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The Characterization of $\{Hg[Co(CO)_4]_3\}^-$: A Reinvestigation of the Anion of Mercury Cobalt Carbonyl

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The anion of mercury cobalt carbonyl, previously formulated as $\{Hg[Co(CO)_4]_2\}^-$, *is in fact* $\{Hg[Co(CO)_4]_3\}^-$, *a complex anion of mercury(II). This complex anion is an intermediate in the reduction of mercury cobalt carbonyl by sodium. It can best be prepared by addition of* $[Co(CO)_4]^-$ *salts to* $Hg[Co(CO)_4]_2$.**

Introduction

Our recent studies[1] have shown that the reduction of octacarbonyldicobalt by alkali metals gives different products from those obtained when sodium amalgam is the reducing agent.[2] As one aspect of our investigations we have found it desirable to prepare tetracarbonylcobaltate(–I) salts by the reaction of alkali metals with *bis*(tetracarbonylcobalt)mercury(II), I. Consequently we were interested in the recent claim by Vizi-Orosz *et al.*[3] that reduction of I proceeds via the $\{Hg[Co(CO)_4]_2\}^-$ anion, II, and can be stopped at this intermediate stage by the use of one g-atom of sodium per mole of I, *viz*:

$$\underset{\text{I}}{Hg[Co(CO)_4]_2} + Na/Hg \longrightarrow$$

$$\underset{\text{II}}{\{Hg[Co(CO)_4]_2\}^-} \xrightarrow{Na/Hg} 2[Co(CO)_4]^- + Hg$$

This suggestion is inconsistent with our observation that reaction of sodium *metal* with I always results in the formation of elemental mercury, regardless of stoichiometry. Furthermore, it was reported that II can be prepared by *reduction* of I with sodium tetracarbonylcobaltate(–I).

$$\text{I} + NaCo(CO)_4 \longrightarrow \text{II}$$

If a redox process were occurring in this reaction, some oxidation product, presumably octacarbonyldicobalt, would be expected. In fact, no such product was reported. These two observations prompted us to reinvestigate this system.

Results and Discussion

According to the mechanism proposed by Vizi-Orosz for the reduction of $Hg[Co(CO)_4]_2$, no mercury should be formed in a stoichiometric reaction with sodium metal. We have found, however, that mercury is slowly deposited under these conditions and much more rapidly if there is an excess of $Hg[Co(CO)_4]_2$. In neither case, though, is a colourless solution of $NaCo(CO)_4$ obtained as the final product; the solution becomes dark orange and further stirring produces no change. Only when sodium metal is present in excess does a colourless solution result. These qualitative observations cannot be rationalized by the proposed reduction mechanism;[3] they are not, however, inconsistent with the existence of an intermediate complex anion of mercury(II).

In order to facilitate our studies, we have investigated the reaction of $Hg[Co(CO)_4]_2$ with the salts $[Fe(C_{12}H_8N_2)_3][Co(CO)_4]_2$ and $[(PBu_3)_2Co(CO)_3][Co(CO)_4]$[4] ($C_{12}H_8N_2$ = 1,10-phenanthroline, PBu_3 = tri-n-butylphosphine). The solid state infrared spectrum of the « ferroin » salt prepared by this method is identical to that of the salt prepared according to the procedure of Vizi-Orosz (broad bands at 2035 and 1960 cm^{-1}). In tetrahydrofuran or methylene chloride solution, however, the spectrum consists of five strong bands at 2075, 2040, 2007, 1970 and 1892 cm^{-1}. The latter absorption is characteristic of $[Co(CO)_4]^-$[5] and the two bands at 2075 and 2007 cm^{-1} are very close to those reported for $Hg[Co(CO)_4]_2$.[6] The spectrum of the $[(PBu_3)_2Co(CO)_3]^+$ salt in the CO region is identical, allowing for absorptions due to the cation. Magnetic measurements of the latter salt show it to be diamagnetic and hence inconsistent with the formulation $\{Hg[Co(CO)_4]_2\}^-$.

The solution spectra, the magnetic data, elemental analyses and the stoichiometry of the preparations show that the anion of mercury cobalt carbonyl is

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(**) Note added in Proof. Since the submission of our paper a more complete report on the nature of the anion of mercury cobalt carbonyl has been published by Burtlitch *et al.* (J. M. Burlitch, R. B. Peterson, H. L. Conder, and W. R. Robinson, *J. Am. Chem. Soc.*, *92*, 1783 (1970). These authors also describe the preparation of other similar complex anions.

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$\{Hg[Co(CO)_4]_3\}^-$, a complex anion of mercury(II). In solution the anion is in equilibrium with $[Co(CO)_4]^-$ and $Hg[Co(CO)_4]_2$. This equilibrium can be further demonstrated by reaction of the anion with triphenylphosphine which results in the precipitation of the well known mercury(II) derivative, $Hg[Co(CO)_3P(C_6H_5)_3]_2$.[7]

$$\begin{tikzcd}\{Hg[Co(CO)_4]_3\}^- \arrow[r, leftrightharpoons] & Hg[Co(CO)_4]_2+[Co(CO)_4]^- \arrow[d, "2P(C_6H_5)_3"] \\ & Hg[Co(CO)_3P(C_6H_5)_3]_2\end{tikzcd}$$

Equilibria of this type are common for complex anions of mercury(II)[8] and Ruff has recently observed a similar equilibrium in the case of the metal carbonyl complex ion, $[Fe(CO)_4InBr_3]^{2-}$.[9]

Conclusions

Our results clearly indicate that during the reaction of $Hg[Co(CO)_4]_2$ with $[Co(CO)_4]^-$ no reduction to mercury(I) occurs; instead, a complex anion $\{Hg[Co(CO)_4]_3\}^-$, is formed which is analogous to other mercurate(II) complexes of the type HgX_3^- (X is a halogen).[8] Furthermore, the fact that $\{Hg[Co(CO)_4]_3\}^-$ is an intermediate in the reduction of $Hg[Co(CO)_4]_2$ suggests the following sequence for the formation of $NaCo(CO)_4$:

$$Hg[Co(CO)_4]_2+2Na \longrightarrow 2NaCo(CO)_4+Hg$$
$$NaCo(CO)_4+Hg[Co(CO)_4]_2 \longrightarrow Na\{Hg[Co(CO)_4]_3\}$$
$$Na\{Hg[Co(CO)_4]_3\}+2Na \longrightarrow 3NaCo(CO)_4+Hg$$

Experimental Section

All operations were carried out under a nitrogen atmosphere. Tetrahydrofuran was purified by distillation from calcium hydride; diethyl ether, from sodium wire. $Hg[Co(CO)_4]_2$ [10] and $[(PBu_3)_2Co(CO)_3][Co(CO)_4]$[4] were prepared by literature methods. Infrared spectra were measured with a Perkin-Elmer 237 B grating spectrometer. Microanalyses were performed by Huffman Laboratories, Inc., Wheatridge, Colorado, U.S.A. Cobalt was determined by the method of Berndt and Šára.[11]

Preparation of $[Fe(C_{12}H_8N_2)_3][Co(CO)_4]_2$. A solution containing 0.014 mole of $NaCo(CO)_4$ [12] in 60 ml of THF was filtered into an aqueous solution containing 0.016 mole of $[Fe(C_{12}H_8N_2)_3][SO_4]$. The dark red precipitate was filtered, washed with water and dried.

Preparation of $[Fe(C_{12}H_8N_2)_3]\{Hg[Co(CO)_4]_3\}_2$. 0.94 g (1.0 mmole) of $[Fe(C_{12}H_8N_2)_3][Co(CO)_4]_2$ was dissolved in 50 ml of THF, 1.08 g (2.0 mmole) of $Hg[Co(CO)_4]_2$ added and the reaction mixture stirred for one hour. The solution was filtered into 100 ml of water resulting in the formation of a red oil. This oil was worked up according to the procedure of Vizi-Orosz.[3]

Preparation of $[(PBu_3)_2Co(CO)_3]\{Hg[Co(CO)_4]_3\}$. To a suspension of 3.59 g (5.0 mmole) of $[(PBu_3)_2Co(CO)_3][Co(CO)_4]$ in 50 ml of diethyl ether were added 2.77 g (5.1 mmole) of $Hg[Co(CO)_4]_2$. The yellow $[Co(CO)_4]^-$ salt immediately dissolved and the solution became dark brown. Removal of ether at reduced pressure afforded a brown crystalline product which was filtered and washed with hexane to remove traces of $Hg[Co(CO)_4]_2$. Yield 5.45 g, 86% based on $[(PBu_3)_2Co(CO)_3][Co(CO)_4]$. (Found: C, 37.16, 36.98; H, 4.44, 4.53; Co, 18.45, 18.69; Hg, 14.86. $C_{39}H_{54}Co_4HgP_2O_{15}$ Calcd: C, 37.14; H, 4.32; Co, 18.69; Hg, 15.91%).

Reaction of $\{Hg[Co(CO)_4]_3\}^-$ with $P(C_6H_5)_3$. 1.26 g (1.0 mmole) of $[(PBu_3)_2Co(CO)_3]\{Hg[Co(CO)_4]_3\}$ were dissolved in 65 ml of THF, 0.55 g (2.1 mmole) of $P(C_6H_5)_3$ added and the mixture stirred at 40° for 15 minutes after which time a yellow precipitate formed. This solid was filtered and washed with THF. It was identified as $Hg[Co(CO)_3P(C_6H_5)_3]_2$ by comparison of its infrared spectrum in chloroform with that of an authentic sample.[13] A spectrum of the THF solution showed only bands characteristic of $[(PBu_3)_2Co(CO)_3][Co(CO)_4]$.

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