

Synthesis and Structural Characterisation of $[\text{TlPt}_3(\text{CO})_3(\text{PCy}_3)_3][\text{Rh}(\eta\text{-C}_8\text{H}_{12})\text{Cl}_2]$ (Cy = Cyclohexyl), a Tetrahedral Pt_3Tl Cluster Compound

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The first example of a thallium–platinum metal cluster cation has been synthesised from Tl^{I} salts and $[\text{Pt}_3(\text{CO})_3(\text{PCy}_3)_3]$ (Cy = cyclohexyl); in $[\text{TlPt}_3(\text{CO})_3(\text{PCy}_3)_3]^+$ the Tl atom caps the Pt_3 triangle with Pt–Tl (average) = 3.038(1) Å.

Although there are no examples of homonuclear cluster compounds of thallium, this element has been incorporated into heterometallic cluster compounds, *e.g.* $[\text{Tl}_2\text{Te}_2]^{2-}$, $[\text{TlSn}_9]^{3-}$, and $[\text{TlSn}_8]^{3-}$.¹ In addition, thallium salts of metal carbonyl anions, $[\text{TlCo}(\text{CO})_4]$, $[\text{Tl}\{\text{Co}(\text{CO})_4\}_3]$, and $[\text{Tl}\{\text{Mn}(\text{CO})_5\}_3]$, are known² and recently Whitmire *et al.*³

have characterised $[\text{Tl}_6\text{Fe}_{10}(\text{CO})_{36}]^{3-}$ which has two Tl_3 triangles linked by two $\text{Fe}(\text{CO})_4$ bridges and capped by $\mu^3\text{-Fe}(\text{CO})_3$ fragments.

Nevertheless, it has generally been assumed that Tl^+ is not capable of forming sufficiently strong metal–metal bonds to the platinum metals. Indeed TlPF_6 is frequently used as a

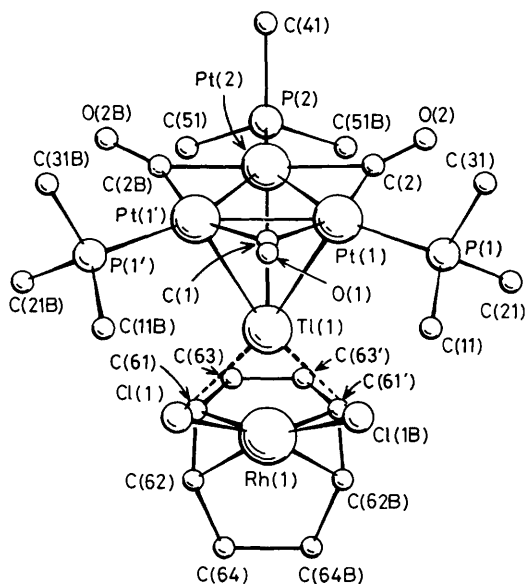


Figure 1. Molecular structure of $[\text{TiPt}_3(\text{CO})_3(\text{PCy}_3)_3][\text{Rh}(\text{C}_8\text{H}_{12})\text{Cl}_2]$ (**1**), showing the inter-ion contacts and co-ordination geometries about the metal atoms, $\text{Ti}(1)\text{--Cl}(1)$ 2.981(9) Å. Important intramolecular bond lengths are: $\text{Ti}(1)\text{--Pt}(1)$ 3.034(1), $\text{Ti}(1)\text{--Pt}(2)$ 3.047(1), $\text{Pt}(1)\text{--Pt}(1')$ 2.668(1), $\text{Pt}(1)\text{--Pt}(2)$ 2.667(1), and $\text{Rh}\text{--Cl}$ 2.369(9) Å. For reasons of clarity the cyclohexyl groups and hydrogen atoms have been omitted.

halide abstracting agent for the addition of AuPR_3^+ to anionic and neutral platinum metal cluster compounds, $\text{Au}(\text{PR}_3)^+$ being formed *in situ* from $\text{AuCl}(\text{PR}_3)$ and TIPF_6 in a polar organic solvent.^{4–7}

Whilst attempting to synthesise some examples of platinum–rhodium cluster compounds $[\text{Rh}_2\text{Cl}_2(\eta\text{-C}_8\text{H}_{12})_2]$ was added to a solution of $[\text{Pt}_3(\eta\text{-CO})_3(\text{PCy}_3)_3]$ ($\text{Cy} = \text{C}_6\text{H}_{11}$) in the presence of a finely ground sample of TIPF_6 . Red crystals of the resulting compound were obtained on recrystallisation from $\text{CH}_2\text{Cl}_2\text{--Et}_2\text{O}$ and shown to analyse satisfactorily for $[\text{TiPt}_3(\text{CO})_3(\text{PCy}_3)_3][\text{RhCl}_2(\mu\text{-C}_8\text{H}_{12})]$ (**1**) [80% yield, $\nu(\text{CO})$ (Nujol) 1865s, 1790m cm^{-1}]. The spectroscopic and analytical data suggested that the Ti^+ ion was capping the Pt_3 triangle, rather than abstracting a chloride ion from $[\text{Rh}_2\text{Cl}_2(\eta\text{-C}_8\text{H}_{12})_2]$, but in order to establish unambiguously the structure of (**1**) a single crystal X-ray diffraction study was completed.[†]

The molecular structure of (**1**) and some important inter-nuclear distances are given in Figure 1. The $[\text{TiPt}_3(\mu\text{-CO})_3(\text{PCy}_3)_3]^+$ cation and the $[\text{RhCl}_2(\eta\text{-C}_8\text{H}_{12})]^-$ anion lie on a crystallographically imposed mirror plane of symmetry. The shortest contacts between cation and anion involve the chlorine atoms and the thallium [$\text{Ti}\text{--Cl}$, 2.981(9) Å], with the

chlorine atoms lying approximately *trans* to two of the platinum atoms of the triangle. The metal atoms in the cluster cation define an elongated tetrahedron with the average $\text{Pt}\text{--Pt}$ distances significantly shorter than the platinum–thallium bond lengths, 2.667(1) vs. 3.038(1) Å.

Besides providing the first example of a thallium–platinum metal cluster, (**1**) represents the third member of a series of tetrahedral clusters with 54 valence electrons, *i.e.* $[(\text{Cy}_3\text{P})\text{AuPt}_3(\text{CO})_3(\text{PCy}_3)_3]^+$,⁵ $[\text{HgPt}_3(\text{CO})_3(\text{PPhPr}^i)_3]$,⁸ and $[\text{TiPt}_3(\text{CO})_3(\text{PCy}_3)_3]^+$. In the gold cluster the average $\text{Au}\text{--Pt}$ distance is 2.758(5) Å, in the mercury complex the $\text{Pt}\text{--Hg}$ distances vary from 2.923 to 3.084(1) Å and the average $\text{Pt}\text{--Ti}$ distance in (**1**) is 3.038(1) Å. This variation clearly reflects the effect of the filled $6s^2$ shell in the latter two compounds.⁹ The mercury compound shows a weak intermolecular interaction leading to dimers linked by a long [3.225(1) Å] $\text{Hg}\text{--Hg}$ bond.⁸ Presumably the residual charge on the thallium prevents such a dimerisation process in (**1**) and instead weak interactions to the chloro-ligands of the rhodium anion are observed. The presence of the large rhodium anion is not necessary for forming stable TiPt_3 clusters, and we have subsequently demonstrated that the addition of TIPF_6 to a benzene–ethanol solution of $[\text{Pt}_3(\mu\text{-CO})_3(\text{PCy}_3)_3]$ gave a 94% yield of $[\text{TiPt}_3(\mu\text{-CO})_3(\text{PCy}_3)_3]\text{PF}_6$ as orange crystals [$\nu(\text{CO})$ (Nujol) 1864s, 1798m, $\nu(\text{PF}_6)$ 837 cm^{-1} ; $^1\text{P}\{^1\text{H}\}$ n.m.r. at 101.26 MHz (CD_2Cl_2) referenced to trimethylphosphate: δ 66.7 p.p.m., $^1\text{J}(\text{Pt}\text{--P})$ 4516, $^1\text{J}(\text{Pt}\text{--Ti})$ 2032 (both estimated from computer simulation), $^2\text{J}(\text{Pt}\text{--P})$ 291, $^2\text{J}(\text{Ti}\text{--P})$ 193, $^3\text{J}(\text{P}\text{--P})$ 44 Hz]. For this salt the retention of the capping thallium atom in solution was clearly indicated by the observation even at room temperature of $^2\text{J}(\text{Ti}\text{--P})$ coupling. In contrast (**1**) showed only broad n.m.r. spectra in the temperature range 300–210 K.

These results clearly indicate that it should be possible to synthesise a wide range of carbonyl cluster compounds with capping thallium atoms, particularly if carbonyl cluster anions are used as precursors. The thallium in this cluster is sufficiently labile to be replaced by other capping metal atoms and for example addition of $[\text{Au}(\text{PCy}_3)\text{Cl}]$ leads to its quantitative conversion into $[(\text{Cy}_3\text{P})\text{AuPt}_3(\mu\text{-CO})_3(\text{PCy}_3)_3]\text{PF}_6$.

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[†] Crystal data for (**1**)· $\text{CH}_2\text{Cl}_2\text{·Et}_2\text{O}$: $[\text{TiPt}_3(\text{CO})_3(\text{PCy}_3)_3][\text{RhCl}_2(\text{C}_8\text{H}_{12})]\text{·CH}_2\text{Cl}_2\text{·Et}_2\text{O}$, $\text{C}_{70}\text{H}_{123}\text{Cl}_4\text{O}_4\text{P}_3\text{Pt}_3\text{RhTi}$, monoclinic, space group $P2_1/m$, $a = 14.526(4)$, $b = 17.720(4)$, $c = 15.553(4)$ Å, $\beta = 96.30(1)^\circ$, $U = 3979$ Å³, $Z = 2$, $D_{\text{calc.}} = 1.80$ g cm^{-3} ; a total of 7786 reflections were measured, $R = 0.051$, $R_w = 0.062$, for 3662 unique, observed reflections [$F_0 \geq 3\sigma(F_0)$; $\theta \leq 25^\circ$]. Intensity data were collected on a Enraf-Nonius CAD4F diffractometer using graphite monochromated $\text{Mo-K}\alpha$ radiation. The structure was solved using Patterson and Fourier methods. Blocked matrix least-squares refinement; anisotropic thermal parameters for all nonhydrogen atoms. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.