thesized reproducibly.[12] Consequently, further studies of these molecules await the development of rational syntheses that will produce them in good yield. Experiments toward this goal are now underway.

Assembly, Disassembly, and Reassembly of a Large Mercury Cobalt Carbonyl Cluster, Hg9Co6(CO)18

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The reaction of an aqueous basic solution of $Hg(CN)_2$ with $Hg[Co(CO)_4]_2$ in methanol/water formed the largest mercury-containing cluster yet reported, $Hg_9Co_6(CO)_{18}$ (1). A single-crystal X-ray structure determination on the bis(acetone) solvate, $Hg_9Co_6(CO)_{18} \cdot 2(CH_3)_2CO$ [$P2_1/c$; $a = 14.339$ (5) Å, $b = 21.024$ (6) Å, $c = 18.535$ (8) Å, $\beta = 94.48$ (3)°; $V = 5570$ (36) Å^3; $Z = 4$; $R_1 = 8.1\%$, $R_2 = 12.0\%$], showed 1 to have *fac*-$(CO)_3Co$ fragments at the corners of a rectangular trigonal prism with a mercury atom at the center of each edge. In addition to forming a 1:3 adduct with $Et_4N^+I^-$, cluster 1 reacted with HgX_2 compounds forming monocobalt compounds $(CO)_3Co(HgX)_3$ (X = I (2), Cl (3), CF_3CO_2). The chloro derivative 3 re-formed 1 in high yield when treated with Ph_3P. Possible mechanisms are discussed. Compound 2 was used to form analogous derivatives, $(CO)_3Co(HgY)_3$: Y = p-$CH_3C_6H_4SO_3$ with silver toluenesulfonate and Y = Ph with phenyllithium. It also formed an 1:1 adduct with n-Bu_4NI.

Introduction

When an attempt was made to recover the starting material from an aborted preparation of $Na^+Co(CO)_4^-$ from $Hg[Co(CO)_4]_2$ and sodium amalgam in methanol, a small quantity of a dark red solid was obtained from the reaction mixture after it had been quenched with aqueous $Hg(CN)_2$. Elemental analysis established the empirical formula as $Hg_3Co_2(CO)_6$, and the simplicity of the infrared spectrum suggested a highly symmetrical structure.

In this paper, we report an improved preparation of this compound, $Hg_9Co_6(CO)_{18}$ (1) the largest mercury-containing cluster yet prepared, and describe some of its reactions.[1] Those with compounds of type HgX_2 provide the first entry point to the chemistry of $(CO)_3CoHgX_3$ compounds from which 1 may be regenerated with surprising efficiency.

Large clusters containing mercury are relatively rare. Prior to preliminary reports of this work,[2,3] the only known mixed-metal clusters containing more than two mercury atoms were $Cp_2Nb[HgS_2CN(Et)_2]_3$,[4] $Hg[NiCp(GePh_3)$-$HgGePh_3]_2$,[5] $Hg_6Rh_4[P(Me)_3]_{12}$,[6] $[Os_3(CO)_{11}Hg]_3$,[7] $[Cp$-$(CO)_3MoHgMo]_4$,[8] $[(MeCp)(CO)_2MgHg]_4$,[9] and $[Cp$-$(CO)_2ReHg]_4$.[10] Except for the last named compound, the structures of these compounds are known; their chemistry has not been reported.

Experimental Section

Unless stated otherwise, all operations were carried out in flame-dried glassware under a purified argon atmosphere, using apparatus and techniques described elsewhere.[11,12] Weighing and preparation of analytical and spectroscopic samples of air-sensitive solids were done in a Vacuum Atmospheres Corp. drybox under prepurified nitrogen. Melting points were observed in sealed capillaries under argon. Molecular weights were determined cryoscopically on freshly prepared samples by using sulfolane as solvent and benzophenone as a standard.[13] Thin-layer chromatography (TLC) was done by using Whatman KC18F plates (200-μm C-18 adsorbant on glass).

Infrared (IR) spectra were obtained on a Perkin-Elmer Model 337 spectrometer, calibrated with the 1944 cm^{-1} line of polystyrene. Unless stated otherwise, elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN, or Analytische Laboratorien, Elbach, Germany. Alternatively, freshly prepared sampes were decomposed by treatment with nitric acid and analyzed for Co and Hg by inductively coupled plasma emission spectroscopy using a Jarrell-Ash 975 spectrophotometer; such analyses were performed by the analytical laboratory of the Cornell University Department of Pomology. Iodide analyses were carried out on similarly prepared samples by the Volhard method.[14a] Proton

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NMR spectra were recorded on a Varian CFT20, Varian XL200, or Bruker WM300 spectrometer and were calibrated by using residual ^{1}H peaks in the deuteriated solvents. Carbon and fluorine NMR spectra were recorded on a JEOL FX90Q spectrometer and were calibrated by using solvent peaks and CFCl$_3$ (external), respectively. Mass spectra were obtained by thermal desorption on an AEI MS902 mass spectrometer equipped with a VG Datasystem 2000 computer; EI ionization (70 eV) was used in all cases. Continuous FAB MS was done on a VG Ind. Model 70-SE using *m*-nitrobenzyl alcohol.[14b] UV/vis spectra were recorded on a Hewlett-Packard 8450A spectrophotometer.

All solvents were reagent grade and were dried and degassed prior to distillation directly into the reaction vessel under an argon atmosphere. Distilled water was deionized on an ion-exchange resin and degassed by several freeze–pump–thaw cycles. The following materials were prepared by literature methods: Hg-[Co(CO)$_4$]$_2$,[15] Hg(O$_2$CCF$_3$)$_2$,[16] (Ph$_3$P)$_2$HgCl$_2$,[17] Hg[Et$_2$NCS$_2$]$_2$,[18] and Na$_3$Co(CO)$_3$.[19] All other starting materials were reagent grade and were used without further purification.

Preparation of 1 (from Sodium Amalgam). Into a 500-mL three-necked flask, equipped with a Teflon stopcock at the bottom, a mechanical stirrer, and a gas inlet tube, was distilled 200 mL of methanol from Mg(OMe)$_2$. Sodium amalgam (prepared from sodium (3.5 g, 0.150 mol) and 40 mL of mercury) was added followed by ca. 5 g of Hg[Co(CO)$_4$]$_2$ with stirring. A vigorous reaction ensued with considerable gas and heat evolution. The gas was determined to be a mixture of CO and H$_2$ by GLC. The vessel was cooled in an ice bath, and, after 20 min, the remainder of the Hg[Co(CO)$_4$]$_2$ (22.5 g, 41.5 mmol total) was added. The mixture was stirred for 30 min with cooling. During this time the solid dissolved and no further gas evolution occurred. The mixture was allowed to warm to room temperature, and stirring was continued for 1 h; a yellowish brown solution resulted. Addition of more sodium amalgam (half of the original amount) caused rapid gas evolution but no change in color.

After having stood for 24 h, the amalgam was drained off and the solution was transferred to a filter tube containing Celite filter aid. A small portion (ca. 25 mL) was reserved for another experiment, and the remaining solution was filtered into 900 mL of a stirred, degassed aqueous solution of Hg(CN)$_2$ (17.6 g, 50.0 mmols) over a 1-h period. An orange precipitate formed immediately and gradually turned dark red during the addition. The solid was filtered in air, washed with water until the washings were neutral, and aspirated dry. The resulting dark red-brown powder (13.6 g) was triturated with 600 mL of acetone; a substantial portion did not dissolve. The orange-red solution was filtered, concentrated to ca. 100 mL by rotary evaporation at reduced pressure, filtered from 1.7 g of a dark, burgundy colored solid (A), and then evaporated to dryness giving 3.25 g of an orange-red crystalline solid (B).

From B, 2.4 g of Hg[Co(CO)$_4$]$_2$, mp 75–78 °C (lit.[20] (mp 81–82 °C), was obtained by trituration with methanol (100 mL) and evaporation of the extracts to dryness. An analytically pure sample of 1 (1.4 g, 3.8%) was obtained from solid A by two recrystallizations from acetone: IR (KBr) 2050 w (sh), 2015 vs, 1975 s (sh), 1930 w (sh), 532 m, 515 m cm^{-1}; IR (THF) 2050 w (sh), 2015 s, 1964 m, 1925 w (sh) cm^{-1}; IR (DMSO) 2010 s, 1968 m cm^{-1}. Anal. Found by M. L. Pascher. (Calcd for Hg$_9$Co$_8$(CO)$_{18}$: Hg, 67.42 (67.79); Co, 12.99 (13.28); O, 10.76 (10.81); C, 8.82, 8.16, 7.99 (8.12)) H, 0.0 (0.00).

Another sample, prepared in essentially the same way and exhibiting the same IR bands, provided the following information. UV/vis (acetone): λ(max) 254, 336 nm. A mass spectrum showed no ions heavier than Hg$^+$ using thermal desorption or fast atom bombardment (FAB). Continuous FAB techniques, however, gave a very nice spectrum. In the region, *m/e* >1700, there were isotope

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clusters centered at the following: *m/e* (relative intensity) 2662 (M$^+$, 25), 2549 (9), 2435 (10), 2406 (14), 2394 (11), 2263 (11), 2005 (70), 1977 (100), 1910 (20), 1890 (13), 1861 (40), 1748 (35), 1720 (11), and 1709 (9). The isotope distribution of the parent ion was nearly Gaussian and was very similar to the calculated distribution. This compound, as the bis(acetone) solvate, was used for the single-crystal X-ray analysis. As shown by the elemental analysis and IR specroscopy, the compound readily lost solvent of crystallization.

Preparation of 1 Using Ba(OH)$_2$. Addition of a solution of 2.50 g (7.93 mmol) of Ba(OH)$_2$·8H$_2$O in 75 mL of degassed distillated water to a solution of 5.00 g (19.5 mmol) of Hg(CN)$_2$ in 75 mL of methanol, followed by stirring for 5 min, gave a cloudy colorless solution. This solution was added to a solution of 5.00 g (9.22 mmol) of Hg[Co(CO)$_4$]$_2$ in 100 mL of methanol over a 30-min period with stirring in the dark, causing gas evolution and a color change from yellow-orange to dark red-brown. This suspension was stirred for 14 h in the dark and then filtered through a "coarse" frit in air, giving a yellow filtrate and a brown solid which was washed with 5 L of distilled water and then dried for 6 h under aspirator suction. The red-brown solid was washed with 400 mL of toluene and dried in air for 1 h, giving a red-black solid. The solid was extracted with 400 mL of acetone, giving a burgundy solution and some red-black acetone-insoluble material. The solution was filtered through filter paper and slowly cooled to −78 °C to afford 0.55 g (7%) of dark burgundy-colored microcrystals of 1. Found (Calcd for Hg$_9$Co$_6$(CO)$_{18}$): Hg, 68.2 (67.8); Co, 13.0 (13.3); mol wt, 2817 (2663). The IR spectrum in THF (2015 (vs) and 1965 (m) cm^{-1}) was the same as that prepared by the above method.

The acetone-insoluble material, formed in variable yields in the range 2–4 g (20–50%), did not react (IR) with a THF solution of HgI$_2$, HgCl$_2$, or P-*n*-Bu$_3$. Found (Calcd for [HgCo(CO)$_3$]$_n$): Hg, 58.1 (58.4); Co, 16.9 (17.2). IR (Nujol): ν(CO) 2035 (s), 1980 (m) cm^{-1}.

Reaction of 1 with HgI$_2$. Preparation of 2. Addition of 0.790 g (1.74 mmol) of HgI$_2$ to a solution of 0.514 g (0.193 mmol) of 1 in 30 mL of THF caused the solution to change from dark burgundy to light red-orange with ν(CO) 2062 (s) and 2024 (m) cm^{-1}. TLC (50:50 THF/CH$_2$Cl$_2$) showed only one component to be present (R_f 0.46). The product, isolated by removing the solvent by TTVD (trap-to-trap vacuum distillation), was soluble in THF and acetone but insoluble in toluene, CH$_2$Cl$_2$, and MeOH; mp decomposition without melting at about 50 °C. The yield was 87%, based on the formula (CO)$_3$Co(HgI)$_3$. Attempts to recrystallize the product by slowly cooling a THF, acetone, or THF/hexane solution were unsuccessful. Slow diffusion of hexane into a THF solution gave a mixture of red, orange, and yellow solids. Another sample prepared by the above reaction, followed by removal of the solvent by TTVD, appeared to be homogeneous and to be pure by IR spectroscopy. A mass spectrum showed only peaks due to Hg$^+$, I$^+$, and Co$^+$. Found (Calcd for (CO)$_3$Co(HgI)$_3$, 2): Hg, 52.9 (53.5); Co, 5.15 (5.24); I, 33.6 (33.8); mol wt, 1094 (1125). IR (THF/CH$_2$Cl$_2$, 1:1): ν(CO) 2056 (s), 2048 (w, sh), 2012 (m) cm^{-1}.

In a similar experiment, the HgI$_2$ was added in portions, 3 equiv (relative to 1) at a time. After 3 equiv had been added, the product had ν(CO) (THF) 2034 (s) and 1989 (m) cm^{-1}. After 6 equiv had been added, the spectrum showed ν(CO) 2051 (s) and 2000 (m) cm^{-1}, and after 9 equiv had been added, the spectrum showed ν(CO) 2063 (s) and 2022 (m) cm^{-1}.

Reaction of 1 with HgCl$_2$. Preparation of 3. Addition of a solution of 0.410 g (1.51 mmol) of HgCl$_2$ in 20 mL of THF to a solution of 0.447 g (0.168 mmol) of 1 in 30 mL of THF with stirring over a 2-h period caused the formation of a yellow-orange suspension. The suspension was allowed to settle, the light blue supernatant liquid was decanted, and the yellow-orange solid was dried in vacuo. The solid was insoluble or very slightly soluble in THF, acetone, ethanol, methylene dichloride, methanol, toluene, and DMSO. UV/vis (CH$_2$Cl$_2$): λ(max) 295, 377 nm. Found (Calcd for (CO)$_3$Co(HgCl)$_3$, 3): Hg, 72.3 (70.71); Co, 6.82 (6.92). IR (Nujol): 2049 (s), 2012 (m) cm^{-1}.

Reaction of 1 with HgBr$_2$. Preparation of 4. When a solution of 0.096 g (0.036 mmol) of 1 in 30 mL of THF was added to a solution of 0.120 g (0.333 mmol) of HgBr$_2$ in 30 mL of THF, a yellow-orange precipitate formed. The mixture was allowed to

settle, and the pale yellow supernatant liquid was decanted. The yellow-orange solid was dried in vacuo. The product presumed to be $(CO)_3Co(HgBr)_3$ (4) was insoluble in THF, acetone, toluene, ethanol, acetonitrile, and thiophene. No ions heavier than Hg^+ were observed in the mass spectrum. IR (KBr): 2044 (s), 1999 (m, sh) cm^{-1}. The product was dissolved in 20 mL of pyridine, giving a red solution with no IR carbonyl absorptions and a gray precipitate. The solution was filtered through a "medium" frit containing Celite, and the solvent was removed via TTVD, giving a red solid. The solid became blue when dried in vacuo. Recrystallization by slowly cooling a toluene solution to -60 °C gave turquoise $(py)_2CoBr_2$.[21] Found (Calcd for $(C_5H_5N)_2CoBr_2$): Br, 41.54 (42.40); N, 7.28 (7.43); C, 31.84 (31.86); H, 2.75 (2.68).

Reaction of 1 with Et_4NI. Preparation of 5. When 0.360 g (1.40 mmol) of $Et_4N^+I^-$ was added to a solution of 0.300 g (0.113 mmol) of 1 in 30 mL of THF, the appearance of the solution did not change. The mixture was stirred for 4 h in the dark and then was filtered through a "medium" frit containing Celite to remove unreacted $Et_4N^+I^-$, giving a clear dark red solution. The solvent was removed via TTVD, and the solid was recrystallized from toluene/THF (2:1), giving red-black needlelike crystals. IR (CH$_2$Cl$_2$): 2050 (w), 2009 (s), 1965 (m) cm^{-1}. ^{1}H NMR (acetone-d_6): δ 3.48 (q, 2 H, J = 7.2 Hz, CH$_2$), 1.39 (t, 3 H, J = 7.2 Hz, CH$_3$). Found (Calcd for $Hg_9Co_6(CO)_{18}\cdot(Et_4NI)_3$, 5): Co, 10.2 (10.3); C, 12.85 (14.69); H, 1.70 (1.76); I, 10.66 (11.08); N, 0.9 (1.2).

Reaction of 1 with $(CF_3CO_2)_2Hg$. Preparation of 6. When 0.193 g (0.453 mmol) of $(CF_3CO_2)_2Hg$ was added to a solution of 0.134 g (0.0503 mmol) of 1 in 10 mL of THF in the dark, the solution immediately changed from burgundy to lemon yellow with ν(CO) 2052 (s) and 2010 (m) cm^{-1}. The solvent was removed by TTVD, and 40 mL of toluene was added in the dark, giving a light-sensitive, yellow solution with a small amount of off-white solid. The mixture was filtered in the dark through a "medium" frit containing Celite, and the resulting yellow solution was slowly cooled to -60 °C, giving 0.25 g (76%) of well-formed yellow to yellow-green crystals, mp 103-104 °C dec. Found (Calcd for $(CO)_3Co(HgO_2CCF_3)_3\cdot^1/_2(C_6H_5CH_3)$, 6): Hg, 52.65 (53.27); Co, 6.49 (5.21); C, 12.78 (13.29); H, 0.39 (0.35). The presence of toluene was confirmed by ^{1}H NMR. ^{19}F NMR (CDCl$_3$): δ -74.54 (s, br, CF$_3$). A mass spectrum showed no ions heavier than Hg^+. When crystals were warmed to room temperature, they became opaque and noncrystalline, as shown by X-ray diffraction, so newly grown crystals were mounted under dim incandescent lights in 0.5-mm X-ray capillaries that contained a small amount of mother liquor. These crystals gave good X-ray rotation photographs, but on continued exposure to the X-ray beam, even at -60 °C, the crystals became black and non-crystalline.

Reaction of 1 with $Hg(S_2CNEt_2)_2$. When 0.557 g (1.12 mmol) of $Hg(S_2CNEt_2)_2$ was added to a solution of 0.330 g (0.124 mmol) of 1 in 30 mL of acetone, the color changed from deep red to orange. On stirring for 10 min in the dark, the solution became green with gray precipitate. The solution was filtered through a "medium" frit containing Celite, giving a dark green solution. On cooling to -60 °C, a dark green, crystalline precipitate formed which was identified as $Co(S_2CNEt_2)_2$ by comparison of its IR and ^{13}C and ^{1}H NMR spectra with those of an authentic sample.[22]

Attempted Reaction of 1 with $(p\text{-}CH_3C_6H_5)_2Hg$. Addition of 0.173 g (0.452 mmol) of $(p\text{-}CH_3C_6H_5)_2Hg$ (Eastman) to a solution of 0.126 g (0.0473 mmol) of 1 did not change the IR spectrum of the solution. The $(p\text{-}CH_3C_6H_5)_2Hg$ was isolated by slowing cooling the solution and identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample. The supernatant liquid contained 1 as shown by its IR spectrum.

Preparation of $(p\text{-}CH_3C_6H_4SO_3Hg)_3Co(CO)_3$ (7). To a solution of 2, prepared from 0.056 g (0.021 mmol) of 1 with 0.087 g (0.192 mmol) of HgI_2 in 20 mL of THF, was added 0.110 g (0.394 mmol) of solid $p\text{-}CH_3C_6H_4SO_3Ag$ (Eastman). The mixture was stirred for 1 h, in which time the solution changed from red-orange to yellow and a flocculent white precipitate formed. The mixture was filtered through a "medium" frit containing Celite, giving a clear yellow solution with ν(CO) 2069 (s) and 2025 (m) cm^{-1}. The product, isolated by removing the solvent by TTVD, was soluble in THF, acetone, and methylene chloride but not in toluene or

diethyl ether. TLC (acetone eluent) gave one spot at R_f 0.49. With THF/CH$_2$Cl$_2$ (1:1) eluent, there was also only one spot (R_f 0.63). Slow cooling of a solution of the product in CH$_2$Cl$_2$/hexanes (2:1) gave a yellow powder that decomposed at room temperature in the dark over a 2-week period, giving a yellow product which was insoluble in THF or acetone. Found (Calcd for $(p\text{-}CH_3C_6H_4SO_3Hg)_3Co(CO)_3$): Hg, 48.1 (47.82); Co, 4.57 (4.68); mol wt, 1295 (1258). ^{1}H NMR (acetone-d_6): δ 7.75 (d, 2 H, J = 8.1 Hz, CH), 7.29 (d, 2 H, J = 7.9 Hz, CH), 2.38 (s, 3 H, CH$_3$).

A similar reaction with $AgNO_3$ gave a yellow product with ν(CO) (THF) 2074 (s) and 2029 (m) cm^{-1}. The product was soluble in THF, acetone, and methanol but not in toluene or methylene chloride. Likewise, $AgBF_4$ (Alfa) gave a yellow product (ν(CO) (THF) 2094 (s) and 2050 (m) cm^{-1}) that decomposed on standing at room temperature for several days. Neither product was characterized.[3]

Reaction of 2 with $n\text{-}Bu_4N^+I^-$. Preparation of 8. To a solution of 2, prepared from 0.308 g (0.116 mmol) of 1 with 0.474 g (1.04 mmol) of HgI_2 in 30 mL of THF, was added 0.507 g (1.37 mmol) of $n\text{-}Bu_4N^+I^-$, causing the solution to change from light red-orange to deep red with ν(CO) 2016 (s) and 1964 (m) cm^{-1}. The solvent was removed by TTVD, and the product was recrystallized by slowly cooling a methylene dichloride/toluene (3:1) solution to -60 °C. The deep red crystals formed were well-shaped rhombohedra, but on warming the solution to room temperature, a dark red oil was formed. This oil was recrystallized again, but the crystals did not diffract X-rays well enough for a unit-cell determination or single-crystal structure analysis. These crystals also changed to an oil on standing. The product decomposed slightly on standing at room temperature in the dark, giving a partially insoluble product over a 4-week period. Found (Calcd for $(C_4H_9)_4N(CO)_3Co(HgI)_3I$, 8): Hg, 40.8 (40.3); Co, 3.65 (3.94); I, 34.6 (34.0); C, 16.78 (15.27); H, 1.87 (2.43); N, 1.01 (0.94). ^{1}H NMR (acetone-d_6) δ 3.48 (m, 2 H, CH$_2$, 1.82 (m, 2 H, CH$_2$), 1.47 (m, 2 H, CH$_2$), 0.99 (t, 3 H, J = 7.1 Hz, CH$_3$).

Reaction of 2 with PhLi. Preparation of 9. To a solution of 2, prepared by the reaction of 1.154 g (0.433 mmol) of 1 and 1.770 g (3.90 mmol) of HgI_2 in 30 mL of THF and cooled to -78 °C, was added 7.8 mmol (4.58 mL of a 1.7 M solution) of phenyllithium (Aldrich) in diethyl ether/cyclohexane, causing the formation of a dark red suspension. The mixture was filtered through a "medium" frit containing Celite, giving a clear dark red solution. The solvent was removed by TTVD, and the solid was dried in vacuo. Methylene dichloride (30 mL) was distilled in, giving a clear red solution with ν(CO) 2020 (s) and 1969 (m) cm^{-1} and an undissolved gray solid. Toluene (25 mL) was distilled in, and the dark red solution was filtered through a "medium" frit containing Celite. The solvent was removed by TTVD, and the resulting red solid was washed with toluene. ^{1}H NMR (acetone-d_6): δ 7.85-7.10 (m, C$_6$H$_5$). IR (CH$_2$Cl$_2$): 2006 (s), 1957 (m) cm^{-1}. A mass spectrum showed peaks due to $C_6H_5^+$, Hg^+, and $(CO)_3Co(HgC_6H_5)^+$ (m/e (relative intensity) 77 (100), 202 (20), 408 (1)). Found (Calcd for $(CO)_3Co(HgC_6H_5)_3$, 9): Hg, 62.0 (61.6); Co, 5.91 (6.04); I, 1.3 (0.0).

Attempted Preparation of $(CO)_3Co(HgBr)_3$ from $Na_3Co(CO)_3$ and HgX_2. To a stirred solution of 2.96 g (8.2 mmol) of $HgBr_2$ in 40 mL of THF was added 0.58 g (2.1 mmol) of $Na_3Co(CO)_3$ as a suspension in THF (40 mL). The mixture became dark brown, and a finely divided, gray-white solid precipitated. The solution was filtered through a "medium" frit and cooled to -60 °C, but no precipitate formed. The product was precipitated as a yellowish brown solid by addition of hexane (150 mL): IR (KBr) 2055 (ms), 2010 (m) cm^{-1}; IR (Nujol) 2075 (m), 2025 (m) cm^{-1}. Since conditions to recrytallize the product could not be found and since its solubility properties and IR spectra indicated it was not the desired product, it was not characterized further.

Collection of X-ray Diffraction Data. Attempts to grow crystals of 1 by slow cooling of an acetone solution gave dark burgundy crystals which fragmented on warming to room temperature. Crystals of $Hg_9Co_6(CO)_{18}\cdot2C_3H_6O$ were prepared by slowly evaporating a solution of 1 in acetone. Since these crystals readily lost solvent, a crystal was selected and mounted in a glovebag under an acetone-saturated nitrogen atmosphere. The crystal was mounted on the tip of a 0.3-mm Lindemann glass capillary that was sealed into a 0.5-mm capillary containing a small

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Table I. Experimental Conditions and Data from the X-ray Structure Analysis of Hg$_9$Co$_6$(CO)$_{18}$·2C$_3$H$_6$O

	Crystal Data
cryst shape	tabular
cryst faces (dist	2$\bar{1}$1, $\bar{2}$11 (0.032); 0$\bar{1}$2, 021,
to cryst center	01$\bar{2}$, 02$\bar{1}$ (0.25); 12$\bar{1}$,
(mm))	$\bar{1}$21, 1$\bar{2}$1, $\bar{1}$2$\bar{1}$ (0.14)
cryst dimens, mm	0.55 × 0.30 × 0.065
cell parameters	a = 14.339 (5), b = 21.024
	(6), c = 18.535 (8) Å;
	β = 94.48 (3)°
cell vol, Å^3	5570.4 (36)
Z	4
ρ_{calcd}, g/cm^3	3.31
Laue symmetry	monoclinic
space group	$P2_1/c$, C_{2h}^5, No. 14[24]
systematic absences	0k0, k = 2n + 1;
	h0l, l = 2n + 1
formula	C$_{24}$H$_{12}$Co$_6$Hg$_9$O$_{20}$
mol wt	2779.4
	Data Collection and Reduction
radiatn	Mo Kα
μ, cm^{-1}	270.9
takeoff angle, deg	6.2
scan type	ω
scan speed, deg min^{-1}	1.5–29.3
scan width, deg	1.0
bkgd(total):scan ratio	0.75:1
std reflctns and freq	3/60
variatn of I_{std}	<4%
2θ limits, deg	0.0–45.0
criterion for observn	4$\sigma(F)$
total reflctns measd	5689
reflctns in unique set	5464
obsd reflctns	2624
transmissn range,^{a} %	1–18
	Structure Solution and Refinement^b
solution	direct methods and difference Fourier
refinement	block-diagonal least squares
anisotropic convergence^c	R_1 = 0.081; R_2 = 0.120
max shifts in parameters	position, 0.14; thermal, 0.43
in final cycle (δ/σ)	
error of fit^d	4.75
data/parameters	8.4

^{a} Analytical absorption correction using ABSORB.[25] ^{b} Structure solution and refinement was done by using REDUCE[26] and CRYS-TALS[27] on a PRIME 850 computer operated by the Cornell University Chemistry Department. $^c R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$. ^{d} Error of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{ref} - N_{var})]^{1/2}$.

amount of mother liquor. The crystal was mounted on a Syntex P2$_1$ automated four-circle diffractometer and was centered with 15 reflections having 15° < 2θ < 21°. Details of the crystal data, data collection, data reduction, and structure solution and refinement are presented in Table I. Metal atoms were given anisotropic thermal parameters and other atoms were refined isotropically. Hydrogen atoms were not included. Atomic coordinates, bond distances, and bond angles are given in Tables II, III, and IV, respectively. Thermal parameters are given in Table V. A PLUTO[23] drawing of the molecule is shown in Figure 1.

Results and Discussion

Preparation of Hg$_9$Co$_6$(CO)$_{18}$. Following its initial isolation as a byproduct, as described in the Introduction,

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(26) Leonowicz, M. E. REDUCE; Cornell University: Ithaca, New York, 1978.

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Table II. Fractional Coordinates for Hg$_9$Co$_6$(CO)$_{18}$·2C$_3$H$_6$O^a

atom	x/a	y/b	z/c	U(iso), Å^2
Hg(1)	0.1414 (4)	−0.1727 (2)	0.9505 (3)	0.073
Hg(2)	0.0865 (4)	−0.2080 (2)	0.7924 (3)	0.072
Hg(3)	0.2978 (4)	−0.1987 (2)	0.8499 (3)	0.071
Hg(4)	0.1416 (4)	0.0305 (2)	0.8823 (3)	0.075
Hg(5)	0.0844 (4)	−0.0110 (2)	0.7265 (3)	0.077
Hg(6)	0.2964 (4)	0.0033 (2)	0.7807 (3)	0.075
Hg(7)	0.2990 (4)	−0.0669 (2)	0.9295 (3)	0.072
Hg(8)	0.0013 (4)	−0.0867 (2)	0.8541 (3)	0.074
Hg(9)	0.2239 (4)	−0.1234 (2)	0.7076 (3)	0.076
Co(1)	−0.0244 (13)	−0.2000 (7)	0.8949 (9)	0.078
Co(2)	0.2291 (13)	−0.2432 (7)	0.7262 (8)	0.068
Co(3)	0.3168 (12)	−0.1756 (7)	0.9865 (9)	0.070
Co(4)	−0.0235 (12)	0.0300 (7)	0.8207 (9)	0.072
Co(5)	0.2288 (13)	−0.0136 (8)	0.6493 (9)	0.076
Co(6)	0.3171 (13)	0.0509 (7)	0.9083 (10)	0.078
C(11)	−0.005 (11)	−0.286 (7)	0.915 (8)	0.11 (5)
O(11)	0.015 (8)	−0.334 (5)	0.929 (5)	0.13 (4)
C(12)	−0.058 (7)	−0.173 (4)	0.966 (5)	0.05 (3)
O(12)	−0.097 (6)	−0.159 (4)	1.029 (4)	0.10 (3)
C(13)	−0.136 (10)	−0.201 (6)	0.842 (7)	0.10 (4)
O(13)	−0.182 (6)	−0.209 (3)	0.794 (4)	0.07 (2)
C(21)	0.224 (9)	−0.312 (6)	0.775 (6)	0.08 (4)
O(21)	0.222 (6)	−0.363 (4)	0.792 (4)	0.10 (3)
C(22)	0.332 (11)	−0.247 (6)	0.700 (7)	0.09 (4)
O(22)	0.410 (8)	−0.247 (5)	0.682 (6)	0.15 (4)
C(23)	0.157 (9)	−0.253 (5)	0.648 (6)	0.07 (4)
O(23)	0.102 (8)	−0.259 (5)	0.605 (6)	0.13 (4)
C(31)	0.303 (12)	−0.266 (8)	0.998 (8)	0.12 (6)
O(31)	0.295 (8)	−0.312 (5)	1.022 (6)	0.14 (4)
C(32)	0.424 (11)	−0.173 (6)	0.973 (7)	0.10 (4)
O(32)	0.514 (7)	−0.166 (4)	0.971 (5)	0.11 (3)
C(33)	0.296 (8)	−0.136 (6)	1.062 (7)	0.08 (4)
O(33)	0.293 (7)	−0.115 (5)	1.124 (6)	0.13 (4)
C(41)	0.000 (11)	0.104 (8)	0.781 (8)	0.12 (5)
O(41)	0.013 (7)	0.158 (4)	0.774 (5)	0.10 (3)
C(42)	−0.132 (9)	0.005 (5)	0.773 (6)	0.07 (3)
O(42)	−0.190 (6)	−0.014 (4)	0.727 (4)	0.09 (3)
C(43)	−0.071 (9)	0.044 (6)	0.899 (7)	0.09 (4)
O(43)	−0.097 (6)	0.046 (4)	0.966 (5)	0.11 (3)
C(51)	0.216 (7)	0.063 (5)	0.638 (5)	0.06 (3)
O(51)	0.202 (7)	0.121 (4)	0.636 (5)	0.12 (3)
C(52)	0.334 (11)	−0.033 (6)	0.622 (7)	0.09 (4)
O(52)	0.410 (8)	−0.048 (5)	0.608 (6)	0.14 (4)
C(53)	0.167 (11)	−0.056 (7)	0.576 (8)	0.10 (5)
O(53)	0.126 (9)	−0.064 (6)	0.529 (7)	0.16 (5)
C(61)	0.311 (13)	0.121 (9)	0.878 (9)	0.15 (7)
O(61)	0.299 (7)	0.180 (5)	0.850 (5)	0.12 (3)
C(62)	0.437 (10)	0.034 (5)	0.902 (6)	0.08 (4)
O(62)	0.514 (9)	0.035 (5)	0.912 (6)	0.14 (4)
C(63)	0.306 (11)	0.070 (7)	0.990 (9)	0.12 (5)
O(63)	0.293 (7)	0.075 (4)	1.064 (5)	0.12 (3)
C(1)	0.588 (20)	−0.038 (13)	0.732 (15)	0.28 (13)
C(2)	0.541 (14)	−0.110 (8)	0.786 (9)	0.14 (6)
O(2)	0.446 (7)	−0.107 (4)	0.790 (5)	0.11 (3)
C(3)	0.581 (12)	−0.184 (7)	0.801 (8)	0.13 (6)
C(4)	0.507 (15)	0.123 (9)	0.696 (10)	0.18 (8)
C(5)	0.569 (17)	0.126 (12)	0.637 (13)	0.20 (9)
O(5)	0.564 (9)	0.191 (7)	0.628 (7)	0.18 (5)
C(6)	0.614 (19)	0.075 (13)	0.582 (14)	0.25 (12)

^{a} The standard deviation of the least significant figure is given in parentheses.

attempts to prepare 1 by the addition of a solution of NaOH and Hg(CN)$_2$ in methanol/water to a methanol solution of Hg[Co(CO)$_4$]$_2$ gave variable yields of 1 and frequently resulted in the formation of a finely divided, red-black, intractable solid with ν(CO) 2035 (s) and 1980 (m) cm^{-1}, instead of 1, a dark, burgundy-red solid. Use of Ba(OH)$_2$, instead of NaOH, along with thorough washing and drying of the product, provided a convenient, albeit low-yield (7–10%), synthesis (eq 1). In most cases, sub-
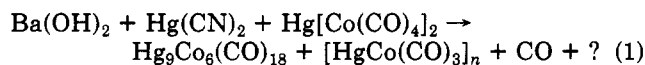
$$Ba(OH)_2 + Hg(CN)_2 + Hg[Co(CO)_4]_2 \rightarrow$$
$$Hg_9Co_6(CO)_{18} + [HgCo(CO)_3]_n + CO + ? \quad (1)$$

Table III. Selected Bond Distances (Å) of Hg$_9$Co$_6$(CO)$_{18}$·2C$_3$H$_6$O^a

Hg(1)–Hg(2)	3.066 (7)	Hg(1)–Hg(3)	3.076 (7)	Hg(2)–Hg(3)	3.138 (8)
Hg(4)–Hg(5)	3.068 (7)	Hg(4)–Hg(6)	3.077 (8)	Hg(5)–Hg(6)	3.141 (8)

Hg(trig)–Hg(trig)(average) = 3.094

Hg(1)–Hg(7)	3.216 (7)	Hg(1)–Hg(8)	3.153 (7)
Hg(2)–Hg(8)	3.086 (7)	Hg(2)–Hg(9)	3.161 (7)
Hg(3)–Hg(7)	3.138 (6)	Hg(3)–Hg(9)	3.185 (7)
Hg(4)–Hg(7)	3.122 (7)	Hg(4)–Hg(8)	3.199 (7)
Hg(5)–Hg(8)	3.160 (7)	Hg(5)–Hg(9)	3.133 (7)
Hg(6)–Hg(7)	3.127 (7)	Hg(6)–Hg(9)	3.130 (7)

Hg(trig)–Hg(square)(average) = 3.151

Hg(1)–Co(1)	2.580 (19)	Hg(1)–Co(3)	2.552 (18)
Hg(2)–Co(1)	2.579 (18)	Hg(2)–Co(2)	2.574 (18)
Hg(3)–Co(2)	2.599 (16)	Hg(3)–Co(3)	2.573 (17)
Hg(4)–Co(4)	2.547 (18)	Hg(4)–Co(6)	2.561 (20)
Hg(5)–Co(4)	2.571 (18)	Hg(5)–Co(5)	2.609 (18)
Hg(6)–Co(5)	2.575 (17)	Hg(6)–Co(6)	2.564 (18)

Hg(trig)–Co(average) = 2.574

Hg(7)–Co(3)	2.521 (16)	Hg(7)–Co(6)	2.525 (16)
Hg(8)–Co(1)	2.535 (16)	Hg(8)–Co(4)	2.548 (15)
Hg(9)–Co(2)	2.541 (15)	Hg(9)–Co(5)	2.553 (17)

Hg(square)–Co(average) = 2.537

Co(1)–C(11)	1.86 (16)	Co(1)–C(12)	1.54 (10)	Co(1)–C(13)	1.81 (14)
Co(2)–C(21)	1.72 (13)	Co(2)–C(22)	1.59 (15)	Co(2)–C(23)	1.72 (13)
Co(3)–C(31)	1.92 (17)	Co(3)–C(32)	1.58 (14)	Co(3)–C(33)	1.67 (13)
Co(4)–C(41)	1.77 (16)	Co(4)–C(42)	1.82 (12)	Co(4)–C(43)	1.67 (13)
Co(5)–C(51)	1.63 (10)	Co(5)–C(52)	1.68 (15)	Co(5)–C(53)	1.80 (16)
Co(6)–C(61)	1.57 (19)	Co(6)–C(62)	1.76 (14)	Co(6)–C(63)	1.59 (16)

Co–C(average) = 1.71

C(11)–O(11)	1.07 (15)	C(12)–O(12)	1.36 (11)	C(13)–O(13)	1.08 (13)
C(21)–O(21)	1.12 (12)	C(22)–O(22)	1.20 (15)	C(23)–O(23)	1.09 (13)
C(31)–O(31)	1.08 (15)	C(32)–O(32)	1.30 (15)	C(33)–O(33)	1.24 (13)
C(41)–O(41)	1.15 (15)	C(42)–O(42)	1.20 (12)	C(43)–O(43)	1.32 (13)
C(51)–O(51)	1.24 (11)	C(52)–O(52)	1.18 (15)	C(53)–O(53)	1.03 (16)
C(61)–O(61)	1.36 (18)	C(62)–O(62)	1.11 (14)	C(63)–O(63)	1.39 (15)

C–O(average) = 1.20

C(1)–C(2)	1.97 (29)	C(4)–C(5)	1.46 (25)
C(2)–C(3)	1.66 (20)	C(5)–C(6)	1.64 (28)
C(2)–O(2)	1.37 (18)	C(5)–O(5)	1.38 (22)

C–C(average) = 1.68
C–O(average) = 1.38

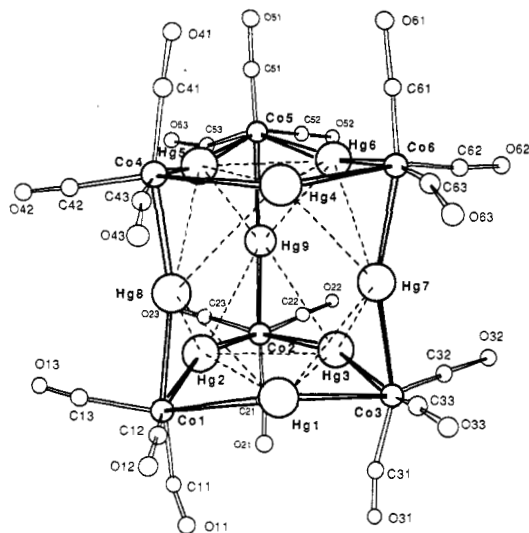^{a} The standard deviation of the least significant figure of each is given in parentheses.

Table IV. Selected Bond Angles (deg) of Hg$_9$Co$_6$(CO)$_{18}$·2C$_3$H$_6$O^a

Co(1)–Hg(1)–Co(3)	163.2 (5)	Co(4)–Hg(4)–Co(6)	161.8 (6)
Co(1)–Hg(2)–Co(2)	158.3 (6)	Co(4)–Hg(5)–Co(5)	157.7 (6)
Co(2)–Hg(3)–Co(3)	160.2 (6)	Co(5)–Hg(6)–Co(6)	159.1 (6)

Co–Hg(terminal)–Co(average) = 160.0

Co(3)–Hg(7)–Co(6)	161.0 (6)	Co(2)–Hg(9)–Co(5)	162.2 (5)
Co(1)–Hg(8)–Co(4)	163.0 (6)		

Co–Hg(central)–Co(average) = 162.1

Hg(1)–Co(1)–Hg(2)	72.9 (5)	Hg(4)–Co(4)–Hg(5)	73.6 (5)
Hg(1)–Co(1)–Hg(8)	76.1 (5)	Hg(4)–Co(4)–Hg(8)	77.8 (5)
Hg(2)–Co(1)–Hg(8)	74.2 (5)	Hg(5)–Co(4)–Hg(8)	76.2 (5)
Hg(2)–Co(2)–Hg(3)	74.7 (4)	Hg(5)–Co(5)–Hg(6)	74.6 (4)
Hg(2)–Co(2)–Hg(9)	76.3 (5)	Hg(5)–Co(5)–Hg(9)	74.7 (5)
Hg(3)–Co(2)–Hg(9)	76.6 (4)	Hg(6)–Co(5)–Hg(9)	75.2 (5)
Hg(1)–Co(3)–Hg(3)	73.8 (5)	Hg(4)–Co(6)–Hg(6)	73.8 (5)
Hg(1)–Co(3)–Hg(7)	78.7 (5)	Hg(4)–Co(6)–Hg(7)	75.7 (5)
Hg(3)–Co(3)–Hg(7)	76.0 (5)	Hg(6)–Co(6)–Hg(7)	75.8 (5)

Hg(terminal)–Co–Hg(terminal)(average) = 73.9
Hg(terminal)–Co–Hg(central)(average) = 76.1

Hg(1)–Co(1)–C(11)	91 (5)	Hg(4)–Co(4)–C(41)	89 (5)
–C(12)	85 (4)	–C(42)	163 (4)
–C(13)	165 (4)	–C(43)	92 (4)
Hg(2)–Co(1)–C(11)	90 (5)	Hg(5)–Co(4)–C(41)	83 (5)
–C(12)	155 (4)	–C(42)	96 (4)
–C(13)	100 (4)	–C(43)	162 (4)
Hg(8)–Co(1)–C(11)	162 (5)	Hg(8)–Co(4)–C(41)	157 (5)
–C(12)	88 (3)	–C(42)	86 (3)
–C(13)	89 (4)	–C(43)	91 (4)
Hg(2)–Co(2)–C(21)	86 (4)	Hg(5)–Co(5)–C(51)	88 (4)
–C(22)	162 (5)	–C(52)	160 (5)
–C(23)	89 (4)	–C(53)	94 (5)
Hg(3)–Co(2)–C(21)	83 (4)	Hg(6)–Co(5)–C(51)	91 (5)
–C(22)	89 (5)	–C(52)	92 (5)
–C(23)	161 (4)	–C(53)	156 (5)
Hg(9)–Co(2)–C(21)	155 (4)	Hg(9)–Co(5)–C(51)	160 (4)
–C(22)	91 (4)	–C(52)	88 (4)
–C(23)	90 (4)	–C(53)	81 (5)
Hg(1)–Co(3)–C(31)	87 (5)	Hg(4)–Co(6)–C(61)	94 (7)
–C(32)	155 (5)	–C(62)	154 (4)
–C(33)	88 (5)	–C(63)	93 (6)
Hg(3)–Co(3)–C(31)	85 (5)	Hg(6)–Co(6)–C(61)	92 (6)
–C(32)	83 (5)	–C(62)	85 (4)
–C(33)	155 (4)	–C(63)	165 (5)
Hg(7)–Co(3)–C(31)	159 (5)	Hg(7)–Co(6)–C(61)	166 (7)
–C(32)	89 (5)	–C(62)	86 (4)
–C(33)	83 (4)	–C(63)	94 (5)

Hg–Co–C(trans)(average) = 160
Hg–Co–C(cis)(average) = 89

C(11)–Co(1)–C(12)	104 (6)	C(41)–Co(4)–C(42)	104 (6)
C(11)–Co(1)–C(13)	102 (6)	C(41)–Co(4)–C(43)	108 (6)
C(12)–Co(1)–C(13)	98 (6)	C(42)–Co(4)–C(43)	95 (6)
C(21)–Co(2)–C(22)	101 (6)	C(51)–Co(5)–C(52)	107 (6)
C(21)–Co(2)–C(23)	107 (6)	C(51)–Co(5)–C(53)	110 (6)
C(22)–Co(2)–C(23)	104 (6)	C(52)–Co(5)–C(53)	93 (7)
C(31)–Co(3)–C(32)	99 (7)	C(61)–Co(6)–C(62)	101 (8)
C(31)–Co(3)–C(33)	112 (6)	C(61)–Co(6)–C(63)	96 (8)
C(32)–Co(3)–C(33)	111 (7)	C(62)–Co(6)–C(63)	106 (7)

C–Co–C(average) = 103

Co(1)–C(11)–O(11)	173 (16)	Co(4)–C(41)–O(41)	162 (13)
–C(12)–O(12)	170 (8)	–C(42)–O(42)	164 (10)
–C(13)–O(13)	155 (12)	–C(43)–O(43)	169 (11)
Co(2)–C(21)–O(21)	165 (11)	Co(5)–C(51)–O(51)	173 (9)
–C(22)–O(22)	177 (13)	–C(52)–O(52)	176 (13)
–C(23)–O(23)	170 (12)	–C(53)–O(53)	160 (15)
Co(3)–C(31)–O(31)	162 (15)	Co(6)–C(61)–O(61)	175 (16)
–C(32)–O(32)	170 (12)	–C(62)–O(62)	162 (12)
–C(33)–O(33)	167 (12)	–C(63)–O(63)	170 (12)

Co–C–O(average) = 168

C(1)–C(2)–C(3)	132 (15)	C(4)–C(5)–C(6)	137 (22)
C(1)–C(2)–O(2)	111 (15)	C(4)–C(5)–O(5)	95 (19)
C(3)–C(2)–O(2)	112 (14)	C(6)–C(5)–O(5)	126 (21)

C–C–C(average) = 134
C–C–O(average) = 111

^{a} The standard deviation of the least significant figure of each angle is given in parentheses.

Figure 1. The structure of Hg$_9$Co$_6$(CO)$_{18}$·2C$_3$H$_6$O as drawn by PLUTO. For clarity, acetone molecules have been omitted.

stantial amounts (up to 40%) of the insoluble component formed. The fate of CN$^-$ is not known. Several attempts to prepare 1 from Na$_3$Co(CO)$_3$ and various mercury(II) salts were not successful; I was not detected by IR spectroscopy in any of the cases. I is moderately soluble in organic solvents of intermediate polarity. It is surprisingly stable to light, air, and water; one sample was unchanged during more than a year in DMSO solution exposed to air. Upon recrystallization from acetone, 1 is initially isolated

Table VI. Infrared [ν(CO)] Spectra and Colors

formula	no.	ν(CO),[a] cm^{-1}	solv	color
Hg$_9$Co$_6$(CO)$_{18}$	1	2015, 1965	THF	burgundy
(CO)$_3$Co(HgI)$_3$	2	2062, 2024	THF	red-orange
(CO)$_3$Co(HgCl)$_3$	3	2049, 2012	Nujol	yellow-orange
(CO)$_3$Co(HgBr)$_3$	4	2044, 1999	KBr	yellow-orange
Hg$_9$Co$_6$(CO)$_{18}$·3(Et$_4$NI)	5	2015, 1955	THF	dark red
(CO)$_3$Co(HgO$_2$CCF$_3$)$_3$	6	2052, 2010	THF	yellow
(p-CH$_3$C$_6$H$_4$SO$_3$Hg)$_3$Co-(CO)$_3$	7	2069, 2025	THF	yellow
(CO)$_3$Co(HgI)$_3$I$^-$NBu$_4^+$	8	2016, 1964	THF	deep red
(C$_6$H$_5$Hg)$_3$Co(CO)$_3$	9	2020, 1969	THF	red

[a] Higher frequency peak is strong and lower frequency peak is weak to medium intensity.

as a bis(acetone) solvate, but the solvent is rapidly lost at room temperature, as shown by the elemental analysis and IR spectroscopy. The IR spectrum (C–O stretching region) of 1 in THF shows two major bands, 2015 (s) and 1965 (m) cm^{-1}, assigned to the A$_1$ and E stretching modes, respectively, of a Co(CO)$_3$ group with C_{3v} geometry.[28] The observed ^{59}Co NMR line width $\Delta\nu_{1/2}$ = 360 Hz (δ −225 vs Co(CO)$_4^-$) is consistent with this symmetry environment.[29] The close similarity of the IR spectra of 1 in DMSO and in THF or Nujol suggests that, as with Hg[Co(CO)$_4$]$_2$,[30] ionic dissociation does not occur to a significant extent. The molecular weight of 1, measured cryscopically in sulfolane, was found to be 2817 g/mol, consistent with the presence of an undissociated hexamer, [Hg$_{1.5}$Co(CO)$_3$]$_6$, in solution.

Crystal Structure of Hg$_9$Co$_6$(CO)$_{18}$·2C$_3$H$_6$O. Because the unusual stability and stoichiometry of 1 suggested an unusual structure, a single-crystal X-ray analysis was carried out, establishing the structure shown in Figure 1. The metal framework is best described as a distorted rectangular trigonal prism with *fac*-(CO)$_3$Co fragments at each corner and a mercury atom at the center of each edge. Mercury atoms Hg(1)–Hg(6), on the edges of the triangular faces (Hg(trig)), are located slighlty inside the two Co$_3$ planes and outside the lines connecting adjacent cobalt atoms. Mercury atoms Hg(7)–Hg(9), on the edges of the square faces (Hg(sq)), are bent toward the center of the cluster. The cobalt atoms exhibit distorted octahedral geometry with the C–Co–C angles averaging 103° while the Hg–Co–Hg angles average 75°. These distortions are at least partly caused by geometric requirements; it is impossible for the cluster to have 90° angles at cobalt and 180° angles at mercury and to maintain the trigonal-prismatic arrangement of metal atoms.

There are several interesting features about the structure. Very few compounds are known to contain *fac*-(CO)$_3$CoX$_3$ units: As$_3$Co(CO)$_3$[31a] and [SbCo(CO)$_3$]$_4$.[31b] The average C–Co–C angle of 100° and Sb–Co–Sb angle of 74.3° are very similar to the C–Co–C and Hg–Co–Hg angles of 103° and 75° in 1, respectively. The Hg(trig)–Co and Hg(sq)–Co distances were 2.574 and 2.537 Å; both values are slightly greater than the Hg–Co distance of 2.499 Å in Hg[Co(CO)$_4$]$_2$.[32] The average distance between Hg(trig) atoms is 3.094 Å, while the average Hg(sq)–Hg(trig) distance is 3.151 Å. These distances are comparable to the 2.99 Å found for nearest neighbors in mercury metal at −40
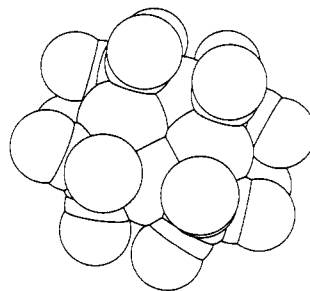
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Figure 2. A space-filling model of Hg$_9$Co$_6$(CO)$_{18}$·2C$_3$H$_6$O as drawn by PLUTO.

°C[33] and the average Hg–Hg distance of 3.142 Å observed in Hg$_6$Rh$_4$[P(Me)$_3$]$_{12}$.[6] Formally, both 1 and Hg$_6$Rh$_4$[P-(Me)$_3$]$_{12}$ are made up of Hg$_{1.5}$ML$_3$ units, and it is not clear why the clusters adopt different degrees of oligomerization.

The nature of the Hg–Hg interactions in this type of cluster is open to question. Although the Hg–Hg distance of ca. 3.1 Å is well within bonding distance, this does not necessarily imply a bonding interaction. As noted by Grdenič, the additivity rule for atomic radii does not work well for mercury;[34] the Hg–Hg distance in Hg(I)–transition-metal compounds can vary from 2.651[35] to 3.225 Å,[36] in spite of the fact that there is clearly a Hg–Hg bond in each case. Extended Hückel calculations on 1 and, for comparison, on (CO)$_4$Fe(HgCl)$_2$ (with a Hg–Hg distance of 3.24 Å) show small overlap populations between mercury atoms, indicating that the bonding interactions, if any, are small.[37]

The stereochemistry observed in several compounds containing two or more mercury atoms bonded to the same transition metal is suggestive of a bonding interaction;[4-10,38] the mercury atoms are cis with an Hg–M–Hg angle of 60–80° and an Hg–Hg distance less than 3.3 Å. In addition, comparison of the analogous clusters Hg[NiCp-(GePh$_3$)HgGePh$_3$]$_2$[5] and Cd[NiCp(GePh$_3$)CdGePh$_3$]$_2$[39] shows a Hg–Hg distance of 3.177 Å in the former, but a Cd–Cd distance of 3.353 Å in the latter, in spite of the similar size of mercury and cadmium atoms.[40] The Hg–Ni–Hg angle of 81° is substantially smaller than the Cd–Ni–Cd angle of 86°. This evidence implies that some interaction occurs between adjacent mercury atoms in clusters of this type, but it is likely that it is much smaller than the covalent Hg–M bonds. The simple valence bond description of the bonding in these clusters (which ignores Hg–Hg interactions) is adequate for understanding the stoichiometry and major structural features of 1.

Reactions of 1 with Lewis Bases. For the linear derivatives, Hg(ML$_n$)$_2$, mercury is known to act as a Lewis

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(36) Albinati, A.; Moor, A.; Pregosin, P. S.; Venanzi, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 7672.
(37) Femec, D. A.; Ragosta, J. M., unpublished observations. Average reduced overlap populations for (CO)$_4$Fe(HgCl)$_2$: Fe–Hg, 0.360; Fe–C, 0.855; Hg–Hg, 0.026; Hg–Cl, 0.296; C–C, 0.031. Average reduced overlap populations for Hg$_9$Co$_6$(CO)$_{18}$: Co–Hg, 0.262; Co–C, 0.868; Hg–Hg, 0.039; C–C 0.035.
(38) (a) Kubicki, M. M.; Kergoat, R.; Guerchais, J. E.; Bois, C.; L'-Haridon, P. *Inorg. Chim. Acta* **1980**, *43*, 17. (b) Kubicki, M. M.; Kergoat, R.; Guerchais, J. E.; Bkouche-Waksman, I.; Bois, C.; L'Haridon, P. *J. Organomet. Chem.* **1981**, *219*, 329. (c) Raston, C. L.; White, A. H.; Wild, S. B. *Aust. J. Chem.* **1976**, *29*, 1905. (d) Baird, H. W.; Dahl, L. F. *J. Organomet. Chem.* **1967**, *7*, 503. (e) Baker, R. W.; Pauling, P. *J. Chem. Soc. D* **1970**, 573. (f) Brotherton, P. D.; Kepert, D. L.; White, A. H.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1871.
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(40) Pauling, L. *The Nature of the Chemical Bond*, 4th ed., Cornell University Press: Ithaca, New York, 1967.

acid, readily forming adducts under favorable conditions.[41] Out of several attempts to form adducts, using 1 and various Lewis bases (I⁻, SCN⁻, and PPh₃), there is evidence for adduct formation in only one case, viz., in the reaction of Et₄N I; elemental analysis showed the presence of three iodide ligands per cluster. The reticence of 1 to form adducts is probably due to steric and electronic factors. A space-filling model (Figure 2) suggests that the coordination of small- to moderate-sized ligands to the square faces of the cluster should be possible. Coordination would also favor a change to trigonal-planar geometry at mercury,[42] but such a major change in geometry at mercury would be accompanied by distortion of the pseudoocta-hedral coordination at cobalt, thereby reducing the driving force for adduct formation.

The coordination of I⁻ has only a slight effect on the IR spectrum of the complex, lowering the highest frequency absorption by about 6 cm⁻¹ from that of 1. This is consistent with a very little donation of electron density to the cobalt carbonyl fragments. The apparent inability of SCN⁻ to form a similar complex surprised us.
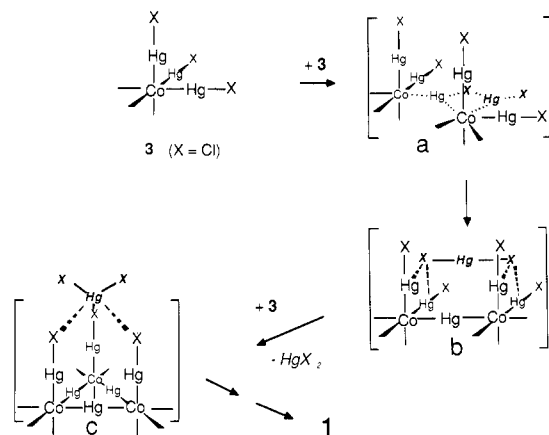
In addition to the Lewis site on mercury, Lewis bases could also react by displacement of CO at cobalt. When a solution of 1 in THF was treated with PPh₃ at room temperature, no reaction was evident (IR). In contrast, when 1 was treated with P-n-Bu₃ at room temperature in THF, there was no change in the IR spectrum for the first 30 min, but after this time, decomposition occurred, giving an uncharacterized product with no ν(CO) absorptions.

Conversion of 1 to (CO)₃Co(HgX)₃ Derivatives. It is well-known that symmetrical transition metal–mercury compounds Hg(ML$_n$)₂ (ML$_n$ = Cp(CO)₃Mo, Cp(CO)₃W, (CO)₄Co, Cp(CO)₂Fe, etc.) react with mercury halides, HgX₂ (X = Cl, Br, I, SCN), to form unsymmetrical compounds L$_n$MHgX.[43] The reaction of 1 with compounds of type HgX₂ (X = Cl, Br, I, CF₃COO) forms new compounds of composition (CO)₃Co(HgX)₃ (eq 2). When X was Ph or p-CH₃C₆H₄, no reaction was observed, whereas with mercury(II), dithiocarbamate, only Co(S₂CNEt₂)₂ was isolated.

$$Hg_9Co_6(CO)_{18} + 9HgX_2 \rightarrow 6(CO)_3Co(HgX)_3 \quad (2)$$
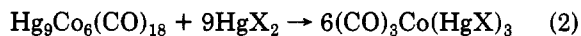
Products from these exchange reactions are yellow to red solids. The iodide 2 and the trifluoroacetate are moderately soluble in polar solvents whereas the chloride 3 and bromide are only sparingly soluble. With the exception of the light-sensitive trifluoroacetate derivative, none could be recrystallized cleanly from the many solvent systems tried; in the case of the bromo derivative, dissolution in pyridine released CO and Hg and formed (py)₂CoBr₂. Slow decomposition occurred when these solids were stored for several days at room temperature; this instability manifested itself as partial insolubility in organic solvents previously found to dissolve the sample completely.[44]

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(42) Petersen, R. B.; Ragosta, J. M.; Whitwell, G. E., II; Burlitch, J. M. *Inorg. Chem.* **1983**, *22*, 3407 and references therein.

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(44) Because of the instability, consistent carbon and hydrogen analyses could not be obtained when samples were sent out for analysis. Consequently, molecular weight determinations and metal and halogen analyses were done locally on freshly prepared samples. The most stable compound in this group, (CO)₃Co(HgO₂CCF₃)₃, could be stored for somewhat longer periods of time, so more complete, though less than ideal elemental analysis data were available. This compound, as a toluene solvate, was crystalline, but the crystals decomposed in an X-ray beam, even at −60 °C, so a structural determination was not possible.

Scheme I

The IR spectra of all the (CO)₃Co(HgX)₃ compounds (see Table V) show the same pattern of ν(CO) as 1 viz. a strong peak between 2000 and 2100 cm⁻¹ and a peak with weak to medium intensity at approximately 50 cm⁻¹ lower frequency. From this, we infer that these compounds have an environment at cobalt similar to that of 1, viz., nearly C_{3v} symmetry. The simplicity of the IR spectra and the observation of only one spot after TLC analysis are consistent with principally one species being present in solution. Mass spectra were obtained for several (CO)₃Co-(HgX)₃ compounds, but parent molecular ions were not observed for any. Cryoscopic molecular weight determination on a freshly prepared sample of 2 showed it to be monomeric.

In an attempt to prepare compounds of type (CO)₃Co-(HgX)₃ by an alternate method, Na₃Co(CO)₃[19] was treated with mercury(II) halides. The reaction of Na₃Co(CO)₃ with HgBr₂ gave a small amount of an unidentified product with ν(CO) (Nujol) 2075 (m) and 2025 (m) cm⁻¹. In none of several attempts was the product the same as the product formed by the reaction of 1 with HgX₂. The extreme reactivity of Na₃Co(CO)₃ may cause it to be oxidized by HgX₂ before it can react to form (CO)₃Co(HgX)₃.

Reassembly of Hg₉Co₆(CO)₁₈. By far, the most unusual reaction of the (CO)₃Co(HgX)₃ compounds, is the efficient conversion of the chloro derivative to 1. Addition of PPh₃ to a suspension of (CO)₃Co(HgCl)₃ (3) gave 92% of the theoretical yield of (PPh₃)₂HgCl₂ and, after recrystallization, 82% of the theoretical yield of 1 (Equation 3). A similar reaction occurred on mixing (CO)₃Co(HgI)₃

$$6(CO)_3Co(HgCl)_3 + \text{excess PPh}_3 \rightarrow$$
$$Hg_9Co_6(CO)_{18} + 9(PPh_3)_2HgCl_2 \quad (3)$$
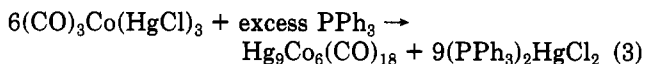
with PPh₃, but it was much slower, requiring several days for completion during which time some decomposition occurred. Compounds of type L$_n$MHgX can be converted to the symmetrical compounds, (L$_n$M)₂Hg, by addition of excess PPh₃.[43b]

Conversion of 3 to 1 gave only one cluster. Such specificity places rather stringent requirements on the spatial orientation of the fac-(XHg)₃Co moieties during cluster growth if this were to occur by a sequence of irreversible reactions. In such a case, this orientation might be provided by coordination of the departing HgX₂ fragments to several Co–HgX units, as shown in Scheme I. In this scenario, the process would begin by coordination of the electron-rich cobalt (formally Co(−III)) of 3 to a mercury atom of a second molecule of 3, forming the intermediate labeled **a**. This intermediate is analogous to the one formed in the ammonia-promoted symmetrization of arylmercuric halides.[45] Adduct formation between a

transition-metal carbonyl anion and mercury is well-documented.[42] Mercuric chloride is then lost from this complex, but it remains coordinated to the condensation product **b** and orients the remaining -HgCl groups for attack by another molecule of **3**. Other reactions of the same type might thus lead to formation of **1**.

Alternatively, if reversible reactions are considered, **1** might simply be the most energetically favorable of a very large number of transient species.

Reactions of $(CO)_3Co(HgI)_3$. The iodo derivative **2** served as a useful precursor for formation of other derivatives by metathetical reactions. The reaction of **2** with silver p-toluenesulfonate in THF resulted in the formation of a new compound, $(p\text{-}CH_3C_6H_4SO_3Hg)_3Co(CO)_3$, and nearly quantitative precipitation of AgI (eq 4, Y = p-$CH_3C_6H_4SO_3$ and M = Ag). The product is a yellow solid,

$$(CO)_3Co(HgI)_3 + 3MY \rightarrow (CO)_3Co(HgY)_3 + 3MI \quad (4)$$

soluble in polar organic solvents. It was recrystallized as a yellow powder from methylene dichloride, but crystals suitable for an X-ray structure determination could not be obtained. Its IR $\nu(CO)$ spectrum (Table V) was similar to that of **2** and showed the highest $\nu(CO)$ of any of the compounds in this study. This is consistent with the weak base character of the p-tosyl group. The observed molecular weight of this product, 1295 g/mol (calculated 1258 g/mol), indicated a monomeric form in solution.

The metathesis reaction of **2** provided a route to a class of previously inaccessible cobalt carbonyl compounds, viz., organomercury derivatives, $(RHg)_mCoL_n$. Treatment of **2** with 3 equiv of phenyllithium (eq 3, Y = Ph, M = Li) gave a dark red product, the mass spectrum of which contained peaks assignable to $(CO)_3Co(HgPh)^+$ but no parent ion. Like other $(CO)_3Co(HgY)_3$ compounds, the phenyl derivative is somewhat thermally unstable but has an IR spectrum consistent with the structure of a *fac* isomer. It is noteworthy that attempts to prepare this derivative and its p-tolyl analogue by direct reaction of the appropriate R_2Hg compound with **1** were not successful.

Compound **2** formed a Lewis acid–base adduct with iodide ion. The product is thermally unstable, but elemental analysis indicated that the stoichiometry is approximately 1:1. The reversible nature of adduct formation was shown by the addition of 1 equiv of Ag$^+$ to a solution of $(CO)_3Co(HgI)_3I^-$, regenerating **2**. Formation of adducts with dimetallic L_nMHgX compounds with halides has been described.[41]

Summary and Conclusions. A novel metal cluster, $Hg_9Co_6(CO)_{18}$ (**1**), has been prepared from $Hg[Co(CO)_4]_2$ and found to consist of *fac*-$Co(CO)_3$ fragments at the corners of a rectangular prism with mercury atoms at the middle of each edge. Through reaction of **1** with mercury(II) halides or $Hg(CF_3CO_2)_2$, new compounds $(CO)_3Co(HgX)_3$ were prepared. One of these, having X = Cl, reformed **1** in high yield when treated with triphenylphosphine; such an efficient reassembly of a large cluster, from a simple precursor under mild conditions, is most unusual and has potential for the preparation of novel, mixed-metal clusters starting with a mixture of ML_nHgX species. Substitution of iodide in the analogous cmpound $(CO)_3Co(HgI)_3$ by p-toluenesulfonato or phenyl ligands gave new compounds, $(CO)_3Co(HgY)_3$ (Y = p-$CH_3C_6H_4SO_3$, C_6H_5). The latter is the second organomercury derivative of a cobalt carbonyl of any type.[46] All of the tris(halomercury) compounds were somewhat unstable and were best prepared in situ (from **1**) and used immediately.

Registry No. 1, 100851-89-6; 1·2C_3H_6O, 100851-90-9; **2**, 102651-39-8; **3**, 102651-40-1; **4**, 113687-17-5; **5**, 113687-18-6; **6**, 102651-41-2; **7**, 102651-43-4; **8**, 102651-45-6; **9**, 102651-42-3; $[HgCo(CO)_3]_n$, 113687-19-7; $Hg[Co(CO)_4]_2$, 13964-88-0; $Na_3(Co(CO)_3$, 90668-30-7; Co, 7440-48-4; Hg, 7439-97-6.

Supplementary Material Available: Table V (thermal parameters) (1 page); a list of structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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