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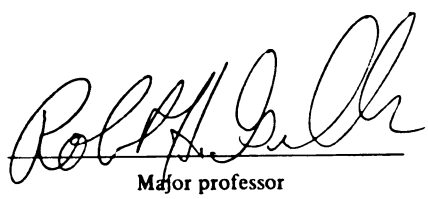
THE PREPARATION AND CHEMISTRY OF NI(II) METALLOCYCLES

presented by

Mei-In Melissa Liu

has been accepted towards fulfillment
of the requirements for

Ph. D. degree in Chemistry



Major professor

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THE PREPARATION AND CHEMISTRY OF NI(II) METALLOCYCLES

BY

Mei-In Melissa Liu

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ABSTRACT

THE PREPARATION AND CHEMISTRY OF NI(II) METALLOCYCLES

By

Mei-In Melissa Liu

Six phosphine nickel cyclopentane complexes ($P\phi_3$, diphos, $\phi_2PCH_2\phi$, PCY_3, $Me\phi_2P$, and $n\text{-}Bu_3P$), two phosphine nickel cyclohexane complexes ($P\phi_3$, diphose) and an acyclic bis(triphenylphosphine)di-n-butyl nickel (II) complex were prepared by the reaction of suitable lithium reagent (1, 4-dilithiobutane, 1, 5-dilithiopentane, or n-butyl lithium) to the appropriate dihalobisphosphine nickel (II) complex at low temperature.

The mode of decomposition of metallocycles under thermolysis and photolysis were examined. The relative ratio of the gaseous products formed in the solvents effected decomposition of metallocycles was studied. It was found that strongly coordinating solvents promoted carbon-carbon fragmentation products. The coordination number of complexes in solution was determined by ^{31}P nmr spectroscopy and/or molecular weight determination. These complexes decompose to give ethylene, cyclobutane, and 1-butene.

Both the theoretical analysis and experimental results provided the conclusion that the ratio of the gaseous products is a function of ligand structure and coordination of the complex. Three coordinate nickellocycle (P_1 species) give 1-butene, four coordinate nickellocycle (P_2 species) give cyclobutane while five coordinate nickellocycle (P_3 species) give ethylene.

ACKNOWLEDGEMENTS

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Gratitude is also extended to the Department of Chemistry, Michigan State University for financial assistance in the form of teaching assistantship and research assistantship from the National Science Foundation in the form of a grant administered by Michigan State University.

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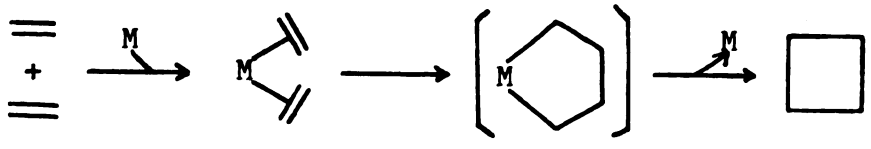
PREPARATION AND ANALYSIS OF NICKEL(II) METALLOCYCLES

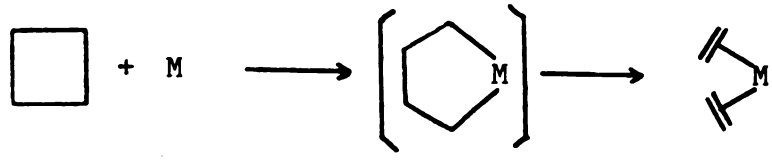
Introduction

Oxygen, nitrogen and sulfur heterocycles have played major roles in the development of organic chemistry. It is becoming apparent that transition metallocycles may have considerable importance in transition metal organic chemistry.

Tetramethylene metallocycles have been proposed as intermediates in a number of transition metal catalyzed (2 + 2) cyclo additions of olefins (scheme 1) and retro cyclo addition of olefins (scheme 2).

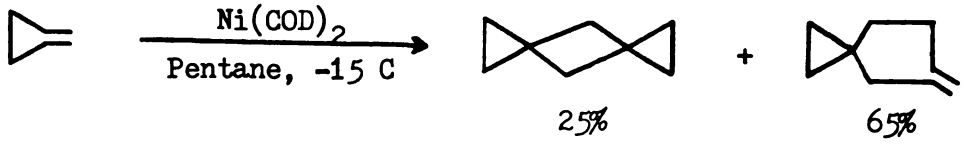


(Scheme 1)



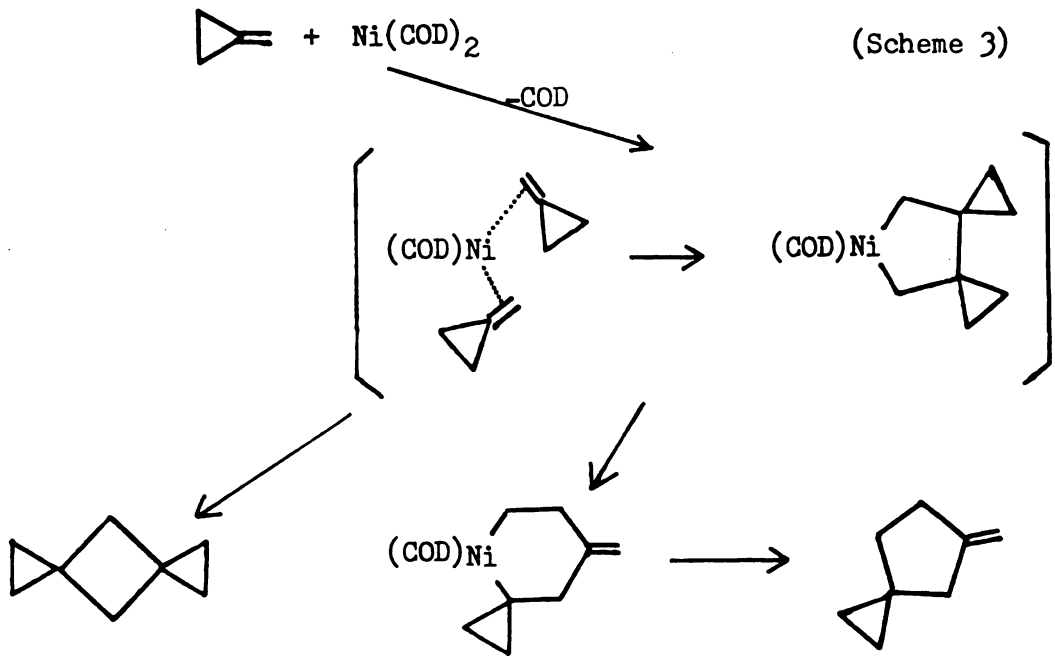
(Scheme 2)

Most cases such as the cyclodimerization of methylenecyclopropanes catalyzed by nickel(0) (eq. 1) reported by Binger (1) in 1972 involve reactive olefins.



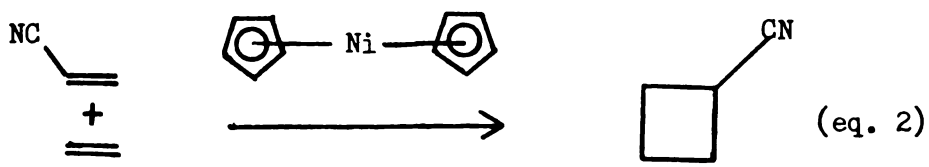
(eq. 1)

Based on the structures of the products the authors proposed that the reaction goes through a metallocycle as show in scheme 3.



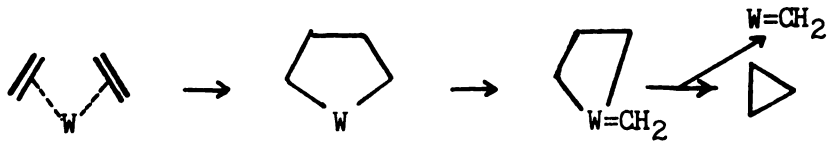
(Scheme 3)

Hall (2) found (eq. 2) in 1973 that ethylene and acrylonitrile produce cyclobutane carbonitrile when catalyzed by nickelocene or cyclopentadienyl nickel carbonyl.



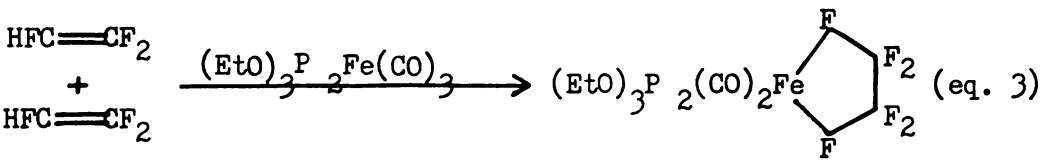
(eq. 2)

Grubbs (3, 4) has suggested that tetramethylene metallocycles could be source of the metal-carbene in some tungsten olefin metathesis catalyst systems (scheme 4).



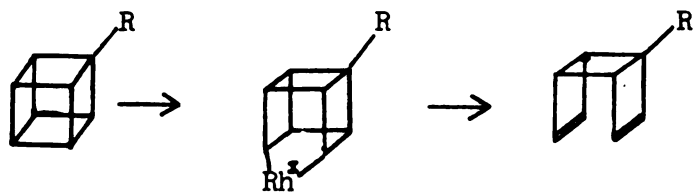
(Scheme 4)

Some metallocycles have been trapped or isolated (5,6) as shown below (eq. 3).



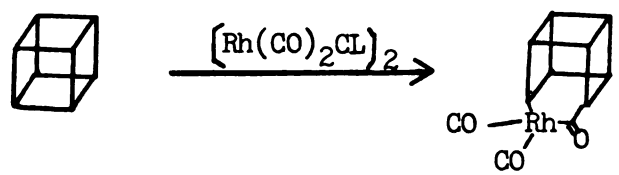
(eq. 3)

Halpern (7) identified metallocycles as intermediates (eq. 4) in the isomerization of cubane derivatives by rhodium(I) catalyst. They trap



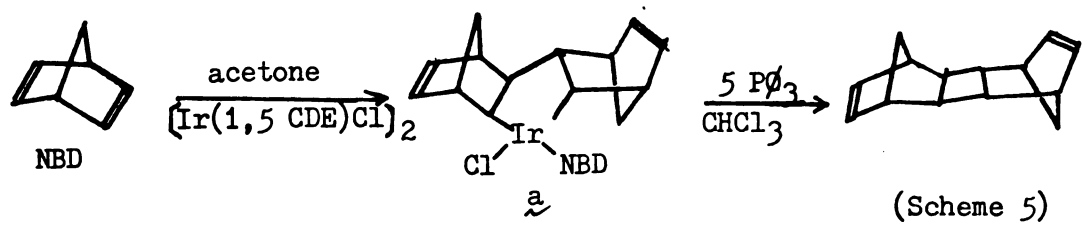
P= $COOCH_3$ (eq. 4)

ped the rhodacycle by using a stoichiometric amount of the catalyst (eq. 5).



(eq. 5)

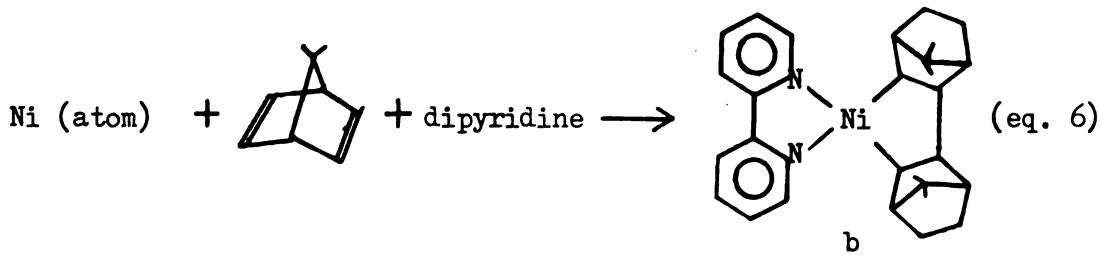
Osborn (8) has isolated a metallocyclic intermediate a from an Ir(I) catalyzed imerization of norbornadiene (scheme 5).



a

(Scheme 5)

Also a nickel type analogue of a (eq. 6) was identified by Blackborow et. al.(9)

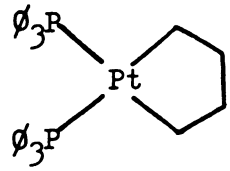


(eq. 6)

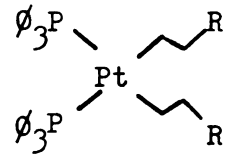
b

The structure of b was confirmed by nmr, mass spectrum and elemental analysis.

Some metallocycles have been prepared as stable complexes. Platinum metallocycle c have been prepared by both Grubbs' and Whiteside's groups independently and confirmed with x-ray diffraction by Grubbs (10). Whiteside (11, 12) has demostrated that platinum metallocycles possess unusual stability relative to acyclic analogue d and did not give C-C bond fragmentation on thermolysis.

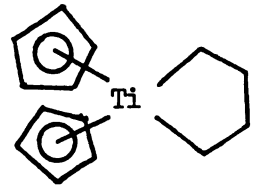


c



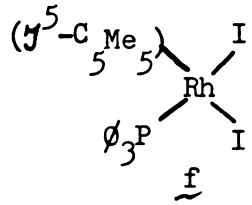
d

Whiteside (13, 14) has also prepared and demostrated that metallocycles e can apparently be formed by the addition of ethylene to reduce titanocene species, however, this titanium species e proved too unstable for spectral analysis.



e

Diversi (15) and his coworker reported in 1977 that the reaction of $RhI_2(P\phi_3)(\eta^5\text{-}C_5Me_5)$ f with di-grignard reagent $BrMg\text{-}(CH_2)_n\text{-}MgBr$ g (n = 5 or 6) led to the rhodacycloalkanes h and i, respectively. Reaction of f and g (n = 4) gave the rhodacyclopentane j and the rhodium(I)-ethylene complex k.

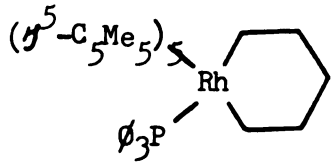


f

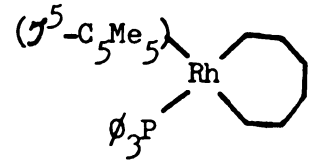
$BrMg\text{-}(CH_2)_n\text{-}MgBr$

g

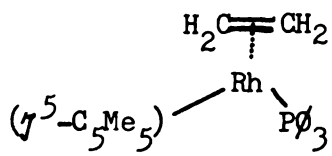
n = 4, 5, or 6



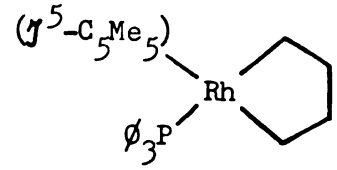
h



i



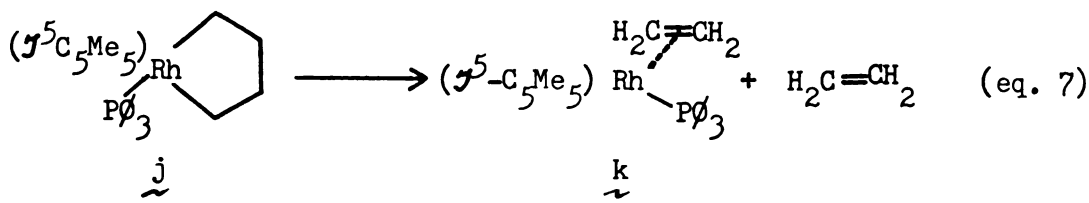
k



j

In the solid state, h and i decomposed at 160°C under argon; no carbon-carbon bond cleavage was observed, the only volatile products being n-pentenes and n-hexenes from h and i respectively. Similar decomposition modes have been observed in the case of some platinum(II) metallocycles.

The method of preparation of k and the simultaneous evolution of ethylene strongly suggest that the metallocyclopetane derivatives j is the precursor of k undergoing carbon-carbon bond cleavage. Efforts to isolate j have so far been unsuccessful, invariably leading to samples contaminated by k.



(eq. 7)

Recently, Grubbs (16) found a simple system, which combines the best properties of the platinum, rhodium, and titanium complexes and undergoes all of the major reactions previously observed for metallocycles: (a) Reductive elimination of cic-alkyl groups, (b) β-hydride elimination, and (c) carbon-carbon bond cleavage. What factors encourage those reactions is an intersting subject for further study.

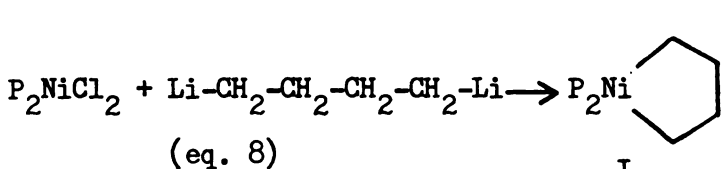
Results and Discussion

This chapter deals with the preparation, purification, and analysis of six phosphine nickel cyclopentane complexes ($P\emptyset_3$, diphos, $\emptyset_2PCH_2P$, PCY_3, $Me\emptyset_2P$, and $n\text{-}Bu_3P$), two phosphine nickel cyclohexane complexes ($P\emptyset_3$ and diphos) and an acyclic bis(triphenylphosphine)di-n-butyl nickel(II) complex.

There are several reasons for choosing tertiary phosphine as ligands: (a) A large number of tertiary phosphine are inert to various substrates in homogeneous catalysis. (b) There exist well-established

synthetic routes to phosphine ligands. (c) One theory suggests the transition metal phosphine bond possesses the proper balance between σ-donating and π-back bonding needed for stabilization of a metal-carbon bond. (d) Tertiary phosphines not only coordinate well on nickel but also readily dissociate again, making available the coordination site necessary for a catalytic system.

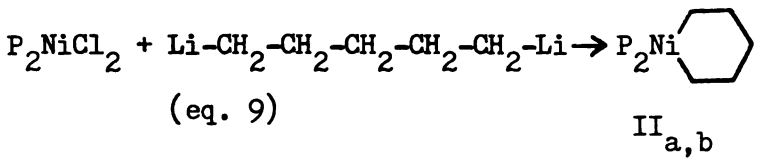
The target complexes were prepared by the addition of a suitable lithium reagent (1,4-dilithiobutane, 1,5-dilithiopentane, or n-butyl lithium) to the appropriate dihalo bisphosphine nickel(II) complex in ether at -78°C. The reaction was slowly warmed to -10°C and the resulting yellow solid was isolated by filtration (eq. 8, 9, and 10).



(eq. 8)

I_{a-f}

a. $P_2 = (P\phi_3)_2$
b. $P_2 = (\phi_2PCH_2\phi)_2$
c. P_2 = Diphos
d. $P_2 = (PCY_3)_2$
e. $P_2 = (PMe\phi_2)_2$
f. $P_2 = (Pn\text{-}Bu_3)_2$



(eq. 9)

$II_{a,b}$

a. $P_2 = (P\phi_3)_2$
b. P_2 = Diphose

$$(\phi_3P)_2NiCl_2 + 2\ n\text{-}BuLi \longrightarrow (\phi_3P)_2Ni(Bu)_2$$

(eq. 10)

III

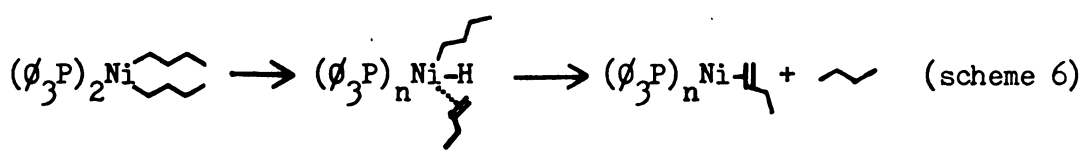
All reaction should be carried out under purified argon and at low temperature below -10°C. If the reaction was carried out with a large excess of dilithium reagent or at higher temperature, other colored solids were produced.

In the synthesis of bis(triphenylphosphine)tetramethylene nickel (II) or bis(triphenylphosphine) pentamethylene nickel(II) the use at a

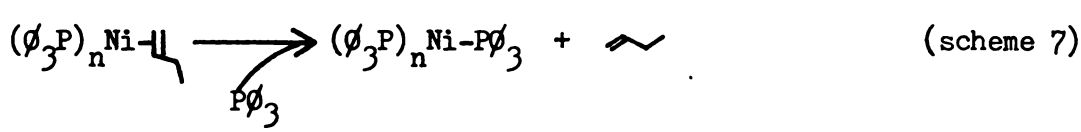
large ratio of dilithium reagent to nickel dichloride resulted in either the precipitation of brown solid or no solid at all. The properties of the brown solid were not investigated.

In the preparation of the yellow bis(diphenylmethylphosphine)tetramethylene nickel(II) complex, raising the temperature resulted in the formation of orange particles. Thermodecomposition gave ethylene (56%) and cyclobutane (33%) only. Once isolated the orange complex was stable at room temperature and fairly stable in deoxygenated water. This could be a nickel mono- or diethylene complex.

In the preparation of bis(triphenylphosphine)di-n-butyl nickel(II) raising the temperature gave a dark brown solid. This dark brown solid was stable at room temperature but gave off butene upon addition of excess triphenylphosphine. An acyclic n-butyl ligand would have no ring strain to hinder β-hydride elimination and could thus generate butene. The possible pathway shown as follow:

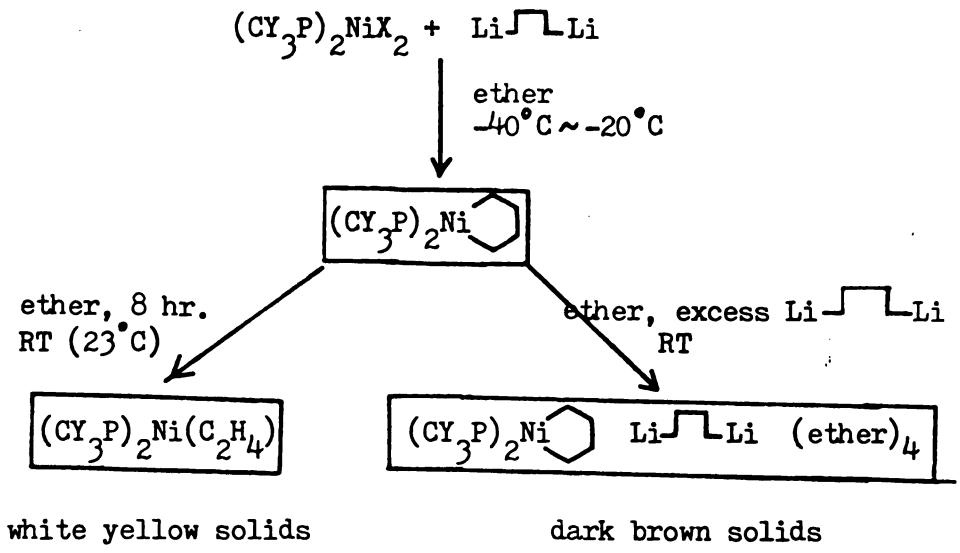


(scheme 6)



(scheme 7)

In the preparation of bis(tricyclohexylphosphine)tetramethylene nickel (II) (scheme 8). Raising the reaction temperature or adding excess dilithium gives a variety of products which have been investigated by Dr. Miyashita in detail. Apparently the ratio of lithium reagent to nickel dihalide, the reaction time, and the temperature are critical factors in the synthesis of the target compounds. The use of fresh lithium ribbon in the preparation of dilithium reagent is also important. It may



(scheme 8)

improve the yield by reducing contamination.

To get rid of contaminants (mainly lithium halide and nickel dihalide), the complexes were recrystalized from toluene, ether, or n-hexane as appropriate solvent. For non-water sensitive complexes, ether is a good solvent (low boiling point, easy to handle, bigger crystals). For water sensitive complexes, toluene is good, since toluene dose not dissolve the main impurities at low temperatures. However, the boiling point of toluene is higher and crystalization is slower than in ether.

Gaseous analysis was carried out in vacuum line at low temperature to avoid the production of thermaldecomposition products.

$$P_2Ni\ (CH_2)_n + H^+\ (-30^\circ C) \longrightarrow H_3C\text{-}(CH_2)_{n-2}\text{-}CH_3 + \text{Solids} \qquad \text{(eq. 11)}$$

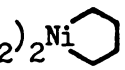
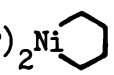
$$n = 4,\ 5$$

Nickel analysis was done using the glyoxime. This extraordinarily sensitive reagent for nickel depends on the fact that α-dimethylglyoxime added to an ammoniacal solution containing a nickel salt

produces an intese scarlet coloration (16). This reaction can routinely detect nickel at a concentration of one part per million in water. With care, it is possible to detect one part in 30,000,000 (17).

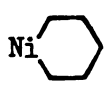
Tertiary phosphine can easily be oxidized to the stable tertiary phosphine oxide. This characteristic was used for phosphine analysis. Diphos tetramethylene nickel(II) is the most stable complex. The chelated ligand and five membered ring angle probably account for this stability. Its molecular weight suggests that it is a monomer. The molecular weight of bis(tricyclohexylphosphine)tetramethylene nickel(II) suggests that in solution one phosphine is completely dissociated from the nickel. Steric hindrance could be the cause since tricyclohexylphosphine is a bulkyl group. The molecular weights were determined by freezing point depression of benzene.

Table 1. The yield and analysis data of tetramethylene nickel metallocycles and III.

Compound	% Yield	M. Wt.	P/Ni	C_4/Ni
I_a $(\phi_3P)_2Ni$ 	36	626 (calc. 639)	2.0 (2.0)	0.98 (1.0)
I_b $(\phi CH_2P\phi_2)_2Ni$ 	32	659 (calc. 667)	2.0 (2.0)	0.99 (1.0)
I_c Diphos Ni 	25	512 (calc. 513)	2.0 (2.0)	0.96 (1.0)
I_d $(CY_3P)_2Ni$ 	43	343 (calc. 675)	2.0 (2.0)	0.97 (1.0)
I_e $(Me\phi_2P)_2Ni$ 	20	-	2.1 (2.0)	1.00 (1.0)
I_f $(n\text{-}Bu_3P)_2Ni$ 	13	-	ND[a]	0.90 (1.0)
III $(\phi_3P)_2Ni(n\text{-}Bu)_2$	21	-	1.9 (2.0)	1.80 (2.0)

[a]ND = not determined

Table 2. The yield and analysis data of pentamethylene nickel metallocycles.

Compound	% Yield	P/Ni	C_5/Ni
II_a $(\phi_3P)_2Ni$ 	40	2.0 (2.0)	0.97 (1.0)
II_b Diphos Ni 	28	2.0 (2.0)	1.10 (1.0)

Experimental

General Methods:

All reaction involving organometalic compounds were carried out under prepurified nitrogen or argon using an activated Q reactant column (18). Diethyl ether, toluene, and benzene were distilled from sodium benzophenone ketyl. Absolute ethanol was used in systhetic work after bubbling with argon.

The solid complexes decompose in the air with the production of smoke. Bistriphenylphosphine tetramethylene nickel(II), bis(benzyldiphenylphosphine) tetramethylene nickel(II), and diphos tetramethylene nickel(II) are not sensitive to water. The other complexes are very sensitive to air or water, however, so all manipulations were carried out under deoxygenated anhydrous conditions.

The ^{1}H nmr spectra were run on a Varian T-60 or a Varian A-56/60 D nmr spectrometer. Chemical shifts are reported in parts per million down field from tetramethylsilane (TMS). The ^{31}P nmr spectra were determined by a multinuclear nmr DA 60 with phosphoric acid as external standard.

Gasses were analyzed by gas chromatography on a Perkin Elmer 900 or a Varian 1400 equipped with flame ionization detectors. Products were identified by comparison of retention times to those authentic samples. identity was considered established when equal retention times on two columns with different stationary phases (19) were obtained. Product yields were determined by the response relative to an internal standard with consideration of a cofactor or by a vacuum line equipped with a barometer. Molecular weight was determined by a cryoscopic method.

Synthesis of bis(triphenylphosphine) nickel(II) dichloride:

The synthetic procedures were modified from Venanzi (20). Triphenylphosphine used was recrystalized from ethanol. To a hot solution of 52.6 g (0.2 mmole) of triphenylphosphine in 500 ml of glacial acetic acid was added with stirring to a solution of 23.8 g (0.1 mmole) of nickel(II) chloride hexahydrate, 20 ml of water, and 250 ml of glacial acid. The olive green microcrystalline precipitate, when kept in contact with the mother liquor overnight, gave dark blue crystals of bis(triphenylphosphine nickel(II) dichloride (80% yield) which were vacuum filtered, washed with glacial acetic acid and dried in vacuo.

Preparation and standardization of 1,4-dilithiobutane: (21)

In a 500 ml three-necked round bottom flask fitted with an argon line, 250 ml dropping funnel, oil bubbler, and stirring magnet were placed 100 cm of shaved lithium ribbon and 250 ml of dry, oxygen free diethyl ether. To the reaction was added, dropwise over two hours, a solution of 25 ml of 1,4-dibromobutane in 150 ml of ether. The reaction was initially allowed to proceed at room temperature for a few minutes, then it was cooled to 0°C. Following the addition of the dibromobutane, the mixture was stirred for 30 minutes. The solution was allowed to settle overnight in a refrigerator. The liquid was then seperated by filtration and stored under nitrogen at 0°C. The 1,4-dilithiobutane was stable for approximately one week at 0°C.

The concentration of 1,4-dilithiobutane solution was determined by removing a 10 ml aliquot of the filtered solution and adding it to 2 ml of chlorotrimethylsilane under nitrogen. This generated quantitatively 1,4-bis(trimethylsilyl)butane. Durene (1,2,4,5-tetramethylbenzene) was

added as a standard (cofactor = 1) and the solution was analyzed by glc (8 ft 5% QF-1 at 80°C flow rate 30 ml/min).

Preparation and purification of bis(triphenylphosphine)tetramethylene nickel(II):

The reaction was carried out under positive N_2 pressure in a 100 ml side-arm round bottom flask equipped with a teflon-coated stirrer bar. Bis(triphenylphosphine) nickel(II) dichloride (4 g, 6.2 mmole) and dry, oxygen free ether (20 ml) were placed in the flask. After cooling the reaction mixture to -78°C (dry-ice-ethanol bath), 62 ml (12.8 mmole) of 1,4-dilithiobutane in ether was slowly added by syringe.

After addition the reaction mixture was stirred for 10 minutes, then the bath was removed and the stirring maintained. On partial warming the black starting material turned to dark violet and then dissolved in the ether, forming a dark solution. On warming still further (-10°C) a bright yellow solid was produced. As soon as the yellow solid ceased forming, the reaction was filtered. Only the top parts of the suspension were taken for filtration. The bright yellow solids were washed with dry, oxygen free ether several times and then dried under vacuum.

The dried yellow solids were dissolved in dry oxygen free toluene at -15°C and then filtered. The resultant clear yellow solution was partially condensed to 90% of the original volume under vacuum, and then 10-20% of n-hexane was added (stop adding n-hexane before the solution become cloudy). The solution was kept in a dry-ice box. Bright yellow crystals were obtained and dried under vacuum giving a yield of 36% based on starting material.

The ^1H nmr spectrum at -10°C in toluene-d_6 showed multipletes at

1.67 and 1.87. A single ^{31}P peak was observed at -42.4 ppm over the temperature range of -10°C to -90°C. The gaseous analysis from acidolysis, nickel analysis, and phosphine analysis showed P/Ni = 2.0 (theo = 2.0), C_4/Ni = 0.98 (theo = 1.0). Molecular weight determined 626 (calc. = 639).

Gaseous products from acidolysis of nickel(II) complexes:

The solid nickel complex was transfered into a small Schlenk tube having two joints and one side-arm, and the weight of the sample was measured. The Schlenk tube was connected to a vacuum line (see Fig. 1) after one joint was fitted with a bent tube containing concentrated sulfuric acid. The tube was evacuated and the whole system was closed. The sample was decomposed with concentrated sulfuric acid at -30°C to 0°C by turning the bent tube up. Gasses formed from the acidolysis were trapped using a cold finger in a liquid nitrogen bath. The pressure was measured with a Hg manometer. Gaseous products were also analyzed with glc or mass spectrometer.

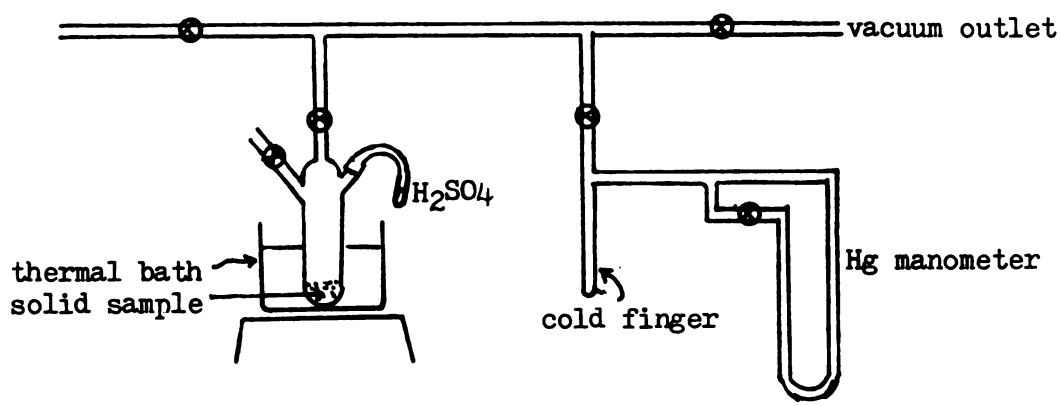


Figure 1. Vacuum line system for acidolysis reaction

Phosphine analysis of bis(triphenylphosphine)tetramethylene nickel(II):

The residue which resulted from the acidolysis was oxidized with hydrogen peroxide at -10°C to giving a white solid (triphenylphosphine oxide). This white solid was extracted with ether several times and the ether solution was neutralized with sodium carbonate. The ether was evaporated off and the triphenylphosphine oxide was weighed until a constant weight was obtained.

Nickel analysis : (22)

To the solution which resulted from the decomposition of bis(triphenylphosphine)tetramethylene nickel(II) with sulfuric acid was added 150 ml of water. A white precipitate (triphenylphosphine and/or triphenylphosphine oxide) formed immediately. To facilitate the removal of this white solid, the mixture was first heated to 70°C, then cooled to room temperature, and finally vacuumed filtered to give a clear solution.

To the clear solution at 60°C was added 20 ml of a freshly prepared 1% solution of dimethyl glyoxime in absolute ethanol. Concentrated ammonium hydroxide was added dropwise very slowly until no more of the bright red flocculent precipitate formed. The mixture was digested for one hour, cooled to room temperature, and vacuum filtered onto a tared fritted glass crucible. The solid was dried for several hours at 130°C, its weight determined, and the percent nickel calculated using the following equation.

$$\% \text{ Ni} = \frac{\text{Wt. of ppt. (g)} \times 20.313}{\text{Wt. of sample (g)}}$$

Synthesis of benzyldiphenylphosphine :

Lithium ribbon (35 cm, 3.5 g, 0.507 mole) was placed in a 500 ml two-side-arm round bottom flask containing 100 ml of tetrahydrofuran. The flask was fitted with a dropping funnel containg 80 ml of tetrahydrofuran and 34 ml (0.188 mole) of diphenyl chlorophosphine. The lithium ribbon was stirred using a magnetic stirring bar. The tetrahydrofuran solution of chlorodiphenylphosphine was added to the lithium over a two hour period. An ice bath was periodically used to prevent the temperature from rising too high. After addition was completed the reaction was stirred for four more hours and then allowed to settle.

The liquid was transferred to another 500 ml two-side-arm round bottom flask which contained a stirring bar. The flask was fitted with a 125 ml dropping funnel containing 80 ml of tetrahydrofuran and 27 ml (0.235 mole) of benzyl chloride. This was degassed with nitrogen for 15 minutes in the addition funnel.

The benzyl chloride solution was added dropwise over a two hour period. After addition of sufficient benzyl chloride to give a reddish brown solution, the addition was stopped, the addition funnel removed, and the reaction stirred for half hour. One hundred milliliters of degassed saturated ammonium chloride solution was added. This was left stirring overnight. The top layer (tetrahydrofuran) was transferred to another side arm round bottom flask containing calcium chloride (degassed by evacuation and diffusion of nitrogen). The aqueous solution was washed with three 75 ml portions of oxygen free benzene which was then added to the flask containing calcium chloride. All removals were made by syringe.

The combined organic layers were condensed and the remaining solvent (about 100 ml remained) was removed by vacuum distilled (with the pot heated to about 100 degrees). The system was filled with argon and cooled

and 400 ml of isopropyl alcohol was added to it and allowed to stand overnight. After filtration the solid was recystalized from isopropyl alcohol again, and gave benzyl diphenylphosphine (yield 54%, m. p. 72°-73°C) (23). The ^1H nmr spectrum showed peaks at 3.37 (2), 7.07 (5), 7.25 (10).

Synthesis of bis(benzyldiphenylphosphine) nickel(II) dichloride:

To a hot solution (60°C) of 2.0781 g (7.53 mmole) of benzyl phosphine in 40 ml of galcial acetic acid was added with stirring a solution of 0.8928 g (3.75 mmole) of nickel(II) chloride hexahydrate in 2 ml of water and 25 ml of glacial acetic acid. The resultant pink solution was kept in a refrigerator overnight where upon dark violet needle crystals formed. The product was vacuum filtered, washed with glacial acetic acid and dried under vacuum to give an 85% yield of bis(benzyldiphenylphosphine) nickel(II) dichloride. The IR spectrum showed Ni-Cl bands at 250 cm^{-1}, 340 cm^{-1}.

Preparation and purification of bis(benzyldiphenylphosphine) tetramethylene nickel(II): I_b

A solution of (2.6 g, 3.8 mmole) bis(benzylphenylphosphine) nickel (II) dichloride in 10 ml of dry oxygen free ether was placed in a 100 ml side-arm round bottom flask equipped with a teflon-coated stirring bar and maintained under argon. After cooling the reaction mixture to -78°C (dry-ice-ethanol bath), 80 ml (8 mmole) of 1,4-dilithiobutane in ether was slowly added by syringe. After addition was complete the reaction mixture was stirred for 10 minutes, and then allowed to warm partially while stirring. On warming the dark violet solid redissolved in the ether

On further warming (-15°C) a bright yellow solid fell out of solution. As soon as precipitation was complete the solid was filtered and washed several time with ether.

The yellow solid was washed with deoxygenated water (not sensitive to water), to get rid of lithium salts. After being washed with ether again the product was dried under vacuum and recrystlized from ether (yield 32% of I_b).

The gaseous analysis from acidolysis, nickel analysis and phosphine analysis from phosphine oxide showed P/Ni = 2.0 (theo = 2.0), C_4/Ni = 0.99 (theo = 1.0).

Synthesis of ethylen bis(diphenylphosphine) nickel(II) dichloride:

A solution of 5.15 g of nickel(II) chloride hexahydrate in 200 ml of ethanol was added to 8.02 g of 1,2-bis(diphenylphosphine)ethane in 600 ml ethanol (50°C). After the reaction had stirred, orange feathery needlelike crystals formed. The solution was allowed to cool and the orange cystals were filtered under vacuum, washed with ether and dried under vacuum giving an 82% yield of ethylene bis(diphenylphosphine) nickel(II) dichloride.

Preparation and purification of ethylene bis(diphenylphosphine) tetramethylene nickel(II): I_c

All procedures were carried under purified argon. A solution of 4 g (7.6 mmole) bis(diphenylphosphine) nickel(II) dichloride in 20 ml of oxygen free ether was placed in a 100ml side-arm round bottom flask equipped with teflon-coated tirring bar. The reaction was cooled to -78°C (dry-ice-ethanol bath) and 54 ml (13 mmole) of 1,4-dilithiobutane in ether was slowly added by syringe.

After addition the reaction mixture was stirred for 10 minutes, then the bath was removed and the stirring maintained. On warming, the orange solid dissolved in the ether giving a dark brown solution. On further warming and stirring a bright yellow solid came out of solution. As soon as precipitation was complete the product was filtered, washed several times with ether until a negative lithium test was obtained (or washed with deoxygenated water and ether) and dried under vacuum.

The dried yellow solids were recrystalized from ether and dried under vacuum giving 25% of ethylen bis(diphenylphosphine) tetramethylene nickel(II). Analysis P/Ni = 2.0 (theo = 2.0), C_4/Ni = 0.96 (theo = 1.0). The ^1H nmr showed a broad peak at 1.1-1.8 range (overlapping the ethane on the phosphine). The ^{31}P nmr showed peak at -45.5 ppm.

Lithium test:

Ferric salts react with periodates to yield a precipitate of a ferric periodate complex. This precipitate is solubale in excess periodate solution and also in excess potassium hydroxide solution. The resulting alkaline solution of the ferric periodate complex is a selective reagent for lithium, since it gives a white precipitate ($LiKFeIO_6$), even from dilute solution and in the cold. Sodium and potassium give no precipitate: ammonium salts, all metals of group I to IV and Mg should be absent. Sensitivity: 0,1 ug lithium, concentration limit = 1 : 100,000.

The ferric periodate reagent is prepared by dissolving 2 g of potassium periodate in 10 ml of freshly prepared 2 N potassium hydroxide solution and diluting with water to 50 ml. Then added 3 ml of 10 percent ferric chloride solution and diluted to 100 ml with 2 N potassium hydroxide solution. The reagent is stable.

Procedure: Place a drop of neutral or alkaline test solution in a micro test tube, and add 1 drop of saturated sodium chloride solution and 2 drops of the ferric periodate reagent. Simultaneously carry out a blank test with a drop of distilled water. Immerse both tubes for 15-20 seconds in water at 40-50°C. A white (or yellow white) precipitation indicates the presence of lithium; the blank remains clear.

Diphenylmethylphosphine:

To a stirred solution of 50 ml (0.278 mmole) of chlorodiphenylphosphine in 90 ml of ether at 0°C was added 135 ml of methyl lithium (0.279 mmole) solution over a two hour period. The ice bath was removed and the mixture was stirred for an additional thirty minutes. The organic layer was filtered (or decanted) and fractionally distilled (b.p. 108-110°C, 0.15 mm Hg vacuum), giving 36 g (66.6%) yield of diphenylmethylphosphine. The ^{1}H nmr showed 1.7 (3) and 7.5 (10).

Bis(diphenylmethylphosphine) nickel(II) dichloride: (24)

A solution of 12 g (60 mmole) of diphenylmethylphosphine dissolved in 200 ml hot ethanol (degassed) was mixed with a solution of 7.13 g (30 mmole) of nickel(II) chloride hexahydrate dissolved in 200 ml of hot ethanol. After mixing, the solution was violet. The solution was kept in a refrigerator overnight and the violet crystals which formed were filtered and dried under vacuum, giving 13.6 g (91.3% yield) of bis(diphenylphosphine) nickel(II) dichloride (m.p. 150°C).

Bis(diphenylmethylphosphine)tetramethylene nickel(II): I_e

A solution of 51.6 g bis(diphenylmethylphosphine) nickel(II) dichloride in 20 ml of ether was placed in a 1000 ml side arm round bottom flask fitted with a stirring magnet, gas outlet valve (oil bubbler) and a dry-ice-ethanol bath. The flask was first purged of air by flushing with argon and start stirring. An excess of 1,4-dilithiobutane in ether (400 ml, 0.056 mole) was added dropwise at -78°C. After addition, the bath temperature was allowed to increase until a light yellow precipitate came out. The precipitate was recooled to -78°C and filtered under argon using cold jacketed fritted filter. The light yellow solids were recrystalized from ether giving 20% yield of bis(diphenylmethylphosphine)tetramethylene nickel(II). Gaseous analysis by acidolysis, nickel analysis, and phosphine analysis (25) by acetoacetate ligand exchanged gave P/Ni = 2.06 (theor = 2.0), C_4/Ni = 1.0 (theor = 1.0). The ^{31}P nmr showed -4.3 ppm (-90°C, ether).

Bis(tri-n-butylphosphine) tetramethylene nickel(II): I_f

A solution of 3 g (0.0056 mmole) of bis(tri-n-butylphosphine) nickel(II) dichloride dissolved in 10 ml of ether was cooled to -78°C. To this was added 51 ml of dilithium butane solution (0.22 M in ether). The reaction mixture was kept under -35°C for several hours (with stirring) until a yellow precipitate formed.

The solvent was evaporated under vacuum at low temperature (-30°C). The product was extracted with pentane several times until only lithium chloride (white solid) remained. The pentane solution was condensed to half its original volume at low temperature (-30°C) and kept in a dry-ice-box for two weeks. The resulting yellow crystals were dried under

vacuum at low temperature. Giving about a 13% yield of bis(tri-n-butylphosphine)tetramethylene nickel(II). The ^{31}P nmr at +1.5 ppm (toluene, -90°C).

Preparation of bis(triphenylphosphine) di-n-butyl nickel(II): III

All steps were carried at below -15°C. A solution of 5 g (7.6 m mole) of bis(triphenylphosphine) nickel(II) dichloride in 70 ml of dry oxygen free ether was placed in a side arm flask equipped with a teflon coated stirring bar. The solution was cooled to -78°C, and 8 ml (2.4 M) of n-butyl-lithium-n-hexane solution was added very slowly. After addition was complete the mixture was warmed up to -20°C ↗ -10°C (with stirring). The yellow red solids which formed from the dark solution were filtered under -20°C using a frit equipped with a cooling jacket (filtration and procedures must be done quickly and at low temperature). The solids were water sensitive and too unstable to recrystalize from toluene. The solids were repeatedly washed with cold ether and then dried under vacuum at -10°C in the dark. Giving a 21% yield of bis(triphenylphosphine) di-n-butyl nickel(II), analysis P/Ni = 1.9 (theor = 2.0), C_4/Ni =1.8 (theor = 2.0).

Deutero chloric acid was generated by slowly combining 10 ml deuterium oxide and 5 ml of acetyl chloride under nitrogen. The deutero chloride solution was then added to bis(triphenylphosphine) di-n-buty nickel(II). The gas above the resultant solution was removed from the flask by syringe and the butane in the gas was isolated by glc. The butane was then analyzed by mass spectroscopy. The mass spectrum exhibited a parent peak of m/e 59 which corresponds to butane-d_1.

Preparation and standardization of 1,5-dilithiopentane:

In a 500 ml three-neck round bottom flask fitted with an argon line, 250 ml dropping funnel, oil bubbler, and stirring magnet were placed 100 cm of shaved lithium ribbon and 200 ml of dry oxygen free diethyl ether. A solution of 30 ml 1,5-dibromopentane in 150 ml of ether was added dropwise over two hours. The reaction was carried out at 0°C. Following the addition of the dibromopentane, the mixture was stirred for 30 minutes. The liquid was separated by filtration and stored under nitrogen at 0°C.

The concentration of the 1,5-dilithiopentane was determined by removing a 10 ml aliquot of the filtered solution and adding to it 2 ml of chlorotrimethylsilane under nitrogen. Durene (1,2,4,5-tetramethylbenzene) was added to the quantitatively generated 1,5-bis(trimethylsilyl)pentane as a standard (cofactor = 0.8) and the solution was analyzed by glc (10% carbonwax on 60/80 mesh Chromosorb W at column temperature 110°C and flow rate 15 ml/min).

Preparation and purification of bis(triphenylphosphine)pentamethylene nickel(II): II_a

A solution of 6.53 g (10 mmole) of bis(triphenylphosphine) nickel (II) dichloride in 30 ml ether was placed in a 300 ml side-arm round bottom flask equipped with teflon-coated stirring bar. After cooling the reaction mixture to -78°C, 77 ml (0.26 M) of 1,5-dilithiopentane in ether was added dropwise by syringe. When the addition was complete the reaction mixture was stirred for 20 minutes and then allowed to warm. On warming, the black starting material dissolved forming a dark brown homogeneous solution. On further stirring yellow orange solids formed

and were then filtered (below -20°C) and dried under vacuum.

The yellow orange solids were dissolved in dry oxygen free toluene at -10°C. After filtration n-hexane was added to the clear yellow solution which was then placed in a dry-ice box. The yellow brown crystals which then formed were dried under vacuum. Giving a 40% yield of bis(triphenylphosphine)pentamethylene nickel(II). The ^{1}H nmr spectrum showed multiplets at 0.96 and 0.73. The ^{31}P nmr spectrum showed a peak at -33.6 ppm. The gaseous analysis from acidolysis, nickel analysis, and phosphine analysis showed P/Ni = 2.1 (theor = 2.0), C_5/Ni = 0.97 (theor = 1.0).

Preparation and purification of the ethylene bis(diphenylphosphine)pentamethylene nickel(II): II_b

An ether solution of ethlene bis(diphenylphosphine) nickel(II) dichloride was cooled to below -45°C with stirring, and to this a ether solution of 1,5-dilithiopentane was added by syringe. After the 1,5-dilithiopentane had been added (1.5-2.0 mole excess) the pot temperature was allowed to increase. On warming the orange solution gave yellow solids. Rapid filtration (below -20°C) of the yellow solids was followed by washing with coold ether. The product was dried under vacuum at -20°C ~ -10°C in the dark. The yellow solids were dissolved in dry oxygen free toluene at -10°C (starting material and lithium halide are not solubale in toluene at this temperature). After filtration a clear yellow solution was obtained. To this was added 10-20% of n-hexane. The solution was cooled to -50°C giving a 28% yield of ethylene bis(diphenylphosphine) pentamethylene nickel(II) as yellow crystals which were dried under vacuum at -10°C in the dark. Analysis P/Ni = 2.0 (theor = 2.0), C_5/Ni = 1.10 (theor = 1.0). The ^{31}P nmr showed at -45.5 ppm.

CHAPTER 2

THE EFFECT OF HEAT, LIGHT, SOLVENTS AND OLEFINS ON THE DECOMPOSITION OF NICKEL(II) METALLOCYCLES

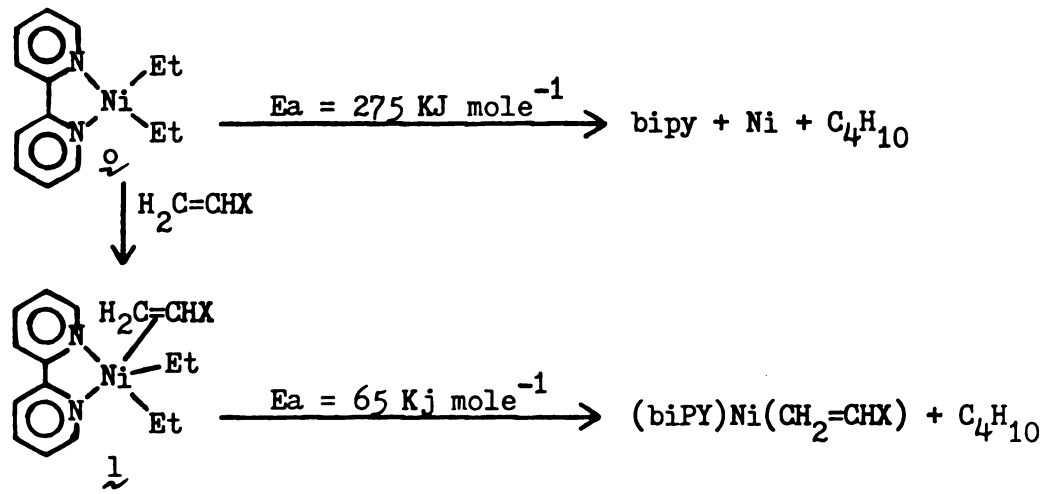
Introduction

The instability of transition metal-carbon bonds is a problem of fundamental importance in organotransition metal chemistry. A theory (26, 27) proposed by Whitesides, Filioppo and Yagupsky et. al., determining the stability of transition metal-carbon bonds stresses the importance of a low energy decomposition pathway being present, such as β-H elimination. Whitesides, Filippo and Yagupsky et. al. ascribed the stabilizing effect of a ligand to its ability to block the coordination site. Stabilization also results when the M-C-C-H dihedral angle is constrained to be far from the zero degree angle that seems to be optimal for metal hydride elimination.

Thermal decomposition of platinum metallocycles gave only those β-hydride elimination products (12) which had been obtained from acyclic analogues. Thermal decomposition of nickel(II) metallocycle in toluene probably occurs by several pathways judging from the analysis of the decomposition products (28). Those pathways (other than β-hydride elimination) which involve C-C bond cleavage give ethylene, cis nickel-carbon bond elimination gives cyclotutane. What factors give those pathways the opportunity to compete with β-hydride elimination is a questions which can only be answered by further investigation of the thermalchemistry and photochemistry of nickel(II) complexes.

Recently Grubbs (29) found that the coordination number of a complex appears to be the major factor controling the mode of its decomposition.

One other theory, originally proposed by Chatt and Show (30) and later modified by Yamamoto (31), used the electronic of constituents to explain the stability of metal-alkyl bonds. In the case of o decomposed in the solid state is 275 KJ mole^{-1}. In the presence of olefins, however, this parameter is reduced to ca. 65 KJ mole^{-1} and an 18-electron intermediates 1 can be isolated (31) (scheme 9).



18-electron intermediate (scheme 9)

A correlation can be drawn between the electron deficiency of the olefin and the ease with which the metal-alkyl bond will cleave. As the electron deficiency of the olefin is increased, a higher rate for the metal-carbon bond cleavage is observed. There is an energy gap between the bonding σR-M orbital and a vacant d orbital. Promotion of an electron from the bonding σR-M orbital to a vacant d orbital would result in the splitting of the R-M bond. Thus, if the energy gap were decreased, promotion

of the electron would become easier, and the cis-metal-alkyl bond would be more susceptible to cleavage. In this chapter strong coordinating olefins were used to investigate the effect of electronic factors on the mode of decomposition.

Results and Discussion

(1). Thermal decomposition:

Samples of nickel(II) complex (solid) were allowed to decompose in a Schlenk tube connected to vacuum line. The temperature of the oil bath was raised slowly until the complex had totally decomposed and the gases produced at each temperature were measured. The product composition was determined by gc. The decomposition temperatures in Table 3 and 4 refer to the temperature at which the gases evolved most rapidly on heating in vacuum. Most of the complexes turned black at or above the decomposition temperature.

The four types of products obtained from the decomposition of solid state metallocycle and III(see Table 3) were as follows:

(a). carbon-carbon bond break: ethylene

(b). hydride-abstration: butane

(c). nickel-carbon cis elimination: cyclobutane

(4). β-hydride elimination: butenes

Observing the product ethylene percentages in Table 3 we see that I_d had the highest (13.2%) and I_a had the lowest (0.7%) percentage. All the compounds had similar decomposition temperatures. Electronially tricyclohexyphosphine in more basic than triphenylphosphine. Stericly tricyclohexyphosphine is a bulky phosphine which easily forms a three

coordinate species by losing on phosphine. According to Whitesides, Filippo and Yagupsky et. al. theory (26, 27) butenes should be the major product when the ligand is the tricyclohexyphosphine and indeed the highest percentage of butene's on I_d (87%). The free phosphine lost from the nickel may coordinate on another molecule of bisphosphine complex. The facts suggested that ethylene formation would be promoted by a more basic ligand or by a higher coordination species. I_c and I_e have electronically similar groups on phosphine. There is a steric difference, I_c has a chelated diphos ligand while I_e has two non-chelated ligands. Examination of the products shows that both complexes gave about the same amount of ethylene. They also gave similar amounts of butene's, but I_c decomposed at a higher temperature than I_e. The amounts of butane and cyclobutane formed were quite difference for the two compounds. The free phosphine methyl group in I_e could be a good hydride source leading to the formation of butane. The formation of cyclobutane from I_c could be promoted by the chelation. III gave typical thermal decomposition products (12) with no ethylene or cyclobutane observed.

In this case nickel(II) complexes C-C bond cleavage and Ni-C cis elimination are due to the nickel(II) complex having cyclic structure. Electron donating ligands can promot C-C bond encourage Ni-C cis elimination. Complexes having a greater tendency to form three coordinate species, also tend to give more butene products.

Six membered ring metallocycles (see Table 4) undergo C^{α}-C^{β}, C^{β}-C^{γ} bond cleavage and Ni-C cis elimination. II_a gives much more β-hydride elimination product than I_a. This compatible with the first hypothesis. The M-C-C-H dihedral angle in the six membered ring compound is much closer to the angle required for β-hydride elimination than it is in the

Table 3. Products(%) formed from the thermal decomposition of tetramethylene nickellocycles and III in solid state.

Compound	Temperature	Products(%)					
		Ethylene	Butane	Cyclobutane	1-Butene	t-2-Butene	c-2-Butene
I_a $(\phi_3P)_2Ni$	100 C±1°C	0.7	1.9	87.5	7.7	1.3	0.9
I_b $(\phi CH_2P\phi_2)_2Ni$ 	112°C±1°C	4.0	5.0	58.4	27.0	3.5	2.2
I_c Diphos Ni 	150°C±2°C	2.3	-	25.0	43.7	15.9	12.7
I_d $(CY_3P)_2Ni$ 	100°C	13.2	-	-	64.4	11.8	10.8
Ie $(Me\phi_2P)_2Ni$ 	100°C±1°C	2.5	24.8	-	43.6	15.1	11.9
I_f $(n\text{-}Bu_3P)_2Ni$ 	80°C±2°C	2.8	35.0	0.3	53.3	5.0	3.4
III $(\phi_3P)_2Ni(n\text{-}Bu)_2$	100°C	-	50.0	-	---------50.0----------		

Table 4. Products(%) formed from the thermal decomposition of pentamethylene nickellocycles in solid state.

Compound	Temperature	Products(%)										
		CH_4	=									
II_a $(\phi_3P)_2Ni$	110°C±2°C	0.1	6.5	0.1	1.8	0.2	0.7	16.7	4.1	44.0	23.0	2.5
II_b Diphos Ni	125°C±2°C	0.9	15.3	1.3	1.5	-	0.5	9.6	70.0	-----	0.9	----

five membered ring complex. II_b also gives $C^{\alpha}-C^{\beta}$ and $C^{\beta}-C^{\gamma}$ bond cleavage products and a Ni-C cis elimination product but there is no suitable six member ring complex for comparison.

(2). Photodecomposition:

Most of the complexes are not thermally stable so two sets of samples were prepared under identical conditions. One set of samples was irradiated with ultraviolet light (450 watt) while the other set was wrapped in aluminum foil and used as a control. The big change accompanying photolysis was an increase in C-C bond cleavage reactions (Table 5, 6, and 7). Five membered ring nickel(II) complexes either in solution (Table 5) or in the solid state (Table 6) gave more ethylene with photolysis. Six membered ring nickel(II) complexes in the solide state (Table 7) gave more $C^{\alpha}-C^{\beta}$ and $C^{\beta}-C^{\gamma}$ cleavage products with photolysis. This phenomenon is probably the result of a bonding electron being promoted to a C-C antibonding orbital by ultraviolet radiation (with more discussion in last chapter).

(3). Solvent effects on the decomposition of nickel(II) metallocycles:

I_a was decomposed in toluene, acetonitrile, or in toluene with added ligand (triphenylphosphine or tricyclohexylphosphine) (see Table 8). Examination of the product ratios, shows that the yield of ethylene increased as the solvent was changed from toluene to acetonitrile to pyridine. Ethylene became the major product in pyridine and in toluene with added phosphine (scheme 10), toluene/$P\emptyset_3$, toluene/PCY_3. These results probably reflect a change in coordination number. The coordinating ability of the solvent increases as its basisity increases going

Table 5. Products(%) formed from the photolysis of I_a, I_c, and I_f at 0°C in solution state.

Compound	Solvent	Light	Products(%)	
			C_2H_4	$C_4H_8 + C_4H_{10}$
I_a	ø-H	UV	21	79
I_a	ø-H	-	6	94
I_a	ø-CH_3	UV	14	86
I_a	ø-CH_3	-	5	95
I_c	ø-H	UV	59	41
I_c	ø-H	-	-	99.9
I_c	ø-CH_3	UV	75.5	24.5
I_c	ø-CH_3	UV	31	69
I_f	ø-H	UV	31	69
I_f	ø-H	-	29	71
I_f	ø-CH_3	UV	19.5	81
I_f	ø-CH_3	-	15	86

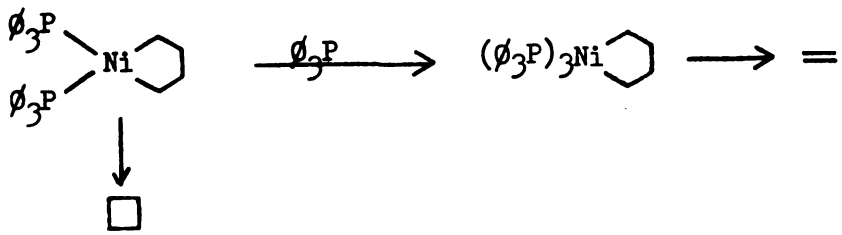
Table 6. Products(%) formed from the photolysis of I_a, I_c, and I_e in solid state.

Compound	Temp.	Time (hr)	Light	Products(%)	
				C_2H_4	$C_4H_8 + C_4H_{10}$
I_a	RT	25	UV	41.9	58.1
I_a	RT	25	-	20.4	79.5
I_c	RT	25	UV	37.4	61.9
I_c	RT	25	-	27.2	72.5
I_e	5°C	8	UV	45.8	54.2
I_e	5°C	8	-	26.1	73.1

Table 7. Products(%) formed from the photolysis and thermolysis of II_a and II_b in solid state.

Compound	Temp.	Light	Products(%)				
			CH_4	C_2H_4	C_3H_6	C_4H_{10}	$C_5H_{10}+C_5H_{12}$
II_a	5°C	UV	4.2	26.6	2.0	2.3	64.8
II_a	110 C	-	0.1	6.5	0.1	2.7	90.3
II_b	5°C	UV	14.7	40.0	8.0	17.4	19.5
II_b	125°C	-	0.9	15.3	1.3	2.0	81.0

from top to bottom in Table 8.



(Scheme 10)

As the concentration of the higher coordination species is increased, the yield of ethylene increases. When I_c chelated diphos ligand was decomposed in toluene, pyridine or toluene with added triphenylphosphine or tri-n-butylphosphine, the mode of decomposition (see Table 9) was quite different from that observed with I_a. Cyclobutane was the major product when the decomposition was carried in toluene, pyridine, or toluene with added triphenylphosphine. In an attempt to alter or otherwise affect the mode of decomposition, higher concentrations of the more basic tri-n-butylphosphine ($n\text{-}Bu_3P:I_c$ = 200 : 1) were used. This changed the major product from cyclobutane to 1-butene. One possible explanation is that the chelated complex I_c does not easily form a higher coordination species. As larger excesses of the more basic tri-n-butylphosphine were added, the reaction went, tri-n-butylphosphine acting as a base can do an intermolecular hydride abstraction on the hydro carbon ring (scheme 11). The pathway is still not fully understood however. The probable reason why I_c, when decomposed in toluene with a large excess of triphenylphosphine, does not give 1-butene as the major product is that triphenylphosphine is not as basic as tri-n-butylphosphine.

Table 8. Products(%) formed from solvent effects on the decomposition of I_a at 9°C±1°C.

Solvent	Products(%)			
	Ethylene	Butane	Cyclobutane	Butene
Toluene	4.6	5.4	68.8	21.1
Acetonitrile	16.3	-	83.7	-
Pyridine	71.8	6.7	21.5	-
Toluene/ϕ_3P *	71.7	2.9	25.3	-
Toluene/CY_3P@	86.5	1.7	11.8	-

*ϕ_3P : I_a = 20 : 1 (mole)

@CY_3P : I_a = 20 : 1 (mole)

Table 9. Products(%) formed from solvent effects on the decomposition of I_c.

Solvent	Temperature	Products(%)					
		Ethylene	Butane	Cyclobutane	1-Butene	t-2-Butene	cis-2- Butene
Toluene	RT (26°C)	2.5	10.1	62.3	11.2	7.1	6.6
Pyridine	RT (26°C)	3.3	4.2	78.4	6.6	5.7	1.8
Toluene	14°C±1°C	2.7	2.3	89.5	2.2	1.5	1.2
Toluene/ϕ_3P	14°C±1°C	2.6	2.3	89.0	------ 4.4 ------		
Toluene/n-Bu_3P*	14°C±1°C	0.6	22.4	7.0	69.7	trace	trace

n-Bu_3P* : I_c = 200 : 1

Table 10. Products(%) formed from solvent effects on the decomposition of I_b and I_e at room temperature.

Compound	Solvent	Products(%)					
		Ethylene	Butane	Cyclobutane	1-Butene	t-2-Butene	cis-2-Butene
I_b	Toluene	3.5	7.0	75.4	10.9	1.8	1.0
I_b	Pyridine	16.0	13.8	42.6	16.5	5.0	2.1
I_e	Toluene	6.0	8.2	46.5	24.5	4.8	10.0
I_e	Pyridine	22.5	10.7	24.5	19.4	11.1	6.9
I_e	Toluene/n-Bu_3P^*	56.7	13.3	9.0	--------	21.0	--------

n-Bu_3P^* : I_e = 30 : 1 (mole)

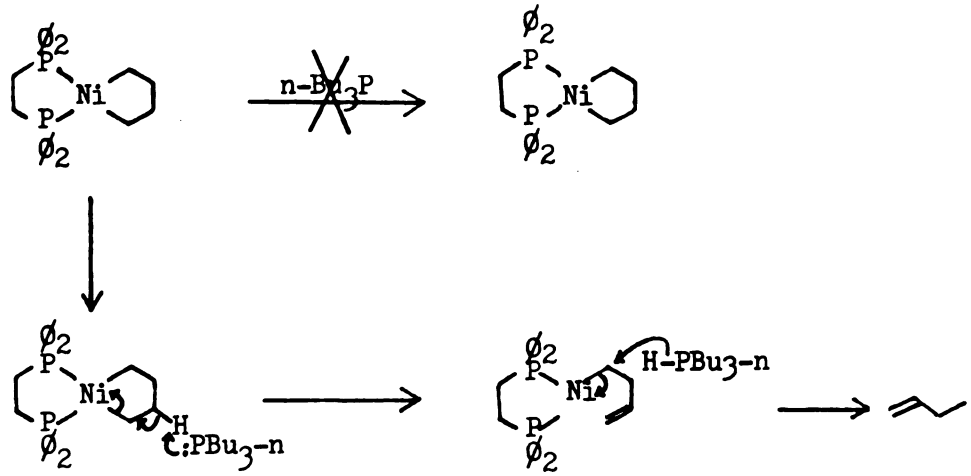
Table 11. Products(%) formed from solvent effects on the decomposition of I_f.

Solvent	Temperature	Products(%)					
		Ethylene	Butane	Cyclobutane	1-Butene	t-2-Butene	cis-2-Butene
Pyridine	8°C	14.5	44.4	1.7	34.0	3.2	1.4
Acetonitrile	8°C	11.7	40.6	2.4	35.0	8.7	1.3
Toluene/n-Bu_3P*	0°C	30.0	31.7	1.9	30.0	2.5	3.7

*n-Bu_3P : I_f = 9 : 1 (mole)

Table 12. Products(%) formed from solvent effects on the decomposition of II_a.

Solvent	Products(%)						
	Methane	Ethylene	Pentane	Cyclopentane	1-pentene	t-2-pentene	cis-2-pentene
Acetonitrile	2.7	23.2	28.2	24.5	16.7	2.8	0.9
Pyridine	3.9	32.6	22.6	19.9	16.0	2.3	1.0
n-Bu_3P	3.9	35.1	25.4	14.2	17.1	2.1	0.8
$N(Et)_3$	3.9	49.5	17.9	12.1	13.1	1.5	0.1

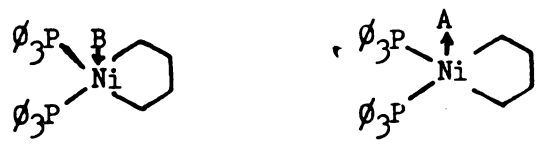


(Scheme 11)

The modes of decomposition of I_b and I_e in pyridine and toluene are shown in Table 10. Ethylene became the major product when I_e was decomposed in toluene with added tri-n-butylphosphine. This behavier is quite different from that of the I_c but it is similar to that of I_a. The decomposition of the nickel(II) metallocycle II_a (six member ring) was also investigated (see Table 12). The formation of ethylene increased as the solvent was changed from acetonitrile to pyridine, tri-n-butylphosphine and finally triethylamine. When II_a was decomposed in triethylamine, strongly coordinating solvent, ethylene become the major product.

(4). Olefin effects on the decomposition of nickel(II) metallocycles:

According to the second theory, complexation of an electron deficient olefin (A) to the nickel may induce charge transfer from the bonding M-C orbital to a vacant metal d orbital and increase cyclobutane formation.



Complexation of an electron rich olefin (B) to the metal should induce electron flow in the other direction, favoring ethylene formation, similar to that observed in photodecomposition. The results are shown in Table 13 and 14. Tetracycanoethylene, acrylnitrile, and ethylene trichloride were used as electron deficient olefins. Cis-2-pentene and cyclohexene were used as electron rich olefins.

Table 13. Products(%) formed from olefine effects on the decomposition of I_e at room temperature.

Olefine	Products(%)					
	Ethylene	Butane	Cyclobutane	1-Butene	t-2-Butene	cis-2-Butene
Tetracynoethylene/ toluene	6.8	8.3	38.6	5.5	11.8	29.0
Cis-2-pentene	66.6	4.2	9.0	2.4	6.8	9.2

Table 14. Products(%) formed from olefine effects on the decomposition of II_a.

Olefine	Products(%)						
	Methane	Ethylene	Pentane	Cyclopentane	1-Pentene	t-2-Pentene	cis-2-Pentene
Acrylnitrile	3.6	32.8	22.8	20.4	14.4	1.7	0.5
1,1,2,trichloro-ethylene	3.4	34.2	18.4	23.5	15.3	2.1	0.7
Cyclohexene	5.1	44.8	17.0	15.3	15.8	1.3	0.2

Experimental

All experiments were carried out under a deoxygenated argon atmosphere, or in a vacuum. Gasses evolved during thermolysis were analyzed with a mass spectrometer. The composition of the gases evolved during thermolysis or photolysis of a complex was determined on a gas chromatograph Varian 1400 or a Perkin Elmer 900 equipped with flame ionization detector. The latter was also hooked up with an Autolab System I integrator. An 8 ft stainless column (1/8 in O.D.) containing ether 7% parafin wax on Al_2O_3 or 120/150 mesh Duropak was used. The column temperature were 80 and 75°C, respectively. The carrier gas (He) flow was 30 ml/min.

Thermal decomposition:

A 15 ml Schlenk tube containing 0.1-0.4 g of complex was connected to avacuum line equipped with a mercury manometer, and was evacuated (Figure 2). The Schlenk tube was placed in a oil bath with thermometer. The temperature of the oil bath was raised very slowly (1°C/min), and the gas evolved at each temperature was recorded.

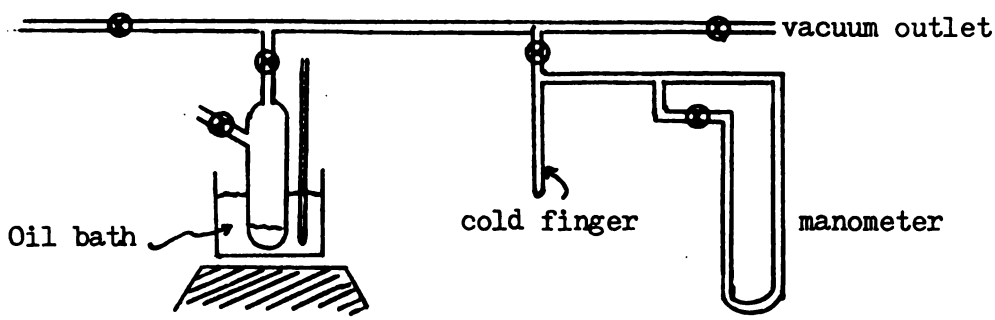


Figure 2: Vacuum line system for thermolysis reaction

Photodecomposition:

A 10 ml quartz tube containing 0.1 g of complex in the solid state or a 50 ml pyrex tube containing 0.1 g of complex in 10 ml of solvent was irradiated under argon using a 450 watt super high-pressure mercury lamp with overal UV wavelenth. The sample tubes were positioned at the same distance from the lamp in a big ice box or water bath. The evolved gas (on top) was analyzed by gc.

Solvent and olefine effect on the decomposition of nickel(II) metallocycles:

Solvents were dried by standard methods and stored under dry oxygen free conditions. The complexes were prepared as previously described. All product gases which had dissolved in the solvent were collected by repeated trap-to-trap distillation as follows (see Figure 3).

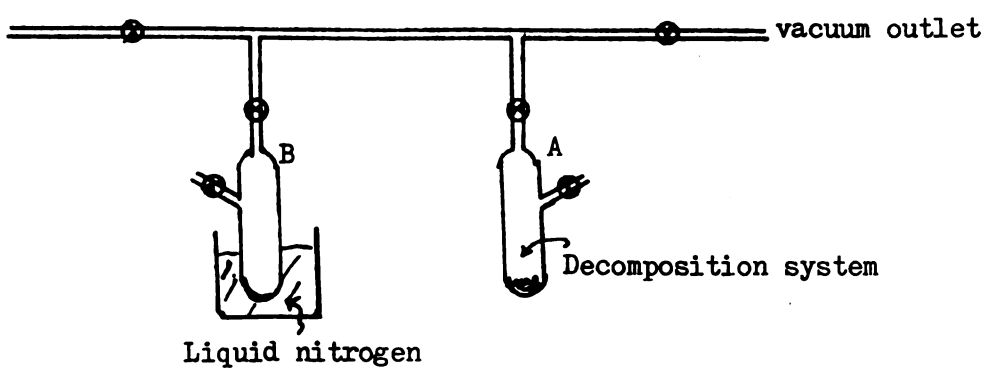


Figure 3: Vacuum line system for trap to trap method

The gas and 50 to 30% of the solvent from the decomposition system in tube A were vacuum distilled into tube B, then a new empty tube A was connected to the joint after tube A was removed. All of the gas in

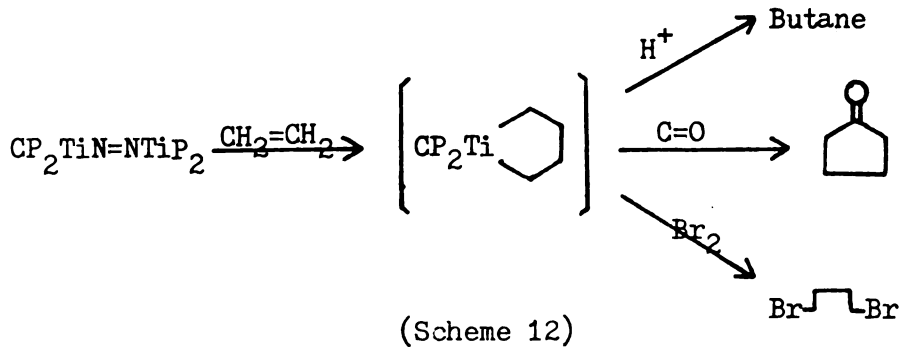
tube B (and 10% of the solvent) was distilled into tube A', and tube B was then dried in vacuum. Finally all of the gas in tube A' was distilled into tube B without solvent. Gas samples for gc analysis were taken from tube B.

CHAPTER 3

ETHYLENE AND CYCLOPENTANE FROM NICKEL(II) METALLOCYCLES

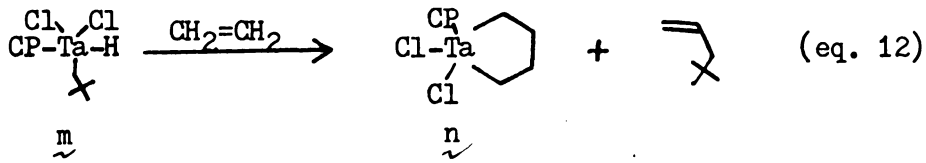
Introduction

In the first chapter the only well characterized metallocyclopentane complexes considered were made from more reactive olefin such as norbornadiene. The formation of unsubstituted metallocyclopentane from ethylene has been observed in two cases (14, 33). In one case ethylene was introduced into a system containing $CP_2TiN{=}NTiCP_2$, which was at a temperature below -30°C. This produced a reaction mixture with chemical properties which suggested the presence of metallocyclopentane (see scheme 12).



(Scheme 12)

Recently, 1977, Schrock gave strong evidence for the formation of a tantalum metallocyclopentane (33) by reaction of m with ethylene (eq. 12). The product n was isolated in 9% yield and characterized by ^1H nmr, and chemical reactions



m n (eq. 12)

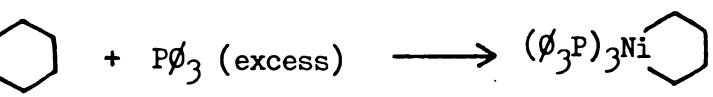
This chapter will focus on the reverse reaction (formation of ethylene from unsubstituted metallocycles) and some oxidative addition reactions of metallocycles.

Results and Discussion

(1). ^{31}P nmr of nickel(II) metallocycles:

The ^{13}C nmr of carbons in subject metallocycles could not be obtanied because of low solubility. The ^{1}H nmr of I_c and I_d were dominated by the resonance of the ligand.

The ^{31}P nmr chemical shift of I_a was observed at -42.5 ppm and a new complex was observed by ^{31}P nmr after excess triphenylphosphine had been added to I_a. This new complex (chemical shift at -27.5 ppm) was isolated (29) and recystalized under low temperature as golden brown cystals. The analysis of this complex showed P/Ni = 2.98 (theor =3.0) and hydrolysis with sulfuric acid (-20°C) produced butane (98%). This indicates that the new species is still a metallocycle (eq. 13).



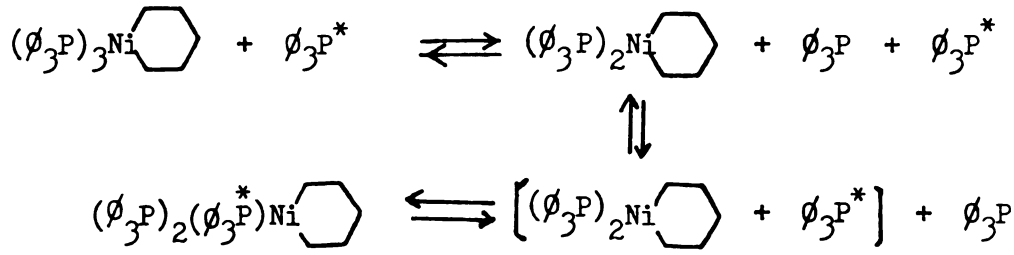
(eq. 13)

When the solid was redissolved, it again showed a ^{31}P signal at -27.5 ppm. The ^{31}P spectrum of I_a in the presence of a 14.1 mole excess

of triphenylphosphine was temperature dependent. As the temperature was raised (Figure 4), the -27.5 ppm peak averaged with the free triphenylphosphine peak while the signal for I_a remained sharp.

The ^{31}P spectra of II_a showed similar behaviour. The chemical shift of II_a was observed at -33.3 ppm. Addition of one mole excess of triphenylphosphine (Figure 5) gave a higher coordination complex. The new peak at -23.5 ppm was assigned to the higher coordinated metallocycle on the basis of the observation of I_a. When a toluene solution of II_a was treated with an excess of triphenylphosphine at -10°C and then stored at -20°C for a week golden brown cystals formed which were then isolated.

The ^{31}P signal of this complex was observed at the same position (-23.5 ppm) at -90°C. As the temperature was raised, the -23.5 ppm peak equlibrated with the triphenylphosphine peak, presumably by a dissociation mechanism (scheme 13). The rate of equlibration depended on the amount of triphenylphosphine added (Figure 6 and 7) with a higher concentration of triphenylphosphine giving a slower rate of exchange.



(Scheme 13)

The ^{31}P spectrum of I_c at -90°C consisted of a single peak at -45.0 ppm, I_c (Figure 8) indicating that neither exchange nor formation

of detectable amounts of higher coordination number complexes and decomposition products are only formed on heating to 80°C. The results are consistent with data in the previous chapter and serve to confirm that four coordinated metallocycles (P_2 species) give cyclobutane while five coordinate metallocycles (P_3 species) give ethylene.

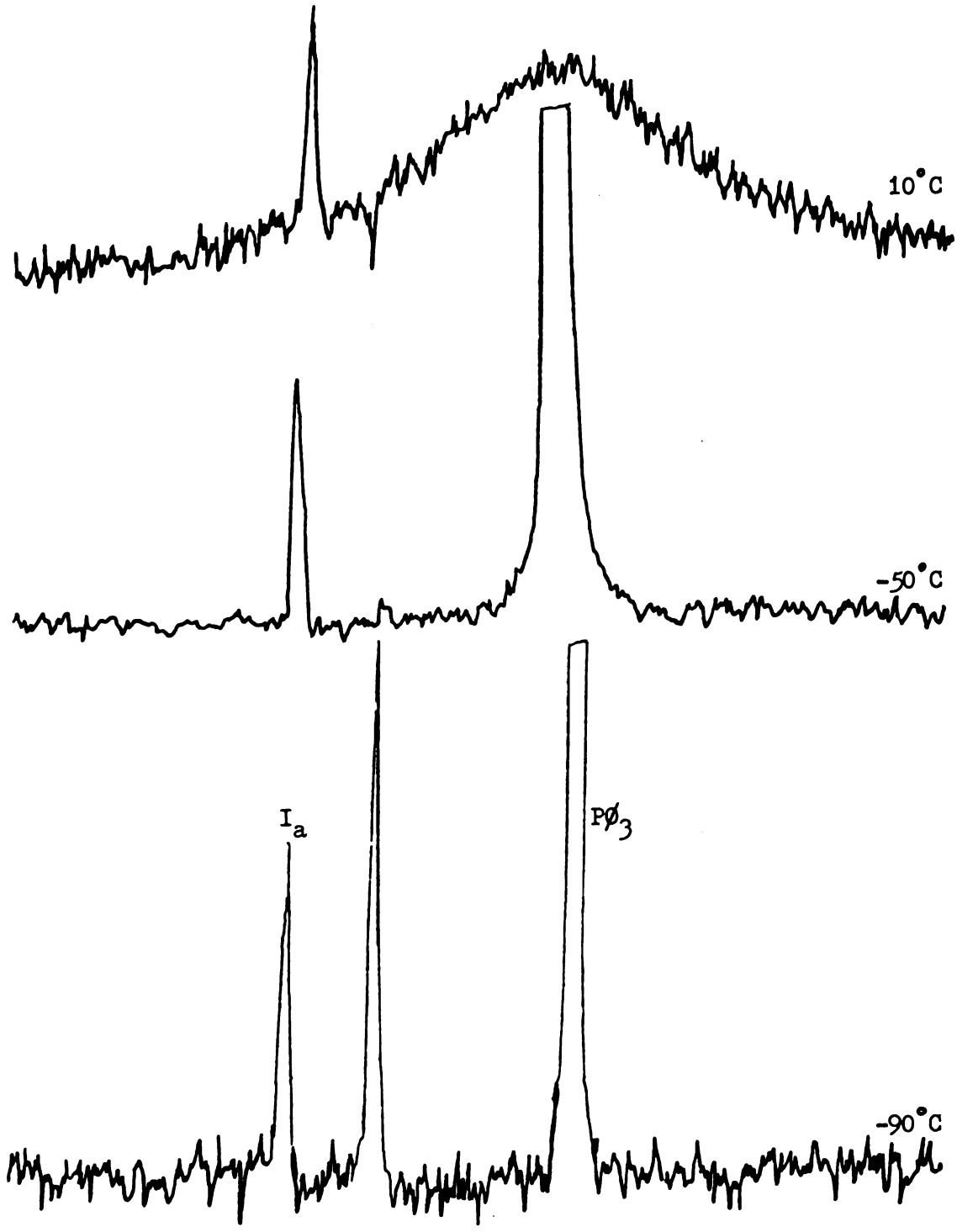


Figure 4. Temperature dependant ^{31}P nmr spectrum of I_a in toluene with added, $P\phi_3$/ I_a = 14.1 (mole).

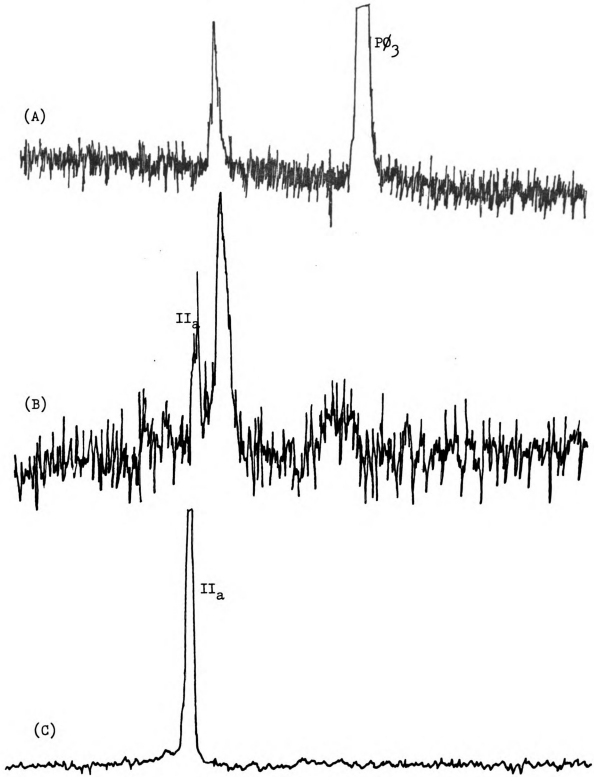


Figure 5. ^{31}P nmr spectrum of II_a in toluene with (A). added, $P\emptyset_3$/ II_a = 4.1 (B). added, $P\emptyset_3$/ II_a = 1 (C). no added $P\emptyset_3$ at -92°C

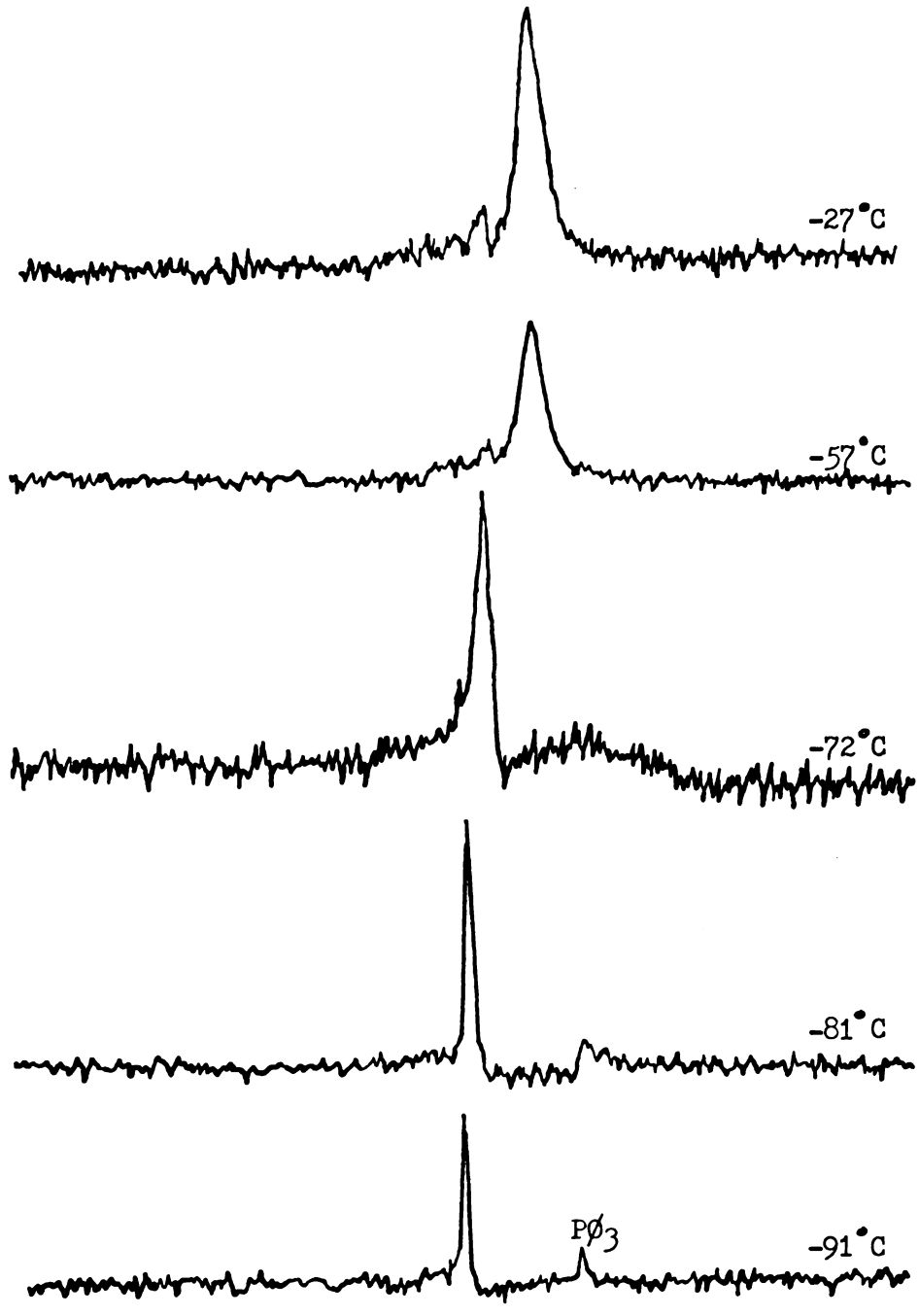


Figure 6. Temperature dependant ^{31}P nmr spectrum of II_a in toluene with added, $P\emptyset_3$ / II_a = 1.2

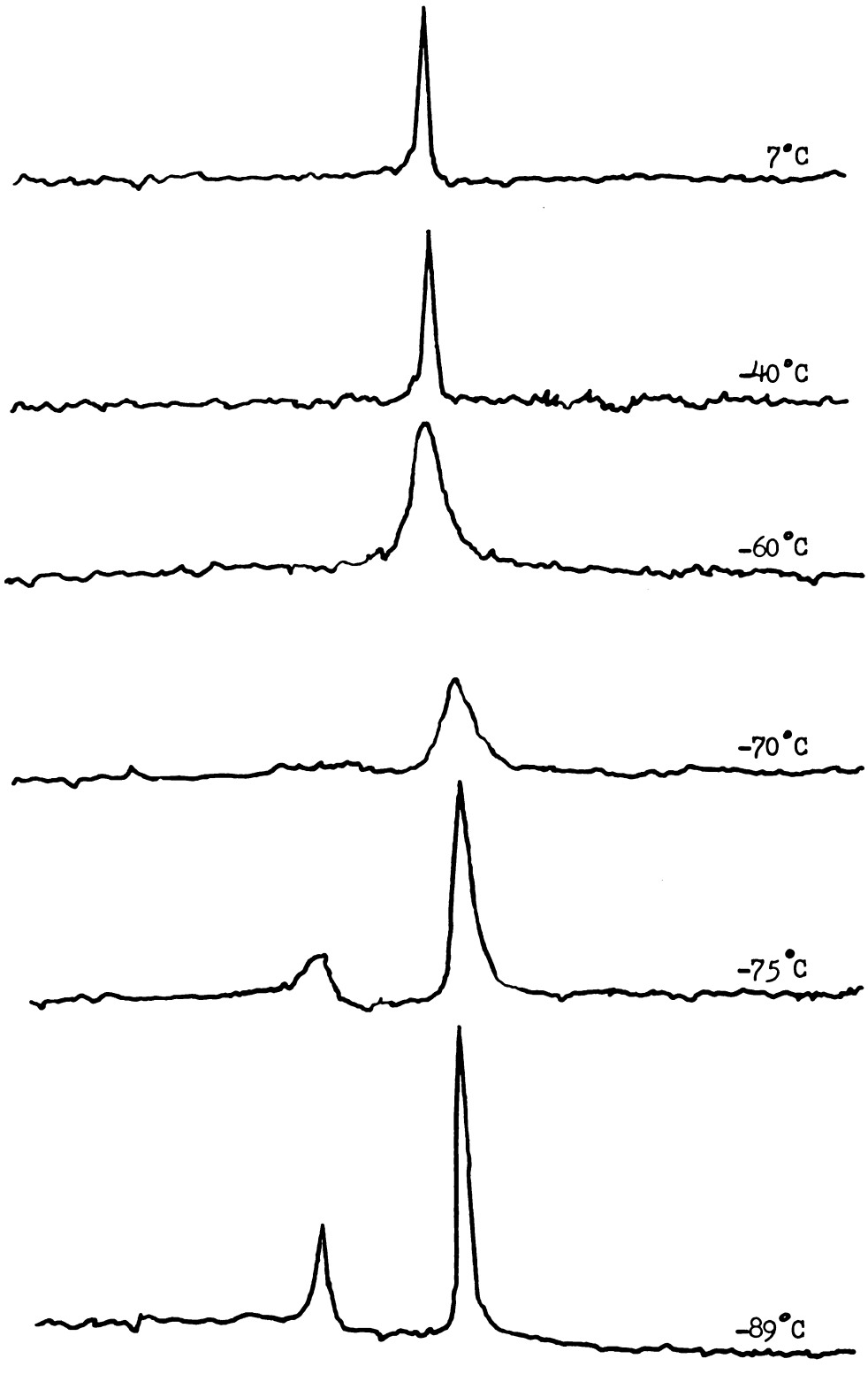


Figure 7. Temperature dependant ^{31}P nmr spectrum of II_a in toluene with added $P\emptyset_3$ / II_a = 4.0

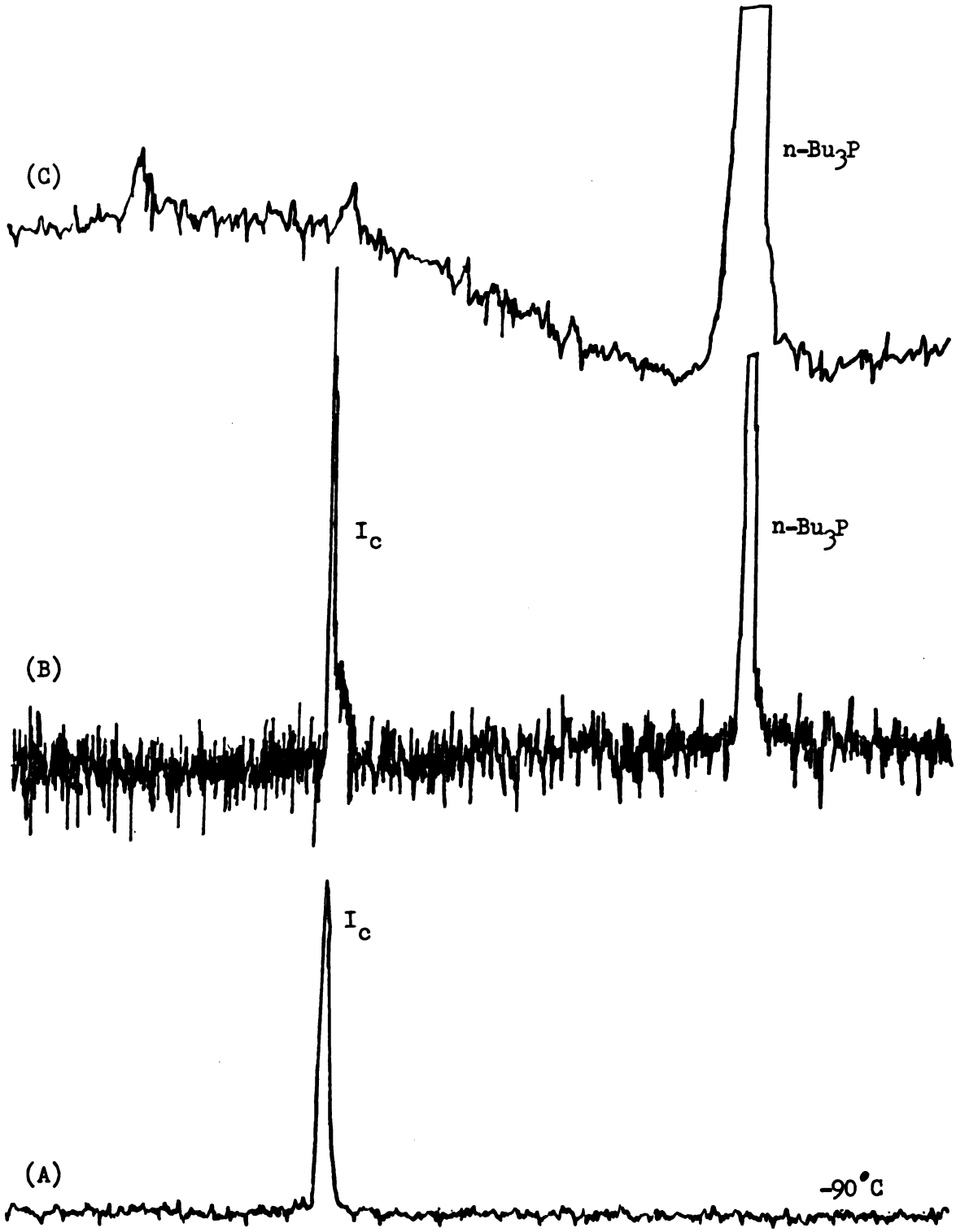


Figure 8. ^{31}P nmr spectrum of I_c in toluene with (A). no added PBu_3-n (B). added PBu_3 (C). added PBu_3-n, heat up to 80°C

(2). Phosphine effects on the mode of decomposition of nickel(II) metallocycles:

Since the coordination numbers of the complexes were a function of the structure of the phosphine, the ratios of the decomposition products as a function of the P/Ni ratio were determined. Plots of the resulting gas composition as a function of added phosphine are shown in Figure 9, 10, 11, 12, and 13.

From the molecular weights in solution, it can be determined that I_a and I_c are present as P_2 species whereas I_d dissociated to a P_1 species. Cyclobutane is the predominate product for both P_2 species at P/Ni = 0. The dissociated I_d produced 1-butene as the major product. As trialkyl phosphine is added to the trichlohexyphosphine complex the amount of cyclobutane increases to a maximum at P/Ni of 4. At this point and at higher P/Ni ratios the decomposition ratios are very similar to those resulting from triphenylphosphine complex at P/Ni = 0 and larger value and only for I_c at P/Ni = 0. The ^{31}P studies showed that I_c did not form higher coordination number complexes when tri-n-butyphosphine was added. Consequently, this requires very high concentration of phosphine appears to induce decomposition to linear butenes by a mechanism not fully understood.

The decomposition curve of I_f shows the same tendencies as described above, but except data (P/Ni ratios) is lacking.

The results combined with nmr data and molecular weight information are most consistent with the following scheme 14.

$$\underset{\downarrow}{PNi(C_4H_8)} \overset{P}{\rightleftharpoons} \underset{\downarrow}{P_2Ni(C_4H_8)} \overset{P}{\rightleftharpoons} \underset{\downarrow}{P_3Ni(C_4H_8)} \qquad \text{(scheme 14)}$$

1-butene cyclobutane ethylene

There are two modes of carbon-carbon fragmentation possible for II_a, $C^{\alpha}-C^{\beta}$ bond cleavage, and $C^{\beta}-C^{\gamma}$ bond cleavage, so the ethylene observed here may not be exclusively from a simple fragmentation. Futher work, such as labeling studies, is required for any conclusion can be drawn.

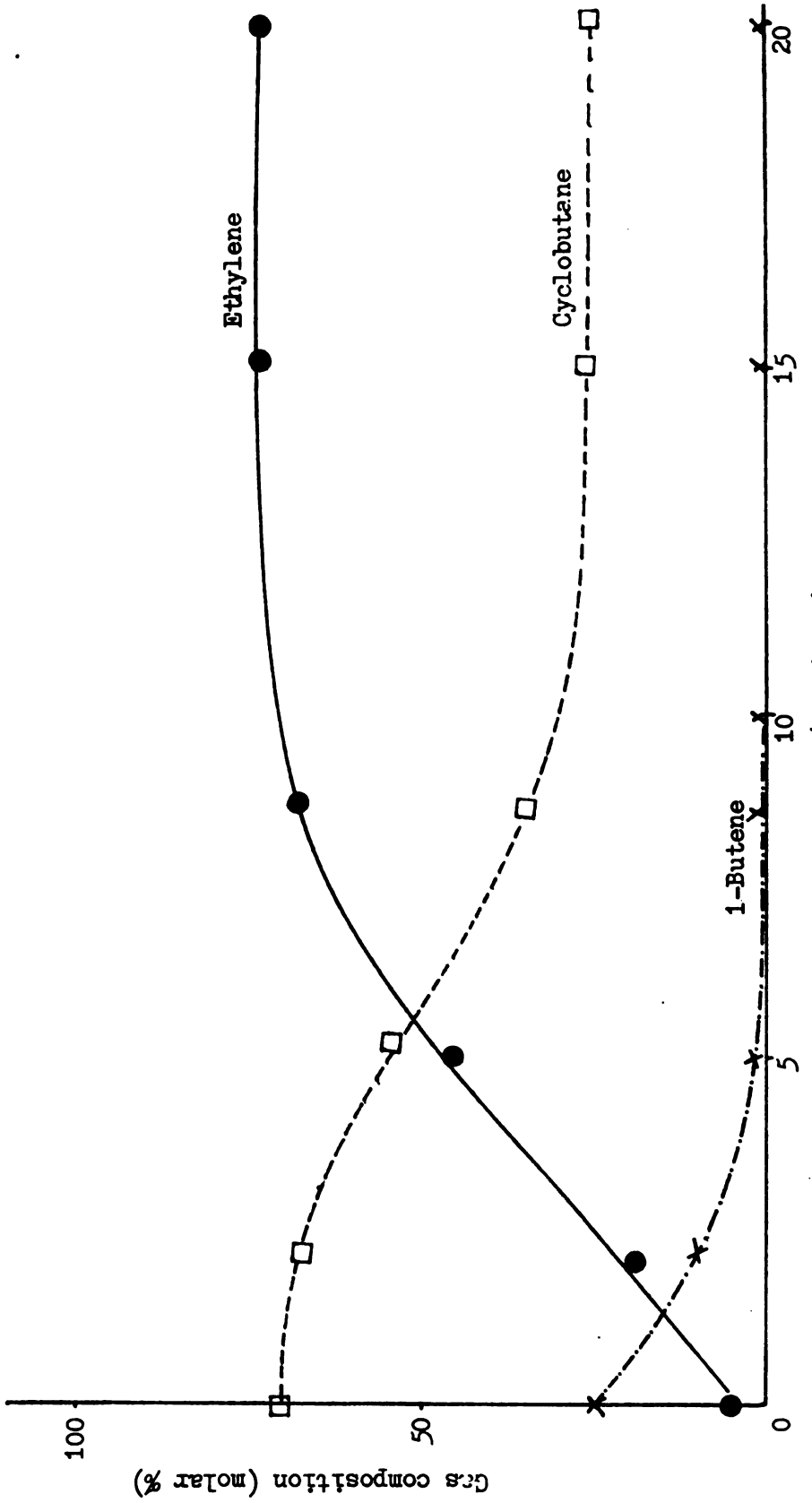


Figure 9. Effect of added PØ3 on the decomposition mode of I_a

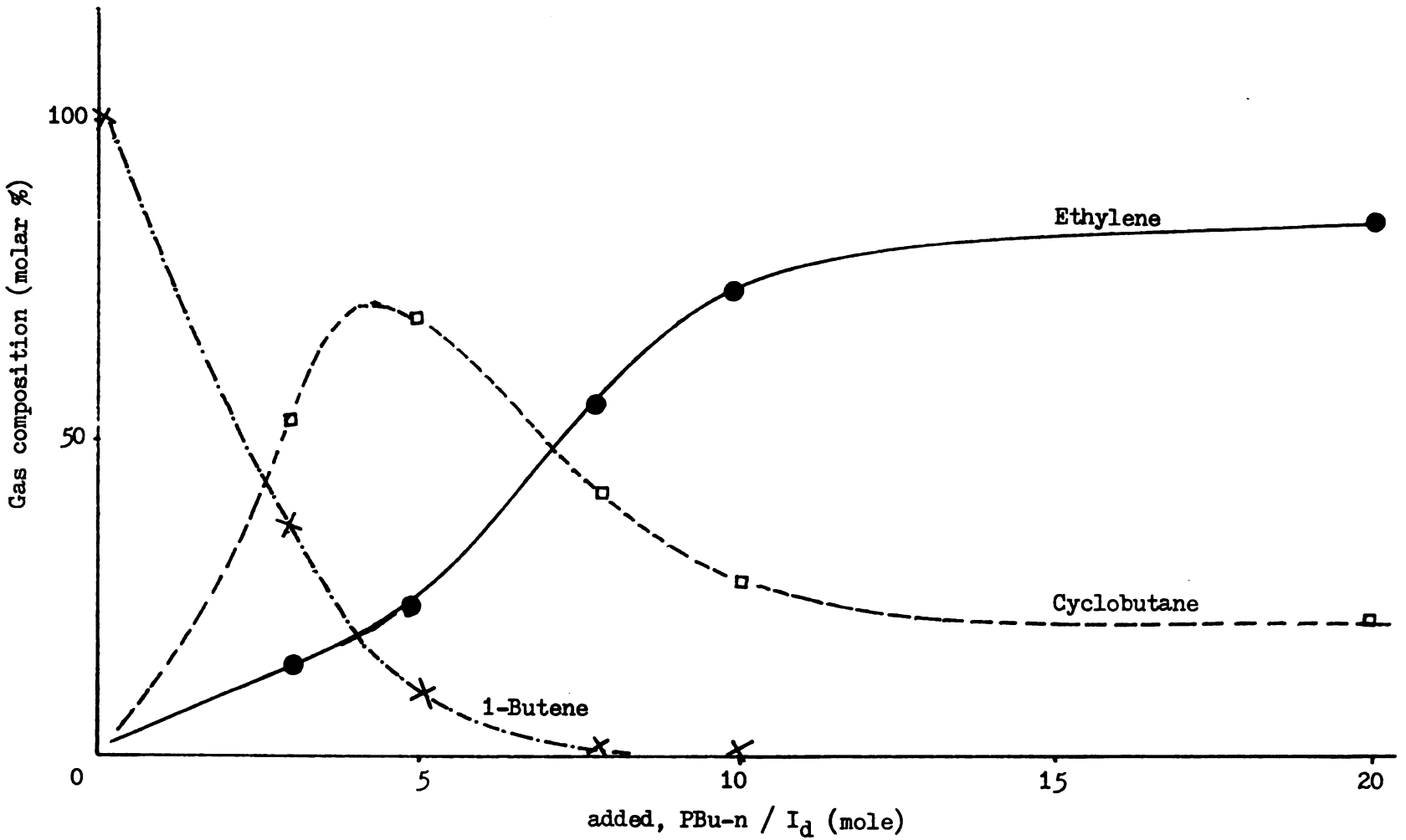


Figure 10. Effect of added n-Bu_3P on the decomposition mode of I_d

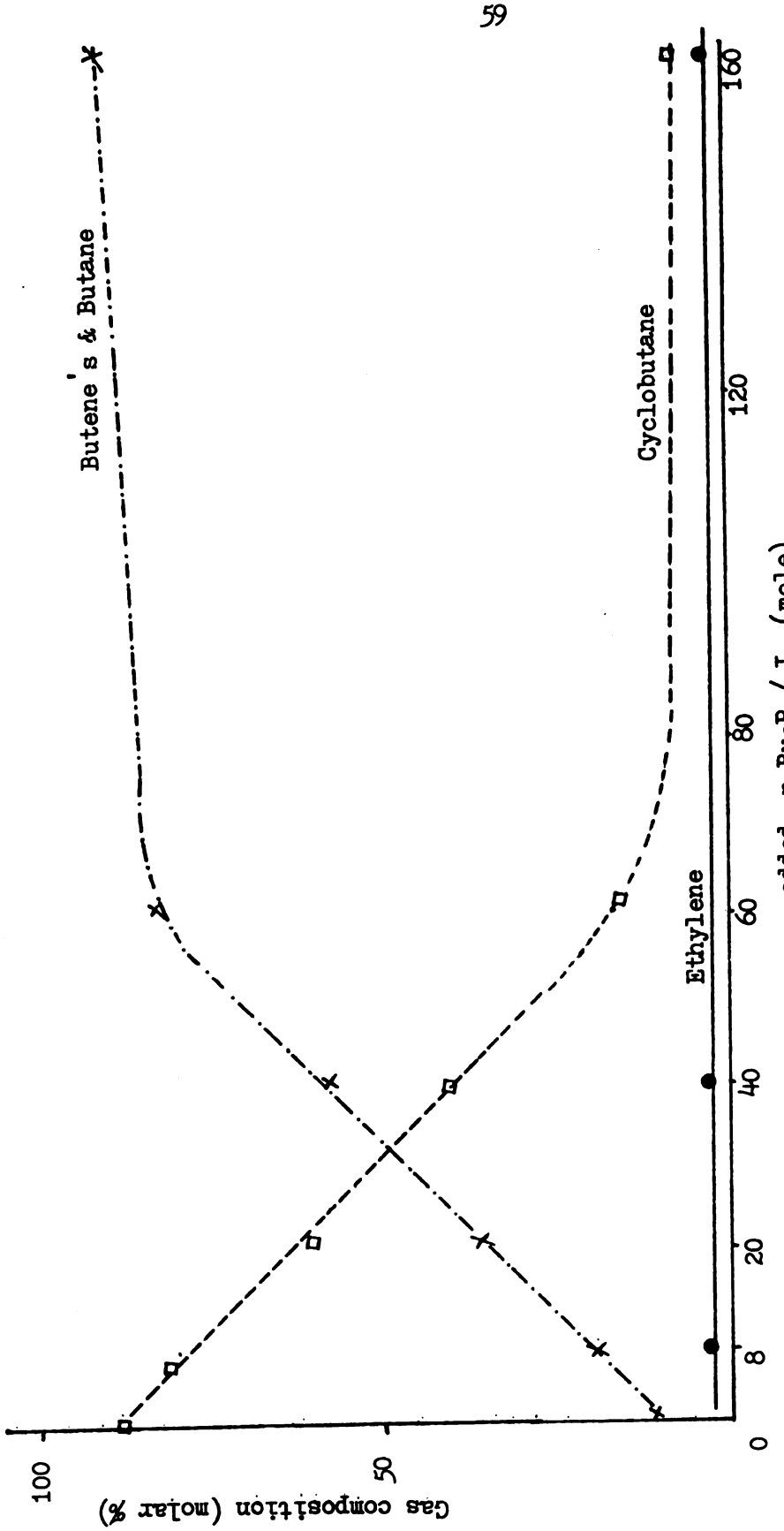


Figure 11. Effect of added n-Bu_3P on the decomposition of I_c

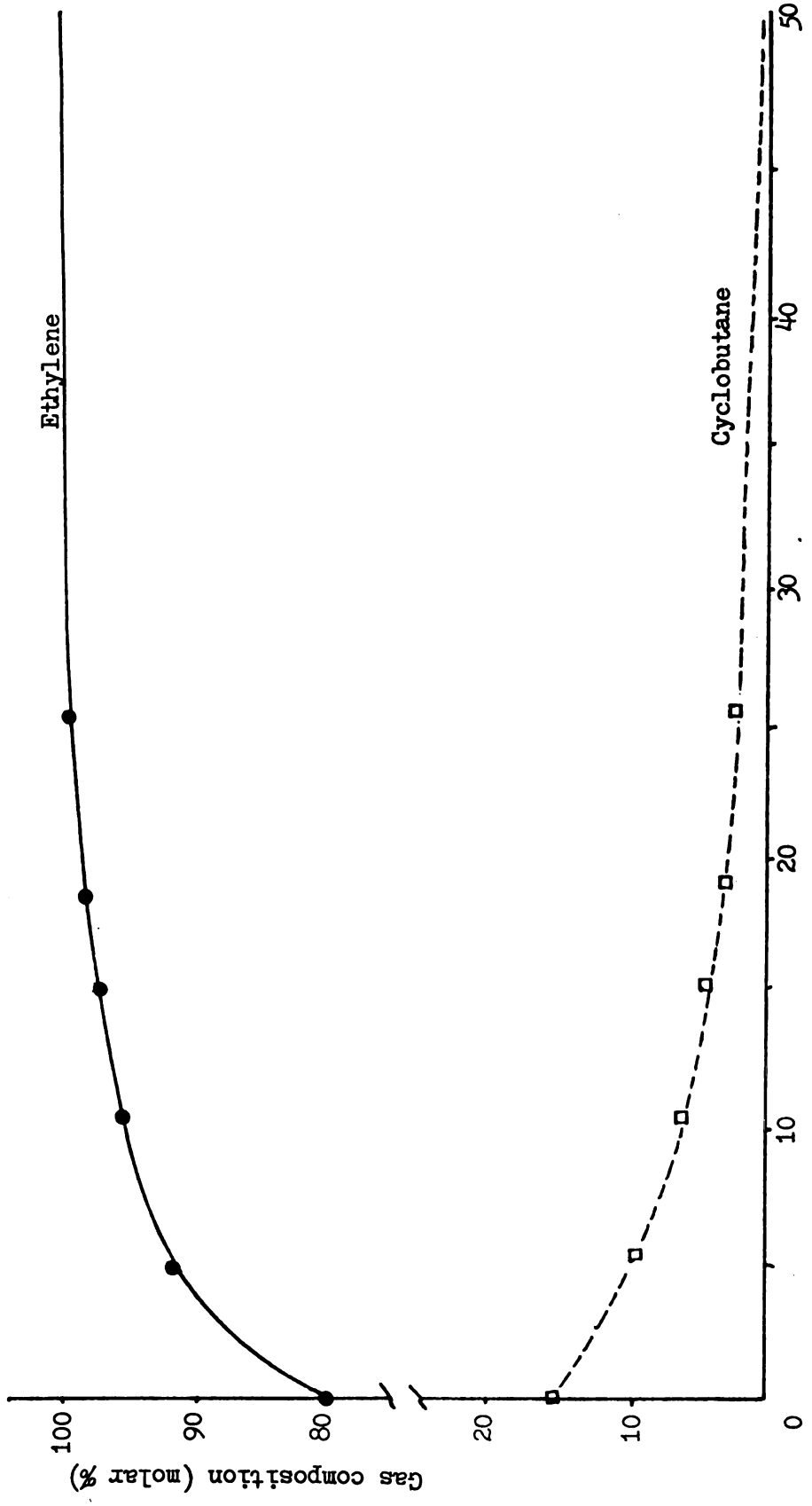


Figure 12. Effect of added n-Bu3P on the decomposition of I_f

Figure 13. Effect of added $P\emptyset_3$ on the decomposition of II_a

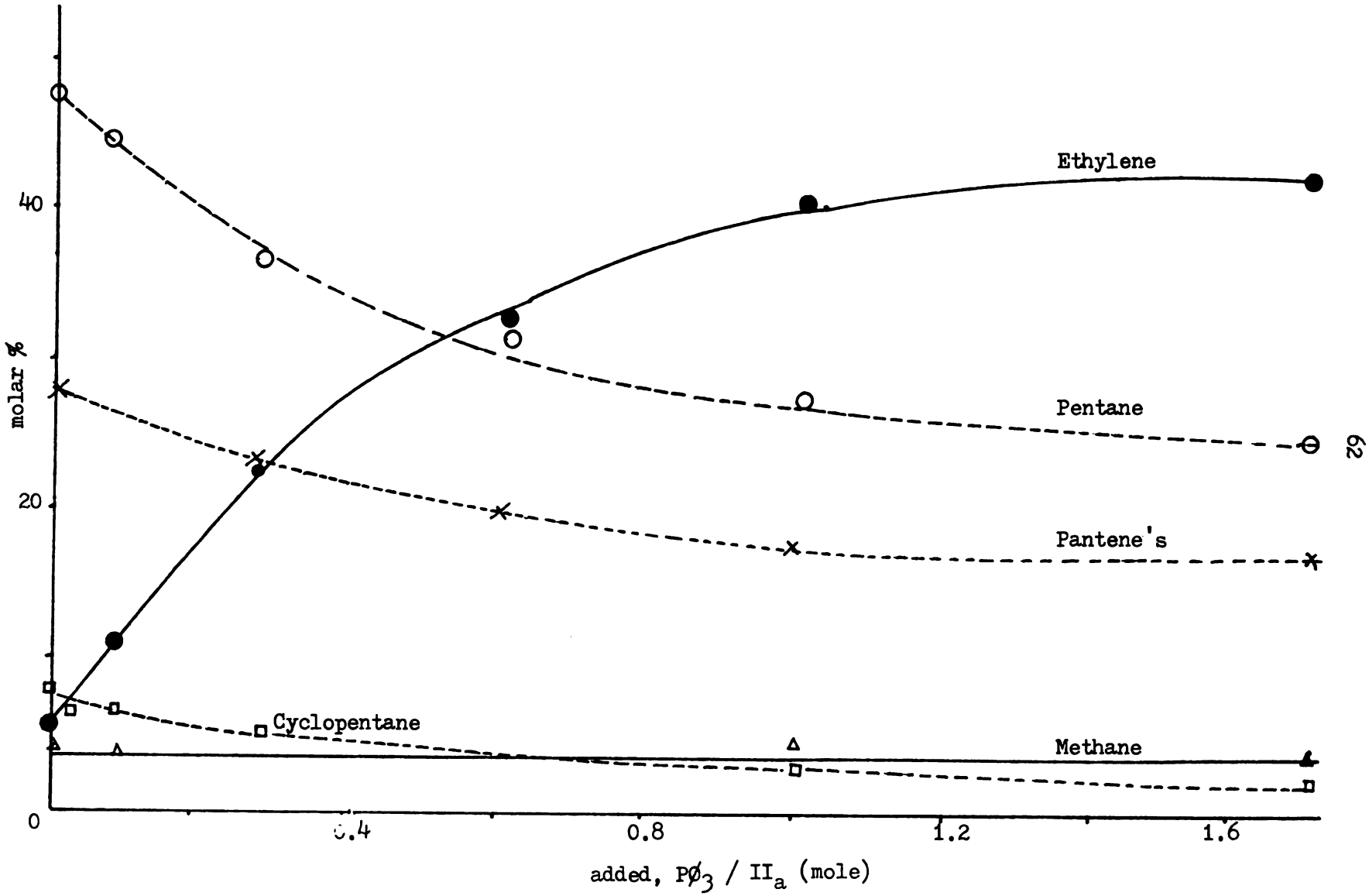

Ethylene
Pentane
Pantene's
Cyclopentane
Methane
molar %
40
20
0
0.4
0.8
1.2
1.6
added, PØ3 / IIa (mole)

Table 15. Products(%) formed from triphenylphosphine effects on the decomposition of I_a at 9°C±1°C in toluene.

ϕ_3P, added/Ni Molar ratio	Products(%)			
	Ethylene	Butane	Cyclobutane	Butene's
2.0	17.2	5.3	67.2	10.3
5.0	44.3	0	53.1	2.6
8.0	64.7	0	34.2	1.1
10.0	70.5	0.9	28.3	0.3
15.0	72.2	1.7	26.1	0
20.0	71.7	2.9	25.3	0

Table 16. Products(%) formed from tri-n-butylphosphine effects on the decomposition of I_c at 14°C±1°C in toluene

n-Bu_3P, added/Ni Molar ratio	Products(%)		
	Ethylene	Cyclobutane	Butene's
0	2.7	89.5	7.2
8	1.6	81.6	15.9
20	2.6	60.9	32.7
40	1.9	38.6	53.5
60	1.2	15.2	81.8
160	0.6	7.4	91.2
200	0.6	7.0	92.1

Table 17. Products(%) formed from tri-n-butylphosphine effects on the decomposition of I_f at -50°C in toluene.

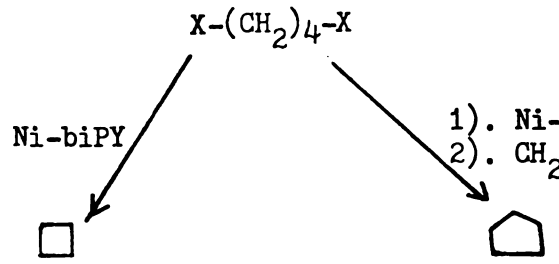
$n\text{-}Bu_3P$,added/Ni Molar ratio	Products(%)	
	Ethylene	Cyclobutane
0	85.0	15.0
5	91.5	8.5
10	94.0	5.9
15	96.0	4.0
20	97.0	2.9
25	98.0	2.0
60	100.0	0

Table 18. Products(%) formed from triphenylphosphine effects on the decomposition of II_a at 16°C in toluene.

ϕ_3P, added/Ni Molar ratio	Products(%)					
	Methane	Ethylene	Iso-pentane	Pentane	Cyclopentane	Pentene's
0	4.65	5.81	7.61	47.57	6.66	27.70
0.01	3.81	6.98	8.25	46.98	6.67	27.31
0.03	5.85	9.15	7.33	45.43	5.71	27.31
0.09	3.56	10.99	7.54	44.61	6.60	26.70
0.28	5.62	23.18	5.62	37.18	5.48	22.92
0.61	4.42	32.88	5.76	32.83	4.03	20.07
1.00	4.09	41.49	4.60	27.96	3.81	18.06
1.70	4.86	43.38	3.75	25.82	3.40	18.79

(3). Cyclopentane formation

Organonickel compounds are widely used as reagents and catalysts in organic synthesis (34). Takahashi, et. al. (35) recently reported that a low valent nickel-bipyridyl complex is a powerful reagent for the cyclo coupling of dihalogenoalkanes,as shown in scheme 15. They suggested that the cyclo coupling reaction might proceed through nickel cycloalkane intermediates.



(Scheme 15)

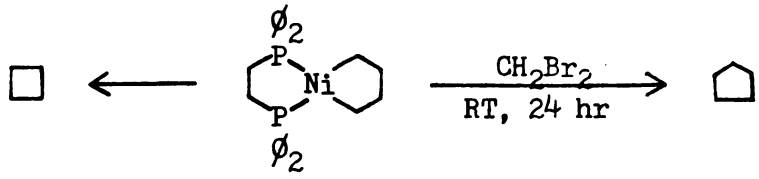
Diphos nickel cyclopentane (I_c) has been isolated : upon treament with oxygen and activated olefin it liberats cyclobutane more than 91%.

Table 19. Cyclobutane formed from oxygen and olefin effected decomposition of I_c.

Reagent	Temp.	Solvent	Products(%)		Products(%)	
			Ethylene	Butane	Cyclobutane	Butene's
Oxygen	26°C	-	1.1	0.4	91.2	7.3
Oxygen	15°C	Toluene	0.4	0.1	95.0	3.2
Oxygen	15°C	Benzene	0.5	0.3	96.0	2.3
Acrylnitrile	15°C	-	0.3	0.6	91.0	6.7

When dibromomethane was added to an ether solution of I_c at 0°C and allowed to reat at room temperature for twenty four hours,cyclopentane

was obtained in 70% yield (Scheme 16).



(Scheme 16)

In the case of I_a, the yield of cyclopentane about 20% was relatively low owing to the low stability of I_a. This method may have a potential application in the synthesis of cyclopentane derivatives by using dibromomethane derivatives as reagents .

Experimental

The ^{31}P spectrum was run by multinucleur nmr spectrometer DA-60 with D_2O external lock, and phospheric acid as external reference. The sample was placed in a sealed vacuumed nmr tube transfered at low temperature and under an inert atmosphere.

Decomposition reactions were carried out on a vacuum line as illustrated in the previous chapter. The decomposition gases were collected by trap to trap distillation and the components were analyzed by gc. They are shown in Table 16, 17, 18 and 19.

Cyclopentane synthesis: Dibromomethane was added at $0^{\circ}C$ under argon to an ether solution of metallocycle (type 1) with 1 : 1 ratio of dibromomethane to I_a or I_c. After addition the reaction was allowed to react at room temperature for twenty four hours. The gas volume and components were analyzed by gc.

CHAPTER 4

APPLICATION OF EXTENDED HÜCKEL CALCULATION TO THE REACTION OF NICKEL(II) METALLOCYCLES

Introduction

The Hückel theory has been widely oxploited in chemistry. Woodward and Hoffmann have developed the concept of symmetry-based selection rules for chemical reactions. They have applied their approach to electrocyclic reactions (36), sigmatropic reactions (37, 38), and concerted cycloaddition reaction (39). Hoffmann also applied these calculations to the bonding capability of transition metal carbonyl fragments and the structure and chemistry participation of transition metal in concerted cycloaddition reactions using the Woodward-Hoffmann scheme. Their methods is to draw a molecular orbital energy level diagram for the reactants and then for the products and finally to correlate the individual final molecular orbitals using symmetry restrictions imposed by an assumed geometry for the transition state. If the correlation connects a filled bonding orbital in the initial state with an empty antibonding orbital in the final state, the reaction is then described as thermally disallowed but photochemically allowed. As pointed out by Eaton (42), a more elegant approach to this is to construct a state correlation digram.

In this chapter the extended Hückel calculation was used and state correlation digram was constructed for the isomerization between square planar $(H_3P)_2Ni(C_4H_8)$ and tetrahedral $(H_3P)_2Ni(C_4H_8)$.

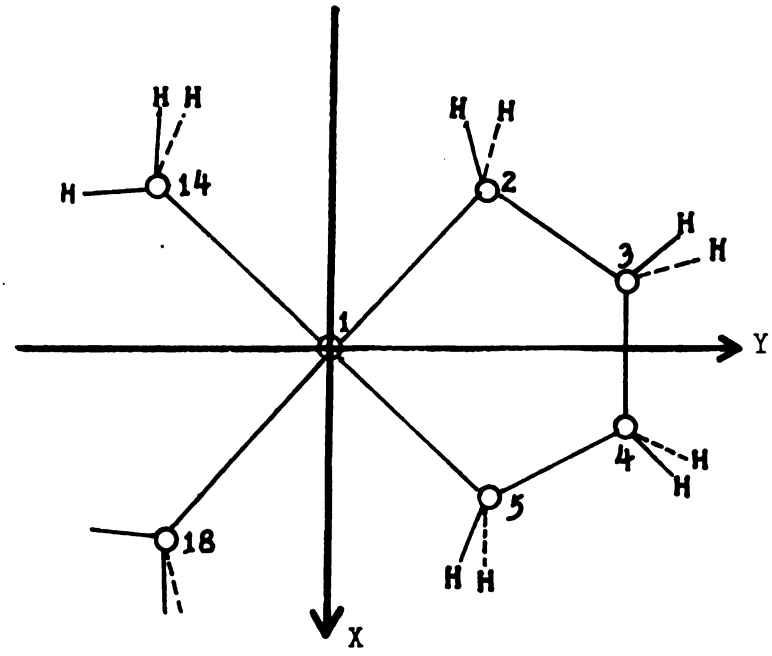
Calculation

A basis set of valence atomic orbital for Ni consisting of 3d, 4s, and 4p, single slater-type orbitals were used for the 4s and 4p wave function, while the 3d wave function was taken as a contracted linear combination of two slater-type wave function. The diagonal H matrix elements, H_{ii}, were as shown in Table 20.

The geometrical approach used here is to perform the calculation at a resonable orientations. The bond lengths used in the calculation were obtained from currently available X-ray data (43). The coordinates are listed in Table 21 and Table 22.

Table 20. Parameter used in the calculation (44) (45).

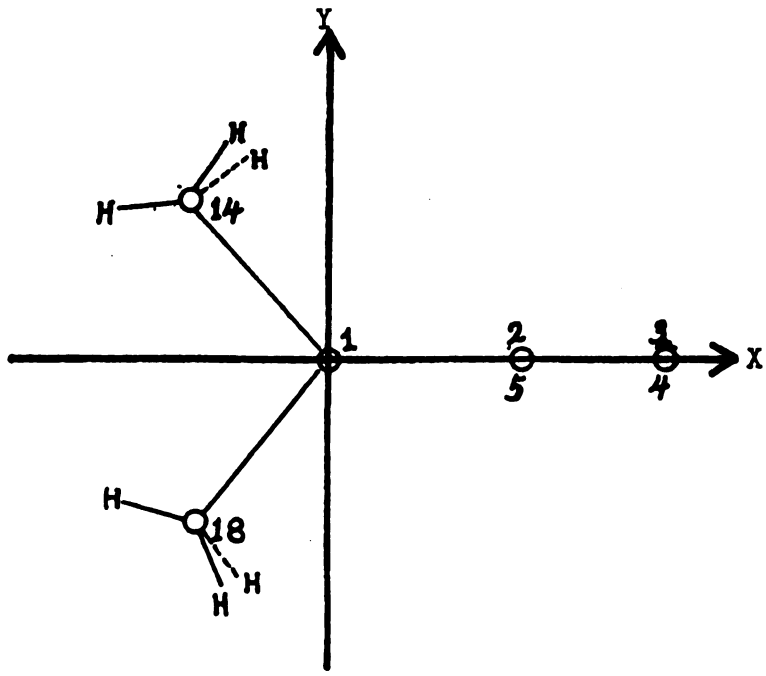
Orbital		Orbital exponent		H_{ii}, ev
		1	2	
Ni	3d	5.75	2.00	-13.2
	4s	1.50		-10.7
	4p	0.86		- 6.3
P	3s	1.18		-19.00
	3p	1.08		-10.04
C	2s	1.63		-19.5
	2p	0.88		- 9.9
H	1s	1.00		-13.60



-1-

Table 21. Coordinates of 1 (square planar metallocycle). $(H_3P)_2Ni$⬡

Atom, #		Coordinate (A°)			Atom, #		Coordinate		
		X	Y	Z			X	Y	Z
Ni	1	0	0	0	H	12	2.48	1.01	0.90
C	2	-1.48	1.48	0	H	13	2.48	1.01	-0.90
C	3	-0.81	2.90	0	P	14	-1.61	0	0
C	4	0.81	2.90	0	H	15	-1.94	0	1.34
C	5	1.48	1.48	0	H	16	-2.76	1.16	-1.34
H	6	-2.48	1.01	0.90	H	17	-1.11	-1.16	-1.34
H	7	-2.48	1.01	-0.90	P	18	1.61	0	0
H	8	-1.34	3.86	0.90	H	19	1.11	-2.74	1.34
H	9	-1.34	3.86	0.90	H	20	1.94	-2.74	-1.34
H	10	1.34	3.86	0.90	H	21	2.76	-2.74	1.34
H	11	1.34	3.86	-0.90					



-2-

Table 22. Coordinates of **2**, (tetrahedral metallocycle). $(H_3P)_2Ni$⬡

Atom, #		Coordinate (A^o)			Atom, #		Coordinate		
		X	Y	Z			X	Y	Z
Ni	1	0	0	0	H	12	1.29	0.90	-2.56
C	2	1.48	0	1.48	H	13	1.29	-0.90	-2.56
C	3	2.90	0	0.80	P	14	-1.30	1.85	0
C	4	2.90	0	-1.80	H	15	-0.83	3.19	1.16
C	5	1.48	0	-1.48	H	16	-0.83	3.19	-1.16
H	6	1.29	0.90	2.56	H	17	-2.67	1.46	0
H	7	1.29	-0.90	2.56	P	18	-1.30	-1.85	0
H	8	3.86	0.90	1.34	H	19	-2.67	-1.46	0
H	9	3.86	-0.90	1.34	H	20	-0.83	-3.19	1.16
H	10	3.86	0.90	-1.34	H	21	-0.83	-3.19	-1.16
H	11	3.86	-0.90	-1.34					

Table 23. Molecular orbital configurations and the associated electronic states of the square planar nickel metallocycle.

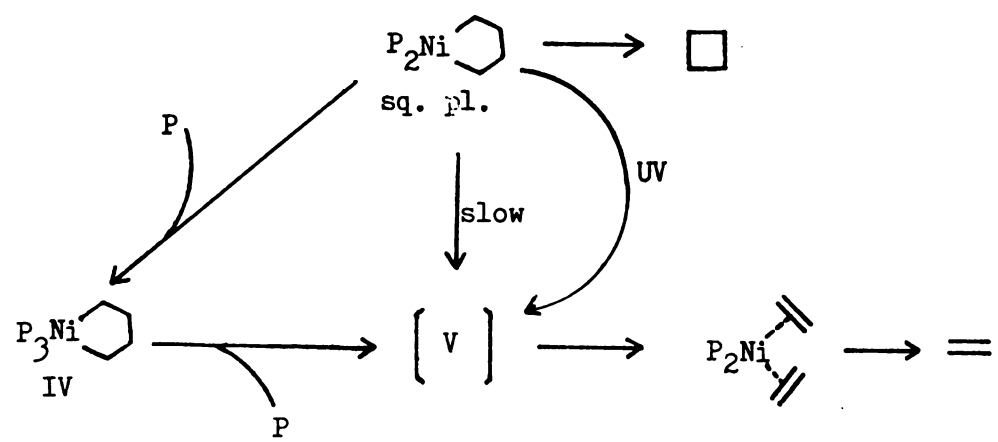
Molecular orbital configuration	State	E (ev)
$4b_2^2\ 9a_1^2\ 8b_1^1\ 9b_1^1$	$^{1,3}A_1$	4.12585
$4b_2^2\ 9a_1^1\ 8b_1^2\ 9b_1^1$	$^{1,3}B_1$	4.31319
$4b_2^1\ 9a_1^2\ 8b_1^2\ 9b_1^1$	$^{1,3}A_2$	5.00864
$4b_2^2\ 9a_1^2\ 8b_1^1\ 9b_2^1$	$^{1,3}A_2$	5.58234
$4b_2^2\ 9a_1^1\ 8b_1^2\ 9b_2^1$	$^{1,3}B_2$	5.76969
$4b_2^1\ 9a_1^2\ 8b_1^2\ 9b_2^1$	$^{1,3}A1$	6.46514
$4b_2^2\ 9a_1^2\ 8b_1^1\ 9b_2^1$	$^{1,3}A_2$	6.93198
$4b_2^2\ 9a_1^1\ 8b_1^2\ 9b_2^1$	$^{1,3}B_2$	7.11933
$4b_2^1\ 9a_1^2\ 8b_1^2\ 9b_2^1$	$^{1,3}A_1$	7.81478

Table 24. Molecular orbital configuration and associated electronic states of the tetrahedral nickel metallocycle.

Molecular orbital configuration				State	E (ev)
$4a_2^2$	$6b_1^2$	$10a_1^1$	$6b_2^1$	$^{1,3}B_2$	0.47849
$4a_2^2$	$6b_1^1$	$10a_1^2$	$6b_2^1$	$^{1,3}A_2$	0.54897
$4a_2^1$	$6b_1^2$	$10a_1^2$	$6b_2^1$	$^{1,3}B_1$	1.49688
$4a_2^2$	$6b_1^2$	$10a_1^1$	$6b_2^1$	$^{1,3}B_2$	5.04815
$4a_2^2$	$6b_1^1$	$10a_1^2$	$6b_2^1$	$^{1,3}A_2$	5.11863
$4a_2^1$	$6b_1^2$	$10a_1^2$	$6b_2^1$	$^{1,3}B_1$	6.06654
$4a_2^2$	$6b_1^2$	$10a_1^1$	$6b_1^1$	$^{1,3}B_1$	5.20841
$4a_2^2$	$6b_1^1$	$10a_1^2$	$6b_1^1$	$^{1,3}A_1$	5.27889

Results and Discussion

The isomerization of a metallocycle (type I) to a bis-olefin-metal complex reduces the oxidation state but retains the same coordination mber of the metal. From previous chapter the triphosphine metal compexes are coordinately saturated the conversion to a lower oxidation state would require the loss of a ligand (scheme 18). The lower coordination mber intermediate (V) required for the phosphine exchange in the nmr is an appealing precusor for the formation of ethylene. This suggests that the ethylene and cyclobutane are produced from isomeric coordinate complexes.

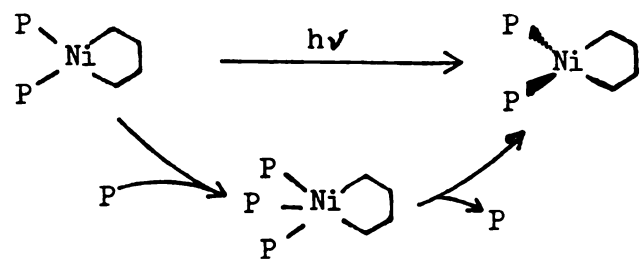


(Scheme 18)

The isomerization of a square planer complex to the isomeric complex (V) could take place through a higher coordination complex (IV) as an intermediate. The isomerization could also be induced with UV irradiation. The conclusion is true if direct isomerization take place very slowly or the direct isomerization is not allowed. The possible choice of V is tetrahedral.

The three highest occupied molecular orbitals and the three lowest

unoccupied molecular orbitals were used to calculate nine low lying excited states as shown in Table 23 and 24. The state correlation diagam was constructed with singlet triplet spliting as 1 ev. As shown in Figure 14, the ground state of the square planar metallocycle correlates with the ground state of the tetrahedral metallocycle by symmetry allowence and the same way for excited states. The ground state of tetrahedral metallocycle is a triplet. These states correlate with square planar excited states. In the square planar metallocycle state diagram there is a large gap between the ground state and excited states. This would indicate that the isomerization of square planar metallocycle to tetrahedral metallocycle will be slow and the isomerization of the ground state of the square planar metallocycle to triplet ground state of tetrahedral metallocycle will not be thermally allowed but photochemically allowed. This calaulation result is compatiable with the experimental results and suggects that the higher coordination species formed are unstable in the square planar configuration and isomerize to the tetrahedral configuration (Scheme 19). Photo irradiation accomplishes the same transformation by exciting the square planar ground state to the excited states thereby making the transformation of square planar metallocycle to tetrahedral metallocycle allowed.



(Scheme 19)

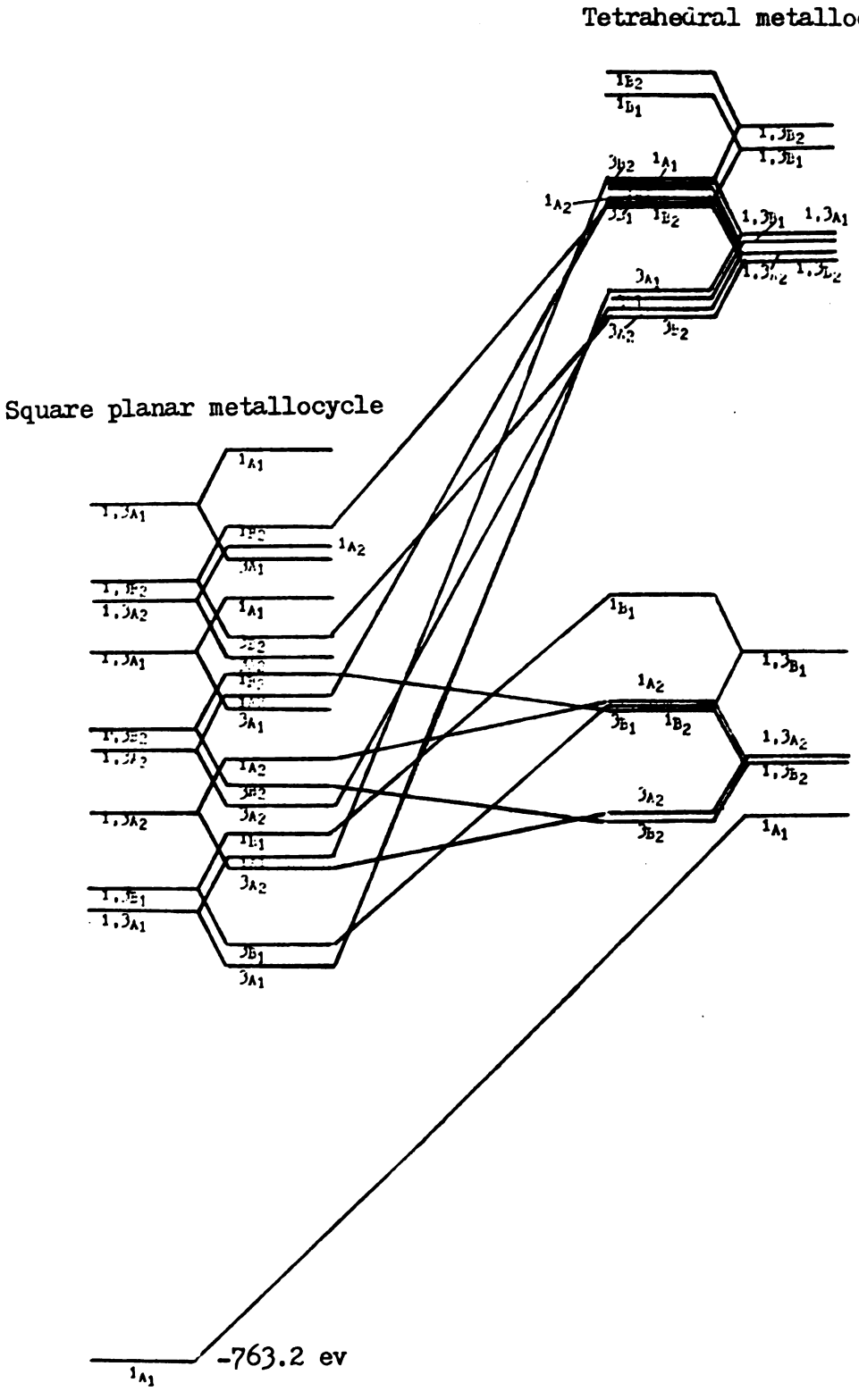


Figure 14. State correlation digram of square planar metallocycle and tetrahedral metallocycle

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