Communications to the Editor

Unsupported Pt(0)−Tl(I) Bonds in the Simple $[Pt(PPh_2Py)_3Tl]^+$ Complexes

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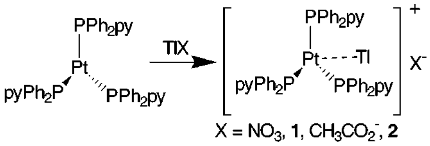
The bonding interaction between closed-shell, heavy metal atoms or ions is gaining increasing attention,[1] and while there are numerous examples of square-planar Pt(II) centers aggregating with s^2 ions such as Tl(I) or Pb(II),[2] there are surprisingly few examples of similar associations in the closely related trigonally coordinated Pt(0) centers. Along these lines, we recently reported the application of d^{10}-based metallocryptands as hosts for the incarceration of metal ions including Tl(I)[3,4] and Pb(II).[5] In these systems the internal ion does not interact with the bridging ligands. Rather, the three-metal assembly is maintained by the short metallophilic bonds formed between the trigonally coordinated d^{10} metals and the internal ion, with separations very close to the sum of the respective covalent radii. The strength of this attraction suggests that the rigid structural framework of the metallocryptand cage may not be essential in maintaining these assemblies, and similar metallophilic attractions may be observed by simple s^2 ion addition to trigonally coordinated $Pt(PR_3)_3$ complexes.

Here, we report the synthesis of $[Pt(PPh_2py)_3Tl]NO_3$ (**1**) and $[Pt(PPh_2py)_3Tl](C_2H_3O_2)$ (**2**, PPh_2py = diphenyl-2-pyridylphosphine) which, to the best of our knowledge, are the first examples of complexes containing unsupported Pt(0)−Tl(I) bonds.

Compound **1** was prepared by the anaerobic addition of a benzene solution of $Pt(PPh_2py)_3$[6] to $TlNO_3$ suspended in CH_3CN/MeOH at room temperature (Scheme 1). The yellow benzene solution turns orange within a few minutes, and orange crystals of **1** are grown by slow diffusion of n-Bu_2O into the reaction mixture. Compound **2** is prepared analogously using ethanolic $Tl(C_2H_3O_2)$. A similar reaction is observed with $Pt(PPh_3)_3$ and Tl(I) ion affording orange solutions, but X-ray quality crystals could not be grown. Interestingly, addition of Tl(I) significantly attenuates the air-sensitivity compared to their respective $Pt(PR_3)_3$ species,[7] and solutions of **1** or **2** can be handled in air with only modest precautions while the solids are air-stable for days to weeks.

Scheme 1



$^{31}P\{^1H\}$, ^{195}Pt, and ^{205}Tl NMR spectroscopy (9:1 toluene/EtOH) indicate that the Pt−Tl interaction is maintained in solution. At 25 °C complexation with Tl^+ shifts the $^{31}P\{^1H\}$ resonance of $Pt(PPh_2py)_3$ from 52.0 ppm ($^1J_{PtP}$ = 4444 Hz) to 44.5 ppm ($^1J_{PtP}$ = 4237 Hz) for **1** and to 45.0 ppm ($^1J_{PtP}$ = 4194 Hz) for **2**. The decrease in the Pt−P coupling constants is consistent with an increase in coordination number upon Tl(I) complexation.[8] The lack of an observable Tl−^{31}P coupling has been noted in the related metallocryptands. The ^{195}Pt NMR spectra of **1** at 25 °C show a doublet of quartets (−4000 ppm, $^1J_{PtTl}$ = 6382 Hz) where direct coupling to Tl is observed. However, in **2** at room temperature the Tl binding is dynamic. The ^{195}Pt NMR spectra of **2** at 25 °C display a broad quartet (−3837 ppm, $^1J_{PtP}$ = 4194 Hz) that resolves into a doublet of quartets at −30 °C (−4112 ppm, $^1J_{PtTl}$ = 7030 Hz) indicating that the acetate ion plays a role in Tl(I) ion binding. For comparison the ^{195}Pt NMR spectra of $Pt(PPh_2py)_3$ exhibit resonances at −4592 and −4630 ppm at 25 and −50 °C, respectively. The ^{205}Tl NMR spectra of **1** show a broad resonance at +1940 ppm[9] similar to that of the metallocryptands.[4] Similar results are obtained using $Pt(PPh_3)_3$. Addition of $Tl(C_2H_3O_2)$ shifts the $^{31}P\{^1H\}$ resonance of $Pt(PPh_3)_3$ from 51.0 ($^1J_{PtP}$ = 4451 Hz) to 34.5 ppm ($^1J_{PtP}$ = 4208 Hz). Likewise, at 25 °C the quartet associated with $Pt(PPh_3)_3$ in the ^{195}Pt NMR spectra shifts from −4550 (q $^1J_{PtP}$ = 4451 Hz) to −4290 ppm (q $^1J_{PtP}$ = 4208 Hz) upon addition of $Tl(C_2H_3O_2)$. The same results are obtained with $Pt(PPh_3)_4$ as the starting material. No changes in color or $^{31}P\{^1H\}$ chemical shift were noted in control experiments where $Na(C_2H_3O_2)$ was added to solutions of either $Pt(PPh_3)_3$ or $Pt(PPh_2py)_3$, and in all cases the product formulation was insensitive to addition stoichiometry. Only the 1:1 adduct was observed based on ^{195}Pt NMR spectra and X-ray crystallography (vide infra).

Similar interactions are observed with the analogous Pd(0) species. The $^{31}P\{^1H\}$ NMR spectrum of $Pd(PPh_3)_3$ with Tl(OAc) exhibits a resonance at 21.9 ppm at −90 °C. Interestingly, unlike **2**, a $^2J_{PTl}$ of 803 Hz is now resolved.

The molecular structures of **1**[10] and **2**[11] determined by X-ray crystallography are similar except that in **1** the asymmetric unit contains two molecules, and in **2** the acetate ion remains coordinated to Tl(I). As seen in Figures 1 and 2, each structure contains a trigonally coordinated Pt(0) center with short Pt−Tl separations of 2.8888(5) and 2.9096(6) Å for the cations of **1** and 2.8653(4) Å for **2**. This is comparable to the sum of the

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[9] ^{205}Tl spectra (288.861 MHz) were referenced vs $TlNO_3$(aq). Low-temperature ^{205}Tl NMR was not possible with use of this probe.

[10] Crystal data for **1** ($C_{102}H_{84}N_8O_6P_6Pt_2Tl_2$): $M = 2502.51$, triclinic, $a = 14.454(2)$ Å, $b = 17.324(3)$ Å, $c = 19.754(2)$ Å, $\alpha = 106.09(1)°$, $\beta = 99.42(1)°$, $\gamma = 102.09(1)°$, $V = 4515(1)$ Å^3, $T = 140$ K, space group $P1$, $Z = 2$, μ(Mo K) = 6.813 mm^{-1}, 50263 reflections measured, 20692 unique ($R_{int} = 0.0537$), $R1(I > 2\sigma) = 0.050$ and $wR2 = 0.1082$. Calcd. elemental anal.: C, 48.95; H, 3.38; N, 4.48: Found: C, 48.86; H, 3.18; N, 4.47.

[11] Crystal data for **2** ($C_{54.25}H_{48}N_3O_{2.75}P_3PtTl$): $M = 1278.33$, triclinic, $a = 11.147(1)$ Å, $b = 11.436(1)$ Å, $c = 20.674(2)$ Å, $\alpha = 101.015(2)°$, $\beta = 95.791(2)°$, $\gamma = 97.056(2)°$, $V = 2546.6(4)$ Å^3, $T = 140$ K, space group $P\bar{1}$, $Z = 2$, μ(Mo K) = 6.042 mm^{-1}, 34689 reflections measured, 11641 unique ($R_{int} = 0.0370$), $R1(I > 2\sigma) = 0.042$ and $wR2 = 0.113$.

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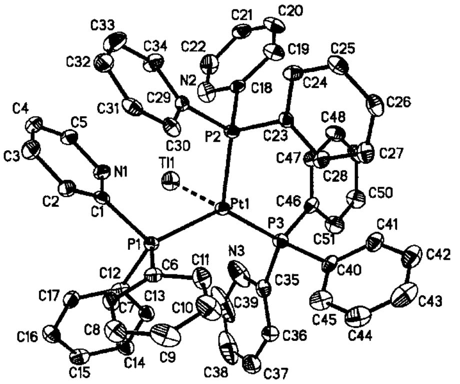

Figure 1. Thermal ellipsoid plot (40%) showing the Pt(1) containing cation of **1**. Selected bond lengths (Å) and angles (deg): Pt(1)−Tl(1) 2.8888(5), Pt(1)−P(1) 2.297(2), Pt(1)−P(2) 2.280(2), Pt(1)−P(3) 2.281(2), P(1)−Pt(1)−P(2) 110.12(7), P(1)−Pt(1)−P(3) 129.15(7), P(2)−Pt(1)−P(3) 120.40(7),

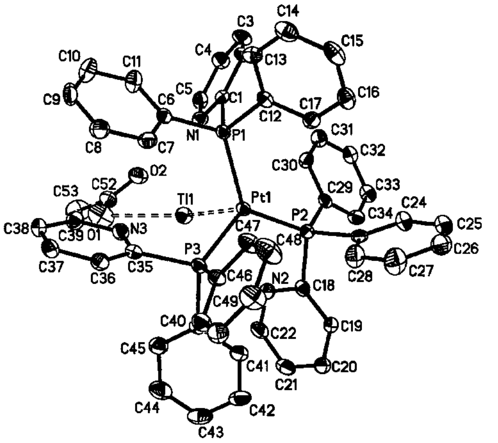

Figure 2. Thermal ellipsoid plot (40%) of **2**. Selected bond lengths (Å) and angles (deg): Pt(1)−Tl(1) 2.8653(4), Pt(1)−P(1) 2.270(1), Pt(1)−P(2) 2.283(1), Pt(1)−P(3) 2.276(1), Tl(1)−O(1) 2.708(6), P(1)−Pt(1)−P(2) 125.31(5), P(1)−Pt(1)−P(3) 115.55(5), P(2)−Pt(1)−P(3) 118.44(5).

covalent bond radii of Pt and Tl (2.78 Å) and close to the separations of ~2.79 Å seen in the related metallocryptates, indicating that the interactions in **1** and **2** are genuine attractive interactions. The nature of this attraction can be rationalized in a manner analogous to that described by Fackler and co-workers[12] for $AuTl(CH_2P(S)Ph_2)_2$ and the closely related Pt_2Tl-metallocryptands[4] reported earlier.

In **1** and **2**, the P−Pt−P angles deviate from the ideal 120°, yet the sum is nearly 360°. Similar to the structure of $Pt(PPh_3)_3$,[13] the Pt centers are slightly distorted out of the phosphorus plane and displaced toward the Tl(I) ion by 0.049 and 0.076 Å for Pt(1) and Pt(2) of **1** and by 0.110 Å for **2**. In **1** the closest contact to a N atom is 2.778(1) Å and the longest is 3.460(1) Å, while in **2** these separations range from 2.884(1) to 3.421(1) Å.[7] As seen in Figure 2 the acetate ion remains coordinated to Tl(1) with the Tl(1)−O(1) separation of 2.798(6) Å. However, in **1** the NO_3^- ions are noninteracting, and the shortest O−Tl contacts are ~2.90 Å for each Tl^+ ion.

FAB-mass spectra (Supporting Information) of both **1** and **2** are nearly identical and show that the Pt(0)−Tl(I) unit remains intact in the gas phase. The spectra clearly show peaks corresponding to $[Pt(PPh_2py)_3Tl]^+$ and to the Tl-free material with the proper isotopomer ratios. The most intense peak centered at 926 amu assigned to $[Pt(PPh_2py)_2Tl]^+$ indicates that ligand loss is preferred over Tl^+ ion dissociation. Peaks assigned to $[Pt(PPh_2py)_2]^+$, $[Pt(PPh_2py)Tl]^+$, and $[Pt(PPh_2py)]^+$ are easily identified. Similar results are seen for $[Pt(PPh_3)_3Tl]^+$, but the peaks are much less intense. No binding of either acetate or nitrate ion was observed in any spectra.

In solution **1** and **2** appear orange in color. Each shows absorptions attributable to $\pi-\pi^*$ transitions between 275 and 375 nm and a large tailing band that extends into the visible. Because of the dynamic nature of these complexes and the air sensitivity of $Pt(PPh_2py)_3$ reliable extinction coefficients could not be determined. In the solid state (Nujol mull) a band at ~500 nm is nearly resolved for **1**. Like $Pt(PPh_3)_3$,[15] solutions of $Pt(PPh_2py)_3$ are weakly emissive; however, no emission could be detected from either the solid or a room temperature solution of either **1** or **2**. A similar behavior is noted in the related metallocryptands.[4]

Pt(0) and Pd(0) complexes find application in organic synthesis and catalysis,[16−18] and it has been shown that in situ addition of Tl(I) salts to some Pd(0)-catalyzed reactions is an efficient method for controlling the regioselectivity[19] and rate[20,21] of catalysis. In the past decade, the formation of a Tl−Pd alloy has been implicated in the selective control of Tl-modified palladium catalysts used in hydrogenation[22] and hydrodechlorination.[23] Only very recently the implications of relativistic effects in coordination, chemisorption, and catalysis have been realized.[24,25] The metallophilic interactions observed in **1** and **2** may be relativistic in nature, although further investigation is warranted.

Our results suggest that the role of metallophilic interactions in Pt(0) or Pd(0) catalysis may be larger than previously thought. We are continuing our systematic investigation of these zerovalent systems and the consequences of metallophilic interactions in catalysis, which may lead to synthetically useful reactions.

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Supporting Information Available: Mass spectral data and complete crystal structural data for **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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