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TRANSITION-METAL MEDIATED FORMATION AND CLEAVAGE OF CARBON-HYDROGEN BONDS: HYDROGENOLYSIS OF TRINUCLEAR ALKYLIDYNE CLUSTERS AND OXIDATIVE ADDITION OF CARBON-HYDROGEN BONDS TO RHENIUM

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TRINUCLEAR ALKYLIDYNE CLUSTERS AND OXIDATIVE
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P.F. Seidler
(Ph.D. Thesis)

March 1985

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Transition-Metal Mediated Formation and Cleavage of Carbon-Hydrogen Bonds:

Hydrogenolysis of Trinuclear Alkylidyne Clusters

and Oxidative Addition of Carbon-Hydrogen Bonds to Rhenium

By

Paul Fredrich Seidler

PH.D. THESIS

MARCH 1985

MATERIALS & MOLECULAR
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**Transition-Metal Mediated Formation and Cleavage of Carbon-Hydrogen
Bonds: Hydrogenolysis of Trinuclear Alkylidyne Clusters and
Oxidative Addition of Carbon-Hydrogen Bonds to Rhenium**

Paul F. Seidler

Abstract

Chapter 1. Treatment of dicobalt alkyne complexes

$\text{Co}_2(\text{CO})_6(\text{HCCR})$ ($\text{R} = \text{alkyl, aryl}$) with H_2 and $\text{Co}_2(\text{CO})_8$ or $\text{CpMo}(\text{CO})_3\text{H}$ leads to μ_3 -alkylidyne complexes with molecular formula $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{R}$ and $\text{CpMo}(\text{CO})_2\text{Co}_2(\text{CO})_6\text{CCH}_2\text{R}$, respectively, in high yield and purity. Hydrogenation of these clusters occurs under mild conditions ($60 - 90^\circ\text{C}$, benzene solution, 3 - 4 atm of H_2) and gives olefins, paraffins, and carbonyl compounds. A radical pathway for the hydrogenolyses is suggested by the observation of CIDNP in the olefinic product from some of the trinuclear clusters. ESR experiments involving the reaction of $\text{Co}_3(\text{CO})_9\text{CCH}_2(\text{CH}_3)_3$ (2) with H_2 in the presence of the spin-trap $t\text{-BuNO}$ confirm the intervention of vinyl radical intermediates and reveal that a hydrogen atom donor is generated as well. Evidence consistent with vinyl radical intermediates is also provided by isotope labelling studies on the hydrogenolysis of 2.

Chapter 2. Inter- and intramolecular C-H oxidative addition reactions have been observed from two related organorhenium intermediates: $\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)$ (11) and $\text{Cp}^*\text{Re}(\text{PMe}_3)_2$ (12)

(Cp* = $\eta^5\text{-C}_5\text{(CH}_3)_5$). Species 11 is formed from irradiation of both Cp*Re(CO)₂PMe₃ (2) and Cp*Re(CO)(PMe₃)₂ (7), and products formed by intermolecular insertion into C-H bonds of benzene and cyclopropane have been observed. Irradiation of 2 in other alkanes such as hexane provided the product of intramolecular insertion, cyclometallated complex 5a. Bis(phosphine) substituted cyclometallation product 5b is formed by exhaustive photolysis of 2 in the presence of excess PMe₃, presumably by photosubstitution of initially formed 5a. The cyclometallated compounds undergo reductive elimination; the coordinatively unsaturated species thus formed can be trapped to give intermolecular C-H activation products under mild thermal conditions. Reductive elimination of cyclometallated material 5c provides the only access to bis(phosphine) substituted intermediate Cp*Re(PMe₃)₂ (12). In contrast to its (carbonyl)phosphine analog 11, 12 is capable of insertion into the C-H bonds of methane as well as cyclopropane and benzene.

Robert B. Beggs

To my Grandparents

Acknowledgements

I owe a debt of gratitude to Professor Robert G. Bergman for the educational opportunities which he has made available to me. His patience and assistance throughout my tenure in graduate school has been appreciated. I would also like to thank collectively the members of the Bergman and E. L. Muetterties research groups for both their scientific and personal support. Each person has contributed in their own way to my development here in Berkeley, and to single out individuals would serve only to unfairly distort my general gratefulness. Special thanks must, however, be given to May Lynne B. Gill for her seemingly tireless assistance in assembling this manuscript. I also find myself feeling a great sense of appreciation towards my twin brother Mark D. Seidler for what can only inadequately be described as an undying fraternity providing the strength for perseverance. Acknowledgement is given to the National Science Foundation for a Predoctoral Fellowship for 1980-1983.

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Chapter 1

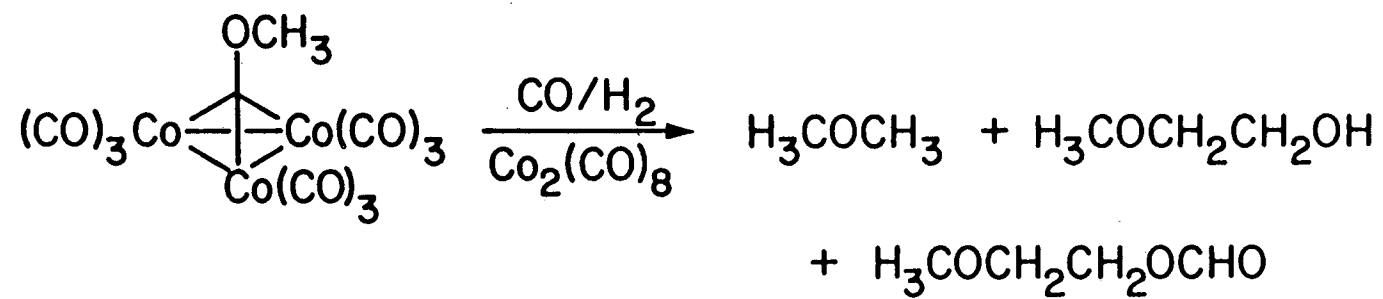
**Synthesis of Trinuclear Alkylidyne Complexes
from Dinuclear Alkyne Complexes and Metal Hydrides.
CIDNP and ESR Evidence for Vinyl Radical Intermediates
in the Hydrogenolysis of These Clusters.**

Introduction

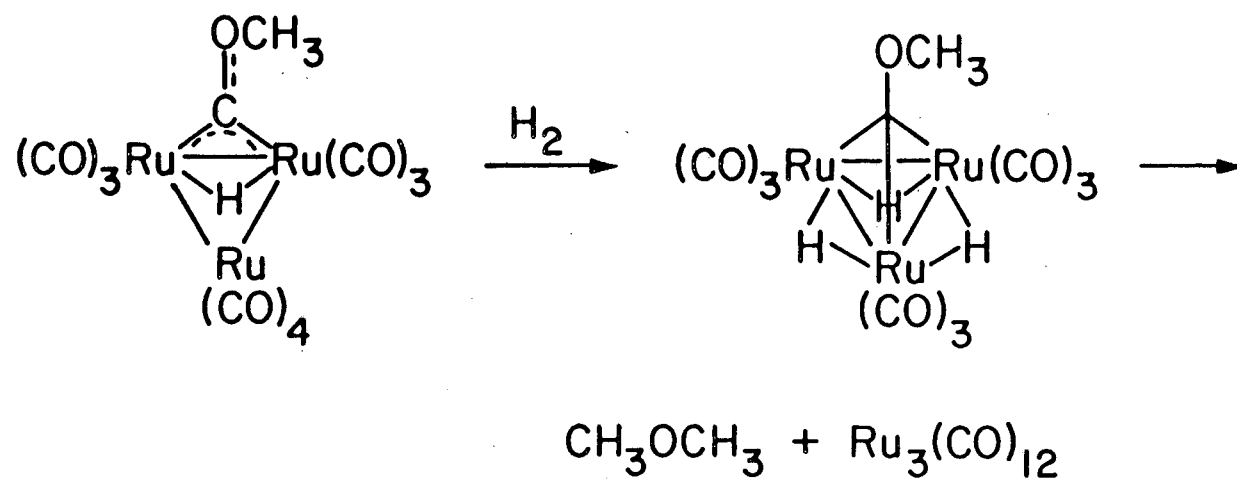
Although metal-carbon bond hydrogenolysis is an important step in many catalytic processes,¹ relatively few direct mechanistic investigations of this reaction exist.² A paucity of such studies exists particularly for alkyl transition-metal cluster complexes. Examination of these species is of added significance because of the suggestion that some metal clusters may provide models for the study of species chemisorbed on metal surfaces³ and the consequent implications for heterogeneous catalytic transformations. As a result, we have undertaken a study of homogeneous reactions of trinuclear alkylidyne complexes with hydrogen to investigate the mechanism by which carbon fragments bound to more than one metal are converted to paraffins and olefins.

Relevant systems⁴ which have been investigated include the hydroformylation of alkylidyne(nonacarbonyl)tricobalt clusters performed by Fachinetti, Lazzaroni, and Pucci (Scheme I).⁵ Mechanistic interpretation of these results is complicated, however, by the presence of $\text{Co}_2(\text{CO})_8$ and CO. More informative is the hydrogenation of trinuclear alkylidyne clusters of the iron triad examined by Keister, Payne, and Muscatella.⁶ They observed the intermediacy of a dihydrogen oxidative-addition adduct leading to the ultimate formation of dimethyl ether from a methoxymethylidyne species (Scheme II). Finally, Geoffroy and Epstein⁷ found that photochemical hydrogenation of $\text{Co}_3(\text{CO})_9\text{CH}$ leads to methane, and similarly hydrogenation of $\text{Co}_3(\text{CO})_9\text{CH}_3$ under the same conditions gives a mixture of ethane and ethene. Homolytic cleavage of Co-Co bonds upon photolysis has been postulated as a possible mechanism leading to

Scheme I



Scheme II



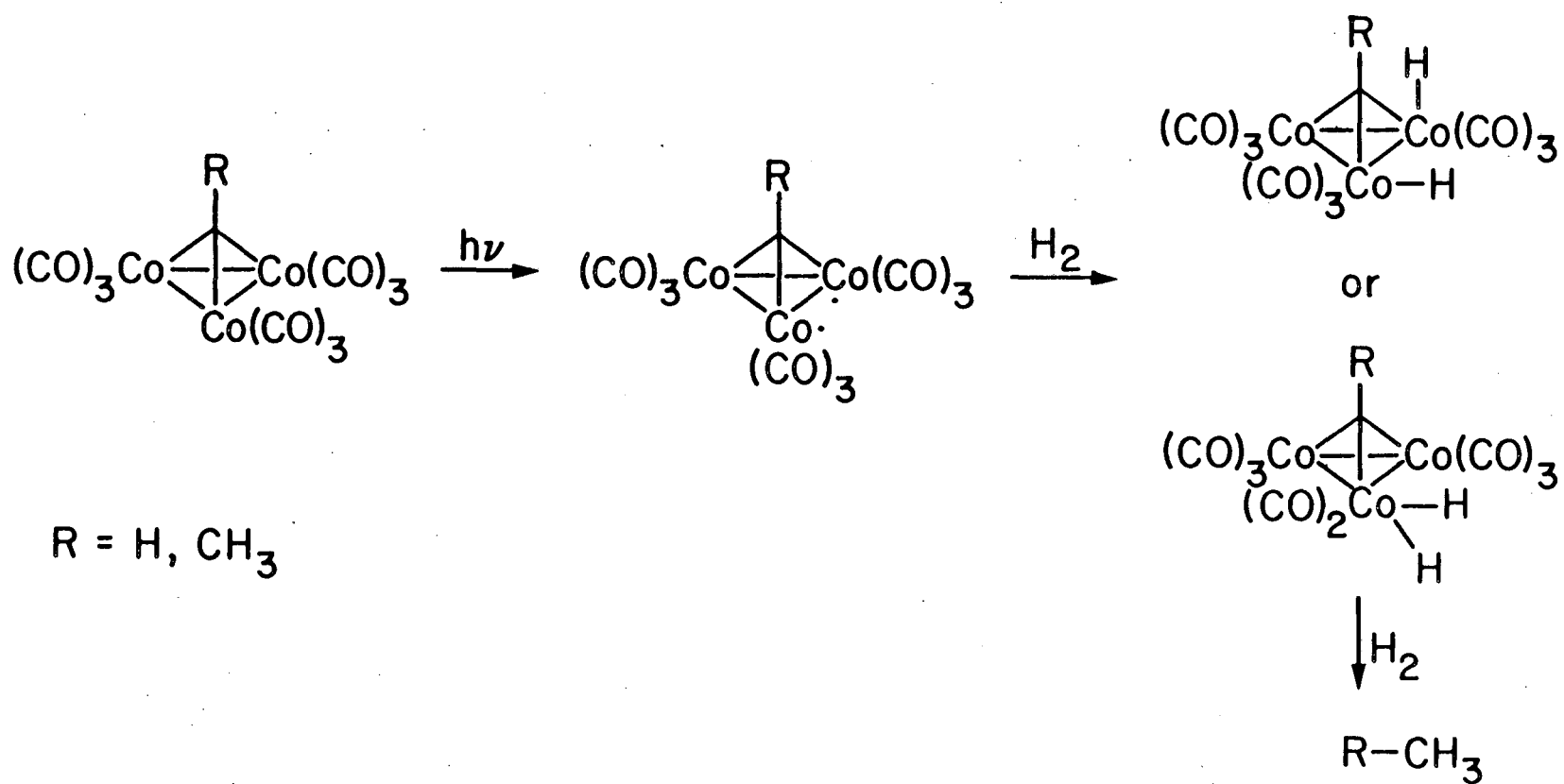
initial activation of dihydrogen. Subsequent carbon-hydrogen bond formation via reductive elimination is presumed to be the route to alkane (Scheme III).

We describe here⁸ a new method for the synthesis of several (alkylidyne)tricobalt nonacarbonyl and [(alkylidyne)cyclopentadienyl-molybdenum]dicobalt octacarbonyl complexes and a study of their hydrogenolysis. Preliminary evidence has been found that suggests a radical mechanism for the latter process, including the first observation of chemically induced dynamic nuclear polarization (CIDNP) in the reaction of an organometallic cluster complex. Some of this work was performed by J. E. Frommer and H. E. Bryndza, and reference to their respective Ph.D. dissertations^{8a,b} is made at various points in the text where they were responsible for or contributed to the particular set of experiments being described. A brief summary of their contributions is also given in the Experimental section.

Results and Discussion

Preparation of trinuclear alkylidyne complexes. Traditionally, complexes of the form $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{R}$ have been prepared by refluxing dicobalt alkyne complexes $\text{Co}_2(\text{CO})_6(\text{HCCR})$ in acidic methanol.⁹ We have found that the interaction of metal hydrides, or their equivalent, with those alkyne complexes generates the desired alkylidyne complexes in high yield and purity;^{8b} this provides a useful alternative in cases where yields in the traditional synthesis are low or workup is difficult. For example, dinuclear cobalt alkyne complex $\text{Co}_2(\text{CO})_6(\text{HCCC}(\text{CH}_3)_3)$ (1), prepared by reaction of $\text{Co}_2(\text{CO})_8$ and 3,3-dimethyl-1-butyne,¹⁰ reacted with 3-4 atm of H_2 and $\text{Co}_2(\text{CO})_8$ in a

Scheme III



sealed vessel in benzene at 65 °C. After 5 days, filtration, solvent removal, chromatography (hexane/silica), and recrystallization from methanol gave an 80 % yield of dark red-purple crystals of tricobalt alkylidyne complex $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_3$ (2) (Scheme IV). Analogous reactions gave the tricobalt clusters $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$ (3), $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{Ph}$ (4), and $\text{Co}_3(\text{CO})_9\text{C}(\text{CH}_2)_4\text{CH}_3$ (5) (Table I). Spectral and analytical data for 2 and 3 are given in the Experimental Section. Clusters 4 and 5 were shown by ^1H NMR to be identical with materials prepared earlier.¹¹

In the above procedure, H_2 and $\text{Co}_2(\text{CO})_8$ presumably act as a source of $\text{HCo}(\text{CO})_n$.¹² If this assumption is correct, direct reaction of 1 with $\text{HCo}(\text{CO})_4$ might conceivably lead to cluster 2. However, Dickson and Tailby found this not to be the case;¹³ decomposition of the cobalt hydride at room temperature seems to occur before reaction with alkyne complexes. The formation of alkylidyne complex 2 is possible under the conditions presented above perhaps because of generation of a small amount of $\text{HCo}(\text{CO})_4$ in equilibrium with H_2 and $\text{Co}_2(\text{CO})_8$ at a temperature where CO loss is facile or reaction with 1 is relatively rapid. In agreement with this interpretation, Fachinetti, Pucci, Zanazzi, and Methong have shown that at temperatures where $\text{HCo}_3(\text{CO})_9$ dissociates into $\text{HCo}(\text{CO})_3$ and $\text{Co}_2(\text{CO})_6$, reaction with acetylene (and ethylene, presumably with H_2 evolution) occurs to produce $\text{Co}_3(\text{CO})_9\text{CCH}_3$.¹⁴

Our results with H_2 and $\text{Co}_2(\text{CO})_8$ suggested the use of other metal hydrides for the preparation of mixed alkylidyne clusters,¹⁵ and reaction of $\text{CpMo}(\text{CO})_3\text{H}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with alkyne complex 1 (45 °C, 20 h) in benzene led to the mixed cluster $\text{CpMoCo}_2(\text{CO})_8\text{CCH}_2\text{C}(\text{CH}_3)_3$ (8).

Scheme IV

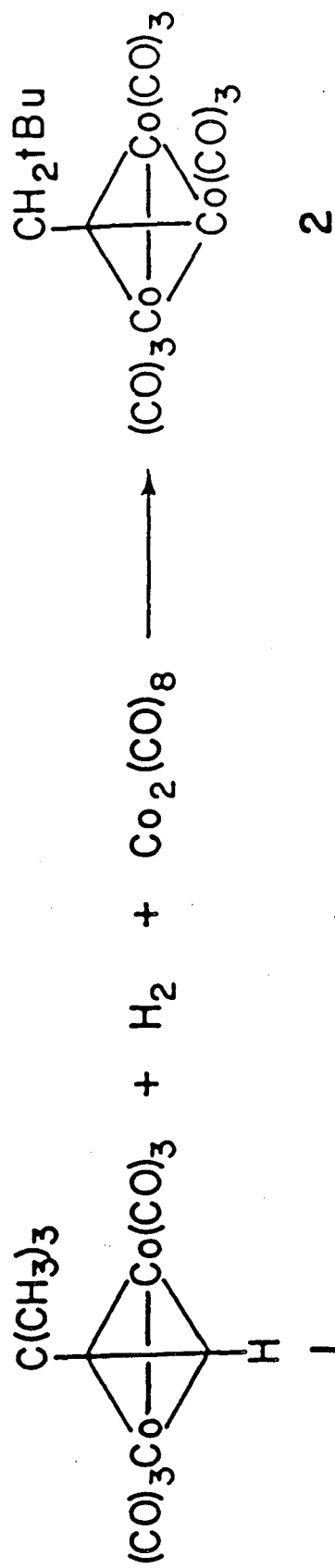


Table I. Synthesis and Hydrogenolysis of Trinuclear Alkylidyne Complexes

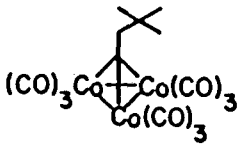
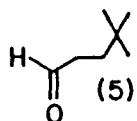
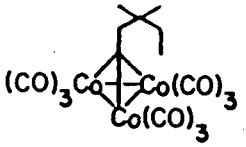
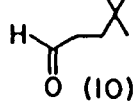
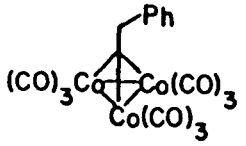
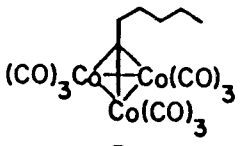
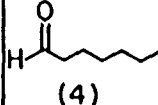
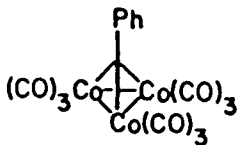
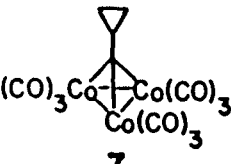
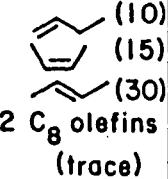
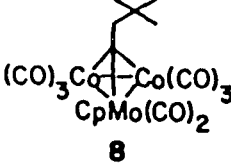
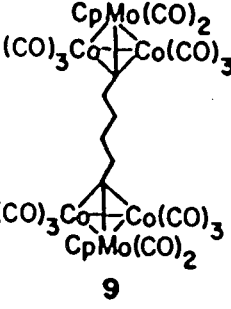
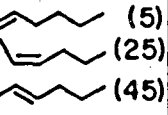
COMPOUND	YIELD	COLOR	HYDROGENATION PRODUCTS (YIELDS) ^a			HYDROGENATION TEMPERATURE	PRODUCT SHOWING CIDNP
			OLEFIN	ALKANE	CARBONYL COMPOUND		
 2	80%	Red-Purple	 (75)	 (20)	 (5)	60°C	
 3	36%	Red-Purple	 (75)	 (15)	 (10)	60°C	
 4	85%	Red-Purple	 (25)	 (75)	—	85°C	None
 5	68%	Red-Purple	 (40)  (10)  (10)	 (40)	 (4)	85°C	None
 6	16%	Red-Purple	—	 (100)	—	85°C	None

Table I. (Continued)

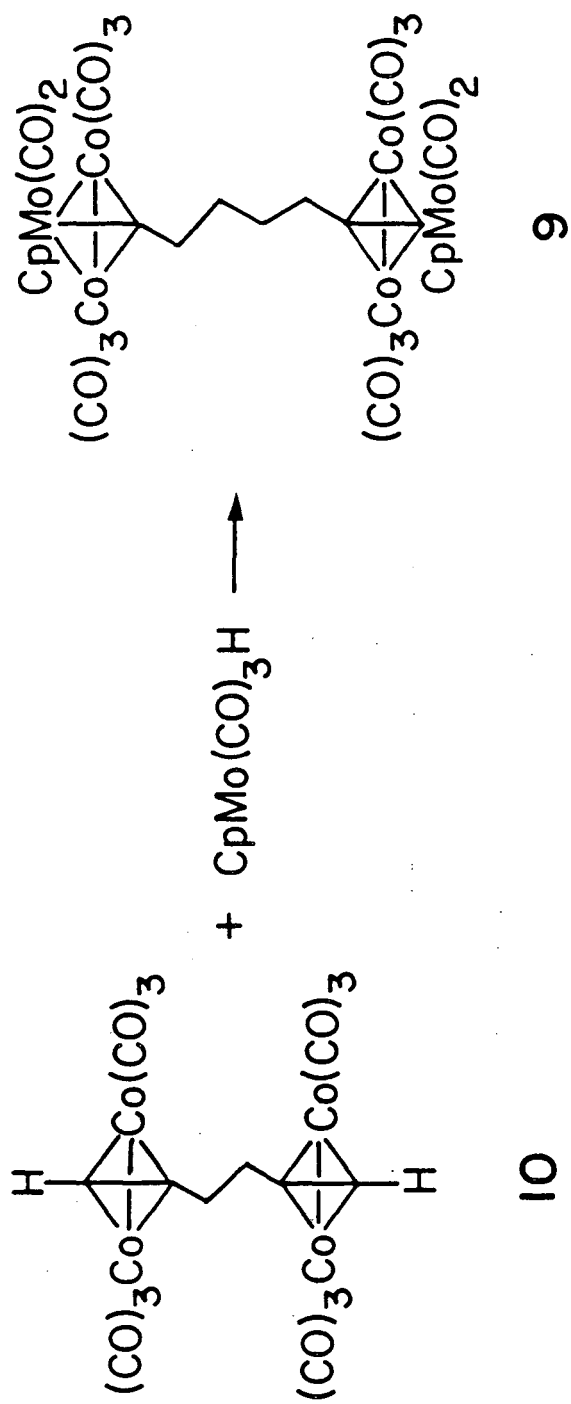
COMPOUND	YIELD	COLOR	HYDROGENATION PRODUCTS (YIELDS) ^a			HYDROGENATION TEMPERATURE	PRODUCT SHOWING CIDNP
			OLEFIN	ALKANE	CARBONYL COMPOUND		
 7	20%	Red-Purple	 2 C ₈ olefins (trace)	 (4)	 (40)	90°C	None
 8	75%	Green	 (100)	—	—	60°C	
 9	77%	Green	 (5) (25) (45)	 (25)	—	90°C	

^a THE RATIOS OF THE HYDROGENATION PRODUCTS VARY DURING THE COURSE OF THE REACTIONS.
THE NUMBERS IN PARENTHESES REPRESENT APPROXIMATE PERCENTAGE YIELDS AT >80% CONVERSION.

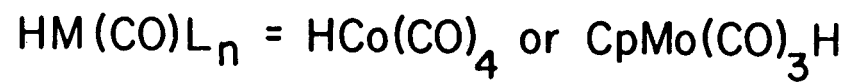
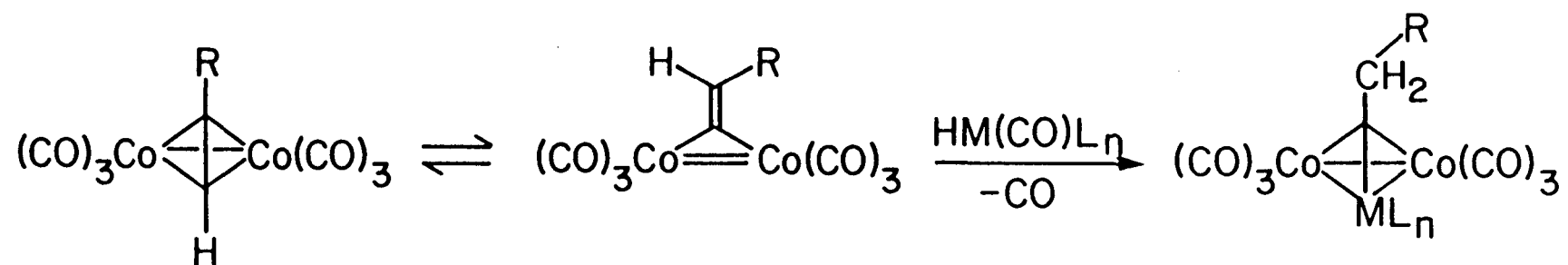
Synthesis of the double mixed cluster $[\text{CpMoCo}_2(\text{CO})_8]\text{C}(\text{CH}_2)_4\text{C}-[\text{CpMoCo}_2(\text{CO})_8]$ (9) was possible from combination (75 °C, 1 h) of $\text{CpMo}(\text{CO})_3\text{H}$ and the double acetylene complex (10) formed in the reaction of 1,5-hexadiyne and $\text{Co}_2(\text{CO})_8$ (Scheme V and Table I). Interestingly, the latter reaction was successful only with the molybdenum hydride; when 10 is treated with H_2 and $\text{Co}_2(\text{CO})_8$ instead, the analogous all-cobalt double cluster $[\text{Co}_3(\text{CO})_9]\text{C}(\text{CH}_2)_4\text{C}[\text{Co}_3(\text{CO})_9]$ was not formed cleanly. Although $[\text{Co}_3(\text{CO})_9]\text{C}(\text{CH}_2)_4\text{C}[\text{Co}_3(\text{CO})_9]$ may be present in the mixture of several compounds produced, only compound 5 could be isolated (9.0 % yield) and identified.¹⁶

While no real evidence concerning the details of the mechanism of formation of trinuclear alkylidyne complexes from dinuclear alkyne complexes and metal hydrides was collected, some speculation is possible. We propose the pathway outlined in Scheme VI. Initial rearrangement of the alkyne complex could generate an unsaturated bridging vinylidene species. Subsequent addition of a metal-hydride across the carbon-carbon double bond, followed by CO loss and metal-metal bond formation, might then lead to the observed alkylidyne clusters. A similar mechanism was suggested by Young for the reaction of dimethylketene with $\text{Co}_2(\text{CO})_8$ to give $\text{Co}_3(\text{CO})_9\text{CCH}(\text{CH}_3)_2$.¹⁷ A dicobalt dimethylvinylidene complex was proposed as an initially formed intermediate in this study. Recently, the first examples of cluster expansion using isolable vinylidene and hydride species have been published. Stone, *et al.*, have described the formation of a trinuclear Mn-Fe-Fe derivative,^{15h} and Jacobsen and Bergman have presented work supporting a non-chain radical mechanism in the

Scheme V



Scheme VI



preparation of Co-Co-Mo and Co-Co-Mn derivatives.^{15i,18}

The synthetic method described here is only applicable to clusters in which a methylene group is attached to the alkylidyne carbon. Consequently, those tricobalt complexes used for the hydrogenolysis studies which do not fit this criterion were prepared by known routes. Namely, the procedures of Seyferth, *et al.*, were used to make phenyl derivative $\text{Co}_3(\text{CO})_9\text{CPh}$ (6)^{4f} and vinyl derivative $\text{Co}_3(\text{CO})_9\text{CCH}=\text{CH}_2$ (11).¹⁹ Reaction of butyl cyclopropyl-dithiocarboxylate with $\text{Co}_2(\text{CO})_8$ in benzene (85 °C, 4 h), followed by chromatography (hexane/silica) and recrystallization from methanol, yielded the new cyclopropylmethylidyne complex 7 (Table I). The latter procedure is an extension of the remarkable yet general method of Patin, Mignani, and van Hulle in which dithioesters have been used to make a variety of tricobalt alkylidyne clusters.²⁰ Data for 6 and 11 are in agreement with previously published preparations.^{4f,19} The characterization of 7 is described in the Experimental Section. Confirmation of the identity of 7 was provided by determination of its crystal and molecular structure by X-ray diffraction, which is presented in the Appendix to this chapter.

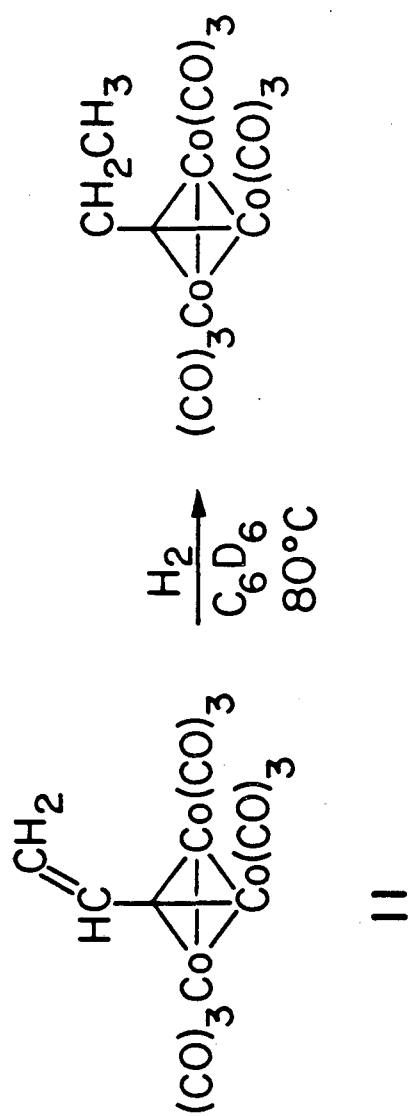
Reaction of trinuclear alkylidyne complexes with H_2 . Reaction of the clusters 2-9 with 3-4 atm of H_2 in benzene leads to the organic products listed in Table I in greater than 95 % yield, as determined by ^1H NMR spectroscopy. The products were identified by GC/MS and/or preparative GC followed by ^1H NMR analysis. Though the product distributions vary during the course of the reactions and depend on solvent, temperature, and concentration of the species involved,^{8a} in most cases the major product is the indicated olefin. Hydrogenation

at 80 °C of vinyl complex 11, however, gave the known saturated species $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{CH}_3$ ²¹ (Scheme VII), and its chemistry was pursued no further.

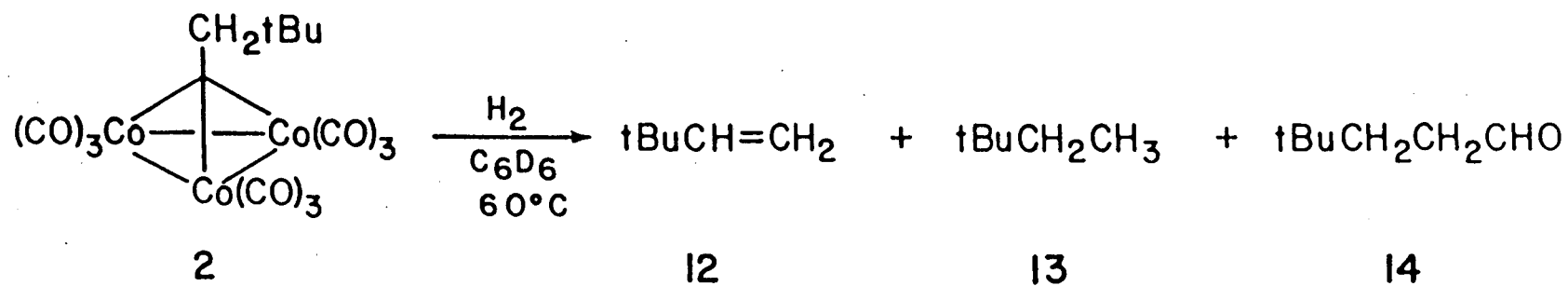
In the case of 3,3-dimethylbutylidyne complex 2 in particular,^{8a,b} the loss of starting complex (and the formation of all products) shows first-order dependence on the concentration of 2; the dependence on the pressure of H_2 above the solution has a nonintegral order. However, rates of individual product formation are less well-defined. The ratio of alkene 12 to aldehyde 14 (Scheme VIII) is constant during the hydrogenation at early reaction times. This suggests that initially 12 and 14 are generated as primary products in concurrent reactions. Later in the reaction, after the concentration of 12 has grown, the concentration of alkane 13 increases rapidly. The rate of production of aldehyde 14 (observed as the ratio $([\text{12}] + [\text{13}])/[\text{14}]$) also seems to increase slightly, though the small amounts of this material involved make the change difficult to analyze. These results suggest that secondary reactions of alkene 12 result in conversion of the olefin into the related alkane (by hydrogenation) and aldehyde (by hydroformylation). In agreement with these conclusions, reaction of alkylidyne complex 2 with H_2 in the presence of added alkene 12 leads to the rapid formation of alkane 13 and aldehyde 14 in excess of that produced in the absence of added 12. Moreover, hydrogenation of 2 in the presence of ethylene gives ethane and propanal as well as 12, 13, and 14.²²

For the hydrogenation of 2, $\text{Co}_4(\text{CO})_{12}$ has been shown to be the final organometallic product.²³ The reactions of complexes 8 and 9

Scheme VII



Scheme VIII



produce $\text{CpMo(CO)}_3\text{H}$; for **8**, the yield of $\text{CpMo(CO)}_3\text{H}$ was measured by ^1H NMR to be > 90 %. No evidence for organometallic intermediates was detected in any of the reactions, particularly no high-field ^1H NMR resonances attributable to metal hydrides. Indeed, when photolysis of **2** under H_2 in toluene- d_8 was carried out at low temperature, formation of alkene **12** was observed at -20°C and higher temperatures, but no new intermediate species were evident by ^1H NMR, even at -75°C . A similar attempt to form a detectable intermediate at low temperature was made by treating **2** with 1 equiv of Me_3NO . Between -25 and -15°C , rapid conversion to intractable materials occurred.

In order to test whether these hydrogenolyses are homogeneous reactions, the reaction of **2** with H_2 was carried out in benzene solution over mercury. The mercury is expected to interact with colloidal metal particles.²⁴ The mercury had no observed effect, even on the CIDNP evident in the ^1H NMR spectra of the reaction mixture (vide infra), indicating that catalytically active colloidal metal particles are not involved in the hydrogenolysis. This is significant in light of the fact that metallic cobalt is observed occasionally in the hydrogenolysis mixtures, particularly if the reactions are carried out at temperatures much higher than those indicated in Table I.

Further mechanistic information is provided by the fact that carbon monoxide strongly inhibits the reaction of **2** with hydrogen²⁵ without the buildup of significant quantities of any detectable Co-CO adduct. In the presence of a 50/50 (mol/mol) mixture of CO/H_2 , heating to 85°C is required to give slow production of aldehyde **14** as the sole product.^{8a} This marked CO inhibition is in agreement with that found in the photochemical hydrogenation of $\text{Co}_3(\text{CO})_9\text{CCH}_3$.⁷

Moreover, treatment of 2 with both triethylphosphine and H_2 at 25 °C results in rapid incorporation of 3 equiv of PEt_3 into the cluster long before any hydrogenation takes place.^{8b} Similar rapid phosphine substitution has been observed for other (alkylidyne)tricobalt nonacarbonyl clusters.²⁶ If the hydrogenation of 2 is carried out under tetrafluoroethylene, no influence on the reaction, including the CIDNP (vide infra) is apparent.

These data are consistent with dissociative CO loss as an initial step in the hydrogenation of 2. One way CO inhibition could be observed without ligand dissociation present on the reaction path is for a new complex, thermodynamically more stable than the starting material, to result from reaction of 2 and CO.²⁷ This is not the case, since no such complex is detected. Alternatively, CO could be scavenging some undetected substance which takes part in the activation of one of the starting materials. This substance could be a reactant involved in the propagation step of a chain reaction or a catalyst for the reaction. However, if this were the case, tetrafluoroethylene would be expected to act in a manner very similar to that of CO, i.e., as an inhibitor,²⁸ and C_2F_4 behaves as an inert spectator. Consequently, CO dissociation from 2 is proposed to be the initial step on the path to alkene 12.

CIDNP observations: Evidence for a radical mechanism. The most striking observation in these hydrogenolyses is the occurrence of CIDNP in the products from some of the trinuclear clusters.^{29,30} As shown in Figures I and II, when a sample of 2 or 8 is heated under 3-4 atm of H_2 in an NMR probe at 60 °C, intense multiplet CIDNP due to the

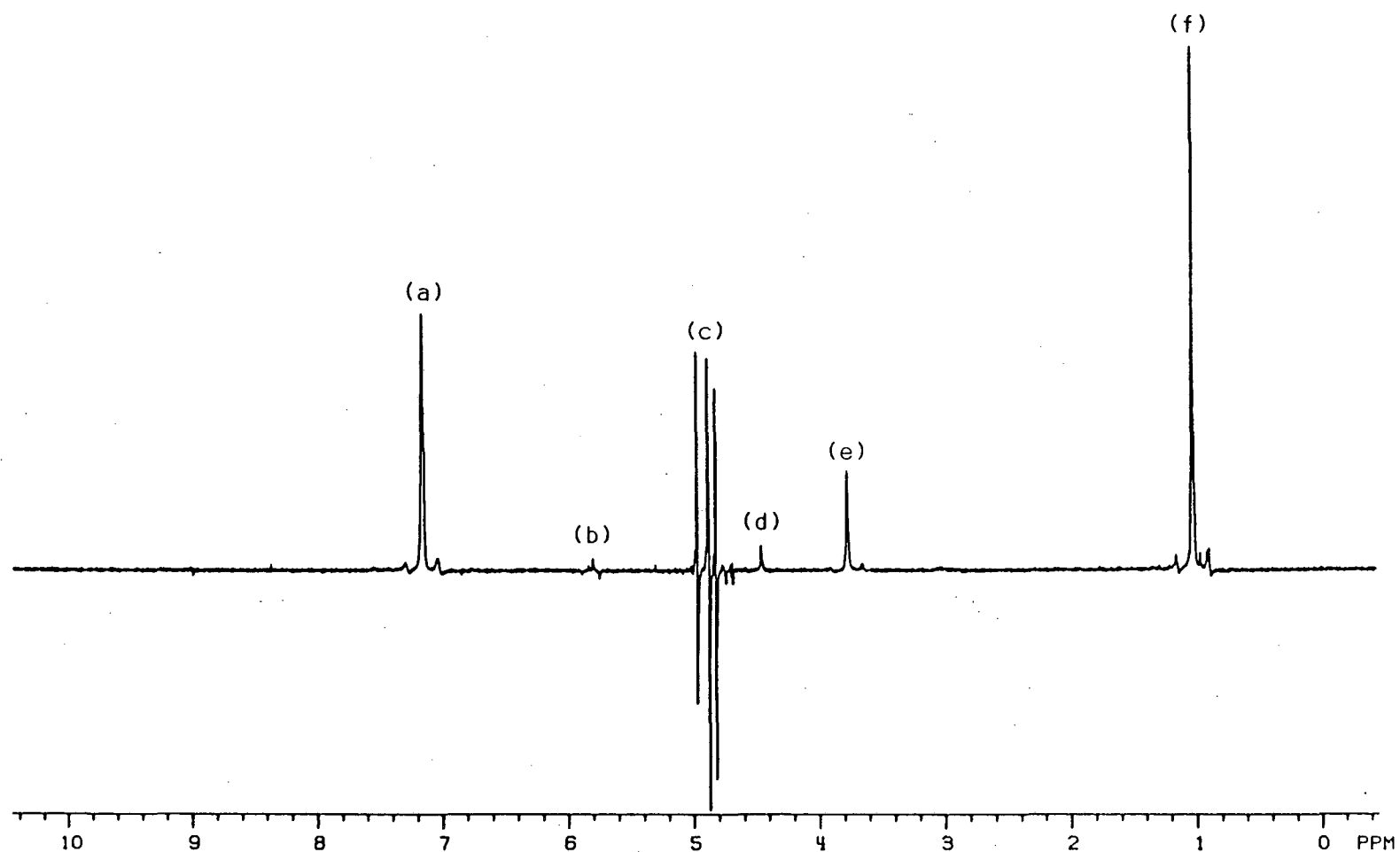


Figure 1. CIDNP observed in ^1H NMR spectrum during hydrogenolysis of **2** in benzene- d_6 . Peak identification: (a) benzene- d_5 ; (b) internal vinyl hydrogen in 3,3-dimethyl-1-butene product; (c) terminal vinyl hydrogens; (d) dissolved H_2 ; (e) CH_2 hydrogens in **2**; (f) t -Bu hydrogens in **2**. Chemical shifts are recorded in ppm downfield from tetramethylsilane.

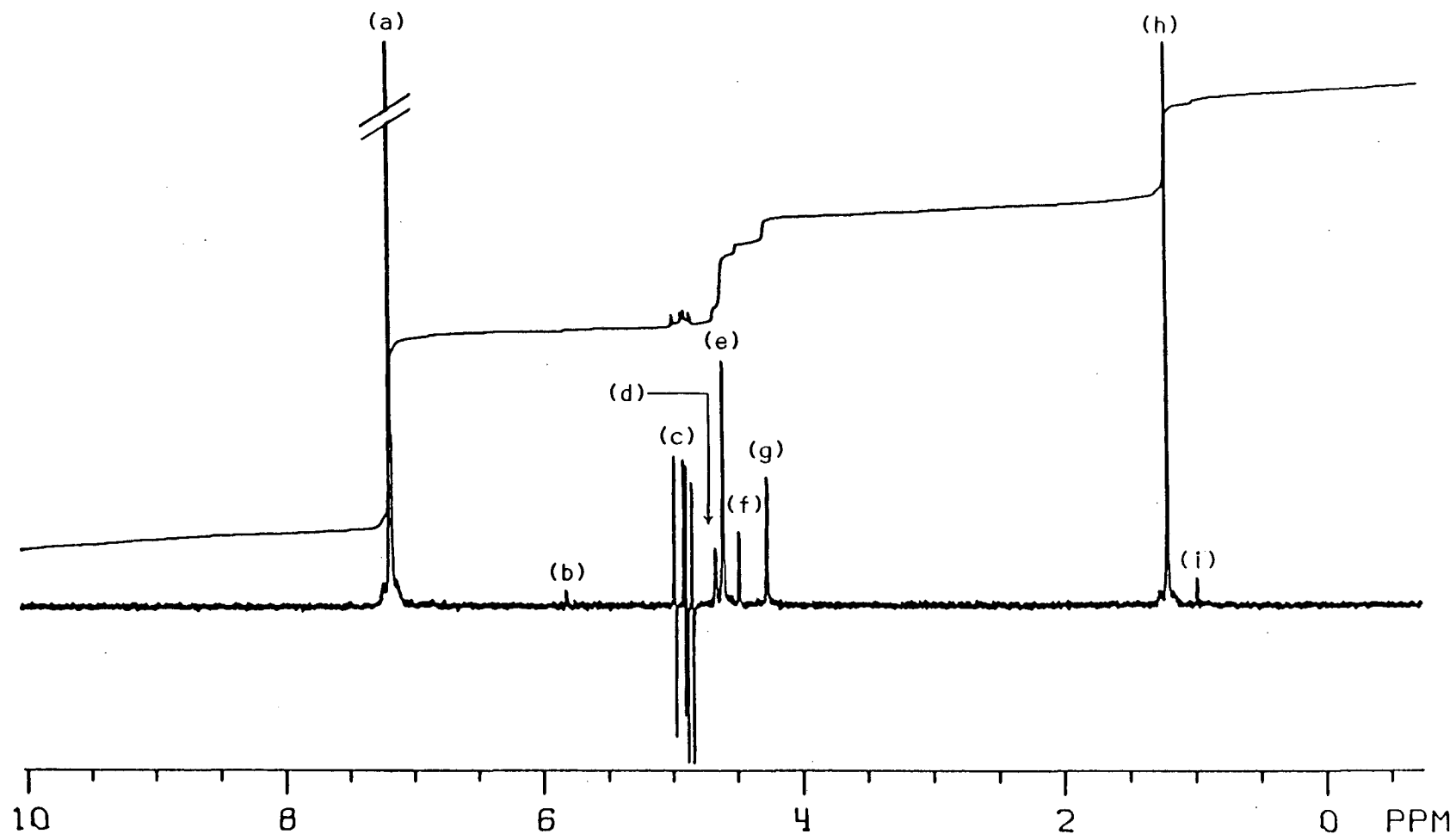


Figure II. CIDNP observed in ^1H NMR spectrum during hydrogenolysis of **8** in benzene- d_6 . Peak identification: (a) benzene- d_5 ; (b) internal vinyl hydrogen in 3,3-dimethyl-1-butene product; (c) terminal vinyl hydrogens; (d) Cp hydrogens in $\text{CpMo(CO)}_3\text{H}$ product; (e) Cp hydrogens in **8**; (f) dissolved H_2 ; (g) CH_2 hydrogens in **8**; (h) t-Bu hydrogens in **8**; (i) t-Bu hydrogens in 3,3-dimethyl-1-butene product. Chemical shifts are recorded in ppm downfield from tetramethylsilane.

terminal vinyl proton signals of the alkene 12 being produced is observed in the ^1H NMR spectra taken throughout the reaction. In addition, less intense multiplet CIDNP combined with slight net enhanced absorption is seen for the proton at the 2 position of 12. The CIDNP pattern is identical regardless of whether the starting material is cluster 2 or 8. Polarization is also observed in the olefinic product from 3; again the terminal vinyl protons show multiplet CIDNP. For the internal vinyl proton, multiplet CIDNP not combined with any detectable net effect is observed (Figure III). Hydrogenation of compound 9 leads to weak polarization (multiplet effect) in the terminal vinyl protons of only the 1-hexene produced (Figure IV). No CIDNP was observed in the hydrogenolyses of the remaining alkylidyne complexes. Furthermore, when hydrogenation of cluster 2 containing the natural abundance level of isotopes was monitored by ^{13}C NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR, no ^{13}C CIDNP could be detected.

The observation of CIDNP signals due to the alkene products requires that at least some of the alkene is produced in a reaction involving radicals, but does not necessitate formation of all of the alkene in this manner. The polarization results from the fact that the rate of singlet/triplet radical pair intersystem crossing and, consequently, the relative amounts of cage-recombination and cage-escape products depends on the g factors and electron-nuclear hyperfine coupling constants of the radicals involved.³¹ Primarily multiplet effect is observed in the systems studied here. Multiplet effect is seen for the products from radicals having hyperfine coupling constants which are much greater than the difference in their g factors. For organic radicals, which generally have small hyperfine

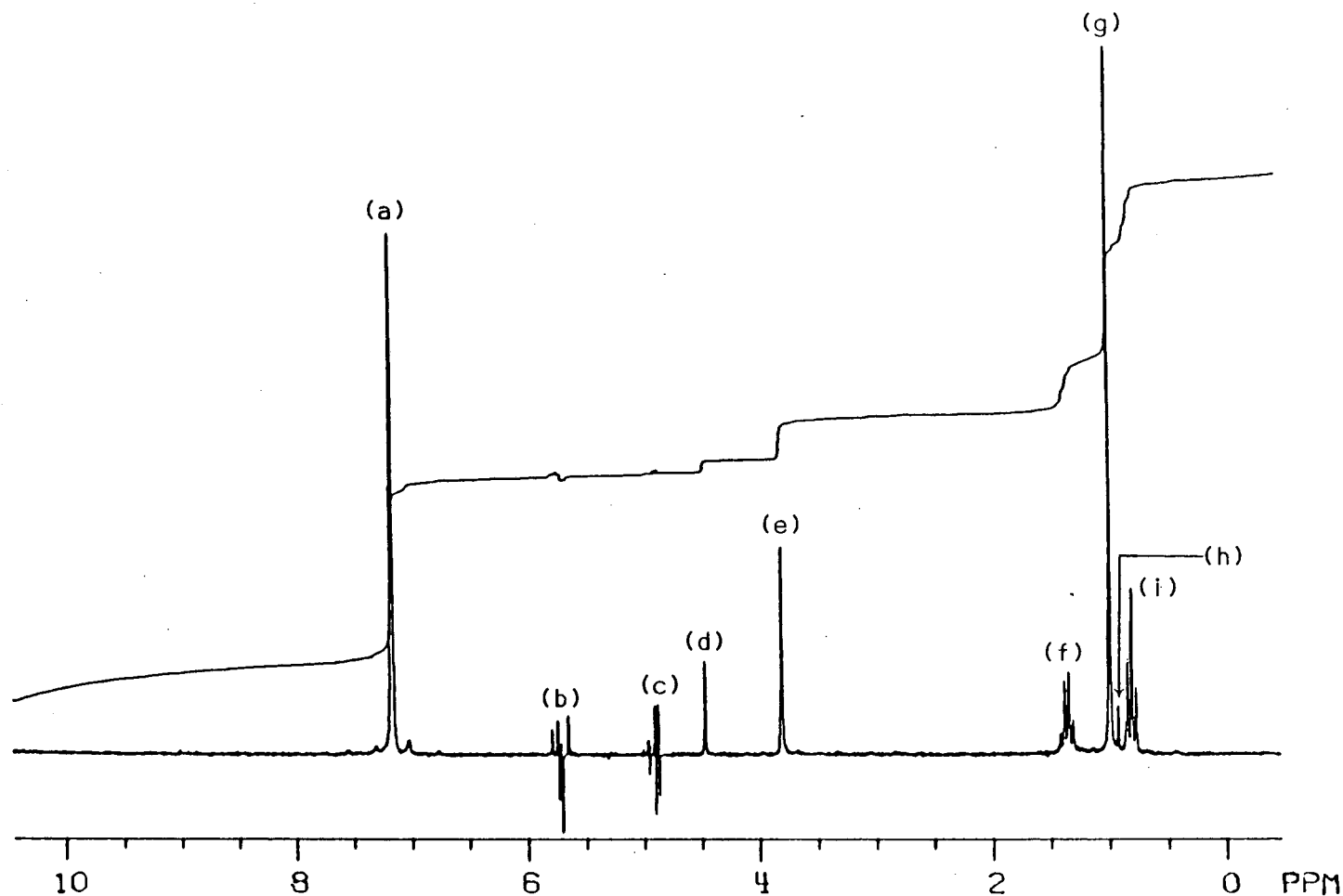


Figure III. CIDNP observed in ^1H NMR spectrum during hydrogenolysis of **3** in benzene- d_6 . Peak identification: (a) benzene- d_5 ; (b) internal vinyl hydrogen in 3,3-dimethyl-1-pentene product; (c) terminal vinyl hydrogens; (d) dissolved H_2 ; (e) CH_2 (position 2) hydrogens in **3**; (f) CH_2 (position 4) hydrogens in **3**; (g) hydrogens of CH_3 groups on carbon 3 in **3**; (h) hydrogens of CH_3 groups on carbon 3 in 3,3-dimethyl-1-pentene product; (i) CH_3 (position 5) hydrogens in **3**. Chemical shifts are recorded in ppm downfield from tetramethylsilane.

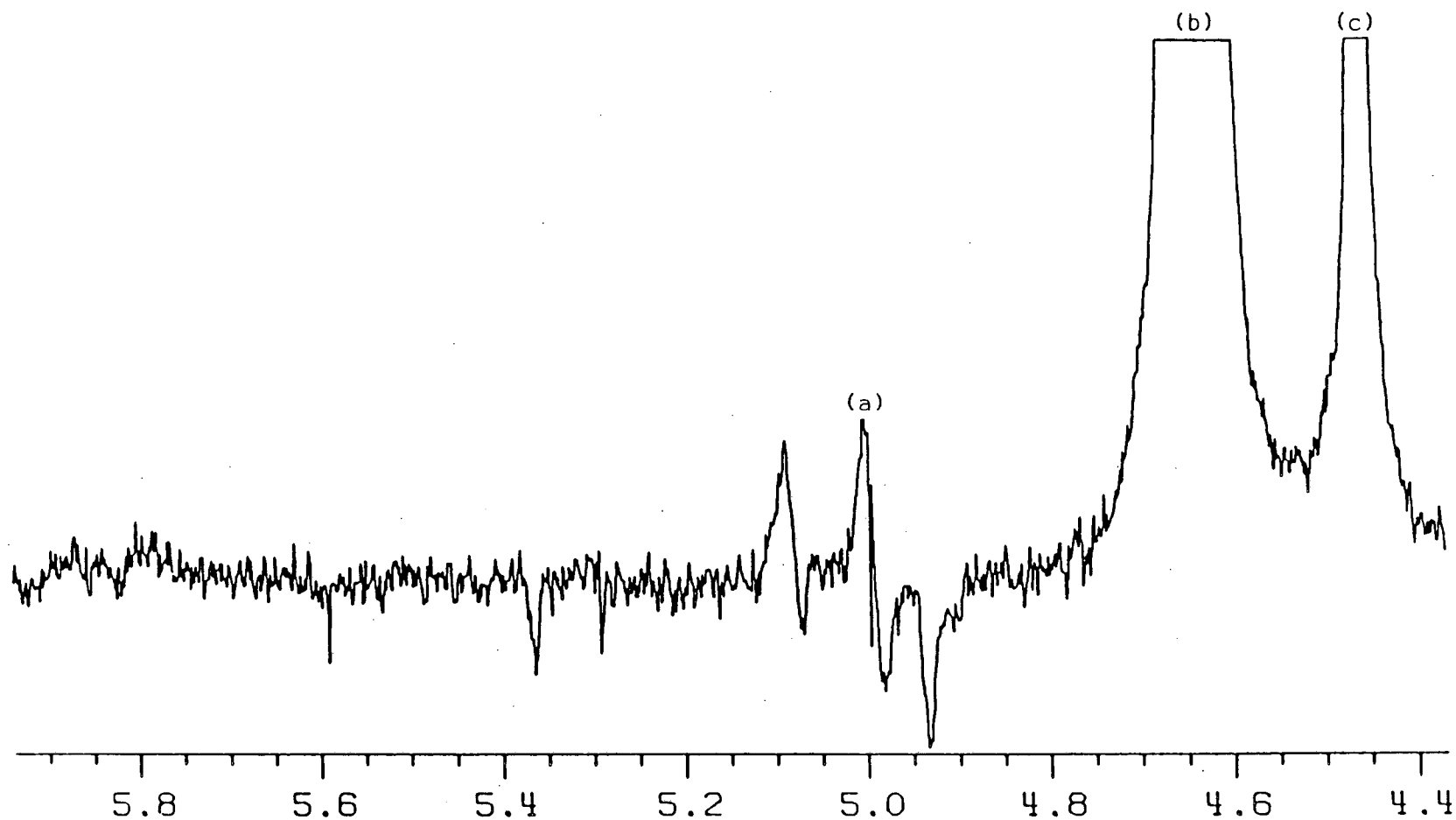


Figure IV. CIDNP observed in ^1H NMR spectrum during hydrogenolysis of **9** in benzene- d_6 . Peak identification: (a) terminal vinyl hydrogens in 1-hexene product; (b) Cp hydrogens in **9**; (c) dissolved H_2 . Chemical shifts are recorded in ppm downfield from tetramethylsilane.

coupling constants, multiplet effect is normally seen only for pairs of radicals which are very similar (nearly equal g factors), but not identical. In the hydrogenation of the alkylidyne complexes, though, only one CIDNP producing organic product, the alkene, is detected. The data are consistent with $t\text{-BuCH}=\dot{\text{C}}\text{H}$ as one radical partner in the pair responsible for the polarization. However, at present we have no completely satisfactory suggestion for the identity of the second radical. One possibility is a metal-containing radical with a very large hyperfine coupling constant to a proton. Such a species might be a cobalt hydride for which a resonance structure putting a large amount of unpaired spin on the hydrogen atom could be drawn (Scheme IX).³² Since a free hydrogen atom is known to have a huge hyperfine splitting constant (509.74 G),³³ contribution of the latter resonance structure could account for the observed multiplet effect.³⁴ The similarity of the CIDNP in the hydrogenations of 2 and 8 indicates that the radical pair responsible for the polarization is identical in these systems. Specifically, the partner to the organic radical precursor to alkene 12 is the same in both systems, and must be cobalt-containing, even when formed from 8, if it is the proposed metal hydride species.

The CIDNP observed during the hydrogenolysis of 2 was examined most extensively.^{8b} Identical spectra were observed in cyclohexane- d_{12} , benzene- d_6 , and toluene- d_8 , but no CIDNP was observed and the spectra became very broad in THF- d_8 or CCl_4 .³⁵ Traces of methanol, anisole, oxygen, and various $\text{Co}_2(\text{CO})_6(\text{HCCR})$ ($\text{R} = n\text{-butyl, } t\text{-butyl, phenyl}$) complexes enhanced the absolute signal intensities in benzene- d_6 , whereas other additives, such as $\text{Co}_2(\text{CO})_8$ and

Scheme IX



benzonitrile, attenuated them. The presence of a large amount (15 equiv) of 9,10-dihydroanthracene, a substance capable of trapping radicals through hydrogen atom donation (vide infra), also severely attenuated the CIDNP signals. No CIDNP at all is observed when the spin-trap $t\text{-BuNO}^{36}$ or the isolable tetramethylpiperidine-N-oxyl radical (TEMPO)³⁷ is present. A third class of compounds including benzophenone, $\text{Co}_2(\text{CO})_6(\text{H}_3\text{CCCC}(\text{CH}_3)_3)$, and $\text{Co}_4(\text{CO})_{12}$ had no effect on signal intensities. Moreover, when 2 was stored for four months at -40°C under air-free conditions, the resulting material showed intensified CIDNP, though no detectable differences in bulk material were evident. These variations in absolute CIDNP signal intensity presumably reflect changes caused by the additives in proton- and electron-spin relaxation times. In the case of stored 2, undetected decomposition to some trace impurity may be the source of change in relaxation times. Another possible explanation is that the foreign materials alter the relative rates of the radical processes which lead to cage-recombination and cage-escape products. This possibility seems likely in the case of 9,10-dihydroanthracene, $t\text{-BuNO}$, or TEMPO. As it stands, though, these phenomena have eluded full understanding.

ESR observations: Evidence for vinyl radicals and a hydrogen atom donor. When solutions of cluster 2 in benzene under 3-4 atm of H_2 were examined over the temperature range of $25\text{--}100^\circ\text{C}$ in an ESR spectrometer, no observable signals were produced.³⁸ However, when a large excess (7-8 equiv) of spin-trap $t\text{-BuNO}$ (a substance known to react with radicals to form new, long-lived, ESR detectable radicals)^{36a,b} was present, new signals in addition to those of the

decomposition product $(t\text{-Bu})_2\dot{\text{N}}\text{O}^{36a,b}$ were observed (Figures V, VI, and VII). Analysis of the overlapping coupling patterns revealed that one radical (15; cf. Scheme X) was initially produced at 25 °C giving a resonance split into a doublet of 1:1:1 triplets ($g = 2.006$, $a_{\text{H}} = 22$ G, $a_{\text{N}} = 15.5$ G). A second resonance pattern of six peaks (radical 16; cf. Scheme X), consisting of a 1:1:1 triplet of doublets ($g = 2.006$, $a_{\text{N}} = 13.5$ G, $a_{\text{H}} = 11$ G), was also present at 25 °C, but became most intense as the reaction mixture was heated to ca. 50 °C. Heating also leads to the gradual disappearance of 15 and the formation of a third species (17; cf. Scheme XIII). The resonance due to radical 17 is most intense at 70 °C and is split into a 1:1:1 triplet of doublets ($g = 2.006$, $a_{\text{N}} = 14$, $a_{\text{H}} = 3$).

While the values of g and a_{N} for 15-17 are typical of tert-butylnitroxyl spin-trapping adducts,^{36a,b} structural assignment from their ESR signals is straightforward only for radical 16, the data for which are consistent with those measured for $t\text{-Bu(H)}\dot{\text{N}}\text{O}$ ($a_{\text{N}} = 13.3$ G, $a_{\text{H}} = 11.6$ in benzene- h_6 at room temperature; varies with solvent and temperature).³⁹ This assignment would agree with the previous hypothesis of a cobalt hydride intermediate, which is expected to be a good hydrogen atom donor (vide infra) and could react with $t\text{-BuNO}$ to give $t\text{-Bu(H)}\dot{\text{N}}\text{O}$ (Scheme X). The tert-butylvinyl radical was postulated earlier as an intermediate species consistent with the observation of CIDNP in alkene 12; it might also account for the production of the other ESR signals. Indeed, assignment of the initially formed radical 15 as a tert-butylvinyl adduct of $t\text{-BuNO}$ (Scheme X) was confirmed by generation of the same resonance pattern on treatment of trans-1-bromo-3,3-dimethyl-1-butene with $(n\text{-Bu})_3\text{SnH}$ in the presence of $t\text{-BuNO}$

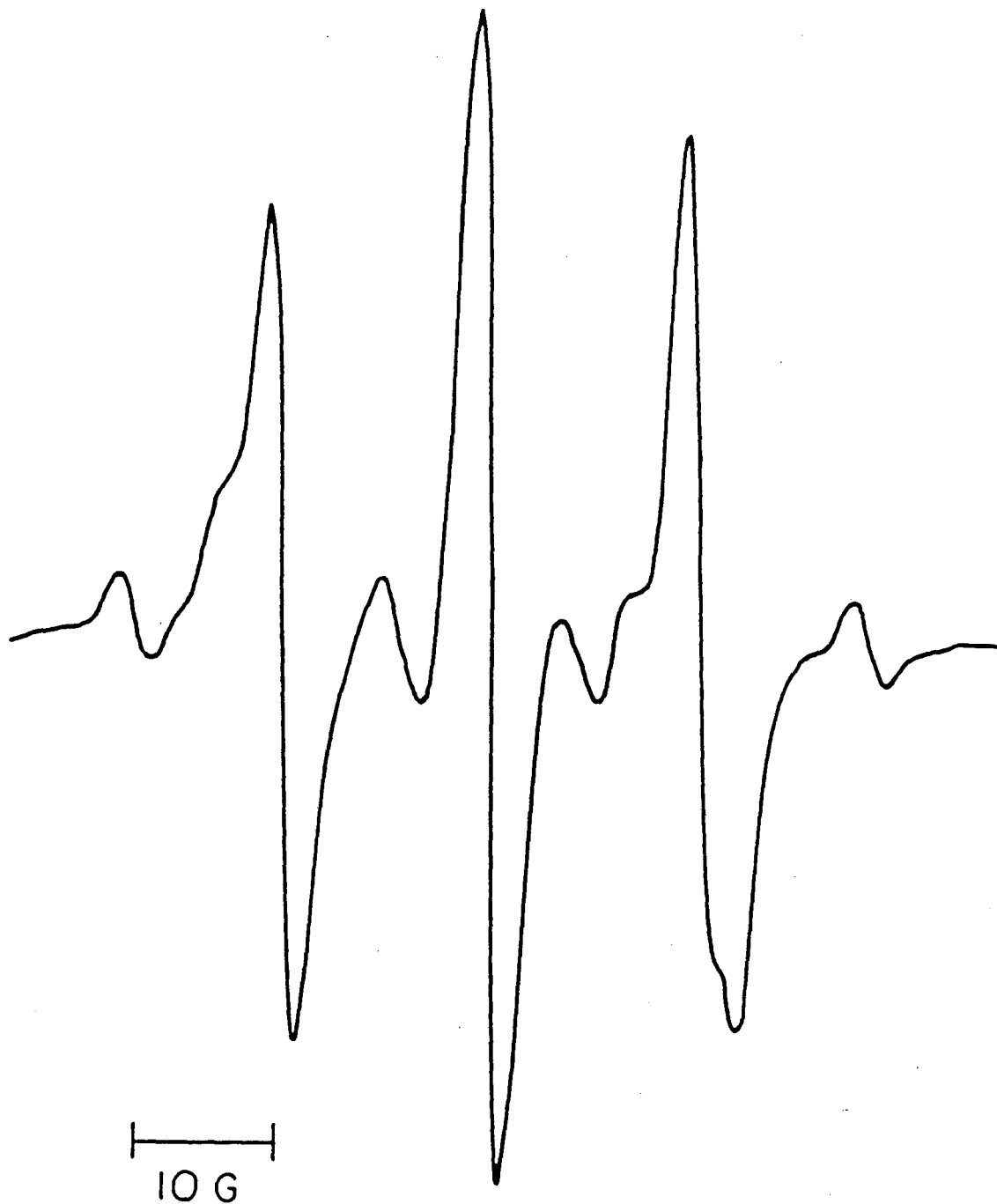


Figure V. Low resolution ESR spectrum of a mixture of **2**, H_2 , and $t\text{-BuNO}$ in benzene- d_6 at 25 °C.

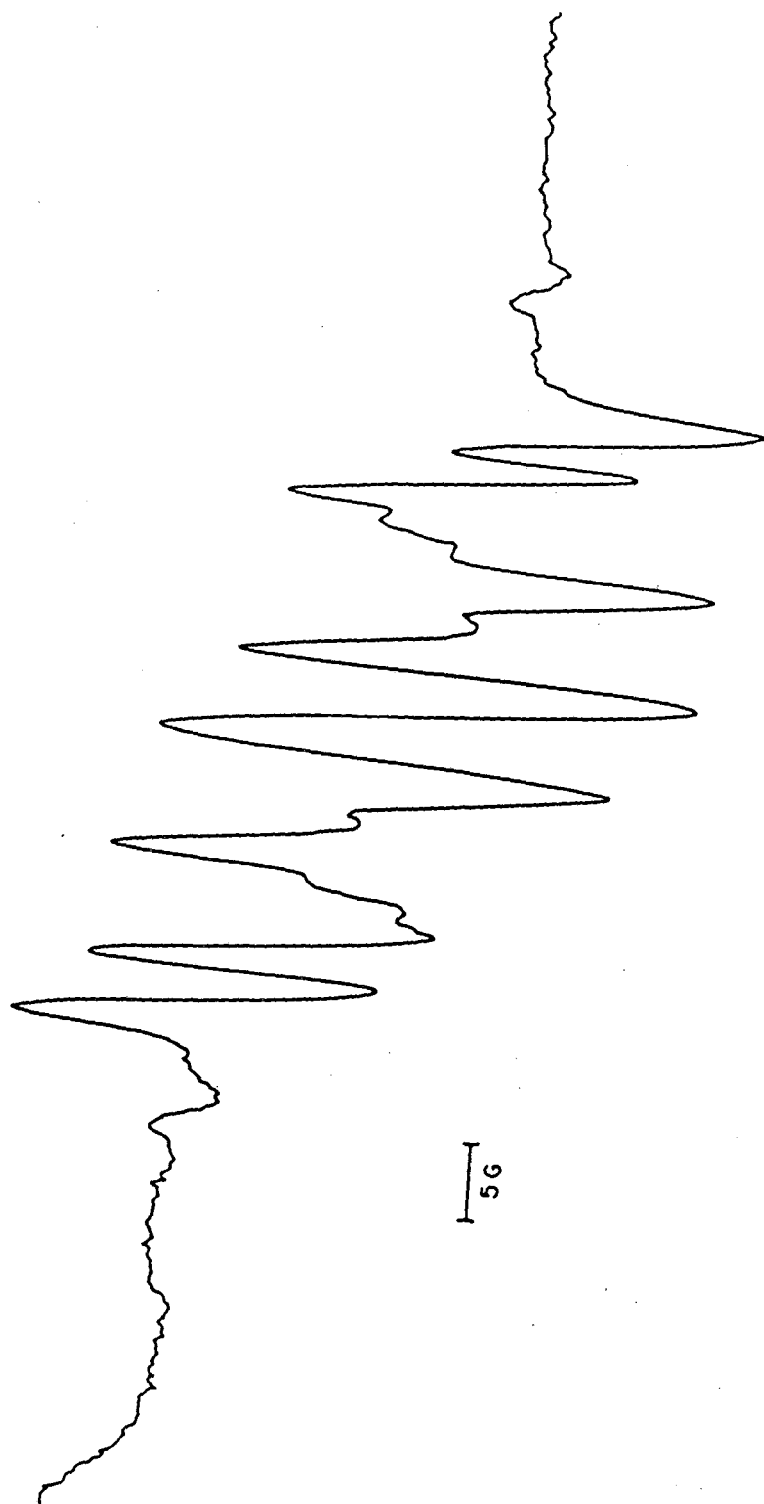


Figure VI. High resolution ESR spectrum of a mixture of 2, H_2 , and $t\text{-Bu}\dot{\text{N}}\text{O}$ in benzene- d_6 at 34 °C.

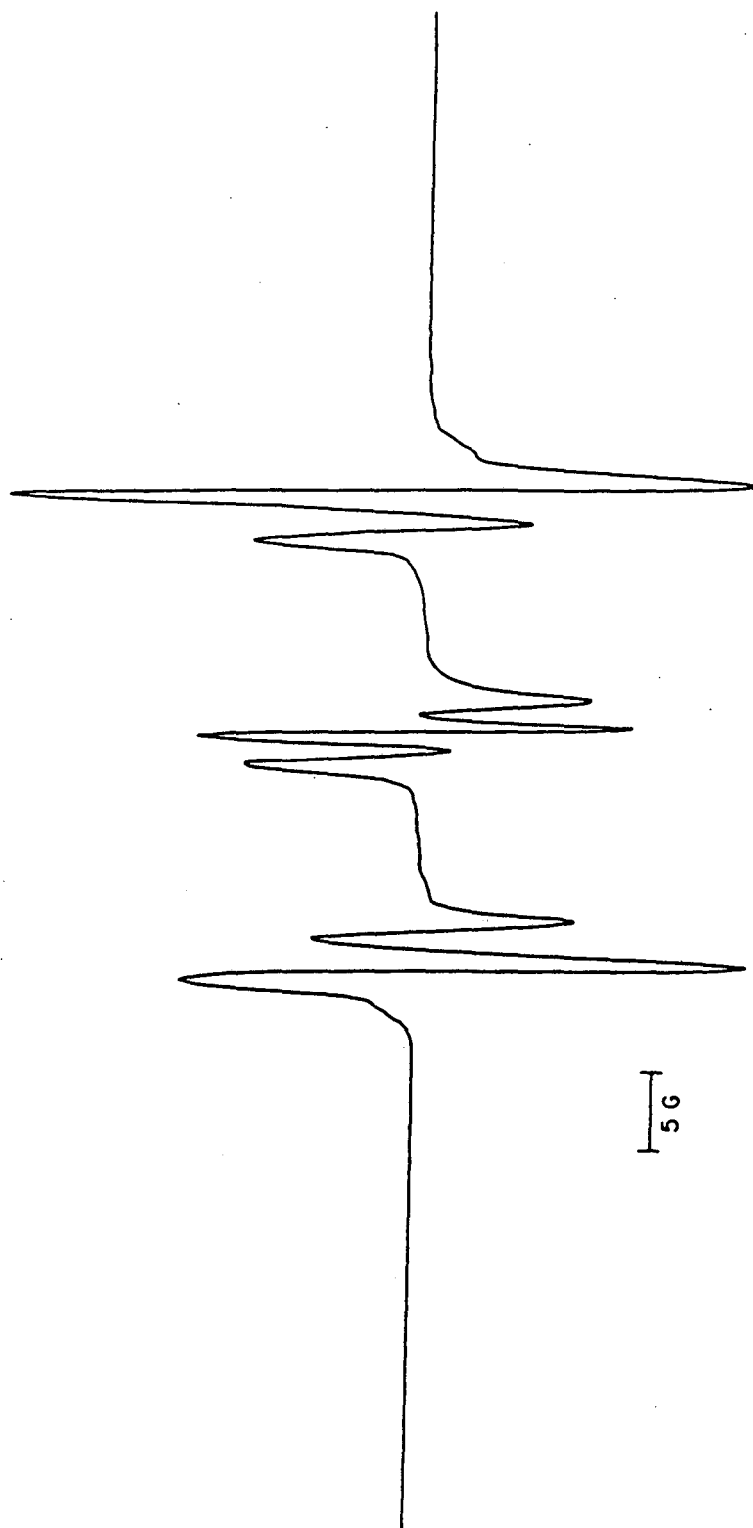
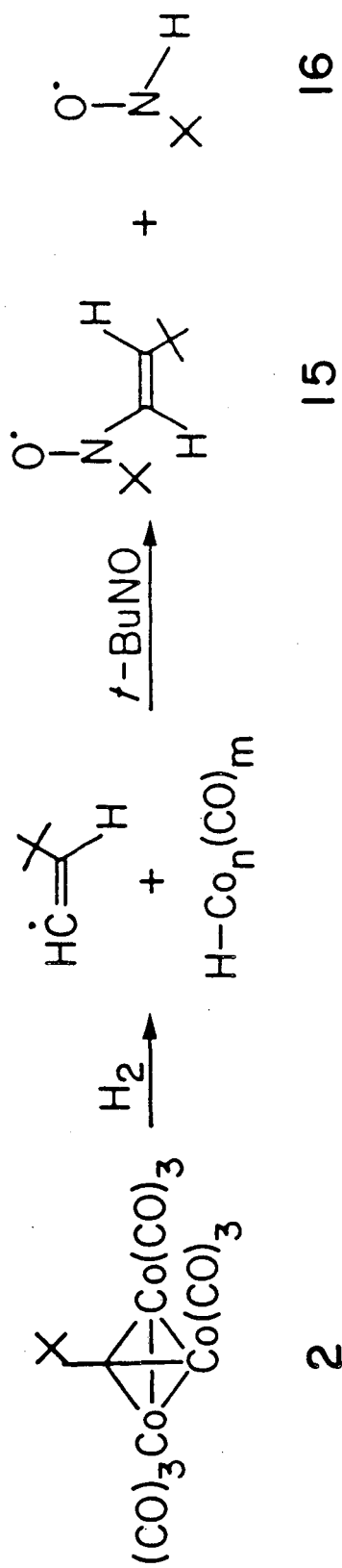


Figure VII. High resolution ESR spectrum of a mixture of 2, H_2 , and $t\text{-BuNO}$ in benzene- d_6 at 70°C .

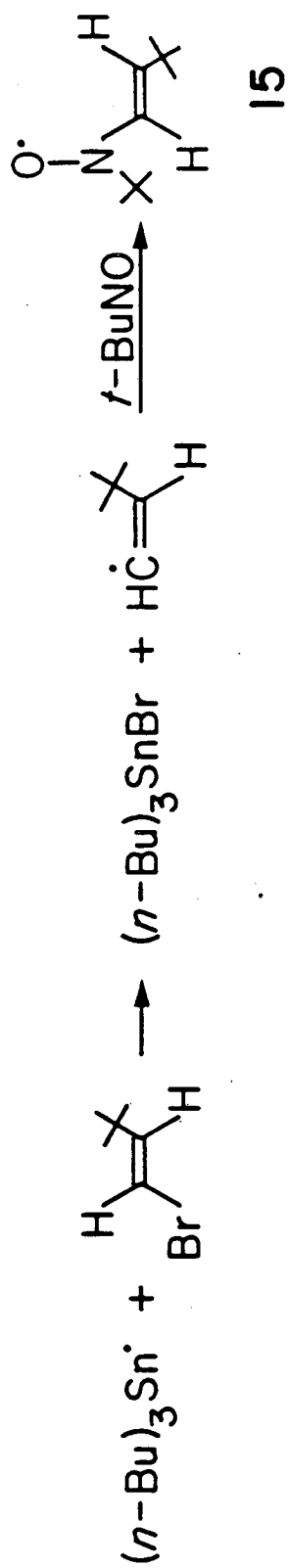
Scheme X



at room temperature (Scheme XI, Figure VIII). In this case each peak of the doublet of 1:1:1 triplets could be partially resolved, revealing fine structure with splitting of ca. 0.5 G. The large hydrogen hyperfine splitting for 15 is indicative of a large spin density near one hydrogen atom, and is explicable by a resonance structure placing the unpaired electron on the β carbon (Scheme XII). The small (ca. 0.5 G) coupling may be due to the hydrogen on the α carbon, or perhaps to some ^{13}C coupling. At any rate, coupling to the α hydrogen is expected to be much smaller than to the β hydrogen.⁴⁰ The fleeting nature of the resonance due to 15 is consistent with the known behavior of such species. Even with bulky substituents, as in the proposed structure for 15, vinylnitroxyl radicals are known to be very reactive and to rapidly combine with a second molecule of $t\text{-BuNO}$ via attack at the β vinyl position. The product of this repeated spin-trapping would be $t\text{-BuN(O)CHCH(t-Bu)\dot{N}(O)(t-Bu)}$, the proposed structure of radical 17 (Scheme XIII). The hyperfine splitting constants and g values measured for 16 and 17 are reasonable in comparison with those observed for other vinylnitroxyl radicals and the products of their subsequent reaction with another molecule of $t\text{-BuNO}$.⁴⁰

Labelling experiments. In order to acquire additional mechanistic information concerning the nature of the radicals involved in the hydrogenolyses and the extent of their participation, labelling experiments were conducted. The complex $\text{Co}_3(\text{CO})_9\text{CCD}_2\text{C}(\text{CH}_3)_3$ (2-d_2) was prepared from 1-deuterio-3,3-dimethyl-1-butyne, D_2 , and $\text{Co}_2(\text{CO})_8$ in a manner completely analogous to that of the perprotio compound.

Scheme XI



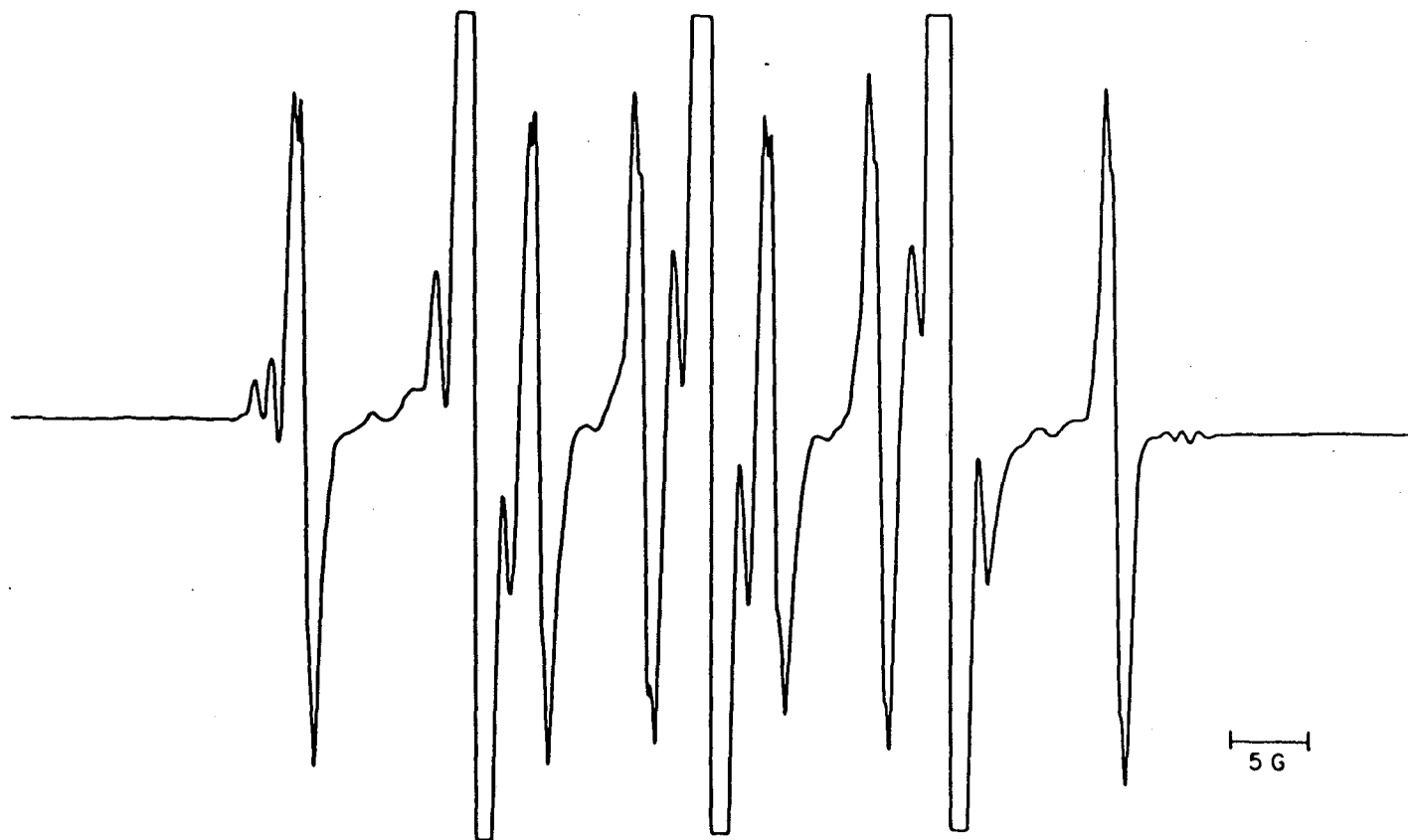
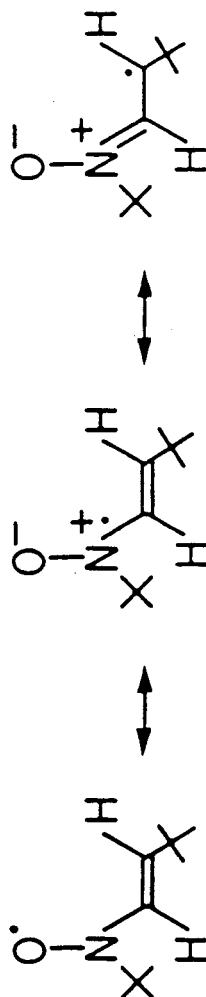
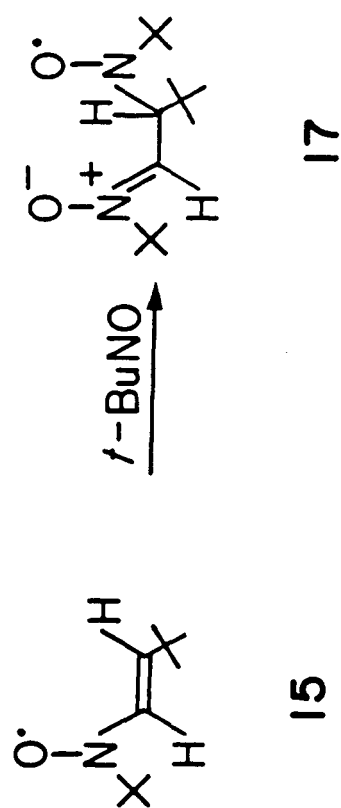


Figure VIII. High resolution ESR spectrum of a mixture of trans-t-BuCH=CHBr, (n-Bu)₃SnH, and t-BuNO at 25 °C.



Scheme XII

Scheme XIII



Reaction of 2-d₂ with H₂, in the presence of a variety of CIDNP-enhancing dicobalt alkyne complexes, gave a new olefinic CIDNP pattern which was independent of the nature of the additive and attributable to t-BuCDCH₂ (Figure IX). The bulk olefin product exhibited the same labelling pattern.^{8b} This result demonstrates that the CIDNP signals arise from 2 and not some impurity, and suggests that all of the olefin is formed via the radical pathway which produces the polarization.

The inverse labelling experiment is not so straightforward. Reaction of perprotio 2 with D₂ in pentane or benzene-d₆ led to a mixture of hydrogen and deuterium in both the 1 position and the 2 position of alkene 12. More precisely, when the experiment was carried out in benzene-d₆ at 60 °C, no CIDNP was observed and the product was found to contain ca. 90 % deuterium and 10 % hydrogen in the 1 positions (average of cis and trans positions) and ca. 30 % deuterium and 70 % hydrogen in the 2 position by ¹H NMR spectroscopy. These percentages were apparent even at early reaction times (< 10 % conversion). Moreover, the ratio of hydrogen in the two positions did not change (measured up to > 60 % conversion).

In direct analogy, complex 3 was treated with D₂ in pentane at 60 °C, followed by preparative GC of the volatile components of the reaction mixture. ¹H NMR analysis showed ca. 70 % deuterium in the 1 positions (average of cis and trans positions) and ca. 40 % in the 2 position of the olefin produced. The aliphatic product was also examined in this case. An average of 40 % deuterium incorporation into the 1 and 5 positions, and an average of 35 % for the 2 and 4 positions, was measured. This corresponds to 100 % D₂ addition to the

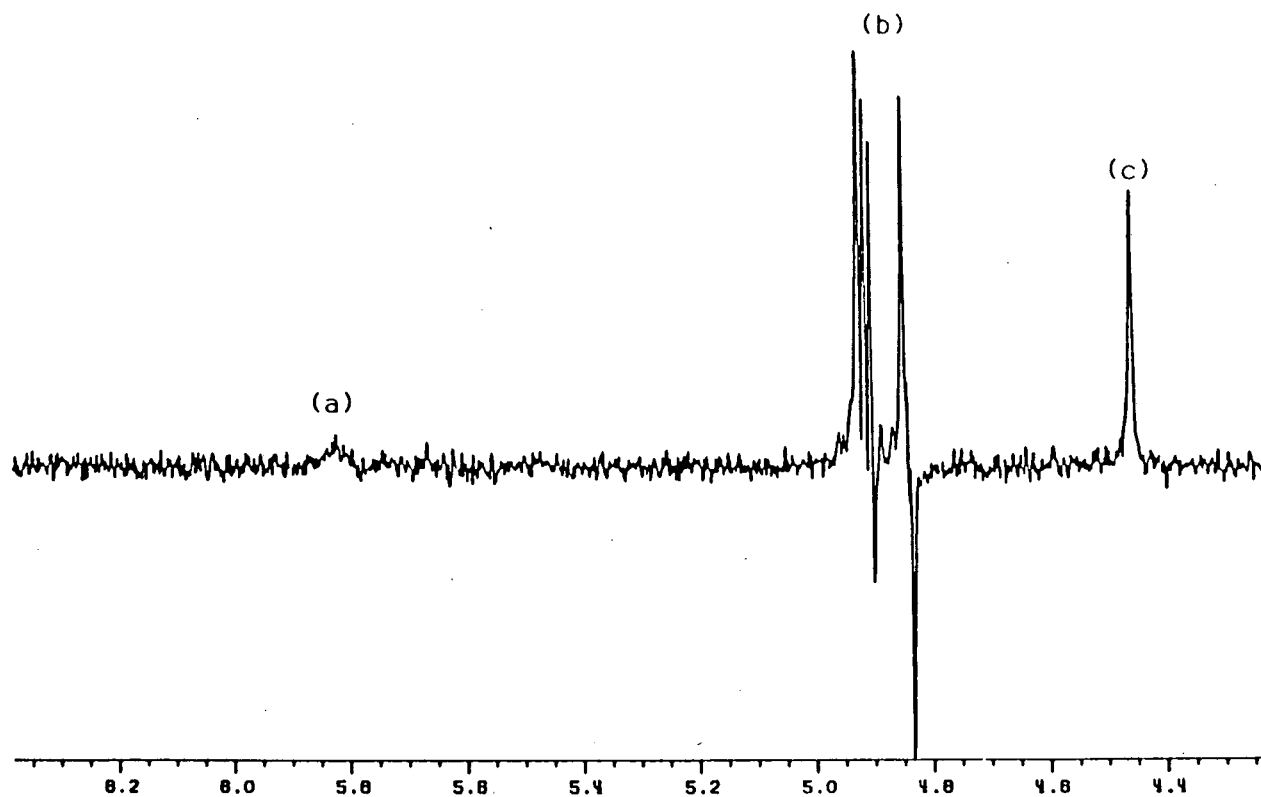


Figure IX. CIDNP observed in ^1H NMR spectrum during hydrogenolysis of 2-d_2 in benzene- d_6 . Peak identification: (a) internal vinyl hydrogen in 3,3-dimethyl-1-butene product; (b) terminal vinyl hydrogens; (c) dissolved H_2 . Chemical shifts are recorded in ppm downfield from tetramethylsilane.

mixed-label olefin. These results also hold qualitatively for reaction in cyclohexane- d_{12} , for which 1H NMR spectroscopy revealed no CIDNP.

The implication from these data is that tert-butylvinyl radicals are intermediates along the reaction path to 12, but some mechanism exists for exchange of external hydrogen into all of the olefinic positions prior to the final step releasing the olefin product. This exchange process does not seem to involve solvent deuterium or hydrogen and, not surprisingly, is accelerated for reaction of 2 with D_2 relative to reaction of 2- d_2 with H_2 .

Trapping experiments. With the hope of trapping free tert-butylvinyl radicals which may be formed in the hydrogenolysis of 2, the reaction of 2 with H_2 was carried out in the presence of radical trapping agents. Use of the stable radical TEMPO as a trapping agent was unsuccessful, yielding no isolable tert-butylvinyl radical adduct.³⁷ Hydrogenolysis of 2 in CCl_4 , however, did lead to the detection of large quantities of Cl_3CCCl_3 by GC/MS, and a large excess (14 equiv) of 1-bromomethyl-4-methylbenzene in benzene gave 1,4-dimethylbenzene and HBr. These reactions are not very clean, and a multitude of tert-butyl containing products are observed by 1H NMR spectroscopy.

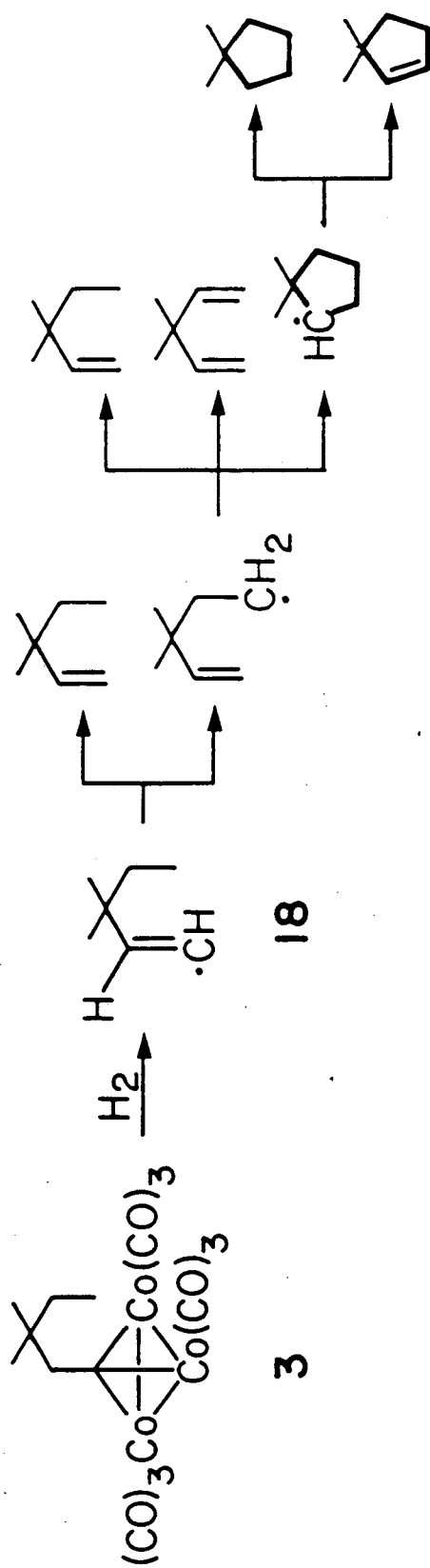
Cleaner results are obtained when the reaction of 2- d_2 with D_2 was carried out in the presence of the following hydrogen atom donors: 9,10-dihydroanthracene, diphenylmethane, and triphenylmethane.^{8b} The resulting 3,3-dimethyl-1-butene was analyzed for hydrogen content by 1H NMR and GC/MS. The largest amount of incorporation was found to be 13 % for dihydroanthracene and was independent of trapping agent

concentration. The trapped alkene was shown to have incorporated only one hydrogen atom by GC/MS. This suggests that tert-butylvinyl radicals are being formed, and virtually all of them which escape the cage containing the second radical are being trapped. The low percentage of trapped material is consistent with the limited cage escape necessary for the observation of CIDNP.³¹ Furthermore, since no combination or disproportionation⁴¹ products have been observed in this or the other hydrogenolyses, except to an extremely small extent for the reaction of complex 7, it is reasonable to assume that cage escape products are relatively minor.

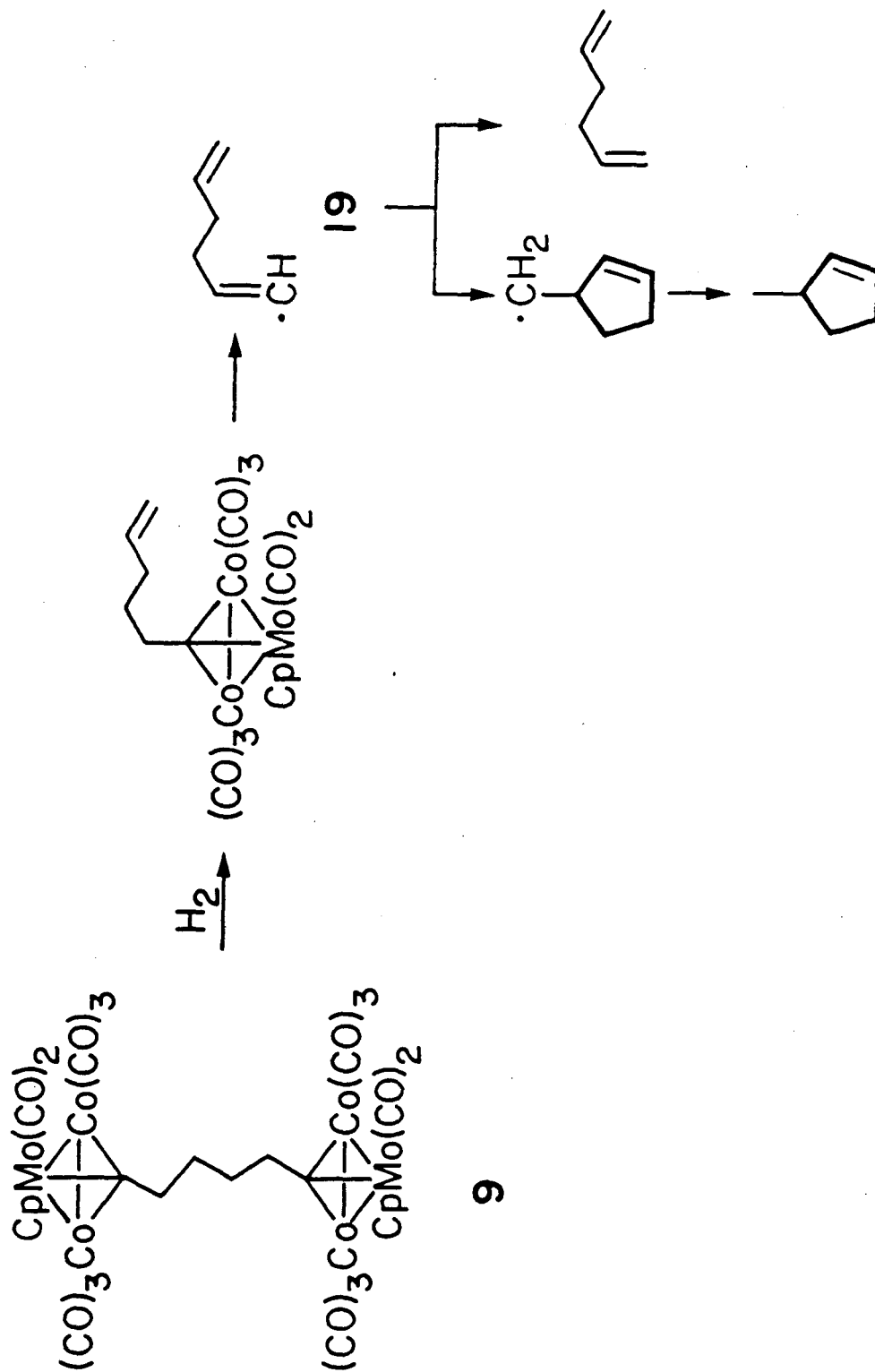
Rearrangement evidence for radicals. Compounds 3, 7, and 9 were prepared for the purpose of obtaining additional information supporting a radical mechanism as a principal pathway for the alkylidyne hydrogenolyses. Rapid rearrangement of an initially formed radical intermediate before interaction with its radical partner would implicate the existence of such species. Compounds 3 and 9 could conceivably lead, in analogy to alkylidyne 2, to the 3,3-dimethyl-1-penten-1-yl (18) and 1,5-hexadien-1-yl (19) radicals, respectively, rearrangement of which might yield the products shown in Schemes XIV and XV, explicable most simply only by radical pathways.⁴² Unfortunately, the second radical in the cage appears to be a very efficient trap for the vinyl radicals, and cage recombination must be occurring before rearrangement can take place; only those unrearranged organic products shown in Table I are produced.

However, the hydrogenolysis of cyclopropylmethyldiyne complex 7 does provide data consistent with a radical mechanism for cleavage of

Scheme XIV



Scheme XV



the organic moiety. No cyclopropyl-containing products are observed in the hydrogenolysis of 7, and a control experiment demonstrated that methylcyclopropane is stable to the reaction conditions. This is consistent with the production of cyclopropylcarbinyl radical as an intermediate,⁴³ which is known to very rapidly rearrange to the homoallylic radical (Scheme XVI),⁴⁴ accounting for the formation of the butenes and butane.

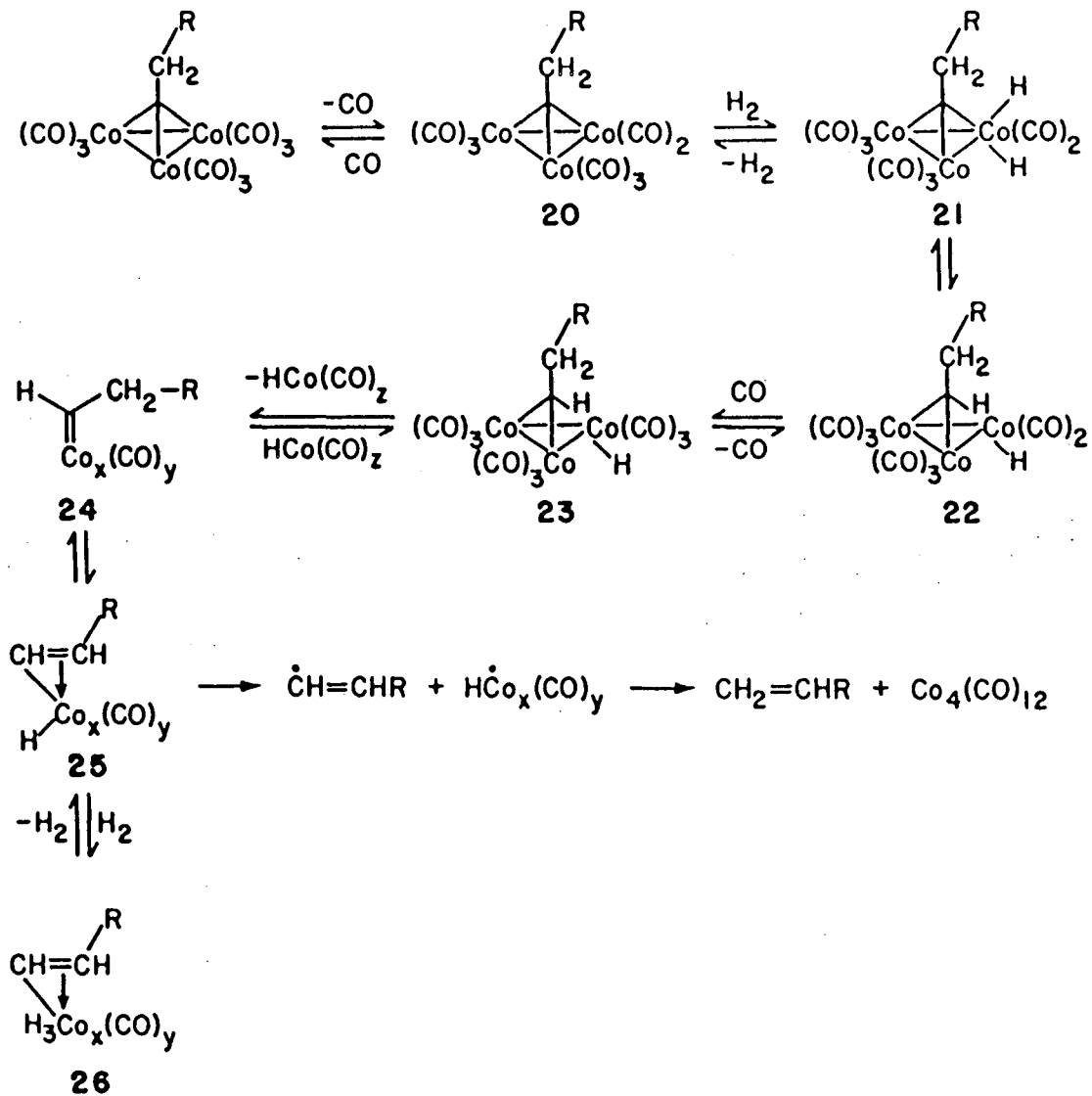
It is intriguing that cyclopentanone is also produced in this reaction; we hope to uncover the pathway by which it is formed. Preliminary investigation has shown that treatment of 7 with D₂ instead of H₂ leads to equal, though incomplete, incorporation of deuterium into the α and β positions of the cyclopentanone. Furthermore, reaction of complex 7 under a 50/50 (mol/mol) mixture of CO/H₂ in the presence of a large excess of trans-2-butene (7.2 equiv) showed no detectable consumption of the trans-2-butene. The large amount of trans-2-butene used prevents making the assertion that none of the cyclopentanone has this olefin as its source, but a rapid catalytic conversion of trans-2-butene to cyclopentanone can be ruled out.

Proposed mechanism. A sequence of reasonable intermediates which accounts for the mechanistic requirements described above is shown in Scheme XVII for the conversion of an alkylidyne complex to the corresponding alkene. We presume the reaction is initiated by CO dissociation from one metal center, followed by H₂ oxidative addition and cleavage, by reductive elimination, of a metal-carbon bond. In this manner, species 22 could be formed via 20 and 21. Intermediate 22 is a coordinatively unsaturated hydridocobalt alkylidene species,

Scheme XVI



Scheme XVII



which can achieve saturation by reassociation of CO to give compound 23. However, the number of carbonyl ligands and, for that matter, the number of cobalt atoms in these proposed intermediates is speculation; no information regarding the nuclearity of these species is available. Subsequent reaction steps are, therefore, presented in general terms which account for the products. Specifically, loss of a cobalt-hydride unit from a structure like 23 would yield a cobalt alkylidene (24) reminiscent of the $(\text{CpCo})_2(\mu\text{-CR}_2)$ species studied by Theopold and Bergman.²⁸ In the case of compounds 8 and 9, loss of a molybdenum hydride in this step would account for the observation of $\text{CpMo}(\text{CO})_3\text{H}$ and the identity of CIDNP from hydrogenolysis of 2 and 8. Rearrangement via β -elimination of alkylidene 24 (in a manner related to the mechanism proposed for the 1,2-carbon-carbon migration of the Theopold and Bergman alkylidenes) could lead to hydridovinyl complex 25. Such σ -bound vinyl structures are preceded in metal cluster chemistry.⁴⁵ Homolytic cleavage of the σ vinyl bond to cobalt would produce a tert-butylvinyl radical and the hypothesized (vide supra) hydridocobalt radical, although it is unclear why this bond should be so weak. The trapping and radical rearrangement experiments indicate that the partner to the tert-butylvinyl radical is an extremely good hydrogen atom donor. Final transfer of a hydrogen atom from the cobalt hydride to the tert-butylvinyl radicals would generate the alkene and a precursor to the ultimate organometallic product, $\text{Co}_4(\text{CO})_{12}$.

Explanation of the results of the labelling experiments is possible if the reasonable assumption is made that cleavage of the σ vinyl bond in 25 is a slow step. Rapid addition and elimination of hydrogen on a coordinatively unsaturated cobalt intermediate, such as

the interconversion of 25 and 26, combined with the reversibility of the steps leading up to 25 would allow introduction of deuterium into both the 1 and 2 positions of the alkene product when the alkylidyne cluster is treated with D_2 . This type of reversible addition and elimination of hydrogen has been well documented, particularly for osmium clusters.⁴⁶

Conclusion

A new, high yield, synthetic route has been found which gives trinuclear alkylidyne clusters from dinuclear alkyne complexes and metal hydrides. Hydrogenolysis of these clusters under mild conditions leads to mixtures of organic products containing (depending on structure) significant amounts of alkenes. Mechanistic studies demonstrate that radicals are involved in the process that leads to the observed organic products of the cluster hydrogenolyses. Substituted vinyl radicals have been identified as specific intermediates in the formation of olefinic products, and a metal hydride radical has been implicated as a potential radical-pair partner; the existence of these species gives rise to intense CIDNP. Indeed, this is the first organometallic cluster reaction for which CIDNP has been detected. Our results suggest that radicals should be considered as viable intermediates in other metal-carbon bond cleavage reactions of clusters, and perhaps of surfaces as well.

Experimental

Experimental details of the work carried out by J. E. Frommer and H. E. Bryndza, some of which have been incorporated into this chapter, can be found in their respective theses.^{8a,8b} In particular, initial product identification and corresponding kinetic studies for the hydrogenolysis of alkylidyne **2** have been described by Frommer. Bryndza is responsible for additional kinetic investigation, some trapping and labelling experiments, and the original detection and examination of CIDNP in this reaction. Preparation of clusters **2**, **2-d₂**, **4**, **5**, and **8** from dinuclear alkyne complexes and metal hydrides, and hydrogenation of **4**, **5**, and **6** were also performed by him. Those experiments not previously reported are described below.

For reference, the following characterizing data are listed for compounds **2**, **2-d₂**, **4**, **5**, and **8**.

For **2**: ¹H NMR (benzene-d₆) δ 3.73 (s, 2H), 0.98 (s, 9H); IR (benzene) 2095 (m), 2050 (s), 2035 (s), 2010 (m), 1975 (w) cm⁻¹; mp 127-128 °C. Anal. Calcd for C₁₅H₁₁Co₃O₉: C, 35.18; H, 2.17; Co, 34.53. Found: C, 35.49; H, 2.37; Co, 34.50.

For **2-d₂**: ¹H NMR (benzene-d₆) δ 1.06 (s); mass spectrum parent ion and ¹H NMR results indicate > 99 atom % D in the methylene group.

For **4**: ¹H NMR (benzene-d₆) δ 7.25-7.05 (m, 5H), 4.53 (s, 2H) in agreement with previously published preparations.^{11a}

For **5**: ¹H NMR (benzene-d₆) δ 3.5 (t, 2H, ³J_{HH} = 8), 1.8 (quintet, 2H, ³J_{HH} = 8), 1.15-1.25 (m, 4H), 0.83 (t, 3H, ³J_{HH} = 6) in agreement with previously published preparations.^{4e,11b,c}

For **8**: ¹H NMR (benzene-d₆) δ 4.43 (s, 5H), 4.26 (s, 2H), 1.18 (s, 9H).

General Information. Manipulations of organometallic compounds were conducted under anaerobic conditions. Experiments in the drybox were performed under a prescrubbed recirculating atmosphere of nitrogen maintained at 10-15 °C in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train and equipped with a -40 °C freezer. Exclusion of oxygen and water in the handling of materials outside of the drybox was accomplished using standard Schlenk or vacuum line techniques.

^1H NMR spectra were recorded on a Varian EM-390 90 MHz spectrometer or at 180, 200, or 250 MHz using Fourier transform NMR spectrometers outfitted with Cryomagnets Inc. magnets, Nicolet Model 1180 data collection systems, and electronics designed and assembled by Mr. Rudi Nunlist of the University of California, Berkeley. The spectra are reported in units of parts per million (ppm) (δ) downfield from tetramethylsilane (TMS). The residual proton resonances occurring at δ 1.93, 7.15, 1.38, and 2.09 ppm were used as internal standards for spectra recorded in acetonitrile- d_3 , benzene- d_6 , cyclohexane- d_{12} , and toluene- d_8 , respectively. ^1H NMR spectra recorded in pentane- h_{12} were referenced to the solvent resonance at δ 0.89 ppm, and were obtained using a PRESAT pulse sequence in which the solvent ^1H resonance was presaturated for 2 s with a decoupling signal at the appropriate frequency prior to the data acquisition pulse. ^{13}C and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 63.1 MHz and are reported in units of ppm (δ) downfield from TMS, with the solvent ^{13}C resonance serving as the internal standard: δ 128.0 ppm for benzene- d_6 and δ 14.3 ppm for pentane.

Electron spin resonance (ESR) spectra were obtained using a Varian E-3 ESR spectrometer. Solution infrared spectra were recorded using 0.10-mm sodium chloride cells on a Perkin-Elmer Model 283 grating spectrometer. Electron impact (EI) mass spectra were acquired at the UCB mass spectrometry laboratory on AEI MS-12 and Finnigan 4000 mass spectrometers. The Finnigan 4000 mass spectrometer was also used for GC/MS analyses. Elemental analyses were conducted by the UCB microanalytical laboratory. Melting points were recorded in sealed glass capillary tubes under nitrogen on a Thomas Hoover capillary melting point apparatus and are not corrected.

Preparative column chromatography was performed using degassed silica gel (70-230 mesh). All columns were packed and chromatograms run under air-free conditions in the drybox. Preparative gas chromatography (GC) was carried out on a Varian Aerograph model 90-P gas chromatograph. Fractions were collected in U-tubes packed with glass helices.

Benzene, diethyl ether, tetrahydrofuran (THF), and toluene were distilled from sodium-benzophenone ketyl under nitrogen before use. Olefin-free hexane was purified by distillation from LiAlH_4 or n-butyllithium. Olefin-free pentane was vacuum transferred from a sodium mirror. Benzene- d_6 and toluene- d_8 were dried over sodium-benzophenone ketyl and vacuum transferred prior to use. Cyclohexane- d_{12} was dried over sodium and then vacuum transferred. Acetonitrile- d_3 was vacuum transferred from 3 Å molecular sieves. 9,10-Dihydroanthracene was recrystallized from boiling ethanol. 3,3-Dimethyl-1-pentyne was prepared according to the method of Moulin,⁴⁷ and purified by preparative GC (10 % SE-30 on 60/80

Chromosorb 10 in a 20 ft. x 0.375 in. stainless-steel column). The procedure of Seyferth, Eschbach, Williams, and Hung¹⁹ was used to make $\text{Co}_3(\text{CO})_9\text{CCH}=\text{CH}_2$ (11). Isomerically pure trans-1-bromo-3,3-dimethyl-1-butene was prepared from 3,3-dimethyl-1-butyne, diisobutylaluminum hydride, and bromine according to the method of Zweifel.⁴⁸ All other solvents and reagents were reagent grade and were used without further purification.

$\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$ (3). In the drybox, a 50-mL single-neck round-bottom flask equipped with a vacuum stopcock and a magnetic stir bar was charged with 1.00 g (2.92 mmol) of $\text{Co}_2(\text{CO})_8$ and 25 mL of hexane. The sealed apparatus was removed from the drybox and attached to a vacuum line. Under a strong flow of argon, the teflon plug was removed from the stopcock, through which 0.297 g (3.09 mmol) of 3,3-dimethyl-1-pentyne was subsequently added to the flask via syringe. The teflon plug was replaced, and the reaction mixture was stirred under argon. Evolution of gas was observed. The reaction was monitored by taking IR spectra of aliquots of the reaction mixture removed periodically by syringe through the vacuum stopcock. Although most of the $\text{Co}_2(\text{CO})_8$ was consumed early on in the reaction, the mixture was stirred overnight in order to drive the reaction as far as possible. After 21.5 h, the volatile components were removed from the flask under vacuum, even though some $\text{Co}_2(\text{CO})_8$ could still be detected, leaving 1.10 g (98.6 %) of a red-brown oil. Although a trace of $\text{Co}_2(\text{CO})_8$ was seen in the IR spectrum, a ^1H NMR spectrum of the product exhibited only resonances attributable to dicobalt alkyne complex $\text{Co}_2(\text{CO})_6(\text{HCCC}(\text{CH}_3)_2\text{CH}_2\text{CH}_3)$. ^1H NMR (benzene- d_6) δ 5.46 (s, 1H), 1.30

(q, 2H, $^3J_{\text{HH}} = 7.4$), 1.00 (s, 6H), 0.71 (t, 3H, $^3J_{\text{HH}} = 7.4$); IR (hexane) 2090 (m), 2050 (s), 2020 (s), 2010 (m), 2085 (w), 1872 (w) cm^{-1} .

In the drybox, a 60-mL glass bomb with a teflon stopcock was charged with 1.35 g (3.95 mmol) of $\text{Co}_2(\text{CO})_8$ and the red-brown oil dissolved in 10 mL of benzene. The bomb was attached to a vacuum line, degassed through three freeze-pump-thaw cycles, and filled at -196°C with 650 torr of hydrogen (6.8 mmol) introduced via a trap cooled to -196°C . After closing off the bomb, it was heated in an oil bath at 65°C for 5 days. The volatile materials were removed from the bomb by vacuum transfer once the mixture had cooled to room temperature. In the drybox, the red-brown residue was extracted with 5-mL portions of hexane until the extracts had turned from red to brown. The combined hexane solution was purified by column chromatography using hexane as eluent. The first material to elute was complex 3. Solvent removal in vacuo from the solution of 3 obtained from the column, followed by recrystallization under argon from boiling methanol gave 0.541 g (35.2 %) of dark red crystals which were pure as judged by ^1H NMR and elemental analysis. ^1H NMR (benzene- d_6) δ 3.75 (s, 2H), 1.31 (q, 2H, $^3J_{\text{HH}} = 7.5$), 0.95 (s, 6H), 0.77 (t, 3H, $^3J_{\text{HH}} = 7.5$); IR (CCl_4) 2095 (m), 2050 (s), 2035 (s), 2010 (m), 1975 (w) cm^{-1} ; mp $47-48^\circ\text{C}$ (decomp). Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{Co}_3\text{O}_9$: C, 36.53; H, 2.49. Found: C, 36.56; H, 2.55.

Butyl cyclopropyldithiocarboxylate. This material was synthesized by a method analogous to that used by Meijer, Vermeer, and Brandsma⁴⁹ for the preparation of other dithioesters. A 25-mL two-neck round-bottom flask containing 0.197 g (8.10 mmol) of Mg turnings

was equipped with a magnetic stir bar, a Friedrich's condenser, and a rubber septum. A vacuum stopcock was attached to the top of the condenser. In the drybox, the flask was charged with 10 mL of THF. The sealed apparatus was removed to a vacuum line, the contents were placed under an argon atmosphere, and 1.00 g (8.26 mmol) of bromocyclopropane was added to the flask over 15 min via syringe through the rubber septum. After 1 h, all of the Mg had reacted. The flask was then cooled in an ice-acetone bath maintained at -10 to -5 °C, and 0.48 mL (8.0 mmol) of CS₂ was added to the reaction mixture over 10 min. via syringe. When the addition of CS₂ was complete, the cooling bath was removed, and the reaction was monitored by taking IR spectra of reaction mixture aliquots. After stirring for 1 h at room temperature, and then 1 h 15 min. while being heated at 65 °C with an oil bath, IR spectroscopy revealed no further change in the reaction mixture. Therefore, the mixture was allowed to cool to room temperature, and 1.00 mL (8.79 mmol) of 1-iodobutane was added dropwise to the flask by means of syringe. The flask was then heated in an oil bath at 50 °C for 1 h. After cooling to room temperature, the contents of the flask were carefully diluted with 25 mL of H₂O and extracted four times with 25-mL portions of diethyl ether. The combined ethereal extracts were dried over MgSO₄ and gravity filtered. Solvent was then removed by vacuum transfer. The yellow oil obtained was purified first by a pot-to-pot distillation at 10⁻⁵ torr using a microdistillation apparatus, followed by vacuum transfer at 10⁻³ torr and room temperature of any remaining 1-iodobutane from the distillate. A yield of 0.750 g (53.8 %) of a yellow liquid was

obtained. ^1H NMR (CDCl_3) δ 3.25 (t, 2H, $J = 7.4$), 2.70 (m, 1H), 1.64 (q, 2H, $J = 7.7$), 1.45 (m, 4H), 1.10 (m, 2H), 0.91 (t, 3H, $J = 7.3$); IR (neat) 3080 (w), 1185 (m), 1000 (m) cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_{14}\text{S}_2$: C, 55.12; H, 8.09. Found: C, 55.15; H, 8.13.

$\text{Co}_3(\text{CO})_9\text{C}(\overline{\text{CHCH}_2}\text{CH}_2)$ (7). Compound 7 was prepared in a manner similar to that used by Patin, Mignani, and van Hulle²⁰ in the synthesis of other alkylidynetricobalt nonacarbonyl complexes from dithioesters. In the drybox, 1.04 g (3.04 mmol) of $\text{Co}_2(\text{CO})_8$ was dissolved in 15.0 mL of benzene in a 25-mL two-neck round-bottom flask equipped with a magnetic stir bar, a straight reflux condenser, and a rubber septum. A vacuum stopcock was attached to the top of the condenser. The sealed apparatus was removed from the drybox and attached to a vacuum line. The contents of the apparatus were placed under an argon atmosphere, and 0.255 g (1.46 mmol) of butyl cyclopropyldithiocarboxylate was added all at once to the flask via syringe through the rubber septum. Gas evolution was observed. After stirring the reaction mixture for 10 min., the flask was heated in an oil bath at 85 °C. IR spectra of aliquots of the mixture removed periodically by syringe allowed monitoring of the progress of the reaction. After 2 h 50 min. the IR bands of 7 had replaced those of $\text{Co}_2(\text{CO})_8$, but heating was continued for a total of 4 h 10 min. to ensure completion of the reaction. The reaction mixture was then allowed to cool to room temperature, and the volatile components were removed in vacuo. In the drybox, the red-brown residue was extracted with 1- to 2-mL portions of hexane until the extract was nearly colorless. Purification of the combined hexane solutions by chromatography on silica using hexane as the eluent gave three bands: a

brown band which stayed near the top of the column; a yellow band which moved slowly; and a red-brown band containing 7, which came off the column first and was collected. The solvent was removed from the solution of 7 obtained from the column by vacuum transfer.

Recrystallization of the red residue from boiling methanol under argon gave 0.143 g (20.3 %) of 7, which was pure as judged by ^1H NMR and elemental analysis. ^1H NMR (benzene- d_6) δ 2.51 (m, 1H), 0.97 (m, 2H), 0.80 (m, 2H); IR (CCl_4) 2095 (m), 2050 (s), 2035 (s), 2010 (m), 1975 (w) cm^{-1} ; mp 160-161 $^\circ\text{C}$ (decomp). Anal. Calcd for $\text{C}_{13}\text{H}_5\text{Co}_3\text{O}_9$: C, 32.40; H, 1.04. Found: C, 32.61; H, 1.03.

$\text{Co}_2(\text{CO})_6[\text{HCC}(\text{CH}_2)_2\text{CCH}]\text{Co}_2(\text{CO})_6$ (10). A 50-mL single-neck round-bottom flask equipped with a vacuum stopcock and a magnetic stir bar was charged with 3.55 g (10.4 mmol) of $\text{Co}_2(\text{CO})_8$ and 25 mL of hexane in the drybox. The sealed apparatus was removed from the drybox and attached to a vacuum line. Under a strong flow of argon, the teflon plug was removed from the stopcock, and 0.50 mL (5.2 mmol) of 1,5-hexadiyne was added to the flask via syringe through the stopcock. The teflon plug was replaced, and the reaction mixture was stirred under argon. Evolution of gas was observed. IR spectra of aliquots of the reaction mixture removed periodically by syringe through the vacuum stopcock allowed observation of the progress of the reaction. After 2 h 30 min., the solvent was removed under vacuum. Extraction of the red-brown solid residue with hexane in the drybox, followed by suction filtration and recrystallization at -40°C from hexane, gave the double acetylene complex 10 in 62 % yield. ^1H NMR (benzene- d_6) δ 5.38 (s, 2H), 2.87 (s, 4H); IR (hexane) 2090 (m), 2055 (s), 2030

(s), 2010 (s), 1988 (w). Anal. Calcd for $C_{18}H_6Co_4O_{12}$: C, 33.26; H, 0.93. Found: C, 33.62; H, 1.08.

Reaction of $Co_2(CO)_6[HCC(CH_2)_2CCH]Co_2(CO)_6$ (10) with H_2 and $Co_2(CO)_8$. An unsuccessful attempt was made to synthesize the double cluster $[Co_3(CO)_9]C(CH_2)_4C[Co_3(CO)_9]$ via the same route as that used for compounds 2 - 5. A 60-mL glass bomb with a teflon stopcock was charged with 1.00 g (1.54 mmol) of 10, 1.01 g (2.95 mmol) of $Co_2(CO)_8$, and 10 mL of benzene in the drybox. The bomb was degassed on a vacuum line through three freeze-pump-thaw cycles and filled at $-196^\circ C$ with 650 torr of hydrogen (6.8 mmol) introduced via a trap cooled to $-196^\circ C$. After closing off the bomb, it was heated in an oil bath at $65^\circ C$ for 5 days. After cooling to room temperature, the solvent was removed in vacuo. 1H NMR analysis of the red-brown residue revealed a mixture of several materials. Column chromatography on silica with hexane as eluent led to several bands, the first of which to elute contained cluster 5. Solvent removal under vacuum from this fraction yielded 70.6 mg (9.0 % based on 10) of red-purple crystalline 5, which was identified by comparison of its 1H NMR spectrum to that of an authentic sample. Clean separation of the other components of the reaction mixture could not be achieved.

$[CpMoCo_2(CO)_8]C(CH_2)_4C[CpMoCo_2(CO)_8]$ (9). A 25-mL two-neck round-bottom flask equipped with a magnetic stir bar and a rubber septum was loaded with 0.403 g (0.620 mmol) of 10, 0.405 g (1.64 mmol) of $CpMo(CO)_3H$, and 10 mL of benzene in the drybox. After fitting the flask with a straight reflux condenser with a vacuum stopcock on top, the sealed apparatus was removed from the drybox and attached to a vacuum line. Argon was introduced through the vacuum stopcock, and

the flask was heated to 75 °C with an oil bath. Monitoring of the progress of the reaction was made possible by taking IR spectra of aliquots removed from the flask by way of syringe through the rubber septum. After 1 h, the IR spectra had ceased changing, and the flask was allowed to cool to room temperature. Solvent removal was by vacuum transfer. The dark green-brown residue was recrystallized twice from toluene/pentane at -40 °C in the drybox to give 0.257 g of green, crystalline double cluster 9. Recrystallization of the residue obtained from concentration of the mother liquor gave another crop of crystals of 9 (0.262 g), bringing the total yield of 9 to 77.1 %.

^1H NMR (benzene- d_6) δ 4.44 (s, 10H), 4.16 (br t, 4H, $J = 8$), 2.24 (br t, 4H, $J = 8$). IR (benzene) 2060 (m), 2020 (s), 2000 (s), 1945 (m) cm^{-1} ; mp > 315 °C. Anal. Calcd for $\text{C}_{32}\text{H}_{18}\text{Co}_4\text{Mo}_2\text{O}_{16}$: C, 35.39; H, 1.67. Found: C, 36.43; H, 1.78.

Hydrogenation of alkylidyne complexes. For the purpose of identifying the organic products of alkylidyne hydrogenolysis, reactions were conducted in a 45-mL glass bomb with a teflon stopcock. In a typical experiment, the bomb was loaded in the drybox with the alkylidyne cluster. Approximately 1-2 mL of the appropriate solvent for subsequent GC analysis was vacuum transferred into the bomb at -196 °C, followed by 650 torr of H_2 (ca. 6.0 mmol) which had passed through a trap cooled to -196 °C. After heating in an oil bath for 1 day at the temperature indicated in Table I, the reaction vessel was cooled to room temperature, and the volatile components of the mixture were vacuum transferred to a Schlenk flask with a rubber septum on the side arm. The products were identified by GC/MS and/or preparative GC

followed by ^1H NMR analysis as described below. Comparison of the ^1H NMR spectrum of the total volatile mixture with the results of separation indicated that all of the products had been identified.

Hydrogenation of $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$ (3). A sample of 3 (101 mg, 0.192 mmol) dissolved in pentane was treated with H_2 (6.0 mmol) in a glass bomb as described above. The organic products listed in Table I were separated by preparative GC with a 20 ft. x 0.25 in. stainless-steel column packed with 10 % SF-96 on acid-washed, dimethylchlorosilane-treated, 60/80 Chromosorb P. Identification was by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy as well as GC/MS analysis of a sample of the total volatile mixture. Observed for 3,3-dimethylpentane: ^1H NMR (benzene- d_6) δ 1.17 (q, 4H, $^3J_{\text{HH}} = 7.5$), 0.79 (s, 6H), 0.78 (t, 6H, $^3J_{\text{HH}} = 7.5$); mass spectrum (EI), m/e 99 ($\text{M}^+ - 1$), 85 ($\text{M}^+ - \text{CH}_3$), 71 ($\text{M}^+ - \text{CH}_2\text{CH}_3$), 43 ($\text{M}^+ - \text{C}_4\text{H}_9$, base).^{50a} Observed for 3,3-dimethyl-1-pentene: ^1H NMR (benzene- d_6) δ 5.70 (dd, 1H, $^3J_{\text{HH}} = 17.2$, $^3J_{\text{HH}} = 11.0$), 4.95 (dd, 1H, $^3J_{\text{HH}} = 11.0$, $^2J_{\text{HH}} = 1.5$), 4.92 (dd, 1H, $^3J_{\text{HH}} = 17.3$, $^2J_{\text{HH}} = 1.5$), 1.23 (q, 2H, $^3J_{\text{HH}} = 7.3$), 0.92 (s, 6H), 0.77 (t, 3H, $^3J_{\text{HH}} = 7.5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (pentane) δ 148.6 (C_2), 110.7 (C_1), 37.3 (C_3), 36.1 (C_4), 26.7 (CH_3 's on C_3), 9.1 (C_5); mass spectrum (EI), m/e 98 (M^+), 83 ($\text{M}^+ - \text{CH}_3$), 69 ($\text{M}^+ - \text{CH}_2\text{CH}_3$), 55 ($\text{M}^+ - \text{C}_3\text{H}_7$), 41 ($\text{M}^+ - \text{C}_4\text{H}_9$, base).^{50b-d} Observed for 4,4-dimethylhexanal: ^1H NMR (benzene- d_6) δ 9.34 (t, 1H, $^3J_{\text{HH}} = 1.7$), 1.77 (td, 2H, $^3J_{\text{HH}} = 8.1$, $^3J_{\text{HH}} = 1.8$), 1.2 (obscured), 0.97 (q, 2H, $^3J_{\text{HH}} = 7.6$), 0.65 (t, 3H, $^3J_{\text{HH}} = 7.5$), 0.60 (s, 6H); mass spectrum (EI), m/e 110 ($\text{M}^+ - \text{H}_2\text{O}$), 99 ($\text{M}^+ - \text{CH}_2\text{CH}_3$), 95 ($\text{M}^+ - \text{CH}_5\text{O}$), 81 ($\text{M}^+ - \text{C}_2\text{H}_7\text{O}$), 71 ($\text{M}^+ - \text{C}_4\text{H}_9$), 43 ($\text{M}^+ - \text{C}_5\text{H}_9\text{O}$, base).

Hydrogenation of $\text{Co}_3(\text{CO})_9\text{C}(\overline{\text{CHCH}_2\text{CH}_2})$ (7). A sample of 7 (43.7 mg, 0.0907 mmol) dissolved in benzene- d_6 was treated with H_2 (6.0 mmol)

in a glass bomb as described above. The C_4 organic products (Table I) were separated by preparative GC on a 24 ft. x 0.25 in. stainless-steel column packed with 15 % DBTCP on acid-washed, dimethylchlorosilane-treated, 60/80 Chromosorb P. A 20 ft. x 0.25 in. stainless-steel column packed with 10 % SF-96 on acid-washed, dimethylchlorosilane-treated, 60/80 Chromosorb P allowed separation of cyclopentanone. Identification was by comparison of retention times and 1H NMR spectra to those of authentic samples. Use of the latter column revealed a trace of other products with olefinic resonances at δ 5.43 (m) ppm. GC/MS analysis of a sample of the total volatile mixture showed that two materials with a composition of C_8H_{16} (m/e 112, M^+) were present, and these materials are listed as C_8 olefins in Table I. GC/MS of the total volatile mixture also confirmed the formation of cyclopentanone.

This experiment was repeated using D_2 (6.0 mmol) instead of H_2 and 74.5 mg (0.154 mmol) of 7. The 1H NMR spectrum of the cyclopentanone obtained after preparative GC showed broadened resonances with equal integrations (1.00:1.00 relative areas) for the α and β positions. This indicated that a comparable amount of deuterium had been incorporated into both positions.

Hydrogenation of $[CpMoCo_2(CO)_8]C(CH_2)_4C[CpMoCo_2(CO)_8]$ (9). A sample of 9 (114 mg, 0.105 mmol) dissolved in C_6D_6 was treated with H_2 in a glass bomb as described above. Separation of the organic products was achieved by preparative GC using a 20 ft. x 0.25 in. stainless-steel column packed with 10 % SF-96 on acid-washed, dimethylchlorosilane-treated, 60/80 Chromosorb P. Agreement of

retention times and ^1H NMR spectra with those of authentic samples, as well as GC/MS analysis of a sample of the total volatile mixture, permitted making the assignments shown in Table I.

NMR and ESR Experiments. Hydrogenation studies conducted by NMR were run as follows. An NMR tube fused to a 14/20 ground glass joint was loaded in the drybox with the alkylidyne starting material and any non-gaseous additive or co-reactant. The tube was capped with a vacuum stopcock and attached to a vacuum line. Approximately 0.6 mL of solvent was vacuum transferred into the tube at -196°C , followed by 650 torr of hydrogen introduced via a trap cooled to -196°C . After equilibrating for one min., the tube was sealed approximately 20 cm above the solution. Thus, the tube contained ca. 3 mL of hydrogen at -196°C (ca. 0.40 mmol). The tube was then heated and observed as described below. For the CIDNP studies, this involved placing the tube in a 20°C NMR probe and taking ^1H NMR spectra as the probe was heated as quickly as possible to the desired hydrogenation temperature (Table I).

In those experiments involving further analysis of the volatile components of the reaction mixture, opening of NMR tubes was done in the tube cracking apparatus shown in Figure X.⁵¹ Prior to placing the tube into the apparatus through Solv-Seal⁵² port A, the tube was scored with a file at the point indicated by the arrow. The apparatus was evacuated and then cooled to -196°C . With valve B closed, teflon plug C was tightened until the NMR tube broke open. If hydrogen was present, it was removed under vacuum while the reaction mixture was held at -196°C . The remaining volatile materials were vacuum transferred from the NMR tube as the apparatus slowly warmed to room

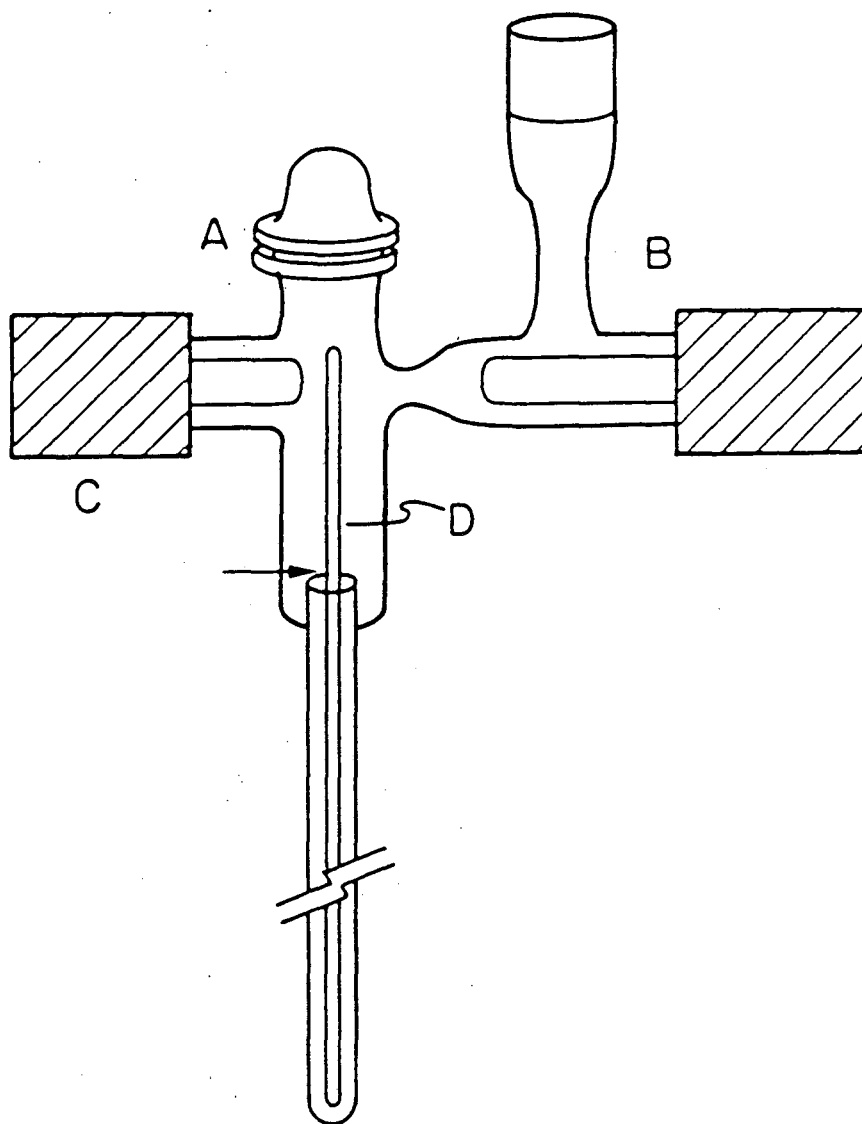


Figure X. Apparatus for opening sealed NMR tubes:
(A) Solv-Seal joint; (B) vacuum stopcock
with teflon plug; (C) teflon plug;
(D) sealed NMR tube. The arrow indicates
the location of the score on the NMR tube.

temperature.

Samples for ESR experiments were prepared in exactly the same manner as the NMR samples, except a quartz ESR tube fused to a 14/20 quartz joint was used. Only 0.15 mL of solvent and ca. 1.5 mL of hydrogen at -196°C (ca. 0.20 mmol) were placed in the tube. ESR spectra of the samples were taken as the temperature of the ESR cavity was raised from 25°C to 100°C .

Hydrogenation of $\text{CpMoCo}_2(\text{CO})_8\text{CCH}_2\text{C}(\text{CH}_3)_3$ (8). An NMR tube was prepared as described above with 10 mg (0.017 mmol) of 8, 0.6 mL of benzene- d_6 , and 0.40 mmol of H_2 . The sealed tube was placed in a 20°C NMR probe and heated to 60°C as quickly as possible. The same CIDNP as observed in the hydrogenation of 2 was exhibited in the ^1H NMR spectra taken throughout the course of the reaction. Approximately 20 % conversion was achieved within 15 min. at 60°C as determined by integration relative to benzene- d_5 , and the reaction was complete after 1.5 h at 60°C . The products were identified by comparison to ^1H NMR spectra of authentic samples.

Hydrogenation of $\text{Co}_3(\text{CO})_9\text{CCH}=\text{CH}_2$ (11). Using the procedure outlined above, an NMR tube containing 20 mg (0.043 mmol) of 11, 0.6 mL of benzene- d_6 , and 0.40 mmol of H_2 was prepared. The sealed tube was placed in a 20°C NMR probe, and ^1H NMR spectra were taken as the probe was heated first to 60°C , and then to 80°C . No CIDNP was detected. In fact, no reaction occurred until the sample reached 80°C , at which point the resonances of 11 gave way to those of the known complex $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{CH}_3$ (δ 3.25 (q, 2H, $^3J_{\text{HH}} = 7.2$), 1.18 (t, 3H, $^3J_{\text{HH}} = 7.2$) ppm)²¹ in 43 % yield as determined by integration using the benzene- d_5 resonance as an internal standard.

Photolysis of $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_3$ (2) under H_2 . An NMR tube containing 21.8 mg (0.0426 mmol) of 2, 0.6 mL of toluene- d_8 , and 0.40 mmol of H_2 was prepared as described above. The tube was immersed in a methanol bath that was cooled with a Neslab Cryocool CC-100 immersion cooler. Irradiation was conducted with a Hanovia 450-W medium-pressure mercury lamp powered by a Model 7830 Ace-Glass power supply and mounted in a vacuum-jacketed quartz cooling immersion well containing circulating water. While being transported for ^1H NMR analysis, the sample was stored in a dry ice/acetone bath. The NMR probe was cooled prior to insertion of the sample tube. Photolysis at -75°C for 1 h, -50°C for 1 h, and -40°C for 7.5 h led to no observable products (2 is not completely dissolved at these temperatures). Only after photolysis at -20°C for 1 h was alkene 12 detected ($< 10\%$ conversion) by ^1H NMR at -20°C . No other materials besides 2 and 12, particularly no hydrogenolysis intermediates or species exhibiting high field resonances, were observed.

Reaction of $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_3$ (2) with Me_3NO . In the drybox, an NMR tube fused to a 14/20 ground glass joint was charged with 25.8 mg (0.0504 mmol) of 2 and 3.8 mg (0.050 mmol) of Me_3NO . The tube was fitted with a vacuum stopcock, attached to a vacuum line, and filled with 0.6 mL of toluene- d_8 by vacuum transfer at -196°C . The reaction mixture was introduced into the NMR probe, which was precooled to -85°C , and examined by taking ^1H NMR spectra as the sample was warmed in 10° intervals. No reaction was observed up to -25°C . Upon warming to -15°C , the ^1H NMR spectrum irreversibly broadened as red-brown material precipitated in the tube. While the Me_3NO was

consumed, the bulk of 2 was not, and it appears that each molecule of 2 reacts with more than one molecule of Me_3NO , even though only 1 equiv of Me_3NO is present. No stable, soluble species, such as an unsaturated intermediate, was detected.

Hydrogenation of $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_3$ (2) over Hg. An NMR tube sample containing 20.8 mg (0.0406 mmol) of 2, 0.400 g (1.99 mmol) of Hg, 0.6 mL of benzene- d_6 , and 0.40 mmol of H_2 was prepared as described above. The sealed tube was placed in a 20 °C NMR probe, and ^1H NMR spectra were taken while the probe was heated to and maintained at 60 °C. The sample was occasionally removed briefly from the probe and shaken to ensure contact of the Hg with any cobalt metal particles possibly produced. The spectra obtained were indistinguishable from spectra of samples prepared without the Hg (20 mg 2, 0.6 mL benzene, 0.40 mmol H_2), including the observed CIDNP resonances for alkene 12. The rate of reaction was also roughly the same, giving approximately 20 % conversion after 0.5 h at 60 °C, as measured by integration of the tert-butyl resonances.

Hydrogenation of $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_3$ (2) under C_2F_2 . Using the method described above, an NMR sample consisting of 20.8 mg (0.0406 mmol) of 2, tetrafluoroethylene, 0.6 mL of benzene- d_6 , and 0.40 mmol of H_2 was prepared. The tetrafluoroethylene (200 torr, 5.72 mL at 298 °K; 0.0615 mmol) was vacuum transferred into the tube from a known-volume bulb prior to the addition of H_2 to the mixture. The sealed tube was placed in a 20 °C NMR probe, and ^1H NMR spectra were taken while the probe was heated to and maintained at 60 °C. Again the spectra obtained were indistinguishable from spectra of samples prepared without C_2F_2 (20 mg 2, 0.6 mL benzene, 0.40 mmol H_2).

including the observed CIDNP resonances for alkene 12. More importantly, the rate of reaction was the same, giving approximately 20 % conversion after 10 minutes, as measured by integration of the tert-butyl resonances. Significant inhibition was evident.

Hydrogenation of $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_3$ (2) in the presence of 9,10-dihydroanthracene. A sample of 2 was prepared as described earlier with 20.0 mg (0.0418 mmol) of 2, 107 mg (0.594 mmol) of 9,10-dihydroanthracene, 0.6 mL of benzene- d_6 to bring the total solution volume to 0.60 mL, and 0.40 mmol of H_2 . The sealed tube was placed in a 20 °C NMR probe, and ^1H NMR spectra were taken while the probe was heated. As the probe temperature reached 60 °C, the CIDNP pattern normally observed for alkene 12 was only weakly apparent and died away quickly. Heating further to 80 °C and then 90 °C only accelerated the formation of 12 with no increase in the CIDNP intensity. At no point was CIDNP for anthracene or 9,10-dihydroanthracene resonances observed.

Hydrogenation of $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_3$ (2) in the presence of *t*-BuNO. In an attempt to form long-lived radicals capable of detection by ESR spectroscopy, the hydrogenolysis of 2 was carried out in the presence of *t*-BuNO. The reaction was first examined by ^1H NMR spectroscopy. An NMR tube sample containing 21.4 mg (0.0418 mmol) of 2, 36.3 mg (0.417 mmol) of *t*-BuNO, 0.6 mL of benzene- d_6 , and 0.40 mmol of H_2 was prepared as indicated above. ^1H NMR spectra recorded as the sample was heated in an NMR probe from 20 °C to 60 °C showed only the shifting of the equilibrium between *t*-BuNO (δ 0.92 ppm) and its dimer

(δ 1.48 ppm) toward the monomer.⁵³ As the sample was maintained at 60 °C, and subsequently heated to 80 °C and then 100 °C, no resonances due to alkene 12 were produced as 2 was consumed, and no CIDNP was observed. A multitude of new, unidentified, t-Bu resonances grew into the spectrum. The t-BuNO was clearly diverting the course of the reaction.

For a typical ESR experiment, a sample was prepared as described above with 14.4 mg (0.0281 mmol) of 2, 18.2 mg (0.209 mmol) of t-BuNO, 0.15 mL of benzene-d₆, and 0.20 mmol of H₂. The sealed tube was placed into an ESR cavity held at 25 °C. A variety of signals were immediately evident. A 1:1:1 triplet ($g = 2.006$, $a_N = 15.5$ G) was assigned to the decomposition product of t-BuNO, namely (t-Bu)₂ $\dot{N}O$.^{36a,b} The remainder of the signals could be accounted for as a composite of two resonances: a doublet of 1:1:1 triplets ($g = 2.006$, $a_H = 22$ G, $a_N = 15.5$ G) (resonance A) and a 1:1:1 triplet of doublets ($g = 2.006$, $a_N = 13.5$ G, $a_H = 11$ G) (resonance B). The sample was heated in the ESR cavity, and spectra were taken of the new radicals up to 86 °C. Above that temperature, the signal due to (t-Bu)₂ $\dot{N}O$ became overwhelmingly intense. Spectra taken above room temperature exhibited a third resonance pattern (C) consisting of a 1:1:1 triplet of doublets ($g = 2.006$, $a_N = 14$, $a_H = 3$). Resonance A slowly disappeared upon heating, and was not evident above 46 °C. Resonance B was most intense at ca. 50 °C, and heating to 70 °C gave resonance C at its highest intensity and in the absence of resonances A and B. See the text for the assignment of structures to A, B, and C.

Reaction of trans-1-bromo-3,3-dimethyl-1-butene, $(n\text{-Bu})_3\text{SnH}$, and $t\text{-BuNO}$. An ESR tube was charged in the drybox with 30.7 mg (0.105 mmol) of $(n\text{-Bu})_3\text{SnH}$, 1.3 mg (0.015 mmol) of $t\text{-BuNO}$, and 0.15 mL of benzene and capped with a rubber septum. The sample was removed to the ESR spectrometer, where only signals due to $(t\text{-Bu})_2\dot{\text{N}}\text{O}$ were detected.^{36a,b} Spectra obtained at room temperature following the injection of 40 μL of an 11 % solution of trans-1-bromo-3,3-dimethyl-1-butene in THF (0.035 mmol) showed a resonance split into a 1:1:1 triplet of doublets ($g = 2.006$, $a_{\text{H}} = 22\text{G}$, $a_{\text{N}} = 15.5\text{G}$), each peak of which exhibited a partially resolved splitting of ca. 0.5 G. The resonance due to $(t\text{-Bu})_2\dot{\text{N}}\text{O}$ was also still present.

Hydrogenation of $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_3$ (2) in the presence of TEMPO. An NMR tube sample containing 14.0 mg (0.0273 mmol) of 2, 42.2 mg (0.270 mmol) of TEMPO, 0.6 mL of benzene- d_6 , and 0.40 mmol of H_2 was prepared as indicated earlier. The sealed tube was placed in a 20 °C NMR probe, and ^1H NMR spectra were acquired as the probe was heated to 60 °C, and then further to 80 °C and 100 °C. No CIDNP was detected at any point during the reaction. While all peaks were severely broadened, resonances due to alkene 12 as well as a variety of unidentified alkyl resonances were observed. Attempts to separate the volatile components of this mixture by GC were unsuccessful.

Hydrogenation of $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_3$ (2) in CCl_4 . A sample for ^1H NMR analysis was prepared with 20.0 mg (0.0390 mmol) of 2, 0.6 mL of CCl_4 , and 0.40 mmol of H_2 in the manner described above. No CIDNP was detected as the sample was heated from 20 °C to 80 °C in an NMR probe, and all of the resonances broadened. After heating the reaction mixture in an oil bath at 60 °C for 2 days, a ^1H NMR spectrum

of the volatile components revealed, among others, a multitude of tert-butyl resonances. GC/MS analysis of the reaction mixture volatiles indicated that several hydrocarbons had been produced, but Cl_3CCCl_3 was the primary chlorine containing product, as confirmed by comparison to an authentic sample. Only traces of other chlorinated materials were detected.

Hydrogenation of $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{C}(\text{CH}_3)_3$ (2) in the presence of 1-bromomethyl-4-methylbenzene. Using the method described above, an NMR sample consisting of 20.4 mg (0.0398 mmol) of 2, 102 mg (0.551 mmol) of 1-bromomethyl-4-methylbenzene, 0.6 mL of benzene- d_6 , and 0.40 mmol of H_2 was prepared. Heating of the sealed tube from 20 °C to 60 °C in an NMR probe showed the usual CIDNP detected for alkene 12. Following heating of the sample for 2 days at 90 °C in an oil bath, a ^1H NMR spectrum showed no alkene 12 and no 2; 1,4-dimethyl benzene (ca. 50 % yield based on 1-bromomethyl-4-methylbenzene, ca. 270 % based on 2) and HBr (ca. 25 % yield based on 1-bromomethyl-4-benzene, ca. 130 % based on 2) had been produced, as confirmed with authentic samples. Several other materials with tert-butyl resonances were also evident. Attempts to separate these compounds by column chromatography were unsuccessful.

Labelling experiments. In addition to those labelling studies executed by Bryndza,^{8b} the following experiments were carried out. An NMR tube was charged with 11.6 mg (0.0226 mmol) of 2, TMS (16 torr, 5.72 mL at 293 °K; 0.0050 mmol), 0.6 mL of benzene- d_6 , and 0.40 mmol of D_2 using the method described above. The sealed tube was heated at 60 °C in a constant temperature water bath, and periodically cooled in

an ice-water bath and analyzed by ^1H NMR spectroscopy. Integration relative to the TMS internal standard gave the hydrogen content of alkene 12, which is presented in the Results and Discussion section.

A second NMR experiment involving 2 (81.4 mg, 0.159 mmol) and D_2 (0.40 mmol) was conducted in 0.50 mL of pentane. After heating at 60 °C in a constant temperature water bath for 2 days, a PRESAT ^1H NMR spectrum of the reaction mixture showed complex multiplet resonances for both internal and terminal olefinic protons of alkene 12, indicating deuterium incorporation into both positions. Significantly, deuterium had not completely washed into either olefinic position.

Similar experiments were performed with cluster 3. In the manner described earlier, a sealed NMR tube sample was prepared with 65.0 mg (0.124 mmol) of 3, 0.40 mL of pentane, and 0.40 mmol D_2 . The sealed tube was heated in an oil bath at 70 °C for 1 day. The 3,3-dimethylpentane and 3,3-dimethyl-1-pentene were isolated from the mixture by preparative GC using a 20 ft. x 0.25 in. stainless-steel column packed with 10 % SF-96 on acid-washed, dimethylchlorosilane-treated, 60/80 Chromosorb P. Integration of the ^1H NMR spectra of these materials in benzene- d_6 gave the hydrogen content listed in the Results and Discussion section.

Another NMR sample containing 15.6 mg (0.0296 mmol) of 3, 0.6 mL of cyclohexane- d_{12} , and 0.40 mmol of D_2 was heated in an NMR probe from 20 °C to 60 °C, and then to 80 °C. No CIDNP was observed. While the products were not separated, complex multiplet resonances for both olefinic positions (internal and terminal) of 3,3-dimethyl-1-pentene were observed. This indicated the presence of hydrogen and deuterium

in both positions, and is consistent with the results obtained in pentane.

Trapping experiments. Confirmation of those trapping experiments carried out by Bryndza^{8b} and GC/MS analysis of the alkene 12 produced were obtained as follows. A typical NMR sample was prepared containing 46 mg (0.090 mmol) of 2-d₂, 191 mg (1.06 mmol) of 9,10-dihydroanthracene, 0.40 mmol of D₂, and enough benzene-d₆ to give 0.60 mL of solution. A control sample was prepared with no 9,10-dihydroanthracene. Both samples were heated for 45 min. at 60 °C, after which the volatiles were analyzed by ¹H NMR spectroscopy. Whereas the alkene 12 produced in the absence of 9,10-dihydroanthracene was found to be > 98 % 12-d₃ from the ¹H NMR analysis, GC/MS examination of the volatiles in the control reaction gave 82 % 12-d₃, 16 % 12-d₂, 3 % 12-d₁, and 0 % 12-d₀. This is presumably an artifact of the GC/MS method of analysis, and may be due to a variation in fragmentation rates with deuterium incorporation or hydrogen-deuterium exchange within the machine. Nevertheless, the mixture containing 9,10-dihydroanthracene gave 73 % 12-d₃, 20 % 12-d₂, 6 % 12-d₁, and 1 % 12-d₀, corresponding to 10 % incorporation of hydrogen (calculated based on the control: 73 % 12-d₃, 22 % 12-d₂, 4 % 12-d₁, < 1 % 12-d₀). This is in agreement with the ¹H NMR results,^{8b} and indicates one hydrogen is incorporated into each molecule of 12 formed from trapping.

Hydrogenation of Co₃(CO)₉C(CHCH₂CH₂) (7) in the presence of methylcyclopropane. An NMR tube sample containing 10.8 mg (0.0224 mmol) of 7, methylcyclopropane (73 torr, 5.72 mL at 298 °K; 0.022 mmol), 0.6 mL of benzene-d₆, and 0.40 mmol of H₂ was prepared. The

reaction mixture was heated in an oil bath at 97 °C and monitored by taking ^1H NMR spectra periodically. Integration using the benzene- d_5 resonance as an internal standard showed that the methylcyclopropane was not consumed during the course of the reaction.

Reaction of $\text{Co}_3(\text{CO})_9\text{C}(\overline{\text{CHCH}_2\text{CH}_2})$ (7) with a mixture of CO , H_2 , and trans-2-butene. A sealed NMR tube was prepared containing 19.4 mg (0.0402 mmol) of 7, trans-2-butene (100 torr, 53.93 mL at 298 °K; 0.290 mmol), 0.60 mL benzene- d_6 , and 650 torr of a 50/50 mixture of CO and H_2 (ca. 0.20 mmol each) in the manner described earlier. The reaction was examined over a temperature range of 25-120 °C. While formation of the products listed in Table I was detected at 85 °C and higher temperatures, no significant change in the amount of trans-2-butene present was observed by ^1H NMR spectroscopy, even after 2 days at 85 °C and 1 h at 120 °C.

Appendix

**X-ray Crystal and Molecular Structure of
1,1,1,2,2,2,3,3,3-Nonacarbonyl- μ_3 -cyclopropylmethylidyne-triangulo-
tricobalt, $(\mu_3\text{-}\xi\text{-C}_3\text{H}_5\text{C})\text{Co}_3(\text{CO})_9$ ⁵⁴**

Abstract. $M_r = 481.98$, triclinic, $P\bar{1}$, $a = 7.8772(6) \text{ \AA}$, $b = 14.3778(17) \text{ \AA}$, $c = 15.7851(16) \text{ \AA}$, $\alpha = 103.700(9)^\circ$, $\beta = 100.877(7)^\circ$, $\gamma = 99.365(8)^\circ$, $V = 1664.9(7) \text{ \AA}^3$, $Z = 4$, $D_x = 1.923 \text{ g/cm}^3$, Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 29.93 \text{ cm}^{-1}$, $F(000) = 944$, $T = 296 \text{ K}$, $R = 2.7\%$, $R_w = 3.6\%$, $R_{\text{all}} = 3.7\%$, $S = 1.67$ for 3691 observations with $I > 3\sigma(I)$. The final structure clearly shows the staggering of the Co-Co-Co and C-C-C rings in a nearly three-fold symmetric environment. There are no intermolecular contacts shorter than $2.70 \text{ \AA}$.

Introduction. A recently developed and important class of organometallic clusters is the alkylidynetricobalt nonacarbonyl series.^{9a} Such compounds have been shown to exhibit interesting reactivity,⁵⁵ and have even found use as catalyst precursors for certain transformations.^{22b}

Sutton and Dahl first structurally characterized a member of this class using film data;⁵⁶ more recently, published reviews have described the interesting structural features of these compounds.^{55a,57} In order to add to the available data, and also to investigate the possibility of interaction between the strained cyclopropyl ring and the tricobalt ring, we chose to determine the molecular structure of the title compound, $(\mu_3\text{-}\xi\text{-C}_3\text{H}_5\text{C})\text{Co}_3(\text{CO})_9$.

Experimental. Material prepared from butyl cyclopropyldithiocarboxylate and $\text{Co}_2(\text{CO})_8$;²⁰ crystallized from hot methanol under argon

as oblong burgundy flakes; data crystal 0.12 x 0.15 x 0.50 mm; mounted on a glass fiber with polycyanoacrylate cement with the major crystal axis approximately perpendicular to the fiber axis; Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo K α radiation; 24 well-centered reflections with $27^\circ < 2\theta < 36^\circ$ used to obtain lattice parameters; 4543 data collected at 296(2) K over 86 h using θ - 2θ scans from $3 < 2\theta < 45^\circ$ with $(\sin \theta/\lambda)_{\max} = 0.538 \text{ \AA}^{-1}$; $h \pm 8$, $k \pm 15$, l 0 to ± 16 ; intensity standards 423, 541, 426 every 2 h of exposure; data corrected for isotropic decay due to radiation damage to a maximum of 21.7%; orientation standards checked every 250 reflections with no reorientation necessary; data reduction through Frenz Structure Determination Package⁵⁸ providing scattering factors and corrections for anomalous dispersion⁵⁹ and all other programs; data analytically corrected for absorption, with correction based on crystal shape; $\mu = 29.93 \text{ cm}^{-1}$, maximum transmission coefficient 0.73, minimum 0.30, average 0.60; corrected for secondary extinction, $g = 1.443 \times 10^{-7}$ (refined); phased via MULTAN 11/82;⁶⁰ balance of non-hydrogen atoms located through combination of difference Fourier and SEARCH techniques and refined anisotropically with full-matrix non-linear least squares; function minimized in least squares was $\sum w(F_o - F_c)^2$ where $w = 1/\sigma(F_o^2)$, and $\sigma(F_o^2) = \{[(\sigma_I)^2 + [0.035(F_o)^2]^2\}^{1/2}$, where σ_I is based on counting statistics; all hydrogen atom positions calculated (not refined) based on the attached carbon at fixed distances (0.95 Å); all hydrogen atoms given fixed isotropic thermal parameters based on the attached carbon; largest feature in final difference Fourier map $0.59 \text{ e \AA}^{-3}$ near C(6); refining 452 variables against 4352 unique data, 3691 with $I > 3\sigma(I)$, $R = 0.027$, $R_w = 0.036$.

$$R_{all} = 0.037, S = 1.67, (\Delta/\sigma)_{max} = 0.15.$$

Discussion. Data appropriate to discussion of the structure are given in Tables 1 and 2.⁶¹ The data clearly demonstrate that $(\mu_3\text{-}\eta\text{-C}_3\text{H}_5\text{C})\text{Co}_3(\text{CO})_9$ exists as discrete molecules in the solid state; no intermolecular contacts shorter than 2.70 Å were observed.

As may be seen from Table 2 and Figure 1, the three cobalt atoms form an equilateral triangle within experimental error, with average bond distances of 2.470(2) Å. The structure of the nonacarbonyl-tricobalt fragment of the molecule is what would be expected intuitively for such a species. The carbonyl ligands have quite normal bonding distances and the Co-C-O angles are essentially linear. One interesting result is that the average Co-C(equatorial carbonyl) bond distance, e.g. Co(1)-C(12), is approximately 0.05 Å shorter than the average Co-C(axial carbonyl) bond distance, e.g. Co(1)-C(11), although all C-O carbonyl bond lengths are experimentally equal. This result has been observed previously for $(\mu_3\text{-HC})\text{Co}_3(\text{CO})_9$ in both neutron and X-ray studies.⁶³

The average Co-C(alkylidyne) bond distance is 1.911(4) Å, with the carbon lying 1.271(3) Å above the tricobalt plane. These distances agree well with the respective values of 1.90(2) Å and 1.25(3) Å determined for $(\mu_3\text{-CH}_3\text{C})\text{Co}_3(\text{CO})_9$.⁵⁶

The effect of increased carbon p orbital contribution to the C-C bonding⁶⁴ may be seen by considering the C-C bond distances of the cyclopropyl fragment. The average C(alkylidyne)-C(cyclopropyl) bonding distance is 1.465(4) Å, significantly shorter than the average $\text{sp}^3\text{-sp}^3$ C-C bond length of 1.54 Å⁶⁵ and shorter even than the

Table 1. Table of positional parameters, equivalent isotropic thermal parameters and their estimated standard deviations

$$B_{eq} = \{a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)\}.$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Co(1)	0.12261 (5)	-0.30524 (3)	0.46586 (3)	2.809 (9)
Co(2)	0.42814 (5)	-0.22137 (3)	0.47705 (3)	2.865 (9)
Co(3)	0.28864 (5)	-0.17659 (3)	0.60421 (3)	2.797 (9)
Co(4)	0.02925 (5)	0.19022 (3)	-0.11764 (3)	3.21 (1)
Co(5)	0.33304 (6)	0.20011 (3)	-0.10367 (3)	3.36 (1)
Co(6)	0.27906 (6)	0.17298 (3)	-0.00576 (3)	3.37 (1)
O(11)	-0.0802 (3)	-0.1916 (2)	0.3684 (2)	5.87 (7)
O(12)	0.1091 (4)	-0.4782 (2)	0.3221 (2)	6.60 (8)
O(13)	-0.1432 (4)	-0.3984 (2)	0.5424 (2)	7.68 (9)
O(21)	0.3487 (3)	-0.0709 (2)	0.3854 (2)	5.75 (7)
O(22)	0.7938 (3)	-0.1460 (2)	0.5792 (2)	6.35 (8)
O(23)	0.5147 (4)	-0.3663 (2)	0.3384 (2)	7.45 (9)
O(31)	0.1776 (3)	-0.0041 (2)	0.5583 (2)	5.57 (7)
O(32)	0.0605 (3)	-0.2224 (2)	0.7215 (2)	6.16 (7)
O(33)	0.6017 (4)	-0.0770 (2)	0.7488 (2)	6.46 (8)
O(41)	0.0177 (4)	0.0168 (2)	-0.2652 (2)	6.34 (8)
O(42)	-0.1675 (4)	0.3124 (2)	-0.2018 (2)	7.46 (8)
O(43)	-0.2524 (3)	0.1174 (2)	-0.0389 (2)	7.44 (9)
O(51)	0.4417 (4)	0.1407 (2)	-0.2422 (2)	7.09 (8)
O(52)	0.6662 (4)	0.4043 (3)	0.0086 (2)	9.4 (1)
O(53)	0.2309 (4)	0.4224 (2)	-0.1975 (2)	7.46 (9)
O(61)	0.3473 (4)	-0.0102 (2)	-0.1121 (2)	6.27 (8)
O(62)	0.0746 (4)	0.0969 (2)	0.1094 (2)	6.75 (8)
O(63)	0.6143 (4)	0.2487 (3)	0.1285 (2)	7.25 (9)
C(1)	0.3388 (4)	-0.2983 (2)	0.5492 (2)	2.86 (7)
C(2)	0.4043 (4)	-0.3764 (2)	0.5812 (2)	3.87 (8)
C(3)	0.5418 (5)	-0.3555 (3)	0.6666 (3)	5.6 (1)
C(4)	0.3591 (5)	-0.4051 (3)	0.6608 (3)	5.3 (1)
C(5)	0.1907 (4)	0.2865 (2)	-0.0177 (2)	3.23 (7)
C(6)	0.1569 (5)	0.1721 (3)	0.0429 (3)	5.1 (1)
C(7)	0.0896 (6)	0.3691 (4)	0.1219 (3)	7.3 (1)
C(8)	0.2729 (6)	0.4242 (3)	0.1313 (3)	6.8 (1)
C(11)	-0.0027 (4)	-0.2339 (2)	0.4063 (2)	3.66 (8)
C(12)	0.1143 (5)	-0.4108 (3)	0.3775 (2)	4.12 (9)
C(13)	-0.0395 (5)	-0.3616 (3)	0.5136 (2)	4.24 (9)
C(21)	0.3809 (4)	-0.1278 (2)	0.4206 (2)	3.67 (8)
C(22)	0.6519 (4)	-0.1731 (3)	0.5403 (2)	3.89 (8)
C(23)	0.4783 (4)	-0.3102 (3)	0.3914 (2)	4.30 (9)
C(31)	0.2166 (4)	-0.0698 (2)	0.5767 (2)	3.55 (8)
C(32)	0.1476 (4)	-0.2043 (3)	0.6756 (2)	3.81 (8)
C(33)	0.4825 (4)	-0.1158 (3)	0.6923 (2)	4.19 (9)
C(41)	0.0188 (5)	0.0826 (3)	-0.2101 (2)	4.29 (9)
C(42)	-0.0899 (5)	0.2654 (3)	-0.1702 (3)	4.7 (1)
C(43)	-0.1418 (4)	0.1454 (3)	-0.0692 (2)	4.46 (9)
C(51)	0.4014 (4)	0.1946 (3)	-0.1898 (2)	4.50 (9)
C(52)	0.5373 (5)	0.3551 (3)	-0.0355 (3)	5.3 (1)
C(53)	0.2697 (5)	0.3672 (3)	-0.1611 (3)	4.9 (1)
C(61)	0.3219 (4)	0.0591 (3)	-0.0712 (2)	4.25 (9)
C(62)	0.1539 (5)	0.1271 (3)	0.0643 (2)	4.48 (9)
C(63)	0.4852 (5)	0.2192 (3)	0.0762 (3)	4.9 (1)

Table 2. Selected bond distances (Å) and angles (°)

Co(1)-Co(2)	2.464 (1)	Co(4)-Co(5)	2.471 (1)
Co(1)-Co(3)	2.474 (1)	Co(4)-Co(6)	2.471 (1)
Co(2)-Co(3)	2.470 (1)	Co(5)-Co(6)	2.471 (1)
Co(1)-C(1)	1.918 (2)	Co(4)-C(5)	1.912 (3)
Co(2)-C(1)	1.913 (3)	Co(5)-C(5)	1.911 (3)
Co(3)-C(1)	1.900 (2)	Co(6)-C(5)	1.911 (3)
C(1)-C(2)	1.463 (4)	C(5)-C(6)	1.466 (4)
C(2)-C(3)	1.494 (4)	C(6)-C(7)	1.452 (5)
C(2)-C(4)	1.497 (4)	C(6)-C(8)	1.465 (5)
C(3)-C(4)	1.473 (5)	C(7)-C(8)	1.492 (5)
Co-C(axial carbonyl) (average)			1.834 (3)
Co-C(equatorial carbonyl) (average)			1.735 (3)
C-O(carbonyl) (average)			1.128 (4)
Co(1)-C(1)-Co(2)	80.1 (1)	Co(4)-C(5)-Co(5)	80.5 (1)
Co(1)-C(1)-Co(3)	80.8 (1)	Co(4)-C(5)-Co(6)	80.6 (1)
Co(2)-C(1)-Co(3)	80.8 (1)	Co(5)-C(5)-Co(6)	80.6 (1)
C(2)-C(3)-C(4)	60.6 (2)	C(6)-C(7)-C(8)	59.7 (3)
C(3)-C(2)-C(4)	59.0 (2)	C(7)-C(6)-C(8)	61.5 (3)
C(1)-C(2)-H(2)	104.0 (2)	C(5)-C(6)-H(6)	100.6 (3)
C(1)-C(2)-C(3)	122.2 (3)	C(5)-C(6)-C(7)	124.0 (3)
C(1)-C(2)-C(4)	122.6 (3)	C(5)-C(6)-C(8)	123.7 (3)
C(1)-Co(1)-C(12)	101.9 (1)	C(5)-Co(5)-C(52)	100.7 (1)
C(1)-Co(1)-C(13)	102.0 (1)	C(5)-Co(5)-C(53)	102.9 (1)
C(1)-Co(2)-C(22)	100.9 (1)	C(5)-Co(4)-C(42)	101.3 (1)
C(1)-Co(2)-C(23)	102.8 (1)	C(5)-Co(4)-C(43)	102.8 (1)
C(1)-Co(3)-C(32)	105.2 (1)	C(5)-Co(6)-C(62)	102.9 (1)
C(1)-Co(3)-C(33)	104.5 (1)	C(5)-Co(6)-C(63)	105.1 (1)
Co-C-O (average)	178.7 (3)		

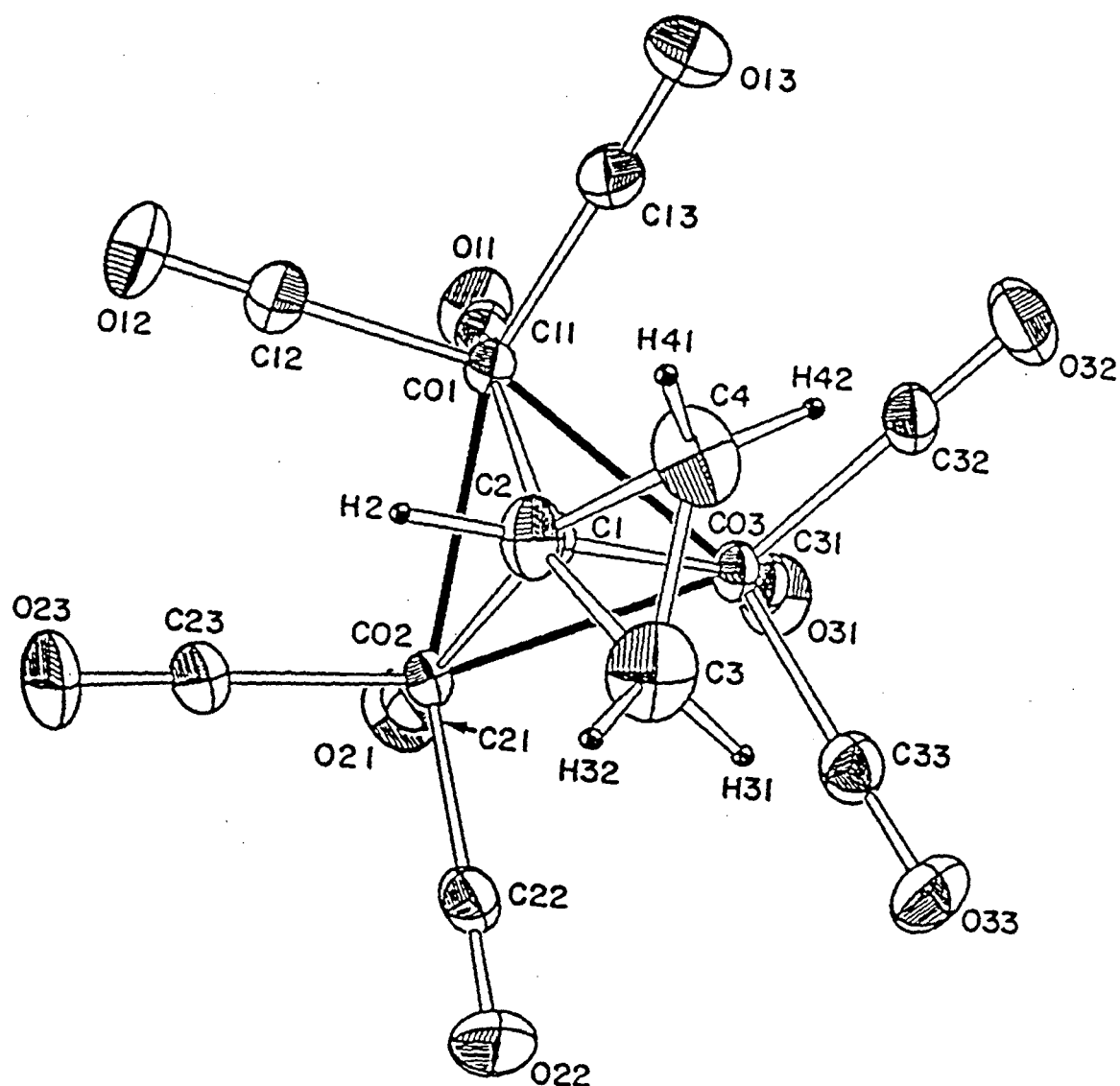


Figure 1. Atomic labelling (ORTEP)⁶² for $(\mu_3\text{-C-C}_3\text{H}_5)\text{Co}_3(\text{CO})_9$, viewed approximately along the methylidyne axis.

analogous bond in methylcyclopropane, observed to be 1.517(2) Å,⁶⁶ and the analogous bond in $(\mu_3\text{-CH}_3\text{C})\text{Co}_3(\text{CO})_9$, reported as 1.53(3) Å.⁵⁶ In fact, this distance approximates the sp-sp^3 C-C bond length of 1.460(3) Å observed for propyne, $\text{CH}_3\text{C}\equiv\text{CH}$.⁶⁵ Unusually short bonds to the alkylidyne carbon have been previously observed in this class of tricobalt clusters.^{57a} For example, a 1.37(1) Å C(alkylidyne)-C(alkylidyne) bond is found in $(\text{CO})_9\text{Co}_3\text{C-CCo}_3(\text{CO})_9$.⁶⁷

The cyclopropyl carbon atoms have bonding distances and angles which suggest, within experimental error, that the atoms form an equilateral triangle, but the bonding distances, which range from 1.452(5) to 1.497(4) Å, are again significantly shorter than the $\text{sp}^3\text{-sp}^3$ value of 1.54 Å quoted above, and in fact are considerably shorter than the distance of 1.510 Å observed for free cyclopropane⁶⁴ and 1.509(1) Å observed for methylcyclopropane.⁶⁶

The three-membered rings adopt a staggered conformation, apparently to minimize nonbonding contacts (Figure 1). As evidence of slight steric repulsion, the data show that the cyclopropyl ligand "pushes" the equatorial carbonyl carbon atoms on the eclipsed cobalt atom (Co(3)) 0.07-0.10 Å closer to the Co_3 plane than the other equatorial carbonyl carbon atoms. However, this push represents the only interaction between the two rings which we could detect.

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Chapter 2

**Inter- and Intramolecular Oxidative Addition of
Phosphine, Alkane, and Arene Carbon-Hydrogen Bonds to Rhenium.
Ancillary Ligand Requirements.**

Introduction

The recent discovery of homogeneous organometallic systems in which the intermolecular oxidative addition of unactivated saturated hydrocarbons to transition metals can be directly observed¹ has provoked a flurry of research aimed at elucidating the mechanism and prerequisites for this heretofore virtually unknown transformation. Interest in this process of C-H activation exists for at least two major reasons.² One is curiosity about the details of reactions of chemically stable organic materials such as alkanes, the relative inertness of which results from high C-H and C-C bond energies and low polarity of these bonds. In addition, the exploitation of saturated hydrocarbons as chemical feedstocks could potentially be greatly enhanced by the use of similar homogeneous organometallic systems capable of selectively functionalizing these important and plentiful substrates.

The insertion of transition metals into carbon-hydrogen bonds can be segregated into two classes: intermolecular and intramolecular reactions (Scheme I).³ The frequently entropically favored intramolecular alternative has, in the past, thwarted the quest for the more intriguing intermolecular process. Many examples of intramolecular insertion are known, especially when the C-H bond is already activated, for example as part of an aromatic ring (eq 1, Scheme II).^{3a} Even when the attacked C-H bond is not made more reactive by low bond dissociation energy or high polarity, intramolecular insertion has been observed (eq 2, Scheme II).^{3b,c}

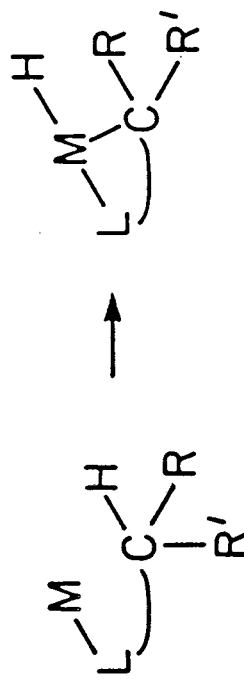
Intermolecular homogeneous analogs to these transformations are by no means unknown, and Scheme III shows three cases in which very

Scheme 1

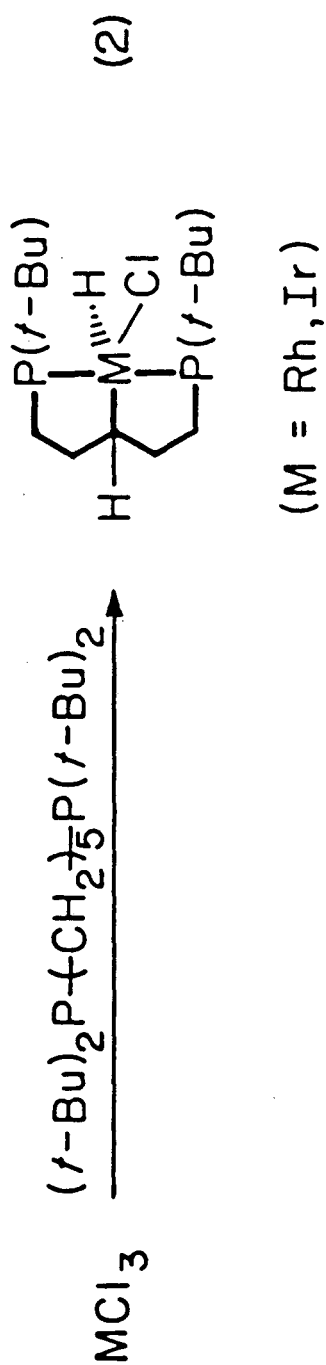
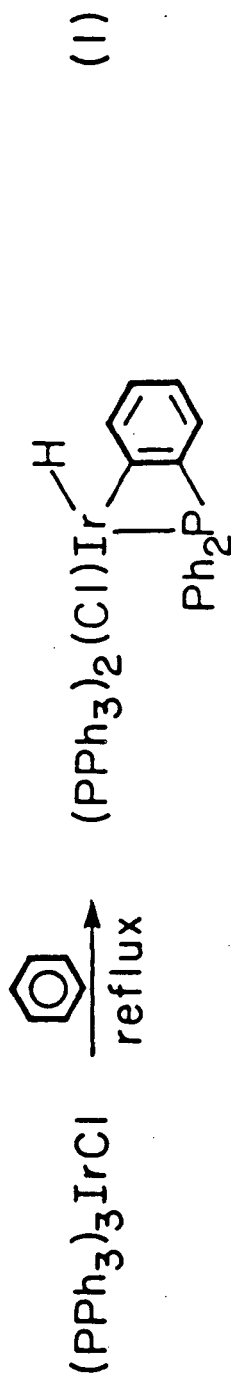
Intermolecular C-H activation:



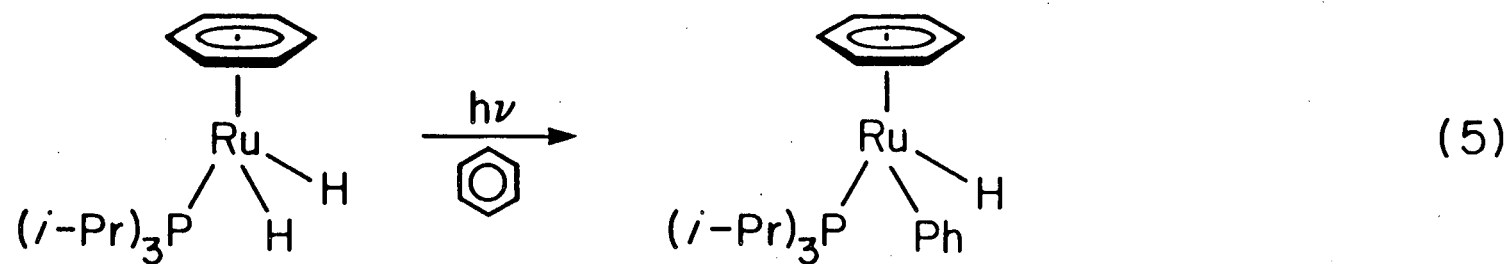
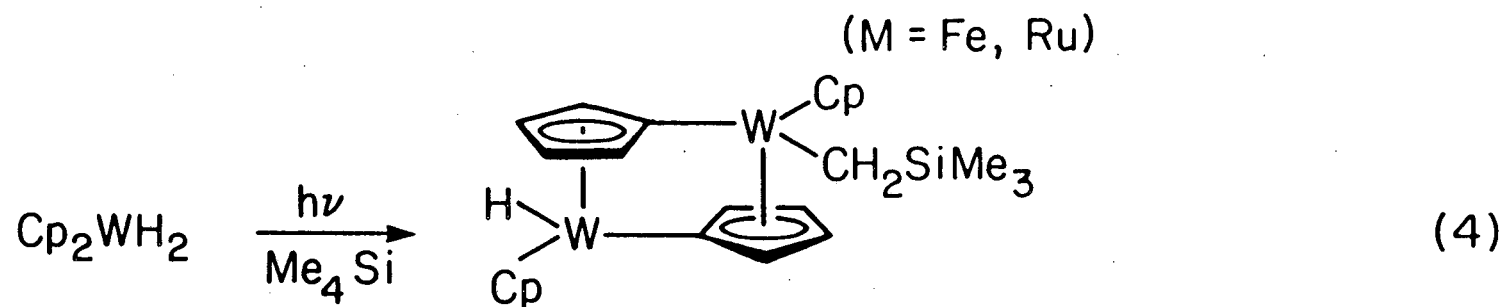
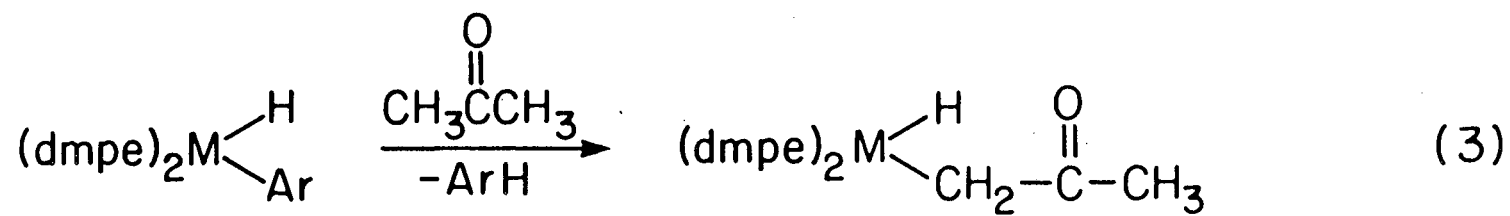
Intramolecular C-H activation:



Scheme II



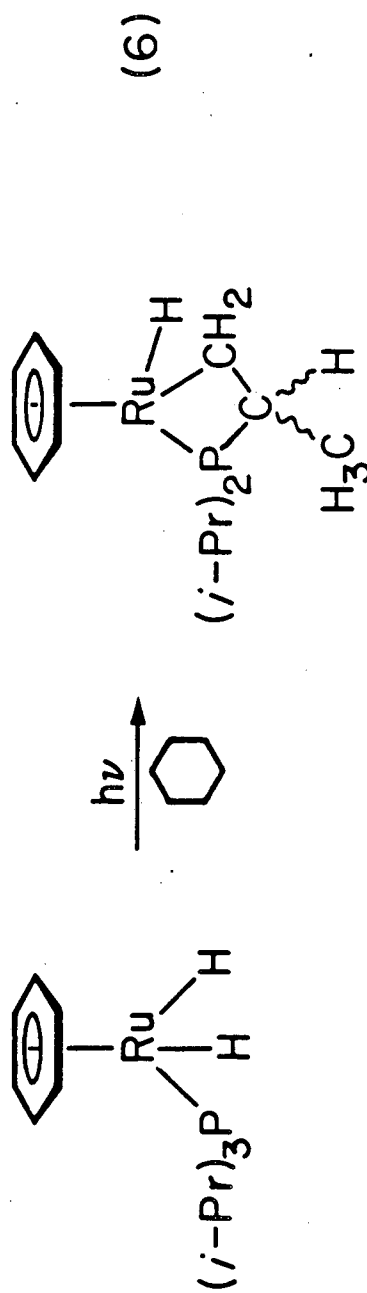
Scheme III



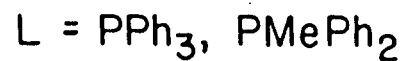
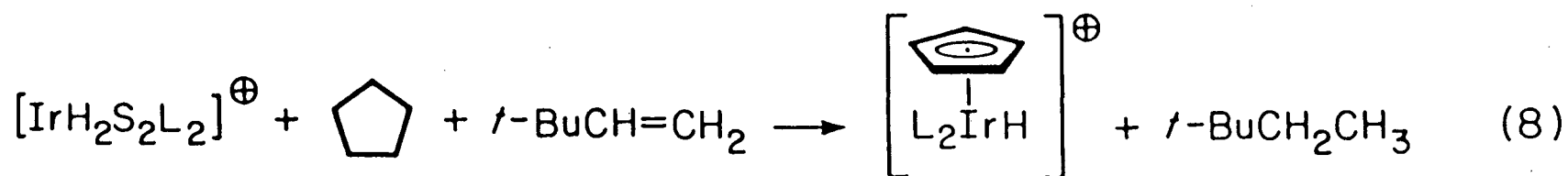
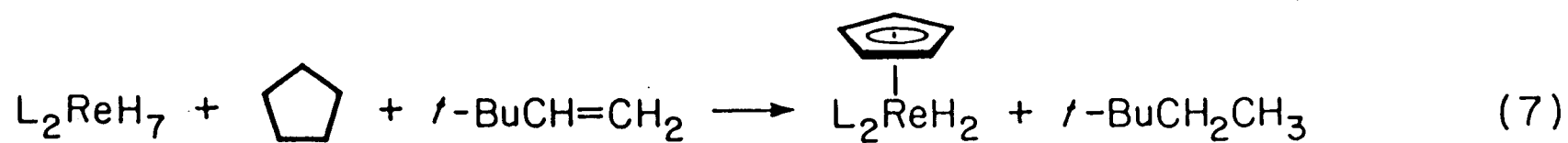
reactive electron-rich metal centers have been found to insert into C-H bonds of separate organic substrates for which adjacent functional groups provide some pre-activation.^{3d-j} In each of these cases, however, attack by the metal centers on C-H bonds of their own ligands occurs in preference to reaction with saturated hydrocarbons (Scheme IV for example).^{3j} Two intriguing homogeneous examples of intermolecular reaction of unactivated saturated-hydrocarbon C-H bonds with transition-metal complexes were discovered by Felkin, *et al.*, and Crabtree, *et al.* (Scheme V).^{3k-o} Several hydrogen atoms are lost from the alkane reactants in these systems, and added alkene is required as a hydrogen acceptor. While oxidative addition of C-H bonds to rhenium and iridium has been postulated, no direct observation of this step has been made. More recently, direct observations have been announced by the groups of Bergman, Graham, and Jones (Scheme VI).¹ In each transformation, a coordinatively-unsaturated sixteen-electron transition-metal complex has been postulated as the species which is capable of inserting into various C-H bonds. Interestingly, only the systems with a triphenylphosphine ligand demonstrate a proclivity for intramolecular reaction.⁴ In particular, the $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligands are not affected, insertion into the C-H bonds of which is well preceded.^{3p-r} Most recently, however, two systems which attack their own $\eta^5\text{-C}_5(\text{CH}_3)_5$ ligands, the lutetium and yttrium methyl complexes of Watson, were found to undergo selective reaction with methane in the presence of cyclohexane (Scheme VII).^{3t}

Our goal was to design in a deliberate manner a new organo-transition metal species capable of C-H activating organic substrates. We hoped to probe the selectivity for the intra- and intermolecular

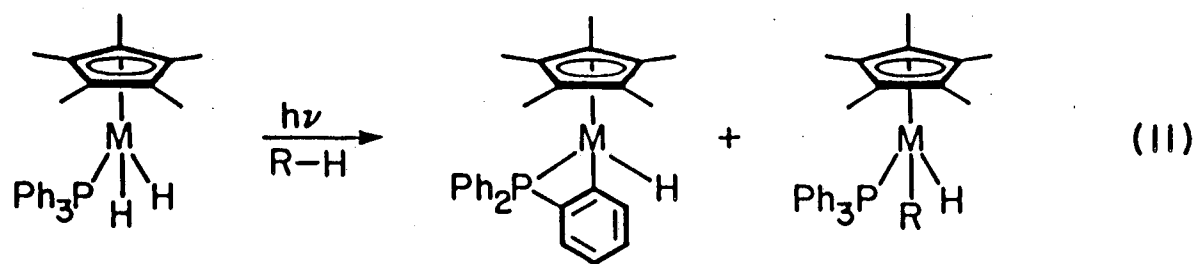
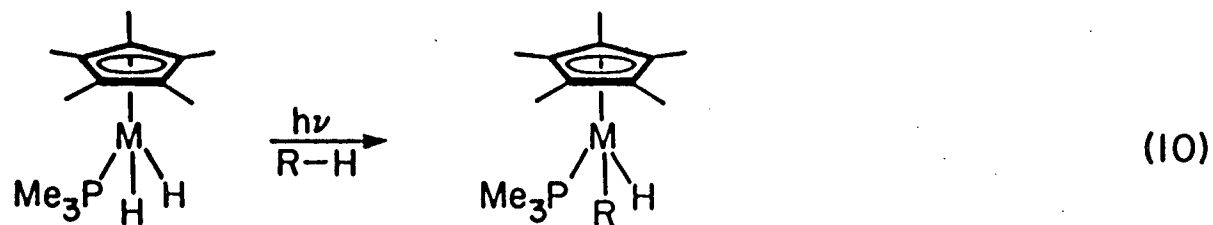
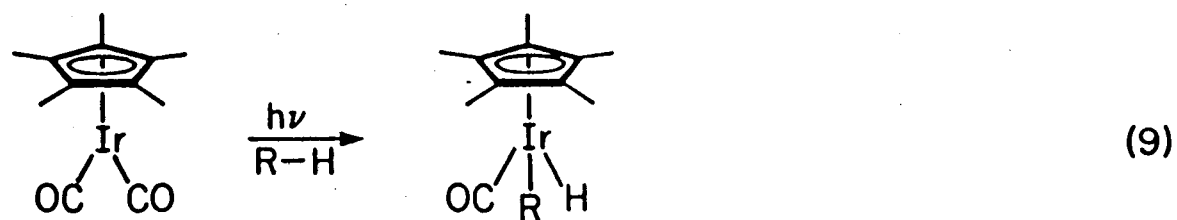
Scheme IV



Scheme V



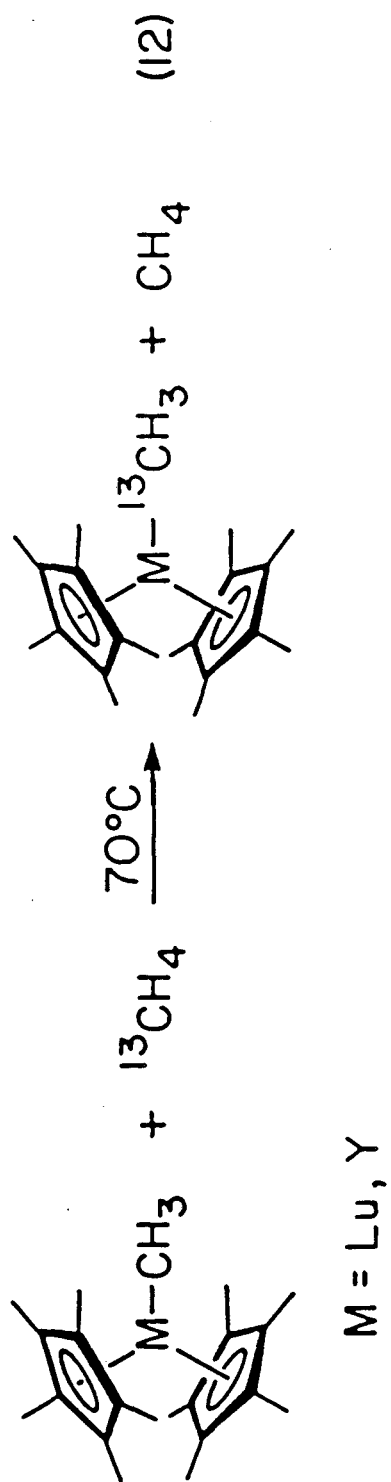
Scheme VI



R-H = arene, alkane

M = Rh, Ir

Scheme VII

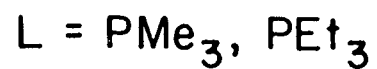
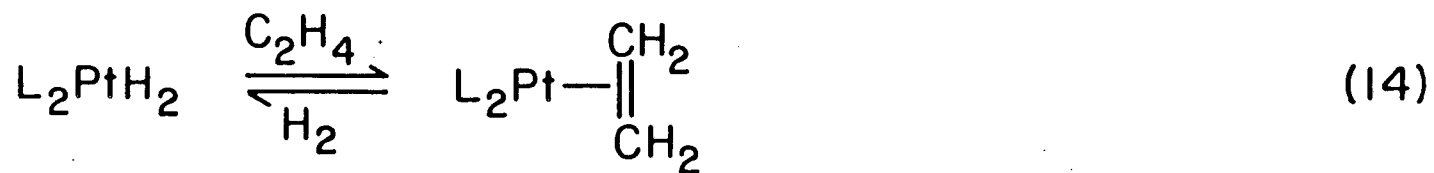
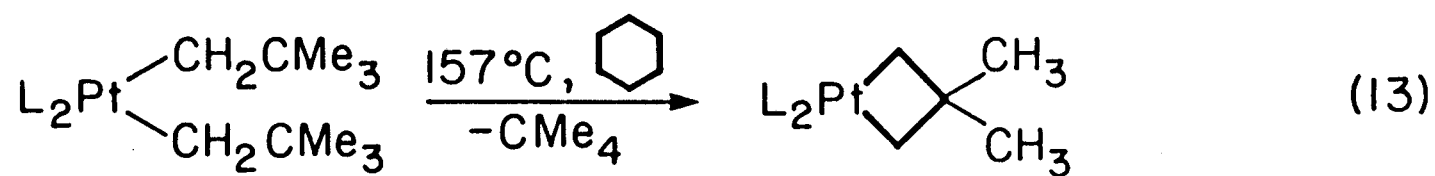


processes, and for insertion into various types of C-H bonds. Moreover, we intended to examine the influence of the ancillary ligands on these transformations. Using the implications of some of the known C-H activating systems, our initial objective was to generate relatively electron-rich, coordinatively unsaturated species for which we had a reasonable expectation of forming relatively strong metal-carbon and metal-hydrogen bonds and, therefore, of forming stable oxidative addition products. High electron density on the metal atom could be promoted by using more electron-donating ligands, such as trialkyl phosphines and per-alkyl π -bound ligands. A later transition metal with higher electronegativity and in a low oxidation state would also be advantageous. Coordinative unsaturation might be achieved with an easily photochemically or thermally dissociated dative ligand like CO, N₂, or a phosphine, or perhaps by way of a facile reductive elimination of an unstable alkyl hydride.

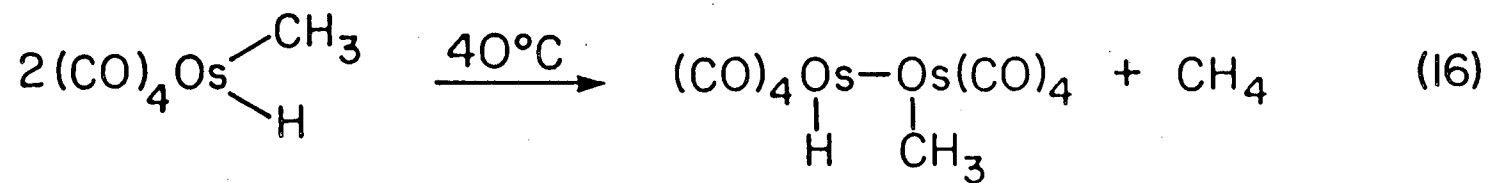
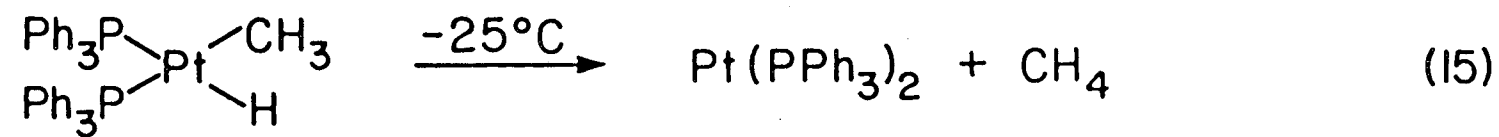
Characteristics favoring strong metal-carbon and metal-hydrogen bonds are more difficult to specify. The observed increase in strength of these bonds and consequent decrease in reactivity observed for larger principle quantum numbers⁵ suggests the choice of a second- or preferably third-row transition metal. Although the electron density argument above implied that the metal should also be late in the transition series, it should not be too late in the series, because of the gradual contraction of the d orbitals relative to the valence s and p orbitals, and the consequent drop in d orbital contribution to bonding to other atoms.⁶

This simplistic reasoning may explain the behavior illustrated in Schemes VIII^{3u,7} and IX.^{8,9} The bis(neopentyl)platinum complex of

Scheme VIII



Scheme IX



Foley and Whitesides, though quite thermally stable, does undergo intramolecular cyclometallation at high temperature, as shown in eq 13. The metal center here fits the criteria for a C-H activating system expounded above. The third row metal has electron donating triethylphosphine ligands and, although already containing an open coordination site, can become even more coordinatively unsaturated by dissociation of one phosphine. No activation of the cyclohexane solvent is observed though. Paonessa and Trogler have described a very similar platinum dihydride system (eq 14) which seems to meet the same criteria. In this case, the ligand C-H bonds are not attacked; perhaps they are sterically inaccessible for oxidative addition. Nevertheless, the platinum center makes considerable use of its open coordination site and high electron density in facile substitution reactions with π acceptors such as CO, $\text{H}_2\text{C}=\text{CH}_2$, and $\text{F}_2\text{C}=\text{CF}_2$, in oxidative addition of Et_3SiH , and in H-D exchange. But again, no tendency to activate C-H bonds in acetonitrile, methanol, tetrahydrofuran, or aromatic solvents is reported. In fact, $\text{Pt}(\text{PEt}_3)_2\text{H}_2$ slowly decomposes in benzene under vacuum to give $\text{Pt}(\text{PEt}_3)_3$. It seems that these platinum species are on a reactivity borderline for which the metal-carbon and metal-hydrogen bonds made from oxidative addition of hydrocarbons are not quite strong enough to give isolable materials from intermolecular reactions under the studied conditions, and the entropic and steric factors discussed by Whitesides^{3u} may be responsible for the accessibility of the intramolecular pathway of eq 13. Indeed, Halpern and co-workers have convincingly argued that the conversion of bis(phosphine)hydrido-alkylplatinum(II) species to bis(phosphine)platinum(0) and alkane

should normally be exergonic.⁸

A comparison of the platinum methyl hydride studied by Halpern, *et al.*, and the osmium methyl hydride of Norton, *et al.*, is also instructive (Scheme IX). Reductive elimination of methane from the platinum complex occurs at -25 °C, whereas heating to 40 °C is required for the osmium species, at which point the reaction goes via a bimolecular pathway. In both cases, the metals are in the third transition series and in a low oxidation state. The osmium complex even has electron-withdrawing carbonyl ligands, which should facilitate reductive elimination,¹⁰ yet it is more stable than the platinum analog.

The argument presented here is a thermodynamic one and does not take into account kinetic barriers which may exist to insertion into hydrocarbon C-H bonds. Moreover, the low temperature stability of platinum alkyl hydrides suggests that it may be possible to form these species from electron-rich coordinatively-unsaturated platinum complexes if the reaction is carried out at a sufficiently low temperature. Be that as it may, the implication from this discussion and from the known rhodium and iridium C-H activation systems as well, is that formation of strong metal-carbon and metal-hydrogen bonds necessary for stable, isolable C-H oxidative-addition adducts might best be anticipated in a new system for osmium or perhaps rhenium, metals which are not too late in the transition series, but still not too electropositive.

Taking into account all of the factors presented above, we chose to examine systems in which species of general formula Cp^*ReL_2

(Cp' = $\eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_5(\text{CH}_3)_5$; L = CO or PMe_3) could be generated, with the expectation that $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Re}(\text{PMe}_3)_2$ might be the unsaturated intermediate most likely to effect C-H activation. We report here the behavior of the $\eta^5\text{-C}_5(\text{CH}_3)_5$ systems,¹¹ including the first direct observation of intermolecular oxidative addition of C-H bonds in alkanes to rhenium. The following differences from the earlier-studied systems are observed: (1) Unlike rhodium and iridium, rhenium exhibits competitive intermolecular C-H activation and intramolecular attack on C-H bonds in PMe_3 ligands. (2) The cyclometallated products obtained from intramolecular reaction provide a route to selective thermal activation of hydrocarbons under relatively mild conditions. (3) Despite the lowered inter/intra selectivity, selectivity with respect to different alkanes is substantially increased. Methyl, cyclopropyl, and aromatic C-H bonds are attacked, but other alkane C-H bonds are not. Thus, alkanes like cyclohexane or hexane can be used as inert solvents, providing a convenient method of activating more reactive substrates like methane. (4) C-H activation at rhodium and iridium occurs successfully with either $\eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_5(\text{CH}_3)_5$ and either CO or PMe_3 attached to the metal center. With rhenium the efficiency of oxidative addition depends markedly upon the ligands attached to the metal, PMe_3 having a more important influence on reactivity than methyl substitution on the cyclopentadienyl moiety.

Results

Our strategy was to examine those complexes which are less electron-rich first, progressively introducing more electron-donating ligands into the coordination sphere of the metal, and investigating

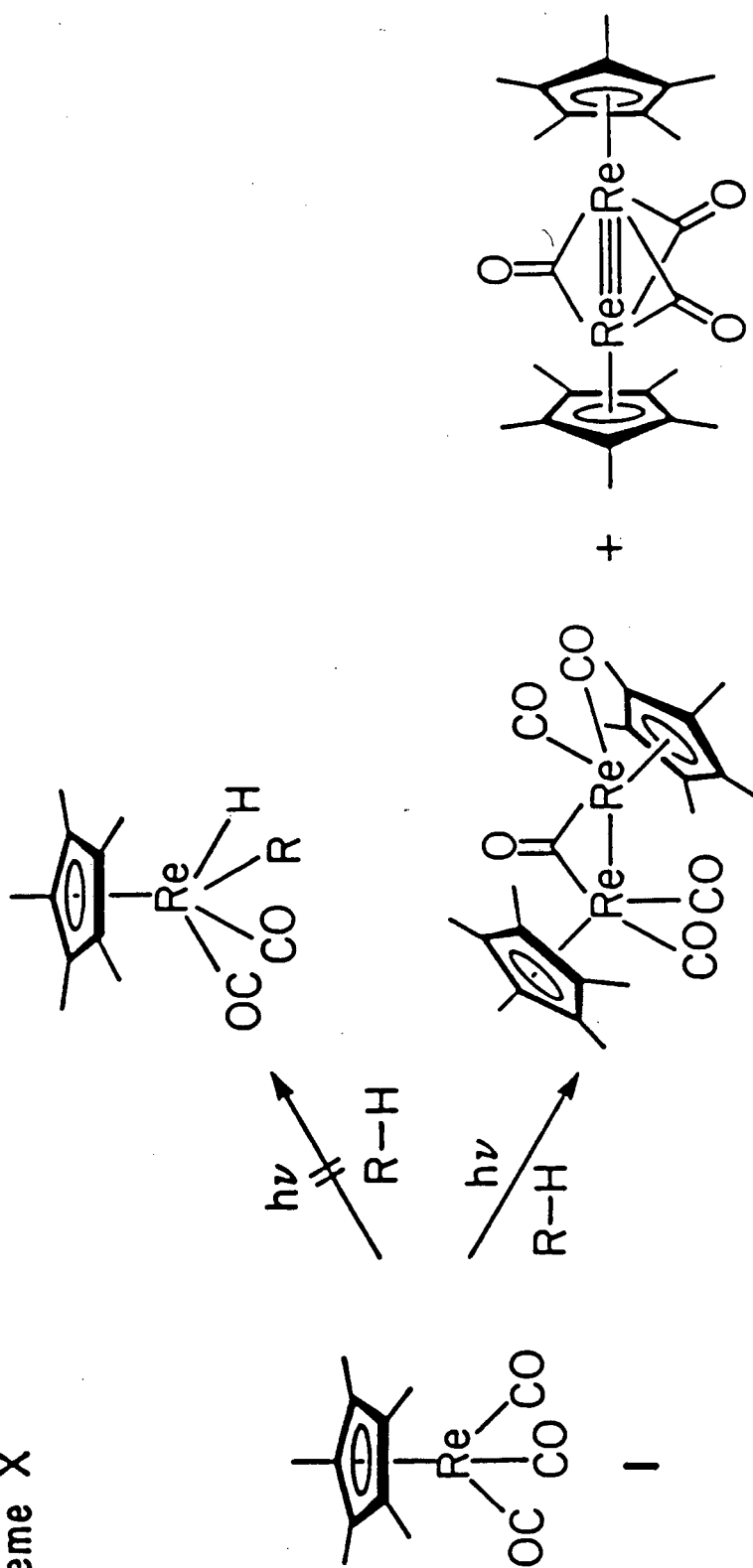
the change in reactivity of the metal center toward various hydrocarbon substrates and bonds within its own ligands. Therefore, initial experiments centered around the known complex $\text{Cp}^*\text{Re}(\text{CO})_3$ ¹² (1) ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$). Irradiation¹³ of this material through pyrex in benzene or neopentane led to no detectable high-field resonances in the ^1H NMR spectra of the reaction mixtures, which would be expected from the hydride ligands in the products of insertion of the metal into C-H bonds of the solvent. The Cp^* resonances of two products were, however, observed in each case. The products were shown to be identical in the two solvents by redissolving in benzene- d_6 the nonvolatiles from the photolysis in neopentane, and assignment was made to those structures reported by Hoyano and Graham:¹⁴

$(\text{Cp}^*\text{Re})_2(\mu\text{-CO})_3$ and $[\text{Cp}^*\text{Re}(\text{CO})_2]_2(\mu\text{-CO})$ (Scheme X). Similarly, no hydride resonances were detected when 1 was photolysized at -80°C in pentane and the reaction monitored by ^1H NMR at -65 to -70°C in an attempt to observe the possible formation of an unstable alkyl hydride.

Synthesis and Reactions of $\text{Cp}^*\text{Re}(\text{CO})_2\text{PMe}_3$ (2).

In order to make the rhenium center more electron-rich, an effort was made to thermally substitute PMe_3 for one of the CO ligands in 1. Heating a mixture of 1 and PMe_3 in benzene- d_6 , however, produced no reaction, even at temperatures as high as 215°C . Rapid initial formation of $\text{Cp}^*\text{Re}(\text{CO})_2\text{PMe}_3$ (2) did occur when 1 (10^{-2} - 10^{-1}M) was irradiated through pyrex in benzene, pentane, neopentane, hexane, or cyclopropane in the presences of excess PMe_3 (ca. 12 equiv). Experimentation with reaction conditions showed that conversion of 1 to 2 becomes more efficient at higher concentrations of PMe_3 ,¹⁵ and

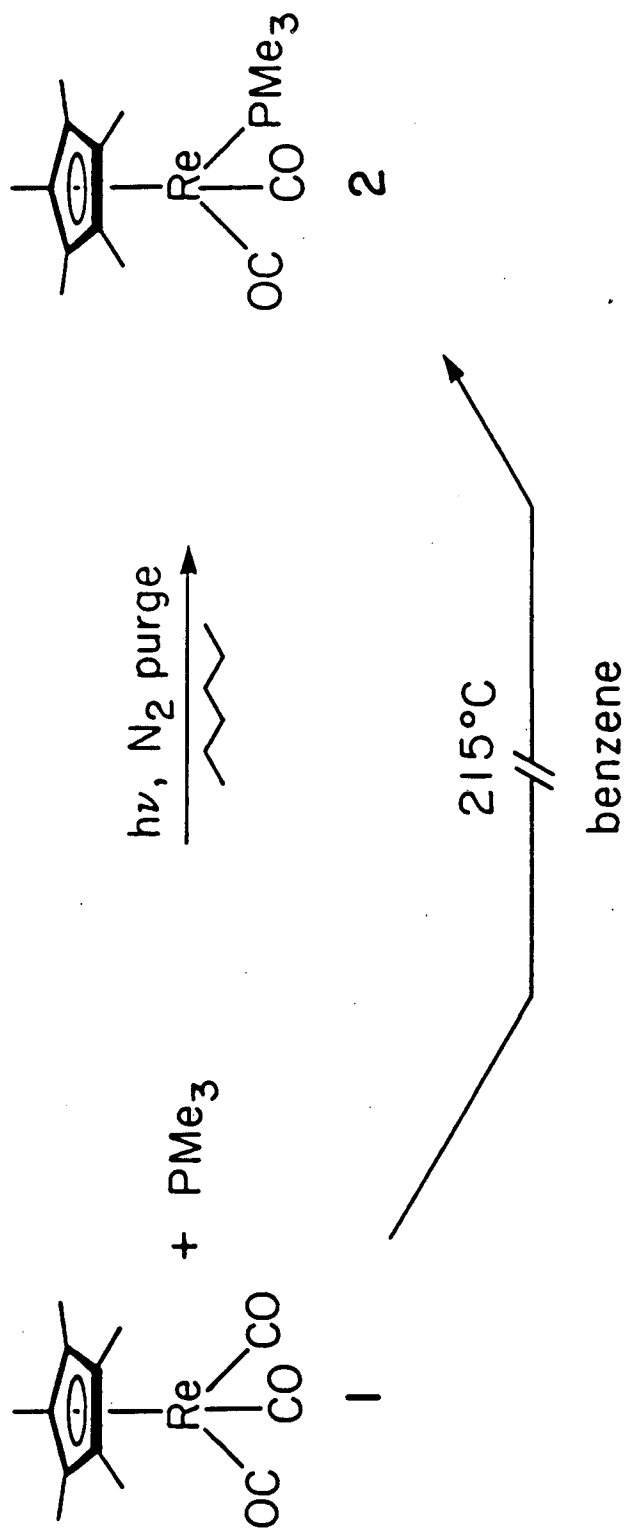
Scheme X



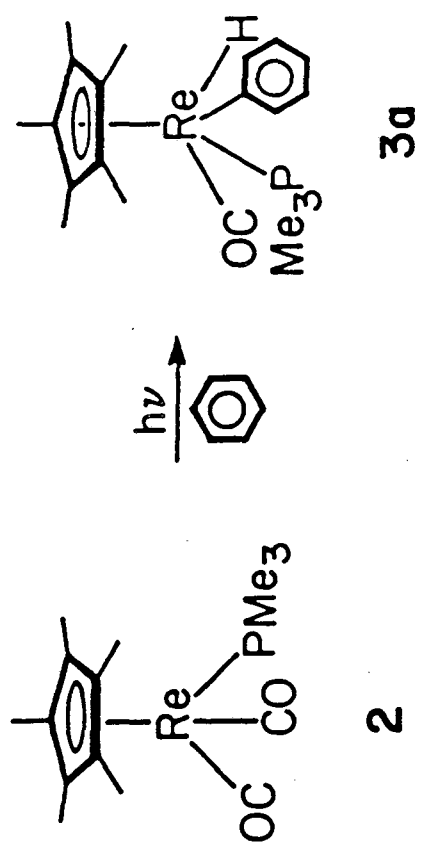
can even be performed in neat PMe_3 . But, since large quantities of PMe_3 are expensive and impractical to use, synthesis of 2 was accomplished on a preparative scale in 38 % yield by photolysis of 1 (ca. $2 \times 10^{-1}\text{M}$) at -5 to -15 °C in a nitrogen purged¹⁶ hexane solution of a three fold excess of PMe_3 (Scheme XI). Purification was by chromatography under nitrogen on silica gel. Compound 2 is a white crystalline material soluble in aliphatic and aromatic hydrocarbons. It has intense IR carbonyl stretching absorptions at 1930 and 1866 cm^{-1} in hexane as compared with the 2014 and 1924 cm^{-1} absorptions of 1. This shift in absorption frequencies is consistent with increased back-bonding to the remaining CO ligands in 2 due to the electron-donating character of the PMe_3 ligand and consequently augmented electron density on rhenium. In addition, the UV/visible spectrum of 2 exhibited one band with λ_{max} at 205 nm and shoulders at 217, 231, and 248 nm.

Photolysis of 2 through pyrex resulted in extrusion of CO and subsequent oxidative addition of C-H bonds to rhenium. In particular, irradiation of 2 in benzene led initially to formation of $\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)\text{Ph}(\text{H})$ (3a) (Scheme XII). Further irradiation, however, caused rapid substitution of CO rather than reductive elimination, giving $\text{Cp}^*\text{Re}(\text{PMe}_3)_2\text{Ph}(\text{H})$ (3b) (Scheme XIII) along with PMe_3 -deficient rhenium containing materials which were not identified. In situ preparation of 2 and conversion to 3a, and subsequently to 3b, could be carried out directly from 1 (10^{-2} - 10^{-1}M) and excess PMe_3 (12 equiv) in an NMR tube. The added free PMe_3 allowed efficient substitution of CO on 3a with minimal loss of rhenium, and after 25 h of irradiation a mixture of 16 % 2, 4 % 3a, and 71 % 3b (absolute yields) could be

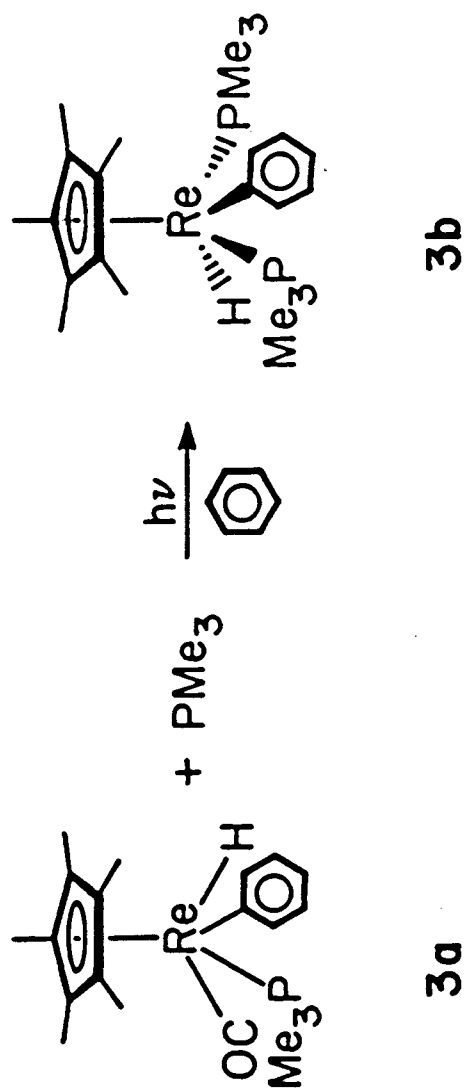
Scheme XI



Scheme XII



Scheme XIII



achieved.

Because of the facile photochemical conversion of **3a** to **3b** even in the absence of added PMe_3 , it was difficult to generate large quantities of **3a**, and it was identified only by ^1H NMR spectroscopy. Specifically, a hydride resonance at δ -9.22 ppm split into a doublet by coupling to phosphorus ($^2J_{\text{PH}} = 66.5$) was attributed to **3a**. This resonance and the phenyl resonances of **3a** were absent when the photolysis was carried out in benzene- d_6 , consistent with the formation of $\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)(\text{C}_6\text{D}_5)\text{D}$ (**3a-d**₆). In addition, the stability of **3a** to reductive elimination at room temperature was demonstrated by the lack of exchange of the hydride and phenyl moieties in **3a-d**₀ with benzene- d_6 .

While preparation of **3b** on a large scale from **1** and PMe_3 in benzene was not possible because of difficulties in driving the reaction past the formation of **2** when more than analytical quantities of reagents were used,¹⁵ isolable quantities of **3b** could be prepared from **2** (10^{-4} - 10^{-3}M)¹⁷ and excess PMe_3 (ca. 50 equiv) in nitrogen purged benzene. After filtration through alumina III at 15 °C and recrystallization from pentane, **3b** was isolated in 63.5 % yield based on **2** as extremely alkane soluble, pale yellow crystals and fully characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR, IR, MS and elemental analysis. In the ^1H NMR spectrum (Figure I), the hydride resonance at δ -11.08 ppm is a triplet ($^2J_{\text{PH}} = 53.9$), indicating coupling to two equivalent phosphorous atoms. Furthermore, a single $^{31}\text{P}\{^1\text{H}\}$ resonance at δ -45.00 (br s) ppm is seen. These data are consistent with either a trans geometry or a highly fluxional structure for **3b** which exchanges the environments of the phosphine ligands rapidly on the NMR

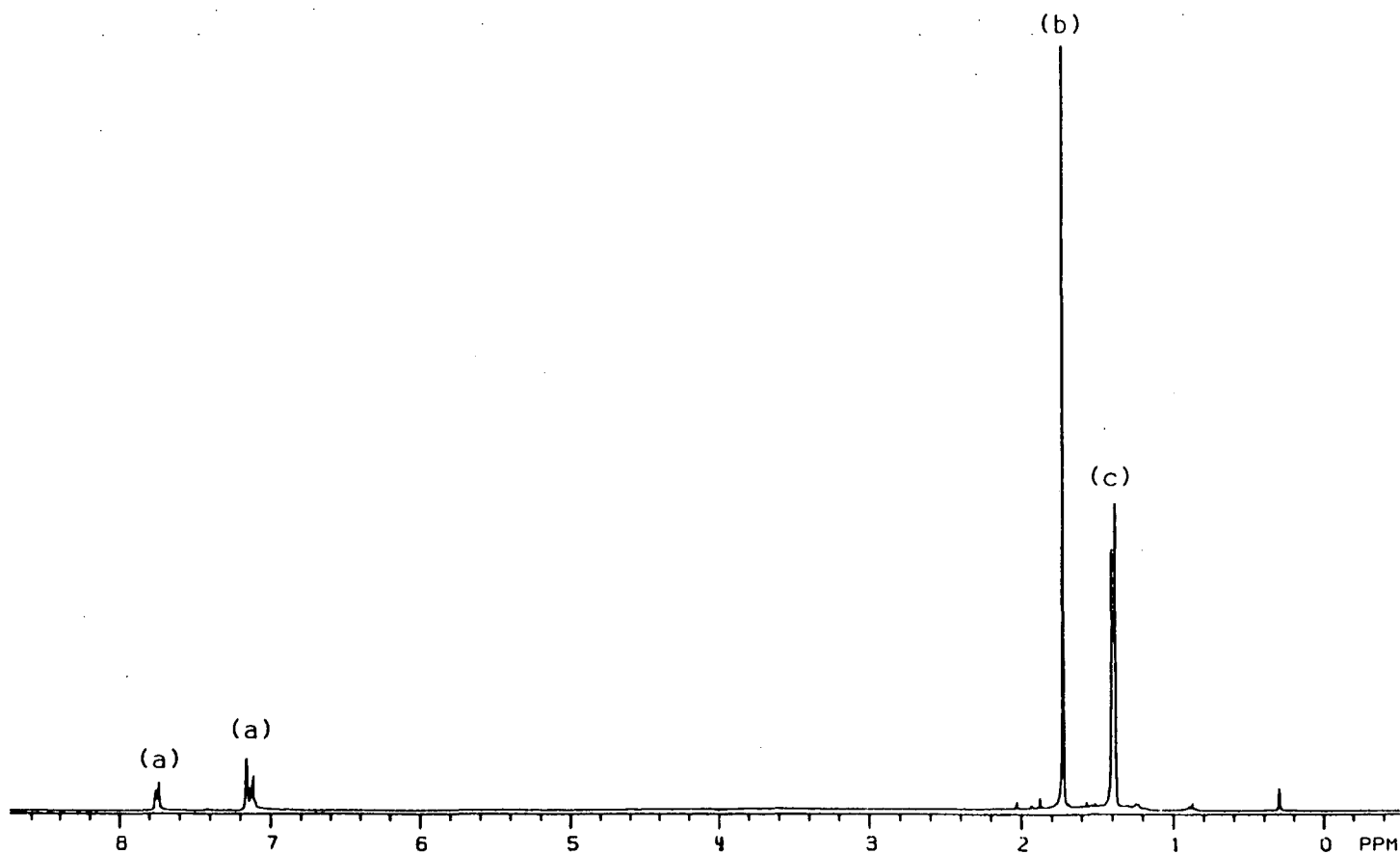


Figure I. 300 MHz ^1H NMR spectrum (benzene- d_6) of **3b**. Peak identification: (a) phenyl protons; (b) Cp^* protons; (c) bound- PMe_3 protons; (d) hydride proton. Chemical shifts are recorded in ppm downfield from tetramethylsilane. Figure continued on next page.

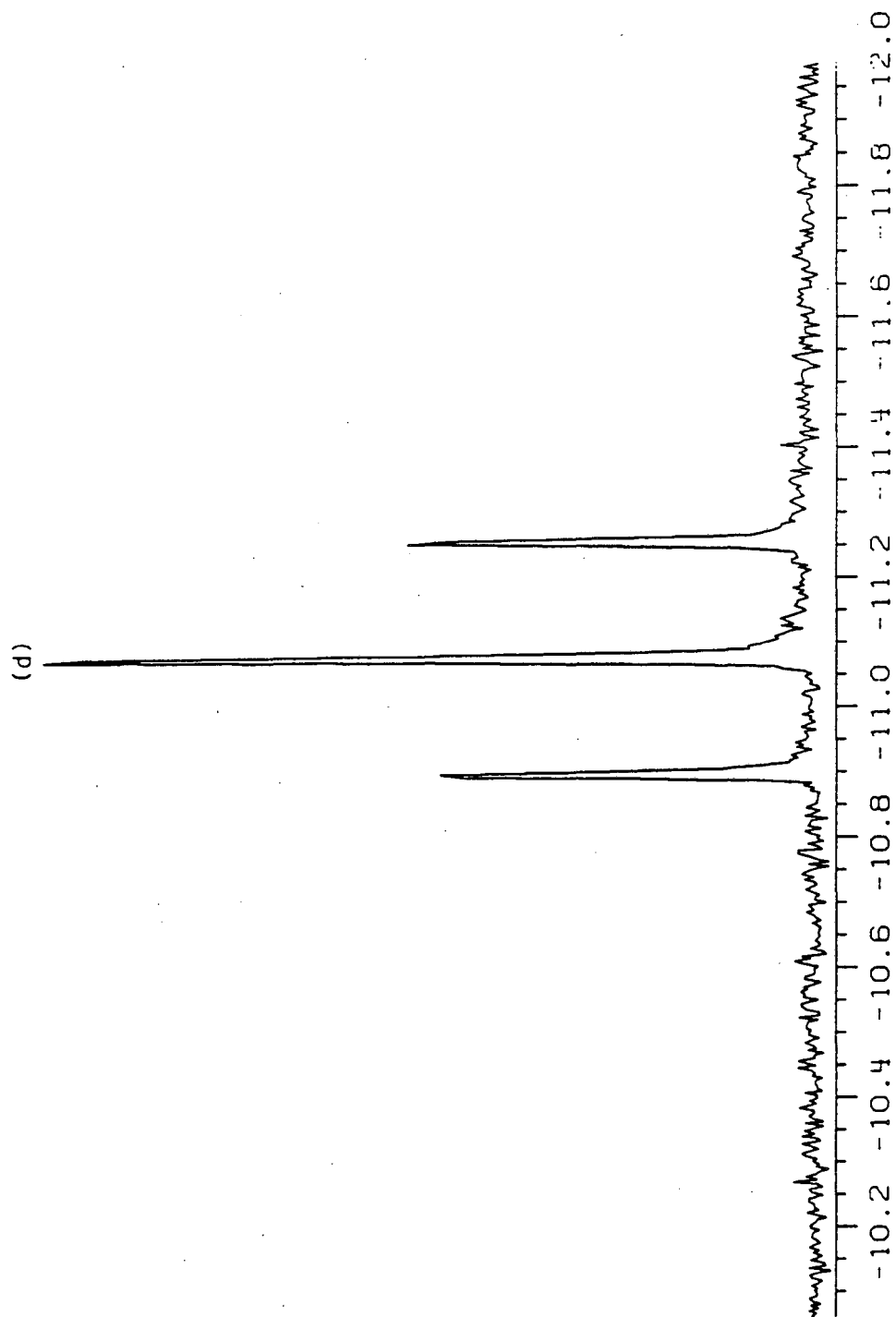


Figure I. (Continued from previous page)

time scale. Another distinguishing feature of the ^1H NMR spectrum of **3b** and other hydrocarbon oxidative addition products (*vide infra*) is the virtual doublet assigned to the PMe_3 ligands. Similarly, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows a complex six-line multiplet for the PMe_3 moieties, which is well preceded for such structures (Figure II).¹⁸ Also, a weak IR Re-H stretching absorption was found at 2015 cm^{-1} .

When the procedure for the preparation of **3b** was performed with benzene- d_6 instead of benzene- h_6 , $\text{Cp}^*\text{Re}(\text{PMe}_3)_2(\text{C}_6\text{D}_5)\text{D}$ (**3b-d₆**) was produced, and no bound phenyl group or hydride resonances were seen by ^1H NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR resonance at $\delta -44.76$ ppm is now a 1:1:1 triplet ($^2J_{\text{PD}} = 7.8$) due to coupling to the rhenium bound deuterium. No exchange of benzene- h_6 with **3b-d₆** or of benzene- d_6 with **3b-d₀** was detected, indicating **3b**, like **3a**, is also stable to reductive elimination at room temperature.

In cyclopropane, irradiation of **2** once again led to a new complex seen to contain a hydride ligand ($\delta -10.32$ (d, $^2J_{\text{PH}} = 62.5$) ppm) and intact Cp^* and PMe_3 groups by ^1H NMR. Its structure was assigned as $\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)(\overline{\text{CHCH}_2\text{CH}_2})\text{H}$ (**4a**) (Scheme XIV). The reaction mixture darkens rapidly, however, and the photolysis can only be taken to low conversions. Consequently, no $\text{Cp}^*\text{Re}(\text{PMe}_3)_2(\overline{\text{CHCH}_2\text{CH}_2})\text{H}$ (**4b**) was observed in analogy to the reaction of **2** in benzene, and **4b** required a different route of preparation (*vide infra*).¹⁹ Low conversion of **2** also precluded isolation, and only ^1H NMR data were obtained.

When **2** was photolyzed in neopentane, pentane, hexane, or cyclohexane, or in cyclohexane under methane, a new Cp^* containing material (**5a**) formed. Although this material reacted rapidly with benzene (*vide infra*), ^1H NMR spectra quickly obtained after

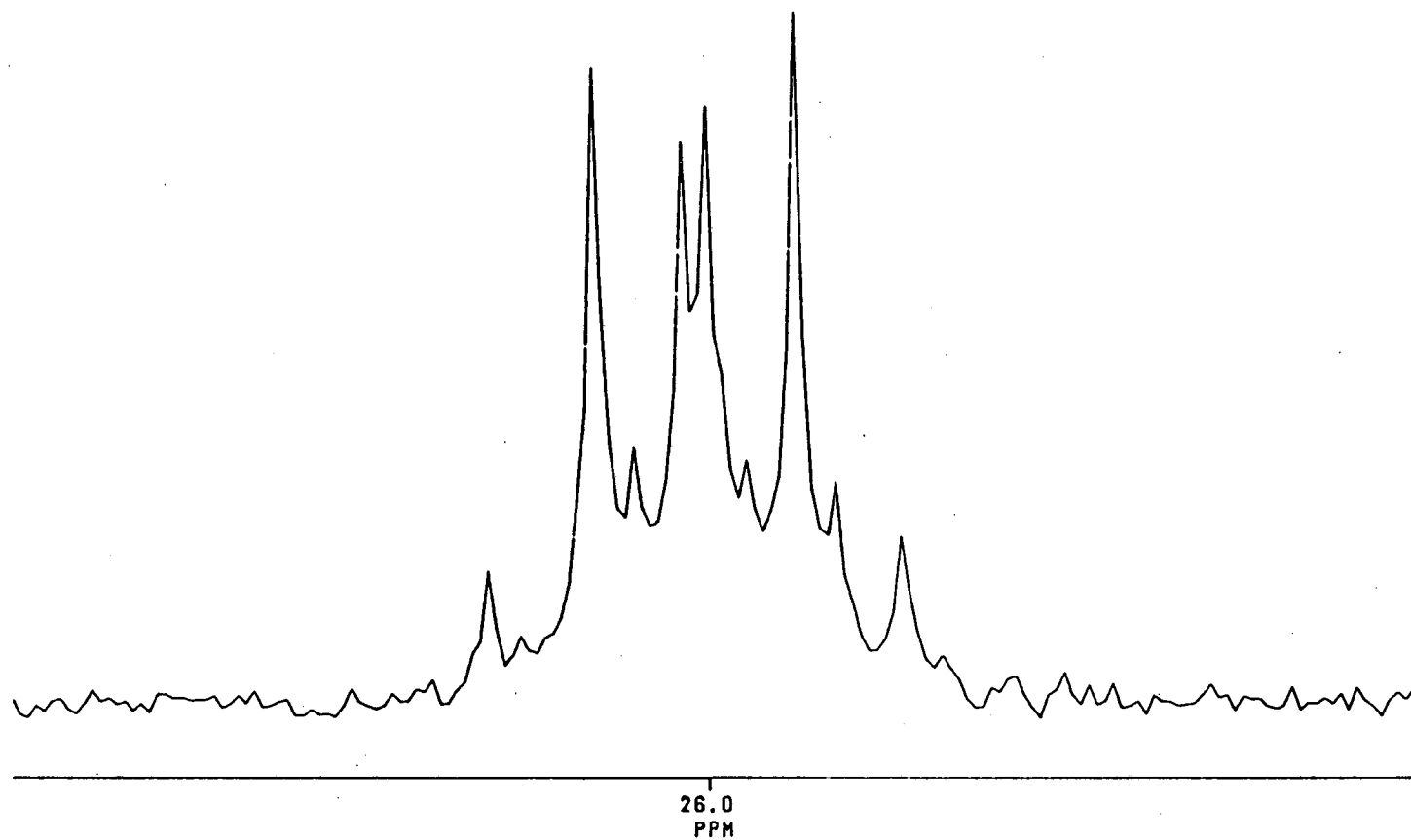
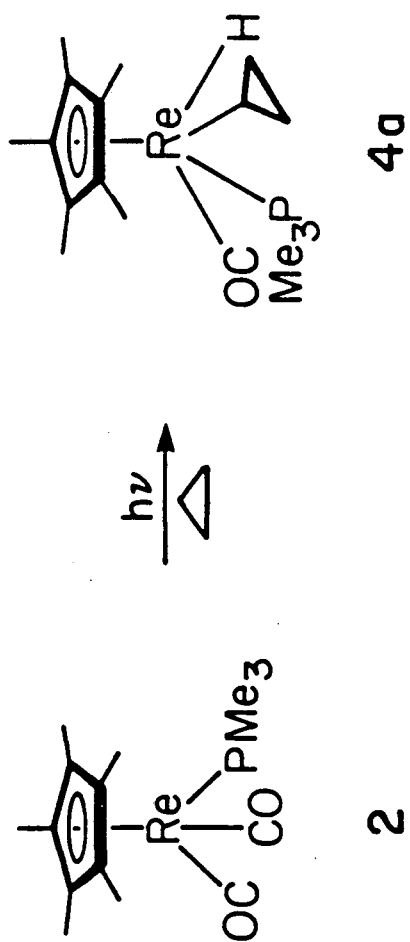


Figure II. 125.8 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (benzene- d_6) of bound- PMe_3 region for **3b**.
Chemical shifts are recorded in ppm downfield from tetramethylsilane.

Scheme XIV



redissolving the nonvolatiles in benzene- d_6 showed this new substance to be the same compound when produced in any of the above solvents. Moreover, ^1H NMR resonances attributable to 5a could also be observed when 2 was irradiated in cyclohexane- d_{12} , consistent with the lack of incorporation of a solvent molecule into the structure of 5a. Even when photolysis of 2 in hexane was performed at -65°C and examined by ^1H NMR spectroscopy at -35°C , no evidence for intermolecular reaction was seen.²⁰ In addition to the Cp^* resonance, the resonances observed in the benzene- d_6 ^1H NMR spectrum of 5a included two doublets (δ 1.33 ($^2J_{\text{PH}} = 12.4$) and 0.94 ($^2J_{\text{PH}} = 12.0$ ppm)), two doublets of doublets (δ 0.85 ($^2J_{\text{HH}} = 7$, $^2J_{\text{PH}} = 4$) and -0.51 ($^2J_{\text{HH}} = 7$, $^2J_{\text{PH}} = 3$)), and a hydride doublet at δ -9.44 ($^2J_{\text{PH}} = 37.8$) ppm. In cyclohexane- d_{12} , a $^{31}\text{P}\{^1\text{H}\}$ resonance shifted to very high field (δ -59.8 (br s) ppm) was seen. These data, particularly the distinguishing $^{31}\text{P}\{^1\text{H}\}$ resonance,²¹ strongly implicated preferential attack by the rhenium center on C-H bonds of the PMe_3 ligand, and the structure of 5a was assigned as $\text{Cp}^*\text{Re}(\text{CO})\text{PMe}_2\text{CH}_2(\text{H})$ (Scheme XV). Preparations of relatively large amounts of 5a were performed with nitrogen purged hexane solutions of 2. The formation of significant amounts of light absorbing impurities made it particularly important in this case to work at low concentration of 2 (10^{-4} - 10^{-3}M) and low light intensity (100-W lamp, 1 h 20 min.). Integration (relative to a tetramethylsilane internal standard) of the ^1H NMR spectra of a carefully prepared sample of 5a, taken up in toluene- d_8 and maintained below -40°C to prevent further reaction, indicated that yields of 30 % at 70 % conversion of 2 could be achieved for 5a (Figure III).

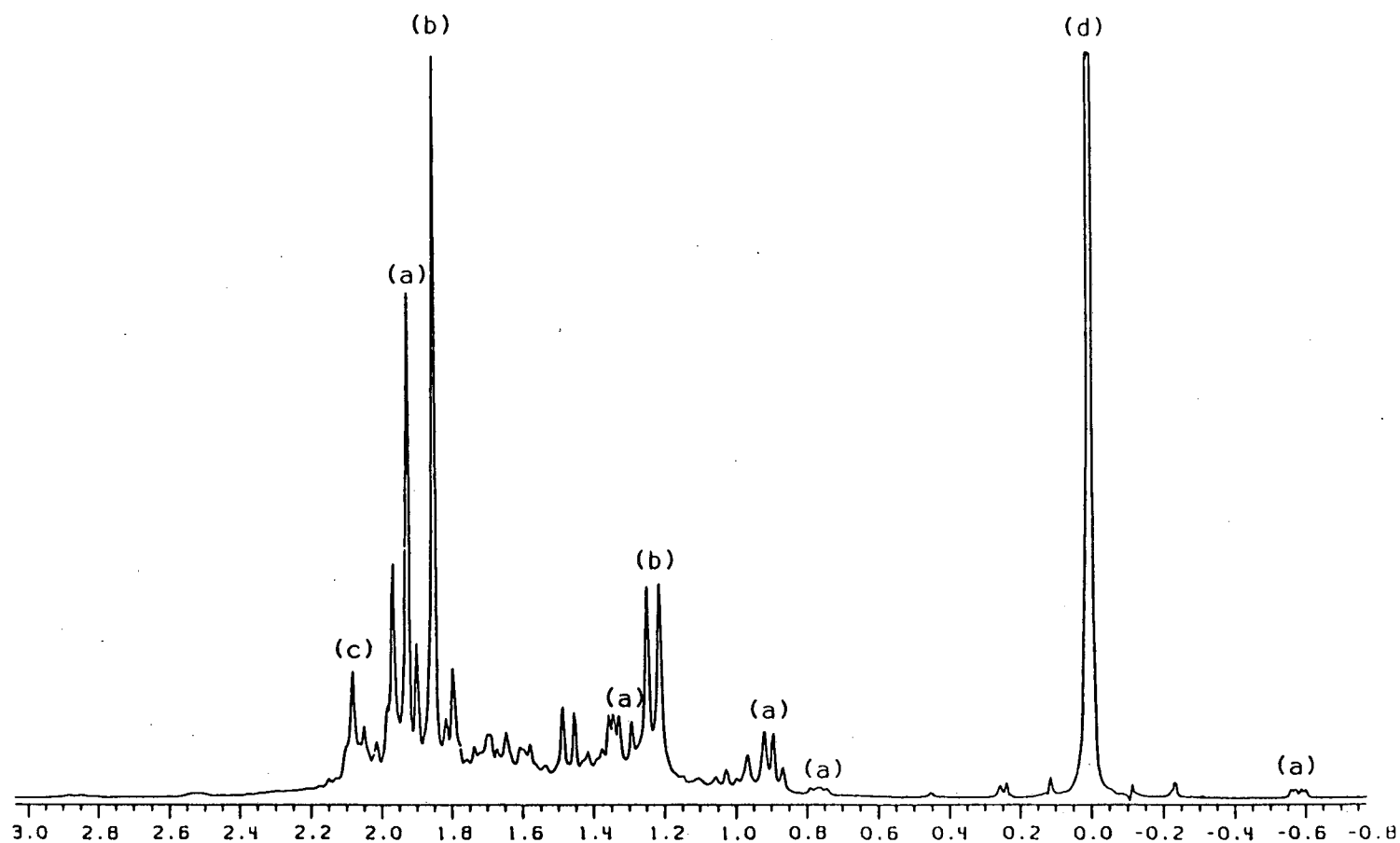


Figure III. 250 MHz ^1H NMR spectrum (toluene- d_8 , -10°C) of a typical mixture containing **5a**. Peak assignment: (a) **5a**; (b) **2**; (c) toluene- d_7 ; (d) tetramethylsilane. Chemical shifts are recorded in ppm downfield from tetramethylsilane. Figure continued on next page.

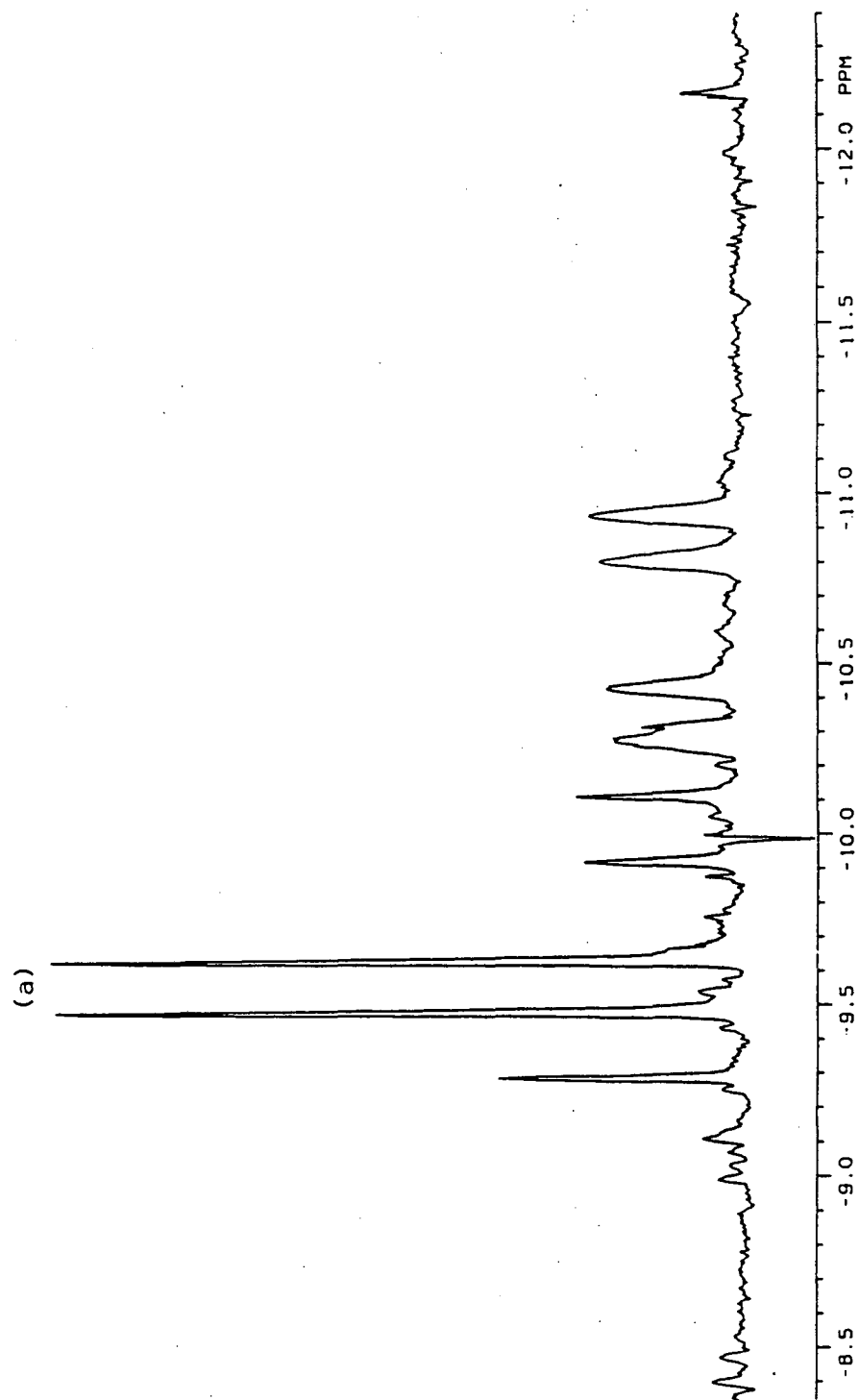
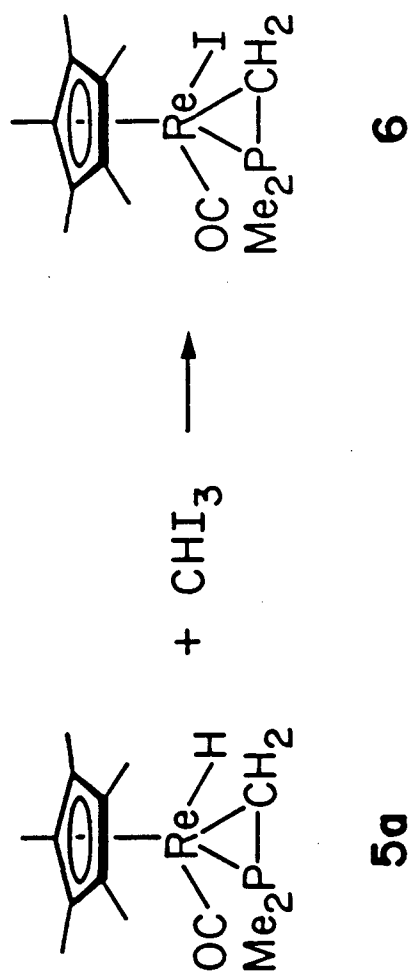


Figure III. (Continued from previous page)

Purification of 5a was not possible, and confirmation of its structure was acquired through derivatization without ring opening to the corresponding iodide $\text{Cp}^*\text{Re}(\text{CO})\text{PMe}_2\text{CH}_2(\text{I})$ (6) by treatment of a mixture containing 5a with iodoform (Scheme XVI). Compound 6, isolated after chromatography on silica in 18 % yield based on the amount of 2 used in making 5a, is a slightly pentane soluble, but highly benzene soluble, yellow solid. It was fully characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{31}P , and $^{31}\text{P}\{^1\text{H}\}$ NMR, IR, and low and high resolution MS. Here the stereotopic methyl groups on phosphorous have resonances observed at δ 1.59 (d, $^2J_{\text{PH}} = 13.4$) and 0.88 (d, $^2J_{\text{PH}} = 12$) ppm, and the stereotopic methylene ^1H peaks are at δ 1.08 (dd, $^2J_{\text{HH}} = 7.7$, $^2J_{\text{PH}} = 3.4$) and -0.04 (dd, $^2J_{\text{HH}} = 7.7$, $^2J_{\text{PH}} = 3.7$) ppm. A single upfield resonance at δ -64.83 ppm is found in the ^{31}P NMR spectrum, characteristic of a cyclometallated trimethylphosphine ligand.²¹ This resonance is a binomial septet ($^2J_{\text{PH}} = 13$) of broadened peaks when no ^1H decoupling is applied to the sample, due to similar coupling constants to the protons of the stereotopic methyl groups on phosphorous and unresolved coupling to the methylene protons. ^1H decoupling collapses the ^{31}P resonance to a broad singlet. The presence of the CO ligand was evident from a $^{13}\text{C}\{^1\text{H}\}$ NMR peak at δ 201.79 (br s) ppm, $\text{M}^+ - \text{CO}$ ions in the mass spectra for the two naturally occurring isotopes of rhenium, and an intense IR absorption at 1886 cm^{-1} .

Although cyclometallated hydride 5a is stable indefinitely at room temperature in alkanes like neopentane, pentane, hexane, and cyclohexane, the transformation of 5a to the phenyl hydride 3a alluded to above takes place rapidly when 5a in a mixture is redissolved in

Scheme XVI

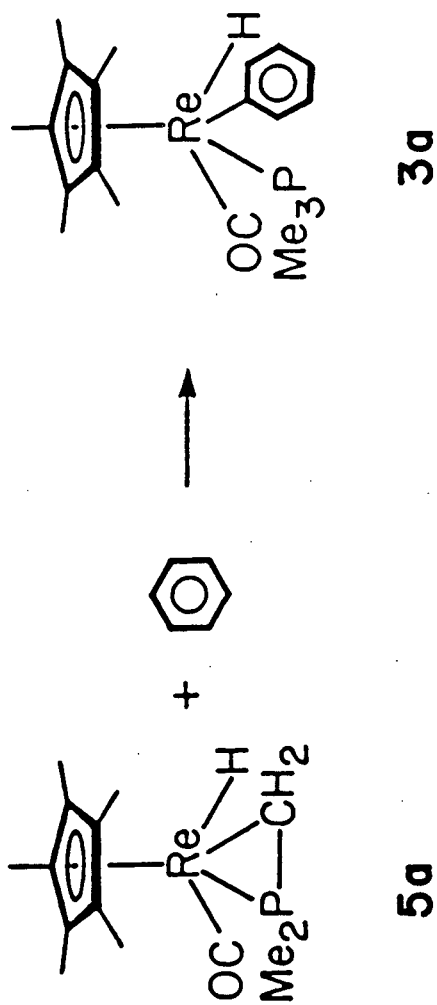


benzene (Scheme XVII). Specifically, observation of the Cp* and hydride resonances by ^1H NMR spectroscopy of a sample of 5a dissolved in benzene- h_6 revealed the quantitative conversion of 5a to 3a with a half life on the order of 0.5 h at 25 °C. If benzene- d_6 was used instead of benzene- h_6 , only $\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)(\text{C}_6\text{D}_5)\text{D}$ (3a- d_6) was formed, and no 3a- d_n ($n < 6$), as indicated by the absence of hydride and bound phenyl group resonances in the ^1H NMR spectra.

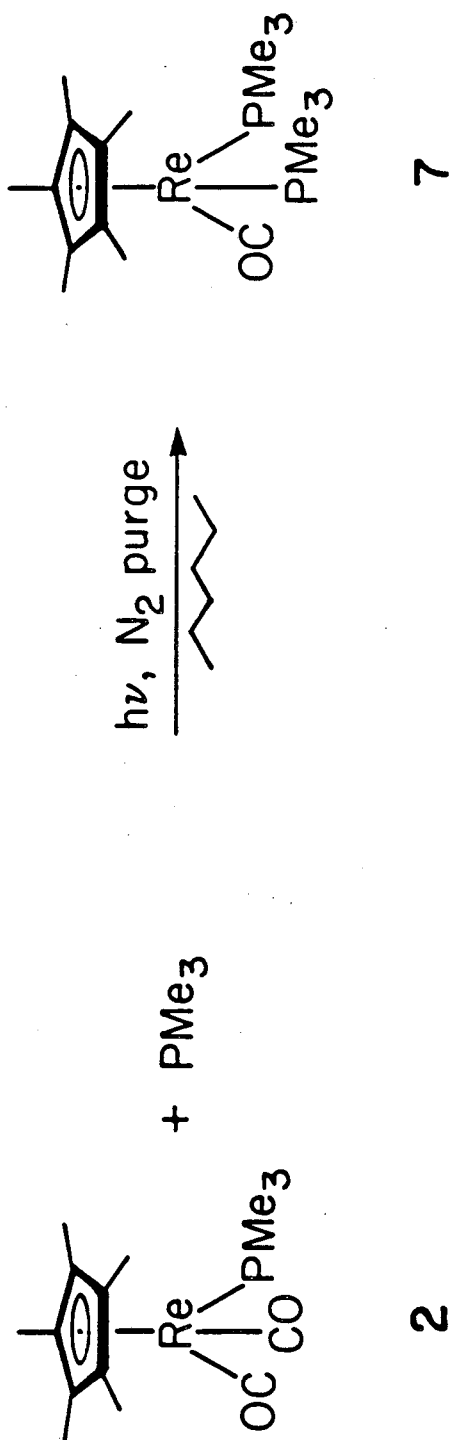
Synthesis and Reaction of $\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)_2$ (7).

Since evidence for intermolecular insertion into C-H bonds was so far procured only for benzene and cyclopropane, and intramolecular attack on PMe_3 ligands was seen in alkane solvents, it would seem necessary to make the metal center in 2 more electron-rich by substitution of a second CO ligand with PMe_3 in order to see alkane C-H activation. This substitution was achieved by photolysis of 2 (ca. 10^{-3}M) in nitrogen purged hexane with a greater than 200 fold excess of PMe_3 to give $\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)_2$ (7) in 22 % yield after chromatography on silica (Scheme XVIII). Like 2, compound 7 could also be prepared on an analytical scale by irradiation in neat PMe_3 . The light tan 7 was fully characterized. Of interest is the virtual doublet observed for the methyl groups bound to phosphorous in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (Figure IV). The remaining CO ligand gave a peak at δ 208.25 (br s) ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum and a very strong IR absorption at 1833 cm^{-1} . The latter is a remarkably low stretching frequency for a terminally bound CO ligand, indicating extensive back-bonding and a quite electron-rich rhenium center.

Scheme XVII



Scheme XVIII



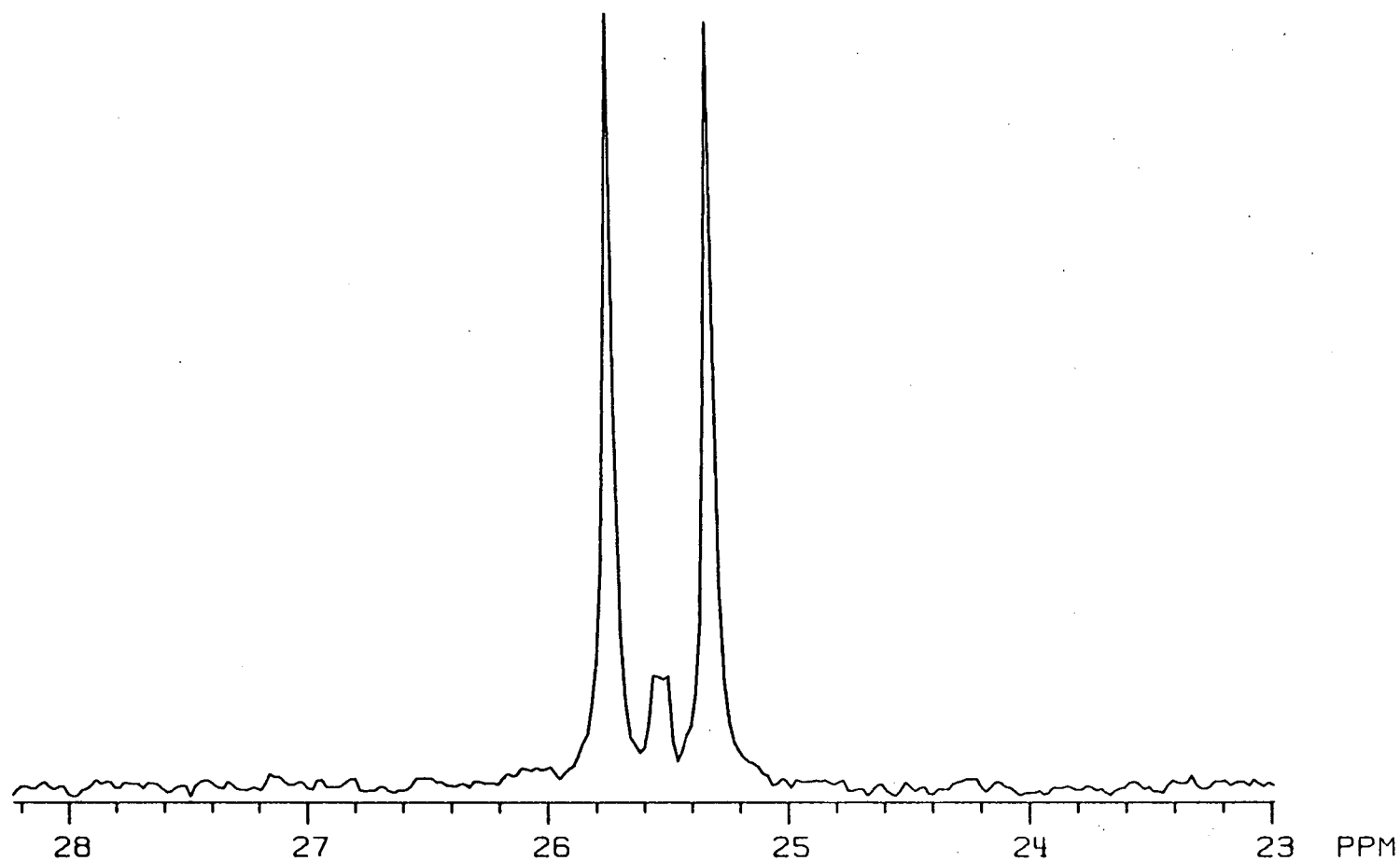


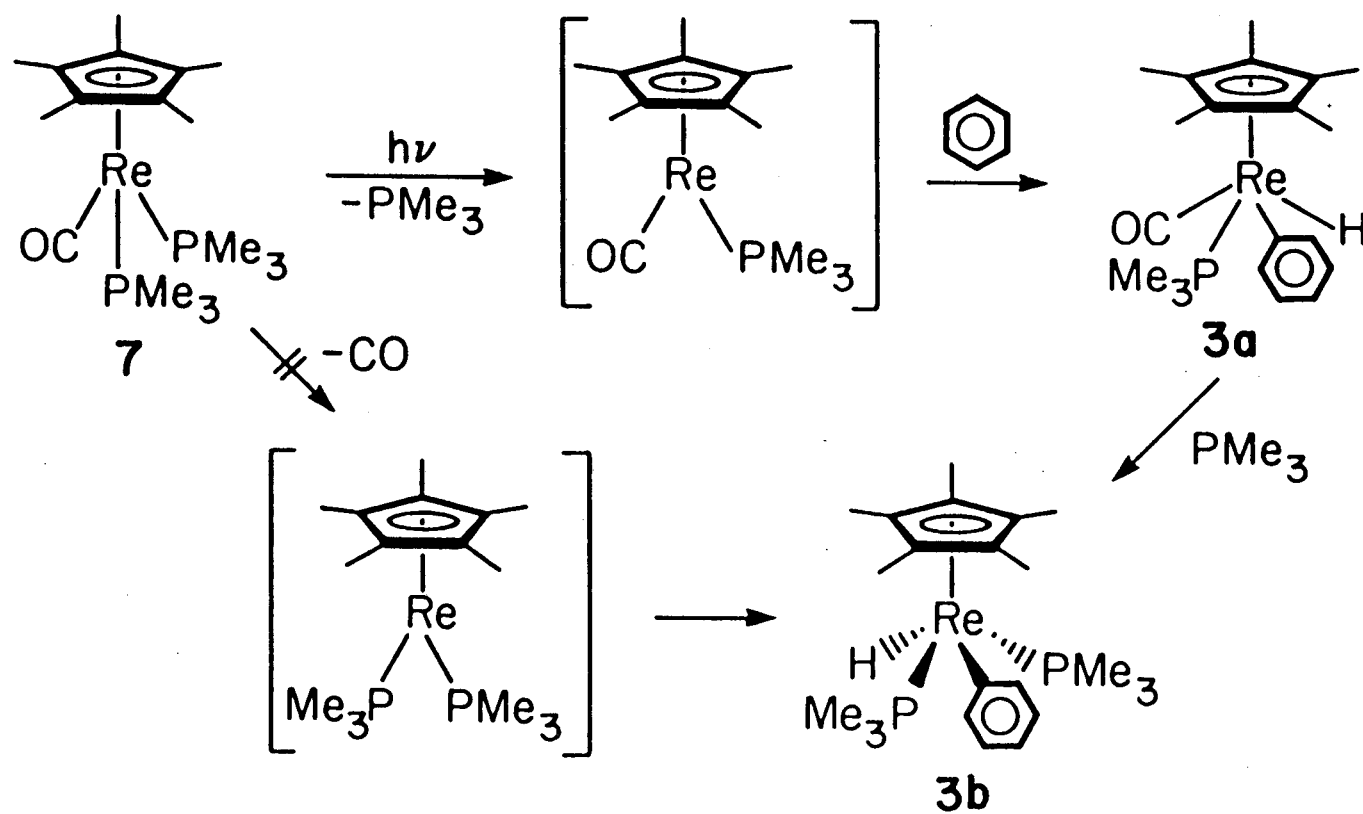
Figure IV. 75.5 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (benzene- d_6) of bound- PMe_3 region for **7**. Chemical shifts are recorded in ppm downfield from tetramethylsilane.

Unfortunately, the low CO stretching frequency is also indicative of a CO ligand which is not easily dissociated, and photolysis of 7 does not lead to extrusion of CO, but rather to loss of PMe_3 . This is apparent from the irradiation of 7 in benzene, in which the initial generation of resonances due to 3a is observed by ^1H NMR spectroscopy. These resonances necessarily give way to those of 3b, as mentioned before (Scheme XIX).

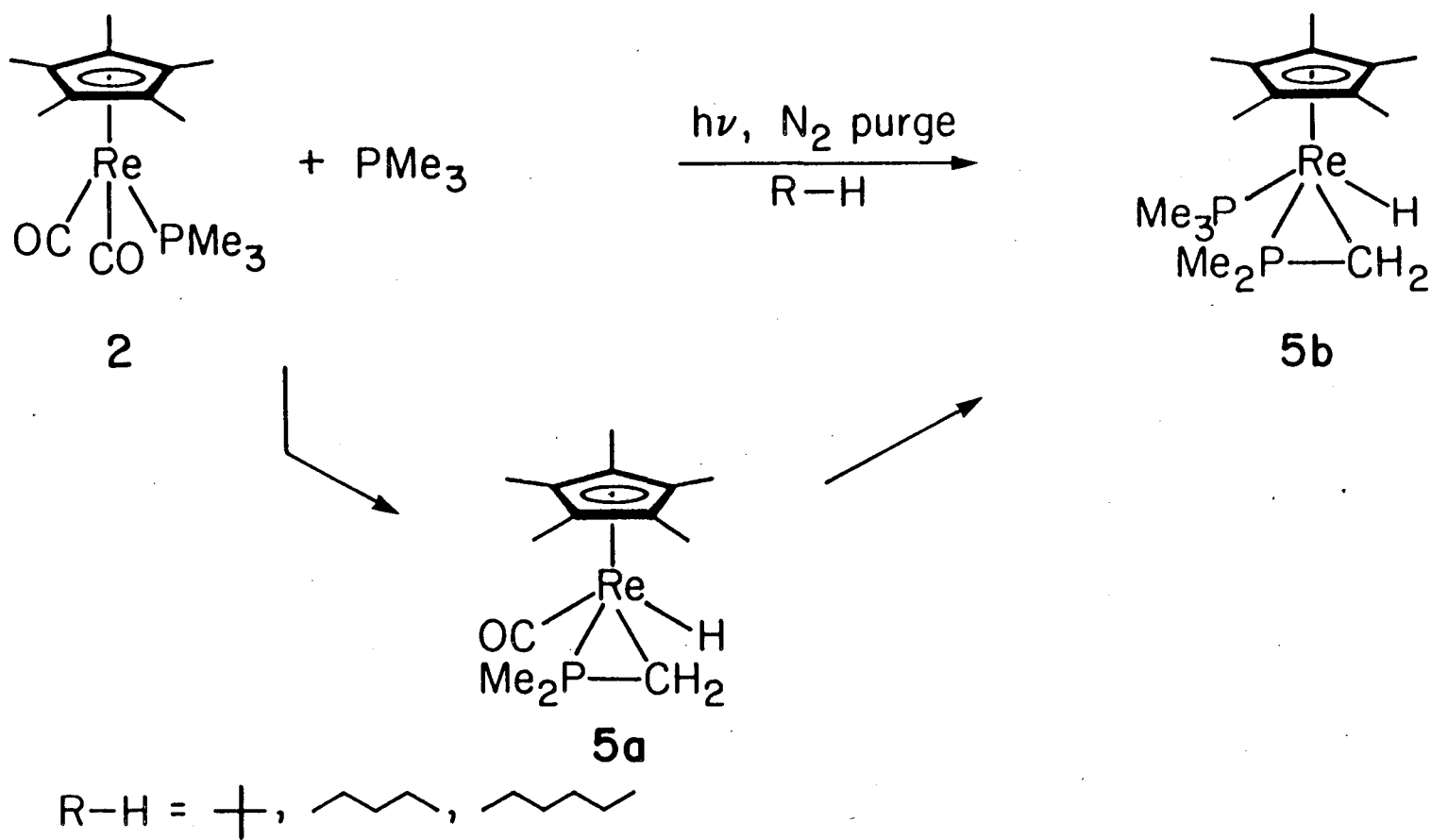
Synthesis and Reactions of $\text{Cp}^*\text{Re}(\text{PMe}_3)_2\text{PMe}_2\text{CH}_2(\text{H})$ (5b).

Just as the photolysis of 2 in benzene did not stop at the formation of carbonyl(phosphine)phenyl hydride 3a, but led on to bis(phosphine)phenyl hydride 3b, so the prolonged irradiation of 2 in alkanes caused cyclometallated complex 5a to be converted to $\text{Cp}^*\text{Re}(\text{PMe}_3)_2\text{PMe}_2\text{CH}_2(\text{H})$ (5b) (Scheme XX). This conversion is best carried out in the presence of added free phosphine. Preparation of 5b can be accomplished starting directly from 1 (10^{-2} - 10^{-1} M) and free PMe_3 in neopentane, pentane, or hexane. However, at low concentrations of PMe_3 (1 equiv), initial formation of 2 was prohibitively slow, and large quantities of PMe_3 (30 equiv) led, after rapid formation of 2, mostly to uncharacterized side products. Thus, on an analytical scale irradiation of 1 (10^{-2} - 10^{-1} M) in the presence of a 12 fold excess of PMe_3 was found to be best. The cyclometallated complex 5a is observed as an intermediate in this process. Preparative scale synthesis of 5b, however, was best carried out by irradiation of 2 (10^{-4} - 10^{-3} M) for 3.3 h in nitrogen purged hexane with an approximately 50 fold excess of PMe_3 . The efficiency of this reaction varied somewhat. In order to measure the yield of 5b, low

Scheme XIX



Scheme XX



temperature ^1H NMR spectra were acquired on a carefully prepared toluene- d_8 solution of **5b** containing tetramethylsilane as an internal standard. The sample of **5b** used was not from a particularly efficient synthesis, and integration of the spectra set a minimum of 23 % yield of **5b** at 88 % conversion of **2**.

Compound **5b** is quite thermally stable in most alkanes, and survived heating in hexane up to 125 °C. Heating above 125 °C led to slow decomposition over several days. Nevertheless, it resisted purification, even decomposing when chromatographed at -110 °C on alumina III. Treatment of a mixture containing **5b** with iodoform converted **5b** to very insoluble unidentified material. Therefore, **5b** was examined as part of mixtures in subsequent reactions (Figure V).

Characterization of cyclometallated compound **5b** consisted of ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, and high resolution MS. A singlet resonance in the ^1H NMR spectrum in benzene- d_6 at δ 1.97 ppm was assigned to the Cp^* moiety, while the conventionally bound PMe_3 ligand gave a doublet at δ 1.29 ($^2J_{\text{PH}} = 7.2$) ppm. The stereotopic methyl groups on phosphorous produced two doublet resonances at δ 1.39 ($^2J_{\text{PH}} = 10$) and 1.31 ($^2J_{\text{PH}} = 10$) ppm, and the stereotopic methylene protons gave a doublet of doublets of doublets at δ 0.09 ($^3J_{\text{PH}} = 13.8$, $^2J_{\text{HH}} = 7.3$, $^2J_{\text{PH}} = 1.9$) ppm and a virtual quartet at δ -0.23 (J = 19.6, separation of the outermost lines of the resonance pattern) ppm. The hydride resonance at δ -12.02 ppm is now split by the two chemically nonequivalent phosphorous atoms into a doublet of doublets ($^2J_{\text{PH}} = 39.0$, $^2J_{\text{PH}} = 32.6$). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the stereotopic methyl groups on phosphorous led to two doublets (δ 17.27 ($^1J_{\text{PC}} = 25.1$) and 10.45 ($^1J_{\text{PC}} = 22.4$) ppm), and the resonance of the methylene

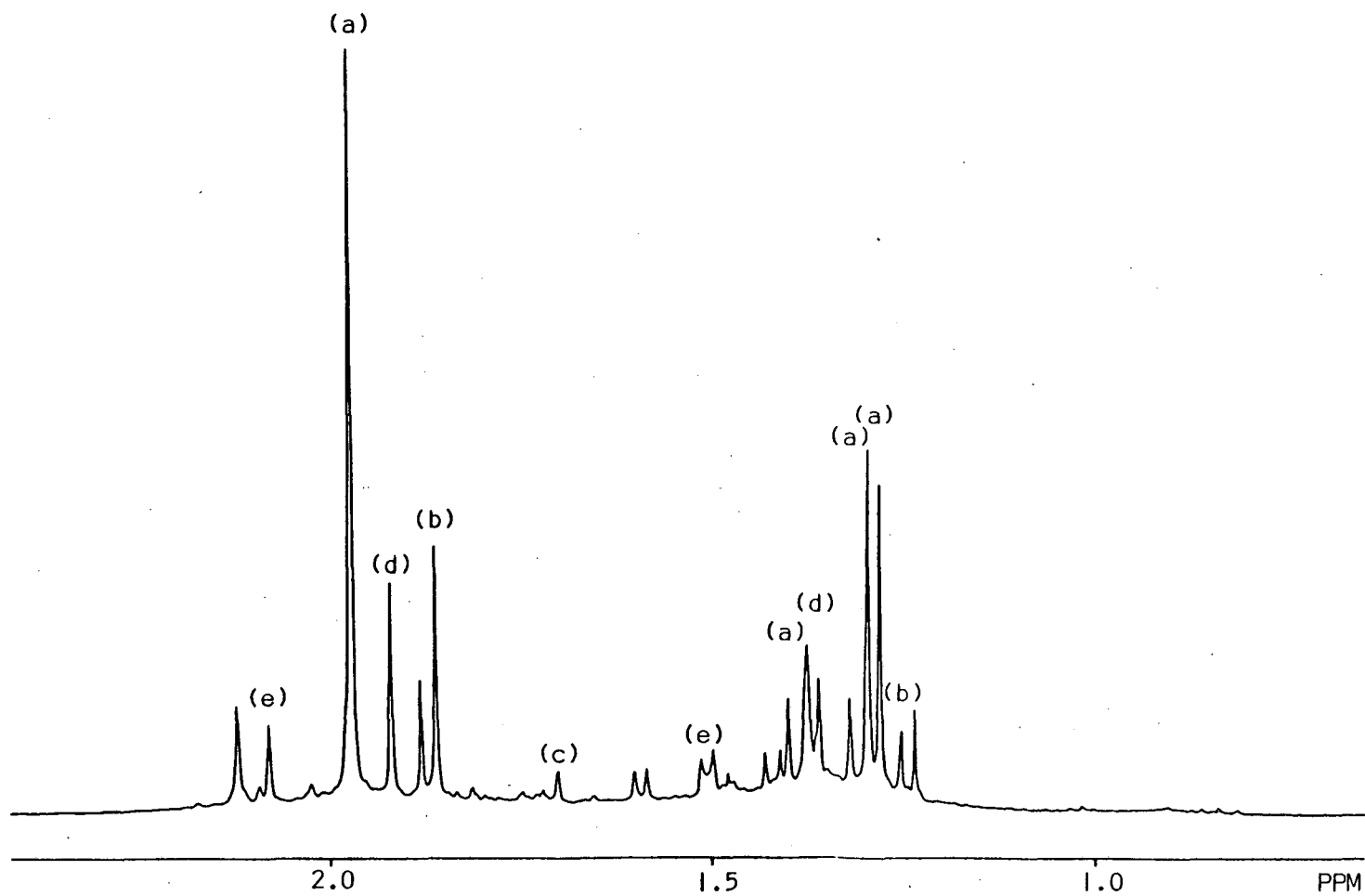


Figure V. 500 MHz ¹H NMR spectrum (benzene-d₆) of a typical mixture containing **5b**. Peak assignment: (a) **5b**; (b) **2**; (c) **3a**; (d) **7**; (e) **8**. Chemical shifts are recorded in ppm down-field from tetramethylsilane. Figure continued on next page.

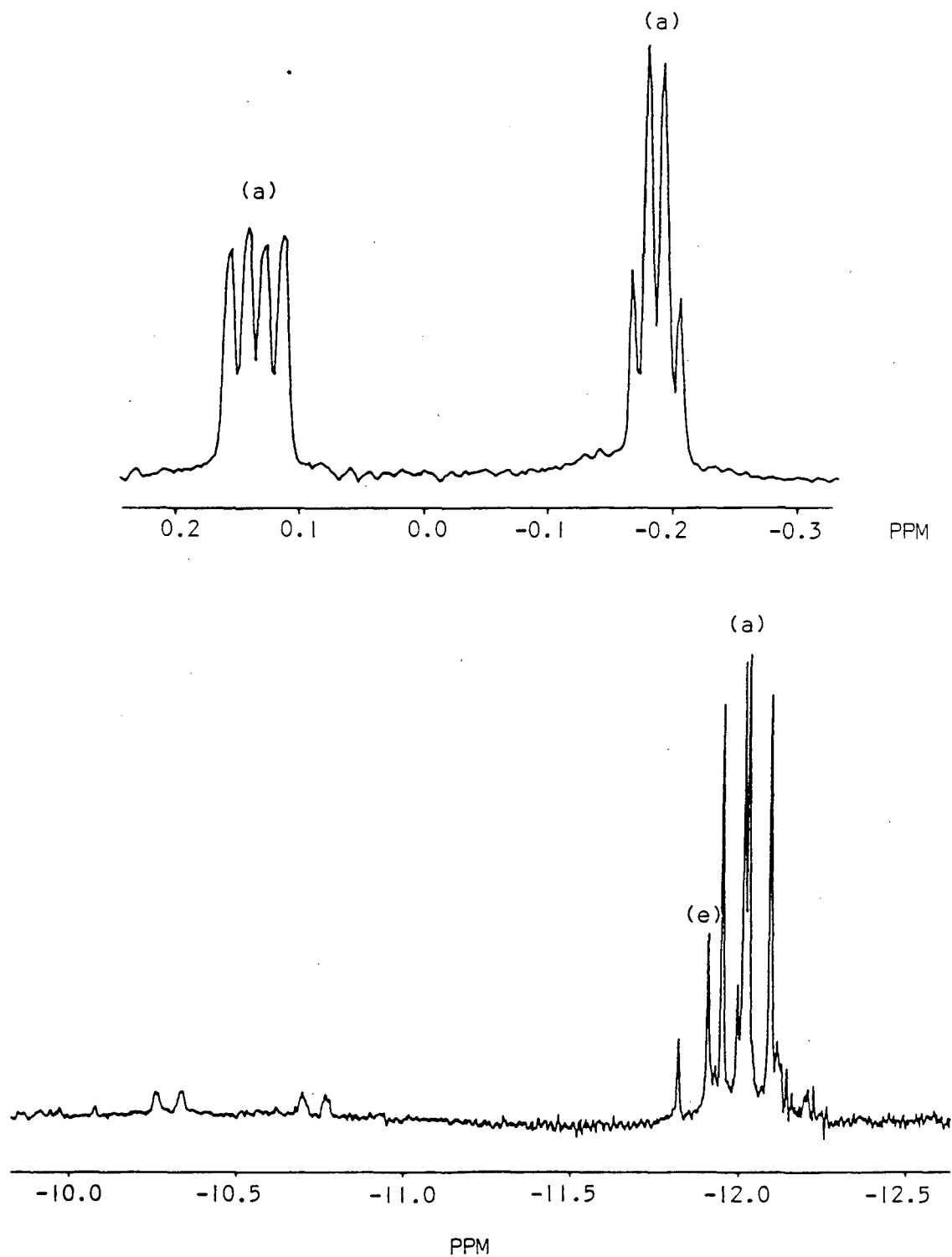


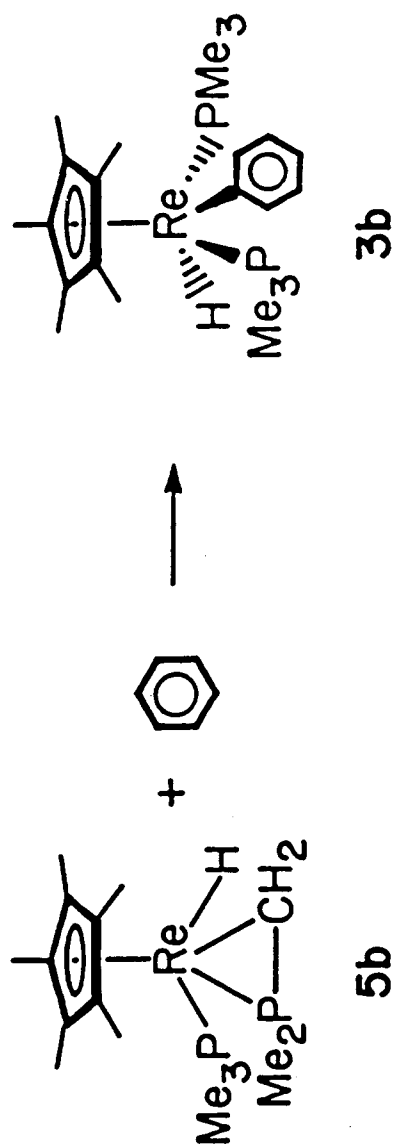
Figure V. (Continued from previous page)

carbon bound to rhenium at δ -31.94 ppm was a triplet ($J_{PC} = 8$), apparently due to fortuitously equal coupling to the two chemically distinct phosphorous atoms. As was true for the other cyclometallated complexes already described, **5a** and **6**, a severely upfield shifted $^{31}\text{P}\{^1\text{H}\}$ resonance was found at δ -76.88 ppm for **5b**. This resonance is a doublet ($^2J_{PP} = 19.7$) due to coupling to the phosphorous of the conventionally bound PMe_3 ligand, the resonance due to which is observed within the expected range (δ -39.41 (d, $^2J_{PP} = 19.8$) ppm).²¹

The synthetic route to **5b** leads to many side products, and reaction mixtures containing small amounts of compounds **2**, **5a**, **7**, and several unidentified materials in addition to **5b** are common. None of these materials appear to be involved in the subsequent thermal reactions of **5b**. One compound in particular, **8**, occasionally is present in a significant amount (Figure V). Compound **8** has only Cp^* , bound PMe_3 , and hydride resonances with the intensity ratio 15:18:2 in its ^1H NMR spectrum. The hydride resonance is a triplet ($^2J_{PH} = 43.5$) at δ -11.89 ppm, and the PMe_3 resonance is a virtual doublet. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the PMe_3 ligands give a six-line complex multiplet. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy shows a single peak at δ -37.57 (br s) ppm, and the $^{31}\text{P}\{^1\text{H}\}$ and ^1H assignments were confirmed by selective ^{31}P decoupling of ^1H NMR spectra. These data suggest that **8** is trans- $\text{Cp}^*\text{Re}(\text{PMe}_3)_2\text{H}_2$. Of course a fluxional compound with the same ligands cannot be ruled out.

In direct analogy to **5a**, cyclometallated compound **5b** is converted at 25 °C in benzene solution into intermolecular C-H activation product **3b** (Scheme XXI). Observation of the Cp^* and hydride resonances by ^1H NMR spectroscopy indicated that this process is

Scheme XXI

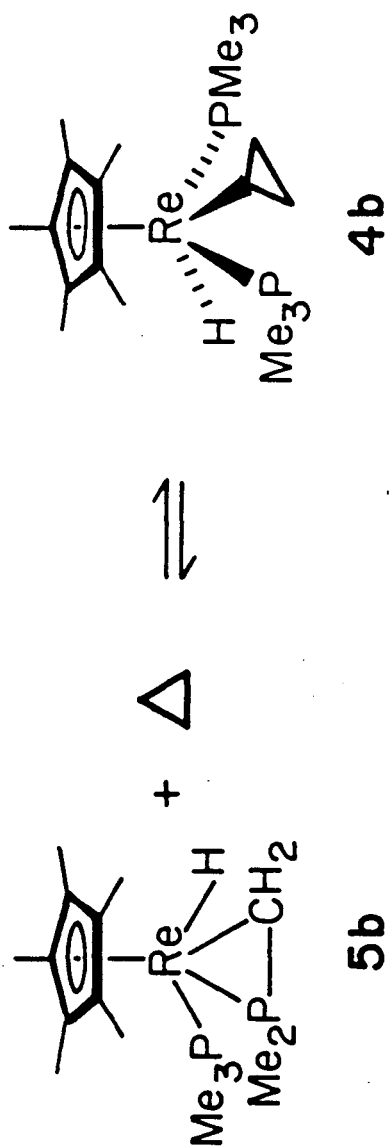


quantitative, with a half life on the order of four days. This is significantly slower than the conversion of **5a** to **3a**. Furthermore, no bound phenyl group or hydride resonances were detected due to **3b** by ^1H NMR when the conversion was carried out with benzene- d_6 , indicating only $\text{Cp}^*\text{Re}(\text{PMe}_3)_2(\text{C}_6\text{D}_5)\text{D}$ (**3b-d₆**) and no **3b-d_n** ($n < 6$) were produced.

The conversion of **5b** to **3b** proved useful in confirming the spectral assignments of **5b**. Compound **5b** was always detected and used in mixtures, but it is the only component of these mixtures which reacts with benzene. After heating a sample of **5b** in benzene- d_6 at 60-70 °C for 1 h, only the **5b** NMR resonances had disappeared, making obvious their location.

The reactivity of **5b** was used to further advantage in activating other hydrocarbons. Thermal intermolecular insertion of rhenium into the C-H bonds of cyclopropane was effected upon heating of **5b** as a mixture in liquid cyclopropane, yielding $\text{Cp}^*\text{Re}(\text{PMe}_3)_2(\overline{\text{CHCH}_2\text{CH}_2})\text{H}$ (**4b**) (Scheme XXII). However, under the reaction conditions the relative stabilities of starting material **5b** and product **4b** are nearly comparable, and an equilibrating mixture of hydrido(cyclopropyl) complex **4b** and cyclometallated complex **5b** was observed by ^1H NMR spectroscopy. As entropic considerations would suggest, formation of **4b** was favored by lower temperatures, while more **5b** was present at higher temperatures. Optimum conversion of **5b** to **4b** in a practical reaction time was 33 % at 45 °C after 37.5 h with cyclopropane as solvent, as measured by ^1H NMR spectroscopy. Hydrido(cyclopropyl) complex **4b** was partially purified by fast chromatography at 15 °C on alumina III (Figure VI). It is a waxy, white, crystalline solid of extraordinary solubility in common organic solvents, including

Scheme XXII



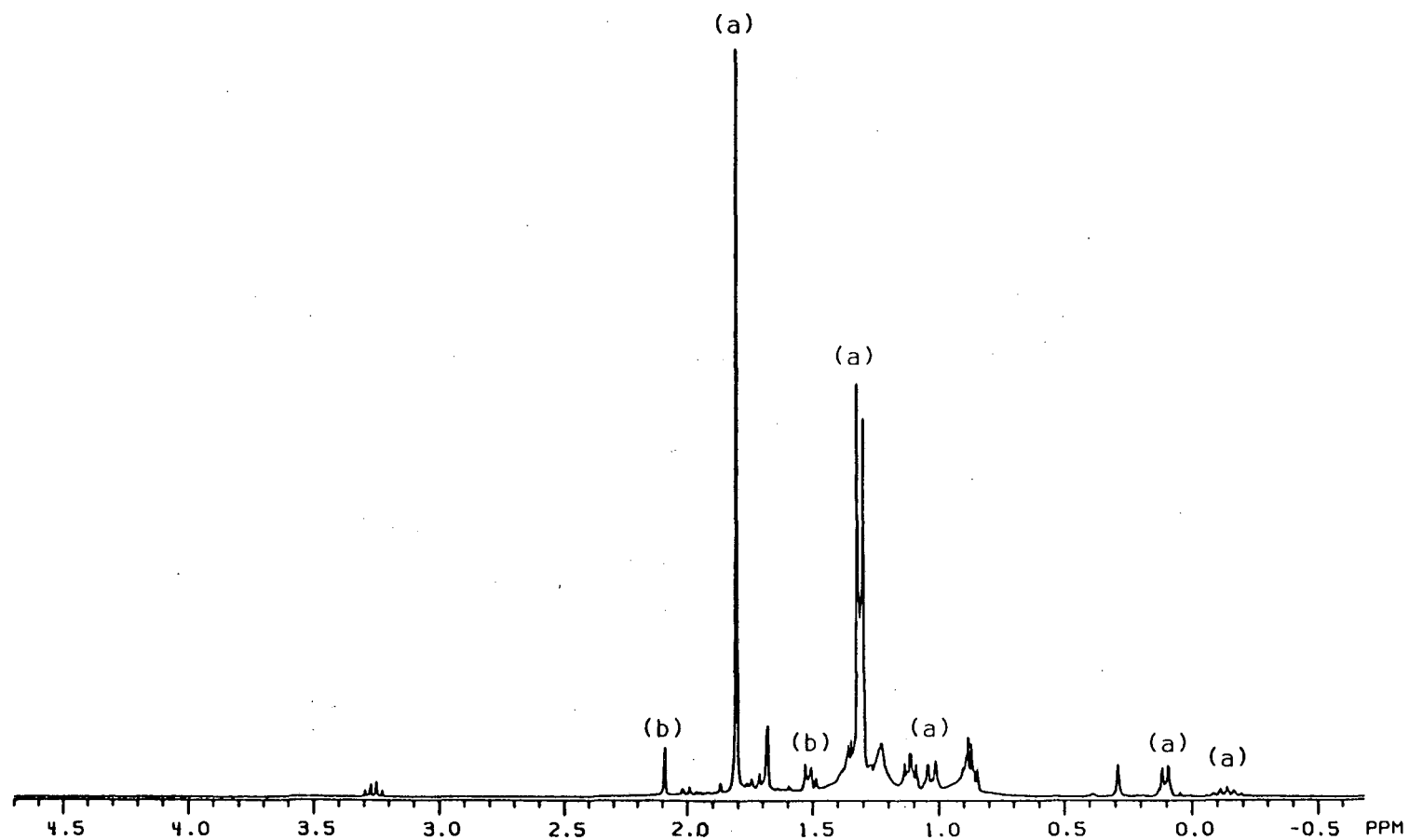


Figure VI. 300 MHz ^1H NMR spectrum (benzene- d_6) of partially purified **4b**. Peak assignment: (a) **4b**; (b) **8**. Chemical shifts are recorded in ppm downfield from tetramethylsilane. Figure continued on next page.

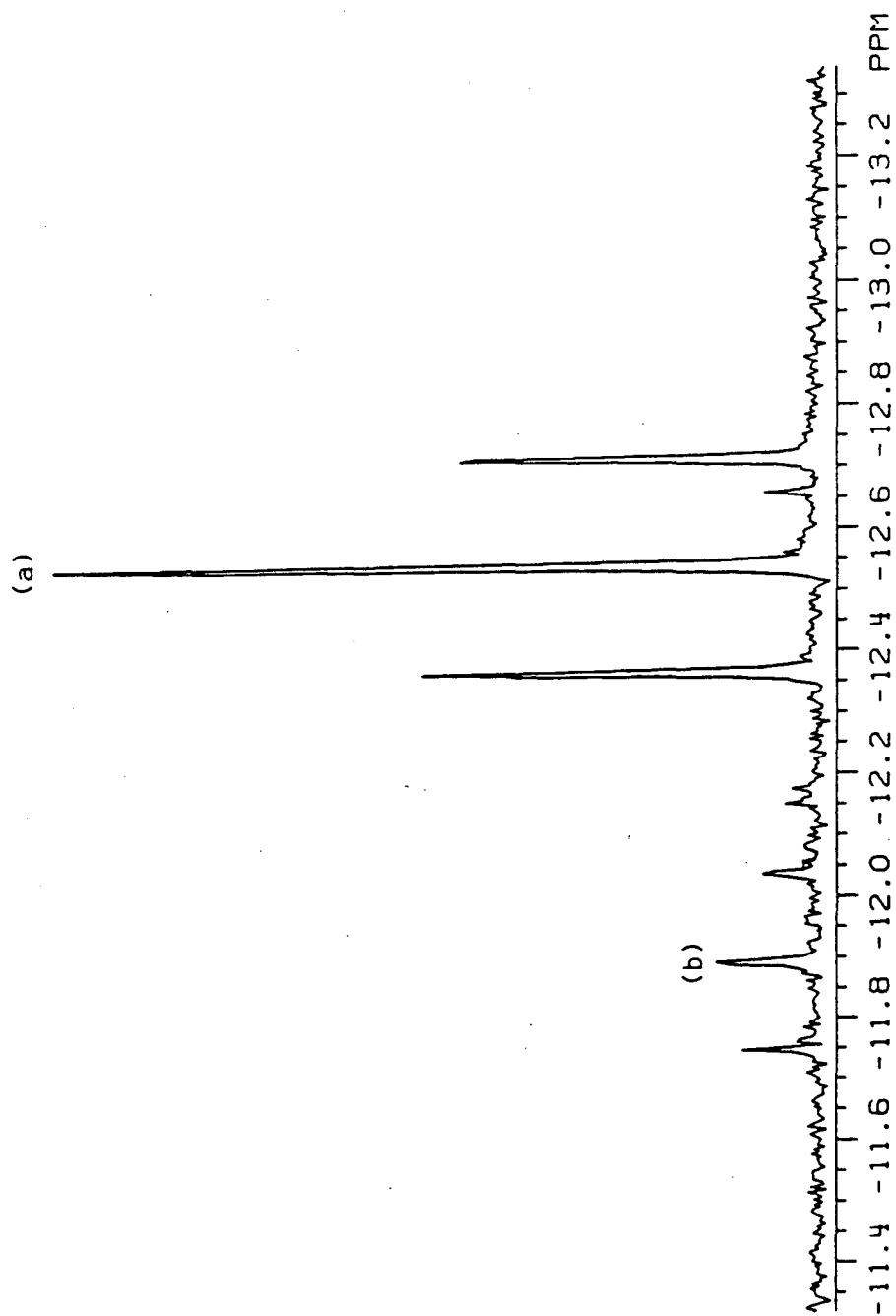


Figure VI. (Continued from previous page)

pentane. Compound **4b** is somewhat thermally sensitive, decomposing when heated above 25 °C. Full spectroscopic characterization was obtained, including low and high resolution mass spectra. In addition to parent ions, the mass spectra showed $M^+ - C_3H_6$ ions for the two naturally occurring rhenium isotopes. In the 1H NMR spectrum, the hydride resonance at δ -12.54 ppm is a triplet ($^2J_{PH} = 52.3$). A single $^{31}P\{^1H\}$ NMR peak at δ -40.06 (br s) ppm is also seen. Like the spectra for bis(phosphine)phenyl hydride **3b**, this implies coupling to two phosphorous atoms which are chemically equivalent, due either to a trans geometry or fluxionality on the NMR time scale. Also similar to the data for **3b** are the characteristic virtual doublet in the 1H NMR spectrum and the complex six-line multiplet in the $^{13}C\{^1H\}$ NMR spectrum for the PMe_3 ligands of **4b** (Figure VII). The bound cyclopropyl moiety of **4b** was evident from two doublet-like multiplets at δ 1.03 and 0.10 ppm integrating to two protons each, due to the β hydrogens, and a septet ($J = 8$) at δ -0.14 ppm, integrating to one proton and assigned to the α hydrogen. The latter resonance is presumably a septet due to nearly equivalent coupling to the two phosphorous atoms and the four β hydrogens. Again, a weak IR Re-H stretching absorption was observed at 1962 cm^{-1} .

In a fashion analogous to the preparation of cyclopropyl hydride **4b**, treatment of cyclometallated complex **5b** with methane in hexane or cyclohexane solution gave $Cp^*Re(PMe_3)_2CH_3(H)$ (**9**) (Scheme XXIII). As was the case for **4b**, the relative stabilities of starting material **5b** and product **9** are nearly comparable under the reaction conditions, and an equilibrating mixture of hydrido(methyl) complex **9** and cyclometallated complex **5b** was likewise observed by 1H NMR spectroscopy.

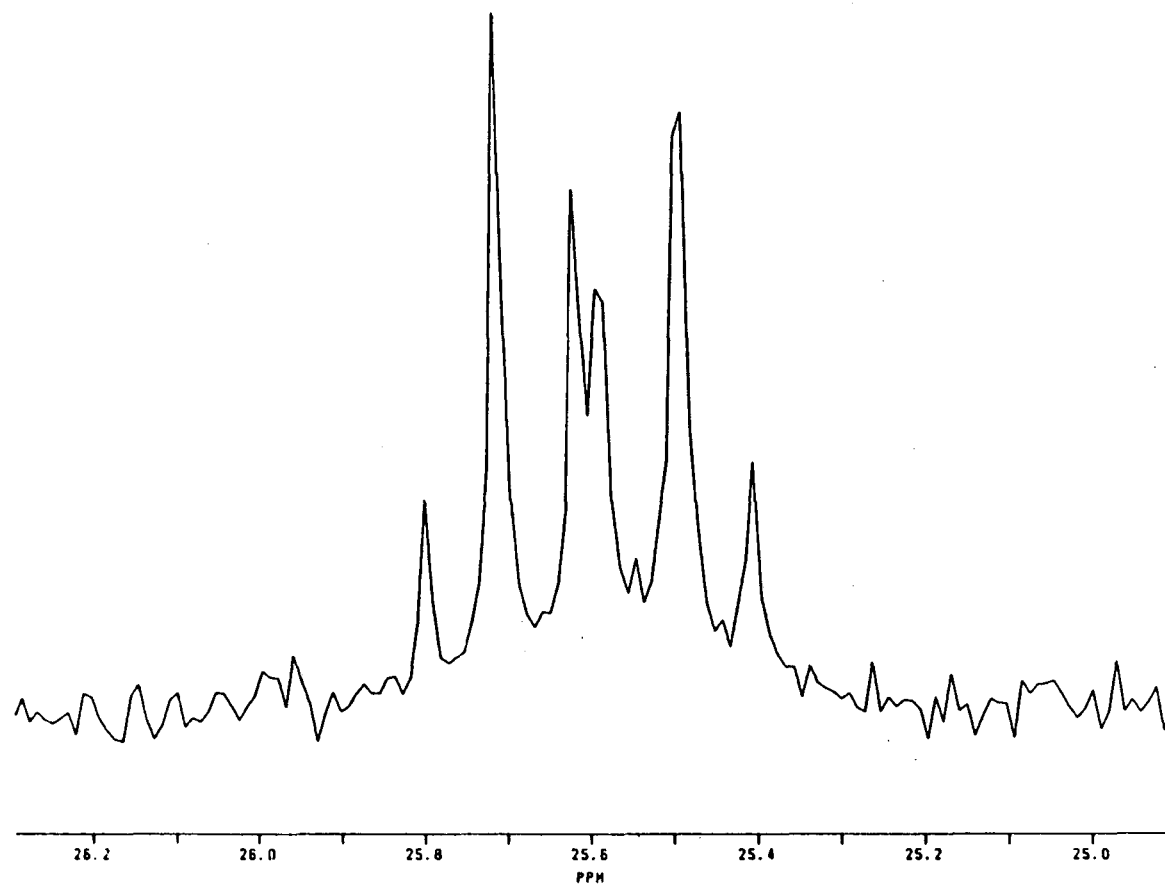
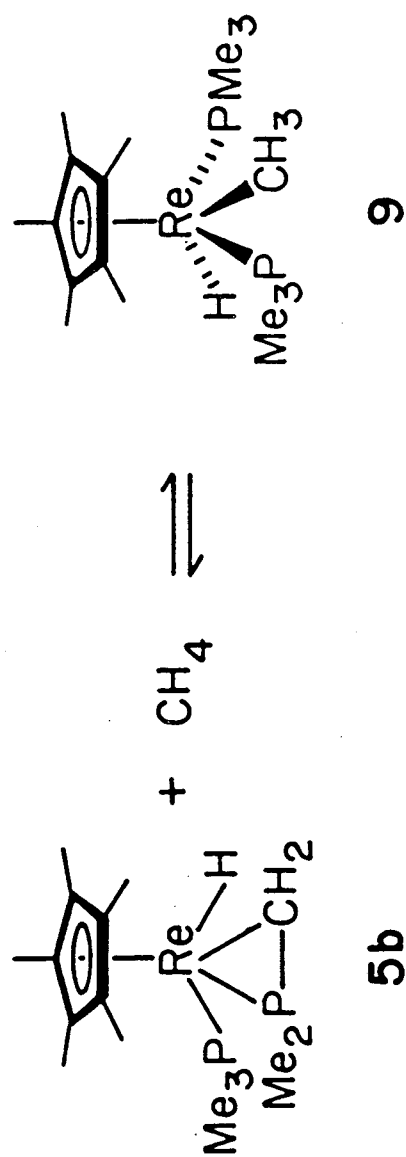


Figure VII. 125.8 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (benzene- d_6) of bound- PMe_3 region for **4b**. Chemical shifts are recorded in ppm downfield from tetramethylsilane.

Scheme XXIII



However, in this case the equilibrium lay further toward **5b**, perhaps because of the difficulty of achieving high methane concentrations. Indeed, the following observations consistent with the laws of mass action and entropy were made: higher methane pressures and lower temperatures favored **9**, whereas lower methane pressures and higher temperatures increased the amount of **5b**. Taking these factors into consideration, preparative scale synthesis of **9** was executed at 70 °C under 82 atm of methane in hexane over 55.5 h to give approximately 20 % conversion of **5b** to **9** as measured by ^1H NMR spectroscopy. Partial purification of **9** with some loss of material was achieved by chromatography at -95 to -110 °C under nitrogen, giving a nearly colorless, highly pentane-soluble oil which was 32 % in **9** (Figure VIII). The structure of **9** was substantiated by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR, and high resolution MS. The high resolution mass spectrum exhibited parent ions as well as M^+-CH_4 peaks for the two naturally occurring rhenium isotopes. In analogy to the other bis(phosphine) hydrocarbon insertion products, the single $^{31}\text{P}\{^1\text{H}\}$ resonance at δ -36.81 (br s) ppm and the ^1H NMR hydride triplet ($^2J_{\text{PH}} = 48.5$) at δ -12.35 ppm indicated a trans or fluxional geometry. The peaks in the hydride triplet were broadened, perhaps due to unresolved coupling to the protons of the methyl group bound to rhenium. In fact this coupling could be seen in the methyl group resonance, which was a triplet of doublets ($^3J_{\text{PH}} = 11.3$, $^3J_{\text{HH}} = 2.1$) at δ -0.01 ppm. Again, a virtual doublet in the ^1H NMR spectrum and a six-line complex multiplet in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum were assigned to the PMe_3 ligands. Selective ^{31}P decoupled ^1H NMR experiments provided confirmation of the ^1H and $^{31}\text{P}\{^1\text{H}\}$ assignments. Additional support for the

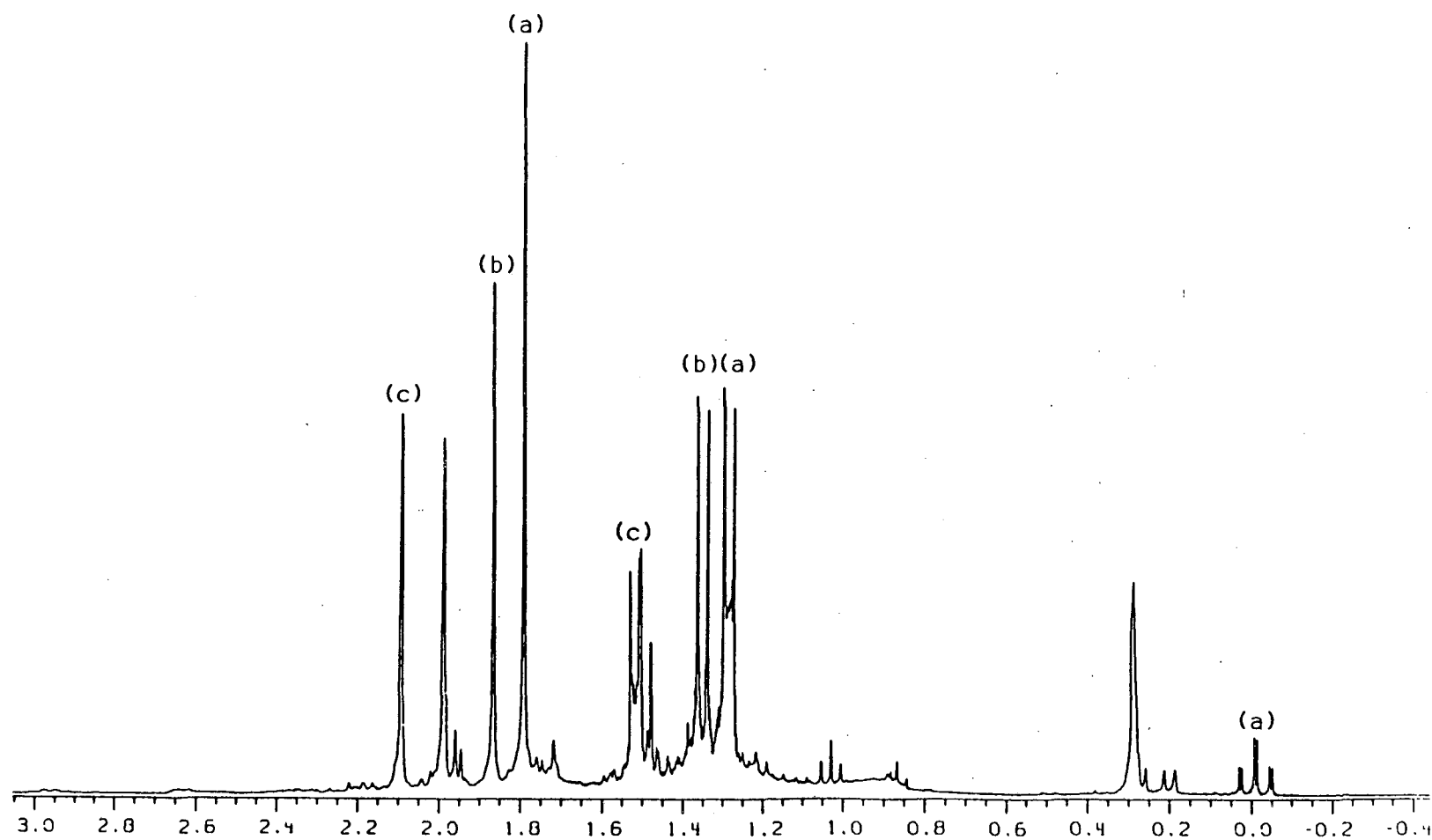


Figure VIII. 300 MHz ^1H NMR spectrum of partially purified **9**. Peak assignment: (a) **9**; (b) **2**; (c) **8**. Chemical shifts are recorded in ppm downfield from tetramethylsilane. Figure continued on next page.

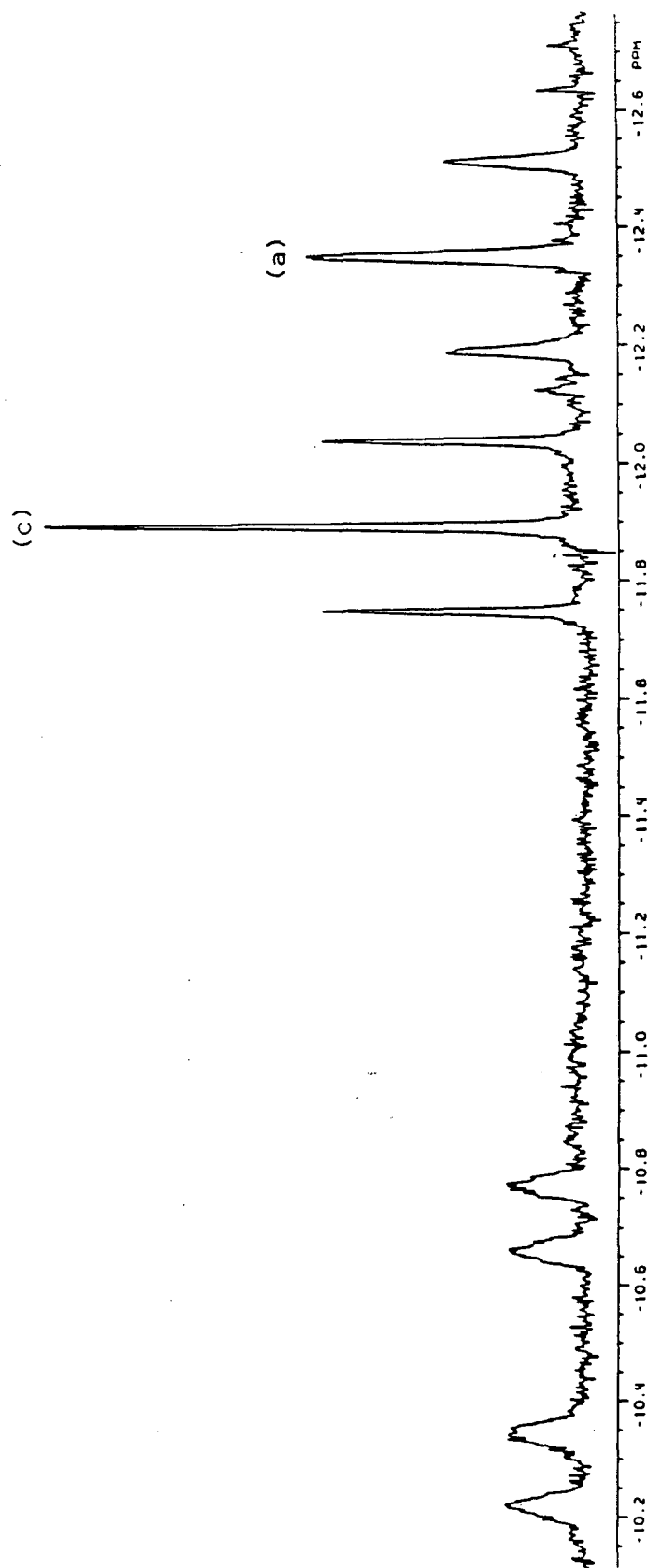


Figure VIII. (Continued from previous page)

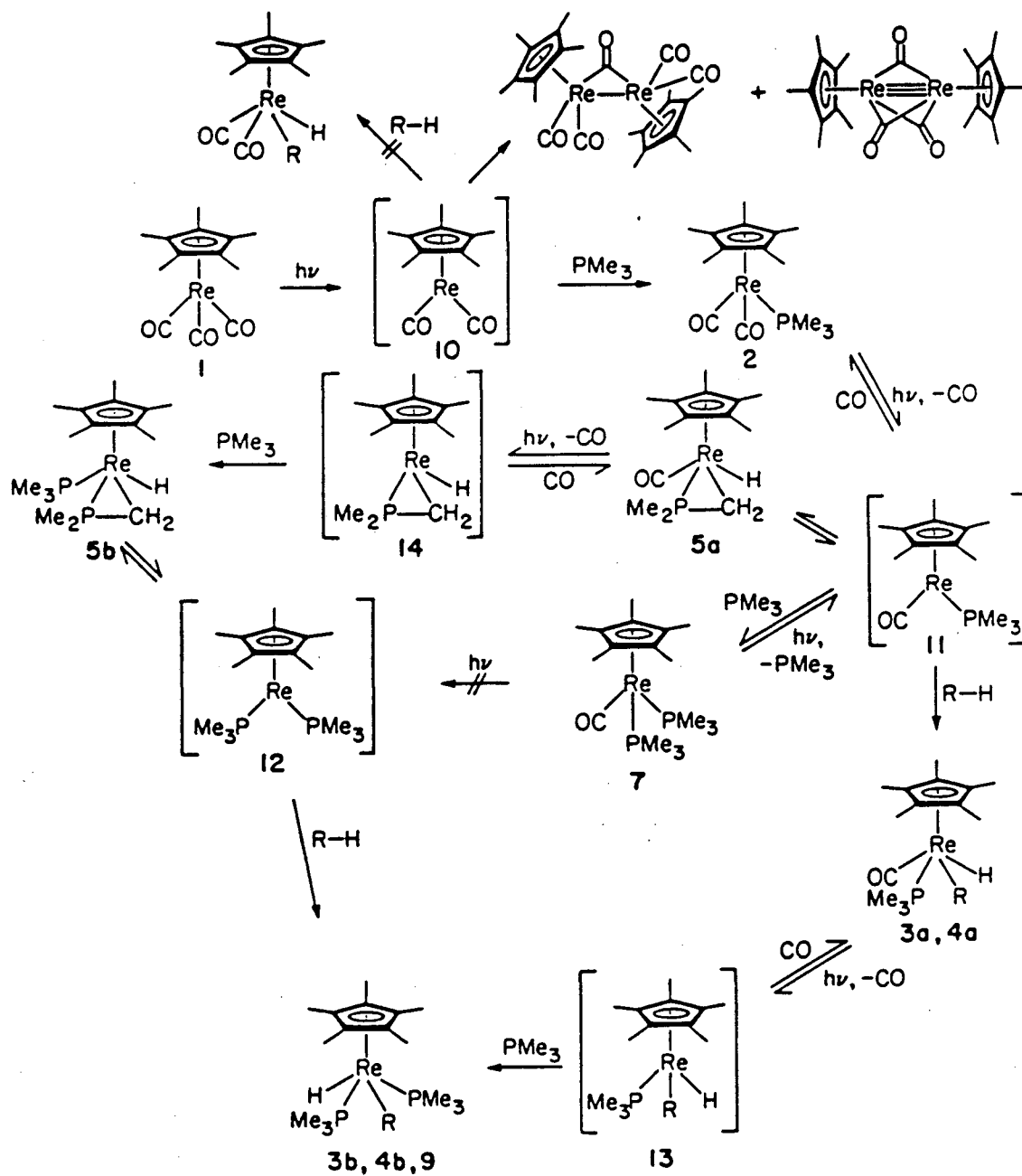
$^{13}\text{C}\{^1\text{H}\}$ NMR assignment of a triplet at $\delta -28.2$ ($^2J_{\text{PC}} = 15.1$) ppm to the methyl group bound to rhenium, as well as for intermolecular activation of methane, was obtained by carrying out the thermolysis of **5b** under 90 % enriched ^{13}C methane. Rapid generation of the Re-CH_3 resonance was observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture.

Discussion

The chemical behavior of a series of pentamethylcyclopentadienyl-rhenium compounds with various phosphine and carbonyl ligands was investigated to establish the limitations and ancillary ligand requirements of the C-H activation process. Examination of the thermal and photochemical reactivity of compounds **1**, **2**, **7**, **5a**, and **5b** provided rhenium systems capable of inserting into progressively less activated (as reflected by lower acidity) C-H bonds, and serendipitously led to the discovery of conditions for selective reaction of several hydrocarbons.

Our proposal as to how these transformations take place involves the postulated intermediacy of sixteen-electron coordinatively unsaturated intermediates and is outlined in Scheme XXIV. The intervention of sixteen-electron intermediates in the oxidative addition of C-H bonds to metal centers was presented as a desirable characteristic in designing a C-H activating system and has already been suggested for the known rhodium and iridium systems.^{1,22} Moreover, the extrusion of CO upon photolysis of transition-metal carbonyl complexes, as in the formation of intermediate **10** from **1** or intermediate **11** from **2** or **7**, is a well-documented process.²³ The

Scheme XXIV



formation of 11 and 12 from cyclometallated complexes 5a and 5b, respectively, is likewise in agreement with the known thermal chemistry of alkyl hydrides²⁴ and similar η^2 -dimethylphosphinomethyl complexes.²¹ The accessibility of the same products from both 2 and 5a is consistent with a species of the structure shown for 11 as a common intermediate. Unfortunately, analogous formation of intermediate 12 from 7 was not possible, as indicated by the inability to form bis(phosphine) complex 3b directly in the photolysis of 7. The unsaturated species 13 and 14 depicted for the ligand substitutions of PMe_3 for CO are only presented as one of several possible types of intermediates. Rearrangement of the pentamethylcyclopentadienyl ring from η^5 to η^3 ligation, followed by association of PMe_3 and subsequent dissociation of CO, might also be considered. However, the observed acceleration of photolyses when purged with nitrogen is in agreement with initial dissociation of CO in these processes and the other reactions in which CO is lost.

While intermediates 10, 11, and 12 are isoelectronic, they demonstrate varying reactivity and allow fine tuning of reaction conditions for selective activation of hydrocarbons. As suggested might be the case in the Introduction, this is apparently due to increasing electron density on the metal as back-bonding CO ligands are progressively replaced with relatively electron donating PMe_3 ligands. Accordingly, dicarbonyl intermediate 10 led to the formation of no stable adducts of the hydrocarbons tested, and its existence was evident only from the resultant dimers originally discovered by Graham and Hoyano.¹⁴ Introduction of one PMe_3 into the coordination sphere of rhenium made intermediate 11 reactive enough to insert into the

fairly acidic C-H bonds of benzene, and less efficiently into the still somewhat activated but less acidic^{25a,b} C-H bonds of cyclopropane. Because of the rapid reaction of 5a with benzene under ambient conditions, mild selective thermal activation of benzene in the presence of less reactive materials, such as alkanes, is possible via intermediate 11. This inspired using 5b for access to the highly electron-rich species 12, with the expectation of increased reactivity of the rhenium center toward hydrocarbons. Admittedly, 5b reacts more slowly than 5a with benzene. However, this almost certainly reflects a difference in the rate of reductive elimination to give 12 and 11, respectively, and the 12 produced from 5b reacts as anticipated with several hydrocarbon substrates. Specifically, 12 reacts with benzene, cyclopropane, and methane at progressively higher temperatures. With other alkanes, decomposition temperature is reached before a stable adduct can be formed. The increasing reaction temperatures provide a method of selective activation of C-H bonds by a thermal route and reflect the decreasing acidities of the hydrocarbon substrates.²⁵

Also understandable in hindsight are the relative stabilities of the C-H activation products, both inter- and intra-molecular. Complexes containing CO ligands, being somewhat less electron-rich, seem to be more sensitive to reductive elimination than alkyl hydrides with two phosphine ligands. This is best shown by the rapid rate of reaction of 5a with benzene relative to 5b. Conversely, while all the complexes dealt with, except 1, are air-sensitive to some degree, the (carbonyl)alkyl hydrides are in general less sensitive to oxidation than the bis(phosphine)alkyl hydrides. The (carbonyl)alkyl hydrides

could be briefly subjected to the presence of air with a minimal effect, whereas even momentary exposure of the bis(phosphine) complexes led to destruction. Moreover, 5a could be converted to its iodide derivative with iodoform, while 5b could not. Presumably rapid electron transfer or direct attack on a phosphine ligand is responsible. The differences in reactivity correlate with the higher electron density on rhenium in the bis(phosphine) complexes.

The factors which determine the capacity of the rhenium species considered here to effect insertion into hydrocarbon C-H bonds are both kinetic and thermodynamic in nature. The failure to observe this process in a given system may be due to thermodynamic instability of the alkyl hydride adducts, as has been hypothesized by Halpern,²⁶ or may result from kinetic barriers to insertion. In designing this rhenium system, naive considerations maximizing metal-carbon and metal-hydrogen bond dissociation energies led to the desired reactivity. This method may not always be successful, and a potentially telling experiment is suggested. Namely, demonstration of the inability of any sixteen-electron intermediate, for which the corresponding alkyl hydride insertion product is known to be stable, to activate the appropriate hydrocarbon would constitute proof of the existence of kinetic barriers possible in C-H activation reactions. Perhaps the osmium mediated activation of methane shown in Scheme XXV might be considered, the product of which has been shown to be stable by Norton.⁹

Finally, while the set of criteria presented in the Introduction for construction of C-H activating transition-metal organometallic species proved useful here, it is by no means an exclusive list for

Scheme XXV



such systems. Indeed, the electron-poor lutetium and yttrium complexes of Watson (Scheme VII) do not meet these criteria. However, drastically different mechanisms are possible and clearly operate in these cases. Consequently, an open-minded approach to full understanding of C-H bond activation and the myriad of potential reactivity pathways must be taken.

Conclusion

In summary, the rhenium complexes studied here appear to lie on a reactivity borderline between a large group of C-H activating systems which undergo only cyclometallation, and the recently discovered rhodium and iridium complexes which, except in certain special cases, overwhelmingly prefer intermolecular reaction. Although the rhenium systems show less selectivity between intermolecular reaction and cyclometallation, the intramolecular rhenium adducts provide a route to thermal activation of hydrocarbons under relatively mild conditions. Moreover, the rhenium systems discriminate much more effectively between different types of hydrocarbons; this provides a means of carrying out intermolecular activation of certain types C-H bonds in the presence of others. Reluctance of cyclohexane and hexane to form stable adducts in the rhenium systems makes available ordinary alkanes which can be used as inert solvents for the activation of gaseous hydrocarbons, a goal difficult to realize in the rhodium and iridium series, due to their more promiscuous reactivity. Thus, selective functionalization of small amounts of important hydrocarbons, such as methane, in the presence of large quantities of higher hydrocarbons may be a feasible goal.

Experimental

General information. Manipulations in the drybox were conducted under a prescrubbed recirculating atmosphere of nitrogen maintained at 10 to 15 °C in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train and equipped with a -40 °C freezer. Oxygen- or water-sensitive materials were handled outside of the drybox using standard Schlenk or vacuum line techniques.

^1H NMR spectra were recorded on a Varian EM-390 90 MHz spectrometer or at 180, 200, 250, or 300 MHz using Fourier transform NMR spectrometers consisting of Cryomagnetics Inc. magnets, Nicolet Model 1180 or 1280 data collection systems, and electronics designed and assembled by Mr. Rudi Nunlist of the University of California, Berkeley. ^1H NMR spectra were also obtained using a Bruker 500 MHz Fourier transform NMR spectrometer equipped with an Oxford/Spectrospin magnet. The 300 MHz Fourier transform machine was used for acquiring $^1\text{H}\{^{31}\text{P}\}$ NMR spectra. The spectra are reported in units of parts per million (ppm) (δ) downfield from tetramethylsilane (TMS). The internal standard used for spectra recorded in toluene- d_8 is TMS. For spectra recorded in benzene- d_6 , cyclohexane- d_{12} , and THF- d_8 the internal standard is the residual proton resonance of these solvents occurring at δ 7.15, 1.38, and 1.73 ppm, respectively. In cyclopropane- h_6 and pentane- h_{12} , the respective solvent resonances at δ 0.22 and 0.89 ppm were used.

Those ^1H NMR spectra which were recorded in perprotio solvents were obtained using a PRESAT pulse sequence in which the solvent ^1H resonance was presaturated for 2 s with a decoupling signal at the appropriate frequency prior to the data acquisition pulse. For

samples in hexane, pentane, or tetrahydrofuran, the two sets of solvent ^1H resonances were presaturated by modulating the decoupling frequency at half the frequency separation of the two groups of resonances, with the decoupler adjusted for the average frequency of the two sets.

$^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 75.5 or 125.8 MHz and are reported in units of ppm (δ) downfield from TMS, with the solvent ^{13}C resonance serving as the internal standard: δ 128.0 ppm for benzene- d_6 , 26.4 ppm for cyclohexane- d_{12} , and δ 14.3 ppm for pentane. ^{31}P and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 81.7 and 121.5 MHz and are reported in units of ppm (δ) downfield of a separate external 85 % $\text{H}_3\text{PO}_4(\text{aq})$ sample used as the standard.

In the ^1H NMR and/or $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of some compounds, virtually coupled resonances were observed. For these resonances, the value given for J is the separation between the outermost lines of the pattern, and is not necessarily a true coupling constant.

Solution infrared spectra were recorded using 0.10-mm sodium chloride cells on a Perkin-Elmer Model 283 grating spectrometer or a Perkin-Elmer 1550 Fourier transform infrared spectrometer equipped with a Perkin-Elmer 7500 Professional Computer. Ultraviolet/visible spectra were recorded on a Hewlett-packard 8450A UV/vis spectrophotometer using 1-cm path length quartz cells. Electron impact (EI) mass spectra were recorded at the UCB mass spectrometry laboratory on AEI MS-12 and Finnigan 4000 mass spectrometers. High resolution electron impact mass spectra were obtained with a Kratos MS-50 mass spectrometer. Elemental analyses were performed by the UCB microanalytical

laboratory. Melting points were recorded in sealed glass capillary tubes under nitrogen on a Thomas Hoover capillary melting point apparatus and are not corrected.

Preparative column chromatography was performed using either neutral alumina (III) or silica gel (70-230 mesh), both of which were degassed before being taken into the drybox. All columns were packed and chromatograms run under air-free conditions.

Cyclohexane and olefin-free pentane and hexane were purified before use by distillation under nitrogen from LiAlH_4 or by vacuum transfer from a sodium mirror. Benzene, diethyl ether, and tetrahydrofuran (THF) were distilled from sodium-benzophenone ketyl under nitrogen. Benzene- d_6 and toluene- d_8 were dried over sodium-benzophenone ketyl and vacuum transferred prior to use. Cyclohexane- d_{12} was dried over LiAlH_4 or sodium, and then vacuum transferred. Neopentane was used as received. Cyclopropane was purified by stirring at room temperature over a mixture of 2 g HgSO_4 , 6 mL concentrated H_2SO_4 , and 25 mL H_2O . The mixture was then cooled to -78°C and the cyclopropane vacuum transferred onto sodium-potassium alloy. The cyclopropane was vacuum transferred from the alloy at -78°C .

Trimethylphosphine was dried over a sodium mirror and vacuum transferred prior to use. Iodoform was recrystallized from boiling methanol. Methane, 90 % ^{13}C enriched methane, and $\text{Re}_2(\text{CO})_{10}$ were used as received. $\text{Cp}^*\text{Re}(\text{CO})_3$ (1) was synthesized according to the method of King and Bisnette,^{12,27} using $\text{Re}(\text{CO})_5\text{Br}$ ²⁸ instead of $\text{Re}(\text{CO})_5\text{Cl}$. Use of $\text{Re}(\text{CO})_5\text{Br}$ constituted a distinct improvement, giving 87 % yield of 1, as compared to the published 4 % yield, and sublimation of 1 was

not necessary. The pentamethylcyclopentadiene used for this procedure was prepared by a modification of the method of Threlkel and Bercaw²⁹ as described in the Appendix.

Photochemical Experiments. All irradiations reported here were done with pyrex filtration of the light to avoid rapid, uncontrolled destruction of starting materials and products. Analytical scale photochemical experiments were carried out in pyrex NMR tubes. A typical sample preparation involved loading an NMR tube fused to a 14/20 ground glass joint with 12 mg of the appropriate rhenium complex (0.026 mmol in the case of $\text{Cp}^*\text{Re}(\text{CO})_2\text{PMe}_3$) in the drybox. The tube was fitted with a vacuum stopcock and attached to a vacuum line. Approximately 0.6 mL of solvent was vacuum transferred into the tube at -196°C . For those reactions requiring it, PMe_3 measured out as a gas in a known-volume bulb was also vacuum transferred into the NMR tube at this point. After sealing off the tube, NMR spectra taken periodically allowed observation of the progress of photolysis of the sample. Irradiation was conducted with a Hanovia 450-W medium-pressure mercury lamp powered by a Model 7830 Ace-Glass power supply and mounted in an Ace-Glass quartz cooling immersion well containing circulating water. The reaction mixtures were immersed in a water bath cooled by a copper coil heat exchanger containing a circulating -10°C ethylene glycol/water mixture from a Forma Scientific Model 2095 refrigerated bath. The heat from the lamp kept the water bath at approximately 6°C .

In those experiments involving highly volatile solvents like cyclopropane or neopentane, opening of NMR tube samples for

purification and further analysis was done in the tube cracking apparatus shown in Figure IX.³⁰ Prior to placing the tube into the apparatus through Solv-Seal³¹ port A, the tube was scored with a file at the point indicated by the arrow. The apparatus was evacuated and then cooled to -196°C . With valve B closed, teflon plug C was tightened until the NMR tube broke open. The volatile materials were vacuum transferred from the NMR tube as the apparatus slowly warmed to room temperature.

A typical preparative scale photolysis was performed as follows. A 250-mL Ace-Glass photochemical reactor equipped with a quartz cooling immersion well, a pyrex filter, a serum cap, a vacuum stopcock, and a magnetic stir bar was charged with reactant and solvent in the drybox and stoppered. Outside of the drybox, the apparatus was connected to a mineral oil bubbler attached to the vacuum stopcock via a gas inlet tube. Nitrogen was bubbled slowly through the solution by way of 18 gauge teflon tubing introduced through the serum cap. In cases in which PMe_3 was used, the PMe_3 was measured out in the gas phase in a known-volume bulb and vacuum transferred to a flask already containing solvent. The resulting solution was transferred via syringe to the photolysis apparatus. The lamp and reaction mixture were cooled with an ethylene glycol/water mixture maintained between -5 and -15°C , which was circulated through the immersion well with a Brinkmann-Instruments Lauda K-4/RD cooling unit. Irradiation was conducted with a Hanovia 100-W or 450-W medium-pressure mercury lamp powered by a Model 7830 Ace-Glass power supply. The progress of the reaction was monitored by taking IR spectra of aliquots removed periodically with a syringe from the reactor. All of

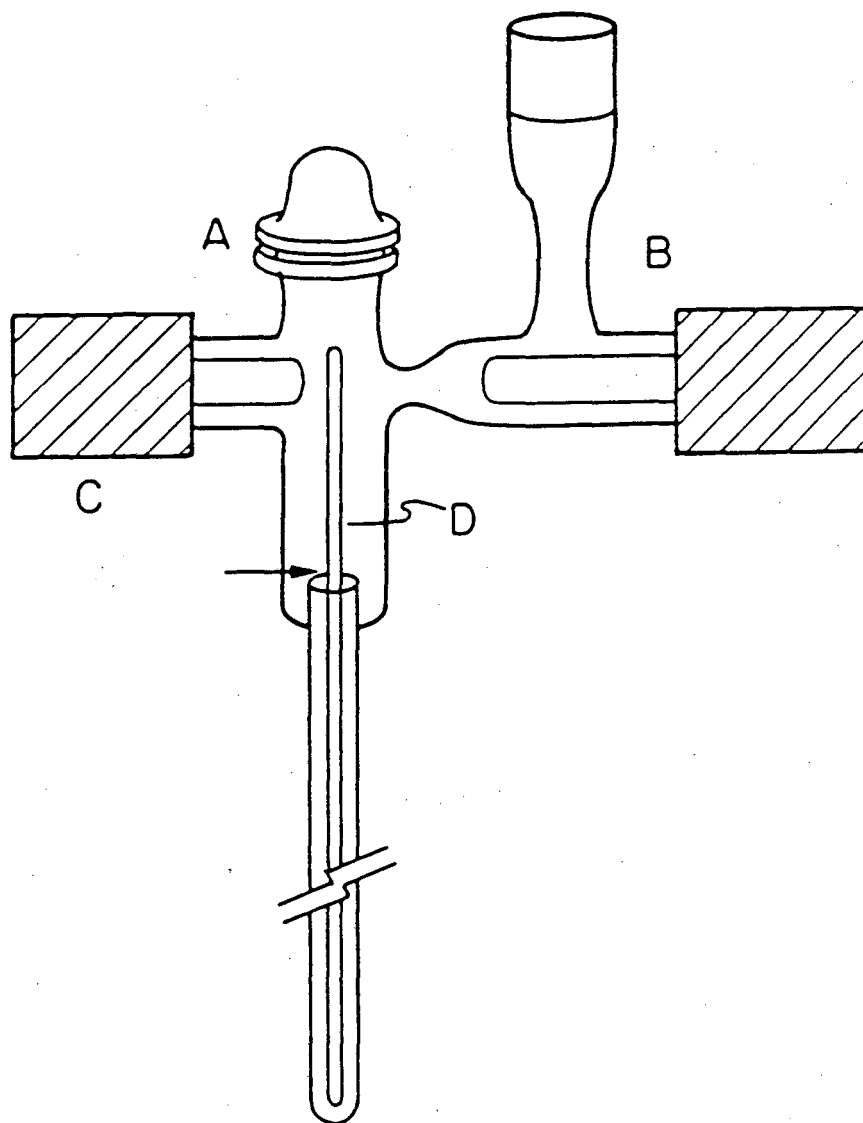


Figure IX. Apparatus for opening sealed NMR tubes:
(A) Solv-Seal joint; (B) vacuum stopcock
with teflon plug; (C) teflon plug;
(D) sealed NMR tube. The arrow indicates
the location of the score on the NMR tube.

the reaction mixtures darkened somewhat, but to varying degrees. The formation of light absorbing material is presumably responsible for the cessation of reaction even when unreacted starting material remained. Upon completion of the photolysis, the reaction mixture was transferred via cannula to a dry, nitrogen-purged 500-mL two-neck round-bottom flask equipped with a vacuum stopcock, a magnetic stir bar, and a serum cap in the side arm. Once the transfer was made, the serum cap was replaced with a stopper, and the solvent was stripped from the flask under vacuum.

The precise details of the larger scale experiments and isolation procedures used are described below. Also listed are the spectral data for those materials identified only by analytical scale experiments.

$\text{Cp}^*\text{Re}(\text{CO})_2\text{PMe}_3$ (2). The 250-mL Ace-Glass photochemical reactor was charged with 2.77 g (6.83 mmol) of 1 and 300 mL of hexane in the dry box. A solution of trimethylphosphine (735 torr, 508.51 mL at 297 °K; 20.2 mmol) in 30 mL of hexane was transferred via syringe to the reactor. The resulting mixture was irradiated with the Hanovia 450-W lamp at -5 to -15 °C for 1 h 20 min. while bubbling nitrogen through the solution. At this point, no further reaction was detected by IR spectroscopy, so the yellow reaction mixture was transferred and the solvent removed as described above. The brown residue was taken up in hexane and chromatographed on silica in the drybox, monitoring the effluent by TLC. The first fraction collected contained $\text{Cp}^*\text{Re}(\text{CO})_3$ and eluted with hexane, after which benzene was gradually added to the eluent. The fraction containing the product 2 was removed from the column with 3:1 (v/v) hexane/benzene eluent and

concentrated under vacuum to give 1.18 g (38 %) of white to pale yellow crystals. ^1H NMR (benzene- d_6) δ 1.86 (s, 15H), 1.24 (d, 9H, $^2J_{\text{PH}} = 8.9$); ^1H NMR (cyclohexane- d_{12}) δ 2.04 (s, 15H), 1.53 (d, 9H, $^2J_{\text{PH}} = 9.5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6) δ 206.22 (br s, CO), 95.56 (s, $\text{C}_5(\text{CH}_3)_5$), 22.34 (d, $^1J_{\text{PH}} = 34.2$, $\text{P}(\text{CH}_3)_3$), 11.10 (s, $\text{C}_5(\text{CH}_3)_5$); $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene- d_6) δ -28.22 (br s); $^{31}\text{P}\{^1\text{H}\}$ NMR (cyclohexane- d_{12}) δ -27.88 (br s); IR (benzene- d_6) 1917 (vs), 1848 (vs) cm^{-1} ; IR (hexane) 1930 (vs), 1866 (vs) cm^{-1} ; UV/visible (pentane) λ_{max} 205 (ϵ 1.2×10^4), 217 (shoulder, ϵ 8.7×10^3), 231 (shoulder, ϵ 6.9×10^3), 248 (shoulder, ϵ 5.2×10^3); mass spectrum (EI), m/e 454 (M^+ , ^{187}Re , base), 452 (M^+ , ^{185}Re); mp 137-139 °C. Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{PRE}$: C, 39.73; H, 5.33; P, 6.83. Found: C, 39.92; H, 5.21; P, 6.52.

Observation of $\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)\text{Ph}(\text{H})$ (3a). A typical analytical scale experiment in which a significant amount of 3a was observed was performed in a sealed NMR tube as described above with 10 mg (0.022 mmol) of 2 dissolved in 0.6 mL of benzene. The behavior of such a solution upon irradiation is described in the Results section. Specifically, integration of the Cp^* resonances after 18 h of photolysis indicated approximately 25 % 3a along with 12 % 2 and 10 % 3b (absolute yields) were present. Data assigned to 3a were: ^1H NMR (benzene- d_6) δ 1.76 (s, 15H), 1.03 (d, 9H, $^2J_{\text{PH}} = 8.7$), -9.22 (d, 1H, $^2J_{\text{PH}} = 66.5$).

Data for $\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)(\text{C}_6\text{D}_5)\text{D}$ (3a- d_6). ^1H NMR (benzene- d_6) δ 1.75 (s, 15H), 1.02 (d, 9H, $^2J_{\text{PH}} = 8.8$).

$\text{Cp}^*\text{Re}(\text{PMe}_3)_2\text{Ph}(\text{H})$ (3b). In the drybox, 95.9 mg (0.211 mmol) of 2

and 300 mL of benzene were placed in the 250-mL Ace-Glass photochemical reactor. A solution of trimethylphosphine (400 torr, 508.51 mL at 298 °K; 10.9 mmol) in 25 mL of benzene was added to the reaction vessel via syringe. Irradiation with the Hanovia 100-W lamp was carried out at -5 to -15 °C for 2.5 h while bubbling nitrogen through the reaction solution. At this point, IR spectroscopy indicated that no further reaction was occurring. The yellow reaction mixture was transferred and the solvent removed under vacuum, as described above. In the drybox, the residue was taken up in hexane and washed rapidly through a 3 cm plug of alumina (III) packed into a fritted-glass funnel. The solvent was removed under vacuum in the drybox. The nearly white residue was recrystallized from pentane at -40 °C to give 74.1 mg (63.5 %) of pale yellow crystalline **3b**. ^1H NMR (benzene- d_6) δ 7.74 (m, 2H), 7.11 (m, 3H), 1.71 (s, 15H), 1.38 (virtual doublet, 18H, $J = 6.5$), -11.08 (t, 1H, $^2J_{\text{PH}} = 53.9$); ^1H NMR (cyclohexane- d_{12}) δ 7.50 (m, 2H), 6.72 (m, 3H), 1.69 (s, 15H), 1.46 (virtual doublet, $J = 6.6$), -11.04 (t, 1H, $^2J_{\text{PH}} = 53.7$); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6) δ 151.00 (t, $^2J_{\text{PH}} = 16.3$, i-Ph), 148.59 (t, $^3J_{\text{PH}} = 7.2$, o-Ph), 126.00 (s, m-Ph), 122.00 (s, p-Ph), 89.87 (s, $\text{C}_5(\text{CH}_3)_5$), 26.02 (6-line multiplet, $J = 59.9$, $\text{P}(\text{CH}_3)_3$), 12.72 (s, $\text{C}_5(\text{CH}_3)_5$); $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene- d_6) δ -45.00 (br s); a $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene- d_6) spectrum in which all but the hydride ^1H resonance were broad-band decoupled gave a resonance at δ -45.00 (br d, $^2J_{\text{PH}} = 53.3$); IR (hexane) 2015 (w) cm^{-1} ; mass spectrum (EI), m/e 551 (M^+-1 , ^{187}Re), 550 (M^+-2 , ^{187}Re), 549 (M^+-1 , ^{185}Re), 548 (M^+-2 , ^{185}Re), 474 (base); mp, decomposes without melting above 70 °C. Anal. Calcd for $\text{C}_{22}\text{H}_{39}\text{P}_2\text{Re}$: C, 47.90; H, 7.12. Found: C, 47.60; H, 7.24.

Data for $\text{Cp}^*\text{Re}(\text{PMe}_3)_2(\text{C}_6\text{D}_5)_2\text{D}$ (3b-d₆). ^1H NMR (benzene-d₆) δ 1.71 (s, 15H), 1.38 (virtual doublet, 18H, $J = 7$); $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene-d₆) δ -44.76 (1:1:1 triplet, $^2J_{\text{PD}} = 7.8$).

Observation of $\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)(\overline{\text{CHCH}_2\text{CH}_2})\text{H}$ (4a). A typical analytical scale experiment in which 4a was observed was performed in a sealed NMR tube as described above with 11 mg (0.027 mmol) of 1, 0.6 mL of cyclopropane, and trimethylphosphine (220 torr, 27.55 mL at 298 °K; 0.326 mmol). Photolysis led to relatively rapid darkening of the solution. After 35.5 h of irradiation, the yield of 4b was estimated to be < 30 %. Resonances due to 1, 2, and 5b as well as unidentified resonances were also evident. Data for this mixture assigned to 4b were: ^1H NMR (benzene-d₆) δ -10.32 (d, $^2J_{\text{PH}} = 62.5$); ^1H NMR (cyclopropane) δ 2.02 (s, $\text{C}_5(\text{CH}_3)_5$), 1.54 (d, $^2J_{\text{PH}} = 7.4$, $\text{P}(\text{CH}_3)_3$), -10.61 (d, $^2J_{\text{PH}} = 63$, ReH).

$\text{Cp}^*\text{Re}(\text{CO})\overline{\text{PMe}_2\text{CH}_2}(\text{H})$ (5a). In order to prepare a relatively large quantity of 5a, the 250-mL Ace-Glass photochemical reactor was filled with a solution of 106 mg (0.234 mmol) of 2 in 300 mL of hexane. The need to work at low concentration, and the consequently large volumes of solvent required, prevented increasing the scale of this reaction further. The Hanovia 100-W lamp was used to irradiate the solution at -5 to -15 °C for 1 h 20 min. while bubbling nitrogen through it. Reaction had ceased to occur at this point, as indicated by IR spectroscopy. The light brown mixture was removed from the reactor and concentrated as described above (Figure III). Attempts to isolate 5a from this mixture by crystallization or chromatography were unsuccessful. Data for this mixture assigned to 5a were:

^1H NMR (benzene) δ 1.94 (s, 15H), 1.33 (d, 3H, $^2J_{\text{PH}} = 12.4$), 0.94 (d, 3H, $^2J_{\text{PH}} = 12.0$), 0.85 (dd, 1H, $^2J_{\text{HH}} = 7$, $^2J_{\text{PH}} = 4$), -0.51 (dd, 1H, $^2J_{\text{HH}} = 7$, $^2J_{\text{PH}} = 3$), -9.44 (d, 1H, $^2J_{\text{PH}} = 37.8$). ^1H NMR (cyclohexane- d_{12}) δ 2.02 (s, $\text{C}_5(\text{CH}_3)_5$), 0.56 (dd, $^2J_{\text{HH}} = 7.1$, $^2J_{\text{PH}} = 4.0$, one stereotopic $\text{P}(\text{CH}_3)_2\text{CH}_2$), -0.57 (dd, $^2J_{\text{HH}} = 7.1$, $^2J_{\text{PH}} = 3.2$, one stereotopic $\text{P}(\text{CH}_3)_2\text{CH}_2$), -9.92 (d, $^2J_{\text{PH}} = 38.2$, ReH); $^{31}\text{P}\{^1\text{H}\}$ NMR (cyclohexane- d_{12}) δ -59.8 (br s).

For the purpose of determining the yield of 5a, the brown residue was taken up in pentane in the drybox, and the resulting solution was pipetted into an NMR tube fused to a 14/20 ground glass joint. The tube was capped with a vacuum stopcock and the pentane removed by vacuum transfer. After prolonged evacuation on a vacuum line, toluene- d_8 (0.6 mL) and TMS (150 torr, 27.55 mL at 297 °K; 0.233 mmol) were vacuum transferred into the NMR tube, which was cooled to -196 °C. After sealing the tube, it was stored at -78 °C to prevent reaction of 5a with the TMS or the toluene- d_8 . Integration of the ^1H NMR spectra of this sample taken at -40 °C and -50 °C indicated that approximately 70 % of 2 had been converted to other materials. Based on the amount of 2 used, 5a was produced in approximately 20 % yield (approximately 30 % yield based on reacted 2). For 5a: ^1H NMR (toluene- d_8 , -10 °C) δ 1.92 (s, 15H), 1.31 (d, 3H, $^2J_{\text{PH}} = 13$), 0.94 (d, 3H, $^2J_{\text{PH}} = 12$), 0.76 (dd, 1H, $^2J_{\text{HH}} = 6.8$, $^2J_{\text{PH}} = 4.6$), -0.58 (dd, 1H, $^2J_{\text{HH}} = 7.5$, $^2J_{\text{PH}} = 3.2$), -9.56 (d, 1H, $^2J_{\text{PH}} = 37.6$).

$\text{Cp}^*\text{Re}(\text{CO})\text{PMe}_2\text{CH}_2(\text{I})$ (6). For the purpose of confirming the assigned structure of 5a, the corresponding iodide derivative 6 was prepared from it. The 250-mL Ace-Glass photochemical reactor was used to prepare a solution of 5a from 42.9 mg (0.0946 mmol) of 2 in 340 mL

of hexane by irradiating for 1 h 20 min. This time, however, the dry, nitrogen-purged 500-mL two-neck round-bottom flask normally used for concentration of the light-brown solution was charged with 55.2 mg (0.140 mmol) of CHI_3 prior to transfer of the reaction mixture into it. After stirring for 3 h, the solvent was removed in vacuo. The brown residue was partially purified by suction filtration in the drybox through a 2 cm plug of silica packed into a fritted glass filter. Using hexane as solvent gave a first fraction containing some CHI_3 , but no 6 by ^1H NMR analysis, so it was discarded. Subsequent washes with benzene and then THF gave fractions which ^1H NMR spectra showed to contain 6. These fraction also contained a considerable amount of 2. These fractions were combined, concentrated, and carefully rechromatographed on silica. Elution first with 3:1 (v/v) benzene/hexane gave a fraction containing 2. The amount of benzene in the eluent was then increased. Compound 6 eluted from silica with 100 % benzene. The solvent was stripped from the fraction containing 6. The residue was washed with pentane and vacuum dried to give 9.2 mg (18 %) of a yellow powder that was > 92 % 6 by ^1H NMR. ^1H NMR (benzene- d_6) δ 1.71 (d, 15H, $^4J_{\text{PH}} = 0.5$), 1.59 (d, 3H, $^2J_{\text{PH}} = 13.4$), 1.08 (dd, 1H, $^2J_{\text{HH}} = 7.7$, $^2J_{\text{PH}} = 3.4$), 0.88 (d, 3H, $^2J_{\text{PH}} = 12$), -0.04 (dd, 1H, $^2J_{\text{HH}} = 7.7$, $^2J_{\text{PH}} = 3.7$); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6) δ 201.79 (br s, CO), 97.83 (s, $\text{C}_5(\text{CH}_3)_5$), 15.73 (d, $^1J_{\text{PC}} = 44.9$, one stereotopic $\text{P}(\text{CH}_3)_2$), 11.03 (s, $\text{C}_5(\text{CH}_3)_5$), 6.18 (d, $^1J_{\text{PC}} = 29.2$, one stereotopic $\text{P}(\text{CH}_3)_2$), -22.99 (d, $^1J_{\text{PC}} = 5.8$, $\overline{\text{P}-\text{CH}_2-\text{Re}}$); ^{31}P NMR (benzene- d_6) δ -64.83 (br septet, $^2J_{\text{PH}} = 13$); $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene- d_6) δ -64.83 (s); IR (benzene- d_6) 1886 (vs) cm^{-1} ; mass spectrum (EI), m/e 552/550

(M^+ , $^{187}\text{Re}/^{185}\text{Re}$), 524/522 ($M^+ - \text{CO}$, $^{187}\text{Re}/^{185}\text{Re}$), 426 (base); high resolution mass spectrum (EI), m/e calcd for $^{12}\text{C}_{14}^{1}\text{H}_{23}^{127}\text{I}^{16}\text{O}^{31}\text{PRe}$: 552.0088/550.0060 (M^+ , $^{187}\text{Re}/^{185}\text{Re}$), 524.0139/522.0111 ($M^+ - \text{CO}$, $^{187}\text{Re}/^{185}\text{Re}$); m/e found: 552.0083/550.0060 (M^+ , $^{187}\text{Re}/^{185}\text{Re}$, deviation = -0.9/-0.1 ppm), 524.0144/522.0129 ($M^+ - \text{CO}$, $^{187}\text{Re}/^{185}\text{Re}$, deviation = 1.0/3.5 ppm); mp 122 °C (decomp.). A satisfactory elemental analysis could not be obtained.

Reaction of $\text{Cp}^*\text{Re}(\text{CO})\text{PMe}_2\text{CH}_2(\text{H})$ (5a) with benzene. A large scale preparation of a mixture containing 5a was carried out in cyclohexane according to the method previously described. The brown residue obtained from solvent removal was redissolved in benzene, and a PRESAT ^1H NMR spectrum was acquired as quickly as possible. Observation of the Cp^* and hydride resonances indicated that 5a was converted to 3a with a half life on the order of 0.5 h at 25 °C. Using the 2 present in the sample as an internal standard, this conversion was found to be quantitative (> 95 % yield of 3a based on 5a). Alternatively, if the brown residue containing 5a was dissolved in benzene- d_6 , rapid reaction of 5a also occurred with the solvent, giving only $\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)(\text{C}_6\text{D}_5)\text{D}$ (3a- d_6) and no 3a- d_n ($n < 6$) by ^1H NMR spectroscopy, as indicated by the absence of the phenyl group and hydride resonances.

$\text{Cp}^*\text{Re}(\text{CO})(\text{PMe}_3)_2$ (7). The 250-mL Ace-Glass photochemical reactor was charged with 213 mg (0.470 mmol) of 2 and 300 mL of hexane in the drybox. Trimethylphosphine (3600 torr, 508.51 mL at 296 °K; 99.1 mmol) dissolved in 20 mL of hexane was transferred via syringe to the photolysis apparatus. Nitrogen was bubbled through the solution while irradiating with the Hanovia 100-W lamp at -5 to -15 °C. After 4.5 h

of photolysis, when darkening of the solution prevented further reaction as determined by IR spectroscopy, the yellow reaction mixture was removed from the reactor, and the solvent was stripped (*vide supra*). In the drybox, the brown residue was taken up in 4:1 (v/v) hexane/benzene and chromatographed on silica, monitoring the column effluent by TLC. A fraction containing 2 eluted first, after which more benzene was gradually added to the eluent. A fraction containing a small amount of several materials, including some 3a, was followed by the fraction containing 7, which eluted with approximately 1:1 (v/v) benzene/hexane. The solvent from this last fraction was removed in vacuo. The residue was redissolved in benzene and lyophilized by removing the volatile materials under vacuum in the drybox at a rate fast enough to keep the benzene solution frozen, giving 52.6 mg (22 %) of a light tan, fluffy solid. ^1H NMR (benzene- d_6) δ 1.92 (s, 15H), 1.37 (d, 18H, $^2J_{\text{PH}} = 7.7$); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6) δ 208.25 (br s, CO), 91.64 (s, $\text{C}_5(\text{CH}_3)_5$), 25.52 (virtual doublet, $J = 31.6$, $\text{P}(\text{CH}_3)_3$), 12.25 (s, $\text{C}_5(\text{CH}_3)_5$); $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene- d_6) δ -34.48 (br s); IR (benzene- d_6) 1812 (vs) cm^{-1} ; IR (hexane) 1833 (s) cm^{-1} ; mass spectrum (EI), m/e 502 (M^+ , ^{187}Re , base), 500 (M^+ , ^{185}Re); mp 100 °C (decomp.). Anal. Calcd for $\text{C}_{17}\text{H}_{33}\text{OP}_2\text{Re}$: C, 40.71; H, 6.63; P, 12.35. Found: C, 41.02; H, 6.69; P, 11.9.

$\text{Cp}^*\text{Re}(\text{PMe}_3)\text{PMe}_2\text{CH}_2(\text{H})$ (5b). In a typical reaction, 88.7 mg (0.196 mmol) of 2 and 300 mL of hexane were loaded into the 250-mL Ace Glass photochemical reactor in the drybox. As was the case for the synthesis of 5a, the scale of this reaction was limited by the need to work at low concentrations. Trimethylphosphine (350 torr, 508.51 mL

at 298 °K; 9.57 mmol) dissolved in 25 mL of hexane was syringed into the reaction vessel. With nitrogen bubbling through the resulting solution, irradiation with the Hanovia 100-W lamp was carried out at -5 to -15 °C for 3.3 h, at which point IR spectroscopy indicated that reaction had ceased. The yellow reaction mixture was then removed from the reactor and the solvent stripped on a vacuum line. Attempts to purify the brown residue by crystallization and chromatography, even at -110 °C, proved unsuccessful. Treatment of the mixture with CHI_3 converted 5b to very insoluble unidentified material.

Consequently, the residue containing 5b was used in subsequent reactions without further purification (Figure V). Data for this mixture assigned to 5b were: ^1H NMR (benzene- d_6) δ 1.97 (s, 15H), 1.39 (d, 3H, $^2J_{\text{PH}} = 10$), 1.31 (d, 3H, $^2J_{\text{PH}} = 10$), 1.29 (d, 9H, $^2J_{\text{PH}} = 7.2$), 0.09 (ddd, 1H, $^3J_{\text{PH}} = 13.8$, $^2J_{\text{HH}} = 7.3$, $^2J_{\text{PH}} = 1.9$), -0.23 (virtual quartet, 1H, $J = 19.6$), -12.02 (dd, 1H, $^2J_{\text{PH}} = 39.0$, $^2J_{\text{PH}} = 32.6$); ^1H NMR (cyclohexane- d_{12}) δ 1.89 (s, 15H), 1.47 (d, 3H, $^2J_{\text{PH}} = 10.5$), 1.37 (d, 3H, $^2J_{\text{PH}} = 10.4$), 1.28 (d, 9H, $^2J_{\text{PH}} = 7.6$), -0.17 (ddd, 1H, $^3J_{\text{PH}} = 14.1$, $^2J_{\text{HH}} = 7.6$, $^2J_{\text{PH}} = 2.0$), -0.48 (virtual quartet, 1H, $J = 19.4$), -12.26 (dd, 1H, $^2J_{\text{PH}} = 39.2$, $^2J_{\text{PH}} = 33.1$); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6) δ 88.74 (s, $\text{C}_5(\text{CH}_3)_5$), 25.57 (d, $^1J_{\text{PC}} = 27.8$, $\text{P}(\text{CH}_3)_3$), 17.27 (d, $^1J_{\text{PC}} = 25.1$, one stereotopic $\text{P}(\text{CH}_3)_2$), 12.97 (s, $\text{C}_5(\text{CH}_3)_5$), 10.45 (d, $^1J_{\text{PC}} = 22.4$, one stereotopic $\text{P}(\text{CH}_3)_2$), -31.94 (t, $J_{\text{PC}} = 8$, $\overline{\text{P}-\text{CH}_2-\text{Re}}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (cyclohexane- d_{12}) δ 89.06 (s, $\text{C}_5(\text{CH}_3)_5$), 25.90 (d, $^1J_{\text{PC}} = 28.0$, $\text{P}(\text{CH}_3)_3$), 17.68 (d, $^1J_{\text{PC}} = 25.0$, one stereotopic $\text{P}(\text{CH}_3)_2$), 13.00 (s, $\text{C}_5(\text{CH}_3)_5$), 10.74 (d, $^1J_{\text{PC}} = 22.7$, one stereotopic $\text{P}(\text{CH}_3)_2$), -32.34 (t, $J_{\text{PC}} = 8.1$, $\overline{\text{P}-\text{CH}_2-\text{Re}}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene- d_6) δ -39.41 (d, $^2J_{\text{PP}} = 19.8$, $\text{P}(\text{CH}_3)_3$), -76.88 (d, $^2J_{\text{PP}} =$

19.7, $\overline{\text{P}(\text{CH}_3)_2\text{CH}_2\text{Re}}$; high resolution mass spectrum (EI), m/e calcd for $^{12}\text{C}_{16}^{1}\text{H}_{33}^{31}\text{P}_2\text{Re}$: 474.1614/472.1586 (M^+ , $^{187}\text{Re}/^{185}\text{Re}$); m/e found: 474.1624/472.1585 (M^+ , $^{187}\text{Re}/^{185}\text{Re}$, deviation = 2.0/-0.2 ppm), the peak at 474.1614 was the highest-mass peak > 2 % relative intensity, a peak at 476.1775 due to side product **8** (M^+ , ^{187}Re , deviation = 0.9 ppm, highest-mass peak > 1 % relative intensity) was also observed.

The side product **8** present in this mixture was assigned to the following data: ^1H NMR (benzene- d_6) δ 2.09 (s, 15H), 1.51 (virtual doublet, 18H, $J = 7.5$), -11.89 (t, 2H, $^2J_{\text{PH}} = 43.5$); $^1\text{H}\{^{31}\text{P}\}$ NMR (benzene- d_6) δ 2.09 (s, 15H), 1.51 (s, 18H), -11.89 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6) δ 87.7 (s, $\text{C}_5(\text{CH}_3)_5$), 30.6 (6-line multiplet, $J = 50$, $\text{P}(\text{CH}_3)_3$), 13.9 (s, $\text{C}_5(\text{CH}_3)_5$); $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene- d_6) δ -37.57 (br s).

The yield of **5b** when prepared by this method was determined as follows. In the drybox, the brown residue was redissolved in pentane and transferred into an NMR tube fused to a 14/20 ground glass joint. The tube was fitted with a vacuum stopcock, and the pentane was stripped under vacuum. Prolonged evacuation on a vacuum line ensured removal of all of the pentane. Toluene- d_8 (0.6 mL) followed by TMS (300 torr, 5.72 mL at 297 °K; 0.0926 mmol) was vacuum transferred into the NMR tube, which was maintained at -196 °C. After sealing the tube, it was stored at -78 °C to prevent any reaction of **5b**. Integration of the ^1H NMR spectra of this sample taken at -40 °C and -10 °C allowed the yield of **5b**, based on the amount of **2** used, to be estimated at 20 % with 88 % conversion of **2** (the yield of **5b** was 23 % based on reacted **2**). For **5b**: ^1H NMR (toluene- d_8 , -10 °C) δ 1.95 (s,

15H), 1.37 (d, 3H, $^2J_{\text{PH}} = 10$), 1.33 (d, 3H, $^2J_{\text{PH}} = 10$), 1.26 (d, 9H, $^2J_{\text{PH}} = 8$), -0.32 (virtual quartet, 1H, $J = 19$), -12.10 (dd, 1H, $^2J_{\text{PH}} = 38.8$, $^2J_{\text{PH}} = 32.4$).

Reaction of $\text{Cp}^*\text{Re}(\text{PMe}_3)\text{PMe}_2\text{CH}_2(\text{H})$ (5b) with benzene. A preparative scale synthesis of 5b was carried out in hexane (vide supra). The brown residue obtained from solvent removal was redissolved in benzene- d_6 . Integration of the Cp^* resonances in the ^1H NMR spectra of this sample, using the 7 present as an internal standard, showed that 5b was converted to 3b quantitatively (> 95 % yield of 3b based on 5b) with a half life on the order of 4 days at 25 °C. No bound phenyl group or hydride resonances due to 3b were observed, indicating only $\text{Cp}^*\text{Re}(\text{PMe}_3)_2(\text{C}_6\text{D}_5)\text{D}$ (3b- d_6) and no 3b- d_n ($n < 6$) were formed.

Reaction of $\text{Cp}^*\text{Re}(\text{PMe}_3)\text{PMe}_2\text{CH}_2(\text{H})$ (5b) with cyclopropane; preparation of $\text{Cp}^*(\text{PMe}_3)_2(\text{CHCH}_2\text{CH}_2)\text{H}$ (4b). Compound 5b was synthesized from 87.7 mg (0.193 mmol) of 2 in 300 mL of hexane and trimethylphosphine (330 torr, 508.51 mL at 292 °K; 9.21 mmol) dissolved in 35 mL of hexane. After solvent removal, the brown residue containing 5b was redissolved in pentane in the drybox and pipetted into a medium-walled NMR tube fused to a 14/20 ground glass joint. The tube was fitted with a vacuum stopcock and removed from the drybox to a vacuum line. After all of the pentane had been evacuated from the NMR tube, cyclopropane was vacuum transferred into the tube at -196 °C. The tube was sealed and warmed to room temperature. No reaction at room temperature was initially detected from observation of the sample by ^1H NMR spectroscopy. Heating to 70 °C, however, led to a 4:1 mixture of 5b:4b after 11 h. Further

heating at 70 °C did not change this ratio. Storage of the sample for several days at room temperature caused an increase in the amount of **4b** relative to **5b**. All of this behavior was indicative of an equilibrium between **5b** and **4b**. In order to maximize the yield of **4b** without making the time for equilibration impractically long, the NMR tube was allowed to equilibrate for 37.5 h at 45 °C to give a 2:1 ratio for **5b**:**4b**, or 33 % yield of **4b**. The tube was then cooled to room temperature, and opened in the tube cracking apparatus (vide supra). In the drybox, the brown oily residue was redissolved and rapidly washed through a 4-cm plug of alumina (III) packed in a fritted glass suction filter using hexane as solvent. Removal of the solvent under vacuum gave 8.4 mg of a waxy, white, semi-crystalline solid. Integration of the Cp* resonances in the ^1H NMR spectrum of this sample indicated that it contained approximately 78 % **4b** and 6 % **8** (Figure VI). The following characterizing data for this mixture were assigned to **4b**: ^1H NMR (benzene- d_6) δ 1.80 (s, 5H), 1.30 (virtual doublet, 18H, $J = 6.6$), 1.03 (m, 2H), 0.10 (m, 2H), -0.14 (septet, 1H, $J = 8$), -12.54 (t, 1H, $^2J_{\text{PH}} = 52.3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6) δ 89.07 (t, $^2J_{\text{PC}} = 2.2$, $\text{C}_5(\text{CH}_3)_5$), 25.60 (6-line multiplet, $J = 49.1$, $\text{P}(\text{CH}_3)_3$), 12.46 (s, $\text{C}_5(\text{CH}_3)_5$), 11.65 (t, $^3J_{\text{PC}} = 5.8$, $\text{ReCHCH}_2\text{CH}_2$), -27.28 (t, $^2J_{\text{PC}} = 19.2$, $\text{ReCHCH}_2\text{CH}_2$); $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene- d_6) δ -40.06 (br s); IR (hexane) 1962 cm^{-1} (w); mass spectrum (EI), m/e 516/514 (M^+ , $^{187}\text{Re}/^{185}\text{Re}$), 474/472 ($\text{M}^+ - \text{C}_3\text{H}_6$, ^{187}Re (base)/ ^{185}Re); high resolution mass spectrum (EI), m/e calcd for $^{12}\text{C}_{19}^{1}\text{H}_{39}^{31}\text{P}_2\text{Re}$: 516.2083/514.2056 (M^+ , $^{187}\text{Re}/^{185}\text{Re}$), 474.1614/472.1587 ($\text{M}^+ - \text{C}_3\text{H}_6$, $^{187}\text{Re}/^{185}\text{Re}$); m/e found:

516.2091/514.2058 (M^+ , $^{187}\text{Re}/^{185}\text{Re}$, deviation = 1.5/0.3 ppm),
 474.1642/472.1596 ($M^+ - \text{C}_3\text{H}_6$, $^{187}\text{Re}(\text{base})/^{185}\text{Re}$, deviation = 5.9/2.0 ppm), the peak at 516.2091 was the highest-mass peak > 0.45 % relative intensity; mmp, decomposes when heated above 25 °C without melting. The sample slowly decomposed and turned green when stored at room temperature.

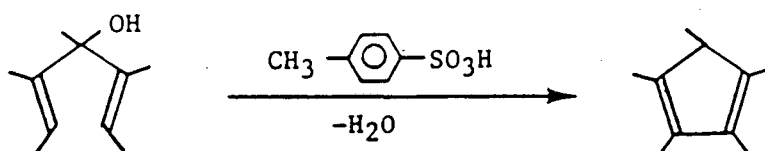
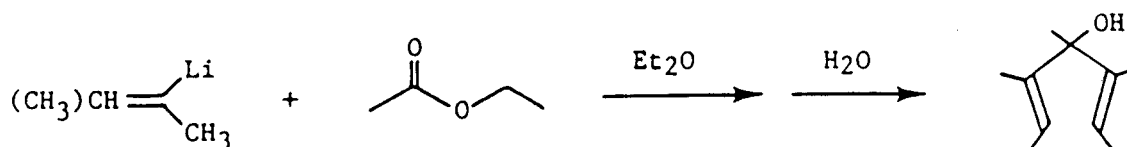
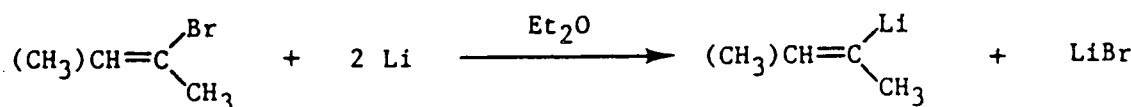
Reaction of $\text{Cp}^*\text{Re}(\text{PMe}_3)_2\text{CH}_2(\text{H})$ (5b) with methane; preparation of $\text{Cp}^*\text{Re}(\text{PMe}_3)_2\text{CH}_3(\text{H})$ (9). Exploratory experiments were carried out in a 45-mL screw-cap stainless-steel Parr bomb equipped with a glass liner sleeve. In a typical experiment, a sample of 5b was synthesized from 85.7 mg (0.189 mmol) of 2 in 300 mL of hexane and a solution of trimethylphosphine (350 torr, 508.51 mL at 297 °K; 9.60 mmol) in 35 mL of hexane. The brown oily mixture including 5b obtained after removal of solvent was transferred in the drybox to the Parr bomb using 10 mL of hexane. Outside of the drybox, the bomb was pressurized with methane while shaking the bomb to ensure complete equilibration with methane dissolved in the hexane. The reaction vessel was then submerged in a constant temperature oil bath. Monitoring of the reaction could be accomplished by allowing the Parr bomb to cool to room temperature, releasing the methane pressure, and removing an aliquot in the drybox for PRESAT ^1H NMR analysis. After acquiring the ^1H NMR spectrum, the aliquot was returned to the bomb, which was then repressurized with methane. No reaction between 5b and methane was observed at room temperature or upon heating to 46 °C. Slow reaction to give 9 occurred at 70 °C, and an approximately 4:1 mixture of 5b to 9 could be achieved. Heating at higher temperatures gave a higher 5b:9 ratio and caused decomposition, as evidenced by a decrease in the

total amount of rhenium present as **5b** or **9**. For the purpose of purification, **9** was prepared by allowing **5b** to equilibrate at 70 °C under 97 atm of methane for 41 h. After removal of the pentane under vacuum in the drybox, the mixture was taken up in 99:1 (v/v) hexane/diethyl ether and cooled in dry ice. Chromatography of the sample was carried out in a vacuum-jacketed column with an inner jacket cooled to -95 °C with liquid nitrogen blow-off. Compound **9** was eluted with 99:1 (v/v) hexane/diethyl ether. It is essential to begin elution with some diethyl ether, since 100 % hexane solvent leads to decomposition of **9** on the alumina III support. The column effluent was monitored with an Altex Model 153 analytical UV detector. The fraction containing partially purified **9** was collected first. Subsequent fractions were collected at -110 °C as more diethyl ether was added to the eluent. These fractions contained **7**, a trace of **5b**, and several unidentified materials. Solvent removal from the first fraction gave 9.5 mg of a colorless oil, which turned green over days at room temperature. Integration of the Cp* region of the ¹H NMR spectrum of this material showed it to be 32 % **9**, 20 % **2**, 19 % **8**, and 19 % of an unidentified material (Figure VIII). The following characterizing data for this mixture were assigned to **9**: ¹H NMR (benzene-d₆) δ 1.79 (s, 15H), 1.28 (virtual doublet, 18H, J = 7.6), -0.01 (td, 3H, ³J_{PH} = 11.3, ³J_{HH} = 2.1), -12.35 (br t, 1H, ²J_{PH} = 48.5); ¹H{³¹P} NMR (benzene-d₆) δ 1.79 (s, 15H), 1.28 (s, 18H), -0.01 (d, 3H, ³J_{HH} = 1.4), -12.35 (br s); ¹³C{¹H} NMR (benzene-d₆) δ 87.79 (s, C₅(CH₃)₅), 23.79 (6-line multiplet, J = 50.9, P(CH₃)₃), 12.06 (s, C₅(CH₃)₅), -28.2 (t, ²J_{PC} = 15.1, ReCH₃); ³¹P{¹H} NMR (benzene-d₆)

δ -36.81 (br s); confirmation of the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR assignments was obtained by examining the ^1H NMR spectrum of this sample while selectively decoupling the observed ^{31}P resonances; high resolution mass spectrum (EI), m/e calcd for $^{12}\text{C}_{17}^{1}\text{H}_{37}^{31}\text{P}_2\text{Re}$: 490.1927/488.1899 (M^+ , $^{187}\text{Re}/^{185}\text{Re}$), 474.1614/472.1586 (M^+-CH_4 , $^{187}\text{Re}/^{185}\text{Re}$); m/e found: 490.1922/488.1895 (M^+ , $^{187}\text{Re}/^{185}\text{Re}$, deviation = -1.0/-0.8 ppm), 474.1620/472.1559 (M^+-CH_4 , ^{187}Re (base)/ ^{185}Re , deviation = 1.2/-5.7 ppm), the peak at 490.1922 was the highest-mass peak > 0.45 % relative intensity.

Reaction of $\text{Cp}^*\text{Re}(\overline{\text{PMe}_3})_2\text{PMe}_2\text{CH}_2(\text{H})$ (5b) with ^{13}C labelled methane. A sample mixture of 5b was prepared from 69.2 mg (0.152 mmol) of 2 in 300 mL of hexane and trimethylphosphine (350 torr, 508.51 mL at 298 °K; 9.57 mmol) dissolved in 25 mL of hexane. The residue obtained after irradiation and solvent removal was taken up in pentane in the drybox and transferred into a medium-walled NMR tube fused to a 14/20 ground glass joint. After capping the tube with a vacuum stopcock, the solvent was reduced in volume on a high vacuum line to approximately 0.3 mL. At -196 °C, 90 % ^{13}C enriched methane (266 torr, 141.23 mL less 17 torr, 290 mL not condensed at 297 °K; 1.76 mmol) was vacuum transferred into the NMR tube. The tube was sealed and then submerged in a 70 °C constant temperature oil bath. Within 11 h, a resonance at δ -28.17 (t, $^2J_{\text{PC}} = 15.1$) ppm due to the methyl carbon bound to rhenium in 9 was already detectable by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, and further heating caused the resonance to become relatively intense. In the PRESAT ^1H NMR spectra, a methyl resonance for the labelled 9 produced was observed at δ -0.44 ppm (dtd, $^1J_{\text{CH}} = 61.5$, $^3J_{\text{PH}} = 11.2$, $^3J_{\text{HH}} = 2.1$).

Appendix

1,2,3,4,5-PENTAMETHYLCYCLOPENTADIENE³²

1. Procedure

A. 3,4,5-trimethyl-2,5-heptadien-4-ol. Lithium wire (1/8") is cut up into approximately 1 cm lengths and washed with hexane (Note 1). A mixture of the cut-up lithium (21 g, 3.0 mol) in 100 mL of diethyl ether from a freshly opened can is stirred well under argon in a 2 L three-necked round-bottom flask equipped with a reflux condenser and a 250-mL addition funnel. 2-bromo-2-butene (cis and trans mixture) is purified and dried by passing it through a 2 x 15 cm column of basic alumina I (Note 2). A small amount of the 2-bromo-2-butene (200 g, 1.48 mol) is added dropwise to the flask via the addition funnel until reaction begins as evidenced by warming of the reaction mixture and formation of bubbles on the surface of the lithium (Note 3). At this

point the mixture is diluted with an additional 900 mL of fresh diethyl ether, and the remainder of the 2-bromo-2-butene is added at a rate sufficient to maintain gentle reflux. Stirring is continued for one hour following completion of this addition, after which ethyl acetate (66 g, 0.75 mol) diluted with an equal volume of fresh diethyl ether is added dropwise via the addition funnel. The reaction mixture turns from yellow-orange to milky-yellow with this addition. It is then poured into 2 L of saturated aqueous NH_4Cl . The ethereal layer is separated, and the pH of the aqueous layer is adjusted to approximately 9 with HCl (aq). The aqueous layer is then extracted three times with diethyl ether. The combined ethereal layers are dried over MgSO_4 , filtered, and concentrated to 100-200 mL by rotary evaporation.

B. 1,2,3,4,5-Pentamethylcyclopentadiene. A mixture of 13 g (0.068 mol) p-toluenesulfonic acid monohydrate and 300 mL diethyl ether is stirred under argon in a 1 L three-necked round-bottom flask equipped with a reflux condenser and a 250 mL addition funnel. The concentrate from above is added as quickly as possible to the flask from the addition funnel, maintaining a gentle reflux. As the reaction proceeds, a water layer separates. The mixture is stirred for one hour after the addition is completed, then extracted with saturated aqueous NaHCO_3 until the extracts remain basic. The ethereal layer is separated, and the combined aqueous layers are extracted three times with diethyl ether. The combined ethereal layers are dried over Na_2SO_4 . Diethyl ether is then removed by rotary evaporation, and the crude product vacuum distilled (bp 55-60°C, 13 torr). Yield 75 g (75%).

2. Notes

1. High sodium lithium (1-2% sodium) is preferred in order to facilitate initiation of the reaction.
2. While published procedures have used samples of 2-bromo-2-butene as obtained from the supplier without further purification, impurities in some batches often make it difficult, if not impossible, to safely start the reaction.
3. Caution! It is imperative to only add a few mL of the 2-bromo-2-butene and patiently wait for the reaction with the lithium to begin. Addition of too much 2-bromo-2-butene too soon may lead to a violent reaction.

3. Discussion

The procedure described here is a modification of that previously published.²⁹ Specifically, it is frequently insufficient to use the 2-bromo-2-butene as obtained from the supplier without purification using basic alumina I. Such purification assures easy starting of the reaction with lithium. Furthermore, the large volumes of diethyl ether used in the past are unnecessary and may inhibit initiation of the reaction of 2-bromo-2-butene with lithium. Finally, while dry solvents and reagents are required, diethyl ether from a freshly opened can is sufficiently free of water, and distillation from LiAlH_4 is unnecessary.

1,2,3,4,5-Pentamethylcyclopentadiene is a useful aromatic building block for the preparation of other compounds. It can be converted to many salts of its conjugate base with alkali metals or

strong bases such as butyl lithium.³³ These pentamethylcyclopentadienyl anion salts as well as the diene itself can be transformed into η^5 -pentamethylcyclopentadienyl ligands of organotransition metal complexes by many known methods.³³

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