$(OMe)_4][NBu_4]$[12] were formed.

The ruthenium alkyl complexes decompose in the solid state and in solution upon exposure to oxygen. In an NMR tube, 10 mg of $[Ru(N)(CH_2SiMe_3)_4][NBu_4]$ was dissolved in 0.3 mL of C_6D_6. Excess O_2 was injected into the sample, and ^1H NMR spectra were obtained periodically. After 80 min, a large amount of black solid had formed on the walls of the NMR tube and there was no $[Ru(N)(CH_2SiMe_3)_4][NBu_4]$ remaining in solution.

We are presently investigating the reaction chemistry of these new ruthenium alkyl complexes with two-electron donors, with electrophiles, and with oxidizing agents.

Acknowledgment. We thank the National Science Foundatioin (Grant CHE-8420768) for support of this work. J.P.W. thanks Allied Chemical for a graduate fellowship 1984–1985. We also thank J. Carter Cooke, Director of the Mass Spectroscopy Laboratory at UIUC, for obtaining the FAB mass spectrum of **3a**.

Registry No. 1, 42862-74-8; **2**, 102649-19-4; **3a**, 102649-21-8; **3b**, 102649-23-0; **4**, 102649-25-2; **5**, 102649-27-4; $NaOSiMe_3$, 18027-10-6; $Mg(CH_2SiMe_3)_2{\cdot}Et_2O$, 63817-04-9; $AlMe_3$, 75-24-1; $MgMe_2$, 2999-74-8; $[Ru(N)(OMe)_4][NBu_4]$, 102681-91-4; methanol, 67-56-1.

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[12] We have not yet obtained analytically pure samples of $[Ru(N)(OMe)_4][NBu_4]$, but the ^1H NMR spectrum (δ 2.03 (s, 3 H, OMe)) is identical with that of the well-characterized osmium analogue $[Os(N)(OMe)_4][NBu_4]$.

Chemical Dissection and Reassembly of a Mixed-Metal Cluster, $Hg_9Co_6(CO)_{18}$

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Summary: The cluster $Hg_9Co_6(CO)_{18}$ reacts with compounds of type HgX_2 to form new monocobalt compounds, $(CO)_3Co(HgX)_3$ ($X = I, Cl, O_2CCF_3$). The iodo derivative was used to prepare $(CO)_3Co(HgI)_3I^-\ Bu_4N^+$, $(CO)_3Co(HgO_3SC_6H_4CH_3)_3$, and $(CO)_3Co(HgPh)_3$. Addition of PPh_3 to $(CO)_3Co(HgCl)_3$ caused reassembly of $Hg_9Co_6(CO)_{18}$ in high yield.

The structure of the novel metal cluster $Hg_9Co_6(CO)_{18}$ (**1**) consists of *fac*-octahedral $(CO)_3Co$ fragments at the corners of a rectangular-trigonal prism with mercury atoms at the centers of each edge.[1] Very little is known about the chemistry of mixed-metal clusters containing several mercury atoms, so a study of the chemistry of this unusual cluster was undertaken. **1** was found to react with compounds of type HgX_2 to form monocobalt clusters of composition $(CO)_3Co(HgX)_3$ (eq 1; $X = Cl, I, O_2CCF_3$), essentially quantitatively. This is analogous to the behavior of simpler compounds, $(L_nM)_2Hg$.[2]

$$1 + 9HgX_2 \rightarrow 6(CO)_3Co(HgX)_3 \qquad (1)$$

Table I. Infrared ν(CO) Frequencies and Colors of Compounds of Type $(CO)_3CoX_3$ and $(CO)_3CoX_3\{B\}$

formula	ν(CO),[a] cm^{-1}	solv	color
$Hg_9Co_6(CO)_{18}$	2015, 1965	THF	burgundy
$(CO)_3Co(HgI)_3$	2062, 2024	THF	red-orange
$(CO)_3Co(HgCl)_3$	2049, 2012	Nujol	yellow
$(CO)_3Co(HgO_2CCF_3)_3$	2052, 2010	THF	yellow
$(CO)_3Co(HgI)_3I^-Bu_4N^+$	2023, 1968	THF	red
$(CO)_3Co(HgC_6H_5)_3$	2012, 1960	THF	red
$(CO)_3Co(HgO_3SC_6H_4\text{-}p\text{-}CH_3)_3$	2069, 2025	THF	yellow
$[(CO)_3CoSb]_4$[b]	2042, 1995	Nujol	black

[a] Peak at higher frequency is strong; lower frequency peak is weak to medium intensity. [b] Reference 4.

The new compounds $(CO)_3Co(HgX)_3$ are yellow to red solids and, with the exception of the slightly soluble chloro derivative, are moderately soluble in polar organic solvents. All of these compounds showed some thermal instability, slowly decomposing into insoluble materials; some even decomposed in the solid state at −60 °C. The trifluoroacetate derivative was the most thermally stable, though, unlike the others, it was light sensitive.[3] Unfortunately, this compound decomposed rapidly in an X-ray beam, even at −60 °C, precluding structural analysis.

Compounds of type $(CO)_3CoY_3$ are rare. In addition to **1**, only one example is known, viz., $[(CO)_3CoSb]_4$ which has a pseudocubic structure with $(CO)_3Co$ fragments and Sb atoms on alternate corners.[4] The new compounds $(CO)_3Co(HgX)_3$ appear to have the same *fac*-octahedral geometry as these two known compounds, based on the similarity of their IR spectra (Table I). The observed molecular weight of 1094 g/mol for $(CO)_3Co(HgI)_3$ (**2**) is within experimental error of the expected value (1125 g/mol) and, along with the IR and analytical data,[3] strongly support a monomeric, *fac*-$(CO)_3Co(HgX)_3$ structure.[8]

Some aspects of the chemical properties of the new compounds resemble those of the bis-metal mercury compounds.[5] As would be expected,[6] mercury in $(CO)_3Co(HgI)_3$ acts as a Lewis acid. Thus, the addition of tetrabutylammonium iodide to **2** gives a 1:1 adduct (eq 2).[7] The addition of 1 equiv of a soluble silver salt to a solution of $(CO)_3Co(HgI)_3I^-$ regenerated **2** in high yield.

$$2 + Bu_4N^+I^- \rightarrow (CO)_3Co(HgI)_3I^-Bu_4N^+ \qquad (2)$$

Replacement of iodine by phenyl at each of the three mercury atoms of **2** was accomplished by treatment with 3 equiv of phenyllithium.[9] The product $(CO)_3Co(HgPh)_3$ is the second example of an organomercury derivative of a cobalt carbonyl of any type;[10a] most $RHgM(L)_n$ deriva-

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[1] Ragosta, J. M.; Burlitch, J. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1187.

[2] Mays, M. J.; Robb, J. D. *J. Chem. Soc. A* **1968**, 329.

[3] Compound **2** was prepared by treating a solution of **1** in THF with the stoichiometric amount of mercuric iodide. Found (Calcd): Hg, 52.9 (53.5); Co, 5.15 (5.24); I, 33.6 (33.8); M_r 1094 (1125).[8] Metal and molecular weight analyses were carried out an a freshly prepared sample. The analogous chloro complex $(CO)_3Co(HgCl)_3$ was prepared in the same way. Found (Calcd): Hg, 72.3 (70.7); Co, 6.82 (6.92). $(CO)_3Co(HgO_2CCF_3)_3$ was prepared by treating a solution of **1** in THF with mercuric trifluoroacetate; the product was recrystallized from toluene. Found (calcd for $(CO)_3Co(HgO_2CCF_3)_3{\cdot}{}^1/_2(C_7H_8)$: Hg, 52.65 (53.27); Co, 6.49 (5.21); C, 12.78 (13.29); H, 0.39 (0.35).

[4] Foust, A. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7337.

[5] Burlitch, J. M. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., eds.; Pergamon Press: Oxford, 1982; Chapter 42.

[6] Conder, H. L.; Robinson, W. R. *Inorg. Chem.* **1972**, *11*, 1527.

[7] $(CO)_3Co(HgI)_3I^-Bu_4N^+$ was prepared by treating a solution of **2** in THF with 1 equiv of $Bu_4N^+I^-$. Found (calcd): 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).

[8] Molecular weights were obtained cryoscopically in sulfolane; with this method, a value of 2817 g/mol was observed for **1** (calculated 2663).

[9] $(CO)_3Co(HgC_6H_5)_3$ was prepared by treating a solution of **2** in THF with the stoichiometric amount of PhLi. Found (calcd): H, 62.0 (61.6); Co, 5.91 (6.04); I, 1.3 (0.0).

[10] (a) Glockling, F.; Mahale, V. B.; Sweeney, J. J. *J. Chem. Soc., Dalton Trans.* **1979**, 767. (b) See ref 5, p 999, for a review.

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tives undergo symmetrization with formation of R_2Hg.[10b]

Treating $(CO)_3Co(HgI)_3$ with 3 equiv of silver *p*-toluenesulfonate in THF resulted in the formation of monomeric, $(p\text{-}CH_3C_6H_4SO_3Hg)_3Co(CO)_3$ and quantitative precipitation of AgI (eq 3).[11] As far as we know, this type

$$2 + 3Ag[p\text{-}CH_3C_6H_4SO_3] \rightarrow (p\text{-}CH_3C_6H_4SO_3Hg)_3Co(CO)_3 + 3AgI \quad (3)$$

of metathesis reaction has not been previously reported for HgX derivatives of transition-metal carbonyls. The product serves as a synthetic intermediate for preparation of other $(CO)_3Co(HgY)_3$ derivatives.[12]

A most intriguing observation was that $Hg_9Co_6(CO)_{18}$ reformed in high yield when $(CO)_3Co(HgCl)_3$ was treated with triphenylphosphine (eq 4.)[13]

$$6(CO)_3Co(HgCl)_3 + 18PPh_3 \rightarrow 1 + 9(PPh_3)_2HgCl_2 \quad (4)$$

It is particularly significant that this reaction proceeds to completion *nearly quantitatively*, forming *only one cluster* out of a large number of possible oligomers or polymers. The reformation of 1 in this way is formally the reverse of the reaction shown in eq 1 with Ph_3P removing the mercuric halide formed. Symmetrization of simple $XHgM(L)_n$ compounds, effected by Ph_3P, has been described.[2]

The reassembly of 1, to the exclusion of other possible oligomers of $(CO)_3CoHg_{1.5}$, places stringent demands on the spatial orientation of each of the six *fac*-$(XHg)_3Co$ moieties during cluster reconstruction. We suggest that the departing HgX_2 may exert the necessary stereochemical influence by coordinating to several Co-HgX units simultaneously.

Acknowledgment. We thank Ace Glass Inc. for partial support of this work.

Registry No. 1, 100851-89-6; 2, 102651-39-8; 3 (X = Cl), 102651-40-1; 3 (X = O_2CCF_3), 102651-41-2; 3 (X = Ph), 102651-42-3; 3 (X = $O_3SC_6H_4$-*p*-CH_3), 102651-43-4; $(CO)_3Co(HgI)_3I^-Bu_4N^+$, 102651-45-6; Co, 7440-48-4; Hg, 7439-97-6.

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[11] A solution of 2 in THF, prepared in situ from 1 and HgI_2, was stirred with slightly more than 3 equiv of $p\text{-}CH_3C_6H_4SO_3Ag$ and then filtered to remove AgI. Removal of the solvent and recrystallization from CH_2Cl_2 gave $(p\text{-}CH_3C_6H_4SO_3Hg)_3Co(CO)_3$ as a yellow powder. Found (calcd): Hg, 48.1 (47.8); Co, 4.57, (4.68); M_r 1295 (1258).[8]

[12] Burlitch, J. M.; Ragosta, J. M., to be submitted for publication.

[13] A suspension of yellow $(CO)_3Co(HgCl)_3$ in THF (prepared in situ) was stirred with a solution of the stoichiometric amount of triphenylphosphine in THF for 3 h. This gave a dark red solution with a gray-white precipitate identified as $(PPh_3)_2HgCl_2$ by mixed melting point with an authentic sample; the yield was 92%. The filtrate contained 1, as identified by its IR spectrum; the yield of recrystallized product was 82%. 2 also reacted with triphenylphosphine to form 1 and $(PPh_3)_2HgI_2$, but the reaction required several days for completion and some decomposition of 2 occurred during this time.

Silicon-Carbon Unsaturated Compounds. 21. Isomerization of a 1-Silapropadiene in the Presence of Tetrakis(triethylphosphine)nickel(0)

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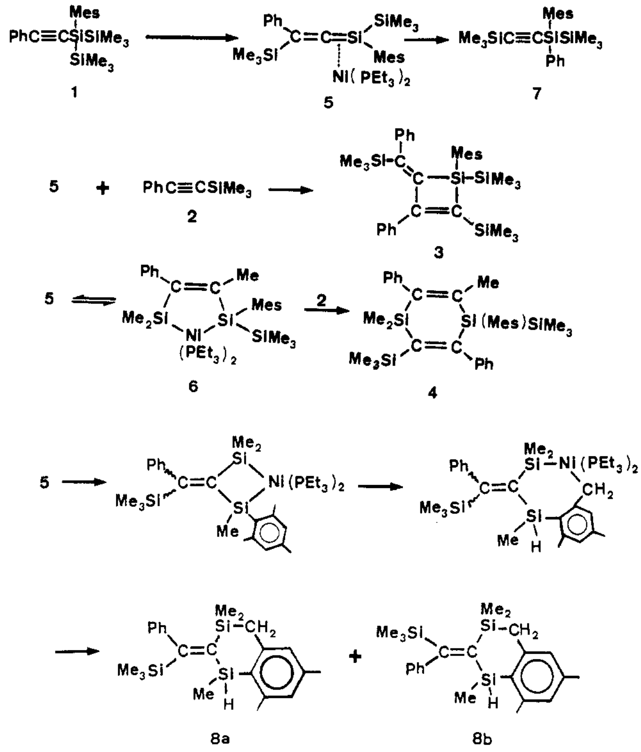
Summary: The nickel-catalyzed reaction of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane (**1**) with phenyl(trimethylsilyl)acetylene (**2**) gave two products arising from the isomerization of **1**, followed by addition to **2**. In the absence of **2**, products derived from the isomerization of a 1-silapropadiene generated from **1**, 5,6-benzo-1,3-disilacyclohexene derivatives, were obtained in high yields.

Scheme I



Recently, we have found that the nickel-catalyzed reaction of phenylethynylpolysilanes and silacyclopropenes with phenyl(trimethylsilyl)acetylene affords products which can be best explained by assuming the formation of 1-silapropadiene-nickel complexes.[1] In this communication we report the novel isomerization of the 1-silapropadiene intermediate generated from 2-mesityl-2-(phenylethynyl)hexamethyltrisilane (1) in the presence of a nickel(0) catalyst.

When 1 was heated with a small excess of phenyl(trimethylsilyl)acetylene (2) in the presence of a catalytic amount of $Ni(PEt_3)_4$ in a sealed glass tube at 195 °C for 20 h, two products, 1-mesityl-3-phenyl-2-[phenyl(trimethylsilyl)methylene]-1,4-bis(trimethylsilyl)-1-silacyclobut-3-ene (**3**) and 2,5-diphenyl-1-mesityl-4,4,6-trimethyl-1,3-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**4**), were obtained in 77 and 11% yields, respectively. Compound **3** could readily be separated from **4** by fractional recrystallization from ethanol. The structures of **3** and **4** were verified by mass and ^1H and ^{13}C NMR spectroscopic analysis.[2,3]

The formation of **3** can be best explained in terms of the reaction of the 1-silapropadiene-nickel complex **5** with acetylene **2**. It seems likely that product **4** would be formed by the reaction of the nickeladisilacyclopentene

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[1] Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. *Organometallics* **1985**, *4*, 2040.

[2] For compound **3**: mp 165-166 °C; 100-MHz ^1H NMR δ (CCl_4) -0.32 (9 H, s, Me_3Si), -0.15 (9 H, s, Me_3Si), 0.40 (9 H, s, Me_3Si), 2.36 (3 H, s, *p*-Me), 2.70 (6 H, s, *o*-Me), 6.64-7.04 (12 H, m, phenyl and mesityl ring protons); ^{13}C NMR δ ($CDCl_3$) -1.0 (Me_3Si), 0.0 (Me_3Si), 1.1 (Me_3Si), 21.1 (*o*- and *p*-Me), 124.5, 125.3, 126.5, 126.8, 127.0, 128.1, 128.9 (two carbons), 131.4, 139.2, 142.2, 142.3 (ring carbons), 144.9, 155.8, 162.6, 174.1 (olefinic carbons); MS, *m/e* 568 (M^+). Anal. Calcd for $C_{34}H_{48}Si_4$: C, 71.76; H, 8.50. Found: C, 71.75; H, 8.64.

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