

# Preparation and Reactions of Phosphine Nickelocyclopentanes

R. H. Grubbs,\* Akira Miyashita, M. Liu, and P. Burk

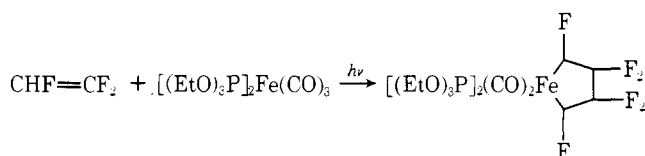
Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. Received September 12, 1977

**Abstract:** Seven phosphine nickelmetallocyclopentanes were prepared by the reaction of 1,4-dilithiobutane with an appropriate dichlorobis(phosphine)nickel(II) complex and were characterized by  $^{31}\text{P}$  and  $^1\text{H}$  NMR, molecular weight, and protolytic decomposition studies. Thermolysis ( $9^\circ\text{C}$ ) of these complexes produced ethylene, cyclobutane, and butenes. The ratio of the gases was a function of the coordination number. Three coordination complexes favored butene formation, four coordinations favored reductive elimination to form cyclobutane, and five coordination complexes produced ethylene. Oxidation induced rapid decomposition of all the complexes to cyclobutane. The excited state of the complexes produced ethylene.

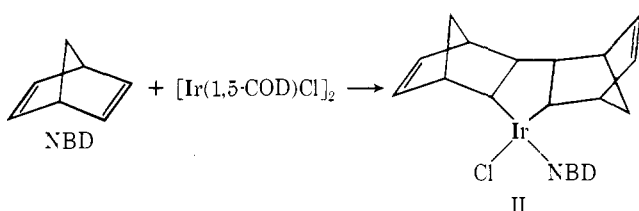
Heterocyclic compounds have played a major role in the development of organic chemistry. It is becoming apparent that heterocycles containing a transition metal play an important role in the transition metal catalyzed reactions of olefins and acetylenes. Stable metallocyclopentadienes have been known for some time and appear to be the major intermediate in many acetylene trimerization reactions.<sup>1,2</sup>

Metallocyclopentanes have been proposed or demonstrated to be intermediates in a number of metal-catalyzed cycloadditions and cycloreversions of olefins.

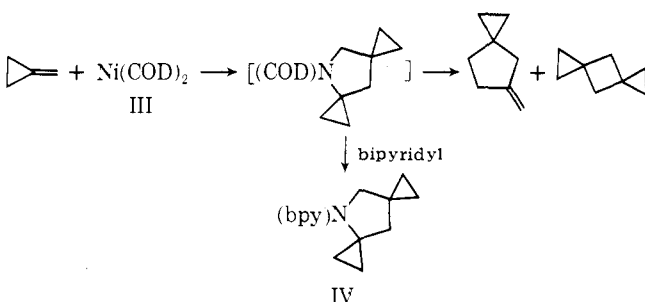
The first systems in which metallocycles were isolated involved the addition of an activated olefin to a metal of reduced coordination number. The first such system was reported by Green<sup>3</sup> from the photolysis of an iron carbonyl complex with trifluoroethylene. A stable metallocycle (I) resulted from this reaction.



Osborn et al.<sup>4</sup> prepared one of the first such systems from a strained olefin.

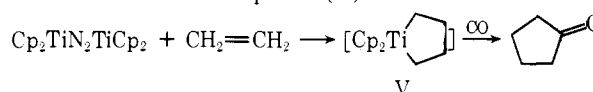


Binger and co-workers reported that bis(cyclooctadiene)-nickel catalyzed the cyclodimerization of methylenecyclopropanes.<sup>5</sup> Recently, they have trapped a metallocyclopentane intermediate (IV) in this reaction.<sup>6</sup>

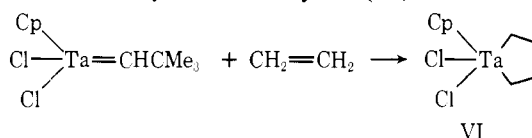


Similar intermediates could be trapped from the reaction of Ni with norbornadiene.<sup>7,8</sup>

Whitesides reported that metallocycles could be prepared in low yields by the reaction of ethylene and other simple olefins with reduced titanocene species (V).<sup>9</sup>

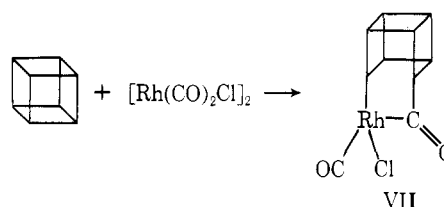


Very recently Schrock has reported the preparation of stable tantalum metallocycles from ethylene (VI).<sup>10</sup>

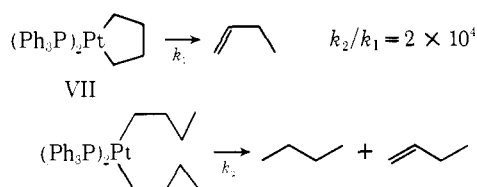


These last two observations, as well as the extensions of the following work, suggest that the investigation of metallocycles may open up new catalytic processes for olefin dimerization and oligomerization.

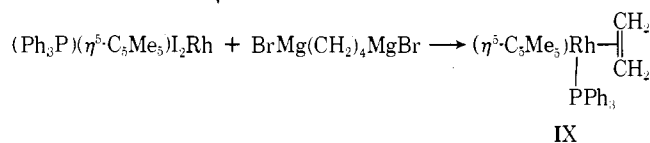
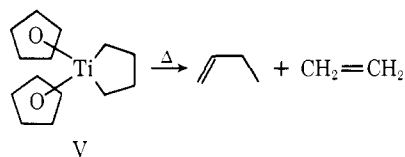
The majority of the evidence for the intermediacy of metallocycles in cycloreversion reactions has resulted from work by the groups of Halpern and Eaton.<sup>11</sup> They found that rhodium(I) complexes catalyzed the ring opening of cubane derivatives and that by using stoichiometric amounts of a rhodium(I) carbonyl complex the intermediate metallocycle (VII) could be trapped.



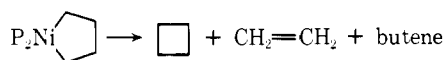
Stable derivatives of the parent complex have been prepared by the reaction of 1,4-dilithiobutane or the Grignard analogue with a variety of transition metal dihalides. Tetramethylene metallocycles containing platinum,<sup>12,13</sup> nickel,<sup>7</sup> titanium,<sup>9</sup> and rhodium<sup>15</sup> have been prepared by this method. The platinum<sup>13</sup> and nickel<sup>14</sup> systems have been characterized by x-ray analysis. Whitesides demonstrated one of the key features of these systems. He found that platinum metallocycles were much more stable toward  $\beta$ -hydride elimination reactions than acyclic analogues.<sup>12</sup>



The key reaction to study for an understanding of the role of intermediates in the reactions of olefins is the carbon-carbon bond cleavage reaction of the metallocycle to produce ethylene. This reaction has only been observed to occur to a small extent in a titanocene (V)<sup>9</sup> and rhodium system (IX).<sup>15</sup>



We have reported earlier that bisphosphenickel metallocycles<sup>16,17</sup> undergo the three major reactions previously observed for metallocycles: (a) reductive elimination, (b)  $\beta$ -hydride elimination, and (c) carbon-carbon bond cleavage to ethylene. In order to explore the factors which control the relative rates of these reactions, a series of complexes containing different ligands and having different coordination numbers have been prepared and characterized.



## Experimental Section

**General Method.** All reactions and other manipulations were performed under prepurified nitrogen or welding-grade argon purified before use by a BASF catalyst and molecular sieves. Diethyl ether, tetrahydrofuran, toluene, and hexane were dried over sodium (with benzophenone added) under an argon atmosphere and were freshly distilled before use. An ethereal solution of 1,4-dilithiobutane was prepared by lithiation of 1,4-dibromobutane at 0 °C. The concentration of dilithium reagent was determined as 1,4-bis(trimethylsilyl)butane, which formed from reaction of the dilithium reagent with trimethylsilyl chloride, by gas chromatography. Bis(triphenylphosphine)nickel(II) dichloride, bis(tricyclohexylphosphine)nickel(II) dibromide, bis(tri-*n*-butylphosphine)nickel(II) dichloride, and diphenylphosphinoethanenickel(II) dichloride were prepared by reported methods.<sup>18</sup> Triphenylphosphine, diphenylphosphinoethane, and tri-*n*-butylphosphine were used as purchased without further purification. Tricyclohexylphosphine was prepared by a literature method.<sup>19</sup> Other chemicals were reagent grade and used without further purification.

**Analytical Methods.** Infrared spectra were measured with a Perkin-Elmer Model 567 instrument using a polystyrene film as a calibration standard. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6 mass spectrometer. <sup>1</sup>H NMR spectra were determined on a Varian T-60 using Me<sub>4</sub>Si as internal standard and <sup>31</sup>P NMR spectra were measured on a Bruker HFX-90 NMR spectrometer and a modified Varian Associates DA-60 NMR spectrometer. Values of chemical shift ( $\delta$ , ppm) are reported positive upfield with respect to external H<sub>3</sub>PO<sub>4</sub> (85%). Hydrocarbon products were analyzed by gas chromatography on a Varian series 1400 instrument equipped with flame ionization detectors, using a Duopak (20 ft) and a Paraffin wax-5% AgNO<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (13 ft) column. Cyclobutane was purified by gas chromatography on a Varian Model 90-P and identified by <sup>1</sup>H NMR and mass spectroscopic comparison with the authentic sample. Product yields were determined by response relative to an internal standard.

**Preparation of Metallocycles. Preparation of Bis(triphenylphosphine)tetramethylenickel(II) (X).** An ether solution of 1,4-dilithiobutane (63 mL, 12.8 mmol) was added slowly to a suspension of bis(triphenylphosphine)dichloronickel(II) (5 g, 7.5 mmol) in 100 mL of ether. The mixture was maintained at -50 °C during the addition and then slowly warmed to 0 °C. A bright yellow solid appeared at -10 to 0 °C and was collected by filtration (-10 °C). The yellow solid was dissolved in oxygen-free toluene and filtered (at -15 °C) to remove lithium chloride and starting material. After partial concen-

tration (-15 °C) of the toluene solution, hexane was added. Bright yellow crystals (1.73 g, 36% yield) formed overnight at dry ice temperature. A portion of the complex was decomposed with hydrogen peroxide-sulfuric acid for analysis. Nickel was determined as the dimethylglyoxime complex<sup>20</sup> and the triphenylphosphine oxide was extracted into ether and weighed after drying. Three samples were analyzed. Anal. Calcd: Ni, 9.18; Ph<sub>3</sub>P, 82.0; PPh<sub>3</sub>/Ni, 2.00. Found: Ni, 9.17; Ph<sub>3</sub>P, 81.7; PPh<sub>3</sub>/Ni, 2.02. Three samples of the complex were decomposed with sulfuric acid at -30 °C and the amount of *n*-butane produced was determined (volumetric). A 98.3% yield of *n*-butane was produced.

The molecular weight of the complex was determined by the cryoscopic method in benzene. Molecular weight: found 626, calcd 639. <sup>1</sup>H NMR (Me<sub>4</sub>Si)  $\delta$  1.67 (m, 4 H), 1.87 (m, 4 H), 6.5 (m, 30 H); with excess Ph<sub>3</sub>P 2.17 (m, 4), 1.88 (m, 4); <sup>31</sup>P NMR (downfield from H<sub>3</sub>PO<sub>4</sub>) -42.4 ppm over temperature range -90 to 10 °C; with excess triphenylphosphine -42.4, -27.5, and +7.5 ppm at -90 °C.

**Preparation of X-d<sub>4</sub>.** The above reaction was repeated using 1,4-dilithiobutane-1,1,4,4-*d*<sub>4</sub> (98% isotopic purity) prepared from 1,4-dibromobutane-1,1,4,4-*d*<sub>4</sub>. The dibromide was prepared in 82% overall yield from diethyl succinate by reduction with lithium aluminum deuteride followed by treatment with 48% HBr in concentrated sulfuric acid.

**Bis(tricyclohexylphosphine)tetramethylenickel(II) (XI).** An ether solution of 1,4-dilithiobutane (6.55 mmol, 26.4 mL) was slowly added to an ether (20 mL) suspension of bis(tricyclohexylphosphine)dibromonickel(II) (3.0 g, 3.85 mmol). The solution was maintained at -50 °C during the addition. As the temperature was slowly raised to -20 °C a yellow-orange solid formed from the deep red homogeneous solution. The solid was rapidly collected at -20 °C and washed with cold ether. After drying in vacuo at -20 °C, the solid was dissolved in toluene at -15 °C and filtered. Hexane (10-20% by volume) was added and the solution cooled overnight at dry ice temperature. The yellow needles which formed were dried in vacuo for several hours at 10 °C in the dark. The yield was 1.1 g (43%) of yellow needles which were extremely air sensitive.

The analysis was performed as before. Anal. Calcd: Ni, 8.69; Cy<sub>3</sub>P, 83.0; PCy<sub>3</sub>/Ni, 2.00; butane, 100. Found: Ni, 8.58; Cy<sub>3</sub>P, 83.7; PCy<sub>3</sub>/Ni, 2.04; butane, 97.3. The molecular weight was determined by the cryoscopic method in benzene: found 343, calcd 675. <sup>31</sup>P NMR (H<sub>3</sub>PO<sub>4</sub>) -33.6 and -7.3 ppm.

**1,4-Dilithiobutane Adduct of (Cy<sub>3</sub>P)<sub>2</sub>Ni(CH<sub>2</sub>)<sub>4</sub> (XII).** When 0.8 g (1.2 mmol) of (Cy<sub>3</sub>P)<sub>2</sub>Ni(CH<sub>2</sub>)<sub>4</sub> was mixed with a solution of 1,4-dilithiobutane in ether at room temperature, a deep brown solution was produced.

After cooling at dry ice temperature overnight, 0.43 g (34%) of fine, deep brown crystals were produced. The extremely air-sensitive compound was decomposed at 99-102 °C and the gases were collected. The gases were determined by GLC (and mass spectrometry). The residue was oxidized and the phosphine collected as the oxide and the nickel was determined as the glyoxime complex. The lithium in the residue was determined as the ferric periodate KLiFe(10<sub>6</sub>) salt. The ether, obtained on pyrolysis of the complex, was determined by GC and identified by mass spectroscopy. Anal. Calcd as XII: Cy<sub>3</sub>P, 53.8; Li, 1.34; Ni, 5.63; C<sub>4</sub>, 100; Et<sub>2</sub>O, 100; Li/Ni, 2.0; PCy<sub>3</sub>/Ni, 2.0; C<sub>4</sub>/Ni, 2.0; Et<sub>2</sub>O/Ni, 4.0. Found: Cy<sub>3</sub>P, 47.7; Li, 1.25; Ni, 4.99; C<sub>4</sub>, 92; Et<sub>2</sub>O, 94; Li/Ni, 2.1; PCy<sub>3</sub>/Ni, 2.0; C<sub>4</sub>/Ni, 2.1; Et<sub>2</sub>O/Ni, 4.2.

An impure sample of this compound was produced (contaminated by LiCl) if the reaction between the dilithiobutane and the nickel dihalide was allowed to warm to room temperature before filtering.

**Preparation of Bis(tri-*n*-butylphosphine)tetramethylenickel(II) (XIII).** A suspension of 5 g (3.96 mmol) of bis(tri-*n*-butylphosphine)dichloronickel(II) was mixed with 74.9 mL (15.7 mmol) of 0.21 mM 1,4-dilithiobutane at -40 °C. The mixture was warmed to -20 °C to produce a deep red solution. All of the solvent was evaporated at this temperature to produce a yellow solid. The solids were extracted with pentane and the red-yellow solution was cooled overnight at dry ice temperature to produce 0.87 g (10%) of yellow, columnar crystals. Anal. Calcd: Ni, 11.3; P(*n*-Bu)<sub>3</sub>, 77.9; P/Ni, 2.0; C<sub>4</sub>, 100. Found: Ni, 11.5; P(*n*-Bu)<sub>3</sub>, 77.4; P/Ni, 1.8; C<sub>4</sub>, 97. Analysis was carried out as before except that the *n*-butylphosphine, extracted with CCl<sub>4</sub> after decomposition of the complex with dilute H<sub>2</sub>SO<sub>4</sub>, was measured on <sup>1</sup>H NMR with benzene as an internal standard.

**Preparation of Tris(triphenylphosphine)tetramethylenickel(II) (XIV).** To a toluene solution of X (5.0 g, 7.8 mmol), cooled below -10 °C, was slowly added an excess of triphenylphosphine (4.0

g, 15.6 mmol). The deep yellow solution was allowed to react at  $-5^{\circ}\text{C}$  for 2 h to give a deep red solution. The golden brown solid which precipitated on cooling the solution to dry ice temperature overnight was collected by filtration and washed with fresh ether several times. The compound was recrystallized at  $-50^{\circ}\text{C}$  from toluene that had been saturated with triphenylphosphine at  $-60^{\circ}\text{C}$ . The compound was very air sensitive and moderately stable at room temperature. Product yield was 67% (4.7 g) after recrystallization.

This compound can also be prepared from bis(triphenylphosphine)nickel dichloride. An ether solution of 1,4-dilithiobutane (31 mL, 6.4 M) was added slowly to a suspension of bis(triphenylphosphine)nickel dichloride (2.5 g, 3.8 mmol) in 80 mL of ether. The mixture was maintained at  $-50^{\circ}\text{C}$  during the addition and allowed to warm slowly to  $0^{\circ}\text{C}$ . The solution was maintained at the temperature until all the chloride had dissolved. When a bright yellow solid started to appear from the deep yellow solution, an excess amount of triphenylphosphine (3.0 g, 11.4 mmol) was slowly added to the solution. The solution color quickly turned to deep brown and a gold-brown solid precipitated. The compound (mp  $128\text{--}130^{\circ}\text{C}$  dec) was quickly isolated by filtration, washed with ether repeatedly, and recrystallized as described above, product yield 1.7 g (51%). Anal. Calcd for  $(\text{Ph}_3\text{P})_3(\text{CH}_2)_4\text{Ni}^{II}$ : Ni, 6.51;  $\text{PPh}_3$ , 87.3; P/Ni, 3.0;  $\text{C}_4$ , 100. Found: Ni, 6.64;  $\text{PPh}_3$ , 86.7; P/Ni, 2.98;  $\text{C}_4$ , 98.0.  $^{31}\text{P}$  NMR  $-27.5$  ppm poorly resolved broad doublet at  $-90^{\circ}\text{C}$ , very broad signal at  $0^{\circ}\text{C}$ .

**Preparation of [Bis(diphenylphosphino)ethane]tetramethylenenickel(II) (XV).** A solution of 4 g (7.6 mol) of bis(diphenylphosphino)ethanenickel(II) dichloride in 20 mL of ether was placed in a 100-mL side arm round-bottom flask. The solution was cooled to  $-78^{\circ}\text{C}$  and 54 mL (13 mmol) of 1,4-dilithiobutane in ether was slowly added with a syringe. On warming the mixture, the starting nickel dichloride dissolved in the solution giving a dark brown solution, then a bright yellow solid slowly precipitated from the solution. As soon as the precipitation was complete, the product was isolated by filtration, washed with (deoxygenated) ether and repeatedly with water until a negative lithium test was obtained, and then dried under vacuum. The product was recrystallized from fresh ether and bright yellow crystals were obtained (25% yield). Anal. Calcd: Ni, 11.4; diphos, 77.6; diphos/Ni, 1.00;  $\text{C}_4/\text{Ni}$ , 1.00. Found: Ni, 11.3; diphos, 78.0; diphos/Ni, 1.01;  $\text{C}_4/\text{Ni}$ , 0.96.

The  $^1\text{H}$  NMR showed a broad peak at  $\delta$  1.1–1.8 ppm range (overlapping with diphenylphosphinoethane signals). The  $^{31}\text{P}$  NMR showed a singlet peak at  $-45.5$  ppm over the temperature range  $-90$  to  $0^{\circ}\text{C}$ . The molecular weight (cryoscopic method): found 512, calcd 513.

**Preparation of Bis(benzylidiphenylphosphine)tetramethylenenickel(II) (XVI).** In a 100-mL Schlenk tube with a stirring bar was placed a solution of bis(benzylidiphenylphosphine)nickel(II) dichloride (2 g, 3.8 mmol) in ether. An ether solution of 1,4-dilithiobutane (80 mL, 8 mmol) was slowly added to the solution below  $-78^{\circ}\text{C}$ . The mixture was allowed to react while the temperature was raised slowly to  $-15^{\circ}\text{C}$ .

The starting nickel dichloride (dark violet) slowly dissolved in the solution to give a dark yellow solution. A yellow solid which precipitated from the solution was isolated by filtration and washed with cold ether repeatedly. The product was also washed with deoxygenated water to remove lithium salts. After being washed with ether again, the compound was dried under vacuum and recrystallized from fresh ether (32% yield). Anal. Calcd: Ni, 8.8;  $\text{PPh}_2\text{CH}_2\text{Ph}$ , 82.8; P/Ni, 2.00;  $\text{C}_4/\text{Ni}$ , 1.00. Found: Ni, 8.4;  $\text{PPh}_2\text{CH}_2\text{Ph}$ , 81.6; P/Ni, 2.0;  $\text{C}_4/\text{Ni}$ , 0.99. The molecular weight (cryoscopic method): found 659, calcd 667.

**Preparation of Bis(methyldiphenylphosphine)tetramethylenenickel(II) (XVII).** This was prepared by the same method described above. The product yield was 20%. Anal. Calcd: Ni, 11.4;  $\text{PPh}_2\text{Me}$ , 76.0; P/Ni, 2.00;  $\text{C}_4/\text{Ni}$ , 1.00. Found: Ni, 10.2;  $\text{PPh}_2\text{Me}$ , 72.3; P/Ni, 2.06;  $\text{C}_4/\text{Ni}$ , 1.0.

**Reaction of Bis(triphenylphosphine)tetramethylenenickel(II) with Carbon Monoxide.** In a pressure bottle fitted with a stirring magnet were placed 1.12 g (1.75 mmol) of bis(triphenylphosphine)tetramethylenenickel (X) and 25 mL of dry oxygen-free heptane. The reaction mixture was cooled to  $0^{\circ}\text{C}$  and while stirring vigorously carbon monoxide (20 psi) was added. As carbon monoxide was taken up by the system, more was added to maintain the pressure above the solution at 20 psi. After stirring for 2 h, the bright yellow starting complex had changed to a grayish white solid. Analysis of the resultant solution

by GLC (10% FFAP 10 ft at  $80^{\circ}\text{C}$ ) showed, using undecane as a standard, that cyclopentanone had been formed in 75% yield.

The light gray solid was isolated by vacuum filtration and was characterized as bis(triphenylphosphine)nickel(0) dicarbonyl (XVIII) in 94% yield: mp  $202\text{--}203^{\circ}\text{C}$  dec (lit.  $210\text{--}215^{\circ}\text{C}$  dec); IR (mull) 2005,  $1954\text{ cm}^{-1}$ .

**Reaction of Bis(triphenylphosphine)tetramethylenenickel(II) (X) with Bromine.** Into a 125-mL Erlenmeyer flask fitted with a rubber septum were placed 0.664 g (1.04 mmol) of bis(triphenylphosphine)tetramethylenenickel and 10 mL of ether. The reaction mixture was cooled to dry ice-ethanol bath temperature and 3 mL of bromine was added by a syringe. The bath was removed and the mixture was shaken until it had reached room temperature at which point 0.10 mL (0.98 mmol) of dodecane was added as a GC standard. An aliquot of the solution was removed and added to an aqueous sodium bisulfite solution which destroyed the excess bromine. The solution was then analyzed by gas chromatograph (10% Carbowax at  $100^{\circ}\text{C}$ ) and 1,4-dibromobutane<sup>9</sup> (100%) was found.

**Decomposition Studies of the Nickelocyclopentanes.** Thermal decomposition reactions employed  $7.8 \times 10^{-5}$  M solution of X in toluene or other solvent as noted. In a 20-mL Schlenk tube equipped with a vacuum stopcock was placed 2.0 mL of the sample solution which was cooled below  $-20^{\circ}\text{C}$ . The tube was connected to a vacuum line ( $\sim 0.002$  Torr) and degassed through three freeze-thaw cycles. The samples were then placed in a water bath constant to  $9 \pm 1^{\circ}\text{C}$ . After complete decomposition (15 h), the gases produced were collected by distillation to a liquid nitrogen trap. On warming to room temperature, the volume of the gases was measured; their composition was determined by GC.

Effects of oxidizing agents on the decomposition mode were performed by introducing pure oxygen gas into the tube containing the complex solution which was under vacuum. After 10 min at  $9 \pm 1^{\circ}\text{C}$ , the samples were refrozen and briefly degassed to remove excess oxygen. The gases produced were collected as described above and analyzed by GC. In the case of Ce(IV)-induced decompositions, ceric(IV) ammonium nitrate (150 mg, 0.2 mmol) was slowly added to the toluene solution of the complex (100 mg, 0.16 mmol) below  $-30^{\circ}\text{C}$ . The tube was degassed and was then placed in a water bath ( $9 \pm 1^{\circ}\text{C}$ ). After 4 h, the product was analyzed by GC.

Olefin effects were performed by the same manner as described above. To the toluene solution of the complex X (0.04 mmol) was transferred 1 mL of acrylonitrile in a vacuum line by trap-to-trap distillation method. The mixture was allowed to react at  $9 \pm 1^{\circ}\text{C}$  for 6 h. The gases evolved were determined by GC. Tetracyanoethylene (50 mg, 0.5 mmol) was added to the toluene solution of X (0.04 mmol) at  $-50^{\circ}\text{C}$ . After the mixture was degassed, it was allowed to react at  $9^{\circ}\text{C}$  for 6 h. The gases produced were analyzed by GC.

**Photolysis.** Two 50-mL Pyrex tubes containing 0.1 g of the complex dissolved in 10 mL of solvent were placed in a large ice bath equidistant from a 450-W high-pressure HG lamp contained in a quartz immersion well. One of the tubes was wrapped in aluminum foil and tubes were irradiated for 8–10 h. The gases above the solution were analyzed by GC as before. The results are presented in Table V.

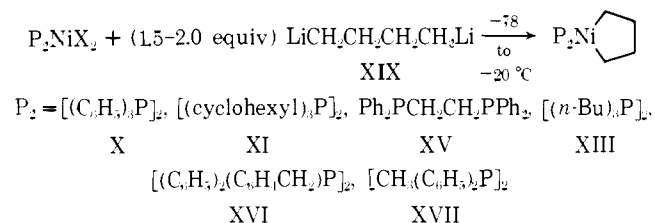
The photolysis of X- $d_4$  (0.2 g in 5 mL of toluene) was carried out in a  $-20^{\circ}\text{C}$  bath in a quartz tube. At this temperature the complex was stable in the dark. The gases produced were collected on a vacuum line and purified by gas chromatography. The mixture contained 85% ethylene and 15%  $\text{C}_4$  products. A mass spectrum of the ethylene showed it to be  $\sim 98\%$  ethylene- $d_2$  (similar isotopic purity to the starting dilithiobutane). A gas phase infrared spectrum showed the ethylene to be 97% ethylene-1,1- $d_2$  (950 and  $750\text{ cm}^{-1}$ ) and 3% of *cis*- and *trans*-ethylene-1,2- $d_2$  (980 and  $720\text{ cm}^{-1}$  *trans* and  $840\text{ cm}^{-1}$  *cis*).

## Results and Discussion

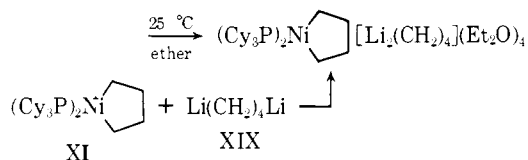
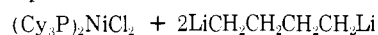
Some time ago we reported that bisphosphinetetramethylenenickel complexes decomposed to produce a mixture of *n*-butene, cyclobutane, and ethylene.<sup>16,17</sup> Since the products of the decomposition of these complexes resulted from competitive reductive elimination, formal  $\beta$ -hydride transfer, and carbon-carbon bond cleavage, a variety of reactions, parameters, and structural variations in the complexes were investigated to define the relationship between metal olefin complexes, metallocyclopentanes, and formal olefin dimerization

products. Only recently have methods been developed which allow these complexes to be produced in high purity for detailed studies.

**Preparation of Bisphosphetetramethylenenickel(II) Complexes.** The desired complexes were prepared in 20–40% yields by the reaction of 1,4-dilithiobutane (XIX)<sup>9,13</sup> with the appropriate dichlorobisphosphinenickel(II) complex at low temperatures. All reactions and manipulations were conducted

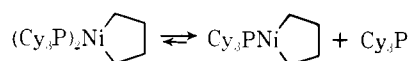


under a deoxygenated argon atmosphere. Traces of air resulted in impure products. The ratio of the dilithium reagent to the nickel complex was also critical since excess dilithium reagent resulted in a brown nickelate complex composed of 2 equiv of the dilithium reagent and one nickel.<sup>21</sup> The same unstable compound was also formed if the temperature of the usual reaction was raised above 0 °C, or if XI was treated with 1 equiv of XIX.

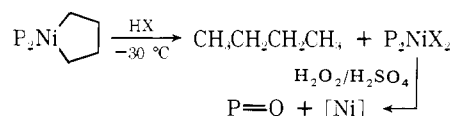


The use of smaller amounts of XIX in the preparation resulted in a decreased yield of product which was difficult to purify. The complexes were purified by low-temperature (−78 °C) recrystallization from toluene–hexane mixtures. The complexes are yellow-orange and are stable at room temperature for short periods of time. Exposure of the solid to oxygen results in rapid decomposition with smoke evolution. Compounds X, XI, and XV were obtained in high enough purity and showed the desired reactions for further study.

**Chemical and Analytical Characterization.** The molecular weights of the complexes were determined by the cryoscopic method in benzene. At 5 °C in benzene, the molecular weights of the triphenylphosphine complex (X) and the diphos complex (XV) are those expected for the four-coordinate complexes. However, the tricyclohexylphosphine complex (XI) appeared to disassociate to form a three-coordinate complex and give a molecular weight of near one-half of that expected.

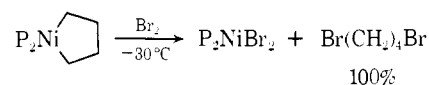


Owing to the extreme air sensitivity, the complexes were analyzed after protonolysis. The composition and quantity of organic products produced after acid cleavage of the Ni–C bond were determined by GC analysis and the nickel was determined gravimetrically.<sup>20</sup> Those phosphines which produced solid oxides with peroxide/H<sub>2</sub>SO<sub>4</sub> were determined gravimetrically while the ligand phosphine oxides were determined by NMR.<sup>22</sup>



Complexes purified by the method outlined above gave the expected analysis. The only product of acidolysis at low temperature was butane. Higher temperatures resulted in mixtures

of butane and 1-butene. Bromination resulted in the production of high yields of 1,4-dibromobutane.<sup>9</sup>



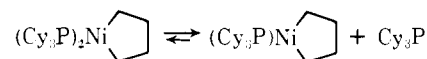
**Spectroscopic Studies.** The <sup>1</sup>H NMR spectra of the diphos (XV) and the tricyclohexylphosphine complexes were dominated by the resonances of the ligands. From the triphenylphosphine complex (X), multiplets were observed at δ 1.67 and 1.87. The shift and coupling patterns were similar to those of the analogous Pt(II)<sup>13</sup> complex whose structure had been determined by x-ray analysis. The <sup>13</sup>C spectra of the carbons in the metalocycle of the triphenylphosphine complex were not obtained owing to the low solubility and phosphorus splitting of the signals.

The <sup>31</sup>P spectra provided considerable evidence concerning the structure and potential reactivity of the complexes.<sup>23</sup>

The triphenylphosphine complex (X) showed a singlet at −42.4 ppm (relative to H<sub>2</sub>PO<sub>4</sub>) in toluene at −90 °C. Neither the line width nor the chemical shift changed over the temperature range of −90 to 0 °C. Addition of 14.1 equiv of triphenylphosphine to X resulted in two new peaks. One peak at +7.5 ppm was due to free triphenylphosphine while the second peak (doublet at high resolution) at −27.5 ppm has been identified as tris(triphenylphosphine)tetramethylenenickel(II) (XIV) (see below). When an isolated, pure sample of the tris(triphenylphosphine) (XIV) complex was dissolved in toluene only a doublet was observed at −27.5 ppm at −90 °C. The <sup>31</sup>P spectrum of XIV was temperature dependent between −90 and 10 °C. However, over this temperature range, there was no evidence for the formation of the biphosphine X or triphenylphosphine. These changes and their relationship to the decomposition mode will be discussed in another paper.<sup>8b</sup>

These results are most consistent with the bis(triphenylphosphine) complex, X, remaining a four-coordinate complex in solution. Addition of excess phosphine results in the slow production of a stable five-coordinate complex. The rate of interchange between the four- and five-coordinate complexes must be slow owing to the stability of the solution of XIV.

A toluene solution (−90 °C) of the bis(tricyclohexylphosphine) complex, XI, showed two <sup>31</sup>P signals of near equal intensity at −7.3 and −33.6 ppm. The line widths and shifts were temperature independent (−90 to −14 °C). The signal at −7.3 ppm was identified as resulting from tricyclohexylphosphine. Owing to the relative intensity and chemical shift of the second peak,<sup>24</sup> it was identified as resulting from (tricyclohexylphosphine)tetramethylenenickel(II). This suggests, as did the molecular weight studies, that this complex forms a three-coordinate complex in solution.



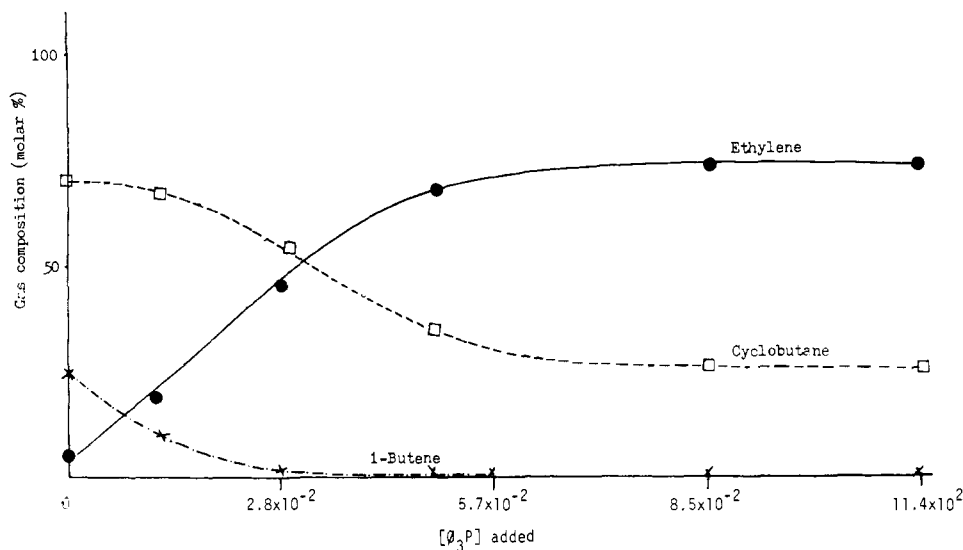
The addition of 2 equiv of tricyclohexylphosphine to the solution resulted in the production of two small, new peaks at −61.1 (0.09) and −52.9 ppm (0.02) (rel intensity). Further work will be required to determine the identity of the complexes which produce these signals.

A toluene solution of the diphos complex, XV, shows a temperature-independent <sup>31</sup>P signal at −45.5 ppm. The lack of temperature dependence and the molecular weight studies show that this complex remains a chelated four-coordinate complex in solution.

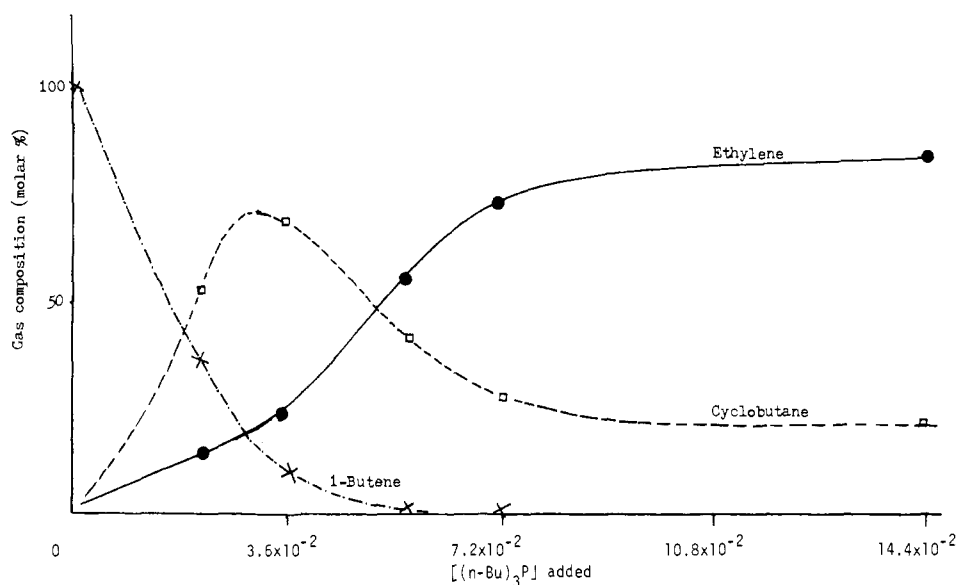
When excess tri-*n*-butylphosphine was added to a sample of XV at temperatures below 10 °C, the only <sup>31</sup>P signals were from the four-coordinate complex and tributylphosphine.

Aging of the sample produced two new signals which were the same as the signals remaining after the sample had been

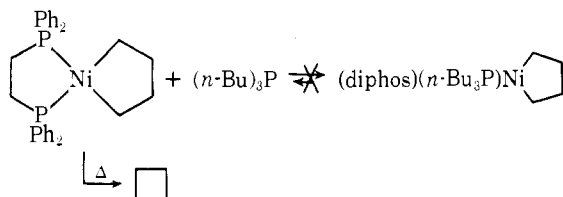




**Figure 1.** Products of decomposition of bis(triphenylphosphine)tetramethylenenickel(II) at 9 °C as a function of the concentration of added triphenylphosphine.  $[X] = 5.7 \times 10^{-3}$  M in toluene.

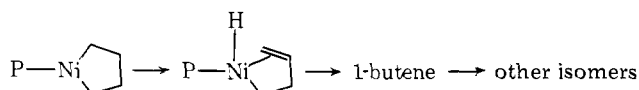


**Figure 2.** Products of decomposition of bis(tricyclohexylphosphine)tetramethylenenickel(II) at 9 °C as a function of the concentration of added tri-*n*-butylphosphine.  $[XI] = 7.2 \times 10^{-3}$  M in toluene.



composition to linear butenes by a mechanism not fully understood, instead of to greater amounts of ethylene.

It is reasonable that the three-coordinate complexes result in  $\beta$ -hydride elimination since this reaction requires an increase in coordination number while the same oxidation state is maintained.



Why the four-coordinate complexes produced cyclobutane and the five-coordinate complexes gave ethylene is much more difficult to answer. Both processes involve reduction of the

**Table II.** Decomposition (9 °C) Mode of Phosphinenickelocyclopentanes as a Function of Solvent

Complex	Solvent	Percent of decomposition products		
		C <sub>2</sub> H <sub>4</sub>	Cyclo-butane	Linear C <sub>4</sub>
XI	Pyridine	50	0	50
X	Pyridine	71.8	21.5	6.7
	Acetonitrile	16.3	83.7	
XV	Pyridine	3.3	78	18.3

metal. Initial considerations of coordination number of the products would suggest the opposite results. The mechanism of the decomposition to ethylene appears to be very complex.<sup>8b</sup>

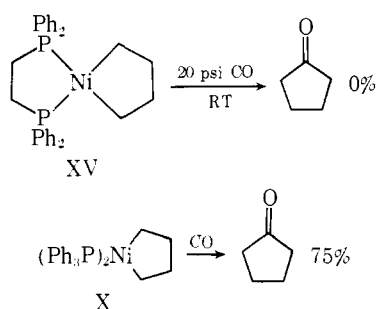
**Solvent Effects.** Good coordinating solvents were used in the decomposition studies. The general effect of these solvents was the same as increasing the phosphine concentration (Table II). Ethylene became the major product when the bistrisphenylphosphine complex, X, was decomposed in pyridine. The ratio

**Table III.** Effect of Oxidizing Agents on the Decomposition Mode

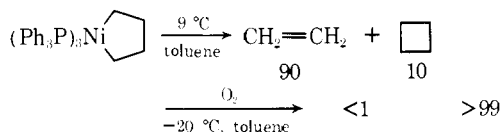
Complex	Oxidizing agent	Added ligand	Percent of decomposition products		
			C <sub>2</sub> H <sub>4</sub>	Cyclo-butane	C <sub>4</sub> linear
X	O <sub>2</sub>	0	5.3	86.9	7.8
X	O <sub>2</sub>	2Ph <sub>3</sub> P	7.9	92.1	0
X	O <sub>2</sub>	5Ph <sub>3</sub> P	0	100.	0
X	O <sub>2</sub>	20Ph <sub>3</sub> P	0	100.	0
X	Ce <sup>IV</sup>	0	7.1	82.4	3.5
X	Ce <sup>IV</sup>	2	8.7	89.4	1.9
XI	O <sub>2</sub>	2( <i>n</i> -Bu) <sub>3</sub> P	8.2	96.9	0
XIV	O <sub>2</sub>	0	Trace	>99.0	0
Diphos XV	O <sub>2</sub>	0	0.4	95	3.8

of the carbon-carbon bond cleavage product (ethylene) to the other gases was similar to that produced in toluene containing a 20-mol excess of triphenylphosphine. Acetonitrile as a solvent gave results comparable to those obtained by adding a 2-mol excess of triphenylphosphine to a toluene solution of the complex. The tricyclohexyl complex, XI, which produced only linear butenes on decomposition in toluene produced a 50% yield of ethylene in pyridine. The relative effectiveness of pyridine and acetonitrile to induce C-C cleavage is related to their relative complexing ability.<sup>25</sup> These complexing solvents appear to result in the production of higher coordination complexes, which show a preference for carbon-carbon bond cleavage reactions. However, the chelated complex, XV, showed little solvent effect owing to its tendency not to form five-coordinate complexes.

**Reaction with Carbon Monoxide.** As reported earlier, metallocyclopentanes react with carbon monoxide to produce cyclopentanone. This reaction with the nickelocycles was dependent on the structure of the supporting ligand. The bis-(triphenylphosphine) complex, X, reacted smoothly to produce cyclopentanone. In contrast, the diphos, XV, produced no cyclopentanone under the same conditions. The low reactivity of the diphos complex, XV, was probably related to the reluctance of this complex to form a five-coordinate complex as discussed earlier.

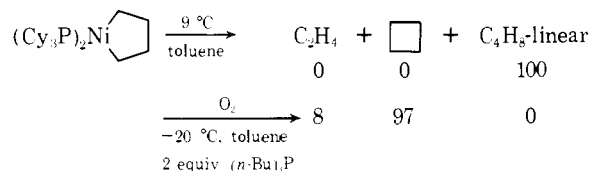


**Oxidizing Agents.** Since good complexing agents appeared to favor the production of ethylene by reductive carbon-carbon bond cleavage, the effect of oxidizing agents was investigated. The results of these studies are presented in Table III. In all cases, the two oxidizing agents promoted the production of cyclobutane by reductive elimination of the metallocycle. The most dramatic case was the oxidative decomposition of the tris(triphenylphosphine) complex, XIV. This complex on thermal decomposition produced ethylene whereas oxidative decomposition produced >99% cyclobutane. Similarly, the

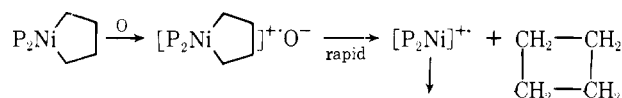
**Table IV.** Effect of Electron-Deficient Olefins on Decomposition Mode

Complex (concn)	Olefin	Mole excess	Percent of decomposition products		
			C <sub>2</sub> H <sub>4</sub>	Cyclo-butane	C <sub>4</sub> linear
X (0.03 M)	TCNE	13	11.8	85.1	3.1
X (0.04 M)	Acrylonitrile	1 mL in toluene	8.8	87.0	4.2
XI (0.03 M)	TCNE	5	2.2	18.2	79.6
XV (0.03 M)	Acrylonitrile	0 as solvent	0.3	91.0	7.2

tricyclohexylphosphine complex which produced 1-butene as the major thermal decomposition product gave a 97% yield of cyclobutane when treated with O<sub>2</sub>. No attempt was made to



isolate the inorganic products of the reaction. These results suggest that the oxidizing agent produces an intermediate cation radical which undergoes rapid reductive elimination.



A similar scheme has been proposed by Kochi<sup>21</sup> for the oxidative decomposition of aryl-alkyl nickel complexes. It is possible that all of the cyclobutane-forming reactions might first involve oxidation of the metal center by either the phosphine ligands or the solvent as has recently been observed for platinum complexes.<sup>12c</sup>

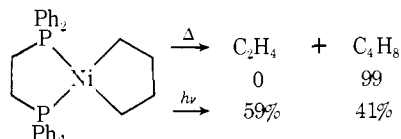
**Electron-Deficient Olefins.** Yamamoto<sup>26</sup> has reported that the complexation of electron-deficient olefins to dialkyldipyridylnickel(II) complexes resulted in an increased rate of decomposition by reductive processes. As can be seen in Table IV, the addition of electron-deficient olefins to the bisphosphine metallocycles results in a small change in the decomposition product ratios. The effect is in the same direction, toward cyclobutane formation, as that observed with strong oxidizing agents. This effect is best explained as resulting from charge transfer from the complex to the added, electron-deficient olefin. This results in oxidation which speeds the reductive process open to the metal. This must dominate the course of the reaction since the phosphine ligands can react rapidly with the added olefin. If this reaction were dominant, the effect of the added olefin would be expected to increase the products (linear butenes) of the lower coordination number complexes. Although these olefins are also complexing agents as are amines and phosphines, their effect is the opposite.  $\sigma$  donors appear to induce ethylene formation while strong  $\pi$  acceptors favor cyclobutane formation.

**Photochemical Decompositions.** Since the decomposition mode of the complexes was sensitive to a variety of factors, the influence of light was explored to determine which of the thermal processes were mimicked. Solutions of the complexes were irradiated at 0 °C and the product ratios were compared to those of a similar sample which had been placed in the same bath for the same period of time wrapped in aluminum foil. As can be seen in Table V, the samples exposed to light produced more ethylene.<sup>27</sup> The less stable complexes underwent a competing thermal reaction. However, the decomposition mode of the more stable diphos complex changed completely.

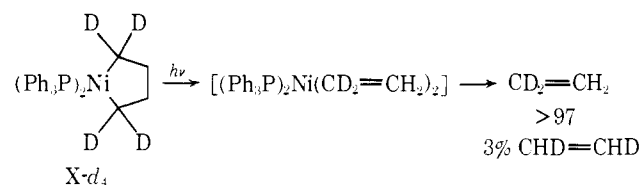
Table V. Photoinduced Decomposition of Complexes in Toluene

Complex	Temp, °C	Light	Composition of gases	
			% C <sub>2</sub> H <sub>4</sub>	% C <sub>4</sub> H <sub>8</sub>
X	0	UV	21	79
	0	Dark	6	94
XV	0	UV	59	41
	0	Dark	0	99.9
XVII	5	UV	19.5	81
	5	Dark	15	86

Thermal decomposition of the complex resulted in complete reductive elimination (cyclobutane) while photolysis resulted in a high yield of ethylene. That this decomposition resulted



from simple carbon-carbon bond cleavage was demonstrated by a labeling study. Labeled bis(triphenylphosphine)tetramethylenenickel(II)-2,2,5,5-*d*<sub>4</sub> (X-*d*<sub>4</sub>) was prepared and photolyzed at -20 °C. The ethylene produced was collected and identified by infrared as 97% ethylene-1,1-*d*<sub>2</sub>. This result is most consistent with a simple carbon-carbon bond cleavage rather than other more complicated rearrangement schemes.



Other labeling and theoretical studies are now in progress which should define the course of this reaction.<sup>28</sup> However, it is apparent that the excited state of the complexes results in a reductive pathway that is different than the ground state and that this decomposition is not that expected from photooxidation.

## Conclusions

The results presented above demonstrate the extreme sensitivity of the reaction modes of these metallocycles to changes in geometry, coordination number, oxidation state, and orbital occupancy. In thermal decompositions the coordination number of the complex was the dominant factor. Changes in the structure of the phosphine supporting ligands were reflected in the control of the relative rates of the possible decomposition modes by changes in the coordination number. A key question which remains to be answered is why the four-coordinate

complexes result in carbon-carbon bond formation while similar five-coordinate complexes result in carbon-carbon bond cleavage.

The oxidative decomposition reactions are surprisingly clean and suggest that removal of an electron from an occupied orbital results in rapid nickel-carbon bond cleavage. These studies should provide information concerning the reactions of metal alkyls in catalytic reactions.

Photolysis of the complexes results in a change in decomposition mode. Excitation of an electron from an occupied orbital to an unoccupied orbital results in carbon-carbon cleavage in systems which normally give reductive eliminations on thermolysis.

**Acknowledgments.** The authors acknowledge the support of this work by the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Dreyfus Foundation through a Camille and Henry Dreyfus Teacher-Scholar Grant.

## References and Notes

- J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, **7**, 1298 (1968).
- J. J. Eisch and G. A. Damasavitz, *J. Organomet. Chem.*, **96**, C19 (1975).
- M. L. H. Green, *Adv. Organomet. Chem.*, **8**, 29 (1970).
- A. R. Fraser et al., *J. Am. Chem. Soc.*, **95**, 597 (1973).
- P. Binger, *Angew. Chem., Int. Ed. Engl.*, **11**, 309 (1972).
- Private communication.
- M. J. Doyle, J. McMeeking, and P. Binger, *J. Chem. Soc., Chem. Commun.*, 376 (1976).
- (a) R. Blackborrow, A. Miyashita, and R. Grubbs, unpublished work; (b) A. Miyashita and R. Grubbs, unpublished work.
- G. Whitesides and J. McDermott, *J. Am. Chem. Soc.*, **96**, 947 (1974); J. McDermott, M. Wilson, and G. Whitesides, *ibid.*, **98**, 6259 (1976).
- S. J. McLain, C. D. Wood, and R. R. Schrock, *J. Am. Chem. Soc.*, **99**, 3519 (1977).
- J. Halpern, P. Eaton, and L. Cassar, *J. Am. Chem. Soc.*, **91**, 2405 (1969).
- (a) G. Whitesides, J. White, and J. McDermott, *J. Am. Chem. Soc.*, **95**, 4451 (1973); (b) *ibid.*, **98**, 6521 (1976); (c) G. Whitesides, private communication.
- R. Grubbs, H. Eick, and C. Biefield, *Inorg. Chem.*, **12**, 2166 (1973).
- C. Kruger and Y.-H. Tsay, unpublished data.
- P. Diversi, G. Ingrosso, and A. Lucherini, *J. Chem. Soc., Chem. Commun.*, 52 (1977).
- R. Grubbs, D. Carr, and P. Burk, *Organotransition-Met. Chem.*, 135 (1974).
- R. Grubbs, A. Miyashita, M.-I. M. Liu, and P. L. Burk, *J. Am. Chem. Soc.*, **99**, 3863 (1977).
- L. Vananzi, *J. Chem. Soc.*, 719 (1958).
- W. H. Gruber and J. Ellerman, *Ber.*, **23**, 1307 (1968).
- R. Belcher and A. Nutten, "Quantitative Inorganic Analysis", A. M. G. MacDonald, Ed., Butterworth, London, 1970, p. 131.
- D. G. Morrell and J. K. Kochi, *J. Am. Chem. Soc.*, **97**, 7262 (1975).
- A. Miyashita and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **50**, 1109 (1977).
- P. Meier, A. Merbach, M. Dartiguenave, and Y. Dartiguenave, *J. Am. Chem. Soc.*, **98**, 6402 (1976).
- A. D. English, P. Meakin, and J. P. Jesson, *J. Am. Chem. Soc.*, **98**, 422 (1976).
- For example, F. Basolo and R. G. Peason, "Mechanisms of Inorganic Reactions", Wiley, New York, N.Y., 1967.
- A. Yamamoto, T. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **93**, 3350 (1971).
- S. Sostero and O. Traverso, *J. Organomet. Chem.*, **134**, 259 (1977).
- J. Harrison, M.-I. Liu, and R. Grubbs, unpublished results.