear that an entirely different mechanism may be responsible for this reaction. An explanation is not immediately obvious. Thermally, it was shown that although both nickel complexes gave 2 + 2 dimers $Ni(CO)_4$ produces the exo-trans-endo dimer and the uncommon endo-trans-endo while $Ni(CO)_2\ P(C_6H_5)_{3\ 2}$ generates exo-trans-endo and exo-trans-exo dimers. This implies that although the metal is the same and the geometry of ligands is essentially the same there is a difference in the active specie which

dictates the variation in the manner in which norbornadiene bonds to it. Since $Ni(CO)_2[P(C_6H_5)_3]_2$ produces the same major dimer photochemically as the rest of the series of complexes it appeared that a closer look at the exceptional $Ni(CO)_4$ dimerization of norbornadiene to try to establish the active complex, produce an active complex similar to those of the other complexes, and find why it does not go through the same reaction sequence as the other members of the series could perhaps elucidate metal and ligand displacement importance. Other reasons for pursuing the $Ni(CO)_4$ experiment were that there would be no interference from other ligands, for example, triphenylphosphine; and here was an unprecedented case in which the dimer products were exactly the reverse of those predicted by orbital symmetry for thermally and photochemically excited reactions of a molecule like norbornadiene.

The latter was important since F. D. Mango[60] had suggested the role of the transition metal d orbitals in allowing the thermally "forbidden" 2 + 2 reactions. His theory was that the bonding of two olefins to a metal resulted in molecular orbitals which allowed electrons from the highest bonding metal olefin orbital (composed of two olefin orbitals which have a node between them in a simple combination without the metal) to flow into an empty d orbital of the metal. At the same time electrons from a d orbital used in backbonding to the empty antibonding orbitals of the two olefins could permit electrons to flow into the antibonding orbitals of the olefins (which do not have a node between the orbitals) thereby resulting in bonding. Applying this theory to the

effect of the nickel carbonyl complexes on norbornadiene when thermally excited explained the formation of the "forbidden" 2 + 2 cycloaddition products.[61] However, all the complexes except $Ni(CO)_4$ gave 2 + 2 cycloaddition products photochemically as well. The fact that $Ni(CO)_4$ gave the thermally allowed 2 + 2 + 2 dimer product photochemically was certainly of interest to contribute to the understanding of effects of transition metals on orbital symmetry conservation during reaction.

Interpretation of Infrared Spectral Data to Determine Species in Solution During Reactions

Transition metal carbonyls have very characteristic C = O stretching frequencies in their ir spectra. The number of peaks observed can generally be justified on the basis of the symmetry of the molecule. The position of peaks is due to the type of bonding involved, whether terminal or bridging, and also the character of other ligands on the central metal. In the particular series of complexes here all C = O stretching frequencies are due to terminally bonded carbon monoxide.

The ir spectra was used to follow the change in the $Ni(CO)_4$ complex as the thermal reaction progressed. This was done to provide information as to what may be happening during the reaction as well as to provide a reference for possible isolated intermediates and as a comparison to the ir spectra of the photochemical reaction. As the thermal reaction progressed the single peak at 2035 cm^{-1} attributed to the C = O stretching of $Ni(CO)_4$ decreased in intensity and simultaneously two other peaks at 2000 and 1970 cm^{-1} grew in. Upon termination of the reaction

(twenty-four hours) and leaving the solution to stand under nitrogen the two new peaks disappeared leaving a peak at 2035 cm^{-1} but of lower intensity than at the onset of heat. When the solution was left standing in the air this peak disappeared too. The above thermal ir spectrum when compared with that of the terminated photochemical reaction also showed peaks at 1970 and 2000 cm^{-1} in addition to the 2035 cm^{-1} peak of $Ni(CO)_4$. However, the peak due to C = O stretching of $Ni(CO)_4$ was so intense in the photochemical case that the other two peaks were seen on the shoulder of the broad $Ni(CO)_4$ peak and was not as well defined as the sharp peaks in the thermal case.

Since the change in intensities of the three peaks in the thermal reaction was not uniform it appeared that more than one complex was responsible for the peaks. Various possible structures exist for these additional peaks, but without knowing whether some peaks were masked by others the assignments would be without meaning. Consequently, the isolation of the complexes responsible for these C = O stretching peaks was begun. Assuming the possibility that one of the peaks may be due to a dimer complex $Ni(CO)_4$ was introduced into a convenient mixture of exo-trans-endo and endo-trans-endo dimers. The peak at 2000 cm^{-1} was found to exist independent of the other two peaks when the dimer complex was isolated from unreacted $Ni(CO)_4$. It was also found that as the dimer complex decomposed the peak at 2035 cm^{-1} ($Ni(CO)_4$) reappeared. By warming a norbornadiene solution of $Ni(CO)_4$ to 40°C for a short period of time ($\approx$12 hours) followed by isolation of the complex an ir spectrum

showed a peak at 1970 cm^{-1} which was attributed to a norbornadiene complex and a peak at 2035 cm^{-1}, presumably, due to $Ni(CO)_4$.

Isolation of the dimers and attempts to find differences in the spectra of their nickel carbonyl complexes was then pursued. The dimer $Ni(CO)_4$ solutions changed from colorless to yellow when heated at 40°C. In the case of the endo-trans-endo dimer almost immediately after turning yellow, decomposition took place and a black precipitate formed. No ir spectrum was ever possible with this complex. On the other hand, the exo-trans-exo dimer formed a bright yellow solid which decomposed in every solvent tested except pyridine. An ir spectrum of that solution, however, showed no peaks around 2000 cm^{-1} except those due to pyridine. An ir spectrum of the latter complex was taken of a nujol mull and a single C = O stretch peak appeared at 1995 cm^{-1}. (A chemical analysis of this complex indicated the possibility of two carbon monoxide ligands on the nickel.) A solution of exo-trans-endo dimer and $Ni(CO)_4$ and also of the major Diels-Alder dimer and $Ni(CO)_4$ turned yellow upon warming between 40 to 50°C for a few hours. Upon isolation of these complexes a single C = O absorption peak at 2000 cm^{-1} in the ir spectra was observed for both. A complex of norbornene and nickel carbonyl was also prepared and its ir spectrum had the same peak at 2000 cm^{-1}. It must be pointed out that each of these complexes were prepared several times in order to obtain acceptable spectra. This was due to the extreme instability of these complexes and the method of purification used. Therefore, no exact concentrations or length of time of heating can be stated since

these were not always the same and conditions were not optimized. It was of interest that in every case some polymeric residue was formed and was not soluble in hexane which was used for the solvent in the chromatographic procedure of purification. Shown in Figures 27 and 28 are the ir spectra of nickel tetracarbonyl and the nickel carbonyl complexes of norbornadiene, exo-trans-endo dimer and exo-trans-exo dimer. The correspondence of these peaks to those seen during the thermal and photochemical reactions indicate the presence of $Ni(CO)_4$, a dimer complex of nickel carbonyl as well as a norbornadiene complex of nickel carbonyl.

The interpretation of the single C = O stretching peak in the ir of each of the experiments above was that the specie observed had either one or two carbon monoxide ligands. This was based on the following rationale. The peaks have been shifted to longer wave length suggesting substitution by an olefin. Substitution of carbon monoxide by other ligands not capable of backbonding to the extent of carbon monoxide (olefins, for example) have been shown to shift the C = O stretching frequency to longer wave lengths.[62] If only one carbon monoxide had been displaced, the geometry of the resultant complex should have at least two peaks, and more probably three, due to the symmetric and asymmetric C = O stretching.[63] The spectra would be expected to exhibit two peaks if two carbon monoxide ligands are left after two have been replaced, due to a symmetric and asymmetric C = O stretch. However, if these two were degenerate in energy or if the tetrahedral configuration has been distorted toward square planar to the point that the symmetric

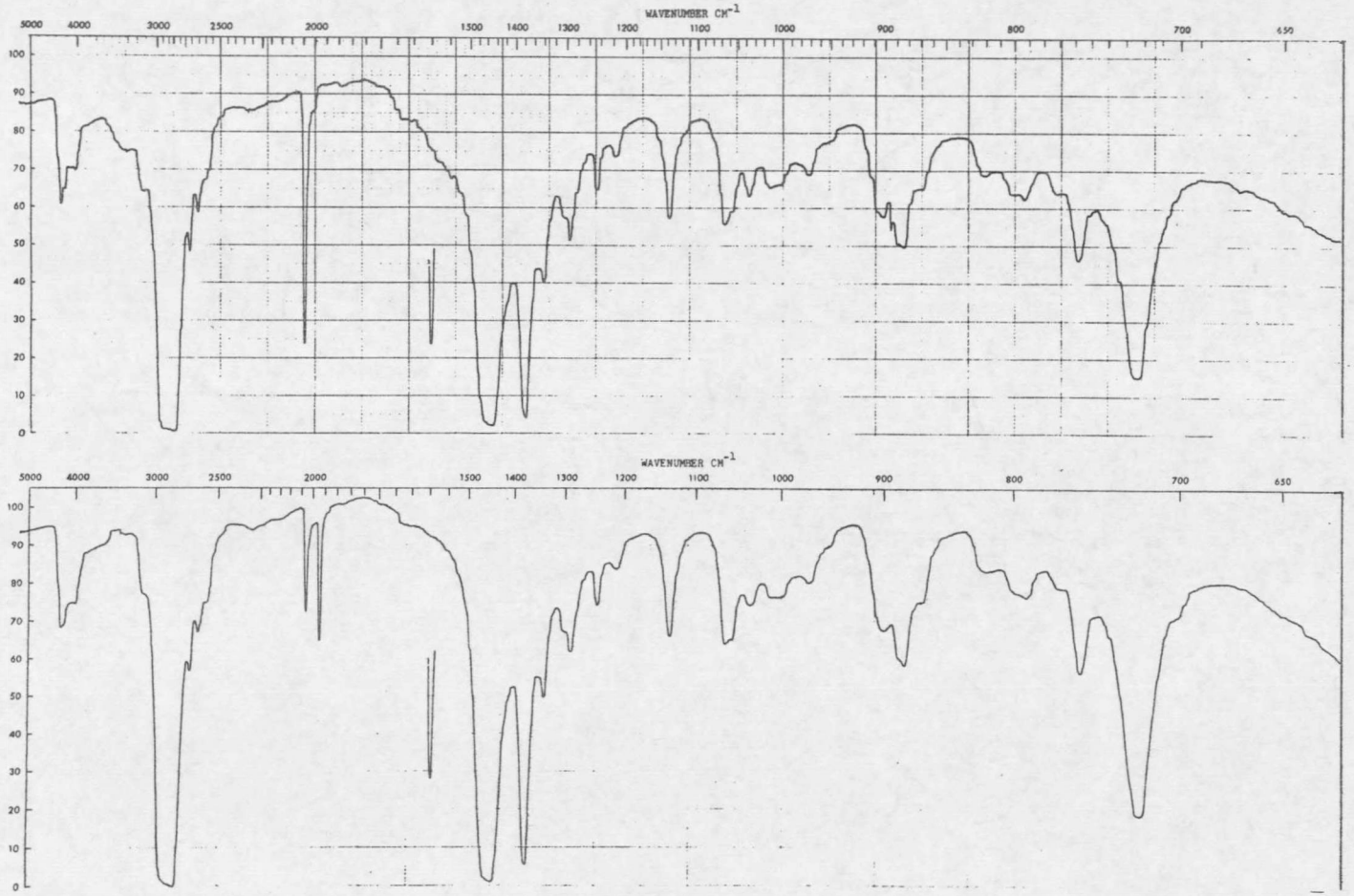


Figure 27

Top: IR Spectrum of a Hexane Solution of $Ni(CO)_4$
Bottom: IR Spectrum of a Hexane Solution of the Isolated Norbornadiene Complex of $Ni(CO)_4$ Containing Some Free $Ni(CO)_4$

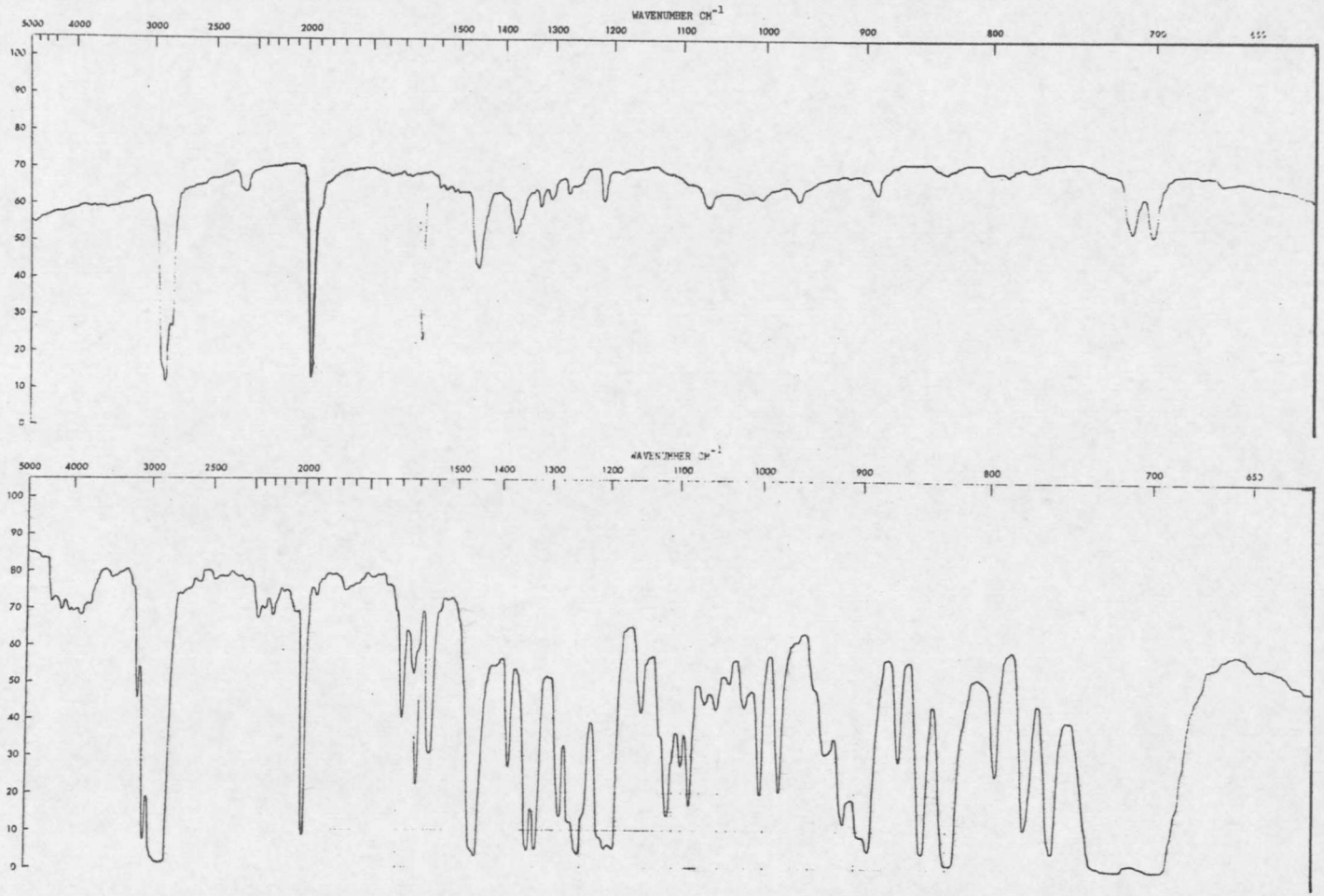


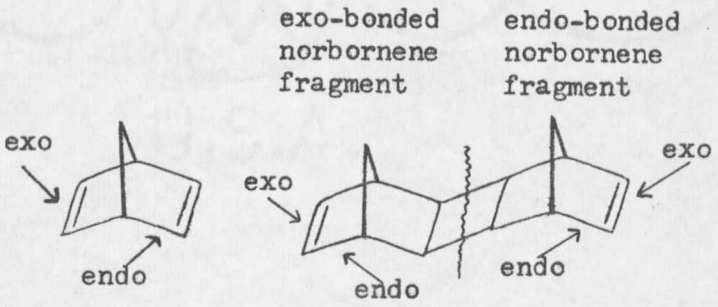
Figure 28

Top: IR Spectrum of a Nujol Mull of the Exo-Trans-Exo Dimer Complex of $Ni(CO)_4$
Bottom: IR Spectrum of a Hexane Solution of the Exo-Trans-Endo Dimer Complex of $Ni(CO)_4$

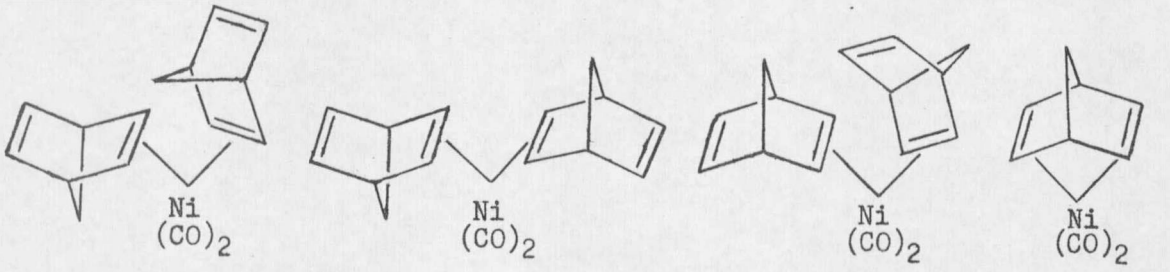
stretch is weak, only one peak would be observed.[64] Also, since ir active bands are dependent on a change in the dipole moment of a molecule, a weak dipole moment change would not be observed as a very strong absorption peak in the ir. Likewise, only one C = O stretch peak would be possible if three carbon monoxide ligands had been replaced by double bonds leaving only one carbon monoxide ligand. However, due to the premise that double bonds are not good backbonders, it is possible in the nickel carbonyl complexes of the dimers and norbornene for two carbon monoxide ligands to be bound to the nickel. In the norbornadiene case the sharp peak at 2035 cm^{-1} has been assigned to $Ni(CO)_4$ and the peak at 1970 cm^{-1} is the single peak for the nickel dicarbonyl norbornadiene specie. It is possible, however, that a second peak for this complex is coincident with the absorption peak of $Ni(CO)_4$.

Results from Attempting to find Bonding Side of Norbornadiene During Reaction via Nuclear Magnetic Resonance Spectroscopy

There are two possible sides, either exo or endo, to which the transition metal could be bonded to the double bonds of norbornadiene (or the dimers) as illustrated below.



This creates the possibility of four different isomers of a norbornadiene complex of nickel containing two carbon monoxide ligands as shown.



exo, exo exo, endo endo, endo endo, endo

There are six possible isomers when only one carbon monoxide remains on the nickel. Four isomers, in brief olefin-bond-to-metal notation, would be (1) exo, exo, exo; (2) exo, exo, endo; (3) exo, endo, endo; (4) endo, endo, endo and two isomers would be endo, endo to one norbornadiene molecule with the second norbornadiene bonded endo or exo. Many of these should be distinguishable by their proton nmr spectra based on shift

positon comparisons with known norbornadiene complexes of transition metal carbonyls. The main difference in shift positions in the complexes is seen, of course, in the olefin protons, since the bonding takes place between the double bond and the transition metal. In comparison to the shift position of the olefin protons in norbornadiene, the complex norbornadiene$Cr(CO)_4$ in which chromium is bonded endo to both double bonds of one molecule of norbornadiene, the olefin protons are shifted upfield 2.20 ppm.[65] In $(\pi C_5H_5)Mn(CO)_2$(norbornadiene) where the norbornadiene is bonded exo to only one double bond, the olefin protons of the metal-bonded double bond are shifted upfield 3.41 ppm while the protons on the non-metal-bonded double bond are shifted upfield 0.62 ppm.[66] There are no known isolated complexes where a transition metal is bonded endo to only one double bond so this cannot be compared to the other examples. Thus, all stable intermediates having a single endo-metal-bond are not considered likely. It can be seen that if only one double bond is exo-bonded to the metal, the protons on the bound double bond will be in a different environment than the protons of the non-bound olefin. If both double bonds are bonded either exo or endo by the nickel only one olefin proton peak would be expected. Therefore, one should be able to assess the side on which the nickel is bonded to the olefin of the various species by inspecting the proton nmr spectra.

The results of investigating the nickel carbonyl complexes, that of norbornadiene in particular, with respect to the change in olefin proton shift positions are best seen in the spectra. These spectra

(Figures 30, 31 and 32) were taken of a hexane solution of principally the norbornadiene complex but with some slight contamination from the dimer complex as can be seen in the ir and nmr spectra. The solution was being reduced in volume by removal of hexane; and since hexane was used no peaks above 1.6 ppm could be seen.

There are five points to consider in comparison of these spectra. First, the peaks in the olefin proton region going from left to right were assigned to norbornadiene, endo-trans-endo dimer, endo-bonded fragment of endo-trans-exo dimer followed by the exo-bonded fragment of the same dimer. These assignments were made based on a spectrum of a hexane solution of norbornadiene and the dimers formed from the thermal reaction of $Ni(CO)_4$ in norbornadiene, endo-trans-endo and exo-trans-endo as shown in Figure 29. The dimers were present since the preparation of the nickel-norbornadiene complex was carried out thermally and form with relative ease under these conditions.

The second point to note is the change in position of the peak assigned to the olefin protons of norbornadiene. As the solution became more concentrated in norbornadiene and dimer complex the shift position of the olefin protons of norbornadiene constantly move upfield with respect to bridgehead protons, moving a total of 0.30 ppm throughout the concentration procedure. The dimer olefin protons positions remained relatively constant. This change in position can be seen in Figures 30, 31 and 32 where the hexane solvent is being reduced. Figure 33 shows a proton nmr spectrum of neat norbornadiene and dimers to show that a

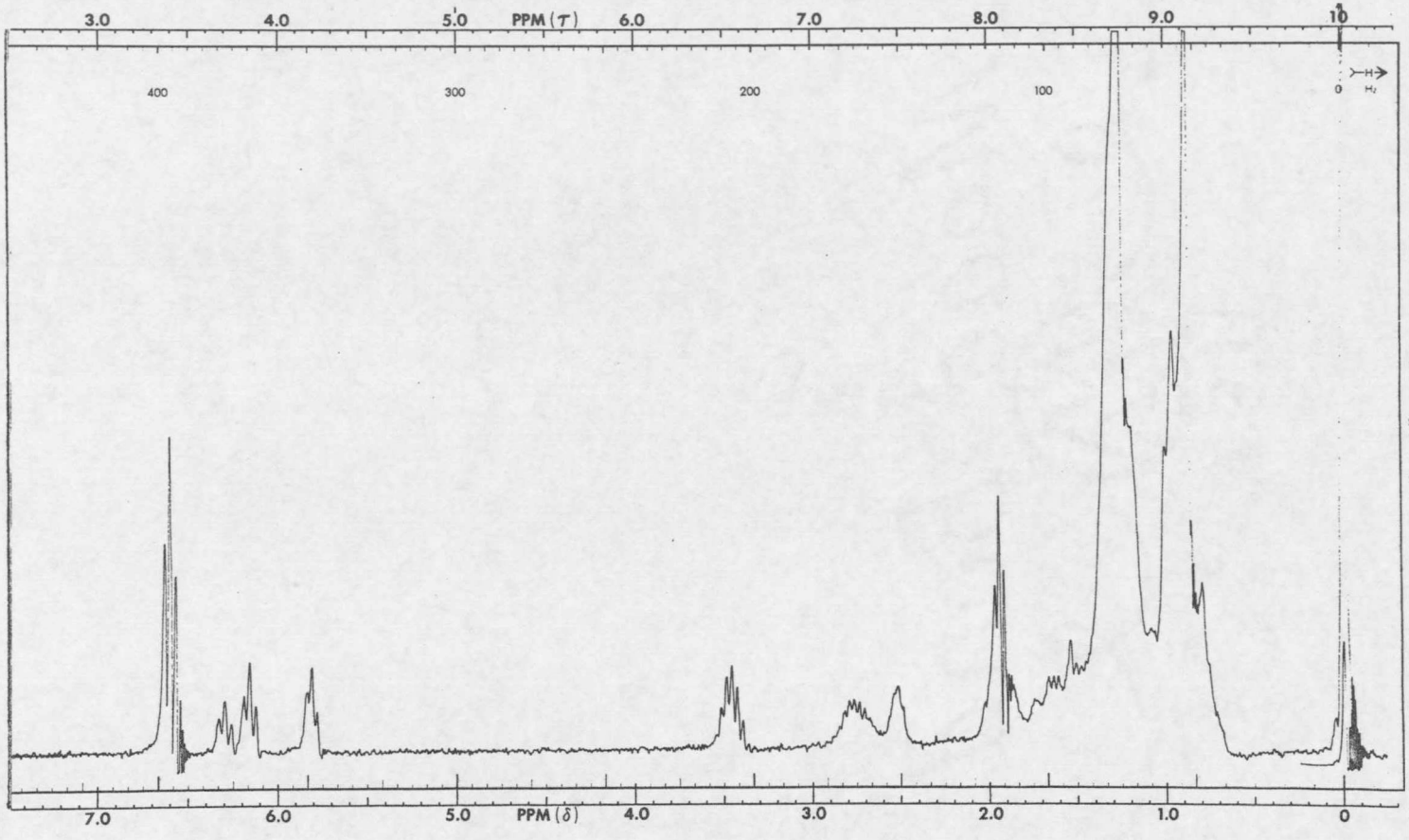


Figure 29

Proton NMR Spectrum of a Hexane Solution of Norbornadiene and the Endo-Trans-Endo and Exo-Trans-Endo Dimers

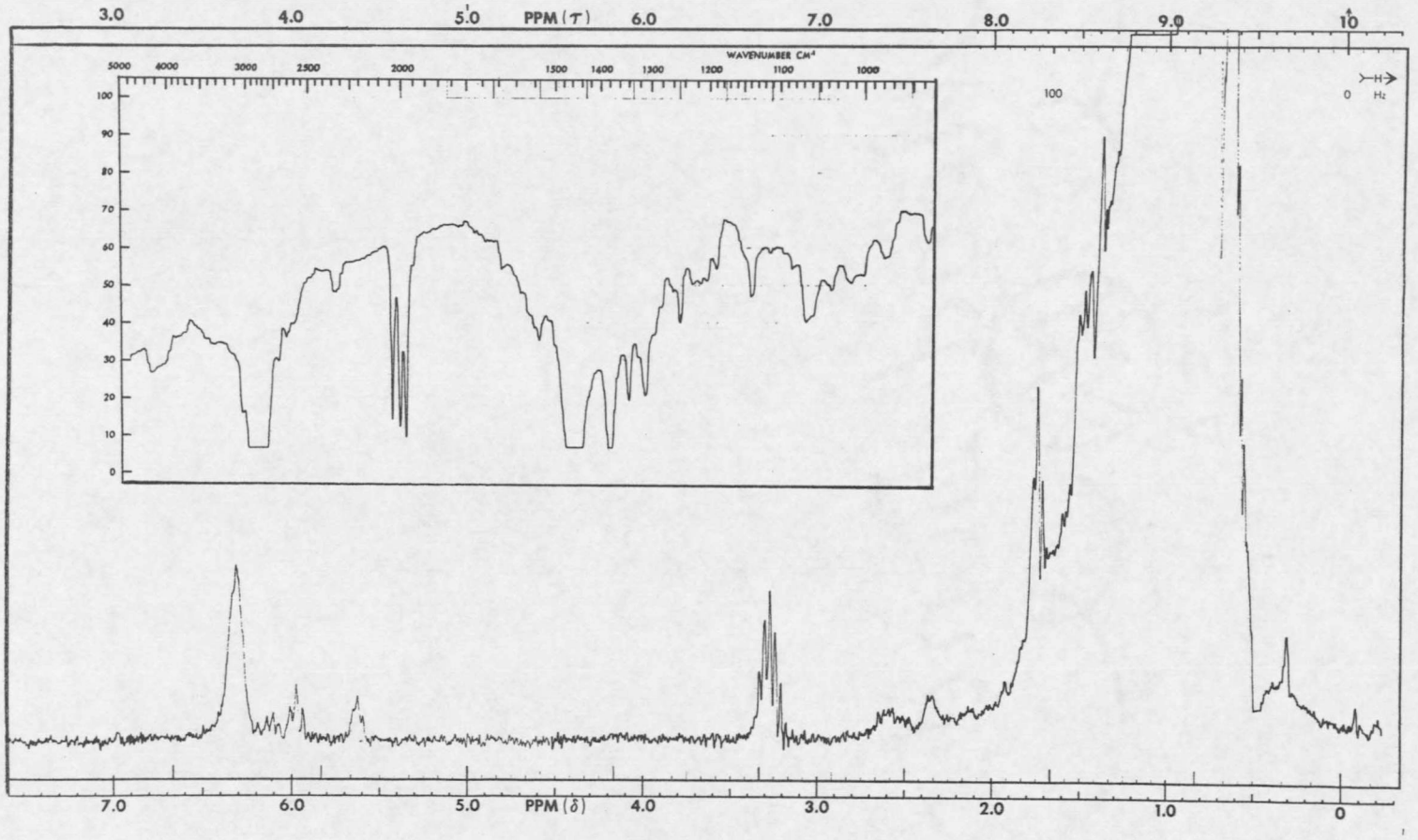


Figure 30

Proton NMR Spectrum of a Dilute Hexane Solution Containing the $Ni(CO)_4$ Complexes of Norbornadiene and the Exo-Trans-Endo Dimer (IR Spectrum in Inset)

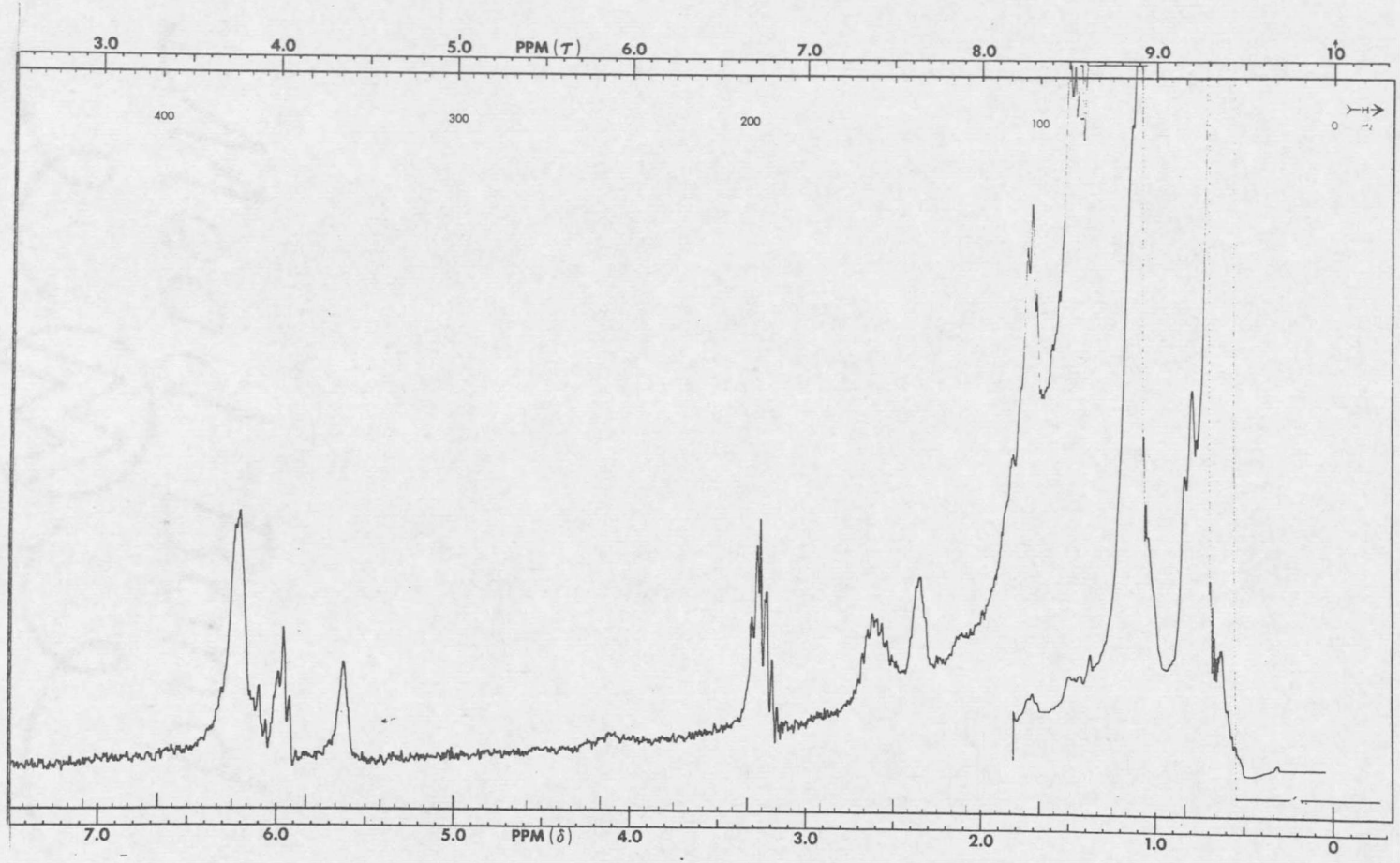


Figure 31

Same Solution as Figure 30 but Reduced to Approximately One Half of Volume

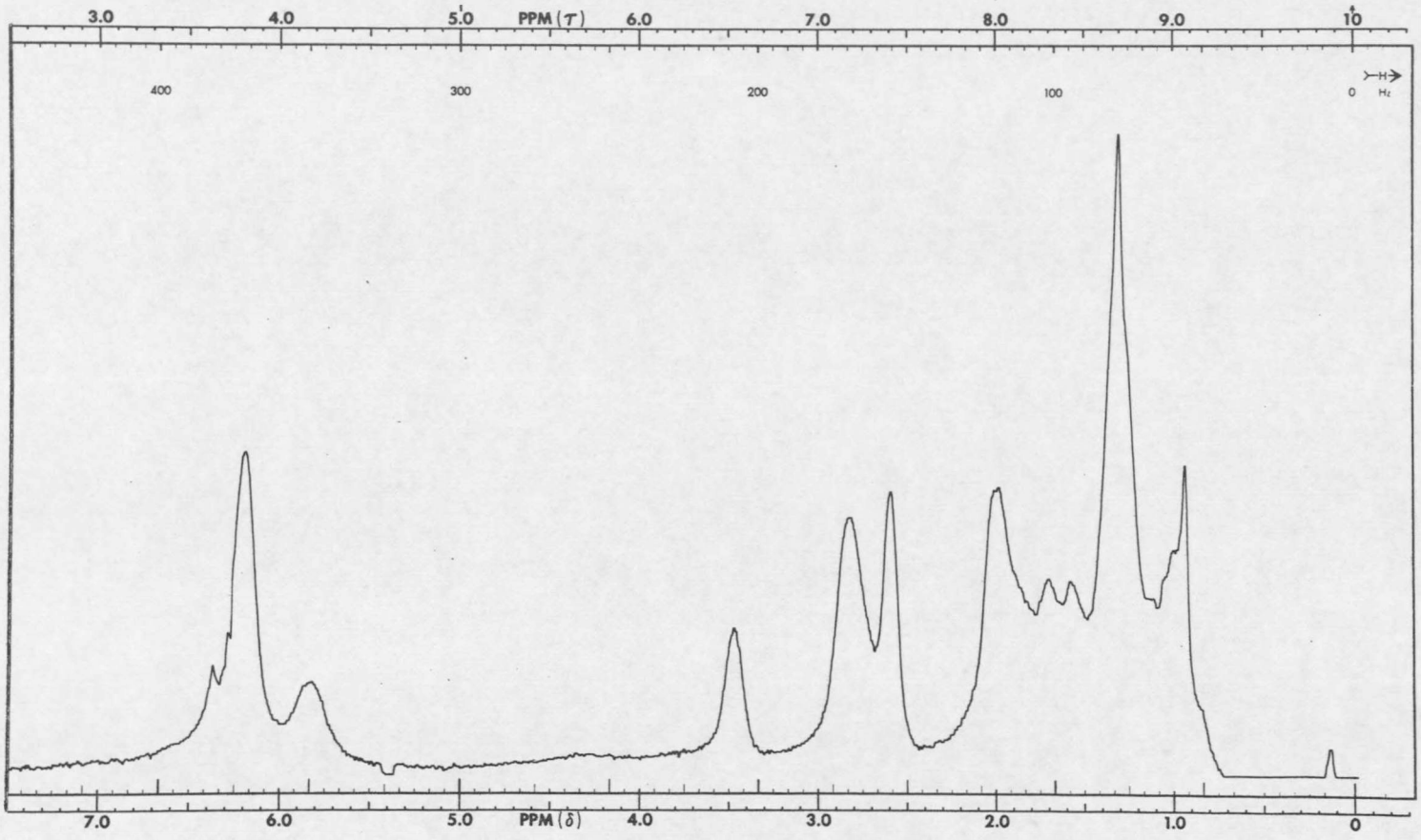


Figure 32

Same Solution as Figure 30 but Reduced to Approximately One Tenth the Original Volume

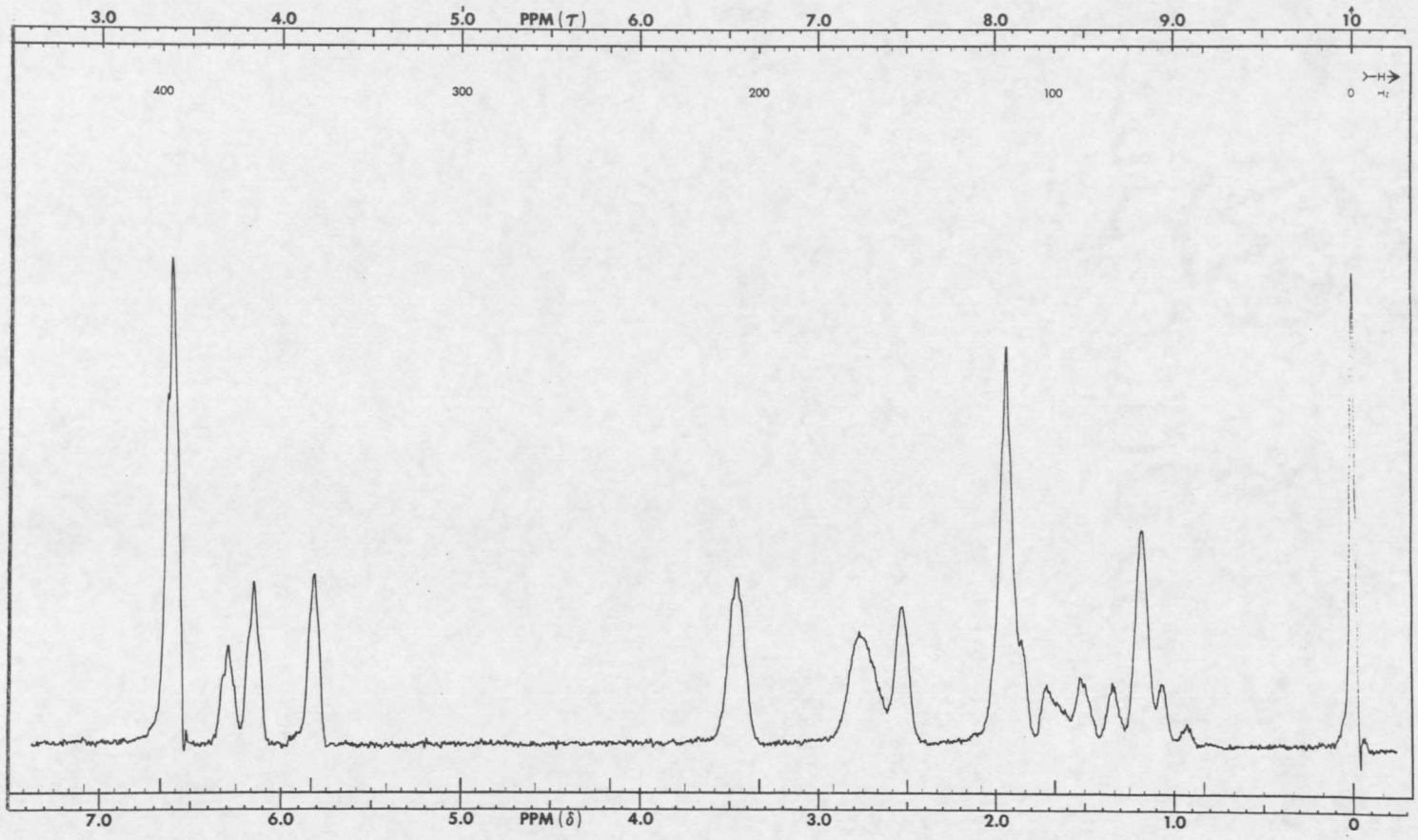


Figure 33

Proton NMR Spectrum of a Solution Containing Norbornadiene and Both the Exo-Trans-Endo and Endo-Trans-Endo Dimers

loss in hexane content was not responsible for the chemical shift.

Also, of importance, is the third observation — the number of olefin proton peaks due to norbornadiene. Although the peak was broad, there was no change in number as it shifted upfield. This implies that both double bonds must be bonded. It is also important to note that whereas the olefin proton peak was broad, the bridgehead proton peak assigned to the multiplet between 3.3 and 3.5 ppm was as sharp, initially, as it was in the reference solution. This suggests tacit bonding between the nickel carbonyl specie and the olefin.

The fourth observation made on these same spectra was the broadened peak assigned to the exo-bonded fragment of the exo-trans-endo dimer compared to the unaffected triplet of the endo-bonded fragment of the exo-trans-endo dimer which stayed nearly the same as the reference spectra. This indicated that the exo fragment of the dimer was bonded to the nickel resulting in the same sort of broadening of the peak as observed in norbornadiene. The peak assigned to the olefin protons of the endo-trans-endo dimer retained the triplet splitting. All the peaks became broadened as hexane content became very low due to the increasing viscosity of the solution, principally because of the presence of the exo-trans-endo dimer. The broadened peaks in a neat nmr spectrum of the norbornadiene-dimers solution is shown in Figure 33.

The fifth observation was the triplet upfield from the bridgehead multiplet. This peak is assigned to the bridge protons of norbornadiene. Either neat or in a hexane solution, this peak lies 1.51 ppm

upfield (located at 1.95 ppm). A triplet peak was observed on the edge of the hexane peak in the solution of nickel-norbornadiene complex and it maintained its positon at 1.52±0.02 ppm from the bridgehead multiplet throughout the volume reduction. From the proton nmr data of $(\pi C_5H_5)Mn(CO)_2$(norbornadiene), the bridge protons were split because of the interference from the exo-bonded manganese. Both protons were shifted upfield, the proton anti to the metal was shifted 1.1 ppm while the proton on the same side as the metal was shifted 1.8 ppm upfield. Since the triplet assigned to the bridge protons of norbornadiene appeared to remain essentially unchanged in the nickel complex experiment, it seems to indicate that the nickel is not bonded on the exo side of the norbornadiene.

In total, the nmr observations indicate that the nickel carbonyl complex of norbornadiene is probably bonded endo to both double bonds of norbornadiene. This conclusion was based principally on the single broad peak of the olefin protons. Although the peak did not shift as far upfield as literature reported values for other transition metal complexes, the shift is in the right direction and is detectable. The broadening of the olefin peak while the peak of bridgehead protons maintained its fine structure indicated that the nickel complex is in equilibrium with its components. Thus, it probably behaves in the same manner as $(COT)Fe(CO)_3$ in solution except intermolecularly rather than intramolecularly. There is the possibility that the nickel carbonyl is exo-bonded to two norbornadiene molecules. However, the two different pairs of

olefin protons would not be expected to average to one peak upon rapid exchange unless both double bonds on each norbornadiene were bonded to nickel. In addition, as the concentration of the complex increased, so did the viscosity, thus, reducing rather than increasing the rate of exchange and, therefore, the appearance of the peak of the protons on the non-metal-bonded double bond should have become apparent. If the nickel were bonded both endo and exo to the different norbornadiene molecules, the protons on the differently bonded double bonds should have had different shift positions. Since there is no precedent for single endo bonded species this complex is discarded. Further, a norbornadiene complex of nickel duroquinone $(C_{10}H_{12}O_2)Ni(C_7H_8)$ has been described as bonding endo to both double bonds of norbornadiene based on its spectral and physical data.[67] In this stable complex the olefin protons were shifted 2.22 ppm upfield to 4.40 ppm (one peak) and only one peak at 1.60 ppm was reported for the bridge protons.

Schrauzer[68] has suggested that the endo-bonded norbornadiene in the duroquinone complex is predominantly an electron donor and a weak electron acceptor to support the shift to longer wave length of the C = O stretch frequency compared to the bis(duroquinone)nickel complex.

The ir spectra for the norbornadiene complex of nickel carbonyl showed the C = O stretching frequency was shifted 30 cm^{-1} to longer wave length than the corresponding dimer and norbornene complexes. From models, it appears that the nickel would not bond to the endo side of a double bond on the dimers or norbornene due to steric hindrance.

Assuming the nickel bonded exo on the dimers and norbornene then the shift of the C = O stretching frequency for the endo-bonded norbornadiene complex would indicate it was different from the dimers or norbornene and could, therefore, possibly be bonded endo.

Reactions of Dimer and Norbornadiene Complexes of $Ni(CO)_4$

The isolation of a complex resulting from a reaction of norbornadiene and nickel tetracarbonyl is not sufficient evidence of the complex being an intermediate in the dimerization reaction. Therefore, these complexes were then reacted with norbornadiene under standard conditions to find if the reaction which followed was the same as or different than the normal reactions.

When the norbornadiene and dimer complexes from a photochemical reaction were isolated and mixed with norbornadiene, then refluxed, the dimer products were the same as those from the normal thermal reaction of nickel tetracarbonyl and norbornadiene. The color change of solution from yellow-orange upon addition of complexes to norbornadiene to red when heated paralleled the color change from yellow to red normally seen in the comparison reaction. All three peaks in the C = O absorption region of the ir spectrum were visible throughout the thermal reaction, again the same as was seen in the standard thermal reaction.

The nickel carbonyl complex of the dimers exo-trans-endo and endo-trans-endo also was added to norbornadiene and refluxed, the yellow solution became yellow-orange, and again, the three C = O stretching

peaks were observed. This solution also turned red as it was refluxed and produced the same dimers as before. It appeared that some sort of equilibrium was formed in these reactions since even though no norbornadiene complex was present until the addition of norbornadiene, in the latter case, this complex as well as $Ni(CO)_4$ was formed in the reaction as indicated by the ir spectrum. The solutions always turned black after a short time when heated and usually a nickel mirror could be seen; thus, some decomposition also took place in these reactions. Presumably, the dimer complex is not as stable under these conditions as the norbornadiene complex, thus decomposing to the norbornadiene complex and $Ni(CO)_4$. During the process some of both complexes could decompose to pure nickel and carbon monoxide.

Similarly, the complexes from the photochemical reaction were isolated and reintroduced to norbornadiene. This solution was sealed in a tube under vacuum as in the normal photochemical reactions. Within six days of irradiation, the solution became solid. The solution during that time had also turned red as in the thermal reaction. The dimer analysis showed only the exo-trans-exo dimer to be present along with some other polymers. Likewise, when the nickel carbonyl complexes from heating nickel tetracarbonyl and norbornadiene were isolated, added to norbornadiene, sealed under vacuum in a tube and irradiated, the contents turned red and became solid within five days. Again, the dimer analysis showed that only the exo-trans-exo dimer was formed along with some polymers.

The interpretation of all this data was that the complexes isolated photochemically and thermally are common intermediates or produce common intermediates which are responsible for the dimer products formed in the thermally excited reaction of $Ni(CO)_4$. Since the dimers as well as norbornadiene form complexes with nickel carbonyl, the formation of trimer and other polymers were as expected. However, the same isolated complexes did not appear to be the complex of $Ni(CO)_4$ which was responsible for the 2 + 2 + 2 dimers under photochemical conditions even though they are apparently formed photochemically. The formation of the exo-trans-exo dimer from these dimer complexes was completely unlike any other experiment with nickel tetracarbonyl in norbornadiene, but did parallel the major dimer formed in the photolysis experiments with all the other members of the pseudo-nickel carbonyl group in which the predominant dimer formed is exo-trans-exo.

One possible explanation for this anomalous dimer formation in the photochemical experiment of preformed nickel complexes was that the carbon monoxide content in the tube was greatly reduced from the normal photochemical nickel tetracarbonyl experiment. In the normal nickel tetracarbonyl photochemical reaction with norbornadiene to form a norbornadiene-nickel dicarbonyl complex, the carbon monoxide concentration would be twice that of the complex based on the assumed reactions — $Ni(CO)_4 + C_7H_8 \rightarrow Ni(CO)_3(C_7H_8) + CO$ and $Ni(CO)_3(C_7H_8) \rightarrow Ni(CO)_2(C_7H_8) + CO$. There is also much unreacted $Ni(CO)_4$ in solution as has been observed in the ir spectrum of photochemical reactions after termination. In the

case of the addition of preformed nickel carbonyl complexes to norbornadiene, there would initially be no carbon monoxide in solution from either the complex formation reaction or $Ni(CO)_4$ dissociation. If a certain concentration of carbon monoxide was necessary to participate in the reaction or was responsible for the formation of a norbornadiene complex in which the orientation of the norbornadiene molecules would permit the formation of the 2 + 2 + 2 dimers, then this participation would be reduced in the norbornadiene-dimer nickel carbonyl complex case.

To substantiate the participation of carbon monoxide in forming 2 + 2 + 2 dimers rather than the exo-trans-exo dimer, an experiment was performed in which nitrogen was bubbled through a tube containing a solution of norbornadiene and nickel tetracarbonyl during irradiation. This was designed to remove excess carbon monoxide during the reaction. The experiment showed the formation of exo-trans-exo dimer in addition to the 2 + 2 + 2 dimers. In comparison to the standard photochemical reaction where only a trace of exo-trans-exo dimer is formed, the enhancement of exo-trans-exo was eight times more than in the standard reaction. Thus, the participation of carbon monoxide in the 2 + 2 + 2 dimers formation in preference to the exo-trans-exo dimer product appeared to be a good possibility.

Proposed Reaction Mechanism for the Thermal Reaction of $Ni(CO)_4$ in Norbornadiene

With the compilation of all this data regarding the nickel

tetracarbonyl-norbornadiene reactions, a mechanism is suggested which incorporates these results for both the thermal and photochemical reactions. Since the mechanism appears to differ, they have been dealt with separately. In both cases, the assumption has been made that the dimerization takes place when both molecules of norbornadiene are in contact with the metal in the conformation of its subsequent dimer until dimerization is completed. This is based on current theories of Schrauzer,[69] Mango,[70] Jolly et. al.[71] and others as well as being the most straightforward way of explaining the formation of the products assuming tetrahedral configuration. Katz[72] has proposed the idea that the metal is only necessary to form one new carbon-carbon bond between the two norbornadiene molecules. The subsequent formation of the other σ bond to complete dimerization is not clear. In view of the apparent specific bonding and geometry of the ligands on metal carbonyls as well as the complexity involved in bonding in metal complexes the ability for free rotation around a carbon-carbon bond with two available sites for bonding in close proximity with the metal seems more complex and more difficult to explain than the complete metal-mediated approach. This idea has not been applied to the system investigated here.

In the thermally excited reaction of nickel tetracarbonyl in norbornadiene the expected first step would be the unimolecular loss of a carbon monoxide ligand followed by the bonding of one double bond of norbornadiene. The suggested homogeneous thermal decomposition of nickel tetracarbonyl by Garrett and Thompson[73] and Callear[74] is the loss

of one carbon monoxide ligand initially. Rate of exchange of carbon monoxide studies and ligand replacement reactions also suggest a rapid loss of carbon monoxide ligand as the initial step.[75]

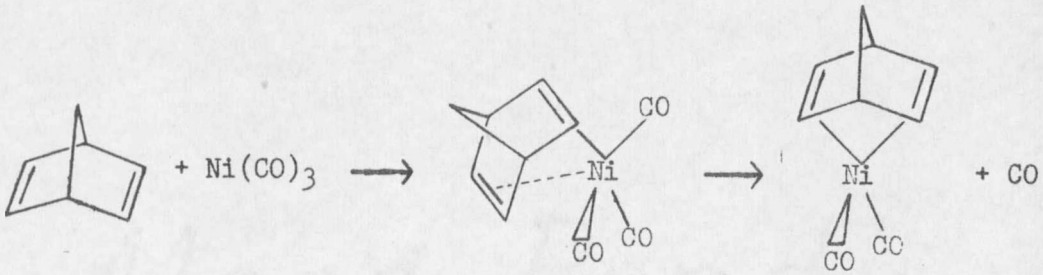
As was pointed out earlier, the norbornadiene molecule can bond either exo or endo to the nickel. Regardless of the way it is bonded the next step in the hypothetical reaction sequence is the loss of another carbon monoxide ligand to give a nickel dicarbonyl specie which is then bonded to another double bond of norbornadiene. The proposed loss of the second carbon monoxide ligand is also precedented by ligand replacement reactions as well as by the thermal decomposition mechanism proposed by Callear.[76] Kimball[77] has suggested that according to valence bond interpretation there are only two metal π bonds available for backbonding to ligands in the tetrahedral nickel carbonyl complexes which predicts easy loss and replacement of two carbon monoxide ligands with the two remaining carbon monoxide ligands being bonded stronger to the metal. Indeed, most of the thermal replacement reactions of carbon monoxide on nickel tetracarbonyl by various phosphine ligands have gone rapidly to, but stopped at, the replacement of two.[78] Consequently, the loss of two carbon monoxide ligands and subsequent bonding to two double bonds of norbornadiene is not incompatible with reported observations.

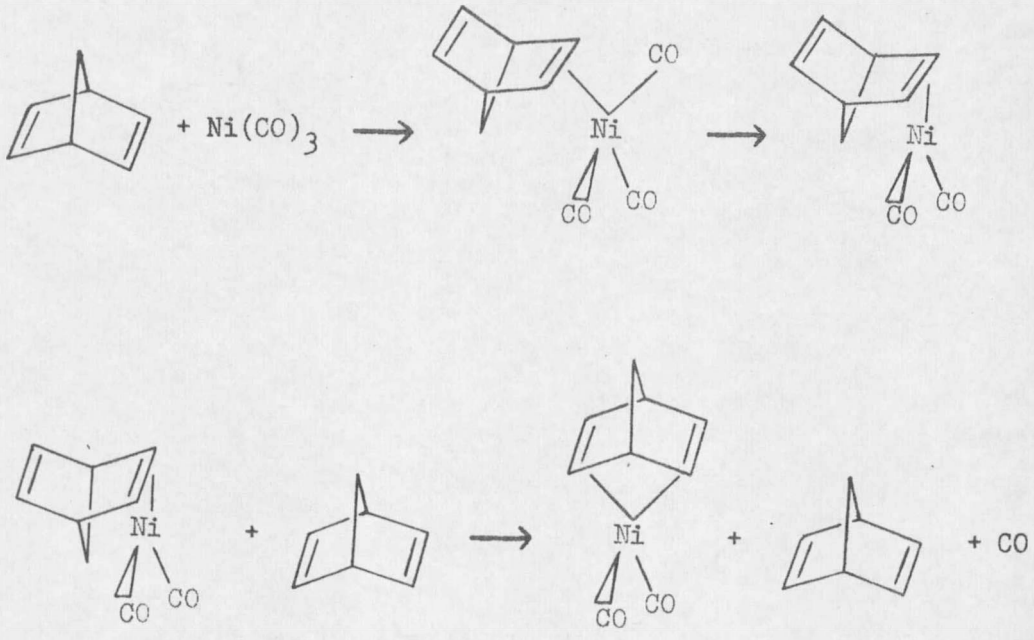
Returning to the manner in which the norbornadiene bonds to nickel, the data from the ir spectra and proton nmr spectra were incorporated in the analysis to rationalize the structure of the intermediate. Since the norbornadiene complex shifted the C = O absorption peak to

longer wave length than did the dimers and also since only one peak appeared for the olefin protons of norbornadiene in the proton nmr spectra, the norbornadiene seems to be bonded endo to both double bonds of one molecule per nickel dicarbonyl specie. In the step-wise sequence prior to formation of this complex, the norbornadiene may have bonded endo initially after the loss of one carbon monoxide and in the process displaced the second carbon monoxide ligand. It is also possible that the first double bond was exo-bonded to the metal but the subsequent loss of another carbon monoxide ligand results in displacement of the exo-bonded norbornadiene by another molecule of norbornadiene which bonds endo to both double bonds. Moreover, the shift to longer wave length of the C = O absorption peak in the ir spectrum inferred that the bidentate norbornadiene may be less capable of backbonding than two single exo-bonded species. This follows from the observation of other metal carbonyl complexes where a higher electron density on the metal creates stronger backbonding onto the carbon monoxide ligands. This reduces the bond order between the carbon and oxygen and lowers the frequency of vibration. The doubly endo-bonded norbornadiene could perhaps be referred to as a relatively stronger σ donor but a relatively weaker π acceptor than exo-bonded double bonds. It should also be pointed out that all of the isolated transition metal carbonyl complexes containing norbornadiene that have been reported are bonded endo to the two double bonds.[79] This di-endo-bonding may also be due to the metal participation in the "homoconjugation" between the double bonds found to exist from

photoelectron spectroscopy of norbornadiene.[80] It was suggested that this double bond interaction produces a slight stabilizing effect (0.1ev) on the strained ring system. The metal could, by bonding to both double bonds simultaneously, allow some redistribution of electrons which may, perhaps, help increase stabilization. This interaction of the π system may also explain why no isolated norbornadiene complex of transition metals has yet been found which bonds endo to only one double bond and could also explain the second carbon monoxide displacement of nickel tricarbonyl if the norbornadiene is approached on the endo side. For the same "homoconjugation" reason, this may explain why the metal would not bond exo on the norbornadiene if the resulting stabilization of the complex did not exceed the destabilization of the norbornadiene "homoconjugation". Below is a diagram to illustrate possible reaction routes to the di-endo norbornadiene nickel dicarbonyl complex.

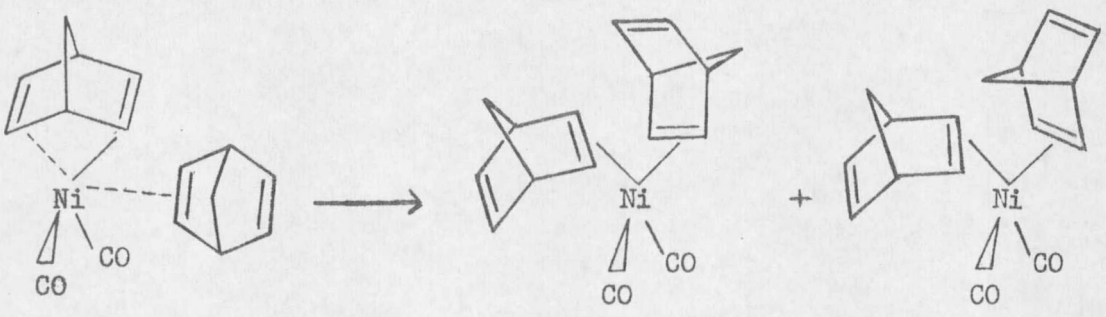
$$Ni(CO)_4 \longrightarrow Ni(CO)_3 + CO$$





After the formation of the di-endo-bonded norbornadiene nickel dicarbonyl specie, it must attack or be attacked by another molecule of norbornadiene to meet the initially assumed requirement that two molecules of norbornadiene be in contact with the metal prior to dimerization. The di-endo norbornadiene complex is, of course, not very stable as indicated by its susceptibility to decomposition in air and the implication by the broad olefin proton peak in the nmr which is proposed to result from a rapid exchange in solution. When this complex is attacked by another molecule of norbornadiene the question of orientation of the reactants again arises. However, the stereochemistry of the dimer products suggests that the attack of the uncomplexed norbornadiene

can be either exo or endo with a preference for exo side based on the 3:1 ratio of exo-trans-endo dimer to endo-trans-endo dimer. The arrangement of these two norbornadiene molecules on the nickel prior to dimerization must be an endo bond to one double bond of one molecule of norbornadiene and either an exo or endo bond to the other molecule. This could arise as a result of a second molecule of norbornadiene attacking the nickel on the opposite side of one of the endo-bonded double bonds of the norbornadiene of the complex with a double bond (exo or endo) in an S_N2 type of displacement. The result would be a single endo bond to a double bond of one norbornadiene and a single bond (exo or endo) to a double bond of the other norbornadiene on the nickel dicarbonyl specie as shown below.



This "complex" would probably be extremely short-lived but dimerization could also take place rapidly. The stereospecificity of the bonding to the second molecule of norbornadiene may be due to the steric factors of the original complex. Thus, the predominant exo bonding may be due to the geometry of the ligands and the resulting steric hindrances.

Cyclobutanation from the above di-norbornadiene complex may be rationalized by orbital symmetry considerations by Mango.[81] According to the conservation of orbital symmetry rules of Woodward and Hoffmann[82] norbornadiene should not undergo a $\pi 2s + \pi 2s$ cycloaddition reaction thermally. However, in the presence of transition metals, a pathway exists to allow the cycloaddition. This pathway exists, according to Mango,[83] in a nickel dicarbonyl specie in which a relatively empty dyz orbital of the nickel participates in a σ donor bond by overlapping with the highest occupied molecular orbital (HOMO) of the two norbornadiene molecules. The π backbonding orbital consists of the relatively filled dxz orbital of the nickel overlapping with the lowest unoccupied molecular orbital (LUMO) of the same norbornadiene molecules. Since orbital symmetry will not permit net bonding considering norbornadiene molecules without metal but will permit overlap between the LUMO's, bonding (dimerization) may proceed on the nickel by donating the pair of electrons from the HOMO to the nickel and removing the pair of electrons of the nickel, accepting them into the LUMO. This has been illustrated on Pages 14 and 15. The nickel will have a total net change in electron density of zero as do the norbornadiene molecules in forming the dimer.

As the dimer forms the nickel dicarbonyl specie can either simultaneously bond to a solution bidentate norbornadiene molecule regenerating another di-endo norbornadiene intermediate (Figure 34) or, because of the geometry of the dimer just formed, could leave by a momentary bonding endo to the double bond of the endo-bonded dimer (Figure 35).

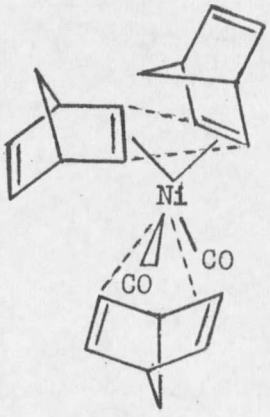


Figure 34

Reformation of Di-endo Norbornadiene Nickel Dicarbonyl Complex during 2 + 2 Dimerization

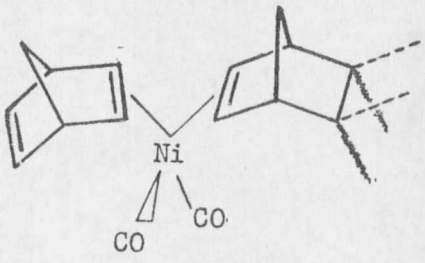


Figure 35

Reformation of Di-endo Norbornadiene Nickel Dicarbonyl Complex after 2 + 2 Dimerization

Trimer formation could be explained in the same fashion except that the attacking molecule on the complex is a dimer which bonds in particular on the exo side of the exo-bonded fragment of the dimer. This stereospecificity may be due to steric hindrance on the underside of the dimer fragment due to the protons of the cyclobutane ring. Another contributing factor might be the through-space electronic effect which the cyclobutane ring has on the endo side of the double bond of the exo-bonded norbornene fragment (Refer to Page 62). Presumably, it is possible that the electron density of the edge of the cyclobutane ring may interfere by electron-electron repulsion with the lobes of the π bond on the endo side of the norbornene fragment creating a larger electron density on the exo side of the double bond. The trimer which

would then form would be the result of the dimer bonding on the exo side of the double bond on the exo-bonded fragment and a norbornadiene molecule endo-bonded. This corresponds to the major trimer formed (Page 37, Figure 21, Structure II) from exo-trans-endo, $Ni(CO)_4$ and norbornadiene thermally; and is added confirmation of a di-endo-bonded norbornadiene nickel dicarbonyl complex.

The formation of the black residue in the thermal reaction, presumed to be nickel due to its metallic appearance and an occasional mirror formation, could come about as a result of the collision of two loosely bonded nickel dicarbonyl species. According to the decomposition mechanism of nickel tetracarbonyl by Callear,[84] nickel and carbon monoxide are the products when two nickel dicarbonyl species collide. Since the nickel dicarbonyl species supposedly are rapidly exchanging norbornadiene molecules, the collision of any two of these moieties could result in the decomposition of the nickel dicarbonyl species in the same manner.

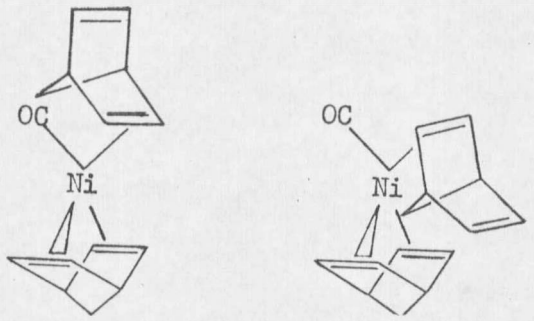
Proposed Reaction Mechanism for the Photochemical Reaction of $Ni(CO)_4$ in Norbornadiene

A proposed mechanism for the photochemical dimerization of norbornadiene by nickel tetracarbonyl is also proposed from the structures of the products and the work done on the isolated intermediates. Callear[85] has shown by flash photolysis that the decomposition of gaseous nickel tetracarbonyl is a two photon process to lose two carbon monoxide ligands generating the nickel dicarbonyl specie via the nickel

tricarbonyl specie. Therefore, it seems logical to assume that the same di-endo norbornadiene nickel dicarbonyl complex is formed photochemically as thermally. Further, comparison of the ir spectra of the photolyzed and refluxed solutions gave evidence that the same complexes are formed in both cases. The isolation of the previously discussed norbornadiene and dimer complexes, subsequent mixing with norbornadiene, and thermally exciting the solution gave the same dimer products as the standard thermal reaction with nickel tetracarbonyl. Hence, it appears that whether photolytically or thermally the same norbornadiene and dimer complexes (except for a difference in dimer) of the nickel dicarbonyl specie are formed. The main difference between the two methods at this point is that the concentration of nickel tetracarbonyl is much higher in the photochemically excited solutions than in the thermally excited solutions. Perhaps this is due to the closed system in the irradiated case where nothing can escape compared to the possibility that some is lost from solution when the norbornadiene is refluxed due to its volatility.

Therefore, in order to produce pseudo-Diels-Alder dimers rather than the 2 + 2 cycloaddition of two double bonds as in the thermally excited experiments the di-endo norbornadiene nickel dicarbonyl complex must lose one carbon monoxide and bond to another molecule of norbornadiene at right angles to the norbornadiene already bonded on the nickel in keeping with the metal-mediated assumption. In addition, the bidentate norbornadiene does not break either of its bonds to the nickel.

The second singly bonded molecule of norbornadiene must be bonded on the exo side since the two dimers formed are both exo-bonded to this norbornadiene molecule. There are two conformational isomers of this complex shown below.

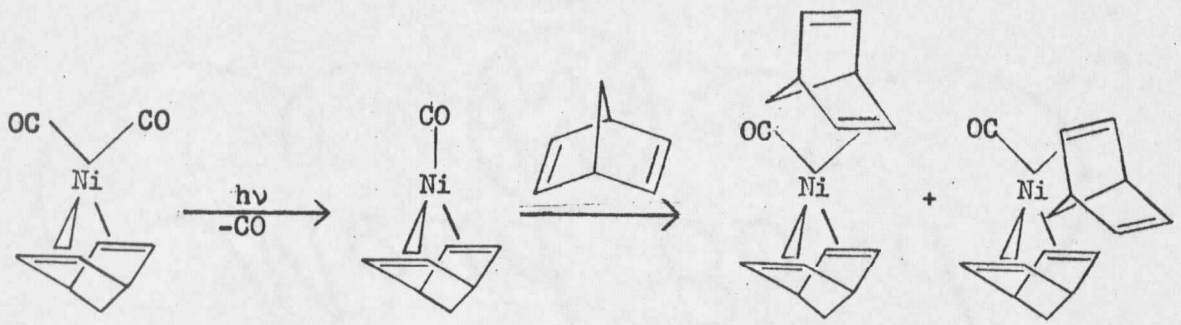


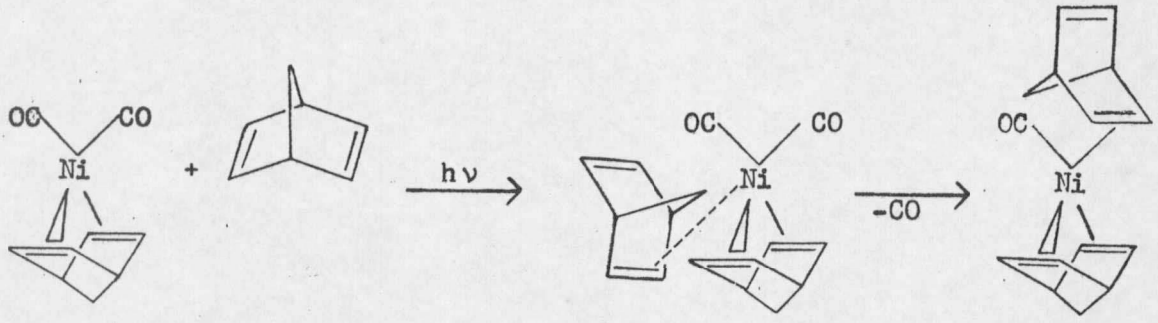
I II

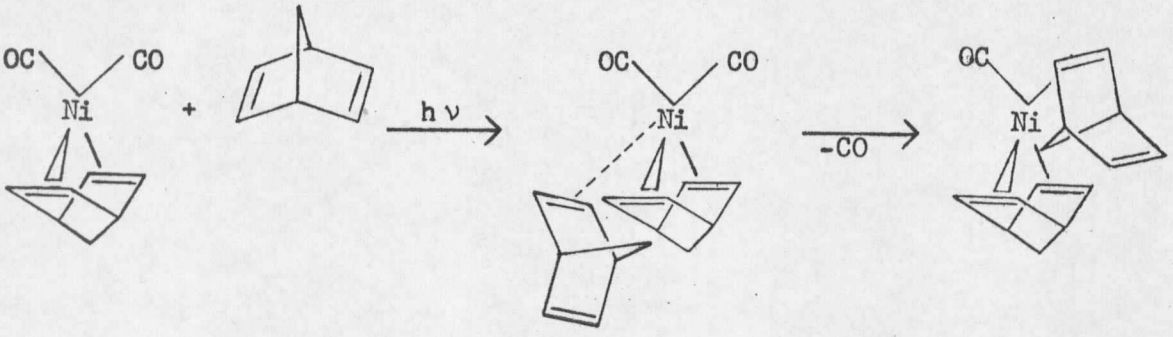
Formation of such monocarbonyl complexes of nickel can be rationalized. Starting with the di-endo norbornadiene nickel dicarbonyl complex, the first step is probably the absorption of light followed by the loss of a carbon monoxide ligand after which a molecule of norbornadiene becomes bonded. This ligand exchange is probably photochemically activated since the loss of an additional carbon monoxide ligand is not usually achieved in most of the disubstituted nickel dicarbonyl complexes when thermally activated. There are, however, many examples where a thermally nonreplaceable carbon monoxide ligand can be replaced when irradiated. The $(\pi C_5H_5)Mn(CO)_3$ is one such case[86] in which photochemically either an olefin or a phosphine ligand will replace a carbon

monoxide ligand. Thermally, carbon monoxide is inert to replacement by either ligand. It is interesting to note in this same example when norbornadiene is the replacing ligand, the manganese bonds exo to only one double bond and with norbornene the bond is exo as well. Since it appears that the norbornadiene must also bond exo to the preformed nickel complex for the proper geometry to form the correct $\pi 2s + \pi 2s + \pi 2s$ products it is reasonable to propose that this step is photochemical. The reason for the exo-bonded norbornadiene may also be that the resultant complex is stabilized more by an exo-bonded double bond than by an endo-bonded norbornadiene. In addition, there is the steric problem which could also be responsible for the exo bond where there appears to be the least amount of unfavorable interactions in molecular models.

The replacement could be either SN_1 or SN_2 which at best, would be very difficult to differentiate with the available data. Although an SN_1 type of mechanism has been shown to take place in many thermal and photochemical substitution reactions in parent transition metal carbonyls[87] this is not necessarily the case in the photolysis of more complex metal carbonyl compounds.[88] Therefore, it is feasible that a norbornadiene molecule could attack a photochemically excited di-endo norbornadiene nickel dicarbonyl complex displacing a carbon monoxide ligand. Illustrations of the possible reaction pathways to the monocarbonyl species follow.


OC
CO
Ni
hν
-CO
CO
Ni
OC
Ni
+
OC
Ni


OC
CO
Ni
+
hν
OC
CO
Ni
-CO
OC
Ni


OC
CO
Ni
+
hν
OC
CO
Ni
-CO
OC
Ni

Likewise photolysis of the monocarbonyl specie could reconvert to the di-endo complex when attacked by carbon monoxide. When a carbon monoxide is in the process of replacing the exo-bonded norbornadiene the norbornadiene orbitals could overlap to dimerize resulting in formation of the 2 + 2 + 2 dimer and a nickel dicarbonyl specie. The specie could then in turn be attacked by norbornadiene to regenerate the original di-endo norbornadiene intermediate or be attacked by carbon monoxide to form nickel tri- or tetracarbonyl complexes. In Figure 36 below the minor dimer would be formed when the bridge methylene of the exo-bonded norbornadiene is pointed toward the other norbornadiene molecule. Figure 37 shows how the major dimer would be formed when the bridge methylene of the exo-bonded norbornadiene is pointed toward the carbon monoxide ligand.

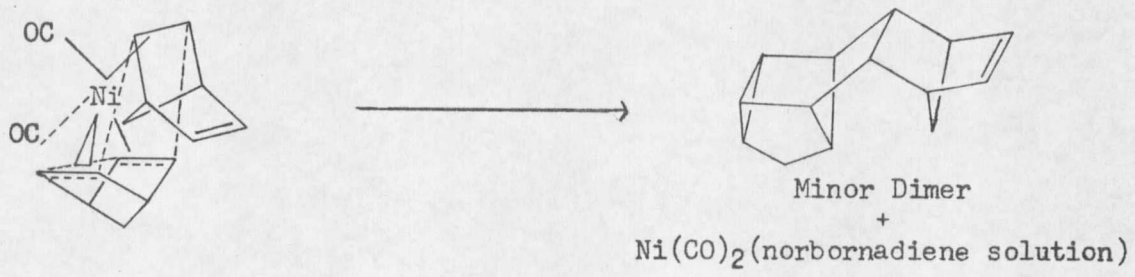
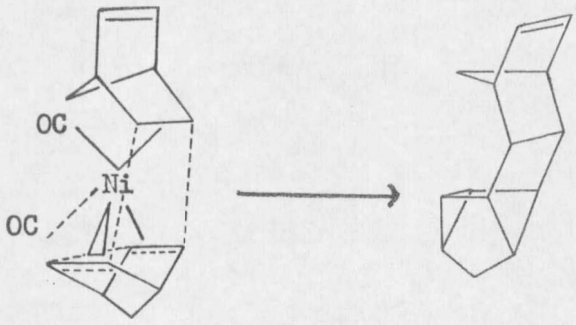


Figure 36

Proposed Intermediate to Minor Dimer Formation in $Ni(CO)_4$ Reaction



+ $Ni(CO)_2$(norbornadiene solution)

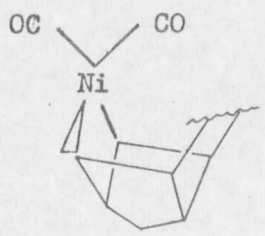
Major Dimer

Figure 37

Proposed Intermediate to Major Dimer Formation in $Ni(CO)_4$ Reaction

The arrangement of the exo-bonded norbornadiene would probably be dependent on steric interaction of the hydrogen on the bridge carbon with the carbon monoxide versus the center of the norbornadiene ligand. The formation of trimer could be possible in the same way because the dimer could be capable of bonding on the exo side resulting in the observed mixture of trimers which exhibit no olefin proton peaks in the proton nmr.

The above postulated reaction sequence could be viewed as a concerted mechanism in which the dimerization takes place with no intermediate steps after the monocarbonyl complex is formed. On the other hand, the reaction pathway for the formation of either dimer could involve an intermediate step which would consist of a nickel dicarbonyl specie sigma bonded to two carbons of the dimer prior to their closure to the cyclopropyl ring. This is illustrated here.



Attack of this specie by the endo side of norbornadiene would also result in the original complex and the dimer. The differentiation between mechanisms would be undeterminable.

The point at which the carbon monoxide attacks the monocarbonyl dinorbornadiene complex is an arbitrary choice which would seem to take place at a logical point in the sequence of events. It could take place before or after dimerization begins but seems to be necessary to get the original di-endo norbornadiene nickel dicarbonyl complex back again. The assumption that this is necessary is based on the nearly exclusive formation of 2 + 2 + 2 dimers which presumably could not be the case with a simple monocarbonyl nickel specie in solution since it would have three sites for bonding to norbornadiene and would conceivably produce 2 + 2 dimers as well.

This same series of reactions will also explain why exo-trans-exo dimer is formed photochemically when the norbornadiene and dimer complexes are used in place of nickel tetracarbonyl. As stated previously the main difference between this photochemical reaction and that of nickel tetracarbonyl is 1) in the latter case there is an excess of

nickel tetracarbonyl and 2) carbon monoxide is in the solution from the reaction sequence of $Ni(CO)_4$ + norbornadiene $\longrightarrow$ (norbornadiene)$Ni(CO)_2$ + 2 CO. As the starting norbornadiene or dimer complex is converted to the monocarbonyl dinorbornadiene nickel complex only a third of the carbon monoxide would be present per molecule as in the reaction starting with nickel tetracarbonyl notwithstanding the contribution of carbon monoxide from the unreacted nickel tetracarbonyl as well. Therefore, there is little possibility of converting the nickel monocarbonyl specie back to the dicarbonyl specie after formation of the dimer because of this lack of carbon monoxide in solution. In order for the monocarbonyl nickel specie to become stabilized the most available ligands would be norbornadiene. The bonding of these norbornadiene molecules could be exo or endo, whichever would stabilize the nickel complex most. Too little is known about a nickel specie such as this to predict which would be the most likely bonding site on norbornadiene. However, since the dimer formed in this reaction was exo-trans-exo the indications that the norbornadiene molecules bonded to the nickel on the exo side. If any norbornadiene bonded endo some endo-bonded dimer or 2 + 2 + 2 dimer would be expected. It has also been shown[89] that when a nickel exo-trans-exo dimer complex was isolated and heated with norbornadiene the only dimer formed was exo-trans-exo. Thus it is even possible but unknown that the last carbon monoxide ligand could be displaced upon irradiation and the nickel would be surrounded by four exo-bonded norbornadiene ligands analogous to the biscycloocta-1,5-diene nickel complex.

Unfortunately, there was no way of accurately measuring the amount of nickel complex put into the norbornadiene prior to photolysis so the activity of the complex responsible for the exo-trans-exo dimer is unknown and no indication of the amount of carbon monoxide released during the reaction is available.

Application of Proposed Reaction Intermediates of $Ni(CO)_4$ to Other Complexes Studied in the Nickel Carbonyl Series

The mechanism for dimerization of norbornadiene by nickel tetracarbonyl could in part be applied to the other members of the pseudo-nickel carbonyl series including the bistriphenylphosphinedicarbonyl nickel complex. However there are enough differences within the series that they clearly would not be expected to be the same in every respect. It would seem that the $Fe(CO)_2(NO)_2$ complex and its triphenylphosphine derivatives are capable of only producing 2 + 2 dimers due possibly to the stabilization of the nitric oxide ligands and the relative ease of forming the $(norbornadiene)_xFe(NO)_2$ (x = 1 or 2). Since a third double bond could not be introduced into the $(norbornadiene)_xFe(NO)_2$ complex without loss of NO the formation of 2 + 2 + 2 dimers would not be expected. However it should be pointed out that other complexes of iron (1,4-diphenylbutadieneirontricarbonyl and the iron complex resulting from the reduction of iron acetyl acetonate by triethyl aluminum in norbornadiene[90]) have been shown to form 2 + 2 + 2 dimers of norbornadiene; so their formation is not without precedent with iron complexes. Since

the major dimer formed by the $Fe(NO)_2L_2$ complexes is the exo-trans-exo dimer it appears that the iron nitrosyl specie bonds to norbornadiene predominantly on the exo side.

Theoretically the $Co(CO)_3NO$ complex and the triphenylphosphine derivatives of it do have the possibility of forming 2 + 2 + 2 dimers. This could result by the replacement of three ligands by two norbornadiene molecules and leaving the one "irreplaceable" NO ligand. The evidence in this thesis, however, indicates that the replacement of the third ligand is questionable and may depend on the replaceable ligands of the cobalt complex. It is difficult to draw very clear analogies between these complexes and either the iron or nickel complexes for explaining the most likely way in which the norbornadiene would bond. There is no parallel to the iron complexes because of the difference in the number of nitric oxide ligands. This difference is not only due to the theoretical replaceable ligands but also to electron density on the metal as well even though all complexes are "isostructural". Ground state kinetics of replacing two of the CO ligands has shown this to be a second order mechanism[91] as compared to a first order mechanism in the replacing of two CO ligands on the $Ni(CO)_4$ complex.[92] Although this may be different in the photochemical reaction of $Co(CO)_3NO$ the complex differs enough from $Ni(CO)_4$ that no clear analogies are apparent. The mono- and bistriphenylphosphine derivatives of $Co(CO)_3NO$ are different from the $Co(CO)_3NO$ complex itself as is the bistriphenylphosphine derivative of $Ni(CO)_4$ and its parent complex $Ni(CO)_4$ because of the difference

in replaceable ligands on the metal. But the cobalt and nickel complexes are not different from each other to the same extent.

Consequently the only conclusion about the mechanism by which the cobalt complexes dimerize norbornadiene is that the predominant mode of bonding to norbornadiene when excited photochemically is on the exo side even in the case of $Co(CO)_3NO$ initially. $Co(CO)_3NO$ is light and heat sensitive and probably falls apart to some other specie $(norbornadiene)_xCoNO$ (x = 2 or 3 perhaps) which is responsible for the additional dimers formed when irradiated for a prolonged period of time with an intense light or heated. This does not appear to be the case with the triphenylphosphine derivatives — probably due to the effect of the triphenylphosphine either by dictating the bonding of the metal to norbornadiene sterically or by stabilizing some intermediate step in the reaction or both.

The role of triphenylphosphine seems to be important in the nickel complexes as well based on the differences in products between the bistriphenylphosphine nickel dicarbonyl and nickel tetracarbonyl. The loss of both of the triphenylphosphine groups from the $Ni(CO)_2[P(C_6H_5)_3]_2$ complex would not be expected since the resulting $Ni(CO)_2$ specie should behave similarly to that proposed in the nickel tetracarbonyl reaction and such is not the case as evidenced by the difference in dimer products. The possibility of losing a CO and a $P(C_6H_5)_3$ ligand or two CO ligands could result in norbornadiene complexes that may be active in dimerizing norbornadiene and would be

expected to produce dimers different than the norbornadiene complex of the $Ni(CO)_2$ specie. The difference would again be expected because of the triphenylphosphine effect either sterically or electronically in the formation of the most stable active complex or a combination of the two effects. It would seem, however, that in the photochemical reaction CO would be one of the ligands on nickel since nickel has a strong affinity for CO. This can be seen in the addition of CO to the nickel complex of trans, trans, trans, cyclododeca-1,5,9-triene upon introduction of CO to the system. Whether the carbon monoxide or triphenylphosphine would be easiest to displace photochemically is not known. Regardless of which ligands are displaced it appears that the norbornadiene complex which results must be exo-bonded primarily again based on the products formed both thermally and photochemically.

Although a rather detailed mechanism can be postulated for nickel tetracarbonyl reacting with norbornadiene more information is needed for the other complexes of the series to be able to gain a better insight into the probability of various pathways in their reaction sequences.

SUMMARY

The research reported in this thesis has been conducted to provide an insight into the reaction mechanisms in homogeneous systems which are responsible for dimerization of norbornadiene via transition metal carbonyls. It was felt that a systematic study of metal carbonyls which had many common factors could contribute most to an understanding of what factors were important in deciding the resultant stereospecific dimers formed. Nickel tetracarbonyl and the pseudo-nickel carbonyls were chosen for this purpose due to their isostructural and isoelectronic properties as well as their ability to form derivatives allowing some lateral alterations in the system. The products from photochemical reactions were contrasted with the dimers reported from thermal reactions. The eight carbonyl complexes investigated were:

A) $Ni(CO)_4$

B) $Ni(CO)_2[P(C_6H_5)_3]_2$

C) $Co(CO)_3(NO)$

D) $Co(CO)_2(NO)[P(C_6H_5)_3]$

E) $Co(CO)(NO)[P(C_6H_5)_3]_2$

F) $Fe(CO)_2(NO)_2$

G) $Fe(CO)(NO)_2[P(C_6H_5)_3]$

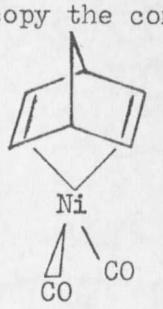
H) $Fe(NO)_2[P(C_6H_5)_3]_2$

In this exploratory investigation it was found that all of these complexes would produce dimers of norbornadiene. Further, except for $Ni(CO)_4$ the major dimer which was formed within an irradiation time of thirty hours was the 2 + 2 dimer, exo-trans-exo. And except for $Co(CO)_3(NO)$ and $Fe(CO)_2(NO)_2$ the remaining complexes continued to produce the exo-trans-exo dimer as the major dimer with longer irradiation

time. $Fe(CO)_2(NO)_2$ completely dimerized norbornadiene within an exceedingly short period of time (one hour) while $Co(CO)_3(NO)$ eventually began to produce other stereoisomers of the dimers in comparable amounts to exo-trans-exo after prolonged irradiation. $Ni(CO)_4$ on the other hand produced nearly exclusively two 2 + 2 + 2 dimers photochemically.

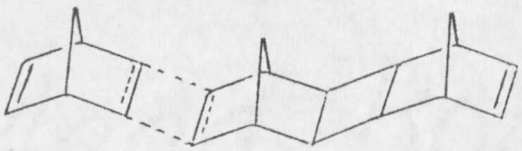
Assuming that the active specie $(norbornadiene)_2Fe(NO)_2$ is responsible in the iron complexes for exo-trans-exo dimer formation then the specie which is responsible for dimerization in the cobalt complexes may be either $(norbornadiene)_2Co(CO)(NO)$ or $(norbornadiene)_2Co(NO)[P(C_6H_5)_3]$ or both in the substituted cobalt complexes. Since the parent complex $Co(CO)_3(NO)$ does not seem to persist in generating the exo-trans-exo dimer predominantly, due to a specie such as $(norbornadiene)_2Co(NO)$, the $(norbornadiene)_2Co(NO)[P(C_6H_5)_3]$ may be the active specie in the $P(C_6H_5)_3$ derivatives of $Co(CO)_3(NO)$. The analogous moiety $(norbornadiene)_2Ni(CO)[P(C_6H_5)_3]$ may be the active specie in the bistriphenylphosphinedicarbonylnickel case although $(norbornadiene)_2[P(C_6H_5)_3]_2Ni$ cannot be ruled out.

The "maverick" complex in this series of compounds is nickel tetracarbonyl. A complex of nickel carbonyl norbornadiene was sought and isolated. By proton nmr and ir spectroscopy the complex appeared to be di-endo norbornadiene dicarbonyl nickel.



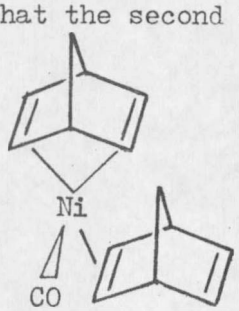
This extremely unstable complex was apparent in both the thermal and photochemical reaction systems. The dimers formed from the thermal reaction of nickel tetracarbonyl and norbornadiene

were predominantly endo-bonded. A trimer was formed thermally from a mixture of the thermal dimer products, $Ni(CO)_4$ and norbornadiene. This trimer was formed as the result of a norbornadiene molecule bonding endo to the exo side of the exo-bonded fragment of the exo-trans-endo dimer.



This confirmed the di-endo-norbornadienedicarbonylnickel complex as the active intermediate. In addition, a preference for exo-attack was observed. Furthermore, since the products formed from this norbornadiene nickel complex when introduced in norbornadiene in place of nickel tetracarbonyl gave the same stereoisomers as with $Ni(CO)_4$ itself, it appeared that the di-endo-norbornadienedicarbonylnickel complex was the active intermediate.

The stereoisomers found in the photochemical reaction indicated that the second norbornadiene molecule must be bonded on the exo side.



In comparison, when the isolated mixture of norbornadiene and dimer complexes of nickel carbonyl were irradiated in norbornadiene only the 2 + 2 dimer exo-trans-exo was formed. The implication from these experiments is that carbon monoxide must be present in solution in order to reform the di-endo-norbornadienedicarbonylnickel intermediate which in turn is responsible for generating the 2 + 2 + 2 dimers observed.

Trimer is formed from the photochemical reaction with the bis-triphenylphosphinedicarbonylnickel complex and norbornadiene. Addition of exo-trans-exo dimer to this reaction solution showed an increase in

amount of trimer formed. The active nickel specie apparently prefers to bond to the exo side of norbornadiene and to the exo side of the dimer as well. This difference in preference for bonding by the nickel species active in dimerization in the nickel tetracarbonyl and in the bistriphenylphosphinedicarbonylnickel cases implies that the ligands on the metal do play an important part in the stereospecificity of the dimers formed by transition metal complexes.

Finally, two crystal structures were done — one by D. L. Ward on $Co(CO)_2(NO)[P(C_6H_5)_3]$ and one by G. D. Smith on the silver nitrate complex of the major 2 + 2 + 2 dimer — to aid in this research. The crystal structure on the cobalt complex was done to corroborate the idea that the complexes in the series studied do tend to be tetrahedral. Positioning of the cyclopropyl ring with respect to the bridge carbon protons was the specific reason for the silver nitrate complex structure determination. This was used in conjunction with proton nmr spin decoupling experiments to determine the shielding effect of the edge of the cyclopropyl ring.

EXPERIMENTAL

Reagents

Norbornadiene was purchased from Frinton Laboratories but required purification by any one of three methods before use. The purity was determined by gas chromatography analysis on a six foot column of 5% SE 30 on 100 - 120 mesh Gas Chrom Z. The method used for purification did not affect the products obtained from the reactions. In most cases the norbornadiene was purified one final time by vacuum distillation prior to use.

The three methods of purification used were: 1) distillation on a spinning band column; 2) decomposition of the silver nitrate complex; and 3) distillation on a Todd column.

Method 1) involved refluxing norbornadiene over neutral alumina for three to six hours under deoxygenated nitrogen. The resulting yellow solution was decanted off and distilled on a Nester-Faust annular teflon spinning band distillation column under deoxygenated nitrogen. The first one fourth to one third of the distillate was discarded and a cut usually amounting to one half of the original solution was pure by gas chromatography analysis.

Method 2) required the formation of the known silver nitrate-norbornadiene complex.[93] This was carried out by slowly adding norbornadiene to a concentrated aqueous solution of silver nitrate (1:2 molar ratio). The precipitate was collected on a Buchner funnel in the dark and was washed with water until the filtrate did not give a positive

chloride test for silver. The precipitate was then recrystallized from 100% ethanol. The crystals ($2AgNO_3 \cdot C_7H_8$) were collected and stored in the dark. To recover the norbornadiene the complex was placed in a round-bottomed flask and joined by a tube containing anhydrous magnesium perchlorate to a vacuum line. The complex was allowed to remain at room temperature under vacuum (10^{-4} mm) for two hours or more, depending on the amount, to remove any residual alcohol which may have remained in the crystals. The complex was then heated to 125°C and the norbornadiene was collected in a U-trap cooled by liquid nitrogen.

Method 3) was a simple distillation of norbornadiene on a Todd Model A Precise Fractionation Assembly complete with automatic reflux ratio and fractionation still head. The column was four feet in length and packed with glass helices. The first one third or more was discarded due to the amount of impurities still present and approximately one half of the remaining solution was pure by gas chromatography analysis.

Gases

The nitrogen (Airco, Dry-High Purity) used for distillations, refluxings, evaporations of solvents, and in all other cases was deoxygenated by the use of BSTS catalyst (BASF Colors and Chemicals, Inc.) and dehydrated by passing it through anhydrous calcium chloride. Argon (Airco, 99.99% pure) was used as obtained. The carbon monoxide (Matheson, C. P.) for the preparations of $Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$ was used from the cylinder. However, for the carbon monoxide enriched reaction

carbon dioxide and oxygen were removed by passing the carbon monoxide through a strongly basic aqueous solution of pyrogallic acid (amounts of pyrogallic acid and sodium hydroxide were adjusted to remove the amount of carbon dioxide and oxygen present in the maximum amount of carbon monoxide that would be used). The $Ni(CO)_4$ (Matheson) which was used in product determination experiments was always distilled under deoxygenated nitrogen before use. It was occasionally used out of the cylinder when preparing some of the nickel intermediates thermally after the experimental procedure was established.

Preparations

Tricarbonylnitrosylcobalt. The successful method used for this preparation was a modification of the method originally described by F. Seel.[94] The entire apparatus and procedure was carried out in the hood. A three-necked liter round-bottomed flask was fitted with a mechanical stirrer, a pressure-equalized dropping funnel, and a gas inlet connected to unpurified carbon monoxide. (The gas inlet was a tube with a scintered glass end which extended three fourths of the way through the solution). Carbon monoxide was slowly bubbled into the solution throughout the preparation using a mercury bubbler for the exhaust. The system was flushed with the gas and 200 ml of 12% ammonium hydroxide was put into the flask. After adding a solution of 8.75 g (30 mmol) of cobaltous nitrate hexahydrate in 20 ml of water the flask was cooled in an ice-water bath to 10° to 15° C. With cooling and

stirring a solution of 8.0 g (46 mmol) of sodium dithionite in 165 ml of 12% ammonium hydroxide was slowly added to the blue solution via a dropping funnel. After the complete addition of the sodium dithionite (eight hours) the solution was stirred until it turned a bright yellow. Upon complete change of color 2.1 g (30.5 mmol) of sodium nitrite in 8 ml of water was slowly added. Following this addition the flask was cooled (-10° to -15°C) in an ice-salt bath and the mechanical stirrer was replaced by a Friedrichs condenser. The condenser was connected to a drying tube filled with calcium chloride. This was then connected to the first of a series of U-traps. On the one end of the U-traps was an oil vacuum pump and between the last two U-traps was a T-joint. After the solution in the flask had turned red a solution of 30 ml acetic acid and 30 ml water was slowly added and the first U-trap was cooled with a dry ice-acetone bath. The red-brown fumes of the tricarbonylnitrosyl-cobalt which were liberated from the system and bubbled out of the flask by the carbon monoxide were trapped as an orange solid in the first U-trap. When no more complex was liberated from the solution the U-traps were closed to both the outside and the reaction flask. The cobalt complex was distilled under vacuum three times (liquid nitrogen in the final trap) until the red solid melted in an ice-water bath at 0° to -2°C. It was then transferred to an ampoule at the T-joint and sealed with a torch. Subsequent uses of the complex required breaking the ampoule open under vacuum; a transfer of the portion to be used followed by a transfer of the remaining complex to another ampoule which was sealed as above. The

ampoule was stored in a refrigerator at -5°C.

Tricarbonylnitrosylcobalt was purchased from Strem Chemicals as more was needed. This complex was purified by the same procedure as above to the same melting point. Ir spectra of the complex was taken in every case in a hexane solution in a solvent cell. The spectra had the characteristic C = O stretching frequencies at 2109 and 2047 cm^{-1} and the N = O band at 1825 cm^{-1}.[95]

Dicarbonylnitrosylphenylphosphinecobalt(0) and carbonylnitrosylbistriphenylphosphinecobalt(0). The method used for this preparation of $Co(CO)_3NO$ derivatives was a modification of the preparation described by Malatesta and Araneo.[96]

To a concentrated toluene solution (50 ml) of triphenylphosphine (4.54 g, 17.3 mmol) in a round-bottomed flask tricarbonylnitrosylcobalt (1.00 g, 5.78 mmol) was added with a syringe. A reflux condenser was attached to the flask containing the red solution and the system was kept under nitrogen while stirred via a magnetic stirrer overnight. Bubbling noted during the first hour of reaction had ceased by morning. Toluene and other volatiles were removed by vacuum and the resulting dark red solid was dissolved in a minimum of methylene chloride. This solution was put onto an alumina column and eluted first with hexane followed by a solution of methylene chloride and hexane (1:5). The unreacted triphenylphosphine was thus eluted first. A red-orange band then moved down the column and the collected red solution was found to

be the monosubstituted derivative. The addition of a 1:1 mixture of hexane:methylene chloride eluted a dark red band which was found to be the bistriphenylphosphine derivative.

The monosubstituted derivative was recrystallized twice from 95% ethanol which resulted in red crystals having a melting point of 136.5° to 138.5° C dec. and an ir spectrum identical to that reported.[97]

The disubstituted derivative was recrystallized twice from methylene chloride with a melting point of 192° to 194° C dec. The ir spectrum was shown to be the same as the reported spectrum.[98]

Crystals of the monosubstituted derivative were used in a structure determination to establish the geometry around the cobalt. The crystal structure was done by D. L. Ward.[99]

Dicarbonyldinitrosyliron(0). To a 250 ml three-necked round-bottomed flask fitted with a gas inlet, Friedrichs condenser, and 50 ml pressure-equalized dropping funnel was added an 80 ml aqueous solution of sodium nitrite (6.0 g, 87 mmol) and sodium hydroxide (10.0 g, 250 mmol). The system was flushed with deoxygenated nitrogen and both the gas inlet and condenser were connected to the nitrogen line in which a mercury bubbler was included. The addition of 5 ml (7.3 g, 3.73 mmol) of iron pentacarbonyl followed by refluxing for four hours with constant stirring with a magnetic stir bar resulted in a homogeneous dark red-brown solution. This solution was cooled to room temperature. A series of U-traps were joined to the condenser through a drying tube filled

with anhydrous calcium chloride. On the other end of this series a vacuum pump was connected for later evacuation but the connection was closed initially. In the first U-trap enough anhydrous P_2O_5 was present to dry the sample to be collected (<6 g) but did not obstruct passage through the trap. A T-connector between the last two traps was open to allow flow of gas through the system. After cooling the first trap with a dry ice-acetone bath the dropping funnel was charged with 20 ml of 50% acetic acid which was added slowly, drop-wise, to the pot while flushing the system with nitrogen and vigorously stirring. The red-brown fumes of $Fe(NO)_2(CO)_2$ appeared in the flask and a dark red-brown solid was condensed in the first trap. The addition of acetic acid was halted when no more fumes were generated from the solution. The connection between the reaction flask and the trap was sealed and an ampoule connected to the opening at the T-joint. The system was then evacuated (10^{-3} Torr) and allowed to warm to room temperature followed by recondensation and evacuation to allow all the $H_2Fe(CO)_4$ condensed in the trap to decompose. When the generation of hydrogen was no longer apparent, as noted by no pressure change in the manometer, the complex was distilled through three traps before sealing in the ampoule.

Carbonyldinitrosyltriphenylphosphineiron(0) and dinitrosylbis-triphenylphosphineiron(0). The method followed for these preparations was a modification of the method described by Malatesta and Araneo.[100] A 3:1 molar ratio of triphenylphosphine and iron complex were combined

to give a dark red solution which yielded both the mono- and disubstituted derivatives. These were separated on an alumina column (as reported by Stone et. al.)[101] with the elution of an orange band (the monosubstituted derivative) using a solution of 1:4 methylene chloride:pentane as eluant. An olive-green band which was then eluted with a 1:1 methylene chloride:pentane solution was the disubstituted derivative.

The two derivatives were recrystallized from the respective eluants used in separation. Dark red crystals of the monosubstituted derivative had a melting point of 137° to 139° C dec. while the melting point of the disubstituted derivative was 190° to 194° C dec. Some triphenylphosphine contaminated the disubstituted compound which would account for the melting point being lower than the 204° C reported. Ir spectra of these two complexes were comparable to the reported spectra.[102]

Bistriphenylphosphinedicarbonylnickel(0). The preparation used is the same as the synthesis reported in Organometallic Synthesis edited by Eisch and King.[103]

To a 25 ml nitrogen-filled round-bottomed flask fitted with a reflux condenser and a 4 mm rubber septum cap was added a solution of 4.0 g (15.2 mmol) of triphenylphosphine in 22 ml of ethyl ether. The solution was then refluxed. With a 1 ml syringe 1.0 ml (1.30 g, 7.6 mmol) of freshly distilled $Ni(CO)_4$ was added drop-wise over a period of five minutes via the septum. The solution was refluxed for an additional

thirty minutes and then cooled to room temperature. Cream-yellow crystals were collected, separated from the ether solution, and washed with dry ether to remove unreacted triphenylphosphine. Decomposition temperature (210°C) and ir spectrum were identical to those reported.

Methods Used in Determining Norbornadiene Products

Determination of dimer and trimer products was done by comparing the retention times of products with known dimers via gas chromatography and with proton nmr spectra analysis. The instruments used were a Varian A-60 Proton NMR and either and F & M Model 400 or a Varian Model 1740 Gas Chromatograph. The columns used for gas chromatography dimer determination were a six foot one eighth inch diameter copper tubing packed with 5% SE 30 on 100 - 120 mesh Gas Chrom Z for the Varian instrument and a four foot glass tube with one fourth inch diameter with the same load and phase on the F & M instrument. For the dimer determination of $Ni(CO)_4$ a six foot one eighth inch diameter copper tubing column was used packed with 20% Carbowax 20 M on 80 - 100 Chromosorb W.

Photolysis of Tricarbonylnitrosylcobalt(0) in Norbornadiene

Approximately 0.5 to 0.75 ml of tricarbonylnitrosylcobalt(0) was transferred on the vacuum line into each of six pyrex tubes. This was followed by the transferral of approximately 6 ml of norbornadiene into the tubes using liquid nitrogen as a coolant. The solution was warmed to room temperature to check the volume of norbornadiene and more norbornadiene was added when needed until 6.5 ml (as marked on the tubes)

was reached. The contents were then frozen with liquid nitrogen and with the total system evacuated, the tubes were sealed with a torch. The tubes were then placed in a merry-go-round and irradiated with a mercury arc lamp filtered with uranyl nitrate glass. The tubes were irradiated zero, six, twelve, eighteen, twenty-four, and thirty hours respectively during which time the red color of the solution seemed to become more orange-red but no precipitate formed. The red color noted initially returned when the irradiation was stopped. A red-brown precipitate was visible in the solution within five minutes after opening in air. The dimer products were found to be predominantly exo-trans-exo from gas chromatography retention time and comparison with an authentic sample of exo-trans-exo dimer on a gas chromatogram. The amount increased with increased irradiation time. The ratio of peak heights after thirty hours of irradiation was 47:5:4:1, the largest number corresponding to the exo-trans-exo dimer. When a similar solution of tricarbonylnitrosylcobalt in norbornadiene was irradiated for three days the ratio of dimer peak heights was found to be 3:1:5:3, the first number corresponding to the exo-trans-exo dimer peak.

Photolysis of Dicarbonyldinitrosyliron(0) in Norbornadiene

Approximately 0.5 to 0.75 ml of dicarbonyldinitrosyliron(0) was transferred on the vacuum line into pyrex tubes. Norbornadiene (approximately 6.0 ml) was then transferred in the same manner and the tube was sealed under vacuum with a torch. Upon irradiating this blood-red

colored solution for one hour in a merry-go-round with an Hg arc lamp fitted with a uranyl nitrate filter the contents became solid. The dimer products were found to be composed principally (peak height ratio of dimers was 9:1) of exo-trans-exo by gas chromatography retention time and properties (white sublimable solid) mp 66° to 67°C.

Photolysis of Dicarbonylnitrosyltriphenylphosphinecobalt(0), Carbonylnitrosylbistriphenylphosphinecobalt(0), Carbonyldinitrosyltriphenylphosphineiron(0), and Dinitrosylbistriphenylphosphineiron(0) in Norbornadiene

Dicarbonylnitrosyltriphenylphosphinecobalt(0). Into a pyrex tube containing 0.0467 g (7.28×10^{-2} mmol) of cobalt complex, 6.0 ml of norbornadiene was transferred via the vacuum line and the tube was then sealed. The solution was irradiated in the merry-go-round for one day. The tube of clear solution was opened (after which a precipitate formed) and the contents were monitored via gas chromatography. The major dimer was exo-trans-exo and by sublimation the weight of dimers formed was 0.0255 g (0.138 mmol). Peak height ratio of dimers from gas chromatography was 16:1:1:1. When a solution of the same concentration (1.21×10^{-2} M) was irradiated for nine days the weight of dimers isolated was 0.4777 g (2.59 mmol) which constitutes approximately an 8% conversion of norbornadiene. The peak height ratio of dimers from the gas chromatography was found to be 21:3:3:1, again the exo-trans-exo dimer being the predominant product. Dimer peak height ratio for three days of irradiation was shown to be 118:13:7:1 with exo-trans-exo dimer the prominent peak.

Carbonylnitrosylbistriphenylphosphinecobalt(0). Using 6 ml solutions of this cobalt complex in norbornadiene of the same concentrations as above (1.21×10^{-2} M) and irradiating for three days and for nine days in the same apparatus as that used for the previous solutions dimers were produced. The gas-liquid chromatograms obtained from these dark red solutions showed a dimer peak height of 83:12:6:1 after three days of irradiation and 8:1:2:1 after nine days of irradiation with exo-trans-exo dimer being the major dimer as shown by retention time. The weight of dimers isolated in these two cases was 0.1671 g (0.908 mmol) and 0.6495 g (3.52 mmol) respectively. These represent a 2.8% conversion of norbornadiene in three days of irradiation and a 11% conversion after nine days of irradiation. Dimer peak height ratio from the gas chromatogram for one day of irradiation was found to be 96:15:8:1, exo-trans-exo dimer the predominant isomer.

Carbonyldinitrosyltriphenylphosphineiron(0). A dark red solution of norbornadiene (6 ml) which was 1.34×10^{-2} M (0.0326 g, 8.03×10^{-2} mmol) in iron complex was irradiated for twenty-four hours in the same apparatus as the parent iron compound. Retention time on the gas liquid chromatograms showed the major dimer to be exo-trans-exo (dimer peak height ratio was 9:1). The total weight of dimers was found to be 0.1266 g (0.686 mmol) which is a 2.2% conversion of norbornadiene.

Dinitrosylbistriphenylphosphineiron(0). This iron complex (0.0406 g, 6.34×10^{-2} mmol) was dissolved by 6 ml of norbornadiene in a

tube resulting in a solution of 1.06 x 10^{-2} M concentration. When the sealed tube of dark yellow-green solution was irradiated for twenty-four hours in the same manner as the parent iron complex the gas chromatography analysis showed only a trace of dimer. The gas chromatography retention time showed it to be exo-trans-exo. No attempt was made to isolate it.

Photolysis of Dicarbonylbistriphenylphosphinenickel(0) in Norbornadiene

Norbornadiene (6.5 ml) was transferred under vacuum into a pyrex tube containing 0.0465 g (7.28 x 10^{-2} mmol) of the nickel complex and the tube was sealed. Since the lowest energy absorption band was at λ = 2700 Å for this complex as compared to λ = 3500 Å for the cobalt and iron complexes the uranyl nitrate filter was not used but the pyrex photolysis well was used instead when this sample was photolyzed. Following irradiation for three days the pale yellow solution turned orange and 1.11 g (5.98 mmol) of dimer was isolated of which exo-trans-exo was the major component. Gas chromatography analysis showed only trace amounts of other dimers (dimer peak height ratio 95:6:1) and the presence of what could be a trimer according to retention time.

Photolysis of Nickel Tetracarbonyl in Norbornadiene

Since the absorption spectrum of nickel tetracarbonyl showed a peak at λ = 2100 Å with shoulders at 2350 Å and 2800 Å (broad) photolysis was carried out in pyrex, vycor, and quartz tubes. Due to the handling procedures of nickel tetracarbonyl the concentrations used were 0.1 M.

To 8.5 ml (as measured by a calibrated flask on the vacuum line) of norbornadiene transferred into each of the pyrex, vycor, and quartz tubes was added 0.110 ml (0.145 g, 0.849 mmol) of freshly distilled nickel tetracarbonyl. The addition was made via a 1 ml syringe with a six inch needle which would project through a septum cap and into the norbornadiene. The solutions were then cooled with liquid nitrogen, evacuated, sealed, and irradiated for four and one half days. (The solutions were colorless initially and were a slight yellow color after being irradiated with no precipitate forming until opened). With the use of an SE 30 column for gas chromatography analysis two peaks in a ratio of 1:76 were observed with a retention time of the major peak similar to that for the endo-trans-endo dimer. Also present were a much smaller peak with a retention time similar to that of a trimer and three very small peaks grouped together between the dimer and trimer peaks. Mass spectral data on the nondimer peaks showed a parent peak at m/e = 212 for the three very small peaks and m/e = 276 for the probable trimer peak. The gas chromatography analysis of the products on Carbowax 20 M showed that the major peak consisted of two peaks (ratio of 2:1). Gas chromatography analysis also showed that the amount of dimer products from the vycor and quartz tubes were essentially equal amounts while the pyrex tube yielded approximately one half that amount.

The dimer and trimer products were isolated by evaporating the unreacted norbornadiene and nickel tetracarbonyl with nitrogen. By use of a sublimation-distillation apparatus the liquid dimers and white

solid trimer were isolated. In the case of the products from the vycor tube the dimers recovered were 0.876 g (4.75 mmol) and 43 mg (0.156 mmol) mp 185° to 186° C of trimer was isolated. The nmr spectrum showed two dimer products (ratio 2:1).

Thermal Reactions of Norbornadiene

Norbornadiene and dicarbonylbistriphenylphosphinenickel(0). A solution of 15 ml (13.6 g, 148 mmol) of norbornadiene and 0.96 g (1.5 mmol) of bistriphenylphosphinedicarbonylnickel was prepared in a 25 ml round-bottomed flask. The flask fitted with a reflux condenser was kept under nitrogen. After wrapping the condenser and flask with a black cloth the flask was immersed in an oil bath. With constant stirring the solution was refluxed for eighteen hours. At the end of this time the contents were checked for dimer products. It was found by gas chromatography and nmr that the major dimer products were exo-trans-endo and exo-trans-exo in a ratio of 2:1 respectively with a small amount of endo-trans-endo present. The solution had changed color from pale yellow to orange. The weight of dimers recovered was 1.63 g (8.85 mmol).

Norbornadiene with nickel tetracarbonyl. Into 8.50 ml (7.73 g, 83.9 mmol) of norbornadiene in a 10 ml round-bottomed flask at room temperature 0.110 ml (0.145 g, 0.849 mmol) of nickel tetracarbonyl was added. The flask was then attached to a reflux condenser which was connected to a nitrogen line and mercury bubbler. After immersing the flask into an oil bath at 85° to 87° C the solution was refluxed for six and one

half hours. The contents were then monitored on the gas chromatograph which showed two major dimer peaks and one major trimer peak. By retention time and nmr the dimer peaks were shown to be exo-trans-endo and endo-trans-endo in a ratio of 3:1 respectively. The dimer products (3.17 g, 17.2 mmol) were isolated by vacuum distillation and represented a 41% conversion of norbornadiene. Although a trimer peak was visible on the gas chromatographs no trimer was isolated.

Characterization of Norbornadiene Products

Characterization of trimer from photolysis of dicarbonylbistriphenylphosphinenickel(0) in norbornadiene. The trimer was separated from dimer products by fractional sublimation. In a sublimation apparatus with all the products from photolysis the system was evacuated and the residue was heated to 60° C. At this temperature all the dimers sublimed onto the cold finger within twenty-four hours. After removing the dimers the sublimation temperature was raised to 110° C whereupon the trimer sublimed within twenty-four hours leaving a fluffy residue. (This residue gave m/e peaks in the mass spectrum at 368, 460, and 552 corresponding to tetramer, pentamer and hexamer respectively.)

The trimer was resublimed twice for purification before the elemental analysis was agreeable (Calc. C - 91.25, H - 8.75; Found. C - 91.43, H - 8.84). The melting point was 205° to 206° C. The m/e parent peak in the mass spectrum was 276.

The nmr spectrum showed one triplet at 5.86 ppm; a multiplet at

2.56 ppm (4H); a broad multiplet at 1.88 ppm (2.5H), and another at 1.71 ppm (3.5H); a split peak at 1.33 ppm (8H); a small broad multiplet at 1.18 ppm (1.5H), and at 1.03 ppm (0.5H) (methylene chloride solvent). The triplet at 5.87 ppm and multiplet at 2.57 ppm had the same integration when the compound was dissolved in Silanor C. When carbon disulfide was used as the solvent the nmr spectrum showed a triplet at 5.77 ppm; a multiplet at 2.48 ppm; a peak at 1.84 ppm; a small peak at 1.75 ppm; a peak at 1.65 ppm with a broad shoulder at approximately 1.60 ppm; a sharp peak at 1.32 ppm and 1.27 ppm with a small peak at 1.18 ppm and another at 1.03 ppm. Thus it appeared that an AB quartet lay at 1.67 ppm and 1.10 ppm.

The trimer was hydrogenated with 5% Pt/C in ethanol at room temperature under a pressure of thirty pounds of hydrogen for nine hours. The mass spectrum showed a peak at m/e - 280 for the saturated trimer.

To help determine the structure of the trimer photochemical reactions were carried out with exo-trans-exo dimer added to norbornadiene and bistriphenylphosphinedicarbonylnickel. For statistical data on trimer enhancement standard solutions were photolyzed as well. To three pyrex tubes, each containing 0.0358 g (0.0560 mmol) of bistriphenylphosphinedicarbonylnickel, three 5.00 ml (4.45 g, 49.4 mmol) volumes of norbornadiene were transferred under vacuum from a calibrated flask and then sealed. To three other pyrex tubes, each containing 0.0358 g of bistriphenylphosphinedicarbonylnickel as well as 0.5000 g. (2.72 mmol) of exo-trans-exo dimer, three 5ml volumes of norbornadiene

were also transferred under vacuum and sealed. These six tubes of pale yellow solution were placed in the merry-go-round and irradiated with an Hg arc lamp for thirty hours. The ratio of dimer and trimer constant in each tube was found by injecting three samples of each tube and averaging the peak area of dimer and trimer. The results still showed only one trimer greatly enhanced when exo-trans-exo was added to the reaction mixture . The nmr spectrum of the trimer was the same in the dimer enhanced reaction as in the standard. The statistical data showed values of 0.34±0.04 (attenuation of 256 x 10^{-10}) for the dimer and 0.57±0.04 (attenuation of 1 x 10^{-10}) for the trimer of the peak areas of the standard solution. For the solution with exo-trans-exo dimer added the peak area values were 0.78±0.06 (attenuation of 256 x 10^{-10}) for the dimer and 1.25±0.17 (attenuation of 2 x 10^{-10}) for the trimer.

Dimer and trimer isolated from the photochemical nickel tetracarbonyl reaction with norbornadiene.

Trimer

In the isolation of products from the photochemical reaction of norbornadiene with nickel tetracarbonyl there was white solid which sublimed onto the cold finger under vacuum when the system was heated with a heating tape. The white solid had a parent peak in the mass spectrum at m/e = 276 which is the correct molecular weight of a trimer. The nmr spectrum of the trimer showed no peak in the region of olefin protons and had the characteristic peak at 0.80 ppm for cyclopropyl protons of a

nortricyclene unit. The rest of the spectrum was grouped between 2.3 and 1.1 ppm. An nmr spectrum of a Diels-Alder product trimer published by Katz[104] closely resembled this spectrum. The white solid melted at 185° to 186°C.

Dimer

The dimer products after isolation by vacuum distillation were separated on a preparative gas chromatograph. A twenty foot column, three eighths inches in diameter, packed with 20% Carbowax 20 M on Chromosorb W (80 - 100 mesh) at 190°C with a helium flow rate of 100 ml/minute separated the two dimers such that three fractions were collected of which two were pure. Both dimers were viscous colorless liquids. The ratio of dimers collected was 2:1. Ir spectra were obtained on both dimers but other than showing peaks between 780 and 810 cm^{-1} indicating the nortricyclene area the spectra were of little help.

The nmr spectrum of the major dimer in Silanor C showed a multiplet at 6.17 ppm (2H); at 2.61 ppm and a small one at 2.42 ppm (3H); a sharp peak at 1.91 ppm with a shoulder at 1.97 ppm (5H); a multiplet at 1.30 ppm with a smaller one at 1.15 ppm (4H); and a doublet at 0.82 ppm (2H).

Also in Silanor C the second dimer had an nmr spectrum with a triplet at 6.08 ppm (2H); a quintet at 2.58 ppm (2H); a multiplet at 2.22 ppm (1H); a peak at 1.88 ppm with a shoulder at 1.87 ppm and at 1.77 ppm (5H); a peak at 1.53 ppm (2H); a series of peaks together at

1.18 ppm, 1.08 ppm, and 1.02 ppm (2H); and a doublet at 0.85 ppm (2H).

Spin decoupling of some of the protons of these two dimers was done on a Varian HA-60. In the experiments on the major dimer the peaks at 6.17 ppm and 2.61 ppm were each irradiated and the area upfield was scanned for decoupling results. Upon irradiation near the peak at 2.61 ppm (approximately 2.50) a peak moved out from under the peak at 1.30 ppm. The multiplet at 1.15 ppm decreased in size as the power of irradiation was increased while the peak growing in at 1.28 ppm grew in size. When the peak at 6.17 ppm was irradiated the multiplet at 2.42 ppm became a triplet and some fine structure of another triplet showed on the upfield edge of the peak at 2.61 ppm. It appeared as if the coupling constant was 10 cps.

Doing the same experiment on the minor dimer the peaks at 6.08 ppm and 2.58 ppm were irradiated. Deuterobenzene was used as a solvent since it split the peak at 1.88 ppm into two peaks (1.87 ppm and 1.78 ppm) with a small peak on the side at 1.67 ppm. The peak at 1.67 ppm became two sharp peaks of an apparent triplet and one peak showed up between the peaks at 1.87 and 1.78 ppm when the peak at 6.08 ppm was irradiated. No other peaks other than the one at 2.58 ppm showed any alteration. Upon irradiation of the quintet at 2.58 ppm the peak at 1.67 ppm changed to a singlet and the peak at 1.18 ppm became sharper. An approximate coupling constant was again 10 cps.

Trimer characterization from the nickel tetracarbonyl/norbornadiene thermal reaction. To a round-bottomed flask fitted with a reflux condenser and containing 20 ml of norbornadiene under nitrogen 10 ml of an exo-trans-endo and endo-trans-endo dimer mixture and 0.5 ml (3.9 mmol) of nickel tetracarbonyl were added. The solution was then heated for nine hours at 100°C and an additional five hours at 120°C. The gas chromatography of the final solution showed dimer peaks, trimer peaks (peak height ratio of 1:2.4:19.4:1.5), and two small peaks between the dimer and trimer peaks. The excess norbornadiene and nickel tetracarbonyl were removed by passing a stream of nitrogen into the flask in the hood. The resulting viscous liquid was then vacuum distilled. The colorless liquid which distilled over was a mixture of the two dimer products. After all the liquid had been distilled the temperature was raised to 100°C and held there until all the white solid had sublimed on to the cold finger. The nmr spectrum of the white solid in Silanor C showed a triplet at 6.22 ppm; a multiplet at 2.78 ppm (which have the same integration); a multiplet at 2.07 ppm; a doublet at 1.85 ppm; a small multiplet at 1.59 ppm and one at 1.33 ppm; and a peak at 1.03 ppm with a small multiplet at 1.18 ppm and at 0.95 ppm. From the nmr spectrum of the trimer in deuterobenzene a shoulder appeared on the upfield side of the peak at 1.03 ppm and the integration of the multiplets at 1.59 ppm and 0.95 ppm were the same indicating an AB quartet centered at 1.46 ppm and at 1.08 ppm. It was obvious that there were some impurities (probably other trimers) present in the sample. The mass spectrum of this compound showed a parent peak at m/e = 276.

Investigation of Interconversion of Products

Photolysis of dimer products from thermal reactions. Dimers exo-trans-endo and endo-trans-endo (6 ml) isolated from the thermal reaction of norbornadiene and nickel tetracarbonyl were placed into a pyrex tube and evacuated. The contents were evacuated and sealed after being taken through two freeze-thaw cycles and adding 0.08 ml (0.11 g, 0.644 mmol) of nickel tetracarbonyl via a 1 ml syringe. The tube was placed in the merry-go-round and irradiated for one week. During this time the colorless solution turned to pale yellow. After photolysis was carried out the contents were freed of unreacted nickel tetracarbonyl and the liquid was vacuum distilled. The nmr spectrum of the distillate was identical to the spectrum taken of the dimers before the reaction.

Thermal reaction of pseudo-Diels-Alder dimers with nickel tetracarbonyl. The dimers used for this reaction were those from the thermal reaction of norbornadiene and rhodium on carbon as described by Katz.[105] The major dimer was the same as the major dimer formed in the photolysis of norbornadiene with nickel tetracarbonyl.

To 5 ml (5.15 g) of this dimer mixture in a 10 ml round-bottomed flask fitted with a reflux condenser connected to nitrogen was added 0.06 ml (0.085 g, 0.50 mmol) of nickel tetracarbonyl. The colorless solution was heated at 92°C for twenty-six hours after which a yellow solution resulted and was treated as in the previous reaction. Following the distillation an nmr spectrum was taken of the distillate. This

spectrum was identical with that of the original starting material.

Preparation of crystals of silver nitrate complexed with dimer. The dimer products from the thermal reaction of norbornadiene and rhodium on carbon were separated via preparative gas chromatography using the same procedure as discussed above for the separation of the dimers in the photolysis of nickel tetracarbonyl. To approximately 100 mg of the major dimer a saturated aqueous solution of silver nitrate was added until no more white precipitate formed. The precipitate was collected on a fritted funnel under vacuum and was washed with water until no silver nitrate was detected in the filtrate. The white solid was then dissolved in a minimal amount of warm ethanol (45°C) and allowed to cool to room temperature. After standing overnight in the dark, colorless crystal plates formed. They were kept under the mother liquor while crystals were secured for the X-ray analysis.

Results of Monitoring the Norbornadiene Thermal Reaction with Nickel Tetracarbonyl

During the thermal reaction of norbornadiene which was 0.1 M with respect to nickel tetracarbonyl ir spectra were obtained of samples taken out of the flask at various times. A round-bottomed flask with a sidearm fitted with a 4 mm septum cap was used from which samples could be withdrawn with a syringe and long needle without disturbing the refluxing solution.

A sample was withdrawn as soon as the nickel tetracarbonyl was

injected into the refluxing norbornadiene. This time was designated as zero time in Table 7 which shows the relative heights of the peaks which appeared in the C = O stretch region.

Table 7

Peak Height Comparison of the Carbonyl Absorption Bands in the Infrared Spectra Taken during a Thermal Reaction of $Ni(CO)_4$ in Norbornadiene

Time	Height of peak in mm from baseline for peaks appearing at: 2070 cm^{-1}	2035 cm^{-1}	2000 cm^{-1}	1970 cm^{-1}	Ratio of heights with 2035 cm^{-1} as reference
0 min.		114 (2.0)[x]	49	86	1:0.4:0.8
20 min.		89 (0.8)	100	104	1:1.1:1.2
40 min.	16	81 (0.7)	111	99	0.2:1:1.4:1.2
60 min.	28	107 (1.4)	87	107	0.3:1:0.8:1.0
85 min.	32	108 (1.4)	88	107	0.3:1:0.8:1.0
135 min.	37	109 (1.4)	86	107	0.3:1:0.8:1.0
210 min.	35	106 (1.3)	85	100	0.3:1:0.8:0.9
390 min.	36	103 (1.2)	78	87	0.4:1:0.8:0.9
540 min.	31	102 (1.2)	71	77	0.3:1:0.7:0.8
1200 min.	30	89 (1.0)	66	56	0.3:1:0.7:0.6
*	30	89 (1.5)	39		0.3:1:0.4

x Peak width in mm at 0.8 of the peak height.

* Solution cooled to room temperature and left to stand.

Nickel tetracarbonyl in norbornadiene at room temperature in the dark for forty-two hours showed a peak at 2035 cm^{-1} (108 mm) and at 2000 cm^{-1} (32 mm) in a ratio of 1:0.3. The 2035 cm^{-1} peak had a width of 2 mm at 0.8 of the peak height.

An ir spectrum of nickel tetracarbonyl in hexane of concentration 0.025 M showed a sharp peak at 2037 cm^{-1} (89 mm peak height - 0.7 mm width at 0.8 of peak height) with a slight shoulder at 2000 cm^{-1}.

Refluxing hexane solutions of nickel tetracarbonyl and norbornadiene in a molar ratio of 1:2 and 1:3 respectively produced ir spectra showing the same changes in the 2000 cm^{-1} region as in the thermal reaction of nickel tetracarbonyl in norbornadiene above.

Preparation of Norbornadiene and Dimer Complexes of Nickel Tetracarbonyl

In preparing these complexes the concentration of crude complex, column separation, and concentration of isolated complex were carried out in the same manner each time.

Due to the instability of these complexes, handling them had to be done under nitrogen or argon. In the first step of the isolation — concentration of crude complex — the flask was connected to a two-holed stopper with a line attached to either nitrogen or argon and the exhaust line led to a two-holed stopper in another flask. This system facilitated the removal of unreacted nickel tetracarbonyl and olefin from the complex and permitted the capture of them in another flask for further use. The second flask was cooled in a dry ice-acetone bath.

The nitrogen or argon was flushed through the system until only a viscous liquid remained in the first flask. At this point the appearance of yellow on the otherwise white condensate in the second flask was apparent.

To the commonly yellow-orange viscous crude complex was added a small amount of pre-purified hexane. The solution was then immediately put onto a column of Florosil for purification.

The Florosil on the column was deactivated from its received condition by slurrying it with a solution of hexane and a volume of methanol corresponding to 5% of the weight of the Florosil being deactivated. This type of column worked better than Florosil, alumina, or silica in their original conditions.

The complex after being adsorbed on the column (the top of the column was kept under nitrogen or argon to reduce decomposition) was eluted with hexane. The complex resulted in a yellow-chartreuse band on the column.

As the yellow-chartreuse band moved off the column the eluant was collected in a special Erlenmeyer flask which had a sidearm with a ground joint. On the sidearm was fitted an nmr tube with a ground joint. Both the flask and nmr tube had been previously flushed with argon and during the collection of the eluant the flask was continually being flushed with argon.

After the complex had been eluted the hexane was reduced or removed entirely (dependent on the following experiments) by fitting a

two-holed stopper connected to the argon on the flask. By maintaining a constant flow of argon through the cooling flask the hexane was removed resulting in a concentration of the complex with a minimal amount of decomposition.

Norbornadiene Complex of Nickel Tetracarbonyl

Thermal. When a 0.1 M solution of nickel tetracarbonyl in norbornadiene was heated at 48° to 50° C under nitrogen for two days the unreacted starting materials were then removed. Upon the addition of hexane to the orange paste under argon a yellow solution resulted. The ir spectrum taken immediately after the addition of hexane contained peaks at 1970, 2000, and 2035 cm^{-1}. The change of peak heights with time were as follows in Table 8.

Table 8

Change in Peak Heights of Carbonyl Absorption Bands in Infrared Spectrum of the $Ni(CO)_4$ Complexes of Norbornadiene and Thermal Dimers with Respect to Time

Time	Peak height in mm		
	2035 cm^{-1}	2000 cm^{-1}	1970 cm^{-1}
0 min.	66	102	85
10 min.	67	79	85
20 min.	71	74	86
30 min.	73	25	85

The complex was then purified via the Florosil column resulting in a yellow hexane solution having peaks at 2035 and 1970 cm^{-1}. The ir spectrum of this solution changed with time as indicated in Table 9.

Table 9

Change in Peak Heights of Carbonyl Absorption Bands in the Infrared Spectrum of $Ni(CO)_4$ and the $Ni(CO)_4$ Complex of Norbornadiene with Respect to Time

Time	Peak height in mm	
	2035 cm^{-1}	1970 cm^{-1}
0 min.	34	44
15 min.	35	44
30 min.	41	33

A similar reaction was carried out and from the purified complex an nmr spectrum was obtained together with an ir spectrum which was comparable to those above. The nmr showed the multiplet with fine structure of norbornadiene at 3.45 ppm and a broad peak at 6.38 ppm (based on hexane).

Photochemical. After irradiating 0.1 M solution of nickel tetracarbonyl in norbornadiene in a pyrex tube for three days and eighteen and one half hours the solution was transferred under vacuum leaving

behind the dimers and trimers. This solution was then run through an alumina column and the hexane solution was evaporated down. An ir spectrum of this solution showed peaks at 2035 cm^{-1} (80 mm), 2000 cm^{-1} (55 mm), and 1975 cm^{-1} (93 mm).

Dimer Complexes of Nickel Tetracarbonyl

A solution of nickel tetracarbonyl and the exo-trans-endo and endo-trans-endo dimers as isolated from the thermal reaction of norbornadiene and nickel tetracarbonyl were heated to 48° to 50° C for thirteen hours under nitrogen. After purification of the complex via gas chromatography and concentration of the complex in hexane the ir spectrum of the yellow solution showed one strong peak at 2000 cm^{-1} with a shoulder at 2037 cm^{-1}. The shoulder was what resulted from concentration of the sample since the original solution off the column had a strong peak at 2031 cm^{-1} plus the peak at 2000 cm^{-1}.

When norbornadiene was added to this yellow solution the ir spectrum showed two peaks grow in — one at 1970 and one at 2037 cm^{-1}. Within a period of thirty minutes the original yellow solution was dark red and the three peaks were nearly of the same intensity.

The exo-trans-endo dimer and nickel tetracarbonyl (1:1.5, molar ratio) under nitrogen were heated at 50° C for one and one half days. The 5 ml solution changed from colorless to a chartreuse-yellow. An nmr spectrum showed only an increase in the shift positions of the two olefin proton peaks of 0.05 ppm as compared to a spectrum of the dimer neat.

When endo-trans-endo dimer was dissolved in nickel tetracarbonyl under nitrogen and heated to 42°C the 3 ml solution began to turn from colorless to chartreuse-yellow as in the experiment with exo-trans-endo dimer. However, soon after the solution had changed color nickel began to plate out and no sample of any complex was available.

When heat was applied to a 5 ml solution of 2 + 2 + 2 dimers (obtained from the thermal reaction of Rh/C) and nickel tetracarbonyl the solution changed color as in the other cases. The ir spectrum of this complex showed on peak at 2000 cm^{-1} but the nmr spectrum showed essentially the same spectrum as the dimers themselves.

The exo-trans-exo dimer (0.500 g, 2.72 mmol) was dissolved in 5 ml of purified nickel tetracarbonyl under nitrogen and the colorless solution was heated to 40° to 45°C for six hours. During heating the solution turned a bright yellow and a yellow precipitate formed. The unreacted nickel tetracarbonyl was flushed off. The bright yellow solid became a grayish-white after standing in the air for approximately one half hour. A nujol mull of this solid showed a peak at 1995 cm^{-1} and one at 2035 cm^{-1} both of which diminished with time. When the yellow solid was put into norbornadiene, however, the yellow solution resulting from the small amount that dissolved exhibited peaks at 2035 cm^{-1}, 2000 cm^{-1}, and at 1970 cm^{-1}. Within two hours after making the solution the peaks at 2035 cm^{-1} and 1970 cm^{-1} became the most prominent while the peak at 2000 cm^{-1} almost disappeared.

The yellow solid was soluble in pyridine and dimethyl formamide

to give yellow solutions. No descriptive ir spectra were obtained from these solutions. However, carbon tetrachloride, ether, chloroform, hexane, benzene and methylene chloride all decomposed the solid leaving a whitish-gray mass. The ir spectrum of the residue had no peaks in the 2000 cm^{-1} region. This complex was, however, soluble in a benzene solution of triphenylphosphine. Again the ir spectrum was not descriptive of the complex. A chemical analysis of this complex showed the relative composition to be: Ni, 14.71; C, 68.45; H, 6.55.

Reaction of Norbornadiene with Nickel Tetracarbonyl

A nickel tetracarbonyl solution of norbornene was heated at 40° C for thirty-nine hours under nitrogen. The chartreuse colored solution was purified and exhibited a peak at 2035 cm^{-1} and at 2000 cm^{-1} of nearly equal intensity. After flushing the hexane solution with argon the height of the peak at 2035 cm^{-1} was reduced to less than 20% of the 2000 cm^{-1} peak. Upon standing at room temperature the 2037 cm^{-1} peak increased in intensity and nickel was plated out as the 2037 cm^{-1} became the predominant peak. Eventually it was the only peak in the spectrum.

Reactions of Complexes

Thermal reactions. After isolation of the complexes of nickel-dicarbonyl from the photochemical reaction of $Ni(CO)_4$ and norbornadiene and the addition of 5 ml of norbornadiene, the resulting red solution was refluxed for twenty-four hours. The dimer products were found to be

exo-trans-endo and endo-trans-endo by nmr spectrum.

Repeating the same reaction with the nickeldicarbonyl complexes isolated from the thermal reaction of norbornadiene and nickel tetracarbonyl produced the same products.

Photochemical reactions. Upon isolation of the complex formed by the thermal reaction of norbornadiene and nickel tetracarbonyl 5 ml of norbornadiene was added and the red-orange solution was put into a pyrex tube. The tube was cooled, evacuated, and sealed. After irradiation for five days during which only a light precipitate formed, the material had become almost completely solid. The solid was white while the overall color remained red-orange. The tube was opened and the contents were found to be principally exo-trans-exo dimer with some trimer as identified by the nmr spectrum.

The same reaction was investigated when the complex came from the photochemical reaction of norbornadiene and nickel tetracarbonyl. Upon addition of norbornadiene to the complex it again became red-orange and within six days of irradiation the material in the tube became solid. Only a slight amount of red-brown precipitate formed in this reaction also. The products were the same as in the preceding experiment.

Results from a Mixture of Norbornadiene and Dimers Complexed with Nickel Tetracarbonyl

A mixture of nickel tetracarbonyl and norbornadiene under nitrogen was heated at 45° to 48° C for several days. The purification of

nickel carbonyl complex from the yellow solution was carried out as before. The ir spectrum of the resulting yellow hexane solution (approximately 50 ml) showed peaks at 2035 cm^{-1} (59 mm), 2000 cm^{-1} (62 mm), and 1970 cm^{-1} (65 mm). The nmr spectrum exhibited a broad featureless peak 183 cps (A) from the septet assigned to the bridgehead protons of norbornadiene as well as two triplets and another broad featureless peak at 170 (B), 162 (C), and 141 (D) cps respectively from the septet in the same olefin proton region. As the solution became more concentrated from flushing the system with argon the relative positions of these peaks changed. When the solution volume was approximately 30 ml the peaks had shifted to relative positions of 178 (A), 171 (B), 163 (C), and 142 (D) cps. A more concentrated solution gave positions relative to the bridgehead proton position of 164 (A), 172 (C), and 143 (D) cps. All peaks at this point were featureless. The small peak (B) was covered by the broad combination of (A) and (C) (which was a shoulder on (A)). When the solution was concentrated to a volume of approximately 3 to 5 ml the nmr spectrum showed the respective positions of the four featureless peaks at 164 (A), 174 (B), 168 (C), and 143 (D) cps. The relative positions of these peaks from a mixture of norbornadiene and the endo-trans-endo and exo-trans-endo dimers in hexane were 189 (A), 171 (B), 162 (C), and 141 (D) cps from the bridgehead protons of norbornadiene. A triplet on the shoulder of the solvent peak was observed 92 cps upfield from the bridgehead septet. This triplet retained its position throughout the volume reduction and its structure remained until

the final volume was reacted.

Investigation of Effects Which May Alter the Dimerization by $Ni(CO)_4$

Four experiments were performed in which $Ni(CO)_4$ (0.1 M) in norbornadiene was excited photochemically using the pyrex well for one week. Pyrex tubes were used in each experiment. One tube of 14.7 ml capacity containing 12.5 ml of a 0.1 M $Ni(CO)_4$ norbornadiene solution was evacuated and sealed under the same conditions as previous photochemical experiments. A tube identical to the previous one in capacity and with the same solution was sealed under a pressure of carbon monoxide (650 mm pressure). In the third experiment the same tube as in the second experiment again containing 12.5 ml of a 0.1 M $Ni(CO)_4$ norbornadiene solution was attached to a reflux condenser and kept under a nitrogen atmosphere throughout irradiation. The fourth tube was a larger one with a fritted disc in the bottom to allow passage of nitrogen through the solution and a ground joint at the top for attaching a condenser. This tube was charged with 27 ml of a 0.1 M $Ni(CO)_4$ solution of norbornadiene. The solution in the first experiment turned pale yellow during the week of irradiation while the solution in the second experiment remained essentially colorless. In the third experiment the solution turned yellow and a brown precipitate formed at the top. The solution in the fourth experiment turned a pale yellow from colorless and eventually yellow-orange by the end of the week of irradiation. The flow rate of nitrogen was not monitored and was not constant but was

slow. The gas chromatograph results of these experiments showed the following with respect to dimers using 2 μl of each solution.

Table 10

Ratio of Peak Areas of Dimers in Four Photochemical Reactions of $Ni(CO)_4$ in Norbornadiene

Conditions	exo-trans-exo:Diels-Alder dimers
Normal	0.2:3.1
CO	0.2:4.5
N_2	0.1:2.2
Bubbled N_2	1.7:3.9
Attenuation:	32×10^{-10}:256×10^{-10}

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