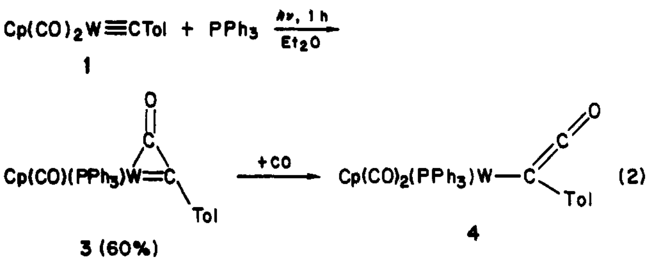
diphenylcyclopropenone and for which a weak metal carbonyl interaction was suggested.[10] Of particular interest in 2 is the acute C(6)–C(5)–C(7) angle of 98°, considering the assumed sp^2 hybridization of C(5). Complex 2 also forms in trace quantities along with unidentified brown decomposition products when solutions of 1 are irradiated in the absence of added CO.

A similar rapid photoinduced carbonylation of the carbyne ligand occurs when 1 is irradiated in the presence of PPh_3 to give the η^2-ketenyl complex 3 (eq 2). When the reaction is performed under a CO atmosphere, 3 is observed as an intermediate, but the final product of this reaction is the η^1-ketenyl complex 4.[11] Complex 4 was independently shown to derive from 3 by a thermal reaction with CO. The 1 to 3 conversion has been previously reported to proceed thermally over 2 days at 25 °C,[12] but we find that if these solutions are rigorously maintained in the dark, 3 forms after 7–8 days and then only as one component in a mixture of decomposition products. In contrast, the similar reaction involving PMe_3 proceeds rapidly in the dark as well as upon irradiation.[12]



We suggest that these carbonylation reactions proceed via initial migration of a coordinated CO to the carbyne ligand in a tungsten-to-carbyne CT excited state. This would yield a coordinatively unsaturated η^2-ketenyl complex which could subsequently be scavenged by PPh_3 to yield 3 or alternatively by CO or the carbyne complex 1 to form binuclear 2 (Scheme I). Support for this suggestion comes from IR monitoring of the photolysis of 1 in the presence of PPh_3 under a ^{13}CO atmosphere. No incorporation of ^{13}CO into the η^2-ketenyl ligand of 3 was observed nor into the η^1-ketenyl ligand of 4 which eventually forms. Metal carbonyl enrichment of 4 did occur since exogenous CO is taken up by 3 to form 4.[14]

The results described here may be of relevance to an earlier study by Fischer and co-workers in which photolysis of *trans*-$Cl(CO)_4W{\equiv}CPh$ with Hacac gave the hydroxyalkyne complex *trans*-$Cl(CO)_2(acac)W(\eta^2\text{-}HOC{\equiv}CPh)$.[15] Although the mechanism for this reaction was not defined, our studies suggest that it proceeds via photoinduced carbonylation of the carbyne ligand followed by protonation of the resulting ketenyl species by Hacac. A similar protonation of a ketenyl ligand has been described by Stone et al.[16]

It is assumed that carbon monoxide migrates from tungsten to the carbyne ligand in a MLCT excited state because of the increased electron density on the carbyne carbon atom. With carbyne complexes that do not possess CO ligands, it may prove possible to capture the "activated" carbyne with other substrates. Such systems are currently under investigation.

Acknowledgment. The donors of the Petroleum Research Fund, administered by the American Chemical Society, are acknowledged for support of this research. The diffractometer at the University of Delaware was purchased with partial support from the National Science Foundation.

Registry No. 1, 60260-15-3; 2, 95029-84-8; 3, 102615-19-0; 4, 102615-20-3.

Supplementary Material Available: Tables of crystallographic data and atomic positional parameters for 2 (28 pages). Ordering information is given on any current masthead page.

---

(10) Carroll, W. E.; Green, M.; Howard, J. A. K.; Pfeffer, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1978, 1472.

(11) 4: IR (CH_2Cl_2) ν(CCO) 2035 (s) cm^{-1}, ν(CO) 1946 (s), 1856 (s) cm^{-1}; ^{31}P NMR (acetone-d_6, −10 °C) δ 33.8 (J_{P-W} = 188 Hz); $^{13}C\{^1H\}$ NMR (acetone-d_6, −10 °C) δ 20.7 (CH_3), 93.0 (Cp), 128–134 (aryl), 158.2 (CCO), 224.8, 224.9, 225.2 (CO); ^1H NMR (acetone-d_6, −10 °C) δ 2.23 (s, CH_3), 5.20 (d, J_{H-P} = 2 Hz, Cp).

(12) Kreissl, F. R.; Eberl, K.; Uedelhoven, W. *Chem. Ber.* 1977, *110*, 3782.

(13) Uedelhoven, W.; Eberl, K.; Kreissl, F. R. *Chem. Ber.* 1979, *112*, 3376.

(14) IR: ν(CCO) 2035 (s) cm^{-1}; ν(CO) 1946, 1856 (m) cm^{-1}; ν(^{13}CO) 1902, 1836 (m) cm^{-1}.

(15) Fischer, E. O.; Friedrich, P. *Angew. Chem., Int. Ed. Engl.* 1979, *18*, 327.

(16) Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Stone, F. G. A. *J. Organomet. Chem.* 1983, *258*, C37.

Synthesis of $[Ru(N)R_4][NBu_4]$, the First Alkyl Complexes of Ruthenium(VI)

Patricia A. (Belmonte) Shapley* and James P. Wepsiec

Department of Chemistry, University of Illinois
Chicago, Illinois 60680

Received March 27, 1986

Summary: The nitridoalkylruthenium(VI) anions $[Ru(N)R_4]^-$, $[Ru(N)Me_2(CH_2SiMe_3)_2]^-$, and $[Ru(N)(CH_2SiMe_3)_2(OSiMe_3)_2]^-$ (where R = CH_3 or CH_2SiMe_3) have been prepared from either $[Ru(N)Cl_4]^-$ or $[Ru(N)(OSiMe_3)_4]^-$ and $Mg(CH_2SiMe_3)_2$ and/or $AlMe_3$. The alkyl complexes are thermally stable, yellow crystalline complexes. They react rapidly with O_2 in solution but are stable to H_2O and MeOH in the absence of light.

Ruthenium tetraoxide is a powerful oxidizing agent, capable of oxidizing olefins to the cis diols or cleaving the C–C double bond to form aldehydes or carboxylic acids.[1] It has been proposed that metal oxides, like RuO_4, react with olefins to form high oxidation state organometallic complexes.[2] Ruthenium(VI) alkyls have also been proposed, recently, as intermediates in C–H activation of hydrocarbons with a ruthenium hydrido complex.[3] While there have been recent reports of osmium(VI) alkyl complexes, organometallic complexes ruthenium(VI) are unknown.[4-6] The most recent advances in Ru(VI) chemistry have been the preparation of nitrido complexes such as $[Ru(N)X_4]^-$ and trans dioxo complexes such as $[Ru(O)_2X_4]^{2-}$.[7]

---

(1) Djerassi, C.; Engle, R. *J. Am. Chem. Soc.* 1953, *75*, 3838. Berkowitz, L. M.; Rylander, P. N. *J. Am. Chem.* Soc. 1958, *80*, 6682. Lee, D. G.; van den Engh, M. In *Oxidation in Organic Chemistry*; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; Part B, Chapter 4. Gore, E. S. *Platinum Metals Review* 1983, *27*, 111–125.

(2) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J. *J. Am. Chem. Soc.* 1977, *99*, 3120–3128. Rappe, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* 1982, *104*, 3288–3294.

(3) Chaudret, B.; Poilblanc, R. *Organometallics* 1985, *4*, 1722–1726.

(4) Alves, A. S.; Moore, D. S.; Andersen, R. A.; Wilkinson, G.; *Polyhedron* 1982, *1*, 83–87.

(5) Belmonte, P. A.; Own, Z.-Y. *J. Am. Chem. Soc.* 1984, *106*, 7493–7496.

(6) (Belmonte) Shapley, P. A.; Own, Z.-Y.; Huffmann, J. C., submitted for publication in *Organometallics*.

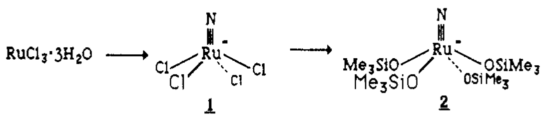
0276-7333/86/2305-1515$01.50/0

Table I. Spectroscopic and Analytical Data

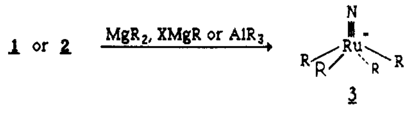
	^1H NMR[9] δ			IR[10] ν(RuN), cm^{-1}	anal.[11]		
	$RuCH_3$	$RuCH_2$	$SiMe_3$		C	H	N
2			0.60 (s, 9 H)	1090	46.98 (47.08)	10.14 (10.16)	3.96 (3.92)
3a		1.28 (s, 2 H)	0.54 (s, 9 H)	1078	54.04 (54.41)	11.22 (11.41)	3.92 (3.97)
3b	1.43 (s, 3 H)			1072	57.76 (57.51)	11.25 (11.58)	6.36 (6.71)
4		1.70 (s, 2 H)	0.62 (s, 9 H), 0.52 (s, 9 H)	1073	50.68 (50.72)	10.98 (10.78)	3.84 (3.94)
5	1.17 (s, 3 H)	1.49 (s, 2 H)	0.57 (s, 9 H)	1071	54.91 (55.56)	10.63 (11.48)	4.89 (4.98)

Here we report that a series of ruthenium(VI) alkyl complexes can be prepared starting from $[Ru(N)Cl_4]^-$. These are the first alkyl complexes of ruthenium in the +6 oxidation state.

$[Ru(N)Cl_4][NBu_4]$ can be prepared in 85% yield from $RuCl_3{\cdot}3H_2O$ by the method of W. P. Griffith.[8] $[Ru(N)Cl_4]^-$ (**1**) reacts with 4 equiv of $NaOSiMe_3$ to form $[Ru(N)(OSiMe_3)_4][NBu_4]$ (**2**). In a typical preparation, 0.450 g (4 mmol) of $NaOSiMe_3$ dissolved in THF was added dropwise to 0.500 g (1 mmol) of $[Ru(N)Cl_4][NBu_4]$ in THF solution at −78 °C. The solution was warmed to room temperature and filtered through Celite and solvent removed from the filtrate under vacuum. The violet residue was recrystallized from toluene/pentane at −30 °C to give 0.57 g of violet needles, an 80% yield of pure **2**.

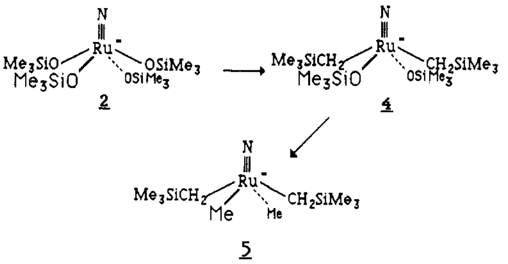


The ruthenium trimethylsiloxy complex **2** reacts with 4 equiv of $Mg(CH_2SiMe_3)_2$ or $ClMg(CH_2SiMe_3)$ to form the corresponding tetraalkyl complex $[Ru(N)(CH_2SiMe_3)_4][NBu_4]$ (**3a**). In a typical reaction, a solution of 0.160 g $Mg(CH_2SiMe_3){\cdot}Et_2O$ in 30 mL of diethyl ether was added to 0.100 g of **2** in 20 mL of toluene at room temperature under N_2. The color of the reaction mixture rapidly changed from violet to yellow. The ether was removed in vacuo, 50 mL of heptane was added, and the solution was cooled to −30 °C. A yellow precipitate was collected by filtration. This was washed with pentane and crystallized from toluene/pentane at −30 °C. An 81% yield, 0.080 g, of analytically pure, yellow crystalline product was obtained. A similar reaction occurs between **2** and excess $AlMe_3$ (or 4 equiv of $MgMe_2$) in toluene. Yellow needles of $[Ru(N)Me_4][NBu_4]$ (**3b**) are obtained from toluene/pentane solution at −30 °C in 20% yield. The tetraalkyl complexes can also be prepared directly from **1** in somewhat lower yield.



$[Ru(N)(CH_2SiMe_3)_2(OSiMe_3)_2][Bu_4N]$ can be prepared by the slow addition of 2 equiv of $Mg(CH_2SiMe_3)_2{\cdot}Et_2O$ to $[Ru(N)(OSiMe_3)_4][Bu_4N]$ in ether/heptane solution at −30 °C. The product is crystallized by concentrating this solution and recrystallized as orange needles in 58% yield from toluene/ether solution at −30 °C. A mixed-alkyl complex, $[Ru(N)Me_2(CH_2SiMe_3)_2][Bu_4N]$, is prepared by the reaction of excess $AlMe_3$ with $[Ru(N)(CH_2SiMe_3)_2(OSiMe_3)_2][Bu_4N]$ in ether/heptane solution. The yellow crystalline product is obtained from ether/heptane solution at −30 ° in 44% yield.

The ruthenium trimethylsiloxy complex **2** and the new ruthenium(VI) alkyl complexes **3–5** have been characterized by ^1H NMR, IR, and elemental analyses. In the FAB mass spectrum of **3a**, the most intense peak at 464 mass units corresponds to $Ru(N)(CH_2SiMe_3)_4^-$. Peaks at *m/e* 377 and 290 result from loss of one and two alkyl groups, respectively, from this anion. The alkyl complexes are thermally stable, showing no decomposition by ^1H NMR after prolonged heating in benzene or toluene solution at 70–80 °C.



The ^1H NMR spectra of **4** and **5** show that these complexes have trans (trimethylsilyl)methyl groups. As with *trans*-$[Os(N)(CH_2SiMe_3)_2Cl_2][NBu_4]$, a singlet is observed for the enantiotopic methylene protons of the equivalent trans (trimethylsilyl)methyl groups. We would expect a doublet of doublets pattern for the diastereotopic methylene protons in a complex with cis (trimethylsilyl)methyl groups as have been observed in the ^1H NMR spectrum of *cis*-$[Os(N)(CH_2SiMe_3)_2Cl_2][NBu_4]$.[5]

The ruthenium tetraalkyl complexes do not react with water or methanol in the absence of light. In an NMR tube, 5 mg (7×10^{-3} mmol) of $[Ru(N)(CH_2SiMe_3)_4][NBu_4]$ was dissolved in 0.3 mL of C_6D_6 and a ^1H NMR spectrum was obtained. Degassed H_2O, 11 μL (0.61 mmol), was injected into the tube giving a cloudy suspension of water in water-saturated C_6D_6. ^1H NMR spectra were obtained periodically for 4 h. There was no change in the NMR spectrum of $[Ru(N)(CH_2SiMe_3)_4][NBu_4]$. Under similar conditions, $[Ru(N)(CH_2SiMe_3)_4][NBu_4]$ and 10 equiv of methanol were dissolved in C_6D_6 in an NMR tube. Again, there was no reaction observed by ^1H NMR even after 3 days.

The alkyl complexes are photosensitive, however. Solutions of these complexes and even crystalline solids decompose upon exposure to light. We have found that light promotes the reaction between $[Ru(N)(CH_2SiMe_3)_4][NBu_4]$ and methanol. A solution of $[Ru(N)(CH_2SiMe_3)_4][NBu_4]$ and 10 equiv of methanol in C_6D_6 changed from yellow to orange upon exposure to room light over a 2-h period. Tetramethylsilane and [Ru(N)-

---

[7] Griffith, W. P. *Chemistry of the Rarer Platinum Metals*; Interscience: London, 1976; Chapter 4. Seddon, K. R.; Seddon, E. A. *The Chemistry of Ruthenium*; Elsevier: New York, 1984; Chapter 5.

[8] Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315–1320.

[9] ^1H NMR were obtained in C_6D_6 at 300 K on a Bruker 200SY FT NMR spectrometer. Resonances for the counterion NBu_4^+ were also observed: δ 2.3–2.7 (m, $NCH_2CH_2CH_2CH_3$), 0.9–1.2 (m, $NCH_2CH_2CH_3$), 0.8–0.9 (t, $NCH_2CH_2CH_3$).

[10] IR spectra were obtained on KBr pellets with an IBM System 9000 FT IR/32 spectrometer.

[11] C, H, and N analyses were obtained from the University of Illinois at Urbana-Champaign analytical service. Calculated values are in parentheses. The error in the analysis of compound **5** is due to the presence of trace amounts of **3a**.

Organometallics **1986**, *5*, 1517–1518

$(OMe)_4][NBu_4]$[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.

---

[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, $Hg_9Co_6(CO)_{18}$

Joseph M. Ragosta and James M. Burlitch*

Department of Chemistry, Baker Laboratory
Cornell University
Ithaca, New York 14853

Received March 25, 1986

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]

$$\mathbf{1} + 9HgX_2 \rightarrow 6(CO)_3Co(HgX)_3 \tag{1}$$

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.

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.

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.

$$\mathbf{2} + Bu_4N^+I^- \rightarrow (CO)_3Co(HgI)_3I^-Bu_4N^+ \tag{2}$$

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-

---

[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.

0276-7333/86/2305-1517$01.50/0