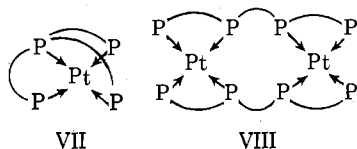


Chelating tetradentate ligands potentially can form tetrahedral platinum(0) derivatives of the type (tetraphos)Pt with all four donor atoms of the ligand bonded to the platinum atom. Such a compound is  $P(-Pf)_3Pt$  (VII) obtained from the chelating tripod tetratertiary phosphine  $P(-Pf)_3$ . The linear tetratertiary phosphine  $Pf-Pf-Pf-Pf$  also forms a zerovalent platinum complex of stoichiometry (tetraphos)Pt, but a solution molecular weight determination indicated it to be the dimeric derivative  $(Pf-Pf-Pf-Pf)_2Pt_2$ . This dimeric derivative can be formulated as VIII.



The zerovalent platinum complexes discussed in this paper were originally prepared for use in oxidative addition reactions. However, up to the present time our attempts to obtain tractable oxidative addition products from these new platinum(0) complexes have given unpromising results. In this connection,  $(cPf=Pf)_2Pt$  was found to be unreactive toward alkynes such as 3-hexyne and phenylacetylene in boiling benzene. Similarly,  $(tPf=Pf)_3Pt$  was unreactive toward air, carbon monoxide (1 atm), carbon disulfide, and 3-hexyne when the reactions were carried out in boiling benzene. Even

when reactions took place (as was the case when some of the zerovalent platinum complexes were treated with dimethyl acetylenedicarboxylate or diethyl azodicarboxylate in boiling benzene), the resulting products did not correspond to obvious stoichiometries and could not be unambiguously characterized by the techniques currently available in our laboratory.

Platinum(II) complexes of the ligands  $Pf-Pf-Pf$ ,<sup>22</sup>  $P(-Pf)_3$ ,<sup>13</sup> and  $Pf-Pf-Pf-Pf$ <sup>13</sup> have been reported in the cited papers. However, platinum(II) complexes of the unsaturated ditertiary phosphines  $cPf=Pf$  and  $tPf=Pf$  have not previously been described. The Experimental Section of this paper describes for the first time the preparation and characterization of the platinum(II) complexes  $(cPf=Pf)PtCl_2$  and  $[(tPf=Pf)_4Pt_2][PF_6]_4$ . The formulations and properties of these platinum(II) complexes of the cis and trans isomers of  $(C_6H_5)_2PCH=CHP(C_6H_5)_2$  correspond completely to the reported<sup>23</sup> platinum(II) complexes of the cis and trans isomers of the closely related olefinic ditertiary arsine  $(CH_3)_2AsCH=CHAs(CH_3)_2$ .

**Acknowledgment.**—We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-71-2000.

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## Reactions of Halides, Amines, and Organometallic Lewis Bases with Bis(tetracarbonylcobalt)mercury(II)

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Bis(tetracarbonylcobalt)mercury(II) reacts with bidentate nitrogen ligands giving the complexes  $(L-L)Hg[Co(CO)_4]$  where  $L-L = 1,10$ -phenanthroline or 2,2'-bipyridyl. With  $Co(CO)_4^-$  or halide,  $Hg[Co(CO)_4]$  forms the three-coordinate species  $XHg[Co(CO)_4]_2^-$  where  $X^- = \text{halide or } Co(CO)_4^-$ . No reaction is observed between  $Hg[Co(CO)_4]_2$  and the neutral organometallic Lewis bases (mesitylene)Mo(CO)<sub>3</sub>, Fe(CO)<sub>5</sub>, Fe(CO)<sub>3</sub>[PPh<sub>3</sub>]<sub>2</sub>, and Fe(CO)<sub>4</sub>AsPh<sub>3</sub>. Neither amines, halides,  $Co(CO)_4^-$ , nor the neutral organometallic bases react with  $Hg[Mn(CO)_5]_2$ ,  $Hg[(\pi-C_5H_5)Mo(CO)_3]_2$ , or  $Hg[(\pi-C_5H_5)Fe(CO)_2]_2$ . The Lewis acidity of mercury in  $HgR_2$  depends greatly on the nature of the metal carbonyl groups, R, bonded to it. With strongly basic carbonyl groups mercury is a weak Lewis acid while with less basic metal carbonyl substituents its Lewis acidity is increased.

### Introduction

Of the group IIb-transition metal carbonyl derivatives, the zinc and cadmium compounds readily add additional ligands giving three- or four-coordinate complexes.  $M[Mn(CO)_5]_2$  (M = Zn, Cd),  $Cd[(\pi-C_5H_5)Mo(CO)_3]_2$ ,<sup>2</sup> and  $Cd[(\pi-C_5H_5)W(CO)_3]_2$ ,<sup>2</sup> for example, add two monodentate nitrogen ligands or a bidentate nitrogen ligand such as 2,2'-bipyridyl.  $ICd[(\pi-C_5H_5)Mo(CO)_3]$  and  $Cd[(\pi-C_5H_5)Mo(CO)_3]_2$  react<sup>2</sup> with iodide giving anions which may be analogous to  $Br_2Cd[Co(CO)_4]^-$  which forms<sup>3</sup> from the reaction of  $Co(CO)_4^-$  with  $CdBr_2$ .

The corresponding mercury compounds in general appear to be less reactive with no reaction of  $Hg[Mn(CO)_5]_2$ ,<sup>1</sup>  $Hg[(\pi-C_5H_5)M(CO)_3]_2$  (M = Mo, W), or  $Hg[(\pi-C_5H_5)Fe(CO)_2]_2$ <sup>2</sup> observed with nitrogen ligands.  $IHg[(\pi-C_5H_5)Mo(CO)_3]$  and  $Hg[(\pi-C_5H_5)Mo(CO)_3]_2$  did not react<sup>2</sup> with iodide. However, a few indications that the mercury in mercury-transition metal carbonyl derivatives may be active as a Lewis acid have been reported. An expanded coordination number about mercury has been observed in the crystal structure<sup>4</sup> of  $Fe(CO)_4(HgCl)_2 \cdot 2py$ . The addition of halide to  $Fe(CO)_4(HgX)_2$ <sup>5</sup> may result from coordination of the

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TABLE I  
 ANALYSES OF COMPOUNDS PREPARED

Compound	Color	Mp, °C	% compn									
			C		H		Hg		N		Halide	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[Fe(1,10-phen) <sub>3</sub> ][HgCo <sub>2</sub> (CO) <sub>12</sub> ] <sub>2</sub>	Dark red	124–127	35.4	35.6	1.18	1.40	19.8	20.1	4.13	4.16		
[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As][HgCo <sub>2</sub> (CO) <sub>12</sub> ]	Red-brown	...	39.3	39.2	1.86	1.89	18.8	18.9				
[(C <sub>7</sub> H <sub>7</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P][ClHgCo <sub>2</sub> (CO) <sub>8</sub> ]	Yellow	104	42.6	42.4	2.36	2.31	21.6	21.5			3.82	3.72
[(C <sub>7</sub> H <sub>7</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P][BrHgCo <sub>2</sub> (CO) <sub>8</sub> ]	Yellow-brown	112–115	40.6	40.7	2.26	2.28	20.6	20.8				
[(C <sub>7</sub> H <sub>7</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P][IHgCo <sub>2</sub> (CO) <sub>8</sub> ]	Brown	107–108	38.7	38.7	2.15	2.23	19.6	19.5				
ClHgCo(CO) <sub>4</sub>	Lemon yellow	102–104 105–107 <sup>a</sup>	11.8	11.7	0	0	49.3	49.5				
BrHgCo(CO) <sub>4</sub>	Orange	102–105	10.6	10.4	0	0	44.5	44.7				
(1,10-phen)HgCo <sub>2</sub> (CO) <sub>8</sub>	Orange	121–124	33.2	33.0	1.11	1.36	27.8	28.0	3.87	4.07		
(2,2'-bipy)HgCo <sub>2</sub> (CO) <sub>8</sub>	Orange	111–114	30.9	31.1	1.15	1.35	28.7	28.7	4.02	4.14		

<sup>a</sup> F. Bonati, S. Cenini, and R. Ugo, *J. Chem. Soc. A*, 932 (1967).

halide to the mercury. Co(CO)<sub>4</sub><sup>-</sup> reacts<sup>6</sup> with Hg[Co(CO)<sub>4</sub>]<sub>2</sub> and (π-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub><sup>-</sup> reacts<sup>7</sup> with Hg[(π-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub> giving three-coordinate Hg(II) complexes. Hg[Co(CO)<sub>4</sub>]<sub>2</sub> has been reported<sup>8</sup> to react with bromide and a chloride adduct of this compound has been isolated.<sup>6</sup>

We now wish to report the characterization of the halide adducts of Hg[Co(CO)<sub>4</sub>]<sub>2</sub> as well as the results of the reaction of a number of neutral Lewis bases and transition metal carbonylate anions with mercury-transition metal carbonyls. The formation of mercury complexes in these systems is related to the base strength of both the metal carbonyl group and the entering ligand.

### Experimental Section

All reactions and purifications were carried out under nitrogen with deoxygenated solvents. Elemental analyses (Table I) were performed by Dr. C. S. Yeh and her staff at the Purdue Microanalytical Laboratory. Mesitylenemolybdenum tricarbonyl,<sup>9</sup> triphenylarsineiron tetracarbonyl,<sup>10</sup> bis(triphenylphosphine)iron tricarbonyl,<sup>10</sup> bis(tetracarbonylcobalt)mercury,<sup>11</sup> bis(pentacarbonylmanganese)mercury,<sup>12</sup> bis(cyclopentadienylmolybdenum tricarbonyl)mercury,<sup>13</sup> bis(cyclopentadienyliron dicarbonyl)mercury,<sup>14</sup> (cobalt tetracarbonyl)(cyclopentadienyliron dicarbonyl)mercury,<sup>15</sup> and (cobalt tetracarbonyl)(cyclopentadienylmolybdenum tricarbonyl)mercury<sup>16</sup> were prepared by reported methods. Solutions of metal carbonyl anions were prepared by the reaction of the required amount of the parent carbonyl with an excess of a 5% sodium amalgam.

Infrared spectra in the 4000–700-cm<sup>-1</sup> range were obtained using a Perkin-Elmer 221 spectrometer equipped with NaCl optics and a 0.025-mm CaF<sub>2</sub> cell. Far-infrared spectra of Nujol mulls were obtained with polyethylene cells using a Beckman IR-11.

**Preparation of Salts of Hg[Co(CO)<sub>4</sub>]<sub>2</sub><sup>-</sup>.**—The anion was prepared in either of two ways. (A) A solution of 8.2 mmol of NaCo(CO)<sub>4</sub> (prepared by reaction of 1.4 g of Co<sub>2</sub>(CO)<sub>8</sub> with an excess of sodium amalgam) in 10 ml of tetrahydrofuran (THF) was filtered into 15 ml of a THF solution of 4.45 g (8.2 mmol) of Hg[Co(CO)<sub>4</sub>]<sub>2</sub>. The yellow solutions turned a deep reddish brown upon mixing. (B) To a solution of 6.65 g (12.3 mmol) of Hg[Co(CO)<sub>4</sub>]<sub>2</sub> in 20 ml of THF was added 0.4 ml of a 5% sodium

amalgam (8.2 g-atom of Na). Following 2–3 hr of stirring, an infrared spectrum of the solution showed that Hg[Co(CO)<sub>4</sub>]<sub>3</sub><sup>-</sup> was the principal species present.

Addition of either of the above THF solutions to 4.1 mmol of tris(1,10-phenanthroline)iron(II) sulfate in 50 ml of water produced a red oil which crystallized upon extraction with 200 ml of water. This red solid was recrystallized from ethanol with water giving fine dark red crystals of [Fe(1,10-phen)<sub>3</sub>][HgCo<sub>2</sub>(CO)<sub>12</sub>]<sub>2</sub>. The tetraphenylarsonium salt of Hg[Co(CO)<sub>4</sub>]<sub>3</sub><sup>-</sup> was prepared by the same technique using an equivalent amount of tetraphenylarsonium acetate in 100 ml of water in place of the solution of the iron compound. Yields were greater than 90% for either preparation.

**Preparation of [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]{XHg[Co(CO)<sub>4</sub>]<sub>2</sub>}** (X = Cl, Br, I).—To an orange solution of 1.4 g (2.6 mmol) of Hg[Co(CO)<sub>4</sub>]<sub>2</sub> in 10 ml of CHCl<sub>3</sub> at -50° was added 0.9 g (2.3 mmol) of benzyltriphenylphosphonium chloride. The orange solution instantly turned deep red, and the Hg[Co(CO)<sub>4</sub>]<sub>2</sub> which had precipitated upon cooling to -50° dissolved rapidly. After 2–3 min of stirring, 20 ml of pentane was added causing immediate precipitation of a yellow solid. This solid was filtered from the solution, washed with two 20-ml portions of pentane to remove excess Hg[Co(CO)<sub>4</sub>]<sub>2</sub>, and then vacuum dried at room temperature. The yield was 100% based on the chloride. Preparations of the bromide and iodide complexes were carried out in an identical fashion with 100% yields of the yellow-brown bromide and brown iodide salts being recovered.

Since solutions of XHg[Co(CO)<sub>4</sub>]<sub>2</sub><sup>-</sup> decompose upon standing, immediate isolation of the product was necessary in order to obtain a pure material. A solution of the benzyltriphenylphosphonium salt of the chloro anion, M{ClHg[Co(CO)<sub>4</sub>]<sub>2</sub>}, in tetrahydrofuran produced a small amount of gray powder, a white precipitate, and blue crystals after standing under nitrogen for 16 hr. The gray powder was insoluble in organic solvents, water, aqueous ammonia, and dilute hydrochloric acid but reacted with nitric acid to give a solution which showed a positive qualitative test for mercury and no test for chloride. The white precipitate was identified as MHgCl<sub>3</sub> by comparison of its melting point with that of an authentic sample. Qualitative tests showed the white precipitate contained both Hg and Cl. The blue crystals contain Co but no Hg. A C and H analysis suggested an empirical formula for M<sub>3</sub>Co<sub>2</sub>Cl<sub>7</sub> for these crystals.

The reaction of halides with Hg[(π-C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>]<sub>2</sub>, Hg[Mn(CO)<sub>5</sub>]<sub>2</sub>, and Hg[(π-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub> under conditions similar to those for the preparation of XHg[Co(CO)<sub>4</sub>]<sub>2</sub><sup>-</sup> produced no halo anions.

**Preparation of (1,10-phen)Hg[Co(CO)<sub>4</sub>]<sub>2</sub>.**—To a solution of 1.35 g (2.5 mmol) of Hg[Co(CO)<sub>4</sub>]<sub>2</sub> in 10 ml of absolute ethanol was added 0.5 g (2.5 mmol) of 1,10-phenanthroline in 10 ml of absolute ethanol. The orange compound began to precipitate immediately. After 10 min, the solution was filtered and the solid was washed with 50 ml of pentane and dried under vacuum at room temperature. The yield was 66%.

**Preparation of (bipy)Hg[Co(CO)<sub>4</sub>]<sub>2</sub>.**—To a solution of 1.04 g (1.92 mmol) of Hg[Co(CO)<sub>4</sub>]<sub>2</sub> in 20 ml of absolute ethanol was added 0.3 g (1.9 mmol) of solid 2,2'-bipyridyl. After 10 min of stirring, the orange compound was precipitated by addition of 100 ml of water. The filtered solid was recrystallized from acetone by addition of water, and the dried material was washed with 50 ml of pentane and dried under vacuum at room temperature. The yield was 90%.

**Preparation of XHgCo(CO)<sub>4</sub>** (X = Cl, Br).—To a stirred

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solution of 1.0 g (1.8 mmol) of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and 0.5 g (1.8 mmol) of  $\text{HgCl}_2$  in 20 ml of acetone was added 10 ml of water. The acetone was removed under the vacuum produced by a water aspirator leaving fine yellow crystals in the water. These crystals were filtered, sucked dry, and then washed with several 20-ml portions of pentane to remove any remaining  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ . The yield was 90%. An identical procedure was used to prepare orange crystals of  $\text{BrHgCo}(\text{CO})_4$  in 90% yield. Use of  $\text{HgI}_2$  in this procedure produced only impure  $\text{IHgCo}(\text{CO})_4$ .

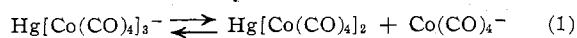
**Reaction of  $\text{XHgCo}(\text{CO})_4$  with  $\text{Co}(\text{CO})_4^-$ .**—The reaction of  $[(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_5)_3\text{P}][\text{Co}(\text{CO})_4]$  with  $\text{XHgCo}_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ) under the conditions described for the preparation of  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  produced a complex mixture.  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  was sublimed from the crude mixture and identified by its infrared spectrum and melting point. Fractional crystallization from chloroform produced two solids which were identified as benzyltriphenylphosphonium salts of  $\text{HgX}_3^-$  and  $\text{X}^-$  by comparison of their melting points and infrared spectra with those of authentic samples. Infrared spectra of the remaining chloroform showed features characteristic of  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  as the only carbonyl-containing species remaining in solution.

**Reactions of Mercury-Transition Metal Carbonyls with Lewis Bases.**—Equivalent amounts of the mercury-transition metal carbonyl and base were dissolved in deoxygenated solvents at room temperature. Concentrations were about 0.1 M with ethanol, tetrahydrofuran, chloroform, and dichloromethane as solvents. Since  $\text{Hg}[\text{Mn}(\text{CO})_5]_2$  is insoluble in these solvents, reactions of this carbonyl were heterogeneous. The resulting solutions were examined by infrared spectroscopy in order to determine if reaction had occurred. No reaction was observed with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ ,  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ ,  $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ , or  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and the following bases:  $\text{Fe}(\text{CO})_5$ ,  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Fe}(\text{CO})_3$ ,  $(\text{C}_6\text{H}_5)_3\text{AsFe}(\text{CO})_4$ , (mesitylene) $\text{Mo}(\text{CO})_3$ , *p*-dithiane. With the exception of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ , no reaction of the mercury compounds with 1,10-phenanthroline, 2,2'-bipyridyl, or halide was observed. Of the symmetrical mercury-metal carbonyls noted above,  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]\text{Hg}[\text{Co}(\text{CO})_4]$ , and  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{Hg}[\text{Co}(\text{CO})_4]$ , only  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  reacted with  $\text{Co}(\text{CO})_4^-$ . Neither  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$  nor  $\text{Mn}(\text{CO})_5^-$  reacted with the symmetrical carbonyls, although  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$  displaced  $\text{Co}(\text{CO})_4^-$  from the asymmetrical mercury compounds. The reaction of  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$  with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and the asymmetrical carbonyls resulted in displacement of  $\text{Co}(\text{CO})_4^-$ . With  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ ,  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$  displaced  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$  producing  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ .

## Results and Discussion

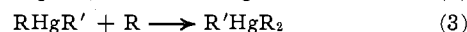
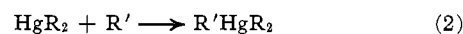
**Reactions with Metal Carbonyls.**—The reaction of a stoichiometric amount of sodium or of  $\text{Co}(\text{CO})_4^-$  with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  produces the anion  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  which can be isolated<sup>6</sup> with large cations such as the tetraphenylarsonium ion or tris(1,10-phenanthroline)-iron(II). A similar reaction between  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$  and  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  has been reported<sup>7</sup> and confirmed by our observations, although no corresponding reaction of  $\text{Mn}(\text{CO})_5^-$  with  $\text{Hg}[\text{Mn}(\text{CO})_5]_2$  or of  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$  with  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  was observed.

Characterization of  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  as a trigonal-planar species which undergoes limited dissociation in tetrahydrofuran solution according to eq 1 has been



reported.<sup>6</sup> We have observed that this dissociation is solvent dependent with the extent of dissociation increasing as the polarity of the solvent increases in the order  $\text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{THF} < \text{CH}_3\text{CN} < \text{DMF} < \text{DMSO}$ . In dichloromethane, only traces of  $\text{Co}(\text{CO})_4^-$  and  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  are observed in the infrared spectrum of the solution, while in DMSO, roughly equivalent amounts of the three species are observed.

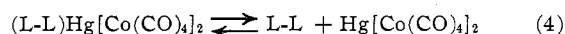
Preparation of mixed-metal complexes of mercury by reaction 2 or 3 in which R and R' were transition



metal carbonyl anions generally were not successful. When R' in reaction 2 was a weaker base than R, no reaction was observed. When R' was a much stronger base than R, the mixed metal complex  $\text{RHgR}'$  was formed. The order of increasing basicity of the transition metal carbonylate anions studied is  $\text{Co}(\text{CO})_4^- < (\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^- < \text{Mn}(\text{CO})_5^- < (\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$ .<sup>16</sup> Thus, mixing solutions of  $\text{Co}(\text{CO})_4^-$  or  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$  with  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  produced no reaction while the reaction of  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$  with  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  produced  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$  and  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]$ ,<sup>15</sup> and the reaction of  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$  with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  produced  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{Hg}[\text{Co}(\text{CO})_4]$ <sup>15,17</sup> and  $\text{Co}(\text{CO})_4^-$ . When R' was the weaker base in reaction 3, the reaction produced the symmetrical product  $\text{RHgR}$ , and when R' was a stronger base than R in reaction 3, no complex was formed.

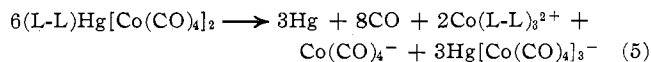
The very weak Lewis bases  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3$ ,  $\text{Fe}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ , and (mesitylene) $\text{Mo}(\text{CO})_3$  form adducts with neither  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ ,  $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ ,  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ , nor  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ , although complexes of these compounds with mercuric halides have been reported.<sup>18,19</sup>

**Reactions with Amines.**—The Lewis bases 2,2'-bipyridyl and 1,10-phenanthroline react with bis(tetracarbonyl-cobalt)mercury giving the yellow crystalline complexes  $(\text{L-L})\text{Hg}[\text{Co}(\text{CO})_4]_2$  where L-L is one of the bidentate ligands. Both complexes are soluble in most polar organic solvents, and both the crystalline solids and their solutions are stable in air for short periods. The presence of strong absorptions due to  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  in their infrared spectra (Table II) indicates the dissociation of these complexes in solution according to eq 4 is quite extensive and that the bidentate ligands are



poor Lewis bases with respect to the mercury in this system. Addition of excess ligand to solutions of  $(\text{L-L})\text{Hg}[\text{Co}(\text{CO})_4]_2$  shifts the equilibrium of eq 4 to the left.

Solutions of these complexes decompose slowly upon standing under nitrogen with the formation of elemental mercury,  $\text{Co}(\text{CO})_4^-$ , and  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$ . The reaction appears similar to that<sup>20,21</sup> of pyridine or ammonia with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and may be described by



Although bipyridyl and phenanthroline form complexes with mercuric halides,<sup>22</sup> they do not react with mercury-transition metal carbonyls other than  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ . Apparently these ligands complex only those mercury(II) compounds in which the mercury is not bonded to a strong Lewis base.

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TABLE II  
 INFRARED SPECTRA OF  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  AND DERIVATIVES

Species	Solvent	Ir spectra, $\text{cm}^{-1}$
$\text{Hg}[\text{Co}(\text{CO})_4]_2$	THF	2072 (s), 2022 (w), 2007 (vs)
$\text{Hg}[\text{Co}(\text{CO})_4]_3^-$ <sup>a</sup>	THF	2071 (vw), <sup>b</sup> 2063 (w), 2041 (s), 2007 (vw), <sup>b</sup> 1973 (vs), 1896 (w) <sup>c</sup>
$\text{bipyHg}[\text{Co}(\text{CO})_4]_2$	$\text{CHCl}_3$	2078 (s), <sup>b</sup> 2058 (m), 2009 (vs), <sup>b</sup> 1985 (s)
$\text{phenHg}[\text{Co}(\text{CO})_4]_2$	$\text{CHCl}_3$	2075 (m), <sup>b</sup> 2056 (s), 2005 (s), <sup>b</sup> 1983 (vs)
$\text{ClHg}[\text{Co}(\text{CO})_4]_2^-$ <sup>d</sup>	$\text{CH}_2\text{Cl}_2$	2076 (w), 2053 (s), 2003 (w, sh), 1984 (vs)
	THF	2075 (w), 2051 (s), 1979 (vs), 1896 (vw) <sup>c</sup>
	DMF	2072 (w), 2050 (s), 1976 (vs), 1898 (w) <sup>c</sup>
$\text{BrHg}[\text{Co}(\text{CO})_4]_2^-$ <sup>d</sup>	$\text{CH}_2\text{Cl}_2$	2075 (w), 2050 (s), 2008 (w, sh), 1980 (vs)
	THF	2071 (w), 2048 (s), 1979 (vs), 1896 (vw) <sup>c</sup>
	DMF	2072 (w), 2049 (s), 1977 (vs), 1897 (w) <sup>c</sup>
$\text{IHg}[\text{Co}(\text{CO})_4]_2^-$ <sup>d</sup>	$\text{CH}_2\text{Cl}_2$	2071 (w), 2048 (s), 2007 (w, sh), 1977 (vs), 1898 (vw) <sup>c</sup>
	THF	2067 (w), 2044 (s), 1974 (vs), 1896 (w) <sup>c</sup>
	DMF	2068 (w), 2048 (s), 1974 (vs), 1897 (mw) <sup>c</sup>
$\text{ClHgCo}(\text{CO})_4$	THF	2093 (m), 2069 (m), 2005 (vs)
$\text{BrHgCo}(\text{CO})_4$	THF	2093 (m), 2072 (m), 2003 (vs)

<sup>a</sup> As  $\text{As}(\text{C}_6\text{H}_5)_4^+$  salt. <sup>b</sup> Peak due to  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ . <sup>c</sup> Peak due to  $\text{Co}(\text{CO})_4^-$ . <sup>d</sup> As  $[\text{C}_6\text{H}_5\text{CH}_2(\text{C}_6\text{H}_5)_3]\text{P}^+$  salt.

**Reactions with Halides.**—Mixing of a colorless solution of lithium bromide and a yellow solution of bis(tetracarbonylcobalt)mercury in tetrahydrofuran produced an immediate color change giving a dark red solution. The similarity of the infrared spectrum of  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  in the carbonyl region to that of the dark red solution containing a 1:1 ratio of lithium bromide to bis(tetracarbonylcobalt)mercury suggested that the bromide ion was adding to the mercury to give the anion  $\text{BrHg}[\text{Co}(\text{CO})_4]_2^-$ . Addition of excess bromide resulted in incomplete displacement of tetracarbonylcobaltate anions as indicated by the increase in intensity of the  $\text{Co}(\text{CO})_4^-$  absorption at  $1896\text{ cm}^{-1}$ . No peaks attributable to a dianion  $\text{Br}_2\text{Hg}[\text{Co}(\text{CO})_4]_2^{2-}$  were observed with an excess of bromide.

Although evaporation of a tetrahydrofuran solution of a 1:1 mixture of lithium bromide and bis(tetracarbonylcobalt)mercury yielded only the starting materials, salts of  $\text{BrHg}[\text{Co}(\text{CO})_4]_2^-$  as well as of the chloro and iodide derivatives could be isolated with large cations,  $\text{M}^+$ , such as the tetraphenylarsonium or benzyltriphenylphosphonium ions. Addition of MX (where X = Cl, Br, or I) to a chloroform solution of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  at  $-50^\circ$  produced an immediate color change from yellow to deep red. Addition of cold pentane precipitated the yellow to brown solids  $\text{M}\{\text{XHg}[\text{Co}(\text{CO})_4]_2\}$  as fine crystalline powders. Since solutions of  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  decomposed upon standing, these materials were isolated promptly (3–5 min) after mixing of the reactants. Longer reaction times or reaction at room temperature consistently gave impure materials.

Solid salts of the yellow chloro-, yellow-brown bromo-, and brown iodobis(tetracarbonylcobaltato)mercurate(II) can be handled in air for short periods (10–15 min) without apparent decomposition, although, even when stored under nitrogen in the dark, the solids de-

compose over a period of months giving green decomposition products which were not characterized. The compounds are soluble in polar organic solvents giving solutions from which elemental mercury as well as halomercurate(II) and halocobaltate(II) species began to precipitate within 5 min at room temperature. The solutions are stable for somewhat longer periods at depressed temperatures. The precipitate from a tetrahydrofuran solution of benzyltriphenylphosphonium chlorobis(tetracarbonylcobaltato)mercurate(II),  $\text{M}\{\text{ClHg}[\text{Co}(\text{CO})_4]_2\}$ , allowed to stand under nitrogen for 16 hr, was identified as a mixture of elemental mercury,  $\text{MHgCl}_3$ , and  $\text{M}_3\text{Co}_2\text{Cl}_7$ . The solution showed spectra characteristic of  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$ .

Attempted reactions of MX with  $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ ,  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ , and  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  gave only the starting materials. Solutions of  $\text{X}^-$  with these mercury-metal carbonyls showed no infrared peaks attributable to formation of halo anions.

The far-infrared spectra of the halo anions all contain two peaks at about  $151$  and  $158\text{ cm}^{-1}$ . Additionally, a third peak is observed at  $200$ ,  $135$ , and  $114\text{ cm}^{-1}$  in the spectra of the chloro, bromo, and iodo anions, respectively. These spectra, as well as the spectra in the CO region, are consistent with a trigonal coordination of the mercury(II) ion by one halide and two  $\text{Co}(\text{CO})_4$  groups. The peaks at  $151$  and  $158\text{ cm}^{-1}$  can be assigned to the infrared-active symmetric and antisymmetric  $\text{HgCo}_2$  stretching modes while the third peak can be assigned to a  $\text{Hg-X}$  stretching mode. Metal-metal vibrations in compounds of this type have been shown to be relatively insensitive to changes in the halide. In  $\text{X}_2\text{Sn}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ,<sup>23</sup> for example, the Sn-Fe modes in the chloro, bromo, and iodo compounds do not differ by more than  $3\text{ cm}^{-1}$ .

The infrared spectra of the halo anions in the CO stretching region are reported in Table II. Since solutions of these anions decompose upon standing, the infrared spectra were run immediately after the solutions were prepared (1–2 min). The weak peaks which appear at about  $1896\text{ cm}^{-1}$  in the more polar solvents may be attributed to small amounts of  $\text{Co}(\text{CO})_4^-$ .

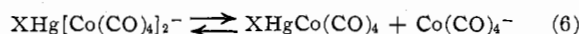
The reaction producing  $\text{Co}(\text{CO})_4^-$  from  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  is solvent and halide dependent. In spectra of the solids in Nujol, no  $\text{Co}(\text{CO})_4^-$  peak is observed, and for a given halo anion, the intensity of the  $\text{Co}(\text{CO})_4^-$  peak increases with the polarity of the solvent. The spectra of  $\text{ClHg}[\text{Co}(\text{CO})_4]_2^-$ , for example, exhibit no  $1896\text{-cm}^{-1}$  peak with dichloromethane or chloroform solutions, a very weak peak with a THF solution, and a weak peak with a dimethylformamide solution. In a given solvent, the intensity of the  $1896\text{-cm}^{-1}$  peak in the spectra of  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  increases in the order  $\text{Cl} < \text{Br} < \text{I}$ , although the amount of  $\text{Co}(\text{CO})_4^-$  present is small in all cases.

This dissociation of  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  appears similar to that of  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  which has been shown to dissociate in a solvent-dependent equilibrium giving  $\text{Co}(\text{CO})_4^-$  and  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  according to eq 1. The increasing dissociation of the halo anions as the halide varies from chloride to iodide is similar to the dissociation<sup>24</sup> of  $(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2\text{HgX}_2$  into  $(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$

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(24) D. J. Cook, J. L. Dawes, and R. D. W. Kemmitt, *ibid.*, 1547 (1967).

and  $\text{HgX}_2$ . This latter equilibrium also increases in the order  $\text{Cl} < \text{Br} < \text{I}$ . In view of these considerations, one is tempted to attribute the presence of  $\text{Co}(\text{CO})_4^-$  in solutions of  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  to the equilibrium



Failure to observe the spectrum of  $\text{XHgCo}(\text{CO})_4$  in the infrared spectrum of dissociated  $\text{XHgCo}(\text{CO})_4$  is not surprising since only small amounts of  $\text{XHgCo}(\text{CO})_4$  would be formed and the weak ir peaks of this compound would be masked by the broad peaks of the halo anion. However, in view of the failure of  $\text{XHgCo}(\text{CO})_4$  to react with  $\text{Co}(\text{CO})_4^-$  to give  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$ , the  $\text{Co}(\text{CO})_4^-$  observed in solutions of  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  may be an intermediate in the decomposition of the halo anions in solution.

The peaks due to  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  in the spectra of all three anions are similar with a shift of the CO absorptions of 30–40  $\text{cm}^{-1}$  to lower energies relative to those in  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  or  $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$ .<sup>25</sup> Such a shift is expected for an increased electron density on the  $\text{Co}(\text{CO})_4$  group resulting from the increased electron density on the mercury due to its coordination by a halide ion. The shifts are of the same magnitude as those observed with  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  relative to  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  or  $\text{In}[\text{Co}(\text{CO})_4]_3^-$ ,<sup>6</sup> with  $\text{FeCo}_3(\text{CO})_{12}^-$  relative to  $\text{Co}_4(\text{CO})_{12}$ ,<sup>26</sup> and with  $\text{Tl}[\text{Co}(\text{CO})_4]_4^-$  relative to  $\text{Tl}[\text{Co}(\text{CO})_4]_3$ .<sup>27</sup>

The small changes of 4–5  $\text{cm}^{-1}$  in CO stretching frequencies associated with variation of the halide in  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  are similar to shifts observed in neutral systems of this type. A shift of only 3–6  $\text{cm}^{-1}$  to lower energies is observed upon changing the halide from chloride to iodide in  $\text{XHg}[\text{Mn}(\text{CO})_5]_2$ ,<sup>28</sup>  $\text{XHg}[(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ ,<sup>29</sup> or  $\text{XHgCo}(\text{CO})_4$ .

The three CO stretching vibrations in the infrared spectra of  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  in THF can be assigned as indicated by Graham<sup>30</sup> with the most intense band being the E mode, the band of medium intensity being the  $A_1^1$  mode involving the axial carbonyl group, and the weakest band being the  $A_1^2$  mode involving the equatorial carbonyl groups of the  $\text{Co}(\text{CO})_4$  unit. If the frequencies of the  $A_1^1$  and  $A_1^2$  modes of  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  are plotted against the electronegativity of X (Figure 1), a linear plot for both sets of frequencies is obtained. The slopes of these two lines are identical which indicates that the effects on the CO electronic configurations of varying X in the halo anion are equally distributed between the axial and equatorial CO groups. An identical shift of CO frequencies with substituent change in systems of this type has been taken<sup>31</sup> as a reflection of little change in  $\pi$  bonding between the metal atoms as the substituent is varied. Since it is expected that  $\pi$  bonding effects, if significant in these systems, should vary with halide, these results suggest that there is little  $\pi$  contribution to the mercury-cobalt bonding.

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(31) W. A. G. Graham, *ibid.*, **7**, 315 (1968); R. Ugo, S. Cenini, and F. Bonati, *Inorg. Chim. Acta*, **1**, 451 (1967).

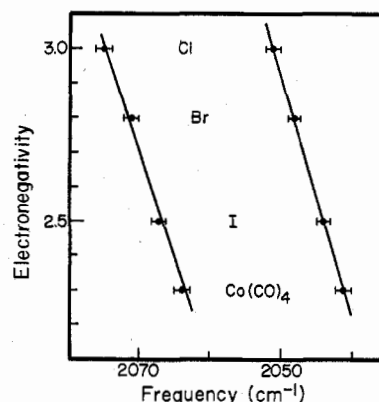
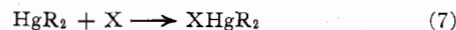


Figure 1.—Plot of the  $A_1^1$  and  $A_1^2$  modes of  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$  vs. the Pauling electronegativity of X.

Since the electronegativity of the  $\text{Co}(\text{CO})_4$  group has not been determined, it is not possible to use the  $A_1^1$  and  $A_1^2$  modes of  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  along with those of the halo anions in the generation of Figure 1. However, when the  $A_1$  modes of  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  are placed on the lines defined by the halo anions, both frequencies fit a group electronegativity of 2.3 for the  $\text{Co}(\text{CO})_4$  moiety. This value is consistent with the results of a  $^{59}\text{Co}$  nqr study<sup>32</sup> which placed the electronegativity of  $\text{Co}(\text{CO})_4$  between that of  $\text{CH}_3$  and  $\text{Cl}$  or  $\text{Br}$ . The observation that the  $\text{Co}(\text{CO})_4$  group fits so well on this plot suggests that there is no significant difference between the  $\text{Hg}-\text{Co}$  and  $\text{Hg}-\text{X}$  bonds in  $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$  and  $\text{XHg}[\text{Co}(\text{CO})_4]_2^-$ .

**Variations of Lewis Acidity of Hg.**—The differences in reactivity of  $\text{HgR}_2$  according to eq 7, where R is a



halide,  $\text{Co}(\text{CO})_4$ ,  $\text{Mn}(\text{CO})_5$ ,  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3$ , or  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ , can be related directly to the nucleophilicity<sup>33</sup> or base strength<sup>16</sup> of the  $\text{R}^-$  anion and the X group where X is  $\text{R}^-$ , 1,10-phenanthroline, 2,2'-bipyridyl, or a neutral organometallic compound. The order of increasing basicity of these ligands is neutral organometallics < amines < halides <  $\text{Co}(\text{CO})_4^-$  <  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$  <  $\text{Mn}(\text{CO})_5^-$  <  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$ . The ordering of organometallic anions has been discussed by Shriver.<sup>16</sup> The relative base strengths of  $\text{Co}(\text{CO})_4^-$ , halide, and the amines have been determined by comparison of the reactions of these ligands with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ . The neutral organometallic compounds  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3$ ,  $\text{Fe}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ , and (mesitylene) $\text{Mo}(\text{CO})_3$  form<sup>17,18</sup> weaker complexes with mercuric halides than do halide ions indicating that the organometallics are weaker bases with respect to mercury than are the halides.

Using this order of base strengths, the following correlations can be made. The neutral organometallic species  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3$ ,  $\text{Fe}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ , and (mesitylene) $\text{Mo}(\text{CO})_3$  form adducts with mercuric halides but not with any  $\text{HgR}_2$  species in which  $\text{R}^-$  is a stronger base than halide. The weakly basic halides and amines complex  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  but not a mercury compound with more strongly basic sub-

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(33) R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, **88**, 5121 (1966).

stituents than  $\text{Co}(\text{CO})_4^-$ .  $\text{Mn}(\text{CO})_5^-$  and  $(\pi\text{-C}_5\text{H}_5)\text{-Mo}(\text{CO})_3^-$  do not form complexes with  $\text{Hg}[\text{Mn}(\text{CO})_5]_2$  or  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  although  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$  reacts with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and  $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ . Apparently, as the base strength of R in  $\text{HgR}_2$  increases, mercury becomes such a weak Lewis acid that only the strongest Lewis bases will form adducts with it, while with weak bases as R, mercury is a sufficiently strong Lewis acid to add other weak bases. There seems to be a balancing of these effects such that three-coordinate mercury complexes  $\text{HgR}_3^-$  can be formed at both ends of the basicity scale of R but not with intermediate ligands.

A similar relationship between reactivity and the base strength of  $\text{R}^-$  in  $\text{ZnR}_2$ ,  $\text{CdR}_2$ ,  $\text{HgR}_2$ , and  $(\text{C}_6\text{H}_5)_3\text{-SnR}$  has been observed<sup>34</sup> for the displacement of  $\text{R}^-$  by dimethylformamide. The extent of dissociation of these compounds in DMF increased as the base strength of  $\text{R}^-$  decreased. Similarly, displacement of  $\text{R}^-$  by

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$\text{Br}^-$  from  $\text{ZnR}_2$  and  $(\text{C}_6\text{H}_5)_3\text{SnR}$  increased as the base strength of  $\text{R}^-$  decreased.<sup>8</sup>

The effect of a strong Lewis base on the bonding of mercury to a weaker base is also apparent in the solid state. The Hg-Co bond distance of 2.573 (12) Å in  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{Hg}[\text{Co}(\text{CO})_4]^{35,36}$  is significantly longer than that of 2.499 (7) Å in  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ .<sup>37</sup> There is no significant difference between the Hg-Co bond lengths in  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and  $\text{BrHgCo}(\text{CO})_4$ <sup>36</sup> in which the  $\text{Br}^-$  is of comparable base strength to  $\text{Co}(\text{CO})_4^-$ .

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## Reactions of *cyclo*-1,5-Bis- $\mu$ -dimethylamino-3,7-di- $\mu$ -hydrido-2,4,6,8-tetrakis(dimethylaluminum) with Lewis Bases

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Treatment of  $\text{Al}_4(\text{CH}_3)_8[\text{N}(\text{CH}_3)_2]_2\text{H}_2$  with excess  $\text{N}(\text{CH}_3)_3$  takes place in either of two ways. One reaction path leads to the formation of  $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$  and  $2(\text{CH}_3)_2\text{AlHN}(\text{CH}_3)_3$ , whereas the second affords  $\text{Al}_3(\text{CH}_3)_6[\text{N}(\text{CH}_3)_2]_2\text{H}$  and  $(\text{CH}_3)_2\text{-AlHN}(\text{CH}_3)_3$ . Ammonia reacts to yield  $[(\text{CH}_3)_2\text{AlNH}_2]$ ,  $\text{HN}(\text{CH}_3)_2$ , and  $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ , while  $(\text{CH}_3)_2\text{O}$  affords  $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]$ ,  $\text{CH}_4$ , and  $[(\text{CH}_3)_2\text{AlO}(\text{CH}_3)_2]_2$ . Treatment of  $\text{Al}_4(\text{CH}_3)_8[\text{N}(\text{CH}_3)_2]_2\text{H}_2$  with  $\text{P}(\text{CH}_3)_3$  leads to partial decomposition as does solution formation in benzene.

### Introduction

The preparation and characterization of  $\text{Al}_4(\text{CH}_3)_8[\text{N}(\text{CH}_3)_2]_2\text{H}_2$  (I) has been reported;<sup>2</sup> the bonding associated with this species involves both electron-sufficient (N) and -deficient bridges (H). A charge refinement of the crystallographic data indicates that the hydride of  $\text{Al}_4(\text{CH}_3)_8[\text{N}(\text{CH}_3)_2]_2\text{H}_2$  has a residual negative charge of  $-0.45 e$ , and the methide has  $-0.39 e$  residual charge.<sup>3</sup> Therefore, it was of interest to investigate the chemistry of I with nucleophiles of various strengths in order to ascertain the stability of H vs. N bridge bonds.

### Experimental Section

**Apparatus and Procedures.**—Because of the pyrophoric nature of many of the reactants and products, materials were manipulated by standard techniques in a vacuum line equipped with mercury float and Kontes 4-mm Teflon valves. Transfer of nonvolatile material was performed in a metal Kewanee dry-box under a nitrogen atmosphere (Burdett high purity grade)

further dried with Linde 4A molecular sieve and  $\text{P}_2\text{O}_5$  "granusic" Boher, reagent grade.

Infrared spectra of volatile materials were obtained in the gas phase using a 10-cm cell fitted with polished KBr plates. Low-volatile solids were milled in the drybox using Nujol or Fluorolube which had been dried and stored over Linde 4A molecular sieve. The mull spectra were run between KBr plates while liquids were run neat. Spectra were obtained on a Perkin-Elmer Model 457 grating spectrometer in the range 4000–400  $\text{cm}^{-1}$  and calibrated by use of the 1376- $\text{cm}^{-1}$  peak of Nujol or by superimposition of the 1601- $\text{cm}^{-1}$  peak of a 0.05-mm polystyrene film. Band intensities are reported following the method of Durkin, DeHayes, and Gloré.<sup>4</sup>

Nuclear magnetic resonance spectra were obtained on solutions hermetically sealed in precision ground 5-mm o.d. Pyrex tubes, Yorde Mfg. Co. Spectra were run on a Varian A60-A spectrometer and were calibrated by using the solvent as an internal standard. All chemical shifts are reported with respect to tetramethylsilane. Analyses were performed as previously described.<sup>5</sup>

**Reagents.**—Solvents unless otherwise specified were obtained from J. T. Baker Chemical Co. as ACS analytical reagent grade and were dried and stored over sodium-potassium liquid alloy (Na/K) until use. Toluene- $d_6$  and benzene- $d_6$ , Diaprep Inc., 99 and 99.5% isotropic purity, were dried and stored over Na/K.

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