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Registry No. $[Co_2(OH)_2(p_3)_2][B(C_6H_5)_4]_2 \cdot xC_3H_6O$, 56172-83-9; $[Co_2Cl_2(p_3)_2][B(C_6H_5)_4]_2$, 56172-85-1; $[Co_2Br_2(p_3)_2][B(C_6H_5)_4]_2$, 56172-87-3; $[Co(ac)(p_3)][B(C_6H_5)_4] \cdot xC_3H_6O$, 56172-90-8; $[Co(acac)(p_3)][B(C_6H_5)_4]$, 56172-92-0; $[Co(NO_3)(p_3)][B(C_6H_5)_4]$, 56172-94-2.

Supplementary Material Available. Tables IV and VIII, listings of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40810Y-10-75.

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Reactions of (RC≡CR')$Co_2(CO)_6$ Complexes with Mono- and Bidentate Group 5 Ligands

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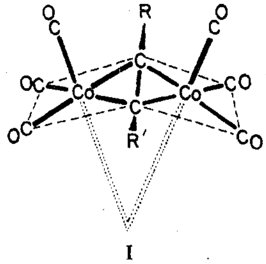
Various (RC≡CR')$Co_2(CO)_6$ derivatives (R, R' = H, CH_2OH, or C_6H_5) undergo replacement of one or both axial CO groups on heating with monodentate phosphines, phosphites, and arsines. Bulky ligands such as $(o\text{-}CH_3C_6H_4)_3P$ do not react, but $(CH_3O)_3P$ may displace up to four carbonyl ligands in a series of reversible reactions. Bidentate fluorocarbon- and hydrocarbon-bridged ligands react similarly but tend to occupy equatorial coordination positions about the metal atoms either by bridging two cobalt atoms in the same molecule or by chelating to one of them. They may displace two or four CO groups. Infrared and NMR spectra are reported.

The products of formula (RC≡CR')$Co_2(CO)_6$, obtained from the reactions of alkynes with dicobalt octacarbonyl, are well-known and have the structure indicated in I.[2] Only a limited number of studies on the reactions of these compounds with group 5 ligands have been made.[2b-5]



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The present work has been carried out to investigate the carbonyl substitution reactions of these compounds with a wide range of monodentate phosphines, phosphites, and arsines, and, of particular interest, with fluorocarbon-bridged di(tertiary ligands). It is an extension of earlier studies on these[5] and the closely related [μ-RSFe$(CO)_3]_2$ compounds.[6]

Experimental Section

Infrared spectra (Tables I and II) were run on Perkin-Elmer Model 337 or 457 spectrometers. NMR spectra (Tables III and IV) were recorded on Varian T-60 and HA-100 or Perkin-Elmer R 12 spectrometers. Chemical shifts are reported in ppm downfield from internal TMS (^1H) and upfield from internal $CFCl_3$ (^{19}F). Molecular weights were determined in benzene solution using a Mechrolab vapor pressure osmometer. Elemental analyses (Tables I and II) were carried out by Mr. P. Borda (University of British Columbia) or Mrs. E. Carey (University College, Dublin).

Ligands and starting materials were prepared as described in the literature. All reactions were carried out in sealed tubes or under an atmosphere of nitrogen using purified solvents.

1. Reaction of (RC≡CR')$Co_2(CO)_6$ with Monodentate Ligands.

Table I. Melting Point, Analytical Data, and Ir Spectra (1700-2100 cm^{-1}) for $L_n(RC{\equiv}CR')Co_2(CO)_{6-n}$ Complexes of Monodentate Ligands

L	n	Mp, °C	% yield	Calcd			Found			ν_{CO},[a] cm^{-1}				
				% C	% H	Mol wt	% C	% H	Mol wt					
$RC{\equiv}CR' = HC{\equiv}CH$														
$(n\text{-}C_4H_9)_3P$	1	25-26	80	46.8	6.0		46.8	6.4		1970 (4)	1997 (2)	2007 (10)	2013 (10)	2069 (9)
$(i\text{-}C_4H_9)_3P$	1	30-32	22	46.8	6.0		47.3	6.1		1969 (4)	1995 (1)	2008 (9)	2013 (10)	2068 (8)
$(C_6H_5)_3P^b$	1	124	20	55.0	3.1		55.2	3.2		1973 (3)	1997 (3)	2009 (10)	2017 (10)	2070 (10)
$(i\text{-}C_4H_9)_3P$	2	30-32	15	54.5	8.5		54.4	8.3		1955 (4)	1965 (10)	1973 (8)	2024 (10)	
$C_6H_5(C_6H_{11})_2P$	2	156-158	34	62.6	7.0		62.2	7.3		1943 (1)	1968 (10)	1975 (9)	2025 (10)	
$(C_6H_5)_3P^b$	2	200 dec	50	64.5	4.1		64.3	3.8		1941 (1)	1965 (10)	1976 (6)	2024 (10)	
$RC{\equiv}CR' = HOCH_2C{\equiv}CCH_2OH$														
$(CH_3O)_3P^c$	1	85	26	47.1	3.4	468	46.6	3.8	444	1980 (6)		2007 (10)	2018 (10)	2068 (7)
$(CH_3O)_3P^c$	2	75	50	29.8	4.3	564	28.8	4.6	575		1973 (10)		2031 (7)	
$RC{\equiv}CR' = C_6H_5C{\equiv}CH$														
$C_6H_5(C_6H_{11})_2P$	1		50							1963 (1)	1994 (1)	2005 (8)	2014 (10)	2064 (7)
$(C_6H_5)_3P$	1	104-107	50	59.8	3.4		59.3	3.2		1973 (4)	1997 (1)	2007 (10)	2017 (10)	2067 (10)
$(n\text{-}C_4H_9)_3P$	2	45–46	72	58.7	8.2		59.2	7.9		1952 sh	1965 (10)	1971 (6)	2020 (9)	
$(i\text{-}C_4H_9)_3P$	2	76-77	8	58.7	8.2		58.2	8.0		1950 sh	1965 (10)	1972 (7)	2018 (10)	
$C_6H_5(C_6H_{11})_2P^b$	2	205-208	16	65.4	6.8		65.9	6.3		1929 (1)	1959 (10)	1969 (7)	2016 (10)	
$(C_6H_5)_3P^b$	2	200 dec	10	67.3	4.2		67.2	4.2		1940 (1)	1965 (9)	1975 (6)	2021 (10)	
$RC{\equiv}CR' = C_6H_5C{\equiv}CC_6H_5$														
$(n\text{-}C_4H_9)_3P$	1	75-76	71	58.3	5.8		58.1	5.8		1964 (4)	1991 (2)	2003 (8)	2011 (10)	2062 (9)
$C_6H_5(C_6H_{11})_2P$	1	150-152	27	62.5	5.2		62.7	5.2		1973 (2)	1997 (3)	2009 (10)	2012 (10)	2059 (9)
$(C_6H_5)_3P$	1	230 dec	84	63.6	3.6		63.6	3.7		1967 (1)	1992 sh	2001 (7)	2015 (8)	2062 (10)
$(CH_3O)_3P$	1	84	85	47.1	3.4	560	46.6	3.8	522	1974 (7)		2002 (10)	2015 (10)	2064 (8)
$(i\text{-}C_4H_9)_3As$	1	56-58	27	54.5	5.4		54.2	5.2		1963 (2)	1987 (1)		2008 (10)	2046 (9)
$(n\text{-}C_4H_9)_3P^b$	2	78	71	62.1	7.9		62.5	7.8		1924 (1)	1950 (10)	1958 sh	2007 (10)	
$(i\text{-}C_4H_9)_3P$	2	121-123	6	62.1	7.9		62.1	7.8			1958 (10)		2013 (10)	
$(C_6H_{11})_3P$	2	186-188	15	66.9	7.9		66.5	8.1			1957 sh	1961 (10)	2014 (9)	
$C_6H_5(C_6H_{11})_2P^b$	2	217-219	13	67.7	6.7		67.8	6.9		1927 (1)	1952 (7)	1970 (6)	2013 (10)	
$(C_6H_5)_2(sec\text{-}C_4H_9)P^b$	2	131-133		67.3	5.4		67.8	5.4		1928 (1)	1956 (7)	1968 (5)	2012 (10)	
$(C_6H_5)_3P^b$	2	200 dec	95	69.5	4.3		69.9	4.4		1942 (1)	1964 (10)	1973 sh	2017 (10)	
$(CH_3O)_3P^c$	2	140	80	43.9	4.3	656	45.1	5.0	615		1971 (10)		2026 (7)	
$(CH_3O)_3P^c$	3	165	30	41.5	5.0	752	42.0	5.4	729	1950 (10)	1997 (9)			
$(CH_3O)_3P^c$	4	95	20	39.6	5.5	848	40.0	5.4	803	1922 (10)	1942 (8)	1996 (2)		

[a] Peak positions with relative peak heights in parentheses; measured in hexane solution unless it is stated otherwise. [b] Ir spectra measured in CS_2 solution. [c] Ir spectra measured in CH_2Cl_2 solution.

Table II. Melting Points, Analyses, and IR spectra (1700-2100 cm^{-1}) of Some Derivatives of $(RC{\equiv}CR')Co_2(CO)_6$ with Bidentate Ligands

	Mp, °C	% yield	Calcd			Found			Absorption bands,[a] cm^{-1}				
			% C	% H	Mol wt	% C	% H	Mol wt					
$f_4fars(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$	175	60	42.0	3.12	742	42.1	3.00	660	1959 (5)	1983 (9)	2002 (10)	2035 (8)	
$f_4AsP(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$	150	20	52.3	3.44	822	52.6	3.19	735	1961 (2)	1981 (8)	2004 (10)	2033 (7)	
$f_4fos(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$	215	66	61.2	3.36	902	60.9	3.50	839	1967 (2)	1987 (7)	2013 (10)	2038 (7)	
$f_6fars(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$	180	50	40.7	2.95	792	40.9	2.81	730	1958 (5)	1980 (9)	2003 (10)	2032 (8)	
$f_6AsP(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$	65	40	52.1	3.01	872	51.5	2.90	833	1964 (4)	1983 (8)	2005 (10)	2034 (7)	2054 (7)
$f_6fos(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$	180	50	60.4	3.60	952	59.2	3.18	905	1963 (2)	1982 (7)	2004 (9)	2056 (10)	
$f_8fos(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$	176	75	57.0	3.12	1002	57.6	3.03	896	1964 (3)	1984 (8)	2004 (9)	2051 (10)	
$dab(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$	80	61	47.1	3.36	780	46.5	3.48	729	1957 (9)	1972 (9)	1999 (10)	2005 (10)	2052 (10)
$dppm(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$	225	80	65.2	4.07	792	64.0	4.32	773	1960 (3)	1980 (9)	1993 (10)	2029 (8)	
$dppe(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$	165	10	65.5	4.26	806	65.0	4.51	812	1954 (4)	1975 (9.5)	1996 (10)	2031 (8)	
$(f_4fars)_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_2$	130	10[b]	37.7	3.37	1020	37.9	3.52	1053	1944 (10)	1951 (7)			
$(dab)_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_2$	190	15[b]	35.5	3 14	1096	35.0	3.13	1131	1898 (10)	1922 (10)			
$(f_4fos)_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_2$	195	40[c]	64.7	3.78	1340	65.2	4.77	1384	1928 (10)	1913 (10)			
$f_4AsP(C_6H_5C{\equiv}CH)Co_2(CO)_4$	135	15	48.3	2.98	746	47.9	3.04	709	1962 (3)	1982 (9)	2006 (10)	2037 (8)	
$f_6fars(C_6H_5C{\equiv}CH)Co_2(CO)_4$	110	50	35.2	2.54	716	35.2	2.63	695	1959 (8)	1974 (8)	2003 (10)	2052 (9)	
$f_8fars(C_6H_5C{\equiv}CH)Co_2(CO)_4$	100	50	34.5	2.37	766	34.7	2.59	730	1967 (3)	1989 (7)	2002 (10)	2050 (9)	
$f_8fos(C_6H_5C{\equiv}CH)Co_2(CO)_4$	190	80	54.3	2.84	926	54.9	3.20	874	1967 (3)	1989 (7)	2002 (10)	2050 (9)	
$dab(C_6H_5C{\equiv}CH)Co_2(CO)_4$	70	30	34.1	2.58	704	33.6	2.30	676		1986 (3)	2022 (10)	2057 (6)	
$f_6fos(C_6H_5C{\equiv}CH)Co_2(CO)_4$	155	50	56.2	3.00	876	55.5	2.75	803	1968 (4)	1990 (7)	2002 (10)	2049 (9)	
$dppm(HC{\equiv}CH)Co_2(CO)_4{}^d$	140	3	60.9	3.9		61.3	4.2		1952 (2)	1971 (8)	1998 (10)	2022 (7)	
$dppb[(HC{\equiv}CH)Co_2(CO)_5]_2{}^d$	162	1	50.7	3.1		50.5	2.9		1964 (3)	1992 sh	2005 (9)	2012 (10)	2066 (9)
$dppb(HC{\equiv}CH)Co_2(CO)_4{}^d$	97	6	59.8	4.4		59.6	4.7		1938 (1)	1962 (10)	1972 sh	2021 (9)	

[a] Peak positions with relative peak heights in parentheses; cyclohexane solutions unless stated otherwise. [b] Photochemical reaction. [c] Thermal reaction. [d] Spectra run in CS_2 solution.

(a) Preparation of $[(CH_3O)_3P](RC{\equiv}CR')Co_2(CO)_5$ Complexes (R, R′ = Ph, CH_2OH). Equimolar quantities (1.0 mmol) of $(CH_3O)_3P$ and $(RC{\equiv}CR')Co_2(CO)_6$ were stirred in benzene (50 ml) at 70° for ca. 3 hr. The solvent was removed under reduced pressure and the residual dark red oil was dissolved in a minimum volume of methylene chloride and chromatographed on Florisil. The unreacted $(RC{\equiv}CR')Co_2(CO)_6$ was eluted with petroleum ether. The product was eluted with a diethyl ether–petroleum ether mixture (1:1) and recrystallized from the same solvent to give dark red crystals of the desired product $[(CH_3O)_3P](RC{\equiv}CR')Co_2(CO)_5$. Other L-

Table III. ^1H NMR Spectra of Some $L_n(RC\equiv CR')Co(CO)_{6-n}$ Complexes of Monodentate Ligands

L	*n*	NMR data[a]
		$RC\equiv CR' = HC\equiv CH$
CO	1	7.89
$(C_6H_5)_3P$	1	5.01 d ($J_{PH} = 5.4$), 7.37 m, 7.28 m
$(C_6H_5)_3P$	2	4.36 t ($J_{PH} = 3.6$), 7.38 m
		$RC\equiv CR' = HOCH_2C\equiv CCH_2OH$
$(CH_3O)_3P$	1	2.45 t ($J_{HH} = 6$), 3.70 d ($J_{PH} = 11$), 4.75 d ($J_{HH} = 6$)
$(CH_3O)_3P$	2	2.40 t ($J_{HH} = 6$), 3.65 t ($J = 5.5$), 4.65 d ($J_{HH} = 6$)
		$RC\equiv CR' = C_6H_5C\equiv CC_6H_5$
$(CH_3O)_3P$	1	3.17 d ($J_{PH} = 11$), 7.21 m, 7.83 m
$(CH_3O)_3P$	2	3.60 t ($J = 6$), 7.55 m, 8.10 m
$(CH_3O)_3P$	3	3.21 m, 3.50 m, 7.23 m, 7.93 m[b]
$(CH_3O)_3P$	4	3.43 s, b, 7.21 m, 7.97 m

[a] All *J* values in hertz. [b] Phosphorus decoupling at 40.4933 MHz caused the two multiplets at 3.0–3.5 ppm to become singlets at 3.06 (area 9) and 3.33 (area 18).

$(RC\equiv CR')Co_2(CO)_5$ (Table I) complexes were prepared similarly. The following reactions did not take place even in refluxing toluene: $(PhC\equiv CPh)Co_2(CO)_6$ with $(i\text{-}Pr)_3P$ or $(s\text{-}Bu)_3P$, $(PhC\equiv CH)Co_2(CO)_6$ with $(s\text{-}Bu)_3P$, and $(HC\equiv CH)Co_2(CO)_6$ with $(s\text{-}Bu)_3P$ or $(o\text{-}CH_3C_6H_4)_3P$.

(b) Preparation of $[(CH_3O)_3P]_2(RC\equiv CR')Co_2(CO)_4$ Complexes (R, R′ = Ph, CH_2OH). Trimethyl phosphite (2 mmol) and the $(RC\equiv CR')Co_2(CO)_6$ (1 mmol) or equimolar quantities (1.0 mmol) of $(CH_3O)_3P$ and $(CH_3O)_3P(RC\equiv CR')Co_2(CO)_5$ were refluxed in benzene (50 ml) for ca. 2 hr. The resulting mixture was recrystallized from diethyl ether–petroleum ether (1:4) to give red crystals of $[(CH_3O)_3P]_2(RC\equiv CR')Co_2(CO)_4$. Other $L_2(RC\equiv CR')Co_2(CO)_4$ complexes were obtained similarly (Table II).

(c) Preparation of $[(CH_3O)_3P]_3(RC\equiv CR)Co_2(CO)_3$ Complexes. Trimethyl phosphite (3.0 mmol) and $(C_6H_5C\equiv CC_6H_5)Co_2(CO)_6$ (1.0 mmol) or equimolar quantities of $(CH_3O)_3P$ and $[(CH_3O)_3P]_2(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$ were refluxed in toluene (25 ml) for 2 hr. After removal of the solvent, the residue was dissolved in a minimum quantity of methylene chloride and chromatographed on a Florisil column. The product was eluted with diethyl ether–petroleum ether mixture (1:10). The dark violet residue obtained after evaporation was recrystallized from methylene chloride–petroleum ether to give red crystals of $[(CH_3O)_3P]_3(C_6H_5C\equiv CC_6H_5)Co_2(CO)_3$. Under the same conditions, $(CH_3O)_3P$ (3.0 mmol) and $(HOCH_2C\equiv CH_2OH)Co_2(CO)_6$ (1.0 mmol) or equimolar quantities (1.0 mmol) of $(CH_3O)_3P$ and $[(CH_3O)_3P]_2(HOCH_2C\equiv CCH_2OH)Co_2(CO)_4$ reacted to give a red oil with $\nu_{CO}(CH_2Cl_2)$ at 1998 (9) and 1953 (10) cm^{-1}. Attempts to purify this compound further were unsuccessful.

(d) Preparation of $[(CH_3O)_3P]_4(C_6H_5C\equiv CC_6H_5)Co_2(CO)_2$. Trimethyl phosphite (4.0 mmol) and $(C_6H_5C\equiv CC_6H_5)Co_2(CO)_6$ (1.0 mmol) or $(CH_3O)_3P$ and $[(CH_3O)_3P]_3(C_6H_5C\equiv CC_6H_5)Co_2(CO)_3$ were refluxed in toluene (25 ml) for 3 hr. After removal of the solvent, the residue was chromatographed on a Florisil column. The unreacted starting material was eluted with diethyl ether–petroleum ether mixtures as in part (c). The product was eluted with (20–100% diethyl ether)–(80–0% petroleum ether) to yield dark brown crystals. These were recrystallized from methylene chloride–petroleum ether to give dark brown needles of $[(CH_3O)_3P]_4(C_6H_5C\equiv CC_6H_5)Co_2(CO)_2$.

2. Reaction of $L_n(RC\equiv CR)Co_2(CO)_{6-n}$ with CO. (a) Reaction of $[(CH_3O)_3P]_4(C_6H_5C\equiv CC_6H_5)Co_2(CO)_2$ with CO. The complex was stirred in benzene (100 ml) at 70° and CO was slowly bubbled into the dark red solution. After 30 min the carbonyl bands at 1942 and 1922 cm^{-1} disappeared and the CO bands at 1997 and 1950 cm^{-1} became very strong. The resulting solution was evaporated, chromatographed, and recrystallized from diethyl ether–petroleum ether (1:10) to give dark red crystals (0.35 g, 80%) with infrared and ^1H NMR spectra identical with those of $[(CH_3O)_3P]_3(C_6H_5C\equiv CC_6H_5)Co_2(CO)_3$.

(b) Reaction of $[(CH_3O)_3P]_3(C_6H_5C\equiv CC_6H_5)Co_2(CO)_3$ with CO. The complex (0.2 g) was stirred in benzene (50 ml) at 70°. After CO was bubbled through this solution for 1 hr, all of the complex was converted to the disubstituted complex which was isolated and purified by recrystallization from petroleum ether.

(c) Reaction of $[(CH_3O)_3P]_2(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$ with CO. Under the same conditions, the disubstituted complex was only ca. 10% converted to the monosubstituted complex after 24 hr.

3. Reaction of $(C_6H_5C\equiv CC_6H_5)Co_2(CO)_6$ with Bidentate Ligands. (a) Preparation of $(L—L)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$. In general, equimolar quantities (1.0 mmol) of ligand L—L and $(C_6H_5C\equiv CC_6H_5)Co_2(CO)_6$ were refluxed in petroleum ether (50 ml) for 5 hr. The solution was concentrated, chromatographed, and recrystallized (petroleum ether) to yield $(L—L)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$ as black or dark green crystals. Thus were prepared the compounds listed in Table II.

(b) Preparation of $(L—L)_2(C_6H_5C\equiv CC_6H_5)Co_2(CO)_2$. The $(L—L)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$ complex (1.0 mmol) and the ligand L—L (1.3 mmol) in 300 ml of benzene were irradiated with a 450-W uv lamp for 8–12 hr. The reaction was monitored spectroscopically by observing the disappearance of the starting material. The final solution was dark brown or black. The benzene was removed under reduced pressure and the resulting oil chromatographed and recrystallized to yield $(L—L)_2(C_6H_5C\equiv CC_6H_5)Co_2(CO)_2$ as dark brown or black crystals (Table II). Alternatively, $(L—L)(C_6H_5\text{-}$

Table IV. NMR Spectra of Some Derivatives of $(RC\equiv CR')Co_2(CO)_6$ with Bidentate Ligands

	^1H NMR data	^{19}F NMR data
$(f_4fars)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$	1.60 s, 7.37 m	105.9 s
$(f_4AsP)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$	1.45 s, 7.40 m	105.2 m, 106.4 m
$(f_6fars)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$	1.60 s, 7.40 m	104.2 m, 130.7 m
$(f_4fos)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$	7.40 m, 7.50 m	105.3 s
$(f_6AsP)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$	1.30 s, 1.50 s, 1.80 s, 7.30 m, 7.50 m	103.1, 104.6, 128.8, 131.1 (all m)
$(f_6fos)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$		109.4 m, 110.5 m, 134.8 m
$(f_8fos)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$		101.5 m, 133.5 m
$(dab)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$	1.45 s, 1.80 s, 7.55 m, 7.60 m	50.5 s
$(dppm)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$	3.20 t (J_{PH}[b] = 10), 7.40 m, 7.50 m	
$(dppe)(C_6H_5C\equiv CC_6H_5)Co_2(CO)_4$	2.5–3.5 m, 7.40 m, 7.55 m	
$(f_4fars)_2(C_6H_5C\equiv CC_6H_5)Co_2(CO)_2$	1.30 s, 1.50 s, 7.20 m	107.2 s
$(dab)_2(C_6H_5C\equiv CC_6H_5)Co_2(CO)_2$	1.45 s, 1.80 s, 7.35 m, 7.60 m	51.3 s
$(f_4fos)_2(C_6H_5C\equiv CC_6H_5)Co_2(CO)_2$		108.0 s
$(f_4AsP)(C_6H_5C\equiv CH)Co_2(CO)_4$	1.50 s, 1.75 s, 5.30 s, 5.60 s, 7.40 m, 7.50 m	
$(f_6fars)(C_6H_5C\equiv CH)Co_2(CO)_4$	1.25 s, 1.60 s, 1.80 s, 1.85 s, 5.45 s, 7.40 m, 7.60 m[a]	
$(f_8fars)(C_6H_5C\equiv CH)Co_2(CO)_4$	*c*	101.7 m, 133.8 m
$(f_8fos)(C_6H_5C\equiv CH)Co_2(CO)_4$	4.60 s, 4.80 s, 7.10 m, 7.50 m	101.7 m, 133.8 m
$(dab)(C_6H_5C\equiv CH)Co_2(CO)_4$	1.25 s, 1.60 s, 1.80 s, 1.85 s, 5.25 s, 7.30 m, 7.50 m	
$(f_6fos)(C_6H_5C\equiv CH)Co_2(CO)_4$	4.60 s, 4.75 s, 7.20 m, 7.55 m	108.5 m, 134.3 m
$(dppm)(HC\equiv CH)Co_2(CO)_4$	2.30 s, 3.31 t ($J_{PH} = 10$), 5.60 t ($J_{PH} = 3.6$), 7.14 m	
$(dppb)(HC\equiv CH)Co_2(CO)_4$	1.77 s, 4.08 s, 7.08 m	

[a] ^1H NMR spectrum unchanged at 70°. [b] All *J* values in hertz. [c] 1.25 t ($J = 1.0$), 1.69 t ($J = 1.3$), 1.77 d ($J = 1.7$) of d ($J = 0.5$), 1.90 d ($J = 1.6$) of d ($J = 0.7$), 5.25 s, 7.30 m, 7.0 m. ^{19}F decoupling at 94.0866352 Hz produces four singlets in the region 1–2 ppm.

$C{\equiv}CC_6H_5)Co_2(CO)_4$ (1.0 mmol) and the ligand L—L (1.0 mmol) were refluxed in toluene (25 ml) for 10 hr. The resulting dark brown solution was evaporated to dryness. The residue was chromatographed and recrystallized from a methylene chloride–petroleum ether mixture (1:20) to yield the desired product.

4. Reaction of $(L{-}L)_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_2$ with CO. The complex $(f_4fos)_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_2$ (0.5 g) was stirred in hexane (50 ml) at 50°, and CO was passed through the solution. After 6 hr ca. 60% conversion to $f_4fos(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$ had occurred, as indicated by the infrared spectrum of the reaction solution.

5. Reaction of $(C_6H_5C{\equiv}CH)Co_2(CO)_6$ with Bidentate Ligands. Equimolar quantities (1.0 mmol) of $(C_6H_5C{\equiv}CH)Co_2(CO)_6$ (prepared in situ) and the ligand L—L were refluxed in benzene (50 ml) for ca. 2 hr. The resulting solution was concentrated, chromatographed, and recrystallized to give dark green or black crystals of $(L{-}L)(C_6H_5C{\equiv}CH)Co_2(CO)_4$ (Table II).

6. Reaction of $(HC{\equiv}CH)Co_2(CO)_6$ with Bidentate Ligands. These were carried out as in part 5. The products are given in Table II.

Results and Discussion

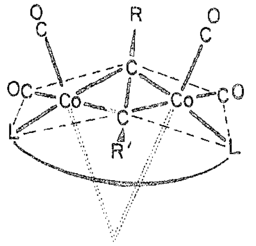
When equimolar quantities of $(RC{\equiv}CR')Co_2(CO)_6$ and monodentate tertiary phosphites, phosphines, or arsines are heated, monosubstituted $L(RC{\equiv}CR')Co_2(CO)_5$ derivatives are generally formed. All have similar infrared spectra in the ν_{CO} region (Table I) and, hence, similar structures. The proton NMR spectra of $[(CH_3O)_3P](HOCH_2C{\equiv}CCH_2OH)Co_2(CO)_5$ and of $(Ph_3P)(HC{\equiv}CH)Co_2(CO)_5$ indicate only one type of $\equiv CCH_2OH$ or $\equiv CH$ group (Table III). Thus monosubstitution gives the more symmetrical axial substituted derivative as in the case of $R_3P(R'S)_2Fe_2(CO)_5$.[6] In this isomer, the steric interactions between the acetylene and the incoming ligand L are probably larger than in the alternative equatorial form. However increasing the bulk of L does not bring about equatorial substitution as such ligands fail to react even in refluxing toluene.

The ir spectra of the disubstituted derivatives $L_2(RC{\equiv}CR')Co_2(CO)_4$ are similar and indicate similar structures in all compounds. The ^1H NMR spectra of $[(CH_3O)_3P]_2(HOCH_2C{\equiv}CCH_2OH)Co_2(CO)_4$ and $(Ph_3P)_2(HC{\equiv}CH)Co_2(CO)_4$ show that the groups R and R' are equivalent (Table III) and that these complexes are diaxial isomers. The reversibility of the reaction between $[(CH_3O)_3P](HOCH_2C{\equiv}CCH_2OH)Co_2(CO)_5$ and $(CH_3O)_3P$ is consistent with this view. The proton NMR spectrum of the bis(trimethyl phosphite) complex indicates that virtual coupling occurs despite the large separation of the two $(CH_3O)_3P$ ligands. The same features, diaxial substitution and virtual coupling, are observed for $[(CH_3)_2PC_6H_5]_2(CH_3S)_2Fe_2(CO)_4$.[6]

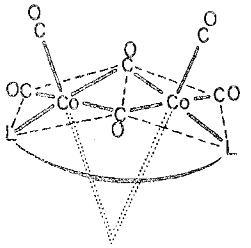
Complexes of formula $L_3(RC{\equiv}CR)Co_2(CO)_3$ and $L_4(RC{\equiv}CR)Co_2(CO)_2$ were characterized only for R = C_6H_5 and L = $(CH_3O)_3P$. The trisubstituted complex can be made by refluxing equimolar quantities of $(CH_3O)_3P$ and the disubstituted complex in toluene. The ^1H NMR spectrum of the product after phosphorus decoupling shows two singlets at 3.06 and 3.33 ppm of relative area 1:2 indicating the presence of at least two different sets of $(CH_3O)_3P$ groups. Since this compound can be converted to the disubstituted one by reaction with CO, the substitution pattern could be two axial and one equatorial phosphites. However one axial (Co_1) and two equatorial phosphites (Co_2) would fit the NMR data better.

Further reaction of the trisubstituted complex results in tetrasubstitution. The NMR spectrum of this complex shows a broad peak for the phosphite resonance indicating four equatorial ligands. The band at 1996 cm^{-1} in the infrared spectrum is probably due to a trace of the trisubstituted complex. The two-band pattern remaining is similar to, but at lower frequency than, that exhibited by the terminal CO bands of $(dppe)_2Co_2(CO)_4$[7] and both isomers of $(f_4fos)_2Co_2(CO)_4$[8,9] which are also believed to have the ligands in equatorial positions.

$(L{-}L)(RC{\equiv}CR')Co_2(CO)_4$ Complexes. Previously[5] it was found that f4fars and f4fos reacted with $(C_6H_5C{\equiv}CH)Co_2(CO)_6$ to give the black $(L{-}L)(C_6H_5C{\equiv}CH)Co_2(CO)_4$ complexes believed to have structure II (R = C_6H_5, R' = H). However, attempts to isolate similar compounds by using f6fos, f6AsP, f8fos, and dab were unsuccessful. In this work, by modifying the reported procedure, the $(L{-}L)(C_6H_5C{\equiv}CH)Co_2(CO)_4$ complexes of these and the related ligands f4AsP, f6fars, and f8fars have been isolated. The main arguments used to assign structure II to $(L{-}L)(C_6H_5C{\equiv}CH)Co_2(CO)_4$[5] (L—L = f4fos, f4fars) were that their infrared spectra were similar to each other and that f4fars shows a reluctance to form chelate complexes presumably because of its large "bite".[10] Furthermore the known[11] structure of $(f_4fars)Co_2(CO)_6$ was as indicated in III, and this complex reacts with $C_6H_5C{\equiv}CH$ to give $f_4fars(C_6H_5C{\equiv}CH)Co_2(CO)_4$. The isomer with R' = C_6H_5 and R = H was eliminated for steric reasons. We now find the mixed ligand f4AsP affords the black solid complex $(f_4AsP)(C_6H_5C{\equiv}CH)Co_2(CO)_4$ whose infrared spectrum is very similar to those of the f4fars and f4fos complexes. The $(CH_3)_2As$ group of the f4AsP moiety is seen as two singlets in the ^1H NMR spectrum (as is the case with the f4fars complex), and the phosphorus evidently couples to the CH group of the acetylene, indicating that the structure is as in II with L—L = f4AsP and R' = H.



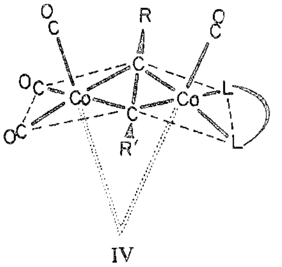
II



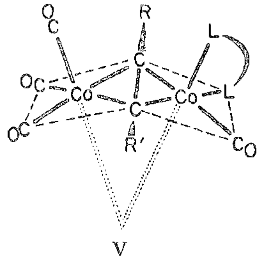
III

Other ligands such as f6fars, f8fars, f6fos, f8fos, and dab afford black complexes $(L{-}L)(C_6H_5C{\equiv}CH)Co_2(CO)_4$ which have different spectroscopic properties. First, their infrared spectra, although similar to each other, are at higher frequencies than those of the derivatives assigned structure II. This same difference of 10 cm^{-1} is seen between the spectra of bridged complexes such as $(f_4fos)Co_2(CO)_6$, III (L—L = f4fos), and its isomer where the ligand is chelated.[8] Thus this information suggests that in these cases the ligands are chelated, not bridged. Second, the ^1H NMR spectra of the arsenic-containing derivatives indicate four inequivalent arsenic methyl groups which again suggests a chelated structure rather than a bridged one. (Bridging as in II would give only two arsenic methyl resonances.) The ^{19}F NMR spectra of all the complexes are little changed from that of the free ligand; however, with one exception this is true of all the cobalt complexes investigated thus far. Possibly the fluorine atoms are too far away to "feel" the effect of the rest of the complex.

If a chelated model is selected for these compounds, then the possibilities are IV and V. In view of the result that, in the derivatives $L(RC{\equiv}CR')Co_2(CO)_5$, L has displaced an axial carbonyl group, V might be considered more likely.



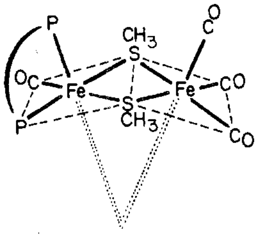
IV



V

However compounds of structure V could exist as two isomers produced by interchanging R and R'. No evidence for the existence of isomers was obtained.

The same sort of decision had to be made in the case of the derivatives of $[SCH_3Fe(CO)_3]_2$,[6] where, to give an example, one isomer of $(f_4fos)(SCH_3)_2Fe_2(CO)_4$ had equivalent iron atoms (by Mössbauer spectroscopy) and was assigned a bridged structure. Another isomer had two inequivalent iron atoms. Its carbonyl infrared spectrum was also at higher frequencies and the chelate structure VI was suggested because, as mentioned above, monosubstitution takes place in an axial position. In this example it is also possible that the chelating ligand occupies two equatorial sites.



VI

The complexes of formula $(L{-}L)(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$ again fall into two classes. Class 1 includes the dark green solids where L—L = f4fars, f4AsP, f4fos, f6fars, dppe, and dppm (the last is dark brown). They all have terminal carbonyl stretching bands similar to those of $(f_4fars)(C_6H_5C{\equiv}CH)Co_2(CO)_4$ and $(f_4fars)Co_2(CO)_6$;[5] hence the bridged structure is suggested for all of these. Recent ^{59}Co NQR studies on $(f_4fars)(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$ reveal that the two cobalt atoms are equivalent supporting the bridged formulation.[12] The number of CO stretching bands, 4, indicates that their structure is probably II ($R = R' = C_6H_5$). However, there is the unexpected result that the appropriate ligands fail to show more than one arsenic methyl resonance in spite of the fact that the corresponding compounds with $R = C_6H_5$ and $R' = H$ do. Assuming that the bridging formulation is correct, it is unusual to find so many ligands forming complexes of this type. Usually only the cyclobutene derivatives yield bridged complexes. The known solid-state structures of $Co_2(CO)_8$,[13] $(f_4fars)Co_2(CO)_6$,[11] and $(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_6$[14] are all very similar and there seems nothing peculiar about the acetylene derivative that would encourage bridging by so many ligands.

The second class of $(L{-}L)(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$ complexes have their carbonyl stretching bands at higher frequencies. Both f6fos and f8fos give complexes of this type which are assumed to be chelates. Although the dab complex has an extra CO stretching band, it is probably of the same type. Two of these complexes, the dab and f8fos derivatives, have ^{19}F spectra very similar to the free ligands and hence are probably equatorial–equatorial substituted (IV, $R = R' = C_6H_5$). The f6fos complex has a less symmetrical structure as judged by its ^{19}F NMR spectrum and could be an axial–equatorial chelate as in V.

The f6AsP complex seems to be a mixture of both chelate and bridged forms as judged by its infrared and NMR spectra.

Both the ir and ^1H NMR spectra of $(dppm)(HC{\equiv}CH)Co_2(CO)_4$ are consistent with its formulation as a bridged complex having structure II. On the other hand, the ir spectrum of $(dppb)(HC{\equiv}CH)Co_2(CO)_4$ ($dppb = Ph_2P(CH_2)_4PPh_2$) is very similar to those of the tetracarbonyl derivatives of monodentate ligands. It is not clear if the dppb ligand bridges two axial coordination positions within the same molecule or within different molecules to give oligomers.

$(L{-}L)_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_2$ Complexes. Three derivatives of this type were obtained by treating the $(L{-}L)(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$ complexes with more L—L (L—L = f4fars, f4fos, dab). The f4fars complex has spectroscopic properties very similar to those of $(f_4fars)(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$ except that there are now only two CO stretching bands. Thus the complex probably has the structure with two bridging ligands occupying the four equatorial positions. A similar structure is suggested for the $(f_4fos)_2$ complex which can be converted back to the singly bridged complex by treatment with CO. In the related $(dab)_2$ complex the ligand is probably chelated. This complex differs from all other tetrasubstituted derivatives of $(RC{\equiv}CR')Co_2(CO)_6$ in that it does not easily react with CO at 50°.

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Registry No. $[(n\text{-}C_4H_9)_3P](HC{\equiv}CH)Co_2(CO)_5$, 55925-98-9; $[(i\text{-}C_4H_9)_3P](HC{\equiv}CH)Co_2(CO)_5$, 55925-99-0; $[(C_6H_5)_3P](HC{\equiv}CH)Co_2(CO)_5$, 55926-00-6; $[(i\text{-}C_4H_9)_3P]_2(HC{\equiv}CH)Co_2(CO)_4$, 55926-01-7; $[C_6H_5(C_6H_{11})_2P]_2(HC{\equiv}CH)Co_2(CO)_4$, 55926-02-8; $[(C_6H_5)_3P]_2(HC{\equiv}CH)Co_2(CO)_4$, 55926-03-9; $[(CH_3O)_3P](HOCH_2C{\equiv}CCH_2OH)Co_2(CO)_5$, 55926-04-0; $[(CH_3O)_3P]_2(HOCH_2C{\equiv}CCH_2OH)Co_2(CO)_4$, 55926-05-1; $[C_6H_5(C_6H_{11})_2P](C_6H_5C{\equiv}CH)Co_2(CO)_5$, 55926-06-2; $[(C_6H_5)_3P](C_6H_5C{\equiv}CH)Co_2(CO)_5$, 55926-07-3; $[(n\text{-}C_4H_9)_3P]_2(C_6H_5C{\equiv}CH)Co_2(CO)_4$, 55926-08-4; $[(i\text{-}C_4H_9)_3P]_2(C_6H_5C{\equiv}CH)Co_2(CO)_4$, 55926-22-2; $[C_6H_5(C_6H_{11})_2P]_2(C_6H_5C{\equiv}CH)Co_2(CO)_4$, 55926-21-1; $[(C_6H_5)_3P]_2(C_6H_5C{\equiv}CH)Co_2(CO)_4$, 55926-20-0; $[(n\text{-}C_4H_9)_3P](C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_5$, 55926-19-7; $[C_6H_5(C_6H_{11})_2P](C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_5$, 55926-18-6; $[(C_6H_5)_3P](C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_5$, 55926-17-5; $[(CH_3O)_3P](C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_5$, 55926-16-4; $[(i\text{-}C_4H_9)_3As](C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_5$, 55926-15-3; $[(n\text{-}C_4H_9)_3P]_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55926-14-2; $[(i\text{-}C_4H_9)_3P]_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55926-13-1; $[(C_6H_{11})_3P]_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55926-12-0; $[C_6H_5(C_6H_{11})_2P]_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55926-11-9; $[(C_6H_5)_2(s\text{-}C_4H_9)P]_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55926-10-8; $[(C_6H_5)_3P]_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55926-09-5; $[(CH_3O)_3P]_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55925-86-5; $[(CH_3O)_3P]_3(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_3$, 55925-87-6; $[(CH_3O)_3P]_4(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_2$, 55925-88-7; $f_4fars(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55925-89-8; $f_4AsP(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55925-90-1; $f_4fos(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55925-91-2; $f_6fars(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55925-95-6; $f_6AsP(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 56086-73-8; $f_6fos(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55975-78-5; $f_8fos(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55975-79-6; $dab(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55975-80-9; $dppm(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55954-95-5; $dppe(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_4$, 55925-96-7; $(f_4fars)_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_2$, 55925-92-3; $(dab)_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_2$, 55925-93-4; $(f_4fos)_2(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_2$, 55937-78-5; $f_4AsP(C_6H_5C{\equiv}CH)Co_2(CO)_4$, 55975-77-4; $f_6fars(C_6H_5C{\equiv}CH)Co_2(CO)_4$, 55975-81-0; $f_8fars(C_6H_5C{\equiv}CH)Co_2(CO)_4$, 55975-82-1; $f_8fos(C_6H_5C{\equiv}CH)Co_2(CO)_4$, 55975-83-2; $dab(C_6H_5C{\equiv}CH)Co_2(CO)_4$, 55975-84-3; $f_6fos(C_6H_5C{\equiv}CH)Co_2(CO)_4$, 55975-85-4; $dppm(HC{\equiv}CH)Co_2(CO)_4$, 55925-97-8; $dppb[(HC{\equiv}CH)Co_2(CO)_5]_2$, 55925-94-5; $dppb(HC{\equiv}CH)Co_2(CO)_4$, 56086-72-7; $(HC{\equiv}CH)Co_2(CO)_6$, 12264-05-0; $(HOCH_2C{\equiv}CCH_2OH)Co_2(CO)_6$, 55975-76-3; $(C_6H_5C{\equiv}CH)Co_2(CO)_6$, 12154-91-5; $(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_6$, 14515-69-6; $(CH_3O)_3P$, 121-45-9.

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dppb is $(C_6H_5)_2PCH_2CH_2CH_2CH_2P(C_6H_5)_2$, and dab is *cis*-$(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2$.
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Oxidation of Chromium, Molybdenum, and Tungsten Dicarbonylbis(diphenylphosphino)methane Complexes

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Chemical oxidation of the series of complexes *cis*-$M(CO)_2(DPM)_2$ (M = Cr, Mo, W; DPM = bis(diphenylphosphino)methane) has been investigated. Products have been characterized by ir, NMR, ESR, electrochemistry, and conductivity. In agreement with electrochemical data, these complexes are easier to oxidize than the analogous DPE complexes (DPE = 1,2-bis(diphenylphosphino)ethane) and both oxidation state I and oxidation state II compounds can be obtained. In oxidation state I complexes containing the low-spin paramagnetic *trans*-$[M(CO)_2(DPM)_2]^+$ cation are formed. ESR studies of the complexes reveal that the electron density on the phosphorus atoms is considerable. Electrochemical reduction of the trans$^+$ cation yields *trans*-$M(CO)_2(DPM)_2$ while oxidation occurs via the pathway

$$trans\text{-}[M(CO)_2(DPM)_2]^+ \rightarrow trans\text{-}[M(CO)_2(DPM)_2]^{2+} + e \rightarrow \text{products}$$

In oxidation state II, six-coordinate dipositive cations are unstable and these species are not isolated. Using $O_2/HClO_4$ as the oxidant, the hydride complexes *trans*-$[MH(CO)_2(DPM)_2]ClO_4$ are formed. With chromium this represents one of the few examples of oxidation state II carbonyl complexes. The hydrides are believed to be seven-coordinate capped octahedra, although a pentagonal-bipyramidal structure cannot be excluded. Products obtained with a range of other oxidants are also discussed.

Introduction

Electrochemical studies on the oxidation of a series of *cis*-$M(CO)_2(DPE)_2$ and *cis*-$M(CO)_2(DPM)_2$ complexes, where M = Cr, Mo, W, DPE = 1,2-bis(diphenylphosphino)ethane, and DPM = bis(diphenylphosphino)methane, have recently been undertaken in these laboratories.[1,2] In both cases a series of complexes $[M(CO)_2(P{-}P)_2]^{0,+,2+}$ (where P–P = DPE or DPM) was shown to exist with cis and trans isomeric forms (isomerism refers to carbonyls) being possible in each oxidation state. In oxidation state zero and II, the cis isomers were shown to be thermodynamically favored, while in oxidation state I, the cis form isomerizes rapidly to the trans isomer, even on the short electrochemical time scale. In oxidation state II, the complexes were demonstrated to be generally unstable and the reaction pathway was described as

$$[M(CO)_2(P{-}P)_2]^{2+} \rightarrow \text{products} \qquad (1)$$

In terms of $E_{1/2}$ values, the oxidation pathway for the reactions

$$\begin{array}{l} cis\text{-}M(CO)_2(P{-}P)_2 \rightleftharpoons cis[M(CO)_2(P{-}P)_2]^+ + e \\ \qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\quad trans\text{-}[M(CO)_2(P{-}P)_2]^+ \end{array}$$

was very similar for both ligands.[1,2] However, it was observed that the $E_{1/2}$ value for the *trans*-$M(CO)_2(DPM)_2|$*trans*-$[M(CO)_2(DPM)_2]^+$ couple was considerably more negative than for the corresponding couple of the DPE complex, and in principle the DPM series of complexes could exhibit different chemical oxidation pathways. Further, $E_{1/2}$ values suggested that oxidation state II could be more readily obtained with DPM as the ligand.

The chemical oxidation of the $M(CO)_2(DPE)_2$ series of complexes has been studied extensively.[3-5] Predominantly, only oxidation state I complexes were obtained. However, no reliable data are available for the DPM complexes, the only report being a reaction of *trans*-$Mo(CO)_2(DPM)_2$ with iodine,[6] which was shown to be probably incorrect.[2] However, many Mo^{II}- and W^{II}-, although no Cr^{II}DPM derivatives, have been prepared directly from carbonyl halides.[7] Oxidation state I complexes do not appear to have been reported for any of the metals with DPM.

The purpose of the present work was to investigate the chemical oxidation of the zerovalent DPM complexes in an endeavor to see whether the products are indeed different from the DPE case. Further, it was hoped to establish the possibility of isolating some higher oxidation state compounds, since with Cr, in particular, these are extremely rare.[8] Finally, detailed characterization of the products in different oxidation states was expected to lead to additional knowledge on the oxidation pathways to supplement that already gained from the electrochemical investigations.

Experimental Section

Reagents. The complexes *cis*-$M(CO)_2(DPM)_2$ and *cis*-$M(CO)_2(DPE)_2$ were prepared as described in the literature.[1,2]

Instrumentation. Electrochemistry. The instrumentation used was as described elsewhere.[2] A.R. grade acetone (0.1 *M* Et_4NClO_4) was used as the solvent and Ag|AgCl (0.1 *M* LiCl) as the reference electrode. All solutions used were 10^{-3} *M*.

NMR. All NMR spectra were recorded on a Varian HA 100 NMR system. Time averaging was undertaken with a D.E.C. PDP 15 computer. Tetramethylsilane was used as an internal reference.

ESR. A varian 450/15 spectrometer was used to record all ESR spectra.

Magnetism. Magnetic measurements were performed on a magneto balance at 20° using the Gouy method.

Results and Discussion

Table I provides ir and conductivity data for representative examples of the complexes characterized in the present work. ESR, NMR, electrochemical, and other data along with detailed discussion on the interpretation of results are presented below for each of the metals in turn.

Oxidation of *cis*-$Cr(CO)_2(DPM)_2$. (i) Iodine. Addition of an excess of iodine in CH_2Cl_2 to a stirred solution of *cis*-$Cr(CO)_2(DPM)_2$ in the same solvent gave a red-brown solution. On addition of *n*-hexane, the yellow-brown *trans*-