erations, and by a comparison with similar bis(salicylidine)ethylenediamine complexes.

With calcium(II) and magnesium(II), it is seen that the order of overall stability is reversed from the situation found with HBED. This is possibly a combination of a steric effect and a coulombic effect, the larger calcium ion being more able to accommodate the bulky phosphonate groups, allowing for stronger interaction between ligand and metal.

Registry No. HBEDPI, 53431-86-0; HBEDPO, 53431-87-1; EDDPI, 34160-37-7; *o*-acetoxybenzyl bromide, 704-65-4; Cu, 7440-50-8; Ni, 7440-02-0; Co, 7440-48-4; Zn, 7440-66-6; Ca, 7440-70-2; Mg, 7439-95-4.

References and Notes

(1) This work was supported by a research grant, A-259, from the Robert A. Welch Foundation.
(2) F. L'Eplattenier, I. Murase, and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 837 (1967).
(3) (a) A. E. Frost, H. H. Freedman, S. J. Westerback, and A. E. Martell, *J. Amer. Chem. Soc.*, **80**, 530 (1958); (b) G. Anderegg and F. L'-Eplattenier, *Helv. Chim. Acta*, **47**, 1067 (1964).
(4) R. J. Motekaitis, I. Murase, and A. E. Martell, *J. Inorg. Nucl. Chem.*, **33**, 3353 (1971).
(5) R. J. Motekaitis, I. Murase, and A. E. Martell, *Inorg. Nucl. Chem. Lett.*, **7**, 1103 (1971).
(6) G. Schwarzenbach and H. Flascha, "Complexometric Titrations," Interscience, New York, N.Y., 1957.
(7) R. J. Motekaitis and A. E. Martell, *J. Amer. Chem. Soc.*, **92**, 4223 (1970).
(8) G. Sillen and A. E. Martell, "Stability Constants," Special Publication No. 25, Chemical Society, London, 1964.
(9) A. E. Martell, U.S. Patent 3,632,637 (1972).

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Tris(trimethylphosphine)cobalt(I) Halides. Preparation and Properties

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Syntheses and properties of stable cobalt(I) halides of the formula $CoXL_3$ ($L = (CH_3)_3P$; X = Cl, Br, I) are reported. In solution these compounds add carbon monoxide under normal pressure to form pentacoordinate complexes of the composition $CoX(CO)L_3$ which, in a subsequent step, are converted into dicarbonyl compounds $CoX(CO)_2L_2$. By addition of a phosphine ligand ionic species $[Co(CO)L_4]^+X^-$ are formed. In the absence of CO the first tetrahedral cobalt(I) cation is isolated in the form $[CoL_4]^+[B(C_6H_5)_4]^-$. An even higher coordination number is accessible in the presence of dimethylphosphine in the form of $[CoL_4L']^+X^-$ ($L = (CH_3)_3P$; $L' = (CH_3)_2PH$; X = Cl, Br). This pentacoordinate species is not formed with trimethylphosphine alone. Infrared, nmr, and magnetic measurements suggest probable structures of these complexes in solution.

Recently we described a tetrahedral chlorotris(trimethylphosphine)cobalt(I) which appears to be indispensable in the preparation of methyltetrakis(trimethylphosphine)cobalt(I).[1] For this type of complex a detailed investigation was desirable not only because its composition matches that of the well-known hydrogenation catalyst chlorotris(triphenylphosphine)rhodium(I) but also since only very few examples of four-coordinate d^8 complexes of cobalt have been reported.[2,3] In contrast to Sacco's Co(I) halides with triphenylphosphine ligands,[3] $CoClL_3$ ($L = (CH_3)_3P$) is stable in the solid state and in solution. Thus a chemistry of tetrahedral Co(I) complexes with simple unidentate ligands has become accessible.[4,5]

Results

Preparation and Characterization of Compounds. In the presence of trimethylphosphine, anhydrous $CoCl_2$ is reduced by metals in THF solution to give tetrakis(trimethylphosphine)cobalt(0).[1,6] In this reduction $CoCl[P(CH_3)_3]_3$ could be isolated as an intermediate. We subsequently found that a comproportionation reaction between Co(0) and Co(II) according to eq 1 provides a simple high-yield synthesis of this

$$CoCl_2 + CoL_4 + 2L \rightarrow 2CoClL_3 \qquad (1)$$

$$CoX_2L_2 + CoL_4 \rightarrow 2CoXL_3 \qquad (2)$$

$$CoL_4 + {}^3/_2I_2 \rightarrow CoIL_3 + (CH_3)_3PI_2 \qquad (3)$$

$$L = (CH_3)_3P;\ X = Cl, Br, I$$

complex. Instead of anhydrous Co(II) salts Jensen's bis(trimethylphosphine)cobalt(II) halides[7] are conveniently employed especially for the bromo and iodo complexes according to eq 2. The oxidation of the Co(0) complex by iodine was found to proceed according to eq 3 with loss of a phosphine ligand. A more general method is based on the cleavage of the CoC bond of methyltetrakis(trimethylphosphine)cobalt(I)[1] by protic acids (eq 4) or, in a smooth reaction, by their ammonia salts (eq 5). The tris(trimethylphosphine)cobalt(I) halides are thermally stable. They are only slightly dissolved in pentane or ether but are quite soluble in benzene, THF, or methanol. Under normal conditions no decomposition products are observed, provided that the material is kept under an inert gas. The deep blue color of the crystals corresponds to the

Table I. Properties of Co(I) Complexes ($L = (CH_3)_3P$)

Compd	Color	Dec pt, °C	Solubility[a]	Magnetism,[b] μ_{eff}, μ_B
$CoClL_3$	Blue	>90	P 1	3.1_0
$CoBrL_3$	Blue	>140	P 1	3.1_8
$CoIL_3$	Violet-blue	>114	P 2	3.3_5
$CoO_2CCH_3L_3$	Dark blue	>135[g]	P 3	~3.0[e]
$[CoL_4]^+[B(C_6H_5)_4]^-$	Green	>188	A-E 3	3.3_9[f]
$CoCl(CO)L_3$	Wine red	>94	P 2	Diamag
$CoBr(CO)L_3$	Red	>65	P 1	Diamag
$CoI(CO)L_3$	Brown-red	>170	E 1	Diamag
$[Co(CO)L_4]^+Cl^-$	Yellow	>110	C[c] 3	Diamag
$[Co(CO)L_4]^+Br^-$	Orange	>115	C[c] 3	Diamag
$[Co(CO)L_4]^+I^-$	Orange	>115	C[c] 3	Diamag
$CoCl(CO)_2L_2$	Yellow	>125	E 1	Diamag
$CoBr(CO)_2L_2$	Yellow	>175	E 1	Diamag
$CoI(CO)_2L_2$	Light brown	>215	E 1	Diamag
$[CoL_4L']^+Cl^-$ [d]	Orange	>60	C[c] 3	Diamag
$[CoL_4L']^+Br^-$ [d]	Orange	>65	C[c] 3	Diamag

[a] A = acetone, C = methylene chloride, E = ether, P = pentane; 1 = 0–10 mg, 2 = 10–500 mg, 3 = 1 g in 10 ml of solvent. [b] In benzene solution (see Experimental Section). [c] Decomposition above 10°. [d] $L' = (CH_3)_2PH$. [e] Some decomposition in solution. [f] In CH_2Cl_2 solution containing 10% cyclohexane. [g] Sealed capillary.

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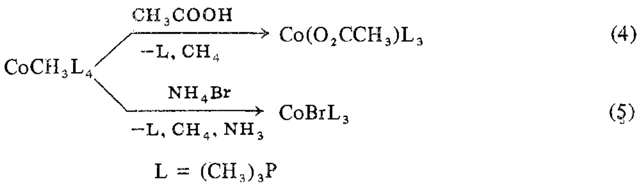


$$CoCH_3L_4 \xrightarrow[-L,\ CH_4]{CH_3COOH} Co(O_2CCH_3)L_3 \quad (4)$$

$$CoCH_3L_4 \xrightarrow[-L,\ CH_4,\ NH_3]{NH_4Br} CoBrL_3 \quad (5)$$

$L = (CH_3)_3P$

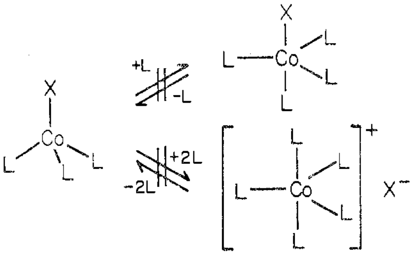
pale blue color of their 0.1 *M* solutions in benzene or THF. Acetatotris(trimethylphosphine)cobalt forms dark blue leaflets (from pentane) and decomposes at ambient temperature to a small extent which is increased *in vacuo*. Excess phosphine ligand enhances the thermal stability both in the solid state and in solution. These observations are readily explained by assuming an equilibrium according to eq 6. As shown by

$$2Co(O_2CCH_3)L_3 \rightleftharpoons CoL_4 + Co(O_2CCH_3)_2 + 2L \quad (6)$$

cryoscopy, the compounds are not associated *via* halogen bridges. Accordingly magnetic measurements (Table I) indicate a local geometry round the Co d^8 center which is close to tetrahedral. The heavier ligands X^- allow for a greater orbital contribution as is shown by increasing values of μ_{eff} following the series Cl < Br < I < L. These values agree well with those obtained by Sacco[3] from solid-state investigations of $CoXL'_3$ ($L' = (C_6H_5)_3P, (C_6H_5CH_2)_3P$; X = Cl, Br, I).

The paramagnetism in solution does not depend on the temperature to an extent that would account for any square-planar species to be present in an equilibrium favored by spin pairing.

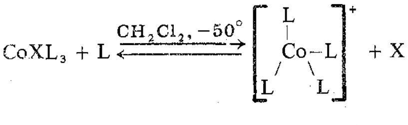
The Tetrakis(trimethylphosphine)cobalt(I) Cation. The blue color of CH_2Cl_2 solutions of $CoXL_3$ ($L = (CH_3)_3P$; X = Cl, Br, I) at 20° does not alter upon addition of trimethylphosphine. But, if cooled to −50°, there is a *reversible* change to green. However, at the same time the magnetic properties do not alter appreciably. At least at low temperatures one would expect some decrease in susceptibility by spin pairing if pentacoordinate species were formed in an equilibrium according to eq 7. The steric requirements of the phosphine ligands possibly prevent the formation of a CoL_5^+ cation. However, this limitation does not apply to other diamagnetic $CoXL_4$ species, since $CoCH_3L_4$[1] is known to be a stable complex.



(7)

$L = (CH_3)_3P$

It is therefore concluded that the green color arises from a tetrahedral CoL_4^+ cation which is formed in equilibrium 8 at low temperatures. This first tetrahedral Co(I) cation can indeed be isolated at ambient temperature if the corresponding anion has very poor ligand properties. Thus, upon adding sodium tetraphenylborate in order to precipitate all Cl^- as NaCl, a *green* solution is formed, from which *green* crystals of tetrakis(trimethylphosphine)cobalt(I) tetraphenylborate are obtained. The magnetic moment of this material (Table I) results basically from the spin value of two unpaired electrons increased by a high orbital contribution as expected for a d^8 configuration of valence electrons in a T_d symmetry case.



$$CoXL_3 + L \underset{}{\overset{CH_2Cl_2,\ -50°}{\rightleftharpoons}} [CoL_4]^+ + X^- \quad (8)$$

$$CoClL_3 + L + NaB(C_6H_5)_4 \rightarrow [CoL_4]^+[B(C_6H_5)_4]^- + NaCl \quad (9)$$

$L = (CH_3)_3P$

Reactions. $CoClL_3$ reacts with $NaOCH_3$ or $LiN(CH_3)_2$ to give coordination polymers of Co(II) and CoL_4. The reaction path according to eq 10 is similar to the alcoholysis of $CoCH_3L_4$.[1] Anionic ligands with a high tendency to bridge formation favor electron transfer and disproportionation into Co(II) and Co(0).

$$2CoClL_3 + 2MX \rightarrow CoL_4 + CoX_2 + 2MCl + 2L \quad (10)$$

$L = (CH_3)_3P$; M = Li, $X = N(CH_3)_2$;
M = Na, $X = OCH_3$

As already pointed out tetrahedral complexes $CoXL_3$ cannot attain closed shells of their valence electrons by adding trimethylphosphine ligands, substitution of the X^- ligand being the only alternative under favorable conditions. On the other hand, they rapidly add carbon monoxide under normal pressure to form diamagnetic carbonyltris(trimethylphosphine)cobalt halides in a first step according to eq 11. Surprisingly, these pentacoordinate monocarbonyl complexes add 1 equiv of trimethylphosphine and, according to eq 12, are converted into ionic carbonyltetrakis(trimethylphosphine)cobalt(I) halides.

$$CoXL_3 + CO \rightarrow CoX(CO)L_3 \quad (11)$$

$$CoX(CO)L_3 + L \rightarrow [Co(CO)L_4]^+X^- \quad (12)$$

$L = (CH_3)_3P$; X = Cl, Br, I

Excess carbon monoxide substitutes a phosphine ligand in a subsequent step according to eq 13. Thus dicarbonylbis(trimethylphosphine)cobalt(I) halides are the final products of the carbonylation of $CoXL_3$ under normal pressure. Since the transfer of CO ligands according to eq 14 is rapid, the preparation of the $CoX(CO)L_3$ (eq 11) is conveniently carried out by combining the two fast reactions according to eq 13 and 14.

$$CoXL_3 + 2CO \rightarrow CoX(CO)_2L_2 + L \quad (13)$$

$$CoXL_3 + CoX(CO)_2L_2 \xrightarrow{+L} 2CoX(CO)L_3 \quad (14)$$

$L = (CH_3)_3P$; X = Cl, Br, I

The lighter halogens are easily replaced by their heavier homologs with LiBr or NaI in THF (eq 15).

$$\left\{\begin{matrix} CoCl(CO)L_3 \\ CoCl(CO)_2L_2 \end{matrix}\right\} + \left\{\begin{matrix} LiBr \\ NaI \end{matrix}\right\} \xrightarrow{THF} \left\{\begin{matrix} CoBr(CO)L_3, CoBr(CO)_2L_2 \\ CoI(CO)L_3, CoI(CO)_2L_2{}^6 \end{matrix}\right\} + \left\{\begin{matrix} LiCl \\ NaCl \end{matrix}\right\} \quad (15)$$

The series of pentacoordinate Co(I) complexes of the general formulas $[Co(CO)_{5-n}L_n]^+$ and $CoX(CO)_{4-n}L_n$, where L is a phosphine ligand, have been prepared from dicobalt octacarbonyl only up to $n = 3$ and $n = 2$, respectively.[8,10] Both series are now complete with $n = 4$ for the cationic species and with $n = 3$ for neutral molecules. They are readily accessible *via* carbonylation of the appropriate trimethylphosphine complexes. Pentacoordinate cobalt(I) cations exclusively substituted by phosphines are formed however when equimolar amounts of trimethylphosphine and dimethylphosphine are added to $CoXL_3$ solutions. The color changes slowly from blue to yellow whereupon a yellow insoluble precipitate is formed according to eq 16. These ionic complexes dissolve in acetone or CH_2Cl_2 and decompose slowly at 20°. In the solid state they are air sensitive but quite stable thermally (Table I). They belong to a type of complexes $[CoL_5]^+X^-$ which is favored by

Table II. Infrared Absorptions of Tetracoordinate Co(I) Complexes (cm^{-1}, Nujol Mull), except for the Regions of Nujol Overlap

$CoClL_3$	$CoBrL_3$	$CoIL_3$	$CoOAcL_3$[a]	CoL_4^+[b]	
2814 m	2811 m	2806 m	2812 m	2810 m	$\nu_s(CH)$
1298 m	1298 m	1298 m	1306 sh	1302 m	$\delta_s(PCH_3)$
			1301 s	1299 sh	
1282 s	1281 s	1284 s	1284 s	1289 s	
		1280 sh			
974 m	971 m	960 sh	968 sh		$\rho_1(PCH_3)$
943 vs	942 vs	935 vs	940 vs	936 vs	
847 w	846 w	838 w	848 m	850 w	$\rho_2(PCH_3)$
			842 sh	842 w	
715 s	715 s	718 s	718 s	705 s	$\nu_{as}(PC_3)$
			700 m	699 sh	
654 s	655 s	657 s	658 s	660 s	$\nu_s(PC_3)$
				654 w	
			385 m		$\nu(CoO)$
343 s	343 s	342 s		344 m	$\delta_s(PC_3)$
306 m			338 s		$\nu(CoCl)$
278 w	255 w		274 w		$\nu(CoP)$ (?)

[a] Acetate absorptions: 1580 vs ($\nu_{as}(CO)$), 1385 vs ($\nu_s(CO)$), 1329 s ($\delta_s(CCH_3)$), 1050 w, 1013 w ($\rho(CCH_3)$), 612 m ($\delta(C_2O_2)$), 300 w. [b] Without tetraphenylborate absorptions.

Table III. Infrared Absorptions of Pentacoordinate Co(I) Complexes (cm^{-1}, Nujol Mull), except for the Regions of Nujol Overlap ($L = (CH_3)_3P$)

$CoCl(CO)L_3$	$CoBr(CO)L_3$	$CoI(CO)L_3$	$CoCl(CO)L_4$	$CoBr(CO)L_4$	$CoI(CO)L_4$	$CoCl(CO)_2L_2$	$CoBr(CO)_2L_2$	$CoI(CO)_2L_2$	Assignment
1877 vs	1872 vs	1882 vs	1901 vs	1908 vs	1909vs	1976 s[a]	1978 s[a]	1980 s[a]	$\nu(CO)$
						1905 vs[a]	1908 vs[a]	1912 vs[a]	
1308 sh	1310 sh	1306 sh	1318 sh	1317 sh	1314 sh	1313 sh			$\delta_s(PCH_3)$
1300 m	1304 s	1301 s	1308 w	1312 w	1309 w	1308 w	1309 w	1308 m	
1286 s	1290 s	1289 s	1296 s	1296 s	1295 s	1294 s	1295 s	1296 s	
1281 sh	1286 sh	1285 s	1286 m	1288 m	1287 m	1288 s	1288 s	1288 s	
1278 m	1280 s	1277 s							
973 sh	973 sh	970 m	987 sh	983 sh	982 sh				$\rho_1(PCH_3)$
941 vs	943 vs	943 vs	955 vs	954 vs	954 vs	945 vs	945 vs	945 vs	
860 m	864 m	867 m	871 m	871 sh	869 sh		860 m	859 m	$\rho_2(PCH_3)$
855 sh	855 m	856 m	865 m	866 m	865 m	861 sh	855 sh	855 sh	
848 m	843 m	845 m	857 sh	857 m	856 sh	857 m			
728 s	725 s	725 s	722 s	723 s	718 s	743 s	743 s	740 s	$\nu_{as}(PC_3)$
723 sh	715 sh	720 sh	717 sh						
711 m	709 m	711 m							
667 s	667 s	667 s	668 s	668 s	666 s	680 s	682 s		$\nu_s(PC_3)$
662 sh	664 sh	662 m				675 s	677 s	675 s	
545 s	547 s	547 s	551 m	546 m	538 s	564 s	567 s	566 s	$\delta(CoCO)$
						553 s	553 m	549 s	
384 s	385 s	382 s	385 m	385 m	385 m	388 m	387 m	387 m	$\delta_s(PC_3)$
364 m	360 m	367 m	342 w, b	342 m, b	340 m				
312 w	310 w, b	310 w	318 w. b	318 w, b	316 w		283 w, b	281 w	$\nu(CoP)$ (?)
268 w						268 m			$\nu(CoCl)$

[a] CH_2Cl_2 solution.

$$CoXL_3 + L + L' \rightarrow [CoL_4L']^+X^- \qquad (16)$$

$L = (CH_3)_3P$; $L' = (CH_3)_2PH$;
$X = Cl, Br$

Co(I) also for $L = P(OR)_3$.[4,8,10] Compared with trimethylphosphine, dimethylphosphine has a similar ligand field strength and a small but in this case decisive steric advantage, which allows us to test the steric and electronic balance of Co(I) in ligand competition reactions.

Infrared Spectra. The infrared data of the new Co(I) complexes (Tables II and III) show several characteristic items connected with the oxidation state and the local geometry. In $CoXL_3$ complexes the number of infrared-active modes of the phosphine ligands is restricted. The $\rho_2(PCH_3)$ absorbs weakly and the $\delta_s(PC_3)$ is shifted to lower wave numbers when compared with those of Table III. In the $\nu(CH)$ region $\nu_s(CH)$ is well separated from the broad Nujol absorption provided CO ligands are absent. $\nu(CoP)$ appears to be inherently weak and is not readily recognized. Only the chloro complexes exhibit a $\nu(CoX)$ absorption above 250 cm^{-1}. In $[CoL_4L']^+$ complexes the dimethylphosphine ligand (=L') is represented by its $\nu(PH)$ at 2278 cm^{-1}.

The $\nu(CO)$ bands of all monocarbonyl complexes appear as strong single absorptions. Dicarbonyl compounds show two bands in solution. Therefore mixtures of structural isomers are not likely to be present.

The ratio of intensities I_{as}/I_s of the antisymmetric and symmetric $\nu(CO)$ frequencies in the $CoX(CO)_2L_2$ complexes are 2.13, 2.40, and 2.14 for the chloro, bromo, and iodo compound, respectively. From these values CO–Co–CO bond angles can be calculated according to a procedure given by Bigorgne.[9] They are 111, 114, and 111°, in the order given above. Thus a trigonal-bipyramidal structure (Chart Ic) with the two phosphine ligands in axial positions is attained in solution according to what has recently been found in related compounds.[10]

In $CoO_2CCH_3L_3$ the difference between the two $\nu(C{=}O)$ absorptions of about 200 cm^{-1} indicates[11] that acetate acts as a unidentate ligand although the high electron density at the Co(I) center lowers both frequencies to an extent that is rarely encountered in covalent metal acetates.

Nmr Spectra. Proton magnetic resonances of all diamagnetic carbonylcobalt(I) complexes consist of only one multiplet in the temperature range between +35 and −80°. These multiplets are characterized by the distance between the intense outer lines corresponding to the totally symmetric transitions in the $(H_9P)_n$ spin systems (Table IV). This can be explained either by a small set of rigid molecular structures or by rapid intramolecular motions of ligands without cleavage of CoP

Table IV. 100-MHz ^1H Nmr Data ($L = (CH_3)_3P$)

Compd	Solvent	T, °C	τ,[a] ppm	N,[b] Hz
$CoCl(CO)L_3$	C_6H_6	30	8.70	8.9
$CoBr(CO)L_3$	C_6H_6	30	8.74	9.0
$CoI(CO)L_3$	C_6H_6	30	8.70	5.4
$[Co(CO)L_4]^+Cl^-$	CH_2Cl_2	0	8.17	6.8
$[Co(CO)L_4]^+I^-$	CH_2Cl_2	0	8.17	6.8
$CoCl(CO)_2L_2$	C_6H_6	30	8.79	9.1
$CoBr(CO)_2L_2$	C_6H_6	30	8.72	8.9
$CoI(CO)_2L_2$	C_6H_6	30	8.60	8.7
$[CoL_4L']^+Br^-$[c]	$(CD_3)_2CO$	−20	(+0.57)[d]	

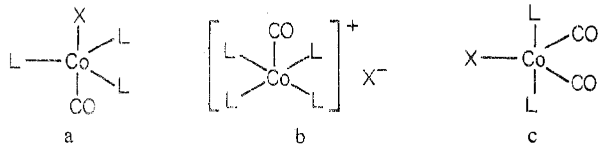
[a] Chemical shifts relative to internal TMS. [b] Peak separations represent $N = |^2J_{PH} + (n-1)^4J_{PH}|$ where n is the number of phosphine ligands. [c] $L' = (CH_3)_2PH$ with $\delta(PH)$[e] −2.70 ppm and $^1J_{PH} = 310$ Hz. [d] Broad singlet; chemical shift relative to acetone-d_5. [e] Chemical shift relative to acetone-d_5.

Table V. 40.5-MHz $\{^1H\}^{31}P$ Nmr Data ($L = (CH_3)_3P$)

Compd	δ,[a] ppm	Compd	δ,[a] ppm
$[Co(CO)L_4]^+Cl^-$	−59.5	$CoBr(CO)L_3$	−68.7[b]
$[Co(CO)L_4]^+I^-$	−61.3	$CoI(CO)L_3$	−67.1[b]
$CoCl(CO)L_3$	−71.6[b]	$CoI(CO)_2L_2$	−85.6

[a] Chemical shifts relative to internal $(CH_3)_3P$ in CH_2Cl_2 solution at −80°. [b] Calculated.

Chart I



a: $X = Cl, Br, I, CH_3$[1]; $L = (CH_3)_3P$

b: $X = Cl, I$; $L = (CH_3)_3P$

c: $X = Cl, Br, I$; $L = (CH_3)_3P$

bonds. Therefore $\{^1H\}^{31}P$ nmr spectra (Table V) at low temperatures[1] are a decisive test. A comparison of activation parameters between $CoCH_3L_4$ and $CoCH_3(CO)L_3$[1] shows that especially with two or more sorts of widely different ligands such as CO, L, or Cl a rigid molecular structure should be attained in solution even at 20°. Since all $\{^1H\}^{31}P$ resonances are singlets at −80°, the probable structures are those given in Chart I.

A successive addition of trimethylphosphine to solutions of $CoCl(CO)L_3$ in CH_2Cl_2 has the following effects. The $\{^1H\}^{31}P$ singlet of $CoCl(CO)L_4$ appears and increases at the expense of the original singlet which finally disappears giving way to the standard signal of free phosphine ligand. A rapid *inter*molecular exchange of phosphine ligands is not observed under these conditions.

In pmr spectra, apart from PCH_3 resonances, dimethylphosphine (=L′) in $[CoL_4L']^+Br^-$ exhibits an *H*–P doublet resonance with $^1J(PH) = 310$ Hz which collapses into a $\{^{31}P\}^1H$ singlet. In ^{31}P nmr spectra of $[CoL_4L']^+X^-$ complexes only one broad signal was obtained.

Experimental Section

Methods and Analyses. Standard high-vacuum techniques were employed in the handling of volatile and air-sensitive materials. The general sequence of operations such as adding a solution under cooling and stirring, removal of insoluble by-products by filtration, evaporating the filtrate *in vacuo*, and crystallization by cooling over a Dry Ice bath were carried out in a bent two-arm glass vessel with a sinter similar to that described earlier by Strohmeier.[12] Combustion analyses were carried out by Mrs. B. Ullrich in our microanalytical laboratory. Molecular masses were determined cryoscopically in benzene under nitrogen and are accurate to ±10%. Melting points and decomposition temperatures were obtained from capillaries under nitrogen and are uncorrected.

Trimethylphosphine was prepared by a recently described new method.[13] Dimethylphosphine was prepared from $(CH_3)_2P(S)$-$P(S)(CH_3)_2$[14] and used as a 1 *M* solution in ether. Other chemicals, with the exception of bulk solvents, were reagent grade. Anhydrous cobalt(II) chloride was obtained from $CoCl_2 \cdot 6H_2O$ (p.a.) by the reaction with excess freshly distilled thionyl chloride and was heated at 150° *in vacuo* before use. Bis(trimethylphosphine)cobalt(II) halides were prepared by Jensen's method.[7]

Spectra. Phosphorus-31 nmr spectra at 40.5 MHz and proton nmr spectra at 60 and 100 MHz were obtained on a Varian T60 and a Varian XL 100 spectrometer, respectively. Magnetic susceptibilities were determined in solution at 30° by the method of Evans[15] using a 10% solution of cyclohexane in benzene as a solvent. These measurements were estimated to be accurate to within ±5% of the μ_{eff} values (Table I).

Preparations and Reactions. Chlorotris(trimethylphosphine)cobalt(I).[1] Tetrakis(trimethylphosphine)cobalt(0)[1] (3.03 g, 8.35 mmol) was added to a suspension of dichlorobis(trimethylphosphine)cobalt(II)[7] (2.35 g, 8.33 mmol) in 50 ml of ether and stirred at 20° for 1 hr. The blue crystals were separated by filtration and washed with two 10-ml portions of ether. The yield was 4.90 g (91%).

Bromotris(trimethylphosphine)cobalt(I). (a) Tetrakis(trimethylphosphine)cobalt(0)[1] (2.00 g, 5.50 mmol) and dibromobis(trimethylphosphine)cobalt(II)[7] (2.04 g, 5.50 mmol) were stirred in 50 ml of ether as above. The solution was cooled to −30°. The blue crystals were separated by filtration and washed with two 10-ml portions of pentane. The yield was 3.84 g (95%).

(b) Methyltetrakis(trimethylphosphine)cobalt(I)[1] (500 mg, 1.32 mmol) and 650 mg of NH_4Br in 50 ml of THF were stirred at ambient temperature for 5 hr. The solvent removed by vacuum distillation at 20° was found to contain trimethylphosphine, identified as $(CH_3)_4P^+I^-$ by its ir spectrum. The blue residue was extracted with ether and the solution was concentrated to 10 ml and cooled to −30°. The blue crystals were isolated as above. The yield was 340 mg (70%). The crystals decompose above 140°.

Anal. Calcd for $C_9H_{27}BrCoP_3$: C, 29.45; H, 7.41. Found: C, 29.21; H, 7.39. Mass spectrum (65°, 70 eV, ^{79}Br): 366 (M^+), 290 ($CoBrL_2^+$), 214 ($CoBrL^+$). Molecule mass: 371 (calcd 367.1).

Iodotris(trimethylphosphine)cobalt(I). (a) Tetrakis(trimethylphosphine)cobalt(0)[1] (2.00 g, 5.50 mmol) and diiodobis(trimethylphosphine)cobalt(II)[7] (2.56 g, 5.50 mmol) in 50 ml of ether were stirred at 20° for 2 hr. The product was isolated as above (method a); yield 4.42 g (97%).

(b) Tetrakis(trimethylphosphine)cobalt(0)[1] (2.00 g, 5.50 mmol) and iodine (2.10 g, 8.25 mmol) were combined in 30 ml of pentane at −50°. The solution was allowed to warm up slowly under stirring. After 24 hr the solution was filtered and the residue was extracted with the same 30 ml of pentane by repeated condensation and filtration. Crystallization at −50° gave 2.20 g (96%) of violet-blue crystals that decompose above 114°. After the extraction, the off-white residue was identified as $(CH_3)_3PI_2$ by its ir spectrum.

Anal. Calcd for $C_9H_{27}CoIP_3$: C, 26.11; H, 6.57. Found: C, 26.08; H, 6.56. Mass spectrum (40°, 70 eV): 414 (M^+), 338 ($CoIL_2^+$), 287 (CoL_3^+), 262 ($CoIL^+$), 211 (CoL_2^+). Molecule mass: 407 (calcd 414.1).

Acetatotris(trimethylphosphine)cobalt(I). A 13.2-ml sample of a 0.1 *M* solution of glacial acetic acid in ether was added to methyltetrakis(trimethylphosphine)cobalt(I)[1] (500 mg, 1.32 mmol) in 30 ml of ether at −50°. When the evolution of gas had ceased, the mixture was slowly warmed up and evaporated to dryness *in vacuo* at −10°. The dark blue residue was dissolved in 50 ml of pentane. Some insoluble impurities were removed by filtration. The dark green solution was kept at −50° overnight. The crystals were isolated as dark blue leaflets (400 mg, 88% yield) that decompose above 135°; mp 48–49° (sealed capillary).

Anal. Calcd for $C_{11}H_{30}CoO_2P_3$: C, 38.16; H, 8.73. Found: C, 38.04; H, 8.68. Molecule mass: 337 (calcd 346.2).

Tetrakis(trimethylphosphine)cobalt(I) Tetraphenylborate. $CoClL_3$[1] ($L = (CH_3)_3P$) (740 mg, 2.29 mmol) and $Na^+B(C_6H_5)_4^-$ (785 mg, 2.29 mmol) were combined in 25 ml of ether containing 0.5 ml of trimethylphosphine (5.26 mmol). The mixture was stirred until the ether was colorless. At −10°, 25 ml of cold acetone was added; the mixture was shaken for 5 sec and filtered rapidly. Further cooling of the green solution yielded green crystals (580 mg, 37%) that decompose above 188°.

Anal. Calcd for $C_{36}H_{56}BCoP_4$: C, 63.36; H, 8.27. Found: C, 62.51; H, 8.02.

Chlorocarbonyltris(trimethylphosphine)cobalt(I). (a) In a closed vessel $CoClL_3$ (720 mg, 2.23 mmol) in 30 ml of ether reacted with 50 ml of CO (2.23 mmol) at ambient temperature for 8 hr. The brown solution was filtered and cooled to −70°. The yield was 735 mg (94%).

(b) A 1.5-ml sample of a 1 *M* solution of L (=$(CH_3)_3P$) in ether was added to a suspension of $CoClL_3$ (480 mg, 1.49 mmol) and $CoCl(CO)_2L_2$ (450 mg, 1.49 mmol) in 30 ml of ether. The reaction mixture was stirred at 30° for 2 hr. A small insoluble portion was removed by filtration. On cooling to −50° wine red crystals were deposited. The yield was 960 mg (92%); mp 76–78°; dec pt >94°.

Anal. Calcd for $C_{10}H_{27}ClCoOP_3$: C, 34.26; H, 7.76. Found: C, 33.81, H, 7.76. Mass spectrum (65°, 70 eV, ^{35}Cl): 274 ($CoCl(CO)L_2^+$), 246 ($CoClL_2^+$).

Bromocarbonyltris(trimethylphosphine)cobalt(I). (a) $CoBrL_3$ (820 mg, 2.23 mmol) was carbonylated as above (method a); yield 810 mg (92%).

(b) $CoCl(CO)L_3$ (350 mg, 1.00 mmol) and excess LiBr (350 mg, 4 mmol) in 20 ml of ether were stirred at ambient temperature for 24 hr. The product was crystallized as described for the chloro complex (method b); yield 360 mg (91%).

(c) $CoBrL_3$ (370 mg, 1.01 mmol) and $CoBr(CO)_2L_2$ (350 mg, 1.01 mmol) in 20 ml of ether containing 1.01 ml of the 1 *M* phosphine solution gave, according to the preparation of $CoCl(CO)L_3$ (method b), 740 mg of red needles (93% yield); dec pt >65°.

Anal. Calcd for $C_{10}H_{27}BrCoOP_3$: C, 30.40; H, 6.89. Found: C, 29.85; H, 6.84. Mass spectrum (65°, 70 eV, ^{79}Br): 366 ($CoBrL_3^+$), 318 ($CoBr(CO)L_2^+$), 290 ($CoBrL_2^+$), 214 ($CoBrL^+$).

Iodocarbonyltris(trimethylphosphine)cobalt(I). (a) $CoIL_3$ (923 mg, 2.23 mmol) was carbonylated as above (method a); yield 900 mg (91%).

(b) $CoCl(CO)L_3$ (390 mg, 1.11 mmol) and excess NaI (1.2 g) in 20 ml of THF were stirred at ambient temperature for 24 hr. The solvent was replaced by 40 ml of pentane. Filtration and crystallization at −30° yielded 440 mg (90%).

(c) From $CoIL_3$ (414 mg, 1.00 mmol) and $CoI(CO)_2L_2$ (394 mg, 1.00 mmol), together with 1.0 ml of the 1 *M* phosphine solution, according to method b, brown-red crystals were obtained; yield 830 mg (94%); mp 130–132°, dec pt >170°.

Anal. Calcd for $C_{10}H_{27}CoIOP_3$: C, 27.17, H, 6.16. Found: C, 26.99; H, 6.15.

Carbonyltetrakis(trimethylphosphine)cobalt(I) Chloride, Bromide, and Iodide. Concentrated solutions of $CoX(CO)L_3$ (X = Cl, Br, I) in ether containing 1 equiv of trimethylphosphine are kept at ambient temperature for 3 days. The supernatant liquor is decanted and the yellow insoluble solid is washed with ether until the solvent is colorless. The product is dried at 20° *in vacuo*; yield 98–100%; dec pt >110° (chloride), >115° (bromide and iodide).

Anal. Calcd for $C_{13}H_{36}ClCoOP_4$: C, 36.59; H, 8.50. Found: C, 36.42; H, 8.41. Calcd for $C_{13}H_{36}BrCoOP_4$: C, 33.14; H, 7.70. Found: C, 32.80; H, 7.60. Calcd for $C_{13}H_{36}CoIOP_4$: C, 30.13; H, 7.00. Found: C, 29.87; H, 6.88.

Chlorodicarbonylbis(trimethylphosphine)cobalt(I). $CoClL_3$ (1.04 g, 3.22 mmol) is dissolved in 30 ml of THF and stirred under 1 atm of CO until the color changes from blue over red to yellow (*ca.* 1 hr). The CO atmosphere is replaced by nitrogen, and the solution is filtered, diluted by adding 30 ml of pentane, and cooled to −50°. The yellow crystals are dried at 20° *in vacuo* for 2 hr; yield 880 mg (90%); dec pt >125°.

Anal. Calcd for $C_8H_{18}ClCoO_2P_2$: C, 31.76; H, 6.00. Found: C, 31.74; H, 5.91. Mass spectrum (50°, 70 eV, ^{35}Cl): 302 (M^+), 274 ($CoCl(CO)L_2^+$), 246 ($CoClL_2^+$), 211 (CoL_2^+), 170 ($CoClL^+$), 135 (CoL^+).

Bromodicarbonylbis(trimethylphosphine)cobalt(I). (a) $CoBrL_3$ (1.1 g, 3.00 mmol) is carbonylated as above; yield 950 mg (91%). (b) $CoCl(CO)_2L_2$ (640 mg, 2.12 mmol) and excess LiBr (500 mg) in 20 ml of THF are stirred at ambient temperature for 20 hr, 80 ml of pentane is added, and the solution is filtered and cooled to −30° to give yellow needles; yield 680 mg (93%); dec pt >175°.

Anal. Calcd for $C_8H_{18}BrCoO_2P_2$: C, 27.69; H, 5.23. Found: C, 27.64; H, 5.03. Mass spectrum (50°, 70 eV, ^{79}Br): 346 (M^+), 318 ($CoBr(CO)L_2^+$), 290 ($CoBrL_2^+$), 214 ($CoBrL^+$), 211 (CoL_2^+).

Iododicarbonylbis(trimethylphosphine)cobalt(I). (a) $CoIL_3$ (970 mg, 2.34 mmol) is carbonylated and crystallized as above; yield 810 mg (88%).

(b) $CoCl(CO)_2L_2$ (413 mg, 1.43 mmol) and excess NaI (1.5 g) in 10 ml THF are stirred as above (method b); yield 490 mg of light brown needles (87%); dec pt >215°.

Anal. Calcd for $C_8H_{18}CoIO_2P_2$: C, 24.39; H, 4.60. Found: C, 24.43; H, 4.49. Mass spectrum (50°, 70 eV): 394 (M^+), 366 ($CoI(CO)L_2^+$), 338 ($CoIL_2^+$), 290 ($CoI(CO)L^+$), 262 ($CoIL^+$), 211 (CoL_2^+), 135 (CoL^+).

Tetrakis(trimethylphosphine)dimethylphosphinecobalt(I) Chloride and Bromide. A 1.00-mmol sample $CoXL_3$ (X = Cl, 323 mg; X = Br, 367 mg) in 40 ml of benzene containing 1.0 ml of a 1 *M* solution of trimethylphosphine and 1.0 ml of a 1 *M* solution of dimethylphosphine in ether were kept at 0° for 24 hr. The orange precipitate was isolated by filtration, washed with pentane until the solvent was colorless, and dried *in vacuo* at 0° for 2 hr. The yield was 320 mg (70%) for X = Cl and 375 mg (74%) for X = Br. Both complex salts can be recrystallized from acetone–ether (1:1) at 0° to give orange needles, the overall yield being 40–50%.

Anal. Calcd for $C_{14}H_{43}ClCoP_5$: C, 36.50; H, 9.41. Found: C, 36.19; H, 9.13. Calcd for $C_{14}H_{43}BrCoP_5$: C, 33.28; H, 8.58. Found: C, 32.20; H, 8.19.

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Registry No. $CoClL_3$, 53432-06-7; $CoBrL_3$, 53432-07-8; $CoIL_3$, 53432-08-9; $CoO_2CCH_3L_3$, 53432-09-0; $[CoL_4][B(C_6H_5)_4]$, 53432-11-4; $CoCl(CO)L_3$, 53432-12-5; $CoBr(CO)L_3$, 53432-13-6; $CoI(CO)L_3$, 53432-14-7; $[Co(CO)L_4]Cl$, 53432-15-8; $[Co(CO)L_4]Br$, 53436-16-9; $[Co(CO)L_4]I$, 53432-17-0; $CoCl(CO)_2L_2$, 53432-18-1; $CoBr(CO)_2L_2$, 53432-19-2; $CoI(CO)_2L_2$, 53495-23-1; $[CoL_4L']Cl$, 53432-20-5; $[CoL_4L']Br$, 53432-21-6; tetrakis(trimethylphosphine)cobalt(0), 33152-37-3; dichlorobis(trimethylphosphine)cobalt(II), 53432-22-7; dibromobis(trimethylphosphine)cobalt(II), 53432-23-8; methyltetrakis(trimethylphosphine)cobalt(I), 53432-25-0; diiodobis(trimethylphosphine)cobalt(II), 53432-24-9; trimethylphosphine, 594-09-2.

References and Notes

(1) H.-F. Klein and H. H. Karsch, *Chem. Ber.*, in press.

(2) A. Yamamoto, S. Kitazume, C. S. Pu, and S. Ikeda, *J. Amer. Chem. Soc.*, **93**, 371 (1971).

(3) M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **3**, 227 (1969).

(4) A recent reinvestigation of the Co^I–$P(OEt)_3$ system[5] has yielded a coordinatively unsaturated $CoClL_3$ (L = $P(OEt)_3$): L. W. Gosser and G. W. Parshall, *Inorg. Chem.*, **13**, 1947 (1974).

(5) M. E. Vol'pin and I. S. Kolomnikov, *Dokl. Akad. Nauk SSSR*, **170**, 1321 (1966).

(6) H.-F. Klein, *Angew. Chem.*, **83**, 363 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 343 (1971).

(7) K. A. Jensen, P. H. Nielsen, and C. T. Petersen, *Acta Chem. Scand.*, **17**, 1115 (1963).

(8) M. S. Arabi, A. Maisonnat, S. Attali, and R. Poilblanc, *J. Organometal. Chem.*, **67**, 109 (1974), and references cited therein.

(9) A. Reckziegel and M. Bigorgne, *J. Organometal. Chem.*, **3**, 341 (1965).

(10) E. Bordignon, U. Croatto, U. Mazzi, and A. A. Orio, *Inorg. Chem.*, **13**, 935 (1974).

(11) G. Winkhaus and P. Ziegler, *Z. Anorg. Allg. Chem.*, **350**, 51 (1967).

(12) W. Strohmeier, *Chem. Ber.*, **88**, 1218 (1955).

(13) W. Wolfsberger and H. Schmidbaur, *Syn. Inorg. Metal.-Org. Chem.*, **4**, 149 (1974).

(14) G. W. Parshall, *Inorg. Syn.*, **11**, 157 (1965).

(15) D. F. Evans, *J. Chem. Soc.*, 2003 (1959); H. P. Fritz and K. E. Schwarzhans, *J. Organometal. Chem.*, **1**, 208 (1964).