Binuclear Dimethylplatinum(II) Complexes: Reactivity and Mechanism in Protonolysis and Oxidative Addition Reactions

Fenbao Zhang, Michael C. Jennings, and Richard J. Puddephatt*

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

Received October 31, 2003

The reaction of [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] with the ligands 1,3- and 1,4-$C_6H_4(CH{=}NCH_2CH_2NMe_2)_2$, 1,3-BAIB, and 1,4-BAIB, respectively, gave the corresponding complexes [Pt_2Me_4(1,3-BAIB)], **1**, and [Pt_2Me_4(1,4-BAIB)], **2**. Complex **1** reacted with 2 equiv of HCl to give [$(PtClMe)_2$(1,3-BAIB)], **3**, in which the chloride ligands are *trans* to the imine nitrogen atoms. Complex **1** undergoes oxidative addition with methyl triflate to give, after recrystallization from moist solvent, the diplatinum(IV) aqua complex [$\{PtMe_3(OH_2)\}_2$(1,3-BAIB)](CF_3SO_3)$_2$, **4**, which has the *anti* stereochemistry of the two aqua ligands. Complex **4** forms a dimer of dimers structure in the solid state through hydrogen bonding between aqua ligands and triflate anions. The reactions of **1** and **2** with HCl are shown to proceed through oxidative addition/reductive elimination sequences, and intermediate hydridoplatinum(IV) intermediates have been identified at low temperature by their ^1H NMR spectra. For example, in reactions with complex **1**, binuclear hydride complexes of the types [$(PtMe_2)(PtHClMe_2)$(1,3-BAIB)], [$(PtHClMe_2)_2$(1,3-BAIB)], and [$(PtClMe)(PtHClMe_2)$(1,3-BAIB)] were identified. The initial oxidative addition reactions occur with *trans* stereochemistry, to give hydride *trans* to chloride, but isomerization was observed in some cases to give complexes with hydride *trans* to a nitrogen donor of the 1,3-BAIB ligand. The reactions with DCl or CF_3SO_3D in CD_3OD or CD_3OD/CD_3CN solvent systems gave all isotopomers of methane CH_nD_{4-n}, indicating that there is an easy equilibrium between hydrido(methyl)platinum(IV) and (methane)platinum(II) complexes and easy hydrogen−deuterium exchange between hydridoplatinum groups and −OD groups of the solvent.

Introduction

The selective, efficient activation of alkanes remains one of the great challenges of contemporary chemistry, and there have been several major reviews of the progress made and the problems that remain to be solved.[1] Within this broad field, the activation of C−H bonds of alkanes by platinum(II) complexes has been particularly important. Platinum complexes gave the first true homogeneous metal complex activation of methane and still maintain a central role in the development of useful catalysis and in studies of the detailed mechanisms of catalysis.[1−12] The emphasis in most previous studies has been on mononuclear platinum complexes, especially those with nitrogen-donor ligands, since these are useful both in alkane activation and in related mechanistic studies.[1−12] In particular, it has been possible to form hydrido(methyl)platinum(IV) complexes, similar to those proposed as reaction inter-

---

(1) (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (b) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *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) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (f) Fekl, U.; Goldberg, K. I. *Adv. Inorg. Chem.* **2003**, *54*, 259.

(2) (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560. (b) Kua, J.; Xu, X.; Periana, R. A.; Goddard, W. A., III. *Organometallics* **2002**, *21*, 511. (c) Xu, X.; Kua, J.; Periana, R. A.; Goddard, W. A., III. *Organometallics* **2003**, *22*, 2057.

(3) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371. (b) Stahl, S. S.; Labinger, J. A.; Bercaw J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (c) Procelewska, J.; Zahl, A.; van Eldik, R.; Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 2808. (d) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378. (e) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846. (f) Heyduk, A. F.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 6366.

(4) (a) Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 8614. (b) Norris, C. M.; Reinartz, S.; White, P. S.; Templeton, J. L. *Organometallics* **2002**, *21*, 5649. (c) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724. (d) Reinartz, S.; Baik, M.-H.; White, P. S.; Brookhart, M.; Templeton, J. L. *Inorg. Chem.* **2001**, *40*, 4726. (e) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3854.

(5) (a) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442. (b) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804. (c) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423. (d) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *Organometallics* **2001**, *20*, 2669. (e) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 1456. (f) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 11900.

(6) (a) Wik, B. J.; Lersch, M.; Tilset, M. *J. Am. Chem. Soc.* **2002**, *124*, 12116. (b) Johansson, L.; Ryan, O. B.; Romming, C.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 6579. (c) Johansson, L.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 739. (d) Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831.

(7) (a) Song, D. T.; Wang, S. *Organometallics* **2003**, *22*, 2187. (b) Konze, W. V.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 12550.

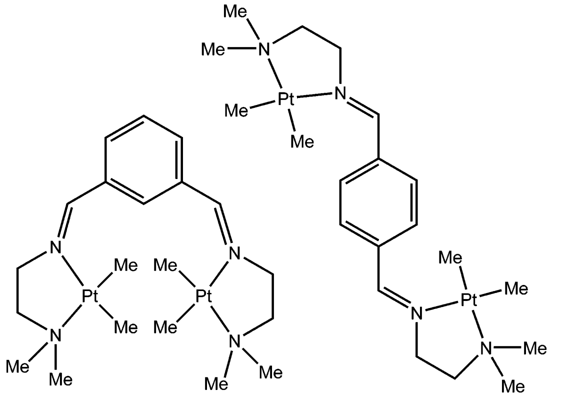
(8) (a) Harkins, S. B.; Peters, J. C. *Organometallics* **2002**, *21*, 1753. (b) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870.

(9) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845.

(10) (a) Vedernikov, A. N.; Huffman, J. C.; Caulton, K. G. *New J. Chem.* **2003**, *27*, 665. (b) Vedernikov, A. N.; Caulton, K. G. *Chem. Commun.* **2003**, 358−359. (c) Vedernikov, A. N.; Caulton, K. G. *Angew. Chem., Int. Ed.* **2002**, *41*, 4102−4104.

10.1021/om030650m CCC: $27.50
Publication on Web 02/18/2004

Chart 1



1 **2**

mediates in methane activation, by protonation of the corresponding methylplatinum(II) complexes. It was of interest to extend these studies of monoplatinum complexes by studying complexes containing two or three platinum atoms. In such compounds, there is the potential for interesting cooperative effects between adjacent metal centers that can give rise to reaction pathways or products that are not possible in the mononuclear analogues.[13] For example, oxidative addition of alkyl halides to bridged binuclear complexes has been studied previously and can yield products formed by single or double oxidative addition.[14] To model intermediates in C−H bond activation of methane, binuclear bis[dimethylplatinum(II)] complexes were required, and the two compounds shown in Chart 1 were designed. These complexes **1** and **2** each contain amine-imine donors, based on *N*,*N*-dimethylethylenediamine, with a phenylene spacer group but with *meta* and *para* substitution, respectively. Through-bond electronic communication between platinum centers is possible in these complexes with arene spacer groups, but the distance between the two dimethylplatinum units is expected to be greater in complex **2** than in **1**.

Results and Discussion

The dimethylplatinum(II) complexes **1** and **2** were prepared by reaction of the appropriate ligand with the complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$[14] and were readily characterized by their ^1H NMR spectra, by comparison with related mononuclear and binuclear dimethylplatinum(II) complexes.[1−12] For example, complex **1** gave two methylplatinum resonances in the ^1H NMR spectrum of equal intensity at $\delta = 0.41$, $^2J(PtH) = 84$ Hz, and at $\delta = -0.06$, $^2J(PtH) = 90$ Hz, corresponding to the nonequivalent methyl groups *trans* to imine and amine donors. The magnitudes of the coupling constants $^2J(PtH)$ are typical for methylplatinum(II) complexes in which the methyl group is *trans* to nitrogen.[2−12] There was a single imine resonance at $\delta = 9.03$ with coupling constant $^3J(PtH) = 45$ Hz. The Me_2N protons gave a single resonance, indicating that the complex has effective C_{2v} symmetry, with a mirror plane containing the $C_6H_4(CH{=}NCCN)_2$ atoms (note that the *effective* symmetry arises from fluxionality between conformers with lower C_2 symmetry, which would give rise to two MeN resonances).

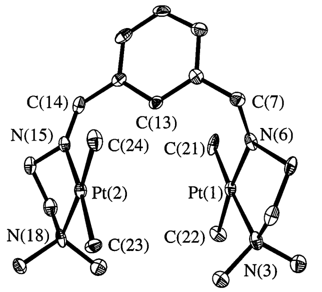


Figure 1. View of the structure of complex **1**.

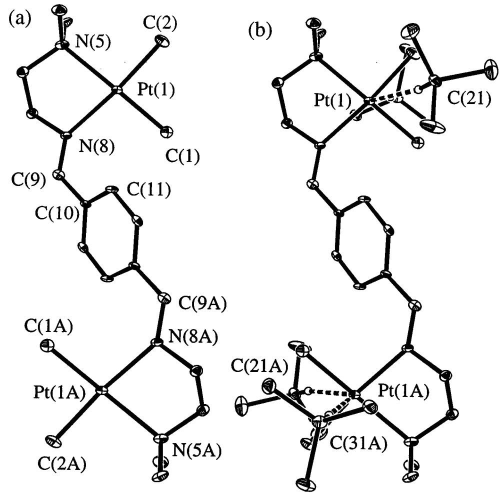


Figure 2. Views of the structure of complex **2**: (a) the molecular structure and (b) with the hydrogen-bonded chloroform solvate molecules.

The structures of complexes **1** and **2** were determined crystallographically, and views of the complexes are shown in Figures 1 and 2, with selected bond distances and angles listed in Table 1. A comparison of the distances between the two platinum atoms and of the angles between the square planes of the two platinum atoms in the complexes is given in Table 2.

In complex **1** (Figure 1), the dimethylplatinum units are skewed on either side of the central arene ring and oriented *syn* to one another. The square planes of the two *syn*-oriented PtC_2N_2 units are close to parallel (angle θ between coordination planes = 6°). In this conformation, the platinum atoms are relatively close with $d(Pt1\cdots Pt2) = 4.70$ Å. The deviation of the imine groups away from coplanarity with the aryl group in **1** is given by the dihedral angles N6−C7−C8−C13 = 42° and N15−C14−C12−C13 = 20°. An idealized structure with the imine coplanar with the aryl group would not

---

(11) (a) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (b) Hill, G. S.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 8745. (c) Prokopchuk, E. M.; Jenkins, H. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 2861. (d) Hinman, J. G.; Baar, C. R.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 563. (e) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219/221*, 157. (f) Jenkins, H. A.; Klempner, M. J.; Prokopchuk, E. M.; Puddephatt, R. J. *Inorg. Chim. Acta* **2003**, *352C*, 72. (g) Prokopchuk, E. M.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 787. (h) Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 261.

(12) De Felice, V.; De Renzi, A.; Panunzi, A.; Tesauro, D. *J. Organomet. Chem.* **1995**, *488*, C13.

(13) (a) Trepanier, S. J.; McDonald, R.; Cowie, M. *Organometallics* **2003**, *22*, 2638. (b) Tejel, C.; Bordonaba, M.; Ciriano, M. A.; Edwards, A. J.; Clegg, W.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **1999**, *38*, 1108.

(14) (a) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 1538. (b) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 2522. (c) Song, D.; Sliwowski, K.; Pang, J.; Wang, S. *Organometallics* **2002**, *21*, 4978.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Binuclear Dimethylplatinum(II) Complexes

Complex **1**			
Pt1−C22	2.05(1)	Pt1−C21	2.05(1)
Pt1−N6	2.10(1)	Pt1−N3	2.17(1)
Pt2−C24	2.02(2)	Pt2−C23	2.04(1)
Pt2−N15	2.08(1)	Pt2−N18	2.19(1)
C22−Pt1−C21	86.2(7)	N6−Pt1−N3	81.4(4)
Complex **2**			
Pt1−C1	2.036(8)	Pt1−C2	2.043(9)
Pt1−N8	2.128(6)	Pt1−N5	2.204(6)
C1−Pt1−C2	88.0(3)	N8−Pt1−N5	81.8(2)
Complex **3**			
Pt−C2	2.111(6)	Pt−Cl1	2.288(2)
Pt−N8	2.006(6)	Pt−N5	2.172(6)
C2−Pt−Cl1	86.9(2)	N8−Pt−N5	83.0(2)

Table 2. Distance [d(Pt⋯Pt), Å] between Platinum Atoms, Angle between the Coordination Planes of the Two Platinum Atoms (θ, deg), and Dihedral Angles Defining the Twist of the Imine Groups Relative to the Aryl Group [Φ(N=CCC), deg] in Complexes 1−4

complex	d(Pt⋯Pt)	θ	Φ
1	4.70	6	20, 42
2	9.54	0	28
3	4.71	1	32
4	8.23	65	38, 126

be possible since there would be major steric repulsions between the methylplatinum groups. There is no crystallographically imposed symmetry, but the symmetry approximates to C_2. The NMR data described above indicate effective C_{2v} symmetry, and so there must be easy rotation about the aryl-imine C−C bonds in solution.

In complex **2** (Figure 2), in which there is a crystallographically imposed inversion center, the platinum atoms are further apart [d(Pt1⋯Pt1A) = 9.54 Å] than in complex **1** and the dimethylplatinum units are oriented *anti* to one another. The angle between the coordination planes of the *anti*-oriented platinum centers is 157°, and the twisting of the imine out of the aryl plane is defined by the dihedral angle N8−C9−C10−C11 = 28°.

The observation of a single NMe resonance in the ^{1}H NMR spectrum of **2** shows that there must be easy rotation about the aryl-imine C−C bonds, as in complex **1**, giving effective C_{2h} symmetry in solution compared to the C_i symmetry in the solid state. The structural data clearly confirm that the two dimethylplatinum(II) centers are further apart in complex **2**, and so would be expected to react more independently of each other, than in complex **1**. The crystals of complex **2** were grown from chloroform solution, and an interesting feature of the structure is that there are two chloroform molecules associated with each dimethylplatinum(II) center, with close contacts Pt⋯H21A = 2.85 Å and Pt⋯H31A = 2.55 Å, presumably with the electron-rich dimethylplatinum(II) center forming a hydrogen bond to each chloroform molecule.

Reaction with HCl and the Structure of [$Pt_2Cl_2Me_2$(1,3-BAIB)]. The reactions of complexes **1** and **2** with HCl were studied in order to determine the selectivity of methyl−platinum bond cleavage. Most of these reactions gave mixtures of products that could not be separated, but the reaction of complex **1** with 2 equiv of HCl occurred to give the complex [$Pt_2Cl_2Me_2$(1,3-BAIB)], **3**, as the major product (eq 1). Complex **3** could be crystallized in pure form from the reaction mixture. In the ^{1}H NMR spectrum, complex **3** gave a methylplatinum resonance at δ = 0.64 with coupling ^2J(PtH) = 80 Hz and a single Me_2N resonance at δ = 2.78. The imine resonance appeared at δ = 8.99, and the coupling constant ^3J(PtH) = 136 Hz was much larger than in complex **1** (45 Hz). This difference arises because the *trans* chloride ligand in **3** has a much lower *trans*-influence than the *trans* methyl group in **1**.

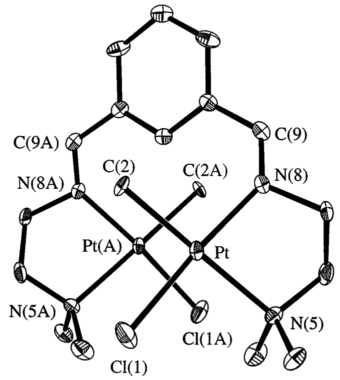
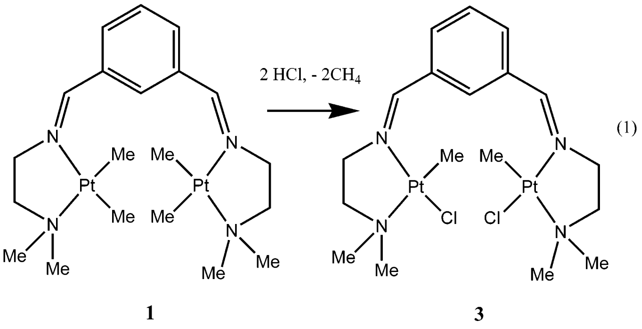


Figure 3. View of the structure of complex **3**.



The structure of complex **3** is shown in Figure 3, with selected bond parameters in Tables 1 and 2. The overall structure is similar to that of complex **1** with mutually *syn* PtClMe groups in which the methyl group is *trans* to NMe_2 and the chloro ligand *trans* to imine. The complex has crystallographically imposed C_2 symmetry in the solid state, but rotation about the aryl-imine C−C bond leads to effective C_{2v} symmetry in solution. The Pt−N (imine) bond is shorter in complex **3** than in **1** (Table 1), as expected from the lower *trans*-influence of chloride compared to methyl.

The minor products formed on reaction of complex **1** with HCl were not identified but are likely to include the two isomers of complex **3** with formula [$(PtClMe)_2$(1,3-BAIB)]. It is established that, in complexes with *cis*-$PtMe_2N_2$ coordination, the first methylplatinum bond is cleaved more easily than the second, but the degree of regioselectivity of cleavage of the methylplatinum group *trans* to imine or amine in complex **1** is not easily predicted. Complex **3** is estimated, on the basis of integration of the ^{1}H NMR spectra of reaction mixtures, to be formed with about 75% selectivity in the reaction of complex **1** with 2 equiv of HCl, but the analogous reaction with complex **2** appears less selective and the complex product mixture could not be separated.

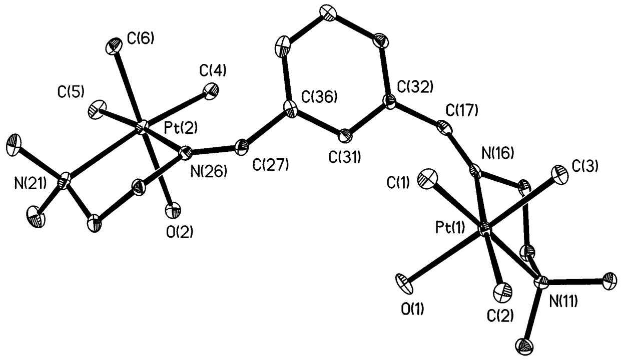


Figure 4. View of the structure of the dicationic complex **4**.

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Binuclear Trimethyl(aqua)platinum(IV) Complex 4

Pt1−C2	2.020(7)	Pt1−C3	2.040(6)
Pt1−C1	2.044(7)	Pt1−O1	2.204(4)
Pt1−N16	2.218(5)	Pt1−N11	2.263(6)
Pt2−C4	2.030(7)	Pt2−C5	2.044(6)
Pt2−C6	2.047(7)	Pt2−O2	2.212(5)
Pt2−N26	2.201(5)	Pt2−N21	2.255(6)
C2−Pt1−C3	87.4(3)	C2−Pt1−C1	85.2(3)
C3−Pt1−C1	85.2(3)	C2−Pt1−O1	90.2(2)
C1−Pt1−O1	91.2(3)	O1−Pt1−N1	691.2(2)
O1−Pt1−N11	87.7(2)	N16−Pt1−N11	80.1(2)
C4−Pt2−C5	86.4(3)	C4−Pt2−C6	91.3(3)
C5−Pt2−C6	87.3(3)	C4−Pt2−O2	88.3(2)
C5−Pt2−O2	94.2(2)	N26−Pt2−O2	86.0(2)
O2−Pt2−N21	84.5(2)	N26−Pt2−N21	80.3(2)

Oxidative Addition of Methyl Triflate to Complex 1. The protonolysis reactions are thought to occur by oxidative addition of HX followed by reductive elimination of methane, and so model oxidative addition reactions were carried out using methyl iodide or methyl triflate with complexes **1** and **2**. The reactions were surprisingly complex, and only in the reaction of complex **1** with methyl triflate was a pure compound crystallized. Thus, treatment of complex **1** with 2 equiv of methyl triflate, followed by recrystallization from dichloromethane/hexane, gave the triflate salt of a dicationic bis[trimethylplatinum(IV)] aqua complex $[Pt_2Me_6(OH_2)_2$-$(1,3\text{-BAIB})](CF_3SO_3)_2$, **4**. The structure of the cationic complex **4** is shown in Figure 4, with selected bond distances and angles listed in Tables 2 and 3.

The structure of the dication shows the presence of two *fac*-trimethylplatinum(IV) centers with the octahedral coordination at each platinum(IV) atom completed by two nitrogen donors of the bridging 1,3-BAIB ligand and an aqua ligand. The ligand geometry is quite different from that seen in the platinum(II) complexes **1** and **3**, in which the orientation of the platinum centers was *syn*, since the conformation in **4** is *anti*. This is most easily demonstrated by the dihedral angles N16−C17−C32−C31 = 38° and N26−C27−C36−C31 = 126°. The change in orientation of the platinum atoms in **4** leads to a longer Pt···Pt separation (8.23 Å) than in complexes **1** and **3**. This conformational change is clearly necessary to minimize steric hindrance between the octahedral platinum(IV) centers in **4**, which are bulkier than the square-planar platinum(II) centers in **1** and **3**. Each platinum(IV) center is chiral, and within a given dication, they have the same chirality, *C*,*C* or *A*,*A*. This stereochemistry leads to the aqua ligands being on the same side of the aryl spacer group. However, the product is formed from **1** by approach of the two methyl triflate reagents from opposite sides of the arene spacer group, as illustrated in Scheme 1. The highest possible symmetry of the dication **4**, through rotation about the aryl-imine C−C bond in solution, is then expected to be C_2.

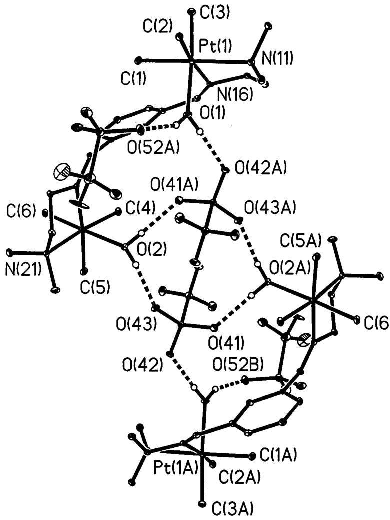
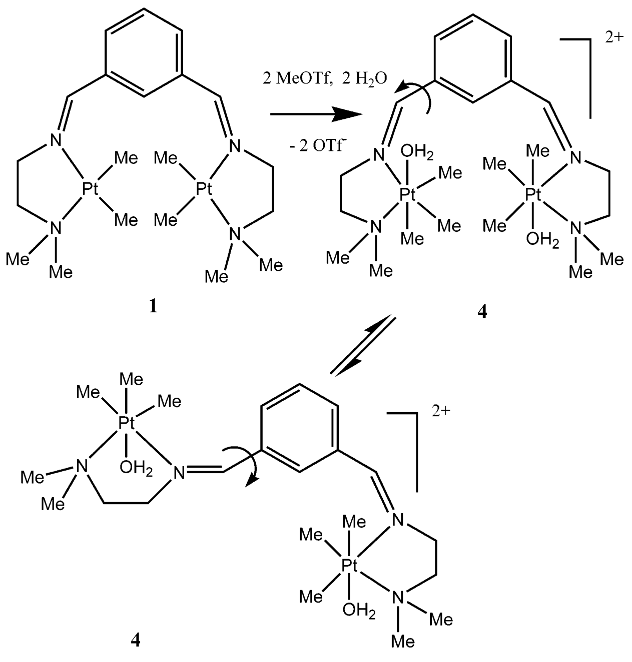


Figure 5. Structure of complex **4**, showing two dications bridged by triflate anions to give a "dimer of dimers" assembly.

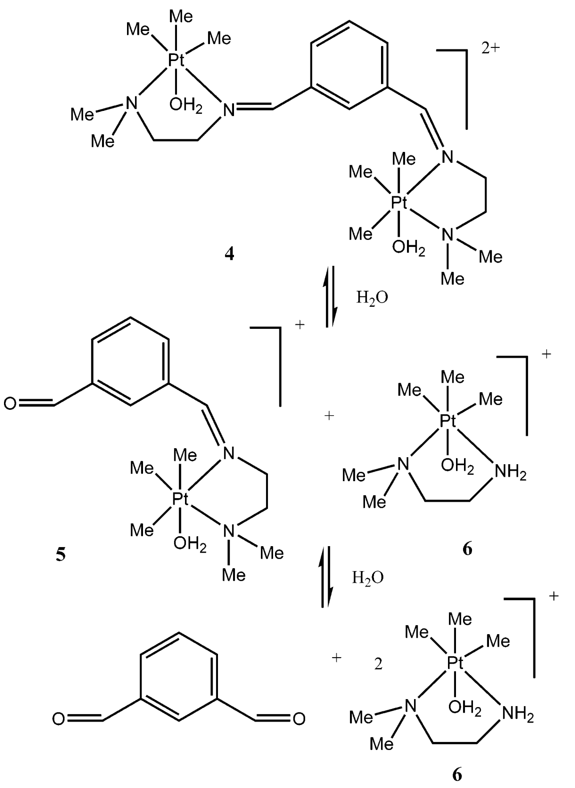
Scheme 1



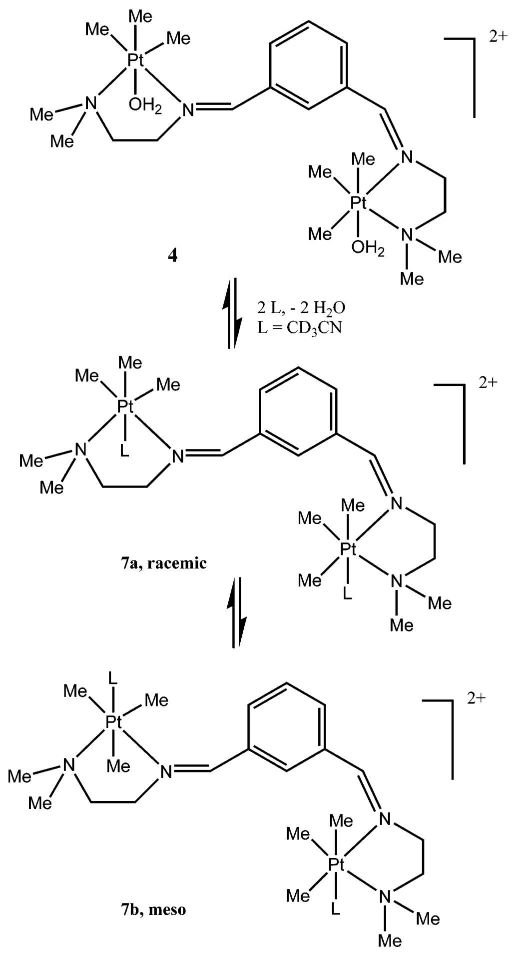
The diplatinum(IV) cations associate pairwise in the crystal lattice by hydrogen bonding between the aqua ligands and triflate anions, as illustrated in Figure 5. Each "dimer of dimers" contains two dications **4** and four triflate anions. There are two bridging triflate anions, each of which hydrogen bonds to three aqua ligands (two of one dication and one of the other) and two triflates that hydrogen bond to just one aqua ligand. There is a center of symmetry at the center of each "dimer of dimers" such that the two units of the dication **4** have opposite chirality, *CC* and *AA*.

The characterization of complex **4** by ^1H NMR was not easy. The complex is sparingly soluble in CD_2Cl_2

Scheme 2



Scheme 3



and the ^{1}H NMR spectrum was broad and poorly resolved. In D_2O solution, the ^{1}H NMR spectrum was consistent with the structure of Figure 4, with easy rotation about the arene-imine C−C bond to give effective C_2 symmetry. Thus there were three methylplatinum resonances at $\delta = 0.23$, $^2J(\mathrm{PtH}) = 70$ Hz; 0.67, $^2J(\mathrm{PtH}) = 67$ Hz for methyl groups *trans* to nitrogen and at $\delta = 0.75$, $^2J(\mathrm{PtH}) = 79$ Hz for the methyl group *trans* to oxygen. However, the imine groups were easily hydrolyzed in water and the spectrum changed over the course of several days as sequential hydrolysis to give the new complexes **5** and **6** and free 1,3-$C_6H_4(CH{=}O)_2$ occurred (Scheme 2).

Complex **4** dissolved in CD_3CN intact, but the aqua ligands were slowly replaced by CD_3CN to give complex **7** (Scheme 3). The ^{1}H NMR spectrum of complex **7** indicated that there were equal amounts of the racemic and meso isomers present. The spectrum was deceptively simple since only one imine resonance and one set of aryl group resonances were present. However, there were four methylplatinum resonances in a 2:2:1:1 ratio [$\delta = 0.24$, $^2J(\mathrm{PtH}) = 70$ Hz; 0.68, $^2J(\mathrm{PtH}) = 70$ Hz; 0.60, $^2J(\mathrm{PtH}) = 75$ Hz; 0.61, $^2J(\mathrm{PtH}) = 75$ Hz, respectively]. This spectrum cannot be rationalized in terms of a single isomer, but is consistent with the presence of an equimolar mixture of racemic and meso isomers, **7a** and **7b**, respectively, in which only the methylplatinum groups *trans* to CD_3CN give separate resonances.

Table 4. Selected ^{1}H NMR Data [δ (J_{PtH}, Hz)] for the Complexes of Scheme 4

	1	8a	8b	9
Pt(IV)−H		−21.28 (1620)	−21.74 (1423)	
Pt(II)−Me	−0.06 (90)	−0.15 (85)	0.01 (80)	−0.16 (86)
	0.41 (84)	0.36 (90)	0.38 (86)	0.34 (80)
				0.64 (80)
Pt(IV)−Me		0.51 (68)	0.70 (68)	
		0.90 (68)	0.86 (68)	
Pt(II)N=CH	9.03 (45)	9.00 (42)	9.04 (42)	8.99 (44)
				8.92 (121)
Pt(IV)N=CH		8.93 (33)	8.69 (32)	

Detection of Intermediates in Protonolysis Reactions. Complex **1** in solution in CD_2Cl_2 was treated with 1 equiv of HCl at −78 °C, and the course of the reaction was monitored by ^{1}H NMR as the temperature was raised slowly to room temperature. Selected data are given in Table 4, the hydride regions of some typical ^{1}H NMR spectra are shown in Figure 6, and the data are interpreted in terms of Scheme 4.

The reaction of complex **1** with 1 equiv of HCl at −78 °C gave complex **8a** as major product. Complex **8a** is characterized by a hydride resonance at $\delta = -21.28$, with satellite peaks due to the coupling $^1J(\mathrm{PtH}) = 1620$ Hz. This coupling constant indicates that the hydride is *trans* to chloride, as expected for *trans* oxidative addition.[3−5,11] There were two methylplatinum(II) and two methylplatinum(IV) resonances, assigned on the basis of the associated coupling constants $^2J(\mathrm{PtH})$ as given in Table 4, and two imine resonances. This complex remained as the major one present at temperatures up to −10 °C. However, above this temperature, isomerization to complex **8b** and reductive elimination of methane to give complex **9** occurred (Scheme 4). At room temperature, complex **8b** was the only hydridoplatinum(IV) complex detected, and reductive elimination to give **9** and methane was complete in about 30

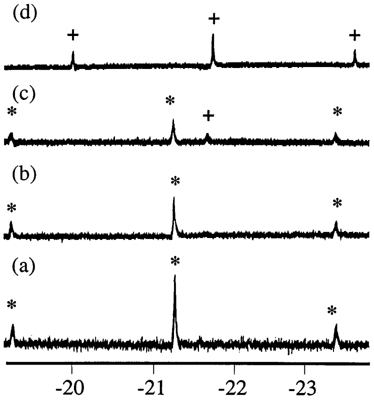
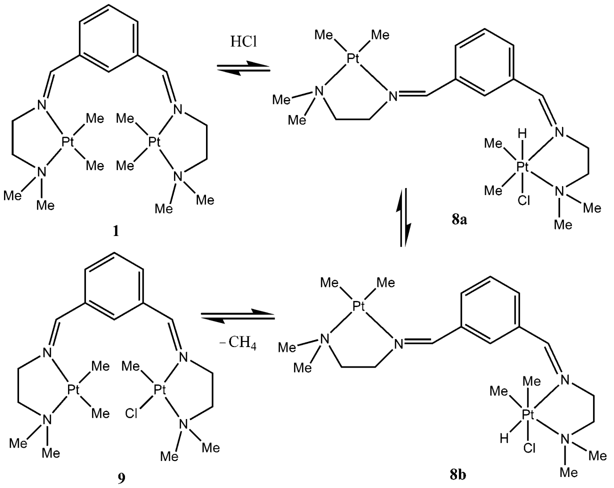


Figure 6. Variable-temperature ^1H NMR spectra (400 MHz) in the hydride region for the protonation of complex **1** in CD_2Cl_2 with 1 equiv of HCl at (a) −30 °C; (b) −20 °C; (c) −10 °C; and (d) 0 °C. The peaks labeled * are assigned to **8a**, and those labeled + are assigned to **8b**.

Scheme 4



min at this temperature. Complex **8b** is characterized by a hydride resonance at $\delta = -21.74$, with coupling constant $^1J(PtH) = 1423$ Hz, corresponding to a hydridoplatinum(IV) complex with the hydride *trans* to a nitrogen-donor ligand.[6] Complex **8b** also gives four methylplatinum and two imine resonances, similar to those of **8a** (Table 4). In complex **9**, the chloride ligand is shown to be *trans* to the imine group by the large value of the coupling constant, $^3J(PtH) = 121$ Hz, which is similar to the value in complex **3** (136 Hz). The minor products present at intermediate stages of reaction were the starting complex **1** and the complexes of formula $[(PtHClMe_2)_2(1,3\text{-BAIB})]$, discussed below, and the final product **9** was accompanied by minor amounts of **1** and **3**, which were not easily separated. Evidently, the first HCl oxidative addition deactivates the second dimethylplatinum(II) center, but not by a large enough factor to give very high selectivity.

The reaction of complex **1** with 2 equiv of HCl at −78 °C gave a mixture of two hydride complexes, formed in about equal yield (Figure 7). These were characterized by hydride resonances at $\delta = -22.2$, $^1J(PtH) = 1610$ Hz, and at $\delta = -21.8$, $^1J(PtH) = 1605$ Hz. The coupling constants indicate hydride *trans* to chloride in both cases, so they are assigned arbitrarily to the products of *syn* and *anti* oxidative addition, **10a** and **10b** (Scheme 5). At −30 °C, the elimination of methane began and a new hydride resonance grew in at $\delta = -21.6$, $^1J(PtH) = 1616$ Hz, which is assigned to complex **11a**. Finally, in the range −20 to −10 °C, a hydride resonance at $\delta = -21.75$, $^1J(PtH) = 1400$ Hz, indicative of hydride *trans* to a nitrogen donor, was observed and tentatively assigned to complex **11b**. At 0 °C, no hydride complexes remained and the final product was complex **3**. The reaction was similar if 3 equiv of HCl was used.

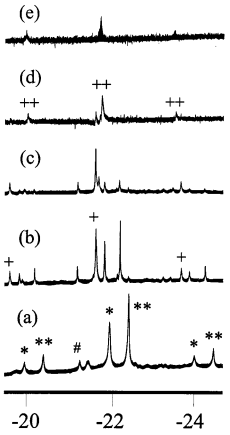
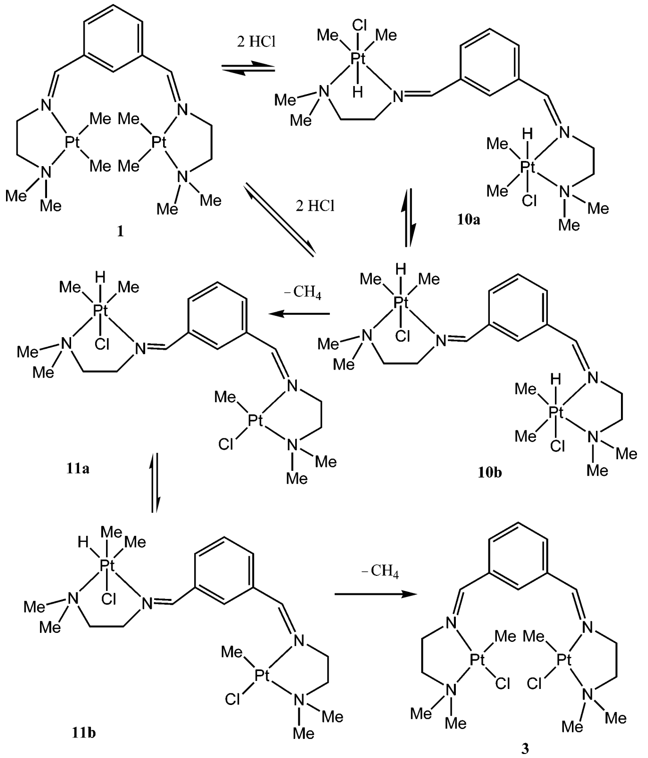


Figure 7. Variable-temperature ^1H NMR spectra (400 MHz) in the hydride region for the protonation of complex **1** in CD_2Cl_2 with 2 equiv of HCl at (a) −78 °C; (b) −30 °C; (c) −20 °C; (d) −10 °C; and (e) 0 °C. Labeled peaks are assigned to the complexes as follows: * and ** to **10a** and **10b**; + to **11a**; ++ to **11b**; # to **8a**.

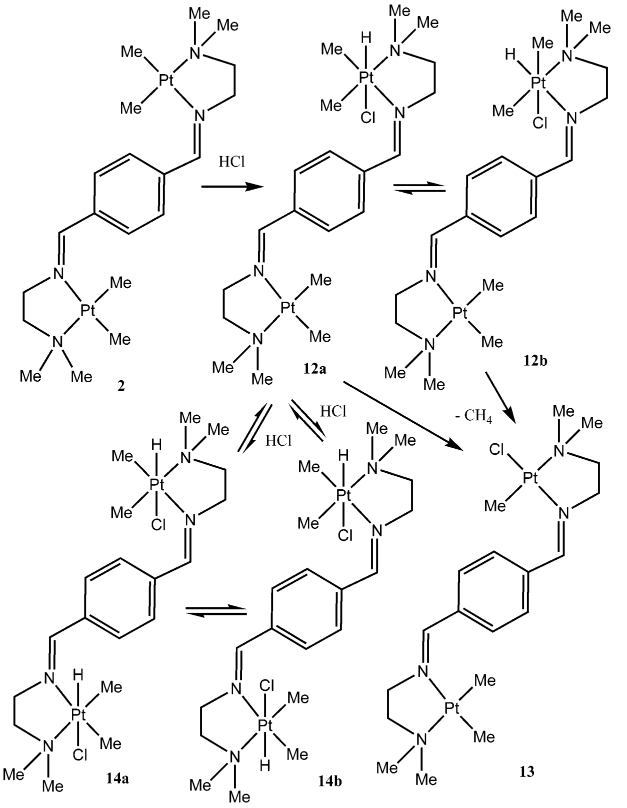
Scheme 5



From these reactions it is clear that the oxidative addition of HCl to the first platinum(II) center of complex **1** deactivates the second one. In addition, the Pt(IV)Pt(IV) complexes **10a** and **10b** undergo reductive elimination of methane more easily than does the analogous Pt(II)Pt(IV) complex **8a**.

The reactions of complex **2** were similar to those of complex **1**. For example, the reaction with 1 equiv of

Scheme 6



HCl occurred according to Scheme 6, with data summarized in Table 5. Complex **12a** is formed at −78 °C, then isomerizes to **12b** in the temperature range −30 to −10 °C and reductively eliminates methane to give **13**. The aromatic protons, H^2 and H^3, are equivalent in complex **2** but not in the unsymmetrical complexes **12** and **13**, and so they appear as apparent pairs of doublets in these complexes. With 2 equiv of HCl at −78 °C, the reaction with complex **2** yields complexes **14a** and **14b**, which have very similar overlapping resonances in the ^{1}H NMR spectrum. For example the hydride resonances occurred at $\delta = -22.0$ and -22.2, each with $^1J(\mathrm{PtH}) = 1620$ Hz. These complexes reacted further over the temperature range −30 to 0 °C by elimination of methane. The complex $[(\mathrm{PtClMe})(\mathrm{PtHClMe_2})(1,4\text{-BAIB})]$, with stereochemistry analogous to **11b**, was formed in low concentration and was identified only by its hydride resonance at $\delta = -21.9$ with $^1J(\mathrm{PtH}) = 1400$ Hz, but it was the most stable complex with respect to loss of methane and could be observed for about 1 h at 20 °C.

H/D Exchange Reactions. The protonolysis of complexes **1** and **2** with DCl or CF_3SO_3D in CD_3OD/CD_3CN solvent was carried out in order to determine if isotopic exchange occurred in the methane produced, under conditions with excess labile deuterium available.[1−4,6,11] The acid addition was made at −20 °C, and then the reactions were monitored by ^{1}H NMR spectroscopy as the temperature was raised to room temperature. Spectra at lower temperatures were unsatisfactory as a result of poor solubility and the freezing out of acetonitrile (mp −45 °C). Some typical data for reactions with complex **1** are listed in Table 6, and typical spectra are in Figure 8; similar data were obtained with complex **2**. Data are given in Table 6 from spectra at −20 °C, at which temperature some intermediates could still be observed, and at 0 °C, at which temperature the reactions were effectively complete. No further isotopic exchange into the methane occurred after this point.

Table 6 and Figure 8 show that all isotopomers of methane CH_4, CH_3D, CH_2D_2, and CHD_3 (and presumably CD_4) were formed under all conditions studied. The simple deuteriolysis would give only CH_3D, and the other products are formed by exchange, as reported previously for several mononuclear dimethylplatinum(II) complexes.[1−4,6,11] Methane, CH_4, can be formed by addition of a single D^+ ion followed by intramolecular isotopic exchange within the hydrido(dimethyl)platinum(IV) and methyl(methane)platinum(II) complexes, but the formation of CH_2D_2 and CHD_3 also requires reversibility of the protonation/deuteration step (shown in simplified form in Scheme 7). For reactions with DCl, Table 6 and Figure 8 show that, relative to CH_3D, the amount of CH_4 produced increases as the concentration of CD_3OD in the CD_3OD/CD_3CN solvent mixture decreases. However, the amounts of CH_2D_2 and CHD_3, relative to CH_3D, vary relatively little over the range of solvent compositions studied and are highest at intermediate solvent compositions. There was even less variation in reactions with CF_3SO_3D, though the formation of CH_2D_2 and CHD_3 was consistently less than in the analogous reactions with DCl (Table 6). Since the reactions with complexes **1** and **2** gave similar results, it is unlikely that binuclear mechanisms play a significant role in these reactions, and so it is reasonable to discuss the chemistry in terms of two independent dimethylplatinum(II) centers. There are too many unknowns in Scheme 7 to allow a quantitative kinetic model for the isotopic distribution to be developed. Most of the key reactions are proposed to occur from isotopically substituted derivatives of the five-coordinate platinum(IV) complex $[\mathrm{PtHMe_2(NN)}]^+$ in easy equilibrium with the methane complex of platinum(II) $[\mathrm{PtMe(CH_4)(NN)}]^+$.[3−11] The complex $[\mathrm{PtHMe_2(NN)}]^+$ can be trapped reversibly as the unreactive six-coordinate complexes $[\mathrm{PtHXMe_2(NN)}]$ and $[\mathrm{PtH(S)Me_2(NN)}]^+$, where S represents the solvent methanol or acetonitrile (of which acetonitrile is expected to be the stronger ligand). The solvent and anion may also play a role in the reversible protonation of the dimethylplatinum(II) complex and in the displacement of methane from the complex $[\mathrm{PtMe(CH_4)(NN)}]^+$. Two recent articles have provided evidence for associative displacement of methane or benzene by solvent molecules in related mononuclear systems.[3,6] If this mechanism of displacement operated in the present system, it might be predicted that the yield of CH_3D would increase as the concentration of the better ligand CD_3CN increased in the solvent mixture CD_3OD/CD_3CN, or for the more strongly ligating $X^- = Cl^-$ over $X^- = CF_3SO_3^-$, but neither of these trends was observed (Table 6). However, since the protonation/deprotonation steps are also likely to be strongly solvent dependent, the observed trends do not constitute definitive evidence for a dissociative mechanism of methane loss.

Overall, there is no evidence for binuclear cooperative mechanisms of reaction in the protonolysis of complexes **1** and **2**. However, the reactions of complex **1** were more selective than those of **2**. The differences appear to be mostly steric in origin. The platinum centers in complex

Table 5. Selected ^{1}H NMR Data [δ (J_{PtH}, Hz)] for the Complexes of Scheme 6

	2	**12a**	**12b**	**13**	**14a/b**
Pt(IV)−H		−22.0 (1616)	−21.7 (1400)		−22.0 (1620)
					−22.1 (1620)
Pt(II)−Me	0.02 (90)	−0.11 (84)	0.01 (85)	−0.09 (90)	
	0.46 (84)	0.36 (84)	0.38 (86)	0.37 (85)	
				0.38 (85)	
Pt(IV)−Me		0.54 (69)	0.75 (68)		0.50 (68)
		0.98 (69)	0.94 (68)		0.96 (68)
Pt(II)N=CH	8.97 (45)	9.01 (50)	9.04 (42)	8.99 (44)	
				8.96 (121)	
Pt(IV)N=CH		8.75 (32)	8.75 (30)		8.82 (32)
$CH^{2,4}$	8.34	8.04, 8.37	8.12, 8.32	8.26, 8.34	8.11

Table 6. Composition of Methane Isotopomers (%) on Deuterolysis of Complex 1 in CD_3OD/CD_3CN

	DCl at −20 °C[b]				DCl at 0 °C[b]			
CD_3OD[a]	CH_4	CH_3D	CH_2D_2	CHD_3	CH_4	CH_3D	CH_2D_2	CHD_3
100	10	43	20	27	7	35	42	16
93	8	47	26	19	5	34	44	17
67	10	33	30	28	7	25	43	24
50	13	35	27	26	10	26	42	23
33	16	38	19	26	10	36	37	17
7	24	45	17	14	19	37	36	8

	CF_3SO_3D at −20 °C[b]				CF_3SO_3D at 0 °C[b]			
CD_3OD[a]	CH_4	CH_3D	CH_2D_2	CHD_3	CH_4	CH_3D	CH_2D_2	CHD_3
100	17	43	29	11	18	48	26	8
93	18	49	26	8	17	48	25	10
67	21	48	20	11	17	47	24	12
50	17	48	27	9	16	45	28	11
33	19	47	24	10	18	46	25	11
7	32	47	16	5	29	45	20	6

[a] The % by volume of CD_3OD in the CD_3OD/CD_3CN solvent mixture. [b] The molar % of each H-containing isotoper of methane, ignoring CD_4, which was not analyzed.

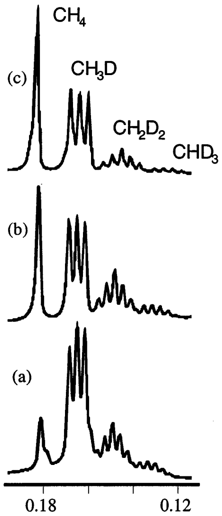
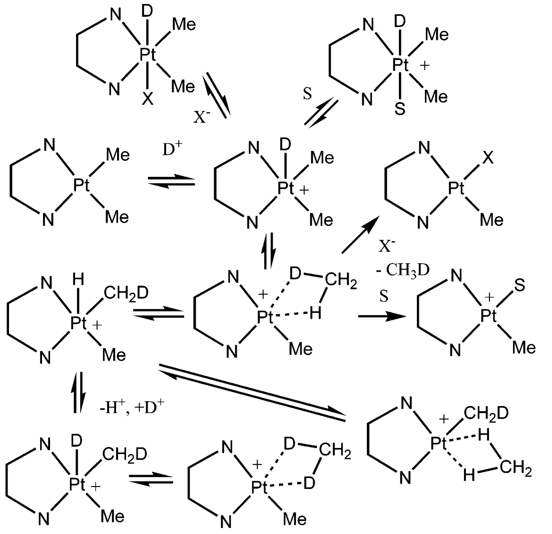


Figure 8. ^{1}H NMR spectra (600 MHz) in the methane region for the protonation of complex **1** with HCl: (a) in CD_3OD; (b) in CD_3OD/CD_3CN, 50:50; and (c) in CD_3OD/CD_3CN, 7:93.

Scheme 7



2 are well separated and so can react essentially independently of one another, whereas the platinum centers in **1** are much closer. The separation between the platinum(II) centers in **1** is short enough to allow a single atom bridge to span between them, but no evidence for this has been found. Instead, the oxidation to octahedral platinum(IV) is accompanied by conformational change to allow a larger separation between the two platinum centers. Nevertheless, the interaction between the two platinum centers does lead to enhanced selectivity in the reactions of complex **1** compared to **2**.

Experimental Section

All reactions were carried out under an N_2 atmosphere using standard Schlenk techniques or using a drybox. Solvents were dried and distilled under N_2 immediately before use. $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and 1,3-BAIB were prepared as described in the literature.[15] NMR spectra were recorded by using a Varian Mercury 400 MHz, Varian Inova 400 MHz, or Varian Inova 600 MHz spectrometer. Analytical data were obtained from Guelph Chemical Labs.

$[Pt_2Me_4(1,3\text{-BAIB})]$, 1. To a solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.230 g) in diethyl ether (20 mL) was added 1,3-BAIB (0.110 g) in diethyl ether (20 mL). The solution immediately turned yellow, and the product **2** precipitated as a bright yellow solid over 40 min. The solvent was removed under vacuum until there was 2 mL of solvent, then 40 mL of pentane was added to complete the precipitation of the product, which was collected by filtration, washed with ether (3 × 2 mL) and pentane (3 × 8 mL), and dried under vacuum. Yield: 91%; mp 205 °C. Anal. Calcd for $C_{20}H_{38}N_4Pt_2$: C, 33.1; H, 5.3; N, 7.7. Found: C, 32.8; H, 5.3; N, 7.8. ^{1}H NMR (CD_2Cl_2): δ −0.06 [s, 6H, ^2J(PtH) = 90 Hz, Pt-Me]; 0.41 [s, 6H, ^2J(PtH) = 84 Hz, Pt-Me]; 2.63 [m, 4H, ^3J(PtH) = 4 Hz, CH_2]; 2.75 [s, 12H, ^3J(PtH) = 19 Hz, N-Me]; 3.99 [m, 4H, ^3J(PtH) = 4 Hz, CH_2]; 7.35 [t, 1H, J(HH) = 8 Hz, H^5]; 8.41 [d, 2H, J(HH) = 8 Hz, $H^{4,6}$]; 9.03 [s, 2H, ^3J(PtH) = 45 Hz, N=CH]; 9.37 [s, 1H, H^2]. ^{13}C NMR ($CDCl_3$): δ −24.8 [^1J(PtC) = 800 Hz, PtMe]; −18.5

---

(15) (a) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643. (b) Yamami, Y.; Tanaka, M.; Sakiyama, H.; Koga, T.; Kobayashi, K.; Miyasaka, H.; Ohba, M.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **1997**, 4595.

Table 7. Crystal Data and Structure Refinement for the Complexes

	1·$C_2H_4Cl_2$	**2**·4$CHCl_3$	**3**·CH_2Cl_2	**4**
formula	$C_{22}H_{42}Cl_2N_4Pt_2$	$C_{24}H_{42}Cl_{12}N_4Pt_2$	$C_{19}H_{32}Cl_4N_4Pt_2$	$C_{24}H_{48}F_6N_4O_8Pt_2S_2$
fw	823.68	1202.20	848.47	1088.96
temp/K	200(2)	200(2)	200(2)	150(2)
λ(Mo Kα)/Å	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$
cell dimens a/Å	8.8641(2)	14.3712(4)	12.7928(3)	11.2493(4)
b/Å	11.4676(3)	11.9440(2)	10.9447(4)	12.0187(3)
c/Å	14.2479(5)	11.8166(2)	19.3462(6)	15.1904(5)
α/deg	88.549(1)	90	90	111.180(1)
β/deg	87.412(1)	104.887(1)	101.317(2)	98.152(1)
γ/deg	76.852(2)	90	90	101.929(2)
volume/Å^3	1408.73(7)	1960.23(7)	2656.06(1)	1820.2(1)
Z	2	2	4	2
d(calc)/Mg m^{-3}	1.942	2.037	2.122	1.987
abs coeff/mm^{-1}	10.125	7.97	10.938	7.869
F(000)	784	1148	1592	1052
no. of reflns/ind reflns	16 510/8255	19 908/4477	11 461, 3037	19 272, 7233
abs corr	integration	integration	integration	integration
no. of data/restr/params	8255/0/272	4477/0/191	3037/2/137	7233/16/483
R1, wR2 [$I > 2\sigma(I)$]	0.072, 0.176	0.049, 0.123	0.036, 0.081	0.039, 0.073

[^1J(PtC) = 840 Hz, PtMe]; 49.7 [NMe_2]; 65.5, 66.3 [CH_2]; 128, 129, 132, 134 [aromatic C].

[Pt_2Me_4(1,4-BAIB)], 2. This was prepared similarly from [$Pt_2Me_4(\mu$-$SMe_2)_2$] (0.0576 g) and 1,4-BAIB (0.0285 g). Yield: 88%; mp 195 °C. Anal. Calcd for $C_{20}H_{38}N_4Pt_2$: C, 33.1; H, 5.3; N, 7.7. Found: C, 33.6; H, 5.7; N, 7.5. ^{1}H NMR (CD_2Cl_2): δ 0.02 [s, 6H, ^2J(PtH) = 90 Hz, Pt-Me]; 0.46 [s, 6H, ^2J(PtH) = 84 Hz, Pt-Me]; 2.63 [m, 4H, ^3J(PtH) = 5 Hz, CH_2]; 2.76 [s, 12H, ^3J(PtH) = 18 Hz, NMe]; 3.98 [m, 4H, ^3J(PtH) = 6 Hz, CH_2]; 8.34 [s, 4H, $H^{2,3,5,6}$]; 8.97 [s, 2H,^3J(PtH) = 36 Hz, N═CH].

[$Pt_2Cl_2Me_2$(1,3-BAIB)], 3. To a solution of complex **1** (0.044 g) in CH_2Cl_2 (20 mL) was added H_2O (3.3 μL) and Me_3SiCl (23 μL) to form HCl in situ. The product formed as a yellow precipitate, which was isolated by filtration, washed with CH_2Cl_2 and pentane, and dried under vacuum. Yield: 63%. Anal. Calcd for $C_{18}H_{32}Cl_2N_4Pt_2$: C, 28.2; H, 4.2; N, 7.3. Found: C, 28.6; H, 4.7; N, 7.4%. ^{1}H NMR (DMSO-d_6): δ 0.64 [s, 6H, ^2J(PtH) = 80 Hz, Pt-Me]; 2.62 [m, 4H, CH_2]; 2.78 [s, 12H, NMe]; 3.99 [m, 4H, CH_2]; 7.37 [t, 1H, H^5]; 8.42 [d, 2H, $H^{4,6}$]; 8.99 [s, 2H, ^3J(PtH) = 136 Hz, N═CH]; 9.41 [s, 1H, H^2].

[$Pt_2Me_6(OH_2)_2$(1,3-BAIB)]($CF_3SO_3)_2$, 4. To a solution of complex **1** (0.15 g) in CH_2Cl_2 (30 mL) was added CF_3SO_3Me (0.12 mL). The solution slowly turned pale yellow in color. After 3 days the solvent was evaporated under vacuum to yield the product, which was recrystallized from CH_2Cl_2/hexane. Yield: 86%. Anal. Calcd for $C_{24}H_{48}F_6N_4O_8Pt_2S_2$: C, 26.5; H, 4.4; N, 5.1. Found: C, 26.6; H, 4.8; N, 4.8%. ^{1}H NMR (CD_3CN): δ 0.24 [s, 6H, ^2J(PtH) = 70 Hz, Pt-Me]; 0.60 [s, 3H, ^2J(PtH) = 75 Hz, Pt-Me]; 0.61 [s, 3H, ^2J(PtH) = 75 Hz, Pt-Me]; 0.68 [s, 6H, ^2J(PtH) = 70 Hz, Pt-Me]; 2.35 [s, 6H, ^3J(PtH) = 16 Hz, N-Me]; 2.69 [s, 6H, ^3J(PtH) = 9 Hz, N-Me]; 2.79 [m, 2H, CHN]; 2.85 [m, 2H, CHN]; 3.92 [m, 2H, CHN]; 3.95 [m, 2H, CHN]; 7.45 [d, 2H, ^3J(HH) = 8 Hz, $CH^{4,6}$]; 7.53 [t, 1H, ^3J(HH) = 8 Hz, CH^5]; 7.54 [s, 1H, CH^2]; 9.05 [s, 2H, ^3J(PtH) = 35 Hz, N═CH]. ^{1}H NMR (D_2O): δ 0.23 [s, 6H, ^2J(PtH) = 70 Hz, Pt-Me]; 0.67 [s, 6H, ^2J(PtH) = 67 Hz, Pt-Me]; 0.75 [s, 6H, ^2J(PtH) = 79 Hz, Pt-Me]; 2.55 [s, 6H, N-Me]; 2.80 [s, 6H, N-Me]; 2.80, 2.88, 3.91, 4.00 [m, 8H, CH_2N]; 7.48 [s, 1H, CH^2]; 7.57 [t, 1H, ^3J(HH) = 8 Hz, CH^5]; 7.71 [d, 2H, ^3J(HH) = 8 Hz, $CH^{4,6}$]; 9.13 [s, 2H, ^3J(PtH) = 34 Hz, N═CH]. Hydrolysis of **4** led to formation of **5** and **6**, identified by their ^{1}H NMR spectra. **5**: δ 0.12 [s, 3H, ^2J(PtH) = 70 Hz, Pt-Me]; 0.66 [s, 3H, ^2J(PtH) = 67 Hz, Pt-Me]; 0.78 [s, 3H, ^2J(PtH) = 80 Hz, Pt-Me]; 2.41 [s, 3H, N-Me]; 2.55 [s, 3H, N-Me]; 2.80, 2.88, 3.92, 4.01 [m, 4H, CH_2N]; 7.61 [t, 1H, ^3J(HH) = 8 Hz, CH^5]; 7.93 [s, 1H, CH^2]; 7.72, 7.98 [d, each 1H, ^3J(HH) = 8 Hz, $CH^{4,6}$]; 9.17 [s, 1H, ^3J(PtH) = 35 Hz, N═CH]; 9.86 [s, 1H, CH═O]. **6**: δ 0.47 [s, 3H, ^2J(PtH) = 70 Hz, Pt-Me]; 0.70 [s, 3H, ^2J(PtH) = 70 Hz, Pt-Me]; 0.71 [s, 3H, ^2J(PtH) = 79 Hz, Pt-Me]; 2.33 [s, 3H, N-Me]; 2.46 [s, 3H, N-Me]; 2.58, 2.59, 2.90, 2.94 [m, 4H, CH_2N].

Characterization of Hydrido(methyl)platinum(IV) Complexes. In a typical experiment, a solution of HCl (0.01 mmol) in CD_2Cl_2 (0.25 mL) (produced by reaction of Me_3SiCl with H_2O) was added by syringe to a solution of complex **1** (7.2 mg, 0.01 mmol) in CD_2Cl_2 (0.30 mL) in a 5 mm NMR tube at −78 °C. The tube was shaken to ensure mixing, then immediately placed in the precooled NMR probe of the Varian Inova 400 MHz spectrometer. ^{1}H NMR data were recorded at −78 °C, and then at −40, −30, −20, −10, 0, and 20 °C as the sample was warmed in steps to room temperature. Complex **9** was characterized by its NMR spectrum: δ(^{1}H) −0.06 [s, 3H, ^2J(PtH) = 92 Hz, Pt-Me]; 0.05 [s, 3H, ^2J(PtH) = 86 Hz, Pt-Me]; 0.41 [s, 3H, ^2J(PtH) = 82 Hz, Pt-Me].

Other experiments were performed in a similar way, and data are listed in Tables 4 and 5.

H/D Exchange Experiments. In a typical experiment, a sample of complex **1** (0.01 mmol) in a 5 mm NMR tube (loaded in a drybox to ensure anhydrous) was dissolved in CD_3OD/CD_3CN (1.0 mL, 1:1 v/v), and the solution was cooled to below −20 °C. Acetyl chloride (1.5 μL, 0.02 mmol) was then added to form DCl. The tube was shaken to give good mixing, then placed in the NMR probe precooled to −20 °C. Spectra were recorded at −20, −10, 0, and 20 °C, as the solution was warmed slowly to room temperature. Other experiments were carried out in a similar way, and selected data are listed in Table 6.

Xray 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 7.

Acknowledgment. We thank the NSERC (Canada) for financial support. R.J.P. thanks the Government of Canada for a Canada Research Chair.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM030650M