Protonolysis of Dimethylplatinum(II) Complexes: Primary Attack at Metal or Ligand

Justin G. Hinman, Cliff R. Baar, Michael C. Jennings, and Richard J. Puddephatt*

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

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The complexes [$PtMe_2$(DMEP)], **1**, and [$PtMe_2$(DMPP)], **2** [DMEP, DMPP = $Me_2N(CH_2)_nN$=CH-2-C_5H_4N, n = 2, 3, respectively], contain ligands that chelate to platinum through the imine and pyridyl groups, with the tertiary amine group not coordinated. Methyl iodide reacted with complex **1** to give [$PtIMe_3$(DMEP)] but reacted with **2** to give a mixture of [$PtIMe_3$(DMPP)] and [$PtMe_3$(DMPP)]I, indicating the greater ability of DMPP to act as a *fac*-tridentate ligand. Complex **2** reacted with MeO_3SCF_3 to form [$PtMe_3$(DMPP)][CF_3SO_3] only. The primary reaction of **1** and **2** with HX (X = Cl, O_2CCF_3, or O_3SCF_3) occurred by protonation of the pendant amine, while with excess acid, a methylplatinum bond trans to imine was cleaved selectively. Two products of protonolysis, namely [PtMe(DMEP)][O_3SCF_3], containing *mer*-tridentate DMEP, and [$PtMe(O_2CCF_3)$(DMEPH)][O_2CCF_3], with a protonated bidentate DMEP ligand, have been characterized by structure determinations, and the reaction pathways have been deduced by monitoring the reactions by ^{1}H NMR at varying temperature. In the reaction of **2** with HCl, an intermediate hydridoplatinum(IV) complex [$PtHClMe_2$(DMPPH)][Cl] was detected and determined to be stable up to −30 °C, when it decomposed to give methane and [PtClMe(DMPPH)][Cl].

Introduction

There have been recent breakthroughs in the study of C−H bond activation, especially of methane, by electrophilic platinum(II) complexes.[1,2] Much mechanistic insight has been gained by studying the microscopic reverse reaction of C−H activation, namely the reductive elimination of methane from hydrido(methyl)-platinum(IV) complexes. Such complexes are most readily generated by oxidative addition of a protic acid to a methylplatinum(II) precursor, and several such complexes have been characterized by low-temperature NMR methods.[3] However, unless carefully designed for stability,[4] the hydrido(methyl)platinum(IV) complexes readily undergo reductive elimination of methane. Indeed, there has been a debate about whether it is necessary that the hydrido(methyl)platinum(IV) intermediate is on the pathway to methane formation in all cases, since cleavage of metal−carbon bonds by direct attack of a proton at the σ(M−C) bond is a well-established mechanism.[5] Most recent experimental and theoretical studies support the oxidative addition/reductive elimination mechanism of protonolysis of methylplatinum bonds.[1−4,6] However, it should be noted that, in the case of hydridoplatinum(II) complexes, cases are known in which a proton may react at the platinum center by oxidative addition, but also in which it may attack the hydride to give a dihydrogen complex or attack another ligand such as cyanide.[7] Clearly there is similar potential for attack of protons at different sites in methylplatinum(II) complexes.

Previous studies have been made of protonation of dimethylplatinum(II) complexes using ligands that have a preference for *fac*-tridentate coordination but which, in the square planar dimethylplatinum(II) precursor

(1) (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560. (b) Johansson, L.; Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1999**, *121*, 1974. (c) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235. (d) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848.

(2) Stahl, S. S.; Labinger J. A.; Bercaw J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2181.

(3) (a) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (b) Stahl, S. S.; Labinger J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961 (c) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371. (d) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75. (e) Hutson, A. C.; Lin, M.; Basickes, N.; Sen, A. *J. Organomet. Chem.* **1995**, *504*, 69. (f) Sen, A.; Lin, M.; Kao, L. C.; Hutson, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6385.

(4) (a) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845. (b) O'Reilly, S. A.; White P. S.; Templeton, J. L.; *J. Am. Chem. Soc.* **1996**, *118*, 5684. (c) Prokopchuk, E. M.; Jenkins, H. A.; Puddephatt R. J. *Organometallics* **1999**, *18*, 2861. (d) Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735.

(5) (a) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U. *Inorg. Chim Acta* **1986**, *112*, L15. (b) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U.; Crociani, B. *Inorg. Chim Acta* **1985**, *100*, 107. (c) Belluco, U.; Michelin, R. A.; Uguagliati. P.; Crociani, B. *J. Organomet. Chem.* **1983**, *250*, 565. (d) Jawad, J. K. Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1977**, 892. (e) Jawad, J. K.; Puddephatt, R. J.; Stalteri M. A. *Inorg. Chem.* **1982**, *21*, 332. (f) Uguagliati, P.; Michelin, R. R.; Belluco, U.; Ros, R. *J. Organomet. Chem.* **1979**, *169*, 115. (g) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57. (h) Romeo, R.; Minniti, D.; Lanza, S.; Uguagliati, P.; Belluco, U. *Inorg. Chem.* **1978**, *17*, 2813. (i) Belluco, U. Guistiniani, M.; Graziani, M. *J. Am. Chem. Soc.* **1967**, *89*, 6494. (j) Belluco, U.; Croatto, U.; Uguagliati, P.; Peitropaolo, R. *Inorg. Chem.* **1967**, *6*, 718. (k) Falk, C. D.; Halpern, J. *J. Am. Chem. Soc.* **1965**, *87*, 3523. (l) Canty, A. J.; Van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406. (m) Romeo, R.; Plutino, M. R.; Elding, L. I. *Inorg. Chem.* **1997**, *36*, 5909.

(6) (a) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478. (b) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. Personal communication. (c) Mylvaganam, K.; Bacskay, G. B.; Hush, N. S. Personal communication.

(7) Stahl, S. S.; Labinger J. A.; Bercaw, J. E. *Inorg. Chem.* **1998**, *37*, 2422.

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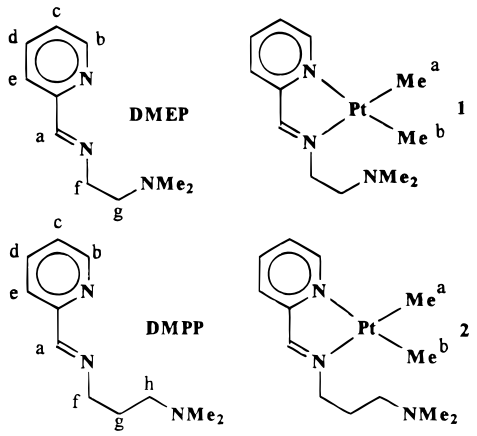
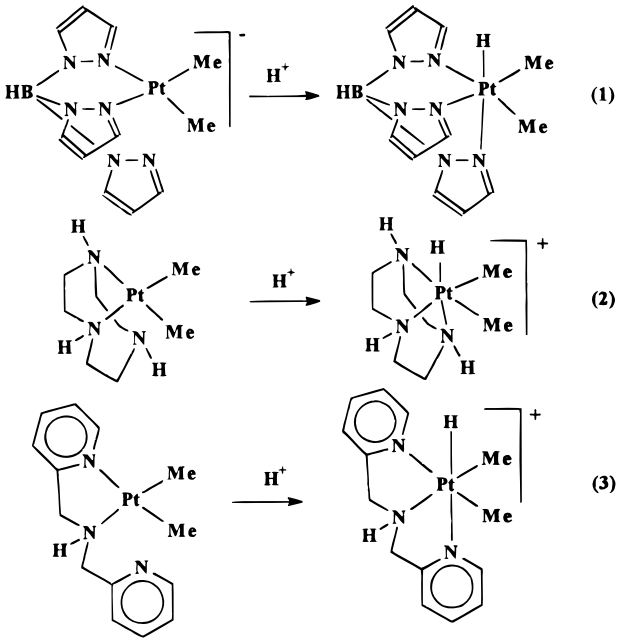
Chart 1. Ligands and NMR Labeling Scheme



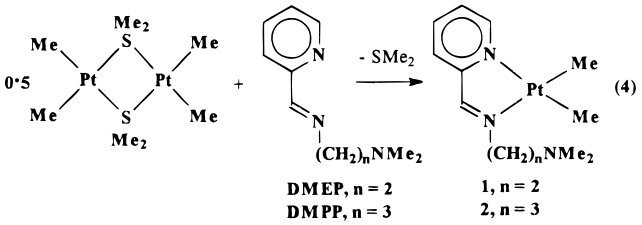
complexes, must be bidentate.[4] In each case, the proton adds to platinum to give very stable hydrido(methyl)-platinum(IV) complexes (eqs 1,2). If the ligand is more flexible, as with bis(pyridylmethyl)amine, BPMA, protonation still occurs at platinum, but the product complex is less thermally stable and undergoes slow loss of methane by reductive elimination (eq 3).[8]



The question then naturally arises as to how well the stability of the hydrido(methyl)platinum(IV) complexes can be controlled by ancillary ligand design. For useful catalytic methane activation, the hydrido(methyl)platinum(IV) complexes need to be easily accessible but not too stable, since further functionalization is required.[1,2] This paper describes chemistry based on the two ligands DMEP and DMPP and their dimethylplatinum(II) complexes defined in Chart 1. These ligands differ from BPMA (eq 3) in two respects. First, they contain an unsaturated imine link that causes strain when bound as *fac*-tridentate ligands, and so they should be less effective in stabilizing the hydrido(methyl)platinum(IV) products. This effect should be most significant with DMEP since it contains a shorter spacer group to the dimethylamino group than in DMPP (Chart 1).[9] Second, the dimethylplatinum(II) complexes **1** and **2** contain a free dimethylamino group, in contrast to the free pyridyl group in the BPMA complex (eq 3). The $-NMe_2$ group is a stronger base toward H^+ than the pyridyl group in BPMA,[10] but not so good a ligand for platinum; this effect might therefore favor protonation of **1** and **2** at nitrogen rather than platinum. The results are reported below.

Results

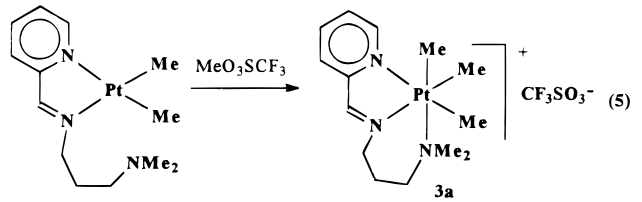
The complexes [$PtMe_2$(DMEP)], **1**, and [$PtMe_2$(DMPP)], **2**, were prepared by reacting [$Pt_2Me_4(\mu$-$SMe_2)_2$] with the corresponding ligand (eq 4). They were isolated as red,



air-stable solids. They are both soluble in dichloromethane, but [$PtMe_2$(DMPP)], **2**, is much more soluble in diethyl ether than [$PtMe_2$(DMEP)], **1**, presumably due to the longer link to the free amine group.

Complexes **1** and **2** were characterized by their ^1H NMR spectra (see Chart 1 for the NMR labeling scheme and Table 1 for selected data). The key question is which two nitrogen atoms of the ligand coordinate to platinum in **1** and **2**, and this is readily determined from the ^{195}Pt satellite spectra of ligand resonances. Thus **1** gives the coupling constants $^3J(PtH_a) = 36$ Hz, $^3J(PtH_b) = 16$ Hz, and $^3J(PtH_f) = 18$ Hz, but there are no resolved platinum couplings for H_g or for the NMe_2 protons. Hence it is clear that the pyridyl and imine groups are coordinated, but the NMe_2 group is not. Complex **1** gave two MePt resonances with couplings $^2J(PtMe) = 88$ and 84 Hz, in the expected range for methyl groups trans to nitrogen in platinum(II) complexes.[8] The assignment of these resonances to specific methyl groups is uncertain, but that with the lower coupling $^2J(PtMe)$ is tentatively assigned to the methyl group trans to the imine group on the basis that the imine is expected to have a slightly greater trans influence. Complex **2** had similar NMR parameters (Table 1) and so is assigned an analogous structure.

Oxidative Addition Reactions of MeO_3SCF_3 and MeI. These reactions were studied as models for the protonation reactions since trimethylplatinum(IV) complexes are stable and are readily characterized by NMR. The reaction of [$PtMe_2$(DMPP)] with MeO_3SCF_3 gave [$PtMe_3$(DMPP)][O_3SCF_3], **3a**, according to eq 5. The ^1H



NMR spectrum gave the ^{195}PtH couplings $^3J(PtH_a) =$

(8) Jenkins, H. A.; Yap, G. P. A.; Puddephatt R. J. *Organometallics* **1997**, *16*, 1946.

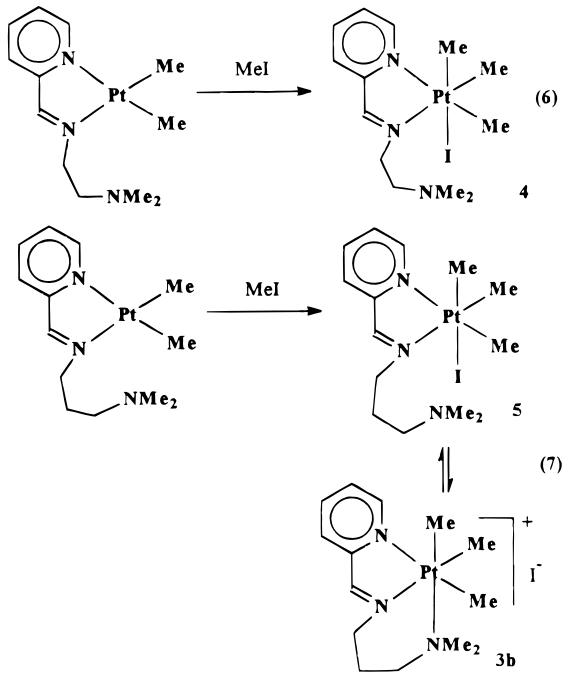
Table 1. Selected NMR Data for the Complexes (see Chart 1 for labels)

complex	$\delta(H_a)$	J(PtH)	$\delta(H_b)$	J(PtH)	δ(NMe)	J(PtH)	δ(PtMe)	J(PtH)
1	9.12	36	9.13	16	2.26		1.10	84
							1.02	88
2	9.12	36	9.14	16	2.18		1.20	84
							1.06	88
3	9.74	36	8.94	13	2.53	16	1.04	68
					2.16	8	0.98	66
							0.34	66
4	9.13	30	8.95	12	2.27		1.36	70
							1.34	72
							0.60	70
5	9.02	30	8.93	12	2.34		1.46	70
							1.43	69
							0.59	71
6	9.65	36	9.04	16	2.75		0.95	84
							0.89	88
7	9.53	36	9.06	16	2.69		0.92	84
							0.81	88
8a	9.54	103	9.38	8	2.34		1.16	80
9a	9.35	103	9.10	8	2.28		1.16	80
10	9.75	48	8.66	48	2.98	46	0.94	77
11	10.29	48	8.83	52	2.90	48	1.06	76
12	9.32	27	8.81		2.77		1.20	67
							1.18	65
13a	9.41	103	9.40	8	2.50		1.12	80
14a	9.86	103	9.50	8	2.80		1.14	80

36 Hz and $^3J(PtH_b) = 13$ Hz, showing that the pyridyl and imine groups were still coordinated. In addition, two resonances were observed for the diastereotopic NMe_2 protons at $\delta = 2.16$ [^3J(PtH) = 8 Hz] and $\delta = 2.53$ [^3J(PtH) = 16 Hz], confirming that this nitrogen atom is now also coordinated. There were three MePt resonances with couplings ^2J(PtMe) in the range expected for methylplatinum(IV) groups trans to nitrogen. Hence the stereochemistry shown in eq 5 is confirmed. However, the reaction of [$PtMe_2$(DMEP)] with MeO_3SCF_3, as monitored by ^{1}H NMR in acetone-d_6, formed a complex mixture of products, which could not be identified. This result clearly shows that the DMEP ligand cannot readily act as a *fac*-tridentate ligand to platinum(IV), whereas DMPP can do so.

The reaction of **1** with MeI gave [$PtIMe_3$(DMEP)], **4**, only. However, the reaction path of **2** with MeI was solvent dependent. Reaction in dichloromethane gave [$PtIMe_3$(DMPP)], **5**, but reaction in acetone-d_6 gave a 1:1 equilibrium mixture of **5** and the ionic [$PtMe_3$-(DMPP)]I, **3b**. Again, this reaction shows that DMPP is more suited for *fac*-tridentate coordination to platinum(IV) than DMEP, and there is a competition between coordination of iodide and the NMe_2 group in this case. As expected, neither DMPP nor DMEP is as effective as BPMA[8] for *fac*-tridentate coordination to platinum(IV), because of their greater rigidity. Under the conditions used, with 1 equiv of MeX, no quaternization of the tertiary amine was observed to occur in **4** or **5**. In these reactions, oxidative addition at platinum(II) is faster than quaternization at nitrogen.

Protonolysis Reactions. Reactions of **1** or **2** with 1 equiv of acid HX at room temperature occurred as shown in Scheme 1 by initial protonation of the free dimethylamino group to give **6** or **7**, respectively. The ^{1}H NMR spectra of **6** or **7** were similar to those of the precursors **1** or **2**, respectively (Table 1), and there was

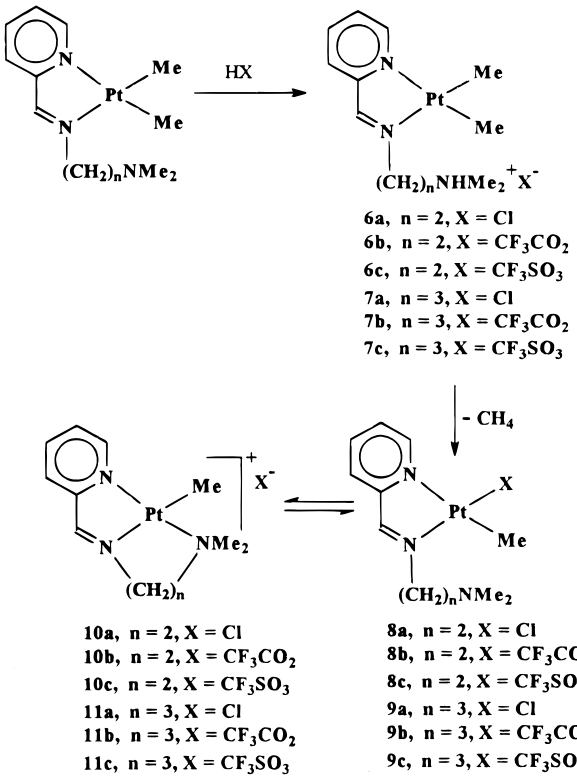


no evidence for formation of hydrido(methyl)platinum(IV) complexes. The complexes **6** or **7** decomposed slowly over a period of hours to give methane, but the nature of the organoplatinum products formed was dependent on the specific acid HX used, as discussed below.

When X = Cl, the complex **6a** slowly eliminated methane to give a mixture of **8a** and **10a**. As monitored by ^{1}H NMR, complex **8a** was the major product initially, but the concentration of **10a** increased in the later stages. Hence it seems that the initial methane loss gives **8a**, which then rearranges to give an equilibrium mixture with **10a**. When X = CF_3CO_2, complex **6b** slowly lost methane to give **8b**, which could be isolated in pure form, but which rearranged slowly to **10b** in solution. Finally, when X = CF_3SO_3, complex **6c** slowly eliminated methane to give **10c**, but the complex **8c** was not observed at any stage of the reaction.

(9) For previous work on these ligands see: Bamfield, P.; Price, R.; Miller R. G. *J. Chem. Soc. (A)* **1969**, 1447.
(10) Issacs, N. *Physical Organic Chemistry*, 2nd ed.: Longman Group: London, UK, 1996.

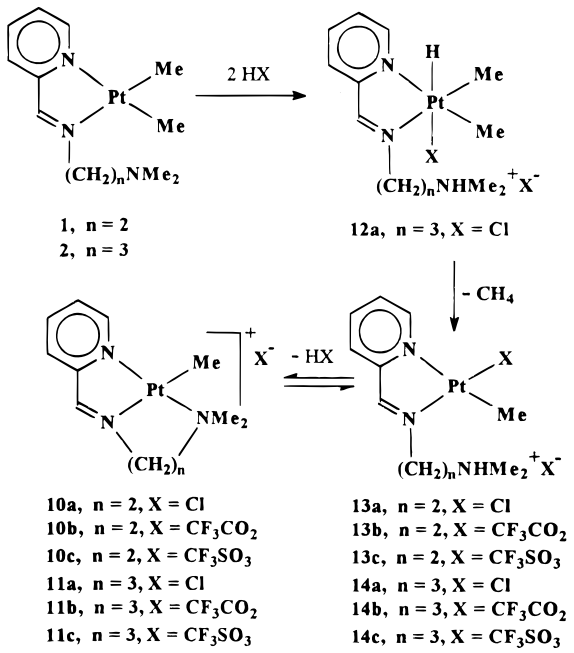
Scheme 1. Protonation with 1 equiv of HX



Similar chemistry was observed for complexes **7** (Scheme 1). When X = Cl, a mixture of **9a** and **11a** was formed and the ratio **9a**:**11a** decreased through the course of reaction, as expected if **9a** is the primary product of methane loss. However, when X = CF_3CO_2 or CF_3SO_3, only the final product **11b** or **11c** was observed after methane loss from **7b** or **7c**, respectively. By analogy with the above observations, we suggest that the primary products are **9b** and **9c**, but that these complexes rearrange faster than they are formed, so are not observed. The rearrangement of **8** to **10** or **9** to **11** is likely to occur by an associative mechanism in which the free dimethylamino group attacks platinum(II) at an axial site, and this is naturally faster for **9** than for **8**, since the intermediate requires DMEP to act as a *fac*-tridentate ligand. We know from the methyl iodide reactions described above that this form of coordination for DMEP is unfavorable due to ring strain. Overall then, there are two important effects in play. First, thermodynamic effects are similar for the DMEP and DMPP complexes. Chloride can compete with the free amine for coordination to platinum, but trifluoroacetate or triflate cannot. Hence an equilibrium is formed between **8a** and **10a** or **9a** and **11a**, when X = Cl, but only the analogous complex **10** or **11** is present after long reaction times when X = CF_3CO_2 or CF_3SO_3. Second, the rate of isomerization is significantly greater for **9** than for **8**, as a result of the greater flexibility of DMPP over DMEP. In the rearrangements of **6** or **7** to **8** or **9**, respectively, it is likely that the proton is transferred from nitrogen to platinum, followed by regioselective reductive elimination of methane.

Reaction of **1** or **2** with 2 equiv of protic acid HX at room temperature leads to immediate loss of methane. When X = Cl or CF_3CO_2, the first organoplatinum products observed were **13** or **14**, and these rearranged

Scheme 2. Protonation with 1 equiv of HX



slowly over a period of about 1 day to give entirely (X = CF_3CO_2) or in large part (X = Cl) the corresponding complexes **10** or **11**, according to Scheme 2. When X = CF_3SO_3, only **10c** or **11c** was observed, and it is presumed that the intermediate **13c** or **14c** rearranges very rapidly in this case (Scheme 2).

A major difference in the chemistry of Schemes 1 and 2 is that the methane loss is very much faster when 2 equiv of acid are used. Clearly, the first equivalent of acid is consumed by reaction with the free amine group of **1** or **2** and the ammonium ion so formed is not sufficiently acidic to react rapidly with the methylplatinum groups with loss of methane (Scheme 1). The second acid equivalent can oxidatively add to platinum(II) to give a hydridodimethylplatinum(IV) intermediate (Scheme 2), but this is not stabilized since the amine group is protonated and does not coordinate. Hence it rapidly loses methane and is not observed in the room-temperature reactions. Since the complexes **13** or **14** are formed rapidly in Scheme 2, they are readily characterized when X = Cl or CF_3CO_2, although, with the very labile triflate ligand, they are still not detected. Complexes **13** or **14** need to lose HX in order to form **10** or **11** (Scheme 2), and so this reaction is slower than the corresponding reaction of Scheme 1.

All the reactions of Schemes 1 and 2 were monitored by low-temperature ^{1}H NMR, by adding the required acid to a solution of **1** or **2** at −78 °C and recording spectra at −80 °C, then at various intermediate temperatures as the solution was warmed in steps to room temperature. No hydridoplatinum intermediates were detected when 1 equiv of acid was used (Scheme 1), and the only successful detection of a hydride was made in the reaction of **2** with 2 equiv of HCl (Scheme 2). The hydride **12a** was formed at −80 °C and decayed to form **14a** at about −30 °C. In this case, the hydride intermediate is slightly less stable than those formed in analogous reactions of dimethylplatinum(II) complexes with simple diimine ligands such as 2,2′-bipyridine.[2,3] In no case did protonation of **1** give a detectable hydride

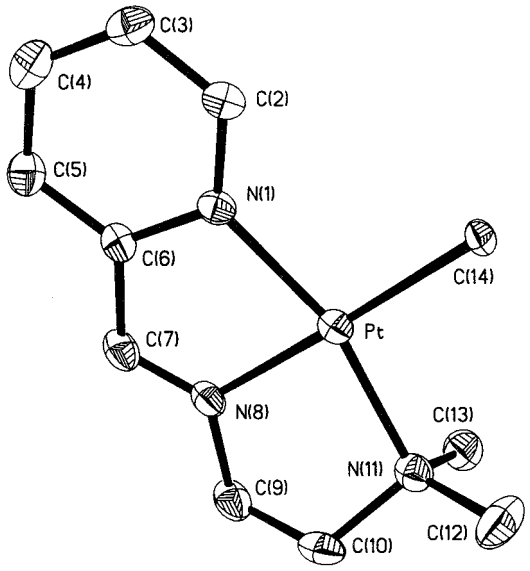


Figure 1. View of the structure of the complex [PtMe(DMEP)]$^+$ in **10c**.

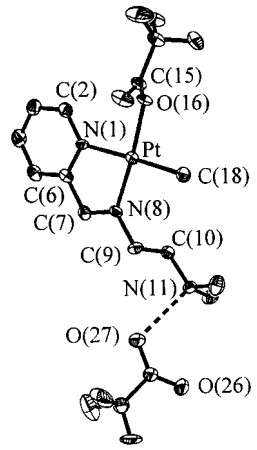


Figure 2. View of the structure of the cation [PtMe(O_2-CCF_3)(DMEPH)]$^+CF_3CO_2^-$, **13b**. The hydrogen bonding between cation and anion is indicated by a dotted line. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 10c

Pt−N(8)	1.994(4)	Pt−N(11)	2.02(3)
Pt−N(1)	2.024(4)	Pt−C(14)	2.099(4)
Pt−N(11)	2.10(2)	N(1)−C(2)	1.342(5)
N(1)−C(6)	1.365(5)	C(7)−N(8)	1.253(6)
N(8)−C(9)	1.463(6)	C(10)−N(11)	1.48(1)
N(11)−C(12)	1.48(1)	N(11)−C(13)	1.49(1)
N(8)−Pt−N(11)	86.1(5)	N(8)−Pt−N(1)	79.6(2)
N(11)−Pt−N(1)	165.7(5)	N(8)−Pt−C(14)	177.91(17)
N(11)−Pt−C(14)	95.2(5)	N(1)−Pt−C(14)	99.08(16)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 13b

Pt−N(8)	2.001(6)	Pt−O(16)	2.026(5)
Pt−C(18)	2.036(7)	Pt−N(1)	2.079(6)
N(1)−C(2)	1.332(9)	N(1)−C(6)	1.354(8)
C(7)−N(8)	1.305(8)	N(8)−C(9)	1.470(9)
C(10)−N(11)	1.463(8)	N(11)−C(12)	1.477(9)
N(11)−C(13)	1.484(8)		
N(8)−Pt−O(16)	173.6(2)	N(8)−Pt−C(18)	97.8(3)
O(16)−Pt−C(18)	88.4(3)	N(8)−Pt−N(1)	79.5(2)
O(16)−Pt−N(1)	94.3(2)	C(18)−Pt−N(1)	177.2(3)

intermediate, and if it is assumed that such species are formed transiently, they clearly undergo very rapid reductive elimination even at −80 °C. The presumed hydridoplatinum(IV) intermediates are apparently destabilized by the adjacent cationic ammonium functionality, especially in complexes of DMEP.

The reactions of Schemes 1 and 2, X = CF_3SO_3, were monitored using deuterium-labeled reagents to search for H−D exchange reactions. The reaction of **1** or **2** with either 1 or 2 equiv of CF_3SO_3D in CD_2Cl_2/CD_3OD solvent medium ultimately gave only CH_3D and **10c** or **11c**, respectively. The reaction with 1 equiv of acid is slow and was monitored over several hours at room temperature, but there was no incorporation of deuterium label in the methylplatinum groups of either the intermediate **6c** or **7c** or in the product **10c** or **11c** (Scheme 1). Hence, unlike some other cases studied,[2,3,8] any CH_3D complex intermediates formed in these reactions are too short-lived to undergo reversible reaction to $H(CH_2D)Pt(IV)$ complexes. The C−H bond formation step is not reversible under the conditions used.

The complexes of Schemes 1 and 2 were characterized by their ^{1}H NMR spectra (Experimental Section, Table 1). For example, referring to the ligand labeling scheme of Chart 1, complex **8a** shows $\delta(H_a) = 9.04$ with $^3J(PtH) = 103$ Hz and $\delta(H_b) = 9.38$ with $^3J(PtH) = 8$ Hz. The much larger coupling $^3J(PtH)$ to the imine proton than to the ortho-pyridyl proton clearly indicates that the pyridyl group is trans to methyl and the imine trans to chloride. The absence of coupling between platinum and the NMe_2 protons shows that the amine group is not coordinated. There was only one methylplatinum resonance, and the coupling $^2J(PtMe) = 80$ Hz shows that it is trans to nitrogen in a platinum(II) complex. Together, these data define the stereochemistry at platinum, and the remaining NMR data are fully consistent with the structural assignment. For the isomerized complex **10a**, the ^{1}H NMR spectrum gave $\delta(H_a) = 9.75$ with $^3J(PtH) = 47$ Hz, much lower than in **8a** since the imine is now trans to methyl with its higher trans-influence. The ortho-pyridyl proton was observed at $\delta(H_b) = 8.66$, and the coupling $^3J(PtH) = 48$ Hz was much larger than in **8a** since the pyridyl group is trans to NMe_2 in **10a**. The NMe_2 resonance of **10a** was observed at $\delta = 2.98$ with $^3J(PtH) = 46$ Hz, showing that this group is now coordinated to platinum. The methylplatinum resonance of **10a** was observed at $\delta = 0.94$ with $^2J(PtMe) = 77$ Hz. The structures of the other platinum(II) complexes of Schemes 1 and 2 were deduced similarly (Table 1).

The hydrido(dimethyl)platinum(IV) complex **12a** was characterized by its NMR spectrum obtained at −80 °C. The hydride resonance was observed at $\delta = -22.0$ with $^1J(PtH) = 1587$ Hz (trans to Cl). Two methylplatinum(IV) resonances were observed at $\delta = 1.20$, $^2J(PtH) = 67$ Hz and $\delta = 1.18$, $^2J(PtH) = 65$ Hz. These parameters are similar to those for several known hydrido(dimethyl)platinum(IV) complexes.[3,4,8] No platinum satellite peaks were observed for the NMe_2 proton resonance, showing that it was not coordinated.

The structures of the DMEP complexes **10c** and **13b** were confirmed crystallographically. The structures are shown in Figures 1 and 2, and selected bond distances and angles are listed in Tables 2 and 3.

The complex **10c** contains DMEP as a *mer*-tridentate ligand, with the methyl group trans to the central imine

nitrogen atom (Figure 1). Interestingly, the shortest Pt−N bond length is Pt−N(8) = 1.994(4) Å, for the imine nitrogen that is trans to methyl, though it is only marginally shorter than the other two, which are mutually trans. Due to chelate constraints of DMEP, the angles N(8)−Pt−N(11) = 86.1(5)° and N(8)−Pt−N(1) = 79.6(2)° are less than 90°, and the angles N(11)−Pt−C(14) = 95.2(5)° and N(1)−Pt−C(14) = 99.1(2)° are greater than 90°. This chelate constraint may be responsible for the short distance Pt−N(8) also.

The structure of **13b** (Figure 2) contains a square-planar platinum(II) center with the protonated DMPP acting as a bidentate ligand, bound through the pyridyl and imine nitrogen atoms. The methyl group is trans to pyridyl, and the trifluoroacetate ligand is trans to imine. The complex **13b** is cationic, and there is a second ionic trifluoroacetate ion that is hydrogen bonded to the NH proton (Figure 2). The bond distance Pt−N(1) (trans to methyl) is longer than Pt−N(8) (trans to oxygen donor), as expected. The angle N(8)−Pt−N(1) = 79.5(2)° is less than 90° due to the chelate constraint, and the angles N(8)−Pt−C(18) = 97.8(3)° and O(16)−Pt−N(1) = 94.3(2)° are greater than 90° as a result.

Discussion

This work has shown that the ligand DMEP can be bidentate or *mer*-tridentate in platinum complexes but not *fac*-tridentate. The more flexible DMPP can coordinate to platinum as a bidentate in a *mer*-tridentate manner or, albeit not very effectively, as a *fac*-tridentate ligand. The ability of the ligands to act as *fac*-tridentates is critical in giving stable hydrido(dimethyl)platinum(IV) complexes, and these ligands therefore do not stabilize such complexes. In addition, the saturated tertiary nitrogen is a relatively hard donor and so has a greater affinity for a proton than for platinum. The effect is that the first proton added to the complexes **1** or **2** adds to the amine and not to platinum. Although a second proton may add at the platinum(II) center, the protonated amine is unable to provide stabilization. Indeed, the positive charge appears to lead to an overall destabilization compared to analogous complexes, such as those derived from [$PtMe_2$(2,2′-bipyridyl)], which contain simpler bidentate diimine ligands. The ligands DMEP and DMPP are thus less effective than BPMA (eq 3) in stabilizing hydrido(dimethyl)platinum(IV) complexes. This is partly because BPMA is more flexible and partly because the dimethylplatinum(II) complexes contain a free pyridyl rather than a tertiary amine donor. The pyridyl group is a better donor to platinum than to the proton (the pK_a's for pyridinium and Me_3NH^+ are 5.21 and 9.80, respectively),[10] and so the first proton attacks [$PtMe_2$(BPMA)] at platinum rather than at the free pyridyl group (eq 3). Comparison of these systems thus defines the factors needed in a tridentate ligand to control the thermal stability of the hydrido(dimethyl)platinum(IV) intermediates in protonolysis of methylplatinum bonds and hence also in alkane activation reactions.[1,2]

The protonolysis reactions lead to selective cleavage of the methyl group trans to the imine rather than that trans to pyridyl. We suggest that this is primarily a result of the greater trans-influence of the imine compared to the pyridyl donor, but it is interesting that the effect is so great. Because of this selectivity, the free amine donor is unable to coordinate to platinum as the methane leaves, and so the anion coordinates to give **8**, **9** (Scheme 1) or **13**, **14** (Scheme 2) depending on the pH. The isomerization of **8**, **9** to **10**, **11** (Scheme 1) requires displacement of X^- by the free amine group, but this must be accompanied by stereochemical change, and this is unusual in square planar substitution reactions. It is possible that the reaction follows a different mechanism. For example, an intermolecular Me for X exchange could lead to stereochemical change at platinum(II),[11] and then, when X is syn to the free amine group, the substitution reaction could occur easily with retention of stereochemistry. In any case, unless the ligand X^- is the very labile triflate, the kinetic product survives long enough to be detected and, in some cases, to be isolated in pure form.

Experimental Section

^{1}H NMR spectra were recorded using a Varian Gemini 200 or 300 MHz spectrometer. Solvents were dried and distilled under N_2 immediately before use. Mass spectra were recorded using a Finnigan-MAT 8200 spectrometer. [$PtMe_2(\mu$-$SMe_2)]_2$ was prepared as described in the literature.[12] Reactions using organometallics were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Several of the salts proved difficult to obtain in analytically pure form, either because they underwent partial deprotonation during crystallization or because they were hygroscopic. Hence some of the analytical data given are outside the normal limits.

DMEP. A mixture of 2-pyridinecarboxaldehyde (0.434 mL, 4.6 mmol) and 2-dimethylaminoethylamine (0.500 mL, 4.6 mmol) in diethyl ether (75 mL) was stirred at room temperature for 24 h with excess magnesium sulfate. The magnesium sulfate was filtered off and the solvent removed by vacuum to give the product as a pale yellow oil. Yield: 90%. NMR in $CDCl_3$: δ(^{1}H) = 8.38 [s, 1H H_a]; 8.62 [d, 1H]; 7.96 [d, 1H]; 7.68 [t, 1H]; 7.26 [t, 1H]; 3.76 [t, 2H, H_f]; 2.65 [t, 2H, H_g]; 2.28 [s, 6H, NMe_2].

DMPP. This was prepared similarly but using 3-dimethylaminopropylamine. Yield: 90%. NMR in $CDCl_3$: δ(^{1}H) = 8.38 [s, 1H, H_a]; 8.61 [d, 1H]; 7.98 [d, 1H]; 7.73 [t, 1H]; 7.29 [t, 1H]; 3.68 [t, 2H, H_f]; 2.33 [t, 2H, H_h]; 2.12 [s, 6H, NMe_2]; 1.85 [t, 2H, H_g].

[$PtMe_2$(DMEP)], 1. A solution of DMEP (0.144 g, 0.814 mmol) in diethyl ether (1 mL) was added via cannula to a solution of [$PtMe_2(\mu$-$SMe_2)]_2$ (0.234 g, 0.407 mmol) in diethyl ether (10 mL) in a Schlenk flask under N_2. The colorless solution turned red immediately, and a red precipitate of the product formed while the reaction mixture stirred overnight. The red precipitate was filtered off and washed with dry pentane (5 mL). Yield: 0.264 g, 81%. Anal. Calcd for $C_{12}H_{21}N_3Pt$: C, 35.8; H, 5.3; N, 10.4. Found: C, 35.4; H, 5.3; N, 10.1. NMR in CD_2Cl_2: δ(^{1}H) = 9.12 [s, 1H, ^3J(PtH) = 36 Hz, H_a]; 9.13 [d, 1H, ^3J(PtH) = 16 Hz, H_b]; 8.09 [t, 1H, H_c]; 7.70 [d, 1H, H_d]; 7.57 [t, 1H, H_e]; 4.14 [t, 2H, ^3J(PtH) = 18 Hz, H_f]; 2.71 [t, 2H, H_g]; 2.26 [s, 6H, NMe_2]; 1.10 [s, 3H, ^2J(PtH) = 84 Hz, PtMe]; 1.02 [s, 3H, ^2J(PtH) = 88 Hz, PtMe].

[$PtMe_2$(DMPP)], 2. This was prepared similarly but using DMPP and was isolated as a red solid. Yield: 0.368 g, 78%. Anal. Calcd for $C_{13}H_{23}N_3Pt$: C, 37.5; H, 5.6; N, 10.1. Found: C, 37.0; H, 5.6; N, 9.8. NMR in $CDCl_3$: δ(^{1}H) = 9.12 [s, 1H, ^3J(PtH) = 36 Hz, H_a trans to Me]; 9.14 [d, 1H, ^3J(PtH) = 16 Hz, H_b]; 8.06 [t, 1H, H_c]; 7.64 [d, 1H, H_d]; 7.56 [t, 1H, H_e]; 4.16 [t, 2H, ^3J(PtH) = 16 Hz, H_f]; 2.30 [t, 2H, H_h]; 2.18 [s, 6H, N-Me_2]; 2.00 [q, 2H, H_g]; 1.20 [s, 3H, ^2J(PtH) = 84 Hz, PtMe]; 1.06 [s, 3H, ^2J(PtH) = 88 Hz, PtMe].

(11) Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1219.
(12) Hill, G. S.; Irwin, M. J.; Rendina, L. M.; Puddephatt, R. J. *Inorg. Synth.* **1998**, *32*, 149.

[PtMe$_3$(DMPP)][CF$_3$SO$_3$], 3a. CF_3SO_3Me (10.3 μL, 0.091 mmol) was added to a solution of **2** (38 mg, 0.091 mmol) in CH_2Cl_2 (5 mL). The initial red solution of **2** immediately turned to a pale amber color. The reaction mixture was stirred overnight, and removal of solvent in vacuo gave the product as a hygroscopic amber powder. Yield: 40 mg, 76%. Anal. Calcd for $C_{15}H_{26}F_3N_3O_3PtS$: C, 31.0; H, 4.5; N, 7.2. Found: C, 30.2; H, 4.4; N, 7.3. MS: *m*/*z* calcd for $PtMe_3(DMPP)^+$: 431. Found: *m*/*z* = 431. NMR in acetone-d_6: $\delta(^1H) = 9.74$ [s, 1H, ^3J(PtH) =36 Hz H_a]; 8.94 [d, 1H, ^3J(PtH) =13 Hz, H_b]; 8.45 [dd, 1H, H_c]; 8.40 [td, 1H, H_d], 8.2 [m, 1H, H_e], 4.35 [t, 2H, ^3J(PtH) = 26 Hz, H_f]; 3.34 [m, 2H, H_h], 2.53 [s, 3H, ^3J(PtH) = 16 Hz, NMe]; 2.16 [s, 3H, ^3J(PtH) = 8 Hz, NMe]; 2.25 [m, 2H, H_g]; 1.04 [s, 3H, ^2J(PtH) = 68 Hz, $PtCH_3$]; 0.98 [s, 3H, ^2J(PtH) = 66 Hz, $PtCH_3$]; 0.34 [s, 3H, ^2J(PtH) = 66 Hz, $PtCH_3$ trans to $-NMe_2$].

The product obtained by similar reaction of **1** with CF_3SO_3-Me was a complex mixture whose NMR spectrum contained over 20 peaks in the PtMe region $\delta = 0.8-1.2$.

[PtIMe$_3$(DMEP)], 4. To a solution of **1** (22 mg, 0.054 mmol) in CH_2Cl_2 (3 mL) was added MeI (3.4 μL, 0.054 mmol), immediately producing a red to light amber color change. Removal of solvent in vacuo and recrystalization from dry CH_2-Cl_2/pentane gave the product as a yellow powder. Yield: 18 mg, 60%. Anal. Calcd for $C_{13}H_{24}IN_2Pt$: C, 28.7; H, 4.4; N, 7.7. Found: C, 29.0; H, 4.4; N, 7.7. NMR in acetone-d_6: $\delta(^1H)$ = 9.13 [s, 1H, ^3J(PtH) = 30 Hz, H_a]; 8.95 [d, 1H, ^3J(PtH) = 12 Hz, H_b]; 8.25 [d, 1H, H_c]; 8.28 [m, 1H, H_d]; 7.84 [m, 1H, H_e]; 4.12 [t, 2H, ^3J(PtH) = 15 Hz, H_f]; 2.79 [m, 2H, H_g]; 2.27 [s, 6H, NMe_2]; 1.34 [s, 3H, ^2J(PtH) = 72 Hz, Pt$-CH_3$]; 1.36 [s, 3H, ^2J(PtH) = 70 Hz, Pt$-CH_3$]; 0.60 [s, 3H, ^2J(PtH) =73 Hz, $PtCH_3$ trans to I].

[PtIMe$_3$(DMPP)], 5. To a solution of [$PtMe_2$(DMPP)] (32 mg, 0.077 mmol) in CH_2Cl_2 (2 mL) was added MeI (4.8 μL, 0.077 mmol). The color changed rapidly from red to pale amber. Removal of solvent in vacuo gave the product as an amber powder. Yield: 30 mg, 70%. Anal. Calcd for $C_{14}H_{26}IN_3Pt$: C, 30.1; H, 4.7; N, 7.5. Found: C, 29.9; H, 4.7; N, 7.2. NMR in $CDCl_3$: $\delta(^1H) = 9.02$ [s, 1H, ^3J(PtH) = 30 Hz, H_a]; 8.93 [d, 1H, ^3J(PtH) = 12 Hz, H_b]; 8.03 [t, 1H, H_c]; 7.95 [d, 1H, H_d]; 7.65 [m, 1H, H_e]; 4.18 [t, 2H, ^3J(PtH) = 18 Hz, H_f]; 3.34 [m, 2H, H_h]; 2.34 [s, 6H, NMe_2]; 2.13 [m, 2H, H_g]; 1.46 [s, 3H, ^2J(PtH) =70 Hz, PtMe]; 1.43 [s, 3H, ^2J(PtH) = 69 Hz, PtMe]; 0.59 [s, 3H, ^2J(PtH) = 71 Hz, Pt$-$Me].

A similar reaction of **2** with MeI in acetone-d_6 gave a mixture of **3b** and **5**, as determined by the ^{1}H NMR spectrum. The parameters for **3b** were similar to those listed above for **3a**.

[PtMe$_2$(DMEPH)]Cl, 6a. Me_3SiCl (12.6 μL, 0.099 mmol) (to produce HCl in situ by reaction with water) was added to a solution of [$PtMe_2$(DMEP)] (40 mg, 0.099 mmol) and H_2O (1.8 μL, 0.10 mmol) in THF/ether (5 mL each). The reaction mixture was stirred for 10 min until a red-orange solid product precipitated. The solvent was separated via cannula, and the product was washed with pentane. Yield: 39 mg, 89%. Anal. Calcd for $C_{12}H_{22}ClN_3Pt$: C, 32.8; H, 5.0; N, 9.6. Found: C, 32.0; H, 4.6; N, 9.3. NMR in DMSO-d_6: $\delta(^1H) = 9.65$ [s, 1H, ^3J(PtH) = 36 Hz, H_a]; 9.04 [d, 1H, ^3J(PtH) = 16 Hz, H_b]; 8.30 [td, 1H, H_c]; 8.05 [d, 1H, H_d]; 7.80 [m, 1H, H_e]; 4.41 [t, 2H, ^3J(PtH) = 16 Hz, H_f]; 3.28 [m, 2H, H_g]; 2.75 [s, 6H, NMe_2]; 0.95 [s, 3H, ^2J(PtH) = 84 Hz, Pt$-$Me]; 0.89 [s, 3H, ^2J(PtH) = 88 Hz, Pt$-$Me].

[PtMe$_2$(DMPPH)]Cl, 7a. This was prepared in a similar way but using [$PtMe_2$(DMPP)]. Yield: 42 mg, 93%. Anal. Calcd for $C_{13}H_{24}ClN_3Pt$: C, 34.5; H, 5.3; N, 9.3. Found: C, 33.9; H, 4.9; N, 9.0%. NMR in DMSO-d_6: $\delta(^1H) = 9.53$ [s, 1H, ^3J(PtH) =36 Hz, H_a]; 9.06 [d, 1H, ^3J(PtH) = 16 Hz, H_b]; 8.31 [td, 1H, H_c]; 8.01 [d, 1H, H_d]; 7.78 [m, 1H, H_e]; 4.06 [t, 2H, ^3J(PtH) = 16 Hz, H_f]; 2.90 [m, 2H, H_h]; 2.69 [s, 6H, NMe_2]; 2.10 [m, 2H, H_g]; 0.92 [s, 3H, ^2J(PtH) = 84 Hz, Pt$-$Me]; 0.81 [s, 3H, ^2J(PtH) = 88 Hz, Pt$-$Me].

[PtMe(DMEP)]Cl, 10a. Me_3SiCl (10.7 μL, 0.086 mmol) was added to a solution of [$PtMe_2$(DMEP)] (35 mg, 0.086 mmol) and MeOH (0.5 mL) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 24 h, and the product was isolated as an amber powder by evaporation of the solvent under vacuum. It was washed with ether and pentane. Yield: 25 mg, 68%. Anal. Calcd for $C_{11}H_{18}ClN_3Pt$: C, 31.2; H, 4.3; N, 9.9. Found: C, 30.7; H, 3.9; N, 9.4. NMR in $CDCl_3$: $\delta(^1H) = 9.75$ [s, 1H, ^3J(PtH) = 48 Hz, H_a]; 8.66 [d, 1H, ^3J(PtH) = 48 Hz, H_b]; 8.09 [m, 1H, H_c]; 8.0 [m, 2H, H_d, H_e], 4.59 [t, 2H, H_f]; 3.48 [t, 2H, H_g]; 2.98 [s, 6H, ^3J(PtH) = 46 Hz, NMe_2]; 0.94 [s, 3H, ^2J(PtH) = 77 Hz, Pt$-CH_3$].

[PtMe(DMPP)]Cl, 11a. This was prepared similarly but using [$PtMe_2$(DMPP)]. Yield: 30 mg, 59%. Anal. Calcd for $C_{12}H_{20}ClN_3Pt$: C, 33.0; H, 4.6; N; 9.6. Found: C, 32.5; H, 4.4; N; 9.3. NMR in CD_2Cl_2: $\delta(^1H) = 10.29$ [s, 1H, ^3J(PtH) = 48 Hz, H_a]; 8.83 [d, 1H, ^3J(PtH) = 52 Hz, H_b]; 8.57 [d 1H, H_d]; 8.18 [d 1H, H_c], 7.58 [t, 1H, H_e], 4.34 [m, 2H, H_f]; 2.98 [m, 2H, H_h]; 2.90 [s, 6H, ^3J(PtH) = 48 Hz, NMe_2]; 2.15 [m, 2H, H_g]; 1.06 [s, 3H, ^2J(PtH) = 76 Hz, Pt$-CH_3$].

[PtClMe(DMEPH)]Cl, 13a. Me_3SiCl (19.0 μL, 0.15 mmol) was added to a solution of [$PtMe_2$(DMEP)] (30 mg, 0.075 mmol) and H_2O (5 μL) in ether/THF (10 mL/4 mL). Immediately, the yellow-orange product precipitated from solution. The solvent was removed via cannula, and the solid was washed with dry ether and dried under vacuum. Yield: 28 mg, 81%. Anal. Calcd for $C_{11}H_{19}Cl_2N_3Pt$: C, 28.8; H, 4.2; N, 9.1. Found: C, 29.4; H, 4.2; N, 8.6. NMR in CD_2Cl_2: $\delta(^1H) = 9.41$ [s, 1H, ^3J(PtH) = 103 Hz, H_a]; 9.40 [d, 1H, ^3J(PtH) = 8 Hz, H_b]; 8.19 [m, 1H, H_c]; 7.89 [d, 1H, H_d]; 7.80 [m, 1H, H_e]; 4.39 [t, 2H, ^3J(PtH) = 54 Hz, H_f]; 3.67 [t, 2H, H_g]; 2.50 [s, 6H, NMe_2]; 1.12 [s, 3H, ^2J(PtH) = 80 Hz, $PtCH_3$].

[PtClMe(DMPPH)]Cl, 14a. This was prepared similarly but using [$PtMe_2$(DMPP)]. Yield: 69%. Anal. Calcd for $C_{12}H_{21}$-Cl_2N_3Pt: C, 30.4; H, 4.5; N, 8.9. Found: C, 30.3; H, 3.8; N, 8.6. NMR in CD_2Cl_2: $\delta(^1H) = 9.86$ [s, 1H, ^3J(PtH) = 103 Hz, H_a]; 9.50 [d, 1H, ^3J(PtH) = 8 Hz, H_b]; 8.12 [m, 1H, H_c]; 7.95 [d, 1H, H_c]; 7.80 [t, 1H, H_e]; 4.48 [t, 2H, ^3J(PtH) = 54 Hz, H_f]; 3.04 [t, 2H, H_h]; 2.80 [s, 6H, NMe_2]; 2.52 [m, 2H, H_g]; 1.14 [s, 3H, ^2J(PtH) = 80 Hz, Pt$-CH_3$]

[PtMe(DMEP)][O$_2$CCF$_3$], 10b. CF_3CO_2H (9.1 μL, 0.117 mmol) was added to a solution of complex **1** (47 mg, 0.117 mmol) in CH_2Cl_2 (5 mL) and MeOH (1 mL). The reaction mixture was stirred for 24 h, and removal of solvent under vacuum gave the product as a hygroscopic amber powder. Yield: 75%. Anal. Calcd for $C_{13}H_{18}F_3N_3O_2Pt$: C, 31.2; H, 3.6; N, 8.4. Found: C, 30.7; H, 3.9; N, 7.8. NMR in $CDCl_3$: $\delta(^1H)$ = 9.85 [s, 1H, ^3J(PtH) = 44 Hz, H_a]; 8.74 [d, 1H, ^3J(PtH) = 50 Hz, H_b]; 8.16 [m, 1H, H_c]; 8.1 [m, 1H, H_d], 7.64 [m, 1H, H_e], 4.46 [t, 2H, H_f]; 3.45 [t, 2H, H_g], 2.95 [s, 6H, ^3J(PtH) = 48 Hz, NMe_2]; 0.96 [s, 3H, ^2J(PtH) = 76 Hz, Pt$-CH_3$].

[PtMe(DMPP)][O$_2$CCF$_3$], 11b. This was prepared similarly but using complex **2**. Yield: 80%. Anal. Calcd for $C_{14}H_{20}F_3N_3O_2Pt$: C, 32.7; H, 3.9; N, 8.2. Found: C, 32.3; H, 3.5; N, 8.0. NMR in $CDCl_3$: $\delta(^1H) = 9.96$ [s, 1H, ^3J(PtH) = 46 Hz, H_a]; 8.80 [d, 1H, ^3J(PtH) = 48 Hz, H_b]; 8.36 [dd, 1H, H_c]; 8.12 [td, 1H, H_d]; 7.56 [tm, 1H, H_e], 4.18 [t, 2H, ^3J(PtH) = 8 Hz, H_f]; 3.00 [t, 2H, H_h]; 2.88 [s, 6H, ^3J(PtH) = 46 Hz, NMe_2]; 2.10 [m, 2H, H_g]; 1.04 [s, 3H, ^2J(PtH) = 76 Hz, Pt$-CH_3$].

[Pt(O$_2$CCF$_3$)Me(DMEPH)][O$_2$CCF$_3$], 13b. CF_3CO_2H (22.4 μL, 0.29 mmol) was added to a solution of complex **1** (59 mg, 0.15 mmol) in CH_2Cl_2 (3 mL). A yellow precipitate slowly formed. After 45 min, pentane (15 mL) was added to the reaction mixture, and the yellow powder was filtered off and washed with pentane (5 mL). Yield: 56 mg, 61%. Anal. Calcd for $C_{15}H_{19}F_6N_3O_4Pt$: C, 29.3; H, 3.1; N, 6.8. Found: C, 29.6; H, 3.1; N, 6.8. NMR in acetone-d_6: $\delta(^1H) = 9.52$ [s, 1H, ^3J(PtH) = 105 Hz, H_a]; 8.66 [d, 1H, ^3J(PtH) =10 Hz, H_b]; 8.38 [td, 1H, H_c]; 8.18 [dt, 1H, H_d]; 8.04 [m, 1H, H_e]; 4.58 [t, 2H, ^3J(PtH) = 54 Hz, H_f]; 3.62 [t, 2H, H_g]; 2.98 [s, 6H, NMe_2]; 1.00 [s, 3H, ^2J(PtH) = 76 Hz, Pt$-CH_3$].

[Pt(O$_2$CCF$_3$)Me(DMPPH)][O$_2$CCF$_3$], 14b. This was prepared similarly but using complex **2**. Yield: 55%. Anal. Calcd for $C_{16}H_{21}F_6N_3O_4Pt$: C, 30.6.; H, 3.4; N, 6.7. Found: C, 31.3; H,3.3; N, 6.7. NMR in acetone-d_6: $\delta(^1H) = 9.52$ [s, 1H, ^3J(PtH)

Table 4. Crystal Data and Structure Refinement

	10c	13b
empirical formula	C12 H18 F3 N3 O3 Pt S	C15 H18 F6 N3 O4 Pt
fw	536.44	613.41
temperature	296(2) K	295(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	monoclinic	monoclinic
space group	*P*2(1)/*c*	*P*2(1)/*c*
unit cell dimens	a = 12.9195(3) Å	a = 9.0192(5) Å
	b = 11.4336(3) Å	b = 18.6474(10) Å
	c = 11.8833(3) Å	c = 12.9098(8) Å
	β = 108.1330(10)°	β = 109.413(3)°
volume	1668.18(7) Å^3	2047.8(2) Å^3
Z	4	4
density (calcd)	2.136 Mg/m^3	1.990 Mg/m^3
abs coeff	8.582 mm^{-1}	6.931 mm^{-1}
F(000)	1024	1172
cryst size	0.21 × 0.20 × 0.02 mm	0.26 × 0.23 × 0.17 mm
θ range	2.70−30.50°	2.00−27.53°
no. of reflns collected	17 760	22 578
no. of ind reflns	5094 [R(int) = 0.0610]	4710 [R(int) = 0.1400]
abs corr	Scalepack	Scalepack
no. of data/restraints/params	5094/8/245	4710/0/289
goodness-of-fit on F^2	1.008	0.896
R indices [$I > 2\sigma(I)$]	R1 = 0.0365, wR2 = 0.0736	R1 = 0.0427, wR2 = 0.0748
R indices (all data)	R1 = 0.0668, wR2 = 0.0815	R1 = 0.1237, wR2 = 0.0918

= 105 Hz, H_a]; 8.66 [d, 1H, ^3J(PtH) = 10 Hz, H_b]; 8.38 [td, 1H, H_c]; 8.16 [d, 1H, H_d], 8.02 [m, 1H, H_e], 4.32 [t, 2H, ^3J(PtH) =56 Hz, H_f]; 3.34 [t, 2H, H_h], 2.98 [s, 6H, NMe_2]; 2.38 [q, 2H, H_g]; 1.04 [s, 3H, ^2J(PtH) = 80 Hz, Pt−CH_3].

[PtMe(DMEP)][O_3SCF_3], 10c. CF_3SO_3H (14.4 μL, 0.162 mmol) was added to a solution of complex **3** (65 mg, 0.162 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 24 h, and removal of solvent under vacuum gave the product as a hygroscopic amber powder. Yield: 51 mg, 58%. Anal. Calcd for $C_{12}H_{18}F_3N_3O_3PtS$: C, 26.9; H, 3.4; N, 7.8. Found: C, 26.7; H, 3.3; N, 7.6. NMR in $CDCl_3$: δ(^{1}H) = 9.70 [s, 1H, ^3J(PtH) = 48 Hz, H_a]; 8.76 [d, 1H, ^3J(PtH) = 48 Hz, H_b]; 8.15 [m, 1H, H_c]; 8.1 [m, 1H, H_d]; 7.7 [m, 1H, H_e]; 4.45 [t, 2H, H_f]; 3.45 [t, 2H, H_g]; 2.98 [s, 6H, ^3J(PtH) =52 Hz, NMe_2]; 0.98 [s, 3H, ^2J(PtH) = 72 Hz, Pt−CH_3].

[PtMe(DMPP)][O_3SCF_3], 11c. This was prepared similarly but using complex **2**. Yield: 93%. Anal. Calcd For $C_{13}H_{20}F_3N_3O_3PtS$: C, 28.4; H, 3.7; N, 7.6. Found: C, 27.9; H, 3.0; N, 7.4. NMR in $CDCl_3$: δ(^{1}H) = 9.58 [s, 1H, ^3J(PtH) =50 Hz, H_a]; 8.82 [d, 1H, ^3J(PtH) = 48 Hz, H_b]; 8.15 [m, 1H, H_c]; 8.15 [m, 1H, H_d], 7.68 [m, 1H, H_e], 4.18 [m, 2H, H_f]; 3.01 [t, 2H, H_h]; 2.89 [s, 6H, ^3J(PtH) = 46 Hz, NMe_2]; 2.12 [m, 2H, H_h]; 1.06 [s, 3H, ^2J(PtH) = 74 Hz, Pt−CH_3].

Monitoring Reactions of 1 and 2 with Acids by NMR. The reactions were monitored by NMR methods to find the conditions needed to form pure products, and then the procedures described above were optimized. In a typical reaction, HO_3SCF_3 (6.0 μL, 0.068 mmol) was added to an NMR tube charged with complex **1** (14 mg, 0.034 mmol) in $CDCl_3$ (0.5 mL) at room temperature. The red color immediately faded, and methane bubbles were observed. The ^{1}H NMR showed that the organometallic product was [PtMe(DMEP)][O_3SCF_3], and methane was also detected (δ = 0.24).

To an NMR tube containing a solution of **2** (16 mg, 0.039 mmol) in CD_2Cl_2 (0.5 mL) at −78 °C was added H_2O (1.4 μL, 0.078 mmol) followed by Me_3SiCl (9.8 μL, 0.078 mmol). The ^{1}H NMR spectrum was recorded at −80 °C, and the product was identified as [$PtHMe_2$(DMPPH)Cl][Cl]. NMR: δ(^{1}H) = 9.32 [s, 1H, ^3J(PtH) = 27 Hz, H_a]; 8.81 [d, 1H, H_b]; 8.1 [s, 2H]; 7.72 [s, 1H]; 4.31 [s, 2H, H_f]; 3.15 [m, 2H, H_g]; 2.77 [s, 3H, N−Me]; 2.73 [s, 3H, N−Me]; 2.58 [s, 1H, H_h]; 2.26 [s, 1H, H_h']; 1.20 [s, 3H, ^2J(Pt−H) = 67 Hz, Pt−Me]; 1.18 [s, 3H, ^2J(PtH) = 65 Hz, Pt−Me]; −22.04 [1H, ^1J(PtH) = 1587 Hz, Pt−H]. The platinum(IV) complex was stable up to −30 °C and then underwent reductive elimination to yield methane (δ = 0.24) and [PtMe(DMPPH)Cl][Cl]. This was the only case in which a methyl(hydrido)platinum(IV) complex intermediate was positively identified.

A deficiency of HO_3SCF_3 (2.3 μL, 0.026 mmol) was added to an NMR tube containing a solution of **1** (21 mg, 0.051 mmol) in a 3:1 mixture of $CDCl_3$/CD_3OD (0.5 mL), as a source of excess labile deuterium. The reaction was monitored over a period of 5 h. Slow partial conversion to [PtMe(DMEP)][O_3SCF_3] and CH_3D/CH_4 occurred.

Structure Determinations. Crystals of **13b** were grown by slow diffusion of pentane into a dichloroethane solution. A red parallelpiped was mounted on a glass fiber. Data were collected at room temperature (22 °C) on a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction was carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and no other absorption corrections were applied. The crystal data and refinement parameters are listed in Table 4.

The SHELXTL 5.1 (Sheldrick, G. M., Madison, WI) program package was used to solve the structure by direct methods, followed by successive difference Fouriers. The anion showed disorder of the CF_3 group, which was modeled as two half-occupancy groups rotated by 60°. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms.

Crystals of [PtMe(DMEP)][CF_3SO_3], **10c**, were grown from a saturated methylene chloride solution by diffusion of pentane. An orange trapezoidal plate was mounted on a glass fiber, and epoxy was sealed around it. Data were collected and treated as above. The refinement of the platinum complex and its anion was straightforward. There was slight disorder at the N(8) through N(11) bridge. C(9) through C(13) were modeled as two moieties in a 60/40 mixture, and the matching bond lengths were constrained to be identical. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms.

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Supporting Information Available: Tables of X-ray data for complexes **10c** and **13b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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