



A study of stereochemical and electronic factors in the nickel promoted dimerization of norbornadiene
[pt.I] : electro-organometallic catalysts [pt.II]
by Dale Grant Pillsbury

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

To gain a better understanding of metal promoted cycloaddition reactions, the nickel promoted dimerization of norbornadiene (NBD) was examined from three aspects; stereochemical and electronic factors in the substrate and the influence of ligands bound to the nickel which are not directly involved in the reaction. As an example of stereochemical perturbation, the 7-methyl derivative of NBD was dimerized using bis(tri-phenylphosphine)dicarbonylnickel, $\text{Ni}(\text{CO})_2(\text{P}(\text{O}i\text{Pr})_3)_2$, as a promoter with both thermal and photochemical activation. It was found by an analysis of the nuclear magnetic resonance spectra of the dimers that both 2+2 and 2+2+2 cyclodimerization products were produced. The major dimers had the same skeletal stereochemical configurations as the dimers produced from the corresponding thermal and photochemical reactions of NBD and to investigate substrate electronic factors, norbornene, pentacyclotetradeca-5,11-diene (exo-trans-exo isomer) and [2,2,2]bicycloocta-2,5-diene were subjected, without success, to conditions found to produce dimers with NBD. A proposal describing the requisite electronic factors for active olefinic substrates was made. The influence of indirectly involved ligands was examined through a study of kinetics parameters in the thermal reaction of $\text{Ni}(\text{CO})_2(\text{P}(\text{O}i\text{Pr})_3)_2$ with NBD. The reaction was found to be very temperature sensitive, to be strongly inhibited by carbon monoxide and triphenylphosphine, and to exhibit an induction period followed by the major reaction period in which the rate of production of the two 2+2 dimers (both known) was constant. The kinetics results were viewed as the initial establishment of equilibrium between a number of competing reactions to produce very low steady state concentrations of active catalytic species. The substrate modification data and kinetics data were coordinated with the work of other investigators to give a unified picture of the nickel promoted cyclodimerization reaction.

The use of electrochemical regeneration of active organometallic coupling reagents was also studied. It was found benzyl halides, bromo-benzene, benzoyl chloride, phenacyl bromide and n-hexyl bromide could be coupled with electrochemically produced metal species. The reactions were run in single compartment cells using N,N-dimethylformamide as solvent, a catalytic amount of a metal ion and stabilizing ligands such as triphenylphosphine to prevent zero valent metal from plating out. Carbonyl insertion and a unique formylation reaction were also studied.

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PART I: A STUDY OF STEREOCHEMICAL AND ELECTRONIC FACTORS
IN THE NICKEL PROMOTED DIMERIZATION OF NORBORNADIENE

PART II: ELECTRO-ORGANOMETALLIC CATALYSTS

by

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fulfillment of the requirements for the degree

of

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in

Chemistry

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PREFACE

At this point it would seem worthwhile to note that this thesis is divided into two separate parts. This has been done to maintain continuity and establish clarity. Thus, despite the fact that all the work reported here involves metal promoted organic reactions, it is felt the two parts differ sufficiently in intent and scope to merit this approach.

ACKNOWLEDGMENTS

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The tangible and intangible sacrifices made by the author's parents Elmer and Agnes Pillsbury, can be best exemplified by their presence during the writing and preparation of this thesis. It is with deepest gratitude that the author acknowledges their many contributions.

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ABSTRACT

To gain a better understanding of metal promoted cycloaddition reactions, the nickel promoted dimerization of norbornadiene (NBD) was examined from three aspects; stereochemical and electronic factors in the substrate and the influence of ligands bound to the nickel which are not directly involved in the reaction. As an example of stereochemical perturbation, the 7-methyl derivative of NBD was dimerized using bis(tri-phenylphosphine)dicarbonylnickel, $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$, as a promoter with both thermal and photochemical activation. It was found by an analysis of the nuclear magnetic resonance spectra of the dimers that both 2+2 and 2+2+2 cyclodimerization products were produced. The major dimers had the same skeletal stereochemical configurations as the dimers produced from the corresponding thermal and photochemical reactions of NBD and $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$. To investigate substrate electronic factors, norbornene, [8,2,1,14,7,2,2,9,03,8]pentacyclotetradeca-5,11-diene (exo-trans-exo isomer) and [2,2,2]bicycloocta-2,5-diene were subjected, without success, to conditions found to produce dimers with NBD. A proposal describing the requisite electronic factors for active olefinic substrates was made. The influence of indirectly involved ligands was examined through a study of kinetics parameters in the thermal reaction of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ with NBD. The reaction was found to be very temperature sensitive, to be strongly inhibited by carbon monoxide and triphenylphosphine, and to exhibit an induction period followed by the major reaction period in which the rate of production of the two 2+2 dimers (both known) was constant. The kinetics results were viewed as the initial establishment of equilibrium between a number of competing reactions to produce very low steady state concentrations of active catalytic species. The substrate modification data and kinetics data were coordinated with the work of other investigators to give a unified picture of the nickel promoted cyclodimerization reaction.

The use of electrochemical regeneration of active organometallic coupling reagents was also studied. It was found benzyl halides, bromobenzene, benzoyl chloride, phenacyl bromide and n-hexyl bromide could be coupled with electrochemically produced metal species. The reactions were run in single compartment cells using N,N-dimethylformamide as solvent, a catalytic amount of a metal ion and stabilizing ligands such as triphenylphosphine to prevent zero valent metal from plating out. Carbonyl insertion and a unique formylation reaction were also studied.

PART I

A STUDY OF STEREOCHEMICAL AND ELECTRONIC FACTORS IN THE
NICKEL PROMOTED DIMERIZATION OF NORBORNADIENE

INTRODUCTION

Toward an Understanding of Metal Promoted Cycloaddition

Among the various classes of organic reactions one may distinguish one group in which the construction of a ring occurs by the creation of two (or more) sides of that ring. The formation of these new sides occurs at the expense of unsaturation - frequently double or triple bonds - in the precursor addends. This class of organic reactions is known as cycloadditions. Thus, the formation of a cyclobutane ring from two molecules of ethylene would be the result of 2π electrons + 2π electrons (two double bonds) going to two single bonds, or in short, a 2+2 cycloaddition. The formation of cyclohexane (three new single bonds) from three molecules of ethylene would be one example of a 2+2+2 cycloaddition. The reaction of 1,3-butadiene (4π electrons) and ethylene (2π electrons) to form cyclohexene (two new single bonds and one new double bond) would be a 4+2 cycloaddition. In this case, the formation of two sides of a six member ring is attended by the creation of a new double bond as well.

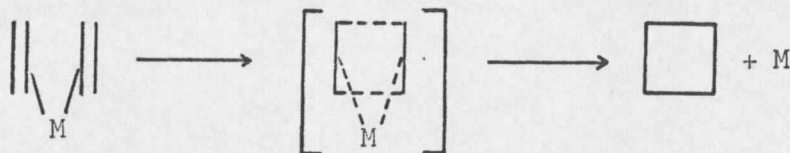
Cycloaddition reactions may be divided into those which require only thermal or photochemical excitation and those in which a catalyst is used in conjunction with such excitation. The former group of cycloaddition reactions encompasses a large body of "classical" organic reactions with such notable examples as the Diels-Alder reaction, ozonization (a dipolar addition), the "ene" reaction, and the

photochemical cyclobutanation of olefins. It appears these reactions follow the conservation of orbital symmetry rules of Woodward and Hoffmann¹, if the reaction follows a concerted mechanism. In brief, the rules state that if there are an odd number of participating π electron pairs, the reaction will be thermally allowed, whereas, an even number of participating π electron pairs results in a photochemically allowed reaction.

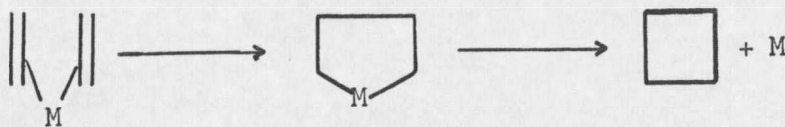
Catalyzed cycloaddition reactions may be subdivided into general acid (or base) catalyzed cycloadditions, e.g. Lewis acid catalyzed Diels-Alder reactions, and metal catalyzed reactions. It is with a specific group of reactions in this latter class - cycloadditions catalyzed by transition metals in low oxidation states - that we shall be concerned here. These reactions hereafter shall be referred to as transition metal mediated (or promoted) cycloaddition reactions.

As implied above, in any cycloaddition reaction two alternative mechanistic pathways are conceivable; one concerted and the other non-concerted. Specifically, with regard to transition metal promoted reactions one may visualize a concerted cycloaddition occurring on a metal template in which all new bonds to form the product ring are formed simultaneously with no intermediates being present from reactants to products. One could also visualize a pathway involving the formation of intermediates incorporating the metal. This non-concerted reaction would lead to the product by elimination of the metal with ring closure.

Examples of these two alternative mechanisms² are given below for a metal promoted ethylene to cyclobutane reaction.



A Concerted Mechanism



A Non-concerted Mechanism

Figure 1

Alternative Cycloaddition Mechanisms

Since the pioneering work of O. Roelen in 1938 on the oxo process, through the increased interest in transition metal promoted reactions during the '50's and '60's, to current work, there has been a keen interest in elucidating the mechanisms of such reactions. To be able to understand the role of a metal in the sequence, and hence predict new reactions, has become a formidable challenge. Some of the basic tenets of the two alternative mechanistic approaches (concerted and non-concerted) as related to transition metal promoted cycloadditions will be considered now. This shall be followed by a few specific examples of reactions which have been controversial.

The fundamental problem faced by advocates of a concerted pathway for metal assisted cycloadditions is the apparent violation of the aforementioned Woodward-Hoffmann rules in metal promoted cycloaddition reactions. Thus, concerted 2+2 cycloadditions are thermally forbidden (photochemically allowed) according to Woodward and Hoffmann, but in the presence of transition metals, reactions of this type occur with thermal excitation. Without going into the details¹ of the conservation of orbital symmetry, one may apply its principals. First, the participating reactant and product orbitals are placed within a system of symmetry elements (planes of reflection, axes of rotation, etc.) and given symmetry designations, e.g. SA (Symmetrical with respect to one symmetry operation and Antisymmetric with respect to another). Second, these orbitals are ordered qualitatively according to energy. Third, the conservation of orbital symmetry restraint is applied, i.e. SS_{reactant} may go only to SS_{product} . Therefore, noting that the tie-lines in Figure 2 correlate symmetry-allowed conversions; for two ethylenes going to a cyclobutane one has:

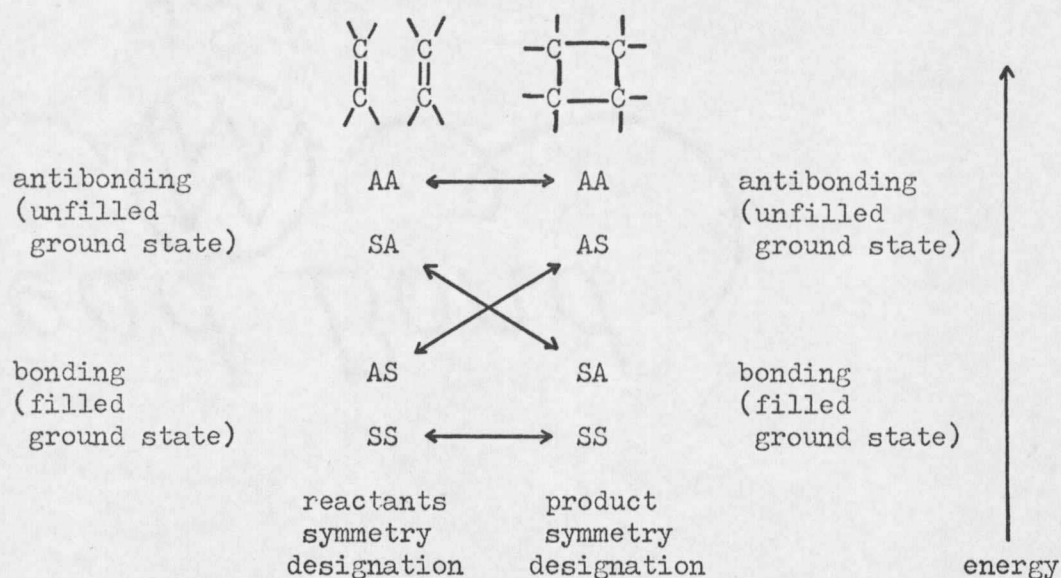


Figure 2

Correlation Diagram for Cyclobutanation of Two Olefins

So thermally, only the SS and AS reactant orbitals would be filled, resulting in an energetically unfavorable path to product. One needs the SS_{reactant} and SA_{reactant} combination for an energetically favorable situation. Photochemically, one electron may be raised to the antibonding SA_{reactant} state, correlating with the SA_{product} orbital, thereby allowing the reaction to occur. Thus one arrives at the rule for 2+2 cycloadditions - thermally forbidden, photochemically allowed.

Mango and Schachtschneider^{3,4} met the "forbidden to allowed" obstacle for thermal transition metal mediated concerted cycloaddition reactions and still worked within the framework of orbital symmetry. They noted that any sequence which could lead to a population of the antibonding SA_{reactant} state would provide a possible pathway. A filled

metal orbital with SA symmetry could "pump" electrons into the anti-bonding SA_{reactant} state. Also another unfilled metal orbital having AS symmetry could simultaneously receive electrons from the bonding AS_{reactant} state. The net result would be an increase in electron density of the SA_{reactant} state at the expense of a decrease in electron density of the AS_{reactant} state. Thus the metal would act as an electron reservoir-pump providing a source of or sink for electrons where needed. The situation is diagrammed below showing the SA and AS orbitals for the reactants, metal and product.⁴ Shading denotes orbitals are filled.

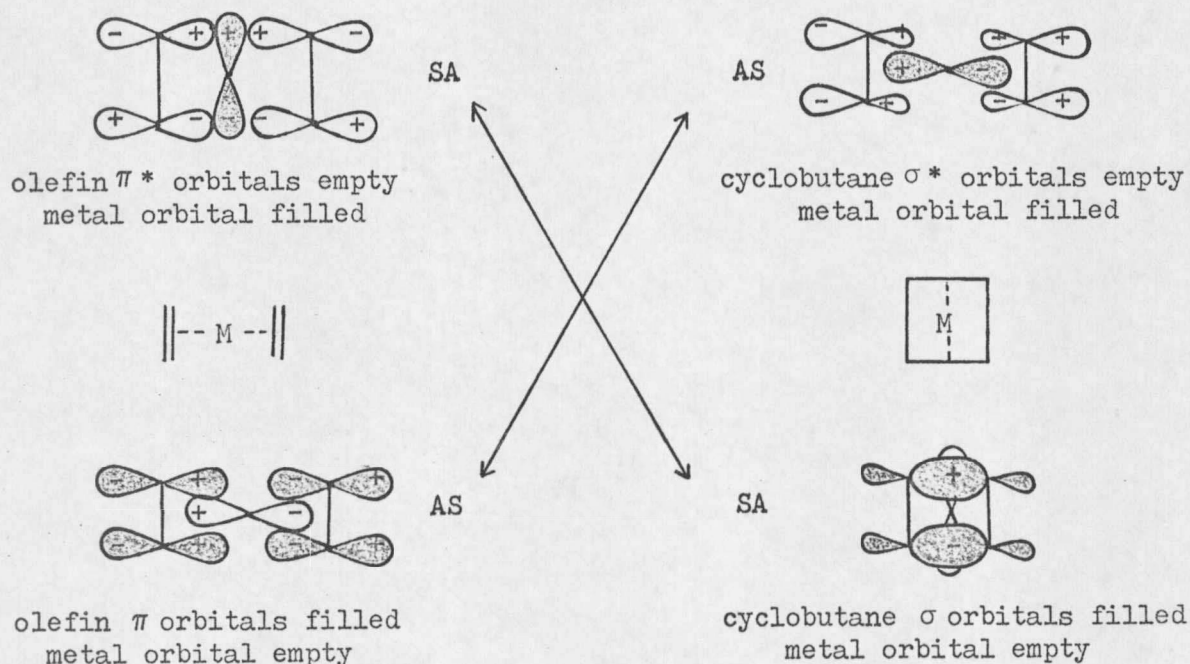


Figure 3

Metal-Olefin Orbital Symmetry
Correlations

It has been suggested by van der Lugt that an alternative to the Mango theory exists involving a lowering of the degree of forbiddenness of thermal 2+2 cycloadditions by metal-substrate configurational interaction.⁵ Mango has answered this challenge⁶ and the Mango theory remains the principal theoretical argument for advocates of a concerted thermal 2+2 cycloaddition mechanism.

Proponents of the non-concerted mechanism circumvent any violation of the Woodward-Hoffmann rules by the very fact that the rules only apply to concerted reactions. The theoretical basis for a non-concerted approach lies in an application of Occum's Razor which may be stated as: there is no necessity to formulate a new mechanism when a reasonable variation of an established theory already exists. However, the very nature of a non-concerted reaction implies the presence of intermediates and the burden of proof for those intermediates lies with the advocates of a non-concerted mechanism. This is not always readily accomplished.

One case which has been examined from both the non-concerted and concerted points of view is the opening of quadricyclane to form norbornadiene. This reaction can be thought of as the reverse of a cyclobutane reaction.

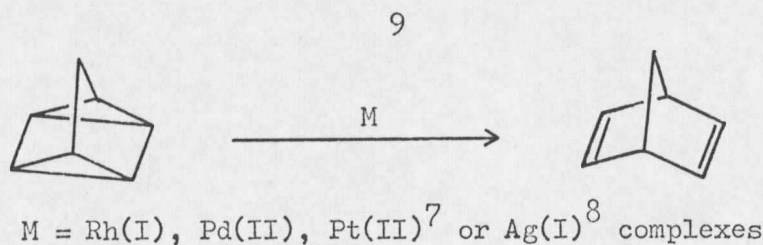


Figure 4

Metal Assisted Conversion of Quadricyclane to Norbornadiene

Mango^{4,9} has asserted the cyclopropane rings fused to the cyclobutane ring ought to promote facile complexation with a metal allowing a concerted reaction to occur. However, L. Cassar and J. Halpern¹⁰ report the isolation of an acyl rhodium complex from the reaction of quadricyclane and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ suggesting a non-concerted mechanism is a reasonable alternative.

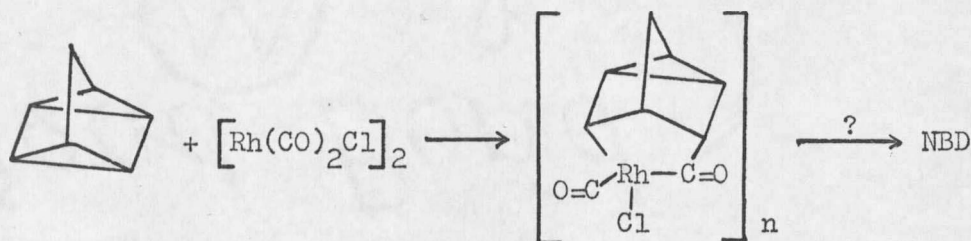


Figure 5

Proposed Path for $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ Assisted Opening of Quadricyclane

It is not clear in this case that the isolated rhodium complex is efficiently converted to norbornadiene, but it is noted that some quadricyclane is transformed to norbornadiene in the formation of the complex. Also, it is not obvious that intermediates are thereby indicated for other metals.

Another case is the dimerization of butadiene to 1,2-divinylcyclobutane with a Ni-ligand catalyst.¹¹

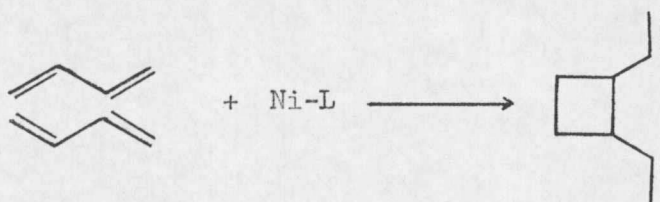


Figure 6

Nickel Promoted Dimerization of Butadiene

Initially, Mango¹² suggested the plausibility of a concerted mechanism, but later he acknowledged a stepwise catalytic process based on isomer distributions.¹³ Intermediates of the type shown below were later isolated by Wilke et al.¹⁴

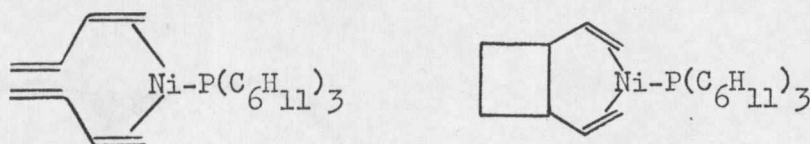
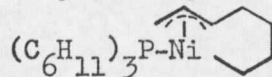


Figure 7

Isolated Intermediates in the Nickel Promoted Dimerization of Butadiene

It is reported these π-bonded intermediates are apparently in equilibrium with a common π allyl-σ allyl bonded species shown by NMR to be:



A third system which has continued to provoke interest is the metal catalyzed conversion of the exo-tricyclooctene (I) to the

tetracyclooctene (II). Two other isomers (III and IV) can also be produced.^{15a-d}

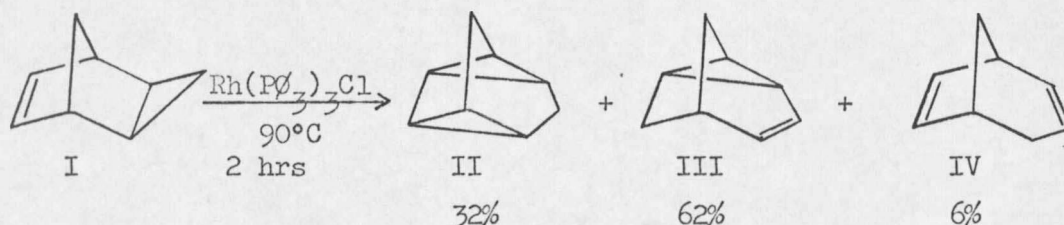
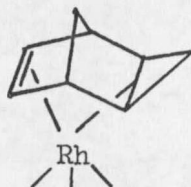


Figure 8

Products from the $\text{Rh}(\text{P}\phi_3)_3\text{Cl}$ Promoted Opening of
Exo- $[3,2,1,0^{2,4}]$ tricycloocta-6-ene

It has been noted by Katz^{15a} that all the products are stable under the reaction conditions and further that it is difficult to relate products III or IV to I by a simple cycloaddition. He has presented arguments to support a common species, of unknown structure from which both II and III are formed. Mango,¹⁶ advocating the possibility of a concerted mechanism, accepts a common origin for the two products. He suggests this "parent" is a complex in which the metal is coordinated to I in a bidentate manner.



He explains the lack of a clean transformation of this complex to II (the by-product formation of III and IV) as due to an energy barrier involving non-reacting ligands. Thus it is proposed that when a metal acts as an electron reservoir-pump, electron density in the metal orbitals is

by necessity somewhat rearranged. If the metal has a strongly interacting ligand field - exclusive of the organic substrate - that field could represent an impedance to the desired cycloaddition reaction. In systems where the ligands act principally as σ donors the effect probably would be minimal, while ligands with strong backbonding capacity could cause a pronounced energy barrier. Since neither the non-concerted nor the concerted arguments can be shown to be faulty, this problem continues to be unresolved.

One final molecule whose behavior in metal mediated cycloadditions remains a puzzle shall be examined. Norbornadiene (V) has been dimerized with a number of transition metal catalysts including derivatives of Cr, Fe, Co, Rh, Ir and Ni. Depending on the catalyst and the reaction conditions a variety of products can be formed. However, the two most frequently encountered types can be considered to be variants of VI (2+2 product) or VII (2+2+2 product).¹⁷

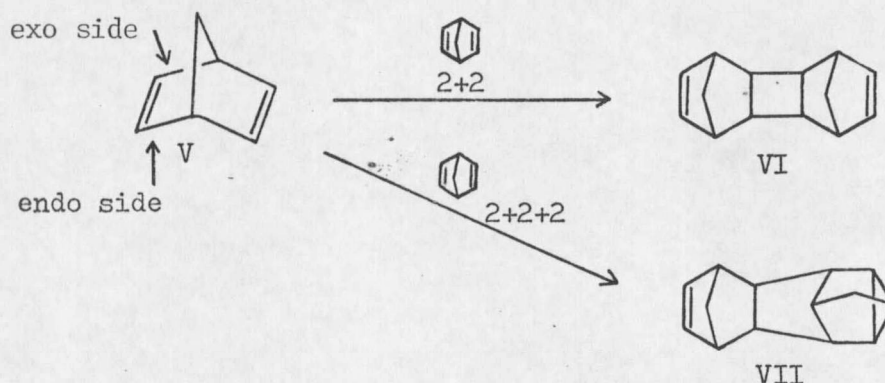


Figure 9

Dimer Types from the Metal Promoted Cycloaddition of Norbornadiene

Both the concerted and non-concerted mechanisms have been applied to the norbornadiene (NBD) system. Advocates for the concerted approach have noted examples of "exo" as well as "endo" bonded transition metal complexes. By selecting a suitable set of bonding modes, concerted pathways may be envisioned leading to the reported dimers.

On the other hand, the recent publication² of the structure (IX) of an Ir complex derived as noted below is offered as proof of a non-concerted mechanism.

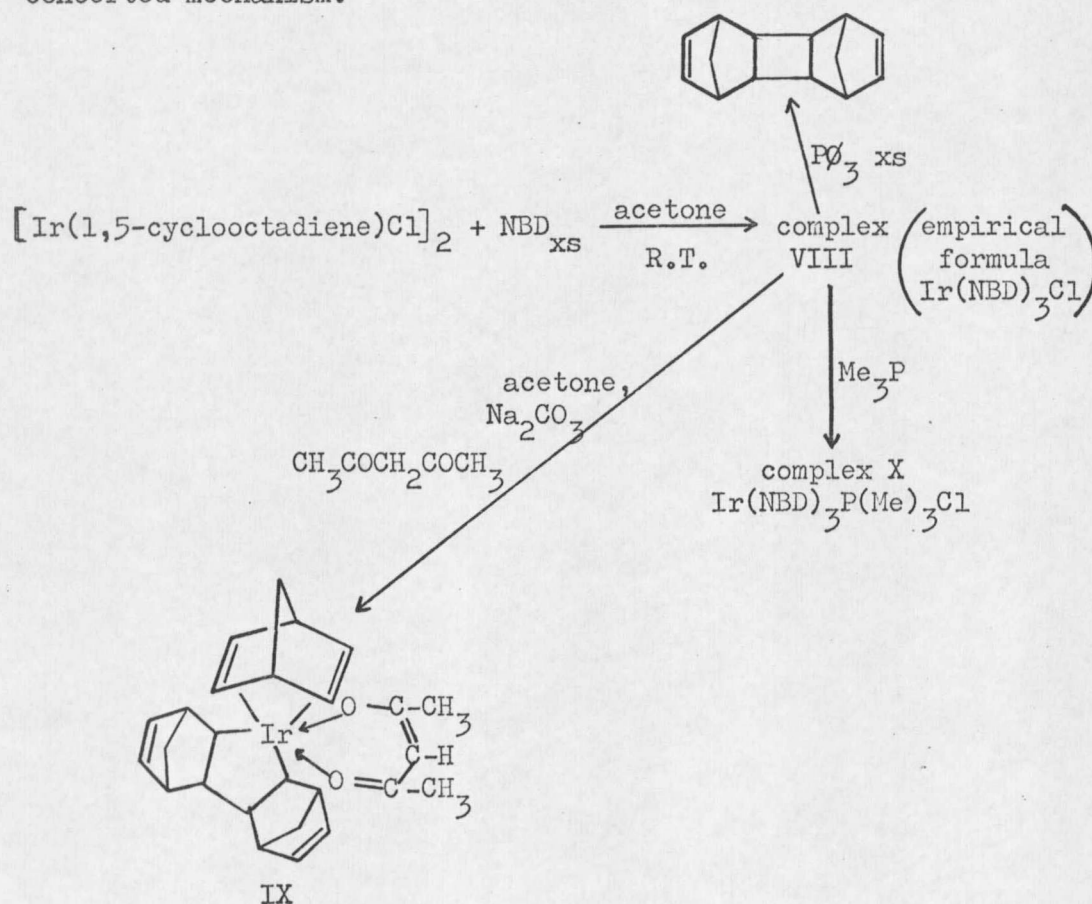


Figure 10

Study of the $[\text{Ir } 1,5(\text{COD})\text{Cl}]_2$ Promoted Dimerization of NBD

It is also noted that there exist pronounced spectral similarities between IX, X and VIII. Nevertheless, even if one accepts this argument as proof for a non-concerted mechanism for an Ir catalyzed dimerization, the concerted alternative cannot be ruled out for other metal and ligand systems.

Based on the four examples just given, one point should be clear: neither the concerted nor the non-concerted mechanism pathways for transition metal promoted cycloadditions can be discarded at this point. While the concerted mechanism is theoretically appealing it has had to be modified to accommodate such realities as the influences of nonreacting ligands. Furthermore, proponents of a concerted mechanism are placed in the difficult situation of either taking a defensive position in what is not clearly an impregnable fortress, or attempting to prove the non-existence of what their opponents claim are tangible species.

Since the proof of intermediates lies with the advocates of the non-concerted mechanism they are faced with a serious epistemological problem. Do efforts to acquire intermediates alter the reaction such as to force the formation of intermediates? If this is the case, proof must be provided that intermediates exist in the unperturbed reaction. Since it would be impossible to observe the reaction without altering it to some extent the observation should be made to alter it as little as possible. Thus neither alternative is without its problems.

It may be worthwhile at this point to summarize some of the important parameters which must be considered in any metal mediated

cycloaddition reaction. The first factor to be considered has just been noted above: when one is attempting to gain information about a reaction mechanism the system under study should be perturbed as little as possible. Frequently, this means only physical data such as spectra can be used. If intermediate species can be isolated, their spectra should be noted and compared to spectra obtainable from the system under actual reaction conditions. However, it is obvious the use of this approach is strongly dependent on the lifetime of the intermediates, the time scale for the method of measurement, and the degree to which a given species may be distinguished from other species in the reaction.

A second factor is the nature of the metal used to catalyze a reaction. It may be worth stressing that rarely, if ever, can the electronic or stereochemical characteristics of one metal-substrate system be duplicated by another. Even for second and third row transition metals in the same column significant differences exist.¹⁸

Very closely related to this is the nature of the ligands. While the nature of ligand-metal-substrate interactions is not completely understood some efforts have been made to correlate experimental facts. One area which has received attention and is particularly relevant to metal mediated cycloadditions is the role of ligands in π to σ transformations. Two examples are given below.

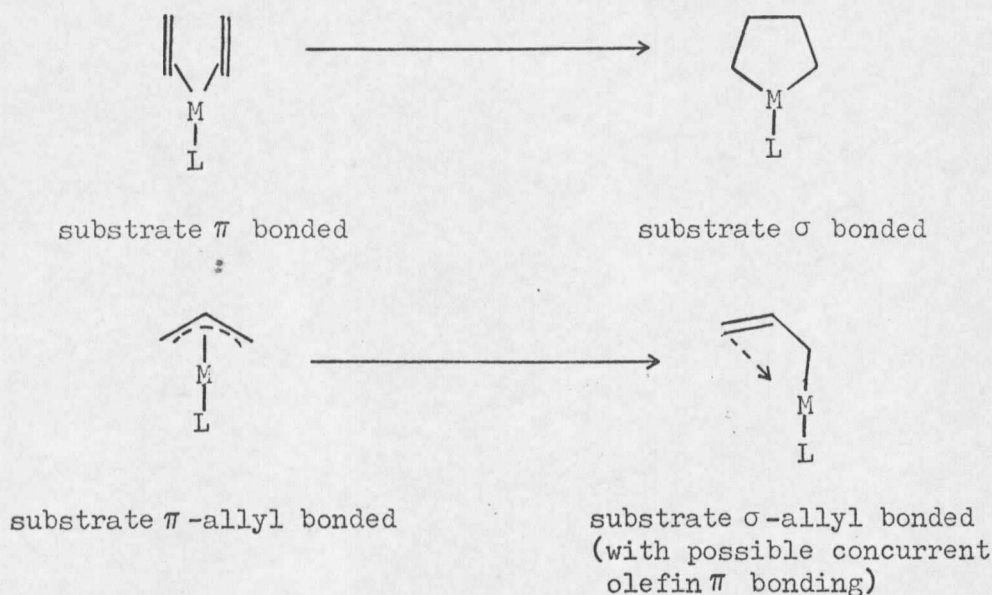


Figure 11

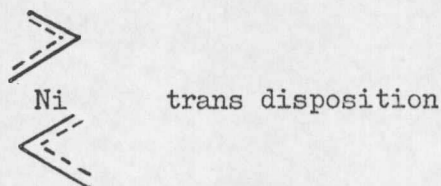
Two Examples of π to σ Transformations

It may be noted that one of these examples has been encountered before in Figure 1 (page 4) to illustrate the non-concerted mechanism for cycloaddition. Species related to the π - σ allyl system have been studied with respect to the dimerization of butadiene.^{11,14} A qualitative theoretical treatment has been given by Tsutsui¹⁹ in which it is proposed that the "Addition of strong π ligands to the central metal is one method of inducing σ - π rearrangements. Only ligands...capable of π bonding are capable of stabilizing the σ state".²⁰ However it has been suggested by Helmbach, Jolly and Wilke¹¹ that π -allyl to σ -allyl conversions are more readily promoted by phosphines than by phosphites. They also note that phosphites are better back-bond acceptor ligands than are phosphines.

Their claim is based on a rather thorough study of the influence of ligands on the nickel catalyzed dimerization of butadiene and appears to be well supported.

This behavior has been explained²¹ by assuming the π -allyl system contributes more electron density than the corresponding σ -allyl system. When the other ligands are strong donors, the σ form is favored. If one considered the formation of a σ bonded complex an oxidative addition to the metal then one would expect ligands which increase electron density - strong σ donors, poor back donation acceptors - to enhance formation of the σ bonds.²²

One final factor that bears mentioning is symmetry considerations. These considerations apply both to the symmetry constraints on orbital interaction for complexation and to the stereochemistry of the products. Thus, in order to secure a clear picture of the bonding in complexes (or intermediates) leading to a product it is necessary to interact substrate and metal orbitals of the same symmetry. For example, the structures of bis(π -allyl)nickel complexes have been found to prefer the geometry given below.²³



A significant alteration of this bonding scheme must occur in the allyl-nickel intermediates leading from butadiene to cis,cis-cyclooctadiene.

To arrive at the *cis,cis* stereochemistry it is suggested that the phosphine ligand (P) allows either a σ -allyl, π -allyl nickel complex (XI) to form or it allows a *cis* disposition of two π -allyl groups as in complex XII.

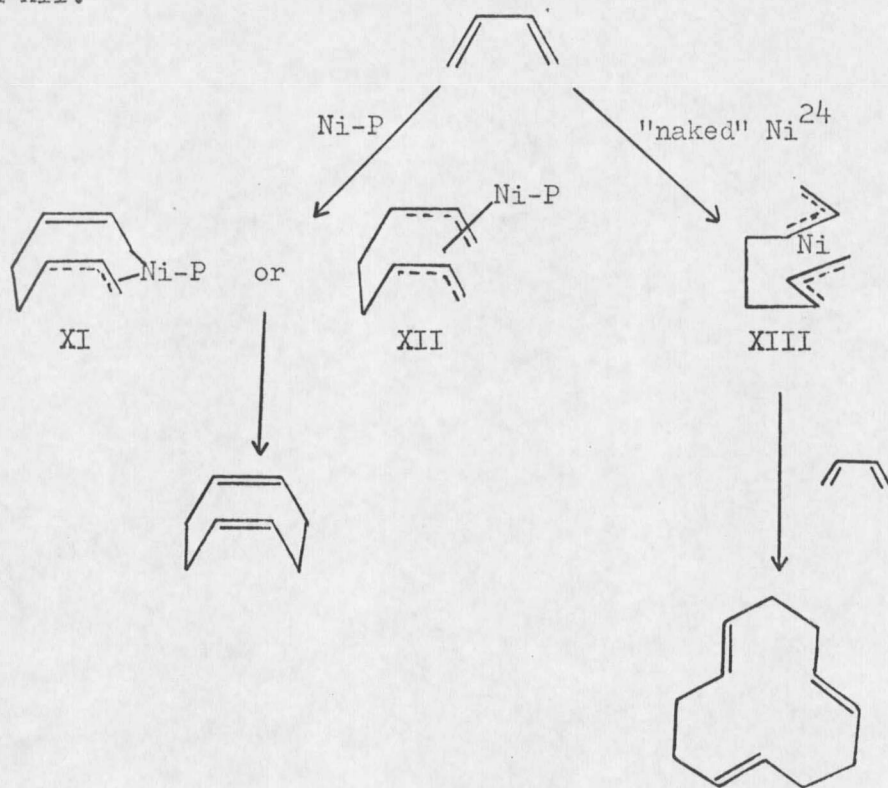
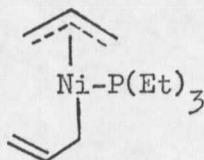


Figure 12

π and σ Bonded Allyl Nickel Intermediates
in the Oligomerization of Butadiene

Since it has been shown the addition of $\text{P}(\text{Et})_3$ to $\text{bis}(\pi\text{-allyl})\text{nickel}$ results in a complex containing one π -allyl and one σ -allyl ligand (see XIV below), complex XI is most reasonable. It may also be noted that in the absence of the phosphine ligand, butadiene is converted to

principally the all trans 1,5,9-cyclododecatriene which could arise from complex XIII.



XIV

As noted before, cycloaddition reactions of norbornadiene have been treated from both a concerted and non-concerted mechanistic viewpoint. However, it may be possible that proponents of neither approach have examined the problem unbiasedly. It is suggested here that the norbornadiene molecule may offer a unique model for examining the mechanism of metal promoted cycloadditions. This is proposed in light of: a) the formation of both 2+2 and 2+2+2 cycloaddition products, b) the number of π -bonded complexes formed by norbornadiene, and c) the report of intermediates whose structures suggest partially formed dimers σ -bonded to a metal.

As an example of the variety one can encounter let us look at the products^{17a} obtained with just two nickel based "catalysts". It may be noted that these "catalysts" have been chosen because of their particular relevance to the work presented in the first part of this thesis and because of the wide spectrum of considerations they introduce.

Nickel tetracarbonyl, Ni(CO)_4 , when used as a promoter with photochemical excitation, produces two specific 2+2+2 dimers (XV and XVI

in Figure 13). Thermal excitation of $\text{Ni}(\text{CO})_4$ and NBD yields two specific 2+2 dimers (XVII and XVIII in Figure 13). The third 2+2 isomer with a trans disposition of norbornene moieties about the cyclobutane ring is a product (XIX in Figure 13) of both the thermally and photochemically induced dimerization of NBD using bis(triphenylphosphine)dicarbonylnickel, $\text{Ni}(\text{P}\phi_3)_2(\text{CO})_2$, as a promoter.

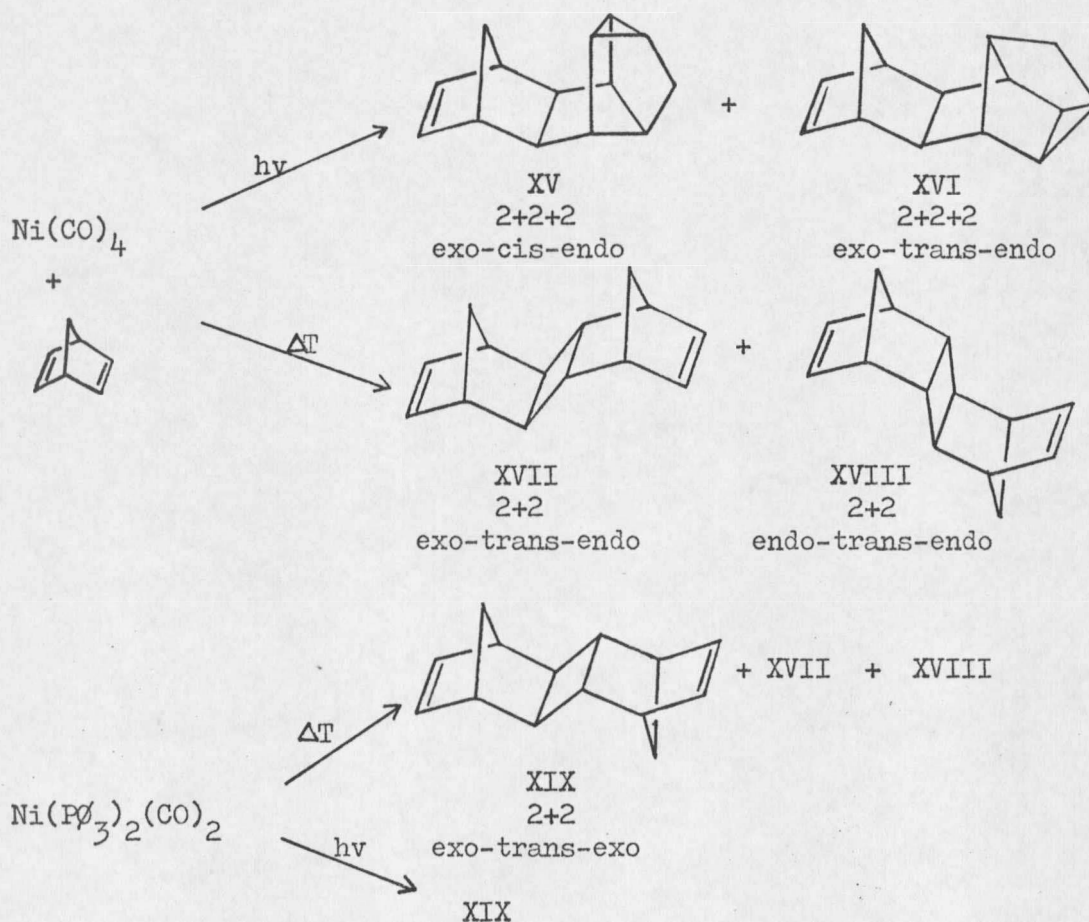


Figure 13

Dimers from the Cycloaddition Reaction of NBD Promoted by $\text{Ni}(\text{CO})_4$ and $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$

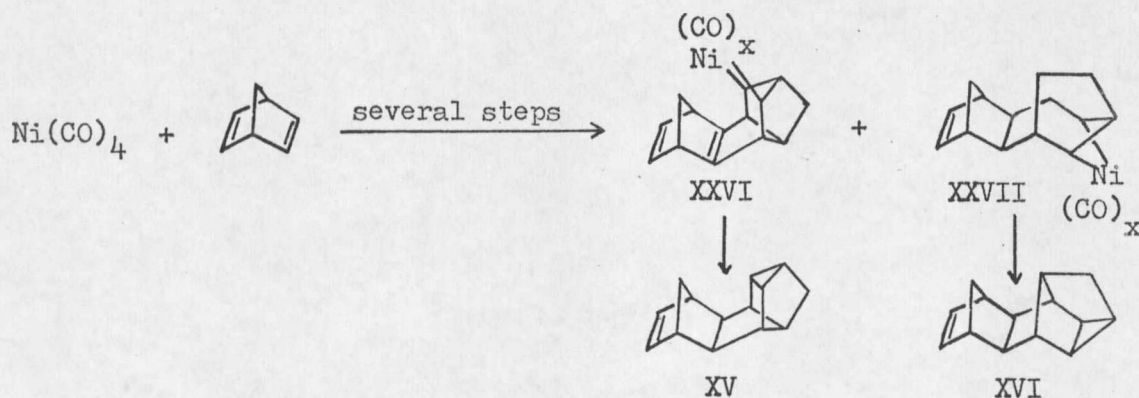
It is suggested that the word promoter be used here rather than the word catalyst, since both Ni(CO)_4 and $\text{Ni(CO)}_2(\text{P}\phi_3)_2$ are apparently converted to other species which act as catalysts for the dimerizations.^{17a,25}

The organic products are stable under the reaction conditions and neither thermal nor photochemical excitation alone (no promoter present) will result in dimerization. Therefore one is faced with accounting for quite an extensive range of products.

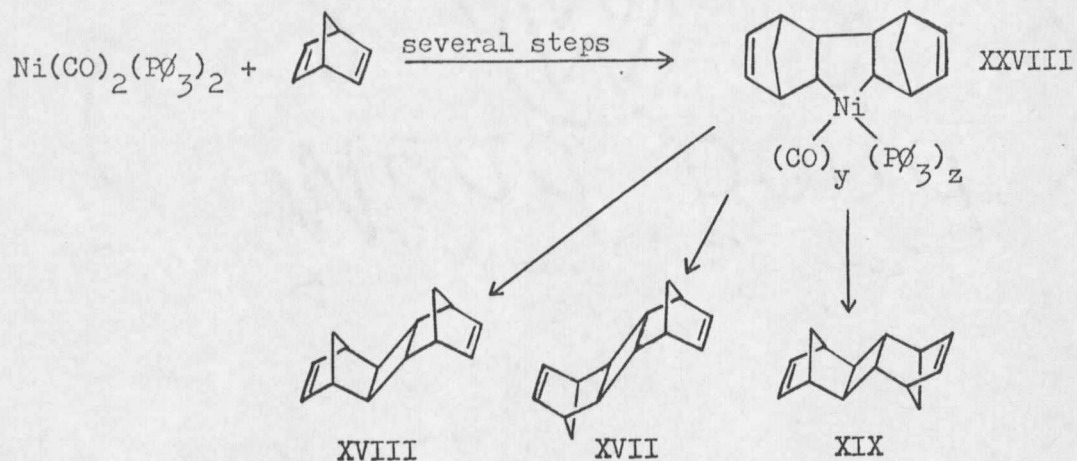
One attempt to account mechanistically for the products would be to propose a number of steps leading to a complex which could undergo a concerted cycloaddition to form dimers. As shown in Figure 14²⁶, nickel carbonyl is converted to nickel tricarbonyl, Ni(CO)_3 , and to nickel dicarbonyl, Ni(CO)_2 . Either Ni(CO)_2 adds to the endo side of NBD in a bidentate manner, or Ni(CO)_3 adds to the endo side in a monodentate manner followed by the loss of another CO. The net result is the formation of endo,endo-NBD Ni(CO)_2 , XX. This molecule may photochemically lose another CO followed by the exo complexation of another NBD molecule to give complex XXI. Complex XXI could undergo a concerted 2+2+2 cycloaddition to give either dimer XV or dimer XVI. Complex XX could also be in thermal equilibrium with the coordinatively unsaturated complex endo-NBD Ni(CO)_2 , XXII. If complex XXII were to bond in an endo fashion to a second NBD molecule, complex XXIII would be formed and this could lead in a concerted fashion to the 2+2 dimer XVIII. On the other hand if complex XXII added another NBD in an exo manner the result would be

complex XXIV. A concerted cycloaddition of XXIV would give dimer XVII. In a similar fashion $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ could lead to complex XXII (and hence to dimers XVII and XVIII) thermally. However, since dimer XIX is produced thermally - and photochemically as well - another precursor complex, e.g. XXV, would have to be formed. This non-carbonyl containing complex might be formed via an intermediate such as bis(triphenylphosphine)nickel, $\text{Ni}(\text{P}\phi_3)_2$, and could lead by a concerted cycloaddition to dimer XIX.

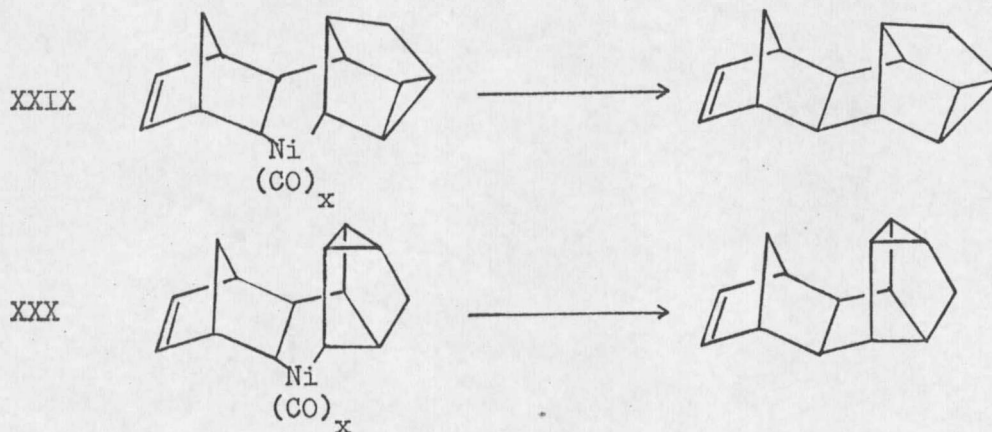
There are also other mechanistic possibilities. A non-concerted cycloaddition sequence based on the concepts developed by Osborn et al.², vide ante, as well as Katz²⁷ might be suggested. Thus 2+2+2 dimers could be explained as arising by the extrusion of a metal species from the incipient cyclopropane ring of the nortricyclane moiety.



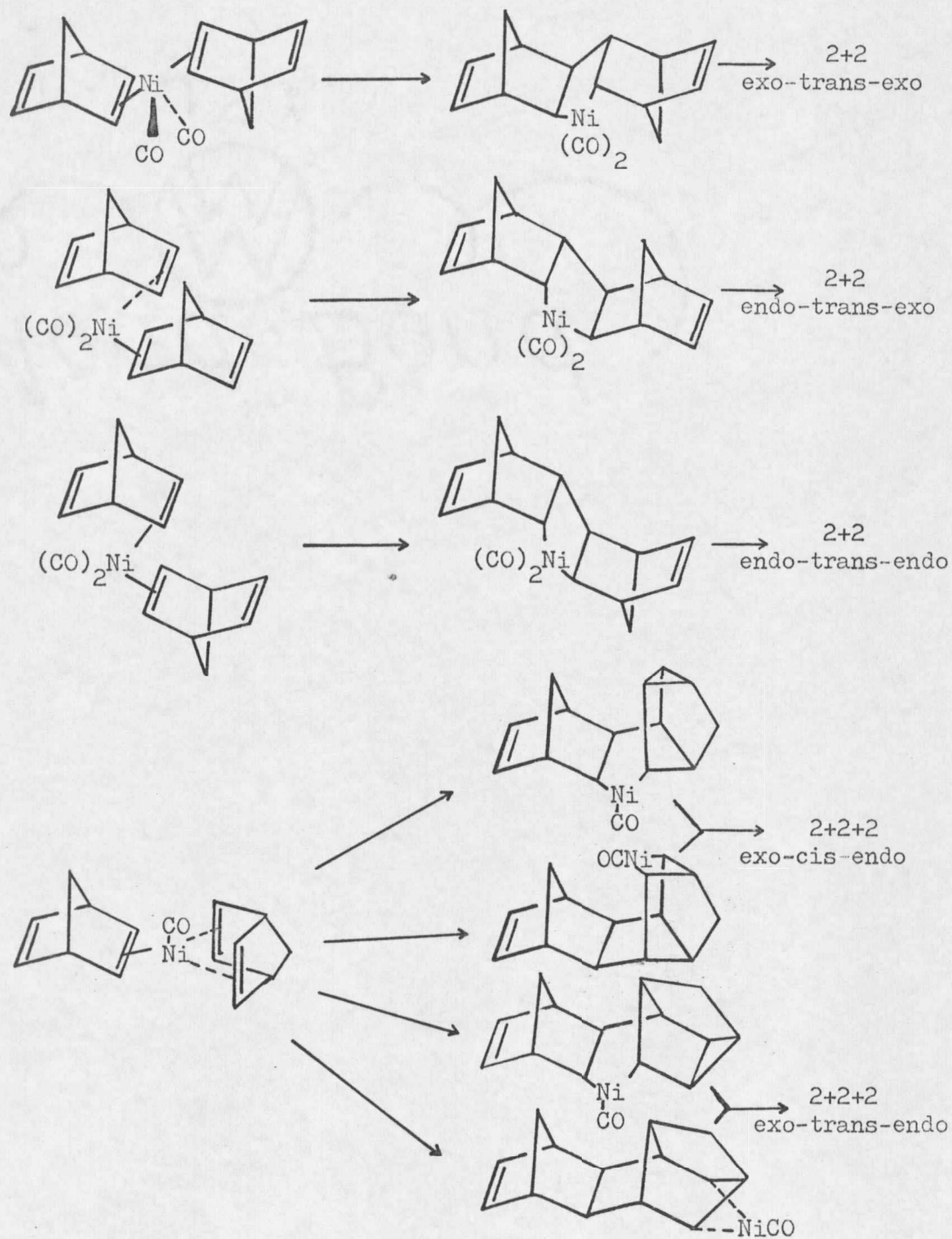
Similarly, the 2+2 dimers would result from extrusion and closure to form the cyclobutane ring.



Another way in which the 2+2+2 dimers might arise by a non-concerted path could be by the closure of the five member ring.



Pathways to these bis(σ -alkyl)nickel species (XXVI-XXX) are many and varied. However, it may be worth-while looking at what appear to be some of the more reasonable possibilities.



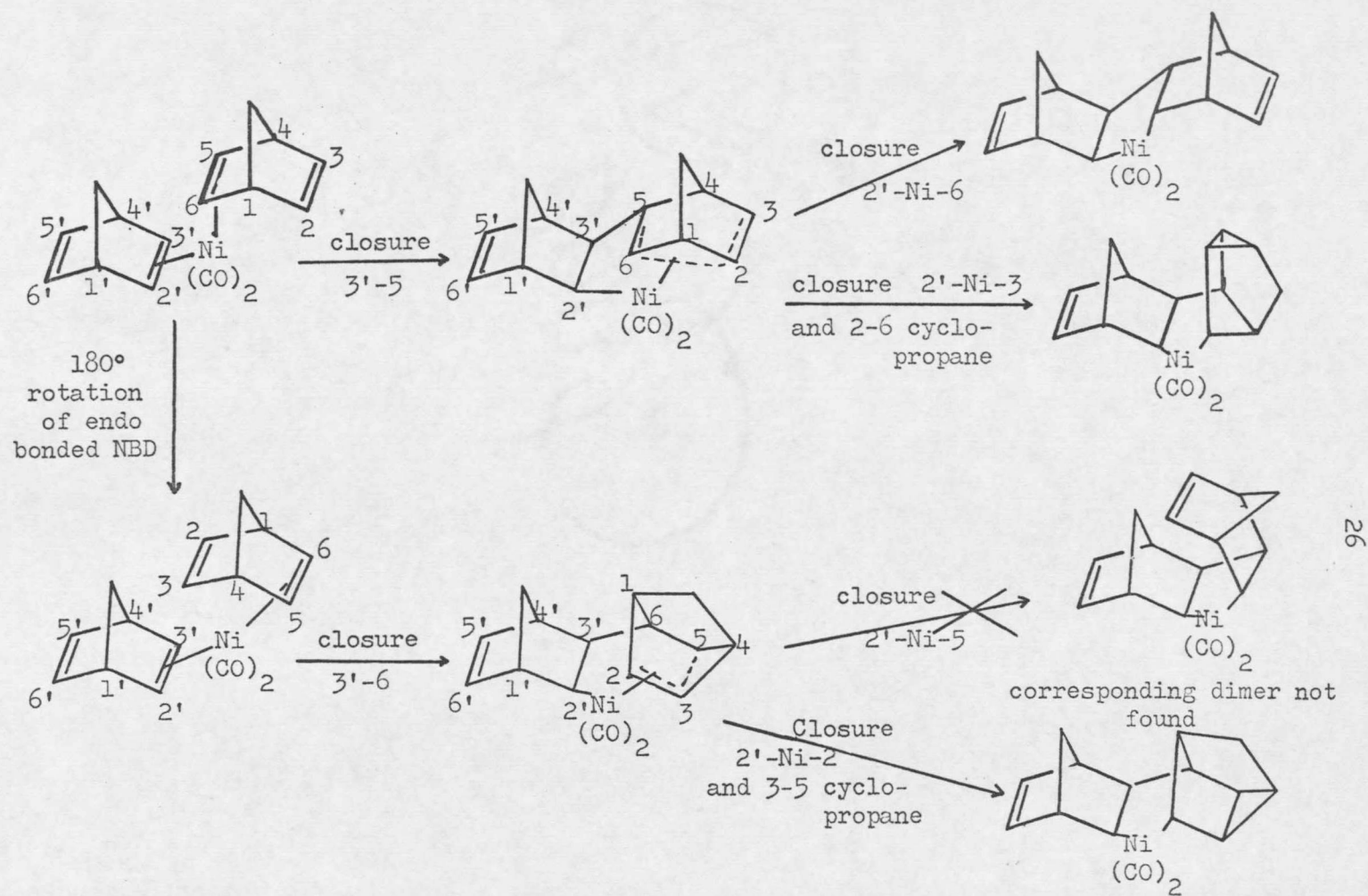
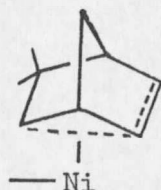


Figure 15

Modes of Closure of Precursor Complexes Leading to NBD Dimers

In each of the above cases the initial complex is the same as that which might lead to product in a concerted fashion. The point of contention is simply the path of getting from these complexes to products. One path which has not previously been suggested as a route for metal mediated cycloadditions of NBD is that involving the so-called homoallylic moiety:



As can be seen in Figure 15, a complex of this type could allow for formation of either 2+2+2 or 2+2 dimers depending on the mode of closure. The invocation of such an intermediate would add unity to the mechanism, and should be considered here.

The formation of a "homoallylic" complex by the addition of methoxide to the di-endo bonded complex (NBD)PdCl₂ has been claimed²⁸ and later this was expanded to the addition of other nucleophiles.^{29a-j}

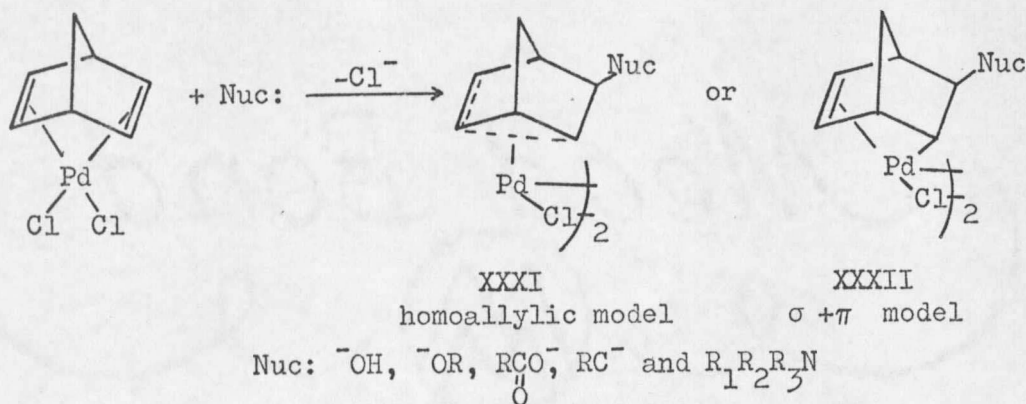


Figure 16

Reactions of PdCl₂•NBD Complex with Nucleophiles

There has been some controversy about the bonding in the product, XXXI or XXXII. The homoallylic model was proposed by Green and Hancock²⁸ to account for their interpretation of NMR spectra of the product. Stille and Morgan^{29c} had originally suggested the product had a Pd-C σ bond and a Pd-C π bond. Chemical reactivity experiments³⁰⁻³² were not very decisive since a dynamic equilibrium between two σ - π contributors and a homoallylic species could readily be displaced by the gain or loss of a ligand,^{19,23,33} as shown below.

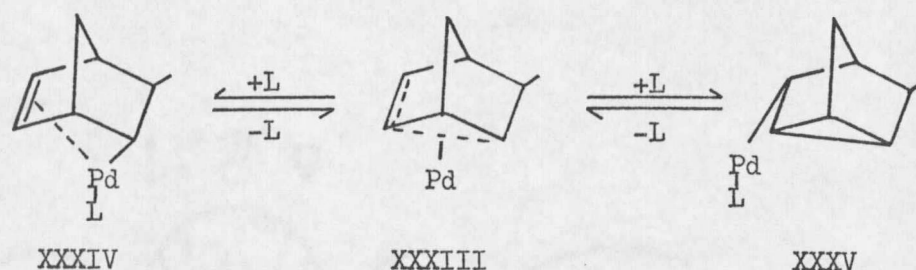


Figure 17

Possible Reaction Pathways for a π -allyl NBD•Pd Complex

Further, proponents^{28,30-32} of the π -homoallylic model in citing supposed similarities between it and known π -allyl palladium compounds have made an analogy which is somewhat dubious. They have implied explicitly or implicitly that the formation of the cyclopropyl ring (forming a nortricyclane) is analogous to the formation of a double bond in π -allylic $\longrightarrow$ σ -allylic transformations. They have apparently dismissed the similar process for norbornenyl systems.

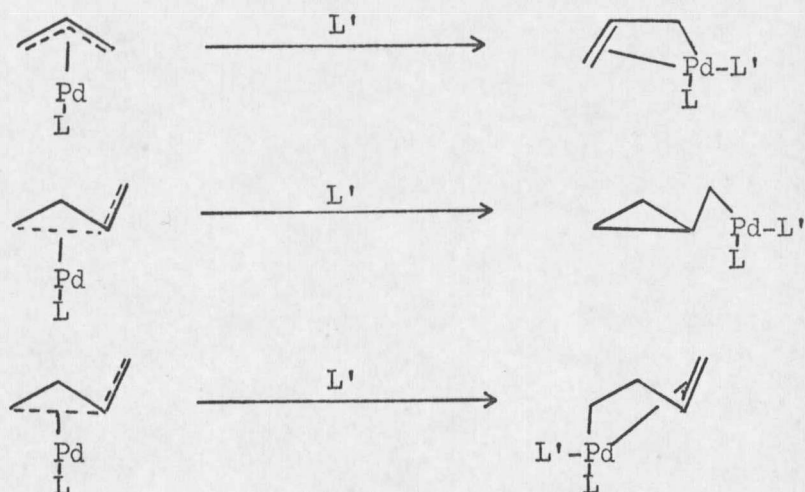


Figure 18

Palladium π and σ Allylic and π and σ Homoallylic Complexes

A later NMR analysis by Haszeldine and workers³⁴ refuted some of Green's assignments. They suggested the one π , one σ bonding picture is more appropriate and explained the propensity of palladium norbornenyl compounds to go to nortricyclane derivatives as being the result of steric approach and electronic factors.

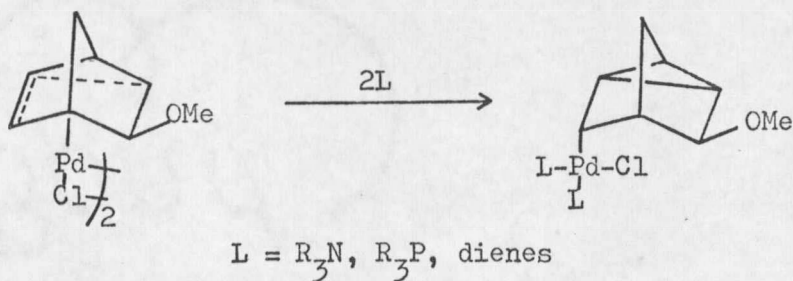


Figure 19

Pd π -allyl NBD to Pd σ -nortricyclane Transformations

Another approach to the question of π homoallylic bonding to metals in norbornenyl systems may come from the bonding picture from the norbornenyl viewpoint. Semmelhack has noted that an allyl group bonded to a transition metal "shows chemical properties consistent with an electron density slightly greater than that of the allyl radical".³⁵ If this is the case, would a delocalized radical be consistent with the behavior of a norbornenyl system? The general consensus appears to be that non-classical norbornenyl radicals such as XXXVI are not a very good representation. Rather there appears to be a preference for an equilibrium between the two classical radicals XXXVII and XXXVIII.

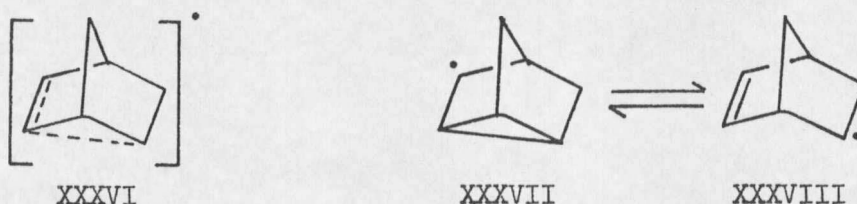


Figure 20

Structural Representations of the Norbornenyl Radical

Based on this consideration, the σ and π model for the 2-methoxy-norbornenyl palladium chloride dimer would seem the more reasonable choice. It should be noted that while the nature of both the metal and any ligands on that metal may alter the situation there does not appear to be any compelling evidence in favor of a π -homoallylic bonding mode.

However, one is still faced with a decision between the concerted path to product or the non-concerted alternative. The problem of

resolving this question still presents a formidable challenge. It would be reasonable to ask if the solution of such a problem could have any significance other than establishing the mechanism for the cyclo-dimerization of one molecule. While norbornadiene must be considered a rather unique molecule, an understanding of the mode by which it dimerizes in the presence of metals could have some far-reaching consequences based on just that uniqueness.

These consequences could reasonably include:

- 1) Contribution to the picture of the fundamental nature of bonding between metals and organic molecules - both π and σ bonded species being known.
- 2) Contributions to the relative significance of steric and electronic factors in metal promoted 2+2+2 as well as 2+2 reactions - thus allowing for the possible expansion of synthetic organic reactions.
- 3) Possible direct extrapolation to other bi- or polycyclic olefins including terpenoid molecules - perhaps providing an insight into the basis for stereoselectivity in natural products.

Thus, while the solution of the problem may present a formidable challenge, the results of that solution would too.

DISCUSSION

The work reported in this thesis is the result of a bifunctional approach to the problem of metal mediated cycloaddition reactions of olefins. The first aspect of this approach is to explore the scope of the reaction and the second is to come to a better understanding of the mechanism or mechanisms operating in such reactions. Since norbornadiene (NBD) presents some particular advantages from both aspects, as noted in the Introduction to this part of the thesis, it was chosen as the molecule to be studied initially.

Although it would be somewhat artificial to isolate the two aspects of the problem from one another, it is considered useful to differentiate them. To do so the following divisions have been made in the work to be reported:

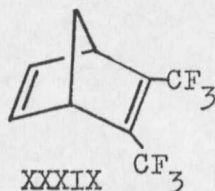
- a) An examination of structural modification of the NBD molecule, while still retaining the NBD skeleton. Emphasis is placed on steric considerations including substrate and metal-substrate factors.
- b) An examination of structural perturbations of the NBD molecule in which the electronic nature of the NBD molecule has been significantly altered. Emphasis is placed here on substrate electronic effects as they influence complexation and subsequent cycloaddition.
- c) A kinetic study with emphasis placed on metal-ligand

interaction.

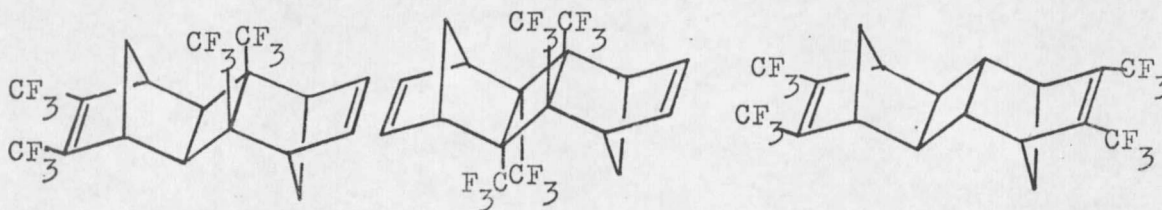
It is realized that any structural modifications in the substrate would necessarily result in changes in electronic factors. Likewise, variations in ligands will result in new stereochemical demands. It is felt, however, that while in any given portion of the discussion emphasis may be placed on a particular point, this emphasis will not preclude the consideration of other factors.

Structural Modifications - Steric Considerations

Preliminary investigations. The first compound to be investigated from a structural viewpoint was 2,3-bis(trifluoromethyl)NBD, XXXIX. From



an analysis of the anticipated 2+2 xtx dimer, vide infra, one might be able to gain an insight into the mode of bonding in intermediate complexes and the role of stereochemistry in determining favorable bonding patterns. The following product variations are among those which could be considered.

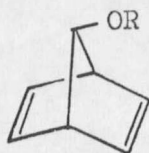


Various concerted and non-concerted pathways involving directly or indirectly, metal mediated reactions could be suggested to account for these products and it was hoped an analysis of dimer product would be informative. Furthermore, the ease with which the molecule could be prepared from bis(trifluoromethyl)acetylene and cyclopentadiene was attractive as compared to the difficulty anticipated with the corresponding hydrocarbon, 2,3-dimethylNBD. However, the extended photolysis* (166 hours) of a benzene solution of this molecule using bis(triphenylphosphine)dicarbonylnickel, $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$, as a promoter showed no apparent dimer formation by gas chromatographic analysis. Bis(triphenylphosphine)dicarbonylnickel was chosen as a promoter in the reaction since, as noted earlier, it produces essentially only one NBD dimer (the 2+2 dimer, XIX) with photochemical activation; it is quite an active catalyst with NBD (20% reaction in 72 hours)^{17a} and it is also a solid air stable compound providing experimental convenience.

Feeling the negative result with 2,3-bis(trifluoromethyl)NBD might be a result of either too severe a steric demand or too drastic a change in the electronic configuration of the olefinic bonds, two 7-substituted derivatives (XL and XLI) were tried. The first of these was commercially available while the second could be fairly readily prepared. Jolly,

* All photolysis reactions were carried out in pyrex tubes unless otherwise noted. The amount of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ used was catalytic (1×10^{-4} to 1×10^{-6} M), which also applies to any thermal reactions run.

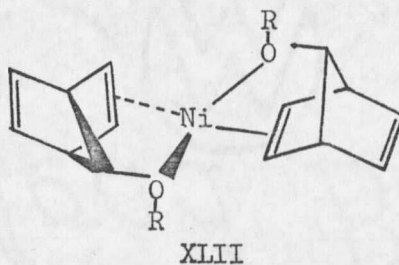
Stone and MacKenzie³⁷ reported XL could be thermally dimerized, albeit low yield, using the very active promoter^{17a} dicarbonyldinitrosyliron. However, irradiation of benzene solutions of XL (135 hours) and XII (140 hours) containing $\text{Ni(CO)}_2(\text{P}\phi_3)_2$ showed no apparent dimer by gas



XL R = t-butyl

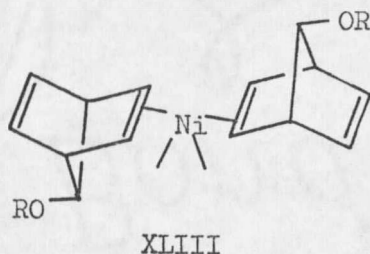
XII R = H

chromatographic analysis. This lack of success could be attributed to a very stable complex such as XLII being formed between the metal and the substrate. The formation of a stable chelate complex such as XLII



might prevent further reaction, since the bonded olefins may not be in a favorable disposition to interact (the bonded olefins are at right angles to each other). Other alternatives to explain the inactivity of this substrate might be suggested. For example, one could envision the blockage of one exo side of each norbornadiene simply by steric bulk. Thus if it were reasonable to assume an exo-exo diNBD specie (XLIII)

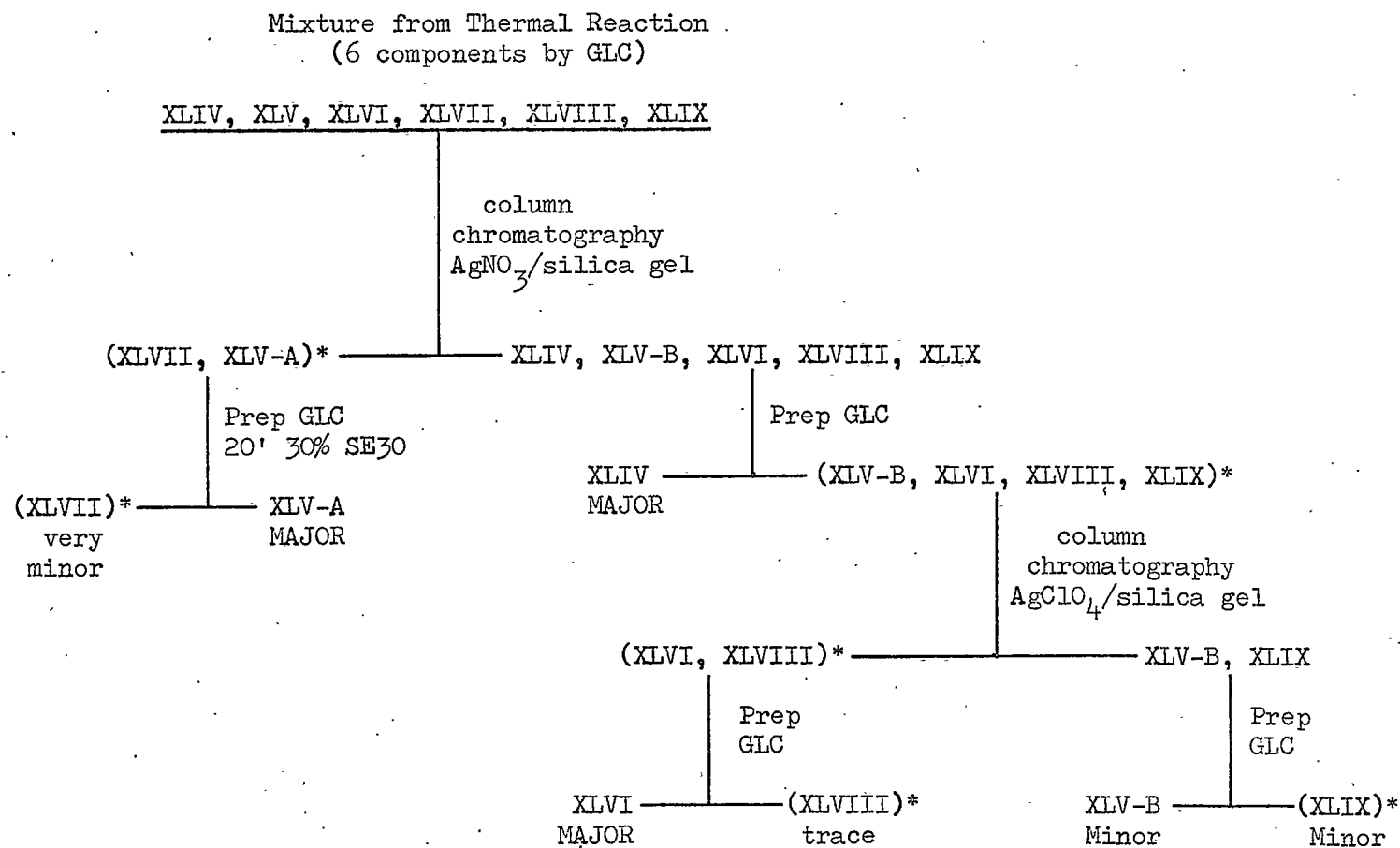
was necessary for dimerization (and involved in the rate expression), the rate would be one quarter of that in the unsubstituted case, based on statistical factors alone. In the case of 7-hydroxy-NBD (XLI),



oxidation of the nickel with concomitant hydrogen gas formation is a reasonable explanation for lack of product formation.

7-Methylnorbornadiene, Reactions and product structure assignments.

In light of the difficulty encountered with substituents containing heteroatoms, the hydrocarbon derivative 7-methylnBD was synthesized and subjected to thermal and photochemical excitation in the presence of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$. After photolyzing undiluted 7-methylnBD for about 210 hours, a significant amount of the olefin had been converted to dimers. A thermal reaction was also run with this molecule. Starting at reflux (92°C) and heating for 40-70 hours (final temperature about 105°C) resulted in nearly complete dimerization. Since gas chromatography showed that the major components of the photochemical reaction were also present in the thermal reaction and because the thermal reaction provided considerably more product to work with, the dimers from the thermal reaction were subjected to the following separation scheme.



Note: Relative yields may be given as; XLV-A ~ XLVI > XLIV >> XLV-B > XLIX >> XLVII >> XLVIII

*Note: In each of the above subseparations, the dimer or dimers denoted by * were retained longer (had longer GLC retention times or required a greater quantity of, or more polar elutant for the column chromatography separations).

Figure 21

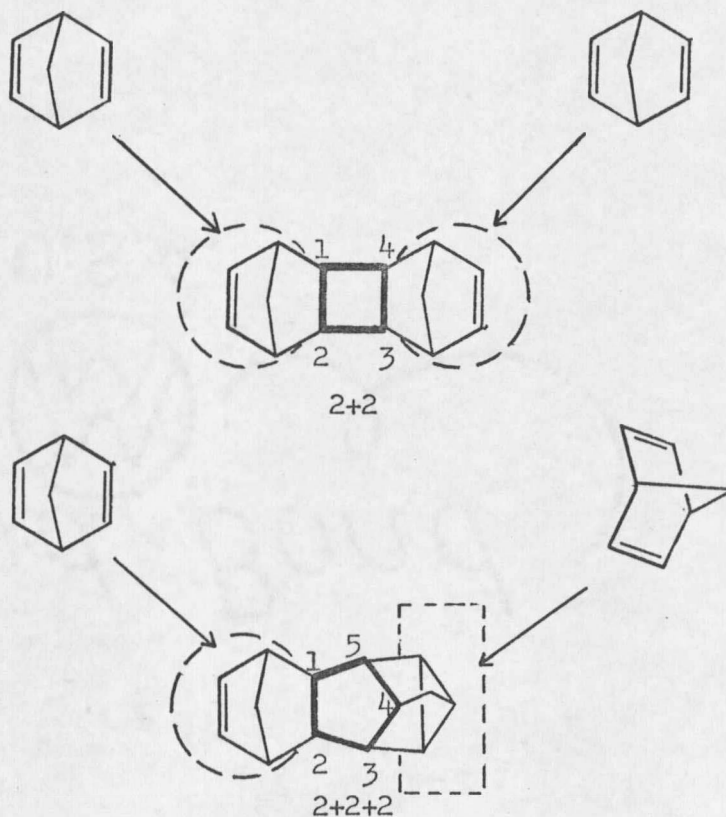
Although the initial gas chromatogram showed six components, column chromatography on silver nitrate impregnated silica gel followed by another gas chromatographic analysis showed one of the "components" (XLV) to be two compounds (XLV-A and XLV-B). Only a limited separation could be achieved with silver nitrate impregnated silica gel column chromatography. However, by the use of preparative gas chromatography as well as column chromatography on silver ion impregnated silica gel (both the perchlorate and the nitrate), one could obtain complete separation. Attention is drawn to the fact that silver perchlorate which probably is a source of "rawer" silver ion^{38,39} could effect a separation which was impossible with silver nitrate.

Once separated, the NMR spectra were taken for all the dimers except XLVIII since it was obtained in a very small quantity. Analysis of the NMR spectra (see Appendix I for the spectral data and its analysis) provided the structural assignments given in Figure 22. Note that the numbers following the thermal and photochemical designations refer to estimations of the relative amounts of a particular dimer formed with the specified mode of excitation. These estimates were based on peak heights from gas chromatographic analysis of the product.

The photochemically obtained products were assigned their structures by comparison with samples from the thermal reaction. Both silver ion impregnated silica gel thin layer plates and gas chromatography were used for these comparisons.

Nomenclature for NBD dimers. An explanation of the nomenclature to be used here as well as in the remainder of this portion of the thesis is given here.

- 1) Dimers are referred to either as 2+2 (two double bonds form a cyclobutane ring) or as 2+2+2 (three double bonds form cyclopentane and cyclopropane rings).



- 2) 2+2 dimers are assigned three stereochemical designations.

- a) Two of these designations concern the stereochemistry of the carbon-carbon bonds to the two norbornene fragments, e.g. exo- -exo (abbreviated x-x). Note that in no case is there

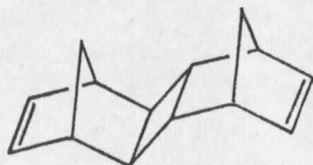
any 1,2 (or 3,4) trans substituted cyclobutane formed, i.e. the cyclobutane ring is flat.

- b) The third designation concerns the disposition of 1,2 substituents (cyclopentene fragments, circled) relative to 3,4 substituents (also circled). Both trans and cis are conceivable, but only the trans disposition is found in the 2+2 dimers reported in the literature.

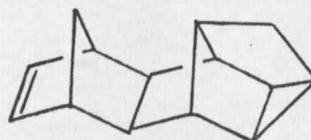
3) 2+2+2 dimers are also assigned three stereochemical designations which are based on the following sequence.

- a) Norbornene fragment (always specified first); carbon-carbon bonds are either exo (x) or endo (n).
- b) The cyclopentane ring; 1,2 substituents (circled) are cis (c) or trans (t) to 3,5 substituents (marked by a square). Note that in all cases a substituent of carbon 1 is cis to one on carbon 2, and a substituent on carbon 3 is cis to one on carbon 5.
- c) Nortricyclane fragment; always bonded on the endo side in 2+2+2 dimers of NBD and always specified last.

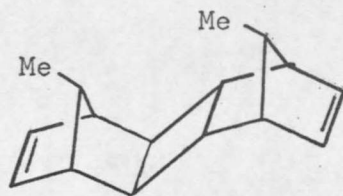
Thus, the total designation of a dimer should be noted since the following dimers might otherwise be confused.



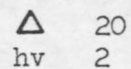
2+2 xtn



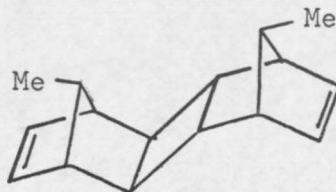
2+2+2 xtn



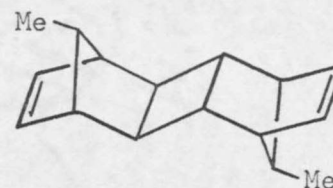
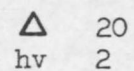
XLV-A



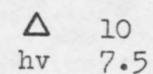
2+2 exo-trans-endo (xtn)



XLVI



XLIV

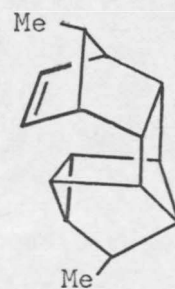
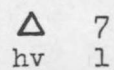


2+2 exo-trans-exo (xtx)



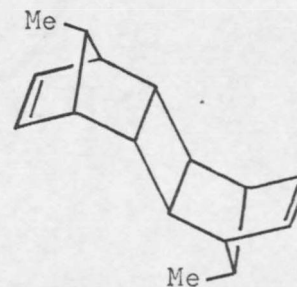
XLV-B

2+2+2 exo-cis-endo (xcn)



XLIX

2+2+2 endo-cis-endo (ncn)



XLVII

2+2 endo-trans-endo (ntn)



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Figure 22
Structures of 7-MethylNBD Dimers

Structure and product distribution relationships for 7-methylNBD

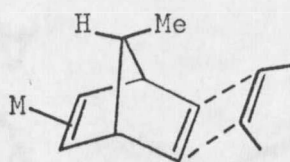
dimers. A cursory examination of these product assignments reveals some general relationships between structure and product distribution.

- a) The major "thermal" dimers are those having the 2+2 xtn and 2+2 xtx skeletons (xtn:xtx, 4:1).
- b) The major photochemical dimer has the xtx skeleton. These findings are qualitatively consistent with the results from the reaction of NBD with $\text{Ni(CO)}_2(\text{P}\phi_3)_2$ run under similar conditions; photochemical xtx > 90%, thermal xtn:xtx, 2:1.
- c) The rate of dimerization is significantly slower than that of NBD itself. Therefore, side reactions in the dimerization of NBD could become more important with 7-methylNBD. However, it should be noted the 2+2 dimers do account for about 81% of the dimers produced.

It is therefore suggested that a similar reaction mechanism is operating for both 7-methylNBD and NBD itself. The 7-methylNBD molecule is a perturbation on NBD and its dimerization reactions do not warrant a completely separate mechanistic picture. On further examination some other points may be made.

- d) There is no dimer formed in which a methyl group is syn to an exo bonded cyclobutane. Brown's work⁴⁰ with 7-substituted NBD derivatives can be noted here. He found 7-methyl groups syn to the olefin would severely inhibit silver ion complexation and

this inhibition can probably be generalized to other metals. Furthermore, there should be a strong steric interaction when a methyl group is syn to an incipient cyclobutane. Thus the possibility of a metal species bonding exo to one side of a NBD, thereby inducing (via a transannular interaction) a propensity for the other exo side to participate in dimer formation is unlikely.



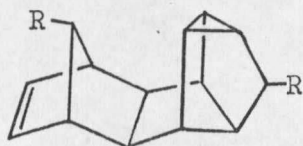
e) In 2+2 dimers there appears to be a statistical distribution of methyl groups on norbornene fragments having the cyclobutane endo bonded, cf. the 2+2 xtn dimers XLV-A and XLVI and the 2+2 ntn dimer XLVII. Thus, formation of an endo bonded cyclobutane probably arises from a specie with the metal bonded endo to the incipient endo fragment.

Based on statements d and e above, and assuming the mechanism for dimer formation involves the stereospecific complexation of two olefins to the same metal,^{4,17a,25} followed by closure in either a concerted or a non-concerted manner, a statistical comparison of 7-methylnbd and nbd dimerizations can be made. Only one of the four possible modes of complexation leading to dimer XLIV is possible with 7-methylnbd. Thus the effective concentration of 7-methylnbd is reduced by $\frac{1}{4}$. Only two of

four possible modes of complexation can lead to dimers XLV-A and XLVI. So the effective concentration of 7-methylNBD is reduced by $\frac{1}{2}$ relative to these dimers.

Since the 2+2 xtx dimer (XLIV) is reduced by $\frac{1}{4}$ and 2+2 xtn dimers (XLV-A and XLVI) are reduced by $\frac{1}{2}$, dimer XLIV is reduced by $\frac{1}{2}$ relative to dimers XLV-A and XLVI. Since the approximate ratio of XLV-A and XLVI to XLIV is experimentally found to be 4:1, a ratio of $(\frac{1}{2})^4$:1 or 2:1 would be suggested for the 2+2 xtn to 2+2 xtx ratio in the dimerization of unsubstituted NBD. This is the value reported. This provides further evidence the mechanism(s) operating in the dimerization is only a perturbation on that (those) for NBD.

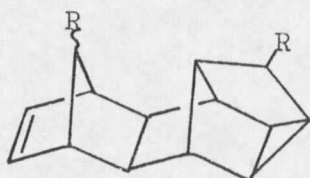
f) It may be noted that the 2+2+2 dimer XLV-B has the skeleton of the major 2+2+2 dimer xcn from $\text{Ni}(\text{CO})_4$. However, the 2+2+2 xtn dimer skeleton is not formed from 7-methylNBD and $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ although the corresponding NBD dimer is produced with $\text{Ni}(\text{CO})_4$.



2+2+2 xcn skeleton

Formed by $\text{Ni}(\text{CO})_4 + \text{NBD}$, $\text{R} = \text{H}$

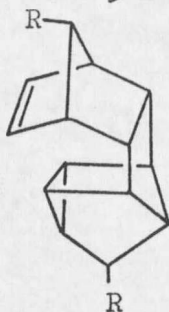
Formed by $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2 + 7\text{-methylNBD}$, $\text{R} = \text{methyl}$



2+2+2 xtn skeleton

Formed by $\text{Ni}(\text{CO})_4 + \text{NBD}$, $\text{R} = \text{H}$

Not formed by $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2 + 7\text{-methylNBD}$, $\text{R} = \text{methyl}$



2+2+2 ncn skeleton

Not formed by $\text{Ni}(\text{CO})_4 + \text{NBD}$, $\text{R} = \text{H}$

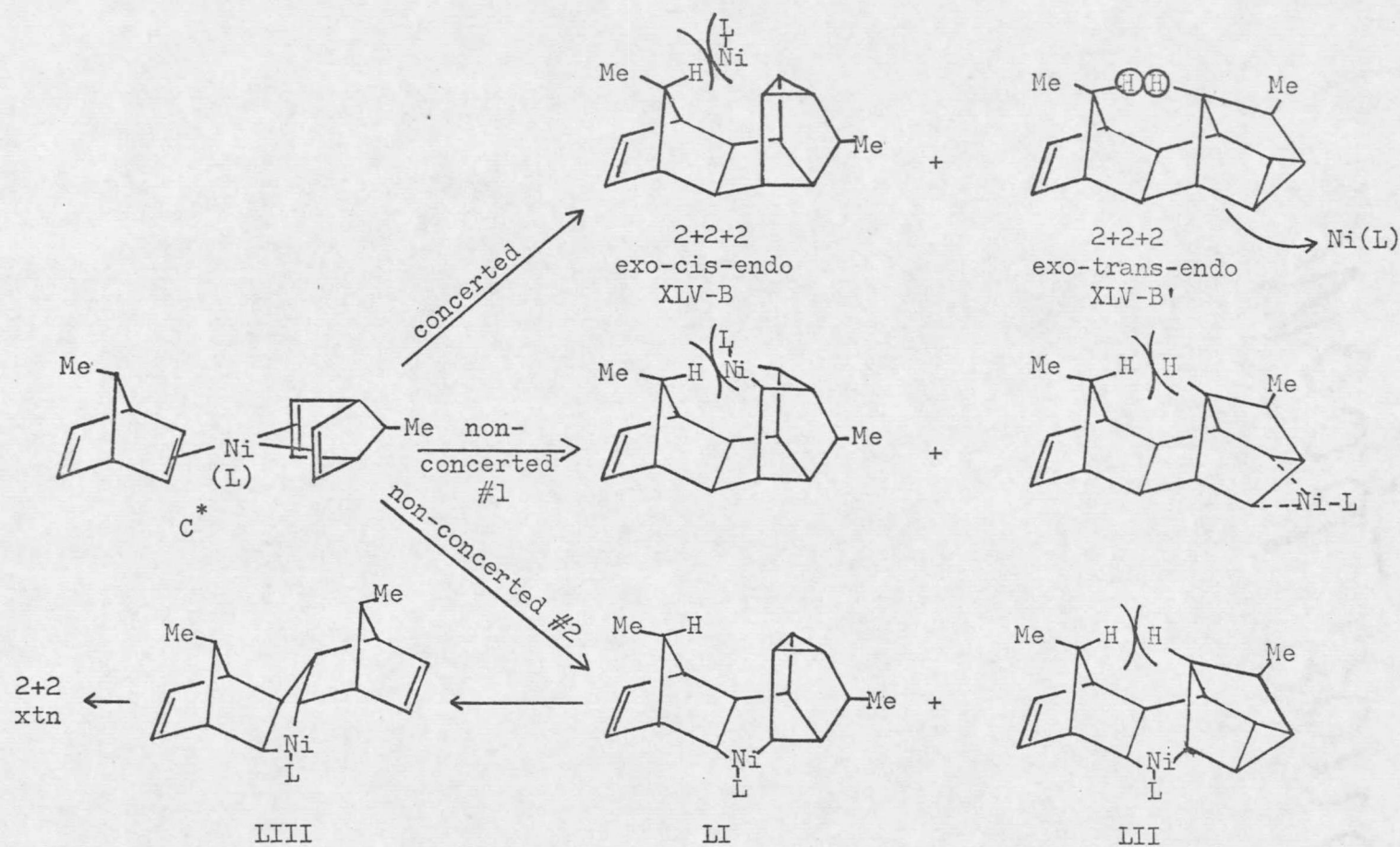
Formed by $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2 + 7\text{-methylNBD}$, $\text{R} = \text{methyl}$

Thus, it is suggested that in the $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2/7\text{-methylNBD}$ reaction, at least, the formation of 2+2+2 xtn and 2+2+2 xcn type dimers are probably independent. The stereochemical combination of 2+2+2 dimer skeletons (xcn and ncn) formed in the 7-methylNBD/ $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ system has been found in at least three other cases. The dimerization of NBD with 5% rhodium on carbon⁴¹ under thermal conditions provides these two, 2+2+2 xcn and 2+2+2 ncn (7:1), as nearly the exclusive dimeric product (2.8% 2+2 xtx is also formed). Dicobaltoctacarbonyl also produced these two 2+2+2 dimers as well as the 2+2 xtx, xtn and ntn dimers.²⁵ Using the promoter 1,4-diphenylbutadienetetracarboxyliron and NBD with photochemical activation, the two 2+2+2 dimers and the 2+2 xtx dimer are

formed.⁴²

At this point one can examine the stereochemical dispositions of the various dimers, both 2+2 and 2+2+2, formed in the thermal reaction of 7-methylNBD, and attempt to correlate their formation with mechanistic hypotheses. As in the application of deductive reasoning to any incomplete body of information, this can only result in the elimination of some possibilities as being unlikely. The application of inductive reasoning to the same body of information can only suggest likely possibilities. Thus, the application of both types of reasoning can possibly provide some working hypotheses to be tested. This is the intended purpose in the following stereochemical-mechanistic correlation.

To explain the absence of the 2+2+2 xtn dimer, a steric interference argument could be made involving the interaction between the bridge hydrogen and the bridgehead hydrogen (both circled) in structure XLV-B' of Figure 23. However, it is not clear that in the concerted or the first non-concerted path shown, the alternative steric interactions forming the 2+2+2 xcn dimer, XLV-B, are any less of a problem. It would seem more reasonable to propose the second non-concerted path as the predominant mode.



* Note: Complex **C** could also be bonded endo to the 7-methylNBD in a monodentate fashion and the steric considerations would still be essentially the same. This is due to the restrictions placed on the spatial disposition of molecules in any intermediate which could reasonably lead to such a rigid structure as the 2+2+2 dimers.

Figure 23

Stereochemical Interactions in Intermediates Leading to 2+2+2 Dimers

Sequences are shown in Figure 24 below, where the two stereoisomers of complex C are distinguished as C_1 and C_2 . In complex C_1 , the ligand L, to relieve steric interaction with the bridge hydrogen, is not in the bridge carbon-nickel-bridgehead carbon plane; the plane of the paper in Figure 24. Thus the two norbornadiene molecules are juxtapositioned to favor formation of LI because carbons a and b are moved closer at the expense of the c-d distance. Furthermore, in the sequence $C_1 \longrightarrow LI$, the formation of the cyclopropane ring probably decreases steric interaction. This is in contrast to the concerted path or the first non-concerted path where, as shown in Figure 23, the Ni-L/bridge hydrogen interactions probably increase as the reaction proceeds. The steric interference between the bridge hydrogen and the bridgehead hydrogen appears to be much more severe and much less readily relieved (by canting of the norbornadiene molecules) in the complex C_2 than are the steric interactions in C_1 . Thus, there ought to be a stereochemical preference in the formation of the initial complex (C_1 or C_2), with the formation of C_1 being favored.

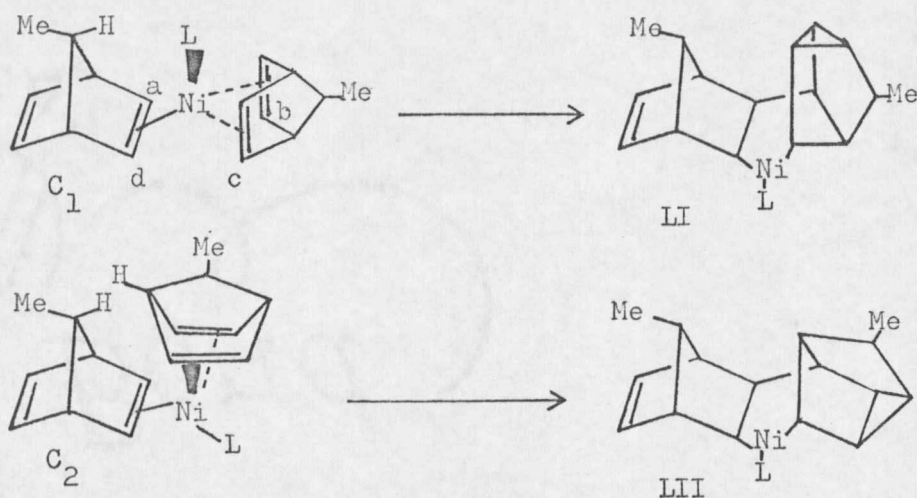


Figure 24

Stereoisomers of Complex C Leading to 2+2+2 xcn and 2+2+2 xtn

Further, in the case of the $C_2 \rightarrow LII$ sequence, steric interactions are also relieved but to a lesser extent than in the $C_1 \rightarrow LI$ sequence. It is suggested complex C_1 leading to intermediate LI therefore is the favored process.

As noted in Figure 23, it is possible to propose that intermediate LI may also serve as one route to the 2+2 xtn dimers XLV-A and XLVI. Thus, in light of the electron donating character of the edge of a cyclopropane ring^{43,44} one could expect the backside of the nickel to be available for attack as shown in Figure 25. Such an attack could lead to the intermediate $LIII$ with no necessity to invoke a "homoallylic" bonding situation, (cf. page 27 ff.) although that possibility could not be ruled out.

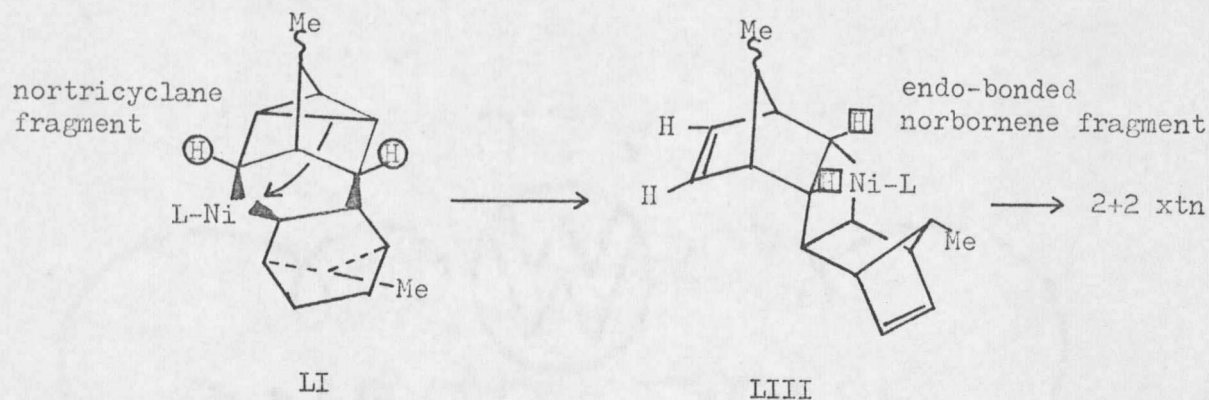


Figure 25

Stereochemical Considerations in Complex LI Influencing
the Position of the Methyl Group in 2+2 xtn 7-methylNBD Dimer

There is, however, one complication which must be considered here. If one proposes complex LI going to complex LIII, then there ought to be a stereochemical preference of the position of the methyl group in the endo bonded norbornene fragment of the product. In the complex LI of Figure 25, both circled hydrogens would interact sterically about equally. These hydrogens constitute by far the major steric effect relative to the methyl group in the nortricyclane fragment. Thus there would be no particular preference for which side the methyl would be on in the nortricyclane fragment. However, in complex LIII the endo bonded norbornene fragment - which was the nortricyclane moiety - presents two rather different steric demands to a bridge methyl group. The incipient cyclobutane side has two exo hydrogens (marked by squares in complex LIII) which ought to present significant steric bulk to a methyl group near

them.⁴⁵ The olefinic side, however, presents no such interaction and, in fact, ought to provide steric interaction which is less than that found in the progenitorial complex LI. Preference for the methyl group being syn to the olefin is not found in the 2+2 dimers XLV-A and XLVI, and thus it is suggested the non-concerted path $C \rightarrow LI \rightarrow LIII \rightarrow 2+2$ xtn dimer is probably not reasonable. It is suggested, based on the same reasoning, that any sequence leading to 2+2 xtn dimer which involves the formation of complex LIII is unlikely, since it is inconsistent with the statistical disposition of methyl groups on the endo bonded norbornene fragment. It is therefore difficult to envision a non-concerted directly metal-mediated path to the 2+2 xtn dimers XLV-A and XLVI.

In a similar fashion one could visualize complex LIV (Figure 26) leading to intermediate LV (and hence to the 2+2+2 non dimer) and possibly intermediate LVI, providing a path to the 2+2 ntn dimer.

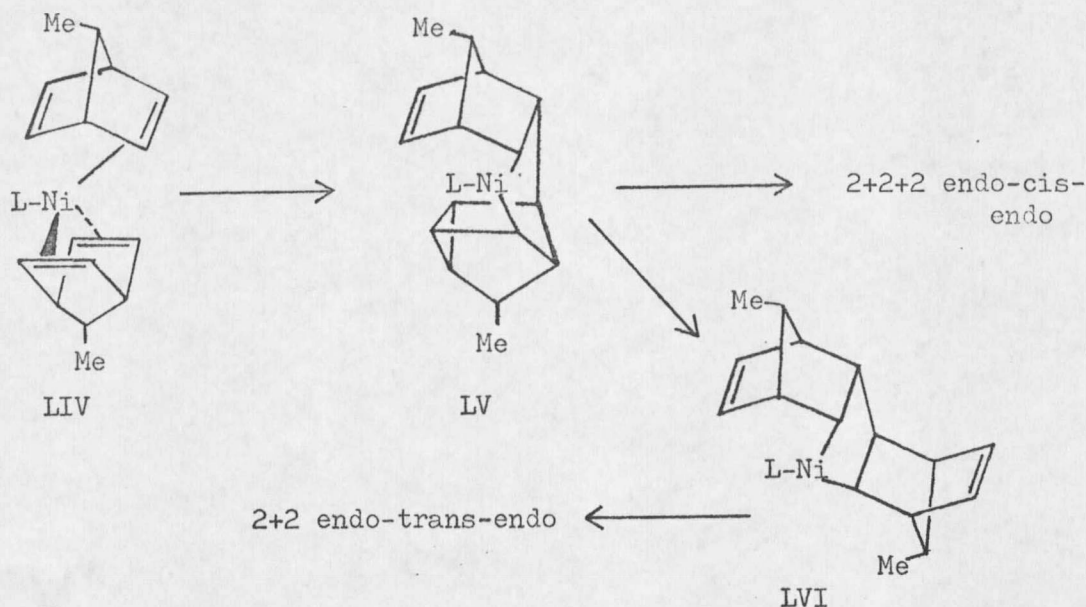


Figure 26

Stereochemical Considerations in the Formation of
2+2+2 ncn and 2+2 ntn 7-MethylNBD Dimers from Complex LV

Why the methyl group should be syn to the olefin in this 2+2+2 product could thus be rationalized by two explanations. The first of these is based on the results of both proton^{46,47} and carbon 13 ^{48,49} nuclear magnetic resonance spectroscopy from which it is clear the presence of a 7-methyl alters the electron density about the olefinic carbons (and presumably the olefinic bond itself). This might result in preferential bond making or breaking.

Another explanation would be to look at complex LIV (Figure 26) as a bis(endo,endo-7-methylNBD)nickel species LIV' (Figure 27). Thus, L in complex LIV is the remaining uncomplexed endo side of the

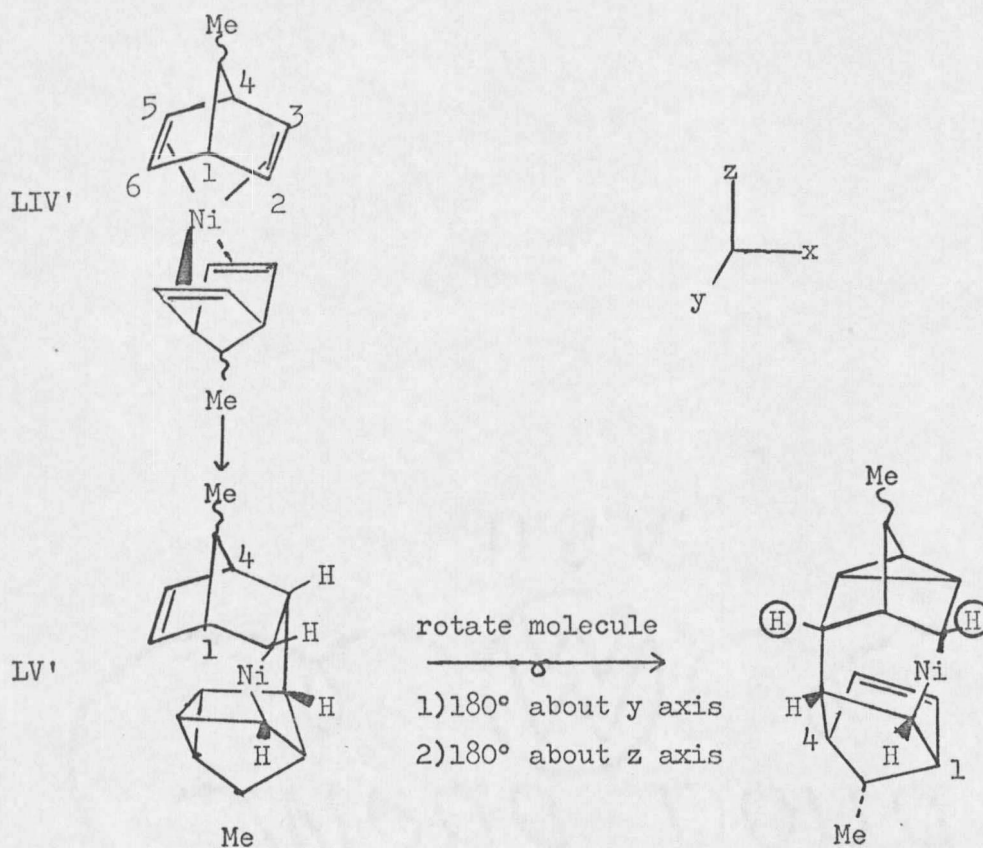


Figure 27

Stereochemical Considerations in the Formation of
the 2+2+2 ncn 7-MethylNBD Dimer

monodentate NBD and both NBD molecules become bidentate in complex LIV'. As the intermediate LV' is formed, the methyl could be either syn or anti to the olefin in the norbornene fragment. In this process of going from the π -bonded intermediate LIV' to the σ -bonded intermediate LV', carbons 2 and 3 change from sp^2 to sp^3 hybrids. This results in the swinging up, to the exo side, of the hydrogens attached to these carbons. If the

methyl group were on the same side as these "new" exo hydrogens the steric interference would be greater than if the methyl group were anti to them (syn to the olefin). Thus, the methyl is predicted to be syn to the olefin as is found to be the case. The position of the methyl on the nortricyclane fragment would be statistical since the steric requirement would be virtually the same on either side.

An analysis of the path $IV \rightarrow LVI \rightarrow 2+2$ ntn dimer (Figure 26) could be made in a fashion similar to that done for the $LI \rightarrow LIII \rightarrow 2+2$ xtn dimer sequence (Figure 25). The prediction would be for a preferential formation of the 2+2 ntn dimer with both methyls syn to olefins. In fact, the statistically favored dimer with one methyl syn and one anti to the respective olefins is found. Thus here as well, it appears a common intermediate leading to both 2+2+2 and 2+2 dimers is unlikely. Further, by analogy with the arguments given for the 2+2 xtn dimers, page 50, it is deemed unlikely that the 2+2 ntn dimer (XLVII) is formed by a non-concerted process.

The result of the dimerization of 7-methylNBD can therefore be summed up as follows:

- 1) The mechanism is probably quite similar to that of NBD itself for both the thermal and photochemical reaction.
- 2) Transannular energy transfer leading to dimer is unlikely.
- 3) 2+2+2 and 2+2 dimers are probably formed by different mechanisms.
- 4) It is suggested that the non-concerted paths $C_1 \rightarrow LI \rightarrow 2+2+2$ xcn (Figures 23 and 24) and $LIV' \rightarrow LV' \rightarrow 2+2+2$ ncn (Figure 27) can

best account for the formation of the observed 2+2+2 dimers.

- 5) Non-concerted mechanisms involving complexes LIIII and LVI cannot explain the formation of the observed 2+2 xtn (XLV-A, XLVI) and 2+2 ntn (XLVII) dimers. Since it is difficult to suggest non-concerted, direct metal-mediated paths which do not involve these complexes, it is suggested a concerted path may be more reasonable.
- 6) Virtually nothing can be said about the formation of the 2+2 xtx dimer XLIV other than its formation may involve the initial complexation of two NBD molecules on the exo side, anti to the methyl group.

Structural Modifications - Electronic Factors

As noted at the outset of this discussion, an examination of structural perturbations of the NBD molecule which result in a significant alteration of the electronic nature of that molecule were also studied. It is very probable that the primary electronic interactions between NBD molecules and nickel species involve the olefinic bonds of NBD. Thus, modification of the olefinic bonds in NBD by alteration of its structure was the method chosen to examine substrate electronic factors. Three molecules were chosen for study: norbornene, the 2+2 xtx NBD dimer and [2,2,2]bicycloocta-2,5-diene. Norbornene could be viewed as a model for one side of a NBD molecule and would provide a probe for the importance of olefin-olefin interaction in the NBD molecule. It is known^{17a} that the 2+2 xtx NBD dimer will co-dimerize with NBD. Thus it was felt

a study of a norbornene-olefin system, perturbed by an exo bonded cyclobutane, might provide a "graded" interaction scale from norbornene to NBD. Finally, the NBD homolog [2,2,2] bicycloocta-2,5-diene was to be studied for similar reasons.

The reaction of norbornene and $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ was run thermally as a melt of neat norbornene. The mixture was heated at about 90°C for three days. However, although the solution became yellowish, no dimeric product could be found by gas chromatographic analysis. A similar experiment was run with the 2+2 exo-trans-exo dimer which may be viewed as a modified norbornene, except in this case just enough hexane was added to effect solution of the dimer. After refluxing six days, the solution had become yellowish, but on work-up no tetramer could be detected.*

It is felt the results of these two experiments suggest either of two alternatives, a) no complex is formed, or b) a complex is formed but it does not lead to cycloaddition products. A thorough investigation of these systems was not attempted. However, the formation of yellow solutions is reminiscent of the behavior of norbornene and the 2+2 xtx dimer with $\text{Ni}(\text{CO})_4$ observed by Voecks. In that system, complex formation was readily observed, but dimerization could not be achieved. Thus

* Note: If one heats a neat mixture of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ and the NBD 2+2 xtx dimer to 160-180°C, a solution is obtained and a gas, presumably carbon monoxide, is evolved. The infrared spectrum shows a significant decrease in the intensity of the two CO peaks (2000 cm^{-1} and 1955 cm^{-1}). Prolonged heating under these conditions results in nickel being plated out.

the second alternative - "unfruitful" complex formation - may be a more suitable description of the observed behavior of norbornene and the 2+2 xtx dimer.

The homolog of NBD, [2,2,2] bicycloocta-2,5-diene (dihydrobarrelene), shown in Figure 28, was synthesized and reacted as an isopentane solution with dinitrosyldicarbonyliron(0), $\text{Fe}(\text{CO})_2(\text{NO})_2$, using photochemical activation. Three other dimerization reactions using thermal activation were also attempted with benzene solutions of dihydrobarrelene and the following promoters: $\text{Fe}(\text{CO})_2(\text{NO})_2$, $\text{Ni}(\text{CO})_4$, and 5% rhodium on carbon. The choice of promoters used was made as follows. The NBD 2+2 xtx dimer is the most frequently encountered NBD dimer, considering all the promoters which have been used for dimerization. Dinitrosyldicarbonyliron is the most active of the promoters reported for producing the 2+2 xtx NBD dimer, when used either photochemically or thermally.^{17a,37} The use of $\text{Ni}(\text{CO})_4$ was prompted by its ability to form the 2+2 xtn and ntn NBD dimers thermally.^{17a} Rhodium on carbon is known to thermally dimerize NBD to give 2+2+2 xcn and ncn dimers.⁵⁰ Thus, although a large number

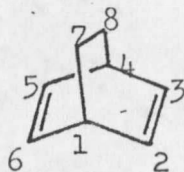


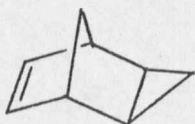
Figure 28

Dihydrobarrelene

of promoters were investigated to provide a wide range of dimer skeletal types, none of the reactions produced dimer as shown by gas chromatographic and/or NMR analysis. It was noted, however, that in the cases of Ni(CO)_4 and $\text{Fe(CO)}_2(\text{NO})_2$, color changes (colorless to yellow and red to dark red, respectively) occurred, suggesting an "unfruitful" complex may have been formed here as suggested in the norbornene and 2+2 xtx dimer reactions with $\text{Ni(CO)}_2(\text{P}\phi_3)_2$ (vide supra).

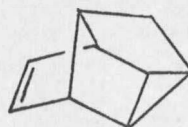
It was felt the reactivity of NBD in transition metal promoted cyclo-dimerization reactions could be interpreted as a function of the interaction of its two double bonds. The lack of reactivity of the mono-olefin, norbornene, would be in accord with this hypothesis. It was hypothesized that interaction of a norbornene-type olefinic bond with the edge of an exo bonded cyclobutane might result in sufficient activation of the double bond to promote dimerization. The 2+2 xtx NBD dimer is an example of just such a system and its known co-dimerization with NBD to form NBD trimer^{17a} was encouraging.

Part of the rationale for possibly expecting the cyclobutane to activate the olefin was based on an analogy with the cyclopropane analogs. It is known that norbornene derivatives such as LVII⁵¹ and LVIII⁵² will dimerize with 5% rhodium on carbon although in much lower yields, considerably higher temperatures and with longer reaction times than those used for NBD.



LVII

130°C
48 hours
15% yield of dimer



LVIII

185°C
42 hours
5% yield of dimer

The dimeric products are suggested to have the 2+2 xtx skeleton. It is also interesting to note that in the case of 5% rhodium on carbon, norbornene was found to be inactive alone or in crosscoupling experiments with NBD.⁵²

As noted, it was found that, in fact, the 2+2 xtx dimer is inactive towards cycloaddition in the absence of NBD, and that dihydrobarrelene is also inactive. These results, in light of the above proposed hypotheses, suggest a re-evaluation of the degree of olefin activation to be expected in these (and similar) cases is necessary. Equally important to consider is the influence of such activation on metal-promoted cyclo-dimerization reactions.

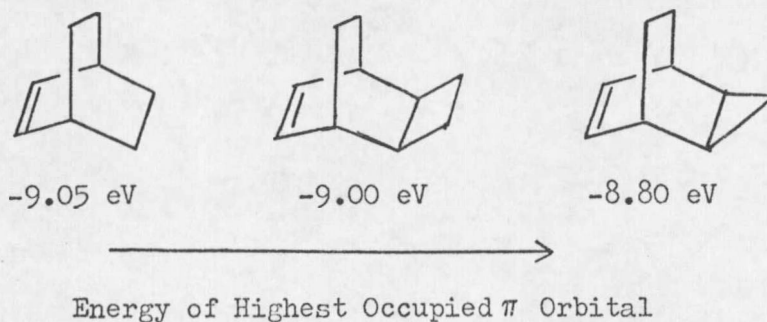
To aid in this re-evaluation, extensive use shall be made of the results from photoelectron spectroscopy, a technique which has been shown to yield valuable information about the nature of electronic interactions in molecules. Photoelectron spectroscopy shows there is an interaction between the exo cyclopropane and the olefin bond in LVII, resulting in a lowering of the energy of the olefin by about .05 eV (interaction

parameter ≈ 0.3 eV) relative to the olefin in norbornene. By comparison, the energy of the highest occupied olefin orbital in NBD is 0.25 eV higher than that in norbornene (interaction parameter ≈ 0.4 eV), and .20 eV higher than the olefin in LVII.⁵³ It is suggested that the cyclobutane moiety would be less effective in raising the energy of the highest filled π orbital than would a cyclopropane or another olefin.* Thus an exo cyclobutane such as is present in the xtx dimer may provide sufficient activation of a neighboring olefin to allow it to react with a complexed NBD (producing trimer), but may be insufficient to activate two dimers to form tetramer.

It may be noted that photoelectron spectroscopy shows the highest occupied π orbital of dihydrobarrelene to be 0.18 eV below that of NBD or about equal to that of the exo cyclopropano-norbornene, LVII.⁵⁵

Note also that there appears to be a significantly

* Support for this argument comes from the photoelectron spectroscopically obtained values for the energy of the highest occupied π orbitals in the following molecules.⁵⁴



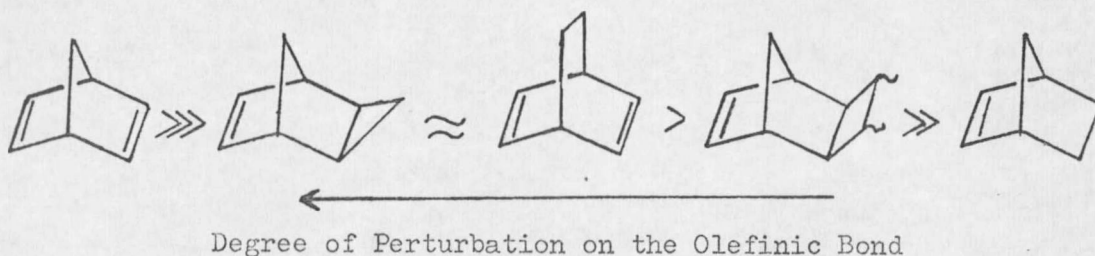
more severe steric demand in the 2+2 dihydrobarrelene dimer with the xtx skeleton compared to the same NBD dimer skeleton.



Since $\text{Fe}(\text{CO})_2(\text{NO})_2$ promotes the formation of the 2+2 xtx NBD dimer,^{17a,37} it might be expected, on steric grounds, to be less effective here than with NBD.

Nickel tetracarbonyl favors the production of 2+2 endo bonded NBD dimers, but since it shows low activity as a promoter for NBD dimerization,^{17a} it may not be effective with dihydrobarrelene. As noted earlier, rhodium on carbon will dimerize the less reactive exo cyclopropano-norbornenes, LVII and LVIII, but only under much harsher conditions than were used in the experiments run with dihydrobarrelene.

As a result of the photoelectron spectral data given above for the various olefins the following sequence can be given.



The influence of the activation of olefins by neighboring moieties in metal promoted cyclodimerizations might best be discussed in terms of the "fruitful" versus the "unfruitful" complex. It is known that both NBD and norbornene are capable of bonding to metals on the exo side of the olefin. In cases where this behavior has been observed (Ag olefin, Cu olefin, $\pi(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{olefin})$), the complexing olefins (norbornene and NBD included) act principally as electron donors, with π -back donation being minimal.⁵⁶ The double bond in these cases is weakened only slightly as shown by the small shift in $\nu_{\text{C}=\text{C}}$ in the infrared spectra. Complexes of this sort do not generally lead to dimeric product (unfruitful complexation).*

In order to have an olefin complex lead to dimeric product, it is suggested that a significant weakening of the olefin bond must occur.

* Note: Photolysis of the AgNO_3 complex of norbornene and NBD does not produce dimers.⁵⁷ The $\pi(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{NBD}$ complex is formed by photolysis of $\pi(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{NBD}$ with no dimer being formed.⁵⁸ The photolysis of the CuI^5 complexes of norbornene, producing norbornene dimer, and NBD, producing quadricyclane,⁵⁹ may well follow a path very much different from that operating with complexes which are known to promote NBD dimerization.

The most probable way this could be achieved would be by π -back donation of electron density into the anti-bonding orbital of the olefin. This can occur only if an approximate energy and symmetry match exists between filled metal d orbitals and olefin anti-bonding orbitals. Based on the photoelectron spectra and molecular orbital assignments for NBD, the following correlation diagram can be drawn.

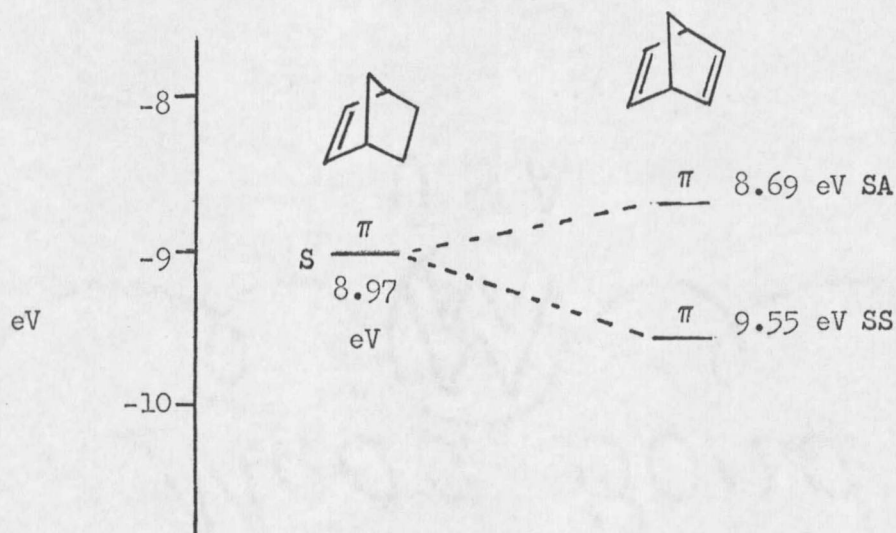


Figure 29

Correlation Diagram for Norbornene-Norbornadiene

Thus the interaction of two "norbornene-type" olefins results in a raising in energy of the highest occupied π orbital, providing activation of the olefin. But, the important effect here is twofold and best illustrated in the diagram given by Hoffmann.⁶⁰

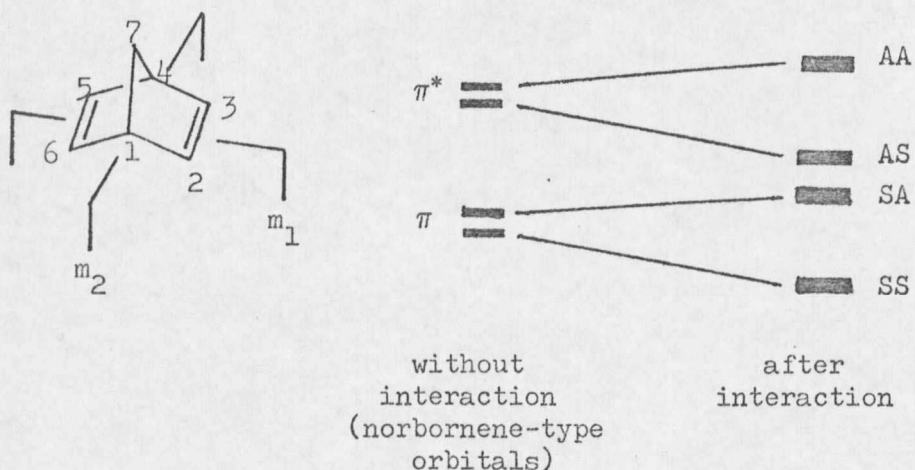


Figure 30

Norbornadiene Orbital Interaction Diagram after Hoffmann⁶⁰

Not only is the highest occupied π orbital raised, but the lowest anti-bonding π orbital is lowered by the interaction process. Lowering the energy of the anti-bonding π orbital would most likely be conducive to a better energy match between it and a filled metal d orbital.

The approximate atomic orbitals for nickel are given by T. L. Brown⁶¹ as 3d, -10.5 eV; 4s, -9.8 eV; and 4p, -9.0 eV. The assignment of π^* orbitals based on ultraviolet spectra of NBD has evoked some controversy in light of the apparent partial mixing of σ and π orbitals in NBD. However, based on the analysis of VanCatledge⁶² and the ultraviolet spectra of NBD and norbornene,⁶³ it appears that norbornene π^* orbitals are considerably more energetic than are the π^* orbitals associated with NBD.

Backbonding should, therefore, be considerably more significant with NBD than with norbornene, and "fruitful" complexation, i.e. complexation leading to weakening of the olefinic bond, ought to be favored with NBD. Thus, a relationship between perturbations on an olefin by another moiety in the molecule and successful metal-mediated cyclodimerization of the perturbed olefins can be given.

Perturbations on olefins which cause an increase in the energy of the highest occupied π orbitals at the expense of the energy of the lowest unoccupied π^* orbitals will favor transition metal cycloaddition reactions of the perturbed olefins.

This proposal can be valid only if approximate metal-olefin energy and symmetry matches exist, and no dramatic new steric demands are introduced by the perturbing moiety.

The sequence given for the degree of perturbation of the olefinic bond, page 61, provides a series of predicted reactivities in transition metal promoted cyclodimerization reactions. Thus, it is predicted that if dihydrobarrelene were subjected to the harsh conditions successful for dimerization of exo cyclopropano-norbornenes LVII and LVIII, it too would dimerize. It is further predicted that the molecule [2,2,2]bicyclo-octatriene (barrelene),⁶⁴ in which olefinic interaction raises the highest occupied π orbital to -8.23 eV (cf. dihydrobarrelene π_{highest} -8.87 eV and NBD π_{highest} -8.69 eV), ought to dimerize. The dimer will

probably not dimerize to tetramer unless the fused cyclobutane activates the remaining two olefins considerably above those in dihydrobarrelene and this is not expected.⁵⁴ It may also be noted the steric requirements imposed by dihydrobarrelene between the bridge hydrogens and the incipient

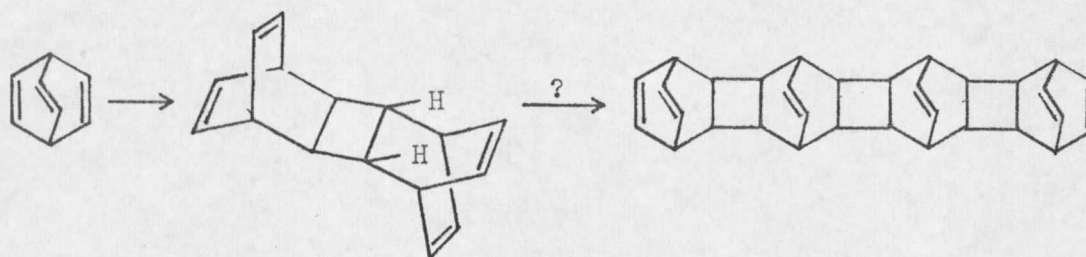


Figure 31

Oligomerization of Barrelene

cyclobutane (vide ante) are absent with barrelene, but are imposed by the dimer, a fact which also disfavors tetramer formation.

Kinetic Considerations

It has been implicitly and explicitly noted throughout the preceding discussion that electronic considerations are very important factors governing the behavior of substrate olefins. As noted at the onset of this discussion, this is also valid for coordinated ligands which are not directly involved in the cyclodimerization reaction. Thus, one is faced with a number of considerations pertinent to these indirectly involved ligands. Which ligands are lost and to what extent...temporarily or permanently? What relation do any remaining ligands have to the

electronic or stereochemical demands of the reaction? What role could ligands play in directing π or σ bonding between the metal and substrate olefin molecules?

It was with these questions in mind that an effort was initiated to probe some of these ligand related factors. A number of reactions were run with NBD, and $\text{Ni}(\text{CO})_2(\text{P}\emptyset_3)_2$ as promoter. Bis(triphenylphosphine) dicarbonylnickel was chosen for a number of reasons. As mentioned before, it is an air stable solid thus allowing for ease of experimental manipulation. Thermally, it promotes the formation of two major dimers, 2+2 xtx and 2+2 xtn, and one minor dimer, 2+2 ntn. Its reaction with 7-methylNBD was investigated. This work provided some insight into the course of the reaction as well as suggesting areas which required further investigation.

With reference to coordination, $\text{Ni}(\text{CO})_2(\text{P}\emptyset_3)_2$ is either a disubstituted nickel tetracarbonyl derivative or a disubstituted tetrakis(triphenylphosphine) nickel derivative. The thermal reaction of nickel tetracarbonyl has been investigated by Voecks^{17a}, and it has been shown to lead to 2+2 xtn (major) and 2+2 ntn (minor) dimers. The hypothesis could be made that if a dicarbonyl nickel specie such as $\text{Ni}(\text{CO})_2(\text{NBD})_2$ was responsible for the formation of xtn (and ntn) dimer in the $\text{Ni}(\text{CO})_4$ case, then the same sort of specie could arise from $\text{Ni}(\text{CO})_2(\text{P}\emptyset_3)_2$ by the loss of two $\text{P}\emptyset_3$ ligands and the addition of two NBD molecules. To carry the hypothesis further, it could be suggested that a $\text{Ni}(\text{P}\emptyset_3)_2(\text{NBD})_2$ specie formed by the loss of two carbon monoxides is responsible for

the formation of the xtx dimer and it would be predicted then, that $\text{Ni}(\text{P}\phi_3)_4$ would lead to only xtx dimer. Thus, two different active complexes could be responsible for the products obtained from $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$.

Exploratory experiments served to demonstrate some of the essential characteristics of the reaction of NBD with $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$.

- a) The reaction is very temperature sensitive; prolonged heating at 75°C produces virtually no dimer, while refluxing at an initial temperature of 85°C allows a facile reaction. This is generally observed with metal carbonyls and has been interpreted as the minimum temperature for ligand expulsion.
- b) Using neat NBD, the reaction temperature increases from 85°C to ca. 100°C during the reaction. The rate of reflux is decreased considerably as the pot temperature increases and the viscosity of the solution appears to increase. This behavior is attributed to the formation of dimer which becomes an increasingly important component in the refluxing medium.
- c) The reaction is very sensitive to refluxing. At a temperature just below reflux, ca. 81°C , very little dimerization occurs. However, if nitrogen is bubbled through the solution, reaction occurs quite readily. This suggests that "liberated" CO probably inhibits reaction by recombination.

- d) The substitution of carbon monoxide for nitrogen as a sweeping gas inhibits the reaction virtually completely.
- e) Monitoring the formation of dimers as the reaction progresses shows that after an induction period, two major 2+2 dimers (xtx and xtn) are formed at a constant rate. A third 2+2 dimer, ntn, is also produced, but only in small amounts.
- f) The xtn:xtx ratio varies with time. Very early in the reaction, during the induction period, this ratio is greater than one. This value decreases to about .25 to .50, depending on the temperature at which the reaction is run, and remains constant after the induction period. One explanation of this result is the process by which xtn is produced is perhaps less energetic than that for the production of xtx.*

As a result of these preliminary runs, a procedure was established for examining some of the kinetic parameters of the thermally induced cycloaddition reaction. The desired amount of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ dissolved in warm NBD was injected into a flask containing NBD which was already in equilibrium with a constant temperature bath. Prior to addition of the $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ solution, a stream of nitrogen was established in the reaction flask by use of a glass tube fitted with a frit. The flow of

* Such an explanation does not distinguish between factors which influence the duration of the induction period and factors which govern dimer formation when the rate of dimer production becomes constant (cf. page 80).

nitrogen was monitored with a soap bubble flowmeter. The flask was fitted with a long glass packed condenser to prevent loss of substrate by evaporation.

Samples were withdrawn from the reaction and analysed by gas chromatography using an internal standard.* A plot of the concentration of dimer versus time was made which provided a graph with the characteristics given below, while data from the various experiments is given in Table 1.

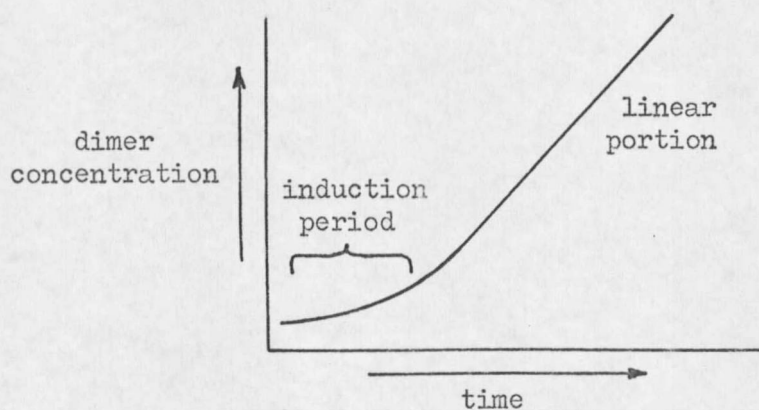


Figure 32

Generalized Concentration versus Time Plot

* For the derivation of the equation relating the standard and the dimer gas chromatographic data, see Appendix II.

Table 1

Tabulation of Kinetic Data

Temperature °C	Promoter (initial concentration)	Least squares slope of linear portion of graph $\times 10^5$		Abscissa intercept ^a $\times 10^{-3}$	
		xtx	xtn	xtx	xtn
74.2°	$\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$.0112 M	.5857	.2484	14.746	9.724
81.2°	$\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$.0112 M	12.165	2.896	5.266	5.354
85.1°	$\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$.0112 M	16.827	4.969	2.634	2.135
81.2°	$\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$.0112 M + added $\text{P}\phi_3$.00128 M	5.378	1.439	4.445	4.051
81.2°	$\text{Ni}(\text{P}\phi_3)_4$ Ca. .0112 M	1.955	.5696	-6.926	-2.953

a calculated from equation of least squares line

It is estimated this data is accurate to about fifteen to twenty-five percent, depending on the particular data. Thus, at best, the results should be treated as trends, not as absolute values. From the data for $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ at the three temperatures, one can obtain an estimate

of the energy of activation ($\Delta H^\ddagger$) for the formation of the 2+2 xtx and xtn dimers. The shape of the plots is given below.

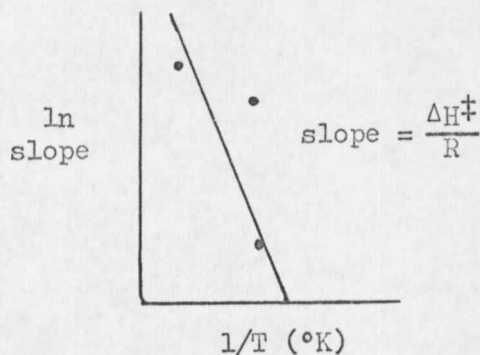


Figure 33

Plot of $\ln$ Slope vs $1/T$

A least squares analysis of the data yields values of $\Delta H^\ddagger_{\text{xtx}} = 79.96$ kcal/mole and $\Delta H^\ddagger_{\text{xtn}} = 70.24$ kcal/mole. It may be noted that during the latter part of the reaction run at 85°C , it appeared that nickel was being plated out. This may imply the actual catalytic nickel specie may have been thermally decomposing, which would account for the non-linearity of the $\Delta H^\ddagger$ plot.

Two important points concerning these reactions should be noted:

a) The reaction has an unusually high energy of activation (vide infra).

b) The implication that $\Delta H^\ddagger_{\text{xtx}}$ is greater than $\Delta H^\ddagger_{\text{xtn}}$ is probably real. For example, if the data from the reaction at 85.2°C is neglected, the two remaining data points yield $\Delta H^\ddagger_{\text{xtx}} = 102.3$ kcal/mole and $\Delta H^\ddagger_{\text{xtn}} = 82.6$ kcal/mole.

One can also examine the ratio of the amount of xtn to xtx produced versus temperature. Comparison can be made for reactions run at 81.2°C and 74.2°C, as well as for other preliminary experiments run under the same conditions except at lower temperatures. This comparison shows that formation of xtn increases in importance at lower temperatures implying its formation is a less energetic process.

As noted, the experimentally determined $\Delta H^\ddagger$ is unusually high. However, extreme sensitivity to temperature is not unprecedented for reactions promoted by carbonyl containing nickel species. Meriwether and co-workers⁶⁵ studied the reaction of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ with acetylenes leading to linear and aromatic oligomers. They reported:

"These reactions are very sensitive to temperature and degree of agitation in the solution. No polymerization was observed in unstirred solutions of 1-heptyne and catalyst in cyclohexane or acetonitrile between 25 and 75°C. However, if the solution was brought to the boiling point (about 81°) or if the solution at 75° was agitated, complete reaction occurred after a short induction period."

They also found that sweeping the solution with nitrogen or with carbon dioxide greatly facilitated reaction, whereas sweeping the solution with carbon monoxide had a strong inhibitory effect. They noted, "These results suggest that the reversible dissociation of carbon monoxide from $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ is an essential step in the formation of the 'active' catalyst. Agitation simply promotes the release of carbon monoxide gas from the carbon monoxide supersaturated solutions." Their proposed

mechanism includes an initial equilibrium step whereby carbon monoxide is reversibly displaced by the acetylene. The acetylene coordinated complex is proposed as the active catalytic specie and thus the large inhibitory effect of carbon monoxide on the rate of reaction can be readily appreciated.

Ellgen also found the expulsion of carbon monoxide from a nickel carbonyl specie to be very temperature sensitive.⁶⁶ The reaction involved the substitution of carbon monoxide by alkynes in di- μ -carbonylbis(cyclopentadienyl)nickel, $(\text{Ni}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2)$.

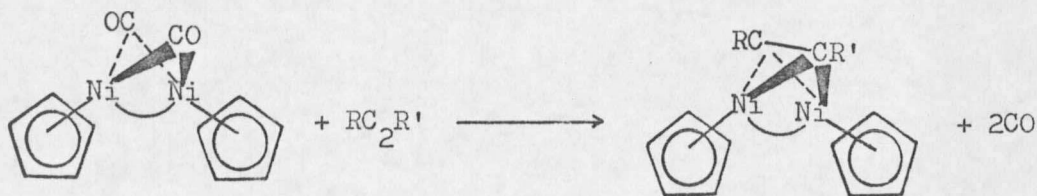


Figure 34

Reaction of Alkynes with $\text{Ni}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2$

Ellgen implies the loss of a carbon monoxide may be the first step in the reaction. It was further noted that the substitution reaction takes place at a convenient rate only at temperatures which are sufficiently high that the decomposition of $\text{Ni}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2$ is difficult to avoid. A compromise temperature of 80°C was chosen.

As will be seen later, these examples are used as models only to the extent they apparently provide instances where:

- a) Difficult initial cleavage of the metal-carbonyl bonds occurs, and/or
- b) Great reluctance for the "liberated" carbon monoxide to be completely lost from the system is observed (recombination is very likely).

Other information concerning the nature of the dimerization is provided by examining various slope ratios based on the data in Table 1.

81.2°C no added $P\phi_3$	$\frac{\text{slope xtn}}{\text{slope xtx}} = .238$	It is suggested either
81.2°C added $P\phi_3$	$\frac{\text{slope xtn}}{\text{slope xtx}} = .268$	one of two explanations may account for
		the observed in-

crease in xtn/xtx ratio. Either a) relatively more xtn is produced with added $P\phi_3$, or b) relatively less xtx is produced with added $P\phi_3$. However,

for the same two reactions as given above	$\frac{\text{slope xtx (added } P\phi_3)}{\text{slope xtx}} = .442$
	$\frac{\text{slope xtn (added } P\phi_3)}{\text{slope xtn}} = .498$

These two ratios provide evidence that the production of xtx is impeded more than is the production of xtn by the addition of $P\phi_3$.

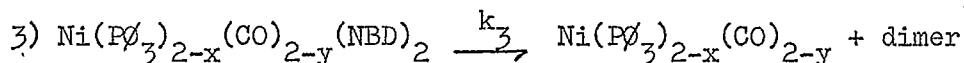
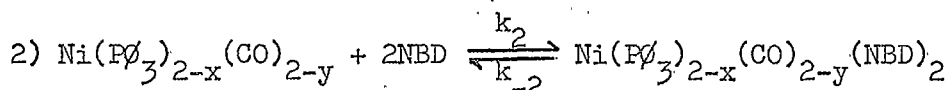
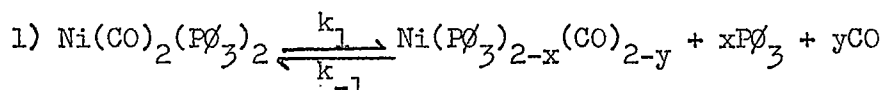
An examination of the data (Table 1) for $Ni(P\phi_3)_4$ and comparison with the data for $Ni(CO)_2(P\phi_3)_2$ is also informative.

$Ni(P\phi_3)_4$	$\frac{\text{slope xtn}}{\text{slope xtx}} = .292$
cf.	
$Ni(CO)_2(P\phi_3)_2$	$\frac{\text{slope xtn}}{\text{slope xtx}} = .238$

Thus it would appear that carbon monoxide ligands are not necessary for the production of either 2+2 xtx or xtn dimers.

It is also informative to note the dependence of the rate on the concentration of $P\phi_3$. It is not unreasonable to expect that the promoter $Ni(CO)_2(P\phi_3)_2$ loses either one or more ligands to form a true catalytic specie which is responsible for the dimerization reaction. Thus a sequence similar to the following may pertain.

$$x+y = 2$$



It is suggested that step 3 is irreversible since the NBD dimers show no apparent tendency to revert to NBD. The reversibility of the first two steps is advocated based on the reported⁶⁷ lability of nickel (as well as other metal-olefin complexes) and the fact that $Ni(CO)_2(P\phi_3)_2$ is known to undergo ligand exchange.⁶⁸ Further, it is suggested the complexation of NBD (step 2) and the formation of dimer from the NBD-nickel complex (step 3) are not intrinsically highly energetic processes.

Support for this proposal comes from two sources:

- a) Skell and co-workers⁶⁹ have found that nickel vapor may be condensed at low temperature in the presence of NBD to yield a product. This product, on warming to room temperature,

yields the 2+2 xtx NBD dimer.

- b) In our own laboratory it has been shown that divalent nickel can be electrochemically reduced in the presence of NBD at room temperature to yield both xtx and xtn 2+2 NBD dimers.

One can write the following general relationships, assuming a steady state for $\text{Ni}(\text{P}\phi_3)_{2-x}(\text{CO})_{2-y}$ and $\text{Ni}(\text{P}\phi_3)_{2-y}(\text{NBD})_2$.

$$\text{rate of formation of dimer} = \frac{k_1 k_2 k_3 [\text{Ni}(\text{CO})_2 (\text{P}\phi_3)_2] [\text{NBD}]^2}{k_{-1} (k_{-2} + k_3) [\text{CO}]^y [\text{P}\phi_3]^x + k_2 k_3 [\text{NBD}]^2}$$

thus,

$$\text{rate of dimer formation} \propto \frac{1}{[\text{P}\phi_3]^x [\text{CO}]^y}$$

Let us denote the concentration of $\text{P}\phi_3$ when no extra $\text{P}\phi_3$ is added as $[\text{P}\phi_3^0]$ and in the experiment where 1.28×10^{-3} mole/liter of $\text{P}\phi_3$ is added. let this concentration range from $1.28 \times 10^{-3} \text{M} + [\text{P}\phi_3^0]$ to $1.28 \times 10^{-5} \text{M}^*$

From the ratios noted before:

$$\frac{\text{xtx rate with added } \text{P}\phi_3}{\text{xtx rate without added } \text{P}\phi_3} = \frac{[\text{P}\phi_3^0]^x}{[\text{P}\phi_3^0 + 1.28 \times 10^{-3}]^x} = .442$$

$$x = 1 \text{ or } 2$$

* Triphenylphosphine does not substitute for carbon monoxide in $\text{Ni}(\text{CO})_2 (\text{P}\phi_3)_2$ even with heating at 210°C in a melt of $\text{P}\phi_3$ for 15 minutes. However, it is possible that NBD might substitute for carbon monoxide and $\text{P}\phi_3$ substitute for NBD. Thus, a reasonable estimate of the lower limit of the $\text{P}\phi_3$ concentration is taken to be $1/100^{\text{th}}$ of the added $\text{P}\phi_3$ concentration.

$$\begin{aligned} \text{for } x = 1 \quad [\text{P}\phi_3] &= 1.01 \times 10^{-3} \text{ to } 5.66 \times 10^{-6} \text{ M} \\ x = 2 \quad [\text{P}\phi_3] &= 2.54 \times 10^{-3} \text{ to } 8.5 \times 10^{-6} \text{ M} \end{aligned}$$

Thus, with these limits on the concentration of $\text{P}\phi_3$ from $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$, one can estimate the concentrations of $\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}$ species to be in the same range (ca. 2.5×10^{-3} to 5.7×10^{-6} M). Since the ratio of the rates without and with added $\text{P}\phi_3$ is similar for the formation of the xtn dimer, the proposed concentration would hold for any $\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}$ species leading to this dimer as well.

Since the initial promoter concentration is $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2 = 1.12 \times 10^{-2}$ M, the concentration of the active catalyst(s), $\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}$ where $x = 0, 1$ or 2 and $y = 0, 1$ or 2 , may be about 2.5×10^{-1} to 5×10^{-4} times this value. The concentration of the complex suggested as leading directly to dimer, $\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2$, is probably lower than this. Assuming the three step sequence, one may write the following relationships.

$$\text{rate of dimer formation} = k_3 [\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2]$$

If $\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2$ is subject to the steady state approximation,

$$\frac{d[\text{complex}]}{dt} = 0, \text{ the slopes of the curves of dimer concentration versus time are } k_3 [\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2].$$

Transition state theory gives the equation $\ln k = \ln(k/h) + \ln T - \Delta H^\ddagger/RT + \Delta S^\ddagger/R$. One can insert $k_3 [\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2]$ for k , add $\ln [\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2]$ to the right side of the equation, put experimental values in for $\Delta H^\ddagger$, and solve for $\Delta S^\ddagger$.

$$\text{xtx} \quad \Delta S^\ddagger = 10.539 \log [\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2] + 147.03$$

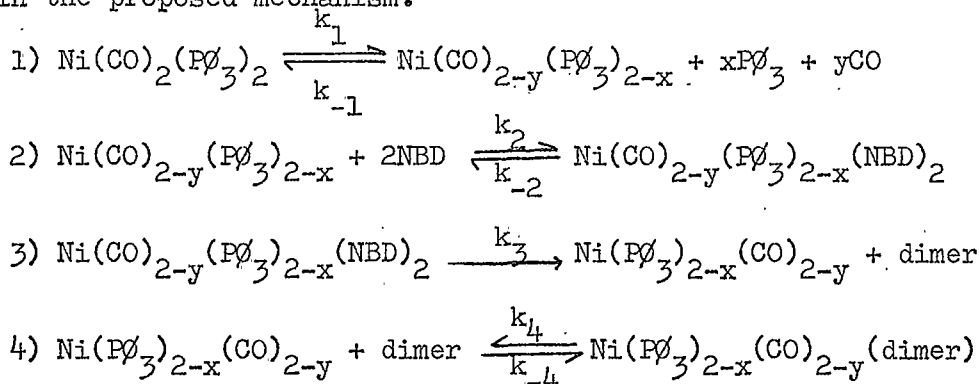
$$\text{xtn} \quad \Delta S^\ddagger = 10.539 \log [\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2] + 116.2$$

If one assumes a reasonable $\Delta S^\ddagger$ value is in the range of -20 to +20 cal/deg.mole, then $[\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2] = 8.9 \times 10^{-13} \text{ m/l}$ to $1.4 \times 10^{-16} \text{ m/l}$ for xtx and $[\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2] = 7.4 \times 10^{-10} \text{ m/l}$ to $1.2 \times 10^{-13} \text{ m/l}$ for xtn.* Although these concentrations are quite small they are not unreasonable as steady state concentrations of catalytic species. One factor which may contribute to low concentrations of species containing coordinated NBD is the presence in the solution of dimers which may competitively complex with any coordinatively unsaturated nickel species. At the point where the [dimer] versus time curves start to be linear, the dimer concentration is at least $3.14 \times 10^{-2} \text{ M}$. This is approximately three times the initial concentration of promoter. It is ca. 12 to 5,000 times the suggested, vide supra, limits on $\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}$ concentrations.

It is suggested the formation of dimer-containing complexes may effectively serve to lower the concentration of NBD-containing complexes. In light of the lack of ability of dimers to themselves dimerize as well

* Monitoring the infrared spectrum during the reaction supports the proposal that only a portion of the $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ is converted to other species during the reaction. The carbonyl absorption peaks at 1940 cm^{-1} and 1995 cm^{-1} decrease in intensity during the initiation period of the reaction, but become quite nearly constant for the remainder of the reaction.

as the relatively low yield of trimeric species in the dimerization reactions, dimers could be visualized as inhibitory ligands. In fact, the inhibitory nature of the dimers can be expressed as an alternative reaction path for the active complex $\text{Ni}(\text{CO})_{2-y}(\text{P}\emptyset_3)_{2-x}$, giving an additional step (4) in the proposed mechanism.



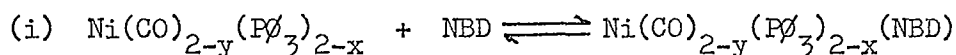
This changes the rate expression to:

$$\frac{d[\text{dimer}]}{dt} = \frac{k_1 k_2 k_3 [\text{Ni}(\text{CO})_2(\text{P}\emptyset_3)_2] [\text{NBD}]^2 + k_2 k_3 k_{-4} [\text{NBD}]^2 [\text{Ni}(\text{P}\emptyset_3)_{2-x}(\text{CO})_{2-y}(\text{dimer})]}{k_{-1}(k_{-2} + k_3) [\text{CO}]^y [\text{P}\emptyset_3]^x + k_2 k_3 [\text{NBD}]^2 + (k_{-2} + k_3) k_4 [\text{dimer}]}$$

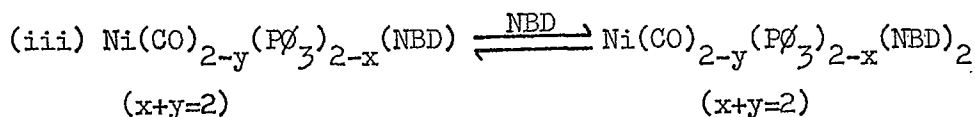
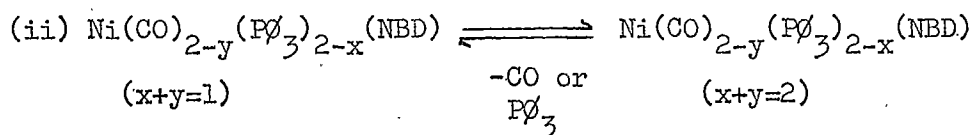
Only four steps are given here, while in fact many other reactions occur.

For example, the addition of NBD to $\text{Ni}(\text{CO})_{2-y}(\text{P}\emptyset_3)_{2-x}$ almost certainly occurs in two steps;

- a) the addition of one NBD molecule to give a saturated complex (see equation 1 where $x+y=1$). So many potential ligands exist in the reaction that the loss of two ligands to give a complex in which two coordination sites are empty is, in reality, improbable.



- b) The loss of a CO or $\text{P}\phi_3$ ligand from this resulting complex to give a coordinatively unsaturated complex (equation ii) which must capture another NBD molecule to give the complex $\text{Ni(CO)}_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2$, equation iii.



The assumption of the simultaneous loss of two ligands in step 1 (page 80), followed by the addition of two NBD molecules in step 2, serves as a simplification for developing the rate equation. Unfortunately, an understanding of the degree of complexity of the equilibria leading to productive complexes $\text{Ni(CO)}_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2$, $x+y=2$, is thereby made less obvious. The important point is that the number of productive (dimer producing) pathways relative to the number of probable reactions occurring is small. The induction period of the reaction involves the establishment of equilibrium among all the reaction steps, and any process which would lead to the relatively easy production of coordinatively unsaturated species ought to shorten this period (vide post). The linear portion of the dimer concentration versus time plots corresponds to a constant rate of production of dimer once the equilibria have been

established, $d[\text{dimer}]/dt = k_3 [\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2] = \text{a constant}$. Since a number of equilibria do exist involving the complex $\text{Ni}(\text{CO})_{2-y}(\text{P}\phi_3)_{2-x}(\text{NBD})_2$, $x+y=2$, which lead to dimer, the slopes of the $[d]$ vs t plots* contain a large number of concentration and rate constant terms. In turn, the use of the slopes of $[d]$ vs t plots for the determination of $\Delta H^\ddagger$ values necessarily implies that a $\Delta H^\ddagger$ value so obtained represents the total $\Delta H^\ddagger$ for a rather large number of reactions, although it is referred to as the enthalpy of activation for the dimerization of NBD to give a specific dimer. Thus, values of $\Delta H^\ddagger_{\text{xtn}} = 70.24$ kcal/mole and $\Delta H^\ddagger_{\text{xtx}} = 79.96$ kcal/mole should each be treated as composite $\Delta H^\ddagger$ values for the various equilibria involving intermediates which lead to each of the two dimers.

The observed influence of the ligands ($\text{P}\phi_3$ and CO) on reaction rates may now be correlated to the mechanistic picture of the dimerization reaction. The production of xtx and xtn are both inhibited by the presence of $\text{P}\phi_3$, which vies for vacant coordination sites on nickel. As noted in the introduction as well as earlier in the discussion, the following scheme can be proposed. To form the 2+2 xtn dimer, one starts with a bidentate endo,endo NBD nickel specie which then goes to a monodentate endo NBD nickel specie and finally to an exo NBD, endo NBD nickel specie, leading to xtn dimer.

* $[d]$ vs t = dimer concentration versus time

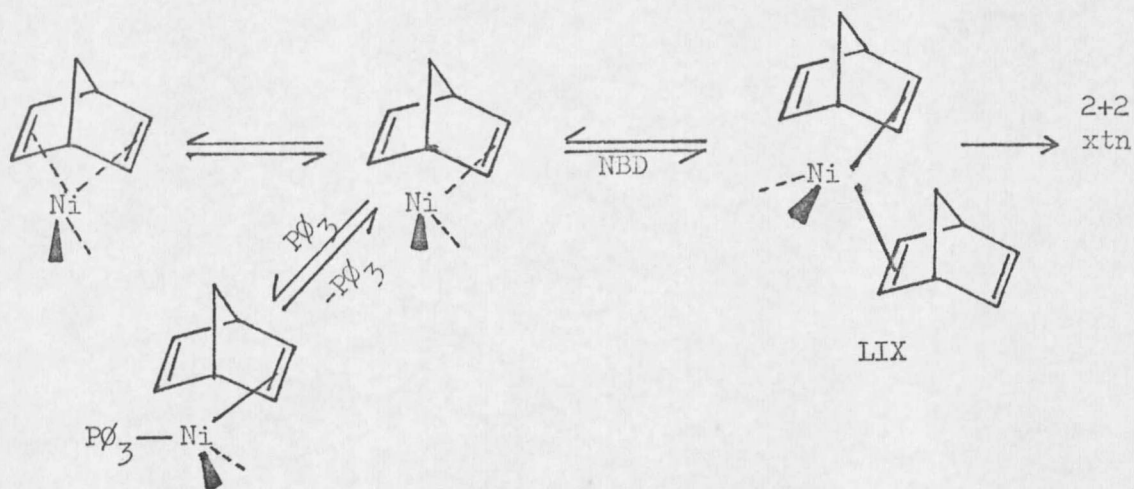


Figure 35

Entropy Effects in Complexes Leading to the 2+2 xtn NBD Dimer

Further, in the case of the 2+2 xtx dimer, the following intermediate (LX) has been proposed.^{17a,25}

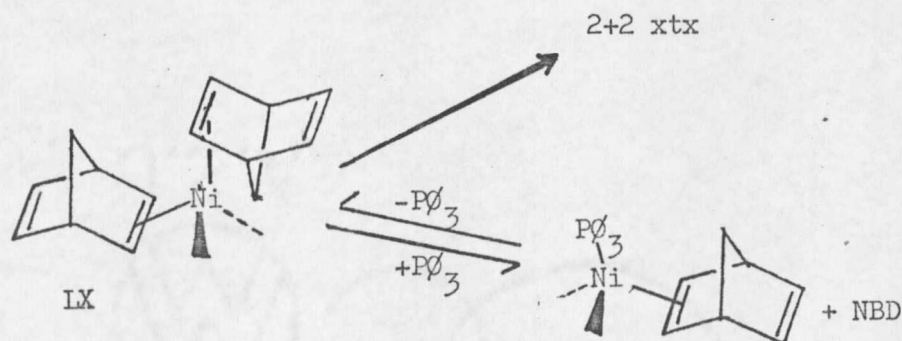


Figure 36

Entropy Effects in Complexes Leading to the 2+2 xtx NBD Dimer

Relative to entropy considerations, it is expected that if the mono-endo bonded NBD nickel specie temporarily complexes with a $P\phi_3$ molecule, the nickel atom will be likely to recomplex with the endo side of the same NBD, since it is still bonded to the remaining endo side (Figure 35). However, if an exo,exo-bis(NBD)nickel specie temporarily forms a $P\phi_3$ bonded complex, it is much less likely to reform an intermediate capable of leading to dimer (Figure 36). Thus, it would be expected that increases in the $[P\phi_3]$ would result in more significant changes in the rate of xtx production than in the rate of xtn production.*

The possibility of two mechanisms for the production of the 2+2 xtn dimer should also be considered. One mechanism would involve the formation of a dicarbonyl endo,endo-NBD nickel catalyst which could be analogous to the proposed^{17a} nickel tetracarbonyl derived specie.

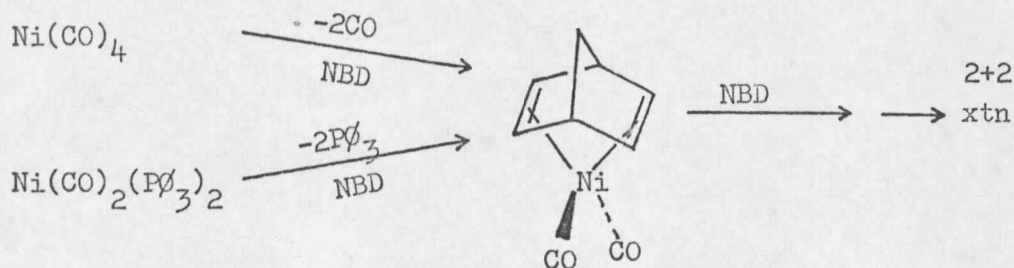


Figure 37

Common Pathway to the 2+2 xtn NBD Dimer

* While it is possible a $P\phi_3$ could substitute for a NBD (either exo or endo bonded) in the endo-NBD, exo-NBD nickel complex (LIX), it is more likely substitution of the exo-NBD by the remaining uncoordinated endo side of the mono-endo coordinated NBD will occur.

In the absence of carbonyl ligands (and to a lesser extent even in their presence), a less efficient path to dimer might be operative involving endo,endo-NBD nickel catalysts.

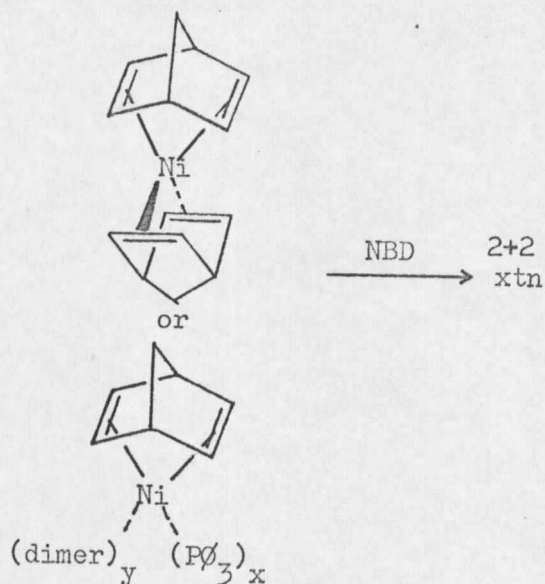


Figure 38

Non-carbonyl Containing Complexes Leading to the 2+2 xtn NBD Dimer

It is not completely clear why a dicarbonyl-endo,endo-NBD-nickel specie should be particularly efficient for the production of the 2+2 xtn dimer. However, a reasonable explanation involves the nature of the interaction between the endo side of NBD and the nickel dicarbonyl moiety. It has been noted⁷⁰ that valence bond theory predicts that in tetrahedral nickel(0) complexes only two orbitals will be available for π -back-bonding. Thus, in nickel tetracarbonyl, two of the four carbonyls are readily removed, while strong π -back-bonding to the remaining two carbonyls prevents their easy displacement. Accordingly, a relatively

stable but labile complex could be envisioned for a NBD-dicarbonylnickel system. The π -back-bonding capability of nickel could be readily satisfied with two carbonyls, leaving two sites available for ligands having principally donor properties. Schrauzer⁷¹ has advocated, based on spectral data for endo, endo-NBD duroquinone nickel, that the endo side of NBD acts principally as an electron donor. This is supported by the lability of NBD duroquinone nickel towards trimethyl phosphite.⁶⁸

Based on photoelectron spectra⁷² it is clear the double bonds in NBD interact in a through-space manner. Thus, in a qualitative way, one could develop the following picture for the orbitals in NBD. In addition to the "normal" interaction between the four p atomic orbitals - producing two π bonding and two π antibonding molecular orbitals - account should be made for interaction between the endo lobes of transannular p orbitals. This interaction may be thought of as a form of partial sigma bond formation. Thus, the situation can be pictured as given below, where π and π^* notation refers to molecular orbitals in which p- π bonding is stressed, while σ and σ^* notation refers to molecular orbitals in which p- σ bonding is stressed.

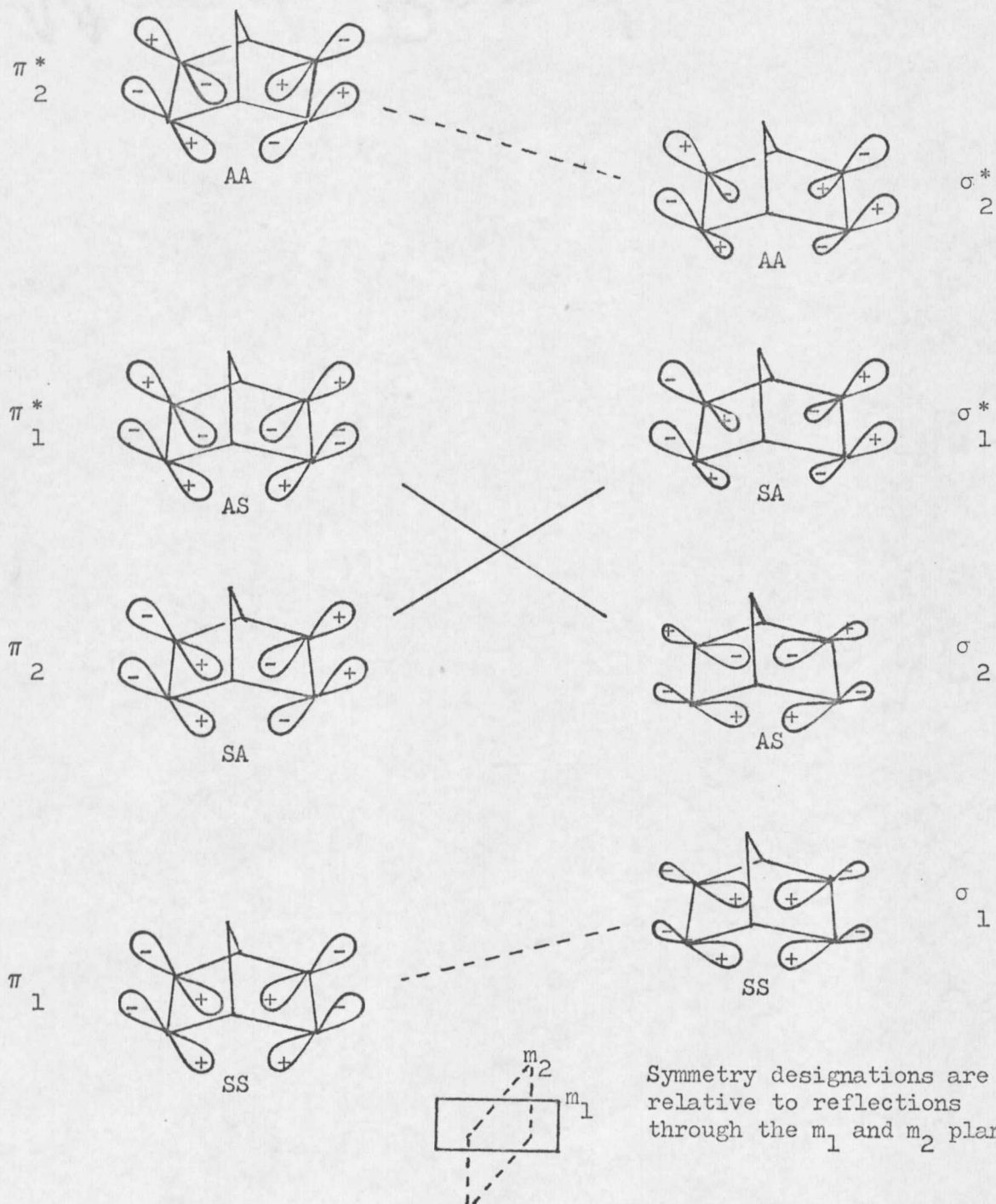


Figure 39

Qualitative Picture of p Orbital Interactions in NBD

In light of the much greater strain energy for quadricyclane (78.7 kcal/mole) versus two norbornene molecules ($2 \times 17.6 = 35.2$ kcal/mole) (NBD strain energy = 25.6 kcal/mole)⁷³, it is possible that energy differences will preclude extensive mixing between the π_{SS} and σ_{SS} states. The $\pi_{AS}^{*-\sigma_{AS}}$ and $\pi_{SA}^{*-\sigma_{SA}}$ states, however, probably do mix, the degree once again depending on the relative energy levels. It is suggested that one result of such mixing would be to increase the electron density on the endo side of NBD. The lowest antibonding orbital would also be altered by mixing. Thus, to the extent mixing obtains, the region of maximum antibonding orbital probability would lie on the exo side of NBD, at the expense of a decrease on the endo side.

This picture, if correct, would explain the preference of a dicarbonyl nickel moiety to be bonded to the endo side since the two carbonyls would act as excellent π -back-bond acceptors, while the endo side of NBD would serve principally as a donor. The proposed model could also be invoked to explain why a $Ni(P\phi_3)_2$ could preferentially bond to the exo side of two NBD molecules and thus lead to the 2+2 xtx dimer. Triphenylphosphine is generally conceded to be a rather poor π -back-bond acceptor,⁷⁴ while nickel has been suggested to be perhaps the most basic metal for π -back donation to olefin π^* orbitals.⁷⁵ Thus, in the absence of carbonyl ligands to act as π -back donation acceptors, olefins (e.g. the exo sides of two NBD molecules) could serve as acceptor ligands. Note that in the above discussion any $Ni(L)_2$ entity in which L is

principally a σ donor (poor π -back-bond acceptor), e.g. a dimer molecule, would be predicted to lead to the 2+2 xtx dimer.

One final point should be made concerning the data from the kinetics experiments: duration of the induction period. From the abscissa intercepts in Table 1, page 71, it can be seen that the trend is as expected; the higher the temperature the shorter the induction period, corresponding to an increased production of unsaturated species (cf. page 80 ff.). In general, the induction period for the 2+2 xtn dimer is shorter than that for the 2+2 xtx dimer. This is consistent with a less energetic process for xtn than for xtx formation, $H^\ddagger_{\text{xtn}} < H^\ddagger_{\text{xtx}}$, provided the factors effecting the establishment of the equilibrium among the various ligands and complexes mirror the factors effecting the maintenance of that same equilibrium.

Since it is known that tetrakis(triphenylphosphine)nickel dissociates in solution at room temperature to tris(triphenylphosphine)nickel and triphenylphosphine,⁷⁴ a coordinatively unsaturated specie can be readily formed and thus, it is not surprising to see the induction period virtually disappear. Further, the absence of the strongly bound carbon monoxide ligand in the promoter, cf. $\text{Ni}(\text{CO})_2(\text{P}(\text{O})_3)_2$, should also contribute to a shortening of the time required to form an intermediate capable of leading to dimer.

Conclusions

At this point it is felt a review of the proposed mechanism for the

dimerization of NBD by nickel promoters is appropriate. This review will be presented in light of the combined results from both the structural modifications and kinetic data reported in this portion of the thesis. In conjunction with these results the work of other investigators will be included (or referred to) as support for the proposed theories. The object of this section will therefore be to describe the author's conception of the mechanistic picture.

First, the formation of both the 2+2 xtx and 2+2 xtn dimers from NBD and $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ involves the coordination of two NBD molecules in a stereo-specific manner. Second, these coordinated NBD molecules join to form dimer.

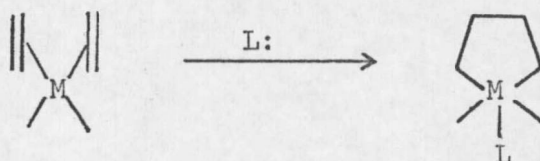
The proposed mechanistic routes for the formation of each of the two 2+2 dimers will now be presented. This will be followed by some comments concerning the production of 2+2+2 dimers.

2+2 xtx: Two molecules of NBD are coordinated to nickel on their exo sides. This exo,exo-bis(NBD)nickel di-ligand complex would be favored by ligands which were not good π -back-bonders, e.g. $\text{P}\phi_3$, dimers⁷⁶ and 1,5-cyclooctadiene.⁷⁷

However, the presence of an excess of strong σ donors will result in the effective inhibition of xtx formation, since once an exo,exo-bis(NBD)nickel di-ligand specie is converted to a mono-exo-NBD tri-ligand moiety (e.g. LX) by replacement of one NBD by a ligand, there are no favorable entropy considerations

present to aid in the reformation of the *exo,exo*-bis(NBD)nickel di-ligand specie (cf. Figure 36).

From the data presented in this thesis it is not possible to distinguish between a concerted or a non-concerted path for the production of the 2+2 xtx dimer from an *exo,exo*-bis(NBD)nickel di-ligand specie. However, it has been suggested the presence of good σ donors ought to favor π to σ transformations.^{21,22}



But as noted above, the presence of excess good σ donors all ought to inhibit the formation of the *exo,exo*-bis(NBD)nickel di-ligand precursor to the di- σ -bonded complex. Thus, one is faced with a dilemma and both factors must be considered in determining the likelihood of any proposed mechanism.

2+2 xtn: Initially a complex involving an *endo,endo*-NBD di-ligand complex must be formed.

This is favored by ligands capable of functioning as strong π -back-bond acceptors such as carbonyls or activated olefins (e.g. acrylonitrile and 1,1-biphenylene-2,2-dicyanoethylene)²⁵ which could satisfy the propensity of nickel for π -back-bonding. The *endo* side of NBD is proposed to be principally a σ donor

and a poor π -back-bond acceptor. The presence of added strong σ donors, e.g. $P\phi_3$, ought to affect a complex of this type less than exo,exo-bis(NBD)nickel di-ligand complexes because of the favorable entropy factor to reform the complex (cf. Figure 35).

Once the endo,endo-NBD-nickel di-ligand complex is formed it may lead by the dissociation of one endo bond and recomplexation with the exo side of a second NBD molecule to the immediate precursor to the 2+2 xtn dimer - an exo-NBD, endo-NBD-nickel di-ligand complex (LIX).

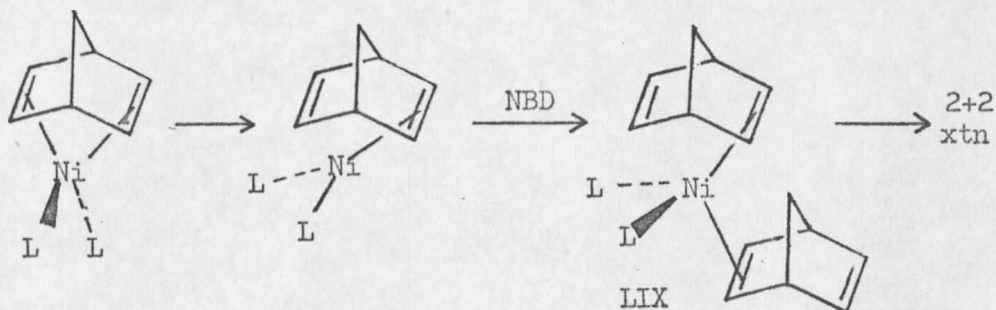


Figure 40

Proposed Intermediates in the Formation of the 2+2 xtn NBD Dimer

Based on the data from the dimerization of 7-methylnbd, it is proposed that to account for the formation of the statistical distribution of methyl groups in the endo-bonded fragment - in both the NBD 2+2 xtn and ntn dimers - a concerted path is most probable. Thus, it is proposed that the xtn dimer and the ntn dimer (by analogy) are produced by the concerted pathway

particularly in cases where carbonyl ligands ($\text{Ni}(\text{CO})_4$ and $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$) are available. In the case of $\text{Ni}(\text{P}\phi_3)_4$, the formation of the 2+2 xtn dimer is accounted for by suggesting a specie such as complex LIX, where L is an exo-bonded NBD molecule, or less likely, $\text{P}\phi_3$, dimers, or similar* molecules.

It is suggested in these cases, the formation of 2+2 xtn dimer via complex LIX is in strong competition with the loss of the endo bonded NBD molecule. For tetrahedral nickel complexes, the presence of any less than two strong π -back donation acceptors will promote the loss of σ donors.⁷⁸

In the case of the $\text{Ni}(\text{P}\phi_3)_4$ promoted dimerization, the best π -back-bond acceptor ligands available are the exo sides on NBD molecules. Since these exo sides are only moderately good π -back-bond acceptors, the loss of ligands including the endo bonded NBD becomes more likely.

2+2+2: It has been proposed in the stereochemical modification portion of this discussion that the formation of 2+2+2 7-methylNBD dimers (using $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$) follows a non-concerted pathway. It is further proposed that if, for stereochemical (or possibly

* As was noted earlier, $\text{Ni}(\text{II})$ has been electrochemically reduced in the presence of NBD to yield the 2+2 xtn and 2+2 xtx dimers. These reactions were run in pyridine and acetonitrile, solvents which may serve as donor ligands.

electronic) reasons, the complex LXII, Figure 42, cannot readily result in 2+2 xtn dimer, it is possible a carbon monoxide may be lost to yield complex LXIII which would yield the five coordinate di- σ -bonded complex, LXVII. This would reductively eliminate the dimer.

Other routes to complex LXIII could be suggested and may be even more probable. Initial complexation of NBD on the exo side could give complex LXIV. The loss of carbon monoxide, prompted by the acceptor properties of the exo side of NBD, followed by complexation of a NBD molecule, this time on the endo side, would give LXVI. Loss of $P\phi_3$ from LXVI would yield LXIII. The complex LXIV could lose $P\phi_3$ instead, giving LXV. This would be promoted by steric considerations of the more hindered 7-methylNBD molecule. The coordinatively unsaturated complex LXV could bind with the endo side of a second 7-methyl-NBD molecule to give LXII and as noted, loss of a carbonyl from LXII would yield LXIII.

Note that whereas Katz²⁷ proposed that a rhodium complex (LXVIII) is responsible for the 2+2+2 exo-cis-endo NBD dimer, it is proposed here, based on stereochemical considerations, that a nickel complex (LXIX) is responsible in the case of 7-methylNBD and $Ni(CO)_2(P\phi_3)_2$.

Proposed Mechanistic Routes to the
2+2+2 xcn 7-MethylNBD Dimer

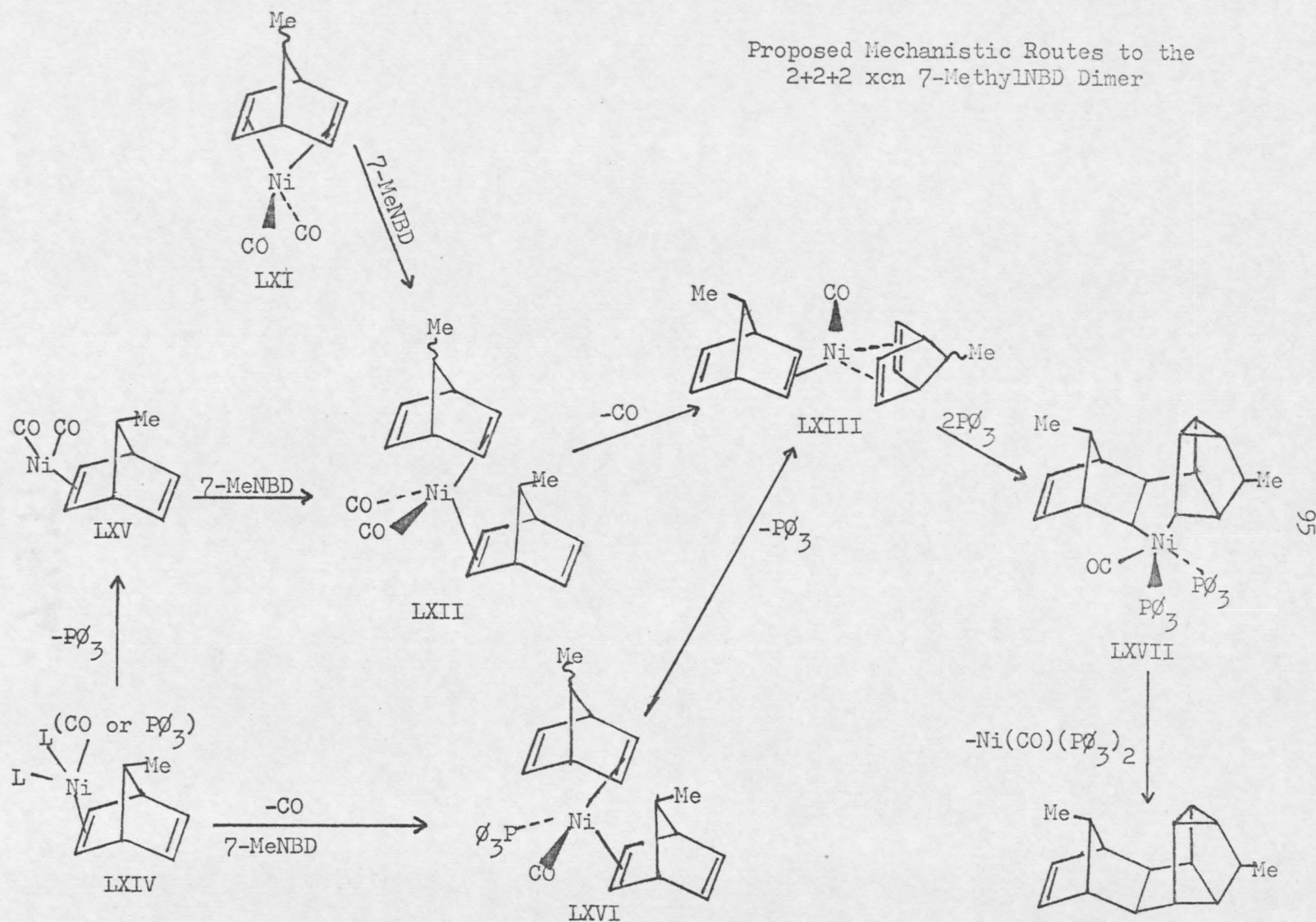


Figure 41

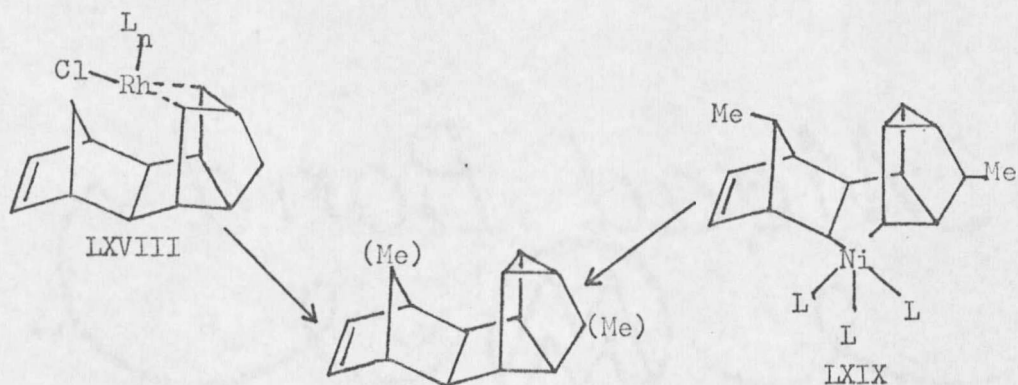
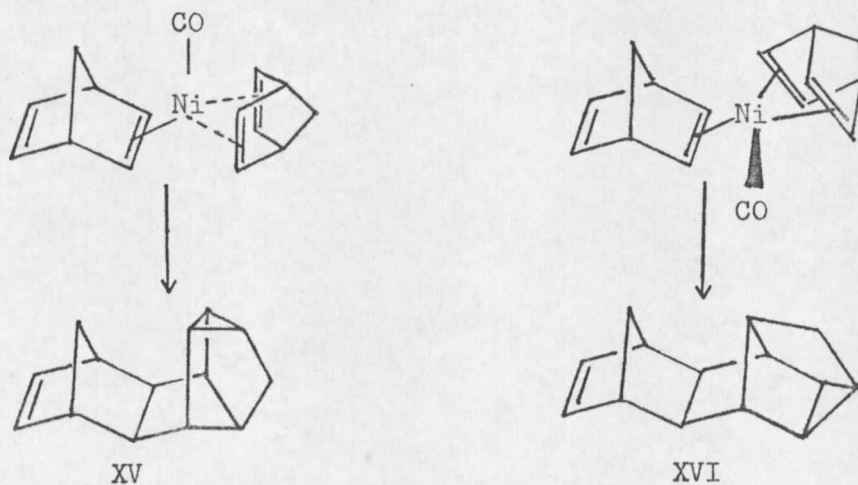


Figure 42

Alternative Pathways for the Non-concerted Production
of the 2+2 xtn Dimer Skeleton

It is also worth-while to note that in the case of nickel tetracarbonyl, the two 2+2+2 dimers (XV and XVI) are formed, and their formation might well be explained by a concerted mechanism noting the presence of carbonyl ligands does not favor an oxidative addition (non-concerted) mechanism.



A concerted pathway for the dimerization promoted by $\text{Ni}(\text{CO})_4$ would be favored from a stereochemical point of view too, since carbon monoxide is sterically quite small. Note that it would be predicted the non-concerted (oxidative addition) mechanism would be favored by the presence of $\text{P}\phi_3$ (vide supra).

The work reported and discussed in this portion of the thesis has been concerned with the cycloaddition reaction of NBD promoted by $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ and to a lesser extent $\text{Ni}(\text{CO})_4$. The metal is the same for both promoters and the number of ligand types initially in solution are reasonable small ($\text{P}\phi_3$, CO and NBD). However, as has been noted, the number of factors to be discussed is already quite large. It can well be imagined that the number of factors which must be considered is very large when: the substrate is changed from NBD; the promoter metal is changed from nickel; the formal oxidation state of the metal is no longer zero and the number of ligand types is increased to include trihalophosphines, phosphites, arsines, stibines, nitrosyls and halide ions. The problem can quickly become virtually insolvable. Thus, despite the limited area of examination which is reported here, it is felt the evidence and proposals presented should aid in suggesting experiments for more detailed studies of metal promoted cycloadditions as a whole.

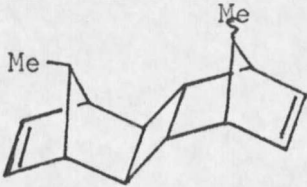
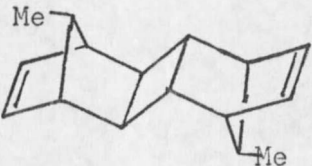
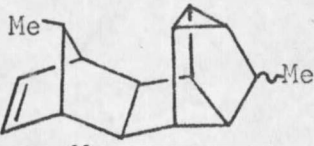
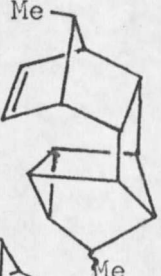
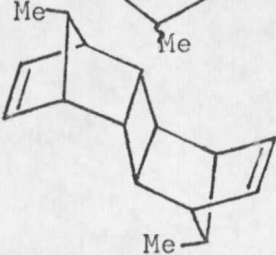
SUMMARY

The work reported in this thesis is the result of a bifunctional approach to the problem of metal mediated cycloaddition reactions of olefins. The first aspect of this approach was to explore the scope of the reaction and the second was to come to a better understanding of the mechanism(s) operating in such reactions. Norbornadiene (NBD) presents some particular advantages from both aspects. Thus this molecule and its derivatives were used as the principal substrates in the work presented here.

The first general area of study was structural modifications. This area was subdivided into two sections. In the first, emphasis was placed on substrate stereochemical considerations, while the second section stressed substrate electronic considerations. The second general area involved a kinetic study, with emphasis being placed on consideration of metal-ligand related phenomena.

A number of substituted NBD derivatives were tried as substrates using bis(triphenylphosphine)dicarbonylnickel as a promoter (promoter being used to describe the initial metal complex which leads to the active catalytic specie during the reaction). The compound 7-methylnbd was found to dimerize using $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ and activation by light or heat. The thermally obtained product mixture was subjected to an extensive separation scheme using silver nitrate and silver perchlorate impregnated silica gel column chromatography in conjunction with preparative gas

chromatography. It was shown there are seven products, six of which were identified. The photochemically obtained product consisted of four major dimers. These were related to thermally produced products by using Ag^+ ion impregnated silica gel thin layer plates and gas chromatography. The product structures are given below. Relative amounts are only internally consistent since amounts of thermally derived products were not compared to amounts of photochemically derived products.

		ΔT	$h\nu$
2+2 xtn both isomers in equal amounts		40	4
2+2 xtx		10	7.5
2+2+2 xcn		7	1
2+2+2 ncn		5	
2+2 ntn		2	
		relative yields	

A study of substrate electronic considerations was also made.

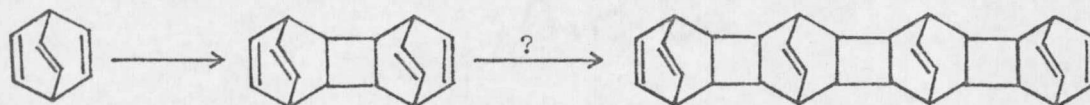
It was assumed that substrate olefin-metal interactions constitute the major substrate electronic factors in metal promoted cycloaddition reactions of olefins. Thus, three olefins having "perturbed" olefin bonds (relative to NBD) were chosen.

Norbornene - only one double bond

The 2+2 xtx NBD dimer - one double bond interacting with a trans-annular exo bonded cyclobutane.

[2,2,2] bicycloocta-2,5-diene (dihydrobarrelene) - a methylene homolog of [2,2,1] bicyclohepta-2,5-diene (NBD).

However, norbornene, the 2+2 NBD xtx dimer, and [2,2,2] bicycloocta-2,5-diene were all found to be inactive toward dimerization. An explanation was offered, based on reported and projected energy levels, for the lack of reactivity in these systems as compared to NBD. The fundamental tenet of the proposal is that both a relatively high-energy filled π olefin orbital and a relatively low-energy unfilled π^* orbital are necessary in the substrate. In NBD this situation is provided by the interaction of the two olefin bonds. It is proposed other similar molecules where such interaction can occur will also be active towards dimerization. Thus, based on photoelectron spectra, it is suggested that [2,2,2] bicycloocta-2,5,7-triene (barrelene) will dimerize, but the dimer being similar to dihydrobarrelene, may be inactive.



The kinetics study, as noted, was directed towards an understanding of metal-ligand interactions. The thermal reaction of NBD with $\text{Ni}(\text{CO})_2^-$ $(\text{P}\phi_3)_2$ and $\text{Ni}(\text{P}\phi_3)_4$ was studied and the following information gathered.

a) The reaction proceeds in two phases - an induction period, followed by the principal reaction where dimers are produced at a constant rate.

b) The reaction is extremely dependent upon three factors.

i) Temperature

ii) The rate at which carbon monoxide can escape from the reaction

iii) The concentration of triphenylphosphine in solution

c) From the data it was found:

i) $\Delta H^\ddagger$ values were obtained for the 2+2 xtx and xtn dimers.

$$\Delta H^\ddagger_{\text{xtx}} = 79.96 \text{ kcal/mole}$$

$$\Delta H^\ddagger_{\text{xtn}} = 70.24 \text{ kcal/mole}$$

ii) Sweeping the reaction solution with N_2 greatly facilitated reaction, while sweeping the reaction with CO caused nearly total inhibition.

iii) $\text{P}\phi_3$ strongly inhibits the reaction, the production of xtx being inhibited somewhat more than the production of xtn.

d) Using $\text{Ni}(\text{P}\phi_3)_4$ instead of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ as promoter:

i) Virtually eliminates the induction period.

ii) Decreases the rates of xtx production (1/6) and xtn production (1/5) for reactions run under the same conditons.

Several inferences were made based on the kinetics data. These were coordinated with the results of the structural modification data as well as with the work of Voecks^{17a,b} and other investigators on similar systems. It is proposed the following picture for the Ni(O) promoted cycloaddition reaction of NBD emerges.

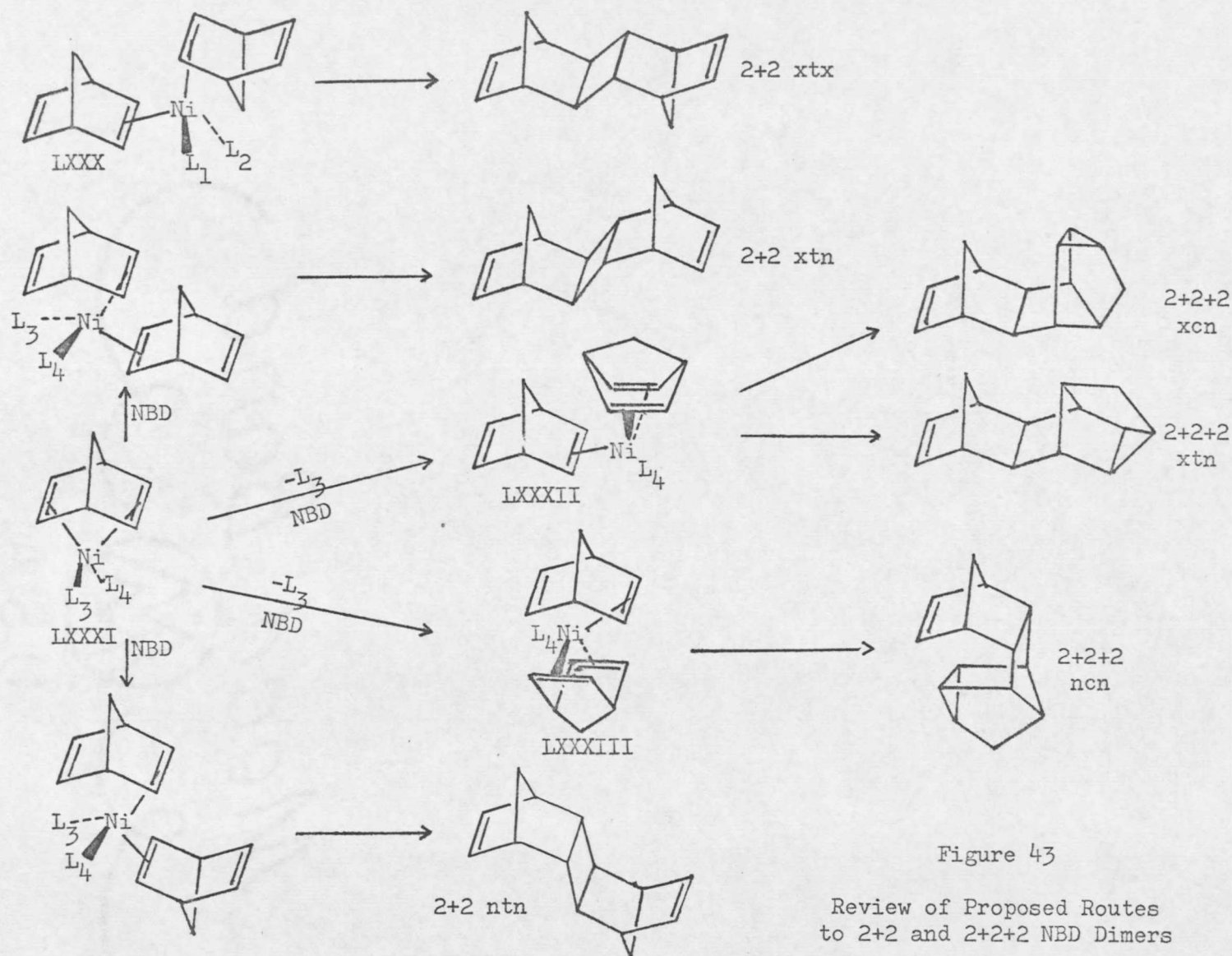
- A) Ligands (both CO and $\text{P}\phi_3$) are lost to produce coordinatively unsaturated nickel species, some of which may be described as "active catalysts". These ligands, as well as NBD and NBD dimers are in constant competition for sites on nickel, thus reducing the concentration of "active catalysts" to very low values. The establishment of an equilibrium between the promoter, the ligands and the various modified nickel species, including "active catalysts" constitutes a mechanistic description of the induction period observed in these metal promoted cyclodimerizations.
- B) Once this equilibrium is established, the rate of dimer production is constant. Because of the very low concentrations of "active catalysts" caused by the efficient competition of inhibitory ligands (e.g. CO, $\text{P}\phi_3$, and NBD dimers) for coordination sites on nickel, the enthalpy of activation for dimer formation

may appear to be very large. What, in fact, is being measured is the composite of enthalpy values for the many equilibrium processes involving the "active catalysts".

- C) NBD molecules stereospecifically disposed on nickel act as precursors to dimer. Which specific precursors are formed in any particular promoter substrate system depends on the nature of the ligands initially on the metal as well as any ligand in solution. This situation also holds for the fate of these precursor molecules with respect to the routes they follow in forming dimer (see Figure 43).

However, some generalizations can be made based on the available data and the proposal that the endo side of NBD is principally a σ donor, while the exo side of NBD is a good π -back-bond acceptor.

- i) Formation of complex LXXX is favored by L_1 and L_2 being good σ donors, e.g. PO_3 .
- ii) A non-concerted path from complex LXXX to the 2+2 xtx dimer is favored by good σ donors in solution, but these ligands would also promote the deactivation of complex LXXX by vying with NBD for coordination sites on nickel.
- iii) The formation of complex LXXXI would be favored by L_3 and L_4 being strong π -back-bond acceptors, e.g. carbonyls.
- iv) The formation of 2+2 xtn and 2+2 ntn dimer proceeds via a concerted pathway.



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Figure 43

Review of Proposed Routes
to 2+2 and 2+2+2 NBD Dimers

v) The formation of 2+2+2 dimer can occur either by a non-concerted route (2+2+2 xcn and 2+2+2 ncn) or by a concerted route (2+2+2 xcn and 2+2+2 xtn). The non-concerted path is favored by steric inhibition to 2+2 xtn formation and the presence of $P\phi_3$. The concerted path is favored by the absence of σ donors and the presence of π -back-bond acceptors. It is expected to be operative in the very energetic process of photochemical activation of complex LXXXI (forming complex LXXXII) when L_3 and L_4 are CO.

D) Trimer formation is expected to be favored when dimers can effectively serve as ligands.

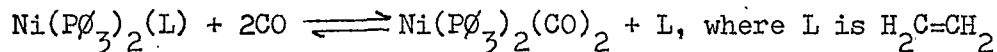
i) Then their concentration is relatively large.

ii) When there are the minimal number of other effective σ donors.

For example, the use of 1,5-bis(cyclooctadiene)nickel promotes extensive trimer formation.⁷⁷

To further explore the above proposals, some experiments can be suggested.

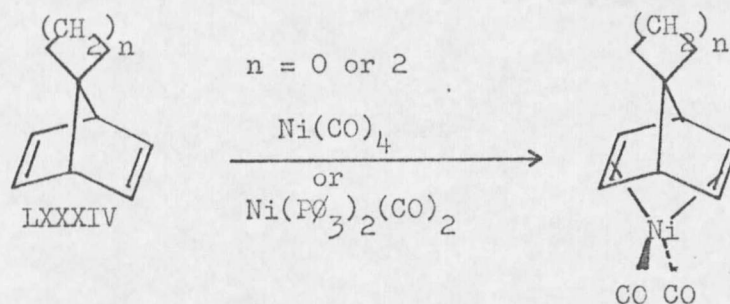
1) To study the dissociation of carbon monoxide from $Ni(CO)_2(P\phi_3)_2$, the experiment can be run in reverse. That is, measure the enthalpy change for the reaction :



or :N=N: .

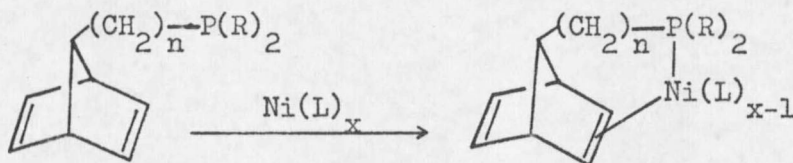
2) By using the substituted NBD, LXXXIV, it may well be possible to obtain the endo,endo-bis(7,7-polymethyleneNBD)nickel dicarbonyl

complex, since with all modes of exo bonding blocked, its rate of dimerization ought to be very slow. Infrared, NMR and UV



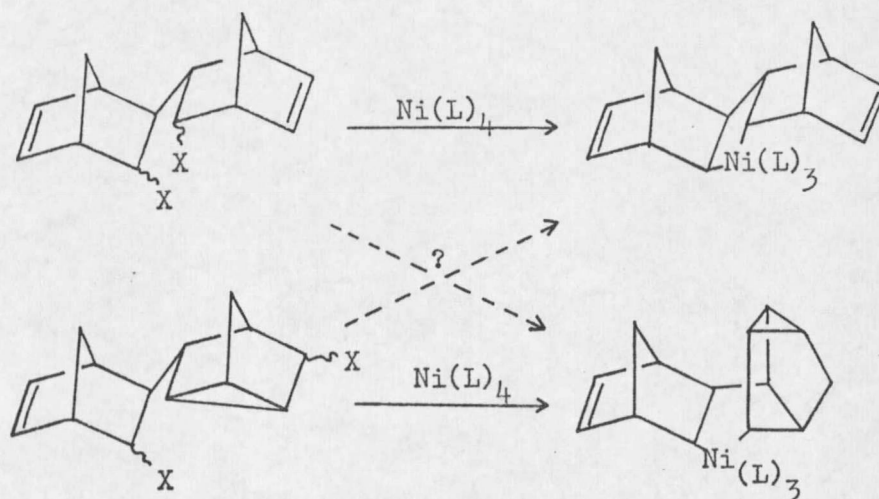
spectra of such a complex could aid in detecting the unsubstituted counterpart.

- 3) By running the reaction of NBD with a specie such as $Ni(P\phi_3)_2N_2^*$ at low temperature under vacuum, one may be able to obtain evidence for NBD- $Ni(P\phi_3)_2$ species.
- 4) To explore attack by nickel on the exo side of NBD, 7-disubstituted methylenephosphinatoNBD⁷⁹ could be used as substrates.



* It has not been possible to exchange norbornene for ethylene in the complex $(P\phi_3)_2Ni(CH_2CH_2)$.⁸⁰ However, with the dinitrogen complex $(P\phi_3)_2NiN_2$,³ NBD exchange may prove possible.

- 5) Finally, to investigate the possibility of non-concerted intermediates in the formation of 2+2 xtn and 2+2+2 xcn, as well as the possible interconversion of such intermediates, the following sequences are suggested.



X = halogen

In these cases, $\text{Ni}(\text{L})_4$ could be $\text{Ni}(\text{CO})_4$, $\text{Ni}(\text{P}\phi_3)_4$, $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$, bis(1,5-cyclooctadiene)nickel or electrochemically obtained low valent Ni species. In light of the success obtained in the use of the dipyridyl ligand for stabilizing low valent bis- σ -alkyl nickel complexes,⁸¹ it may prove to be a suitable ligand for these reactions.

EXPERIMENTAL

Instruments and Equipment

Gas chromatographic analyses were run on a Varian Model 1740 Gas Chromatograph using 1/8 inch six or twenty foot columns of 5% SE 30 on 100-120 mesh Gas Chrom Z. Preparative gas chromatography for 7-methylnorbornadiene dimers were run on an Aerograph Model A-700 Autoprep Gas Chromatograph, using a 3/8 inch twenty foot column of 30% SE 30 on 80-100 mesh Chromosorb W at a column temperature of 225°C and helium flow of 200 ml/min.

Nuclear Magnetic Resonance spectra were obtained on a Varian A-60 Proton NMR

The light source for photochemical reactions was a Hanovia Type A 450 watt high pressure mercury arc. A pyrex filter was used for the $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ promoted reactions, while a uranyl glass filter was used for the reaction of dinitrosyldicarbonyliron and 2,5-[2,2,2]-bicyclooctadiene.

Reagents

Norbornadiene was purchased from Frinton Laboratories and was purified by distillation under nitrogen 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 chromatographic analysis on a six foot column of 5% SE 30 on 100-120 mesh Gas Chrom Z.

Seven-t-butoxy-norbornadiene was purchased from Frinton Laboratories and was purified by column chromatography using Alfa Inorganics Alumina CAMAG NEUTRAL 507-C-1 as an absorbant and n-hexane as an elutant.

Triphenylphosphine (Alfa Inorganics) was sublimed prior to use.

Bis(triphenylphosphine)dicarbonylnickel was prepared by the method reported in Organometallic Synthesis edited by Eisch and King.⁸²

Dicarbonyldinitrosyliron(O) was a gift of G. Voecks.

The 2+2 norbornadiene exo-trans-exo dimer was doubly sublimed from a dimer mixture and was free of impurities by gas chromatographic analysis.

Dodecane, used as a standard for the gas chromatographic analysis of dimers in kinetics experiments was purchased from the Eastman Kodak Co. It showed one peak under the conditions of analysis: 20 foot column (vide supra), linear temperature program of 6-10°C per minute, starting at 50°C.

Purification of di-n-amyl ether used in the preparation of 7-methyl norbornadiene was accomplished by running the ether through an activated alumina column followed by simple distillation under nitrogen.

Seven-hydroxy-norbornadiene was prepared by an established literature procedure via a benzoyl norbornadiene intermediate.⁸³

Gases

Hexafluoro-2-butyne was purchased from Peninsular ChemResearch and was used without further purification for the preparation of 2,3-bis(trifluoromethyl)norbornadiene.

Nickel carbonyl (Matheson) was used without purification for the preparation of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$.

Carbon monoxide (Matheson C.P.), used to sweep the $\text{NBD-Ni}(\text{CO})_2(\text{P}\phi_3)_2$ reaction, was deoxygenated by the use of BSTS catalyst (BASF Colors and Chemicals, Inc.).

Nitrogen (Airco, Dry-High Purity) was used for distillations, re-fluxings, sweeping, and in all other cases was deoxygenated by use of BSTS catalyst.

Preparations

2,3-bis(trifluoromethyl)norbornadiene. Eight ml (.137 moles) of freshly distilled 1,3-cyclopentadiene was placed at 0°C in a bomb reactor. The bomb was sealed and cooled to -78°C. Hexafluoro-2-butyne (22.2 g, .137 moles) was introduced via an inlet valve. Gradually, the mixture was allowed to come to room temperature. The product was purified by distillation at 120 mm, bp 68.5-69.0°C. Its nuclear magnetic resonance as a neat sample, with tetramethyl silane added as a standard, showed:

Triplet	2H	6.83	olefin
Multiplet	2H	3.85	bridgeheads
Multiplet	2H	2.125	bridge

Note the bridge and bridgehead protons appear to show extensive splitting presumably due to ^{19}F coupling.

7-Methyl-norbornadiene. The preparation of P. R. Story⁸⁴ was modified in the following manner. Methyl iodide (92 g, .65 moles) in 200 ml of di(n-amy)l ether was added dropwise to 158 g (.65 moles) of magnesium turnings, maintaining the temperature at 35-45°C. Thus a di(n-amy)l ether solution of methyl Grignard was prepared. Fifty grams (.305 moles) of 7-t-butoxy-norbornadiene was added and the solution heated (refluxing ensues) to 140°C for 15 minutes. It was then cooled to 120°C and the 7-methyl-norbornadiene was removed by vacuum distillation through a 30 cm glass-packed column at 100 mm. The product was collected in a -87°C (ethyl acetate slush) trap. The distillation was continued until the di(n-amy)l ether began to distill and provided a 25.17 g (77.8% yield) of nearly pure 7-methyl-norbornadiene. The bp is consistent with Story's value and the NMR spectrum identical. This method of preparation is not only an improvement over Story's method based on yield, 77.8% vs 57.6%, but also based on convenience - Story's procedure requires several days while the procedure reported here takes sixteen hours.

[2,2,2]cycloocta-2,5-diene. The most facile route to this diene involved a modification of the electrochemical reduction of [2,2,2]bicyclo-oct-2-ene-5,6-dicarboxylic acid.⁸⁵ The acid was prepared by the base hydrolysis of the corresponding anhydride, followed by careful acidification. Care must be exercised in acidification since the diacid readily

reconverts to the anhydride. The anhydride was synthesized from cyclohexa-1,3-diene and maleic anhydride.⁸⁶ The reaction was run as a 10% water-90% pyridine solution with a small amount of tri-ethylamine added to aid in carboxylate formation. Because of the low conductivity of the reaction medium, a considerable amount of heat is evolved. Thus, in light of the extreme volatility of the product,⁸⁷ some provision had to be made to effectively disperse this heat from the reaction mixture. Using a thin-walled steel reaction vessel, a mechanical stirrer, a cold bath and two concentric platinum electrodes, the reaction could be conveniently carried out on a reasonably large scale with the minimal supervision. Work-up consists of adding water to the reaction mixture, extracting with isopentane and careful distillation to remove the solvent. Thus, one can convert 5.88 g (.03 moles) of [2,2,2]bicyclooct-2-ene-5,6-dicarboxylic acid to 1.11 g-1.27 g of product (35-40% yield). The yields are compatible with reported results for reactions run on one-sixth the scale.

Tetrakis(triphenylphosphine)nickel(0). All procedures were carried out under a protective atmosphere of nitrogen. A solution of sodium benzophenone ketyl was prepared by combining benzophenone (1.83 g, .01 moles) and sodium (.23 g, .01 moles) in 10 ml of anhydrous ether. The ketyl solution was added dropwise to a vigorously stirred solution of bis(pentan-2,4-dione)nickel(II) (1.0 g, .00389 moles) and triphenylphosphine (4.2 g, .016 moles) in 20 ml of anhydrous ether until the dark blue color of the ketyl just persisted. The mixture was centrifuged and the

red-brown precipitate washed with anhydrous ether, and the mixture centrifuged again. This operation was repeated two more times. The product was finally dried under a slow stream of nitrogen to yield 3.45 g (80%) $\text{Ni}(\text{P}\phi_3)_4$.

Dimerization Reactions

These reactions can be put into two general classes, thermal and photochemical. The general procedure for each is as follows.

Thermal. The reactions were run with or without solvent under nitrogen at a specific temperature or at reflux. Gas chromatographic analysis of an aliquot sample was carried out using either a six foot or twenty foot 1/8 inch 5% SE 30 column. Nuclear magnetic resonance and ir spectra were also used to confirm gas chromatographic data.

Photochemical. These reactions were normally run in evacuated pyrex tubes. The appropriate amount of substrate was either added to the tube or transferred into the tube by a trap to trap distillation on a vacuum line. The promoter was either directly added, $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$, or transferred into the tube on a vacuum line. The charged tubes were subjected to several freeze-thaw cycles on a vacuum line, then sealed with a torch. The tubes were placed in a merry-go-round for irradiation with a high pressure mercury arc. Samples from the reaction mixtures were analyzed as in the thermal reactions.

In Table 2 below, a compilation of several specific experiments is given.

Table 2

Compilation of Attempted Dimerization Reactions with
Norbornene, 2+2 xtx NBD dimer, and [2,2,2]bicycloocta-2,5-diene

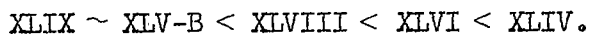
Substrate	Promoter	Activation Mode photochemical, hv thermal, (temp.) Activation time Solvent (if any)	Method(s) of Analysis GC (gas chromatography) NMR (nuclear magnetic resonance spectra)	Result of Analysis and/or any other comments concern- ing experiment
2,3-bis(tri- fluoromethyl)- norbornadiene	$\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$	hv, 166 hours benzene	GC	no dimer
7-t-butoxy- norbornadiene	$\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$	hv, 135 hours benzene	GC	no dimer
7-hydroxy- norbornadiene	$\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$	hv, 140 hours benzene	GC	no dimer
norbornene	$\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$	$\Delta(90^\circ\text{C})$, 3 days neat	GC	no dimer, solution became yellowish
2+2 xtx norbornadiene dimer	$\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$	reflux, 6 days hexane	GC	no tetramer, solution became yellowish ^a
[2,2,2]bicyclo- octa-2,5-diene	$\text{Fe}(\text{CO})_2(\text{NO})_2$	Δ , 3 hours isopentane	GC	no dimer, solution turns from red to dark red
	$\text{Fe}(\text{CO})_2(\text{NO})_2$	hv, 5 hours benzene	GC	no dimer, solution turns from red to dark red
	5% Rh/C	reflux, 27 hours benzene	GC NMR	no dimer
	$\text{Ni}(\text{CO})_4$	Δ , 71°C(reflux) 7 hours isopentane-benzene	GC NMR	no dimer, solution turns from colorless to yellow

^a heating xtx + $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ results in apparent complex formation. See page 56.

7-Methyl-norbornadiene. This molecule was dimerized in the presence of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ by thermal and photochemical activation.

Thermal. Nine ml of 7-methyl-norbornadiene was distilled on a vacuum line and transferred on the line into a flask containing .20 g (.31 moles) of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$. The reaction was run under nitrogen at reflux for 36 hours. The pot temperature rose from an initial 92°C to a final temperature of 105°C. After cooling, the unreacted 7-methyl-norbornadiene was removed under aspirator vacuum at 0-5°C. The resultant dimer mixture was subjected to the separation scheme diagrammed on page 36. Preparative column chromatography was performed on a 3/8 inch 20 foot 30% SE 30 column. Silver nitrate impregnated silica gel was prepared by adding a concentrated aqueous solution containing 10 g of silver nitrate to 90 g of silica gel in a 500 ml round bottom flask. The water was slowly removed under aspirator vacuum in the dark. In a similar fashion, a twenty weight percent silver perchlorate impregnated silica gel was prepared.

Two dimers (XLV-A and XLVII) were retained by silver nitrate impregnated silica gel. The column was eluted with hexane, hexane-benzene, and finally benzene alone. Silver perchlorate impregnated silica gel retained five dimers. Hexane, hexane-benzene, benzene was the elution sequence, although a hexane, hexane-ethanol sequence could also be used. The five dimers in increasing order of retention tenacity were:



See Appendix I for structure assignments of the isolated dimers

based on their NMR spectra.

Photochemical. Five ml of 7-methyl-norbornadiene were transferred on a vacuum line into a pyrex tube containing .064 g (1×10^{-4} moles) of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$. This was irradiated in a merry-go-round with a high pressure mercury arc using a pyrex filter for 8 days, 18 hours and 30 minutes. The excess 7-methyl-norbornadiene was removed under aspirator vacuum at $0-5^\circ\text{C}$. Comparison of dimeric products was made by gas chromatographic analysis using a 1/8 inch 20 foot 5% SE 30 column and by use of silver nitrate and silver perchlorate impregnated silica gel thin layer plates. These plates were prepared by dipping pre-cut Baker-flex Silica Gel 1B thin layer plates into a saturated methanol solution of the appropriate silver salt. The degree of impregnation is determined by the concentration of the solution and the duration of submersion of the plates. The eluted (hexane or hexane-ethanol) plates were developed by spraying with a potassium permanganate solution.

Kinetics Experiments

The reaction vessel was a 50 ml 14/20 three neck flask. The middle neck was fitted with a water cooled condenser which was packed (45 cm) with short lengths of 3 mm glass tubing to prevent losses by evaporation. One of the exterior necks was stopped with a septum cap while the other was fitted by means of tygon tubing with a glass tube having a medium porosity frit. This system allowed sweeping of the reaction by nitrogen or carbon monoxide gas. Gas flow was monitored by a soap bubble flowmeter.

The flow rate was kept at 13.5-14.5 ml/minute during all reactions. The temperature was maintained to $\pm 0.3^\circ\text{C}$ by a large constant temperature bath. All reactions were run at a promoter concentration of 1.12×10^{-2} M. The promoter ($.2148 \text{ g Ni(CO)}_2(\text{P}\phi_3)_2$ or $.3 \text{ g Ni(P}\phi_3)_4$) was dissolved in 7 ml of norbornadiene which had been warmed to about 60°C . The solution was quickly injected through the septum cap into the reaction flask, which contained 23 ml of norbornadiene (and any added ligands) already in thermal equilibrium with the constant temperature bath. Prior to the addition of the $\text{Ni(CO)}_2(\text{P}\phi_3)_2$ solution, a stream of the sweeping gas had been established in the reaction flask. Samples (ca. .2 ml each) were withdrawn from the reaction and quickly cooled. The samples were prepared for analysis by adding the appropriate amount of a benzene solution of dodecane (standard). The standard solution and diluted reaction sample solutions were prepared so as to produce gas chromatographic peaks of similar intensity for the standard and principal dimer at a given attenuation setting on the gas chromatograph. Each prepared sample was analyzed at least three times.

The analyses were carried out using a 1/8 inch 20 foot 5% SE 30 column with a linear temperature program of $6^\circ\text{-}10^\circ\text{C/minute}$ starting at 50°C . The data was obtained as integrated areas under peaks and was treated as described in Appendix II to give concentrations of dimer. Dimer concentration vs time values were subjected to least squares analyses. The slopes and abscissa intercepts of the least squares lines are recorded in Table 1 on page 71.

PART II

ELECTRO-ORGANOMETALLIC CATALYSTS

INTRODUCTION

Transition Metal Organometallic Reagents and the Application of Electrochemistry to Their in situ Generation

A large proportion of the organic reactions used to form carbon-carbon bonds can be thought of as involving organometallic reagents. This includes such well-known cases as the Reformatsky and Grignard reactions as well as the less obvious base-catalyzed condensations involving alkali metal salts of stabilized carbanions such as enolates. There also exists within this large group, a body of classical coupling reactions in which the reagent is usually generated in situ. Under this heading the following reactions may be noted.

1) Wurtz reaction: $RX + RX \longrightarrow R-R$

- a) Primary halides work best.
- b) Metallic sodium is used except for ring closure of α, ω polymethylene dihalides, where Zn is favored.
- c) Cross coupling reactions generally give poor yields.
- d) Only ethers, of the common functional groups can survive reaction conditions.

2) Wurtz-Fittig reaction: $RX + ArX \longrightarrow R-Ar$

- a) This reaction works well for bromides with sodium as a coupling agent.
- b) Most functional groups interfere with the reaction.

3) Ullman reaction: $ArX + Ar'X \longrightarrow Ar-Ar'$

- a) Supplants Fittig reaction by substituting copper for sodium.

- b) High temperature is required (150° - 240°C).
- c) Functional groups with hydrogens attached to oxygen or nitrogen inhibit reaction.
- d) Coupling of like substrates generally gives reasonable yields.
- e) Cross-coupling yields rarely exceed 50% and are usually lower.

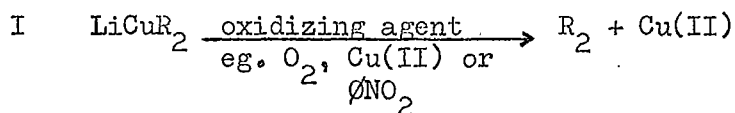
The general impression one gains upon examination of these reactions is the prevalence of harsh conditions. As a result of the demand in modern synthesis for the formation of carbon-carbon bonds under mild conditions, efforts have been made to avoid these classical reactions, and a search made for new approaches. The majority of success in the area of reactions applicable to laboratory synthesis has come from two areas: the chemistry of organo-copper reagents and organo-nickel reagents. These reagents and their reactions shall now be discussed from the viewpoint of their scope and limitations. Other pertinent reactions shall also be mentioned.

Organo-copper Reagents

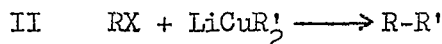
Two reviews^{1,2} have recently appeared covering organo-copper reagents and these will be heavily relied upon in this portion of the introduction. The chemistry of organo-copper reagents could be divided into three areas based on reagent types: RCu , RCu -ligand and LiCuR_2 . However, in practice, it is only the more readily available and versatile lithium disubstituted cuprates (LiCuR_2), which have found general use among chemists. Thus, this is the only reagent type to be discussed here.

These reagents are most often prepared in tetrahydrofuran from an organolithium and a cuprous halide in situ. In some cases it was found advantageous to add a ligand such as bipyridyl or triphenylphosphine during the preparation of the reagent. It is useful to classify reactions using LiCuR_2 as coupling and addition reactions. Representative examples of reactions in each of these categories are given below to provide an insight into the scope of these reagents.

Coupling reactions:



R = Alkyl, vinyl, aryl



- a) RX = 1° alkyl chloride, bromide, iodide or tosylate
 = 2° alkyl bromide (if R' = aryl)
 = α-bromoketone or α-bromocarboxylic ester

R' = alkyl or aryl

An oxidizing agent, eg. O_2 or O_2NO , is necessary to effect coupling.

- b) RX = aryl or vinyl bromides or iodides

R' = alkyl, aryl, vinyl

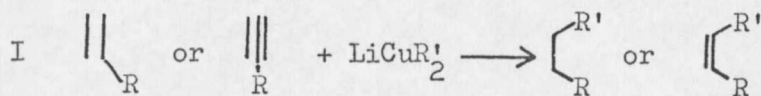
- c) RX = allyl or propargyl bromides

R' = alkyl, aryl

- d) $\text{RX} = \text{Ar} \overset{\text{O}}{\parallel} \text{C} - \text{Cl}$ or $\text{RC} \overset{\text{O}}{\parallel} - \text{Cl}$

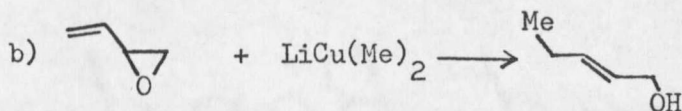
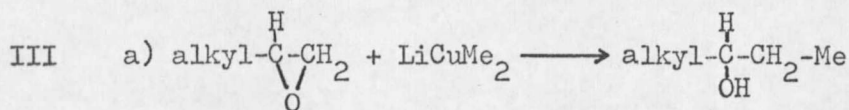
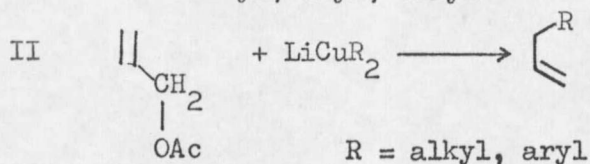
R' = alkyl, aryl or vinyl

Addition reactions:



R = carbonyl group, $\text{C}(=\text{O})\text{-R}''$, $\text{C}(=\text{O})\text{-O-R}''$

R' = alkyl, aryl, vinyl



In the majority of the above cases it has been found a stoichiometry of greater than one mole of organo-copper reagent to one mole of substrate is optimum. Although it is not stated in the literature for each specific case, it appears that generally one obtains RCu molecules as relatively unreactive by-products in the above reactions. These two points can mean a considerable amount of organo-cuprate is not effectively used. If the organic moiety in the cuprate is difficult to obtain, this can be a severe limitation. If there is excess organo-lithium (or Grignard) reagent in a reaction to regenerate the disubstituted cuprate anion, only a catalytic amount of cuprous salt is necessary. However, this "catalytic" route, due to side reactions, is often less efficient for the production of the desired molecule.

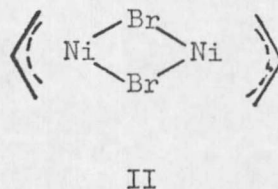
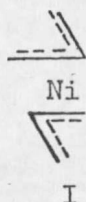
One further limitation on the use of organo-copper reagents concerns the protection of functional groups. The reaction of LiCuR_2 with carbonyl groups is slow and thus carbonyls in the substrate do not need to be protected when such a reagent is used. However, one must protect carbonyl groups in the substrate if the above, simpler "catalytic" procedure is used since a very active organometallic is always present. Nor can one incorporate unprotected carbonyl functions in the cuprate since its preparation involves the use of active organometallics. This is probably also true for other carbonyl-type functional groups, eg. nitriles and imines.

The presence of other functional groups also alters organo-copper reagents; amines tend to act as ligands, thereby altering the stereochemical course of reactions, while active hydrogen groups, eg. $-\text{OH}$ and $-\text{NH}$, oxidize the reagent. Thus, while organo-copper reagents are very useful synthetic tools, there are several restrictions on their application.

Organo-nickel Reagents

The most highly developed area of nickel reagent chemistry is that involving π -allylic nickel compounds, either as discrete reagents or as transient intermediates. This area has also recently been reviewed^{3,4} in detail and the following discussion relies extensively on these reviews, although reference will be made to other reports concerning related areas when appropriate.

Two types of π -allylic nickel reagents exist: bis(π -allylic)nickel species, I, and π -allylic nickel halides, II.



Both types of reagents are air sensitive and involve inconvenient preparations, as shown below.

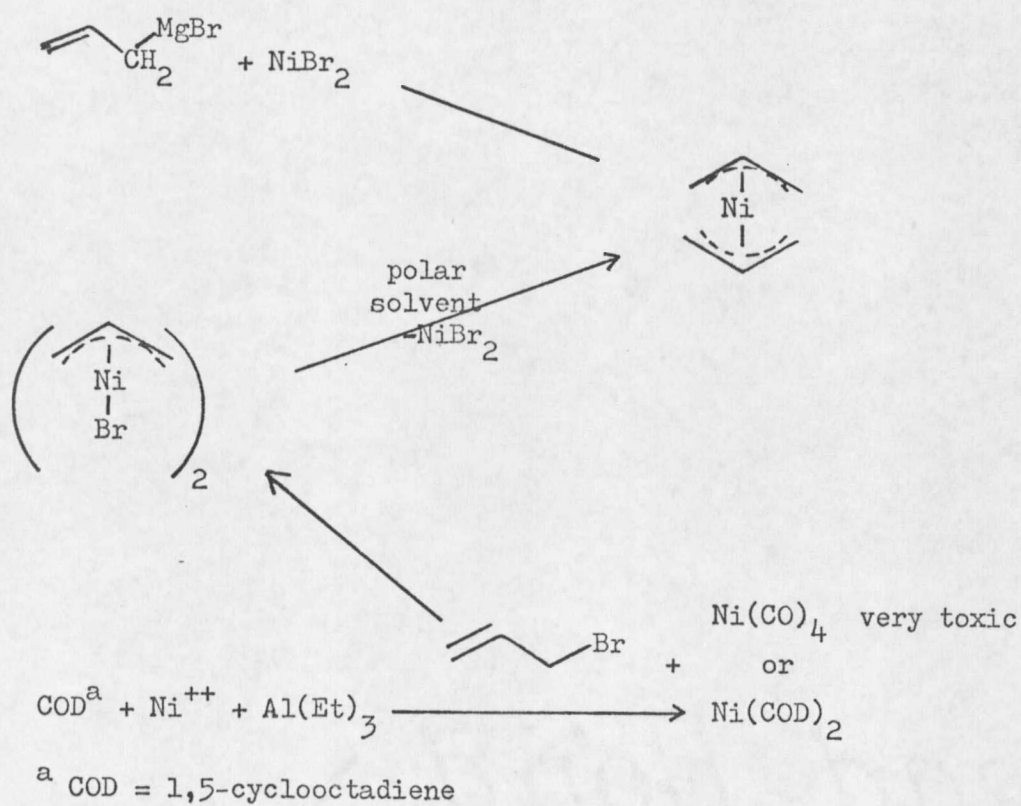
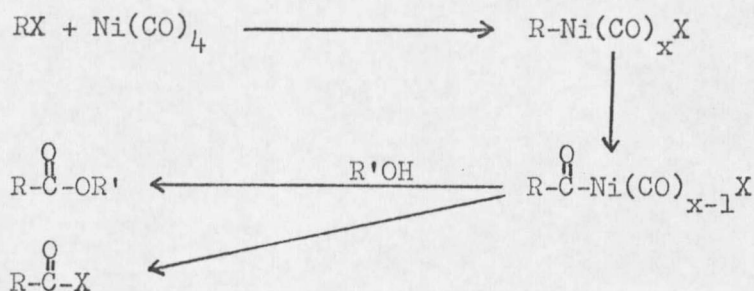


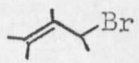
Figure 1
Preparations of Allyl Nickel Reagents

The reaction of an allylic Grignard with nickel bromide to give the bis(π -allylic)nickel complex would appear to be the most facile approach, but it is not well documented. Semmelhack states the Grignard route to bis(π -allylic)nickel complexes is less convenient than the route via allyl nickel halides. However, this latter path involves the use of either the very toxic nickel tetracarbonyl or bis(1,5-cyclooctadiene) nickel, $\text{Ni}(\text{COD})_2$, which itself must be synthesized. The bis(π -allylic)nickel complexes are generally thermally unstable, very volatile (the parent bis(π -allyl)nickel co-distills with ether) often making purification difficult. In general, synthetically, bis(π -allylic)nickel species offer no particular advantages over π -allylic nickel halide complexes. The one significant exception is in the case of the oligomerization reactions of butadiene to give various products (eg. 1,2-divinylcyclobutane, 4-vinylcyclohexene, 1,5-cyclooctadiene or 1,5,9-cyclododecatriene) depending on the conditions used. In this case, as well as in the crossed oligomerization of 1,3-butadiene and ethylenes, bis(π -allylic)nickel species appear as transient intermediates.

Whether generated as discrete reagents or as transient intermediates, the chemistry of π -allylic nickel halides can be divided into three reaction types; carbonyl insertion, coupling and addition.

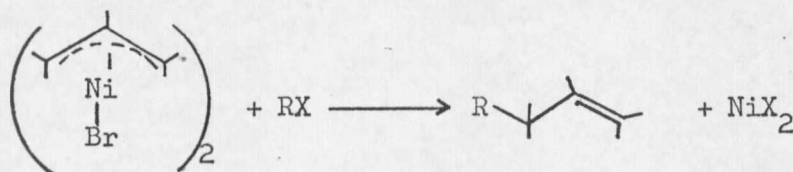
Carbonyl insertion reactions are most often carried out by the in situ generation of active nickel species from nickel tetracarbonyl. The reaction can be diagrammed as follows:



$\text{RX} =$ , , Ar(I or Br) , alkyl-I. Often, a strong base, eg. NaOMe or Ca(OH)_2 ⁵, is required for these substrates.

At least with allylic halides, it is not easy to predict whether carbonyl insertion or coupling will occur for a given structure. However, complementary carbonylation reactions are available using sodium tetracarbonylferrate(II)⁶ or the olefin/palladium chloride/CO system.⁷

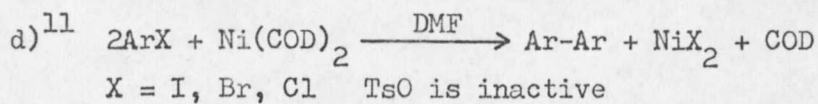
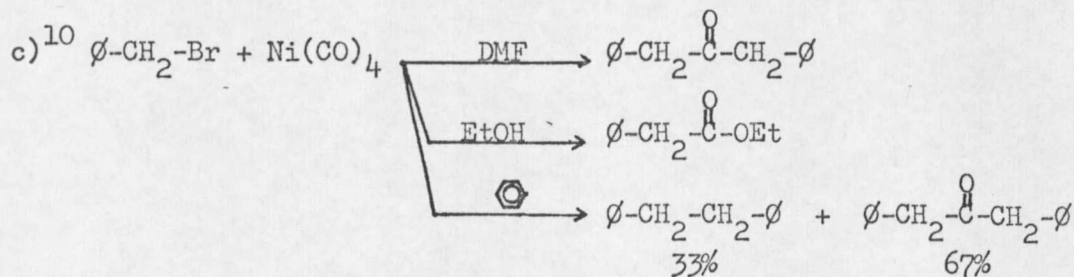
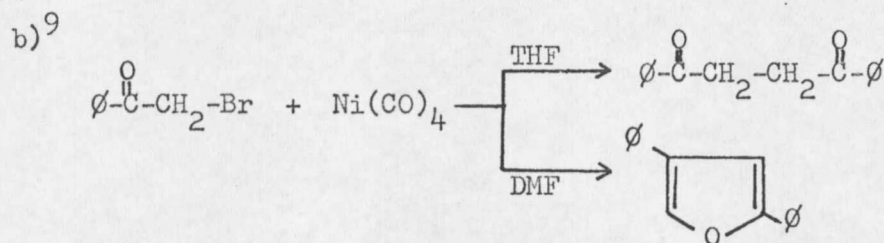
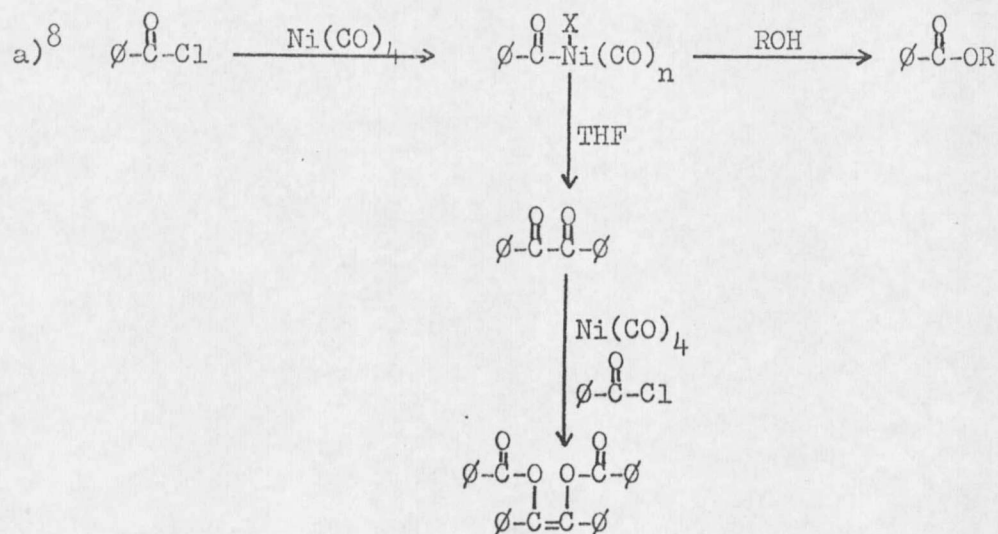
Coupling reactions with π -allylic nickel halides or the in situ generation of such species from allylic halides and nickel, offers a general route for the addition of an allyl group. Thus, in the sequence

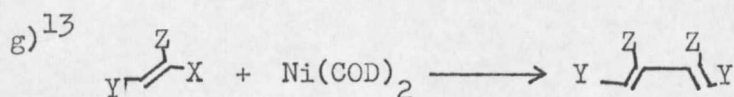
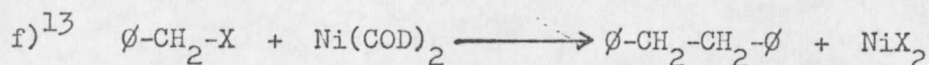
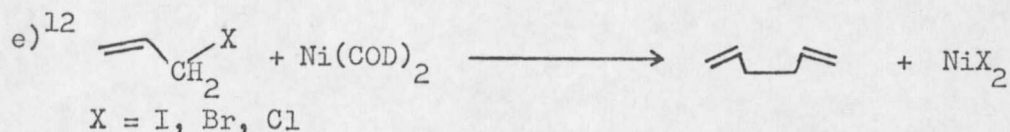


R can be allyl, benzyl, alkyl, vinyl or aryl. X is usually Br or I, although in the allyl case the following relative reaction rate sequences have been established: $\text{I} > \text{Br} > \text{Cl}$ and $\text{TsO} > \text{OAc}$. In general, bromides or iodides (2° alkyl, aryl) are used and the reaction is run in polar solvents (eg. dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone or hexamethylphosphoramide). Yields are usually quite good, 70-90%.

However, this reaction is stoichiometric in the nickel reagent.

Other organic halogen compounds can be coupled by the action of Ni(CO)_4 or Ni(COD)_2 .





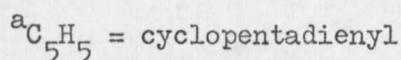
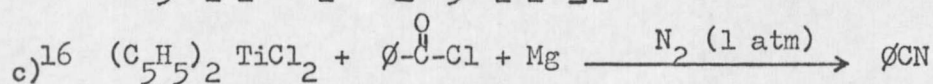
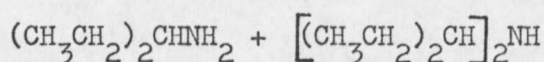
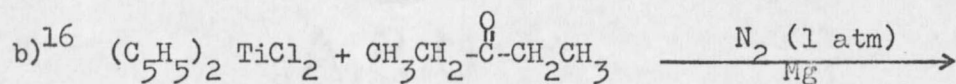
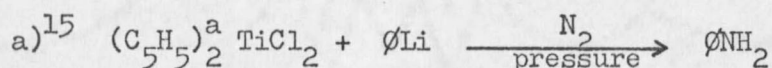
$\text{X} = \text{Br}$ or Cl

Y and Z are often carbonyl functionalities, although fair to good yields can be obtained when they are H , alkyl or aryl groups.

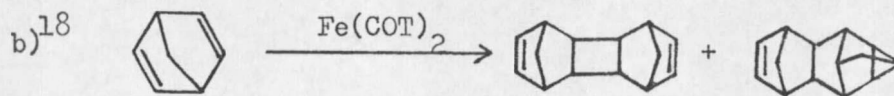
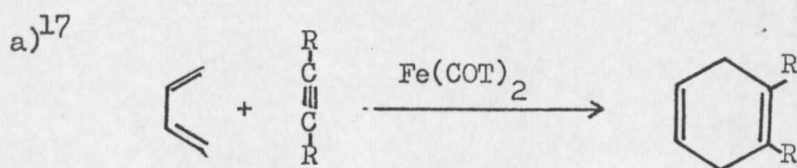
A number of addition reactions involving a Ni(O) complex, butadiene and an organic carbonyl compound have been developed by Wilke.³ Cassar¹⁴ has found Ni(CO)_4 , an allylic compound, acetylene and carbon monoxide can be added to give 2,5-dienoic acids. While these reactions are useful, they have not found widespread use among chemists and will not be discussed here.

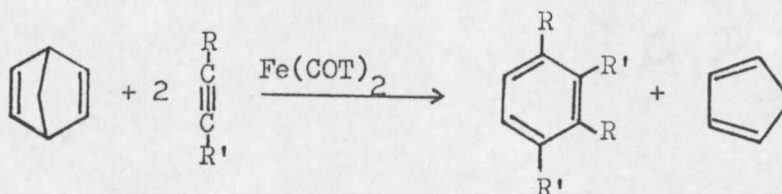
However, it has been found that in polar solvents at $50-60^\circ\text{C}$, π -allylic nickel halides can add across ketone carbonyls to give β - γ unsaturated alcohols. Similarly, epoxides can be opened. It is interesting that acrolein undergoes 1,2 addition of an allyl group to the carbonyl function while methyl acrylate affords the 1,4 addition product. In general, these additions may find special synthetic applications, but they do not offer any particular advantage over magnesium or lithium reagents.

Although organo-cuprates and organo-nickel species are the most versatile transition metal organometallics, there exists a considerable body of data on reactions promoted by other transition metal organometallic reagents. Sodium tetracarbonyl ferrate and the olefin-PdCl₂-CO system have already been noted. The fixation of nitrogen by low valent titanium compounds has also been realized.

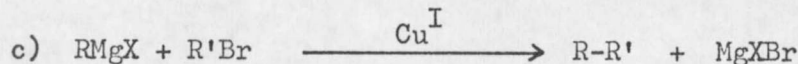
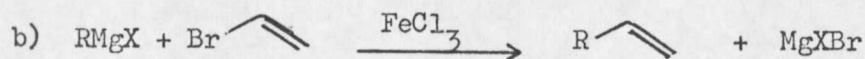
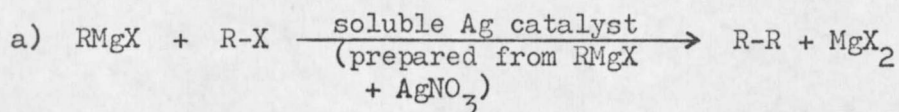


Using bis(cyclooctatetraene)iron, (COT)₂Fe, it has been possible to effect Diels-Alder type reactions.



c)¹⁹

Often, the active catalytic species are not isolated or even identified. For example, Kochi has reported²⁰ the following useful reactions which have been distilled from a large body of data.²¹



The last reaction can be recognized as probably involving an organocuprate reagent. In fact, reactions of this type have served as, and will continue to be, a source of inspiration and motivation for detailed investigations of transition metal based catalytic systems.

One underlying similarity between the various organometallic reagents which have been discussed here is the preponderance of stoichiometric reactions. Thus, in most cases, unless the reactions are run in the presence of a strong reducing reagent (eg., an organo-lithium or Grignard reagent) to regenerate the catalyst, a relatively large amount of "catalyst" is needed. As noted in this discussion, the catalysts often are not

readily available for large scale use, and the presence of strong reducing agents can limit synthetic scope and certainly encumber it.

Thus, it would be desirable to have a reduction method available that allows the production of "catalytic" species, but which does not cause unwanted side reactions. In light of the reduction potential range of transition metal cations and their compounds (relatively low) and the polar nature of the solvents in which many of the above discussed "catalytic" reactions are run, electrochemistry suggests itself as a reduction mode. This method of producing active metal species shall now be discussed to provide background as well as an understanding of the principles upon which this portion of this thesis is based.

The electrochemical generation of organometallic compounds can be divided into two general areas, non-transition metal organometallics and transition metal organometallics. The former area has received the greatest attention and organic derivatives of the following elements have been prepared electrochemically: Zn, Cd, Hg, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, and Bi. In most cases one of two techniques was used.^{22,23a}

1. Reduction of an organic halide at a cathode of the appropriate element, or
2. Reaction of an alkyl metal compound, AlR_3 , $RMgX$ or their alkali metal derivatives, eg. $NaAlR_4$, with an anodically generated cation of the appropriate element.

Undoubtedly, the interest shown in electrochemically produced non-transition organometallics is motivated by possible industrial applications.

In fact, a large portion of the tetraalkyl lead compounds produced are prepared electrochemically.

The electrochemical generation of transition metal compounds has been much more limited in scope. Exemplary of the work which has been done is that of Lehmkuhl and workers, who have prepared Ni, Co and Ti containing organometallics by the electrochemical reduction of $\text{Ni}(\text{acac})^*_2$, $\text{Co}(\text{acac})_2$ and TiCl_4 in the presence of organic ligands. In this manner they have prepared, for example, bis(1,5-cyclooctadiene)nickel(0)²⁴, π -cyclooctenyl-1,5-cyclooctadienecobalt(I)²⁵ and cyclooctatetraene titaniumchloride pyridinate.²⁶

The area of intentional in situ generation of very reactive metallic or organometallic reagents has been even more limited. Some representative examples are given below.

1. The generation of a metal in an oxidation state suitable for reaction as a catalyst or reagent.
 - a. Reduction of aromatics with Li° from LiCl .²⁷
 - b. Oxidation of aromatics with Mn, Co or Ag in high oxidation states to give aldehydes.^{23b}
 - c. Hydroxylation of aromatics with molecular oxygen and electrochemically generated Cu^{I} .^{23b}
 - d. Formation of "univalent magnesium" (benzophenone to benzopinacol) and "univalent aluminum" (nitrosobenzene to

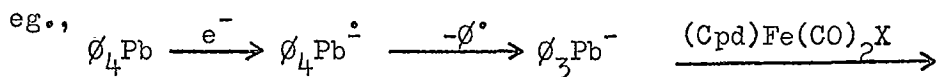
* acac refers to the mono anion of acetylacetone (pentan-2,4-dione).

sym-diphenyl hydrazine).^{23b}

- e. Electrochemical generation of Ni^{28} and Co^{29} catalysts for conversion of butadiene to 4-vinyl cyclohexene and 1,5-cyclooctadiene.

2. Preparation of amalgams for hydrodimerizations of activated olefins,^{23b} eg. $(\text{R}_4\text{N})(\text{Hg})_x$ $\xrightarrow{\text{CN-CH=CH}_2}$ $\text{NC-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CN}$ 100%

3. Generation of reactive radical anions suitable as reagents^{23c},



Although these examples are not exhaustive they do show the trend of in situ generation of reactive metal containing species and imply the potential for further investigation.

With a background of the sort of systems to which the electrochemical technique has been applied, it is now appropriate to discuss the basis for application of the technique to coupling and insertion reactions of organic substrates. As noted in the first portion of this introduction, frequently one encounters reactions in which the coupling of two organic substrate molecules is promoted by the presence of a transition metal in a low oxidation state. In addition to the coupled organic product, one obtains the oxidized transition metal. If the oxidized transition metal is electrochemically reduced, it is possible to provide the system with an electrochemically regenerated "catalyst".

The situation for a divalent metal can be diagrammed as follows, where RX refers to the substrate to be coupled.

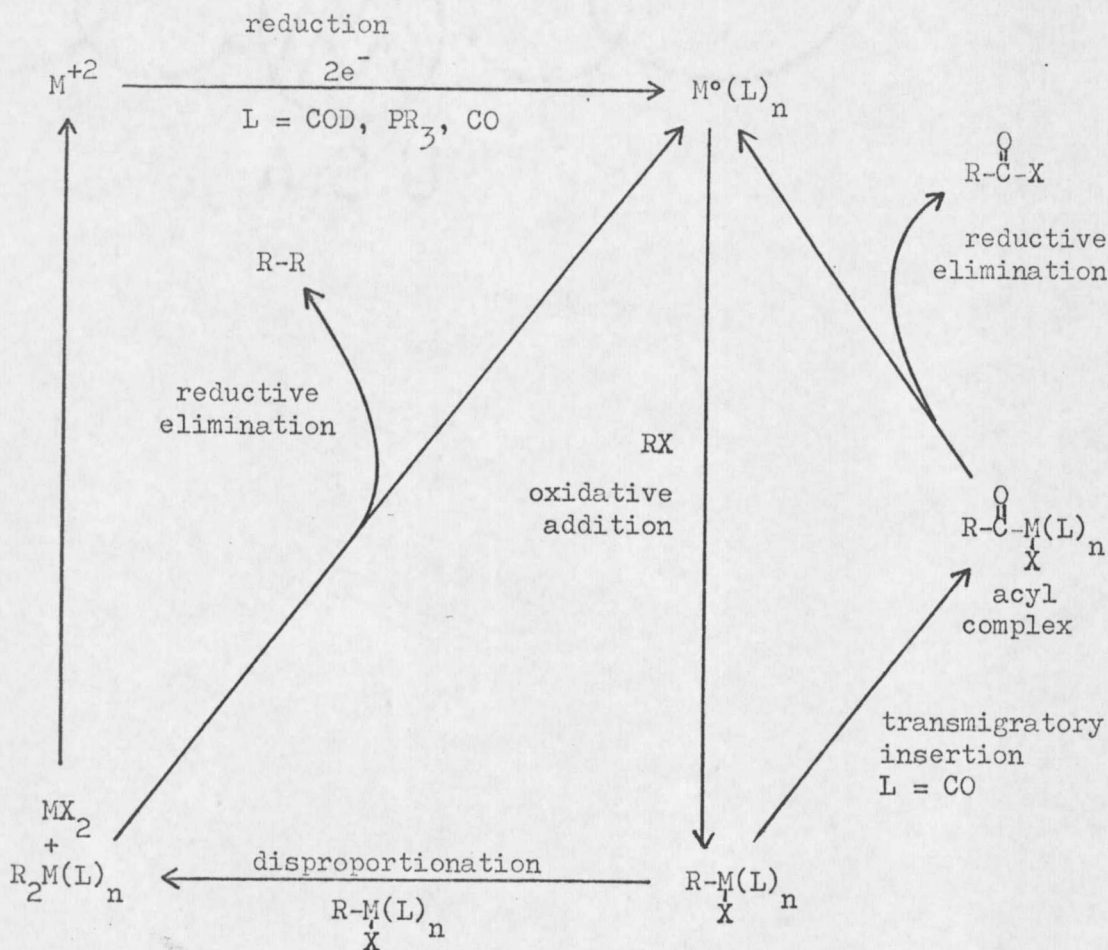


Figure 2

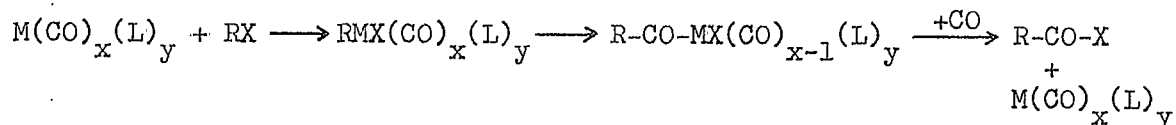
Schematic for Electro-organometallic Catalysis

Note, that included in the sequence is the alternative route involving carbonyl insertion.

The initial step is reduction of the transition metal in the presence of a number of possible ligands to yield the active transition metal complex. This reduction should be carried out at a potential low enough

to avoid reduction of the common functional groups. This, in fact, is possible for the majority of common functional groups, although closer regulation of potentials is required when transition metals on the left-hand side of the periodic table are used than when metals from the VII-B and VIII groups are used.* The oxidative addition step is strongly influenced by the nature of the metal and the coordinated ligands, L. Collman, in two reviews,^{31,32} has pointed out that d^{10} complexes undergo oxidative addition more easily than do d^8 complexes. He has also noted³³ that oxidative additions are promoted by the presence of strong electron donors, eg. R_3P , and the absence of strong π -back-bond acceptors, eg. CO. The complex, $RMX(L)_n$, which is formed in the oxidative addition reaction, may be either π - or σ -bonded. As noted in part I of this thesis, page 15, the presence of strong σ -donor ligands favor $\pi \rightarrow \sigma$ reactions. This complex may follow either of two routes depending on the nature of the ligands, L. If at least some of the ligands are carbonyls, then trans-migratory insertion can occur to give an acyl complex. The nature of the R group, the metal and any remaining coordinated ligands can determine the probability of this route. If excess CO is present, the resultant acyl complex can reductively eliminate to give a carbonylated organic product and the active catalyst. Thus, this cycle can be catalytic.

* To aid in the determination of the appropriate reduction potentials and the feasibility of any given reaction, reference can be made to the extensive lists of polarographic data available.³⁰ This, of course, can be supplemented by small-scale control potential electrolyses.



Two molecules of the $RMX(L)_n$ complex can also undergo disproportionation to give a $R_2M(L)_n$ complex and MX_2 . Thus, one M is returned to be reduced again while the other reductively eliminates to give product and a M^0 species.

If oxidative addition is promoted by σ -donors³³ and if σ -donors also stabilize resultant σ -bonded organometallics (alkyl, aryl or acyl complexes),³⁴ it is probable that replacement of a σ -bonded ligand by a strong π -back-bond acceptor will promote the reverse process of reductive elimination. One is therefore faced with a dilemma, and the best compromise may be to use ligands such as triaryl phosphines, which can act as acceptors to at least some extent.

The net result of such a cycle is the use of catalytic amounts of metal and associated ligands, and the flow of two faradays of charge for each mole of coupled product produced.

Finally, one may consider some of the electrochemical variables which influence these "catalytic" coupling reactions. Although there are a very large number of variables associated with any electrochemical reaction only three of these shall be distinguished as being clearly important here. These are electrode potential, electrode material and solvent. As will be seen, the first two of these variables are perhaps best treated together. It may be argued that the careful control of the

electrode potential is critical to any electrochemical reaction and the importance of such control cannot be denied. The manner in which the potential is controlled, however, can vary widely. In the case of the proposed "catalytic" coupling reactions there are two types of reduction potentials to be considered; the metal reduction potential and the substrate reduction potential. Since most common functional groups have more negative reduction potentials than do transition metal ions, it is generally possible to reduce the metal without reducing the substrate. Furthermore, in light of the cyclic nature of the coupling reactions ($M^{+n} + ne^- \longrightarrow M^0 \xrightarrow{RX} \longrightarrow M^{+n} + R-R$), the concentration of metal ions reaches an equilibrium value. The following points may be made:

- a) the metal ions are present in concentrations which are only a fraction of the substrate concentration(although they are, speaking from a classical electrochemical point of view, quite high).
- b) the coupling reactions occur quite readily and hence
- c) the concentration of metallic "catalyst" species is probably quite low.

Thus, the concentration of the metal ions doesn't change very much until the substrate is nearly completely reacted.* Thus, monitoring the applied potential provides a reasonable check on the cathode potential.

* Note that the relation between emf and concentration is given by the Nernst equation as $E = E^0 + \frac{0.0591}{n} \log \frac{[ox]}{[red]}$. Thus to change the

value of E by 0.1 volt for a two electron reduction, one must change the ratio $[ox]/[red]$ by 2400, which is a very large change for this system.

In order for an electrochemical reduction to occur, there must be an electrochemical oxidation as well. There are several ways to avoid difficulties with concurrent oxidation processes. The conceptually easiest route, and experimentally most inconvenient route is to use a divided cell. An alternative which is experimentally advantageous is to allow an innocuous oxidation to occur in an undivided cell. One of the most facile approaches is to use a sacrificial anode. This route was chosen in the electrochemical preparation of Ni(COD)_2 by Lemkuhl²⁴ who used two aluminum electrodes in a pyridine electrolyte. The two half reactions can be written:

$$\text{Ni}^{++} + 2\text{e}^- \longrightarrow \text{Ni}^0 \xrightarrow{2\text{COD}} \text{Ni(COD)}_2$$

$$\text{Al}^0 \longrightarrow 3\text{e}^- + \text{Al}^{+++}$$

The anodically generated aluminum ions were probably quite readily complexed by pyridine. It can be noted also that a cell composed of these two half reactions would result in a spontaneous reaction (act as a battery) if it were not for the internal resistance of the cell. In fact, an applied voltage of about 18 volts is required for significant reaction. One could also use an anode made of the same metal as is used for the "catalyst". The concentration of metal ions in solution would thus steadily increase as the reaction proceeded. But, since the half cell reactions are identical, there is only one solution; and barring concentration gradients, only one concentration of metal ions, the cell potential would remain zero. The only significant change would be in the ionic strength of the solution, which initially is quite high in light of supporting electrolyte concentration and concentration of metal ion originally in

the cell.

As noted in the first part of this introduction, many of the coupling reactions have been found to work best in highly polar solvents and it has been suggested by Semmelhack¹³ that this may be due to their role as very labile ligands. In particular, the aprotic, water soluble, high dielectric constant solvent N,N-dimethylformamide has been found to be very useful, although, other similar solvents such as dimethylsulfoxide and hexamethylphosphoric triamide have found some use. The presence of $P\phi_3$ or other good σ -donor ligands would allow the use of acetonitrile as well. All of the above solvents dissolve organics, inorganics and organometallics readily. Dimethylformamide offers the additional advantage of low reactivity towards anion radicals.

In light of the introduction presented here it ought to be evident that the application of the electrochemical reduction technique to transition metal organometallic promoted reactions ought to be quite fruitful.

DISCUSSION

Coupling Reactions

Several coupling reactions of organic halogen compounds have been run in our laboratory. The reactions were conducted under a nitrogen atmosphere in glass, single compartment cells. Two general electrode systems were used: two aluminum electrodes or a copper cathode and nickel anode. Nickel ion was introduced as $\text{Ni}(\text{acac})_2$, while tetraethyl ammonium bromide was the supporting electrolyte. The solvent was N,N-dimethylformamide in all cases. Unless otherwise noted, the products were indentified by infrared spectra (ir) comparisons and mixed melting point determinations with known samples.

Chronologically the first, as well as the most thoroughly investigated reaction, was the coupling of benzyl halide with low valent nickel species. The applied potential was such that in the absence of Ni^{++} no appreciable current would flow, ie. no reaction would occur, while in the presence of Ni^{++} , appreciable reaction would result. The results can be tabulated as follows, where COD = cyclooctadiene.

Table 1
Benzyl Halide Coupling Reactions

Substrate	Added Ligand	Electrodes (cathode/anode)	Isolated Yields
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	$\text{P}\phi_3$	Al/Al	69%
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	COD	Cu/Ni	56%
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}^{35}$	$\text{P}\phi_3$	Cu/Ni	87
$\text{C}_6\text{H}_5\text{CH}_2\text{Br}^{35}$	$\text{P}\phi_3$	Cu/Ni	85%
$\text{C}_6\text{H}_5\text{CH}_2\text{I}^{35}$	$\text{P}\phi_3$	Cu/Ni	—

These results can be examined from the viewpoint of four closely interrelated variables: electrode material, added ligands, the halogen (X), and the appearance of side reactions.

Using Al electrodes, $P\phi_3$ as an added ligand and ϕCH_2Cl as the substrate, a 69% isolated yield of bibenzyl could be realized. During the course of the work-up, it was noticed there appeared to be a very fragrant by-product. Thin layer chromatography (TLC) of the crude product showed the presence of a more polar component, while an infrared spectrum showed a carbonyl peak at ca. 1705 cm^{-1} . Based on this ir spectrum and a comparison of TLC R_f values with those of a known sample, this compound was identified as phenylacetaldehyde.

By changing to a nickel anode and a copper cathode and using the same substrate and added ligand ($P\phi_3$), the elimination of this side product could be achieved. The yield of bibenzyl rose to 87%.

The yield of coupled product would be predicted to decrease, cf. page 134 of the Introduction, with the substitution of $P\phi_3$ (a good σ -donor) by cycloocta-1,5-diene (a poorer σ -donor) and this is observed (56% vs 87% yields).

When the substitution of benzyl bromide for benzyl chloride is made keeping the concentration of substrate, $P\phi_3$, $Ni(acac)_2$ and supporting electrolyte constant, and using a Cu/Ni electrode system, very little difference is observed in the course of the reaction. Thus the applied potential for a current of 50 mA remains constant during reaction and is the same value for both ϕCH_2Cl and ϕCH_2Br . The yields of coupled

product are also similar ($\phi\text{CH}_2\text{Cl} = 87\%$, $\phi\text{CH}_2\text{Br} = 85\%$).

That the potentials are nearly identical suggests the same specie is being reduced in both cases. While it is conceivable this could be an organic substrate, it is very unlikely based on published³⁰ reduction potentials of the various possible species.

$\phi\text{CH}_2\text{Br}$	-1.22 vs SCE in DMF
	-1.324 vs Ag/AgCl in methanol
$\phi\text{CH}_2\text{P}^+\text{O}_3^-\text{Cl}$	-1.826 vs Ag/AgCl in methanol
Ni^{++}	-0.855 vs SCE in DMF
	-0.917 vs Ag/AgCl in methanol

Since the reduction potential of $\text{RCl} > \text{RBr}$, it can be assumed from the above data, that Ni^{++} would reduce at a less negative potential than $\phi\text{CH}_2\text{Cl}$.

Furthermore, as noted earlier, in the absence of Ni^{++} very little current ($< 5 \text{ mA}$) flows at a potential sufficient to cause a 50 mA current in the presence of Ni^{++} .

When $\phi\text{CH}_2\text{I}$ was used as a substrate, the liberation of iodine appeared to occur at the anode and the reaction did not run cleanly.

To explore the scope of the application of this electrochemical technique to coupling reactions, bromobenzene was chosen as an example of an aryl halide. It could be coupled using $\text{Ni}(\text{acac})_2$ and either COD or P^-O_3 as an added ligand. The goal of the preliminary investigation using an Al/Al electrode system and COD as an added ligand was simply to establish the feasibility of the reaction. When the reaction was

run* using $P\phi_3$, a nickel anode and a copper cathode, a 65% yield of biphenyl was isolated. No effort was made to optimize the yield of this reaction.

Exploratory coupling reactions were also run with benzoyl chloride and $Ni(acac)_2$. With a Cu cathode and a nickel anode, and COD as an added ligand, the major product was the 1,2-diketone, benzil. Using $P\phi_3$ as an added ligand and two aluminum electrodes, the benzoate ester of the corresponding ketol, benzoin, was formed. This product was identified by comparison of ir spectra, melting point and a mixed melting point with a sample of benzoin benzoate prepared by the reaction of benzoyl chloride and benzoin**. It is reasonable to propose that the dibenzoate of benzoin (esterification of both the ketone and the alcohol) is actually produced in this latter reaction. This would be in accord with the reported⁸ result of coupling acyl halides using $Ni(CO)_4$. However, in the work-up procedure employed by Kiely, acidic water (ca. 2M HCl) is used to facilitate the break-up of emulsions. These conditions would probably result in hydrolysis of the enol ester function, giving the observed α -ketobenzoate.

From the coupling of α -bromoacetophenone with $Ni(acac)_2$, $P\phi_3$, and using a copper cathode and a nickel anode, crystals of 1,2-dibenzoyl ethane could be readily isolated. The identification of this compound was made

* This reaction was run by Mr. Dennis Miller, Montana State University.

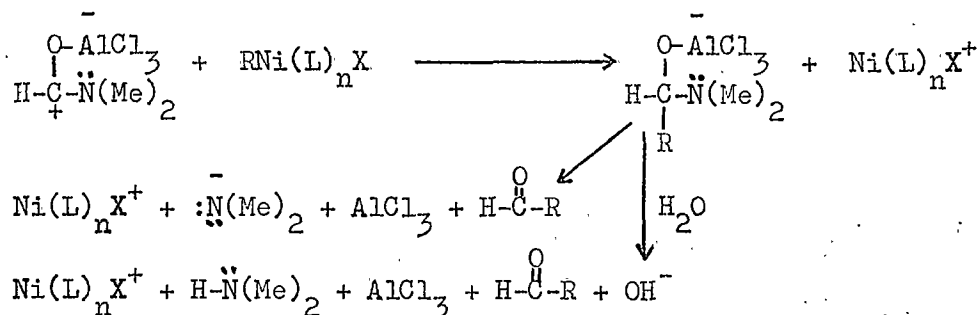
** This electrolysis and the subsequent product identification were carried out by Mr. John Kiely, Montana State University.

by comparison with the reported³⁶ ir spectrum and melting point.

As noted earlier, when benzyl chloride is coupled in an Al/Al electrode system, a by-product suggested to be phenylacetaldehyde is formed. Although Al^{+++} and Cl^- ions are formed in this reaction, dilution of the electrolyte with water results in an essentially neutral solution. When a nickel anode and copper cathode are used instead, no phenylacetaldehyde is produced. This situation was enigmatic until it was found that a DMF solution of AlCl_3 , when diluted with water, also produced an essentially neutral solution. It has been found that DMF forms a strong complex with AlCl_3 and evidence has been presented for complexation occurring through the carbonyl oxygen.³⁷ It is suggested such complexation would result in an activation of the carbonyl carbon.



It would be expected such an activated carbonyl could react with an organometallic specie, $\text{R-Ni(L)}_n(\text{X})$, such as would be produced by the oxidative addition of RX to Ni(L)_n .



Thus, either with or without the addition of water, one could visualize the formation of an aldehyde and an essentially neutral solution.

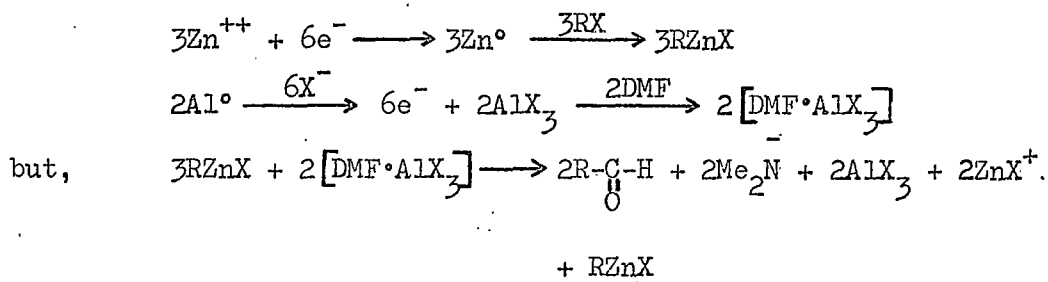
To gain the maximum synthetic utility from such a reaction, several features would be helpful.

- a) Coupling of RX molecules by the metal promoter $M(L)_n$ should be minimized; a non-transition metal might be more suitable.
- b) The reactivity of the complex $RMX(L)_n$, resulting from oxidative addition, would increase if the R-M bond were made more ionic; a non-transition metal complex would be expected to have a more ionic R-M bond than would a transition metal complex.
- c) However, to achieve substitution of the halide in RX by a formyl group, $R-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-H$, without subsequent reaction of the aldehyde, the complex $RMX(L)_n$ should not be too reactive. Moderated activity would also help to obviate the problem of the protection of other reactive functional groups which might be present in a substrate.
- d) The electrochemical generation of the low valent metal specie $M(L)_n$ and its ease of subsequent reaction with RX to give the $RMX(L)_n$ complex should also be compatible with the above points.

Zinc was chosen as the most suitable metal to meet these requirements. Its reduction potential and reactivity toward oxidative addition is a good compromise in light of the moderately ionic character of the R-Zn

bond. However, the reactivity of organo-zinc compounds toward common functional groups is quite low.³⁸ Further, organo-zinc compounds do not couple readily and dimethylformamide has been recommended as a solvent for their preparation from zinc dust and alkyl halides.^{39a,b}

It was found that electrolysis of a DMF solution of n-hexylbromide and ZnI_2 resulted in the formation of a 40% yield of heptaldehyde, isolated as the 2,4-dinitrophenylhydrazone derivative. It was felt this yield could be improved. One factor limiting the yield could be the stoichiometry of the reaction.



It can, therefore, be seen that for the flow of six faradays of charge, three moles of RZnX are formed and two moles of $\text{DMF} \cdot \text{AlX}_3$, activated DMF complex, are formed. If the reaction of one mole of RZnX with one mole of $\text{DMF} \cdot \text{AlX}_3$ results in the effective neutralization of the mole of AlX_3 then only two-thirds of the RZnX would form product (RCHO).

One way to approach this stoichiometry problem would be to add the "deficient" amount of AlCl_3 to the DMF prior to electrolysis. However, it was found that under these conditions (a high concentration of $\text{DMF} \cdot \text{AlCl}_3$ complex), the reaction did not run cleanly and little aldehyde was formed.

This problem could also be approached by changing from an aluminum anode to an anode made of a metal which preferentially oxidizes to a divalent cation showing reasonable Lewis acidity. It is now felt that this would be the most successful solution to the stoichiometry problem.

The approach which was, in fact, used involved the substitution of zinc by a trivalent metal, providing a balanced redox system. Thus $\text{Fe}(\text{acac})_3$ was used with a copper cathode, an aluminum anode and n-hexylbromide as a substrate. A gas chromatographic analysis of the product showed that the formation of heptaldehyde had not occurred to any major extent. It was established by sample admixture that the major product was n-dodecane.

As noted in the Introduction, coupling methods are often limited by the reactivity of precursor organometallics. This has been especially true for the coupling of alkyl halides and thus the discovery of a new mild coupling method would be advantageous. The reaction has not been extensively studied but it does show promise.

Carbonyl Insertion

Some success was also achieved with carbonyl insertion using the electro-organometallic technique. A DMF solution of $\phi\text{CH}_2\text{Cl}$ and $\text{Ni}(\text{acac})_2$ was reduced between two Al electrodes in the presence of a carbon monoxide atmosphere. Thin layer chromatography of the crude product showed the presence of unreacted $\phi\text{CH}_2\text{Cl}$, $\phi\text{CH}_2\text{CH}_2\phi$ and two other more polar

components, one of which appeared to be $\phi\text{CH}_2\text{CHO}$. The crude product was chromatographed on silica gel and the remaining unidentified component isolated. This compound's infrared spectrum was identical with that of dibenzylketone, while its NMR spectrum was also consistent with this assignment. It is suggested the formation and reaction of $\text{Ni}(\text{CO})_4$ may have occurred in the system, thus providing a route to the insertion product. Since the insertion product was obtained in low yield by the initial technique of exposure to a carbon monoxide atmosphere, some reactions were carried out in which a stream of CO was swept through the system at a pressure of about 1.2 atm. However, this did not improve the yield of insertion product. It did result in removal of nickel from the reaction vessel, presumably as $\text{Ni}(\text{CO})_4$, since nickel could be readily detected as nickelbis(dimethylglyoximate) in a trap placed in the effluent CO stream. It is suggested a closed pressure electrolysis cell would be required to exploit this reaction.

Suggestions for further Work in this Area

At this point a number of suggestions will be made for further exploration of the use of the electro-organometallic technique in organic chemistry. It is probable that not all the suggested reactions will behave as anticipated. However, it is hoped all will provide stimulation for further development and exploitation of this technique.

Organic Coupling Reactions. While crosscoupling experiments were not investigated, the ability to perform this sort of reaction would increase

the scope of the reaction. Since the reduction potential of alkyl tosylates is well above that of most transition metals³⁰ and since they appear to have relatively low reactivity towards oxidative addition, it is suggested that crosscoupling may best be carried out using the $\text{RMX} + \text{R}'\text{OTs} \rightarrow \text{R-R}'$ system. A likely possibility for a metal (M) would be copper.

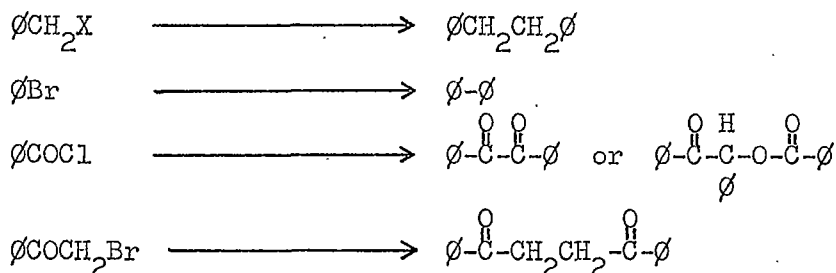
By using nickel as a metal, bipyridyl as a stabilizing ligand and a small amount of tetracyanoethylene to promote coupling,⁴⁰ it may be possible to improve the coupling of two alkyl groups.

Formylation by Bimetallic Activation. (The Halide/Formyl Substitution Reaction). It is suggested the stoichiometry problem ($\text{Al}^\circ/\text{Al}^{+++}$ and $\text{Zn}^{++}/\text{Zn}^\circ$) may best be met using a magnesium anode since MgX_2 would be formed, and it is a good Lewis acid allowing activation of the DMF. It is also suggested that other amides may prove to be reactive in this system enlarging the scope of the reaction.

Insertion Reactions. As noted, the use of a closed pressure electrolysis cell would probably increase the production of carbonyl insertion product. It is also possible other metals, especially iron and cobalt, could be used to insert carbon monoxide into carbon-carbon or carbon-halogen bonds. Other groups such as SO_2 and NO might also be incorporated. In particular the in situ generation of a tri- or tetranitrosyl substituted alkyl chromium species from $\text{Cr}(\text{acac})_3$, RX and NO or NOCl could be suggested.

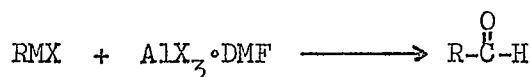
SUMMARY

It has been found that using electrochemically generated low valent nickel species, the following substrates may be coupled to give the specified products.



In these reactions it was found $\text{P}\phi_3$ was a suitable added ligand. It probably acts a) by stabilizing transient low valent nickel species, preventing the plating out of nickel on the cathode, and b) as a good σ donor.

The use of an aluminum anode, generating Al^{+++} ions which can complex with the dimethylformamide solvent, promotes a halide-formyl substitution reaction.



Zinc is suggested to be the best choice for a metal in RMX. However, because zinc favors a +2 oxidation state while aluminum favors a +3 state, problems with the stoichiometry of the reaction occur.

It was also found that n-hexylbromide would couple in the presence of an $\text{Fe}/\text{P}\phi_3$ "catalyst" to give dodecane.

Carbonyl insertion was also observed, using the electro-organometallic technique. Thus, benzyl chloride could be converted to

dibenzyl ketone in low yield.

It is felt the success of this preliminary work in the area of electro-organometallic catalysis provides a reasonable basis for expecting the technique to have wide application to organic synthesis. Further, based on preliminary experiments, some of which are referred to in part I of this thesis, page 77, it is expected at least two more areas of application exist.

The first of these involves the application of the electrochemical technique to the synthesis of new organometallic compounds. The chemistry of transition metal organometallics not having carbonyl or cyclopentadienyl ligands is very limited, but potentially very useful. Thus, the ability to synthesize such compounds would be advantageous and it is suggested the selectivity of the electrochemical reduction technique would be particularly helpful. It may also be noted the electrochemical technique may prove valuable in the synthesis of rare earth and actinide organometallics. Another area would be the selective generation of ligand stabilized metals in high or unusual oxidation states. In addition to the intrinsic value of synthesizing exotic compounds of this sort, they may prove to be useful as synthetic reagents themselves. For example, the availability of an organic solvent soluble form of the ceric ion would provide organic chemists with a potentially very useful oxidizing agent.

The second area involves the integration of electro-organometallic synthesis and electro-organometallic catalysis, ie. a study of the

mechanisms of coupling or insertion reactions. Unlike many other methods of generating highly reactive organometallic catalytic species, eg. the thermal or photochemical activation of relatively stable complexes, the electrochemical technique, because of its selectivity should allow the low energy generation of reactive organometallic species. The approach would be to build up the reactive species from reactive precursors under mild conditions, rather than tearing stabilizing ligands off a stable complex to produce this same reactive species. It may also be noted that specific ligand combinations which were otherwise difficult to produce might become available for investigation by the electrochemical technique.

EXPERIMENTAL

Instruments and equipment

Gas chromatographic analyses were run on a Varian Model 1740 Gas Chromatograph using 1/8 inch, six or twenty foot columns of 5% SE 30 on 100-120 mesh Gas Chrom Z.

Nuclear Magnetic Resonance spectra were obtained on a Varian A-60 Proton NMR.

Electrolyses were carried out with regulated voltage power supplies equipped with current limiters. Several power supplies were used, the only requirement being the ability to deliver from 0 to ca. 20 volts at currents at least up to ca. 250 mA.

Reagents

All of the organic substrates and the ligand 1,5-cyclooctadiene, were distilled under nitrogen prior to use.

Triphenylphosphine was sublimed under vacuum.

Gases

Carbon monoxide (Matheson, C.P.) used for carbonyl insertion reactions, was deoxygenated by the use of BSTS catalyst (BASF Colors and Chemicals, Inc.).

Nitrogen (Airco, Dry High Purity) used for distillation and as a protective atmosphere for electrochemical reactions, was deoxygenated by the use of BSTS catalyst.

Solvent

The solvent for all electrolyses was N,N-dimethylformamide. It was dried over Linde 4-A molecular sieves and distilled under a N_2 atmosphere.

Preparations

Ni(acac)₂. This was prepared by a variation of the procedure of Watson. An ammoniacal solution of $NiCl_2$ was prepared by the addition of just enough water to effect the solution of a mixture of $NiCl_2$ (32.4 g, 0.25 moles) and 150 ml of concentrated ammonia solution. This solution was added with vigorous stirring to an ammoniacal solution prepared by the addition of just enough water to effect the solution of a mixture of acetylacetone (55 ml, .535 moles) and concentrated ammonia (40 ml, .60 moles). The resulting thick blue mixture was vigorously stirred for one-half hour, filtered, and air dried to give the di-ammine derivative of $Ni(acac)_2$. To obtain ammonia free $Ni(acac)_2$, the di-ammine derivative was boiled in toluene, or more quickly in xylene, to give a dark green solution of $Ni(acac)_2$. The solution was concentrated and hexane added to precipitate the light green $Ni(acac)_2$. After washing the precipitate several times with hexane, it was filtered, vacuum dried and stored in a desiccator.

Fe(acac)₃. This was prepared from a stoichiometric amount of $FeCl_3$ and sodium acetylacetonate (1:3) in an aqueous solution. The dark red product was extracted with chloroform, washed with water and the chloroform was removed. The red $Fe(acac)_3$ was recrystallized from ethanol-water and air dried.

Tetraethylammonium Bromide. This was prepared from equal molar quantities of triethylamine and ethyl bromide by refluxing overnight in a toluene solution. The precipitate was washed with toluene and filtered. It was recrystallized from a benzene-ethanol mixture, dried under vacuum at 80°C and stored in a desiccator.

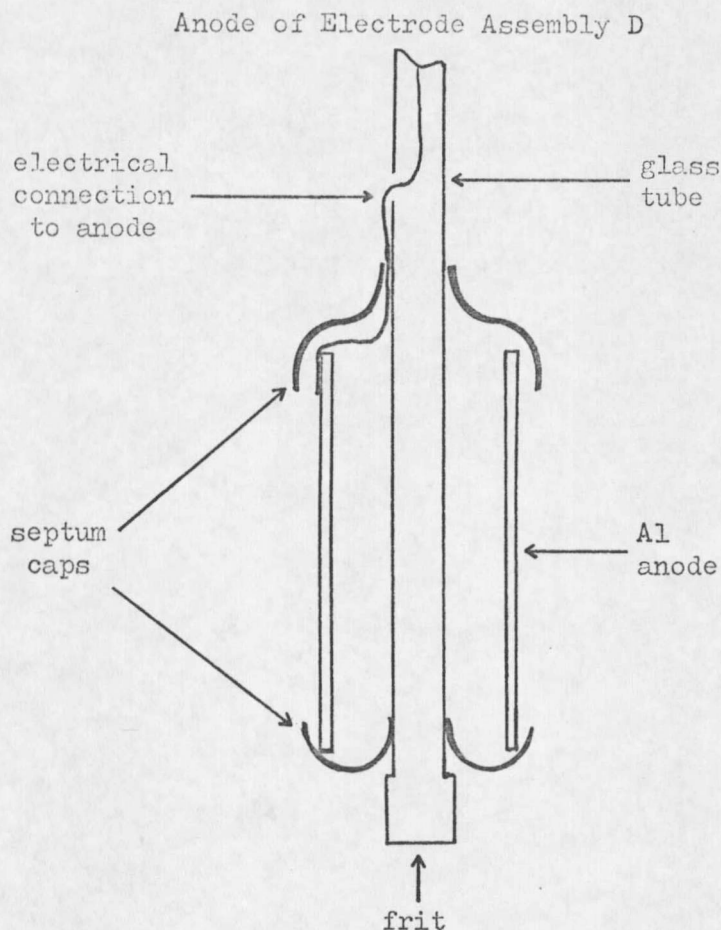
Electrochemical Cells and Electrode Assembly

The cells were pyrex cylinders of various diameters closed at one end.

The electrode assemblies were of four types.

- A) Two parallel rectangular aluminum plates.
- B) Two parallel wires, one made of copper (cathode) and the other (anode) made of either aluminum or a heavily nickel plated copper wire. This assembly was used principally for small scale (.005 moles) reactions or about one-tenth of the scale of the reactions with other assemblies and cells.
- C) Two concentric cylindrical electrodes, the outer cathode made of copper screen and the inner anode made of nickel foil wrapped around a long glass tube which had been closed off.
- D) Two concentric cylindrical electrodes, the outer cathode made of copper screen and the inner anode a short cylinder of aluminum attached by means of septum caps to a long glass tube which was fitted with a frit. This electrode assembly was used for carbonyl insertion reactions so the electrolyte could be swept with carbon monoxide.

Stirring could be effected by a teflon covered magnetic stir bar.



Procedures for Electrolysis Reactions

General Considerations. The cell was charged with the appropriate metal salt (ca. 0.1 M $\text{Ni}(\text{acac})_2$, $\text{Fe}(\text{acac})_3$ or ZnI_2), the supporting electrolyte (ca. 0.1M) and the added ligand ($\text{P}\phi_3$ or COD). The cell was flushed with nitrogen, and under a protective atmosphere of N_2 gas, the substrate and solvent added. The appropriate electrode assembly was then inserted in the electrolyte. The system was maintained under N_2 during

the electrolyses, except in the carbonyl insertion reactions where either a carbon monoxide atmosphere or sweeping of the system by carbon monoxide was used. The electrolysis was usually carried out at constant current (ca. 50 mA, fixed by the current limiter) and both potential and current were monitored frequently during the reaction. In cases where an aluminum anode was used, a short period of electrode activation was observed. During this period, usually about an hour, the voltage dropped when the current was held constant. This period of activation is not observed when a nickel anode is used. It is probably attributable to the oxide coating on aluminum and can probably be eliminated by pre-electrolysis prior to the addition of the substrate. To obviate the activation period, it has been found advantageous to increase the voltage to a high value (ca. 10-15 V, corresponding to a current value of ca. 1 amp) for a very short (30 seconds) time, and returning it to the normal (ca. 1.0 V) range to maintain a current of about 50 mA. The electrolyses were run for about 5% more time than that required by Faraday's laws. Work-up consisted of addition of the electrolyte to water* followed by repeated extraction of the organics by ether. The combined ether extracts were washed with water several times, washed with a saturated salt solution and dried over magnesium sulphate.

In the following portion of the experimental, the treatment of the

* In some cases the acidification of the water was found to be helpful in eliminating emulsions.

dried ether extracts from the various reactions will be described. The reactions were frequently carried out more than once in different cells with different electrode assemblies. Further, some of the reactions were not carried out by the author, although he supervised their running. Thus, in the following section of the experimental, only the electrode assembly types (designated as A,B,C or D), the approximate ratio (1:1:5, 1:2:6, etc.) of metal (ca. 0.1 M) to added ligand, to substrate, the nature of the metal and ligand, the temperature of the reaction (if not room temperature), and the product isolation procedure shall be given.

As noted, the approximate concentration of metal salt and supporting electrolyte was 0.1 M. Since the applied potential for any electrolysis is dependent on electrode assembly construction and many electrode assemblies were used, only guideline values for applied potentials will be given. For the electrode assemblies A,C and D an applied voltage in the range of ca. .8-1.5 volts was sufficient to maintain a current of 50 mA. For electrode assembly B, an applied potential of 3-4 volts was required to maintain a current of 50 mA. Since it was felt this potential would be apt to produce side reactions, an applied voltage of 1.5 to 2.2 volts, corresponding to a current of between 30 and 40 mA was used.

Table 3

Tabulation of Experimental Data from Electrochemical Reactions

Substrate (Reaction Temperature)	Electrode Assembly type (cathode/anode)	Metal ^b /Ligand/Substrate, ^s	Work-up ^c
$\phi\text{CH}_2\text{Cl}$ (RT) ^a	A (Al/Al)	Ni(1)/ $\text{P}\phi_3$ (.4)/S(11)	solvent removed from ether extract, ^c re-crystallized from 95% ethanol
$\phi\text{CH}_2\text{Cl}$ (RT)	C (Cu/Ni)	Ni(1)/COD(1.4)/S(7.45)	
$\phi\text{CH}_2\text{Cl}$ (RT)	C (Cu/Ni) ^a	Ni/ $\text{P}\phi_3$ /S ^e	solvent removed from ether extract under aspirator at 0°C, residue sublimed
$\phi\text{CH}_2\text{Br}$ (RT)	C (Cu/Ni) ^d	Ni/ $\text{P}\phi_3$ /S ^e	
$\phi\text{CH}_2\text{I}$ (RT)	B (Cu/Ni)	Ni/ $\text{P}\phi_3$ /S ^e	ether extract subjected to gas chromatographic analysis
ϕBr (50-60°C)	C (Cu/Ni)	Ni/ $\text{P}\phi_3$ /S ^f	solvent removed from ether extract, re-crystallized from 95% ethanol
ϕBr (50-60°C)	A (Al/Al)	Ni(1)/ $\text{P}\phi_3$ (1)/S(8.2)	
$\phi\text{C}(=\text{O})\text{Cl}$ (RT)	C (Cu/Ni)	Ni(1)/COD(.7)/S(7.4)	solvent removed from ether extract, residue sublimed
$\phi\text{C}(=\text{O})\text{Cl}$ (RT)	A (Al/Al)	Ni/ $\text{P}\phi_3$ /S ^g	
$\phi\text{C}(=\text{O})\text{CH}_2\text{Br}$ (RT)	B (Cu/Ni)	Ni(1)/ $\text{P}\phi_3$ (1)/S(8.2)	solvent removed from ether extract, re-crystallized from methanol

Substrate (Reaction Temperature)	Electrode Assembly type (cathode/anode)	Metal/Ligand/Substrate,s	Work-up
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{Br}$ (95°C) (Br/formyl substitution)	A (Al/Al)	$\text{Zn}(\text{ca.}.18\text{M})/\text{S}(\text{ca.}.8\text{M})$	ether extract was added dropwise to hot acetic acid, kept on steam bath ½ hour, solvent removed. Recrystallized from ethanol-water.
n-hexyl Br (33°C) (coupling)	B (Cu/Al)	$\text{Fe}(1)/\text{P}\phi_3(1.35)/\text{S}(2.5)$	ether extract subjected to gas chromatographic analysis
$\phi\text{CH}_2\text{Cl}$ (RT) (carbonyl insertion)	A (Al/Al)	$\text{Ni}(1)/\text{Co atm.}/\text{S}(12)$	ether extract evaporated and residue chromatographed on silica gel. Use hexane to elute non-polar components and use 15 vol% $\phi\text{H}/85$ vol% hexane to get $\phi\text{CH}_2\text{COCH}_2\phi$ product.
$\phi\text{CH}_2\text{Cl}$ (RT)	D(Cu/Al)	$\text{Ni}(1) \begin{array}{c} \text{stream} \\ \text{of CO at} \\ 760-770\text{mm} \\ \text{pressure} \end{array} / \text{S}(12)$	ether extract concentrated and analyzed by thin layer chromatography.

- a RT = room temperature
b concentration of metal equals ca. .1 molar unless otherwise noted
c for origin of ether extract see general work-up procedure in General Procedure (previous) section
d the same electrode assembly and cell were used for these two reactions
e these reactions were run by Mr. Gary Hass
f This reaction was run by Mr. Dennis Miller
g This reaction was run by Mr. John Kiely

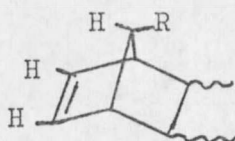
APPENDICES

APPENDIX I

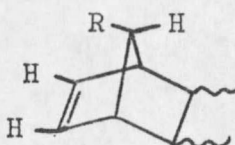
Nuclear Magnetic Spectral Data of Dimers Obtained from $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ and 7-Methylnbd with Thermal Excitation and Their Structural Assignments

Prior to assigning structural features responsible for resonances found in the spectra some assumptions and their bases should be noted.

Assumption A:



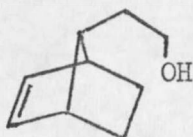
When R group anti to olefin, olefinic protons are a "clean" triplet.



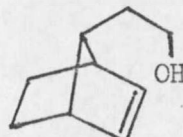
When R group syn to olefin, olefinic protons are a perturbed triplet, usually a septet.

Basis:

- 1) NMR assignments of the two compounds shown; structures are based on oxymercuration studies.⁸⁸



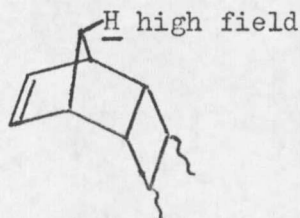
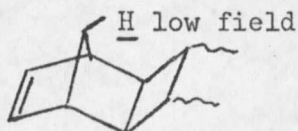
olefin protons clean triplet



olefin protons perturbed triplet

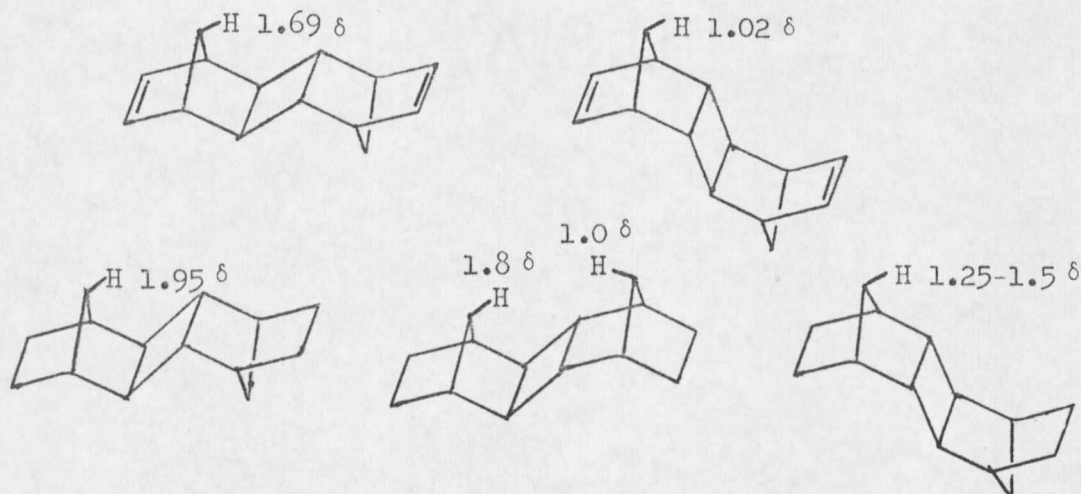
- 2) Integration of these assignments and those for a number of 7-substituted norbornenes and norbornadienes.⁴⁶

Assumption B: Bridge protons syn to an "exo" bonded cyclobutane ring resonate at relatively low field compared to protons syn to an "endo" bonded cyclobutane.



Basis:

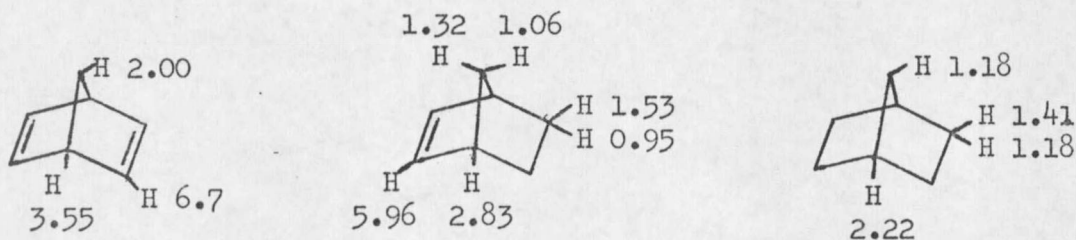
- 1) Comparison with assignments for dimers from NBD itself and the corresponding saturated dimers.⁷⁶ⁱⁱⁱ

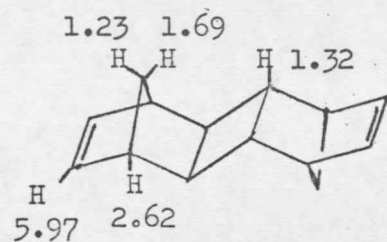


- 2) Assignments for resonances of protons over (low field) and edgewise (high field) to cyclobutane rings.⁸⁹

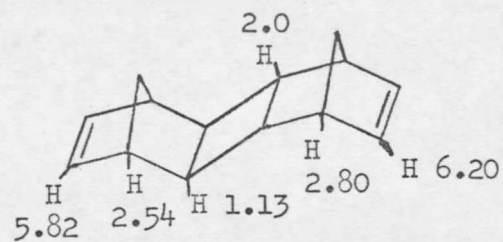
Based on these assumptions, and the assignments (vide infra) from reference 76iii for norbornadiene and norbornene dimers, preliminary assignments may be made.

Chemical Shifts (δ) in Norbornene Derivatives



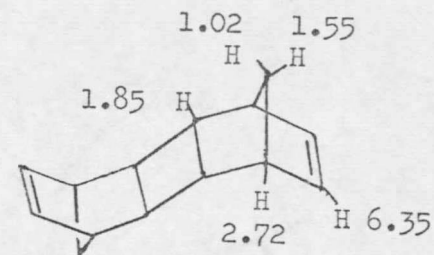


exo trans exo
xtx

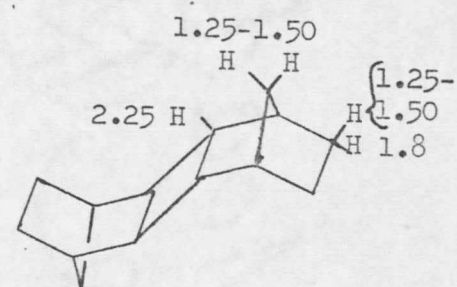
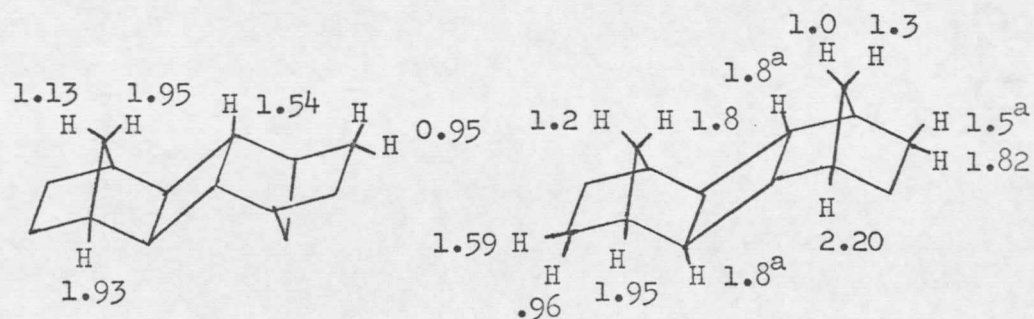


bridge protons not assigned

exo trans endo
xtn



endo trans endo
ntn



a = mean value for both fragments

Preliminary Structural Assignments of Selected 7-MethylNBD Dimers

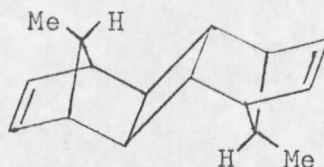
Sample in CDCl ₃	Olefin(s)	Methyl(s)	Cyclobutane(s)	Bridgeheads	Bridges
XLIV	5.84 dSept	.84 D	1.43 M	2.38 M	2.35 Q
integration	4	6	4	6	
XLV-A	6.22 T 5.73 dSept	.69 D .87 D	1.21 M	2.51 M, 2.33 M 2.12 M, 2.01 M	
integration	2 2	3 3	2	8	
XLVI	6.02 dSept 5.66 dSept	.85 D	1.17 M, 2.54 M, 2.30 M, 2.08 M, 1.84 M		
integration	2 2	6	2 3 1	2 2	
XLVII	6.34 T 6.19 dSept	.53 D .80 D	2.41 M	1.94 M, 1.67 M	
integration	2 2	3 3	4	6	

dSept = dirty septet D = doublet M = multiplet Q = quartet
T = triplet

Assignment for Dimer XLIV:

- One kind of olefin at 5.84 δ dSept, therefore methyl group syn to olefin.
- One kind of methyl at .84 δ D
- One kind of cyclobutane at 1.43 δ M

Therefore, highly symmetric dimer either xtx or ntn skeleton; the chemical shift for the olefin supports an assignment of xtx. NBD dimer xtx 5.97, ntn 6.35.



Note the similarity between chemical shift of methyl group here (.84) and in 7-methyl NBD (.87).

Assignment for Dimer XLV-A:

a) Two kinds of olefins

- i) Triplet 6.22 δ
- ii) Septet 5.73 δ

b) Two kinds of methyl

- i) Doublet .69 δ
- ii) Doublet .87 δ

c) Two kinds of cyclobutane

d) Unsymmetrical; suggests xtn skeleton, cf. NBD xtn

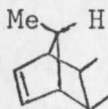
olefins - exo fragment 5.82 δ
 endo fragment 6.20 δ

e) Assign 6.22 to endo fragment, and 5.73 to exo fragment

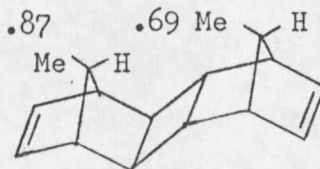
f) Since 6.22 is a triplet,



and since 5.73 is a septet,



g) Thus assignment is:



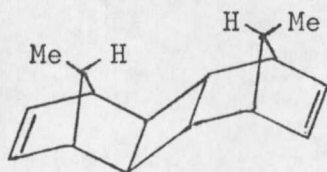
Methyl groups are assigned as shown based on:

- i) exo methyl would be closest to methyl in 7-methyl (.87)
- ii) the methyl on the endo portion ought to feel influence of the edge of the cyclobutane ring, therefore it ought to be shifted upfield and it is (.69).

Assignment for Dimer XLVI:

- a) Two kinds of olefins
- b)

i) Dirty septet 6.02 ii) Dirty septet 5.66	}	so both fragments have methyl syn to the olefin
---	---	--
- b) Although in DCCl_3 only one methyl appears to be present, in D_6 benzene two kinds of methyl are present (.97 D, and .92 D).
- c) Two types of cyclobutanes
- d) Probably xtn skeleton; cf. NBD xtn olefins - exo 6.20, endo 5.82



Since neither methyl feels direct influence of cyclobutane ring, both would be similar (.85) to 7-methyl NBD (.87)

Assignment for Dimer XLVII:

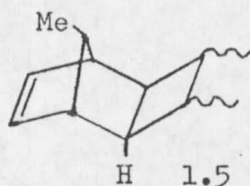
- a) Two kinds of olefins
 - i) Triplet 6.34 δ
 - ii) Septet 6.19 δ

b) Two kinds of methyl

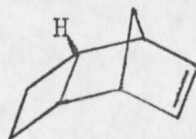
i) .53 δ

ii) .80 δ

c) Cyclobutane protons uncertain but no resonances at higher field than 1.5 δ ; also note assignments for XLIV, XLV-A and XLVI where it appears the cyclobutane protons at an exo norbornene cyclobutane fusion resonate at a higher field than 1.5 δ .

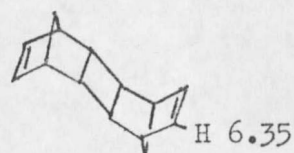
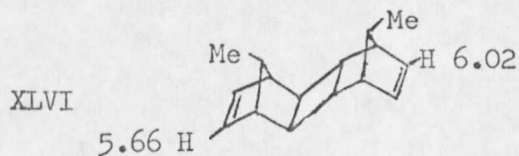
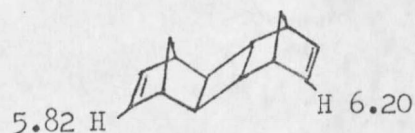
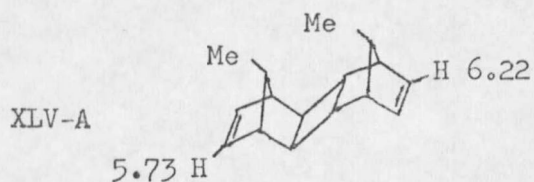


This is also true in NBD dimers. Likewise in NBD dimers, protons at the fusion of an endo norbornene-cyclobutane are at lower field than 1.50 δ .



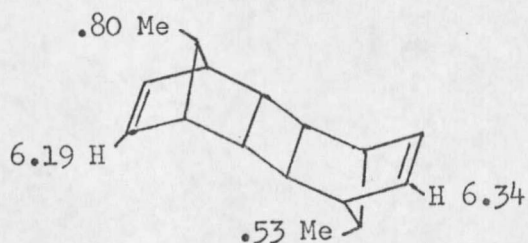
d) Thus in light of these considerations and the chemical shifts for the olefins, an endo-trans-endo skeleton is suggested.

e) Comparing the olefin chemical shifts:



XLVII 6.19, 6.34

The most reasonable possibility is an ntn skeleton with one methyl syn and one anti to the olefins.



One methyl is quite close to the 7-methyl NBD value (.87) while the other is shifted upfield considerably (edge effect of cyclobutane). The olefins may also be assigned since the 6.34 resonance is a triplet (a methyl is anti to it) and likewise the 6.19 resonance should be a septet. Notice that when a methyl is anti to an olefin its resonance is about that of the NBD dimer, while the presence of a syn methyl group shifts the resonance to a higher field. Thus,

Dimer	NBD (olefin)	7-methylNBD (olefin)*			
xtx	5.97	syn,syn dimethyl xtx		5.84	
xtn	exo 5.82	syn,anti dimethyl xtn		exo	5.73 (syn)
	endo 6.20			endo	6.22 (anti)
		syn,syn dimethyl xtn		exo	5.66 (syn)
				endo	6.02 (syn)
ntn	6.35	syn,anti dimethyl ntn		6.19 (syn)	
				6.34 (anti)	

* Methyl syn and anti relative to olefin bond of that fragment

This can also be seen in the parent 7-methylNBD vs NBD.

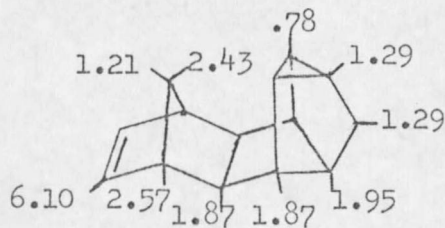
7-methylNBD	6.715	triplet (methyl anti)
	6.47	septet (methyl syn)
NBD	6.7	septet

The structures for two dimers remain to be assigned. The NMR data is given below.

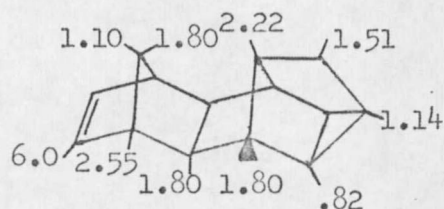
XLV-B	5.98 dSept	.83 D	.80 D	3.30 Q	2.38 M	a series of resonances at 2.25-0.75	
integration	2	3	3	1	2	9	
XLIX	5.74 dSept	.84 D	.75 D	2.5 M	a series of resonances at 2.3-0.7 M		.39 D
integration	2	3	3	4	6		2

Based on the relative integration values for methyls and olefins (6:2), it appears there is only one olefin bond in these dimers, suggesting 2+2+2 dimers. This tends to be confirmed by the presence of high field (less than 1.0) resonances expected from the cyclopropane moiety which is found in 2+2+2 dimers.

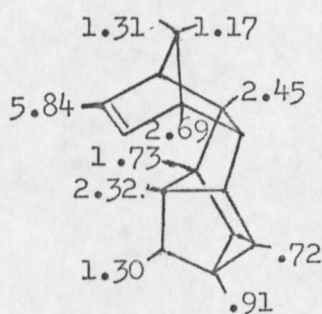
The following assignments have been made for 2+2+2 dimers of NBD



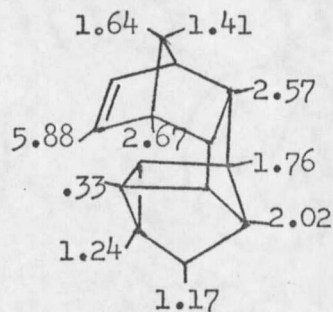
A



B



C

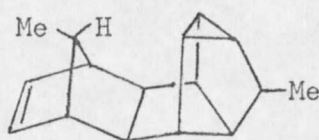


D

Assignment for Dimer XLV-B:

- a) Olefin 5.98 septet, methyl syn to olefin
- b) A quartet (one proton) appears at low field (3.30 δ). The coupling constant for this quartet matches the coupling constants for the methyl groups.
- c) In only one dimer, A, does the norbornene hydrogen, anti to the olefin, appear at an unusually low field. Since the published spectra of the NBD 2+2+2 dimers show no resonances which could

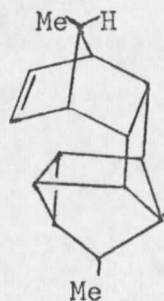
reasonably correspond in multiplicity to the quartet at 3.30δ in XLV-B, this quartet must be the result of a methyl group splitting a bridge hydrogen. Thus the structure is assigned as:



Assignment for Dimer XLIX:

- a) Olefin septet at 5.74δ , so methyl syn to olefin.
- b) Two cyclopropyl hydrogens at unusually high field (0.39δ).
- c) Only one 2+2+2 NBD dimer (D) has such high field cyclopropyl protons.

Furthermore, D shows a relatively high field olefin resonance (5.88δ) which would be shifted to higher field by the presence of a syn methyl group. Thus the structure is assigned as:



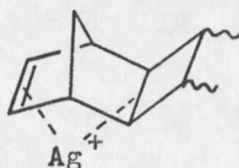
It may also be noted these assignments are consistent with behavior of the dimers on silver ion impregnated silica gel plates: XLV-A and XLVII retained with silver nitrate; XLIV, XLV-B, XLVI and XLIX not retained with silver nitrate.

Decreasing order of retention with silver perchlorate:

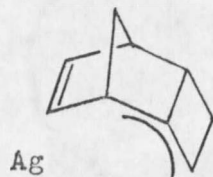


It is most likely that dimers with the exo side of the olefin free from the shielding of a methyl group ought to be bonded the strongest; XLV-A and XLVII are retained on silver nitrate while the others are not.

It is also probable that any complexing that the remaining dimers show is due to endo side bonding of the dimer to the rawer silver ion of silver perchlorate. Further, to account for the given order of retention it is suggested an exo bonded cyclobutane either decreases the steric hinderance to endo bonding or the edge of the cyclobutane actually provides some electron density to aid complexation.



Thus dimer XLIV has two sites for this type of bonding to occur while dimer XLVI has only one (an endo bonded cyclobutane only provides steric hinderance).



Dimers XLV-B and XLIX do not have any available double bonds to complex with and are not retained even with silver perchlorate.

APPENDIX II

Derivation of Equation Relating Gas Chromatographic Data

All experimental data was reduced to ratios, relating the dimer concentrations of all samples to the concentration of the 2+2 xtx dimer in one particular experimental sample (base sample) containing both the 2+2 xtx and 2+2 xtn dimers. The 2+2 xtn values were related first to the 2+2 xtn value in the base sample. They were then related to the xtx value in the base sample by the ratio of xtn to xtx in the base sample. It was assumed xtx and xtn would analyze similarly using a flame ionization detector. This assumption is supported by noting the heat of combustion of the two isomers differs only by 2.4%.⁷⁶ It is also supported by the fact that a comparison of the ratios from a gas chromatographic analysis agrees with integration data of the olefin NMR peak spectra for the two dimers. The molar concentration of the 2+2 xtx dimer in the base sample was determined by use of a calibration curve prepared using known amounts of pure 2+2 xtx dimer.

The following symbols will be used in the derivation of the equation.

$[A^0]$ = concentration of 2+2 xtx dimer in base sample

$[A^1]$ = concentration of 2+2 xtx dimer in base sample after it is diluted with a benzene solution of standard (dodecane)

Thus A^0 refers to data for base sample before dilution and A^1 refers to data for base sample after dilution.

$[B^0]$ = concentration of 2+2 xtx dimer in any other experimental sample

$[B^1]$ = concentration of 2+2 xtx dimer in this sample after it
is diluted with a benzene solution of standard (dodecane)

Thus B^0 refers to data for any other particular sample prior to dilution,
whereas B^1 refers to data for that sample after dilution.

S refers to standard (dodecane) related data

X refers to 2+2 xtx related data

CNTS (counts) refers to the integrated area (in arbitrary units)
under a particular gas chromatographic peak.

OBS refers to an observed variation

ATT refers to an attenuation setting on the gas chromatograph

INJ = injected sample

OBS CNTS of S in $A^1 \propto [S_A^1]$ (ml of A^1 INJ)(ATT. A^1 for S)

OBS CNTS of S in $B^1 \propto [S_B^1]$ (ml of B^1 INJ)(ATT. B^1 for S)

OBS CNTS of X in $A^1 \propto [X_A^1]$ (ml of A^1 INJ)(ATT. A^1 for X)

OBS CNTS of X in $B^1 \propto [X_B^1]$ (ml of B^1 INJ)(ATT. B^1 for X)

$$\frac{\text{OBS CNTS of S in } B^1}{\text{OBS CNTS of S in } A^1} = \frac{[S_B^1] (\text{ml of } B^1 \text{ INJ})(\text{ATT. } B^1 \text{ for S})}{[S_A^1] (\text{ml of } A^1 \text{ INJ})(\text{ATT. } A^1 \text{ for S})}$$

$$\frac{\text{ml of } B^1 \text{ INJ}}{\text{ml of } A^1 \text{ INJ}} = \frac{(\text{OBS CNTS of S in } B^1) [S_A^1] (\text{ATT. } A^1 \text{ for S})}{(\text{OBS CNTS of S in } A^1) [S_B^1] (\text{ATT. } B^1 \text{ for S})} \quad (1)$$

Thus the sizes of injected samples can be related to the size of the injected sample of diluted base sample.

Similarly:

$$\frac{X_{B1}}{X_{A1}} = \frac{(\text{OBS CNTS of X in } B^1)(\text{ATT. } A^1 \text{ for X})}{(\text{OBS CNTS of X in } A^1)(\text{ATT. } B^1 \text{ for X})} \frac{1}{\left(\frac{\text{ml of } B^1 \text{ INJ}}{\text{ml of } A^1 \text{ INJ}}\right)} \quad (2)$$

Substitution of equation 1 into equation 2, and assuming:

$$\text{ATT. } A^1 \text{ for S} = \text{ATT. } A^1 \text{ for X}$$

$$\text{ATT. } B^1 \text{ for S} = \text{ATT. } B^1 \text{ for X}$$

Gives:

$$\frac{[X_{B1}]}{[X_{A1}]} = \frac{\text{OBS CNTS of X in } B^1 / \text{OBS CNTS of S in } B^1}{\text{OBS CNTS of X in } A^1 / \text{OBS CNTS of S in } A^1} \frac{[S_{B1}]}{[S_{A1}]} \quad (3)$$

Thus the X_{B1}/X_{A1} ratio is independent of ATT. values so long as they are consistent for any given run (ie. $\text{ATT. } S_i = \text{ATT. } X_i$).

We want $[X_{B0}]$, not $[X_{B1}]$, that is, the actual concentration of X in the undiluted experimental sample.

In making up the diluted samples:

$$[X_{A1}] = \frac{(\text{ml of } X_{A0} \text{ added}) [X_{A0}]}{\text{ml of } X_{A0} \text{ added} + \text{ml of standard solution added to } X_{A0}}$$

$$[X_{B1}] = \frac{(\text{ml of } X_{B0} \text{ added}) [X_{B0}]}{\text{ml of } X_{B0} \text{ added} + \text{ml of standard solution added to } X_{B0}}$$

Let

- $\text{ml}_{XA0} = \text{ml of } X_{A0} \text{ added}$
- $\text{ml}_{SA} = \text{ml of standard solution added to } X_{A0}$
- $\text{ml}_{XB0} = \text{ml of } X_{B0} \text{ added}$
- $\text{ml}_{SB} = \text{ml of standard solution added to } X_{B0}$

$$\frac{[X_A^1]}{[X_A^0]} = \frac{(ml_{XA^0}) [X_A^0]}{ml_{XA^0} + ml_{SA}}$$

$$\frac{[X_B^1]}{[X_B^0]} = \frac{(ml_{XB^0}) [X_B^0]}{ml_{XB^0} + ml_{SB}}$$

From these two relationships one can write:

$$\frac{\frac{[X_B^0]}{[X_A^0]}}{\frac{[X_B^1]}{[X_A^1]}} = \frac{\left(1 + \frac{ml_{SB}}{ml_{XB^0}}\right) [X_B^1]}{\left(1 + \frac{ml_{SA}}{ml_{XA^0}}\right) [X_A^1]} \quad (4)$$

Substituting equation 3 into equation 4:

$$\frac{\frac{[X_B^0]}{[X_A^0]}}{\frac{[X_B^1]}{[X_A^1]}} = \frac{\left(1 + \frac{ml_{SB}}{ml_{XB^0}}\right) \left(\frac{\text{OBS CNTS of X in B}^1}{\text{OBS CNTS of S in B}^1}\right) [S_B^1]}{\left(1 + \frac{ml_{SA}}{ml_{XA^0}}\right) \left(\frac{\text{OBS CNTS of X in A}^1}{\text{OBS CNTS of S in A}^1}\right) [S_A^1]}$$

In an exactly analogous fashion, an equation relating xtn concentrations in general samples to the xtn concentration in the base sample can be written. As noted, xtn data can be related to xtx data by the ratio of xtn to xtx in the base sample.

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