Notes

A Carbidoheptarhenate Complex of Thallium(I)

Udo Brand and John R. Shapley*

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

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Introduction

We have examined in previous papers[1] the analogy between the carbidoheptarhenate cluster $[Re_7C(CO)_{21}]^{3-}$ and the cyclopentadienide ion as ligands by the synthesis of $[Re_7C(CO)_{21}ML_n]^{2-}$ complexes corresponding to known $CpML_n$ complexes. The thallium(I) complexes of the cyclopentadienide,[2] dicarbollide,[3] and pyrazolylborate[4] ligands are key reagents for the formation of the corresponding organometallic complexes. Our aim was to synthesize the thallium complex of the carbidoheptarhenate cluster, namely $[Re_7C(CO)_{21}Tl]^{2-}$ ($\mathbf{1}^{2-}$), in order to explore the use of this complex as an intermediate in mixed metal cluster synthesis.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of nitrogen by using standard Schlenk techniques. Solvents for preparative use were dried with use of standard methods and distilled. $[PPN]_3[Re_7C(CO)_{21}]$ was prepared by the literature method.[5] The PPh_4^+ salt of $[Re_7C(CO)_{21}]^{3-}$ was prepared in a similar fashion. $TlPF_6$ was purchased from Strem Chemicals and used without further purification. Infrared spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. Negative ion fast atom bombardment (FAB) mass were obtained 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.

Table 1. Crystallographic Data for $[PPh_4]_2[Re_7C(CO)_{21}Tl]$

formula	$C_{70}H_{40}O_{21}P_2Re_7Tl$	D_{calc} ($g{\cdot}cm^{-3}$)	2.629
fw	2786.73	μ(Mo Kα) (cm^{-1})	14.381
space group	$P\bar{1}$	λ(Mo Kα) (Å)	0.710 69
temp (K)	198(2)	F(000)	2528
a (Å)	13.5354(5)	θ range (deg)	1.46−28.32
b (Å)	14.1170(5)	no. of reflcns collcd	22 326
c (Å)	18.6611(6)	no. of indep reflcns	15 724
α (deg)	81.9330(10)	$R_{int.}$	0.0616
β (deg)	85.6790(10)	no. of obsd data [$I > 2\sigma(I)$]	10 720
γ (deg)	89.3430(10)	R_1 [$I > 2\sigma(I)$][a]	0.0547
V ($Å^3$)	3520.4(2)	wR2 (all data)[b]	0.1866
Z	2		

[a] $R_1 = \sum|(F_o - F_c)|/\sum F_o$. [b] $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum F_o^4\}^{1/2}$ with $w = 1/[\sigma^2(F_o^2) + (0.0799p)^2 + 96.6097p]$ where $p = (F_o^2 + 2F_c^2)/3$.

Caution! Thallium(I) compounds are highly toxic.

Synthesis of $[PPN]_2[Re_7C(CO)_{21}Tl]$. A mixture of $[PPN]_3[Re_7C(CO)_{21}]$ (169 mg, 0.0480 mmol) and $TlPF_6$ (30 mg, 0.086 mmol) was dissolved in 10 mL of dry dichloromethane in a Schlenk tube, and the reaction was monitored by IR spectroscopy over a period of 2 h until complete. The reaction solution was layered with 40 mL of 2-propanol and let stand for 4 d at room temperature. The red crystalline precipitate was washed with methanol and dried under vacuum (144 mg, 0.0453 mmol, 94%). $[PPN]_2[\mathbf{1}]$: IR (CH_2Cl_2) ν(CO), 2044 (w), 1990 (vs), 1961 (w), 1935 (w), 1914 (w), 1878 (vw) cm^{-1}. MS (^{187}Re, ^{205}Tl): m/z 2646 (M − PPN), 2447 ($[Re_7C(CO)_{21}][PPN]$, 2108 (M − 2PPN), 1909 ($Re_7C(CO)_{21}$), $1909 - 28x$, x = 1, 3, 4, 5, 6 ($Re_7C(CO)_{21} - x$CO). Anal. Calcd for $C_{94}H_{60}N_2O_{21}P_4Re_7Tl$: C, 35.45; H, 1.90; N, 0.88. Found: C, 35.73; H, 2.12; N, 0.71.

$[PPh_4]_2[Re_7C(CO)_{21}Tl]$ was prepared in the same fashion in slightly lower yield.

X-ray Structure Determination of $[PPh_4]_2[Re_7C(CO)_{21}]$. Suitable single crystals of $[PPh_4]_2[\mathbf{1}]$ were grown from layering 2-propanol on a dichloromethane solution and subsequent diffusion. The red, transparent, prismatic crystal (0.16 × 0.16 × 0.32 mm^3) was mounted using oil (Paratone-N, Exxon) to a thin glass fiber. Diffraction data were collected on Siemens Platform/CCD automated diffractometer at 198 K. Of a total of 22 326 data collected (θ-range 1.46−28.32°, $-18 \le h \ge 17$, $-18 \le k \ge 18$, $-24 \le l \ge 13$, $\omega/2\theta$ scan, Mo Kα) 15 724 were independent ($R_{int} = 0.0616$); these data (with maximum 0.2399 and minimum 0.0133 transmission) were corrected for absorption. A summary of crystallographic details is given in Table 1.

The structure was solved by direct methods; hydrogen atoms were fixed on calculated positions. Full-matrix least-squares refinement, based on F^2, of the positional and anisotropical thermal parameters for all non-hydrogen atoms converged at $R_1 = 0.0547$ (wR2 = 0.1375) for those data with $I > 2\sigma(I)$ and $R_1 = 0.0935$ (wR2 = 0.1866) for all data.

All software and sources of scattering factors are contained in several versions of SHELXTL programs (G. M. Sheldrick, Siemens XRD, Madison, WI).

Complete details of the crystallographic study and atomic coordinates for $[PPh_4]_2[\mathbf{1}]$ are provided as Supporting Information. Selected bond lengths and angles for the cluster molecule are given in Table 2, and Figure 1 shows the molecule with the crystallographic labeling scheme.

Results and Discussion

The reaction of $TlPF_6$ with the rhenium cluster compound $[PPN]_3[Re_7C(CO)_{21}]$ ($PPN^+ = (Ph_3P)_2N^+$) in dichloromethane

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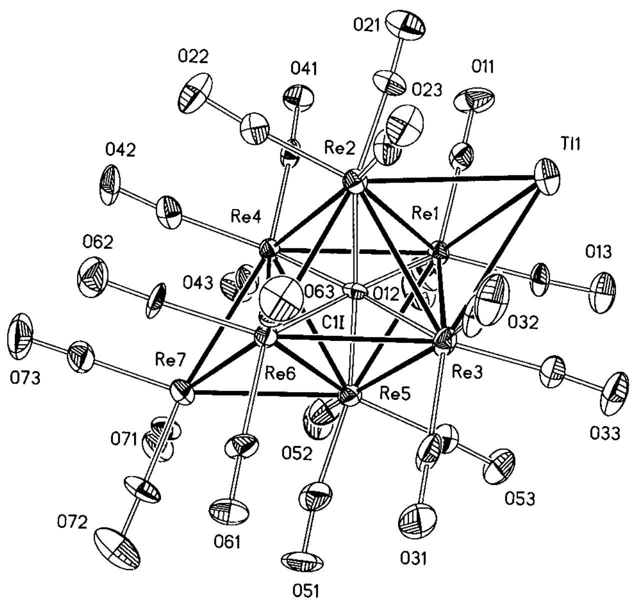


Figure 1. ORTEP diagram of the molecular structure of $[\mathrm{Re_7C(CO)_{21}Tl}]^{2-}$ with 35% thermal ellipsoids.

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

Bond Distances (Å)					
Tl1−Re1	3.2797(9)	Tl1−Re2	3.1957(9)	Tl1−Re3	3.2333(10)
Re1−Re2	3.0647(8)	Re2−Re3	3.0618(9)	Re1−Re3	3.0515(8)
Re1−Re4	3.0219(8)	Re1−Re5	3.0035(8)	Re2−Re4	2.9844(8)
Re2−Re6	2.9947(8)	Re3−Re5	3.0024(9)	Re3−Re6	2.9788(8)
Re4−Re5	2.9628(8)	Re4−Re6	2.9635(8)	Re5−Re6	2.9587(8)
Re4−Re7	2.9813(8)	Re5−Re7	2.9817(9)	Re6−Re7	2.9351(9)
Re1−C1I	2.132(14)	Re2−C1I	2.112(14)	Re3−C1I	2.130(14)
Re4−C1I	2.116(14)	Re5−C1I	2.137(13)	Re6−C1I	2.121(14)

Bond Angles (deg)			
Re1−Tl1−Re2	56.48(2)	Re1−Tl1−Re3	55.87(2)
Re2−Tl1−Re3	56.88(2)	Re1−Re2−Tl1	63.14(2)
Re1−Re3−Tl1	62.83(2)	Re2−Re3−Tl1	60.94(2)
Re2−Re1−Tl1	60.38(2)	Re3−Re2−Tl1	62.18(2)
Tl1−Re1−C1I	89.4(4)	Tl1−Re2−C1I	92.0(4)
Tl1−Re3−C1I	90.6(3)	Tl1−Re1−C11	76.2(5)
Tl1−Re1−C12	150.4(5)	Tl1−Re1−C13	68.9(5)
Tl1−Re2−C21	71.6(6)	Tl1−Re2−C22	149.1(5)
Tl1−Re2−C23	72.5(5)	Tl1−Re3−C31	152.4(6)
Tl1−Re3−C32	73.7(6)	Tl1−Re3−C33	73.5(5)

produced the bimetallic cluster derivative $[\mathrm{PPN}]_2[\mathrm{Re_7C(CO)_{21}Tl}]$ ($[\mathrm{PPN}]_2[\mathbf{1}]$), which was isolated in 94% yield. The infrared spectrum of the dianion $\mathbf{1}^{2-}$ shows several weak absorptions and one strong carbonyl absorption at 1990 $\mathrm{cm^{-1}}$. The principal CO stretching band is shifted 22 $\mathrm{cm^{-1}}$ from that for $[\mathrm{Re_7C(CO)_{21}}]^{3-}$ (1968 $\mathrm{cm^{-1}}$), which is comparable with the shift observed for other mixed-metal−rhenium carbido clusters $[\mathrm{Re_7C(CO)_{21}ML}_n]^{2-}$.[1,6]

The structure of $[\mathrm{Re_7C(CO)_{21}Tl}]^{2-}$ was confirmed by a single-crystal X-ray diffraction study of the tetraphenylphosphonium salt, and a diagram depicting the results is shown in Figure 1. The cluster is a 1,4-bicapped octahedron, with the Tl atom nearly symmetrically disposed over three rhenium atoms of one octahedral face, with the opposite face capped by the $\mathrm{Re(CO)_3}$ unit (Re7). The Re−Re distances of the Tl-capped face are longer (average 3.059 Å) than the Re−Re distances in the face capped by Re7 (average 2.962 Å). The average Tl−Re distance is 3.236 Å, which is significantly longer than the value of 3.05 Å estimated from summing covalent radii of 1.48 Å for Re (from the bonding to Re7) and 1.57 Å for $\mathrm{Tl^+}$.[7] This discrepancy may be due to relatively ionic bonding of the thallium ion, as has been suggested for a number of analogous complexes (see below). The Re atoms constituting the octahedral $\mathrm{Re_6C}$ core are nearly equidistant from the interstitial carbon atom, with an average Re−C distance of 2.125 Å.

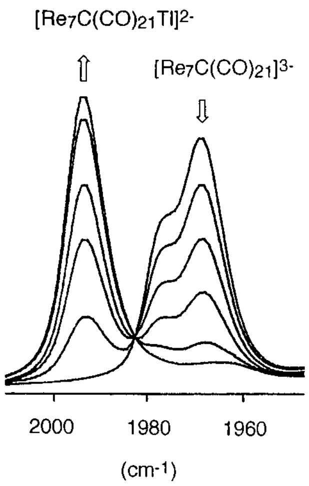
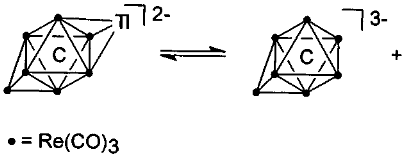


Figure 2. Infrared spectra of $[\mathrm{PPN}]_3[\mathrm{Re_7C(CO)_{21}}]$ (4.2×10^{-4} M) in acetone with different $\mathrm{Tl^+}$ concentrations ($(0 - 1) \times 10^{-3}$ M).

Scheme 1



It is of interest that the thallium ion in the solid state interacts also very weakly with the oxygen atom of carbonyl 23 (Tl−O: 3.553 Å) on an equivalent molecule related by an inversion center. A figure showing this interaction is provided in the Supporting Information.

The monomeric structure of $\mathbf{1}^{2-}$ is similar to the structures adopted by thallium complexes of several pyrazolylborate ligands,[4a−g] where the $\mathrm{Tl^+}$ ion is bonded equidistant to three pyrazole nitrogen atoms. Less symmetrical structures are adopted by the dicarbollide complexes of thallium;[3a−c] the thallium is coordinated to the open $\mathrm{B_3C_2}$ face of the dicarbollide ligand with three short and two longer bonds, and in one case weak ancillary Tl−H interactions enforce a dimer structure.[3a] Polymeric[2a−e] or oligomeric[2c] structures are usually observed with cyclopentadienide ligands with the $\mathrm{C_5}$ ring bridging two thallium ions. In one case with a very bulky ligand, however, a direct thallium−thallium interaction stabilizes the dimer $[\mathrm{Tl}(\eta^5\text{-}\mathrm{C_5(CH_2Ph)_5})]_2$.[8,9]

Infrared spectra show that the complex $\mathbf{1}^{2-}$ is stable in dichloromethane solution. On the other hand, the complex dissociates in coordinating solvents such as acetone and acetonitrile (Scheme 1). A set of infrared spectra of $[\mathrm{Re_7C(CO)_{21}}]^{3-}$ in acetone with different $\mathrm{Tl^+}$ concentrations exhibits an isosbestic point (Figure 2), indicating that there are only two absorbing species in solution. We calculated the association constant K_a from the change in absorbance ΔA of the most intense band (1992 $\mathrm{cm^{-1}}$) in the IR spectrum of the product

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$\mathbf{1}^{2-}$ with increasing Tl^+ concentration $[Tl^+]_0$. The equation used (modified Benisi-Hildebrand)[10] was $[C_0]/\Delta A = K_a/\Delta\epsilon[Tl^+]_0 + 1/\Delta\epsilon$, where $[C_0]$ is the starting concentration of $[Re_7C(CO)_{21}]^{3-}$ and $\Delta\epsilon$ is the difference of the molar absorptivity of the two observed compounds. Plotting $1/\Delta A$ vs $1/[Tl^+]_0$ and dividing the slope by the intercept provided a value of $K_a = 2.1(9) \times 10^{-3}$ mol/L. Thus, an acetone solution of complex $\mathbf{1}^{2-}$ will be highly dissociated (ca. 99%) at typical concentrations such as that used for Figure 2.

The dissociation of complex $\mathbf{1}^{2-}$ in dichloromethane is promoted by halide ion sources. When tetrabutylammonium bromide is added to a solution of $\mathbf{1}^{2-}$ in dichloromethane, a precipitate of TlBr is immedately formed, and the IR spectrum of the solution shows CO absorption bands only for the trianion $[Re_7C(CO)_{21}]^{3-}$. This behavior contrasts with that of the corresponding silver complex $[Re_7C(CO)_{21}Ag]^{2-}$, which is generated from $[Re_7C(CO)_{21}]^{3-}$ and $AgBF_4$ and is stable in acetone or acetonitrile solution. In the presence of tetrabutylammonium bromide the Ag^+ complex forms the bromide-bridged compound $[(Re_7C(CO)_{21}Ag)_2(\mu\text{-}Br)]^{5-}$,[6] and not, as might be expected, silver bromide and $[Re_7C(CO)_{21}]^{3-}$.

The cluster complex $\mathbf{1}^{2-}$ also reacts easily and cleanly with (triphenylphosphine)gold(I) chloride in dichloromethane to form the known compound $[Re_7C(CO)_{21}AuPPh_3]^{2-}$ [1a,6] and insoluble TlCl. Thus, complex $\mathbf{1}^{2-}$ should be able to react with halide-containing organometallic compounds of the general formula XML_n to generate new complexes of the formula $[Re_7C(CO)_{21}\text{-}ML_n]^{2-}$. These reactions are under current investigation.

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Supporting Information Available: Tables of the details of crystallographic data collection and atomic coordinates for $[PPh_4]_2[\mathbf{1}]$ and a figure of two symmetry equivalent molecules showing the Tl−carbonyl interaction (4 pages). Ordering information and instructions for Internet access are given on any current masthead page.

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