Refluxing a THF solution of $(OC)_5WPPh_2H$ (1.0 mmol) and KO-*t*-Bu (1.0 mmol) for 6 h resulted in the precipitation of III (10%). The ^{31}P NMR spectrum of III shows signals at −99.2 ppm (J_{WP} = 156.0 Hz). The infrared spectrum of III, consisting of three medium and one strong absorption, matches in appearance that reported for $[Cr_2(CO)_8(PMe_2)]_2^{2-}$, an anion previously obtained electrochemically.[9] The yellow anion, III, reacts rapidly with air to give red IV but is stable in oxygen-free dry THF or CH_3CN. The infrared spectrum of IV is in agreement with literature reports.[2] ^{31}P resonance occurs at 180.0 ppm (J_{WP} = 162 Hz).

A reasonable reaction sequence for the production of I, II, III, and IV is presented in Scheme I.

Of particular interest is the dramatic change in the ^{31}P chemical shift which accompanies formation of a metal–metal bond. Thus our work adds further support to the notion that ^{31}P chemical shifts diagnose the presence or absence of metal–metal bonds in phosphido bridged complexes.[10]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank David Vander Velde and Dennis Warrenfeltz of the University of Illinois for obtaining ^{31}P spectra.

Registry No. I, 80049-78-1; II, 80049-80-5; III, 80049-81-6; IV, 80049-82-7; $(OC)_5WPPh_2H$, 18399-62-7.

(9) Dessey, R. E.; Weiczorek, L. *J. Am. Chem. Soc.* **1969**, *91*, 4963. Dessey, R. E.; Rheingold, A. L.; Howard, G. D. *Ibid.* **1972**, *94*, 746.
(10) Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051. Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. Brandon, J. B.; Dixon, K. R. *Can. J. Chem.* **1981**, *59*, 1188.

Role of Heteroatoms in the Formation of Higher Nuclearity Transition-Metal Carbonyl Cluster Compounds. The Condensation of Small Clusters

Richard D. Adams,* Zain Dawoodi, and Donald F. Foust
Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received November 9, 1981

Summary: The molecules $HOs_3(\mu_3\text{-S})(\mu\text{-HCNR})(CO)_9$, R = C_6H_5, Ia, and *p*-C_6H_4F, Ib, lose carbon monoxide when heated and condense to form the higher nuclearity carbonyl clusters $H_2Os_6(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-HC=NR})_2(CO)_{17}$, R = C_6H_5, IIa, and *p*-C_6H_4F, IIb, and $H_2Os_6(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-HC=NR})_2(CO)_{16}$, R = C_6H_5, III. The compounds have been characterized by IR and ^1H NMR spectroscopies, and IIb and III have also been characterized by X-ray crystallographic methods. For IIb: space group $P\bar{1}$ at 28 °C; a = 9.865 (7) Å, b = 14.735 (6) Å, c = 15.926 (10) Å, α = 69.08 (5)°, β = 79.63 (6)°, γ = 86.40 (6)°, Z = 2, ρ_{calcd} = 3.01 g/cm^3. The structure was solved by a combination of Patterson and difference Fourier techniques. Refinement on 3584 reflections ($F^2 \geq 3.0\sigma(F^2)$) produced the final residuals R_1 = 0.032 and R_2 = 0.030. For III: space group $P2_1/n$ at 28 °C; a = 10.506 (4) Å, b = 23.145 (12) Å, c = 16.933 (5) Å, β = 97.60 (3)°, Z = 4, ρ_{calcd} = 3.03 g/cm^3. This structure was solved by a combination of direct methods and difference Fourier techniques. Refinement on 2347 reflections ($F^2 \geq 3.0\sigma(F^2)$) produced the final residuals R_1 = 0.052 and R_2 = 0.043. IIb contains two groups of "open" clusters of three metal atoms linked by a tetracoordinate bridging sulfur atom. The metal–metal bonding in each of the "open" cluster groups is analogous to that in the molecules I. In III the metal atoms are arranged in groups of four and two with the two groups linked by a tetracoordinate bridging sulfur atom. It is believed that III is formed by the decarbonylation of IIa. A reorganization of the metal–metal bonding then occurs in which an $Os(CO)_3$ unit is shifted from one group of three to the other.

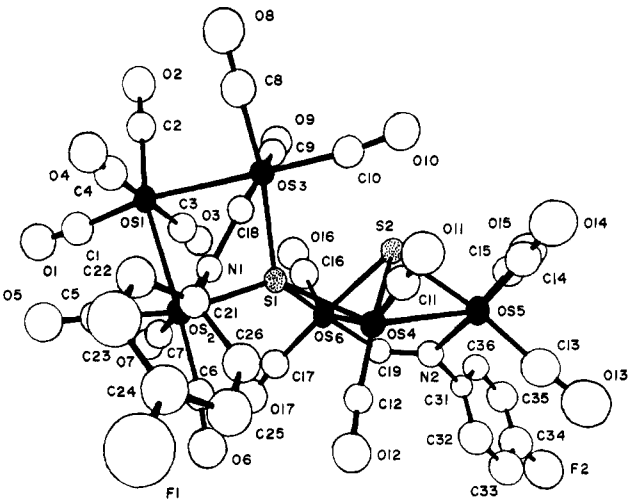
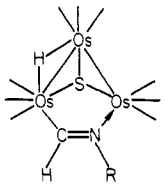


Figure 1. An ORTEP drawing of $H_2Os_6(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-HC=N-}p\text{-}C_6H_4F)_2(CO)_{17}$, IIb, showing 50% electron density probability ellipsoids.

The decarbonylation of metal carbonyl compounds is the most successful and widely used method for the preparation of high nuclearity transition-metal carbonyl cluster compounds.[1] In this process, metal–metal bonds replace the metal–carbon bonds of the eliminated ligands. It is well-known that heteronuclear bridging ligands will enhance the stability of polynuclear metal complexes.[2] Recently it has been proposed that these heteronuclear bridging ligands can play an important role in the systematic synthesis of higher nuclearity cluster compounds.[3]

We wish to report that we have now observed an example of the aggregation of two transition-metal clusters which unequivocally shows the importance and role of the heteronuclear bridging ligand in preliminary cluster condensation and the eventual reorganization of the metal–metal bonds within the clusters.

We have recently reported the synthesis of the cluster compounds $HOs_3(\mu_3\text{-S})(\mu\text{-HC=NR})(CO)_9$, R = C_6H_5, Ia, and *p*-C_6H_4F, Ib.[4] When heated to reflux in octane solvent



I

(1) (a) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285. (b) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2606. (c) Lewis, J.; Johnson, B. F. G. *Gazz. Chim. Ital.* **1979**, *109*, 271. (d) Lewis, J.; Johnson, B. F. G. *Pure Appl. Chem.* **1975**, *44*, 43.
(2) (a) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322. (b) Marko, L. *Gazz. Chim. Ital.* **1979**, *109*, 247.
(3) Vahrenkamp, H.; Wucherer, E. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 680.

0276-7333/82/2301-0411$01.25/0 © 1982 American Chemical Society

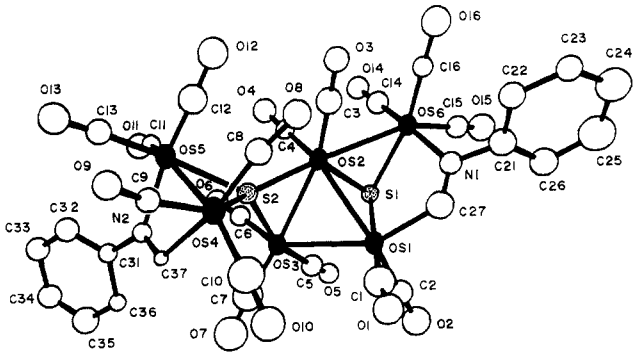
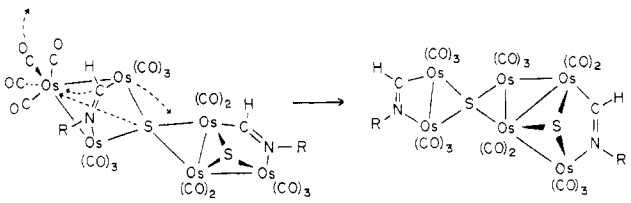


Figure 2. An ORTEP drawing of $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NC_6H_5)_2(CO)_{16}$, III, showing 50% electron density probability ellipsoids.

for 3 h, these molecules are converted into a number of new higher nuclearity clusters, two of which have now been isolated and characterized by IR and ^1H NMR spectroscopic and X-ray crystallographic methods.[5,6] The first of these has the formula $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)_2(CO)_{17}$, R = C_6H_5, IIa, and $p\text{-}C_6H_4F$, IIb.[7] They can be assumed to be formed by the condensation of two moles of I accompanied by the loss of 1 mol of CO. The molecular structure of IIb is shown in Figure 1.[8,9] The molecule consists of two "open" cluster groupings of three osmium atoms which are linked by a tetrahedrally coordinated bridging sulfur atom, S(1). The cluster group Os(4)–Os(5)–Os(6) is very similar to I with the exception that two of the equatorially coordinated carbonyl ligands have been replaced by donor bonds from the bridging sulfur atom, S(1). Cluster Os(1)–Os(2)–Os(3) differs from I in that the sulfur atom is bonded only to two of the metal atoms, Os(1) and Os(2), while Os(3) has four carbonyl ligands. As in I, each cluster grouping in IIb contains an η^2-formimidoyl ligand bridging the open edge of the cluster.

The formation of II was probably initiated via a dissociative loss of CO from I. The empty coordination site was then filled by donation of the lone pair of electrons of the triply bridging sulfur atom from a second molecule of I. In this close proximity, an intercluster carbonyl shift might easily follow the cleavage of an osmium–sulfur bond in the added cluster and this would complete the formation of II.

Scheme I



The second type of molecule isolated from the pyrolysis of I has the formula $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)_2(CO)_{16}$, R = C_6H_5, III.[10] The molecular structure of III is shown in Figure 2.[6,11,12] III contains six osmium atoms which are arranged in groups of four and two. Within the group of four osmium atoms, three, namely, Os(1), Os(2), and Os(6), can be compared with Os(4), Os(5), and Os(6) in the "open" cluster in IIb. These three metal atoms contain a triply bridging sulfur atom and an η^2-formimidoyl ligand bridging the nonbonded pair of metal atoms, Os(1) and Os(6). The fourth metal atom, Os(3), in the form of an $Os(CO)_3$ unit bridges the Os(1)–Os(2) edge of this grouping of three. A tetrahedrally coordinated sulfur atom, S(2), bridges the Os(2)–Os(3) bond and links the two atom group Os(4)–Os(5) to the first four. The Os(4)–Os(5) group consists of two $Os(CO)_3$ units joined by a metal–metal bond and contains a bridging η^2-formimidoyl ligand.

We feel it is significant that III contains one carbonyl ligand less than II and thus believe that the molecules II are precursors to III. The transformation of II into III can be imagined in the following way (see Scheme I). If the $Os(CO)_4$ unit in II loses one carbonyl ligand, the formimidoyl ligand can then move either its carbon or nitrogen atom to that metal atom. According to the labeling scheme in IIb, the remaining $Os(CO)_3$ unit, either that of Os(2) or Os(3), can then insert into the Os(6)–S(1) bond. This involves cleavage of either the Os(1)–Os(2) or the Os(1)–Os(3) metal–metal bond and formation of metal–metal bonds to both Os(4) and Os(6). A metal–sulfur bond between Os(1) and S(1) is also formed.

The principal steps represented by II and III in the condensation of the clusters of I are (1) metal–sulfur coordination which leads to the initial link between the clusters and (2) reorganization of the metal–metal bonds which occurs in the formation of III. The first step is facilitated by the ability of the sulfur ligand to serve as a polycoordinate multielectron donor.[13]

(4) Adams, R. D.; Dawoodi, Z. *J. Am. Chem. Soc.* **1981**, *103*, 6510.

(5) In a typical preparation 180 mg of Ia was refluxed 3 h in octane solvent under a nitrogen atmosphere. The products were isolated by TLC on silica gel plates using a hexane/10% CH_2Cl_2 solvent mixture. At least six compounds were isolated in yields ranging from 5 to 15%. Accurate yields are difficult to obtain because of the small amounts of material involved. Of the six product bands which followed residual starting material on the plate, IIa and IIIa were the fifth and second bands, respectively. All the products are air-stable. ^1H NMR spectra were recorded at 270 MHz on a Bruker HX-270 spectrometer.

(6) X-ray crystallographic data were collected on an Enraf-Nonius CAD-4 automatic diffractometer using molybdenum radiation. Structure solution and refinement calculations were done on a Digital PDP 11/45 computer by using the Enraf-Nonius SDP program library, Version 16.

(7) For IIa: IR ν (CO) (in hexane) 2111 (m), 2096 (m), 2085 (sh), 2066 s), 2053 (sh), 2044 (vs), 2029 (vs), 2008 (s), 1990 (s), 1979 (s), 1960 (m); ^1H NMR (in $CDCl_3$), δ 12.38 (s, 1 H), 11.25 (s, 1 H), 7.30 (m, 10 H), −13.82 (s, 1 H), −17.44 s, 1 H). For IIb: IR ν(CO) (in hexane), 2110 (m), 2095 (m), 2080 (w), 2067 (vs), 2050 (sh), 2043 (s), 2025 (s), 2005 (m), 1980 (m), 1975 (m), 1955 (w); ^1H NMR (in $CDCl_3$), δ 12.40 (s, 1 H), 11.27 (s, 1 H), 7.20 (m, 8 H), −13.87 (s, 1 H), −17.46 (s, 1 H).

(8) For IIb: space group $P\bar{1}$ at 28 °C; a = 9.865 (7) Å, b = 14.735 (6) Å, c = 15.926 (10) Å, α = 69.08 (5)°, β = 79.63 (6)°, γ = 86.40 (6)°, Z = 2, ρ_{calcd} = 3.01 g/cm^3. The structure was solved by a combination of Patterson and difference Fourier techniques. Least-squares refinement on 3584 reflections ($F^2 \geq 3.0\sigma(F^2)$) produced the final residuals R_1 = 0.032 and R_2 = 0.030.

(9) Selected bond distances (Å) and angles (deg) for IIb: Os(1)–Os(2) = 2.914 (1), Os(1)–Os(3) = 2.918 (1), Os(4)–Os(5) = 2.951 (1), Os(4)–Os(6) = 2.803 (1), Os(3)–C(18) = 2.10 (1), Os(2)–N(1) = 2.12 (1), Os(6)–C(19) = 2.02 (2), Os(5)–N(2) = 2.16 (1); Os(2)–S(1) = 2.447 (4), Os(3)–S(1) = 2.481 (3), Os(4)–S(1) = 2.441 (4), Os(6)–S(1) = 2.509 (4); Os(2)–Os(1)–Os(3) = 75.28 (2), Os(5)–Os(4)–Os(6) = 80.93 (2), Os(2)–S(1)–Os(3) = 92.54 (13), Os(4)–S(1)–Os(6) = 68.96 (10), Os(2)–S(1)–Os(4) = 124.05 (13), Os(2)–S(1)–Os(6) = 129.54 (15), 68.96 (10), Os(2)–S(1)–Os(4) = 124.05 (13), Os(2)–S(1)–Os(6) = 129.54 (15), Os(3)–S(1)–Os(4) = 113.61(14), Os(3)–S(1)–Os(6) = 129.38 (14), Os(4)–S(1)–Os(6) = 68.96 (10).

(10) For III: Ir ν(CO) (in hexane) 2100 (m), 2077 (vs), 2054 (vs), 2039 (s), 2024 (s), 2007 (vs), 1979 (s), 1953 (m), 1932 (w); ^1H NMR (in $CDCl_3$) δ 10.89 (s, 1 H), 10.38 (s, 1 H), 7.30 (m, 10 H), −17.57 (s, 1 H), −17.72 (s, 1 H).

(11) For III: space group $P2_1/n$ at 28 °C; a = 10.506 (4) Å, b = 23.145 (12) Å, c = 16.933 (5) Å, β = 97.60 (3)°, Z = 4, ρ_{calcd} = 3.03 g/cm^3. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. Least-squares refinement on 2347 reflections ($F^2 \geq 3.0\sigma(F^2)$) produced the final residuals R_1 = 0.052 and R_2 = 0.043.

(12) Selected bond distances (Å) and angles (deg) for III: Os(1)–Os(2) = 2.865 (2), Os(1)–Os(3) = 3.070 (2), Os(2)–Os(3) = 2.839 (2), Os(2)–Os(6) = 2.917 (2), Os(4)–Os(5) = 2.769 (2), Os(2)–S(2) = 2.372 (8), Os(3)–S(2) = 2.417 (7), Os(4)–S(2) = 2.425 (7), Os(5)–S(2) = 2.403 (8), Os(1)–C(27) = 2.07 (4), Os(6)–N(1) = 2.16 (3), Os(4)–C(37) = 2.11 (3), Os(5)–N(2) = 2.11 (2); Os(2)–S(2)–Os(3) = 72.7, Os(2)–S(2)–Os(4) = 132.2 (3), Os(3)–S(2)–O(4) = 130.5 (4), Os(3)–S(2)–Os(5) = 131.9 (3), Os(4)–S(2)–Os(5) = 70.0 (2), Os(1)–Os(2)–Os(6) = 81.04 (5), Os(1)–Os(2)–Os(3) = 65.13 (5), Os(1)–Os(3)–Os(2) = 57.85 (5), Os(2)–Os(1)–Os(3) = 57.02 (5), Os(3)–Os(2)–Os(6) = 128.76 (6).

Further loss of carbon monoxide from III should lead to the formation of clusters with still more metal–metal bonds. These studies are now in progress.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-78ER04900 and the Alfred P. Sloan Foundation through a fellowship to R. D. A. NMR studies were supported by Grant No. CHE-7916210 to the Northeast Regional NSF-NMR Facility from the National Science Foundation. We wish to thank Engelhard Industries for a loan of osmium tetroxide.

Registry No. Ia, 80399-46-8; Ib, 79790-55-9; IIa, 80409-94-5; IIb, 80409-95-6; III, 80409-96-7.

Supplementary Material Available: Tables of final fractional atomic coordinates, bond distances and angles, and structure factors (35 pages). Ordering information is given on any current masthead page.

(13) Coleman, J. M.; Wojcicki, A.; Pollick, P. J.; Dahl, L. F. *Inorg. Chem.* **1967**, *6*, 1236.

Direct Observation of a Cationic Intermediate in the Acid-Catalyzed Decomposition of (2-Hydroxy-, (2-Ethoxy-, and (2-Phenoxyethyl)cobaloximes

Kenneth L. Brown* and Sheela Ramamurthy

Department of Chemistry
The University of Texas at Arlington
Arlington, Texas 76019

Received October 21, 1981

Summary: The kinetics of the acid-catalyzed decomposition of the title compounds to form ethylene and cobaloxime(III) have been studied by UV and visible spectroscopy as well as manometrically in both weakly and strongly acidic H_2SO_4/H_2O mixtures. Compelling kinetic evidence has been obtained for formation of a cationic intermediate (upon loss of the β-leaving group) which accumulates in strongly acidic media where the activity of water is low. The ^1H NMR spectrum of the intermediate and its temperature dependence are consistent with its assignment as a cobaloxime(III)–ethylene π complex with two preferred conformations, although a σ-bonded ethylcobaloxime carbonium ion cannot be ruled out.

Cobalt(III) olefinic π complexes and/or electronically equivalent σ-bonded alkylcobalt carbonium ions have been suggested as intermediates in the alcoholysis of (2-acetoxyalkyl)cobaloximes,[1–4] in the acid-catalyzed rearrangements of (2-hydroxy-*n*-propyl)- and (2-hydroxyisopropyl)cobaloximes[5,6] and decomposition of (2-hydroxyethyl)cobaloxime[6] as well as in the synthesis of organo-

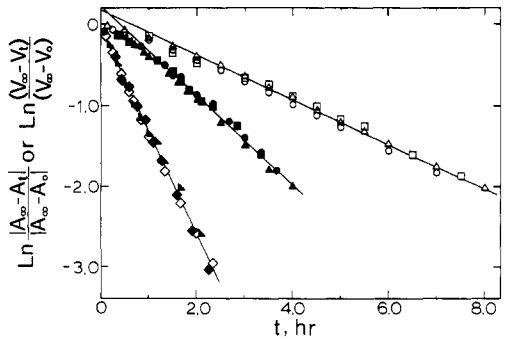
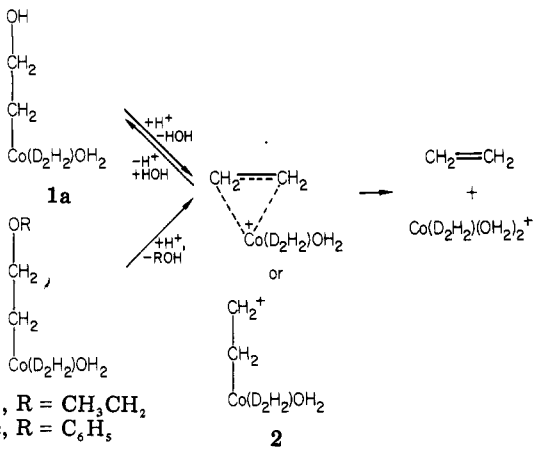


Figure 1. Normalized, semilogarithmic plots of the UV (255 nm), visible (445 nm), and manometric kinetics of the decomposition of **1a**, **1b**, and **1c** at $H_o = 1.70 \pm 0.01$, 25.0 ± 0.1 °C: **1c**, UV (○), visible (△), manometric (□), $k_{obsd} = (7.65 \pm 0.18) \times 10^{-5}$ s^{-1}; **1b**, UV (●), visible (▲), manometric (■), $k_{obsd} = (1.53 \pm 0.04) \times 10^{-4}$ s^{-1}; **1a**, UV (♦), visible (◇), manometric (◣), $k_{obsd} = (3.53 \pm 0.05) \times 10^{-4}$ s^{-1}.

Scheme I



cobalt complexes from vinyl ethers and cobalt(III) complexes in nucleophilic solvents.[4,7–9] To date, all evidence presented for the existence of such intermediates has been indirect. We would now like to report firm kinetic evidence for the existence of an intermediate in the acid-catalyzed decomposition of (2-hydroxyethyl)cobaloxime to cobaloxime(III) and ethylene[10] and direct observation of this intermediate by ^1H NMR spectroscopy.

The decomposition of (2-hydroxyethyl)aquocobaloxime (**1a**)[11] in weakly acidic H_2SO_4/H_2O mixtures ($H_o = 1.70 \pm 0.01$)[14–16] (Figure 1) was found to be a strictly first-order process when monitored by UV or visible spectroscopy, as well as manometrically. In contrast, the decomposition of (2-ethoxyethyl)-(**1b**) and (2-phenoxyethyl)aquocobaloxime (**1c**) in the same media shows a distinct lag followed by a first-order decay using the same three techniques. The observed first-order rate constants decrease markedly

(1) Golding, B. T.; Holland, H. L.; Horn, U.; Sakrikar, S. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 959–960.
(2) Golding, B. T.; Sakrikar, S. *J. Chem. Soc., Chem. Commun.* **1972**, 1183–1184.
(3) Silverman, R. B.; Dolphin, D.; Babior, B. M. *J. Am. Chem. Soc.* **1972**, *94*, 4028–4030.
(4) Silverman, R. B.; Dolphin, D. *J. Am. Chem. Soc.* **1976**, *98*, 4626–4633.
(5) Brown, K. L.; Ingraham, L. L. *J. Am. Chem. Soc.* **1974**, *96*, 7681–7686.
(6) Espenson, J. H.; Wang, D. M. *Inorg. Chem.* **1979**, *18*, 2853–2859.
(7) Silverman, R. B.; Dolphin, D. *J. Am. Chem. Soc.* **1973**, *95*, 1686–1688.
(8) Silverman, R. B.; Dolphin, D. *J. Am. Chem. Soc.* **1974**, *96*, 7094–7096.
(9) Silverman, R. B.; Dolphin, D.; Carty, T. J.; Krodel, E. K.; Abeles, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 7096–7097.
(10) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 143–147.
(11) The title complexes were synthesized by published procedures[10,12,13] and characterized by ^1H NMR spectroscopy and elemental analysis.
(12) Brown, K. L.; Awtrey, A. W. *Inorg. Chem.* **1978**, *17*, 111–119.
(13) Brown, K. L. *J. Am. Chem. Soc.* **1979**, *101*, 6600–6606.
(14) Hammett, L. P.; Deyrup, A. J. *J. Am. Chem. Soc.* **1932**, *54*, 2721–2739.
(15) Bascombe, K. N.; Bell, R. P. *J. Chem. Soc.* **1959**, 1096–1104.
(16) Ryabova, R. S.; Medvetskaya, I. M.; Vinnik, M. T. *Zh. Fiz. Khim.* **1966**, *40*, 339–345.

0276-7333/82/2301-0413$01.25/0 © 1982 American Chemical Society