An Unbridged Platinum(III) Dimer with Added Chloro Ligands in Equatorial Sites, $[Pt_2Cl_2(phpy)_4]$ (Hphpy = phenylpyridine), Synthesized by an Oxidation with Aurous Complex

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An unsupported platinum(III) dimer having added chloro ligands at equatorial sites and novel axial-equatorial chelate ligands, $[Pt_2Cl_2(phpy)_4]$ (Hphpy = phenylpyridine) was obtained from an oxidative addition reaction of $[Pt(phpy)_2]$ with $[AuCl(SMe_2)]$.

The chemistry involving platinum(III) has centered mainly around the development of platinum dimers with a metal–metal (d^7–d^7) bond[1] except for $[Pt^{III}(C_6Cl_5)_4]^-$.[2] Many examples of platinum(III) dimers have been reported since Muraveiskaya and co-workers first reported the structure of $K_2[Pt_2(SO_4)_4(H_2O)_2]$.[3] While most of these complexes have bridging ligands, the X-ray structure of four dimers without bridging ligand have been reported.[4–6] Natile and co-workers suggest that platinum(III) complexes may sometimes be an important intermediate in the oxidation of platinum(II) complexes to platinum(IV) complexes,[5] and in this case, the platinum(III) complexes would not have any bridging ligands. Heath and co-workers prepared the platinum(III) dimers $[Pt_2Cl_2(\alpha\text{-dioximato})_2]$[6] and $[Pt_2Cl_2(\beta\text{-diketonato})_2]$[7] by the partial oxidative addition of platinum(II) bis-chelate complexes but only the α-dioximato complex structure has been reported. In both cases, the addition of chloro ligands occurred at the axial sites and all of the chelating ligands are in the equatorial positions. We, now, report the synthesis of an unsupported platinum(III) dimer, $[Pt_2Cl_2(phpy)_4]$ (Hphpy = 2-phenylpyridine) with the added chloro ligands in equatorial positions.

When $[Pt(phpy)_2]$ (**1**) was mixed with an equimolar amount of $[AuCl(SMe_2)]$ in CH_2Cl_2, metallic gold precipitated upon the oxidation of **1**. This is quite different from the similar reaction involving Ag^+ or Cd^{2+} in place of $[AuCl(SMe_2)]$, in which Pt → M dative bonds form (vide infra). The product was isolated with a low yield using column chromatography.[8] ESIMS was used to determine the formula, $[Pt_2Cl_2(phpy)_4]$ (**2**), and two sets of phpy peaks in the ^1H NMR spectrum suggested that the chloro ligands were not in axial position as found in other complexes. X-ray structural analysis of $\mathbf{2}\cdot 4CH_2Cl_2$[9] confirmed that the chloro ligands are in equatorial positions, Figure 1a. The dimer has an approximate 2-fold axis bisecting the Pt–Pt bond and each phpy has adopted a chelating confirmation. However, each ligand coordinates in a different fashion. One has coordinated in an axial and an equatorial position (ax–eq phpy), and the other in two equatorial sites (eq–eq phpy). Two Pt–C bonds on each platinum are in equatorial positions with a *cis* arrangement. Thus, the two Pt–C bonds and one Pt–Pt bond occupy a facial site of the platinum octahedron to avoid any pairs of strong *trans*-effectors, i.e. Pt–C and Pt–Pt bonds, being colinear. The remaining equatorial sites are occupied by chloro ligands, introduced by oxidative addition. This is in contrast to other platinum(III) dimers in that the chloro ligands occupy the axial positions.[7] The equatorial coordination of the chloro ligands helps to alleviate the steric repulsion between *o*-protons of adjacent phpy ligands. In complex **1**, the phpy plane is distorted (mean deviation 0.15 Å) in a bow-like fashion due to the repulsion,[10] but in **2**, the phpy ligands are almost planer with mean deviations from the best plane of 0.04 Å. The Pt–Pt distance (2.7269(3) Å) in **2** is slightly longer, about 0.15 to 0.3 Å, than those of the supported dimers and similar to other unsupported platinum(III) dimers (2.694(1)–2.765(2) Å).[4–6] The difference is probably due to the lack of supporting bridging ligands combined with steric repulsion between the equatorial ligands. The long Pt–N distances in the axial positions (2.158(4) and 2.165(5) Å) are due to the *trans* influence of the Pt–Pt bond and the long equatorial Pt–N lengths

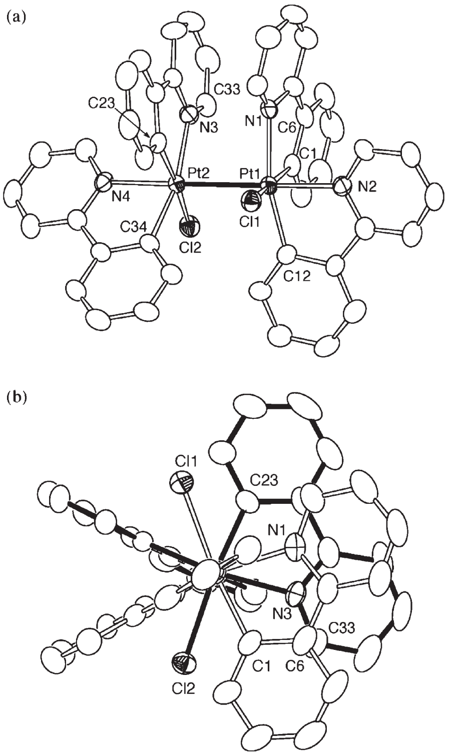

Figure 1. ORTEP drawing of $[Pt_2Cl_2(phpy)_4]$ (**2**). (a) Side view. (b) Projection view along the Pt–Pt bond. Relevant bond distances (Å) : Pt(1)–Pt(2) 2.7269(3), Pt(1)–Cl(1) 2.470(2), Pt(2)–Cl(2) 2.467(1), Pt(1)–C(1) 2.001(6), Pt(2)–C(23) 1.988(6), Pt(1)–C(12) 2.024(6), Pt(2)–C(34) 2.034(5), Pt(1)–N(1) 2.143(5), Pt(2)–N(3) 2.133(5), Pt(1)–N(2) 2.165(5), Pt(2)–N(4) 2.158(4).

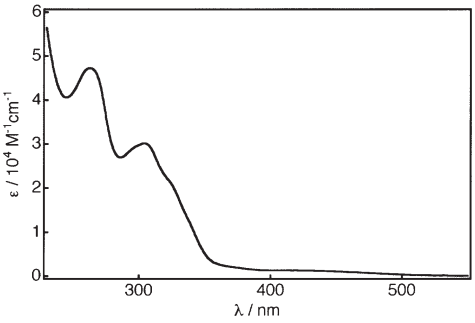

Figure 2. UV–vis spectra of $[Pt_2Cl_2(phpy)_4]$ in CH_3CN.

(2.133(5) and 2.143(5) Å) are due to *trans* influence of the Pt–C bond. As well the long Pt–Cl lengths (2.467(1) and 2.470(2) Å) are due to the *trans* influence of the Pt–C bond. To alleviate steric repulsion, the complex is staggered along the Pt–Pt bond with a Cl–Pt–Pt–Cl dihedral angle of 141.01(5)° (Figure 1b). The two phpy ligands are almost parallel, but there is a small amount of repulsion with a dihedral angle of 19.7°. The shortest C–C contact between the two ligands is 2.98(1) Å (C6–C33).

A solution of **2** is stable in the dark for at least a few days. The stability is similar to dioximato complex, $[Pt_2(\alpha\text{-dioximato})_2Cl_2]$,[6] but different from other unbridged platinum(III) dimers which undergo disproportionation within half an hour[4] or immediately.[5,7] The UV–vis spectrum of **2** in acetonitrile shows intense bands around 263 nm (ε 47000) and 304 nm (ε 30000) with weak sholder at ca. 420 nm (ε 1300), Figure 2. Although some ligand (phpy) based transition may obscure, the bands tentatively assigned according to the assignment of phosphate, sulfate, or pyrophoshite bridged platinum(III) dimer. One of two intense bands is assigned to $\sigma(L) \rightarrow \sigma^*$ and weak shoulder to $\pi \rightarrow \sigma^*$ transition. In contrast with parent platinum(II) mononuclear complex, $[Pt(phpy)_2]$, possesses strong emission at room temperature, **2** dose not show such emission.

The ^{195}Pt NMR spectrum of **2** in DMF/DMSO-d_6(3:1) shows a singlet at -736 ppm vs K_2PtCl_4/D_2O, Figure 3. While the chemical shift lies between $[Pt^{II}(phpy)_2]$ (-1926 ppm) and $[Pt^{IV}Cl_2(phpy)_2]$ ($+240$ ppm), the peak is shifted closer to the platinum(IV) complex. This is similar to the β-diketonato and α-dioximato systems.[7] The major reason is because the ^{195}Pt chemical shifts depend both on the coordination number around the metal as well as the oxidation state of the metal. When the Pt–Pt bond is included, the coordination sphere resembles the platinum(IV) complex more. As well, the Pt $4f_{7/2}$ binding energy (74.1 eV), determined from X-ray photoelectron spectroscopy, shows a similar phenomenon in that the value is closer to the platinum(IV) complex $[Pt^{IV}Cl_2(phpy)_2]$ (75.0 eV) than the platinum (II) complex $[Pt^{II}(phpy)_2]$ (72.6 eV).

Finally, It is noteworthy to compare the present reaction with reactions of $[Pt(phpy)_2]$ with other d^{10} metal ions. In contrast to aurous complex $[AuCl(SMe_2)]$, the reactions of $[Pt(phpy)_2]$ with Ag^I or Cd^{II} compounds give complexes with Pt → M dative bonds[11,12] instead of oxidative addition. The phpy ligands in the $[Pt(phpy)_2]$ exert high ligand field due to carbon coordination and thus can make strong Pt → M dative bonds with metal ions having appropriate acceptor orbital. However, if the energy of acceptor orbital is rather low, an electron transfer occurs from platinum to the acceptor, resulting in the oxidation of platinum complex.

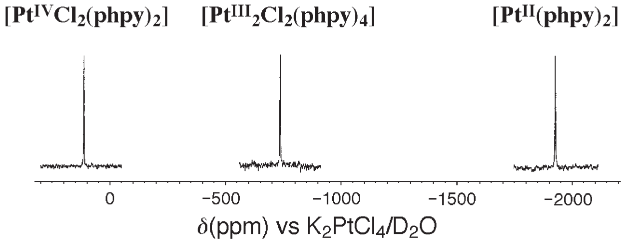

Figure 3. ^{195}Pt NMR spectra of $[Pt^{II}(phpy)_2]$, $[Pt_2{}^{III}Cl_2(phpy)_4]$, and $[Pt^{IV}Cl_2(phpy)_2]$.

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8 To a CH_2Cl_2 solution (5 mL) of $[Pt(phpy)_2]$ (50 mg, 0.1 mmol) was added a CH_2Cl_2 solution (5 mL) of $AuClSMe_2$ (30 g, 0.1 mmol) at −80 °C, and the resulting solution was warmed to room temperature in the dark, during which time the color of the solution changed from orange to yellow and a black precipitate formed. The precipitate was removed by filtration and the solvent was evaporated. The crude compound was separated by a gel-filtration column (Bio-beads XS-3) using CH_2Cl_2 as the eluent, and main yellow band was collected and evaporated to yield $[Pt(phpy)_2Cl]_2$ (20 mg, yield 37%). Anal. Calcd for $\mathbf{2}\cdot 1/2CH_2Cl_2\cdot H_2O$: C, 46.95; H, 3.10; N, 4.92%. Found: C, 47.06; H, 3.47; N, 4.92%. ^1H NMR (DMSO-d_6, 300 Hz, TMS): $\delta =$ 5.781 (d, 1H), 6.770–6.850 (m, 3H), 6.923–6.994 (m, 3H), 7.158 (d, 1H, $J_{Pt\text{–}H} = 48$ Hz), 7.290 (d, 1H), 7.622 (d, 1H), 7.691–7.795 (m, 3H), 7.849 (d, 1H), 8.004 (d, 1H), 9.204 (d, 1H). ESIMS: $m/z = 1077$ (calcd.1078).

9 Crystal of $[Pt(phpy)_2Cl]_2\cdot 4(CH_2Cl_2)$ for X-ray analysis was obtained by slow evaporation from a CH_2Cl_2 solution. Crystal data : $C_{48}H_{40}Cl_{10}N_4Pt_2$, $M_r = 1417.52$, Monocinic, $a = 16.7022(6)$, $b = 18.1145(6)$, $c = 18.0675(6)$ Å, $\beta = 115.061(1)°$, $V = 4951.7(3)$ Å^3, $T = 213(2)$ K, space group $P2_1/n$ (no, 14), $Z = 4$, $\mu = 6.223$ mm^{-1}, 37325 reflections measured, 11409 unique ($R_{int} = 0.0801$), $R_1 = 0.036$ (for $I > 2\sigma(I)$), $wR_2 = 0.1134$ (for all data).

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