4896 *Inorg. Chem.* **2001,** *40,* 4896−4901

Synthesis and Characterization of the Dimercury(I)-Linked Compound $[PPN]_4[(Re_7C(CO)_{21}Hg)_2]$. Oxidative Cleavage of the Mercury−Mercury Bond Leading to Carbidoheptarhenate Complexes of Mercury(II), Including $[PPN][Re_7C(CO)_{21}Hg(S{=}C(NMe_2)_2)]$

Chris A. Wright, Udo Brand, and John R. Shapley*

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Received October 6, 2000

The reaction of $[PPN]_3[Re_7C(CO)_{21}]$ with $Hg_2(NO_3)_2{\cdot}2H_2O$ in dichloromethane formed the complex $[PPN]_4[(Re_7C(CO)_{21}Hg)_2]$ ($[PPN]_4[\mathbf{1}]$), isolated in 60% yield. Analogous salts of $[\mathbf{1}]^{4-}$ with $[PPh_4]^+$ and $[NEt_4]^+$ were also prepared. The crystal structure of $[PPN]_4[\mathbf{1}]$ showed that two carbidoheptarhenate cores are linked by a dimercury(I) unit ($d(Hg-Hg) = 2.610(4)$ Å), with each individual mercury atom face-bridging. Oxidative cleavage of the Hg−Hg bond in $[\mathbf{1}]^{4-}$ was effected by 4-bromophenyl disulfide to form $[Re_7C(CO)_{21}HgSC_6H_4Br]^{2-}$ ($[\mathbf{4}]^{2-}$), by I_2 to form $[Re_7C(CO)_{21}HgI]^{2-}$ ($[\mathbf{5}]^{2-}$), and by Br_2 to form $[Re_7C(CO)_{21}HgBr]^{2-}$ ($[\mathbf{6}]^{2-}$). Oxidation of $[\mathbf{1}]^{4-}$ by ferrocenium ion (2 equiv) in the presence of tetramethylthiourea resulted in the derivative $[Re_7C(CO)_{21}HgSC(NMe_2)_2]^-$ ($[\mathbf{7}]^-$). The molecular structure of $[PPN][\mathbf{7}]$ was determined by X-ray crystallography. This is the first example of a carbidoheptarhenate−mercury complex with a neutral ligand on mercury, and ligand exchange was demonstrated by displacement with triethylphosphine. Complex $[\mathbf{7}]^-$ can also be prepared by protonating $[Re_7C(CO)_{21}HgO_2CCH_3]^{2-}$ in the presence of tetramethylthiourea. Cyclic voltammetry data to calibrate and compare the redox properties of compounds $[\mathbf{1}]^{4-}$ and $[\mathbf{7}]^-$ have been measured.

Introduction

In previous papers, we have described the synthesis and characterization of various carbidoheptarhenate complexes of mercury(II) moieties with the general formula $[Re_7C(CO)_{21}HgX]^{2-}$.[1−4] Our previous attempt to generate a compound in which two carbidoheptarhenate units are linked by a single mercury(II) ion was unsuccessful,[4] apparently because of charge or steric repulsion between the two cluster units. However, we have provided evidence for a compound with a three-atom Hg−S−Hg bridge, namely, $[(Re_7C(CO)_{21}Hg)_2S]^{4-}$, which is in labile equilibrium with H_2S and the hydrosulfide complex $[Re_7C(CO)_{21}HgSH]^{2-}$.[2]

There are many reported examples of clusters that are linked by mercury centers,[5−18] but there are only a few that contain a dimercury unit.[15−18] Of these, two reports[15,16] describe compounds that have a dimercury(0) unit encapsulated end-on between the faces of two triangular Pt_3 cluster units. A set of osmium−mercury clusters have Hg_2 units sandwiched sideways between triangular faces of two Os_9C moieties,[17,18] but the oxidation state for mercury is indeterminate.[5] Only one example of a structurally characterized compound that contains a discrete dimercury(I) unit bound between two transition metal atoms has appeared, namely, $[(N(CH_2CH_2PPh_2)_3Co)_2Hg_2]$.[19,20] Two other notable molecular compounds that contain the dimercury(I) moiety are $[Hg_2(Me_6C_6)_2][AlCl_4]_2$,[21] which has the unit asymmetrically complexed by hexamethylbenzene, and $[(Me_3SiMe_2Si)_3Si]_2Hg_2$,[22] which has the unit bound linearly between two silicon atoms. Two recent reviews of structural data pertaining to dimercury units in organometallic compounds[23] and in minerals[24] are available.

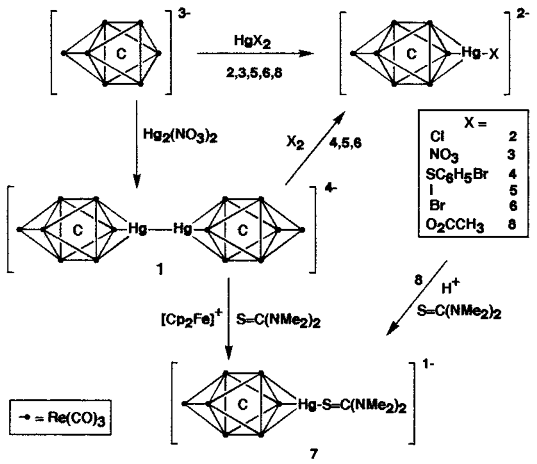
We now report the synthesis and characterization of $[(Re_7C(CO)_{21}Hg)_2]^{4-}$ ($[\mathbf{1}]^{4-}$), which provides the first unam-

---

(1) Brand, U.; Shapley, J. R. *Inorg. Chem.* **2000**, *39*, 32.
(2) Brand, U.; Shapley, J. R. *Inorg. Chem.* **1998**, *37*, 5697.
(3) Brand, U.; Coffer, J. L.; Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1997**, *36*, 3386.
(4) Henly, T. J.; Shapley, J. R. *Organometallics* **1989**, *8*, 2729.
(5) Gade, L. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 24.
(6) 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.
(7) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; p 598.
(8) Rosenberg, E.; Hardcastle, K. I.; Day, M. W.; Gobetto, R.; Hajela, S.; Muftikian, R. *Organometallics* **1991**, *10*, 203.
(9) Braunstein, P.; Rosé, J.; Tiripicchio, A.; Camellini, M. T. *J. Chem. Soc., Dalton Trans.* **1992**, 911.
(10) Bianchini, A.; Farrugia, L. J. *Organometallics* **1992**, *11*, 540.
(11) Gade, L. H.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Powell, H. R. *J. Chem. Soc., Dalton Trans.* **1992**, 921.
(12) Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Scowen, I. J. *J. Chem. Soc., Dalton Trans.* **1996**, 597.
(13) Hao, L.; Vittal, J. J.; Puddephatt, R. J. *Inorg. Chem.* **1996**, *35*, 269.
(14) Au, Y.-K.; Wong, W.-T. *Inorg. Chem.* **1997**, *36*, 2092.
(15) Albinati, A.; Moor, A.; Pregosin, P. S.; Venanzi, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 7672.
(16) Tanase, T.; Horiuchi, T.; Yamamoto, Y.; Kobayashi, K. *J. Organomet. Chem.* **1992**, *440*, 1.
(17) Gade, L. H.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Kotch, T.; Lees, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 8698.
(18) Gade, L. H.; Johnson, B. F. G.; Lewis, J.; Conole, G.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1992**, 3249.
(19) Ghilardi, C. A.; Midollini, S.; Moneti, S. *J. Chem. Soc., Chem. Commun.* **1981**, 865.
(20) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Moneti, S. *J. Chem. Soc., Dalton Trans.* **1983**, 349.
(21) Frank, W.; Dincher, B. *Z. Naturforsch., B* **1987**, *42*, 828.
(22) Bravo-Zhivotovskii, D.; Yuzefovich, M.; Bendikov, M.; Klinkhammer, K.; Apeloig, Y. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1100.
(23) Holloway, C. E.; Melník, M. *J. Organomet. Chem.* **1995**, *495*, 1.
(24) Pervukhina, N. V.; Romanenko, G. V.; Borizov, S. V.; Magarill, S. A.; Palchik, N. A. *J. Struct. Chem.* **1999**, *40*, 461.

10.1021/ic0011213 CCC: $20.00

Scheme 1



biguous example of a dimercury(I) bridge between two cluster faces. Furthermore, we show that the unsupported mercury−mercury bond is susceptible to oxidative cleavage, which affords a new route to carbidoheptarhenate complexes of mercury(II) centers, including the first case with a neutral ligand on mercury. The chemistry described in this paper is summarized in Scheme 1.

Experimental Section

General Procedures. All reactions were carried out at room temperature under an atmosphere of nitrogen by using standard Schlenk techniques. Solvents were distilled from appropriate drying agents under nitrogen before use. The compounds $[PPN]_3[Re_7C(CO)_{21}]$,[25] $[PPh_4]_3[Re_7C(CO)_{21}]$,[25] $[PPh_4]_2[Re_7C(CO)_{21}HgO_2CCH_3]$,[1] and 4-bromophenyl disulfide[26] were prepared by literature procedures. Mercurous nitrate (Baker), mercurous chloride (Mallinckrodt), mercuric nitrate (Aldrich), iodine (Fisher), bromine (Aldrich), 4-bromothiophenol (Aldrich), 1,1,3,3-tetramethylthiourea (Aldrich), and tetrabutylammonium tetrafluoroborate (TBAB, Aldrich) were used as received. Infrared spectra were recorded on Perkin-Elmer 1600 or 1750 FT-IR spectrometers. Proton NMR spectra were obtained on Varian U400 or U500 NMR spectrometers. Electrochemical experiments were performed with a Bioanalytical Systems 100B/W electrochemical analyzer, using a standard three-electrode cell equipped with a platinum working electrode, a Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. Dichloromethane solutions, 0.1 M in TBAB and 0.5 mM in analyte, were purged initially with nitrogen and were maintained under nitrogen during measurements. Negative ion electrospray ionization mass spectra (ESI) were obtained on a VG Quattro spectrometer, and fast atom bombardment mass spectra (FAB), using 3-nitrobenzyl alcohol as the dispersing medium, were obtained on a VG ZAB-SE spectrometer by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences (SCS) at the University of Illinois. Microanalyses were performed by the staff of the SCS Microanalytical Laboratory.

Synthesis of $[PPN]_4[(Re_7C(CO)_{21}Hg)_2]$ ($[PPN]_4[1]$). In a 50 mL Schlenk tube, 81.9 mg (0.0233 mmol) of $[PPN]_3[Re_7C(CO)_{21}]$ and 6.5 mg (0.012 mmol) of $Hg_2(NO_3)_2{\cdot}2H_2O$ were stirred in 20 mL of dichloromethane for 8 h. The reaction was monitored by IR spectroscopy until complete. The reaction mixture was reduced to dryness under vacuum, and the residue was dissolved in minimal dichloromethane (4 mL). The solution was filtered and then layered with 24 mL of methanol. After 2 days, the brown fibers formed were collected by filtration, washed with methanol and diethyl ether, and dried under vacuum (44.2 mg, 0.0070 mmol, 60%). Anal. Calcd for $C_{188}H_{120}Hg_2N_4O_{42}P_8Re_{14}$: C, 35.49; H, 1.90; N, 0.88; Re, 40.97. Found: C, 35.32; H, 1.84; N, 0.88; Re, 40.82. IR (CH_2Cl_2) ν(CO): 2040 (w), 1999 (vs), 1967 (w), 1935 (w), 1919 (w), 1879 (w) cm^{-1}. ESI-MS (^{187}Re, ^{202}Hg) *m/e*: 2648 $\{[PPN]_2[(Re_7C(CO)_{21}Hg)_2]\}^{2-}$, 1586 $\{[PPN][(Re_7C(CO)_{21}Hg)_2]\}^{3-}$, 1055 $\{[(Re_7C(CO)_{21}Hg)_2]\}^{4-}$. A red transparent prismatic single crystal ($0.04 \times 0.06 \times 0.12$ mm^3) of $[PPN]_4[\mathbf{1}]$ suitable for X-ray diffraction analysis was grown by layering 2-propanol on an acetone solution and allowing subsequent slow interdiffusion at room temperature.

The tetraphenylphosphonium salt of $[\mathbf{1}]^{4-}$ can be prepared by starting from $[PPh_4]_3[Re_7C(CO)_{21}]$, and the tetraethylammonium salt of $[\mathbf{1}]^{4-}$ can be prepared from $[NEt_4]_3[Re_7C(CO)_{21}]$ by using acetone as the reaction solvent.

Attempted Synthesis of $[PPN]_4[1]$ Using Mercurous Chloride. In a 50 mL Schlenk tube, 102.2 mg (0.0290 mmol) of $[PPN]_3[Re_7C(CO)_{21}]$ and 7.2 mg (0.015 mmol) of Hg_2Cl_2 were stirred in 20 mL of dichloromethane for 4 h. The reaction was monitored by IR spectroscopy until the reaction progress had ceased, at which time only the characteristic bands for $[Re_7C(CO)_{21}]^{3-}$ and $[Re_7C(CO)_{21}HgCl]^{2-}$ were present. An additional 6.2 mg (0.013 mmol) of Hg_2Cl_2 was added, which converted the remaining $[Re_7C(CO)_{21}]^{3-}$ to $[Re_7C(CO)_{21}HgCl]^{2-}$ after another 2 h. The reaction mixture was reduced to dryness under vacuum, and the residue was dissolved in minimal CH_2Cl_2 (3 mL). The solution was filtered to remove a small amount of silver-gray material, and the filtrate was then layered with 20 mL of methanol. After 5 days, the pale supernatant was decanted, and the crystals obtained were washed with methanol and diethyl ether and then were dried under vacuum (65.3 mg, 0.020 mmol, 70%). The identity of the product as $[PPN]_2[Re_7C(CO)_{21}HgCl]$ ($[PPN]_2[\mathbf{2}]$) was confirmed by IR and mass spectral data in agreement with literature data.[4]

Synthesis of $[PPh_4]_2[Re_7C(CO)_{21}Hg(NO_3)]$ ($[PPh_4]_2[3]$). In a 20 mL Schlenk tube, 75.8 mg (0.0259 mmol) of $[PPh_4]_3[Re_7C(CO)_{21}]^{3-}$ and 14.4 mg (0.0420 mmol) of $Hg(NO_3)_2{\cdot}H_2O$ were combined in 10 mL of acetone with stirring. After 10 min, the IR spectrum indicated a complete reaction. The solution volume was reduced under vacuum to 2 mL, and the remainder was layered with 12 mL of methanol. After 6 days, the pale supernatant was decanted from black crystals, which were washed with methanol and dried under vacuum (63.8 mg, 0.022 mmol, 87%). Anal. Calcd for $C_{70}H_{40}HgNO_{24}P_2Re_7$: C, 29.55; H, 1.42; N, 0.49. Found: C, 29.68; H, 1.39; N, 0.38. IR (acetone) ν(CO): 2056 (w), 2003 (vs), 1975 (w), 1948 (w), 1929 (w), 1889 (w) cm^{-1}. ESI-MS (^{187}Re, ^{202}Hg) *m/e*: 2512 $\{[PPh_4][Re_7C(CO)_{21}HgNO_3]\}^-$, 2450 $\{[PPh_4][Re_7C(CO)_{21}Hg]\}^-$.

Reaction of $[PPN]_4[1]$ with 4-Bromophenyl Disulfide. Formation of $[PPN]_2[Re_7C(CO)_{21}HgSC_6H_4Br]$ ($[PPN]_2[4]$). In a 10 mL Schlenk tube, 9.13 mg (0.001 44 mmol) of $[PPN]_4[\mathbf{1}]$ and 1.2 mg (0.0032 mmol) of 4-bromophenyl disulfide were combined in 4 mL of dichloromethane at room temperature with stirring. The reaction was monitored periodically by IR spectroscopy until complete (7 days). The solution was then concentrated under vacuum to 1 mL in volume, and the remainder was layered with 3 mL of diethyl ether. The precipitate, which formed after 3 days, was washed with diethyl ether and dried under vacuum (5.0 mg, 0.0015 mmol, 52%). The identity of the product was confirmed by IR, NMR, and ESI-mass-spectral data in agreement with literature data.[3]

Reaction of $[PPh_4]_4[1]$ with I_2. Formation of $[PPh_4]_2[Re_7C(CO)_{21}HgI]$ ($[PPh_4]_2[5]$). $[PPh_4]_4[\mathbf{1}]$ (21.2 mg, 0.004 34 mmol) and I_2 (1.21 mg, 0.004 77 mmol) were dissolved in 10 mL of dichloromethane in a 20 mL Schlenk tube. The reaction was monitored by IR spectroscopy until complete (15 min), after which time the solvent was removed in vacuo. The residue was dissolved in minimal dichloromethane (1.5 mL), and the solution was layered with methanol (10 mL). After 7 days, the nearly colorless supernatant was decanted. The black crystals obtained were washed with methanol and diethyl ether and then were dried under vacuum (16.2 mg, 0.0056 mmol, 73%). Anal. Calcd for $C_{70}H_{40}HgIO_{21}P_2Re_7$: C, 28.89; H, 1.39. Found: C, 28.84; H, 1.46. IR (acetone) ν(CO): 2055 (vw), 2002 (vs), 1985 (vw), 1973 (w), 1947 (w), 1930 (w), 1889 (vw) cm^{-1}. ESI-MS (^{127}I, ^{187}Re, ^{202}Hg) *m/e*: 2577 $\{[PPh_4][Re_7C(CO)_{21}HgI]\}^-$, 2238 $\{[Re_7C(CO)_{21}HgI]\}^-$, 1119 $\{[Re_7C(CO)_{21}HgI]\}^{2-}$.

Reaction of $[PPN]_4[1]$ with Br_2. Formation of $[PPN]_2[Re_7C(CO)_{21}HgBr]$ ($[PPN]_2[6]$). $[PPN]_4[\mathbf{1}]$ (24.1 mg, 0.003 79 mmol) was dissolved in 10 mL of dichloromethane in a 20 mL Schlenk tube. Bromine (0.5 μL, 0.01 mmol) was added to this solution with stirring.

---

(25) Hayward, C.-M. T.; Shapley, J. R. *Organometallics* **1988**, *7*, 448.

(26) Crank, G.; Makin, M. I. H. *Tetrahedron Lett.* **1979**, 2169.

Table 1. Crystallographic Data for $[PPN]_4[\mathbf{1}]$ and $[PPN][\mathbf{7}]\cdot H_2O$

	$[PPN]_4[\mathbf{1}]$	$[PPN][\mathbf{7}]\cdot H_2O$
formula	$C_{188}H_{120}N_4O_{42}P_8Re_{14}Hg_2$	$C_{63}H_{42}N_3O_{21}P_2SRe_7Hg\cdot H_2O$
fw	6362.62	2790.99
space group	$P\bar{1}$	$P\bar{1}$
temp (K)	198(2)	198(2)
a (Å)	15.9548(9)	11.1239(3)
b (Å)	17.3419(10)	15.5365(4)
c (Å)	18.1696(11)	21.0417(5)
α (deg)	81.939(1)	87.451(1)
β (deg)	76.479(1)	78.011(1)
γ (deg)	89.014(2)	89.895(1)
V (Å^3)	4839.0(5)	3553.6(2)
Z	1	2
D_{calcd} (g cm^{-3})	2.183	2.608
μ(Mo Kα) (cm^{-1})	104.31	141.70
λ(Mo Kα) (Å)	0.710 73	0.710 73
R1^a	0.0638	0.0491
wR2 (all data)^b	0.2031	0.1267

^{a} $R1 = \sum|(F_o - F_c)|/\sum F_o$. ^{b} $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4\}^{1/2}$.

The IR spectrum indicated a complete reaction after 15 min, after which time the solvent was removed in vacuo. The residue was redissolved in minimal dichloromethane (1.5 mL), and the solution was layered with methanol (10 mL). After 7 days, the pale supernatant was decanted. The dark crystals remaining were collected, washed with methanol, and dried under vacuum (15.8 mg, 0.0048 mmol, 64%). The identity of the product was confirmed by IR and ESI-mass-spectral data in agreement with literature data.[4]

Synthesis of $[PPN][Re_7C(CO)_{21}HgSC(NMe_2)_2]$ ($[PPN][\mathbf{7}]$) from $[PPN]_4[\mathbf{1}]$. $[PPN]_4[\mathbf{1}]$ (32.8 mg, 0.005 16 mmol) was dissolved with $[Cp_2Fe][PF_6]$ (5.2 mg, 0.016 mmol) in 15 mL of acetone contained in a 30 mL Schlenk tube. The reaction was stirred and monitored by IR spectroscopy. After 1 h, the major band had shifted from 2001 to 2004 cm^{-1}. At this point, tetramethylthiourea (7.9 mg, 0.0060 mmol) was added to the reaction solution. After an additional 2 h, the IR spectrum showed a small shift to 2003 cm^{-1}. The solvent was removed in vacuo, and the residue was dissolved in minimal acetone (2 mL). This solution was layered with 2-propanol (12 mL). After 3 days, the nearly colorless supernatant was decanted, and the dark brown residue was washed with methanol and dried under vacuum (20.4 mg, 0.0062 mmol, 60%). Anal. Calcd for $C_{63}H_{42}HgN_3O_{21}P_2Re_7S$: C, 27.27; H, 1.53; N, 1.51. Found: C, 27.65; H, 1.59; N, 1.32. IR (acetone) ν(CO): 2056 (vw), 2003 (vs), 1974 (w), 1949 (w), 1930 (w), 1890 (vw) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 3.47 (s, 12H, 4Me), 7.43−7.52 (m, 24H, Ph, *o*-H, *m*-H), 7.63−7.68 (m, 6H, Ph, *p*-H). ESI-MS (^{32}S, ^{187}Re, ^{202}Hg) *m/e*: 2243 $\{[Re_7C(CO)_{21}HgSC(NMe_2)_2]\}^-$. Single crystals of $[PPN][\mathbf{7}]\cdot H_2O$ suitable for X-ray diffraction were grown by layering 2-propanol on a dichloromethane solution and allowing subsequent slow interdiffusion at room temperature.

Synthesis of $[PPh_4][Re_7C(CO)_{21}HgSC(NMe_2)_2]$ ($[PPh_4][\mathbf{7}]$) from $[PPh_4]_2[Re_7C(CO)_{21}HgO_2CCH_3]$ ($[PPh_4]_2[\mathbf{8}]$). A sample of tetramethylthiourea (5.86 mg, 0.0443 mmol) was combined with $[PPh_4]_2$-$[Re_7C(CO)_{21}HgO_2CCH_3]$ (26.4 mg, 0.009 20 mmol) and stirred in 10 mL of dichloromethane contained in a 20 mL Schlenk tube. After the solids had dissolved, trifluoroacetic acid (1.0 μL, 0.013 mmol) was added. The solution was stirred for 5 h, and then it was evaporated to dryness in vacuo. The residue was dissolved in minimal dichloromethane (1 mL), and the resulting solution was layered with hexanes (10 mL). After 3 days, the nearly colorless supernatant was decanted from dark brown crystals. The crystals were washed with methanol and diethyl ether and then were dried under vacuum (22.2 mg, 0.008 mmol, 82%). The identity of the product was confirmed by IR and NMR spectroscopy.

X-ray Crystal Structure Determinations. A summary of selected crystallographic data for $[PPN]_4[\mathbf{1}]$ and $[PPN][\mathbf{7}]\cdot H_2O$ is given in Table 1. The data sets for both compounds were collected on a Siemens Platform/CCD automated diffractometer. The structures were solved by direct methods;[27] hydrogen atoms were fixed on calculated positions. The structures were refined by full-matrix least-squares procedures,[28] based on F^2, of the positional, isotropic, and anisotropic thermal parameters. The crystallographically independent half of the cluster anion in $[PPN]_4[\mathbf{1}]$ exhibits an orientation disorder such that about 90% of the mercury atoms are near the inversion center at ($^1/_2$ $^1/_2$ $^1/_2$), and the other 10% are near the inversion center at ($^1/_2$ 0 0); this disorder could be solved for all metal atoms but not for the carbide atom and carbonyl atoms of the minor species. In the case of $[PPN][\mathbf{7}]\cdot H_2O$, the largest residual electron density was located in the vicinity of the lattice water, but this does not perturb the cluster parameters. Structural diagrams of the cluster anions $[\mathbf{1}]^{4-}$ and $[\mathbf{7}]^-$ with their crystallographic labeling schemes are shown in Figures 1 and 2, respectively, drawn with 35% thermal probability ellipsoids. Tables 2 and 3 provide selected bond lengths and angles for $[\mathbf{1}]^{4-}$ and $[\mathbf{7}]^-$, respectively.

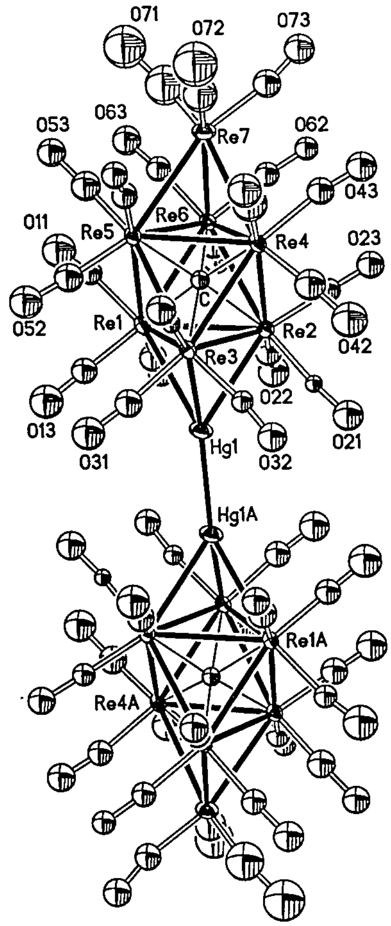


Figure 1. An ORTEP diagram of $[(Re_7C(CO)_{21}Hg)_2]^{4-}$ ($[\mathbf{1}]^{4-}$) with 35% probability ellipsoids.

Results and Discussion

Dimercury(I) Complex. The stoichiometric reaction of mercurous nitrate with 2 equiv of the trianion $[Re_7C(CO)_{21}]^{3-}$ in dichloromethane formed the dimercury-linked cluster compound $[\mathbf{1}]^{4-}$, which was isolated in 60% yield with $[PPN]^+$, $[PPh_4]^+$, or $[NEt_4]^+$ counterions. The fact that this cluster is a tetraanion suggests that our previous attempt to form the monomercury-linked complex $[(Re_7C(CO)_{21})_2(\mu\text{-}Hg)]^{4-}$ failed because of substantial steric interactions between the two cluster

---

[27] Sheldrick, G. M. *SHELXTL*; Siemens Analytical X-Ray Instruments Inc.: Madison, WI, 1990.

[28] Sheldrick, G. M. *SHELXTL PC,* version 5.0; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

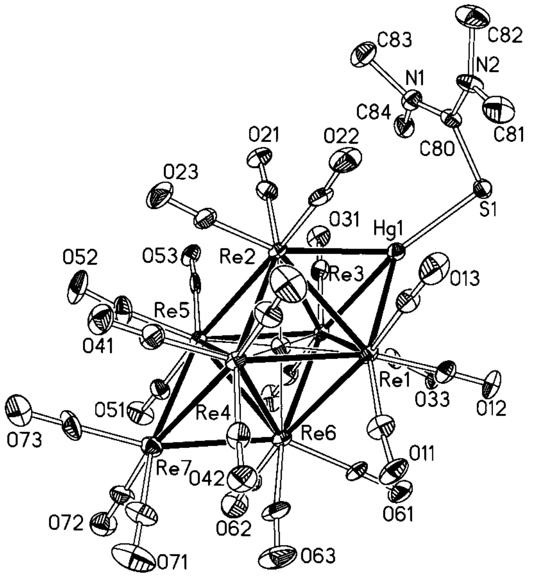


Figure 2. An ORTEP diagram of $[Re_7C(CO)_{21}HgSC(NMe_2)_2]^-$ ($[\mathbf{7}]^-$) with 35% probability ellipsoids.

Table 2. Selected Structural Parameters for $[PPN]_4[\mathbf{1}]^a$

Bond Distances (Å)

Hg1−Re1	2.965(3)	Hg1−Re2	2.911(3)	Hg1−Re3	2.944(3)
Re1−Re2	3.059(2)	Re1−Re3	3.034(2)	Re2−Re3	3.079(2)
Re1−Re5	3.014(3)	Re1−Re6	2.995(3)	Re2−Re4	2.968(3)
Re2−Re6	2.991(3)	Re3−Re4	2.997(3)	Re3−Re5	3.008(3)
Re4−Re5	2.986(2)	Re4−Re6	2.989(3)	Re5−Re6	2.964(2)
Re4−Re7	2.931(3)	Re5−Re7	2.985(3)	Re6−Re7	2.968(3)
Re1−C	2.23(4)	Re2−C	2.19(4)	Re3−C	2.20(4)
Re4−C	2.01(4)	Re5−C	2.07(4)	Re6−C	2.06(4)
Hg1−Hg1#	2.610(4)				

Bond Angles (deg)

Re1−Hg1−Re2	62.74(6)	Re1−Hg1−Re3	61.78(6)
Re2−Hg1−Re3	63.44(6)	Re1−Re2−Hg1	59.49(6)
Re2−Re1−Hg1	57.77(6)	Re1−Re3−Hg1	59.45(7)
Re2−Re3−Hg1	57.76(6)	Re3−Re2−Hg1	58.81(6)
Re3−Re1−Hg1	58.77(6)	Re1−Hg1−Hg1#	147.52(12)
Re2−Hg1−Hg1#	138.78(11)	Re3−Hg1−Hg1#	142.77(12)
Hg1−Re1−C	88.8(9)	Hg1−Re2−C	91.0(10)
Hg1−Re3−C	90.0(10)	Hg1−Re1−C11	160.1(12)
Hg1−Re1−C12	74.7(13)	Hg1−Re1−C13	78.6(12)
Hg1−Re2−C21	73.8(10)	Hg1−Re2−C22	80.4(13)
Hg1−Re2−C23	154.2(11)	Hg1−Re3−C31	75.8(13)
Hg1−Re3−C32	79.2(11)	Hg1−Re3−C33	157.1(10)

[a] Symmetry transformations used to generate equivalent atoms: # $-x - 1, -y + 1, -z + 1$.

subunits, since the longer bridge with two mercury atoms provides a stable link.

The electrospray ionization mass spectrum of $[\mathbf{1}]^{4-}$ in acetone contains peaks corresponding to $[(Re_7C(CO)_{21}Hg)_2]^{4-}$, $[PPN][(Re_7C(CO)_{21}Hg)_2]^{3-}$, and $[PPN]_2[(Re_7C(CO)_{21}Hg)_2]^{2-}$, which supports the formulation of the compound and its stability in solution. However, another feature in the mass spectrum is a peak corresponding to the formula $[Re_7C(CO)_{21}Hg(CH_3COCH_3)]^{2-}$. The intensity of this peak increases with time of observation, suggesting that Hg−Hg bond cleavage occurs under the ionizing conditions involved (vide infra).

The infrared spectrum of $[\mathbf{1}]^{4-}$ in dichloromethane shows several weak carbonyl absorptions along with one strong carbonyl absorption at 1999 cm^{-1}. This principal carbonyl stretching band is also an attribute of the related mercuric complexes $[Re_7C(CO)_{21}HgX]^{2-}$.[1−4] However, a characteristic feature in the infrared spectrum of $[\mathbf{1}]^{4-}$ is the relatively weak band at 2040 cm^{-1}. A similarly weak band in the infrared spectra of $[Re_7C(CO)_{21}HgX]^{2-}$ complexes occurs at significantly higher frequencies, in the range of 2049−2057 cm^{-1} depending on the substituent X.[1−4] The shift of the weak band from 2040 to ca. 2050 cm^{-1} or higher is a good indicator of a reaction that converts the dimercury(I) cluster to a monocapped mercury(II) cluster. This shift is often easier to observe than the change in the principle carbonyl band at 1999 cm^{-1}, the position of which may increase by only 1−3 cm^{-1} for the same reaction.

Table 3. Selected Structural Parameters for $[PPN][\mathbf{7}]$

Bond Distances (Å)

Hg1−Re1	2.8877(7)	Hg1−Re2	2.84878(7)	Hg1−Re3	2.8156(7)
Re1−Re2	3.0911(7)	Re1−Re3	3.0729(7)	Re2−Re3	3.0727(7)
Re1−Re4	3.0085(8)	Re1−Re6	3.0006(7)	Re2−Re4	2.9993(7)
Re2−Re5	3.0008(7)	Re3−Re5	2.9907(7)	Re3−Re6	3.0126(7)
Re4−Re5	2.9971(7)	Re4−Re6	2.9929(7)	Re5−Re6	2.9866(7)
Re4−Re7	2.9856(8)	Re5−Re7	2.9589(7)	Re6−Re7	2.9928(8)
Re1−C	2.136(11)	Re2−C	2.157(11)	Re3−C	2.179(12)
Re4−C	2.088(12)	Re5−C	2.132(11)	Re6−C	2.117(11)
Hg1−S1	2.421(3)	S1−C80	1.744(13)	N1−C80	1.310(16)
N1−C83	1.544(17)	N1−C84	1.472(16)	N2−C80	1.363(15)
N2−C81	1.460(16)	N2−C82	1.448(16)		

Bond Angles (deg)

Re1−Hg1−Re2	65.218(18)	Re1−Hg1−Re3	65.190(17)
Re2−Hg1−Re3	65.713(17)	Re1−Re2−Hg1	58.014(17)
Re2−Re1−Hg1	56.767(17)	Re1−Re3−Hg1	58.538(17)
Re2−Re3−Hg1	57.648(17)	Re3−Re2−Hg1	56.640(16)
Re3−Re1−Hg1	56.273(16)	Re1−Hg1−S1	127.92(9)
Re2−Hg1−S1	136.74(8)	Re3−Hg1−S1	155.44(8)
Hg1−Re1−C	85.4(3)	Hg1−Re2−C	86.0(3)
Hg1−Re3−C	86.4(3)	Hg1−S1−C80	101.9(4)
S1−C80−N1	121.1(9)	S1−C80−N2	116.7(11)
N1−C80−N2	122.2(12)	C83−N1−C84	112.1(11)
C81−N2−C82	114.1(11)	C80−N1−C83	123.8(11)
C88−N1−C84	123.6(11)	C80−N2−C81	122.7(11)
C80−N2−C82	122.8(12)		

It is noteworthy that $[\mathbf{1}]^{4-}$ is not the product when $[Re_7C(CO)_{21}]^{3-}$ is treated with mercurous chloride in place of mercurous nitrate. The reaction proceeds instead to the mercury(II) chloride-capped cluster complex $[\mathbf{2}]^{2-}$, which was previously isolated (in higher yield) from the direct reaction of $[Re_7C(CO)_{21}]^{3-}$ with $HgCl_2$.[4] There is no evidence of intermediate tetraanion formation by IR spectroscopy. The disproportionation of mercury(I) chloride to form mercury(II) chloride and mercury(0) is a likely cause of this result, as such reactions are known to occur for solutions of mercury(I) salts.[29] This conclusion is supported by the observations that a 1:1 mole ratio of $[Re_7C(CO)_{21}]^{3-}/Hg_2Cl_2$ is required for complete reaction and that a silver-gray precipitate, which likely contains mercury(0), is formed during the reaction. We note, however, that the direct reaction of $[Re_7C(CO)_{21}]^{3-}$ with a mercury(II) precursor, $Hg(NO_3)_2$, forms the mercury(II) nitrate-capped complex $[\mathbf{3}]^{2-}$, as in analogous cases where mercuric reagents are used to cap the carbidorhenate cluster unit.[1−4]

X-ray Crystallographic Study of $[PPN]_4[\mathbf{1}]$. The molecular structure of $[\mathbf{1}]^{4-}$ is depicted in Figure 1. The cluster itself is best described as two 1,4-bicapped {Re(Re$_6$)Hg} octahedral units related by a center of inversion located at the middle of the linking Hg−Hg bond. The mercury atom caps the face described by Re1, Re2, and Re3, with distances of 2.965(3), 2.911(3), and 2.944(3) Å, respectively. The average distance of 2.94 Å is 0.15 Å longer than the sum of the covalent radii of rhenium (taken as 1.48 Å from the bonds to Re7) and mercury (taken as 1.31 Å from the Hg1−Hg1# bond), which may indicate the residual effects of steric interactions between the cluster subunits. This average distance of 2.94 Å is also nearly 0.1 Å longer than the average Re−Hg(II) distance found for the structurally characterized rhenium carbido cluster complexes

($[Re_7C(CO)_{21}HgML_n]^{2-}$).[1−3] The remaining Re−Re bond distances and angles are similar to those found in the previously described complexes.

The crystallographic inversion center is located in the center of the Hg1−Hg1# bond, which has a length of 2.610(4) Å (2.71(10) Å in the disordered molecule). This distance is within the range observed for mercurous compounds with halide and related simple ligands (2.50−2.70 Å),[23,24] and it is quite similar to the Hg−Hg bond lengths found in two compounds containing an unsupported dimercury(I) unit linking either two cobalt atoms in $(N(CH_2CH_2PPh_2)_3Co)_2Hg_2$ (2.651(4) Å)[19,20] or two silicon atoms in $((Me_3SiMe_2Si)_3Si)_2Hg_2$ (2.6569(8) Å).[22] The Hg−Hg distance of 2.521(2) Å in $[Hg_2(Me_6C_6)_2][AlCl_4]_2$ is considerably shorter, although in this complex the Hg_2^{2+} unit interacts unsymmetrically with the two hexamethylbenzene units and also has close contacts with several chlorine atoms.[21]

Other reported examples of cluster compounds containing dimercury units display longer mercury−mercury distances and do not appear to involve formal Hg_2^{2+} units. Thus, the triplatinum cluster $Pt_3(\mu\text{-}CO)_3(PPh^iPr_2)_3$ reacts with metallic mercury to cap the metal triangle, and the product crystallizes in dimeric units with the capping mercury atoms interacting weakly (3.225(1) Å) between the two Pt_3 layers.[15] However, when the distance between the two Pt_3 triangles is compressed by bridging diphosphine ligands in the analogous compound $Pt_6(PPh_2(CH_2)_6PPh_2)_6(\mu\text{-}CN{-}C_6H_3Me_2)_6Hg_2$, the Hg−Hg distance in the encapsulated dimercury(0) unit shortens markedly to 2.872(7) Å.[16] Similar distances are observed for the imbedded dimercury units in $[Os_{18}Hg_2C_2(CO)_{24}]^{2-}$(2.744(5) Å)[17] and $[Os_{18}Hg_2C_2)CO)_{24}]^{4-}$(2.820(3) Å),[18] but neither their bonding modes nor their formal oxidation states[5] are analogous to the situation observed for [**1**]$^{4-}$

Mercury−Mercury Bond Cleavage Reactions. The dimercury(I) cluster [**1**]$^{4-}$ is apparently stable indefinitely as a crystalline salt. It is also stable in solution under a nitrogen atmosphere and normal lighting conditions. However, [**1**]$^{4-}$ reacts readily with an equivalent of iodine or bromine in dichloromethane solution to form the known Hg(II) derivatives $[Re_7C(CO)_{21}HgX]^{2-}$ (X = I [**5**], X = Br [**6**]).[4] The analogous reaction of [**1**]$^{4-}$ with 4-bromophenyl disulfide, forming the known compound $[Re_7C(CO)_{21}HgSC_6H_4Br]^{2-}$ [**4**],[3] is significantly slower and requires days instead of minutes for completion at room temperature. The slow pace of this reaction can be attributed to the crowded environment around the Hg−Hg bond combined with the moderate bulk of the oxidant. From a preparative viewpoint, the previously reported method of reacting $[Re_7C(CO)_{21}]^{3-}$ directly with the electrophile HgX_2 provides the mercuric halide cluster complexes ([**5**]$^{2-}$ and [**6**]$^{2-}$) in higher yields,[4] and the direct reaction of $[Re_7C(CO)_{21}HgOH]^{2-}$ with 4-bromothiophenol is a higher yield method for synthesis of [**4**]$^{2-}$.[3]

Mercury(II) Complex with a Neutral Ligand. One peak observed in the electrospray mass spectrum of [**1**]$^{4-}$ corresponds to a cleavage product in which the mercury center is coordinated to acetone, presumably as a neutral molecule. In an attempt to prepare this complex, 2 equiv of ferrocenium ion was added to a solution of [**1**]$^{4-}$ in acetone. This caused a shift in the principal carbonyl IR band from 2001 to 2004 cm^{-1}, but no stable adduct was isolated after evaporation of the solvent. However, when the oxidation reaction of [**1**]$^{4-}$ is carried out in the presence of a stronger neutral ligand, such as tetramethylthiourea (TMTU), a stable complex of the formula $[Re_7C(CO)_{21}HgL]^-$ (L = TMTU) is formed, and it has been isolated as the salt [PPN][**7**]. This compound is the first example of a carbidoheptarhenate cluster complex of a mercury center bound to a neutral ligand, which means that the overall charge on the cluster anion is now 1− instead of the usual 2−. Furthermore, this complex suggests the possibility of changing the coordination at the mercury center by exchange of neutral ligands (vide infra).

The TMTU complex [**7**]$^-$ can be synthesized also by an entirely different reaction sequence that is independent of [**1**]$^{4-}$, beginning instead with the mercury acetate complex $[Re_7C(CO)_{21}HgO_2CCH_3]^{2-}$([**8**]$^{2-}$). If complex [**8**]$^{2-}$ is treated with trifluoroacetic acid in the presence of TMTU, the acetate ligand is replaced by TMTU to give [**7**]$^-$. This reaction likely occurs via neutral ligand exchange wherein the acetate ligand is first protonated and then acetic acid is displaced by the softer sulfur donor. This procedure conveniently allows isolation of [**7**]$^-$ in higher yield than that obtained by oxidizing [**1**]$^{4-}$ with ferrocenium ion in the presence of tetramethylthiourea.

The infrared spectrum of [**7**]$^-$ is very similar to that of carbidoheptarhenate complexes of mercuric centers with anionic ligands in that it shows several weak carbonyl absorptions and one strong carbonyl band at 2003 cm^{-1}.[1−4] The electrospray ionization mass spectrum of [**7**]$^-$ in acetone contains a peak corresponding to $[Re_7C(CO)_{21}Hg{-}S{=}C(NMe_2)_2]^-$ but none corresponding to the analogous acetone complex. The proton NMR spectrum of [PPN][**7**] in CD_2Cl_2 contains peaks for the cation as well as a singlet at $\delta = 3.47$ due to the 12 methyl hydrogens of the TMTU ligand. If this sample is exposed to an equivalent amount of triethylphosphine, the TMTU singlet shifts upfield to $\delta = 3.01$, which is the chemical shift position of free TMTU. Thus, direct substitution of one neutral ligand by another at the mercury center is indicated.

X-ray Crystallographic Study of [PPN][7]. The molecular structure of [**7**]$^-$, as determined by a single-crystal X-ray diffraction study of the [PPN]$^+$ salt, is shown in Figure 2, and structural parameters are collected in Table 3. The cluster unit displays characteristics very similar to those found previously in carbidoheptarhenate complexes of mercury(II) centers.[1−3] As noted in these cases, the average Re−Re distance for the mercury-capped face is slightly longer (∼0.08 Å) than that for the uncapped faces, which is 2.99 Å. The average Re−Hg distance of 2.85 Å also compares well with previously obtained values and is again slightly shorter than that of [**1**].$^{4-}$

The TMTU ligand is bound through its sulfur atom to the mercury center at a distance of 2.421(3) Å, with an Hg1−S1−C80 angle of 101.9(4)°, and a S1−C80 distance of 1.744(13) Å. These parameters compare closely with those reported previously for a mercury−TMTU complex, $[Hg_2(TMTU)_4(\mu\text{-}Br)_2][BF_4]_2$: av Hg−S distance of 2.41 Å, av S═C distance of 1.74 Å.[30] The S1−C80 distance in particular indicates the double-bond character present in this bond. The remaining bond distances and bond angles within the TMTU ligand are essentially the same as those found in other TMTU complexes.[31,32] The SCN_2 skeleton of the TMTU ligand is nearly planar, with the methyl carbon atoms twisted slightly above and below this plane to minimize steric interactions.

Cyclic Voltammetry of [1]$^{4-}$ and [7]$^-$. To better understand the redox behavior of [**1**]$^{4-}$ and its oxidative conversion to [**7**]$^-$,

---

(29) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: Oxford, U.K., 1997; p 1213.

(30) Battaglia, L. P.; Corradi, A. B.; Marcotrigiano, G.; Pellacani, G. C. *J. Chem. Soc., Dalton Trans.* **1979**, 1089.

(31) Gambino, D. G.; Kremer, E.; Baran, E. J.; Mombrú, A.; Suescun, L.; Mariezcurrena, R.; Kieninger, M.; Ventura, O. *Z. Anorg. Allg. Chem.* **1999**, *625*, 813.

(32) Bierbach, U.; Hambley, T. W.; Farrell, N. *Inorg. Chem.* **1998**, *37*, 708.

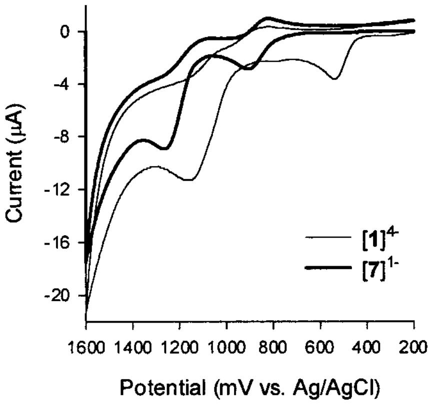


Figure 3. Cyclic voltammograms of $[PPN]_4$[**1**] (0.50 mM) and $[PPh_4]$-[**7**] (0.58 mM) in CH_2Cl_2/0.1 M $[NBu_4][BF_4]$ vs Ag/AgCl.

Table 4. Anodic Current Peak Potentials for [**1**]$^{4-}$, [**7**]$^{-}$, and Related Complexes[a]

compound	E_{pa} (mV)	E'_{pa} (mV)	ref
$[(Re_7C(CO)_{21}Hg)_2]^{4-}$ ([**1**]$^{4-}$)	538	1160	this work
$[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$	687	1000	ref 4
$[Re_7C(CO)_{21}HgCl]^{2-}$	802	1131	ref 4
$[Re_7C(CO)_{21}Hg(CN)]^{2-}$	841	1108	ref 4
$[Re_7C(CO)_{21}Hg(TMTU)]^{-}$ ([**7**]$^{-}$)	907	1262	this work

[a] Versus Ag/AgCl in $CH_2Cl_2/[Nbu_4][BF_4]$.

cyclic voltammograms (CV) were obtained for both compounds (see Figure 3). In the CV of [**7**]$^{-}$, there are two anodic current peaks, the first at 907 mV and the second at 1262 mV (vs Ag/AgCl). The first oxidation process appears quasi-reversible, with a corresponding cathodic peak present at 821 mV, but the second oxidation process appears irreversible. This behavior is completely analogous to that found previously for $[Re_7C(CO)_{21}HgX]^{2-}$ complexes (see Table 4),[4] but replacement of the anionic ligand by a neutral TMTU ligand in [**7**]$^{-}$ causes both anodic peaks to shift to higher potentials.

In the CV of [**1**]$^{4-}$, there are also two anodic current peaks, the first at 538 mV and the second at 1160 mV. Neither of these oxidation processes appears reversible. The first anodic peak occurs at a potential over 100 mV lower than that for the first anodic peak of any $[Re_7C(CO)_{21}HgX]^{2-}$ complex (650−800 mV) previously examined, whereas the position of the second anodic peak compares more closely with these complexes (see Table 4).[4] Although the shift of the first anodic peak to a lower potential may be partly due to the higher charge of [**1**]$^{4-}$, this feature does not exhibit quasi-reversibility, which is a characteristic aspect of the first oxidation process of $[Re_7C(CO)_{21}HgX]^{2-}$ complexes. This distinction, in conjunction with the more comparable second anodic peak potential, indicates that the first oxidation process is likely due to oxidation of the mercury−mercury bond. (For comparison, the reduction potential for $2Hg^{2+} + 2e^- = Hg_2^{2+}$ is 0.698 V vs Ag/AgCl.[33]) In practical terms, the enhanced ease of oxidation for [**1**]$^{4-}$ is sufficient to allow its oxidation chemically by ferrocenium ion to form a carbidohexarhenate mercury(II) complex.

Summary

We have shown that the compound $[Re_7C(CO)_{21}]^{3-}$ reacts readily with mercurous nitrate to form the dimercury(I)-bridged cluster $[(Re_7C(CO)_{21}Hg)_2]^{4-}$. This unique example of a cluster with a bridging μ_3:μ_3'-Hg_2^{2+} unit can be oxidized to cleave the mercury−mercury bond, forming mercuric derivatives of the general formula $[Re_7C(CO)_{21}HgX]^{2-}$. In the presence of tetramethylthiourea (TMTU), oxidation forms $[Re_7C(CO)_{21}Hg(TMTU)]^{-}$, which can also be synthesized in high yield by protonation of $[Re_7C(CO)_{21}HgO_2C_2H_3]^{2-}$ in the presence of TMTU. The singly charged cluster may have utility as a building block for supermolecular assemblies and as an electron-dense, site-selective cluster tag for macromolecules.

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 Sciences was supported by NSF Grant CHE 95-03145. Funding for the NMR instrumentation was provided in part by the W. M. Keck Foundation, NIH (Grant PHS 1 S10 RR10444-01), and NSF (Grant CHE 96-10502). We thank Dr. Scott R. Wilson for collection of the X-ray diffraction data and A. Babcock for assistance with the electrochemical experiments.

Supporting Information Available: An X-ray crystallographic file in CIF format for compounds $[PPN]_4[(Re_7C(CO)_{21}Hg)_2]$ ($[PPN]_4$[**1**]) and $[PPN][Re_7C(CO)_{21}HgS{=}C(NMe_2)_2]$ ([PPN][**7**]). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0011213

---

(33) Rubinson, K. A.; Rubinson, J. F. *Contemporary Instrumental Analysis*; Prentice-Hall: Saddle River, NJ, 2000; p 815.