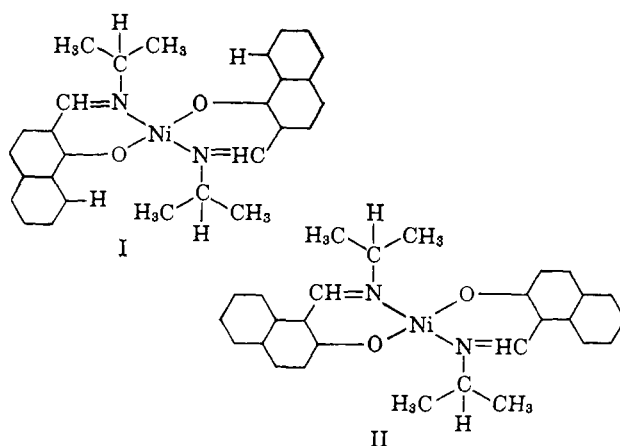


6700 cm^{-1} of this complex, and thus the percentage of tetrahedral form, is practically independent of temperature, indicating that the energies of formation of planar and tetrahedral allomers are practically equal. For the 3,4-benzo-substituted complexes, the reason for this behavior appears to be essentially steric in nature. Trials with Stuart models, in fact, show a considerable steric interaction between the 3,4-benzo group and the isopropyl group (I). In the case of the 5,6-benzo-substituted complexes (II), the steric reasons do not seem to play any role, and the factors affecting the stereochemistry must be essentially of an electronic nature. The importance of the electronic effects in determining the percentages of tetrahedral species is evident also from the thermodynamic data for the isopropyl complexes in Table V. In fact, the 5-substituted complexes, in which the steric factors do not come into play, have percentages of planar forms, and hence values of ΔF , larger than that of the unsubstituted isopropyl complex. In the case of 3-substitution the influence of electronic factors is even more evident, and while the steric effect of a chloro substituent in position 3 could favor the tetrahedral form, the 3-chloro *n*-propyl derivative is exclusively planar, even at elevated temperatures. The 3-chloro isopropyl derivative has small percentages of tetrahedral forms, both at and above room temperature.

The differences in entropy of formation between tetrahedral and planar species of *n*-propyl and isopropyl complexes are always positive in the range 4–10 e.u. The entropy factor favors the attainment of a pseudo-tetrahedral structure, particularly at high temperatures. A part of the entropy difference can be attributed to statistical factors. The ground state of a



trans-planar nickel(II) complex is $^1A_{1g}$ with onefold degeneracy whereas that of a tetrahedral nickel(II) complex is 3T_1 with ninefold degeneracy. In a field of pseudo-tetrahedral symmetry the 3T_1 level will be split, although the splitting is probably small compared with kT . Therefore a statistical ΔS is expected with a value of approximately $R \ln 9/1 = 4.4$ e.u. Part of the entropy change can also be attributed to the greater freedom of rotation of the alkyl groups in the tetrahedral structure compared with that in the planar structure. Another contribution to the entropy difference may be the greater probability of solvation of the planar species, as in the case of the troponimine-nickel(II) complexes.¹⁵

(15) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH 13, PENNA.]

Phosphorus- and Arsenic-Bridged Complexes of Metal Carbonyls. III.¹ Cobalt and Manganese Complexes²

BY R. G. HAYTER

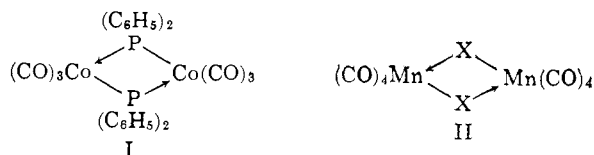
RECEIVED JULY 19, 1963

Tetrasubstituted biphosphines react with $\text{Co}_2(\text{CO})_8$ to give $[\text{Co}\{\text{P}(\text{C}_6\text{H}_5)_2\}(\text{CO})_3]_2$ or $[\text{Co}_3\{\text{P}(\text{CH}_3)_2\}_2(\text{CO})_7]$. $[\text{Mn}\{\text{P}(\text{C}_6\text{H}_5)_2\}(\text{CO})_4]_2$ and $[\text{Mn}\{\text{As}(\text{CH}_3)_2\}(\text{CO})_4]_2$ were obtained either from $\text{Mn}_2(\text{CO})_{10}$ and the corresponding biphosphine or biarsine or from $\text{NaMn}(\text{CO})_5$ and the monochlorophosphine or arsine. $(\text{CH}_3)_2\text{PCl}$ and $\text{NaMn}(\text{CO})_5$ react at room temperature to give $[\text{Mn}_2\{\text{P}(\text{CH}_3)_2\}_2(\text{CO})_8]$, which decomposes to give $[\text{Mn}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_4]_2$ at higher temperature. On the basis of infrared and proton nuclear magnetic resonance spectra, structures containing phosphorus or arsenic bridges are proposed.

We have previously investigated the reactions of the dimeric cyclopentadienyl metal carbonyl compounds of iron, molybdenum, tungsten, and nickel with tetrasubstituted biphosphines and a biarsine, R_4E_2 ($\text{E} = \text{P}$, $\text{R} = \text{CH}_3$, C_6H_5 ; $\text{E} = \text{As}$, $\text{R} = \text{CH}_3$).^{1,3} The majority of the complexes which are obtained form part of a series of general formula $[\text{C}_5\text{H}_5\text{M}(\text{ER}_2)(\text{CO})_n]_2$ ($\text{M} = \text{Mo}$, W , $n = 2$; $\text{M} = \text{Fe}$, $n = 1$; $\text{M} = \text{Ni}$, $n = 0$), all of which have been shown to contain M_2E_2 heterocyclic rings. It was therefore of interest to study the analogous reactions of the pure metal carbonyls, with the aim of preparing a similar series of complexes. For this purpose we chose to study initially the reactions of the biphosphines and tetramethylbiarsine (cacodyl) with cobalt and manganese carbonyls, since both of these compounds contain metal-metal bonds, a structural feature which appears to facilitate the cleavage

of the phosphorus-phosphorus or arsenic-arsenic bonds in the ligands. Since these carbonyls also form sodium salts, an alternative possible method of synthesis is available by reaction of the salts with the chlorophosphines and -arsines, R_2ECl .

It has previously been reported in a patent that $\text{Co}_2(\text{CO})_8$ reacts with tetraphenylbiphosphine, $(\text{C}_6\text{H}_5)_4\text{P}_2$, to give a rose-red compound $(\text{C}_6\text{H}_5)_4\text{P}_2 \cdot 2\text{Co}(\text{CO})_3$.⁴ The structure of the compound was not discussed but our present reinvestigation indicates structure I. Analogous compounds containing bridging SR groups, $[\text{Co}(\text{SR})(\text{CO})_3]_2$, are also known.⁵ The corresponding



(1) Part II: R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

(2) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1963.

(3) R. G. Hayter, *J. Am. Chem. Soc.*, **85**, 3120 (1963).

(4) W. Schweckendiek, German Patent 1,072,244 (Dec. 31, 1959).

(5) W. Hieber and P. Spacu, *Z. anorg. allgem. Chem.*, **233**, 359 (1937).

derivatives of manganese carbonyl differ in the number of carbonyl groups attached to the metal and are known when $X = SR$,⁶ TeR ,⁷ $P(C_6H_5)_2$,⁸ and $As(C_6H_5)_2$,⁹ the metal atoms being univalent and octahedrally coordinated.

Experimental

Microanalyses and molecular weight determinations (by the osmometer method) were by Schwarzkopf Laboratories, Woodside, N. Y.; Huffman Microanalytical Laboratories, Wheatridge, Colo.; and Dr. A. Bernhardt, Max-Planck Institut für Kohlenforschung, Mülheim, Germany. Melting points were determined in evacuated capillaries and are uncorrected.

Infrared spectra were measured on a Beckman IR-9 spectrophotometer unless otherwise indicated and the proton nuclear magnetic resonance spectra on Varian Associates A-60 and HR-60 instruments. From the evidence of sharp n.m.r. spectra, the compounds are presumed to be diamagnetic. The magnetic susceptibility was measured by the Faraday method using a sensitive magnetobalance which had been calibrated with a piece of high purity platinum metal.

All operations, except the handling of the solid complexes, were carried out in a nitrogen atmosphere. Chromatographic separations were done on Merck acid-washed alumina. The phosphine and arsine ligands were prepared by established methods, as previously indicated.³ The metal carbonyls were purchased from commercial sources.

Preparation of Complexes. Di- μ -(diphenylphosphido)-bis-(tricarboxylcobalt).—Diphenylchlorophosphine (6.15 g., 27.9 mmoles) was added dropwise with stirring to a solution of $NaCo(CO)_4$ (27.9 mmoles, prepared from $Co_2(CO)_8$ (4.8 g., 13.95 mmoles) and sodium (0.64 g., 27.9 mmoles) as a 3% amalgam in dry tetrahydrofuran (100 ml.). Vigorous gas evolution occurred and the solution turned deep red. Stirring was continued for 2 hr. after the addition was complete and the solvent then removed at 15 mm., leaving a dark red-brown solid. Crystallization from benzene-hexane gave the pure compound as reddish orange crystals (m.p. 150–152°, yield 45%). The compound decomposes slowly in air, especially on exposure to fluorescent light. The n.m.r. spectrum in carbon disulfide solution shows peaks at τ 2.60 and 2.78 due to phenyl protons.

Anal. Calcd. for $C_{30}H_{20}Co_2O_6P_2$: C, 54.9; H, 3.1; Co, 18.0; O, 14.6; P, 9.4. Found: C, 54.45; H, 3.2; Co, 17.35; O, 14.1; P, 9.1.

This compound was also prepared by a method similar to that described by Schweckendiek.⁴

$Co_2(CO)_8$ (5.0 g., 14.6 mmoles) was added to a solution of tetraphenylbiphosphine (14.6 mmoles) in toluene to give gas evolution and a dark red solution. After stirring at room temperature for 8 hr., the solution was evaporated to dryness and the residual solid crystallized from benzene-hexane to give the compound in 67% yield. It was shown to be identical with $[Co\{P(C_6H_5)_2\}(CO)_3]_2$ obtained by the sodium salt method by m.p., m.m.p., and infrared spectrum.

The Reaction between Cobalt Carbonyl and Tetramethylbiphosphine.—Tetramethylbiphosphine (1.29 g., 10.6 mmoles) was added to $Co_2(CO)_8$ (3.62 g., 10.6 mmoles) in benzene (200 ml.) with stirring. Gas evolution occurred immediately and a red oil was precipitated from the red-brown solution. The solution was refluxed for 90 min., during which time the oil dissolved and an intense green solution was formed. After filtration, solvent was removed at 15 mm. and the residual green oil treated with hexane and cooled to -78° overnight. The hexane solution was decanted from the resulting solid which was crystallized from hexane at -78° to give dark green crystals (m.p. 175–185° dec., yield 15%).

Anal. Calcd. for $C_{11}H_{12}Co_3O_7P_2$: C, 26.7; H, 2.4; Co, 35.7; O, 22.6; P, 12.5; mol. wt., 495. Found: C, 26.35; H, 2.5; Co, 36.0; O, 22.2; P, 12.1; mol. wt. (C_6H_6), 521.

The n.m.r. spectrum in $CDCl_3$ solution shows complex absorption in the methyl proton region with peaks at τ 7.85 (5), 7.91 (4), 7.99 (8), 8.05 (10), 8.13 (3) (relative intensities on an arbitrary scale given in parentheses). A benzene solution showed no absorption between τ 10 and 42.

Measurement of magnetic susceptibility gave $10^6 \chi_M = +205$, $10^6 \chi_M(\text{cor.}) = +337$, $\mu_{\text{eff}} = 0.90$ Bohr magnetons.¹⁰

A number of reactions were also carried out between $NaCo(CO)_4$ and $(CH_3)_2PCl$ (the conditions were the same as for the

analogous reaction with $(C_6H_5)_2PCl$). Dark red oily materials were obtained which could not be satisfactorily purified owing to air sensitivity and extensive decomposition on attempted chromatography. If the reaction mixture is refluxed before attempting to isolate the products, the red solution becomes an intense green, but again no crystalline products could be isolated.

The reactions of $Co_2(CO)_8$ with $(CH_3)_2As$ in boiling benzene and of $NaCo(CO)_4$ with $(CH_3)_2AsCl$ in tetrahydrofuran at room temperature both gave intense red solutions with evolution of gas. The only product which could be isolated in both cases was a red jelly-like material which could not be freed completely of solvent or induced to crystallize.

Di- μ -(diphenylphosphido)-bis-(tetracarbonylmanganese).—Manganese carbonyl (2.0 g., 5.14 mmoles) was added to tetraphenylbiphosphine (5.14 mmoles) in toluene (100 ml.) and the solution refluxed for 14 hr. After filtration from some pale yellow insoluble solid the solution was evaporated at 15 mm. and the residual solid sublimed, first at 80° to remove $Mn_2(CO)_{10}$ (0.10 g.) and then at 160° to give traces of yellow oily crystals. The nonvolatile residue was crystallized from methylene chloride to give bright yellow crystals of the product (m.p. 249–252° dec., yield 46%).

Anal. Calcd. for $C_{32}H_{20}O_8P_2Mn_2$: C, 54.6; H, 2.9; O, 18.2; Mn, 15.6; P, 8.8; mol. wt., 704. Found: C, 54.2; H, 2.7; O, 18.4; Mn, 16.0; P, 8.5; mol. wt. (ebullioscopically in C_6H_6), 962.

This compound was also prepared as follows: Manganese carbonyl (2.0 g., 5.14 mmoles) was stirred in dry tetrahydrofuran (50 ml.) with an amalgam of sodium (0.31 g., 13.4 mmoles) and mercury (10 ml.). After about 1 hr., the excess amalgam was removed from the very pale yellow solution of $NaMn(CO)_5$, and diphenylchlorophosphine (2.28 g., 10.28 mmoles) was added with stirring. A slow evolution of gas took place and the solution became orange. After stirring for 1 hr., solvent was removed at 15 mm., toluene (75 ml.) added, and the mixture refluxed for 16 hr. During this time the color of the solution changed from red to light orange and yellow solid was precipitated. After evaporation of the solvent, the residue was treated as described above to give $Mn_2(CO)_{10}$ (0.15 g.) and a small amount of yellow oil volatile at 160° and 0.1 mm. The residue was crystallized from chloroform to give $[Mn\{P(C_6H_5)_2\}(CO)_4]_2$ in 20% yield. Its identity was established by analysis and by comparison of m.p. and infrared spectrum with those of the compound prepared from $Mn_2(CO)_{10}$ and $P_2(C_6H_5)_4$.

Anal. Found: C, 54.2; H, 3.3; O, 18.9, 19.0; P, 9.1.

Attempts were also made to work up the reaction mixture after stirring for several hours in tetrahydrofuran at room temperature. The product appeared to be a complex mixture and only very low yields of impure $[Mn\{P(C_6H_5)_2\}(CO)_4]_2$ could be isolated by crystallization. Recovery from the chromatography column was also very poor and no further attempts at separation were made.

μ -(Diphenylphosphido)-hydrido-bis-(tetracarbonylmanganese).—Manganese carbonyl (4.4 g., 11.3 mmoles), tetraphenylbiphosphine (5.67 mmoles), and toluene (75 ml.) were refluxed together for 6 hr. to give a dark red solution and a slight yellow precipitate. After filtration, the solution was evaporated to dryness at 15 mm. and the sticky orange residue sublimed at 0.2 mm. Unreacted $Mn_2(CO)_{10}$ (1.5 g.) was recovered at 85° and a yellow sublimate (0.765 g.) was obtained on raising the temperature to 160° . The 160° sublimate was dissolved in hexane and chromatographed. Hexane eluted a faint yellow band due to $Mn_2(CO)_{10}$ and 20% ether-hexane eluted two distinct yellow bands, the larger faster band yielding yellow crystals on evaporation of the eluate. These crystals were recrystallized from hexane to give yellow needles (m.p. 159–160° dec., yield 12%, based on $Mn_2(CO)_{10}$ consumed).

Anal. Calcd. for $C_{20}H_{11}Mn_2O_8P$: C, 46.2; H, 2.1; Mn, 21.1; O, 24.6; P, 5.95; mol. wt., 520. For $C_{21}H_{11}Mn_2O_9P$: C, 46.0; H, 2.0; Mn, 20.0; O, 26.25; P, 5.65; mol. wt., 548. Found: C, 46.0; H, 2.2; Mn, 21.3, 21.2; O, 25.3, 24.4, 24.5; P, 6.1; mol. wt. (C_6H_6), 502.

The second band from the chromatogram yielded 20 mg. of yellow crystals (m.p. 128–130° dec.).

The orange residue from the sublimation was washed with hexane and crystallized from methylene chloride to give $[Mn\{P(C_6H_5)_2\}(CO)_4]_2$ in 40% yield (based on available $P_2(C_6H_5)_4$).

μ -(Dimethylphosphido)-(dimethylphosphido)-enneacarbonyldimanganese.—Dimethylchlorophosphine (0.63 g., 6.5 mmoles) was added slowly with stirring to a solution of $NaMn(CO)_5$ (6.5 mmoles, prepared as described above) in tetrahydrofuran (50 ml.). Vigorous evolution of gas occurred and the color of the solution changed from pale yellow to orange. Stirring was continued for 1 hr. after the addition was complete and solvent was then removed, initially at 15 mm. and finally at 0.2 mm. The residual yellow solid was extracted into hexane and the filtrate, on cooling, deposited yellow crystals. Sublimation at 90° and 0.2 mm. gave the pure product (decomposes above 240° , yield 35%). The

(6) P. M. Treichel, J. M. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963); W. Hieber and W. K. Schropp, *Z. Naturforsch.*, **14b**, 460 (1959).

(7) W. Hieber and T. Kruck, *Chem. Ber.*, **95**, 2027 (1962).

(8) M. L. H. Green and J. T. Moelwyn-Hughes, *Z. Naturforsch.*, **17b**, 783 (1962).

(9) R. F. Lambert, *Chem. Ind. (London)*, 830 (1961).

(10) The diamagnetic correction was evaluated using Pascal's constants obtained from P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 91.

n.m.r. spectrum shows two doublet peaks due to the methyl protons at τ 8.29 (J_{HP} 6.5 c.p.s.) and 9.08 (J_{HP} 7.6 c.p.s.) in benzene solution, at τ 8.00 (J_{HP} 6.4 c.p.s.) and 8.59 (J_{HP} 7.5 c.p.s.) in deuteriochloroform solution, and at τ 8.00 (J_{HP} 6.2 c.p.s.) and 8.61 (J_{HP} 7.4 c.p.s.) in carbon disulfide solution.

Anal. Calcd. for $C_{13}H_{12}Mn_2O_9P_2$: C, 32.3; H, 2.5; Mn, 22.7; O, 29.75; P, 12.8; mol. wt., 484. Found: C, 32.2, 32.1; H, 3.0, 2.45; Mn, 23.1, 22.75; O, 30.1, 30.2, 30.3; P, 12.7, 12.8; mol. wt. (C_6H_6), 472.

The compound could also be purified by chromatography, although it showed unusual behavior. The reaction mixture was dissolved in hexane, filtered, and poured onto an alumina column which had been made up in hexane. Elution with hexane gave a yellow band which, on evaporation of the eluate, gave yellow crystals. These were shown by analysis, m.p., n.m.r. spectrum, and X-ray powder pattern to be identical with the previously characterized $[Mn_2\{P(CH_3)_2\}_2(CO)_9]$.

Anal. Found: C, 32.4; H, 2.5.

Elution of the chromatogram with benzene gave a yellow-orange band, a yellow eluate, and yellow crystals. These were similarly characterized as $[Mn_2\{P(CH_3)_2\}_2(CO)_9]$.

Anal. Found: C, 32.05; H, 2.4.

Each fraction, on repeated chromatography, gave two yellow bands, eluted by hexane and benzene, respectively. The resulting four crystalline fractions were all identical with $[Mn_2\{P(CH_3)_2\}_2(CO)_9]$. The recovery from each chromatogram was about 50%, being approximately equally divided between the two fractions.

Di- μ -(dimethylphosphido)-bis-(tetracarbonylmanganese).—The reaction between dimethylchlorophosphine (1.14 g., 11.8 mmoles) and $NaMn(CO)_5$ (11.8 mmoles) in tetrahydrofuran (50 ml.) was carried out as described above and the solvent removed at 15 mm. Toluene (75 ml.) was then added and the solution refluxed with stirring for 16 hr. After filtration, the red solution was evaporated to dryness leaving oily orange crystals. These were washed with hexane (2×5 ml.) and crystallized from benzene to give pale yellow crystals of the pure product (decomposes above 200° , yield 42%). The n.m.r. spectrum shows a 1:2:1 triplet due to the methyl protons at τ 8.66 (splitting 4.7 c.p.s.) in benzene solution and at τ 8.30 (splitting 5.2 c.p.s.) in deuteriochloroform solution. The compound is eluted from alumina by benzene as a single yellow band, the recovery being 65%.

Anal. Calcd. for $C_{12}H_{12}Mn_2O_8P_2$: C, 31.6; H, 2.65; Mn, 24.1; O, 28.1; P, 13.5; mol. wt., 456. Found: C, 31.6; H, 2.7; Mn, 24.0; O, 28.4, 28.55; P, 13.9; mol. wt. (C_6H_6), 430.

In another attempt to prepare this compound, manganese carbonyl (3.5 g., 9.1 mmoles), tetramethylbiphosphine (1.11 g., 9.1 mmoles), and methylcyclohexane (75 ml.) were refluxed together for 16 hr., an orange precipitate being formed. After cooling, the reaction mixture was filtered to give a yellow solid (1.63 g.) which was only very sparingly soluble in organic solvents; all attempts at purification by crystallization were unsuccessful.

Anal. Found: C, 31.3; H, 4.0; P, 18.1.

On evaporation of the red filtrate, brown crystals were obtained; these were dissolved in hexane and chromatographed. Hexane eluted a yellow band due to unreacted manganese carbonyl (0.94 g.) which was identified by m.p. and m.m.p. Continued elution with hexane and benzene gave two faint yellow bands, neither of which contained sufficient crystalline material for positive identification.

Di- μ -(dimethylarsenido)-bis-(tetracarbonylmanganese).—Manganese carbonyl (1.5 g., 3.86 mmoles), cacodyl (0.811 g., 3.86 mmoles), and ethylcyclohexane (75 ml.) were refluxed together with stirring for 16 hr. to give a red solution. After filtering to remove a small amount of yellow solid, the solution was evaporated at 15 mm. and the residual orange solid dissolved in chloroform and chromatographed. Elution with hexane gave a yellow-orange band, which, after evaporation of the eluate, afforded a yellow solid. Crystallization from benzene-hexane gave yellow-orange prisms of the pure complex (sublimes at 150° and decomposes above 235° , yield 39%). The n.m.r. spectrum in carbon disulfide solution shows a sharp singlet due to the methyl protons at τ 8.41.

Anal. Calcd. for $C_{12}H_{12}As_2Mn_2O_8$: C, 26.5; H, 2.2; Mn, 20.2; O, 23.5; mol. wt., 544. Found: C, 27.0; H, 2.4; Mn, 21.1; O, 23.5; mol. wt. (C_6H_6), 509.

This compound could also be prepared, although only in about 5% yield, by the reaction of $NaMn(CO)_5$ with $(CH_3)_2AsCl$, using boiling toluene to complete the reaction, as described for the preparation of $[Mn\{P(CH_3)_2\}_2(CO)_4]_2$. The major product was an insoluble yellow solid, but $[Mn\{As(CH_3)_2\}_2(CO)_4]_2$ was isolated from the toluene solution by crystallization and was identified by m.p. and infrared spectrum.

Di- μ -(diphenylarsenido)-bis-(tetracarbonylmanganese).— $MnCl(CO)_5$ ¹¹ (1.0 g., 4.34 mmoles), diphenylarsine (1.0 g., 4.34 m-

moles), and *p*-toluidine (0.47 g., 4.34 mmoles) were heated together in benzene solution (50 ml.). Vigorous gas evolution occurred and a yellow precipitate was formed from a red solution. After refluxing for 1 hr., the precipitate was filtered and the filtrate, on cooling, deposited yellow crystals and a green non-crystalline solid. The crystals were separated from the green solid by washing with cold benzene and were recrystallized from hot benzene. The product was identified as $[Mn\{As(C_6H_5)_2\}_2(CO)_4]_2$ (4% yield) by comparison of melting point and infrared spectrum with an authentic specimen.⁹

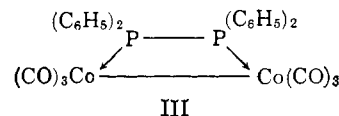
Reaction between $[Mn_2\{P(CH_3)_2\}_2(CO)_9]$ and Mercuric Bromide.— $[Mn_2\{P(CH_3)_2\}_2(CO)_9]$ (0.33 g., 0.68 mmoles), $HgBr_2$ (0.26 g., 0.68 mmoles) and benzene (20 ml.) were refluxed together for 2 hr. to give a yellow solid, which was filtered and washed with ethanol. Precipitation from hot dimethylformamide solution with ethanol gave yellow crystals (dec. 146° , yield 33%).

Anal. Calcd. for $C_{13}H_{12}Br_2HgMn_2O_9P_2$: C, 18.5; H, 1.4; Br, 18.9; Mn, 13.0; P, 7.3. Found: C, 18.9; H, 1.2; Br, 19.2; Mn, 12.6; P, 7.2.

Discussion

Cobalt Complexes.—The reactions of $Co_2(CO)_8$ with tetraphenylbiphosphine and of $NaCo(CO)_4$ with diphenylchlorophosphine both yield a red-orange crystalline compound which appears to be identical with Schweckendiek's $(C_6H_5)_4P_2 \cdot 2Co(CO)_3$.⁴ The compound is soluble in most organic solvents and crystallizes well from benzene-hexane mixtures. Molecular weight measurements in benzene either by osmometry or by boiling point elevation gave unexpectedly high values, in the range 6000–8000, probably owing to decomposition, since the solubility of the compound does not indicate a high degree of polymerization. In the n.m.r. spectrum, the expected absorption due to aromatic protons was observed and the sharpness of the spectrum showed the compound to be diamagnetic. Thus the molecule probably contains an even number of cobalt atoms (most probably two).

The infrared spectrum (Table I) shows carbonyl absorption in the region characteristic of terminal groups but none in the bridging carbonyl region. These data are consistent with structure I, although the alternative structure III is not definitely excluded. The metal-metal bond in III is necessary to account for the observed diamagnetism, and the cobalt-cobalt distance



is estimated to be about 3.3 \AA .¹² Although this distance is not improbably large, the ease with which cleavage of $(C_6H_5)_4P_2$ has previously been found to occur^{1,3} suggests that structure I is more likely than III.

The corresponding dimethylphosphorus-bridged complex has not been isolated, although there are indications that the compound may be an air-sensitive orange or red liquid. Attempts to purify this material were not successful. Similar attempts to prepare $[Co\{As(CH_3)_2\}_2(CO)_3]_2$ gave red semisolid materials, which also could not be crystallized or purified.

The reaction between $Co_2(CO)_8$ and $(CH_3)_4P_2$ in boiling benzene gave a dark green crystalline compound which was shown by complete elemental analysis and molecular weight measurement to have the unexpected composition $[Co_3\{P(CH_3)_2\}_2(CO)_7]$. The infrared spectrum shows bands due to terminal carbonyl absorption between 1922 and 2060 cm^{-1} and a doublet band in the bridging carbonyl region. The n.m.r. spectrum shows complex absorption in the methyl proton region. The apparent diamagnetism, as indicated by the n.m.r. spectrum, was not expected in view of the odd number of cobalt atoms in the molecule. Anom-

(11) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

(12) Estimated using Fisher-Hirschfelder-Taylor molecular models.

TABLE I
INFRARED SPECTRA OF THE COBALT AND MANGANESE COMPLEXES

Compound	Absorption bands in the carbonyl region, cm. ⁻¹		
	Soln. in 1,2-dichloroethane	Halocarbon mulls	Other absorption bands, cm. ^{-1a}
[Co{P(C ₆ H ₅) ₂ }(CO) ₃] ₂ ^b	2030 (m), 2020 (vs) 2001 (vs), 1986 (vs)	2060 (w), 2045 (m) 1996 (vs), 1968 (sh)	1480 (w), 1438 (sh), 1432 (m), 1218 (w) 1208 (w), 1186 (w), 1130 (s), 1083 (m) 1070 (w), 1045 (m), 1023 (m), 998 (m) 972 (w), 845 (w), 740 (s), 726 (s) 692 (vs), 554 (vs), 522 (vs), 511 (vs), 488 (vs)
[Co ₃ {P(CH ₃) ₂ }(CO) ₇] ^c	2060 (m), 1995 (vs) 1988 (vs), 1964 (vs) 1922 (s), 1852 (w) 1812 (vs), 1804 (vs)	1420 (w), 1408 (w), 1282 (m), 958 (s) 950 (s), 888 (s), 875 (w), 725 (sh) 710 (s)
[Mn ₂ {P(CH ₃) ₂ }(CO) ₇]	2077 (w), 2053 (s) 2045 (sh), 1984 (vs) 1960 (sh)	2120 (s), 2072 (vs) 2040 (vs), 2025 (vs) 2000 (vs), 1992 (sh) 1982 (vs), 1962 (vs) 1932 (sh), 1898 (sh)	2985 (w), 2974 (w), 2912 (m), 1626 (s) 1588 (m), 1437 (m), 1430 (m), 1429 (m) 1408 (sh), 1302 (m), 1294 (m), 1288 (m) 1280 (m), 938 (m), 908 (s), 855 (w) 838 (w), 738 (w), 718 (s), 685 (s) 666 (sh), 662 (sh), 657 (vs), 638 (vs) 618 (s), 545 (w), 501 (m), 488 (w) 480 (w), 470 (w)
[Mn{P(CH ₃) ₂ }(CO) ₄] ₂	2044 (s), 1978 (vs) 1955 (vs)	2040 (vs), 1993 (sh) 1980 (vs), 1960 (vs) 1920 (vs, broad)	2985 (w), 2906 (w), 1428 (s), 1416 (s) 1298 (w), 1284 (s), 1063 (w), 948 (s) 909 (s), 866 (w), 844 (m), 826 (s) 692 (s), 658 (vs), 642 (vs), 542 (w) 518 (s), 493 (m), 472 (m), 438 (w)
[Mn ₂ H{P(C ₆ H ₅) ₂ }(CO) ₈]	2093 (s), 2063 (vs) 2008 (vs), 1962 (vs)	2094 (s), 2065 (s) 2013 (vs), 1968 (vs)	3064 (w), 1582 (m), 1434 (m), 1303 (w) 1180 (w), 1155 (w), 1088 (m), 1071 (w) 1048 (w), 1027 (m), 998 (m), 913 (w) 842 (w), 751 (s), 742 (s), 722 (w) 701 (vs), 696 (vs), 692 (sh), 670 (vs) 655 (vs), 630 (vs), 616 (vs), 543 (w) 517 (vs), 503 (vs), 473 (m), 465 (m) 448 (sh), 438 (w)
[Mn{P(C ₆ H ₅) ₂ }(CO) ₄] ₂	2053 (s), 1992 (vs) 1957 (s)	2072 (w), 2052 (s) 2000 (vs), 1992 (vs) 1977 (vs), 1960 (vs) 1942 (vs)	3060 (w), 1477 (m), 1432 (s), 1268 (w) 1182 (m), 1157 (w), 1080 (m), 1026 (w) 1000 (m), 968 (w), 913 (w), 836 (w) 752 (s), 747 (sh), 738 (s), 696 (s) 640 (vs), 615 (sh), 510 (s), 494 (s) 460 (m), 415 (s)
[Mn{As(CH ₃) ₂ }(CO) ₄] ₂	2039 (vs), 1975 (vs) 1952 (s)	2040 (vs), 1982 (vs) 1962 (vs), 1932 (vs)	2920 (w), 1424 (m), 1416 (m), 1250 (w) 904 (m), 864 (sh), 860 (m), 655 (s) 642 (vs), 582 (w), 510 (m), 491 (w)
[Mn{As(C ₆ H ₅) ₂ }(CO) ₄] ₂	2050 (vs), 1987 (vs) 1955 (s)	2072 (w), 2050 (s) 2000 (vs), 1992 (vs) 1976 (vs), 1961 (vs) 1944 (s)	3075 (w), 3060 (w), 1580 (w), 1482 (m) 1437 (m), 1434 (m), 1298 (w), 1184 (w) 1158 (w), 1070 (m), 1024 (m), 1000 (m) 968 (w), 912 (w), 840 (w), 745 (s) 740 (s), 733 (s), 656 (sh), 649 (vs) 648 (sh), 646 (vs), 614 (sh), 540 (w) 502 (m), 480 (s), 462 (m)
[Mn ₂ {P(CH ₃) ₂ }(CO) ₇].HgBr ₂	2130 (s), 2074 (m) 2048 (vs), 2020 (vs) 1956 (vs), 1932 (sh)	1433 (m), 1420 (w), 1308 (w), 1292 (m) 1284 (w), 952 (m), 942 (sh), 912 (sh) 904 (vs), 872 (w), 838 (w), 830 (w) 741 (w), 722 (m), 684 (m), 671 (vs) 653 (vs), 648 (vs), 634 (vs), 477 (m), 458 (m)

^a Nujol mull 400–1300 cm.⁻¹, halocarbon mull 1300–4000 cm.⁻¹. ^b Solution in CS₂. ^c Measured on a Beckman IR-4 spectrophotometer.

alies of this kind have occasionally been resolved in the past by the discovery of metal–hydrogen bonds in the molecule.¹³ However no absorption was found in the region of the n.m.r. spectrum characteristic of transition metal hydrides,¹⁴ although the absorption due to a single proton could possibly have been overlooked if coupling to phosphorus and perhaps also to the

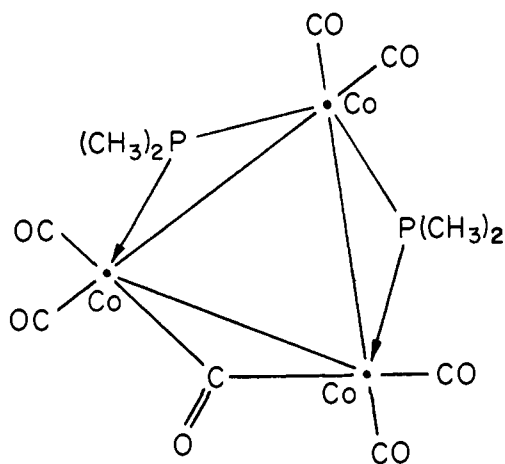
(13) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **77**, 3421 (1955)

(14) M. L. H. Green, *Angew. Chem.*, **17**, 719 (1960).

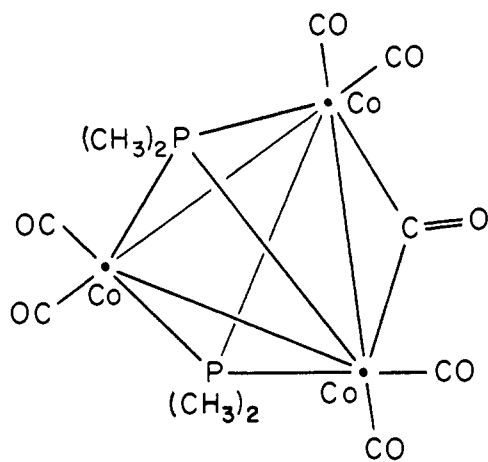
methyl protons had split the resonance into a number of very weak bands.

In the solid state, the compound has a magnetic moment of 0.9 B.M., which is considerably less than that expected for one unpaired electron. In the solid state, however, it is feasible that partial electron pairing may occur between molecules (super exchange). There is no evidence from molecular weight measurements for association in solution.

The present evidence is insufficient to indicate an unambiguous structure for the compound, although some possibilities may be indicated. In order to allow the cobalt atoms to attain an inert gas structure as far as possible, it is necessary to assume metal-metal bonding in a triangular skeleton and that each phosphorus atom acts as a three-electron donor as far as the metal atoms are concerned. The trinuclear molecule should then have one unpaired electron, although, as we have seen, the compound appears to be essentially diamagnetic, both in solution and in the solid state. Since both terminal and bridging carbonyl groups are present and since it is possible for the carbonyl and phosphido groups to be bound either along an edge or to the triangle as a whole,¹⁵ several structures are feasible. Two examples are IV and V.



IV



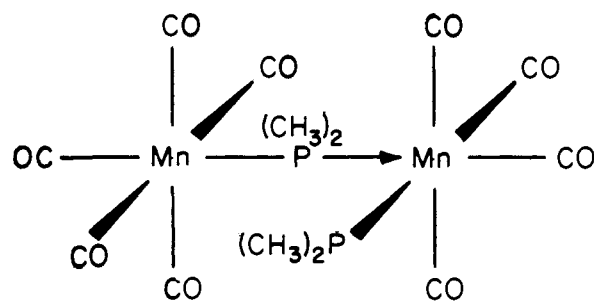
V

Manganese Complexes.—Dimethylchlorophosphine reacts with $\text{NaMn}(\text{CO})_5$ to give, at room temperature, $[\text{Mn}_2\{\text{P}(\text{CH}_3)_2\}_2(\text{CO})_9]$, which loses a further molecule of carbon monoxide on heating in boiling toluene to give $[\text{Mn}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_4]_2$.¹⁷ Both compounds show only terminal carbonyl absorption in their infrared spectra (Table I); more detailed structural information

(15) The carbonyl groups in $[(\text{C}_6\text{H}_5)_3\text{Ni}_3(\text{CO})_2]$ are symmetrically bound above and below the plane of the equilateral triangle formed by the three nickel atoms.¹⁶

(16) A. A. Hock and O. S. Mills, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 640.

(17) For a preliminary account, see R. G. Hayter, *Z. Naturforsch.*, **18b**, 581 (1963).



VI

is obtained from n.m.r. spectra. Thus, $[\text{Mn}_2\{\text{P}(\text{CH}_3)_2\}_2(\text{CO})_9]$ shows two doublets of approximately equal intensity due to the presence of two kinds of methyl group, each resonance being split into a doublet by spin-spin coupling with a phosphorus nucleus ($I = 1/2$). These data are consistent with structure VI, in which the nonequivalence of the methyl groups is due to the presence of two kinds of phosphorus atoms—bridging and terminal. It can be seen from structure VI that the molecule may exist in *cis* or *trans* isomeric forms depending on the relative positions of the two phosphorus atoms which are attached to the same manganese (VI is the *cis* isomer). Although only one crystalline form of $[\text{Mn}_2\{\text{P}(\text{CH}_3)_2\}_2(\text{CO})_9]$ was isolated, its behavior on a chromatography column suggests that under certain conditions, two forms of different polarity may exist. Chromatography on alumina gave two bands, one eluted by hexane and the other by benzene. Both bands yielded the same crystalline compound and each fraction split again into two similar bands on repeated chromatography. This behavior suggests an equilibrium between two isomeric forms, the equilibrium being frozen when the isomers become absorbed on suitable alumina sites. As often happens with a labile equilibrium, only the less soluble component can be isolated by crystallization. The n.m.r. spectrum apparently shows the presence of only one species, although small equilibrium amounts of the second isomer might well be undetected.

$[\text{Mn}_2\{\text{P}(\text{CH}_3)_2\}_2(\text{CO})_9]$ reacts with mercuric bromide to give a 1:1 adduct in which the terminal $(\text{CH}_3)_2\text{P}$ group is probably acting as a donor ligand. The compound is presumably dimeric,¹⁸ although the solubility was too low for a determination of molecular weight. It can be readily understood from structure VI that at elevated temperatures $[\text{Mn}_2\{\text{P}(\text{CH}_3)_2\}_2(\text{CO})_9]$ decomposes with loss of carbon monoxide to give the cyclic compound $[\text{Mn}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_4]_2$ (II, $\text{X} = \text{P}(\text{CH}_3)_2$). In the n.m.r. spectrum, the methyl resonance is a 1:2:1 triplet and this pattern can be attributed to relatively strong phosphorus-phosphorus coupling in the molecule.^{17,19} Similar methyl resonances have also been observed in the n.m.r. spectra of $[\text{C}_6\text{H}_5\text{M}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_n]_2$ ($\text{M} = \text{Mo}, \text{W}, n = 2$; $\text{M} = \text{Fe}, n = 1$; $\text{M} = \text{Ni}, n = 0$).^{1,3}

The reaction of $\text{NaMn}(\text{CO})_5$ with $(\text{C}_6\text{H}_5)_2\text{PCl}$ has previously been found to give low yields of $[\text{Mn}\{\text{P}(\text{C}_6\text{H}_5)_2\}(\text{CO})_4]_2$ (II, $\text{X} = \text{P}(\text{C}_6\text{H}_5)_2$) and a binuclear hydrido complex formulated as VII.⁸ Our investigation of this reaction has confirmed the formation of II, $\text{X} = \text{P}(\text{C}_6\text{H}_5)_2$, and, although under our conditions

(18) By analogy with other complexes of the type $[\text{HgBr}_2 \cdot \text{PR}_3]_2$; see, for example, R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J. Chem. Soc.*, 1209 (1940).

(19) This phenomenon is discussed in more detail in ref. 3 with respect to the spectra of $[\text{C}_6\text{H}_5\text{Fe}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_2]_2$. For a general treatment, see R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

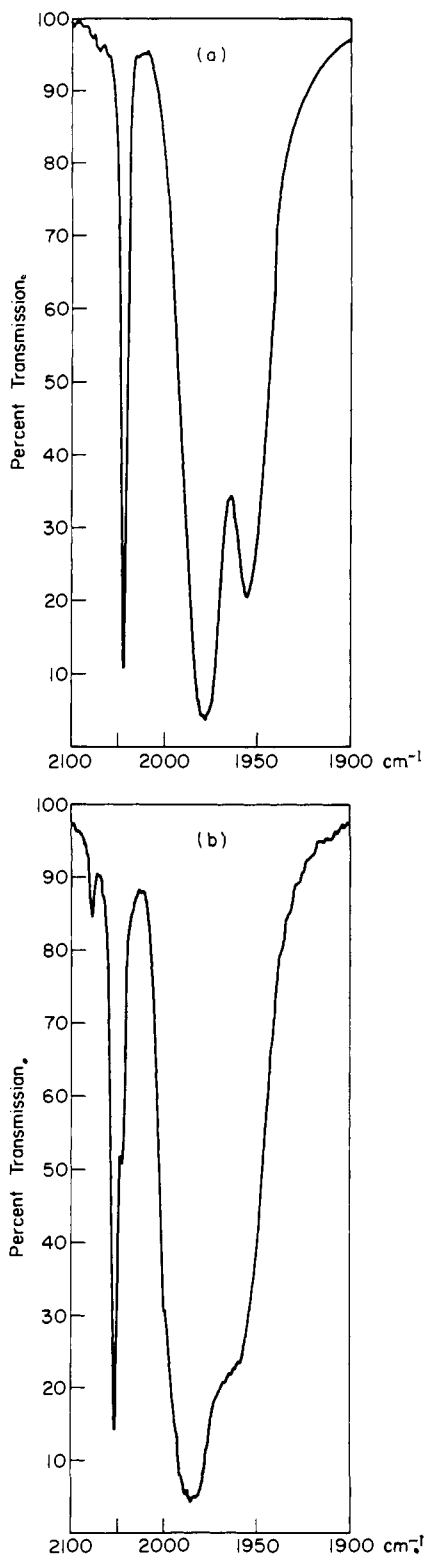
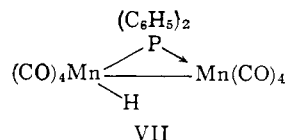


Fig. 1.—Infrared spectra in the carbonyl stretching region of (a) $[\text{Mn}\{\text{P}(\text{CH}_3)_2\}(\text{CO})_4]_2$ and (b) $[\text{Mn}_2\{\text{P}(\text{CH}_3)_2\}_2(\text{CO})_9]$ in 1,2-dichloroethane solution.

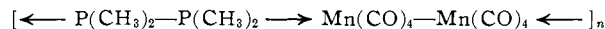
(unlike Green and Moelwyn-Hughes⁸ we used boiling toluene to complete the reaction) the yield was increased to about 20%, only trace amounts of the hydride were obtained. We have previously shown that binuclear hydrides related to VII can be prepared by reaction between the cyclopentadienyliron and -molybdenum carbonyl dimers and biphosphines,^{1,3} the yields being highest when the metal to phosphorus ratio of the reactants is 2:1.²⁰ Reactions between $\text{Mn}_2(\text{CO})_{10}$ and P_2 -



$(\text{C}_6\text{H}_5)_4$ in boiling toluene were therefore carried out with metal to phosphorus ratios of both 1:1 and 2:1. The hydride was obtained in ~ 0 and 12% yields and $[\text{Mn}\{\text{P}(\text{C}_6\text{H}_5)_2\}(\text{CO})_4]_2$ in 40 and 46% yields, respectively.

The properties of the hydrido complex (m.p., volatility, infrared spectrum in the carbonyl region, and behavior during chromatography on alumina) confirm that it is identical with that previously reported.⁸ Complete elemental analysis also confirms the original formulation as an *octacarbonyl* complex VII, although we have suggested on the basis of the previously published analytical data⁸ that the complex may contain *nine* carbonyl groups, $[\text{Mn}_2\text{H}\{\text{P}(\text{C}_6\text{H}_5)_2\}(\text{CO})_9]$, and have an open structure similar to VI.¹⁷ This suggestion can now be withdrawn in favor of VII.

In contrast to the behavior of $(\text{C}_6\text{H}_5)_4\text{P}_2$, tetramethylbiphosphine reacts with manganese carbonyl to give an insoluble, intractable yellow solid, which may be a polymer of the type



Since excess manganese carbonyl was recovered, further displacement of carbon monoxide by the biphosphine may have occurred. This could lead to cross linking. In contrast, cacodyl and $\text{Mn}_2(\text{CO})_{10}$ react smoothly with cleavage of the arsenic-arsenic bond to give $[\text{Mn}\{\text{As}(\text{CH}_3)_2\}(\text{CO})_4]_2$. The proton n.m.r. spectrum of this compound consists of a sharp singlet due to the equivalent methyl protons, as expected for a symmetrical compound. We have also prepared the analogous $[\text{Mn}\{\text{As}(\text{C}_6\text{H}_5)_2\}(\text{CO})_4]_2$ by reaction between $\text{MnCl}(\text{CO})_5$, diphenylarsine, and *p*-toluidine. This method is similar to that previously used to prepare phosphorus-bridged complexes of palladium(II),²¹ although attempts to prepare $[\text{Mn}\{\text{P}(\text{C}_6\text{H}_5)_2\}(\text{CO})_4]_2$ in this way were not successful.

The infrared spectra (Table I, Fig. 1a) of the four complexes of type II all show three bands due to carbonyl stretching vibrations. The complexes can be considered to have essentially the same symmetry properties as *cis*- $[\text{ML}_2(\text{CO})_4]$ ($\text{M} = \text{Cr}, \text{Mo},$ or W ; $\text{L} =$ neutral ligand), and, since no coupling between carbonyl vibrations is expected to occur through the bridge, four infrared-active carbonyl stretching modes are expected.²² Previous measurements on *cis*- $[\text{ML}_2(\text{CO})_4]$ complexes^{22,23} have usually shown the expected four bands, although the two bands of intermediate frequency often occur close together and are not well resolved. In the spectra of the bridged complexes, both the lower frequency bands are relatively broad and one of them probably conceals the expected fourth band. The infrared spectrum of $[\text{Mn}_2\{\text{P}(\text{CH}_3)_2\}_2(\text{CO})_9]$ in the carbonyl region (Fig. 1b) is very complex, as might be expected for an unsymmetrical molecule containing both tetra- and pentacarbonyl groups.

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(20) R. G. Hayter, unpublished observations.

(21) R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, **2**, 306 (1963).

(22) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(23) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961); R. Poilblanc and M. Bigorgne, *Bull. soc. chim. France*, 1301 (1962); C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).