32 *Inorg. Chem.* **2000,** *39,* 32−36

Carbidohexarhenate Cluster Cores Bicapped by Mercury with Acetate or Thiolate Ligands[†]

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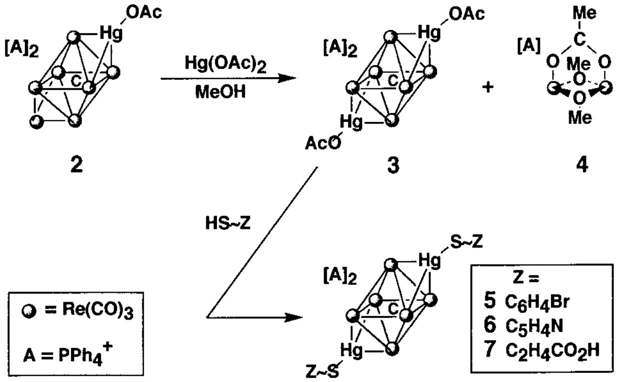
Received June 22, 1999

The reaction of $[PPh_4]_3[Re_7C(CO)_{21}]$ (**1**) with 1 or more equiv of $Hg(OAc)_2$ in dichloromethane provides the monomercury derivative $[PPh_4]_2[Re_7C(CO)_{21}HgOAc]$ (**2**) in high yield. However, in the presence of methanol the reaction of **1** with 2 equiv of $Hg(OAc)_2$ yields the dimercury hexarhenium cluster compound $[PPh_4]_2[Re_6C(CO)_{18}(HgOAc)_2]$ (**3**) together with the dirhenium complex $[PPh_4][Re_2(CO)_6(\mu\text{-OMe})_2(\mu\text{-OAc})]$ (**4**). The dimercury compound **3** reacts with various thiols HS-Z to form thiolate-substituted derivatives $[PPh_4]_2[Re_6C(CO)_{18}(HgS\text{-}Z)_2]$ [Z = C_6H_4Br (**5**); C_5H_4N (**6**); C_2H_4COOH (**7**)]. All new compounds have been characterized by a combination of analytical and spectroscopic data, and the molecular structures of compounds **3**−**6** have been determined by X-ray crystallography.

Introduction

A number of compounds have been described in which an octahedral $[Re_6(\mu_6\text{-C})(CO)_{18}]^{4-}$ cluster core is formally *hetero*-bicapped by different electrophilic metal units, viz., $[Re_6C(CO)_{18}\{Re(CO)_3\}\{ML_n\}]^{2-}$, where M includes a variety of second- and third-row transition and post-transition metals.[1−9] However, only two examples of *homo*bicapped derivatives have been reported, namely, $[Re_8C(CO)_{24}]^{2-}$ [10] and $[Re_6C(CO)_{18}(AuPPh_3)_2]^{2-}$,[11] where the two caps are $[Re(CO)_3]^+$ and $[AuPPh_3]^+$ units, respectively. Further study of our mercury(II) derivatives $[Re_7C(CO)_{21}HgY]^{2-}$ [7−9] has revealed a new decapping reaction in which one rhenium cap is removed and replaced by a second mercury cap (see Scheme 1). Rhenium vertex removal has been carried out previously with such reagents as carbon monoxide, phosphines, or acetonitrile, which typically stabilize the eliminated metal vertex as a mononuclear complex.[12−17] In the present case the decapping reagent is mercury acetate in the presence of methanol, and the eliminated rhenium carbonyl fragment is isolated as a dinuclear complex with bridging methoxy and acetate ligands. Furthermore, ligand exchange with the initially formed Hg_2Re_6 cluster readily replaces the acetate ligands attached to mercury by thiolate ligands. Related examples of mercury−transition metal cluster compounds have been reviewed.[18−20]

Scheme 1



Experimental Section

General Procedures. All reactions were carried out at room temperature; reactions with thiol compounds were conducted under a nitrogen atmosphere by using standard Schlenk techniques. The solvents used were distilled from appropriate drying agents and degassed before use. The compounds $[PPh_4]_3[Re_7C(CO)_{21}]$[21] and mercury(II) acetate[22] were prepared as reported. The reagents 4-bromothiophenol (Aldrich), 4-mercaptopyridine (Aldrich), and 3-mercaptopropionic acid (Aldrich) were used as received. Infrared spectra were recorded on Perkin-Elmer 1750 FT-IR spectrometer. ^{1}H NMR spectra were obtained on a Varian

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[†] Dedicated to Prof. Dr. Heinrich Vahrenkamp on the occasion of his 60th birthday.

(1) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1985**, *295*, C7.
(2) Henly, T. J.; Shapley, J. R.; Rheingold, A. L. *J. Organomet. Chem.* **1986**, *310*, 55.
(3) Henly, T. J.; Shapley, J. R.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 441.
(4) Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1988**, *27*, 2551.
(5) Ma, L.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1990**, *29*, 5133.
(6) Brand, U.; Shapley, J. R. *Inorg. Chem.* **1997**, *36*, 253.
(7) Henly, T. J.; Shapley, J. R. *Organometallics* **1989**, *8*, 2799.
(8) Brand, U.; Coffer, J. L.; Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1997**, *36*, 3386.
(9) Brand, U.; Shapley, J. R. *Inorg. Chem.* **1998**, *37*, 5697.
(10) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 705.
(11) Latten, J. L.; Hsu, G.; Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1998**, *37*, 2520.
(12) Beringhelli, T.; D'Alfonso, G.; Molinari, H.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1992**, 689.
(13) Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Sironi, A.; Molinari, H. *J. Chem. Soc., Dalton Trans.* **1990**, 1901.
(14) Ma, L.; Brand, U.; Shapley, J. R. *Inorg. Chem.* **1998**, *37*, 3060.
(15) Hsu, G.; Wilson, S. R.; Shapley, J. R. *Organometallics* **1994**, *13*, 4159.
(16) Simerly, S. W.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1992**, *31*, 5146.
(17) Hsu, G.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1991**, *30*, 3881.
(18) Gade, L. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 24.
(19) Rosenberg, E.; Hardcastle, K. I. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Elsevier: Oxford, U.K., 1995; Vol. 10, Chapter 6, p 323.
(20) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; p 623.
(21) Hayward, C.-M. T.; Shapley, J. R. *Organometallics* **1988**, *7*, 448.
(22) Meyer, R. J. *Gmelins Handbuch der Anorganischen Chemie, Quecksilber Teil B*; VCH: Weinheim, Germany, 1968; Vol. 34, p 1268.

10.1021/ic990722v CCC: $19.00

Table 1. Summary of Crystallographic Data

	3	**4**·0.5CH$_2$Cl$_2$	**5**·2CH$_3$OH	**6**
formula	C$_{71}$H$_{46}$O$_{22}$P$_2$Re$_6$Hg$_2$	C$_{34.5}$H$_{30}$O$_{10}$PClRe$_2$	C$_{81}$H$_{56}$O$_{20}$P$_2$S$_2$Br$_2$Re$_6$Hg$_2$	C$_{77}$H$_{48}$N$_2$O$_{18}$P$_2$S$_2$Re$_6$Hg$_2$
fw	2831.40	1043.40	3153.52	2933.61
space group	$P1$	$C2/c$	$P1$	$P2_1/n$
temp (°C)	−75(2)	−75(2)	−75(2)	−75(2)
a (Å)	12.4969(3)	34.9361(7)	12.3703(7)	14.4679(2)
b (Å)	12.8877(3)	7.1538(2)	13.8241(7)	14.7984(2)
c (Å)	13.4070(3)	29.6569(7)	15.0331(8)	18.1199(2)
α (deg)	113.297(1)	90	107.560(1)	90
β (deg)	92.406(1)	104.001(1)	102.199(1)	90.160(1)
γ (deg)	110.780(1)	90	113.872(1)	90
V (Å$^{3)}$	1811.95(7)	7191.8(3)	2070.9(2)	3879.49
Z	1	8	1	2
ρ_{calcd} (g·cm^{-3})	2.595	1.927	2.529	2.511
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73	0.710 73
μ(Mo Kα) (cm^{-1})	143.15	69.00	135.45	134.26
R_1 [$I > 2\sigma(I)$]^a	0.0339	0.0238	0.0730	0.0466
wR2 (for all data)^b	0.0850	0.0622	0.2051	0.1020

^{a} $R_1 = \sum|(F_o - F_c)|/\sum F_o$. ^{b} wR2 $= \{\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4\}^{1/2}$.

U400 instrument. Electrospray ionization mass spectra (ESI) were obtained on a VG Quattro and fast atom bombardment (FAB) mass spectra, using 3-nitrobenzyl alcohol as the dispersing medium, on a VG ZAB-SE spectrometer by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences. Microanalyses were performed by the staff of the School Microanalytical Laboratory.

Synthesis of [PPh$_4$]$_2$[Re$_7$C(CO)$_{21}$HgOAc] (2). A mixture of 60.1 mg (0.021 mmol) of [PPh$_4$]$_3$[Re$_7$C(CO)$_{21}$] and 17.0 mg (0.053 mmol) of Hg(OAc)$_2$ in 5 mL of dichloromethane was stirred for 15 min. The solution was then evaporated to dryness. The solid residue was dissolved in 1 mL of dichloromethane; the solution was filtered and then layered with hexane. Subsequent solvent diffusion yielded a dark precipitate of **2**, which was isolated, washed with chloroform, and dried under vacuum (45.9 mg, 0.016 mmol, 78%). Anal. Calcd for C$_{72}$H$_{43}$O$_{23}$P$_2$Re$_7$Hg: C, 30.43; H, 1.53. Found: C, 30.16; H, 1.43. IR (Me$_2$CO): ν(CO) 2056 (vw), 2004 (vs), 1975 (w), 1949 (vw), 1930 (w), 1889 (vw) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.03 (s, 3H, Me), 7.57−7.64 (m, 16H, Ph o-H), 7.72−7.77 (m, 16H, Ph m-H), 7.89−7.94 (m, 8H, Ph p-H). ESI-MS (^{187}Re, ^{201}Hg): *m*/*e* 1081.2, {[Re$_7$C(CO)$_{21}$(HgOAc)]}$^{2-}$.

Synthesis of [PPh$_4$]$_2$[Re$_6$C(CO)$_{18}$(HgOAc)$_2$] (3) and Isolation of [PPh$_4$][Re$_2$(CO)$_6$(μ-OMe)$_2$(μ-OAc)] (4). A mixture of 312 mg (0.107 mmol) of [PPh$_4$]$_3$[Re$_7$C(CO)$_{21}$] and 69.9 mg (0.219 mmol) of Hg(OAc)$_2$ in 12 mL of dichloromethane was stirred for 30 min. (The IR spectrum showed formation of **2**, ν(CO), 2004 (vs) cm^{-1}.) The solution was layered with 25 mL of methanol and was allowed to stand for 6 days before the dark crystals were filtered out and washed with methanol. Concentration of the mother liquor yielded further crystals of **3** (total 220 mg, 0.0776 mmol, 73%). Anal. Calcd for C$_{71}$H$_{46}$O$_{22}$P$_2$Re$_6$Hg$_2$: C, 30.12; H, 1.64. Found: C, 30.09; H, 1.78. IR (Me$_2$CO): ν(CO) 2056 (vw), 2000 (vs), 1985 (m), 1970 (w, sh), 1942 (w), 1930 (w), 1887 (vw) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.04 (s, 6H, Me), 7.57−7.63 (m, 16H, Ph o-H), 7.73−7.77 (m, 16H, Ph m-H), 7.89−7.94 (m, 8H, Ph p-H). ESI-MS (^{187}Re, ^{201}Hg): *m*/*e* 1076.4 ([Re$_6$C(CO)$_{18}$(HgOAc)$_2$]$^{2-}$), 871.1 ([Re$_6$C(CO)$_{18}$]$^{2-}$).

The mother liquor from above was evaporated, and the residue was extracted with a small amount of methanol. The methanol solution was dried under vacuum, and the remaining solid was dissolved in dichloromethane. This solution was layered with hexane, and after 3 days a few colorless crystals of **4** were isolated (5.2 mg, 0.0052 mmol, 5%). IR (Me$_2$CO): ν(CO) 2010 (m), 1997 (m), 1878 (vs) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.96 (s, 3H, Me), 4.14 (s, 6H, OMe), 7.57−7.65 (m, 8H, Ph o-H), 7.73−7.79 (m, 8H, Ph m-H), 7.90−7.96 (m, 4H, Ph p-H). FAB-MS (^{187}Re, ^{201}Hg): *m*/*e* 660.9 ([Re$_2$(CO)$_6$(OMe)$_2$(OAc)]$^-$). The crystal used for the X-ray study of **4** was taken directly from the batch initially isolated.

Synthesis of [PPh$_4$]$_2$[Re$_6$C(CO)$_{18}$(HgSC$_6$H$_4$Br)$_2$] (5). A solution of 18.2 mg (0.00643 mmol) of **3** and 6.8 mg (0.036 mmol) of 4-bromothiophenol in 8 mL of dichloromethane was stirred for 24 h. The solution was concentrated in vacuo until a precipitate was formed, and then it was layered with diethyl ether. After 1 day of diffusion, the precipitate was washed three times with diethyl ether and dried under vacuum (15.9 mg, 0.005 15 mmol, 80%). Anal. Calcd for C$_{79}$H$_{48}$O$_{18}$P$_2$S$_2$Br$_2$Re$_6$Hg$_2$: C, 30.71; H, 1.57. Found: C, 30.60; H, 1.47. IR (Me$_2$CO): ν(CO) 2054 (vw), 1998 (vs), 1981 (m), 1972 (w, sh), 1943 (w), 1926 (w), 1892 (vw) cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.29 (d, ^3J = 8.0 Hz, 4H, C$_6$H$_4$Br), 7.46 (d, ^3J = 8.0 Hz, 4H, C$_6$H$_4$Br), 7.82−7.88 (m, 32H, Ph o-H and m-H), 7.97−8.02 (m, 8H, Ph p-H). ESI-MS (^{187}Re, ^{201}Hg): *m*/*e* 2749.7 ([PPh$_4$][Re$_6$C(CO)$_{18}$(HgSC$_6$H$_4$Br)$_2$]$^-$), 1205.6 ([Re$_6$C(CO)$_{18}$(HgSC$_6$H$_4$Br)$_2$]$^{2-}$). Single crystals of **5**·2MeOH suitable for X-ray data collection were grown by layering an acetone solution with methanol and subsequent diffusion.

Synthesis of [PPh$_4$]$_2$[Re$_6$C(CO)$_{18}$(HgSC$_5$H$_4$N)$_2$] (6). A solution of 44.5 mg (0.0157 mmol) of **3** and 11.1 mg (0.0998 mmol) of 4-mercaptopyridine in 10 mL of dichloromethane/methanol (8:2) was stirred for 24 h. The solution was extracted with 10 mL of 0.4 M NaHCO$_3$ solution. The aqueous layer was washed once with 10 mL of dichloromethane, and the combined organic phases were washed with water, dried over Na$_2$SO$_4$, and evaporated under vacuum. The residue was redissolved in 4 mL of dichloromethane, and this solution was layered with 6 mL of diethyl ether. Subsequent diffusion led to the formation of black crystals (32.0 mg, 0.0111 mmol, 70%). Anal. Calcd for C$_{77}$H$_{48}$N$_2$O$_{18}$P$_2$S$_2$Re$_6$Hg$_2$: C, 31.52; H, 1.65; N, 0.95. Found: C, 31.08; H, 1.54; N, 0.93. IR (Me$_2$CO): ν(CO) 2055 (vw), 1998 (vs), 1982 (m), 1945 (w), 1927 (w), 1892 (vw) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.47(d, ^3J = 6.4 Hz, 4H, py β-H), 7.57−7.64 (m, 16H, Ph o-H), 7.72−7.77 (m, 16H, Ph m-H), 7.89−7.94 (m, 8H, Ph p-H), 8.23 (d, ^3J = 6.4 Hz, 4H, py α-H). ESI-MS (^{187}Re, ^{201}Hg): *m*/*e* 2595.8 ([PPh$_4$][Re$_6$C(CO)$_{18}$(HgSC$_5$H$_4$N)$_2$]$^-$), 2256.3 ([Re$_6$C(CO)$_{18}$(HgSC$_5$H$_4$N)$_2$H]$^-$), 1127.2 ([Re$_6$C(CO)$_{18}$(HgSC$_5$H$_4$N)$_2$]$^{2-}$). Single crystals of **6** suitable for X-ray data collection were obtained directly from the reaction.

Synthesis of [PPh$_4$]$_2$[Re$_6$C(CO)$_{18}$(HgSC$_2$H$_4$COOH)$_2$] (7). A solution containing **3** (16.0 mg, 0.00565 mmol) and 3-mercaptopropionic acid (25.6 mg, 0.241 mmol) in dichloromethane (5 mL) was stirred for 15 h. Then the volume of solution was reduced by half in vacuo, and the remainder was layered with hexane. After 3 d, dark crystals were isolated, washed with hexane, and dried under vacuum (12.1 mg, 0.0414 mmol, 73%). Anal. Calcd for C$_{73}$H$_{50}$O$_{22}$P$_2$S$_2$Re$_6$Hg$_2$: C, 29.99; H, 1.72. Found: C, 29.54; H, 1.68. IR (Me$_2$CO): ν(CO) 2053 (vw), 1994 (vs), 1979 (m), 1940 (w, sh), 1923 (w), 1912 (w, sh) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.81−2.88 (m, 4H, CH$_2$), 3.66−3.71 (m, 4H, CH$_2$), 7.57−7.64 (m, 16H, Ph o-H), 7.72−7.77 (m, 16H, Ph m-H), 7.89−7.94 (m, 8H, Ph p-H). ESI-MS (^{187}Re, ^{201}Hg): *m*/*e* 2586.0 ([PPh$_4$][Re$_6$C(CO)$_{18}$(HgSC$_3$H$_5$O$_2$)$_2$]$^-$), 1122.9 ([Re$_6$C(CO)$_{18}$(HgSC$_3$H$_5$O$_2$)$_2$]$^{2-}$).

X-ray Structure Determinations. A summary of crystallographic data for **3**, **4**·0.5CH$_2$Cl$_2$, **5**·2MeOH, and **6** is given in Table 1. The data sets for all compounds were collected on a Siemens Platform/CCD automated diffractometer and were corrected for absorption. All

Table 2. Selected Bond Distances for Compounds **3**, **5**, and **6**

	3	5	6
Hg1−Re1	2.8207(6)	2.8697(10)	2.8720(8)
Hg1−Re2	2.8188(6)	2.8702(11)	2.8523(8)
Hg1−Re3	2.8636(6)	2.8798(10)	2.8777(7)
Re1−Re2	3.0711(6)	3.0643(11)	3.0482(7)
Re1−Re3	3.0712(6)	3.0591(11)	3.0579(7)
Re2−Re3	3.0735(6)	3.0382(12)	3.0622(14)
Re1−Re2#[a]	3.0020(6)	3.0004(10)	2.9955(7)
Re1−Re3#[a]	2.9871(6)	3.0029(11)	2.9951(8)
Re2−Re3#[a]	3.0058(6)	3.0021(10)	2.9999(7)
Re1−C	2.1400(4)	2.1520(7)	2.1384(5)
Re2−C	2.1546(4)	2.1366(8)	2.1353(5)
Re3−C	2.1443(4)	2.1346(8)	2.1419(5)
Hg1−O1A	2.370(6)		
Hg1−O2A	2.682(11)		
Hg1−S1		2.383(6)	2.373(4)

[a] Symmetry transformations used to generate equivalent (#) atoms: for **3**, $-x$, $-y$, $-z$; for **5**, $-x + 1$, $-y + 1$, $-z$; for **6**, $-x + 2$, $-y + 1$, $-z$.

Table 3. Selected Bond Angles (deg) for Compounds **3**, **5**, and **6**

	3	5	6
Re1−Hg1−Re2	65.99(2)	64.53(3)	64.35(2)
Re1−Hg1−Re3	65.40(2)	64.29(3)	54.26(2)
Re2−Hg1−Re3	65.48(2)	63.79(3)	64.29(2)
Re1−Hg1−O1A	142.0(3)		
Re2−Hg1−O1A	152.0(3)		
Re3−Hg1−O1A	121.2(3)		
Hg1−O1A−C1A	105.1(8)		
Re1−Hg1−S1		149.6(2)	138.0(1)
Re2− Hg1−S1		138.1(2)	152.4(1)
Re3−Hg1−S1		137.9(2)	134.0(1)
Hg1−S1−C101		102.5(6)	
Hg1−S1−C3			108.3(5)

Table 4. Selected Structural Parameters for $[PPh_4][Re_2(CO)_6(\mu\text{-}OMe)_2(\mu\text{-}OAc)]$ (**4**)

Bond Distances (Å)

Re1−C11	1.888(6)	Re1−C12	1.889(6)	Re1−C13	1.898(7)
Re1−O1	2.129(4)	Re1−O2	2.115(4)	Re1−O3	2.166(4)
Re2−C21	1.896(7)	Re2−C22	1.878(7)	Re2−C23	1.894(6)
Re2−O1	2.118(4)	Re2−O2	2.120(4)	Re2−O4	2.148(4)
Re1−Re2	3.3599(3)	O1−C1	1.421(7)	O2−C2	1.421(7)

Bond Angles (deg)

C11−Re1−C12	88.8(2)	C11−Re1−C13	87.6(3)
C12−Re1−C13	88.2(3)	C11−Re1−O2	171.5(2)
C12−Re1−O3	176.7(2)	C13−Re1−O1	173.3(2)
C21−Re2−C22	88.4(3)	C21−Re2−C23	90.8(3)
C22−Re2−C23	86.8(3)	C21−Re2−O2	168.9(2)
C22−Re2−O4	178.5(2)	C23−Re2−O1	172.3(2)

structures were solved by direct methods;[23] hydrogen atoms were fixed on calculated positions. The structures were refined by full-matrix least-squares procedures, based on F^2, of the positional and anisotropic thermal parameters for all non-hydrogen atoms. Selected structural parameters are provided in Tables2−4. Structural diagrams for the molecular anions, Figures1−4, are drawn with 30% thermal ellipsoids.

Results and Discussion

Formation of Compounds 2−4. When $[PPh_4]_3$ $[Re_7C(CO)_{21}]$ (**1**) is treated with 1 or more equiv of mercury(II) acetate in dichloromethane followed by layering with hexane, the monomercury derivative $[PPh_4]_2[Re_7C(CO)_{21}HgOAc]$ (**2**) is isolated in high yield. This result is analogous to the our previous observations with mercury(II) chloride and related compounds.[7] However, if at least 2 equiv of mercury acetate is used and the reaction mixture in dichloromethane is layered with methanol, a dimercury complex $[PPh_4]_2[Re_6C(CO)_{18}(HgOAc)_2]$ (**3**) is isolated. In this compound one $[Hg(OAc)]^+$ unit has displaced a $[Re(CO)_3]^+$ fragment, and the latter has been isolated in the form of a dinuclear methoxy acetate complex $[PPh_4]_2$ $[Re_2(CO)_6(\mu\text{-}OMe)_2(\mu\text{-}OAc)]$ (**4**). The mono- and dimercury complexes **2** and **3** can be distinguished by their IR υ(CO) spectra, since **2** shows just one strong band at 2004 cm^{-1}, whereas **3** shows both a strong band at 2000 cm^{-1} and a medium-intensity band at 1985 cm^{-1}.

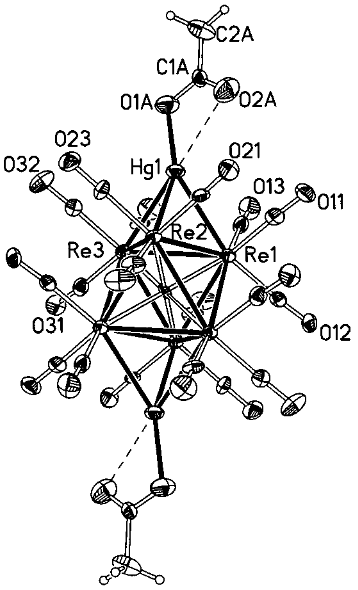

Figure 1. Structural diagram of the cluster $[Re_6C(CO)_{18}(HgOAc)_2]^{2-}$ in compound **3**.

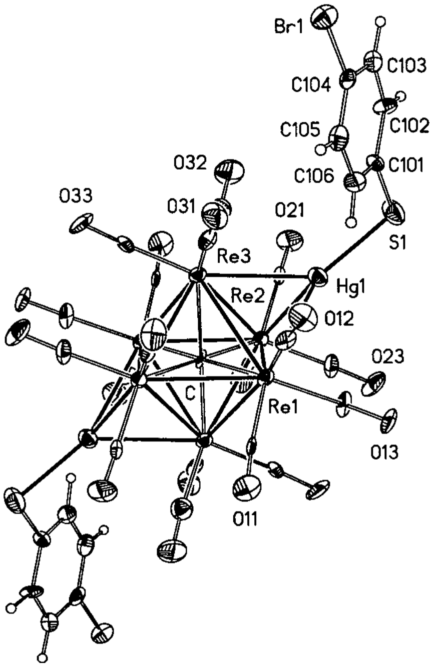

Figure 2. Structural diagram of the cluster $[Re_6C(CO)_{18}(HgSC_6H_4Br)_2]^{2-}$ in compound **5**.

Formation of Derivatives 5−7. We have shown previously that the cluster $[PPh_4]_2[Re_7C(CO)_{21}HgOH]$ reacts easily with a variety of thiols, including those bearing other functional groups, to replace the hydroxyl group with a thiolate.[8,9] The new dimercury complex $[PPh_4]_2[Re_6C(CO)_{18}(HgOAc)_2]$ (**3**) also reacts with thiols HS-Z to form thiolate ligand derivatives

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(23) Sheldrick, G. M. *SHELXTL-PC, v. 5.0*; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

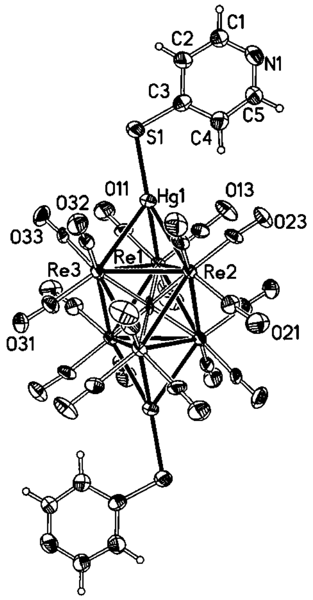

Figure 3. Structural diagram of the cluster $[Re_6C(CO)_{18}(HgSC_5H_4N)_2]^{2-}$ in compound **6**.

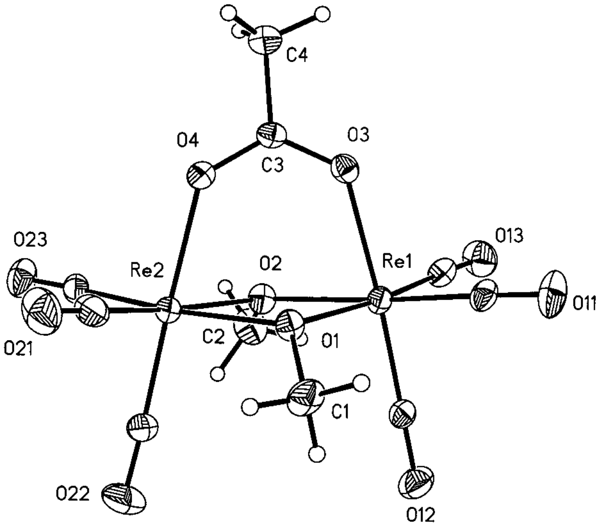

Figure 4. Structural diagram of the unit $[Re_2(CO)_6(\mu\text{-}OMe)_2(\mu\text{-}OAc)]^-$ in compound **4**.

$[PPh_4]_2[Re_6C(CO)_{18}(HgS\text{-}Z)_2]$ in very good yields. The reaction of **3** with 4-bromothiophenol in dichloromethane gave the thiophenolate-substituted cluster $[PPh_4]_2[Re_6C(CO)_{18}(HgSC_6H_4\text{-}Br)_2]$ (**5**) in 80% isolated yield. Treatment of **3** with 4-mercaptopyridine in dichloromethane/methanol (8:2) provided the thiopyridyl derivative $[PPh_4]_2[Re_6C(CO)_{18}(HgSC_5H_4N)_2]$ (**6**) (70%). We avoided protonation of the pyridine nitrogen by extracting the reaction mixture with a basic solution. Finally, by treatment of **3** with 3-mercaptopropionic acid in dichloromethane, $[PPh_4]_2[Re_6C(CO)_{18}(HgSC_2H_4COOH)_2]$ (**7**) was formed, and the compound was isolated in 73% yield. All of the substituted dimercury complexes show similar CO absorption bands in their IR spectra. However, the position of the strongest band does vary with the substituent on mercury, ranging from 1994 cm^{-1} for **7**, through 1998 cm^{-1} for **5** and **6**, to 2000 cm^{-1} for **3**.

Crystal Structures of the Clusters in Compounds 3, 5, and 6. The molecular structure of the cluster derivative $[(Re_6C(CO)_{18}(HgOAc)_2]^{2-}$, as determined by a single-crystal X-ray diffraction study of its $[PPh_4]^+$ salt **3**, is shown in Figure 1. Selected bond lengths and angles are given in Tables 2 and 3. The structure is best described as an octahedron of rhenium atoms, centered on an interstitial carbon atom, with two mercury atoms bonded to opposite faces of the octahedron. The cluster unit is centrosymmetric, with the carbide atom lying on the crystallographic inversion center. There are only small variations in Re−Hg and Re−Re distances, although the Re−Re distances for the mercury-capped faces are slightly longer (ca. 0.06 Å) than those for the uncapped faces. The acetate ligand is bonded to the mercury atom with one strong bond (Hg−O1A = 2.370(6) Å) and one weak bond (Hg−O2A = 2.682(11) Å). This picture is supported by the O−C distances observed for the acetate ligand (1.27(1) Å to O1A and 1.20(1) Å to O2A), which indicate partial double-bond character for the O2A−C1A bond. The Hg−O distances are consistent with those reported for other mercury acetate complexes, which display a wide range from 2.1 to 2.6 Å.[24−26]

Diagrams of the molecular cluster units in compounds **5** and **6** are depicted in Figures 2 and 3, respectively. Selected bond distances and bond angles comparing these two clusters as well as the acetate derivative in **3** are collected in Tables 2 and 3. The cluster cores in all three compounds are centrosymmetric and display very little variation in the Re−Re and Re−Hg bond distances. The Hg−S distances, 2.383(6) Å in **5** and 2.373(4) Å in **6**, are closely similar to that found in the complex $[PPh_4]_2[Re_7C(CO)_{21}HgSC_6H_4Br]$ (2.395(5) Å)[8] as well as those reported for other mercury thiolate complexes.[27−30] In both cases the thiolate ligands are bent slightly off axis toward one edge of the mercury-capped rhenium triangles: the Re−Hg−S angles are 149.6(2), 138.1(2), and 137.9(2)° in **5** and 152.4(1), 138.0(1), and 134.0(1)° in **6**. The aromatic substituents attached to the sulfur atom are oriented quite differently with respect to the Hg−S bond in the two compounds: in **5** the dihedral angle between the two planes (Hg1, S1, C101) and (C102, C101, C106) is 42°, whereas in **6** the dihedral angle for the corresponding planes (Hg1, S1, C3) and (C2, C3, C4) is much smaller at 9°. However, we see no reason to ascribe this behavior to anything other than different packing in the respective crystals.

Crystal Structure of 4. The decapped rhenium vertex formed a dinuclear complex, which was isolated as its $[PPh_4]^+$ salt **4**. A structural diagram of the anion is shown in Figure 4. Selected bond distances and angles from the crystallographic study are displayed in Table 4. The two rhenium centers are linked by two bridging methoxy groups and one bridging η^1,η^1-acetate group. Each rhenium atom has a distorted octahedral environment with three facial carbonyl groups and three facial oxygen donor atoms. The Re−O distances are in the same range observed for related dirhenium compounds with three bridging hydroxo,[31] alkoxo,[32,33] or phenoxo[34] ligands. However, in comparison with these symmetric compounds, the multiatomic

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(24) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014.
(25) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L.; Duisenberg, A. J. M. *J. Chem. Soc., Chem. Commun.* **1980**, 469.
(26) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Khan, M. A. *J. Chem. Res., Synop.* **1979**, 360.
(27) Wang, S.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 2615.
(28) Casals, I.; Gonzáles-Duarte, P.; Clegg, W. *Inorg. Chim. Acta* **1991**, *184*, 167.
(29) Gruff, E. S.; Koch, S. A. *J. Am. Chem. Soc.* **1990**, *112*, 1245.
(30) Block, E.; Brito, M.; Gernon, M.; McGowty, D.; Kang H.; Zubieta, J. *Inorg. Chem.* **1990**, *29*, 3172.
(31) Alberto, R.; Egli, A.; Abram, U.; Hegetschweiler, K.; Gramlich, V.; Schubiger, P. A. *J. Chem. Soc., Dalton Trans.* **1994**, 2815.
(32) Hermann, W. A.; Mihalios, D.; Öfele, K.; Kiprof, P.; Belmedjahed, F. *Chem. Ber.* **1992**, *125*, 1795.
(33) Ciani, G.; Sironi, A.; Albinati, A. *Gazz. Chim. Ital.* **1979**, *109*, 615.
(34) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Sironi, A.; Freni, M. *J. Chem. Soc., Dalton Trans.* **1985**, 1507.

bridge formed by the acetate ligand in **4** distorts the remainder of the $Re_2(\mu\text{-}OR)_2$ core in ways that more closely parallel the effect of a bridging diphosphine ligand.[35] Thus, the nonbonding Re⋯Re distance of 3.3599(3) Å in **4** is ca. 0.2 Å longer than those found in the $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ compounds,[31−34] but it is only 0.04 Å shorter than the analogous distance in $Re_2(\mu\text{-}OMe)_2(\mu\text{-}dppf)(CO)_6$.[35] Furthermore, the two bridging oxygen atoms of the methoxy groups are flattened almost into a plane with the two rhenium atoms (the dihedral angle between the two planes (Re1, O1, Re2) and (Re1, O2, Re2) is 171.1°), and the Re−O−Re angles at these bridging atoms (104.6(2) at O1 and 105.0(2)° at O2) are significantly larger than typical values (ca. 95°) found in the symmetrical $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ complexes.[31−35]

Conclusion

We have shown that the reaction of mercury acetate with $[Re_7C(CO)_{21}]^{3-}$ leads not only to the well-precedented, monomercury-capped *hepta*rhenium cluster $[Re_7C(CO)_{21}HgOAc]^{2-}$ but also, in the presence of methanol, to the new dimercury *hexa*rhenium cluster $[Re_6C(CO)_{18}(HgOAc)_2]^{2-}$ by loss of a rhenium vertex. If this decapping reaction can be applied more generally to $[Re_7C(CO)_{21}ML_n]^{2-}$ derivatives, it will lead to a new series of compounds in which the carbidohexarhenate core is heterobicapped by one mercury center and by one different metal−ligand moiety. Furthermore, we have demonstrated that the new dimercury acetate complex reacts with various thiol compounds to form the thiolate derivatives $[Re_6C(CO)_{18}(HgS\text{-}Z)_2]^{2-}$, including cases in which the substituent Z contains a carboxyl or pyridyl functionality. These new *bi*functionalized hexarhenium clusters together with our previous *mono*functionalized heptarhenium clusters $[Re_7C(CO)_{21}HgS\text{-}Z]^{2-}$ [9] should prove useful as links and anchors, respectively, in the construction of supermolecular metal complex entities.

Acknowledgment. This work was supported in part by National Science Foundation Grant CHE 94-14217. Purchase of the Siemens Platform/CCD diffractometer by the School of Chemical Science was supported by National Science Foundation Grant CHE 95-03145. We thank Dr. S. R. Wilson for X-ray data collection. Funding for the NMR instrumentation was provided in part from the Keck Foundation, the National Institutes of Health, and the National Science Foundation.

Supporting Information Available: An X-ray crystallographic file in CIF format for compounds $[PPh_4]_2[Re_6C(CO)_{18}(HgOAc)_2]$ (**3**), $[PPh_4][Re_2(CO)_6(OMe)_2(OAc)]$ (**4**), $[PPh_4]_2[Re_6C(CO)_{18}(HgSC_6H_4Br)_2]$ (**5**), and $[PPh_4]_2[Re_6C(CO)_{18}(HgSC_5H_4N)_2]$ (**6**). This material is available free of charge via the Internet at http://pubs.acs.org.

IC990722V

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(35) Jiang, C.; Wen, Y.-S.; Liu, L.-K.; Hor, T. S. A.; Yan, Y. K. *Organometallics* **1998**, *17*, 7, 173.