Inorg. Chem. **1997**, *36,* 3386−3389

Carbidoheptarhenate Complexes of Mercury Hydroxide and Arenethiolate. Crystal Structures of $[NEt_3Bz]_2[Re_7C(CO)_{21}HgOH]$ and $[PPh_4]_2[Re_7C(CO)_{21}HgSC_6H_4Br]$

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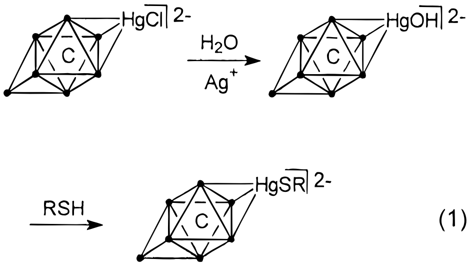
Received January 22, 1997

Introduction

Metal clusters that undergo substitution in well-defined ways have potential utility as markers for macromolecular systems. For example, recent reports illustrate various applications of labeled macromolecules with such techniques as IR spectroscopy (for the carbonylmetalloimmunoassay procedure),[1] scanning transmission electron microscopy,[2] and X-ray crystallography.[3] In an earlier paper we mentioned the apparent transformation under FAB-MS conditions of $[Re_7C(CO)_{21}HgCl]^{2-}$ into $[Re_7C(CO)_{21}HgSR]^{2-}$ when the dispersing matrix was a dithioerythritol/dithiothreitol mixture.[4] We have subsequently investigated such substitution reactions under preparative conditions and now report the formation of the novel hydroxide derivative $[Re_7C(CO)_{21}HgOH]^{2-}$ and its facile transformation into the thiolate complex $[Re_7C(CO)_{21}HgSC_6H_4Br]^{2-}$ (eq 1).



(1)

Experimental Section

General Procedures. $[Et_3BzN]_2[Re_7C(CO)_{21}HgCl]$ was prepared as previously reported.[4] The salt $[PPh_4][Re_7C(CO)_{21}HgCl]$ was prepared in a similar manner (91%). Silver nitrate (Allied Chemical) and 4-bromothiophenol (Aldrich) were used as received. Reactions with the 4-bromothiophenol were conducted under a nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. Negative ion fast atom bombardment (FAB) mass spectra, 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. Microanalyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences.

Synthesis of $[PPh_4]_2[Re_7C(CO)_{21}HgOH]$. A solution of $AgNO_3$ (8.0 mg, 0.047 mmol) in water (4 mL) was added to a solution of $[PPh_4]_2[Re_7C(CO)_{21}HgCl]$ (128 mg, 0.0453 mmol) in acetone (20 mL). The reaction mixture was stirred for 1 h, the precipitated AgCl was separated by filtration, and the filtrate was allowed to evaporate slowly under ambient conditions. After 7 days the remaining colorless supernatant was decanted, and the precipitate was washed with methanol/water (80:20) and then diethyl ether and finally dried under vacuum. $[PPh_4]_2[\mathbf{1}]$ was isolated as black crystals (120 mg, 0.0429 mmol, 95%). IR (CH_2Cl_2): ν(CO) 2056 (vw), 2002 (vs), 1973 (w), 1948 (w), 1926 (w), 1886 (vw) cm^{-1}. Anal. Calcd for $C_{70}H_{41}HgO_{22}P_2Re_7$: C, 30.03; H, 1.48. Found: C, 30.17; H, 1.38.

Table 1. Crystallographic Data for $[Et_3BzN]_2[\mathbf{1}]$ and $[PPh_4]_2[\mathbf{2}]$

	$[Et_3BzN]_2[\mathbf{1}]$	$[PPh_4]_2[\mathbf{2}]$
formula	$^1/_2(C_{48}H_{45}HgN_2O_{22}Re_7)$	$C_{76}H_{44}BrHgO_{21}SP_2Re_7\cdot 0.5CH_2Cl_2$
fw	1252.94 (2505.9)	3013.48
space group	$P\bar{1}$	$P\bar{1}$
temp (°C)	27	−75(2)
a (Å)	10.915(4)	12.4099(1)
b (Å)	13.572(6)	13.7639(1)
c (Å)	10.781(5)	25.8584(5)
α (°)	95.87(4)	79.390(1)
β (°)	94.96(3)	79.927(1)
γ (°)	70.74(3)	65.511(1)
V (Å^3)	1497(1)	3926.72(9)
Z	2 (1)	2
D_{calc} (g.cm^{-3})	2.779	2.549
μ(Mo Kα) (cm^{-1})	169.1	133.71
λ(Mo Kα) (Å)	0.710 73	0.710 73
F(000)	1128	2750
Θ range (°)	1.5−26.5	1.61−21.50
no. of rflns collcd	6797	15202
no. of indep rflns	6205	8970
R_{int}	0.028	0.0507
no. of obsd data [$I > 2\sigma(I)$]	4528	7915
R_1[a]	0.051 [$I > 2.58\sigma(I)$]	0.0433 [$I > 2\sigma(I)$]
weighted residual indexes	$R_w = 0.067$[b]	$wR_2 = 0.1021$ for all data[c]

[a] $R_1 = \sum|(F_o - F_c)|/\sum F_o$. [b] $R_w = \{\sum w(F_o - F_c)^2/\sum F_o^2\}^{1/2}$. [c] $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum F_o^4\}^{1/2}$.

The triethylbenzylammonium salt was prepared in a similar manner. Opaque, black, prismatic crystals of $[NEt_3Bz]_2[\mathbf{1}]$ used for the X-ray data collection were grown from an aqueous acetone solution by slow evaporation in air.

Synthesis of $[PPh_4]_2[Re_7C(CO)_{21}HgSC_6H_4Br]$. $[PPh_4]_2[\mathbf{1}]$ (17.7 mg, 0.00632 mmol) and 4-bromothiophenol (3.0 mg, 0.016 mmol) were stirred under a nitrogen atmosphere in dichloromethane (6 mL) for 14 h. The solution was then concentrated under vacuum by half and layered with diethyl ether (6 mL). After 4 days at room temperature the precipitate formed was isolated, washed with diethyl ether, and dried under vacuum. Analytically pure $[PPh_4]_2[\mathbf{2}]$ was obtained as a dark red crystalline solid (16.0 mg, 0.00539 mmol, 85%). IR (CH_2Cl_2): ν(CO) 2055 (vw), 2001 (vs), 1972 (w), 1947 (w), 1926 (w), 1887 (vw) cm^{-1}. FAB-MS (^{32}S, ^{79}Br, ^{187}Re, ^{201}Hg): m/z 2636 $(M - PPh_4)^-$, 2297 $(M - 2PPh_4)^-$, 1909 − 28x, x = 0, 1, 3, 4, 5, 6, 7 $(Re_7C(CO)_{21-x})^-$, 1638 $(Re_6C(CO)_{18})^-$. Anal. Calcd for $C_{76}H_{44}BrHgO_{21}SP_2Re_7$: C, 30.72; H, 1.49. Found: C, 31.02; H, 1.28. Platy, red crystals of $[PPh_4]_2[\mathbf{2}]\cdot 0.5\ CH_2Cl_2$ were obtained by layering a dichloromethane solution with diethyl ether and subsequent solvent diffusion.

X-ray Crystal Structure Determinations. A summary of selected crystallographic data for $[NEt_3Bz]_2[\mathbf{1}]$ and $[PPh_4]_2[\mathbf{2}]\cdot 0.5CH_2Cl_2$ is given in Table 1. Diffraction data for $[NEt_3Bz]_2[\mathbf{1}]$ were collected on a Syntex $P2_1$ automated four-circle diffractometer. Correction for absorption was applied with 0.109 maximum and 0.045 minimum transmission. The structure was solved by direct methods,[5] and hydrogen atoms were fixed on calculated positions. Full-matrix least-squares refinement,[6] based on F, of the positional, isotropic, and anisotropic thermal parameters for all non-hydrogen atoms converged at $R_1 = 0.051$ for $I > 2.58\sigma(I)$ and $R_w = 0.067$ for all data. Selected bond lengths and angles for

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S0020-1669(97)00068-2 CCC: $14.00

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

Bond Distances (Å)					
Hg−Re1	2.949(8)	Hg−Re2	2.832(9)	Hg−Re3	2.889(8)
Re1−Re2	3.0150(8)	Re1−Re3	3.0105(7)	Re2−Re3	3.0153(8)
Re1−Re2A	3.0046(8)	Re1−Re3A	2.9907(7)	Re1A−Re4A	2.939(7)
Re2−Re3A	2.9855(8)	Re2A−Re4A	3.008(8)	Re3A−Re4A	2.922(7)
Re1−C	2.128(5)	Re2−C	2.128(5)	Re3−C	2.115(5)
Hg−O	2.22(2)				

Bond Angles (deg)			
Re1−Hg−Re2	62.8(2)	Re1−Hg−Re3	62.1(2)
Re2−Hg−Re3	63.6(2)	Re1−Re2−Hg	60.5(2)
Re2−Re1−Hg	56.7(2)	Re1−Re3−Hg	59.9(2)
Re2−Re3−Hg	57.3(2)	Re3−Re2−Hg	59.1(2)
Re1−Hg−O	134.1(7)	Re2−Hg−O	151.6(7)
Re3−Hg−O	141.1(7)	Hg−Re1−C	86.3(2)
Hg−Re2−C	89.4(2)	Hg−Re3−C	88.2(2)
Hg−Re1−C11	158.0(5)	Hg−Re1−C12	79.8(5)
Hg−Re1−C13	77.6(5)	Hg−Re2−C21	76.6(5)
Hg−Re2−C22	77.9(5)	Hg−Re2−C23	155.1(5)
Hg−Re3−C31	78.4(5)	Hg−Re3−C32	155.8(5)
Hg−Re3−C33	78.9(6)		

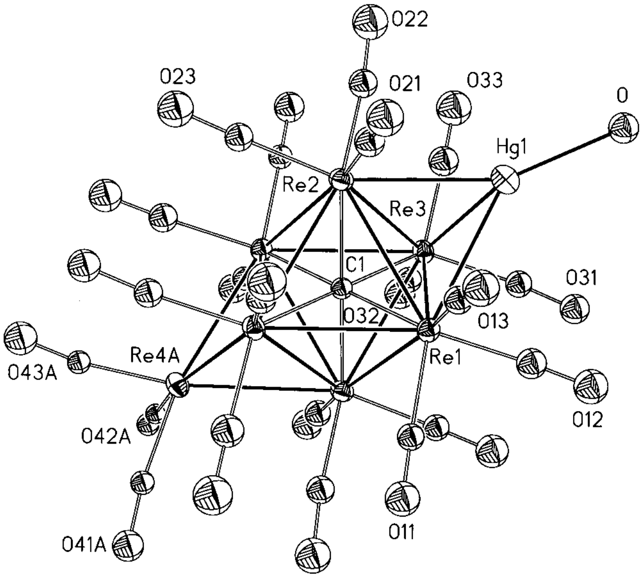


Figure 1. An ORTEP diagram of the molecular structure of $[Re_7C(CO)_{21}HgOH]^{2-}$ with 35% thermal probability.

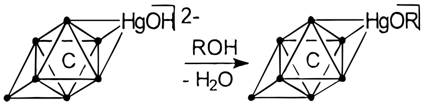
$[NEt_3Bz]_2[\mathbf{1}]$ are given in Table 2. Figure 1 shows the molecule $[\mathbf{1}]^{2-}$ with the crystallographic labeling scheme.

The data for $[PPh_4]_2[\mathbf{2}]\cdot 0.5CH_2Cl_2$ were collected on a Siemens Platform/CCD automated diffractometer. Absorption correction was applied with 0.5842 maximum and 0.0972 minimum transmission. The structure was solved by direct methods,[7] and hydrogen atoms were fixed on calculated positions. Full-matrix least-squares refinement, based on F^2, of the positional, isotropic, and anisotropic thermal parameters for all non-hydrogen atoms converged at $R_1 = 0.0433$ ($wR_2 = 0.0797$) for $I > 2\sigma(I)$ and $R_1 = 0.0897$ ($wR_2 = 0.1021$) for all data. Selected bond lengths and angles for $[PPh_4]_2[\mathbf{2}]$ are given in Table 3. Figure 2 shows the molecule with the crystallographic labeling scheme.

Results and Discussion

We have found that halide abstraction from $[Re_7C(CO)_{21}HgCl]^{2-}$ with an equimolar amount of $AgNO_3$ in aqueous acetone forms the hydroxy-substituted compound $[Re_7C(CO)_{21}HgOH]^{2-}$ ($[\mathbf{1}]^{2-}$), which can be isolated in high yield after slow evaporation of the reaction solvent. This hydroxomercury compound shows reactivity toward sulfhydryl groups, which is not surprising due to the high thiophilicity of mercury.[8,9] The reaction of $[\mathbf{1}]^{2-}$ with an excess of 4-bromothiophenol (eq 1) generates the thiophenolate-substituted compound $[Re_7C(CO)_{21}HgSC_6H_4Br]^{2-}$ ($[\mathbf{2}]^{2-}$), which was isolated in 85% yield. The infrared spectra of both clusters show nearly the same carbonyl absorption bands; for example, the principal CO absorption of $[\mathbf{2}]^{2-}$ is shifted by only 1 cm^{-1} to lower energy compared to that of $[\mathbf{1}]^{2-}$, which makes it difficult to monitor intermediate stages of the reaction.

Negative ion FAB mass spectra of both cluster complexes as the PPh_4^+ salts were obtained with 3-nitrobenzyl alcohol as the dispersing medium. For the complex $[PPh_4]_2[\mathbf{2}]$ peaks corresponding to $[M - PPh_4]^-$, $[M - 2PPh_4]^-$, and $[Re_7C(CO)_{21}]^-$ were observed. For the hydroxo complex $[PPh_4]_2[\mathbf{1}]$ the signal attributed to $[Re_7C(CO)_{21}]^-$ was observed but no signals for $[M - PPh_4]^-$ and $[M - 2PPh_4]^-$ were detected. Instead, ion multiplets at 2257 ($[Re_7C(CO)_{21}HgOR]^-$) and 2596 ($[Re_7C(CO)_{21}HgOR][PPh_4]^-$) were observed, which values correspond to a mercury alcoholate complex resulting from a condensation reaction between the hydroxo complex $[\mathbf{1}]^{2-}$ and the 3-nitrobenzyl alcohol matrix (eq 2).



(2)

The crystal structure of the complex ion $[\mathbf{1}]^{2-}$ (Figure 1) shows that the cluster unit consists of a 1,4-bicapped octahedron, where the mercury is located on a face opposite that of the capping $Re(CO)_3$ unit (Re4A). In the solid state $[NEt_3Bz]_2[\mathbf{1}]$ has pseudo inversion symmetry, which results in end-for-end disorder of the cluster molecule with the carbide atom at the inversion center. This kind of disorder of the octanuclear metal framework has been observed also for several related complexes, including $[Re_7C(CO)_{21}Pt(C_4H_7)]^{2-}$.[10] The mercury atom caps the face described by Re1, Re2, and Re3 with distances of 2.832(9) Å (Hg−Re2), 2.889(8) Å (Hg−Re3), and 2.949(8) (Hg−Re1). The average distance of 2.89 Å is 0.14 Å longer than the sum of the covalent radii of rhenium (taken as 1.48 Å from

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Table 3. Selected Structural Parameters for $[\mathbf{2}]^{2-}$

Bond Distances (Å)					
Hg1−Re1	2.8801(11)	Hg1−Re2	2.8735(10)	Hg1−Re3	2.8546(10)
Re1−Re2	3.0458(10)	Re1−Re3	3.0642(9)	Re2−Re3	3.0547(10)
Re1−Re5	2.9926(10)	Re1−Re6	2.9926(10)	Re2−Re4	2.9915(10)
Re2−Re6	3.0033(11)	Re3−Re4	2.9989(10)	Re3−Re5	2.9913(11)
Re4−Re5	2.9769(10)	Re5−Re6	2.9931(10)	Re4−Re6	2.9867(9)
Re4−Re7	2.9606(11)	Re5−Re7	2.9520(10)	Re6−Re7	2.9572(9)
Re1−C	2.15(2)	Re2−C	2.15(2)	Re3−C	2.16(2)
Re4−C	2.10(2)	Re5−C	2.09(2)	Re6−C	2.11(2)
Hg1−S1	2.395(5)	S1−C101	1.78(2)		

Bond Angles (deg)			
Re1−Hg1−Re2	63.93(3)	Re1−Hg1−Re3	64.59(3)
Re2−Hg1−Re3	64.45(2)	Re1−Re2−Hg1	63.14(2)
Re2−Re1−Hg1	60.38(2)	Re1−Re3−Hg1	62.83(2)
Re2−Re3−Hg1	60.94(2)	Re3−Re2−Hg1	62.18(2)
Hg1−Re1−C	86.9(5)	Hg1−Re2−C	87.1(4)
Hg1−Re3−C	87.3(4)	Hg1−Re1−C11	153.3(5)
Hg1−Re1−C12	82.0(5)	Hg1−Re1−C13	75.5(6)
Hg1−Re2−C21	80.7(5)	Hg1−Re2−C22	156.8(6)
Hg1−Re2−C23	75.7(6)	Hg1−Re3−C31	79.8(5)
Hg1−Re3−C32	78.6(5)	Hg1−Re3−C33	159.5(5)
Re1−Hg1−S1	137.2(1)	Re2−Hg1−S1	136.8(1)
Re3−Hg1−S1	150.9(1)	Hg1−S1−C101	102.1(6)

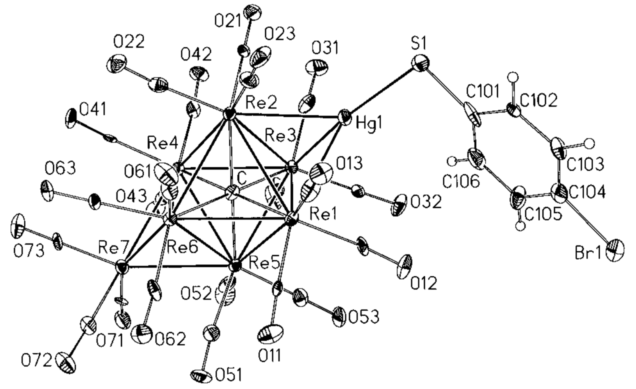

Figure 2. An ORTEP diagram of the molecular structure of $[Re_7C(CO)_{21}HgSC_6H_4Br]^{2-}$ with 35% thermal probability.

the bonds to Re4A) and mercury (1.27 Å from $[Hg_2(NO_3)_2 \cdot 2H_2O]$,[11] which may indicate some ionic character in the Re−Hg bonds. The Re−Re distances in this compound are comparable to those found in $[\mathbf{2}]^{2-}$ (see below) as well as those in other rhenium carbido clusters of the type $[Re_7C(CO)_{21}ML_n]^{2-}$.[10,12]

The mercury atom in $[\mathbf{1}]^{2-}$ also binds a hydroxy group with a Hg−O bond length of 2.22(2) Å. To our knowledge there is no reported solid state structure of a mercury complex with a terminal hydroxo group, although a few mercury complexes with bridging hydroxide ligands must be noted.[13] A study of the structure of hydroxomethyl mercury in solution by X-ray scattering reported a Hg−O distance of 2.06(2) Å.[14] There are also some known mercury complexes with monodentate anionic oxygen donor ligands, such as nitrate, acetate, or trifluoroacetate, where the Hg−O bond length is in the range from 2.10(2) to 2.28(4) Å,[15] which is comparable to the bond distance reported herein. It is of interest that the oxygen of the hydroxo group is bent slightly toward Re1, which makes the longest bond to the mercury atom, and away from Re2, which has the shortest Re−Hg bond. The Re−Hg−O angle varies from 134.1(7)° for Re1 to 141.1(7)° for Re3 to 151.6(7)° for Re2.

The solid state structure of complex $[PPh_4]_2[\mathbf{2}]$ (Figure 2) shows the same cluster framework as in $[\mathbf{1}]^{2-}$. The mercury atom in $[\mathbf{2}]^{2-}$ is more symmetrically bonded to the face described by Re1, Re2, and Re3 than in complex $[\mathbf{1}]^{2-}$, with distances of 2.855(1) Å (Re3−Hg1), 2.874(1) Å (Re2−Hg1), and 2.880(1) Å (Re1−Hg1), averaging 2.87 Å. The thiolate ligand displays a Hg1−S1 distance of 2.395(5) Å and an angle Hg1−S1−C101 of 102.1(6)°. These values are similar to those found in some known mercury thiolate complexes, such as $[Hg(C_5H_4NS)(CH_3CO_2)]_n$,[16] $[Hg(S(CH_2)_3N(CH_3)_3)][PF_6]_2$,[17] $[Hg(SC_6H_2\text{-}2,4,6\text{-i-}Pr_3)_2]$,[18] and $[MeHgSC_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3)_2]$.[19] The thiolate ligand is bent toward the edge described by Re1 and Re2, which is shown by the Re−Hg−S angles, and there are two small angles, 136.8(1)° to Re2 and 137.2(1)° to Re1, and one larger angle of 150.9(1)° to Re3. In the unit cell there is also a disordered solvent molecule near the inversion center, but this does not appear to affect the structure of the cluster complex.

Conclusion

We have shown that the cluster-complexed hydroxomercury compound $[\mathbf{1}^{2-}]$ reacts with a thiol group at room temperature to form a corresponding thiolate derivative. This result suggests that it should be possible to bind $[\mathbf{1}^{2-}]$ onto macromolecules that contain sulfhydryl groups to provide derivatives labeled with electron-dense markers. This prospect is under current investigation.

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Acknowledgment. This work was supported 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.

Supporting Information Available: Tables of crystal data and structure refinement and positional and thermal parameters for $[NEt_3Bz]_2[\mathbf{1}]$ and table of atomic coordinates and equivalent isotropic displacement parameters for $[PPh_4]_2[\mathbf{2}]$ (7 pages). An X-ray crystallographic file for $[PPh_4]_2[\mathbf{2}]\cdot 0.5CH_2Cl_2$, in CIF format, is available on the Internet only. Access and ordering information is given on any current masthead page.

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