

# Methyl(hydrido)platinum(IV) Complexes That Are Resistant to Reductive Elimination, Including the First ( $\mu$ -Hydrido)diplatinum(IV) Complex

Geoffrey S. Hill and Richard J. Puddephatt\*

Department of Chemistry  
The University of Western Ontario  
London, Ontario, Canada N6A 5B7

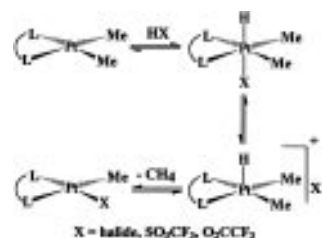
Received April 29, 1996

The first examples of methyl(hydrido)platinum(IV) complexes, which are proposed intermediates in the protonolysis of the methylplatinum(II) bond and in methane activation by platinum(II), were reported very recently (Scheme 1).<sup>1</sup> In most cases, these complexes [PtHXMe<sub>2</sub>(LL)], where LL is a bidentate nitrogen-donor ligand and X = halide, SO<sub>3</sub>CF<sub>3</sub>, or O<sub>2</sub>CCF<sub>3</sub>, are characterized only in solution at low-temperature since, at room temperature, they decompose rapidly. The mechanism of decomposition is proposed to involve dissociation of the ligand X *trans* to the hydride, to form a five-coordinate intermediate which then undergoes easy reductive elimination of methane (Scheme 1).<sup>1b–d</sup>

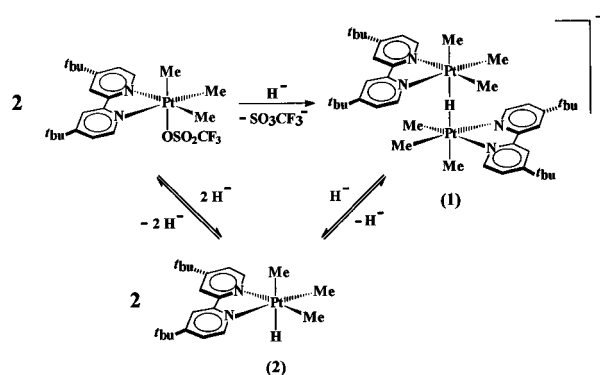
If this mechanism is correct, a complex [PtHXMe<sub>2</sub>(LL)] should be stable to reductive elimination of methane if the group X cannot easily undergo dissociation from platinum. This suggested that a complex [PtHMe<sub>3</sub>(LL)], in which all ligands are strongly bound, would be stable to reductive elimination. In addition, this complex would have mutually *trans* hydrido and methyl ligands (both with large *trans* effects) and so should, by analogy with the related tetramethylplatinum(IV) complex [PtMe<sub>4</sub>(NN)] (NN = 2,2'-bipyridine),<sup>2</sup> give a rich reaction chemistry. Thus the plan was to prepare *fac*-[PtHMe<sub>3</sub>(bu<sub>2</sub>bpy)] (2) (bu<sub>2</sub>bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) from NaBH<sub>4</sub> and *fac*-[PtMe<sub>3</sub>(O<sub>3</sub>SCF<sub>3</sub>)(bu<sub>2</sub>bpy)], with the O<sub>3</sub>SCF<sub>3</sub> ligand acting as a good leaving group (Scheme 2).<sup>3</sup> Although this reaction did occur if a large excess of hydride was present, it proceeded through the unexpected cationic intermediate, [Pt<sub>2</sub>( $\mu$ -H)Me<sub>6</sub>(bu<sub>2</sub>bpy)<sub>2</sub>]<sup>+</sup> (1), which is the first example of a ( $\mu$ -hydrido)diplatinum(IV) complex (Scheme 2).

Treatment of *fac*-[PtMe<sub>3</sub>(O<sub>3</sub>SCF<sub>3</sub>)(bu<sub>2</sub>bpy)]<sup>4</sup> with a stoichiometric amount of NaBH<sub>4</sub> in THF solution affords the cationic [Pt<sub>2</sub>( $\mu$ -H)Me<sub>6</sub>(bu<sub>2</sub>bpy)<sub>2</sub>]<sup>+</sup> (1) which, as the BPh<sub>4</sub><sup>−</sup> salt, can be isolated as a yellow powder in 65% yield. Complex 1 is indefinitely stable at room temperature, both as a solid and in solution, which allowed full characterization by <sup>1</sup>H and <sup>195</sup>Pt NMR spectroscopies.<sup>5</sup>

Scheme 1



Scheme 2



The <sup>1</sup>H NMR spectrum (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of complex 1 shows the expected three aromatic resonances and one *tert*-butyl resonance due to the two equivalent pyridine moieties of the bu<sub>2</sub>bpy ligand. These data rule out the alternative isomer with  $\mu$ -H *trans* to nitrogen, which would have nonequivalent pyridyl groups. There were two methylplatinum resonances in a 2:1 intensity ratio due to the methylplatinum groups *trans* to bu<sub>2</sub>bpy [ $\delta$  = 0.47, <sup>2</sup>J(PtH) = 69.6 Hz] and *trans* to hydride [ $\delta$  = 0.13, <sup>2</sup>J(PtH) = 65.9 Hz], respectively. Both peaks showed a small coupling with the hydrido ligand. The most convincing evidence for a bridging hydrido ligand comes from the low-frequency Pt–H resonance at  $\delta$  = −11.7 with <sup>1</sup>J(PtH) = 442 Hz (Figure 1). The resonance appears as a 1:8:18:8:1 multiplet due to coupling to <sup>195</sup>Pt, thus proving the presence of a Pt<sub>2</sub>( $\mu$ -H) group.<sup>6</sup> This Pt–H resonance is absent in the <sup>1</sup>H NMR spectrum of [Pt<sub>2</sub>( $\mu$ -D)Me<sub>6</sub>(bu<sub>2</sub>bpy)<sub>2</sub>]<sup>+</sup> (1\*), prepared using NaBD<sub>4</sub>. The <sup>2</sup>H{<sup>1</sup>H} NMR spectrum (30.70 MHz, CH<sub>2</sub>Cl<sub>2</sub>) of complex 1\* shows only the expected resonance at  $\delta$  = −11.7 with <sup>1</sup>J(PtD) = 68.4 Hz.<sup>7</sup> The <sup>1</sup>H-coupled <sup>195</sup>Pt NMR spectrum (42.92 MHz, THF-*d*<sub>8</sub>) of 1 contains a doublet at  $\delta$  = −1238 (from K<sub>2</sub>[PtCl<sub>4</sub>] in D<sub>2</sub>O) due to coupling with the bridging hydrido ligand [<sup>1</sup>J(PtH) = 440 Hz], thus proving the presence of only a single  $\mu$ -H ligand. The <sup>195</sup>Pt NMR spectrum (CD<sub>2</sub>-Cl<sub>2</sub>) of [Pt<sub>2</sub>( $\mu$ -D)Me<sub>6</sub>(bu<sub>2</sub>bpy)<sub>2</sub>]<sup>+</sup> (1\*) shows only a broad singlet at  $\delta$  = −1240, since the line width ( $\Delta\nu^{1/2}$  = *ca.* 160 Hz) is greater than the coupling <sup>1</sup>J(PtD).

Complex 1 is stable in solution in common organic solvents. The presence of a large excess of NaBH<sub>4</sub> results in formation of an equilibrium mixture of 1 and 2 equiv of [PtHMe<sub>3</sub>(bu<sub>2</sub>bpy)] (2) (Scheme 2).<sup>8</sup> Under these strongly basic conditions, the complexes decompose slowly with precipitation of metallic platinum, but 2 was readily characterized by <sup>1</sup>H NMR spec-

(1) (a) De Felice, V.; De Renzi, A.; Panunzi, A.; Tesaro, D. J. *Organomet. Chem.* **1995**, 488, C13. (b) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, 14, 4966. (c) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, 117, 9371. (d) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. Personal communication. (e) Canty, A. J. Personal communication.

(2) (a) Hux, J. E.; Puddephatt, R. J. *Inorg. Chim. Acta.* **1985**, 100, 1. (b) Hux, J. E.; Puddephatt, R. J. *J. Organomet. Chem.* **1988**, 346, C31.

(3) Note that this route is formally H<sup>−</sup> + Pt(IV) → Pt(IV)–H, in contrast to the route H<sup>+</sup> + Pt(II) → Pt(IV)–H used previously.<sup>1</sup>

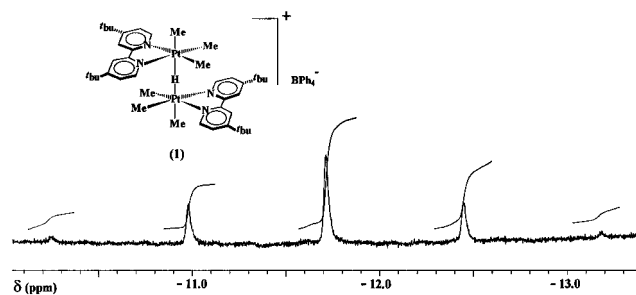
(4) (a) [PtMe<sub>3</sub>(O<sub>3</sub>SCF<sub>3</sub>)(bu<sub>2</sub>bpy)] is conveniently prepared by reaction of [PtMe<sub>2</sub>(bu<sub>2</sub>bpy)]<sup>4b</sup> with MeO<sub>3</sub>SCF<sub>3</sub> in ether at room temperature. NMR in CDCl<sub>3</sub>:  $\delta$ (<sup>1</sup>H) = 0.66 [d, 4H, <sup>3</sup>J(H<sup>6</sup>H<sup>5</sup>) = 84 Hz, PtMe *trans* to triflate]; 1.26 [s, 6H, <sup>2</sup>J(PtH) = 67 Hz, PtMe *trans* to bu<sub>2</sub>bpy]. (b) Achar, S.; Scott, J. D.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1993**, 12, 4592. Note that [PtMe<sub>2</sub>(bu<sub>2</sub>bpy)] is stable in the presence of NaBH<sub>4</sub>.

(5) Spectroscopic data for 1 as the BPh<sub>4</sub><sup>−</sup> salt. NMR (300 MHz) in CD<sub>2</sub>Cl<sub>2</sub>:  $\delta$ (<sup>1</sup>H) = 8.21 [d, 4H, <sup>3</sup>J(H<sup>6</sup>H<sup>5</sup>) = 6.3 Hz, <sup>3</sup>J(PtH) = 14.0 Hz, H<sup>6</sup>]; 8.09 [d, 4H, <sup>4</sup>J(H<sup>3</sup>H<sup>5</sup>) = 2.0 Hz, H<sup>3</sup>]; 7.51 [dd, 4H, <sup>4</sup>J(H<sup>5</sup>H<sup>6</sup>) = 1.9 Hz, <sup>3</sup>J(H<sup>5</sup>H<sup>6</sup>) = 6.2 Hz, H<sup>5</sup>]; 1.49 [s, 36H, <sup>4</sup>bu]; 0.47 [s, 12H, <sup>2</sup>J(PtH) = 69.6 Hz, <sup>3</sup>J(HH) = *ca.* 1.0 Hz, Pt–Me (*trans* to bu<sub>2</sub>bpy)]; 0.13 [s, 6H, <sup>2</sup>J(PtH) = 65.9 Hz, <sup>3</sup>J(HH) = *ca.* 1.0 Hz, Pt–Me (*trans* to H)]; −11.7 [s, 1H, <sup>1</sup>J(PtH) = 442 Hz, Pt–H]. <sup>195</sup>Pt NMR (42.92 MHz) in THF-*d*<sub>8</sub>:  $\delta$  = −1238 [d, <sup>1</sup>J(PtH) = 440 Hz]. We draw 1 with a linear PtHPT bond though M<sub>2</sub>( $\mu$ -H) groups are usually bent. The degree of bending must be small in this case due to steric effects between substituents on platinum.

(6) (a) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 516. (b) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlovic-Muir, L. J.; Muir, K. W.; Puddephatt, R. J.; Thompson, M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 299.

(7)  $\gamma_H/\gamma_D$  = 6.51  $\approx$  <sup>1</sup>J(PtH)/<sup>1</sup>J(PtD) = 6.47.

(8) Spectroscopic data for 2. NMR (300 MHz) in acetone-*d*<sub>6</sub>:  $\delta$ (<sup>1</sup>H) = 8.58 [d, 2H, <sup>3</sup>J(H<sup>6</sup>H<sup>5</sup>) = 6.0 Hz, H<sup>6</sup>]; 8.51 [d, 2H, <sup>4</sup>J(H<sup>3</sup>H<sup>5</sup>) = 2.0 Hz, H<sup>3</sup>]; 7.85 [dd, 2H, <sup>4</sup>J(H<sup>3</sup>H<sup>5</sup>) = 2.0 Hz, <sup>3</sup>J(H<sup>5</sup>H<sup>6</sup>) = 6.0 Hz, H<sup>5</sup>]; 1.45 [s, 18H, <sup>4</sup>bu]; 0.75 [s, 6H, <sup>2</sup>J(PtH) = 66.0 Hz, Pt–Me (*trans* to bu<sub>2</sub>bpy)]; −0.79 [s, 3H, <sup>2</sup>J(PtH) = 43.0 Hz, Pt–Me (*trans* to H)]; −7.0 [s, 1H, <sup>1</sup>J(PtH) = 805 Hz, Pt–H]. Complex 2 is also formed on reaction of 1 with PPh<sub>3</sub> in refluxing acetone and is stable under these conditions.



**Figure 1.** Low-frequency region of the  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2$  at  $25^\circ\text{C}$ . The 1:8:18:8:1 intensity ratio in the multiplet due to  $^{195}\text{Pt}^1\text{H}$  coupling is characteristic of a doubly bridging hydride.

troscopy (acetone- $d_6$ ) and appears stable to reductive elimination of methane, which would give the stable complex  $[\text{PtMe}_2(\text{bu}_2\text{bpy})]$ .<sup>4b</sup> Again, the two equivalent bipyridine moieties of the  $\text{bu}_2\text{bpy}$  give rise to three aromatic and one *tert*-butyl resonance. The methylplatinum resonances appear in a 2:1 ratio at  $\delta = 0.75$  (*trans* to  $\text{bu}_2\text{bpy}$ ) and  $-0.79$  (*trans* to H) with  $^2J(\text{PtH}) = 66.0$  and  $43.0$  Hz, respectively. Note that the methyl group *trans* to the hydrido ligand has a very low value of  $^2J(\text{PtH})$ , which is significantly smaller than that of the methylplatinum ligand *trans* to the bridging hydride in complex **1** [ $^2J(\text{PtH}) = 65.9$  Hz] but is similar to that of the mutually *trans* methylplatinum ligands in  $[\text{PtMe}_4(\text{bpy})]$  [ $^2J(\text{PtH}) = 44$  Hz].<sup>2</sup> Thus the terminal hydrido ligand in complex **2** has a stronger *trans* influence than the bridging hydride in **1**. The Pt–H ligand resonates at  $\delta = -7.0$  with  $^1J(\text{PtH}) = 805$  Hz. This resonance appears as a 1:4:1 multiplet due to coupling to  $^{195}\text{Pt}$ , thus proving the presence of a terminal Pt–H group. This coupling constant has approximately twice the magnitude of that found in **1**, which is reasonable since the s-electron density of the hydride is shared between two platinum centers in **1**. Nevertheless, the value of  $^1J(\text{PtH})$  for complex **2** is still significantly smaller than that of  $[\text{PtHMe}_2\text{X}(\text{bu}_2\text{bpy})]$  (X = Cl, Br, I;  $^1J(\text{PtH}) = 1589.7$ ,  $1630.5$ ,  $1655.5$ , respectively) again illustrating the effect of the *trans* methyl ligand.<sup>1b</sup> The hydride ligand in **2** is *trans* to the strong  $\sigma$ -donor methyl group and so is expected to be much more

hydridic in nature than in the latter complexes. It is presumably this hydridic character that leads to reaction of **2** with  $[\text{PtMe}_3(\text{O}_3\text{SCF}_3)(\text{bu}_2\text{bpy})]$  with displacement of triflate to give the stable complex **1**.<sup>9</sup>

In a very recent study, it was shown that the protonolysis of the Pt–C bond by DCl in  $[\text{PtMe}_2(\text{tmeda})]$  (tmeda = *N,N,N',N'*-tetramethylethylenediamine) proceeds through the detectable Pt(IV)-deuteride,  $[\text{PtD}(\text{Cl})\text{Me}_2(\text{tmeda})]$  and that deuterium incorporation into the methylplatinum groups of  $[\text{PtD}(\text{Cl})\text{Me}_2(\text{tmeda})]$  occurs faster than the reductive elimination of methane.<sup>1c,d</sup> It was proposed that this occurred by dissociation of the chloride ligand to form a five-coordinate complex as in Scheme 1, followed by easy, reversible formation of a  $\text{Pt}(\text{CH}_3\text{D})$   $\sigma$ -complex.<sup>1d</sup> Since neither  $[\text{PtDMe}_3(\text{bu}_2\text{bpy})]$  nor  $[\text{Pt}_2(\mu\text{-D})\text{Me}_6(\text{bu}_2\text{bpy})_2]^+$  can readily undergo ligand dissociation to form the required five-coordinate intermediate, no isotopic H–D exchange within PtDMe groups would be expected. This prediction was upheld; for example, both the  $^1\text{H}$  and  $^2\text{H}\{^1\text{H}\}$  NMR spectra of **1\*** showed the absence of deuterium incorporation into the MePt groups or of H into the PtD groups, even after several days in solution.

In conclusion, the new methyl(hydrido)platinum(IV) complexes  $[\text{PtHMe}_3(\text{bu}_2\text{bpy})]$  (**2**) and  $[\text{Pt}_2(\mu\text{-H})\text{Me}_6(\text{bu}_2\text{bpy})_2]^+$  (**1**), which have no ligand which can easily dissociate, are thermally stable to reductive elimination of methane and to isotopic exchange within PtD(CH<sub>3</sub>) groups, thus giving strong support to the theory that both reactions occur within a five-coordinate intermediate  $[\text{PtHMe}_2(\text{bu}_2\text{bpy})]^+$ .<sup>1</sup> It is the strongly hydridic nature of **2** which leads to formation of the unique ( $\mu$ -hydrido)-diplatinum(IV) complex **1**. The remarkable thermal stability of **1** is probably due to three factors, namely, the absence of an easily dissociable ligand (see above discussion), the less hydridic nature compared to **2**, and steric protection of the hydride ligand.

**Acknowledgment.** We thank the NSERC (Canada) for financial support to R.J.P. and a postgraduate scholarship to G.S.H.

JA961404N

(9) The ligating ability of terminal hydrides in the synthesis of  $\mu$ -hydrido complexes has been exploited before. Venanzi, L. M. *Coord. Chem. Rev.* **1982**, 43, 251.