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Complexes of Trivalent Phosphorus Derivatives. X. Reactions of Ditertiary Phosphines with Alkyl Derivatives of Cyclopentadienylmolybdenum Tricarbonyl[1]

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Within the past few years transition metal σ-alkyl derivatives of the types $C_5H_5MR_2(PR'_3)$ (M = Co[4,5] and Rh[6]) and $C_5H_5NiR(PR'_3)$,[7] which contain both π-cyclopentadienyl and tertiary phosphine ligands, have been reported. In attempts to prepare similar molybdenum compounds, the reactions of the alkyls $RMo(CO)_3C_5H_5$ (R = CH_3 or $C_6H_5CH_2$) with ditertiary phosphines of various types have now been investigated. This note describes the products obtained from reactions of this type when carried out in acetonitrile solution.[8]

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra were taken in potassium bromide pellets or dichloromethane solutions and recorded on a Perkin-Elmer Model 621 spectrometer. Proton nmr spectra were taken in chloroform-*d* solutions and recorded on a Varian HA-100 spectrometer at 100 Mc. Melting and decomposition points were taken of samples in capillaries and are uncorrected. A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admitting to evacuated vessels.

The acetylenic ditertiary phosphine $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ (Pf≡Pf) was prepared by treatment of $(C_6H_5)_2PCl$ (Eastern Chemical Corp., Pequannock, N. J.) with $BrMgC{\equiv}CMgBr$.[9] The remaining ditertiary phosphine ligands were prepared by various published methods[10] all based on the reaction of 1,2-dichloroethane or one of the isomeric 1,2-dichloroethylenes with the appropriate alkali metal dialkylphosphide, MPR_2, in liquid ammonia (R = CH_3; M = Na) or tetrahydrofuran (R = C_6H_5; M = Li). The alkyls $RM(CO)_3C_5H_5$ (M = Mo, R = CH_3 or $C_6H_5CH_2$; M = W, R = CH_3) were prepared by published methods[11,12] using reactions of the sodium salts $NaM(CO)_3C_5H_5$ with appropriate organic halides (methyl iodide or benzyl chloride).

Reactions of $RMo(CO)_3C_5H_5$ with Ditertiary Phosphines in Acetonitrile Solution.—A mixture of 0.4–2.0 g of the $RMo(CO)_3C_5H_5$ derivative (R = CH_3 or $C_6H_5CH_2$) and the stoichiometric quantity of the ditertiary phosphine (Pf—Pf, tPf=Pf, Pf≡Pf, or Pm—Pm) was stirred for several hours in acetonitrile solution (100–250 ml). The $(diphos)[Mo(CO)_2(COR)(C_5H_5)]_2$ derivative separated gradually as a yellow crystalline precipitate. This product was filtered off and purified by recrystallization from a mixture of dichloromethane and hexane. The analyses and melting points of the new $(diphos)[Mo(CO)_2(COR)(C_5H_5)]_2$ derivatives are given in Table I.

Infrared Spectra of $(diphos)[Mo(CO)_2(COR)(C_5H_5)]_2$ Derivatives.—The ν(CO) frequencies of all of the $(diphos)[Mo(CO)_2(COR)(C_5H_5)]_2$ derivatives are given in Table I. The infrared spectra of representative compounds in other regions taken in potassium bromide pellets are given below.

(a) **(Pm—Pm)$[Mo(CO)_2(COCH_2C_6H_5)(C_5H_5)]_2$.**—$\nu$(CH) frequencies at 3085 (vw), 3077 (vw), 3055 (vw), 3020 (vw), 3012 (vw, sh), 2970 (vw), 2957 vw), 2928 (vvw), and 2902 (vw) cm^{-1}; other bands at 1493 (m), 1450 (w), 1417 (m), 1406 (w), 1302 (w), 1287 (m), 1267 (w), 1243 (w), 1169 (w), 1084 (m), 1063 (w), 1025 (w), 1020 (vw), 998 (w), 935 (m), 915 (m), 894 (s), 877 (m), 823 (w), 802 (m), 791 (m), 747 (w), 743 (m), 733 (w), 713 (w), and 695 (s) cm^{-1}.

(b) **(tPf=Pf)$[Mo(CO)_2(COCH_3)(C_5H_5)]_2$.**—$\nu$(CH) frequencies too weak to be unequivocally observed; other bands at 1480 (m), 1428 (m), 1324 (m), 1310 (w, sh), 1265 (vw), 1150 (m), 1083 (m), 1053 (s), 1010 (m), 1000 (m), 974 (w), 955 (vw), 915 (vw, sh), 890 (m), 832 (w), 804 (s), 740 (s), 730 (s), and 688 (s) cm^{-1}.

Proton Nmr Spectra of $(diphos)[Mo(CO)_2(COR)(C_5H_5)]_2$ Derivatives.—Many of these compounds were too sparingly soluble in suitable organic solvents for satisfactory proton nmr spectra to be obtained. However, the following data were obtained in chloroform-*d* solution.

(a) **(Pf—Pf)$[Mo(CO)_2(COCH_3)(C_5H_5)]_2$.**[13]—Resonances at τ ~2.6 (apparent doublet), 5.08 (triplet, separation 0.5 cps), 7.29 (singlet), and 7.34 (singlet) of approximate relative intensities 10:5:2:3 corresponding to the 20 aromatic protons of the Pf—Pf ligand, the 10 equivalent protons of the 2 π-cyclopentadienyl rings, the 4 methylene protons of the Pf—Pf ligand, and the 6 protons of the 2 acetyl groups, respectively.

(b) **(Pf—Pf)$[Mo(CO)_2(COCH_2C_6H_5)(C_5H_5)]_2$.**—Resonances at τ ~2.6 (apparent doublet), 2.7–2.9 (complex multiplet), 5.11 (triplet, separation 0.5 cps), 5.59 (singlet), and 7.16 (broad singlet) of approximate relative intensities 10:5:5:2:2 corresponding to the 20 aromatic protons of the Pf—Pf ligand, the 10 aromatic protons of the 2 phenylacetyl groups, the 10 equivalent protons of the 2 π-cyclopentadienyl rings, the 4 methylene protons of the 2 phenylacetyl groups, and the 4 methylene protons of the Pf—Pf ligand, respectively.

(c) **(Pf≡Pf)$[Mo(CO)_2(COCH_3)(C_5H_5)]_2$.**—Resonances at τ 2.5 (apparent triplet), 4.99 (doublet, separation 1.5 cps), and 7.49 (singlet) of approximate relative intensities 10:5:3 corresponding to the 20 aromatic protons of the Pf≡Pf ligand, the 10 equivalent protons of the 2 π-cyclopentadienyl rings, and the 6 protons of the 2 acetyl groups, respectively.

Preparation of *cis*-(cPf=Pf)$_2$Mo(CO)$_2$. (a) From the alkyls $RMo(CO)_3C_5H_5$ and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$.—An acetonitrile solution containing stoichiometric quantities of the alkyl $RMo(CO)_3C_5H_5$ (R = CH_3 or $C_6H_5CH_2$) and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ was stirred for several hours at room temperature. The yellow precipitate was filtered and purified by crystalliza-

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[1] For part IX of this series see R. B. King, L. W. Houk, and K. H. Pannell, *Inorg. Chem.*, **8**, 1042 (1969).

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[4] R. B. King, *Inorg. Chem.*, **5**, 82 (1966).

[5] H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Japan*, **38**, 2212 (1965).

[6] A. Kasahara, T. Isumi, and K. Tanaka, *ibid.*, **40**, 699 (1967).

[7] H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida, and N. Hagihara, *J. Organometal. Chem.* (Amsterdam), **6**, 86 (1966).

[8] Portions of this work were presented at the Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., Dec 1968.

[9] H. Hartmann, C. Beerman, and H. Czempik, *Z. Anorg. Allgem. Chem.*, **287**, 261 (1956).

[10] For the preparations of the ditertiary phosphines see the following references: (a) $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$: J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960); (b) *cis*- and *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$: A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964); (c) $(CH_3)_2PCH_2CH_2P(CH_3)_2$: J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 896 (1961). However, in this work the $NaP(CH_3)_2$ was obtained by cleavage of $(CH_3)_2P{-}P(CH_3)_2$ with sodium metal in liquid ammonia.

[11] For the preparation and properties of $CH_3Mo(CO)_3C_5H_5$ see T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[12] For the preparation and properties of $C_6H_5CH_2Mo(CO)_3C_5H_5$ see R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966).

[13] This spectrum was also reported by K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967). However, these workers reported neither the splitting of the π-cyclopentadienyl resonance nor the separation of the acetyl and methylene resonances.

TABLE I

SOME (diphos)[$Mo(CO)_2(COR)(C_5H_5)]_2$ COMPOUNDS PREPARED IN THIS WORK

Compound[a,b]			Yield,[c]		Analysis, %				ν(CO), cm^{-1}		
diphos	R	Mp, °C	%		C	H	O	P	Medium[d]	Metal (terminal)	Acyl
Pm—Pm	CH_3	181–182	53	Calcd	43.1	4.8	14.3	9.2	Nujol	1930, 1836	1597
				Found	43.1	4.7	14.3	9.0	CH_2Cl_2	1939, 1850	1602
Pm—Pm	$C_6H_5CH_2$	174	57	Calcd	52.5	4.9	11.7	7.5	CH_2Cl_2	1940, 1852	1613
				Found	52.7	4.9	11.6	7.7			
Pf—Pf	CH_3	228 dec	76	Calcd	57.5	4.4	10.4		KBr	1940, 1850	1600
				Found	57.6	4.9	9.8		CH_2Cl_2	1940, 1854	
Pf—Pf	$C_6H_5CH_2$	170 dec	75	Calcd	62.8	4.5	9.0	5.8	KBr	1934, 1840	1605
				Found	62.5	4.5	9.0	6.1	CH_2Cl_2	1940, 1852	
tPf═Pf	CH_3	220 dec	76	Calcd	57.7	4.2	10.5	6.8	KBr	1945, 1860	1590
				Found	58.0	4.2	10.6	7.1	CH_2Cl_2	1945, 1860	
tPf═Pf	$C_6H_5CH_2$	160–161 dec	53	Calcd	62.9	4.3	9.0	5.8	KBr	1938, 1845	1608
				Found	63.4	4.3	9.4	5.9	CH_2Cl_2	1945, 1860	
Pf≡Pf	CH_3	204 dec	73	Calcd	57.8	4.0	10.5	6.8	KBr	1954, 1867	1597
				Found	57.9	4.0	10.4	6.8	CH_2Cl_2	1952, 1869	1615

[a] In order to conserve space only the R group and the diphos ligand of the (diphos)[$Mo(CO)_2(COR)(C_5H_5)]_2$ compounds are indicated. Pm—Pm = $(CH_3)_2PCH_2CH_2P(CH_3)_2$; Pf—Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; tPf═Pf = *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$; Pf≡Pf = $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$. [b] All of these compounds are yellow. [c] The indicated per cent yields were obtained from the reaction of the ditertiary phosphine with the $RMo(CO)_3C_5H_5$ derivative in acetonitrile solution at room temperature. [d] CH_2Cl_2, dichloromethane solution; Nujol, Nujol mull; KBr, potassium bromide pellet.

tion from mixtures of dichloromethane and hexane to give a yield of up to 60% of *cis*-(cPf═Pf)$_2$Mo(CO)$_2$, dec pt 340°.

(b) **From $(1,3\text{-}C_6H_8)_2Mo(CO)_2$ and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$.**—A mixture of 0.2 g (0.64 mmol) of freshly sublimed bis(1,3-cyclohexadiene)dicarbonylmolybdenum,[14] 0.50 g (1.26 mmol) of *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$, and 50 ml of methylcyclohexane was boiled under reflux for 3 hr. Yellow crystals separated. After cooling these were filtered and washed with methylcyclohexane to give 0.4 g (75% yield) of yellow solid (cPf═Pf)$_2$Mo(CO)$_2$, dec pt 340°, identified by comparison of its infrared spectrum with that of an authentic sample prepared by procedure a. *Anal.* Calcd for $C_{54}H_{44}MoO_2P_4$: C, 68.6; H, 4.7; O, 3.4; P, 13.1. Found (product from $CH_3Mo(CO)_3C_5H_5$ and cPf═Pf): C, 68.6; H, 4.6; O, 4.0; P, 12.2. Found (product from $C_6H_5CH_2Mo(CO)_3C_5H_5$ and cPf═Pf): C, 67.8; H, 4.8; O, 3.9.

Infrared Spectrum of *cis*-(cPf═Pf)$_2$Mo(CO)$_2$.—ν(CO) frequencies at 1857 (s) and 1795 (s) cm^{-1} (KBr pellet) or 1878 (s) and 1810 (s) cm^{-1} (CH_2Cl_2 solution); ν(CH) frequencies at 3058 (vw), 3039 (w), 3025 (vw, sh), 3019 (vvw), and 2987 (vvw) cm^{-1} (KBr pellet); other bands (KBr pellet) at 1479 (m), 1430 (s), 1298 (vw), 1265 (vw, br), 1175 (vw), 1149 (vw), 1083 (m), 1061 (w), 1018 (w), 990 (vw), 956 (vw), 830 (vw), 760 (w), 746 (m), 728 (s), 692 (s), 682 (s), and 668 (s) cm^{-1}.

Discussion

The reactions of the alkyls $RMo(CO)_3C_5H_5$ (R = CH_3 or $C_6H_5CH_2$) with the ditertiary phosphines Pf—Pf, Pm—Pm, tPf═Pf, and Pf≡Pf in acetonitrile solution at room temperature proceed without evolution of carbon monoxide to give binuclear derivatives according to

$$2RMo(CO)_3C_5H_5 + \text{diphos} \longrightarrow (\text{diphos})[Mo(CO)_2(COR)(C_5H_5)]_2$$

Similar reactions of the alkyls $RMo(CO)_3C_5H_5$ with the monotertiary phosphines R'_3P were previously found by Craig and Green[15] to proceed readily in acetonitrile solution to give the related mononuclear derivatives $C_5H_5Mo(CO)_2(R'_3P)(COR)$. Barnett and Treichel[16] also prepared the derivatives $C_5H_5Mo(CO)_2[P(C_6H_5)_3](COCH_3)$ and (Pf—Pf) $[Mo(CO)_2(COCH_3)(C_5H_5)]_2$ by heating $CH_3Mo(CO)_3C_5H_5$ with the tertiary phosphine in tetrahydrofuran solution.

The new (diphos) $[Mo(CO)_2(COR)(C_5H_5)]_2$ derivatives are yellow solids exhibiting in their infrared spectra the expected two metal carbonyl ν(CO) frequencies at 1942 ± 12 and 1852 ± 17 cm^{-1} and the expected single acyl carbonyl ν(CO) frequency at 1602 ± 13 cm^{-1}. The limited solubility of the (diphos) $[Mo(CO)_2(COR)(C_5H_5)]_2$ derivatives in organic solvents prevented satisfactory nmr spectra from being obtained for many of the compounds. The nmr data which could be obtained (mainly on Pf—Pf derivatives) exhibited only a single π-cyclopentadienyl resonance indicating the compounds to be single isomers and both halves to have the same stereochemistry about the molybdenum atom. An X-ray crystallographic study by Churchill and Fennessey[17] indicated the molybdenum atom to have the diagonal ("*trans*") stereochemistry in the triphenylphosphine–acetyl complex π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3](COCH_3)$ obtained by Barnett and Treichel[16] from $CH_3Mo(CO)_3C_5H_5$ and triphenylphosphine.

The π-cyclopentadienyl nmr resonances in the complexes (Pf—Pf) $[Mo(CO)_2(COR)(C_5H_5)]_2$ and in the complex (Pf≡Pf) $[Mo(CO)_2(COCH_3)(C_5H_5)]_2$ were appreciably different. In the former cases the π-cyclopentadienyl resonance was a triplet indicating appreciable phosphorus–phosphorus spin–spin coupling in the complexed $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ ligand.[18] In the latter case the π-cyclopentadienyl resonance was only a doublet indicating negligible phosphorus–phosphorus spin–spin coupling in the complexed $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ ligand. This apparent difference in the coupling between phosphorus atoms across different types of two

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[14] The $(1,3\text{-}C_6H_8)_2Mo(CO)_2$ was prepared according to R. B. King, *J. Organometal. Chem.* (Amsterdam), **8**, 139 (1967).

[15] P. J. Craig and M. Green, *J. Chem. Soc., A*, 1978 (1968).

[16] K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).

[17] M. R. Churchill and J. P. Fennessey, *ibid.*, **7**, 953 (1968).

[18] For a more detailed discussion of spectra of this type see R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

carbon bridges is a novel effect which merits further investigation.

A few attempts were made to prepare (diphos)[$Mo(CO)_2(COR)(C_5H_5)]_2$ derivatives with other types of R groups. Reactions of $CF_3Mo(CO)_3C_5H_5$ and of $(CH_3)_3SnMo(CO)_3C_5H_5$ with the very reactive $(CH_3)_2PCH_2CH_2P(CH_3)_2$ in acetonitrile solution failed to give any precipitate or other evidence of forming a (diphos)[$Mo(CO)_2(COR)(C_5H_5)]_2$ derivative. This is consistent with all previous data which repeatedly indicate the inability for both trifluoromethyl and trialkyltin derivatives of transition metals to undergo carbon monoxide insertion reactions. The reaction between $CH_3CO_2CH_2Mo(CO)_3C_5H_5$ and $(CH_3)_2PCH_2CH_2P(CH_3)_2$ in acetonitrile solution gave a small quantity of a yellow precipitate indicated by its infrared spectrum to be a $C_5H_5Mo(CO)_2LR$ derivative (ν(CO): 1966 and 1882 cm^{-1}) but exhibiting no acyl or ketonic ν(CO) frequency and giving analyses not corresponding to a likely $CH_3CO_2CH_2$ derivative.

In an attempt to prepare a tungsten derivative analogous to the molybdenum derivatives reported in Table I, the reaction between $CH_3W(CO)_3C_5H_5$ and $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ in acetonitrile solution was investigated. After 4 days at room temperature, the infrared spectrum in the ν(CO) region indicated the presence of unchanged $CH_3W(CO)_3C_5H_5$. This is a further example of the lower reactivity of a tungsten derivative relative to the analogous molybdenum derivative. When the mixture of $CH_3W(CO)_3C_5H_5$ and $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ in acetonitrile was boiled under reflux for 14 days, a mixture was obtained which deposited a yellow precipitate. The low oxygen analysis and the absence of an acyl ν(CO) infrared frequency around 1600 cm^{-1} indicated this yellow compound to be the methyl derivative (Pf$\equiv$Pf)[$W(CO)_2(CH_3)(C_5H_5)]_2$ rather than an acetyl derivative.

The reaction between the $RMo(CO)_3C_5H_5$ derivatives (R = methyl or benzyl) and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (cPf$=$Pf) failed to give a (cPf$=$Pf)[$Mo(CO)_2(COR)(C_5H_5)]_2$ derivative. The same yellow crystalline substance was obtained from either the methylmolybdenum or the benzylmolybdenum derivative and was shown by analyses to be (cPf$=$Pf)$_2$Mo(CO)$_2$. The presence of two infrared ν(CO) frequencies of approximately equal relative intensities (1878 and 1810 cm^{-1}) in this complex indicates the two carbonyl groups to be in relative *cis* positions as expected. The reactions between $RMo(CO)_3C_5H_5$ and the excellent chelating agent cPf$=$Pf thus result in the removal of not only the R group but also the π-cyclopentadienyl ring from the molybdenum atom by the chelating ditertiary phosphine. A related example of the cleavage of the π-cyclopentadienyl ring from the halides $C_5H_5Mo(CO)_3X$ upon reactions with phosphines has been reported.[19] The compound *cis*-(cPf$=$Pf)$_2$Mo(CO)$_2$ is a new one not prepared in the previous study of metal carbonyl complexes of cPf$=$Pf.[20] An alternate preparation of *cis*-(cPf$=$Pf)$_2$Mo(CO)$_2$ utilizes the displacement of the two 1,3-cyclohexadiene ligand in (1,3-$C_6H_8)_2Mo(CO)_2$ with two molecules of the chelating ditertiary phosphine. Abel, Bennett, and Wilkinson[21] first reported a similar synthesis of *cis*-$(R_3P)_3Mo(CO)_3$ derivatives by the displacement of the cycloheptatriene ligand in $C_7H_8Mo(CO)_3$ with the three R_3P ligands; the present work appears to represent the first application of this synthetic technique to a (diene)$_2$M(CO)$_2$ complex.

The isolation of a (diphos)$_2$Mo(CO)$_2$ derivative rather than the usual (diphos)[$Mo(CO)_2(COR)(C_5H_5)]_2$ from the reactions of $RMo(CO)_3C_5H_5$ derivatives with *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ suggests that this ditertiary phosphine cannot act as a bridging ligand although it is now well established[20,22] to be an excellent chelating ligand. The inability for *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ to act as a bridging ligand may be attributed to the rigidity of the carbon–carbon double bond forcing the phosphorus atoms to remain so close together in *cis* positions that serious steric interference would occur between other ligands on the two metal atoms being bridged. By contrast, the free rotation around the carbon–carbon single bond in the link between the two phosphorus atoms in the likewise chelating ditertiary phosphines $R_2PCH_2CH_2PR_2$ permits the phosphorus atoms to assume transoid positions in bridging complexes thereby eliminating steric interference between other ligands on the two metal atoms being bridged.

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Mixed-Ligand Complexes of Triethylenetetramine and Ethylenediamine with Cobalt(III)

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Octahedral complexes containing a linear tetramine ligand can exist in nine different geometrical and optical isomers (Figure 1). In the case of triethylenetetramine disubstituted complexes of cobalt(III), most of these possibilities have been realized. Sargeson and Searle[1]

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(1) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965); **6**, 787 (1967).