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Synthesis, Characterization, and Molecular Structure of the First Metal Complex Containing TlCl as a Ligand. A Novel Carrier of Thallium(I)

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Considerable attention has recently been focused on metal complexes capable of binding main group ions with an s^2 electronic configuration.[1] A general strategy requires the design of metal complexes able to form a direct metal to ion bond. We are developing a different approach, which involves interaction of coordinated ligands exhibiting residual nucleophilic character, with electrophilic main group ions.

Here we describe the interaction of the pale yellow cis hydride chloride Ru(II) complex $[(PP_3)RuH(Cl)]^2$ (**1**) with Tl^+ [$PP_3 = P(CH_2CH_2PPh_2)_3$]. Compound **1** in dichloromethane extracts Tl^+ from an aqueous solution of $TlPF_6$ (Scheme I). As a result, the complex $[(PP_3)RuH(\eta^1\text{-}ClTl)]PF_6{}^3$ (**2**) is quantitatively isolated as yellow green crystals from the organic layer.

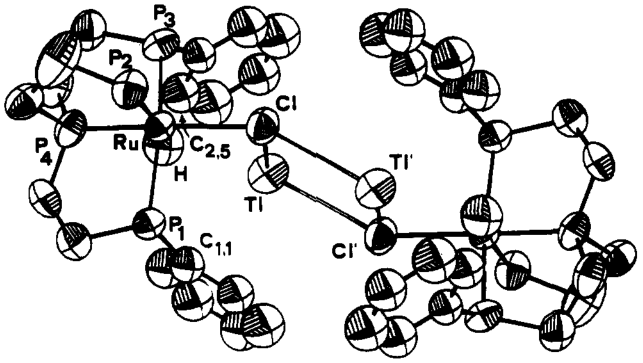
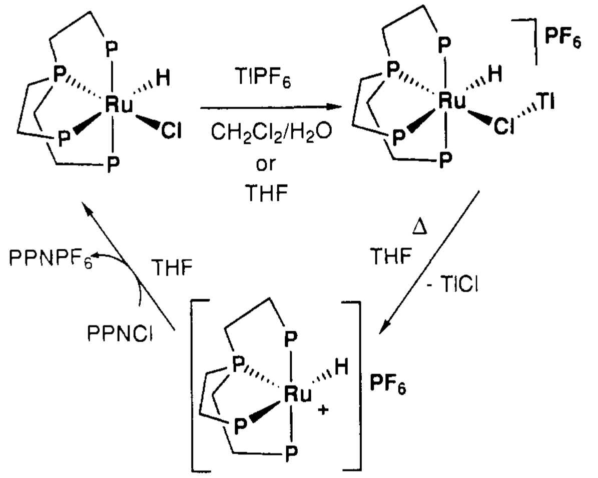


Figure 1. ORTEP drawing of the centrosymmetric aggregate of two $[(PP_3)RuH(ClTl)]^+$ cations in the structure of **2**. For clarity, only the phenyl rings which shield the Tl_2Cl_2 unit are shown. Selected bond distances (Å) and angles (deg): Ru–Cl 2.534 (5), Ru–H 1.8 (2), Tl–Cl 2.815 (4), Tl···Cl′ 3.365 (4), Tl···H 2.6 (2), Ru–P_1/P_3 (average) 2.35 (2), Ru–P_4 2.213 (5), Tl–Cl–Ru 82.7 (1), H–Ru–Cl 98 (6), Tl–Cl–Tl′ 99.2 (1).

Scheme I



The structure of **2** contains a $[(PP_3)RuH(TlCl)]^+$ cation and a $PF_6{}^-$ anion per asymmetric unit.[4] Dimeric aggregates of two centrosymmetrically related cations are shown in Figure 1. In each unit, the Ru atom is pseudooctahedrally coordinated by the four phosphorus atoms of PP_3, a Cl atom, trans to the bridgehead P atom [P_4–Ru–Cl = 177.3 (2)°], and a hydride ligand, trans to one of the terminal P atoms [P_2–Ru–H = 162 (6)°]. It is noteworthy that the P_4 atom, trans to chlorine, suffers the weakest trans-influence, being ca. 0.15 Å closer to the metal than the other P donors [2.213 (5) vs 2.35 (2) Å (average)]. The P_1–Ru–P_3 bond angle of 153.9 (2)° manifests the distortion from ideal octahedral geometry. The Ru–H bond length is 1.8 (2) Å. The Tl–H contact distance of 2.6 (2) Å, although not excluding some residual electrostatic interaction, is certainly much longer than the sum of Tl–H covalent radii (1.8 Å). The remarkable aspect of the structure is the Tl(I) atom bonded to the coordinated Cl atom, which behaves as a bridging ligand. The Ru–Cl–Tl bond angle is 82.7 (1)°, and the Tl–Cl bond length is 2.815 (4) Å. The latter is somewhat shorter than the interionic distance in TlCl (3.15 and 3.32 Å for the NaCl and CsCl forms, respectively) and slightly longer than that found for gaseous TlCl (2.55 Å).[6] The Ru···Tl separation of 3.545 (2) Å is too long to permit a substantial direct metal–metal interaction. It is noteworthy that two of the phenyl groups of PP_3 are oriented toward the Tl atom, so as to create a sort of shielding about thallium. The shortest contacts are the distances Tl···$C_{1,1}$ [3.218 (1) Å] and Tl···$C_{2,5}$ [3.303 (1) Å]. A similar structural feature has been observed for the two different modifications of $[(PhCH_2)_5C_5]Tl$ with the shortest contacts Tl···C(Ph) of 3.382 and 3.410 Å for the kinetic[7] and thermodynamic[8] products, respectively.

As shown in Figure 1, the structure may be also interpreted as a dimeric aggregate of two $[(PP_3)RuH(TlCl)]^+$ cations in

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(3) The compound is stable in the solid state and in deoxygenated solutions where it behaves as a 1:1 electrolyte ($\Lambda_M = 81\ \Omega^{-1}\ cm^2\ mol^{-1}$ in 1×10^{-3} M nitroethane solution). $^{31}P\{^1H\}$ NMR (THF-d_8, 293 K, 121.42 MHz, H_3PO_4 85% reference): temperature-invariant AM_2Q spin system with $\delta(P_A) = 153.61$ ppm, $\delta(P_M) = 47.73$ ppm, $\delta(P_Q) = 49.36$ ppm, $J(P_{AM}) = 9.2$ Hz, $J(P_AP_Q) = 5.8$ Hz, $J(P_MP_Q) = 19.2$ Hz. ^1H NMR (THF-d_8, 293 K, 299.94 MHz, Me_4Si reference): Ru–*H*, δ –6.57 ppm, ddt, $J(HP_M) = 71.0$ Hz, $J(HP_A) \cong J(HP_Q) = 22.5$ Hz. ^{205}Tl NMR (CD_2Cl_2; 293 K; 52.09 MHz; reference, Tl^+ aqueous solution at infinite dilution): s, 1338 ppm, $w_{1/2} = 50$ Hz. IR: ν(Ru–H) 1770 cm^{-1}, s, (Nujol mulls), 1754 cm^{-1} (CD_2Cl_2 solution). UV–vis (THF, 293 K): 364 nm ($\epsilon = 6871$), 377 nm ($\epsilon = 1484$), 425 nm ($\epsilon = 645$). Anal. Calcd for $C_{42}H_{43}ClF_6P_5RuTl$: C, 44.27; H, 3.80; Cl, 3.11. Found: C, 44.08; H, 3.71; Cl, 2.98.

(4) Crystal data: $C_{42}H_{43}P_5F_6Cl_1Ru_1Tl_1$, yellow parallelepiped crystal, monoclinic, $a = 29.422$ (6) Å, $b = 14.876$ (4) Å, $c = 24.633$ (3) Å, $\beta = 114.53$ (2)°, with $Z = 8$ in space group $C2/c$ (No. 15). Data collected at 20 °C on Philips PW1100 diffractometer with monochromated Cu Kα radiation ($\lambda = 1.5418$ Å). Empirical absorption correction made using the program DIFABS.[5] $R = 0.066$ and $R_w = 0.079$ for 3093 reflections (θ–2θ scan) with $I > 3\sigma(I)$ (total reflection number 5436) and anisotropic thermal parameters for Ru, Tl, P, Cl, and the C atoms of the ligand chain. The ruthenium-coordinated H atom was located in a ΔF map and the relative parameters were refined in the least-squares cycles.

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which two asymmetric chlorine atoms bridge two thallium atoms. Although one Tl-Cl separation is as long as 3.365 (4) Å, it can be reasonably assumed that there is a residual interaction between the two atoms. This intermolecular interaction is irretrievably lost in dichloromethane or tetrahydrofuran solution in which the compound is monomeric (molar conductivity and molecular weight measurements) and maintains an octahedral geometry (^{31}P NMR AM_2Q spin system, temperature invariant over the range 303–193 K). Also, no interaction between thallium and the terminal hydride ligand is apparent in solution as shown by the NMR parameters of the hydride resonance (ddt at −6.57 ppm with $J(HP_M) = 71.0$ Hz; $J(HP_A) \cong J(HP_Q) = 22.5$ Hz) and by the proton-coupled ^{205}Tl NMR spectrum which consists of a singlet at 1338 ppm. Indeed, even though no ^1J(HTl) values for Tl(I) compounds are reported in the literature, such coupling constants are expected to be very large [^2J(HTl) values in Tl(III) compounds range from 180 to 400 Hz].[9]

Interestingly, compound **2** decomposes in refluxing THF under argon, separating TlCl and forming the unsaturated $[(PP_3)RuH]^+$ moiety, which, by addition of (PPN)Cl, restores the starting chloride **1** quantitatively (Scheme I). The latter complex is capable of transporting Tl^+ from one aqueous solution through a dichlorometane solution into a second aqueous phase. In a typical U-tube experiment employing 7.2×10^{-2} M CH_2Cl_2 solution of **1**, transport from an aqueous 0.1 M solution of Tl^+ yields detectable thallium concentrations in the second aqueous phase after 4 h.[10] Equal concentrations of Tl(I) in the two aqueous phases is observed after 12 h. During the process, the organic phase acquires the yellow color characteristic of **2** with an intensity that persists for at least 10 days.

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Note Added in Proof. After submission of this paper a report on a complex incorporating a $RuCl_2Tl_2Ru$ ladder appeared.[11]

Supplementary Material Available: Text giving experimental details for the synthesis of **2** and tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (7 pages). Ordering information is given on any current masthead page.

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