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Carbidoheptarhenate Cluster Complexes of Mercury with Hydrosulfide or Functionalized Thiolate Ligands

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Introduction

In previous papers we have described the synthesis and properties of mercury derivatives of the carbidoheptarhenate cluster, namely, $[Re_7C(CO)_{21}HgL]^{2-}$,[1] including formation of the hydroxo mercury compound $[Re_7C(CO)_{21}HgOH]^{2-}$ and its facile transformation to an arylthiolato complex $[Re_7C(CO)_{21}HgSAr]^{2-}$.[2] In this paper we report on an expanded range of sulfur derivatives of this cluster-supported mercury center, including the hydrosulfide derivative as well as a set of thiolate derivatives in which the sulfur ligand bears an additional functional group (see Scheme 1).

Experimental Section

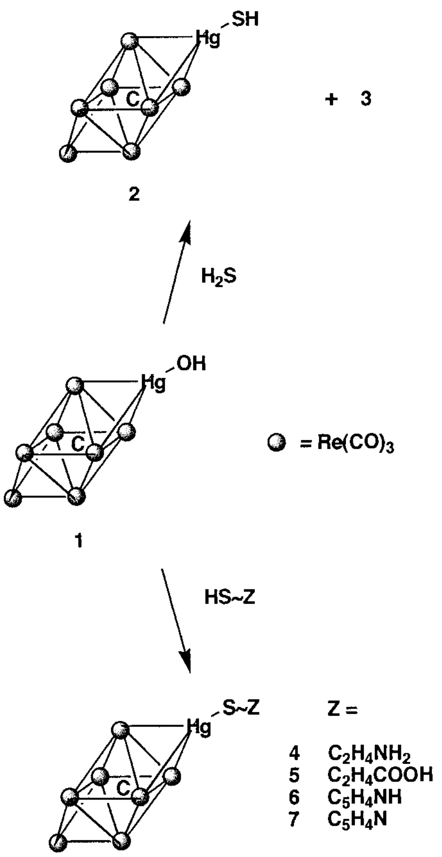
General Procedures. All reactions were carried out at room temperature; reactions with thiol compounds were conducted under a nitrogen atmosphere by using standard Schlenk techniques. The solvents used were distilled from appropriate drying agents and degassed before use. The compounds $[PPh_4]_3[Re_7C(CO)_{21}]$[3,4] and $[PPh_4]_2[Re_7C(CO)_{21}HgOH]$[2] were prepared as reported. The reagents 4-bromothiophenol (Aldrich), 4-mercaptopyridine (Aldrich), 3-mercaptopropionic acid (Aldrich), and cysteamine (Fluka) were used as received. Infrared spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. ^1H NMR spectra were obtained on a Varian U400 NMR instrument. Electrospray ionization (ESI) mass spectra were obtained on a VG Quattro spectrometer or on a VG ZAB-SE spectrometer by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences at the University of Illinois. Microanalyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences.

Synthesis of $[PPh_4]_2[Re_7C(CO)_{21}HgSH]$ (2). A dichloromethane solution of $[PPh_4]_2[Re_7C(CO)_{21}HgOH]$ (**1**) (37.0 mg 0.0132 mmol) was treated with H_2S over a period of 1 h and then stirred in a closed system for 1 day. The solution was then concentrated to 2 mL and layered with methanol. Subsequent diffusion over 4 days yielded dark red crystals (26.1 mg, 0.00927 mmol, 70%). Anal. Calcd for $C_{70}H_{41}HgO_{21}P_2Re_7S$: C, 29.77; H, 1.46. Found: C, 29.72; H, 1.60. IR (CH_2Cl_2) ν(CO), 2040 (w), 1999 (vs), 1967 (w), 1935 (w), 1919 (w), 1879 (w) cm^{-1}. ESI-MS 2480 $\{[PPh_4][Re_7C(CO)_{21}HgSH]\}^-$, 1069 $\{[(Re_7C(CO)_{21}HgSH]\}^{2-}$.

If hydrogen sulfide was bubbled through the solution for only 20 min, a mixture of $[PPh_4]_2[Re_7C(CO)_{21}HgSH]$ (**2**) and $[PPh_4]_4[(Re_7C(CO)_{21}Hg)_2S]$ (**3**) was obtained, as evidenced by ESI mass spectra. However, we were unable to isolate the sulfide bridged complex in pure form. Data for a mixture of **2** and **3**: ESI-MS 2480 $\{[PPh_4][Re_7C(CO)_{21}HgSH]\}^-$, 2460 $\{[PPh_4]_2[(Re_7C(CO)_{21}Hg)_2S]\}^{2-}$, 1527 $\{[PPh_4][(Re_7C(CO)_{21}Hg)_2S]\}^{3-}$, 1069 $\{[(Re_7C(CO)_{21}HgSH]\}^{2-}$.

Synthesis of $[PPh_4]_2[Re_7C(CO)_{21}HgSC_2H_4NH_2]$ (4). In 5 mL of dichloromethane, 40.8 mg (0.0146 mmol) of $[PPh_4]_2[Re_7C(CO)_{21}HgOH]$ and 14.1 mg (0.180 mmol) of cysteamine were stirred together for 2 days. The mixture was layered with diethyl ether, and after 1 day of subsequent diffusion, black crystals were isolated, washed with diethyl ether, and dried under vacuum (34.8 mg, 0.0122 mmol, 83%). Anal. Calcd for $C_{72}H_{46}HgNO_{21}P_2Re_7S$: C, 30.25; H, 1.62; N, 0.49. Found: C, 30.22; H, 1.60; N, 0.37. IR (CH_3COCH_3) ν(CO), 2053 (w), 2001 (vs), 1972 (w), 1946 (w), 1927 (w), 1888 (w) cm^{-1}. ^1H NMR (CD_2Cl_2) δ 3.02 (m, 2H, CH_2), 3.51 (m, 2H, CH_2), and 7.5−7.9 (m, 40H, C_6H_5). ESI-MS 2181 $\{[Re_7C(CO)_{21}HgSC_2H_4NH_3]\}^-$, 1090 $\{[Re_7C(CO)_{21}HgSC_2H_4NH_2]\}^{2-}$, 1069 $\{[Re_7C(CO)_{21}HgSH]\}^{2-}$.

Scheme 1



Synthesis of $[PPh_4]_2[Re_7C(CO)_{21}HgSC_2H_4COOH]$ (5). A solution containing 47.0 mg (0.0168 mmol) of $[PPh_4]_2[Re_7C(CO)_{21}HgOH]$ and 18.3 mg (0.172 mmol) of 3-mercaptopropionic acid in 5 mL of dichloromethane was stirred for 15 h. The solution was concentrated to 3 mL and layered with hexane. After 2 days of subsequent diffusion, dark crystals were isolated, washed with methanol, and dried under vacuum (41.2 mg, 0.0143 mmol, 85%). Anal. Calcd for $C_{73}H_{45}HgO_{23}P_2Re_7S$: C, 30.27; H, 1.57. Found: C, 29.97; H, 1.49. IR (CH_3COCH_3) ν(CO), 2056 (vw), 2002 (vs), 1974 (m), 1948 (w), 1929 (w), 1889 (w) cm^{-1}. ^1H NMR (CD_2Cl_2) δ 2.84 (m, 2H, CH_2), 3.70 (m, 2H, CH_2), and 7.5−7.9 (m, 40H, C_6H_5). ESI-MS 2548 $\{[PPh_4][Re_7C(CO)_{21}HgSC_3H_4O_2H]\}^-$, 2479 $\{[PPh_4][Re_7C(CO)_{21}HgSH]\}^-$.

Synthesis of $[PPh_4][Re_7C(CO)_{21}HgSC_5H_4NH]$ (6). In a Schlenk flask, 34.3 mg (0.0122 mmol) of $[PPh_4]_2[Re_7C(CO)_{21}HgOH]$ and 11.8 mg (0.106 mmol) of 4-mercaptopyridine were stirred together in 5 mL of dichloromethane/methanol (4:1). After 15 h the volume of solution was reduced under vacuum to 2 mL, and a layer of methanol was added. After 6 days of solvent diffusion, black crystals were isolated, washed with methanol, and dried under vacuum (25.2 mg, 0.00986 mmol, 81%). Anal. Calcd for $C_{51}H_{25}HgNO_{21}PRe_7S$: C, 23.90; H, 0.98; N, 0.55. Found: C, 23.46; H, 0.86; N, 0.50. IR (CH_3COCH_3) ν(CO), 2056 (w), 2003 (vs), 1974 (w), 1949 (w), 1929 (w), 1890 (w) cm^{-1}. ^1H NMR (CD_3COCD_3) δ 7.83−7.90 (m, 16H, phenyl *o*-H, *m*-H), 7.98−

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Table 1. Crystallographic Data for $[PPh_4]2[Re_7C(CO)_{21}HgSH]$

empirical formula	$C_{70}H_{41}HgO_{21}P_2Re_7S$
fw	2816.02
space group	$P\bar{1}$
temp (°C)	−15
a (Å)	12.2171(2)
b (Å)	14.0044(2)
c (Å)	21.0822(2)
α (deg)	96.218(1)
β (deg)	93.917(1)
γ (deg)	92.418(1)
V (Å^3)	3572.95(8)
Z	2
D_{calcd} (g cm^{-3})	2.618
μ(Mo Kα) (cm^{-1})	140.93
λ(Mo Kα) (Å)	0.710 73
F(000)	2560
θ range (deg)	1.67−28.30
no. of reflcns collcd	23 370
no. of indep reflcns	16 159
R_{int}	0.0650
no. of obsd data [$I > 2\sigma(I)$]	16 153
R_1 [$I > 2\sigma(I)$]^a	0.0604
wR_2 (all data)^b	0.1795

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

8.04 (m, 4H, phenyl *p*-H), 8.06 (d, 2H, ^3J = 6.8 Hz, pyridine *β*-H), 8.68 (d, 2H, ^3J = 6.8 Hz, pyridine α-H). ESI-MS 2215 $\{[Re_7C(CO)_{21}HgSC_5H_4NH]\}^-$, 1107 $\{[Re_7C(CO)_{21}HgSC_5H_4N]\}^{2-}$.

Synthesis of $[PPh_4]_2[Re_7C(CO)_{21}HgSC_5H_4N]$ (7). In 10 mL of dichloromethane/methanol (4:1), $[PPh_4]_2[Re_7C(CO)_{21}HgOH]$ (57.6 mg, 0.0206 mmol) and 4-mercaptopyridine (22.3 mg, 0.0.201 mmol) were stirred together for 14 h. The reaction mixture was extracted with 10 mL of 0.4 M sodium bicarbonate solution, and this aqueous layer was washed once with dichloromethane. The combined organic phase was washed once with water, dried over Na_2SO_4, and finally evaporated under vacuum. The residue was redissolved in dichloromethane and layered with diethyl ether. After 1 day a black crystalline solid was isolated, washed with diethyl ether, and dried under vacuum (46.1 mg, 0.0159 mmol, 79%). Anal. Calcd for $C_{75}H_{44}HgNO_{21}P_2Re_7S$: C, 31.14; H, 1.53; N, 0.48. Found: C, 31.19; H, 1.44; N, 0.51. IR (CH_3COCH_3) *ν*(CO), 2055 (w), 2003 (vs), 1973 (w), 1948 (w), 1928 (w), 1889 (w) cm^{-1}. ^{1}H NMR (CD_3COCD_3) *δ* 7.50 (d, 2H, ^3J = 5.4 Hz, pyridine *β*-H), 7.83−7.91 (m, 32H, phenyl *o*-H, *m*-H), 7.98−8.05 (m, 8H, phenyl *p*-H), 8.28 (d, 2H, ^3J = 5.4 Hz, pyridine α-H). ESI-MS 2554 $\{[PPh_4][Re_7C(CO)_{21}HgSC_5H_4N]\}^-$, 2215 $\{[Re_7C(CO)_{21}HgSC_5H_4NH]\}^-$, 1107 $\{[Re_7C(CO)_{21}HgSC_5H_4N]\}^{2-}$, 1069 $\{[Re_7C(CO)_{21}HgSH]\}^{2-}$.

X-ray Crystal Structure Determination. A summary of selected crystallographic data for $[PPh_4]_2[Re_7C(CO)_{21}HgSH]$ is given in Table 1. A red transparent single crystal (0.02 × 0.10 × 0.50 mm^3) suitable for X-ray diffraction was grown by layering methanol on a dichloromethane solution and subsequent diffusion. The crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber. Diffraction data were collected on a Siemens Platform/CCD automated diffractometer. All data processing was performed with the integrated program package SHELXTL.[5] For $[PPh_4]_2[Re_7C(CO)_{21}HgSH]$ a total of 23 370 data were collected, of which 16 159 were independent (R_{int} = 0.0650); these data were corrected for absorption (with transmission maximum 0.6912 and minimum 0.3109). The structure was solved by direct methods.[6] Figure 1 depicts the cluster anion with its crystallographic labeling scheme. Complete details of the crystallographic study for $[PPh_4]_2[Re_7C(CO)_{21}HgSH]$ are provided as Supporting Information. Selected bond lengths and angles are given in Table 2.

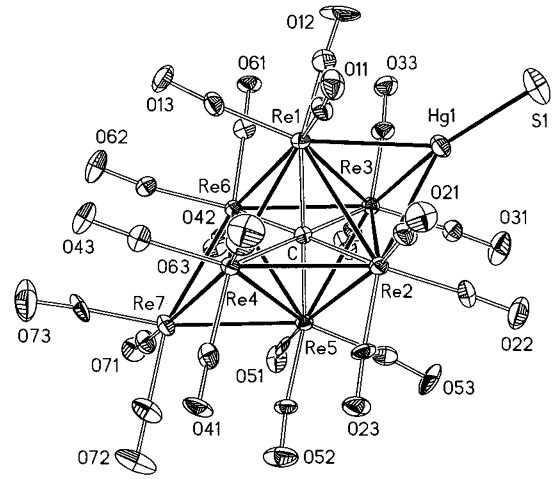

Figure 1. ORTEP diagram of the cluster unit $[Re_7C(CO)_{21}HgSH]^{2-}$ in **2** (30% thermal ellipsoids).

Table 2. Selected Structural Parameters for the Cluster Unit in $[PPh_4]_2[Re_7C(CO)_{21}HgSH]$

Bond Distances (Å)					
Hg1−Re1	2.8854(10)	Hg1−Re2	2.8605(10)	Hg1−Re3	2.8646(10)
Re1−Re2	3.0720(9)	Re1−Re3	3.0470(9)	Re2−Re3	3.0509(9)
Re1−Re4	3.0096(9)	Re1−Re6	2.9867(9)	Re2−Re4	3.0032(10)
Re2−Re5	2.9841(9)	Re3−Re5	2.9943(9)	Re3−Re6	3.0009(9)
Re4−Re5	3.0000(9)	Re4−Re6	2.9805(9)	Re5−Re6	2.9738(9)
Re4−Re7	2.9850(10)	Re5−Re7	2.9679(10)	Re6−Re7	2.9668(10)
Re1−C	2.14(2)	Re2−C	2.14(2)	Re3−C	2.15(2)
Re4−C	2.11(2)	Re5−C	2.11(2)	Re6−C	2.11(2)
Hg1−S1	2.370(6)				

Bond Angles (deg)			
Re1−Hg1−Re2	64.64(2)	Re1−Hg1−Re3	64.00(2)
Re2−Hg1−Re3	64.40(2)	Re1−Re2−Hg1	58.07(2)
Re2−Re1−Hg1	57.29(2)	Re1−Re3−Hg1	58.33(2)
Re2−Re3−Hg1	57.73(2)	Re3−Re2−Hg1	57.86(2)
Re3−Re1−Hg1	57.67(2)	Re1−Hg1−S1	139.2(2)
Re2−Hg1−S1	135.3(2)	Re3−Hg1−S1	150.5(2)

Results and Discussion

Formation and Structure of 2. The reaction of the hydroxo complex $[PPh_4]_2[Re_7C(CO)_{21}HgOH]$ (**1**) with H_2S led to two products, depending on the reaction time. If the gas flow was maintained for at least an hour, only the hydrosulfide complex $[PPh_4]_2[Re_7C(CO)_{21}HgSH]$ (**2**) was isolated. However, if the reaction was stopped after 20 min, a mixture of **2** and the bridging sulfide complex $[PPh_4]_4[(Re_7C(CO)_{21}Hg)_2S]$ (**3**) was obtained. The two complexes could be distinguished by electrospray mass spectroscopy; the mixture of complexes showed ion signals derived from both $[Re_7C(CO)_{21}HgSH]^{2-}$ and $[(Re_7C(CO)_{21}Hg)_2S]$, but the spectrum of pure **2** showed no signals due to **3**. Therefore, the formation of **3** is not induced by the conditions of obtaining the mass spectrum. In the early stage of the reaction the hydrosulfide complex **2** is in the presence of significant amounts of the hydroxide precursor **1**, and elimination of water presumably gives the sulfide bridged product **3**. However, a direct attempt to carry out this reaction failed to give **3** in pure form. Recently reported organo(hydrosulfido)gold(I) complexes display similar lability and (cation-dependent) condensation reactions.[7]

The solid-state structure of complex **2** showed the expected cluster framework of a 1,4 bicapped octahedron (see Figure 1), where the mercury is on the face opposite that of the capping $Re(CO)_3$ unit (Re7).[2] To our knowledge $[PPh_4]_2[Re_7C(CO)_{21}HgSH]$ represents the first isolated and structurally characterized mercury complex with a terminal hydrogensulfide ligand. The Hg−S distance of 2.370(6) Å is comparable to the distance

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found in many mercury thiolate complexes, such as $[PPh_4]_2[Re_7C(CO)_{21}HgSC_6H_4Br]$,[2] $[Hg(C_5H_4NS)(CH_3CO_2)]_n$,[8] $[Hg(S(CH_2)_3N(CH_3)_3)][PF_6]_2$,[9] $[Hg(SC_6H_2\text{-}2,4,6\text{-i-}Pr_3)_2]$,[10] and $[MeHgSC_6H_2\text{-}2,4,6\text{-i-}Pr_3)_2]$.[11] The mercury−rhenium distances to the face described by Re1, Re2, and Re3 are 2.885(1) (to Re1), 2.861(1) (to Re2), and 2.865(1) Å (to Re3). The average of 2.87 Å is identical to that found for the arenethiolate complex $[Re_7C(CO)_{21}HgSC_6H_4Br]^{2-}$.[2] The Re−Re distances in the hydrosulfide complex **2** are closely comparable to those found in other carbidoheptarhenate clusters of the type $[Re_7C(CO)_{21}ML_n]^{2-}$.[2,3]

Formation of the Thiolate Derivatives 4−7. The reaction of hydroxo complex **1** with cysteamine in dichloromethane led to the complex $[PPh_4]_2[Re_7C(CO)_{21}HgSC_2H_4NH_2]$ (**4**), which was isolated in 83% yield. The ^1H NMR spectrum of **4** showed signals for the methylene and phenyl protons; however, no signal for the amino protons was observed. The reaction of complex **1** with 3-mercaptopropionic acid resulted in the formation of $[PPh_4]_2[Re_7C(CO)_{21}HgSC_2H_4CO_2H]$ (**5**), which was also isolated in high (85%) yield. Again, the ^1H NMR spectrum of **5** showed appropriate signals for the methylene and phenyl protons, but the carboxyl proton signal was not detected.

The reaction of 4-mercaptopyridine with complex **1** led to two compounds, depending on the workup procedure. If the reaction in dichloromethane/methanol was concentrated and layered with methanol, only the complex with a pyridinium group $[PPh_4][Re_7C(CO)_{21}HgSC_5H_4NH]$ (**6**) was isolated (81% yield). If the reaction mixture was extracted first with aqueous bicarbonate solution, the unprotonated pyridine derivative $[PPh_4]_2[Re_7C(CO)_{21}HgSC_5H_4N]$ (**7**) was obtained in 79% yield. These two complexes could easily be distinguished by their ^1H NMR spectra. The signals for the protonated pyridine ring protons of **6** appeared at δ 8.06 (H_β) and 8.68 (H_α), whereas the ring proton signals for unprotonated **7** were observed upfield at δ 7.50 and 8.28, respectively. The relative intensity of the pyridine signals to the $[PPh_4]^+$ signals also indicated that in compound **6** only one $[PPh_4]^+$ counterion per cluster unit was present.

The IR spectra of the heptarhenate complexes **4**−**7** show very similar frequencies for the CO absorption bands, with only very small shifts compared to the absorption bands of the hydroxo complex **1**. Thus, the charge on the cluster core is perturbed very little by changes in the substituent on the mercury center, even with the addition of a proton to **7** to give **6**. These cluster derivatives with free functional groups are of interest as possible ligands to other metal centers.[12]

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Supporting Information Available: Tables of crystallographic details and atomic coordinates for $[PPh_4]_2[Re_7C(CO)_{21}HgSH]$ (3 pages). Ordering information is given on any current masthead page.

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