

3 hr the green needles of the *trans* complex were filtered off and washed with a little water and then with acetone (0.66 g). *Anal.* Calcd for $C_7H_{18}N_2O_4S_2Cl_3Co$: C, 19.9; H, 4.3; N, 6.6; Cl, 25.1. Found: C, 19.5; H, 4.3; N, 6.5; Cl, 24.9.

cis-β-[CoETeCl₂]ClO₄.—After the addition of perchloric acid (1 ml; concentrated), the red-violet filtrate obtained after the separation of the *trans* isomer was allowed to stand in a refrigerator for 1 day. The red-violet needles thus obtained were washed with a little iced water and then with methanol (0.5 g). *Anal.* Calcd for $C_7H_{18}N_2O_4S_2Cl_3Co$: C, 19.9; H, 4.3; N, 6.6; Cl, 25.1. Found: C, 19.7; H, 4.3; N, 6.6; Cl, 25.2.

[CoTETCl₂]ClO₄.—The ligand TET (6.3 g) in methanol (30 ml) and hydrochloric acid (30 ml; 1 *N*) was added to an ice-cold solution of cobalt acetate tetrahydrate (7.5 g) in methanol (100 ml), followed by sodium nitrite (4.5 g) in water (10 ml). Air was passed through the solution for 2 hr during which time the initial bluish color faded and a brown solid precipitated. The resulting mixture was transferred to an evaporating dish on a steam bath and urea (3.6 g) in water (10 ml) was added. The solution was warmed and hydrochloric acid (30 ml; 10 *M*) was slowly added. The brown solid gradually dissolved with the evolution of gas to form, after about 0.5 hr of heating, a deep brown solution. After heating on the steam bath for a further 0.25 hr the solution became bluish. The clear solution was filtered and perchloric acid (6 ml; concentrated) was added. It was again heated on a steam bath under a current of air for 5 min whereupon deep purple crystals began to deposit. After cooling in an ice bath for 1 hr, these were collected and washed with a little iced water and then methanol. These crystals consisted of a mixture of the blue *cis-α*-[CoTETCl₂]ClO₄ and the red-violet *cis-β*-[CoTETCl₂]ClO₄ complexes. They were separated as follows.

cis-β-[CoTETCl₂]ClO₄.—The mixture of isomers (2.1 g) was taken up in boiling hydrochloric acid (35 ml; 5 *M*) and filtered. Red-violet needles were obtained after the filtrate was allowed to stand at room temperature for 3 hr. These were collected and washed with a little iced water followed by acetone. The filtrate remaining was brought to boiling and set aside overnight in a

refrigerator. A second crop of red-violet crystals was obtained. These were filtered and washed as before (total yield 1.0 g). *Anal.* Calcd for $C_8H_{20}N_2O_4S_2Cl_3Co$: C, 22.0; H, 4.6; N, 6.4; Cl, 24.3. Found: C, 22.1; H, 4.7; N, 6.4; Cl, 24.4.

cis-α-[CoTETCl₂]ClO₄.—The filtrate remaining from the second crop of red-violet crystals was boiled for 5 min, and perchloric acid (1 ml; concentrated) was added. After allowing the now blue solution to stand in a refrigerator overnight, the resultant blue crystals were filtered and washed with a little iced water and then with acetone (0.4 g). *Anal.* Calcd for $C_8H_{20}N_2O_4S_2Cl_3Co$: C, 22.0; H, 4.6; N, 6.4; Cl, 24.3. Found: C, 21.6; H, 4.6; N, 6.4; Cl, 24.2.

All of these compounds were stored over calcium chloride.

Chemical Interconversions.—The following general method was used for converting the dichloro complexes to the dinitro derivatives and then back to the dichloro complexes. The dichloro complex (5×10^{-5} mol) and sodium nitrite (10^{-4} mol) were dissolved in water (25 ml) and were heated to 80°. The color changed within a few minutes to orange and the solution was heated for a further 5 min and cooled, and the visible spectrum was taken. (The rate of nitrite substitution is more than ten times as fast as aquation, which suggests that the former is Co(II) catalyzed.) The resulting solution (20 ml) was made up to 25 ml with concentrated hydrochloric acid and heated with urea (1.1×10^{-4} mol) at 80°. The color changed rapidly and the conversion was complete in 0.5 hr. (This time is insufficient for complete equilibration of the dichloro complexes and any isomers formed in greater than 10% yield would be detected.) The solutions were cooled and the dichloro products were analyzed spectrophotometrically.

Instruments.—The absorption spectra were measured using a Unicam SP 800 (recording) spectrophotometer and the nmr spectra were taken by means of a Varian HA-100 spectrometer.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA, AND STANFORD UNIVERSITY, STANFORD, CALIFORNIA

Synthesis of σ -Bonded Allenyl Complexes of Iridium, Platinum, and Cobalt

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A series of complexes containing the novel σ -bonded allenyl ligand has been prepared from iridium(I), platinum(0), and cobalt(I) compounds. The complexes were formed by $SN2'$ attack on substituted 3-halopropynes. Provisional structures have been assigned to these complexes on the basis of their infrared, Raman, and nmr spectra. Kinetic evidence is presented demonstrating the second-order nature of the reaction. The reductive cleavage of the metal-carbon bond in the cobalt complexes, yielding allenes and the regenerated cobalt(I) species, has been demonstrated.

Introduction

The central element in low-valent organo-transition metal complexes often possesses nonbonded d-electron pairs which can act as nucleophilic centers.¹ Alkylation of such a metal is a conceptual oxidation. Thus reactions between alkylating or acylating agents and low-valent transition metals can be included in the broad class of *oxidative-addition* processes.² In the course of

studying oxidative additions of d^8 complexes, we treated Vaska's³ iridium(I) complex 1 with α -haloacetylenes and were surprised to find σ -bonded metalloallenes to be the major products of this reaction. Further investigation revealed that other transition metal centers which are susceptible to oxidative addition react with α -haloacetylenes in this way and that the σ -bonded metalloallenes are stable members of a hitherto little-known type of transition metal complex.

(1) J. P. Collman, *Accounts Chem. Res.*, **1**, 137 (1968).

(2) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 54 (1968).

(3) L. Vaska and J. W. DeLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).

That σ -bonded allene complexes would be stable and could be prepared by an apparent $\text{S}_{\text{N}}2'$ type of process is, in retrospect, not surprising. The stability of transition metal vinyl derivatives is well recognized,⁴ and in 1966 Green⁵ described the preparation of a perfluoroallenylrhodium carbonyl from the reaction of hexafluorobut-2-yne with the rhodium pentacarbonyl anion. During the writing of this paper, a preliminary report described the preparation of one of the cobalt allenyl derivatives reported herein.⁶

It seems probable that other metal-promoted allene syntheses pass through such σ -bonded allenyl complexes. An example is the synthesis of alkyl-substituted allenes by reaction between ethynylcarbinol acetates and lithium dialkylcopper reagents recently described by Rona and Crabbé.⁷ The possible relationships between such reactions and those described in this paper are considered below.

Results and Discussion

Reaction between the iridium(I) carbonyl **1** and three α -chloroacetylenes gave rise to the three iridium(III) allenic derivatives **2a**, **2b**, and **2c** (Figure 1). In each case the metal-carbon bond formed at the terminal acetylene atom in an apparent $\text{S}_{\text{N}}2'$ process. Two of the allenyl complexes **2a** and **2c** were also prepared by reaction of the Vaska complex **1** with the corresponding chloroallenes, seemingly by direct displacement. In both instances it seems probable that the reaction proceeds through initial coordination with the acetylene or allene but this point remains speculative.

The acetylenic carbon which forms a σ bond to the metal must be terminal and thus unhindered for the reaction to yield an allenyl complex. For instance, treatment of **1** with 1-chloro-2-butyne does not yield an allene, but affords an unstable acetylene complex **3** which probably exists as a mixture of isomers. The synthesis and probable structures of acetylene complexes such as **3** have been described earlier,⁸ and it was found that the stability (toward dissociation) of such acetylene complexes is dependent on the presence of electron-withdrawing substituents on the acetylene group. Steric effects on the supposed $\text{S}_{\text{N}}2'$ oxidative addition are further illustrated by reactions of the cobalt complex described further on.

It is now recognized that d^{10} complexes can engage in a variety of oxidative-addition reactions,⁹ the most widely studied case being tetrakis(triphenylphosphine) platinum(0) (**4**) and its derivatives.¹⁰ When **4** was allowed to react with haloacetylenes, the allenic platinum(II) complexes **5a**, **5b**, and **5c** were isolated in good yield. As before, **5a** and **5c** were also prepared by treating **4** with the corresponding chloroallenes.

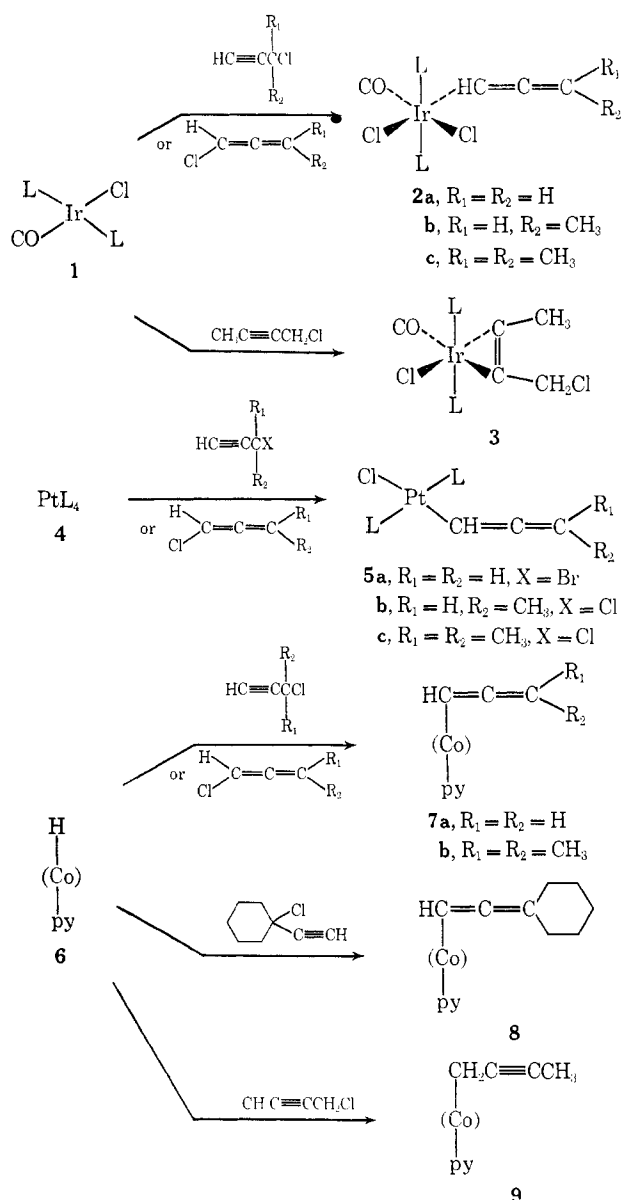


Figure 1.—Reactions of α -haloacetylenes with metal complexes. L signifies triphenylphosphine and dimethylglyoxime ligands are symbolized by parentheses.

As a third metal complex to test with this novel oxidative addition, we chose the cobaloxime **6**, widely heralded as a model for vitamin B₁₂.¹¹ Pyridinebis(dimethylglyoxime)cobalt chloride was converted to the reduced (cobalt(I)) form with sodium borohydride. Although this species is written as a hydride in Figure 1, its actual nature is unclear. This form reacted smoothly with 3-chloropropyne and 2-chloro-2-methyl-3-butyne affording the corresponding allenylcobaloximes **7a** and **7b**. Again, chloroallene also reacted to form the allenyl complex **7a**. Treatment of the reduced cobaloxime with 1-chloro-1-ethynylcyclohexane yielded the allenyl complex **8**.

The nonterminal haloacetylene 1-chloro-2-butyne again behaved differently. In this case the normal $\text{S}_{\text{N}}2$ product **9** was formed by reaction with the reduced cobaloxime.

(4) H. D. Kaesz and F. G. A. Stone, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp 88-149.

(5) M. Green, N. Mayne, and F. G. A. Stone, *Chem. Commun.*, 755 (1966).

(6) M. D. Johnson and C. Mayle, *ibid.*, 192 (1969).

(7) P. Rona and P. Crabbé, *J. Am. Chem. Soc.*, **91**, 3289 (1969).

(8) J. P. Collman and J. W. Kang, *ibid.*, **89**, 844 (1967).

(9) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968).

(10) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Am. Chem. Soc.*, **90**, 4491 (1968).

(11) G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).

With each of the three metals it seems appropriate to describe the formation of allenyl complexes from α chloroacetylenes as an $\text{SN}2'$ process. Halpern¹² has demonstrated that alkylations of the iridium complex **1** and of the platinum(0) complex **4**¹⁰ are $\text{SN}2$ reactions, although in the latter case the kinetics are complicated by prior dissociation of two phosphine ligands to yield the reactive coordinatively unsaturated form. Similarly, Schrauzer has presented kinetic evidence which suggests that the reduced cobaloximes react with alkyl halides by an $\text{SN}2$ mechanism.¹³ The reactions with chloroallene have precedent in reactions of the palladium analog of complex **4** and the cobaloxime **6** with vinyl halides,¹⁴ but Vaska's compound **1** or other neutral d^8 complexes have not been reported to react so. It is our opinion that these reactions are facilitated by prior coordination with the acetylene or the olefin. Isolation of the acetylene complex **3** provides some support for this hypothesis.

Preliminary kinetic studies on the formation of the iridium complexes **2a** and **2c** show that the reaction is clearly second order. The rate law is of the form $-d[\text{IrClL}_2\text{CO}]/dt = k_2[\text{IrClL}_2\text{CO}][\text{HC}\equiv\text{CCR}_1\text{R}_2\text{Cl}]$. The rate constants (Table I) and thermodynamic

TABLE I
SECOND-ORDER RATE CONSTANTS FOR THE REACTION
 $\text{IrClL}_2\text{CO} + \text{R}_1\text{R}_2\text{CICCC}\equiv\text{CH} \longrightarrow \text{IrCl}_2(\text{CH}=\text{C}=\text{CR}_1\text{R}_2)\text{L}_2\text{CO}$

Complexes formed	Solvent	Temp, °C	$k_2, M^{-1} \text{sec}^{-1}$
2a	Benzene	22	6.41×10^{-4}
2a	Benzene	30	9.12×10^{-4}
2a	Benzene	40	1.36×10^{-3}
2c	Benzene	22	3.03×10^{-4}
2c	Benzene	30	4.97×10^{-4}
2c	Benzene	35	6.64×10^{-4}
2c	CDCl_3	35	5.15×10^{-3}

parameters appear to parallel Chock and Halpern's data on the reaction of methyl iodide with **1**. The enthalpies of activation for the formation of **2a** and **2c**, $\Delta H^\ddagger = 7.05$ and 10.4 kcal/mol, are larger than those of the CH_3I reaction (5.6 kcal/mol). The entropies of activation ($\Delta S^\ddagger = -49$ and -40 eu), however, are the same within experimental error. The rate undergoes a similar enhancement in a polar solvent (CDCl_3). Both reactions thus present the same picture of an $\text{SN}2$ -type reaction with a somewhat polar transition state. Further studies are being done to determine the detailed mechanism of the reaction.

The provisional structures assigned to these allenyl complexes are based on ir and pmr spectral data. As shown in Table II, each purported allenyl complex exhibits a stretching band weak in the infrared spectrum, but intense in the Raman spectrum in the range 1900–1930 cm^{-1} . On the other hand, the supposed iridium-acetylene complex **3** exhibits a strong ir band at 1590

cm^{-1} . Such a band is in the range of a strongly coordinated acetylene.⁸ The cobalt-propargy derivative **9** shows a Raman-active band at 2198 cm^{-1} in the range for an uncoordinated acetylene. The carbonyl frequency is increased from 1960 cm^{-1} in the iridium(I) compound **1** to 2050 cm^{-1} in the iridium(III) adducts (Table II). Inasmuch as these carbonyl modes are intense in the infrared spectrum but weak in the Raman spectrum, they are easily distinguished from the allene and acetylene bands.

The pmr spectra summarized in Table III provide further support for the suggested structures. The chemical shifts of the protons directly attached to the allene group (H_a and H_b) are clearly in the olefin rather than the acetylene or alkyl region. The H_a protons are all shifted downfield from the allene position (τ 5.45), and the H_b protons are all shifted upfield. Since the normal tendency of transition metals is to shift nearby protons upfield, the behavior of the H_b protons is not surprising. At present we have no adequate explanation for the downfield shift of the H_a protons. There is also a trend to lower field of both the H_a and H_b protons with increasing methyl substitution of the allene. This is in accord with the normal inductive effect of the methyl group.

The long-range coupling constants found in these compounds are one of the strongest indications of allenic structures. The five-bond coupling constant (J_{ac}) is 2–3 Hz, a value which agrees with that found in other allenes, such as $(\text{CH}_3)_2\text{C}=\text{C}=\text{CHCl}$ ($J_{ac} = 2.1$ Hz). With acetylenes such as $(\text{CH}_3)_2\text{CICCC}\equiv\text{CH}$, such five-bond coupling was not observed within the resolution of our instrument (0.4 Hz). The four-bond coupling constant (J_{ab}) was measurable only in the cobalt compounds, for in the iridium and platinum compounds it was obscured by $^{31}\text{P}-\text{H}$ coupling. In the cobalt complex **7a**, J_{ab} was 5.6 Hz, which is in better agreement with an allenic structure (6–7 Hz) than an acetylenic structure (2–3 Hz).

Since it is well known that the cobalt-carbon bonds in complexes derived from **6** are reactive, we investigated the possibility of cleaving this bond in the cobalt-allenyl complexes. Attempts at oxidative cleavage of **7a** with H_2O_2 and at gentle reductive cleavage with H_2 and hydrazine failed. Irradiation at 300-nm light in CH_3OH resulted in an explosion.

Treatment of **7a** with the more vigorous agent NaBH_4 reductively cleaved the cobalt-carbon bond to produce allene and regenerate the nucleophilic cobalt(I) species **6** (Figure 2). If more α -haloacetylene was then added, **7a** was re-formed and the cycle could be repeated. The product allene was isolated by sweeping nitrogen through the system for several cycles of reaction and condensing the gas in a Dry Ice–2-propanol trap. Vinylidenecyclohexane was prepared by the analogous reaction with **8**, but the product decomposed on contact with the basic NaBH_4 solution. Rapid extraction of the products into pentane allowed a small amount of vinylidenecyclohexane to be identified, as well as several other of the rearrangement and reduction products.

(12) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966).

(13) (a) G. N. Schrauzer, E. Deutsch, and R. J. Windgassen, *ibid.*, **90**, 2441 (1968); (b) G. N. Schrauzer and E. Deutsch, *ibid.*, **91**, 3341 (1969).

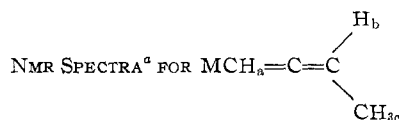
(14) P. Fitton and J. E. McKeon, *Chem. Commun.*, 4 (1968).

TABLE II
INFRARED^{a,b} AND RAMAN^c SPECTRA

Compound	$\nu(\text{C}=\text{C}=\text{C})$	$\nu(\text{C}=\text{O})$	$\nu(\text{M}-\text{Cl})$
$\text{IrCl}_2(\text{CH}=\text{C}=\text{CH}_2)((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$	1920 vw	2050 s	305
$\text{IrCl}_2(\text{CH}=\text{C}=\text{CHCH}_3)((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$	1920 vw (1922 m)	2050 s	305
$\text{IrCl}_2(\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$	1925 vw (1930 m)	2050 s	305
$\text{PtBr}(\text{CH}=\text{C}=\text{CH}_2)((\text{C}_6\text{H}_5)_3\text{P})_2$	1910 vw		
$\text{PtCl}(\text{CH}=\text{C}=\text{CHCH}_3)((\text{C}_6\text{H}_5)_3\text{P})_2$	1915 vw		
$\text{PtCl}(\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)((\text{C}_6\text{H}_5)_3\text{P})_2$	1910 vw (1925 m)		280 (278)
$\text{Co}(\text{dmgh})_2(\text{CH}=\text{C}=\text{CH}_2)(\text{py})^d$	1910 m		
$\text{Co}(\text{dmgh})_2(\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)(\text{py})$	1910 m		
$\text{Co}(\text{dmgh})_2(\text{CH}=\text{C}=\text{C}(\text{CH}_2)_5)(\text{py})$	1915 w		
$\text{IrCl}((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})(\text{CH}_3\text{C}\equiv\text{CCH}_2\text{Cl})$	1590 s $\left(\begin{array}{c} \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{Ir} \end{array} \right)$		
$\text{Co}(\text{dmgh})_2(\text{CHC}\equiv\text{CCH}_3)(\text{py})$	(2198 m) $(-\text{C}\equiv\text{C}-)$		

^a KBr pellets. Intensities of spectral bands are designated by: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. Frequencies reported in cm^{-1} measured on a grating instrument. ^c In parentheses. ^d dmgh = monoanion of dimethylglyoxime.

TABLE III



Compound	H _a	H _b	H _c	Coupling constants ^b
$\text{IrCl}_2(\text{CH}=\text{C}=\text{CH}_2)((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$	4.82 m	6.46 m		
$\text{IrCl}_2(\text{CH}=\text{C}=\text{CHCH}_3)((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$	4.72 m	6.05 m	8.75 m	$J_{ac} = 3.0, J_{bc} = 7$
$\text{IrCl}_2(\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$	4.70 m		8.93 d	$J_{ac} = 2.7$
$\text{PtBr}(\text{CH}=\text{C}=\text{CH}_2)((\text{C}_6\text{H}_5)_3\text{P})_2$	5.13 m	7.22 m		
$\text{PtCl}(\text{CH}=\text{C}=\text{CHCH}_3)((\text{C}_6\text{H}_5)_3\text{P})_2$	5.07 m	6.80 m	8.95 m	
$\text{PtCl}(\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)((\text{C}_6\text{H}_5)_3\text{P})_2$	5.00 m		9.16 d	
$\text{Co}(\text{dmgh})_2(\text{CH}=\text{C}=\text{CH}_2)(\text{py})$	5.10 t	5.48 d		$J_{ab} = 5.6$
$\text{Co}(\text{dmgh})_2(\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)(\text{py})^c$	5.4 ^d		8.62 d	$J_{ac} = 2.2$
$\text{Co}(\text{dmgh})_2(\text{CH}=\text{C}=\text{C}(\text{CH}_2)_5)(\text{py})$	5.18		e	

^a Spectra taken in CDCl_3 unless otherwise specified. Chemical shift in τ units relative to TMS at τ 10. Multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet. The observed areas of the signals agree with suggested formulas in all instances. ^b J in hertz. Assignments in complex multiplets made by spin decoupling. ^c Spectrum taken in CD_3OD . ^d Signal obscured by residual CD_3OH in solvent; located by irradiation of area until H_a protons decoupled. ^e Obscured by other signals.

Experimental Section

General Information.—Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer. Nmr spectra were recorded on a Varian T-60 instrument, a Varian A-60 instrument, or a Varian HA-100 instrument. Nmr analysis was done with the spin-decoupling accessory on the Varian T-60 instrument. Unless otherwise specified, the infrared spectra were run as KBr pellets and the nmr spectra were run in CDCl_3 solution with TMS as an internal reference. Raman spectra were recorded on a laser-excited Cary 81 Raman spectrophotometer. The elemental analyses are due to Messrs. E. Meier and J. Consul, Stanford Microanalysis Laboratory.

Preparation of α -Chloroacetylenes. **A. 3-Chloro-1-butyne.**—1-Butyn-3-ol (14 g, 0.2 mol) was dissolved in 50 ml of dry ether. PCl_3 (8.8 g, 0.066 mol) was slowly added with stirring. The solution was stirred 1 hr and washed with two 25-ml portions of cold H_2O and 25 ml of saturated sodium bicarbonate. The ether layer was dried with MgSO_4 and distilled. $\text{CH}_3\text{CHClC}\equiv\text{CH}$ distilled at 28–32° (100 mm); lit.^{15a} 68.5° (760 mm).

B. 1-Chloro-2-butyne.—By the same procedure 2-butyne-1-ol (14 g, 0.2 mol) and PCl_3 (8.8 g, 0.066 mol) gave 1-chloro-2-butyne, distilling at 38–40° (35–40 mm); lit.^{15b} 104–106° (760 mm).

C. 2-Chloro-2-methyl-3-butyne.—By the same procedure 2-methyl-3-butyne-2-ol (16.8 g, 0.2 mol) and PCl_3 (8.8 g, 0.066 mol) gave 2-chloro-2-methyl-3-butyne, distilling at 42–46° (110–120 mm); lit.^{15a} 74–76° (760 mm).

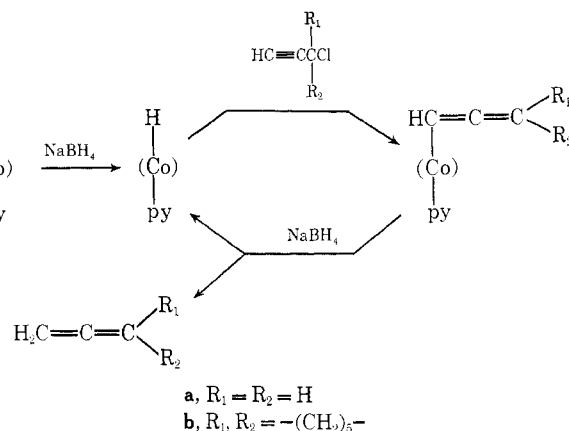


Figure 2.—Formation and reduction of cobalt allenyl complexes.

D. 1-Chloro-1-ethynylcyclohexane was prepared by the procedure of Hennion and Bouselle.^{15b}

Preparation of Chloroallenes. **A. 1-Chloro-1,2-propadiene** was prepared by the method of Jacobs and Brill^{16b} and purified by preparative glpc.

(15) (a) G. F. Hennion and J. M. Campbell, *J. Org. Chem.*, **21**, 791 (1956); (b) G. F. Hennion and A. P. Bouselle, *ibid.*, **26**, 725 (1961).

(16) (a) F. F. Hatch and V. Chiola, *J. Am. Chem. Soc.*, **73**, 360 (1951); (b) T. L. Jacobs and W. F. Brill, *ibid.*, **75**, 1314 (1953).

B. 1-Chloro-3-methyl-1,2-butadiene was prepared by the method of Favorskaya.¹⁷

$\text{IrCl}((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$ was prepared by the method of Collman.¹⁸ $\text{Pt}((\text{C}_6\text{H}_5)_3\text{P})_4$ was prepared by the method of Ugo.¹⁹ $\text{Co}(\text{dmgh})_2\text{Cl}(\text{py})$ ²⁰ was prepared by the method of Schrauzer.²¹

Preparation of Iridium-Allene Complexes. A. $\text{IrCl}_2(-\text{CH}=\text{C}=\text{CH}_2)((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$.— $\text{IrCl}((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$ (320 mg, 0.4 mmol) was dissolved in 10 ml of degassed CHCl_3 under nitrogen. Prop-2-ynyl chloride (35 mg, 0.5 mmol) was injected and the solution was stirred for 1 hr. The solution became colorless rapidly. The resulting complex was precipitated with hexane, redissolved in a minimum amount of chloroform, and crystallized by addition of methanol. *Anal.* Calcd for $\text{IrC}_{40}\text{H}_{38}\text{Cl}_2\text{O}_2\text{P}_2$: C, 56.23; H, 3.90; P, 7.25. Found: C, 55.91; H, 3.91; P, 7.70.

By the same procedure $\text{IrCl}((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$ (320 mg, 0.4 mmol) and chloroallene (35 mg, 0.5 mmol) gave the same complex, identified by comparison of infrared and nmr spectra.

B. $\text{IrCl}_2(-\text{CH}=\text{C}=\text{CHCH}_3)((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$.—By the same procedure $\text{Ir}((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})\text{Cl}_2$ (320 mg, 0.4 mmol) and 3-chloro-1-butyne (40 mg, 0.5 mmol) gave $\text{IrCl}_2(-\text{CH}=\text{C}=\text{CHCH}_3)((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$. *Anal.* Calcd for $\text{IrC}_{41}\text{H}_{39}\text{Cl}_2\text{O}_2\text{P}_2$: C, 56.68; H, 4.06; P, 7.14; Cl, 8.16. Found: C, 56.61; H, 4.06; P, 7.46; Cl, 8.42.

C. $\text{IrCl}_2(-\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$.—By the same procedure $\text{Ir}((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})\text{Cl}$ (320 mg, 0.4 mmol) and 2-chloro-2-methyl-3-butyne (45 mg, 0.5 mmol) gave $\text{IrCl}_2(-\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$. *Anal.* Calcd for $\text{IrC}_{42}\text{H}_{37}\text{Cl}_2\text{O}_2\text{P}_2$: C, 57.14; H, 4.23; P, 7.02. Found: C, 56.77; H, 4.20; P, 7.23.

By the same procedure $\text{IrCl}((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$ (320 mg, 0.4 mmol) and 1-chloro-3-methyl-1,2-butadiene (45 mg, 0.5 mmol) gave the same complex, identified by comparison of infrared and nmr spectra.

Preparation of Platinum-Allene Complexes. A. $\text{PtBr}(-\text{CH}=\text{C}=\text{CH}_2)((\text{C}_6\text{H}_5)_3\text{P})_2$.— $\text{Pt}((\text{C}_6\text{H}_5)_3\text{P})_4$ (124 mg, 0.1 mmol) was dissolved in 2 ml of degassed benzene under nitrogen. 3-Bromopropyne (13 mg, 0.11 mmol) was added and the mixture was stirred for 30 min. The solution rapidly became colorless. The solvent was evaporated and the resulting white solid was washed with ether and recrystallized from chloroform-methanol; yield, 53 mg of white crystals (63%). *Anal.* Calcd for $\text{PtC}_{39}\text{H}_{38}\text{BrP}_2$: C, 55.85; H, 3.97; P, 7.40; Br, 9.56. Found: C, 55.91; H, 3.98; P, 7.15; Br, 9.56.

B. $\text{PtCl}(-\text{CH}=\text{C}=\text{CHCH}_3)((\text{C}_6\text{H}_5)_3\text{P})_2$.—By the same procedure $\text{Pt}((\text{C}_6\text{H}_5)_3\text{P})_4$ (250 mg, 0.2 mmol) and 3-chloro-1-butyne (25 mg, 0.3 mmol) gave $\text{PtCl}(-\text{CH}=\text{C}=\text{CHCH}_3)((\text{C}_6\text{H}_5)_3\text{P})_2$ (120 mg, 75%) as white needles. *Anal.* Calcd for $\text{PtC}_{40}\text{H}_{38}\text{ClP}_2$: C, 59.33; H, 4.32. Found: C, 59.30; H, 4.39.

C. $\text{PtCl}(-\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)((\text{C}_6\text{H}_5)_3\text{P})_2$.—By the same procedure $\text{Pt}((\text{C}_6\text{H}_5)_3\text{P})_4$ (250 mg, 0.2 mmol) and 2-chloro-2-methyl-3-butyne (30 mg, 0.3 mmol) gave $\text{PtCl}(-\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)((\text{C}_6\text{H}_5)_3\text{P})_2$ as white crystals. *Anal.* Calcd for $\text{PtC}_{41}\text{H}_{37}\text{ClP}_2$: C, 59.89; H, 4.54; P, 7.54. Found: C, 59.77; H, 4.60; P, 7.63.

By the same procedure $\text{Pt}((\text{C}_6\text{H}_5)_3\text{P})_4$ (250 mg, 0.2 mmol) and 1-chloro-3-methyl-1,2-butadiene (30 mg, 0.3 mmol) gave the same complex, identified by comparison of infrared and nmr spectra and thin layer chromatography.

Preparation of Cobalt-Allene Complexes. A. $\text{Co}(\text{dmgh})_2(-\text{CH}=\text{C}=\text{CH}_2)(\text{py})$.— $\text{Co}(\text{dmgh})_2\text{Cl}(\text{py})$ (300 mg, 0.75 mmol) was suspended under nitrogen in 20 ml of degassed methanol. NaBH_4 (18 mg, 0.5 mmol) was added to form a dark blue solution. 3-Chloropropyne (60 mg, 0.8 mmol) was added with stirring; the solution rapidly became light red-brown. After 10 min the solvent was evaporated and the resulting solid was recrystallized from hot 30% aqueous ethanol to form thin orange needles. *Anal.* Calcd for $\text{CoC}_{16}\text{H}_{22}\text{N}_5\text{O}_4$: C, 47.17; H, 5.41; N, 17.18. Found: C, 46.75; H, 5.28; N, 17.04.

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By the same procedure $\text{Co}(\text{dmgh})_2\text{Cl}(\text{py})$ (300 mg, 0.75 mmol) and chlorallene (60 mg, 0.8 mmol) gave $\text{Co}(\text{dmgh})_2(-\text{CH}=\text{C}=\text{CH}_2)(\text{py})$ identified by comparison of infrared and nmr spectra.

B. $\text{Co}(\text{dmgh})_2(-\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)(\text{py})$.—By the same procedure $\text{Co}(\text{py})(\text{dmgh})_2\text{Cl}$ (300 mg, 0.75 mmol) and 2-chloro-2-methyl-3-butyne (100 mg, 1.0 mmol) gave $\text{Co}(\text{py})(\text{dmgh})_2(-\text{CH}=\text{C}=\text{C}(\text{CH}_3)_2)$ (200 mg, 60%) as dark red thick needles. *Anal.* Calcd for $\text{CoC}_{18}\text{H}_{26}\text{N}_5\text{O}_4$: C, 49.66; H, 6.01; N, 16.08. Found: C, 49.51; H, 5.95; N, 15.76.

C. $\text{Co}(\text{dmgh})_2(-\text{CH}=\text{C}=\text{C}(\text{CH}_2)_2)(\text{py})$.—By the same procedure $\text{Co}(\text{py})(\text{dmgh})_2\text{Cl}$ (200 mg, 0.5 mmol) gave $\text{Co}(\text{dmgh})_2(-\text{CH}=\text{C}=\text{C}(\text{CH}_2)_2)(\text{py})$ as dark red needles. *Anal.* Calcd for $\text{CoC}_{21}\text{H}_{30}\text{N}_5\text{O}_4$: C, 53.05; H, 6.46; N, 14.73. Found: C, 53.10; H, 6.34; N, 14.78.

Preparation of Other Complexes. A. $\text{Ir}((\text{C}_6\text{H}_5)_3\text{P})(\text{CO})(\text{CH}_3\text{C}=\text{CCH}_2\text{Cl})$.—By the same procedure as used for the iridium-allene complexes above, $\text{IrCl}((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})$ (240 mg, 0.3 mmol) and 1-chloro-2-butyne (40 mg, 0.5 mmol) gave $\text{Ir}((\text{C}_6\text{H}_5)_3\text{P})_2(\text{CO})(\text{CH}_3\text{C}=\text{CCH}_2\text{Cl})$ as a yellow powder relatively insoluble in organic solvents. Because of its insolubility it could not be purified and hence failed to give a good elemental analysis. Ir spectrum: 1590 cm^{-1} (C=C); 2050 cm^{-1} (C=O). Nmr spectrum: τ 6.78 s ($-\text{CH}_2\text{Cl}$); 8.83 s ($-\text{CH}_3$).

B. $\text{Co}(\text{dmgh})_2(-\text{CH}_2\text{C}=\text{CCH}_3)(\text{py})$.—By the same procedure as used for the cobalt-allene complexes above, $\text{Co}(\text{dmgh})_2\text{Cl}(\text{py})$ (200 mg, 0.5 mmol) and 1-chloro-2-butyne (50 mg, 0.63 mmol) gave $\text{Co}(\text{dmgh})_2(-\text{CH}_2\text{C}=\text{CCH}_3)(\text{py})$. Raman spectrum: 2198 cm^{-1} ($-\text{C}\equiv\text{C}-$). Nmr spectrum: 8.17 (q) ($\text{CoCH}_2\text{C}\equiv$); 8.55 (t) ($=\text{CCH}_3$); $J = 2.8$ Hz. *Anal.* Calcd for $\text{CoC}_{17}\text{H}_{24}\text{N}_5\text{O}_4$: C, 48.40; H, 5.71; N, 16.63. Found: C, 48.21; H, 5.68; N, 16.48.

Reduction of $\text{Co}(\text{dmgh})_2(\text{CH}=\text{C}=\text{CH}_2)(\text{py})$.— $\text{Co}(\text{dmgh})_2(-\text{CH}=\text{C}=\text{CH}_2)(\text{py})$ (100 mg, 0.25 mmol) was dissolved in 25 ml of degassed methanol. NaBH_4 was added until the solution abruptly turned the dark blue of $\text{Co}(\text{py})(\text{dmgh})_2\text{H}$. 3-Chloropropyne was then added until the solution again became light red-brown. This cycle was repeated ten times with nitrogen gas sweeping above the solution and passing through a trap cooled with Dry Ice-2-propanol. The liquid in the trap was shown to contain allene by comparison of vpc retention times (2-m Poropak column at 75°) and by nmr spectra (τ 5.30 (s); lit.²² τ 5.34 (s)).

Reduction of $\text{Co}(\text{dmgh})_2(-\text{CH}=\text{C}=\text{C}(\text{CH}_2)_2)(\text{py})$.—By the same procedure $\text{Co}(\text{dmgh})_2(-\text{CH}=\text{C}=\text{C}(\text{CH}_2)_2)(\text{py})$ (120 mg, 0.25 mmol) was taken through five cycles of reduction with NaBH_4 . Water was then added to the solution and the solution was extracted three times with 20 ml of pentane. The pentane layers were combined, dried with MgSO_4 , and distilled. Nearly all of the high molecular weight material distilled at 28–29° (90–100 mm). Vpc (3 m \times 6 mm 10% Carbowax on Chromosorb W) indicated the presence of six components, three of which could be isolated by preparative vpc. They were identified by their nmr spectra as vinylcyclohexane, ethylidenecyclohexane, and vinylidenecyclohexane.

In a blank experiment, 1-chloro-1-ethynylcyclohexane was stirred with NaBH_4 in methanol. After extraction with pentane and distillation as above, vpc indicated that none of the above six products was formed.

Kinetic Studies. Method A.—The disappearance of 2-methyl-2-chloro-3-butyne and the formation of 2c were followed simultaneously with an nmr spectrometer. The relative concentrations of the two compounds were determined from the integrals of the signals of their methyl protons (τ 8.13 and 8.75, respectively). Equimolar quantities of the two reactants were used and second-order rate constants (Table I) were determined from the slope of a plot of [butyne]/[complex] against time.

Solutions of 1 in degassed CDCl_3 (ca. 3.6×10^2 M) were prepared in standard nmr tubes fitted with septum caps and thoroughly flushed with nitrogen. The tube was equilibrated at

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35° in the sample holder of a Varian T-60 nmr spectrometer, and 2-methyl-2-chloro-3-butyne was injected through the septum. The tube was shaken and rapidly placed in the spectrometer probe. The reaction was followed for one second-order half-life and the second-order rate constant based on the best straight line through 10–15 points. The time required to sweep through the two peaks caused a systematic time error of 8 sec which was significant for the first few points. The average of five runs gave $k_2 = 5.15 \times 10^{-2} M^{-1} \text{sec}^{-1}$ with a standard deviation of $0.8 \times 10^{-2} M^{-1} \text{sec}^{-1}$.

Method B.—The disappearance of 1 was followed spectrophotometrically. At least a 15-fold excess of α -chloroacetylene was used and pseudo-first-order rate constants were determined from the slope of a plot of $\ln(D_\infty - D_t)$ against time, where D_t is the absorbance at time t and D_∞ the absorbance after at least 10 half-lives. Absorption was measured at the peaks at both 440 and 387 nm. Ten milligrams of 1 was weighed into a small bottle fitted with a septum. The bottle was thoroughly flushed

with nitrogen and 1.5 ml of a solution of the α -chloroacetylene (*ca.* 0.2 M) in degassed benzene was injected. The bottle was shaken thoroughly and placed in a water bath held to within 0.1° of the stated temperature. Aliquots (100- μ l) were taken at intervals and diluted to 1.6 ml with degassed benzene. The spectrum was taken in a 1.0-cm cell. Reactions were followed for 1–2 half-lives, and pseudo-first-order rate constants were based on the least-squares line through 5–10 points. Second-order rate constants (Table I) calculated from these values were satisfactorily independent of acetylene concentration.

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Nuclear Magnetic Resonance Line-Broadening Study of Cobalt(II) and Nickel(II) in Dimethyl Sulfoxide and Trimethyl Phosphate

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The effects of cobalt(II) and nickel(II) on the proton nmr of dimethyl sulfoxide (DMSO) and trimethyl phosphate (TMPA) have been studied. Chemical exchange controlled line broadening was found only for nickel(II) in DMSO, in which case the exchange rate is $4.2 \times 10^3 \text{sec}^{-1}$ at 25° with $\Delta H^\ddagger = 12.1 (\pm 0.3) \text{kcal mol}^{-1}$ and $\Delta S^\ddagger = 1.3 (\pm 0.5) \text{eu}$. In all other cases the chemical exchange was too fast to measure and only dipolar line broadening was observed. Chemical shifts were measured in all cases. The hyperfine coupling constants (A/h) for Ni^{2+} in DMSO and TMPA are 7.50×10^4 and $7.16 \times 10^3 \text{Hz}$, and for Co^{2+} in DMSO, the constant is $2.08 \times 10^4 \text{Hz}$. The chemical shift for the Co^{2+} -TMPA system changes from positive to negative as the temperature decreases. This observation, combined with a spectrophotometric study, indicates an octahedral-tetrahedral equilibrium of the type $\text{Co}(\text{TMPA})_4^{2+} + 2\text{TMPA} \rightleftharpoons \text{Co}(\text{TMPA})_6^{2+}$. The position of this equilibrium does not permit the extinction coefficient or hyperfine coupling constant of the tetrahedral species to be determined with any certainty. However if an extinction coefficient of 500 is assumed for $\text{Co}(\text{TMPA})_4^{2+}$, then a self-consistent fit of the temperature dependence of the absorbance, chemical shift, and line broadening can be obtained. The fit is far from unique however and a range of extinction coefficients from about 400 to 1200 would also fit the data. It has been found that the activation enthalpy for solvent exchange in a number of systems may be predicted by assuming that the activation enthalpy is made up of a general solvation term, which is constant for a given solvent and charge on the metal ion, and a crystal field contribution.

Introduction

The method of studying solvent-exchange rates by nmr line broadening has become widely used since the original work of Swift and Connick¹ on the water exchange rate of various transition metal ions. It is hoped that studies with several metal ions in a number of solvents will lead to an understanding of the factors controlling the exchange rate of solvent molecules from the inner coordination sphere of the metal ion. A number of studies of nmr line broadening by nickel(II), cobalt(II),^{2–7} and vanadyl ion^{8,9} have recently appeared

in the literature. The present study attempts to fill in some of the gaps so that comparisons can be made between these metal ions in a more extended range of solvents.

The results in dimethyl sulfoxide (DMSO) are an extension of previous results of Thomas and Reynolds.⁷ Only the nickel(II) in DMSO system shows chemical-exchange control of the nmr line broadening and only upper or lower limits can be established for the exchange rates of cobalt(II) in DMSO and for both cobalt(II) and nickel(II) in trimethyl phosphate (TMPA). Interpretation of the chemical shift and visible spectral data for cobalt(II) in TMPA indicates the presence of an equilibrium mixture of tetrahedral and octahedral species.

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