Table I. Kinetic and Thermodynamic Data^a for the Reaction (L)Cr(TPP)Cl + X → (X)Cl(TPP)Cl + L

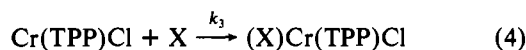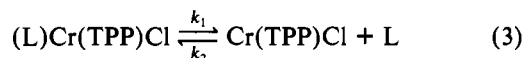| leaving group (L)	10^2 [L]/M	nucleophile (X)	10^2 [X]/M	k_1/s^{-1}	k_3/k_2	log K^b
PPh$_3$	0.46–9.5	MeIm	0.01–1.0	4.6 ± 0.3	1030 ± 200	4.8 ± 0.3
P(OPr)$_3$	9.4	MeIm	0.093–9.3	95 ± 12	24 ± 5	4.1 ± 0.6
P(C$_2$H$_4$CN)$_3$	0.10	MeIm	0.0063–0.63	80 ± 10	~200	5.3 ± 0.5^c
py	10.0	MeIm	1.0–58	5.0 ± 0.8	1.7 ± 0.4	2.5 ± 0.1
PPh$_3$	9.5	py	1.0–50	3.6 ± 0.5	600^d	2.6 ± 0.2
P(OPr)$_3$	9.5	py	1.0–40	90 ± 4	14^d	1.9 ± 0.1
P(C$_2$H$_4$CN)$_3$	0.10	py	0.0063–0.63	90 ± 10		3.1 ± 0.3^c
P(C$_2$H$_4$CN)$_3$	0.10	PPh$_3$	4.6–32	76 ± 15		0.5 ± 0.2

^{a} In toluene at 25 °C; errors are at least one standard deviation. ^{b} Determined from eq 2. ^{c} Calculated from data in this table. ^{d} Calculated by dividing ratio with X = MeIm by 1.7.

metal concentration, which was approximately (1–2) × 10^{-5} M. Pseudo-first-order rate constants, k_{obsd}, were obtained from standard least-squares fitting of ln ($A_\infty - A$) vs. time data.

Results and Discussion

Equilibrium constants for reaction 1 are given in Table I. The spectrophotometric measurements showed that reaction 1 accurately describes the equilibrium with only one axial position being substituted. No evidence was obtained for chloride displacement; e.g., addition of excess PPh$_3$ to Cr(T-PP)Cl followed by addition of py gave the same spectrum as that produced by addition of Cr(TPP)Cl to a solution of py, which is known[5] to yield (py)Cr(TPP)Cl.

Rate constants are given in Table I and representative kinetic plots shown in Figures 1 and 2. The curvature in these plots suggests a simple dissociative reaction mechanism (eq 3 and 4). Applying the usual steady-state approximation to

$$(L)Cr(TPP)Cl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr(TPP)Cl + L \qquad (3)$$

$$Cr(TPP)Cl + X \xrightarrow{k_3} (X)Cr(TPP)Cl \qquad (4)$$

the Cr(TPP)Cl intermediate gives eq 5 and 6. All kinetic

$$k_{obsd} = \frac{k_1 k_3 [X]}{k_2[L] + k_3[X]} \qquad (5)$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{1}{k_1}\left(\frac{k_2}{k_3}\right)\left(\frac{[L]}{[X]}\right) \qquad (6)$$

results were consistent with this mechanism. With MeIm as the nucleophile, double-reciprocal plots of eq 6 gave values for k_3/k_2, which is a measure of the discriminating ability of the five-coordinate Cr(TPP)Cl intermediate. With py as the nucleophile, the observed rate constant k_{obsd} was independent of [L] and [py] at all accessible concentrations, which were constrained because of the magnitude of the equilibrium constant. This simply means that k_3[py] was much greater than k_2[L], so that $k_{obsd} = k_1$. Table I shows that k_1 is nucleophile independent as required by a dissociative mechanism.

The results show that ligands trans to chloride to (L)Cr-(TPP)Cl are clearly labilized compared to those in most reactions of chromium(III).[6] The thermodynamic stability of (L)Cr(TPP)Cl follows the order MeIm > py > P(OPr)$_3$ > PPh$_3$ > P(C$_2$H$_4$CN)$_3$. This is also the order of decreasing proton basicity, and a Brønsted plot of log K vs. pK_a of the nucleophile conjugate acid gives a slope of 0.9 and a correlation coefficient of 0.99. Considering the diversity of nucleophile types, the correlation may be fortuitous in a quantitative sense, but qualitatively it shows that the Cr(III) center is a hard acid and that π bonding involving the ligand L is probably not important. The order of leaving group dissociation (k_1) is P(OPr)$_3$ ≥ P(C$_2$H$_4$CN)$_3$ > py ≥ PPh$_3$ > MeIm (90:80:5:4:0.1). The place of PPh$_3$ in this series is surprising

in view of the stability order. As discussed below, this anomaly is probably steric in origin.

The Cr(TPP)Cl intermediate discriminates among nucleophiles according to MeIm > py > P(OPr)$_3$ > P(C$_2$H$_4$CN)$_3$ > PPh$_3$ (1030:600:40:5:1). Five-coordinate metalloporphyrins, in contrast to other macrocyclic complexes, possess unusual stability and, therefore, selectivity.[2a] The interesting feature here is the inability of phosphorus bases to compete effectively with nitrogen donors, a situation that does not hold[7] with the iron(III) porphyrin Fe(TPP)(HIm)$^+$. The conclusion is that the chromium(III) center is quite hard in Cr(TPP)Cl. As a nucleophile PPh$_3$ is relatively ineffective, yet it is slow to dissociate from (Ph$_3$P)Cr(TPP)Cl. Ineffectiveness as a nucleophile can reasonably be ascribed to a steric barrier encountered as the Cr–PPh$_3$ bond begins to form but before the metal has moved toward the center of the porphyrin core. Movement of the metal approximately into the porphyrin plane would relax the steric interactions. By microscopic reversibility the same steric barrier must be transversed upon PPh$_3$ dissociation, and this would account for the relatively small k_1.

In dry toluene displacement of chloride from (L)Cr(TPP)Cl to yield Cr(TPP)(L$_2$)$^+$, Cl$^-$ was not observed for the nucleophiles in Table I. Lack of chloride dissociation could be due to thermodynamics or due to the poor solvent medium for an ionization process. In acetone, the phosphorus donors (but not the nitrogen donors) displayed biphasic kinetics that may indicate trans activation of chloride in (R$_3$P)Cr(TPP)Cl. Cyanide ion (in acetone) also gave evidence for chloride dissociation. That phosphorus donors would be expected to be much more trans labilizing than nitrogen donors is expected.[2a,7]

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Chemistry of Transition-Metal Phosphine and Phosphite Complexes. 2. Preparation and Properties of XHgCo[P(OC$_6$H$_5$)$_3$]$_3$L

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During the past 30 years there have appeared an astounding number of mercury derivatives of transition-metal carbonyls

Table I. Spectral and Analytical Data

compd	color	mp,[a] °C	% compn			ν(CO), cm⁻¹	
			C	H	X	Nujol mull	THF
ClHgCo[P(OC₆H₅)₃]₄	orange	83–86	calcd 56.20	3.90	2.30		
			obsd 56.04	3.92	2.49		
BrHgCo[P(OC₆H₅)₃]₄	orange	94–96	calcd 54.60	3.79	5.05		
			obsd 54.78	3.90	4.95		
IHgCo[P(OC₆H₅)₃]₄	orange	95–98	calcd 53.05	3.60	7.78		
			obsd 53.79	3.81	7.74		
ClHgCo[P(OC₆H₅)₃]₃(CO)	yellow	109–111	calcd 52.68	3.59	2.83	1968	1967 (br)
			obsd 52.80	3.80	2.59	1973	2004 (sh)
BrHgCo[P(OC₆H₅)₃]₃(CO)	orange	100–105	calcd 50.80	3.46	6.15	1966	1967 (br)
			obsd 50.92	3.72	5.96		2004 (sh)
IHgCo[P(OC₆H₅)₃]₃(CO)	orange	127–130	calcd 49.10	3.35	9.44	1963	1967 (br)
			obsd 48.76	3.39	9.44		2003 (sh)
ClHgCo[P(OC₆H₅)₃]₂(CO)₂	yellow	115–117	calcd 46.93	3.09	3.65	1958	1965 (s)
			obsd 47.16	3.34	3.27	2005	2009 (m)
							2034 (w)
BrHgCo[P(OC₆H₅)₃]₂(CO)₂	yellow	118–119	calcd 45.00	2.95	7.87	1951	1964 (s)
			obsd 44.94	3.10	7.10	2000	2007 (m)
							2033 (w)
BrHgCo[P(OC₆H₅)₃]₃P(OCH₃)₃	yellow	65–70	calcd 49.20	3.87	5.74		
			obsd 49.84	3.98	5.41		

[a] Decomposition accompanied melting in all cases.

of the general type HgM₂, MHgM′, or XHgM, where M and M′ represent metal carbonyl groups, e.g., Mo(CO)₃(η⁵-C₅H₅), Co(CO)₄, etc., and X represents a halide or pseudohalide. For example, Mays and Robb have reported the preparation of the XHgM (where X = Cl, Br, I, or SCN and M = Fe(CO)₂-(η⁵-C₅H₅), Mo(CO)₃(η⁵-C₅H₅), W(CO)₃(η⁵-C₅H₅)) complexes and the MHgM′ (where M = Fe(CO)₂(η⁵-C₅H₅), Mo-(CO)₃(η⁵-C₅H₅), W(CO)₃(η⁵-C₅H₅); M′ = Co(CO)₄) complexes by the exchange reaction between the two symmetrical mercurials HgX₂ and HgM₂.[2] A similar procedure has also been reported for the preparation of the XHgCo(CO)₄ (where X = Cl or Br) complexes.[3,4]

However, the XHgCoL₄ (where L = phosphine or phosphite) complexes have not yet been reported. In fact, the only symmetrical mercurial of this type reported to date is Hg-{Co[P(OCH₃)₃]₄}₂ and it was found to be thermally unstable, decomposing measurably fast at 80 °C.[5,6] Presently, the possibility of the preparation of the XHgCoL₄ complexes by a metathetic exchange between the unknown symmetrical mercurials is not synthetically available.

Mercuric salts, HgX₂, have been known for some time to react with HRhCl₂[As(CH₃)(C₆H₅)₂]₃ to give RhCl₂-(HgX)[As(CH₃)(C₆H₅)₂]₃[7] and with HIrCl₂(CO)[P(C₆H₅)₃]₂ to give IrCl₂(HgX)(CO)[P(C₆H₅)₃]₂.[8] On the other hand only the symmetrical mercurial Hg[Co(CO)₂(PF₃)₂]₂ was reported to be formed when HgCl₂ was reacted with HCo-(CO)₂(PF₃)₂,[9] while HgI₂ did not react with HCo(CO)₂(PF₃)₂ at all.

During the course of our studies on the chemistry of HCoL₃L′ (Where L = phosphite; L′ = phosphite or CO) complexes, we have found that the unsymmetrical mercurials XHgCoL₃L′ could readily be prepared by the reaction between HCoL₃L′ and HgX₂ (where X = Cl, Br, or I) under ambient conditions. Herein, we wish to report the preparation and properties of this new class of complexes.

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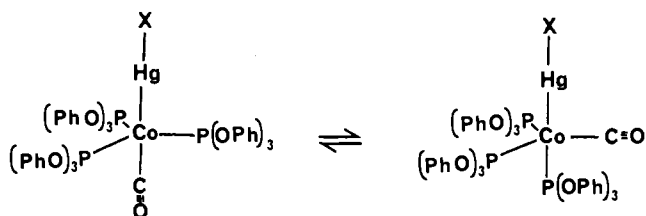(8) Nyholm, R. S.; Vrieze, K. *J. Chem. Soc. A* **1965**, 5337.
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Experimental Section

No precautions were taken to exclude air or moisture from the reaction mixtures or workups unless otherwise specified. The complex HCo[P(OC₆H₅)₃]₄ was prepared by standard literature methods.[10] All other HCoL₃L′ and HCoL₂L′₂ complexes were prepared by standard photochemical methods.[11] All reagents were purchased in their highest purity available and used as received.

Melting points are uncorrected. The infrared spectra were recorded on either a Perkin-Elmer 735B or a Beckman IR12 spectrophotometer. Elemental analyses (see Table I) were performed by Galbraith Laboratories Inc., Knoxville, TN.

Preparation of XHgCo[P(OC₆H₅)₃]₄ and XHgCo[P(OC₆H₅)₃]₃CO Complexes (X = Cl, Br, or I). To a solution containing a 10% molar excess of HgX₂ in 200 mL of acetone was added 2.0 g (1.5 mmol) of HCo[P(OC₆H₅)₃]₄ or 2.0 g (1.96 mmol) of HCo[P(OC₆H₅)₃]₃CO with stirring. The initially light yellow solution became orange-yellow over 10–15 min. The solution was filtered and sufficient water added to cause cloudiness. Removal of the acetone on a water aspirator vacuum gave yellow-orange crystals. Recrystallization of the chloride and iodide complexes from acetone–water and the bromide complexes from benzene–methanol followed by vacuum drying afforded yellow to orange (see Table I) crystalline products (40–90% yields).

Preparation of XHgCo[P(OC₆H₅)₃]₂(CO)₂ Complexes (X = Cl or Br). To a degassed solution of 0.5 g (1.056 mmol) of HgCl₂ in 25 mL of tetrahydrofuran was added a degassed solution of 1.0 g (1.358 mmol) of HCo[P(OC₆H₅)₃]₂(CO)₂ in 25 mL of tetrahydrofuran under a nitrogen atmosphere. The solution turned orange immediately upon mixing. After 15 min of stirring, 10 mL of water was added, the nitrogen atmosphere was discontinued, and the volume reduced on a water aspirator vacuum to yield an orange oil. The orange oil was recrystallized from acetone–pentane to yield fluffy yellow needles of product (0.959 g, 73%).

Preparation of BrHgCo[P(OC₆H₅)₃]₃P(OCH₃)₃. To a solution of 0.70 g (1.94 mmol) of HgBr₂ in 100 mL of acetone was added 2.0 g (1.79 mmol) of HCo[P(OC₆H₅)₃]₃P(OCH₃)₃ with stirring. After 15 min, sufficient water was added to cause cloudiness. Removal of the acetone on a water aspirator vacuum afforded an orange tar. The liquid was decanted and the residue dissolved in 25 mL of acetone. Addition of an equal volume of pentane caused cloudiness, and a white impurity was filtered off. The resulting bright yellow solution was set in a freezer overnight to yield a bright yellow crystalline product (0.70–1.0 g, 28–40%).

Results and Discussion

The XHgCo[P(OC₆H₅)₃]₄ (where X = Cl, Br, or I) complexes have now been prepared by a facile, high-yield synthesis.

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Scheme I

The method involves the direct reaction of the appropriate mercury halide salt with hydridotetrakis(triphenyl phosphite)cobalt(I) in acetone according to reaction 1.

$$HgX_2 + HCoL_3L' \rightarrow XHgCoL_3L' + HX \qquad (1)$$

Although the reaction appears to be the same as that used by MacDiarmid et al.[9] to prepare $Hg[Co(CO)_2(PF_3)_2]_2$, our reactions of $HCo[P(OC_6H_5)_3]_3L$ with mercuric halides provided no evidence for formation of the symmetrical mercurials, $Hg\{Co[P(OC_6H_5)_3]_3L\}_2$, even when large excess of $HCo[P-(OC_6H_5)_3]_3L$ were used. Furthermore, it was reported that $HCo(CO)_2(PF_3)_2$ did not react with HgI_2 and no mention was made of reaction with $HgBr_2$, while we find that both react quickly and cleanly with $HCo[P(OC_6H_5)_3L]_2L$ according to reaction 1.

The yield of $XHgCo[P(OC_6H_5)_3]_4$ was found to be independent of whether or not anaerobic techniques were used. The respective monocarbonyl-substituted $XHgCo[P-(OC_6H_5)_3]_3CO$ complexes were prepared in an analogous manner. The dicarbonyl substituted $XHgCo[P(OC_6H_5)_3]_2-(CO)_2$ complexes were, however, prepared with standard airless ware techniques since the starting hydride $HCo[P(OC_6-H_5)_3]_2(CO)_2$ was extremely air sensitive.[11] All of the resulting mercury salts are yellow to orange, air- and moisture-stable, crystalline solids.

Thermal decomposition occurred during melting (see Table I) for all the reported complexes. The noncarbonyl-containing complexes decomposed slowly even at room temperature; however, all complexes appeared to be stable indefinitely when stored in a freezer.

All of the complexes are highly soluble in benzene, dichloromethane, acetone, and tetrahydrofuran but only sparingly soluble in alcohols and nonhalogenated saturated hydrocarbon solvents. On standing for several hours, solutions of the complexes in chloroform were found to decompose to unidentified products.

The solution infrared of analytically pure samples of the monocarbonyl complexes (e.g., $XHgCo[P(OC_6H_5)_3]_3CO$) all exhibited two carbonyl absorptions (see Table I) of approximately equal intensity. The lower frequency absorption was found to be much broader than the higher frequency absorption. Several possible explanations exist for the two carbonyl stretching frequencies with only one carbonyl group in the molecule. The possibility of the presence of a dimer with halogen bridges between mercury atoms or a molecular dissociation into ionic species was shown to be incompatible with molecular weight determinations in benzene.[12] The results are, in fact, consistent with the presence of undissociated monomers in solution.

A dynamic equilibrium between two isomeric structures with the carbonyl either axial or equatorial to the mercury (Scheme I) seems most consistent with the existing data.[13] It would

be expected that two different carbonyl stretching frequencies would result, one for each isomer since the force constants for the carbonyl bonds in $(C_6H_5)_3PFe(CO)_4$ and $(C_6H_5)_3MCo-(CO)_4$ (where M = Sn or Pb) have been shown to be different for the axial and equatorial carbonyls. Indeed the work of Darensbourg and Darensbourg[14] has clearly shown that the axial carbonyl force constant is consistently larger than the equatorial for $LM(CO)_4$ type molecules. Therefore, one might speculate that the higher frequency absorption ($\sim$2004 cm^{-1}), in our solution spectra, corresponds to the axial isomer while the lower frequency absorption ($\sim$1967 cm^{-1}) is the equatorial isomer.

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Crystal and Molecular Structure of Tris[*P,P,P',P'*-tetraphenylamidobis(phosphine sulfido)-*S,S'*]bismuth(III)

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A number of structural studies have been reported for AX_6E^1 complexes of Pb(II),[2,3] As(III),[4,5] Sb(III),[6–8] Te(IV),[9] Se(IV),[10] and Bi(III).[8,11,12] In some instances, the molecular geometry conforms to VSEPR[13] expectations, whereas in other cases, the geometry is octahedral about the central atom A with no evidence for the nonbonded pair of electrons (E). The lone pair of electrons appears to be stereoactive in structures where X is a hard donor in the HSAB definition[14] or a donor atom associated with a "narrow bite" bidentate ligand such as dialkyldithiocarbamates or alkyl xanthates. On the other hand, the lone pair is stereoinactive in complexes where X is a soft donor as first noted by Wynne.[15]

We have been probing this relationship further by preparing AX_6E complexes in which X is either a hard or soft donor of a bidentate ligand which forms six-membered rings with the central atom. Little structural work has been done with these ligands in hypervalent main-group complexes as the examples cited earlier contain monodentate ligands or bidentate ligands which form four- (narrow bite) or five-membered rings with the central atom.

In this study we present the crystal and molecular geometry of $Bi(SPPh_2NPh_2PS)_3$ which is the first structural example

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