Methyl(hydrido)platinum(IV) Complexes with Flexible Tridentate Nitrogen-Donor Ligands

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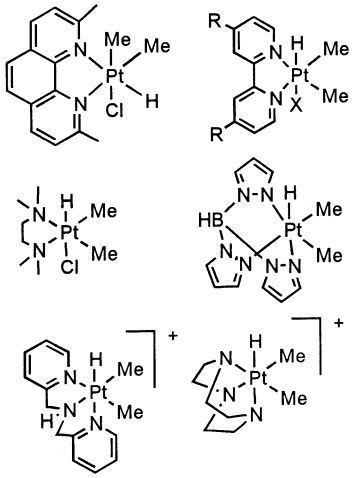
The flexible, unsymmetrical triamine ligands NNN = *N*,*N*,*N*′-trimethyl-*N*′-(2-pyridylmethyl)ethylenediamine (PICO), *N*-benzyl-*N*′,*N*′-dimethyl-*N*-(2-picolyl)ethylenediamine (BPICO), and *N*,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) act as bidentate ligands in forming square-planar dimethylplatinum(II) complexes *cis*-[$PtMe_2$(NNN)]. These complexes undergo oxidative addition with MeI to give the platinum(IV) complexes *fac*-[$PtMe_3$(NNN)]I, in which the ligand NNN is *fac*-tridentate in [$PtMe_3$(NNN)]I when NNN = PICO or BPICO, but in equilibrium with bidentate NNN in [$PtIMe_3$(NNN)] when NNN = PMDETA. Protonation of the complexes *cis*-[$PtMe_2$(NNN)] gave the corresponding dimethyl(hydrido)platinum(IV) complexes, [$PtHMe_2$(NNN)]X (X = BF_4^-, $CF_3SO_3^-$, $CF_3CO_2^-$), often as a mixture of isomers whose structures were deduced from the NMR spectra. These hydridoplatinum(IV) complexes undergo reductive elimination of methane to give the methylplatinum(II) complexes [PtMe(NNN)]X, in which NNN is a *mer*-tridentate ligand, with the rate of reaction for NNN = PMDETA > PICO, BPICO. In all cases, H/D exchange experiments indicate reversibility of the protonation and methyl(hydride) to methane complex steps in the reaction sequence.

Introduction

Alkyl(hydrido)platinum(IV) complexes are important intermediates in several catalytic reactions, most notably in the activation of alkanes by oxidative addition of C−H bonds to platinum(II) complexes, and so there has been intense interest in the synthesis and properties of such complexes.[1−8] The first examples of these complexes, including [$PtHXMe_2$(NN)] (X = Cl, Br, I; NN = 2,9-dimethyl-1,10-phenanthroline, 2,2′-bipyridine or its derivatives; and tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, Chart 1), containing bidentate nitrogen-donor ligands, had limited thermal stability and were characterized by low-temperature NMR techniques.

Chart 1[a]



[a] R = H, Me, *t*-Bu; X = Cl, Br, I.

These complexes decomposed easily by reductive elimination of methane to give the corresponding platinum(II) complex [PtXMe(NN)].[4] The mechanism of reductive elimination involves the dissociation of the ligand X^- to generate the cationic, 5-coordinate intermediate $[PtHMe_2(NN)]^+$, which then undergoes loss of methane.[1,4] Stable methyl(hydrido)platinum(IV) complexes were formed if there was no easily dissociated ligand, as in neutral complexes such as [$PtHMe_3$(bu_2-bpy)] (bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine)[5] or [$PtHMe_2$Tp′], where Tp′ = tris(methylpyrazolyl)borate.[6] The cationic complex $[PtHMe_2(9N3)]^+$, with the *fac*-coordinating ligand 9N3 = 1,4,7-triazacyclononane, had thermal stability comparable to that of [$PtHMe_2$Tp′],[9] while the complex cation $[PtHMe_2(BPMA)]^+$, with the more flexible tridentate ligand BPMA = bis(2-pyridyl-

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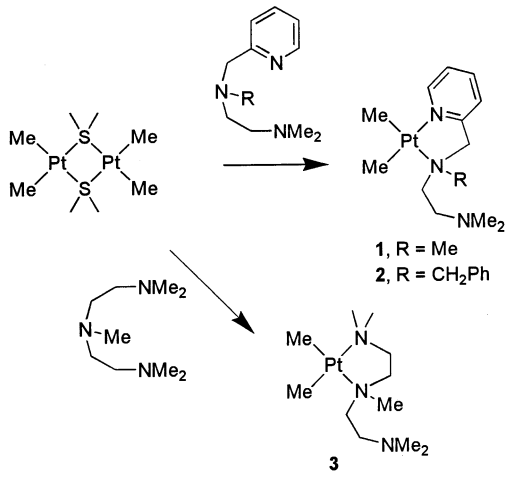
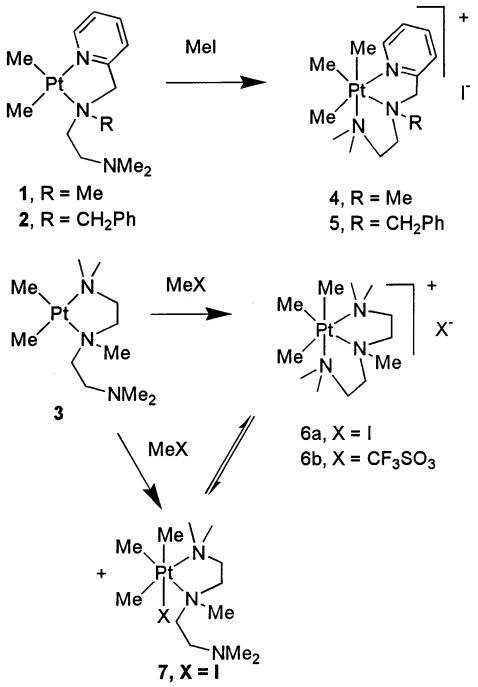
Scheme 1. Synthesis of Platinum(II) Complexes



Scheme 2. Trimethylplatinum(IV) Complexes



methyl)amine (Chart 1), had intermediate thermal stability and decomposed in solution to give methane and $[PtMe(BPMA)]^+$ over a period of about 1 day at room temperature.[7] This intermediate thermal stability allows easy study of further reactions, such as H/D exchange between the hydrido and methyl ligands and the mechanism of the reductive elimination of methane.[7] Thus it was of interest to study analogous chemistry with other flexible tridentate nitrogen-donor ligands, to determine how ligand structure affects the reactivity and selectivity.

The ligand BPMA = $NH(CH_2\text{-}2\text{-}py)_2$ contains two 2-picolyl units and a central NH group. The NH group can cause complications in H/D exchange reactions and was substituted in the present work by NMe or NCH_2Ph groups. In addition, one or both of the 2-picolyl groups in BPMA was replaced by $CH_2CH_2NMe_2$ groups to study the relative effects of pyridyl and amine ligands on the reaction chemistry. The ligands used were $Me_2NCH_2CH_2N(R)CH_2\text{-}2\text{-}py$ (PICO, R = Me; BPICO, R = CH_2Ph) and $(Me_2NCH_2CH_2)_2NMe$ (PMDETA), and the resulting methyl(hydrido)platinum(IV) chemistry is reported below.

Results and Discussion

Preparation of Dimethylplatinum(II) Complexes. The synthetic chemistry is shown in Scheme 1. Reaction of the appropriate ligand with $[PtMe_2(\mu\text{-}SMe_2)]_2$ gave the corresponding dimethylplatinum(II) complex $[PtMe_2(NNN)]$ (**1**, NNN = PICO; **2**, NNN = BPICO; **3**, NNN = PMDETA) by displacement of the dimethyl sulfide ligands. The complexes all contain free $CH_2CH_2NMe_2$ groups and, though they were formed in good yield, all were easily oxidized in solution and were difficult to crystallize for purification. In most cases the complexes were characterized spectroscopically, and were prepared and used in situ for further reaction chemistry. The ^1H and ^{13}C NMR spectra of **1** each contained two methylplatinum resonances at $\delta(^1H)$ 0.54 $[^2J(PtH) = 90$ Hz] and 0.49 ppm $[^2J(PtH) = 86$ Hz], and at $\delta(^{13}C)$ −19.24 $[^1J(PtC) = 838$ Hz] and −21.35 ppm $[^1J(PtC) = 843$ Hz], typical of methylplatinum(II) complexes with methyl groups trans to nitrogen donors.[4−9] The mode of coordination of the PICO ligand in **1** was determined by the ^{195}Pt satellite spectra of the ligand resonances in the ^1H NMR spectrum. Thus, satellite spectra were observed for the *o*-pyridyl proton at $\delta(H^6)$ 8.72 ppm $[J(PtH) = 22$ Hz] and for the NMe group at δ 2.69 ppm $[^3J(PtH) = 14$ Hz], but not for the NMe_2 resonance, showing that the ligand PICO is coordinated through the pyridyl and central NMe nitrogen atoms, with the terminal NMe_2 group free (Scheme 1). Complex **2** was characterized similarly, and the structures of **1** and **2**, with coordinated 2-pyridyl groups and free $CH_2CH_2NMe_2$ groups, clearly show the preference for pyridine over amine coordination at platinum(II). The ^1H NMR spectrum of $[PtMe_2(PMDETA)]$, **3**, contained methylplatinum resonances at δ 0.17 $[^2J(PtH) = 89$ Hz] and 0.12 ppm $[^2J(PtH) = 87$ Hz]. Singlet resonances were observed at δ 2.55 ppm $[^3J(PtH) = 21$ Hz] for the coordinated terminal Me_2N groups, at δ 2.60 ppm $[^3J(PtH) = 21$ Hz] for the coordinated central MeN group, and at δ 2.15, with no resolved coupling to ^{195}Pt, for the uncoordinated Me_2N groups. There was no indication of fluxionality involving intramolecular nitrogen ligand substitution for any of these complexes **1**−**3**.

Oxidative Addition Reactions with MeI. The reactions with methyl iodide are useful as models for oxidative additions, since the products are thermally stable and so benchmark spectroscopic data can be obtained. The products formed are shown in Scheme 2. The oxidative addition of MeI to complexes **1** or **2** in acetone or thf solution gave the stable trimethylplatinum(IV) complexes $[PtMe_3(PICO)]I$, **4**, or $[PtMe_3(BPICO)]I$, **5**, respectively. Consider the NMR spectrum of complex **4** as an example. Since the ligand *fac*-PICO is unsymmetrical, the three methylplatinum groups in **4** are nonequivalent and three methylplatinum resonances were observed in both the ^1H and ^{13}C NMR spectra, as expected. Since ^{195}Pt satellite spectra were observed for all NMe resonances, it is clear that the

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Table 1. Selected NOESY NMR Data for Complexes 3 in Acetone-d_6

proton	δ (ppm); coupling (Hz)	NOESY[a]
	$[PtMe_3(PICO)]^+$, **3**	
Pt-Me (*trans*-py)	0.79; $^2J(PtH) = 69$	Pt-NMe_2, Pt-NMe
Pt-Me (*trans*-NMe)	0.95; $^2J(PtH) = 68$	Pt-NMe_2
Pt-Me (*trans*-NMe_2)	0.54; $^2J(PtH) = 69$	Pt-NMe
Pt-NMe_2	2.29; $^3J(PtH) = 10$	Me_2N-CH_2CH_2-NMe, PtMe (*trans*-NMe)
	2.59; $^3J(PtH) = 17$	Me_2N-CH_2CH_2-NMe, Pt-Me (*trans*-py)
Pt-NMe	2.94; $^3J(PtH) = 16$	py-CH_2, Me_2N-CH_2CH_2-NMe, Pt-Me (*trans*-NMe_2), Pt-Me (*trans*-py)
	$[PtHMe_2(PICO)]^+$, **8a**	
Pt-H	−21.18; $^1J(PtH) = 1438$	
Pt-Me (*trans*-py)	0.86; $^2J(PtH) = 69$	Pt-NMe_2, Pt-NMe
Pt-Me (*trans*-NMe)	0.97; $^2J(PtH) = 66$	Pt-NMe_2
Pt-NMe_2	2.17; $^3J(PtH) = 9$	Me_2N-CH_2CH_2-NMe, PtMe (*trans*-NMe)
	2.48; $^3J(PtH) = 17$	Me_2N-CH_2CH_2-NMe, Pt-Me (*trans*-py)
Pt-NMe	3.05; $^3J(PtH) = 19$	py-CH_2, Me_2N-CH_2CH_2-NMe

[a] Correlation underlined.

PICO is tridentate, and it follows that iodide is not coordinated. It was important to assign the ^{1}H NMR peaks to specific methylplatinum and methylnitrogen groups, since complex **4** is a model for the hydridoplatinum(IV) compounds. The assignments of methylplatinum resonances could not be made on the basis of coupling constants since all MePt groups are trans to nitrogen and so give similar values of ^2J(PtH) and ^1J(PtC) {δ(MePt) 0.95 [$^2J(PtH) = 68$ Hz], 0.79 [$^2J(PtH) = 69$ Hz], 0.54 ppm [$^2J(PtH) = 69$ Hz]; δ(MePt) −3.90 [$^1J(PtC) = 712$ Hz], −4.53 [$^1J(PtC) = 677$ Hz], −7.62 ppm [$^1J(PtC) = 674$ Hz]}. However, a positive assignment of the ^{1}H NMR resonances was accomplished by analysis of the ^{1}H NOESY spectrum (Table 1). The CH_2 resonances of the ligand were readily identified on the basis of their multiplicity in the ^{1}H NMR spectrum and were thus used as the basis for the rest of the peak assignments. Next, correlation of the NMe resonances to those of the neighboring CH_2 protons in the NOESY spectrum led to their assignments. In turn, the correlations between the NMe resonances and the nearby PtMe resonances led to the final assignments (Table 1).

The reaction of CD_3I with **1** in acetone-d_6 gave the corresponding complex $[PtMe_2(CD_3)(PICO)]I$, **4′**. The ^{1}H NMR spectrum of **4′** showed only two of the three methyl resonances observed for **4**, the missing one indicating that the site of the CD_3 group in **4′** is trans to the NMe_2 group. The spectrum of **4′** was unchanged over several days in solution, indicating that scrambling of the methyl groups is a slow process. The isomer of **4′** is that expected based on the usual mechanism of oxidative addition, since the formation of the new $PtCD_3$ bond will be accompanied by coordination of the free NMe_2 group in the trans position.

The reaction of MeI with complex **2** in acetone or thf occurred similarly to give $[PtMe_3(BPICO)]I$, **5** (Scheme 2). Again using the ^{1}H NOESY NMR data, the three methylplatinum groups were assigned at δ 0.90 [$^2J(PtH) = 68$ Hz, trans to pyridyl], 1.02 [$^2J(PtH) = 68$ Hz, trans to NBz], and 0.66 ppm [$^2J(PtH) = 69$ Hz, trans to NMe_2]. The resonance at δ 0.66 was of very low intensity in **5′**, formed by reaction of **2** with CD_3I, and no change in the relative peak heights was observed in the ^{1}H NMR spectra over several days at room temperature. The structure of complex **5** was confirmed crystallographically; a view of the cation is shown in Figure 1 and selected bond distances and angles are given in Table 2.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $[PtMe_3((BPICO)]I$, 5

Pt(1)−C(2)	2.040(6)	Pt(1)−C(3)	2.059(6)
Pt(1)−C(1)	2.065(5)	Pt(1)−N(1)	2.164(5)
Pt(1)−N(2)	2.219(5)	Pt(1)−N(3)	2.247(5)
C(2)−Pt(1)−C(3)	86.9(2)	C(2)−Pt(1)−C(1)	86.5(3)
C(3)−Pt(1)−C(1)	88.1(2)	C(2)−Pt(1)−N(1)	89.1(2)
C(3)−Pt(1)−N(1)	174.7(2)	C(1)−Pt(1)−N(1)	95.1(2)
C(2)−Pt(1)−N(2)	95.0(2)	C(3)−Pt(1)−N(2)	99.3(2)
C(1)−Pt(1)−N(2)	172.5(2)	N(1)−Pt(1)−N(2)	77.6(2)
C(2)−Pt(1)−N(3)	176.4(2)	C(3)−Pt(1)−N(3)	91.6(2)
C(1)−Pt(1)−N(3)	96.8(2)	N(1)−Pt(1)−N(3)	92.2(2)
N(2)−Pt(1)−N(3)	82.0(2)		

The crystal structure contains well-separated cations of **5** and iodide ions. The platinum center in **5** has distorted *fac*-PtC_3N_3 coordination. The major distortions from octahedral geometry arise from the constraints of the tridentate BPICO ligand, with angles N(1)PtN(2) = 77.6(2)° and N(2)PtN(3) = 82.0(2)°. The three platinum−nitrogen bond lengths are significantly different from each other, with the shortest distance being to the pyridyl nitrogen [PtN(1) = 2.164(5) Å] and the longest distance to the dimethylamine nitrogen [PtN(3) = 2.247(5) Å]. The Pt−NMe_2 bond appears weak and it is probably for this reason that the Pt−C distance trans to NMe_2 is shorter at Pt−C(2) = 2.040(6) Å than the other two [Pt(C(1) = 2.065(5) Å, Pt(C3) = 2.059(6) Å]. The benzyl group of the BPICO ligand is directed away from the platinum center, so there is no intramolecular

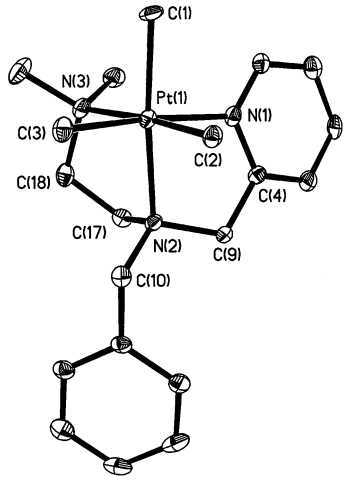
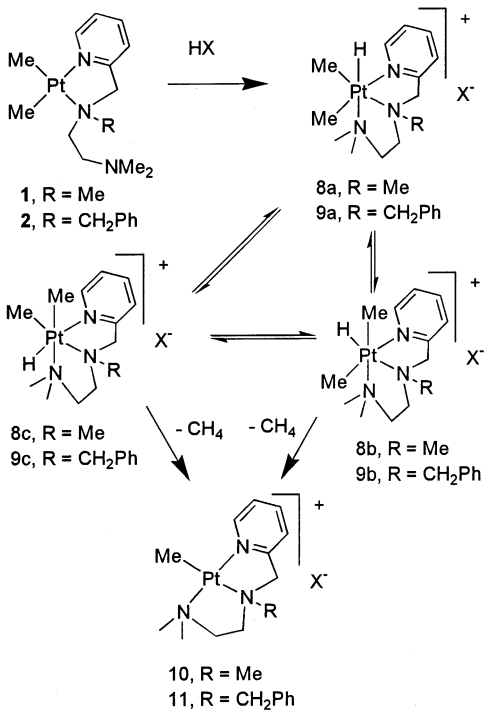


Figure 1. A view of the molecular structure of $[PtMe_3(BPICO)]^+$, showing 25% thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Scheme 3. Hydrido(dimethyl)platinum(IV) Complexes



π-stacking. However, there is an edge-to-face aryl−aryl interaction between the benzyl and pyridyl rings of neighboring cations, with a distance of 3.89 Å between the center of the benzyl ring and the α-proton of the pyridyl ring (a distance of 5.19 Å between the centers of the rings), with an angle of 103° between the planes of the two rings.

Oxidative addition of MeI to complex **3** in acetone or thf occurred to give a mixture of complexes [$PtMe_3$-(PMDETA)]I, **6a**, and [$PtIMe_3$(PMDETA)], **7**, according to Scheme 2. In this case there is competition between iodide and one of the NMe_2 groups for the sixth coordination site. The similar reaction of methyl triflate with **3** gave only [$PtMe_3$(PMDETA)][CF_3SO_3], **6b**, as expected since triflate is a poor ligand for platinum. The complex cation [$PtMe_3$(PMDETA)]$^+$, **6**, has C_s symmetry and so gives two methylplatinum resonances in a 2:1 ratio for **6a** or **6b**. However, complex **7** is unsymmetrical and gives three MePt resonances. The free NMe_2 group was identified by the presence of closely spaced resonances at δ 2.16 and 2.15, similar to the chemical shift of the free (diastereotopic) Me_2N protons in the precursor complex **2**. The ratio of **6a**:**7** formed in the initial reaction of **3** with MeI was about 3:2, and a very slow isomerization of **7** to **6a** was then observed. After one month, approximately 20% of **7** had isomerized to **6a**.

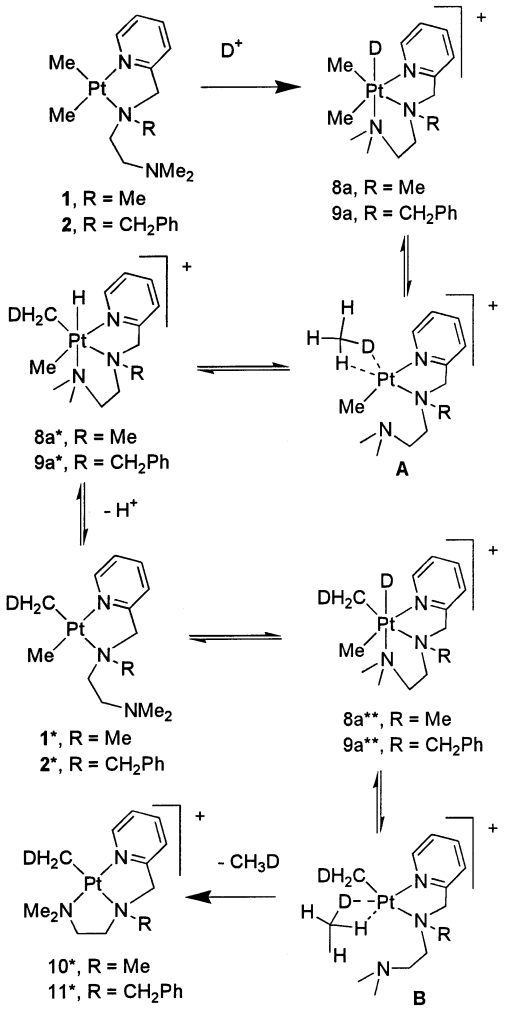
These results show that all three ligands can be *fac*-tridentate in platinum(IV) complexes but the competition with iodide shows that PICO and BPICO are more effective *fac*-tridentate ligands than PMDETA.

Protonation Reactions: (a) Reactions of Complexes 1 and 2 with H^+ and D^+. The reaction of complex **1** at room temperature with 1 equiv of acid HX (X^- = $CF_3SO_3^-$, $CF_3CO_2^-$, BF_4^-) in acetone or dichloromethane solution generally gave a mixture of all three possible isomers of the corresponding cationic complex [$PtMe_2H$(PICO)]$^+$, **8a**−**c** (Scheme 3). Only in the case with X = BF_4 was the protonation product isolated in solid form, since reaction of **1** with H[BF_4] in THF solution led to precipitation of **8c**[BF_4], as essentially a single isomer. Over the course of 7 days in CD_2Cl_2 solution at room temperature, the mixtures of cations **8a**−**c** was converted slowly to give **8c** (H trans to pyridyl), which must therefore be the thermodynamically most stable dimethyl(hydrido)platinum(IV) isomer. However, the isomerization was accompanied by slow reductive elimination of methane to give the corresponding complex cation **10**, as described below. The reaction of complex **1** with excess acid in acetone solution gave only isomer **8a** (H trans to NMe_2), and its subsequent isomerization to **8b** and **8c** was very slow under these conditions. This indicates that **8a** is the product of kinetic control. If a solution containing mostly **8a** was neutralized (for example, by addition of **1**) or if <1 equiv of acid was used in the reaction with complex **1**, the thermodynamic product **8c** was the major product detected and this was the isomer that precipitated on reaction of **1** with H[BF_4] in THF solution. These observations show that the isomerization process involves catalysis by free complex **1**, perhaps involving direct proton transfer between platinum centers.

The structural assignments for complexes **8a**−**c** were made, based on the NOESY ^{1}H NMR spectra, as described above for complex **3**. Thus, the product of kinetic control, cationic complex **8a**, is formed from **1** by addition of a proton with coordination of the Me_2N group in the trans position, as expected and proved by the NOESY data (Table 1).[4] The structure of **8c** was deduced similarly, and it is shown to have the hydride trans to the pyridyl nitrogen donor. The structure of **8b** is then the isomer with hydride trans to the central MeN nitrogen donor, and this was confirmed by the NOESY spectrum of the isomeric mixture containing **8a**, **8b**, and **8c**. It should be noted that **8a**−**c** have similar structures and considerable overlap of the methylplatinum resonances occurred. However, since reaction conditions were found that gave **8a** and **8c** in almost isomerically pure form, and since mixtures of **8a**−**c** were formed with a range of compositions, it was still possible to assign these resonances with confidence.

In the solid state, reductive elimination of methane from **8c**[BF_4] occurred slowly, going to half completion in 1.5 months with formation of [PtMe(PICO)][BF_4], **10**[BF_4]. The cationic methylplatinum(II) complex **10** was characterized by its ^{1}H NMR spectrum, which contained a Pt−Me resonance at δ 0.50 ppm [^2J(PtH) = 79 Hz] and three Pt−NMe resonances at δ 2.61 [^2J(PtH) = 16 Hz], 2.79 [^2J(PtH) = 45 Hz], and 2.93 ppm [^2J(PtH) = 49 Hz]. If the mixture of cationic complexes **8a**−**c** was prepared in solution in CD_2Cl_2 at room temperature, reductive elimination of methane typically occurred over the course of 2 weeks at room temperature to give complex **10**, and the rate was similar for all anions studied. The reductive elimination of methane from initially pure **8c**[BF_4] dissolved in acetone-d_6 required 4 weeks for completion but, in the presence of free H[BF_4], both the isomerization to give **8a**[BF_4] and **8b**[BF_4] and the reductive elimination of methane were inhibited. The reductive elimination from **8c**[BF_4] was catalyzed modestly by the product **10**[BF_4]. Thus, for a sample containing initially an equimolar mixture of

Scheme 4. Methane Complexes and H/D Exchange



8c[BF_4] and **10**[BF_4], reductive elimination of methane from **8c** was complete in 8 days. Since excess acid destroys complex **10** by cleavage of the methylplatinum(II) bond, the autocatalysis is not observed in the presence of excess acid and **8c** is stable under these conditions for several weeks in solution at room temperature. The reaction of **10** with triflic acid was studied separately by monitoring at low temperature, using ^{1}H NMR. At −80 °C there was no reaction, but reaction occurred at −60 °C with formation of methane. No intermediate hydridoplatinum(IV) complex was detected so it is not determined if the methane formation involves oxidative addition/reductive elimination or direct protonolysis.

The reaction of complex **1** in methanol-d_4 with CF_3SO_3D allowed the observation of H/D exchange (Scheme 4). The methane formed contained the isotopomers CH_4, CH_3D, CH_2D_2, and CHD_3 detectable by ^{1}H NMR spectroscopy. Furthermore, the PtMe region of the ^{1}H NMR spectrum showed deuterium incorporation into the methylplatinum groups of all cationic methylplatinum complexes **8a**, **8b**, **8c**, and **10** present during the reaction. Figure 2 shows the presence of $PtCH_3$, $PtCH_2D$, and $PtCHD_2$ groups in the product **10**. These observations indicate that exchanges between isomers of **8** and a methane complex [$PtMe(CH_3D)(PICO)$]$^+$, probably having a bidentate PICO ligand,[10] and between the hydride(deuteride) ligand in **8** and the deuterium rich

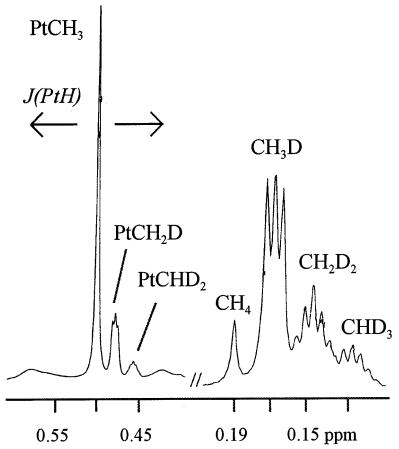


Figure 2. ^{1}H NMR spectrum following the reaction of [$PtMe_2$(PICO)] with CF_3SO_3D in CD_3OD, showing deuterium incorporation into the methane and the remaining methylplatinum group of the product [PtMe(PICO)]$^+$.

environment are faster than the methane dissociation (Scheme 4). Scheme 4 is simplified since it does not show the isomers of **8** (Scheme 3), which will lead to scrambling of partially deuterated methyl groups, and it shows only the first stages of H/D exchange. It follows that repetition of the steps leading from **1** to **1*** or **8a** to **8a**** in Scheme 4 will lead to multiple H/D exchange. Scheme 4 also shows how the proposed intermediate methane complex can be formed with methane trans to NR (**A**) or trans to pyridyl (**B**). Reversibility of the methane complex with the hydrido(methyl)platinum(IV) complex is intuitively more likely for **A**, since intramolecular displacement by the free NMe_2 group is not possible while such displacement is possible for **B** (Scheme 4). Once the reductive elimination to give methane and **10** was complete, no further H/D exchange into the methane or into the methylplatinum group of **10** was observed. Also, the isolated complex **10**[CF_3SO_3], when dissolved in CD_3OD, did not incorporate deuterium into the CH_3Pt group and did not catalyze H/D exchange of added CH_4. Clearly then, there is no easy route back to a methane complex from **10**.

The complex **10**, as the triflate salt, was structurally characterized; details are given in Figure 3 and Table 3. The structure is very similar to that of the BPICO analogue **11** as discussed below.

The protonation of complex **2** occurred in a similar way to that of **1**. Thus, three isomers of [$PtMe_2H$(BPICO)]X (X = $CF_3SO_3^-$ (**9a**), $CF_3CO_2^-$ (**9b**), BF_4^- (**9c**)), were observed (Scheme 3). The reaction of **2** with excess acid gave the kinetic isomer **9a**, but less selectively (ca. 60% yield) than with **1** (ca. 90% yield). This isomer **9a** has a hydride resonance at δ −20.99 ppm [^1J(PtH) = 1435 Hz], and methylplatinum resonances at δ 1.05 [^2J(PtH) = 66 Hz] and 1.01 ppm [^1J(PtH) = 68 Hz], and the NOESY NMR confirmed that the hydride was trans to NMe_2. The isomerization of **9a** to **9c** was complete in one week, even in the presence of excess acid, and so was faster than the corresponding reaction of **8a**. The thermodynamically most stable isomer **9c** could be prepared by using <1 equiv of acid

(10) The role of ligand dissociation in such reactions has been widely discussed.[1−9] See also: Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 261.

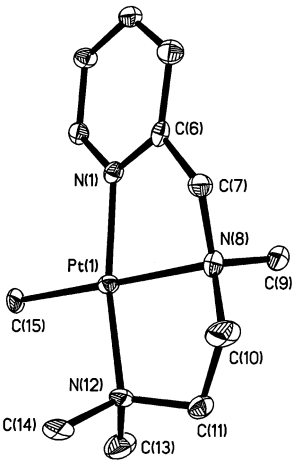


Figure 3. A view of the molecular structure of [PtMe(PICO)]$^+$, showing 25% thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for [PtMe(PICO)]CF_3SO_3, 9

Pt(1)−C(15)	2.035(8)	Pt(2)−C(35)	2.037(8)
Pt(1)−N(1)	2.004(8)	Pt(2)−N(21)	2.013(7)
Pt(1)−N(12)	2.045(8)	Pt(2)−N(32)	2.078(9)
Pt(1)−N(8)	2.119(7)	Pt(2)−N(28)	2.119(7)
N(1)−Pt(1)−C(15)	98.2(3)	N(21)−Pt(2)−C(35)	97.9(3)
N(1)−Pt(1)−N(12)	166.0(3)	N(21)−Pt(2)−N(32)	167.2(3)
C(15)−Pt(1)−N(12)	95.2(4)	C(35)−Pt(2)−N(32)	94.0(3)
N(1)−Pt(1)−N(8)	80.8(3)	N(21)−Pt(2)−N(28)	81.2(3)
C(15)−Pt(1)−N(8)	179.1(4)	C(35)−Pt(2)−N(28)	179.1(3)
N(12)−Pt(1)−N(8)	85.8(3)	N(32)−Pt(2)−N(28)	86.9(3)

in the protonation reaction. This isomer **9c** was identified by the hydride resonance at δ −20.65 ppm [^1J(PtH) = 1412 Hz], and by methylplatinum resonances at δ 1.04 [^2J(PtH) = 67 Hz] and 0.65 ppm [^2J(PtH) = 67 Hz]. The third isomer **9b** was observed as a minor species during the isomerization process, and was characterized by a hydride resonance at δ −21.05 ppm [^1J(PtH) = 1440 Hz] and methylplatinum resonances at δ 1.01 [^2J(PtH) = 68 Hz] and 0.65 ppm [^2J(PtH) = 67 Hz].

The reductive elimination of methane from **9** to give [PtMe(BPICO)]X (X = $CF_3SO_3^-$, $CF_3CO_2^-$, BF_4^- (**11**), occurred in a similar way as for the conversion of **8** to **10**. Addition of a second equivalent of triflic acid to **11** led to cleavage of the methylplatinum group with formation of methane and [Pt(CF_3SO_3)(BPICO)]CF_3SO_3. No intermediate hydrido complex was detected when this reaction was monitored by low-temperature NMR so the mechanism is not known. Complex **11**, as the triflate salt, was structurally characterized; the structure is shown in Figure 4 and selected bond distances and angles are given in Table 4. There are two independent cations and anions in the unit cell but they have very similar structures (Table 4). Each complex has distorted square-planar stereochemistry with *mer*-tridentate BPICO ligand. The greatest angle distortions for Pt(1) are N(1)Pt(1)N(3) = 81.1(2)° and N(1)Pt(1)N(3) = 167.9(2)°, arising from geometrical constraints of the BPICO ligand. The pattern of Pt−N distances is different from that in the trimethylplatinum(IV) complex **5**, which has the *fac*-tridentate ligand with all nitrogen atoms trans to methyl, in which the Pt−NMe_2 bond was clearly weakest (Figure 1, Table 2). In complex **11**, the longest PtN distance is Pt−NBz, which is trans to

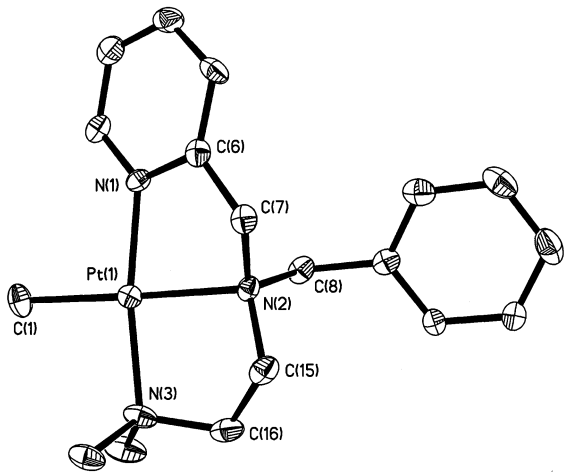


Figure 4. A view of the molecular structure of [PtMe(BPICO)]$^+$, showing 25% thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths [Å] and Angles [deg] for [PtMe(BPICO)]CF_3SO_3, 11

Pt(1)−C(1)	2.039(6)	Pt(2)−C(19)	2.042(7)
Pt(1)−N(1)	2.004(6)	Pt(2)−N(4)	2.013(6)
Pt(1)−N(2)	2.127(5)	Pt(2)−N(5)	2.130(5)
Pt(1)−N(3)	2.064(6)	Pt(2)−N(6)	2.060(7)
N(1)−Pt(1)−C(1)	97.3(3)	N(4)−Pt(2)−C(19)	96.2(3)
N(1)−Pt(1)−N(3)	167.9(2)	N(4)−Pt(2)−N(6)	167.3(2)
C(1)−Pt(1)−N(3)	94.1(3)	C(19)−Pt(2)−N(6)	95.9(3)
N(1)−Pt(1)−N(2)	81.1(2)	N(4)−Pt(2)−N(5)	81.2(2)
C(1)−Pt(1)−N(2)	177.8(3)	C(19)−Pt(2)−N(5)	176.7(3)
N(3)−Pt(1)−N(2)	87.4(2)	N(6)−Pt(2)−N(5)	86.5(2)

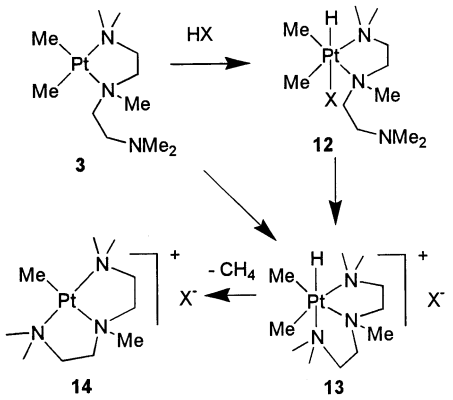
methyl, the shortest is Pt−N(pyridyl), and the Pt−NMe_2 distance is intermediate (Table 4).

The H/D exchange that occurred on reaction of complex **2** with CF_3SO_3D in CD_3OD was very similar to those described for complex **1**, and can be fully explained by the reaction sequence of Scheme 4. However, the reaction of complex **11** with CF_3SO_3D in CD_3OD gave only [Pt(CF_3SO_3)(BPICO)]CF_3SO_3 and CH_3D, a clear indication that methane loss is irreversible in this case.

(b) Reaction of Complex 3 with H^+ and D^+. Reaction of [$PtMe_2$(PMDETA)], **3**, in acetone-d_6 solution with 1 equiv of triflic acid at −78 °C gave a mixture of two cationic dimethylhydridoplatinum(IV) complexes in a 1:3 ratio, characterized as **12** and **13**[CF_3SO_3] (Scheme 5), but at −50 °C only **13**[CF_3SO_3] was present, as monitored by ^{1}H NMR spectroscopy. On warming to −10 °C, loss of methane occurred with formation of the methylplatinum(II) complex **14**[CF_3SO_3] (Scheme 5).

The hydrido(dimethyl)platinum(IV) complex **13** was readily characterized by its ^{1}H NMR spectrum at −50 °C. The hydride resonance was at δ −22.60 ppm, with ^1J(PtH) = 1484 Hz, and there were two equal intensity methylplatinum(IV) resonances at δ 0.80 [^2J(PtH) = 68 Hz] and 0.77 ppm [^2J(PtH) = 64 Hz]. These data define the stereochemistry as **13** (Scheme 5) since the other possible isomer with hydride trans to the NMe group would give only one methylplatinum resonance. The second isomer was formed as a minor component only at very low temperature, and its characterization is less certain. At −80 °C, the hydride resonance was at δ −22.24 ppm [^1J(PtH) = 1474 Hz]. There was a methylplatinum resonance at δ 0.76 ppm [^2J(PtH) = 66 Hz],

Scheme 5. Methyl(hydrido) Complexes with PMDETA



and another was tentatively identified at δ 0.30 ppm, but with platinum satellites obscured. By analogy with the chemistry of Scheme 2, it is likely that the reluctance of PMDETA to act as a *fac*-tridentate ligand leads to partial formation of the hydride **12** with bidentate PMDETA at −78 °C, with very easy conversion to **13** complete by −50 °C. Complex **13** was stable at −50 °C but it had decomposed to give methane and the methylplatinum(II) complex **14** by −10 °C. The hydrides are clearly much less stable than with PICO or BPICO ligands. We suggest that this correlates with the tendency of the ligands to form strong *fac*-tridentate binding to platinum(IV).

Complex **14** is formed rapidly by reaction of complex **3** with triflic acid at room temperature. It is characterized in the ^{1}H NMR spectrum by the methylplatinum resonance at δ 0.25 ppm [^2J(PtH) = 78 Hz]. The structure of complex **14** was determined and is illustrated in Figure 5, with selected bond distances and angles given in Table 5. The complex has distorted square-planar stereochemistry, the largest deviation being the angle N(1)Pt(1)N(3) = 166.5(2)°, which is probably to minimize ring strain in the *mer*-tridentate ligand. The mutually trans nitrogen atoms have almost equal Pt−N distances and, as expected, both are shorter than the Pt−N distance trans to the methylplatinum group.

Reaction of complex **3** with CF_3SO_3D in methanol-d_4 at room temperature gave complex **14** and methane, and

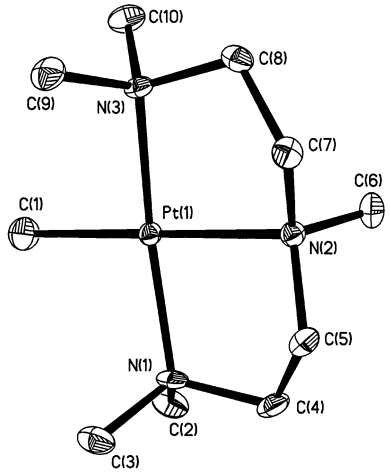


Figure 5. A view of the molecular structure of [PtMe(PMDETA)]$^+$, showing 25% thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Lengths [Å] and Angles [deg] for [PtMe(PMDETA)]CF_3SO_3, 14

Pt(1)−C(1)	2.027(7)	Pt(1)−N(3)	2.072(5)
Pt(1)−N(1)	2.076(5)	Pt(1)−N(2)	2.106(5)
C(1)−Pt(1)−N(3)	94.9(2)	C(1)−Pt(1)−N(1)	94.7(2)
N(3)−Pt(1)−N(1)	166.5(2)	C(1)−Pt(1)−N(2)	179.1(2)
N(3)−Pt(1)−N(2)	84.9(2)	N(1)−Pt(1)−N(2)	85.4(2)

both show clear evidence of deuterium incorporation. In the case of methane, all isotopomers observable by ^{1}H NMR, CH_4, CH_3D, CH_2D_2, and CHD_3 were shown to be present. This is indicative of H/D exchange similar to that shown in Scheme 4. This is clearly a rapid process, since it occurs during the brief time that the hydride complex exists at room temperature. No further H/D exchange into the methane or the methylplatinum group of complex **14** occurred after one month of reaction time, confirming that **14** is inactive as a catalyst for H/D exchange. The reaction of **14** with triflic acid-*d* in CD_3OD gave CH_3D only.

Conclusions

This work shows how the stability of hydrido(dimethyl)platinum(IV) complexes can be fine-tuned by modification of a supporting, flexible tridentate ligand. The ligands PICO and BPICO give hydridodimethylplatinum(IV) derivatives that decompose only slowly at room temperature, while PMDETA gives a much less stable hydride and is independently shown to be a poorer *fac*-tridentate ligand for platinum(IV). In all cases the thermal stability of the hydridodimethylplatinum(IV) complexes with flexible tridentate ligands is intermediate between derivatives with rigidly *fac*-tridentate ligands (very stable) and those with bidentate ligands (low thermal stability).[6−9] The hydridodimethylplatinum(IV) complexes with PICO or BPICO ligands can exist in three isomeric forms as shown in Scheme 3, and all three isomers have been identified by NMR spectroscopy. Protonation of the dimethylplatinum(II) precursor gives the product of kinetic control, in which the hydride is trans to the NMe_2 group, which can then isomerize to the other two isomers. The product of thermodynamic control has the hydride trans to the pyridyl nitrogen donor. Hydrogen−deuterium exchange reactions occur when the protonation reactions are carried out in CD_3OD solvent, and are interpreted in terms of easy reversibility of the protonation of the dimethylplatinum(II) complexes and easy equilibration of the hydridodimethylplatinum(IV) complexes with corresponding methyl(methane)platinum(II) complexes. However, none of these platinum complexes activates free methane at room temperature.

Experimental Section

NMR spectra were recorded by using Varian Mercury 400 or Inova 400 spectrometers and chemical shifts are reported relative to TMS. All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk or drybox techniques. The complex [$Pt_2Me_4(\mu$-$SMe_2)_2$] was prepared according to the literature method.[11a]

(11) (a) Scott, J. D.; Puddephatt, R. J. *Organometalllics* **1983**, *2*, 1643. (b) Abdel-Magid, A. F.; Maryanoff, C. A.; Carson, K. G. *Tetrahedron Lett.* **1990**, *31*, 5595.

***N,N,N′*-Trimethyl-*N′*-(2-picolyl)ethylenediamine, PICO.** A mixture of 2-pyridinecarboxaldehyde (1.5 mL, 15.6 mmol), *N,N,N′*-trimethylethylenediamine (2.3 mL, 17.2 mmol), and sodium triacetoxyborohydride (4.8 g, 21.5 mmol) in dry THF (60 mL) was stirred for 3 days. The reaction was quenched by adding saturated $NaHCO_3$ solution (120 mL) and the mixture was extracted with $CHCl_3$ (3 × 70 mL). The organic phase was dried over anhydrous $MgSO_4$ and filtered, and the solvent evaporated to give the product as a colorless oil.[11b] Yield 1.8 g, 60%. NMR ($CDCl_3$): δ(^{1}H) 8.46 [dd, 1H, ^3J(HH) = 5 Hz, ^4J(HH) = 2 Hz, py]; 7.57 [td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py]; 7.35 [d, 1H, ^3J(HH) = 8 Hz, py]; 7.05 [dd, 1H, ^3J(HH) = 8 Hz, 5 Hz, py]; 3.60 [s, 2H, CH_2]; 2.48 [m, 2H, CH_2]; 2.38 [m, 2H, CH_2]; 2.21 [s, 3H, NMe]; 2.14 ppm [s, 6H, NMe_2]. δ(^{13}C) 159.50 [s, py]; 149.23 [s, py]; 136.55 [s, py]; 123.33 [s, py]; 122.12 [s, py]; 64.60 [s, CH_2]; 57.53 [s, CH_2]; 55.67 [s, CH_2]; 46.00 [s, NMe_2]; 43.00 ppm [s, NMe].

***N*-Benzyl-*N′*,*N′*-dimethyl-*N*-(2-picolyl)ethylenediamine, BPICO.** BPICO was prepared similarly from *N*-benzyl-*N′*,*N′*-dimethylethylenediamine. Yield 88%. NMR ($CDCl_3$): δ(^{1}H) 8.48 [d, 1H, ^3J(HH) = 6 Hz, ^4J(HH) = 2 Hz, py]; 7.62 [td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py]; 7.52 [d, 1H, ^3J(HH) = 8 Hz, py]; 7.35 [d, 2H, ^3J(HH) = 7 Hz, Ph]; 7.28 [t, 2H, ^3J(HH) = 7 Hz, Ph]; 7.27 [t, 1H, ^3J(HH) = 7 Hz, Ph]; 7.10 [t, 1H, ^3J(HH) = 6 Hz, py]; 3.77 [s, 2H, NCH_2Ph]; 3.65 [s, 2H, NCH_2py]; 2.62 [m, 2H, NCH_2CH_2N]; 2.45 [m, 2H, NCH_2CH_2N]; 2.15 ppm [s, 6H, NMe_2]. δ(^{13}C) 160.28 [s, py]; 148.97 [s, py]; 139.42 [s, Ph]; 136.55 [s, py]; 128.98 [s, Ph]; 128.40 [s, ph]; 127.12 [s, Ph]; 122.99 [s, py]; 122.05 [s, py]; 60.88 [s, CH_2]; 59.42 [s, CH_2]; 57.88 [s, CH_2]; 52.26 [s, CH_2]; 46.21 ppm [s, NMe_2].

[$PtMe_2$(PICO)], 1. A mixture of [$PtMe_2$($\mu$$SMe_2$)]$_2$ (150 mg, 0.261 mmol) and pico (103 mg, 0.532 mmol) in THF (5 mL) was stirred for 2 h to give an orange solution of the product, which was usually used in situ for further reactions. Complex **1** could be isolated by evaporation of the solvent and was crystallized with difficulty from CH_2Cl_2/thf/pentane. Anal. Calcd for $C_{13}H_{25}N_3Pt$·thf: C, 41.61; H, 6.78; N, 8.57. Found: C, 41.17; H, 6.34; N, 8.29. NMR (acetone-d_6): δ(^{1}H) 8.72 [d, 1H, ^3J(PtH) = 22 Hz, ^3J(HH) = 7 Hz, py]; 8.02 [td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py]; 7.52 [d, 1H, ^3J(HH) = 8 Hz, py]; 7.32 [td, 1H, ^3J(HH) = 7 Hz, ^4J(HH) = 0.4 Hz, py]; 4.24 [d, 1H, ^2J(HH) = 15 Hz, NCH_2py]; 3.90 [d, 1H, ^2J(HH) = 15 Hz, NCH_2py]; 2.97 [m, 1H, NCH_2CH_2N]; 2.81 [m, 1H, NCH_2CH_2N]; 2.69 [s, 3H, ^3J(PtH) = 14 Hz, Pt−NMe]; 2.68 [m, 2H, NCH_2CH_2N]; 2.08 [s, 6H, NMe_2]; 0.54 [s, 3H, ^2J(PtH) = 90 Hz, Pt-Me]; 0.49 ppm [s, 3H, ^2J(PtH) = 86 Hz, Pt−Me]. δ(^{13}C) 160.38 [s, py]; 145.81 [s, ^2J(PtC) = 33 Hz, py]; 135.86 [s, py]; 124.36 [s, ^2J(PtC) = 20 Hz, py]; 123.09 [s, py]; 67.69 [s, CH_2]; 57.81 [s, CH_2]; 56.86 [s, ^2J(PtC) = 26 Hz, CH_2]; 48.11 [s, NMe]; 45.39 [s, NMe_2]; −19.24 [s, ^1J(PtC) = 838 Hz, Pt−Me]; −21.35 ppm [s, ^1J(PtC) = 843 Hz, Pt−Me].

[$PtMe_2$(BPICO)], 2. 2 was prepared similarly using BPICO. Anal. Calcd for $C_{19}H_{29}N_3Pt$: C, 46.14; H, 5.91; N, 8.50. Found: C, 45.81; H, 6.12; N, 8.23. NMR (acetone-d_6): δ(^{1}H) 8.72 [d, 1H, ^3J(PtH) = 26 Hz, ^3J(HH) = 5 Hz, py]; 7.97 [td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 1 Hz, py]; 7.70 [m, 2H, Ph]; 7.45 [d, 1H, ^3J(HH) = 8 Hz, py]; 7.30−7.25 [m, 4H, py/Ph]; 4.60 [d, 1H, ^2J(HH) = 11 Hz, CH_2Ph]; 4.12 [d, 1H, ^2J(HH) = 11 Hz, CH_2Ph]; 4.11 [d, 1H, ^2J(HH) = 15 Hz, CH_2py]; 3.99 [d, 1H, ^2J(HH) = 15 Hz, CH_2py]; 3.25 [m, 1H, NCH_2CH_2N]; 2.98 [m, 1H, NCH_2CH_2N]; 2.84 [m, 1H, NCH_2CH_2N]; 2.59 [m, 1H, NCH_2CH_2N]; 2.09 [s, 6H, NMe_2]; 0.62 [s, 3H, ^2J(PtH) = 90 Hz, Pt−Me]; 0.49 ppm [s, 3H, ^2J(PtH) = 85 Hz, Pt−Me]. δ(^{13}C) 160.77 [s, py]; 145.71 [s, ^2J(PtC) = 34 Hz, py]; 135.79 [s, py]; 133.67 [s, Ph]; 132.31 [s, Ph]; 128.27 [s, Ph]; 127.98 [s, Ph]; 124.17 [s, ^2J(PtC) = 20 Hz, py]; 123.18 [s, py]; 63.84 [s, CH_2]; 62.91 [s, CH_2]; 57.16 [s, ^2J(PtC) = 28 Hz, CH_2]; 54.59 [s, CH_2]; 45.54 [s, NMe_2]; −18.34 [s, ^1J(PtC) = 843 Hz, Pt−Me]; −21.08 ppm [s, ^1J(PtC) = 853 Hz, Pt−Me].

[$PtMe_2$(PMDETA)], 3. 3 was prepared similarly using PMDETA. Anal. Calcd for $C_{11}H_{29}N_3Pt$·H_2O: C, 31.72; H, 7.50; N, 10.09. Found: C, 31.22, H, 7.26; N, 10.03. NMR (acetone-d_6): δ(^{1}H) 3.49 [td, 2H, ^3J(HH) = 13 Hz, ^2J(HH) = 3 Hz, CH_2]; 3.36 [m, 2H, CH_2]; 2.85 [m, 4H, CH_2]; 2.60 [s, 3H, ^3J(PtH) = 21 Hz, Pt−NMe]; 2.55 [s, 6H, ^3J(PtH) = 21 Hz, Pt−NMe_2]; 2.15 [s, 6H, NMe_2]; 0.17 [s, 3H, ^2J(PtH) = 89 Hz, Pt-Me]; 0.12 ppm [s, 3H, ^2J(PtH) = 87 Hz, Pt−Me]. δ(^{13}C) 61.95 [s, ^2J(PtC) = 7 Hz, CH_2]; 57.82 [s, ^2J(PtC) = 6 Hz, CH_2]; 57.23 [s, CH_2]; 57.05 [s, CH_2]; 49.58 [s, ^2J(PtC) = 10 Hz, Pt−NMe_2]; 47.79 [s, NMe_2]; 46.74 [s, NMe]; −22.00 [s, ^1J(PtC) = 859 Hz, Pt−Me]; −23.30 ppm [s, ^1J(PtC) = 855 Hz, Pt−Me].

[$PtMe_3$(PICO)]I, 4. To a solution of [$PtMe_2$(PICO)] (0.55 mmol) in THF (5 mL), prepared in situ, was added MeI (34 μL, 0.55 mmol). The product formed as a pale yellow precipitate. The mixture was stirred for 30 min, pentane (30 mL) was added to complete precipitation of the product, the solvent was removed by cannula, and the solid product was dried under vacuum. Yield 153 mg, 52%. Anal. Calcd for $C_{14}H_{28}N_3IPt$: C, 30.01; H, 5.04; N, 7.50. Found: C, 30.44; H, 5.05; N, 7.27. NMR (acetone-d_6): δ(^{1}H) 8.75 [d, 1H, ^3J(HH) = 6 Hz, ^3J(PtH) = 11 Hz, py]; 8.24 [td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py]; 7.98 [d, 1H, ^3J(HH) = 8 Hz, py]; 7.76 [td, 1H, ^3J(HH) = 6 Hz, ^4J(HH) = 1 Hz, py]; 4.98 [d, 1H, ^3J(PtH) = 19 Hz, ^2J(HH) = 16 Hz, NCH_2py]; 4.47 [d, 1H, ^2J(HH) = 16 Hz, NCH_2py]; 3.21−3.09 [m, 4H, NCH_2CH_2N]; 2.90 [s, 3H, ^3J(PtH) = 17 Hz, Pt−NMe]; 2.55 [s, 3H, ^3J(PtH) = 17 Hz, Pt−NMe_2]; 2.24 [s, 3H, ^3J(PtH) = 10 Hz, Pt−NMe_2]; 0.95 [s, 3H, ^2J(PtH) = 68 Hz, Pt−Me trans NMe]; 0.79 [s, 3H, ^2J(PtH) = 69 Hz, Pt−Me trans py]; 0.54 ppm [s, 3H, ^2J(PtH) = 69 Hz, Pt−Me trans NMe_2]. δ(^{13}C) 159.02 [s, py]; 146.85 [s, ^3J(PtC) = 11 Hz, py]; 140.48 [s, py]; 126.15 [s, ^2J(PtC) = 12 Hz, py]; 125.19 [s, ^3J(PtC) = 9 Hz, py]; 66.91 [s, CH_2]; 61.19 [s, CH_2]; 59.88 [s, CH_2]; 47.50 [s, NMe_2]; 47.33 [s, NMe_2]; 45.14 [s, NMe]; −3.90 [s, ^1J(PtC) = 712 Hz, Pt−Me]; −4.53 [s, ^1J(PtC) = 677 Hz, Pt−Me]; −7.62 ppm [s, ^1J(PtC) = 674 Hz, Pt−Me].

[$PtMe_3$(BPICO)]I, 5. 5 was prepared similarly from [$PtMe_2$-(BPICO)]. Yield 72%. Anal. Calcd for $C_{20}H_{32}N_3IPt$: C, 37.74; H, 5.07; N, 6.60. Found: C, 37.42; H, 5.22; N, 6.23. NMR (acetone-d_6): δ(^{1}H) 8.77 [d, 1H, ^3J(PtH) = 12 Hz, ^4J(HH) = 6 Hz, py]; 8.19 [td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py]; 7.88 [d, 1H, ^3J(HH) = 8 Hz, py]; 7.74 [t, 1H, ^3J(HH) = 6 Hz, py]; 7.68 [m, 2H, Ph]; 7.47 [m, 3H, Ph]; 4.82 [d, 1H, ^2J(HH) = 16 Hz, CH_2]; 4.52 [d, 1H, ^2J(HH) = 14 Hz, ^3J(PtH) = 5 Hz, CH_2]; 4.31 [d, 1H, ^2J(HH) = 16 Hz, ^3J(PtH) = 20 Hz, CH_2]; 4.18 [d, 1H, ^2J(HH) = 14 Hz, ^3J(PtH) = 5 Hz, CH_2]; 3.45−3.33 [m, 4H, NCH_2CH_2N]; 2.63 [s, 3H, ^3J(PtH) = 16 Hz, Pt−NMe]; 2.27 [s, 3H, ^3J(PtH) = 10 Hz, Pt−NMe]; 1.02 [s, 3H, ^2J(PtH) = 68 Hz, Pt−Me trans N]; 0.90 [s, 3H, ^2J(PtH) = 68 Hz, Pt−Me trans py]; 0.66 ppm [s, 3H, ^2J(PtH) = 69 Hz, Pt−Me trans NMe_2]. δ(^{13}C) 146.56 [s, ^3J(PtC) = 12 Hz, py]; 140.44 [s, py]; 132.72 [s, Ph]; 131.44 [s, Ph]; 129.26 [s, Ph]; 128.84 [s, Ph]; 126.07 [s, ^{2}J(PtC) = 13 Hz, py]; 125.29 [s, br, py]; 63.60 [s, CH_2]; 60.98 [s, CH_2]; 58.72 [br, CH_2]; 47.51 [s, NMe_2]; 47.21 [s, NMe_2]; −3.42 [s, Pt−Me]; −3.96 [s, Pt−Me]; −7.15 ppm [s, Pt−Me].

[$PtMe_3$(PMDETA)]I, 6a, and [$PtMe_3$I(PMDETA)], 7. 6a and **7** were prepared similarly, as a mixture of isomers, from [$PtMe_2$(PMDETA)]. Yield 52%. Anal. Calcd for $C_{12}H_{32}N_3IPt$: C, 26.67; H, 5.97; N, 7.78. Found: C, 26.80; H, 5.97; N, 7.33. NMR (acetone-d_6): **6a**: δ(^{1}H) 2.81 [s, 6H, ^3J(PtH) = 8 Hz, Pt−NMe_2]; 2.71 [s, 3H, ^3J(PtH) = 18 Hz, Pt−NMe]; 2.51 [s, 6H, ^3J(PtH) = 16 Hz, Pt−NMe_2]; 0.88 [s, 6H, ^2J(PtH) = 69 Hz, Pt−Me trans NMe_2]; 0.73 ppm [s, 3H, ^2J(PtH) = 66 Hz, Pt−Me trans NMe]. **7**: δ(^{1}H) 3.22 [s, 3H, ^3J(PtH) = 11 Hz, Pt−NMe]; 2.48 [s, 3H, ^3J(PtH) = 16 Hz, Pt−NMe]; 2.42 [s, 3H, ^3J(PtH) = 15 Hz, Pt−NMe]; 2.41 [s, ^3J(PtH) = 16 Hz, Pt−NMe]; 2.16 [s, 6H, uncoord NMe_2]; 1.26 [s, 3H, ^2J(PtH) = 70 Hz, Pt−Me]; 1.25 [s, 3H, ^2J(PtH) = 72 Hz, Pt−Me]; 1.21 ppm [s, 3H, ^2J(PtH) = 71 Hz, Pt−Me]. The CH_2 resonances were observed in the range δ(^{1}H) = 2.90−4.00, as complex, overlapping multiplets, and were not assigned to specific protons.

[$PtMe_3$(PMDETA)]CF_3SO_3. This was prepared similarly from CF_3SO_3Me and [$PtMe_2$(PMDETA)]. NMR(acetone-d_6): δ(^{1}H) 3.25 [m, 2H, CH_2]; 3.08 [m, 2H, CH_2]; 3.05 [m, 2H, CH_2]; 2.96 [m, 2H, CH_2]; 2.78 [s, 6H, ^3J(PtH) = 8 Hz, Pt−NMe_2]; 2.68 [s, 3H, ^3J(PtH) = 18 Hz, Pt−NMe]; 2.49 [s, 6H, ^3J(PtH) = 16 Hz, Pt−NMe_2]; 0.87 [s, 6H, ^2J(PtH) = 69 Hz, Pt−Me trans NMe_2]; 0.72 ppm [s, 3H, ^2J(PtH) = 66 Hz, Pt−Me trans NMe].

[$PtMe_2$H(PICO)]BF_4, 8c. To a solution of complex **1** (0.53 mmol) in THF (5 mL) was added HBF_4 (54% solution in Et_2O, 133 μL, 0.53 mmol). A pale yellow precipitate of the product was formed. After 2 min, pentane (30 mL) was added to ensure complete precipitation. The solvent was removed by cannula, and the product was dried under vacuum. Yield 180 mg, 68%. Anal. Calcd for $C_{13}H_{26}N_3PtBF_4$: C, 30.84; H, 5.18; N, 8.30. Found: C, 30.37; H, 4.73; N, 7.89. The complex was identified as **8c** with traces of isomers **8a** and **8b** present. NMR (acetone-d_6): **8c**: δ(^{1}H) 8.59 [d, 1H, ^3J(PtH) = 17 Hz, ^3J(HH) = 6 Hz, py]; 8.17 [td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py]; 7.80 [d, 1H, ^3J(HH) = 8 Hz, py]; 7.71 [t, 1H, ^3J(HH) = 6 Hz, py]; 4.62 [d, 1H, ^3J(HH) = 16 Hz, NCH_2py]; 4.50 [d, 1H, ^3J(HH) = 16 Hz, NCH_2py]; 3.31−3.00 [m, 4H, NCH_2CH_2N]; 3.24 [s, 3H, ^3J(PtH) = 22 Hz, Pt−NMe]; 2.95 [s, 3H, ^3J(PtH) = 25 Hz, Pt−NMe_2]; 2.27 [s, 3H, ^3J(PtH) = 10 Hz, Pt−NMe_2]; 0.97 [s, 3H, ^2J(PtH) = 67 Hz, Pt−Me trans NMe]; 0.60 [s, 3H, ^2J(PtH) = 68 Hz, Pt−Me trans NMe_2]; −20.95 ppm [s, 1H, ^1J(PtH) = 1425 Hz, Pt−H]. IR(Nujol): ν_{Pt-H} = 2261 cm^{-1}.

Complexes 8a−c. The selectivity of isomer formation was studied by NMR in a typical experiment as follows. To a solution of complex **1** (0.105 mmol) in acetone-d_6 (0.5 mL) was added CF_3SO_3H (0.105 mmol), and the isomeric mixture of **8a−c** was analyzed by ^{1}H NMR spectroscopy. NMR (acetone-d_6): **8a**: δ(^{1}H) 8.75 [d, 1H, ^3J(PtH) = 17 Hz, ^3J(HH) = 6 Hz, py]; 8.21 [td, 1H, ^4J(HH) = 2 Hz, ^3J(HH) = 8 Hz, py]; 7.91 [d, 1H, ^3J(HH) = 8 Hz, py]; 7.73 [td, 1H, ^3J(HH) = 6 Hz, py]; 4.91 [d, 1H, ^3J(HH) = 16 Hz, ^3J(PtH) = 25 Hz,NCH_2py]; 4.64 [d, 1H, ^3J(HH) = 16 Hz, NCH_2py]; 3.30−3.00 [m, 4H, NCH_2CH_2]; 3.05 [s, 3H, ^3J(PtH) = 19 Hz, Pt−NMe]; 2.48 [s, 3H, ^3J(PtH) = 17 Hz, Pt−NMe_2 trans H]; 2.17 [s, 3H, ^3J(PtH) = 9 Hz, Pt−NMe_2 trans H]; 0.97 [s, 3H, ^2J(PtH) = 66 Hz, Pt−Me trans NMe]; 0.86 [s, 3H, ^2J(PtH) = 69 Hz, Pt−Me trans py]; −21.18 ppm [s, 1H, ^1J(PtH) = 1438 Hz, Pt−H trans NMe_2]. **8b**: This was always a minor isomer and many resonances were obscured. δ(^{1}H) 0.86 [s, 3H, ^2J(PtH) = 69 Hz, Pt−Me trans py]; 0.62 [s, 3H, ^2J(PtH) = 67 Hz, Pt−Me trans NMe_2]; −20.65 [s, 1H, ^1J(PtH) = 1406 Hz, Pt−H trans NMe]. **8c**: See above.

[$PtMe_2$H(BPICO)]CF_3SO_3, 9a−c. To a solution of complex **2** in THF (5 mL) was added triflic acid (48.5 μL, 0.55 mmol). After 1 min, ether (25 mL) was added to precipitate the product. The solvent was removed by cannula, and the residue was dried under vacuum to give an off-white solid, identified as a mixture of isomers **9a−c**. Yield 246 mg, 73%. Anal. Calcd for $C_{20}H_{30}N_3PtF_3SO_3$: C, 37.27; H, 4.69; N, 6.52. Found: C, 36.83; H, 4.37; N, 6.17. NMR (acetone-d_6): **9a**: δ(^{1}H) 8.78 [d, 1H, ^3J(PtH) = 12 Hz, ^3J(HH) = 6 Hz, py]; 4.94 [d, 1H, ^2J(HH) = 16 Hz, CH_2]; 4.60 [d, 1H, ^2J(HH) = 14 Hz, ^3J(PtH) = 5 Hz, CH_2]; 4.48 [d, 1H, ^2J(HH) = 16 Hz, CH_2]; 4.43 [d, 1H, ^2J(HH) = 14 Hz, CH_2]; 2.55 [s, 3H, ^3J(PtH) = 16 Hz, Pt−NMe_2]; 2.19 [s, 3H, ^3J(PtH) = 9 Hz, Pt−NMe_2]; 1.05 [s, 3H, ^2J(PtH) = 66 Hz, Pt−Me trans N]; 1.01 [s, 3H, ^2J(PtH) = 68 Hz, Pt−Me trans py]; −20.99 ppm [s, 1H, ^1J(PtH) = 1435 Hz, Pt−H trans NMe_2]. **9b**: This was always a minor isomer and most resonances were obscured. δ(^{1}H) −21.05 ppm [s, ^1J(PtH) = 1440 Hz, Pt−H trans NBz]. **9c**: δ(^{1}H) 8.63 [d, 1H, ^3J(PtH) = 13 Hz, ^3J(HH) = 6 Hz, py]; 4.86 [d, 1H, ^2J(HH) = 16 Hz, CH_2]; 4.76 [d, 1H, ^2J(HH) = 14 Hz, ^3J(PtH) = 9 Hz, CH_2]; 4.54 [d, 1H, ^2J(HH) = 14 Hz, ^3J(PtH) = 12 Hz, CH_2]; 4.40 [d, 1H, ^2J(HH) = 16 Hz, ^3J(PtH) = 19 Hz, CH_2]; 2.94 [s, 3H, ^3J(PtH) = 25 Hz, Pt−NMe_2]; 2.27 [s, 3H, ^3J(PtH) = 10 Hz, Pt−NMe_2]; 1.04 [s, 3H, ^2J(PtH) = 67 Hz, Pt−Me trans N]; 0.65 [s, 3H, ^2J(PtH) = 67 Hz, Pt−Me trans NMe_2]; −20.65 ppm [s, 1H, ^1J(PtH) = 1412 Hz, Pt−H trans py]. The following resonances overlapped and were not assigned to a specific isomer. δ 8.17−7.64 [m, py]; 7.64−7.46 [m, Ph]; 3.76−3.35 ppm [m, NCH_2-CH_2N].

H/D Exchange with [$PtMe_2$(PICO)]. To a solution of [$PtMe_2$(PICO)] (0.11 mmol) in methanol-d_4 (0.5 mL) was added CF_3SO_3D [18.5 μL, 0.209 mmol] in an NMR tube. The reaction was monitored by ^{1}HNMR spectroscopy. As reductive elimination of methane progressed, over 1 day at room temperature, the peaks for [Pt($CH_{3-n}D_n$)(PICO)]$^+$ (n = 1, 2) appeared: δ(^{1}H) 0.52 [s, 3H, ^2J(PtH) = 78 Hz, Pt−Me]; 0.50 [t, ^2J(HD) = 2 Hz, Pt−CH_2D]; 0.48 ppm [m, Pt−CHD_2]; as well as peaks for the isotopomers of methane, δ(^{1}H) 0.19 [s, CH_4]; 0.17 [t, ^2J(HD) = 2 Hz, CH_3D]; 0.15 [quint,^2J(HD) = 2 Hz, CH_2D_2]; 0.13 ppm [sept, CHD_3].

H/D Exchange with [$PtMe_2$(BPICO)]. This was carried out similarly but using [$PtMe_2$(BPICO)]. ^{1}H NMR (CD_3OD): [$PtCH_{3-n}D_n$(BPICO)]$^+$ (n = 0, 1, 2): δ(^{1}H) 0.58 [s, 3H, ^2J(PtH) = 79 Hz, Pt−Me]; 0.56 [t, ^2J(HD) = 2 Hz, Pt−CH_2D]; 0.54 ppm [m, Pt−CHD_2]; and CH_nD_{4-n}: δ(^{1}H) 0.19 [s, CH_4]; 0.17 [t, ^2J(HD) = 2 Hz, CH_3D]; 0.15 [quint, ^2J(HD) = 2 Hz, CH_2D_2]; 0.13 ppm [m, CHD_3].

[$PtMe$(PICO)][CF_3SO_3]. To a solution of [$PtMe_2$(PICO)] (0.52 mmol) in THF (5 mL) was added triflic acid (46.5 μL, 0.53 mmol) to give a pale orange solution. The solution was stirred at 60 °C for 3 h, then for 12 h at 53 °C, followed by addition of pentane (20 mL) to precipitate the product, which was separated and dried under vacuum. Yield 225 mg, 78%. Anal. Calcd for $C_{13}H_{22}N_3F_3O_3SPt$: C, 28.26; H, 4.01; N, 7.61. Found: C, 28.20; H, 4.11; N, 7.26. NMR (acetone-d_6): δ(^{1}H) 8.54 [d, 1H, ^3J(HH) = 6 Hz, ^3J(PtH) = 49 Hz, py]; 8.18 [td, 1H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, py]; 7.69 [d, 1H, ^3J(HH) = 8 Hz, py]; 7.52 [t, 1H, ^3J(HH) = 6 Hz, py]; 4.62 [d, 1H, ^2J(HH) = 15 Hz, NCH_2py]; 4.40 [d, 1H, ^2J(HH) = 15 Hz, NCH_2-py]; 3.79 [td, 2H, ^2J(HH) = 3 Hz, ^3J(HH) = 14 Hz, NCH_2CH_2N]; 3.72 [td, 2H, ^2J(HH) = 2 Hz, ^3J(HH) = 14 Hz, NCH_2CH_2N]; 3.03 [s, 3H, ^3J(PtH) = 12 Hz, Pt−NMe]; 2.88 [s, 3H, ^3J(PtH) = 44 Hz, Pt−NMe]; 2.74 [s, 3H, ^3J(PtH) = 16 Hz, Pt−NMe]; 0.52 ppm [s, 3H, ^2J(PtH) = 78 Hz, Pt−Me]. δ(^{13}C) 165.82 [s, py]; 149.31 [s, ^2J(PtC) = 38 Hz, py]; 139.40 [s, py]; 125.65 [s, ^2J(PtC) = 44 Hz, py]; 124.99 [s, ^3J(PtC) = 27 Hz, py]; 70.71 [s, ^2J(PtC) = 22 Hz, CH_2]; 65.51 [s, ^2J(PtC) = 29 Hz, CH_2]; 57.98 [s, ^2J(PtC) = 16 Hz, CH_2]; 52.58 [s, Pt−NMe]; 50.88 [s, Pt−NMe]; 43.21 [s, ^2J(PtC) = 48 Hz, Pt−NMe]; −13.10 ppm [s, ^1J(PtC) = 811 Hz, Pt−Me].

[$PtMe$(BPICO)][CF_3SO_3]. To a solution of [$PtMe_2$(BPICO)] (0.52 mmol) in THF (5 mL) was added triflic acid (46 μL, 0.52 mmol). The solution was stirred overnight at 45 °C, then cooled to room temperature, and ether (30 mL) was added to precipitate the product, which was separated and dried under vacuum. Yield 246 mg, 75%. Anal. Calcd for $C_{19}H_{26}N_3F_3O_3$-SPt: C, 36.31; H, 4.17; N, 6.69. Found: C, 36.45; H, 4.15; N, 6.44. NMR (acetone-d_6): δ(^{1}H) 8.39 [d, 1H, ^3J(HH) = 6 Hz, ^3J(PtH) = 50 Hz, py]; 7.99 [td, 1H, ^4J(HH) = 1 Hz, ^3J(HH) = 8 Hz, py]; 7.59 [m, 2H, Ph]; 7.48 [d, 1H, ^3J(HH) = 8 Hz, py]; 7.33 [t, 1H, ^3J(HH) = 6 Hz, py]; 7.21 [m, 3H, Ph]; 4.61 [s, 2H, NCH_2py]; 4.29 [d, 2H, ^2J(HH) = 4 Hz, NCH_2Ph]; 3.81 [d, 2H, ^3J(HH) = 10 Hz, NCH_2CH_2N]; 3.32 [t, 2H, ^3J(HH) = 10 Hz, NCH_2CH_2N]; 3.06 [s, 3H, ^3J(PtH) = 48 Hz, Pt−NMe_2]; 2.92 [s, 3H, ^3J(PtH) = 43 Hz, Pt−NMe_2]; 0.58 ppm [s, 3H, ^2J(PtH) = 79 Hz, Pt−Me].

[$PtMe_2$H(PMDETA)][CF_3SO_3], 13, and [$PtMe_2$H-(PMDETA)(acetone)][CF_3SO_3], 12. To a solution of [$PtMe_2$-(PMDETA)] (0.11 mmol) in acetone-d_6 (0.5 mL) in an NMR tube at −78 °C was added triflic acid (10 μL, 0.11 mmol). The reaction was monitored as a function of temperature. NMR (acetone-d_6, 193 K): **13**: δ(^{1}H) 0.80 [s, 3H, ^2J(PtH) = 68 Hz, Pt−Me]; 0.77 [s, 3H, ^2J(PtH) = 64 Hz, Pt-Me]; −22.60 ppm [s, 1H, ^1J(PtH) = 1484 Hz, Pt−H]. **12**: δ(^{1}H) 0.76 [s, 3H, ^2J(PtH) = 66 Hz, Pt−Me]; 0.30 [s, 3H, ^2J(PtH) not resolved, Pt−Me]; −22.24 ppm [s, ^1J(PtH) = 1474 Hz, Pt−H]. Ligand resonances were not assigned, but were observed in the ranges 3.6−3.0

Table 6. Crystal Data and Structure Refinement for Complexes 5[I], 9[CF_3SO_3], 11[CF_3SO_3], and 14[CF_3SO_3]

	5[I]	**9**[CF_3SO_3]	**11**[CF_3SO_3]	**14**[CF_3SO_3]
formula	$C_{20}H_{32}IN_3Pt$	$C_{13}H_{22}F_3N_3O_3PtS$	$C_{19}H_{26}F_3N_3O_3PtS$	$C_{11}H_{26}F_3N_3O_3PtS$
fw	636.48	552.49	628.58	532.50
T/K	200(2)	200(2)	200(2)	200(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
cryst sys	orthorhombic	monoclinic	triclinic	monoclinic
space group.	$P2_12_12_1$	$P2_1/c$	P-1	$C2/c$
a/Å	12.533(3)	22.3918(6)	13.0580(2)	25.8182(11)
b/Å	17.008(3)	8.8440(2)	13.2793(2)	8.3118(3)
c/Å	10.243(2)	20.0096(5)	15.5937(3)	19.7761(8)
α/deg	90	90	105.8830(7)	90
β/deg	90	116.477(2)	98.5800(8)	122.889(1)
γ/deg	90	90	116.5400(8)	90
V/Å^3, Z	2183.4(7), 4	3546.9(1), 8	2207.84(6), 4	3563.7(2), 8
d_c/Mg/m^3	1.936	2.069	1.891	1.985
abs coeff/mm^{-1}	7.848	8.076	6.500	8.033
F(000)	1216	2128	1224	2064
no. of reflns, ind reflns	6371, 6371	51105, 15589	15223, 10090	19129, 5220
abs corr	integration	integration	integration	integration
no. of data/restraints/ parameters	6371/0/231	15589/3/434	10090/12/547	5220/0/200
goodness-of-fit on F^2	1.001	1.073	1.010	1.019
$R[I > 2\sigma(I)]$: R1, wR2	0.0393, 0.0616	0.0547, 0.1369	0.0455, 0.1101	0.0410, 0.0995
R(all data): R1, wR2	0.0666, 0.0679	0.0775, 0.1454	0.0718, 0.1217	0.0548, 0.1035

[CH_2]; 3.0−2.3 [NMe]. At 223K, resonances of **12** were very weak and **13** was the major complex present. At 263K, reductive elimination to give methane and complex **14** (NMR data given below) was complete.

H/D Exchange with [$PtMe_2$(PMDETA)]. This reaction was carried out similarly but using excess triflic acid-*d* (18.5 μL, 0.21 mmol) with [$PtMe_2$(PMDETA)] (0.11 mmol) in methanol-d_4 (0.5 mL) at room temperature. After 40 min, the ^{1}H NMR spectrum indicated formation of [$PtCH_nD_{3-n}$(PMDETA)]CF_3SO_3: δ(^{1}H) 0.24 [s, 3H, ^2J(PtH) = 78 Hz, Pt−Me]; 0.23 [br, Pt−CH_2D]; 0.21 ppm [br, Pt−CHD_2]; and methane: δ(^{1}H) 0.15 [s, CH_4]; 0.14 [t, ^2J(HD) = 2 Hz, CH_3D]; 0.13 [quint, CH_2D_2]; 0.11 ppm [m, CHD_3]. Within 4 h, further reaction occurred to give CH_nD_{4-n} and [Pt(O_3SCF_3)(PMDETA)]CF_3SO_3.

[PtMe(PMDETA)][CF_3SO_3]. To a solution of [$PtMe_2$(PMDETA)] (0.41 mmol) in THF (5 mL) was added triflic acid (37 μL, 0.42 mmol). The solution was stirred for 20 min, then pentane (20 mL) was added to give the product as a white precipitate, which was separated and dried under vacuum. Yield 150 mg, 70%. Anal. Calcd for $C_{11}H_{26}N_3F_3O_3SPt$: C, 24.81; H, 4.92; N, 7.89. Found: C, 25.29; H, 4.90; N, 7.70. NMR (acetone-d_6): δ(^{1}H) 3.62 [td, 4H, ^2J(HH) = 3 Hz, ^3J(HH) = 14 Hz, CH_2]; 3.55 [td, 4H, ^2J(HH) = 2 Hz, ^3J(HH) = 14 Hz, CH_2]; 2.94 [s, 6H, ^3J(PtH) = 50 Hz, Pt−NMe_2]; 2.77 [s, 3H, ^3J(PtH) = 46 Hz, Pt−NMe]; 0.25 ppm [s, 3H, ^2J(PtH) = 78 Hz, Pt−Me]. δ(^{13}C) 69.97 [s, ^2J(PtC) = 21 Hz, CH_2]; 58.16 [s, ^2J(PtC) = 17 Hz, CH_2]; 52.85 [s, Pt−NMe_2]; 51.89 [s, Pt−NMe_2]; 41.90 [s, Pt−NMe]; −13.30 ppm [s, ^1J(PtC) = 845 Hz, Pt−Me].

Structure Determinations. Crystals of complexes **5**, **9**, **11**, and **14** were grown by slow diffusion of pentane into concentrated acetone solutions and then mounted on glass fibers. Data were collected at −73 °C using a Nonius Kappa-CCD diffractometer with COLLECT (Nonius B.V., 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using DENZO (Nonius B.V., 1998). The data were scaled using SCALEPACK (Nonius B.V., 1998). The crystal data and refinement parameters are listed in Table 6. The SHELXTL V5.1 (Sheldrick, G. M.) suite of programs were used to solve the structures, followed by refinement using successive difference Fouriers.

One of the triflate anions of **11** shows relatively large thermal parameters on the O and F atoms, and an ISOR restraint was placed on O6 and F6. All of the non-hydrogen atoms in all three structures were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

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Supporting Information Available: X-ray crystallographic data for the structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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