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Synthesis, Characterization, and Some Ligand-Redistribution Reactions of the Mercuric Complexes $[Re_7C(CO)_{21}HgY]^{2-}$

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The cluster anion $[Re_7C(CO)_{21}]^{3-}$ reacts with various mercuric compounds to yield a set of clusters $[Re_7C(CO)_{21})HgY]^{2-}$ (Y = halide, pseudohalide, or hydrocarbyl) that have been isolated as crystalline $[PPN]^+$ salts and characterized by IR, mass, and ^1H NMR spectroscopies as well as by cyclic voltammetry. ^{13}C NMR studies of selected clusters indicate that these compounds adopt a (1,4)-bicapped octahedral geometry in solution. Some of the compound $[Re_7C(CO)_{21}HgY]^{2-}$ undergo ligand-redistribution reactions of the type: $[Re_7C(CO)_{21}HgY]^{2-} + YHgZ \rightleftarrows [Re_7C(CO)_{21}HgZ]^{2-} + HgY_2$. The facility of the ligand redistribution appears to depend on the bridging capabilities of the exchanging substituents.

Introduction

Recent work in our group[1-3] has dealt with the addition of metal complex electrophiles (ML_n^+) to the basic cluster $[Re_7C(CO)_{21}]^{3-}$. These efforts have led to a variety of mixed-metal clusters $[Re_7C(CO)_{21}ML_n]^{2-}$, where M = Rh, Ir, Pd, Pt, and Au. It was therefore of interest to examine the reactions of $[Re_7C(CO)_{21}]^{3-}$ with sources of HgY^+ (Y = halide, pseudohalide, or hydrocarbyl).

Hg^{2+} can bond to transition metals in a variety of configurations. The most familiar metal–metal bonding geometry involving mercury is the linear M–Hg–M or M–Hg–Y; such compounds have been known for many years.[4] In contrast, a metal–metal edge-bridging mercury complex was first structurally characterized in 1980[5] and a cluster face-bridging complex in 1983.[6]

Mercury compounds participate in a wide range of ligand-redistribution reactions. The redistribution chemistry of organomercurial compounds, shown in eq 1, has been extensively investigated.[7] Analogous reactivity has been

$$HgR_2 + HgX_2 \rightleftarrows 2RHgX \qquad (1)$$

well documented for heterometallic complexes of mercury, as indicated by eq 2 (M = mononuclear organometallic fragment, e.g. $CpW(CO)_3$).[4,8] In recent years, redistribution reactions have also been reported for tricoordinate

$$HgM_2 + HgX_2 \rightleftarrows 2MHgX \qquad (2)$$

tion reactions have also been reported for tricoordinate mercury, i.e., complexes in which the HgY^+ moiety bridges a metal–metal bond.[9-11] In one study,[10] Mays observed the interconversions of $Mn_2(\mu\text{-}HgPh)(\mu\text{-}PPh_2)(CO)_8$, $Mn_2(\mu\text{-}HgCl)(\mu\text{-}PPh_2)(CO)_8$, and $Hg\{Mn_2(\mu\text{-}PPh_2)(CO)_8\}_2$ (eq 3–5). The work described in this paper explores similar reactions with organometallic clusters containing face-bridging mercury atoms.

$$Mn_2(\mu\text{-}HgCl)(\mu\text{-}PPh_2)(CO)_8 \underset{HgCl_2}{\overset{[Mn_2(\mu\text{-}PPh_2)(CO)_8]^-}{\rightleftarrows}} Hg\{Mn_2(\mu\text{-}PPh_2)(CO)_8\}_2 \qquad (3)$$

$$Mn_2(\mu\text{-}HgPh)(\mu\text{-}PPh_2)(CO)_8 \xrightarrow{PhHgCl} Mn_2(\mu\text{-}HgCl)(\mu\text{-}PPh_2)(CO)_8 \qquad (4)$$

$$Mn_2(\mu\text{-}HgPh)(\mu\text{-}PPh_2)(CO)_8 \xrightarrow[\text{in } CH_2Cl_2]{\text{dissolve}} Hg\{Mn_2(\mu\text{-}PPh_2)(CO)_8\}_2 \qquad (5)$$

Experimental Section

General Data. Instrumentation and methods have been described previously.[2] $HgCl_2$ (Mallinckrodt), $HgBr_2$ (Baker), $Hg(CN)_2$ (Aldrich), C_6H_5HgCl (Alfa), CH_3HgCl (Pfaltz and Bauer), and $Hg(C_6H_5)_2$ (Eastman) were obtained commercially and were used without further purification. $Hg(C(CH_3)_3)_2$ and $(CH_3)_3CHgCl$ were provided by Dr. Vera Mainz of the School of Chemical Sciences.

$[PPN]_2[Re_7C(CO)_{21}HgCl]$. $[PPN]_3[Re_7C(CO)_{21}]$ (70.8 mg, 0.0201 mmol) and $HgCl_2$ (18.9 mg, 0.0696 mmol) were stirred in acetonitrile for 10 min at room temperature to give a brown solution. The solvent was removed under vacuum and the residue dissolved in 10 mL of acetone. Addition of 40 mL of methanol, followed by concentration and cooling of the solution, precipitated brown crystals of product (45.8 mg, 71%). Anal. Calcd for $C_{94}H_{60}P_4N_2Re_7HgClO_{21}$: C, 35.10; H, 1.88; N, 0.87; Cl, 1.10. Found: C, 34.83; H, 1.89; N, 0.80; Cl, 1.40. The ^1H NMR spectrum showed only cation signals. ^{13}C NMR (CD_2Cl_2, −85 °C): δ 181.9 (3), 186.2 (3), 190.9 (6), 191.2 (6), 204.1 (3) (all s, Re–CO).

$[PPN]_2[Re_7C(CO)_{21}HgBr]$. $[PPN]_3[Re_7C(CO)_{21}]$ (71.8 mg, 0.0204 mmol) and $HgBr_2$ (19.1 mg, 0.0530 mmol) were stirred in acetonitrile for 15 min. Removal of the solvent and crystallization from acetone/methanol as described for the chloro compound yielded 49.0 mg (74%) of the brown bromo complex. Anal. Calcd for $C_{94}H_{60}P_4N_2Re_7HgBrO_{21}$: C, 34.62; H, 1.85; N, 0.86; Br, 2.45. Found: C, 34.60; H, 1.80; N, 0.77; Br, 2.82. The ^1H NMR spectrum showed only cation signals.

$[PPN]_2[Re_7C(CO)_{21}Hg(CN)]$. $[PPN]_3[Re_7C(CO)_{21}]$ (101 mg, 0.0287 mmol) and $Hg(CN)_2$ (17.0 mg, 0.0673 mmol) were stirred in acetone for 30 min. Methanol (40 mL) was added; concentration and cooling of the resulting solution afforded brown crystals of the cyano complex (50.2 mg, 55%). Anal. Calcd for

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$C_{95}H_{60}P_4N_3Re_7HgO_{21}$: C, 35.58; H, 1.89; N, 1.31. Found: C, 35.40; H, 1.91; N, 1.31. The ^{1}H NMR spectrum showed only cation signals. No infrared band for ν(CN) was observed.

$[PPN]_2[Re_7C(CO)_{21}Hg(C_6H_5)]$. $[PPN]_3[Re_7C(CO)_{21}]$ (85.3 mg, 0.0242 mmol) and C_6H_5HgCl (7.8 mg, 0.025 mmol) were stirred in dichloromethane to give a dark red solution. After 20 min, the solution volume was reduced under vacuum to ca. 5 mL and 40 mL of methanol was added. Concentration of this solution under vacuum gave a cloudy mixture, which when gently heated precipitated brown crystals (50.8 mg, 64%). Addition of more than 1 equiv of C_6H_5HgCl caused conversion of the phenyl compound to the chloro compound (see below). Anal. Calcd for $C_{100}H_{65}P_4N_2Re_7HgO_{21}$: C, 36.86; H, 2.01; N, 0.86. Found: C, 36.88; H, 2.02; N, 0.82. ^{1}H NMR of Et_4N^+ salt ($(CD_3)_2CO$, 20 °C): δ 1.39 (tt, 24 H, NCH_2CH_3), 3.48 (q, 16 H, NCH_2CH_3), 7.1–8.0 (m, 5 H, C_6H_5). ^{13}C NMR (CD_2Cl_2, −85 °C): δ 184.3 (3), 187.3 (3), 191.9 (6), 193.9 (6), 205.1 (3) (all s, Re–CO). FAB-MS (negative ion): m/z (^{187}Re, ^{201}Hg) 2725 (M − PPN), 2447 ($[PPN][Re_7C(CO)_{21}]$), 2187 (M − 2PPN), 1909 ($Re_7C(CO)_{21}$), $1909 - 28x$, $x = 1$, 3–6($Re_7C(CO)_{21} - x$CO's).

$[PPN]_2[Re_7C(CO)_{21}Hg(CH_3)]$. $[PPN]_3[Re_7C(CO)_{21}]$ (55.4 mg, 0.0157 mmol) and CH_3HgCl (8.7 mg, 0.035 mmol) were dissolved in dichloromethane and stirred for 45 min. Methanol (ca. 30 mL) was added, and the resulting solution was concentrated under vacuum to afford dark red crystals of product (41.7 mg, 83%). Anal. Calcd for $C_{95}H_{63}P_4N_2Re_7HgO_{21}$: C, 35.70; H, 1.99; N, 0.88. Found: C, 35.57; H, 2.06; N, 0.92. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 0.50 (s, 3 H, $J_{Hg-H} = 162$ Hz, CH_3), 7.4–7.8 (m, 60 H, PPN^+ protons). FAB-MS (negative ion): m/z (^{187}Re, ^{201}Hg) 2664 (M − PPN), 2447 ($[PPN][Re_7C(CO)_{21}]$), 2126 (M − 2PPN), 1909 ($Re_7C(CO)_{21}$), $1909 - 28x$, $x = 1$, 3–7($Re_7C(CO)_{21} - x$CO's).

$[PPN]_2[Re_7C(CO)_{21}HgC(CH_3)_3]$. $[PPN]_3[Re_7C(CO)_{21}]$ (79.6 mg, 0.0226 mmol) and $(CH_3)_3CHgCl$ (14.9 mg, 0.0508 mmol) were dissolved in dichloromethane and stirred for 20 min. Methanol (50 mL) was then added, and the resulting solution was concentrated under vacuum to afford dark brown crystals of product (58.9 mg, 80%). Anal. Calcd for $C_{98}H_{69}P_4N_2Re_7HgO_{21}$: C, 36.35; H, 2.15; N, 0.87. Found: C, 35.98; H, 2.05; N, 0.88. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 2.02 (s, 9 H, $J_{Hg-H} = 214$ Hz, CH_3), 7.4–7.8 (m, 60 H, PPN^+ protons). FAB-MS (negative ion): m/z (^{187}Re, ^{201}Hg) 2705 (M − PPN), 2447 ($[PPN][Re_7C(CO)_{21}]$), 2167 (M − 2PPN), 1909 ($Re_7C(CO)_{21}$), $1909 - 28x$, $x = 1$, 3 ($Re_7C(CO)_{21} - x$CO's).

Attempted Synthesis of $[PPN]_4[\{Re_7C(CO)_{21}\}_2Hg]$. $[PPN]_3[Re_7C(CO)_{21}]$ (81.3 mg, 0.0231 mmol) and $HgCl_2$ (3.5 mg, 0.0129 mmol) were stirred in acetonitrile for 75 min. An infrared spectrum of the reaction mixture showed a 1:1 mixture of $[Re_7C(CO)_{21}HgCl]^{2-}$ and unreacted $[Re_7C(CO)_{21}]^{3-}$. Similarly, a 1:1 mixture of $[Re_7C(CO)_{21}Hg(CN)]^{2-}$ and $[Re_7C(CO)_{21}]^{3-}$ was formed upon mixing acetonitrile solutions of $[PPN]_3[Re_7C(CO)_{21}]$ (66.3 mg, 0.0188 mmol) and $Hg(CN)_2$ (2.2 mg, 9.5 μmol). Heating the solution at 70 °C for 20 h or adding excess $Hg(CN)_2$ did not cause a change in the IR spectrum. Acetone solutions of $[Re_7C(CO)_{21}HgY]^{2-}$ (Y = Cl, C_6H_5) showed no change in their ^{13}C NMR spectra over a period of 2 months, so the symmetrization reaction represented by eq 12 does not take place for these compounds on this time scale.

Formation of $[Re_7C(CO)_{21}HgCl]^{2-}$ from $[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$ and C_6H_5HgCl. A ^{13}C-enriched sample of $[Et_4N]_2[Re_7C(CO)_{21}Hg(C_6H_5)]$ (27 mg, 0.011 mmol) was allowed to react with C_6H_5HgCl (4.1 mg, 0.013 mmol) in CD_3CN. The ^{13}C NMR spectrum of the resulting solution showed resonances arising from $[Re_7C(CO)_{21}HgCl]^{2-}$ and $[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$ in a 64:36 molar ratio. In order to confirm that this was an equilibrium solution, 4.2 mg more of C_6H_5HgCl was added (total C_6H_5HgCl added: 8.3 mg, 0.027 mmol). The resulting chloro:phenyl ratio, as determined by ^{13}C NMR, was 81:19.

Formation of $[Re_7C(CO)_{21}HgCl]^{2-}$ from $[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$ and $HgCl_2$. A ^{13}-enriched sample of $[Et_4N]_2[Re_7C(CO)_{21}Hg(C_6H_5)]$ (27 mg, 0.011 mmol) was treated with $HgCl_2$ (3.5 mg, 0.013 mmol) in CD_3CN. A ^{13}C NMR spectrum of the resulting solution showed only the characteristic carbonyl resonances of $[Re_7C(CO)_{21}HgCl]^{2-}$.

Formation of $[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$ from $[Re_7C(CO)_{21}HgCl]^{2-}$ and $Hg(C_6H_5)_2$. An acetonitrile solution of $[Et_4N]_2[Re_7C(CO)_{21}HgCl]$ (53 mg, 0.022 mmol) was treated with $Hg(C_6H_5)_2$ (20.9 mg, 0.059 mmol) to give a mixture of the phenyl and chloro derivatives, as determined by ^{13}C NMR spectroscopy.

Table I. Infrared Data[a] for the Complexes $[Re_7C(CO)_{21}HgY]^{2-}$

complex (as PPN^+ salt)	ν_{CO}, cm^{-1}
$[Re_7C(CO)_{21}HgCl]^{2-}$	2057 (w), 2003 (vs), 1986 (w), 1975 (w, sh), 1948 (w), 1931 (w), 1891 (vw)
$[Re_7C(CO)_{21}HgBr]^{2-}$	2056 (w), 2002 (vs), 1985 (w), 1976 (w, sh), 1947 (w), 1930 (w), 1890 (vw)
$[Re_7C(CO)_{21}Hg(CN)]^{2-}$	2057 (w), 2004 (vs), 1975 (w), 1950 (w), 1929 (w), 1892 (vw)
$[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$	2051 (w), 1998 (vs), 1969 (w), 1942 (w), 1923 (w), 1884 (vw)
$[Re_7C(CO)_{21}Hg(CH_3)]^{2-}$	2051 (w), 1997 (vs), 1968 (w), 1941 (w), 1922 (w), 1884 (vw)
$[Re_7C(CO)_{21}HgC(CH_3)_3]^{2-}$	2049 (w), 1996 (vs), 1967 (w), 1939 (w), 1922 (w), 1884 (vw)

[a] Acetone solution.

Formation of $[Re_7C(CO)_{21}HgCl]^{2-}$ from $[Re_7C(CO)_{21}Hg(CH_3)]^{2-}$ and $HgCl_2$. $[Et_4N]_2[Re_7C(CO)_{21}Hg(CH_3)]$ (63.5 mg, 0.0267 mmol) and $HgCl_2$ (14.7 mg, 0.0541 mmol) were dissolved in CD_3CN. A ^{13}C NMR spectrum of the resulting solution showed only resonances due to $[Re_7C(CO)_{21}HgCl]^{2-}$.

Attempted Conversion of $[Re_7C(CO)_{21}HgCl]^{2-}$ to $[Re_7C(CO)_{21}Hg(C(CH_3)_3)]^{2-}$. A dichloromethane solution of $[PPN]_2[Re_7C(CO)_{21}HgCl]$ (56.7 mg, 0.0176 mmol) was treated with $Hg(C(CH_3)_3)_2$ (13.8 mg, 0.0438 mmol). A ^{13}C NMR spectrum of the resulting solution showed only resonances arising from the chloro complex.

Attempted Conversion of $[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$ to $[Re_7C(CO)_{21}Hg(C(CH_3)_3)]^{2-}$. An acetonitrile solution of $[PPN]_2[Re_7C(CO)_{21}Hg(C_6H_5)]$ (110 mg, 0.0338 mmol) was treated with $Hg(C(CH_3)_3)_2$ (13.4 mg, 0.0426 mmol). A ^{13}C NMR spectrum of the resulting solution showed only resonances arising from the phenyl complex.

Results and Discussion

Synthesis. $[Re_7C(CO)_{21}]^{3-}$ displaced a halide or pseudohalide from $HgCl_2$, $HgBr_2$, $Hg(CN)_2$, C_6H_5HgCl, CH_3HgCl, and $(CH_3)_3CHgCl$ to afford the mixed-metal clusters $[Re_7C(CO)_{21}HgY]^{2-}$, where Y = Cl, Br, CN, C_6H_5, CH_3, and $C(CH_3)_3$. The clusters were isolated as their bis(triphenylphosphine)nitrogen(1+) ($[PPN]^+$) salts in generally good yields; all are brown, crystalline, air-stable solids. The complexes have been fully characterized by elemental analyses as well as by several physical techniques.

Infrared Spectroscopy. The carbonyl IR spectra of the rhenium–mercury compounds (Table I) are very similar to those observed for other Re_7M complexes.[1-3,12] The main absorptions of the halide and cyanide compounds are about 5 cm^{-1} higher in energy than those of the hydrocarbyl compounds, consistent with the stronger electron-withdrawing properties of Cl, Br, and CN relative to C_6H_5, CH_3, and $C(CH_3)_3$.

Mass Spectrometry. Negative-ion FAB mass spectra were obtained for each compound as its PPN^+ salt dispersed in a mixture of isomeric dithioerythritol and dithiothreitol, $HSCH_2CH(OH)CH(OH)CH_2SH$ ("magic bullet"); other dispersing media (e.g., tetraglyme) did not give satisfactory ion currents. The phenyl, methyl, and *tert*-butyl compounds showed spectra typical of other Re_7M derivatives[2] with prominent ion multiplets due to $[M - PPN]^-$ and $[M - 2PPN]^-$; ions resulting from loss of the mercury cap were present as well. For the complexes $[PPN]_2[Re_7C(CO)_{21}HgY]$ (Y = Cl, Br, CN), peaks corresponding to $[PPN][Re_7C(CO)_{21}Hg]^-$ and $[Re_7C(CO)_{21}Hg]^-$ were observed for each of these compounds, but no signals attributable to $[M]^-$, $[M - PPN]^-$, or $[M - 2PPN]^-$ were

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Table II. Cyclic Voltammetry Data[a] for Selected Complexes [Re$_7$C(CO)$_{21}$HgY]$^{2-}$

complex	1st ox. $E_{1/2}$, mV	1st ox. ΔE_p, mV	2nd ox. E_p, mV
[Re$_7$C(CO)$_{21}$Hg(CN)]$^{2-}$	793	95	1108
[Re$_7$C(CO)$_{21}$HgCl]$^{2-}$	734	136	1131
[Re$_7$C(CO)$_{21}$Hg(C$_6$H$_5$)]$^{2-}$	650	74	ca. 1000
[Re$_7$C(CO)$_{21}$HgC(CH$_3$)$_3$]$^{2-}$	689	104	825[c]

[a] Reference electrode: Ag/AgCl. Conditions are given in ref 2. [b] $E_{1/2} = (E_p{}^a + E_p{}^c)/2$. [c] This cluster exhibited a third oxidation wave at 999 mV.

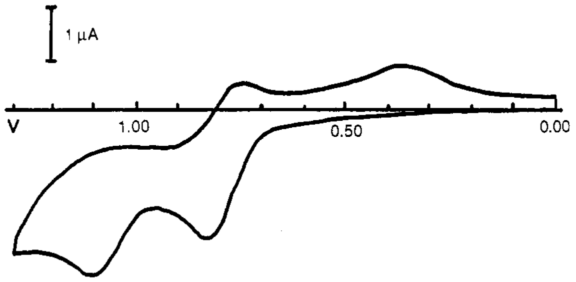

Figure 1. Positive-scan cyclic voltammogram of [PPN]$_2$[Re$_7$C(CO)$_{21}$Hg(CN)]$^{2-}$ (100 mV/s vs Ag/AgCl).

seen. Instead, each spectrum displayed strong ion multiplets at m/z 2263 and 2801. (Weak peaks at these masses also appeared in the spectra of the phenyl and methyl compounds.) These unexpected signals are attributed to a compound formed in the mass spectrometer by reaction between [Re$_7$C(CO)$_{21}$HgY]$^{2-}$ and the dispersing medium. This reaction with the mercury compounds is probably a simple substitution (eq 6), resulting in the usual ions [M − PPN]$^-$ and [M − 2PPN]$^-$. This reactivity is not surprising in view of the high affinity of mercury for sulfur ligands.[13]

$$[\mathrm{Re_7C(CO)_{21}HgY}]^{2-} + \mathrm{HSCH_2CH(OH)CH(OH)CH_2SH} \rightarrow \mathrm{HY} + [\mathrm{Re_7C(CO)_{21}HgSCH_2CH(OH)CH(OH)CH_2SH}]^{2-}\ m/z\ 2263\ (^{187}\mathrm{Re},\ ^{201}\mathrm{Hg}) \quad (6)$$

Cyclic Voltammetry. Cyclic voltammograms were obtained for [Re$_7$C(CO)$_{21}$HgY]$^{2-}$, where Y = Cl, CN, C$_6$H$_5$, and C(CH$_3$)$_3$. The data are presented in Table II. Again, the electron-withdrawing properties of Cl and CN are reflected in the higher potentials needed to oxidize these compounds. The anodic-scan voltammogram of [Re$_7$C(CO)$_{21}$Hg(CN)]$^{2-}$ is shown in Figure 1. In addition to the two expected oxidation waves, there is a reduction wave at 363 mV. The latter feature disappeared when the system was cycled only through the first oxidation. Evidently, the second oxidation—which is irreversible—leads to a new product that is then less easily reduced. The chloride compound exhibited similar behavior, with a very broad, weak reduction peak at 201 mV. The fact that these reduction potentials on Y implies that Y is not lost in the second oxidative process. The complexes [Re$_7$C(CO)$_{21}$HgR]$^{2-}$ did not exhibit this behavior.

^{1}H NMR Spectroscopy. Proton–mercury coupling was observed in the ^{1}H NMR spectra of the methyl and *tert*-butyl derivatives, with $^2J(^{199}\mathrm{Hg}{-}^1\mathrm{H})$ = 162 Hz and $^3J(^{199}\mathrm{Hg}{-}^1\mathrm{H})$ = 214 Hz, respectively. These coupling constants for RHgX compounds are sensitive to the electronic character of the X moiety, and the values determined in this work for the case where X = [Re$_7$] suggest that its

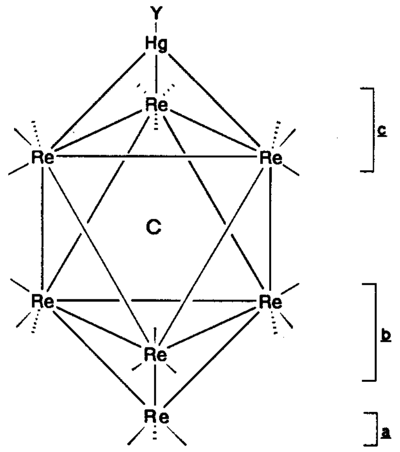

Figure 2. Diagram of the (1,4)-bicapped octahedral geometry postulated for the complexes [Re$_7$C(CO)$_{21}$HgY]$^{2-}$. Groups of carbonyls equilibrated by fast localized exchange are indicated.

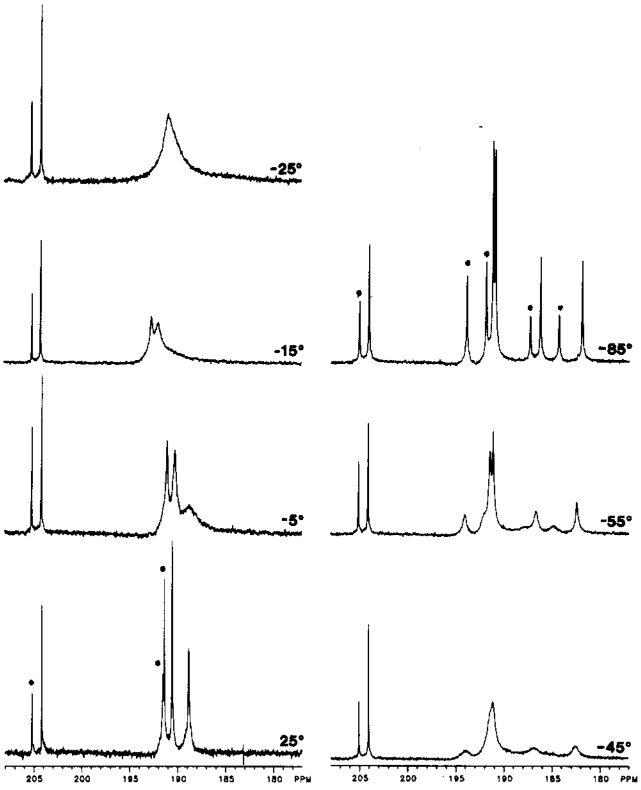

Figure 3. Variable-temperature ^{13}C NMR spectra (carbonyl region, 90 MHz) of a mixture of [PPN]$_2$[Re$_7$C(CO)$_{21}$HgCl] and [PPN]$_2$[Re$_7$C(CO)$_{21}$Hg(C$_6$H$_5$)] (ca. 2:1) Resonances arising from the phenyl complex are marked by a dot in the +25 and −85 °C spectra.

electronic properties parallel those of "soft" thiolate substituents.[14]

^{13}C NMR Spectroscopy. Several clusters of the composition [Re$_7$C(CO)$_{21}$ML$_n$]$^{2-}$ have been characterized by variable-temperature ^{13}C NMR spectroscopy.[1,2] The spectra were readily interpreted in terms of temperature-dependent local carbonyl scrambling within each Re(CO)$_3$ group constituting the C_{3v} (1,4)-bicapped octahedral metal framework (see Figure 2). In the fast-exchange limit three signals of relative intensity 3:9:9 (carbonyl groups a:b:c in Figure 2) were observed. At lower temperatures, freezing out of the local exchange resulted in a pattern of five signals of relative intensity 3:6:6:3:3.

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Table III. ^{13}C NMR Data[a] for Selected Complexes $[Re_7C(CO)_{21}HgY]^{2-}$

complex	δ_{CO} (rel intensity)[b]
$[Re_7C(CO)_{21}HgCl]^{2-}$	188.8 (9) 190.6 (9) 204.2 (3)
$[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$	191.4 (9) 191.5 (9) 205.2 (3)
$[Re_7C(CO)_{21}Hg(CH_3)]^{2-}$	191.6 (9) 192.3 (9) 205.5 (3)
$[Re_7C(CO)_{21}Hg(C(CH_3)_3)]^{2-}$	191.6 (9) 192.6 (9) 205.7 (3)

[a] CD_2Cl_2 solutions at 20–25 °C. [b] Carbide signals were observed at δ 436.5 and 434.9 for the chloro and phenyl complexes, respectively; no carbide signals were observed under these conditions for the methyl and *tert*-butyl complexes.

This behavior was seen also for the clusters $[Re_7C(CO)_{21}HgY]^{2-}$, where Y = Cl or C_6H_5. The ^{13}C NMR spectra obtained for a mixture of the two compounds (see below) are shown in Figure 3, and the limiting chemical shift data are summarized in Table III. These data suggest that both compounds adopt the (1,4)-bicapped octahedral geometry in solution. Preliminary X-ray crystallographic results on the derivative $[Re_7C(CO)_{21}HgOH]^{2-}$ establish this structure type for the solid state as well.[15]

Ligand-Redistribution Reactions. The spectra shown in Figure 3 are for a sample resulting from the reaction of ^{13}C-enriched $[Re_7C(CO)_{21}]^{3-}$ with 1.8 equiv of C_6H_5HgCl to give what was originally expected to be $[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$. However, the presence of a considerable amount of $[Re_7C(CO)_{21}HgCl]^{2-}$ suggested that it was caused by the excess C_6H_5HgCl. Indeed, if only 1 equiv of C_6H_5HgCl was used, pure $[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$ was isolated. In contrast, when $[Re_7C(CO)_{21}]^{3-}$ was allowed to react with 2.2 equiv of either CH_3HgCl or $(CH_3)_3CHgCl$, only one product, the corresponding alkyl mercury complex, was observed by ^{13}C NMR.

When pure $[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$ was allowed to react with C_6H_5HgCl, an equilibrium was established (eq 7). ^{13}C

$$[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-} + C_6H_5HgCl \rightleftarrows [Re_7C(CO)_{21}HgCl]^{2-} + Hg(C_6H_5)_2 \quad (7)$$

NMR spectra were recorded after the addition of 1.3 and 2.7 equiv of C_6H_5HgCl. Equilibrium concentrations were reached within the few minutes required to take the spectrum. Increasing the amount of C_6H_5HgCl added shifted the equilibrium to the right, as expected. The equilibrium constant was calculated for both mixtures, yielding values of 2.05 and 2.12. The value of K_{eq} for eq 7 is therefore set at 2.1 ± 0.1. Equilibrium was also established from the opposite direction, i.e., by adding $Hg(C_6H_5)_2$ to a solution of $[Re_7C(CO)_{21}HgCl]^{2-}$.

In contrast to the reaction with C_6H_5HgCl, treatment of $[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$ with 1.2 equiv of $HgCl_2$ gave $[Re_7C(CO)_{21}HgCl]^{2-}$ quantitatively. No trace of the $[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$ starting material was observed in the ^{13}C NMR spectrum. Assuming that the minimum amount observable is 2% of the total carbonyl-containing species in solution, a lower limit of $K_{eq} \geq 200$ for the reaction in eq 8 can be estimated.

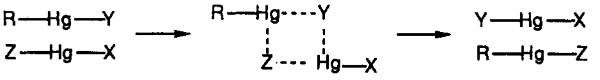
$$[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-} + HgCl_2 \rightleftarrows [Re_7C(CO)_{21}HgCl]^{2-} + C_6H_5HgCl \quad (8)$$

Table IV. Observed and Attempted Redistribution Reactions for Selected $[Re_7C(CO)_{21}HgY]^{2-}$ Complexes

reactants		result
$[Re_7C(CO)_{21}Hg(CH_3)]^{2-}$	$HgCl_2$	$[Re_7C(CO)_{21}HgCl]^{2-}$
$[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$	$HgCl_2$	$[Re_7C(CO)_{21}HgCl]^{2-}$
$[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$	$Hg(C_6H_5)Cl$	$[Re_7C(CO)_{21}HgCl]^{2-}$
$[Re_7C(CO)_{21}HgCl]^{2-}$	$Hg(C_6H_5)_2$	$[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$
$[Re_7C(CO)_{21}HgCl]^{2-}$	$Hg(C(CH_3)_3)_2$	no reaction
$[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$	$Hg(C(CH_3)_3)_2$	no reaction
$[Re_7C(CO)_{21}Hg(CH_3)]^{2-}$	$Hg(CH_3)Cl$	no reaction
$[Re_7C(CO)_{21}Hg(C(CH_3)_3)]^{2-}$	$Hg(C(CH_3)_3)Cl$	no reaction

The alkyl-substituted mercuric compound $[Re_7C(CO)_{21}Hg(CH_3)]^{2-}$ was also cleaved quantitatively to $[Re_7C(CO)_{21}HgCl]^{2-}$ by treatment with $HgCl_2$. However, as previously noted, $[Re_7C(CO)_{21}HgR]^{2-}$ showed no tendency to react with excess RHgCl to give $[Re_7C(CO)_{21}HgCl]^{2-}$ and HgR_2. Furthermore, neither $[Re_7C(CO)_{21}HgCl]^{2-}$ nor $[Re_7C(CO)_{21}Hg(C_6H_5)]^{2-}$ underwent reaction with $Hg(C(CH_3)_3)_2$. A summary of the reactivity we have observed for the complexes $[Re_7C(CO)_{21}HgY]^{2-}$ is presented in Table IV.

Ligand-redistribution reactions of mercuric compounds are believed to proceed through four-center bridged transition states (eq 9).[7b] Good evidence that the rates of these



(9)

reactions depend strongly on the bridging capabilities of the exchanging groups has been presented.[14] For our heptarhenium complexes $[Re_7C(CO)_{21}HgY]^{2-}$, forming the four-center transition state would appear to lead to increased steric congestion around the mercury atom, although it is possible that the mercury atom could move from a triply bridging toward a doubly bridging configuration in the process. Although we do not know the kinetic or thermodynamic limitations for all of the reactions listed in Table IV, the observed reactivities are generally in accord with the expected abilities of the exchanging moieties to form bridges, i.e., Cl > Ph > CH_3 > $C(CH_3)_3$.

For simple organomercuric compounds the equilibrium shown in eq 1 usually lies far to the right;[7a] driving the interconversion to the left (symmetrization) requires a separate means of removing HgX_2 from the reaction. Nevertheless, examples of apparently spontaneous symmetrization reactions are known both for dinuclear compounds (e.g., eq 5) and for cluster compounds. Thus, Rosenberg has reported that the equilibrium in eq 10 re-

$$2Ru_3(CO)_9(\mu_3\text{-}C_2{}^tBu)HgX \rightleftharpoons Hg\{Ru_3(CO)_9(\mu_3\text{-}C_2{}^tBu)\}_2 + HgX_2 \quad (10)$$

quires about 1 month to achieve, with K_{eq} = 0.5 (X = I) or 0.8 (X = Br).[9] Similarly, $Hg[RuCo_3(CO)_{12}]_2$ and $HgBr_2$ are formed from the disproportionation of $RuCo_3(CO)_{12}HgBr$,[16] and the complex $Ru_3(CO)_9(\mu_3\text{-}C_2{}^tBu)Hg[Mo(CO)_3Cp]$ irreversibly decomposes to $Hg[Ru_3(CO)_9(\mu_3\text{-}C_2{}^tBu)]_2$ and $Hg[Mo(CO)_3Cp]_2$ at elevated temperatures.[11] Symmetrization to form $Hg(CH_3)_2$ has been suggested[17] in the decomposition of $[Fe_4(CO)_{13}HgCH_3]^-$, but the related compounds $[Fe_4(CO)_{13}HgMo(CO)_3Cp]^-$ and $[Fe_4(CO)_{13}HgFe(CO)_2Cp]^-$ show no evidence for this type of reaction.[18] Finally, the reaction shown in eq 11 occurs in 1 week at room temperature, although the transformation

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is accompanied by a gross change in cluster geometry.[19]

$$2[Os_{10}C(CO)_{24}HgR]^- \rightarrow [Os_{20}C_2(CO)_{48}Hg]^{2-} + HgR_2 \qquad (11)$$

We have sought evidence for the symmetrization reaction represented by eq 12. This reaction, however, has

$$2[Re_7C(CO)_{21}HgY]^{2-} \rightleftharpoons [\{Re_7C(CO)_{21}\}_2Hg]^{4-} + HgY_2 \qquad (12)$$

not been observed. Furthermore, the symmetric cluster $[\{Re_7C(CO)_{21}\}_2Hg]^{4-}$ cannot be synthesized from 2:1 mixtures of $[Re_7C(CO)_{21}]^{3-}$ and HgX_2 (X = Cl, CN). $Hg(\eta^3\text{-}M_3)_2$ complexes are known in which a mercury atom is triply bridging two triangular faces,[16,20,21] but in all cases the triply bridged faces are sterically uncongested. The structures of $[Re_7C(CO)_{21}ML_n]^{2-}$ derivatives[1-3] show that six CO ligands are oriented markedly toward the capping metal center; thus, steric interactions around the Hg center may strongly disfavor formation of $[\{Re_7C(CO)_{21}\}_2Hg]^{4-}$. On the other hand, the high overall charge density (4–) on the symmetrization product would likely also be a barrier to its formation.

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Communications

Scope of the Cobalt-Catalyzed [2 + 2 + 2] Homo-Diels–Alder Reaction

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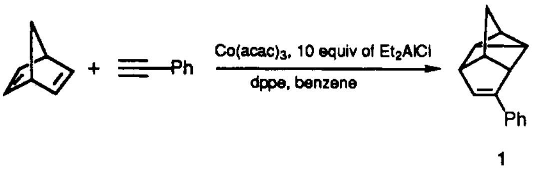
Summary: A cobalt-catalyzed homo-Diels–Alder reaction between norbornadiene and several acetylenes is described. Azeotropic drying of $Co(acac)_3$ is found to increase the reactivity of the catalyst such that sterically hindered and silylsubstituted acetylenes participate in the cycloaddition.

The discovery that metal catalysts can promote cycloadditions has become a powerful tool in organic synthesis.[2,3] The homo-Diels–Alder reaction,[4] in which two new rings are created in the deltacyclic product, is an example of a multi-ring-forming reaction, but one that thus far has found few applications in synthesis. This situation has arisen due to the lack of generality with respect to dienophiles that participate in the coupling and the competing [2 + 2] cycloadditions.[4h] In this letter we describe results that substantially increase the scope of [2 + 2 + 2] cycloadditions between norbornadiene and various acetylenes catalyzed by cobalt–phosphine complexes.

Simple unactivated acetylenes are notoriously poor dienophiles in cycloaddition reactions.[5] We were intrigued, therefore, by a report[6] which indicated that acetylenes react with norbornadiene in the presence of low-valent cobalt complexes to yield a mixture of cycloadducts in which the major product arises via a [2 + 2 + 2] coupling (eq 1). A severe limitation in the reported reaction was that substitution of an aryl group for a simple alkyl group resulted in low yields of the desired coupling products, the major adduct arising from a homocoupling of two norbornadienes.[6] This lack of reactivity and the resulting competitive side processes had to be overcome before the reaction could be sufficiently reliable for use in total synthesis.



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In our initial experiments we isolated deltacyclene 1 in 75–80% yield when a benzene solution of norbornadiene and phenylacetylene was treated with a catalytic quantity (1–5 mol %) of commercially available $Co(acac)_3$ with added 1,2-bis(triphenylphosphino)ethane (1:1) which was reduced with Et_2AlCl. Any change in solvent, ligand, or the use of other acetylenes led to unacceptable yields and

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