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Platinum Cluster Cryptates: Trapping of Mercury(0) and Thallium(I)

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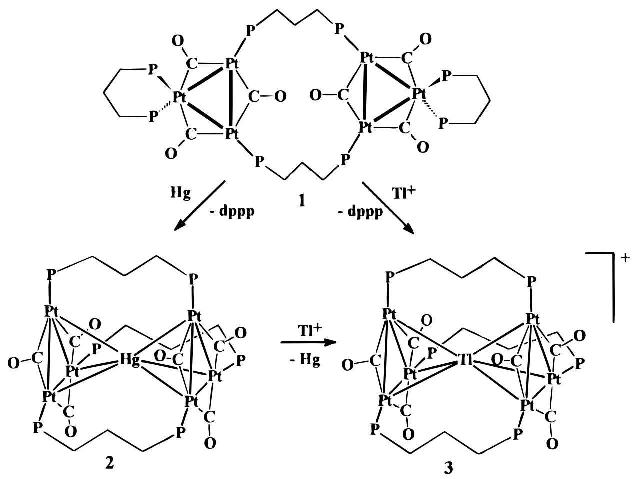
The encapsulation of a metal ion by a cryptand ligand has dramatic effects on both the thermodynamic stability and kinetic reactivity of the resulting cryptate complex since the metal ion is physically trapped and cannot easily escape.[1] This paper describes examples of cluster cryptate complexes in which mercury(0) or thallium(I) is entrapped and in which binding of the metal triggers the encapsulation process.

Reduction of $[PtCl_2(Me_2S)_2]$ with excess $NaBH_4$ in the presence of dppp = $Ph_2P(CH_2)_3PPh_2$ and CO gave the new cluster complex $[Pt_6(\mu\text{-}CO)_6(\mu\text{-dppp})_2(dppp)_2]$, **1**, in 85% yield as a brown-red solid. Cluster **1** can be considered to contain two separate Pt_3 clusters bridged by two μ-dppp ligands, and it was readily characterized spectroscopically[2] by comparison to the known trinuclear complex $[Pt_3(\mu\text{-}CO)_3(PCy_3)_2(dppp)]$.[3] At room temperature, the NMR spectra indicate an effective plane of symmetry containing all platinum atoms, the carbonyl ligands, and phosphorus atoms of the μ-dppp ligands and bisecting the chelating dppp ligands. Thus, for example, only two ^{31}P resonances of equal intensity are observed, one due to the bridging and one to the chelating dppp ligands. However, at low temperature, two resonances are observed for the phosphorus atoms of the chelating dppp ligand, indicating somewhat lower symmetry while maintaining the open structure.[2]

Cluster **1** reacted with either mercury or $Tl[PF_6]$ to give free dppp and the closed cluster **2** (6 h to completion, 75% yield) or **3** (10 min to completion, 82% yield), respectively, in high yield (Scheme 1). Solutions of **1**−**3** are red, green, and green-blue, respectively, and so the reactions are easily monitored by the color changes as well as by NMR spectroscopy. Large crystals of **2** and **3** appear black. The clusters were readily characterized by their spectroscopic properties,[2] and the structure of **3**$[BPh_4]$ was determined crystallographically.[4] The thallium is bonded in sandwich fashion to all six platinum atoms, which themselves have a geometry intermediate between the trigonal prism and antiprism [the dihedral angles typified by P(1)Pt(1)Pt(5)P(5) and P(1)Pt(1)Pt(4)P(4) fall in the ranges 32.4−34.4 and −79.0 to −86.8°; ideal values would be 0 and −120° for the trigonal prism and 60° and −60° for the trigonal antiprism]. The high symmetry of **2**, for example, is demonstrated by the presence of single resonances in the ^{13}C (for ^{13}CO ligands), ^{31}P, and ^{195}Pt NMR spectra.[2] While one other sandwich cluster of mercury is known,[5] **3** appears to be the first example of a sandwich cluster of thallium(I), and the easy formation of a

Scheme 1



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[1] (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (b) Mertes, K. B.; Lehn, J.-M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Vol. 2, Chapter 21.3.

[2] Spectroscopic data are given in the Supporting Information. Satisfactory C, H analyses were obtained for **1**−**3**.

[3] Hallam, M. F.; Howells, N. D.; Mingos, D. M. P.; Wardle, R. W. M. *J. Chem. Soc., Dalton Trans.* **1985**, 845.

[4] Crystal data for $[TlPt_6(dppp)_3(CO)_6](BPh_4)\cdot CH_2Cl_2$: monoclinic, space group $P2_1/n$, $a = 16.571(4)$ Å, $b = 26.030(6)$ Å, $c = 27.447(6)$ Å, $\beta = 95.80(2)°$, $V = 11778(4)$ Å^3, $Z = 4$; Mo Kα radiation, $\lambda = 0.710\ 73$ Å, $R_1(F) = 0.0999$.

[5] Yamamoto, Y.; Yamazaki, H.; Sakurai, T. *J. Am. Chem. Soc.* **1982**, *104*, 2329.

[6] (a) Ezomo, O. J.; Mingos, D. M. P.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1987**, 924. (b) Imhof, D.; Venanzi, L. M. *Chem. Soc. Rev.* **1994**, 185 and references therein. (c) Yamamoto, Y.; Yamazaki, H. *Inorg. Chim. Acta* **1994**, *217*, 121. (d) Gould, R. A. T.; Craighead, K. L.; Wiley, J. S.; Pignolet, L. H. *Inorg. Chem.* **1995**, *34*, 2902. (e) Schoettel, G.; Vittal, J. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 6400.

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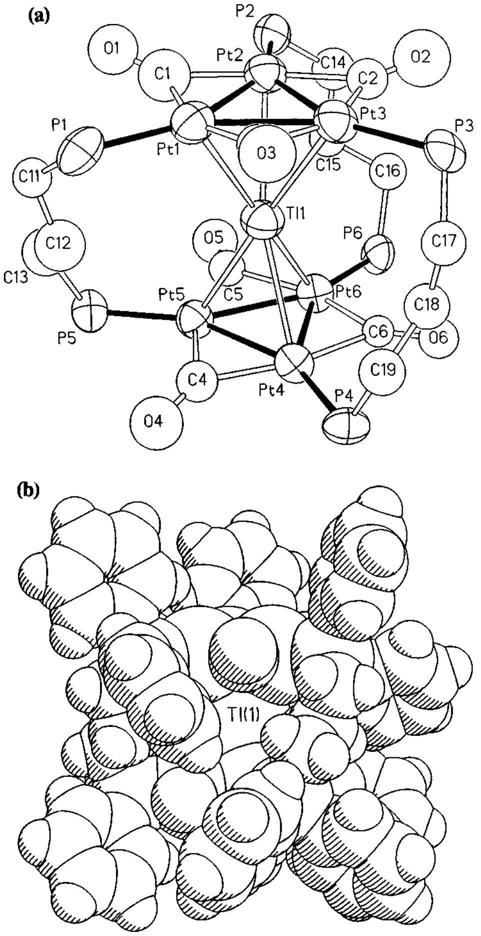

Figure 1. (a) View of the structure of the cluster cation **3**. Metal–metal distances are in the ranges Pt–Tl = 2.860(3)–2.992(3) Å and Pt–Pt = 2.658(3)–2.682(3) Å; the closest intertriangle Pt••Pt distance is Pt(2)Pt(6) = 5.036(3) Å, which is clearly nonbonding. The angle between the planes Pt(1)Pt(2)Pt(3) and Pt(4)Pt(5)Pt(6) is 2.0(1)°. (b) Space-filling model showing the encapsulation of the thallium(I) ion. This is a view along the largest channel for entrance to or exit from the cage.

cryptate cluster (**2**, **3**) from an open cluster (**1**) is also unprecedented.[3,6]

Why are these reactions so selective? Attempts to prepare $[\mathrm{Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppp)_3}]$, with no "guest" metal incorporated, by using the procedure for synthesis of **1** but with reduced amounts of dppp, have been unsuccessful since only **1** and decomposition products are formed, but if the reaction is carried out in the presence of mercury, **2** is formed easily. It may be that the 44-electron configuration of each $\mathrm{Pt_3}$ unit in **1** is preferred to the 42-electron configuration in the hypothetical closed cluster or that entropy effects favor the open structure. Clearly, the sandwich-type coordination of mercury[5] or thallium(I) is sufficient to overcome these effects and the structure is easily closed by formation of the third μ-dppp group, thus leading to encapsulation of the guest metal. Can the metal escape the cage? The presence of the short $\mathrm{(CH_2)_3}$ bridges (the cage bars) leads to a relatively rigid structure with holes that are too small to permit a heavy metal to pass through (Figure 1), but an experimental test of guest metal inertness was needed. Cluster **3** failed to react with mercury, but **2** did react slowly with $\mathrm{Tl[PF_6]}$ over 24 h to give **3**. It is proposed that this metal replacement reaction occurs by at least partial opening of the cluster to allow the mercury to leave and the thallium to enter, thus accounting for the much slower reaction of $\mathrm{Tl^+}$ with **2** compared to **1**. In contrast, in the absence of the cryptand effect, the binding of Hg(0) or Tl(I) to $\mathrm{Pt_3}$ clusters is weak and easily reversible.[6]

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Supporting Information Available: Text giving spectroscopic data for the complexes and details of the X-ray structure determination and tables of crystal data, X-ray experimental details, atomic coordinates, thermal parameters, bond distances and angles, torsion angles, and least-squares planes (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the internet; see any current masthead page for ordering information and Internet access instructions.

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