Hydridodimethylplatinum(IV) Complexes with Bis(pyridine) Ligands: Effect of Chelate Ring Size on Reactivity

Fenbao Zhang, Ernest M. Prokopchuk, Michael E. Broczkowski, Michael C. Jennings, and Richard J. Puddephatt*

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

Received November 15, 2005

The effect of changing the bite angle of the dipyridyl ligand LL on the reactivity of the dimethylplatinum(II) complexes [$PtMe_2$(LL)] has been studied, by comparing complexes with the ligands LL = di-2-pyridylamine (DPA) or di-2-pyridyl ketone (DPK), which form a six-membered chelate ring, to compounds with 2,2′-bipyridyl derivatives, which form a five-membered chelate ring. The complex [$PtMe_2$(DPA)] undergoes easy oxidative addition of methyl iodide to give the corresponding platinum(IV) complex [$PtIMe_3$(DPA)]. Both [$PtMe_2$(DPA)] and [$PtMe_2$(DPK)] are protonated by acids HX at low temperature to give the hydridodimethylplatinum(IV) complexes [$PtHXMe_2$(NN)] and [$PtH(S)Me_2$(NN)]X (S = solvent), which can exist in two isomeric forms with H trans to X or N. The structure of the complex [$PtHClMe_2$(DPK)] was determined crystallographically. In a solution containing excess CD_3OD, extensive hydrogen/deuterium exchange occurs into the methylplatinum groups and methane product at low temperature, indicating very easy reversibility of the exchange between hydridomethylplatinum(IV) and (methane)platinum(II) complexes. The hydridomethylplatinum(IV) complexes reductively eliminate methane at room temperature in solution but have significantly higher thermal stability and undergo more extensive H−D exchange than when NN = 2,2′-bipyridyl. The reaction of [$PtMe_2$(DPA)] with excess HCl gave [$PtCl_2$(DPA)], and the reaction of [$PtMe_2$(DPK)] with excess CF_3SO_3H gave the aqua complex [$Pt(OH_2)_2$(DPK)](CF_3SO_3)$_2$ or the binuclear hydroxo complex [$Pt_2(\mu$-OH)$_2$(DPK)$_2$](CF_3SO_3)$_2$, depending on the experimental conditions.

Introduction

The chemistry of alkylhydridoplatinum(IV) complexes,[1−10] particularly the equilibration with alkane complexes of platinum(II), has given important insights into the mechanism of C−H bond activation by electrophilic organoplatinum(II) complexes.[11−17] Most methylhydridoplatinum(IV) complexes have been prepared by protonation of the corresponding methylplatinum(II) complexes.[3] Complexes of the type [$PtHXMe_2$(LL)], with LL typically a bidentate diamine or dimine ligand, are short-lived intermediates,[1−4] which are most readily detected by NMR at low temperature, but stable derivatives have been formed by use of a strongly coordinating *fac*-tridentate ligands,

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

(2) (a) Belluco, U.; Giustiniani, M.; Graziani, M. *J. Am. Chem. Soc.* **1967**, *89*, 6494. (b) Jawad, J. K.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1977**, 892. (c) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2119. (d) Kalberer, E. W.; Houlis, J. F.; Roddick, D. M. *Organometallics* **2004**, *23*, 4112.

(3) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219*−*221*, 157.

(4) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (b) Zhang, F.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2004**, *23*, 1396.

(5) (a) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684. (b) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845. (c) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724. (d) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2001**, *20*, 1709. (e) Norris, C. M.; Reinartz, S.; White, P. S.; Templeton, J. L. *Organometallics* **2002**, *21*, 5649. (f) Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 8614.

(6) (a) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235. (b) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 11900. (c) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804. (d) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442.

(7) (a) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946. (b) Hill, G. S.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 8745. (c) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209. (d) Prokopchuk, E. M.; Jenkins, H. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 2861. (e) Hinman, J. G.; Baar, C. R.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 563. (f) Prokopchuk, E. M.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 563. (g) Ong, C. M.; Jennings, M. C.; Puddephatt, R. J. *Can. J. Chem.* **2003**, *81*, 1196. (h) Prokopchuk, E. M.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 787. (i) Jenkins, H. A.; Klempner, M. J.; Prokopchuk, E. M.; Puddephatt, R. J. *Inorg. Chim. Acta* **2003**, *352*, 72.

(8) Fekl, U.; Zahl, A.; van Eldik, R. *Organometallics* **1999**, *18*, 4156.

(9) (a) Vedernikov, A. N.; Caulton, K. G. *Angew. Chem., Int. Ed.* **2002**, *41*, 4102. (b) Vedernikov, A. N.; Fettinger, J. C.; Mohr, F. *J. Am. Chem. Soc.* **2004**, *126*, 11160. (c) Vedernikov, A. N.; Binfield, S. A.; Zavalij, P. Y.; Khusnutdinova, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 82.

(10) (a) Lo, H. C.; Haskel, A.; Kapon, M.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 3226. (b) Iron, M. A.; Lo, H. C.; Martin, J. M. L.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 7014.

(11) (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (b) Webster, D. E. *Adv. Organomet. Chem.* **1997**, *15*, 147. (c) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2181. (d) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550. (e) Crabtree, R. H. *Dalton Trans.* **2001**, 2437. (f) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (g) Fekl, U.; Goldberg, K. I. *Adv. Inorg. Chem.* **2003**, *54*, 259. (h) Labinger, J. A. *J. Mol. Catal.* **2004**, *220*, 27.

(12) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560.

(13) (a) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. (b) Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *270*, 467. (c) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378. (d) Procelewska, J.; Zahl, A.; van Eldik, R.; Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 2808. (e) Iverson, C. N.; Carter, C. A. G.; Baker, R. T.; Scollard, J. D.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 12674. (f) Driver, T. G.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2005**, *24*, 3644.

10.1021/om050982m CCC: $33.50
Publication on Web 02/24/2006

Chart 1. Hydridoplatinum(IV) Complexes

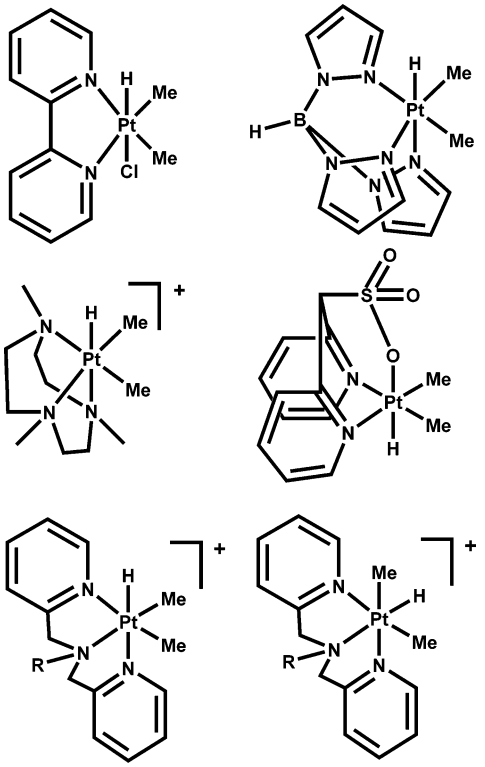
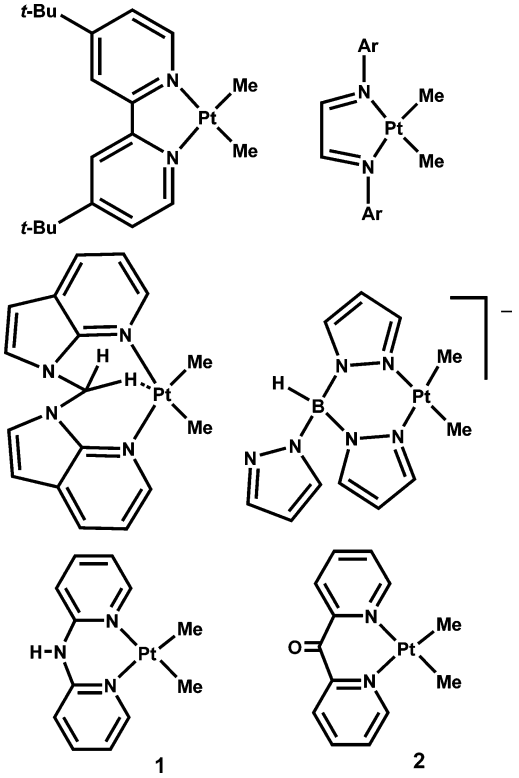


Chart 2. Dimethylplatinum Complexes



such as the anionic tris(pyrazol-1-yl)borate and bipyridylmethylsulfonate or the neutral bis(2-pyridylmethyl)amine and 1,4,7-triazacyclononane (Chart 1).[5−10] The complexes $[PtHXMe_2(LL)]$ decompose by dissociation of the anionic ligand X^- followed by reductive elimination of methane from the 5-coordinate intermediate $[PtHMe_2(LL)]^+$, and the ligand dissociation is more difficult in the complexes $[PtHMe_2(LLL)]^+$, where LLL is a tridentate ligand.[5−10] Stable complexes with bidentate ligands can be formed if none of the ligands are easily dissociated, such as in the complexes $[PtHMe_3(LL)]$ with LL = 4,4′-di-*tert*-butyl-2,2′-bipyridine, bis(diphenylphosphino)ethane.[6,7]

Alkylhydridoplatinum(IV) complexes are important intermediates in the activation of alkanes by oxidative addition of a C−H bond to platinum(II).[1−17] For the C−H activation reaction to occur easily, the complexes [PtMeX(LL)] and $[PtMe(S)(LL)]^+$ are most reactive if the anionic ligand X^- or solvent molecule S is weakly bound, because the first step involves their displacement by alkane to form the "alkane complex" $[PtMe(R\text{-}H)(LL)]^+$, which can equilibrate with the 5-coordinate platinum(IV) complex $[PtHRMe(LL)]^+$.[11−17] While bidentate ligands do not usually give stable alkylhydridoplatinum(IV) complexes, their platinum complexes have found use in catalysis. A recent example is the use of the complex [Pt(bpym)Cl$_2$] (bpym = 2,2′-bipyrimidyl) in sulfuric acid solution to catalyze the conversion of methane to methyl bisulfate.[12] The catalytic cycle is proposed to involve oxidative addition of a C−H bond of methane to give a hydridomethylplatinum(IV) intermediate as a key step, though electrophilic activation is also considered possible.[12,17]

In efforts to optimize C−H activation by organoplatinum complexes, the design of the supporting ligands is crucially important. Bidentate nitrogen-donor ligands have shown the greatest promise and, in addition to 2,2′-bipyrimidine, the most studied ligands have been the diimines ArN=CHCH=NAr, with bulky aryl groups,[13,14] which have proved to be more reactive than 2,2′-bipyridine and its derivatives.[4,7] All of these ligands form five-membered chelate rings. The bis(7-azaindolyl) ligands form much larger eight- or nine-membered chelate rings, and in the platinum(II) complexes, one side of the square plane is blocked (Chart 2). These ligands give platinum(II) complexes which can activate the C−H bonds of benzene under mild conditions.[16] We have independently studied the effect of increasing the chelate ring size by using the ligands di-2-pyridylamine (DPA) and di-2-pyridyl ketone (DPK). These both form six-membered chelate rings, and previous studies have shown that the ligands are similarly bowed rather than planar in their platinum complexes.[18−20] The electronic effects of the bridging NH group in DPA[18] or C=O group in DPK[19,20] are

(14) (a) Johansson, L.; Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc*. **1999**, *121*, 1974. (b) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc*. **2000**, *122*, 10846. (c) Johansson, L.; Tilset, M. *J. Am. Chem. Soc*. **2001**, *123*, 739. (d) Johansson, L.; Ryan, O. B.; Romming, C.; Tilset, M. *J. Am. Chem. Soc*. **2001**, *123*, 6579. (e) Wik, B. J.; Lersch, M.; Tilset, M. *J. Am. Chem. Soc.* **2002**, *124*, 12116. (f) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471.

(15) (a) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc*. **2003**, *125*, 8870. (b) Thomas, C. M.; Peters, J. C. *Organometallics* **2005**, *24*, 5858.

(16) (a) Song, D.; Wang, S. *Organometallics* **2003**, *22*, 2187. (b) Song, D.; Jia, W. L.; Wang, S. *Organometallics* **2004**, *23*, 1194. (c) Song, D.; Wang, S. *Comments Inorg. Chem.* **2004**, *25*, 1. (d) Zhao, S.-B.; Song, D.; Jia, W.-L.; Wang, S. *Organometallics* **2005**, *24*, 3290.

(17) (a) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478. (b) Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831. (c) Mylvaganam, K.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **2000**, *122*, 2041. (d) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *Organometallics* **2001**, *20*, 2669. (e) Gilbert, T. M.; Hristov, I.; Ziegler, T. *Organometallics* **2001**, *20*, 1183. (f) Kua, J.; Xu, X.; Periana, R. A.; Goddard, W. A., III. *Organometallics* **2002**, *21*, 511. (g) Hristov, I.; Ziegler, T. *Organometallics* **2003**, *22*, 1668.

(18) (a) Romeo, R.; Nastasi, N.; Scolaru, L. M.; Plutino, M. R.; Albinati, A.; Macchioni, A. *Inorg. Chem.* **1998**, *37*, 5460. (b) Raterkus, M. J.; Fakih, S.; Mock, C.; Puscasu, I.; Krebs, B. *Inorg. Chim. Acta* **2003**, *350*, 355.

(19) (a) Zhang, F.; Broczkowski, M. E.; Jennings, M. C.; Puddephatt, R. J. *Can. J. Chem.* **2005**, *83*, 595. (b) Zhang, F.; Kirby, C. W.; Hairsine, D. W.; Jennings, M. C.; Puddephatt, R. J. *J. Am. Chem. Soc.* **2005**, *127*, 14196.

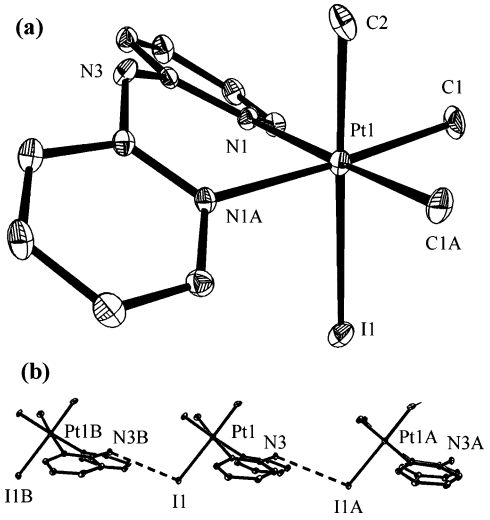


Figure 1. Views of the structure of [PtIMe$_3$(DPA)] (**3**): (a) molecular structure; (b) polymer formed by NH···I hydrogen bonding. Selected parameters: Pt(1)−C(1) = 2.065(5), Pt(1)−C(2) = 2.058(9), Pt(1)−N(1) = 2.162(4), Pt(1)−I(1) = 2.7796(7) Å; N(1)−Pt(1)−N(1A) = 84.8(2)°; H-bond N(3)···I(1A) = 3.809(6) Å, N(3)−H(3)−I(1A) = 162(7)°.

different, thus making it possible to distinguish between geometrical and electronic effects on the reactivity of complexes [PtMe$_2$(DPA)] (**1**) and [PtMe$_2$(DPK)] (**2**) in comparison with [PtMe$_2$(bipy)]. This article shows that the ligands DPA and DPK both give more stable hydridoplatinum(IV) complexes and easier H−D exchange reactions in comparison with 2,2′-bipyridine ligands[1,4] and reports the first structure determination of a hydridomethylplatinum(IV) complex of the type [PtHXMe$_2$(LL)], with an easily dissociated halide ligand.

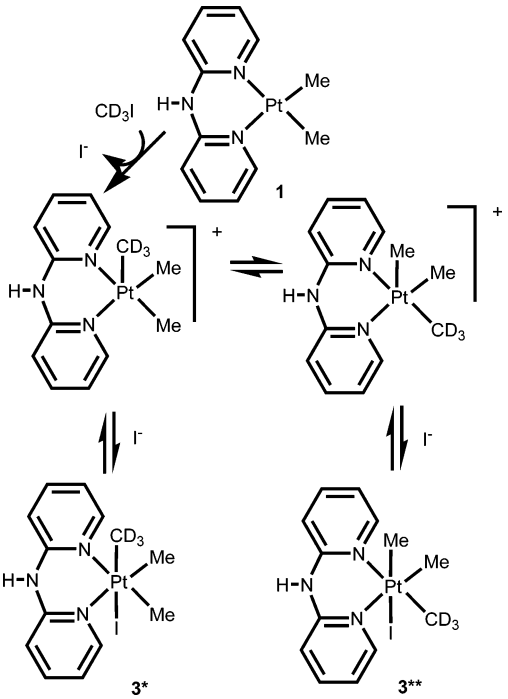
Results and Discussion

Oxidative Addition of MeI to [PtMe$_2$(DPA)]. The dimethylplatinum(II) complex [PtMe$_2$(DPA)] (**1**) was prepared by the reaction of dipyridylamine (DPA) with [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$].[21] It is characterized by a single methylplatinum resonance at δ 0.56 ppm (^2J(PtH) = 86 Hz) in the ^{1}H NMR spectrum in CD_2Cl_2.

The reaction of **1** with MeI gave the stable trimethylplatinum(IV) complex *fac*-[PtIMe$_3$(DPA)] (**3**). The ^{1}H NMR spectrum of **3** contained two methyl resonances, with relative peak intensities of 2:1 at δ 1.24 (^2J(PtH) = 71 Hz, Me trans to N) and 0.87 ppm (^2J(PtH) = 72 Hz, Me trans to I). The structure of complex **3** is shown in Figure 1a. The platinum atom displays octahedral geometry, and there is a plane of symmetry containing the atoms Pt(1)I(1)C(2)N(3). The DPA ligand adopts a boat conformation with the bridging NH group directed toward C(2) and away from I(1). The molecules associate into supramolecular polymeric chains through weak intermolecular NH···IPt hydrogen bonding (Figure 1b), with N(3)···I(1) = 3.809(6) Å.

The reaction of complex **1** with CD_3I in CD_2Cl_2 solution was carried out at −78 °C, and the reaction was monitored by ^{1}H NMR spectroscopy. The oxidative addition was complete at −60 °C to give [PtIMe$_2$(CD$_3$)(DPA)] (**3*** and **3****) (Scheme 1), with

Scheme 1



complete scrambling between the CH_3 and CD_3 groups. In contrast, the oxidative addition of CD_3I to [PtMe$_2$(bipy)] occurs regioselectively to give [PtIMe$_2$(CD$_3$)(bipy)] by trans oxidative addition (CD_3 trans to I), and subsequent CH_3/CD_3 scrambling occurs only slowly at room temperature.[22] These results indicate that the ionic 5-coordinate intermediate in oxidative addition, namely [PtMe$_2$(CD$_3$)(DPA)]$^+$I$^-$, is sufficiently long-lived to undergo intramolecular Me/CD_3 exchange before iodide coordination to give [PtIMe$_2$(CD$_3$)(DPA)] occurs (Scheme 1). Therefore, in comparison to the 2,2′-bipyridine system studied earlier,[21] either the rearrangement step in Scheme 1 is faster or the iodide coordination step is slower in the DPA system (or a combination of both).

Protonolysis Reactions of Complexes 1 and 2. The reactions of complexes **1** and **2** with acids at room temperature gave the overall reactions shown in Scheme 2. The reactions with HCl gave methane and the corresponding complex [PtClMe(LL)] (**4a**, LL = DPA; **5a**, LL = DPK) and then, in a much slower reaction, [PtCl$_2$(LL)] (**6a**, LL = DPA; **7a**, LL = DPK). The reactions with CF_3CO_2H and CF_3SO_3H in nonpolar solvents occurred similarly: for example, to give first the methylplatinum complexes [Pt(O$_2$CCF$_3$)Me(DPA)] (**4b**) and [Pt(O$_3$SCF$_3$)Me(DPA)] (**4c**) or, in more polar solvents, solvent complexes such as [PtMe(NCMe)(DPK)][CF_3CO_2] (**9a**) and [PtMe(NCMe)(DPK)][CF_3SO_3] (**9b**).[23] There is an easy equilibrium between the neutral and cationic complexes in such cases; for example, the complex [Pt(O$_2$CCF$_3$)Me(DPA)] (**4b**) reacted very rapidly with Me$_2$S to give [PtMe(SMe$_2$)(DPA)][CF_3CO_2] (**8a**). After long reaction times, both methylplatinum groups of complexes **1** and **2** could be cleaved.

(20) Crowder, K. N.; Garcia, S. J.; Burr, R. L.; North, J. M.; Wilson, M. H.; Conley, B. L.; Fanwick, P. E.; White, P. S.; Sienerth, K. D.; Granger, R. M., II. *Inorg. Chem.* **2004**, *43*, 72.

(21) (a) Hill, G. S.; Irwin, M. J.; Levy, C. J.; Rendina, L. M.; Puddephatt, R. J. *Inorg. Synth.* **1998**, *32*, 149. (b) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.

(22) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, 6, 2548.

(23) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809. The complexes [PtMe(OTf)(LL)] obtained from methanol or acetone solution did not contain coordinated solvent. However, in solution it is likely that there is an easy equilibrium with the corresponding solvent complexes [PtMe(S)(LL)]OTf. We note that the ^{1}H NMR spectra of the triflate and tetrafluoroborate derivatives in methanol or acetone are essentially identical. For simplicity, they are referred to as the structures present in the solid state.

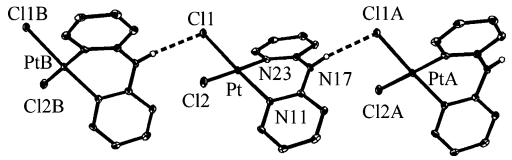
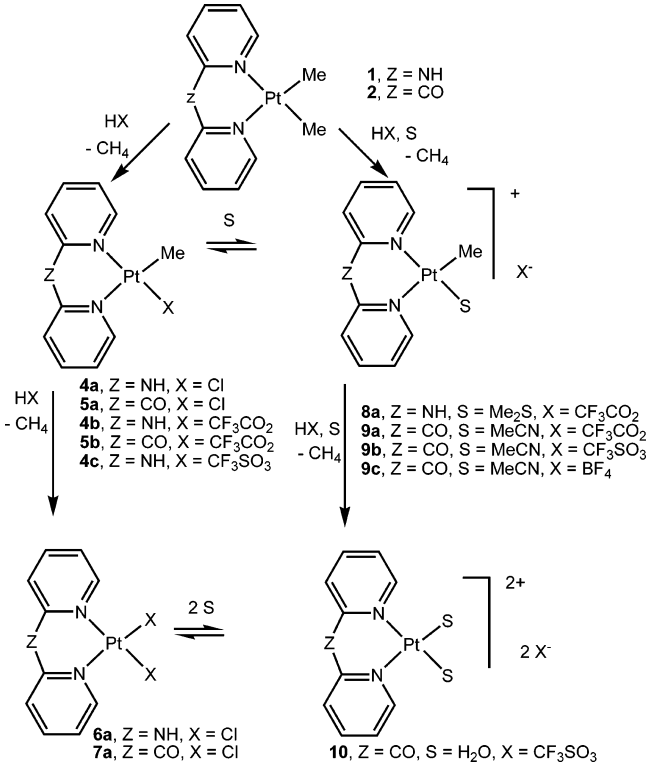


Figure 2. View of the structure of $[PtCl_2(DPA)]$ (**6a**) showing the polymer formed by NH···Cl hydrogen bonding. Selected parameters: Pt−N(11) = 2.015(5), Pt−N(23) = 2.018(4), Pt−Cl(2) = 2.299(1), Pt−Cl(1) = 2.307(1) Å; N(11)−Pt−N(23) = 88.7(2)°.

Scheme 2



In reactions carried out in moist acetone with excess CF_3SO_3H, the aqua complex $[Pt(OH_2)_2(DPK)][CF_3SO_3]_2$ (**10**) or the binuclear hydroxo complex $[Pt_2(\mu\text{-}OH)_2(DPK)_2][CF_3SO_3]_2$ (**11**) were crystallized from solution. Similar chemistry has been established with other bidentate nitrogen-donor ligands,[4,7,13,14,23,24] so characterization of the complexes was straightforward. Several complexes were structurally characterized in order to prove the stoichiometry and to establish the ligand conformations.

The structure of the DPA complex **6a** is shown in Figure 2. The ligand adopts a boat conformation similar to that in the platinum(IV) complex **3**. The deviation of the six-membered chelate ring from planarity can be measured by the displacement of the NH nitrogen atom from the plane defined by the platinum atom and its in-plane ligating atoms (1.28 Å in **3**, 1.39 Å in **6a**) or by the angle between the same platinum plane and the plane defined by the CN(H)C atoms (116° in **3**, 114° in **6a**), and the similarity of the conformations in **3** and **6a** is evident.

The structures of the DPK complexes **5a**, **10**, and **11** are shown in Figures 3−5, respectively. In all three complexes the Pt(DPK) chelate ring adopts the boat conformation. The distortions from planarity, as measured by the displacement of the carbonyl carbon atom from the platinum(II) plane (1.54 Å in **5a**, 1.60 Å in **10**) or by the angle between the CC(O)C atoms and the platinum plane (108° in **5a**, 106° in **10**), are similar in the mononuclear complexes. The chelate rings are somewhat flatter in the binuclear complex **11** (displacement of C atom 1.08−1.45 Å (mean value 1.20 Å); angle between planes 115−132° (mean value 126°)). Complex **10** forms a network structure through hydrogen bonding between triflate anions and aqua ligands (Figure 4), while pairs of binuclear molecules of **11** stack one above the other with resulting long contacts between them (Pt(1)···Pt(3) = 3.61 Å; Pt(2)···Pt(4) = 3.65 Å) (Figure 5). An interesting feature of complex **11** is that the two independent molecules have different conformations. The molecule containing Pt(1) and Pt(2) is folded such that the angle between the two platinum planes is 28°, whereas the molecule containing Pt(3) and Pt(4) is almost flat with an angle between the two platinum planes of only 1°.

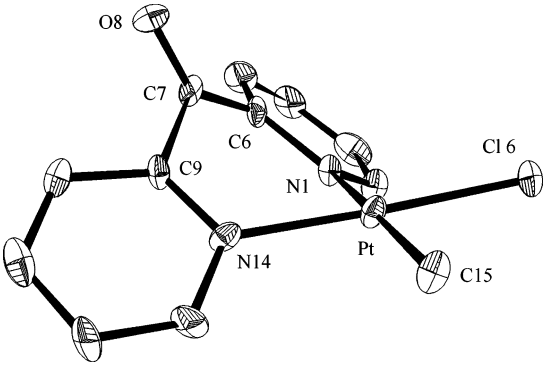


Figure 3. View of the structure of [PtClMe(DPK)] (**5a**). Selected parameters: Pt−N(1) = 2.04(2), Pt−N(14) = 2.07(3) Å; N(1)−Pt−N(14) = 88.7(9)°.

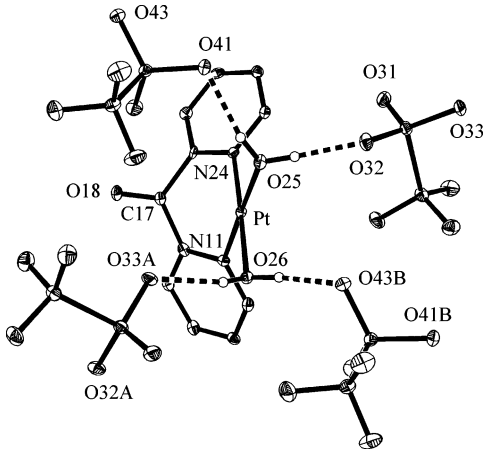


Figure 4. View of the structure of $[Pt(OH_2)_2(DPK)][CF_3SO_3]_2$ (**10**). Each triflate anion is hydrogen-bonded to two aqua ligands to form a network structure. Selected parameters: Pt−N(11) = 1.994(6), Pt−N(24) = 1.990(6), Pt−O(25) = 2.036(5), Pt−O(26) = 2.043(5) Å; N(24)−Pt−N(11) = 90.5(2)°; H-bond distances O(25)···O(41) = 2.636(8), O(25)···O(32) = 2.596(7), O(26)···O(43B) = 2.660(7), O(26)···O(33A) = 2.631(7) Å.

Identification of Hydridoplatinum(IV) Intermediates. The reactions of complexes **1** and **2** with HCl gave the relatively stable hydridoplatinum(IV) intermediates **12** and **13**, shown in Scheme 3, with NMR data summarized in Table 1. When the reactions were carried out at low temperature, the complexes could be isolated in pure form, though as a mixture of isomers.

Complex **13a** was crystallized at low temperature, and its structure is shown in Figure 6. This is the first structural

(24) (a) Ackerman, L. J.; Sadighi, J. P.; Kurtz, D. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2003**, *22*, 3884. (b) Li, J. J.; Li, W.; Sharp, P. R. *Inorg. Chem.* **1996**, *35*, 604. (c) Fallis, S.; Anderson, G. K.; Rath, N. P. *Organometallics* **1991**, *10*, 3180.

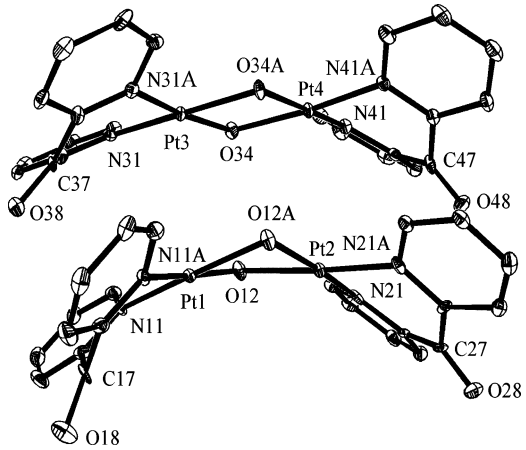
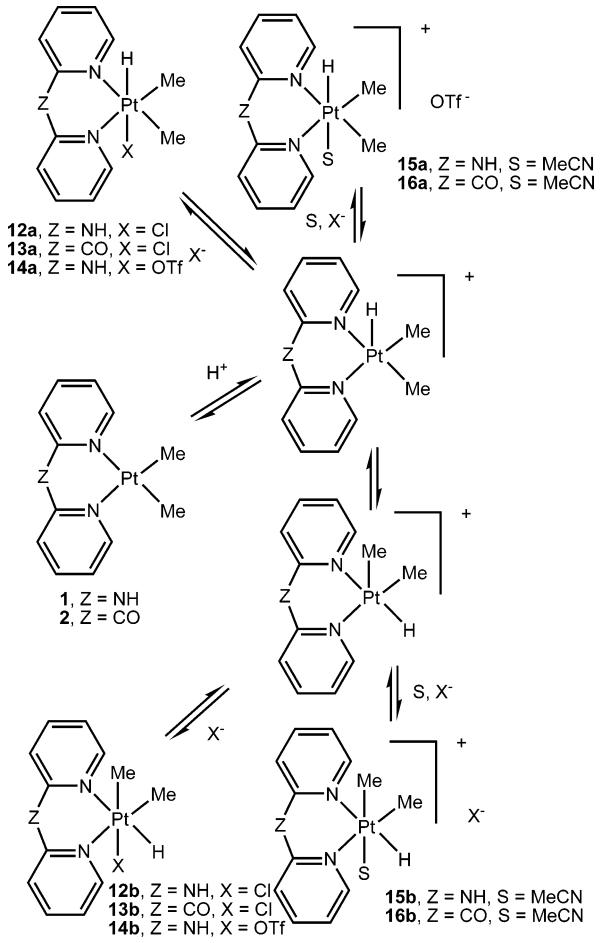


Figure 5. View of the structure of $[Pt_2(\mu\text{-}OH)_2(DPK)_2][CF_3SO_3]_2$ (**11**). Each hydroxo ligand is hydrogen-bonded to one triflate anion (not shown). There are two independent molecules, each of which contains a plane of symmetry. Selected parameters: Pt(1)−N(11) = 1.978(8), Pt(1)−O(12) = 2.025(7), Pt(2)−N(21) = 2.007(8), Pt(2)−O(12) = 2.033(7), Pt(3)−N(31) = 1.999(8), Pt(3)−O(34) = 2.026(6), Pt(4)−N(41) = 1.979(8), Pt(4)−O(34) = 2.022(7) Å; N(11)−Pt(1)−N(11A) = 91.8(5), N(21)−Pt(2)−N(21A) = 92.1(5), N(31)−Pt(3)−N(31A) = 92.1(5), N(41)−Pt(4)−N(41A) = 90.6(5)°.

Scheme 3



characterization of a hydridomethylplatinum(IV) complex with a bidentate nitrogen-donor ligand and with a relatively weakly bonded chloride ligand. The platinum atom has octahedral stereochemistry with the hydride trans to chloride and with no short contacts to the hydride atom (the shortest nonbonding distance is ca. 2.4 Å to a hydrogen atom of each PtMe group). The distance Pt−Cl = 2.446(3) Å is long, as a result of the high trans influence exerted by the hydride ligand. It is the easy dissociation of this ligand in solution to generate a 5-coordinate cation that allows the easy interconversion between isomers and ultimately the reductive elimination of methane. The distortion of the DPK ligand from planarity, as measured by the displacement of the carbonyl carbon atom from the platinum(II) plane (1.57 Å in **13a**, 1.54 Å in **5a**, 1.60 Å in **10**) or by the angle between the CC(O)C atoms and the platinum plane (106° in **13a**, 108° in **5a**, 106° in **10**) is similar to the distortion in the mononuclear platinum(II) complexes **5a** and **10**. The carbonyl group is directed toward the smaller axial ligand, the hydride in **13a**, and so there is not significant steric hindrance.

Table 1. Selected NMR Data for the Hydridoplatinum(IV) Complexes

complex	HX	solvent	δ(PtH)	^1J(PtH) trans, Hz	atom	δ(Pt-Me)	^2J(PtH) trans, Hz	atom
13a	HCl	CD_2Cl_2	−20.36	1586	Cl	1.17	68	N
13b	HCl	CD_2Cl_2	−21.00	1392	N	1.01	71	N
						1.23	78	Cl
14a	HOTf	$(CD_3)_2CO$	−26.21	1774	O	1.07	63	N
14b	HOTf	$(CD_3)_2CO$	−20.15	1391	N	1.22	80	O
						0.85	64	N
15a	HOTf	CD_3CN	−22.55	1584	N	0.98	70	N
15b	HOTf	CD_3CN	−20.43	1376	N	0.93	67	N
						0.80	65	N
16a	HOTf	CD_3CN	−22.03	1554	N	1.09	65	N
16b	HOTf	CD_3CN	−20.18	1393	N	*a*		

[a] This was a minor product, and the methylplatinum resonances were not resolved.

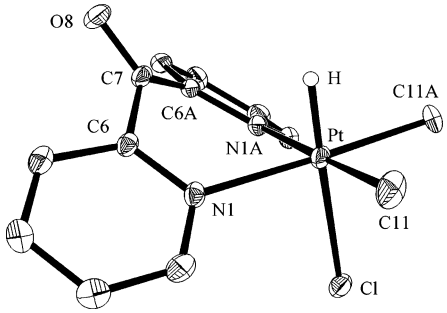


Figure 6. View of the structure of $[PtHClMe_2(DPK)]$ (**13a**). There is a plane of symmetry containing the atoms PtHClC(7)O(8). Selected parameters: Pt−C(11) = 2.073(8), Pt−N(1) = 2.154(6), Pt−Cl = 2.446(3), Pt−H = ca. 1.4 Å; C(11)−Pt−C(11A) = 87.2(6), N(1)−Pt−N(1A) = 85.6(3)°.

The complex **13** was also characterized by its ^{1}H NMR spectra (Table 1, Figure 7). Thus, reaction of complex **2** with HCl at −30 °C gave complex **13a** by trans oxidative addition. At 0 °C, isomerization of **13a** to **13b** was observed and, at 20 °C, slow reductive elimination of methane occurred to give [PtClMe(DPK)] (**5a**). Figure 7 shows the ^{1}H NMR spectra in the hydride region as the isomerization of **13a** to **13b** occurred. Complete isomerization was not observed in this case. The PtH coupling is considerably higher in **13a** (δ(PtH) −20.36, ^1J(PtH) = 1586 Hz) than in **13b** (δ(PtH) −21.00, ^1J(PtH) = 1392 Hz).

The reaction of complex **1** in acetone or dichloromethane solution with triflic acid at −80 °C gave the hydridoplatinum-(IV) complex $[PtHMe_2(CF_3SO_3)(DPA)]$ (**14**) (Scheme 3) as a mixture of the isomers **14a** (δ(PtH) −26.21, ^1J(PtH) = 1774 Hz) and **14b** (δ(PtH) −20.15, ^1J(PtH) = 1391 Hz), as shown in Figure 8.[23] Complex **14a** gave only one methylplatinum resonance in the ^{1}H NMR spectrum, whereas the less symmetrical complex **14b** gave two (Table 1, Figure 9). At −60

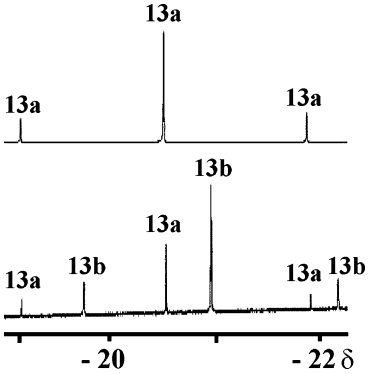


Figure 7. ^{1}H NMR spectra of complex **13** in the hydride region: (top) spectrum at −20 °C, showing selective formation of **13a**; (bottom) spectrum at 20 °C, showing partial isomerization to **13b**.

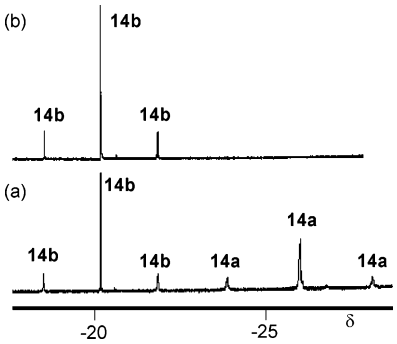


Figure 8. ^{1}H NMR spectra of complex **14** in the PtH region: (a) spectrum at −80 °C, showing the presence of both **14a** and **14b**; (b) spectrum at −60 °C, showing the presence of **14b** only.

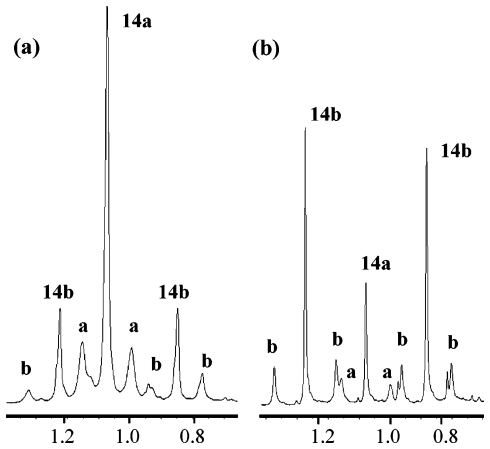


Figure 9. ^{1}H NMR spectra of complex **14** in the MePt region: (a) spectrum at −80 °C, showing the presence of both **14a** and **14b**; (b) spectrum at −65 °C, showing the isomerization to **14b**.

°C, complex **14a** had completely isomerized so that the only hydridoplatinum complex present was **14b** (Figures 8 and 9). At −40 °C, only the reductive elimination product [PtMe(CF_3SO_3)(DPA)] (**4b**) was present.[23] The complex **14** clearly has low thermal stability, but it was positively identified, whereas analogous complexes formed by reaction of complex **2** or [$PtMe_2$(bipy)] with triflic acid were unstable, even at −80 °C.

More stable hydridoplatinum(IV) complexes were formed in reactions with triflic acid when the reactions were carried out in the presence of acetonitrile, which can form the complexes [$PtHMe_2$(NCMe)(DPA)]$^+$(CF_3SO_3)$^-$ (**15**) and [$PtHMe_2$(NCMe)(DPK)]$^+$(CF_3SO_3)$^-$ (**16**). In a typical experiment, a solution of **2** in a $(CD_3)_2CO/CD_3CN$ solvent mixture at −78 °C was treated with triflic acid and NMR spectra were recorded as the solution was warmed to room temperature. The complex **16a** was formed as the product of trans oxidative addition, which was stable to −40 °C but then decomposed by reductive elimination of methane between −40 and 0 °C. The cis isomer **16b** was identified as a minor product in solution only by its characteristic hydride resonance (Table 1). Similar experiments were carried out by varying the concentration of CD_3CN from 0.2 to 2 mol L^{-1}, and the rate of decomposition of the hydride derivative was shown to decrease and then reach a roughly steady value at higher concentrations of CD_3CN. The order of stability of the hydridoplatinum(IV) derivatives was **15** > **16** > [$PtHMe_2$(MeCN)(bu_2bipy)]CF_3SO_3 (bu_2bipy = 4,4-di-*tert*-butyl-2,2′-bipyridine) under similar conditions.

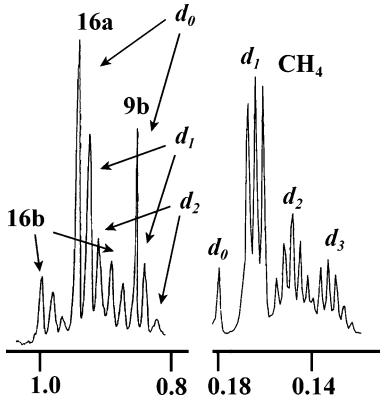


Figure 10. ^{1}H NMR spectrum at −20 °C of a solution obtained by reaction of complex **2** with triflic acid in a 3:1 mixture of CD_3OD and CD_3CN, showing the methylplatinum (left) and methane (right, recorded at higher sensitivity) regions. The major product is **16a**, with smaller amounts of **16b**, **9b**, and methane. The $PtCH_{3-n}D_n$ and $CH_{4-n}D_n$ isotopomers are indicated for the compounds **16a**, **9b**, and CH_4.

H−D Exchange Reactions. Hydrogen/deuterium exchange reactions in hydridomethylplatinum(IV) complexes have been studied by several groups.[4,7,13,14] If the dimethylplatinum(II) complex [(LL)$PtMe_2$] is treated with D^+, reversible intramolecular reactions of the initially formed 5-coordinate complex [(LL)$PtD(CH_3)_2$]$^+$ can give the methane complex [(LL)Pt(CH_3D)(CH_3)]$^+$ and then [(LL)$PtH(CH_2D)(CH_3)$]$^+$ and [(LL)Pt(CH_4)(CH_2D)]$^+$. At each stage, the platinum(IV) complexes can be trapped by addition of anion or solvent to make a 6-coordinate complex, or the methane complex of platinum(II) can react with anion or solvent to form free methane (CH_4 or CH_3D). In the presence of a deuterated solvent, such as the alcohol ROD, intermolecular exchange between PtH and ROD groups can lead to multiple deuterium incorporation into the methane or methylplatinum products. Thus, there are three critical rate constants whose relative magnitudes determine the observed isotope distribution in the products: the rate of intramolecular H−D exchange (step ***A***), the rate of intermolecular H−D exchange with solvent (step ***B***), and the rate of methane displacement from platinum (step ***C***).[13,14]

Complexes **1** and **2** can give particularly easy H−D exchange reactions, as illustrated by Figure 10 and the selected data given in Table 2. The experiments were carried out by reaction of of a dimethylplatinum(II) complex in a deuterium-labeled solvent in an NMR tube with a protic acid at −78 °C. The NMR tube was then inserted into the NMR probe, which was precooled to −80 °C, and the course of the reaction was monitored by recording spectra at 20 °C intervals as the solution was warmed slowly to room temperature in the NMR probe. For example, the ^{1}H NMR spectrum shown in Figure 10 was recorded from

Table 2. H−D Exchange Reactions

reagent	solvent	% reacn[a]	CH_4 d_0:d_1:d_2:d_3	$PtMe$[b] d_0:d_1:d_2
1	CD_3OD	20	1:17:20:32	1:1.9:1.4
TfOD		100	1:16:20:35	1:1.9:2.1
1	CD_3OD[c]	50	1:15:21:39	1:1.8:1.8
TfOD	CD_3CN[c]	100	1:15:23:48	1:2.1:2.3
2	CD_3OD	15	1:10:5:4	*d*
TfOD		100	1:11:10:17	*d*
2	CD_3OD[c]	25	1:15:9:7	1:1.0:0.5
TfOD	CD_3CN[c]	100	1:13:11:17	1:1.0:0.6
2	CD_3OD	5	1:35:6:4	1:0.2:0.1
DCl		20	1:35:13:6	1:0.8:0.4
		100	1:33:28:30	1:0.9:0.6
$[PtMe_2(NN)]$[e] TfOD	CD_3OD	100	1:10:11:9	1:0.7:0.4

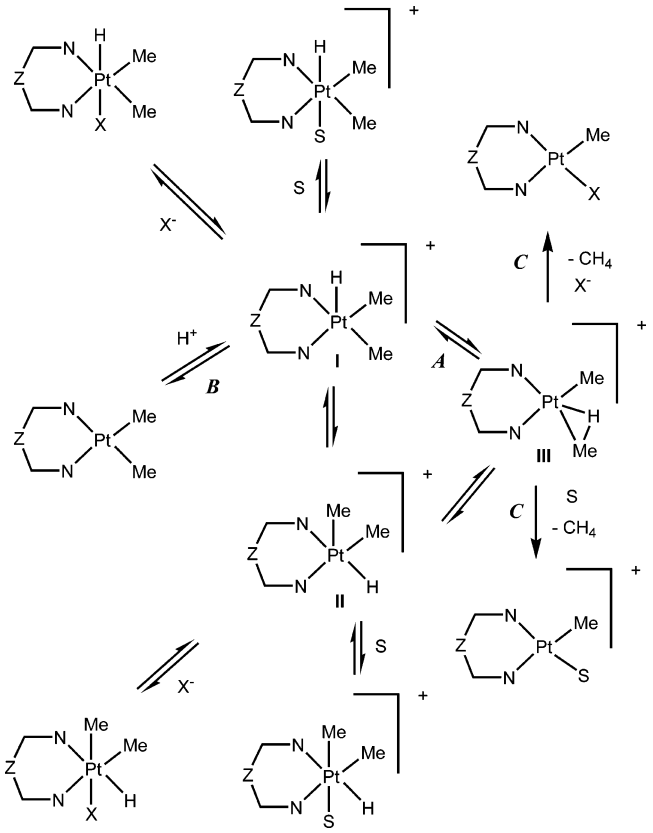
[a] Estimated percent reaction to give methane. [b] Data for the methylplatinum(II) product. [c] Solvent mixture 3:1 CD_3OD:CD_3CN. [d] Overlap of peaks did not allow integration. [e] NN = 4,4′-di-*tert*-butyl-2,2′-bipyridine.

a solution obtained by reaction of complex **2** with triflic acid in a 3:1 CD_3OD/CD_3CN solvent mixture at −78 °C and then warmed to −20 °C in the NMR probe. At this point about 25% reaction to form methane had occurred; thus, the reaction mixture contained about 25% of the products methane and $[PtMe(MeCN)(DPK)]^+$ (**9b**) and about 75% of the hydridoplatinum(IV) intermediate $[PtHMe_2(MeCN)(DPK)]^+$ (**16**), as a mixture of isomers **16a** and **16b**. There was extensive deuterium incorporation into the methane product and into the methylplatinum groups of both the intermediate **16a/16b** and the product **9b**. The peaks for isotopomers containing $PtCH_3$, $PtCH_2D$, and $PtCHD_2$ groups were resolved for each complex, as shown in Figure 10, and the extent of H/D exchange increased during the reaction. Of course, $PtCD_3$ groups and CD_4 are also formed but cannot be observed in the ^1H NMR spectrum. The cleavage of (and H−D exchange into) the remaining methylplatinum bond in complex **9b** was slow, and further H−D exchange of the free methane did not occur.

Because equilibrium and kinetic isotope effects, which have not been determined, affect the H−D exchange and because peak overlap can make it difficult to integrate the peaks due to the isotopomers accurately, only a qualitative interpretation of the data in Table 2 will be given. First, it is clear in all cases that multiple deuterium incorporation into the methane and methylplatinum(II) products is observed. In addition, the extent of deuterium incorporation increases during the reaction, indicating that methane displacement (step ***C***) is the slow step in the overall H−D exchange reaction in each case.[7,13,14] The differences in relative rates are, however, not great enough to lead to complete H−D equilibration in the methane product. Table 2 also indicates that, for a given acid and solvent, the degree of deuterium incorporation into the methane product follows the sequence $[PtMe_2(DPA)]$ > $[PtMe_2(DPK)]$ > $[PtMe_2(bu_2bpy)]$. This is the same sequence as the order of stability of a given hydridoplatinum(IV) complex, $[PtHMe_2X(LL)]$ or $[PtHMe_2(S)(LL)]^+$, as described above. Finally, there is little effect of the acid CF_3SO_3D versus DCl, or of the presence or absence of CD_3CN in the CD_3OD solvent in reactions with CF_3SO_3D, on the overall extent of deuterium incorporation, although the overall rates of reaction to give methane are affected greatly. The reaction of complex **1** with acids DX also led to NH/ND exchange, but this is likely to occur independently of the exchange involving the methylplatinum groups.

The results can be interpreted in terms of Scheme 4, which, for simplicity, omits the deuterium labels. In the presence of acid, none of the starting material $[PtMe_2(NZN)]$ or the key

Scheme 4 [a]



[a] The labels ***A***−***C*** denote the key mechanistic steps leading to H−D exchange (see text) when reactions are carried out in methanol-d_4.

intermediates **I**−**III** are directly detectable, but it is the easy exchange between them that is the key to H−D exchange in the deuterated solvent medium. The initial resting state is the protonated 6-coordinate platinum(IV) complex $[PtHMe_2X(NZN)]$ or $[PtHMe_2(S)(NZN)]^+$, each of which can exist as trans or cis isomers. The greater stability of these complexes in the order X = Cl > CF_3SO_3 or S = MeCN > MeOH is a function of the ligating ability of X^- or S, with the better ligands giving a lower steady-state concentration of the key intermediates **I**−**III**.[4−10,13,14,25] The extent of deuterium incorporation into the methane product depends on how much slower step ***C*** is than the slower of steps ***A*** and ***B***. It was expected that there would be a dependence on the acid HX or the solvent, since the associative displacement of methane from **III** is expected to follow the sequence X = Cl > CF_3SO_3 or S = CD_3CN > CD_3OD, but no significant effect was observed. This would be consistent with dissociative methane loss or, in view of convincing evidence for associative displacement in related complexes,[13,14] with a lack of discrimination between incoming nucleophiles for complexes with the good leaving group methane.

It is important to determine if the observed differences between the reactivity of the complexes with DPA, DPK, and bu_2bipy ligands arise from electronic or steric effects. If the chelate ligand effect is primarily electronic, it can be understood in terms of the stronger donors increasing the steady-state concentrations of the platinum(IV) intermediates **I** and **II** over

(25) The role of 5-coordinate platinum(IV) complexes in organometallic reaction mechanisms has been discussed. (a) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 6425. (b) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423. (c) Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 261.

the platinum(II) intermediate **III**, giving slower rates for the nucleophilic displacement of methane. The carbonyl stretching frequencies of the carbonyl derivatives $[PtMe(CO)(LL)]^+$ are 2105, 2119, and 2109 cm^{-1} for LL = DPA, DPK, bu_2bipy, respectively,[19b] indicating that DPA is the strongest donor (as a result of the π-donor property of the NH group) and DPK is the weakest donor (as a result of the electron-withdrawing properties of the carbonyl group). The differences between DPA/DPK and bu_2bipy are therefore not due to electronic effects and, thus, are proposed to arise from differential steric effects, with the roughly planar bu_2bipy promoting faster displacement of methane.[19b]

Experimental Section

All reactions were carried out under nitrogen, either using Schlenk techniques or in a drybox, unless otherwise specified. NMR spectra were recorded by using Varian Mercury 400 or INOVA 400 or 600 spectrometers. ^1H NMR chemical shifts are reported relative to TMS, and ^{19}F NMR chemical shifts are reported relative to $CFCl_3$. The complexes $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, $[PtMe_2(DPA)]$ (**1**), and $[PtMe_2(DPK)]$ (**2**) were prepared according to the literature procedures.[19,21]

[PtIMe$_3$(DPA)] (3). To a solution of $PtMe_2$(DPA) (89.1 mg, 0.225 mmol) in THF (5 mL) was added MeI (15:l, 0.241 mmol), and the solution was stirred for 2 h. After 2 h, diethyl ether (30 mL) was added to precipitate the product as a white solid, which was separated, washed with ether, and dried under vacuum. Yield: 88.3 mg, 73%. Anal. Calcd for $C_{13}H_{18}IN_3Pt$: C, 29.01; H, 3.37; N, 7.81. Found: C, 28.74; H, 3.29; N, 7.72. ^1H NMR (acetone-d_6): δ 0.87 (s, 3H, ^2J(PtH) = 72 Hz, Pt−Me trans to I); 1.24 (s, 6H, ^2J(PtH) = 71 Hz, Pt−Me trans to py); 7.14 (t, 2H, ^3J(HH) = 6 Hz, py); 7.27 (d, 2H, ^3J(HH) = 8 Hz, py); 7.87 (td, 2H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py); 8.75 (dd, 2H, ^3J(PtH) = 21 Hz, ^3J(HH) = 6 Hz, ^4J(HH) = 2 Hz, py); 9.65 (br, 1H, NH).

[PtMe(DPK)(NCMe)][BF$_4$] (9c). To a solution of complex **2** (0.410 g, 0.1 mmol) in CH_3CN (15 mL) was added HBF_4 (14 μL, 54% in ether, 0.1 mmol). The solution was stirred for 2 h, and then the solvent was evaporated to give the product as a yellow solid, which was washed with pentane (25 mL) and dried under vacuum. Yield: 86%. Anal. Calcd for $C_{14}H_{14}BF_4N_3OPt$: C, 32.20; H, 2.70; N, 8.05. Found: C, 31.82; H, 2.66; N, 8.01. ^1H NMR (CD_3CN): δ 0.96 (s, 3H, ^2J(PtH) = 76 Hz, PtMe); 2.74 (s, 3H, ^4J(PtH) = 12 Hz, PtCNMe); 7.93 (t, 1H); 8.01 (t, 1H); 8.19 (d, 1H); 8.33 (d, 1H); 8.44 (t, 1H); 8.48 (t, 1H); 8.94 (d, 1H, ^3J(HH) = 6 Hz, ^3J(PtH) = 69 Hz, PtNCH, trans to NCMe); 8.88 (d, 1H, ^3J(HH) = 6 Hz, PtNCH, trans to Me).

[PtMe(DPK)(NCMe)]$^+$CF$_3$CO$_2^-$ (9a). This was prepared similarly from complex **2** and CF_3CO_2H. Yield: 89%. Anal. Calcd for $C_{16}H_{14}F_3N_3O_3Pt$: C, 35.04; H, 2.57; N, 7.66. Found: C, 34.99; H, 2.48; N, 7.47. NMR in CD_3CN: as for **9c**.

[PtClMe(DPK)] (5a). This was prepared similarly from complex **2** and HCl. Yield: 90%. Anal. Calcd for $C_{12}H_{11}ClN_2OPt$: C, 33.54; H, 2.58; N, 6.52. Found: C, 34.33; H, 2.51; N, 6.34. ^1H NMR (CD_2Cl_2): δ 1.04 (s, ^2J(PtH) = 77 Hz, PtMe); 7.50 (t, 1H); 7.66 (t, 1H); 7.95 (d, 1H); 8.06 (d, 1H); 8.07 (t, 1H); 8.10 (t, 1H); 8.84 (d, ^3J(HH) = 6 Hz, ^3J(PtH) = 67 Hz, PtNCH, trans to Cl); 9.23 (d, ^3J(HH) = 5 Hz, ^3J(PtH) = 17 Hz, PtNCH, trans to Me). ^{195}Pt NMR (CD_2Cl_2): δ 514.4 ppm.

[PtMe(CF$_3$CO$_2$)(DPA)] (4b). To a solution of $[PtMe_2(DPA)]$ (50 mg, 0.126 mmol) in THF (5 mL) was added excess CF_3CO_2H (19.0 μL, 0.247 mmol). After 30 min, pentane (30 mL) was added to precipitate the product as a pale yellow solid, which was separated, washed with pentane (5 mL), and dried under vacuum. Yield: 74%. Anal. Calcd for $C_{13}H_{12}F_3N_3O_2Pt$: C, 31.59; H, 2.45; N, 8.50. Found: C, 31.88; H, 2.62; N, 8.24. ^1H NMR (acetone-d_6): δ 0.67 (s, 3H, ^2J(PtH) = 77 Hz, Pt−Me); 6.86 (t, 1H, ^3J(HH) = 6 Hz, py); 7.02 (t, 1H, ^3J(HH) = 6 Hz, py); 7.13 (d, 1H, ^3J(HH) = 8 Hz, py); 7.18 (d, 1H, ^3J(HH) = 8 Hz, py); 7.71 (td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py); 7.85 (td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py); 8.23 (dd, 1H, ^3J(HH) = 6 Hz, ^4J(HH) = 1 Hz, py); 8.38 (dd, 1H, ^3J(HH) = 6 Hz, ^4J(HH) = 1 Hz, py); 10.66 (1H, NH).

[PtMe(CF$_3$SO$_3$)(DPA)] (4c). This compound was prepared similarly. Yield: 58%. Anal. Calcd for $C_{12}H_{12}F_3N_3O_3PtS$: C, 27.17; H, 2.28; N, 7.92. Found: C, 26.95; H, 2.42; N, 8.01. ^1H NMR (acetone-d_6): δ 0.52 (s, ^2J(PtH) = 77 Hz, PtMe); 7.14 (m, py); 7.45)m, py); 8.08 (br, py); 8.58)br, py); 10.26 (br, NH). ^{19}F NMR (acetone-d_6): 76 (s, CF_3).

[PtMe(DPA)(SMe$_2$)]CF$_3$CO$_2$ (8a). To a solution of complex **4b** (10 mg) in acetone (2 mL) was added excess SMe_2 (0.15 g). After 10 min, the solvent was evaporated and the pale yellow solid product was washed with pentane (2 × 10 mL) and dried under vacuum. Yield: 85%. Anal. Calcd for $C_{15}H_{18}F_3N_3O_2PtS$: C, 32.38; H, 3.26; N, 7.55. Found: C, 32.03; H, 3.07; N, 7.56. ^1H NMR (acetone-d_6): 0.75 (s, 3H, ^2J(PtH) = 75 Hz, Pt−Me); 2.43 (s, 6H, ^3J(PtH) = 59 Hz, Pt−SMe_2); 7.13 (td, 1H, ^3J(HH) = 6 Hz, ^4J(HH) = 1 Hz, py); 7.18 (td, 1H, ^3J(HH) = 6 Hz, ^4J(HH) = 1 Hz, py); 7.30 (d, 1H, ^3J(HH) = 8 Hz, py); 7.32 (d, 1H, ^3J(HH) = 8 Hz, py); 7.92 (td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py); 7.95 (td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py); 8.32 (dd, 1H, ^3J(HH) = 6 Hz, ^4J(HH) = 2 Hz, py); 8.52 (dd, 1H, ^3J(HH) = 6 Hz, ^4J(HH) = 2 Hz, py); 11.96 (br, 1H, NH).

[PtHClMe$_2$(DPK)] (13a/13b). To a solution of complex **2** (0.102 g, 0.25 mmol) in CH_2Cl_2 (20 mL) was added a solution of HCl in ether (250 μL, 1.0 M, 0.25 mmol). The product precipitated as a yellow solid, which was collected by filtration, washed with ether (3 × 2 mL) and pentane (3 × 8 mL), and dried under vacuum. The product was isolated as a mixture of isomers. Yield: 83%. Anal. Calcd for $C_{13}H_{15}ClN_2OPt$: C, 35.02; H, 3.39; N, 6.28. Found: C, 34.46; H, 3.09; N, 5.99. ^1H NMR (CD_2Cl_2): **13a**, δ −20.36 (1H, ^1J(PtH) = 1586 Hz, PtH, trans to Cl), 1.17 (6H, ^2J(PtH) = 68 Hz, 2PtMe), 7.60 (t, 2H), 8.03 (d, 2H), 8.19 (t, 2H), 9.35 (d, 2H); **13b**, δ −21.00 (1H, ^1J(PtH) = 1392 Hz, PtH, trans to N), 1.01 (3H, ^2J(PtH) = 71 Hz, PtMe trans to Cl), 1.23 (3H, ^2J(PtH) = 78 Hz, PtMe trans to N), 7.51 (t, 2H), 7.67 (t, 2H), 7.96 (d, 1H), 8.09 (d, 1H), 8.14 (t, 1H), 8.17 (t, 1H), 8.86 (d, 1H), 9.25 (d, 1H).

[PtHMe$_2$(DPA)(CF$_3$SO$_3$)] (14a/14b). To a solution of $[PtMe_2$-(DPA)] (19 mg, 0.049 mmol) in acetone-d_6 (0.5 mL) in an NMR tube, cooled to −78 °C, was added triflic acid (4.5 μL, 0.051 mmol). The tube was then placed in the precooled probe of the NMR spectrometer at −80 °C, and ^1H NMR spectra were obtained at 20 °C intervals from −80 to +20 °C. At −60 °C, complex **14b** was the only hydride complex observed. Complex **4c** was observed as an impurity with increasing presence as the temperature was increased. ^1H NMR (acetone-d_6, −80 °C): **14a**, δ −26.21 (s, ^1J(PtH) = 1774 Hz, Pt−H trans to O), 0.85 (s, ^2J(PtH) = 64 Hz, Pt−Me trans to N), 1.07 (s, 6H, ^2J(PtH) = 63 Hz, Pt−Me trans to N), 8.44−7.04 (m, 8H, py), 10.09 (br, 1H, NH); **14b**, δ −20.15 (s, ^1J(PtH) = 1391 Hz, Pt−H trans to N), 0.85 (s, ^2J(PtH) = 64 Hz, Pt−Me trans to N), 1.22 (s, ^2J(PtH) = 80 Hz, Pt−Me trans to O), 8.44−7.04 (m, 8H, py), 10.30 (br, 1H, NH). ^{19}F NMR: δ 75 (s, CF_3).

At −60 °C, complex **14b** was the only hydride complex present. Above −20 °C, complex **4c** was the major complex present. The resonance due to methane at $\delta(^1H)$ 0.2 grew over this temperature range.

Other unstable hydride complexes were characterized similarly, and data are given in Table 1.

H/D Exchange Reactions. A solution of $[PtMe_2(DPK)]$ (0.01 mmol) in methanol-d_4 (0.5 mL) in an NMR tube was cooled to −78 °C, and triflic acid-*d* (5:l, 0.02 mmol) was added. The ^1H NMR spectrum was recorded at −80 °C and then at 20 °C intervals

Table 3. X-ray Data for the Complexes

	3	**5a**	**6a**	**10**	**11**·0.5thf	**13a**·CH_2Cl_2
formula	$C_{13}H_{18}IN_3Pt$	$C_{12}H_{11}ClN_2OPt$	$C_{10}H_9Cl_2N_3Pt$	$C_{13}H_{12}F_6N_2O_9PtS_2$	$C_{26}H_{22}F_6N_4O_{10.5}Pt_2S_2$	$C_{14}H_{17}Cl_3N_2OPt$
fw	538.29	429.77	437.19	713.46	1126.78	530.74
T/K	200(2)	150(2)	150(2)	150(2)	150(2)	150(2)
λ/Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
space group	$P2_1/m$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	*Pnma*	*Pnma*
cell dimens						
a/Å	6.7464(5)	4.0239(3)	9.9704(3)	8.2846(2)	22.1033(4)	15.7153(8)
b/Å	14.248(1)	19.568(1)	10.1342(3)	14.8183(4)	21.9063(3)	12.4400(5)
c/Å	8.4038(6)	15.316(1)	11.7173(4)	16.5000(4)	12.9826(2)	8.7904(4)
β/deg	112.833(4)	96.298(4)	94.027(2)	90	90	90
V/Å^3	744.49(9)	1198.7(1)	1181.02(6)	2025.60(9)	6286.2(2)	1718.51(14)
Z	2	4	4	4	8	4
D_c/Mg m^{-3}	2.401	2.381	2.459	2.339	2.381	2.051
μ/mm^{-1}	11.484	11.911	12.306	7.240	9.125	8.630
R1 ($I > 2\sigma(I)$)	0.0327	0.0988	0.0334	0.0333	0.0485	0.0473
wR2 ($I > 2\sigma(I)$)	0.0569	0.2624	0.0606	0.0726	0.1147	0.1105

as it was warmed to room temperature. Other experiments were run in a similar way, with products identified by their NMR spectra, and deuterium incorporation was estimated from the peak intensities in the methylplatinum or methane regions.

X-ray Structure Determinations. A suitable crystal was mounted on a glass fiber, and data were collected by using a Nonius Kappa-CCD diffractometer. Details of the data collections and structure refinements are given in Table 3. Solution and refinement of the structures was carried out by using the SHELXTL version 5.1 (G. M. Sheldrick) suite of programs.

Acknowledgment. We thank the NSERC (Canada) for financial support and for a scholarship to E.M.P. R.J.P. thanks the government of Canada for a Canada Research Chair.

Supporting Information Available: X-ray crystallographic data as a CIF file for the structure determination of complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050982M