Electrophilic Platinum Complexes: Methyl Transfer Reactions and Catalytic Reductive Elimination of Ethane from a Tetramethylplatinum(IV) Complex

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Received November 20, 1998

Methyl ligand transfer reactions occur easily between tetramethylplatinum(IV) complexes $[PtMe_4(LL)]$ [LL = 4,4′-di-*tert*-butyl-2,2′-bipyridine (bu_2bpy) (**1**), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) (**2**), bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (Ar_2NN) (**3**), 1,2-bis(diphenylphosphino)ethane (dppe) (**4**)] and electrophilic platinum complexes *fac*-$[PtMe_3(SO_3CF_3)(LL)]$ [LL = bu_2bpy (**6a**), tmeda (**7a**), Ar_2NN (**8a**)] or $[PtMe(SO_3CF_3)(dppe)]$ (**10a**). It is proposed that the complexes **6a**, **7a**, **8a**, or **10a** undergo initial dissociation of the triflate ligand to give an electrophilic platinum cation which attacks one of the mutually trans methylplatinum ligands of $[PtMe_4(LL)]$. The reaction of $[PtMe_4(LL)]$ [LL = bu_2bpy (**1**), tmeda (**2**), Ar_2NN (**3**)] with *fac*-$[PtMe_3(SO_3CF_3)(L'L')]$ [L′L′ = bu_2bpy (**6a**), tmeda (**7a**), Ar_2NN (**8a**)] gives an equilibrium mixture between the reactants and *fac*-$[PtMe_3(SO_3CF_3)(LL)]$ and $[PtMe_4(L'L')]$, in which $[PtMe_4(LL)]$ is favored in the same order as the π-accepting properties of the LL ligand ($Ar_2NN \gg bu_2bpy >$ tmeda). The reaction of $[PtMe_4(dppe)]$ (**4**) with **6a**, **7a**, **8a**, or **10a** results in rapid room-temperature catalytic, C−C bond reductive elimination to give C_2H_6 and $[PtMe_2(dppe)]$ (**5**). It is proposed that the actual reductive elimination step occurs from the five-coordinate species $[PtMe_3(dppe)]^+$, formed by methyl ligand transfer from **4** to the electrophilic platinum complex (**6a**, **7a**, **8a** or **10a**). The triflato complexes **6a**−**10a** are in rapid equilibrium with the cationic aqua complexes *fac*-$[PtMe_3(OH_2)(LL)]SO_3CF_3$ [LL = bu_2bpy (**6b**), tmeda (**7b**), Ar_2NN (**8b**), dppe (**9b**)] and $[PtMe(OH_2)(dppe)]SO_3CF_3$ (**10b**), respectively, thus confirming lability of the triflate ligands.

Introduction

Alkyl ligand transfer reactions from main-group to transition-metal atoms are ubiquitous in the field of organometallic chemistry and provide a classic route to the synthesis of alkyl transition-metal complexes, and it is now well established that the transfer of alkyl ligands *between* two transition-metals can occur readily.[1−4] Whether the reaction occurs by the transfer of a nucleophilic alkyl group ($R^{\delta-}$) to an electrophilic complex ($M^{\delta+}$),[2] by the transfer of an electrophilic alkyl group ($R^{\delta+}$) to a nucleophilic complex ($M^{\delta-}$),[3] or by a free-radical mechanism[4] is highly dependent on the electronic properties of the transition-metal complexes involved. For example, the reaction of *cis*-$[PtMe_2(PMe_2Ph)_2]$ with *cis*,*cis*,*trans*-$[PtMe_2(NO_3)_2(PMe_2Ph)_2]$ to give *trans*-$[PtMe(NO_3)(PMe_2Ph)_2]$ and *fac*-$[PtMe_3(NO_3)(PMe_2Ph)_2]$ occurs by the transfer of a nucleophilic methylplatinum(II) ligand to the electrophilic platinum(IV) complex.[2c,f] In contrast, the methyl ligand exchange reaction between *fac*-$[M(X)Me_3(NN)]$ and $[PtMe_2(NN)]$ [M = Pt, Pd; X = halide; NN = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen)] to yield $[MMe_2(NN)]$ and *fac*-$[PtXMe_3(NN)]$ proceeds by the S_N2 mechanism and involves a redox reaction initiated by nucleophilic attack of the electron-rich $[PtMe_2(NN)]$ on an electrophilic M−CH_3 ligand in *fac*-$[M(X)Me_3(NN)]$ (Scheme 1).[3]

The research reported below was prompted by the following observations. An attempt to prepare the alkyl-

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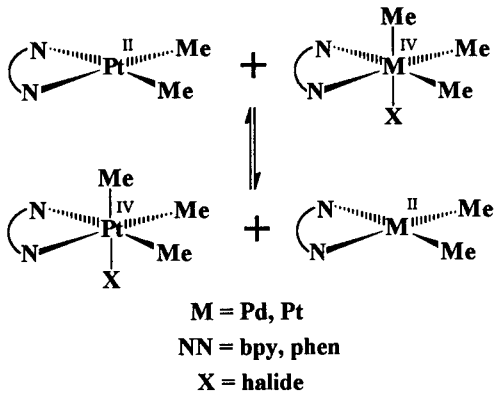
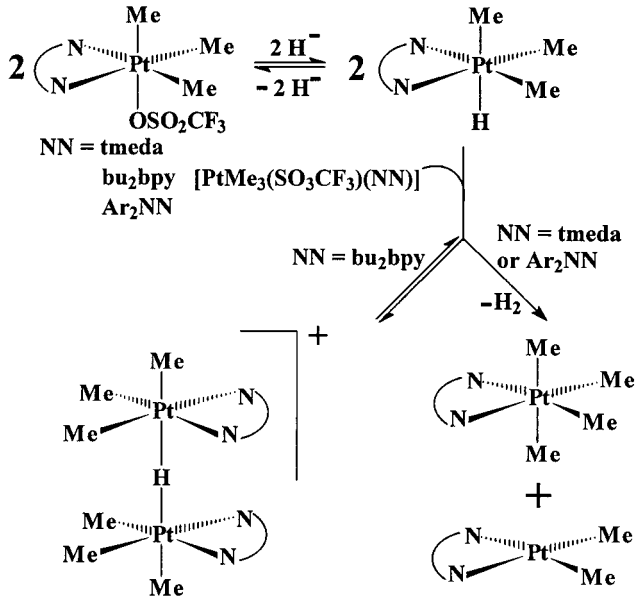
10.1021/om9809419 CCC: $18.00
Publication on Web 03/16/1999

Scheme 1



Scheme 2



(hydrido)platinum(IV) complex *fac*-[PtHMe$_3$(bu$_2$bpy)] (bu$_2$bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) by treatment of *fac*-[PtMe$_3$(SO$_3$CF$_3$)(bu$_2$bpy)] with NaBH$_4$ gave instead the (μ-hydrido)diplatinum(IV) complex [Pt$_2$(μ-H)Me$_6$(bu$_2$bpy)$_2$]SO$_3$CF$_3$.[5] It was proposed that [Pt$_2$(μ-H)Me$_6$(bu$_2$bpy)$_2$]SO$_3$CF$_3$ is formed by electrophilic attack of *fac*-[PtMe$_3$(SO$_3$CF$_3$)(bu$_2$bpy)] on the nucleophilic hydrido ligand of the anticipated product, *fac*-[PtHMe$_3$(bu$_2$bpy)] (Scheme 2). This mechanism suggested that the formation of *fac*-[PtHMe$_3$(NN)] should be favored in these reactions if the NN ligand used is bulky enough to prevent the reaction between *fac*-[PtHMe$_3$(NN)] and *fac*-[PtMe$_3$(SO$_3$CF$_3$)(NN)] to give [Pt$_2$(μ-H)Me$_6$(NN)$_2$]SO$_3$CF$_3$. The reaction of *fac*-[PtMe$_3$(SO$_3$CF$_3$)(NN)] [NN = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda), bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (Ar$_2$NN)] with NaBH$_4$ gave neither *fac*-[PtHMe$_3$(NN)] nor [Pt$_2$(μ-H)Me$_6$(NN)$_2$]SO$_3$CF$_3$, but gave a 1:1 mixture of [PtMe$_2$(NN)] and [PtMe$_4$(NN)] (Scheme 2). A possible mechanism might involve an electrophilic attack of *fac*-[PtMe$_3$(SO$_3$CF$_3$)(NN)] *not* on the *hydrido* ligand but on the *methyl* ligand trans to hydride of *fac*-[PtHMe$_3$(NN)]. Complete methyl ligand transfer would then give 1 equiv of [PtMe$_4$(NN)] and 1 equiv of [PtHMe$_2$(NN)]$^+$, which would be deprotonated by H$^-$ to give [PtMe$_2$(NN)] (Scheme 2).

It is probably the large trans influence of the hydride ligand that is responsible for the enhanced nucleophilic character of the trans methylplatinum ligand of *fac*-[PtHMe$_3$(NN)] and thus the reactivity shown in Scheme 2.[5] This then suggested that the mutually trans methylplatinum ligands of the analogous tetramethylplatinum(IV) complexes [PtMe$_4$(LL)] (LL = diimine, diphosphine)—which have been shown to be highly nucleophilic and very susceptible to electrophilic attack by a variety of reagents[6]—should exhibit chemistry similar to *fac*-[PtHMe$_3$(NN)] shown in Scheme 2. In this paper we report a study of the methyl ligand transfer reactions from electron-rich tetramethylplatinum(IV) complexes of the type [PtMe$_4$(LL)] [LL = bu$_2$bpy (**1**), tmeda (**2**), Ar$_2$NN (**3**), 1,2-bis(diphenylphosphino)ethane (dppe) (**4**)] to electrophilic platinum complexes either of the type *fac*-[PtMe$_3$(SO$_3$CF$_3$)(NN)] [NN = bu$_2$bpy (**6a**), tmeda (**7a**), Ar$_2$NN (**8a**)], *fac*-[PtMe$_3$(SO$_3$CF$_3$)(dppe)] (**9a**), or [PtMe(SO$_3$CF$_3$)(dppe)] (**10a**). It is also shown by low-temperature NMR [^{1}H, ^{19}F, ^{31}P{^{1}H}] spectroscopic studies that the electrophilic triflato complexes **6a**−**10a** are in rapid equilibrium with the corresponding cationic complexes *fac*-[PtMe$_3$(OH$_2$)(LL)]SO$_3$CF$_3$ [LL = bu$_2$bpy (**6b**), tmeda (**7b**), Ar$_2$NN (**8b**), dppe (**9b**)] and [PtMe(OH$_2$)(dppe)]SO$_3$CF$_3$ (**10b**), in moist solvent, respectively. In the case where LL = Ar$_2$NN, both of the isomers *fac*-[PtMe$_3$(SO$_3$CF$_3$)(Ar$_2$NN)] and *fac*-[PtMe$_3$(OH$_2$)(Ar$_2$NN)]SO$_3$CF$_3$ have been characterized based on X-ray crystallographic data, confirming the presence of the coordinated water ligand. The methyl transfer reactions reported here provide the first examples of the transfer of a nucleophilic methylplatinum(IV) ligand to an electrophilic transition-metal complex. All previous reports of the transition-metal to transition-metal methyl ligand transfers from Pt(IV) were shown to follow the nucleophilic, redox mechanism shown in Scheme 1.[3] Furthermore, it is shown that electrophilic methyl ligand abstraction from [PtMe$_4$(dppe)] (**4**) results in rapid room-temperature catalytic C−C bond reductive elimination to give exclusively [PtMe$_2$(dppe)] (**5**) and C$_2$H$_6$. This result is remarkable since the reductive elimination of ethane from complexes of the type *fac*-[PtXMe$_3$(P$_2$)] (X = halide, CH$_3$; P = phosphine, $^1/_2$ diphosphine) generally occurs only at high temperatures.[6,7] A likely mechanism for this unprecedented catalysis is presented, and its relevance to the fundamentally important area of C−C bond formation/cleavage reactions is discussed. A preliminary account of parts of this work has been published.[5c]

Results and Discussion

Synthesis and Characterization of Complexes. The complexes [PtMe$_4$(LL)] [LL = bu$_2$bpy (**1**), tmeda (**2**),

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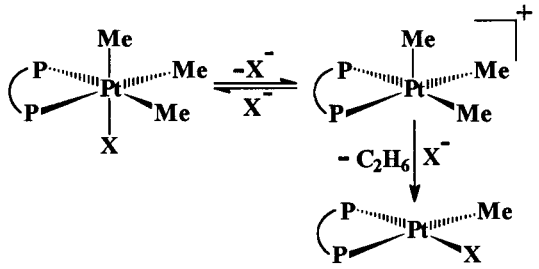
Scheme 3



Ar_2NN (**3**), dppe (**4**)] were prepared by the reaction of $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ with 2 equiv of the ligand LL. The ^1H NMR spectra of $[PtMe_4(LL)]$ showed the expected two sets of methylplatinum resonances for the Pt−Me ligands trans to LL [$^2J(PtH) = 62-73$ Hz] and trans to methyl [$^2J(PtH) = 41-44$ Hz] and require no further discussion.[5b,6e]

The complexes *fac*-$[PtMe_3(SO_3CF_3)(NN)]$ [NN = bu_2bpy (**6a**), tmeda (**7a**), Ar_2NN (**8a**)] were prepared by treatment of the corresponding dimethylplatinum(II) complex $[PtMe_2(NN)]$ with $CH_3OSO_2CF_3$. In contrast, treatment of $[PtMe_2(dppe)]$ (**5**) with $CH_3OSO_2CF_3$ gives exclusively C_2H_6 and $[PtMe(SO_3CF_3)(dppe)]$ (**10a**). Monitoring this reaction in acetone-d_6 at −70 °C by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy revealed that the reaction initially gave the oxidative addition product, *fac*-$[PtMe_3(SO_3CF_3)(dppe)]$ (**9a**), which upon warming to room temperature reductively eliminated ethane to give **10a**. Ethane was detected by ^1H NMR ($\delta = 0.82$ in acetone-d_6) and by GC−MS. Because of this instability toward reductive elimination, **9a** could not be isolated, but it was fully characterized by low-temperature (−70 °C) ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (see later). Since the analogous iodo complex, *fac*-$[PtIMe_3(dppe)]$, is stable to room-temperature reductive elimination (decomposing only at 150−200 °C in the solid state),[7] the instability of **9a** observed here must be due to the presence of the weakly coordinating SO_3CF_3 ligand. It is known[7] that reductive elimination from complexes of the type *fac*-$[PtXMe_3(PP)]$ (X = halide; PP = diphosphine) to give $[PtXMe(PP)]$ and C_2H_6 proceeds by dissociation of the ligand X to give the five-coordinate cationic intermediate $[PtMe_3(PP)]^+$, which then undergoes easy reductive elimination (Scheme 3).[7,8] Dissociation of the weakly coordinating SO_3CF_3 ligand in complex **9a** is a facile process,[9] and thus the exceptionally high reactivity of **9a** toward C_2H_6 reductive elimination relative to that of *fac*-$[PtIMe_3(dppe)]$ (in which iodide is a good ligand for platinum and thus does not readily dissociate) is fully consistent with the mechanism shown in Scheme 3.

The marked difference in stability toward ethane reductive elimination between *fac*-$[PtMe_3(SO_3CF_3)(NN)]$ [NN = bu_2bpy (**6a**), tmeda (**7a**), Ar_2NN (**8a**)] (which are stable to reductive elimination) and *fac*-$[PtMe_3(SO_3CF_3)$-(dppe)] (**9a**) is presumably due to the greater steric effects and more electron-withdrawing properties of the chelating diphosphine compared to diimine ligand.[7,8]

Selected NMR [^1H, ^{19}F, $^{31}P\{^1H\}$] spectroscopic data for complexes **6**−**9** in CD_2Cl_2 and acetone-d_6 recorded at 22 and −70 °C are presented in Table 1. NMR spectra for *fac*-$[PtMe_3(SO_3CF_3)(dppe)]$ (**9a**) were recorded only at −70 °C because of its thermal instability. Variable temperature ^1H NMR experiments performed between 30 and 0 °C with the complexes *fac*-$[PtMe_3(SO_3$-$CF_3)(NN)]$ [NN = bu_2bpy (**6a**), tmeda (**7a**), Ar_2NN (**8a**)] suggest a rapid scrambling of the methylplatinum ligands about the platinum center as shown in Scheme 4. At low temperature (ca. 0 °C for **7a**, **8a** and ca. 20 °C for **6a**) the ^1H NMR spectra of these complexes exhibit a pattern typical for a complex with a *fac*-$[PtMe_3X(NN)]$ arrangement with two sets of methylplatinum resonances in a 2:1 ratio for the Pt−Me ligands trans to NN [$^2J(PtH) =$ ca. 66 Hz] and trans to SO_3CF_3 [$^2J(PtH) =$ ca. 80 Hz], respectively.[5b] These two sets of signals coalesce into one resonance with statistically averaged values of δ and $^2J(PtH)$ upon warming the solution (to ca. 20 °C for **7a**, **8a** and ca. 30 °C for **6a**) (Table 1). Intramolecular methyl ligand scrambling within $[MMe_3$-$(X)L_2]$ complexes is common when either the ligand X or L is readily dissociated.[7c,8,10] Dissociation of the SO_3-CF_3 ligand in complexes **6a**−**8a** is particularly facile,[9] and thus the scrambling of the methylplatinum ligands observed here is very fast.

Upon further cooling of the NMR solutions of *fac*-$[PtMe_3(SO_3CF_3)(NN)]$ [NN = bu_2bpy (**6a**), tmeda (**7a**), Ar_2NN (**8a**)], the ^1H NMR resonances broaden and eventually (at ca. −70 °C) separate into two distinct sets, both displaying the typical *fac*-$[PtMe_3X(NN)]$ pattern. Furthermore, the single room-temperature ^{19}F resonance observed for **6a**−**8a** separates into two distinct resonances at −70 °C. This phenomenon is reversible, as raising the temperature of the solution again results in coalescence of the two sets of resonances. We propose that, in solution in moist solvent, the electrophilic triflato complexes **6a**−**8a** are in rapid equilibrium with the corresponding cationic complexes *fac*-$[PtMe_3(OH_2)$-$(NN)]SO_3CF_3$ [NN = bu_2bpy (**6b**), tmeda (**7b**), Ar_2NN (**8b**)] (Scheme 5). The reactions are strongly affected by traces of adventitous water which coordinates in strong preference to the solvent, which is present in large excess. The ratios of the triflato complexes (**a**) to the

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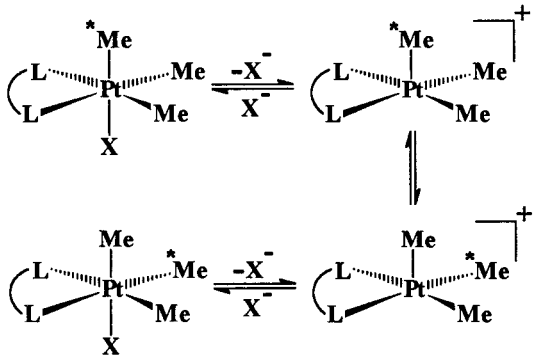
Table 1. Selected NMR Spectroscopic Data for Complexes 6−10[a]

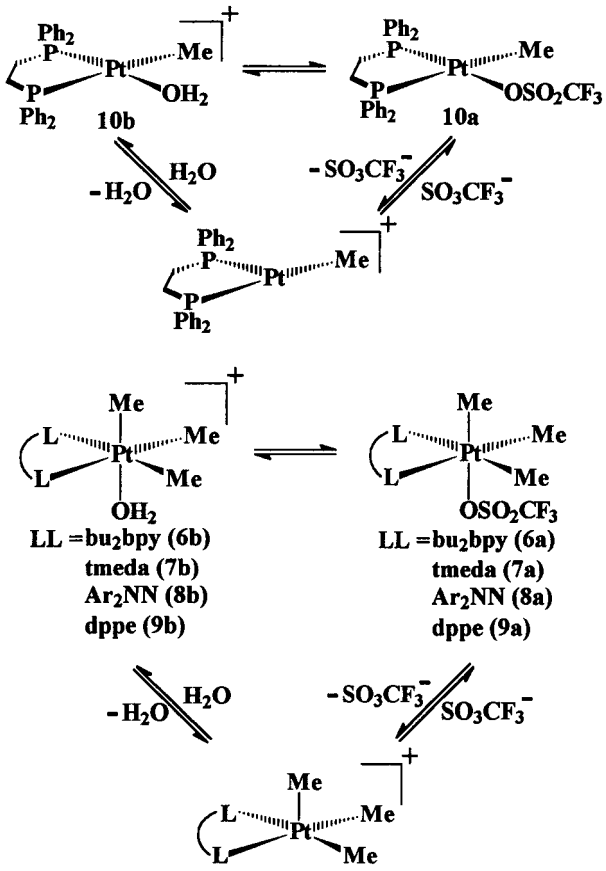
complex	temp (°C)	solvent	X	complex ratio (X = H_2O:X = SO_3CF_3)	δ ^{19}F	δ $^{31}P\{^1H\}$	δ ^1H, Pt−Me	
							trans to X	trans to LL
$[PtMe_3X(LL)]$	−70	acetone-d_6	SO_3CF_3 (**6a**)	2:1−5:1	−75 (s)		0.62 [s, ^2J(PtH) = 84]	1.17 [s, ^2J(PtH) = 66]
				2:1−5:1				
LL = bu_2bpy (**6**)	−70	acetone-d_6	H_2O (**6b**)	2:1−5:1	−74 (s)		0.56 [s, ^2J(PtH) = 80]	1.15 [s, ^2J(PtH) = 65]
	22[b]	acetone-d_6			−79 (s)		0.64 [s, ^2J(PtH) = 83]	1.21 [s, ^2J(PtH) = 67]
	−70	CD_2Cl_2	SO_3CF_3 (**6a**)	1:5−1:9	−75 (s)		0.65 [s, ^2J(PtH) = 84]	1.18 [s, ^2J(PtH) = 66]
				1:5−1:9				
	−70	CD_2Cl_2	H_2O (**6b**)	1:5−1:9	−74 (s)		0.44 (s)	0.98 [s, ^2J(PtH) = ca. 66]
	22[b]	CD_2Cl_2			−79 (s)		0.72 (br s)	1.26 [br s, ^2J(PtH) = ca. 66]
LL = tmeda (**7**)	−70	acetone-d_6	H_2O (**7b**)	∞	−74 (s)		0.76 [s, ^2J(PtH) = ca. 81]	0.78 [s, ^2J(PtH) = 67]
	22[b]	acetone-d_6			−79 (s)			0.96 [s, ^2J(PtH) = 72][c]
	−70	CD_2Cl_2	SO_3CF_3 (**7a**)	5:1−7:1	−75 (s)		0.81 (s)	0.92 [s, ^2J(PtH) = 68]
				5:1−7:1				
	−70	CD_2Cl_2	H_2O (**7b**)	5:1−7:1	−74 (s)		0.64 [s, ^2J(PtH) = 78]	0.74 [s, ^2J(PtH) = 66]
	22[b]	CD_2Cl_2			−79 (s)			0.90 [s, ^2J(PtH) = 66][c]
LL = Ar_2NN (**8**)	−70	acetone-d_6	SO_3CF_3 (**8a**)	2:1−5:1	−76 (s)		0.84 (s)	0.99 [s, ^2J(PtH) = ca. 68]
				2:1−5:1				
	−70	acetone-d_6	H_2O (**8b**)	2:1−5:1	−75 (s)		0.60 [s, ^2J(PtH) = 82]	0.90 [s, ^2J(PtH) = 69]
	22[b]	acetone-d_6			−79 (s)			1.05 [br s, ^2J(PtH) = 74][c]
	−70	CD_2Cl_2	SO_3CF_3 (**8a**)	1:10−1: 15	−75 (s)		0.60 [s, ^2J(PtH) = 80]	0.99 [s, ^2J(PtH) = ca. 67]
				1:10−1: 15				
	−70	CD_2Cl_2	H_2O (**8b**)	1:10−1: 15	−74 (s)		0.42 [s, ^2J(PtH) = ca. 80]	0.84 [s, ^2J(PtH) = ca. 68]
	22[b]	CD_2Cl_2			−79 (s)			1.05 [br s, ^2J(PtH) = 70][c]
LL = dppe (**9**)	−70	acetone-d_6	SO_3CF_3 (**9a**)	1:1−3:1	−76 (s)	25.5 [s, ^1J(PtP) = 1120]	0.25 [br t, ^2J(PtH) = ca. 75, ^3J(PH) = ca. 5]	1.22 [br t, ^2J(PtH) = ca. 55, ^3J(PH) + ^3J(P′H) = ca. 5]
				1:1−3:1				
	−70	acetone-d_6	H_2O (**9b**)	1:1−3:1	−75 (s)	20.5 [s, ^1J(PtP) = 1115]	0.02 [br t, ^2J(PtH) = ca. 75, ^3J(PH) = ca. 5]	1.23 [br t, ^2J(PtH) = ca. 55, ^3J(PH) + ^3J(P′H) = ca. 5]
$[PtMeX(LL)]$ LL = dppe (**10**)	−70	acetone-d_6	SO_3CF_3 (**10a**)	8:1−10:1	−77 (s)	39.2 [s, ^1J(PtP) = 4650]		0.42 [br d, $^3J(P^aH)$ = ca. 8]
				8:1−10:1		52.5 [s, ^1J(PtP) = 1860]		
	−70	acetone-d_6	H_2O (**10b**)	8:1−10:1	−76 (s)	37.2 [s, ^1J(PtP) = 4520]		0.24 [br dd, ^2J(PtH) = ca. 48, $^3J(P^aH)$ = ca. 2, $^3J(P^bH)$ = ca. 8]
						56.0 [s, ^1J(PtP) = 1840]		
	22[b]	acetone-d_6			−79 (s)	36.0 [s, ^1J(PtP) = 4646]		0.38 [br dd, ^2J(PtH) = 48, $^3J(P^aH)$ = 1.5, $^3J(P^bH)$ = 7.5]
						56.0 [s, ^1J(PtP) = 1853]		

[a] Quoted multiplicites do not include ^{195}Pt satellite signals. Coupling constants are given in Hz. [b] Resonances due to the complexes with X = H_2O and with X = SO_3CF_3 are averaged due to a rapid exchange process (see text). [c] Methylplatinum resonances are averaged due to a rapid exchange process (see text).

Scheme 4



Scheme 5



cationic complexes (**b**) are difficult to reproduce since they are highly dependent on the purity of the solvent. For example, using capped rather than flame-sealed NMR tubes, the ratio of **b** to **a** increases during the course of the low-temperature NMR experiment in CD_2Cl_2 and especially in the relatively hygroscopic acetone-d_6, as the concentration of adventitous water in solution increases. Furthermore, NMR spectra recorded in the presence of 1 equiv of H_2O showed only the presence of the proposed aqua species (**b**) at −70 °C (Scheme 5). Neither of the two species **a** or **b** appears to be the cationic solvated species, *fac*-$[PtMe_3(S)(NN)]^+$ (S = CD_2Cl_2), since rigorously dried ^{1}H NMR solutions of *fac*-$[PtIMe_3(NN)]$ and $AgPF_6$ (presumably, generating *fac*-$[PtMe_3(S)(NN)]^+$ in situ) showed no resonances comparable to those due to either **a** or **b** and since the low-temperature spectra of **6**−**8** in rigorously dry CD_2Cl_2 solvent in flame-sealed NMR tubes did not give resonances due to cationic complexes **b**. In dry acetone-d_6, the NMR spectra of **6**−**8** in sealed NMR tubes at low temperature still did give minor peaks assigned to the cationic complexes, and in this case, it is possible that these are due to the acetone-solvated cations, whose NMR spectra are indistinguishable from the aqua complexes. However, the data clearly show a remarkable preference for aqua over acetone coordination.

The methylplatinum ^{1}H NMR resonances for all of the proposed aquated complexes (**b**) are shifted to lower frequency relative to those of the corresponding triflato complexes (**a**). This trend has been observed before in complexes of the type *fac*-$[PtMe_3(X)(NN)]$ (NN = diimine: X = halide, solvent) and fully supports our proposed formulations for complexes **a** and **b**.[10,11] The NMR spectra for all **a** and **b** show a strong temperature dependence of proton or fluorine chemical shifts, with ^{1}H NMR resonances generally shifting to lower frequency and ^{19}F NMR resonances shifting to higher frequency at lower temperatures (Table 1). This observation as well as the inherent complexity of a system undergoing reversible intramolecular scrambling (Scheme 4) as well as reversible intermolecular H_2O (and possibly acetone) for SO_3CF_3 exchange (Scheme 5) rendered the extraction of any kinetic or thermodynamic data virtually impossible.[12]

Similarly, low-temperature (−70 °C) NMR (^{1}H, ^{19}F, ^{31}P{^{1}H}) spectra of *fac*-$[PtMe_3(SO_3CF_3)(dppe)]$ (**9a**) (which is unstable at elevated temperatures, see earlier) revealed the presence of two species, and by analogy with the complexes *fac*-$[PtMe_3(X)(NN)]$ [NN = bu_2bpy (**6**), tmeda (**7**), Ar_2NN (**8**); X = SO_3CF_3 (**a**), H_2O (**b**)], these are assigned to *fac*-$[PtMe_3(SO_3CF_3)(dppe)]$ (**9a**) and *fac*-$[PtMe_3(OH_2)(dppe)]SO_3CF_3$ (**9b**) (Table 1, Scheme 5). The NMR data for **9a** and **9b** are fully consistent with the proposed formulations and require no further discussion (Table 1), except to reiterate that the cationic complex may be present as a mixture of acetone and aqua complexes.

The room-temperature ^{1}H and ^{31}P{^{1}H} NMR spectra of $[PtMe(SO_3CF_3)(dppe)]$ (**10a**) confirm the expected structure. The ^{1}H NMR spectrum displays a resonance for the methylplatinum ligand at $\delta = 0.38$ [dd, $^3J(P^aH) = 1.5$ Hz, $^3J(P^bH) = 7.5$ Hz] with the magnitude of ^2J(PtH) typical for a Pt−Me ligand trans to P (48 Hz).[5b,9a,13] Furthermore, the two phosphorus atoms of dppe resonate in the ^{31}P{^{1}H} NMR at $\delta = 56.0$ and 36.0 with a magnitude of ^1J(PtP) typical for P trans to methyl (1853 Hz) and SO_3CF_3 (4646 Hz), respectively.[5b,9a,13] As for the platinum(IV) complexes **6**−**9**, H_2O (and, possibly, acetone) for SO_3CF_3 exchange was observed in the low-temperature (−70 °C) ^{1}H and ^{31}P{^{1}H} NMR spectra of acetone-d_6 solutions of $[PtMe(SO_3CF_3)(dppe)]$ (**10a**) (Scheme 5). The data are presented in Table 1, and no further discussion is necessary.

The most convincing evidence for the proposed formulations of complexes **a** and **b** comes from an X-ray crystallographic study of *fac*-$[PtMe_3(X)(Ar_2NN)]$ [X =

(11) (a) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548. (b) Puddephatt, R. J.; Scott, J. D. *Organometallics* **1985**, *4*, 1221.

(12) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

(13) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444.

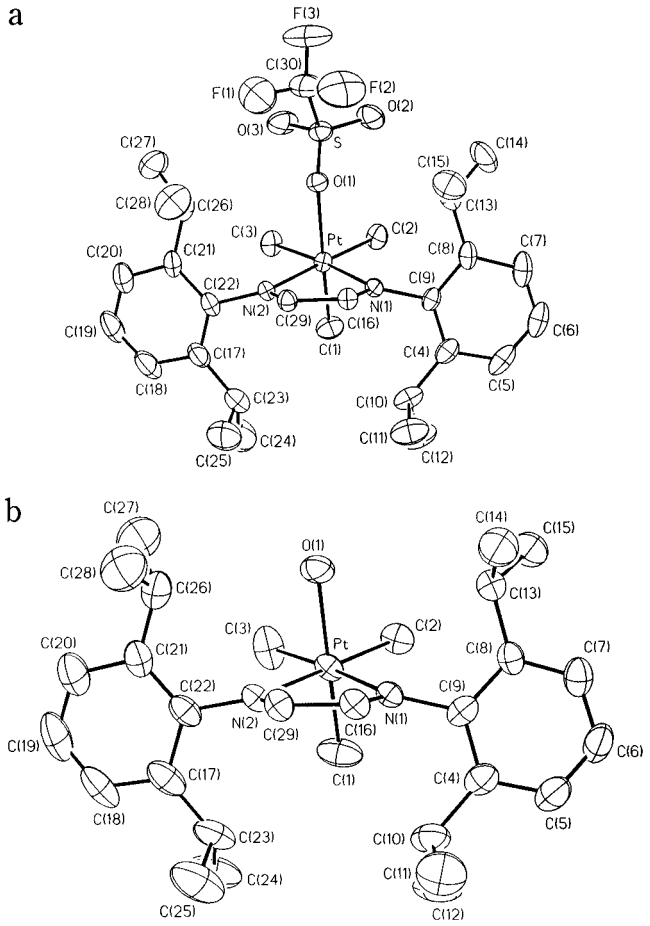


Figure 1. ORTEP diagrams of (a) *fac*-[$PtMe_3(SO_3CF_3)(Ar_2NN)$] (**8a**) and (b) *fac*-[$PtMe_3(OH_2)(Ar_2NN)]^+$ (**8b**). Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for *fac*-[$PtMe_3(SO_3CF_3)(Ar_2NN)$] (8a)

(a) Bond Distances			
Pt−C(1)	2.021(5)	Pt−N(1)	2.213(3)
Pt−C(2)	2.044(4)	Pt−N(2)	2.191(3)
Pt−C(3)	2.030(4)	Pt−O(1)	2.276(3)
(b) Bond Angles			
C(1)−Pt−C(2)	85.9(2)	C(2)−Pt−O(1)	92.3(2)
C(1)−Pt−C(3)	87.2(2)	C(3)−Pt−N(1)	171.6(2)
C(1)−Pt−N(1)	93.9(2)	C(3)−Pt−N(2)	96.5(2)
C(1)−Pt−N(2)	96.2(2)	C(3)−Pt−O(1)	93.0(2)
C(1)−Pt−O(1)	178.1(2)	N(1)−Pt−N(2)	75.0(2)
C(2)−Pt−C(3)	89.4(2)	N(1)−Pt−O(1)	86.2(1)
C(2)−Pt−N(1)	99.0(2)	N(2)−Pt−O(1)	85.6(1)
C(2)−Pt−N(2)	173.8(2)		

SO_3CF_3 (**8a**), H_2O (**8b**)]. Slow solvent evaporation of a THF solution of *fac*-[$PtMe_3(X)(Ar_2NN)$] gave large orange crystals of **8a**, and an ORTEP diagram is shown in Figure 1a. Slow diffusion of *n*-pentane into an acetone solution of *fac*-[$PtMe_3(X)(Ar_2NN)$] gave yellow platelike crystals of **8b**·acetone, and an ORTEP diagram is shown in Figure 1b. Tables2 and 3 contain selected bond distances and angles of **8a** and **8b**·acetone, respectively.

The X-ray molecular structures of **8a** and **8b**·acetone are very similar (Figure 1). In both complexes, the Ar_2-NN ligand shows no exceptional features with the Ar rings twisted nearly orthogonal to the $PtMe_2N_2$ coordination plane. The geometries at both the platinum centers are close to octahedral with the only notable

Table 3. Selected Bond Distances (Å) and Angles (deg) for *fac*-[$PtMe_3(OH_2)(Ar_2NN)]SO_3CF_3$·acetone (8b)

(a) Bond Distances			
Pt−C(1)	2.052(10)	Pt−N(1)	2.205(6)
Pt−C(2)	2.060(9)	Pt−N(2)	2.200(7)
Pt−C(3)	2.049(10)	Pt−O(1)	2.207(7)
(b) Bond Angles			
C(1)−Pt−C(2)	86.1(4)	C(2)−Pt−O(1)	91.8(3)
C(1)−Pt−C(3)	87.9(6)	C(3)−Pt−N(1)	172.4(3)
C(1)−Pt−N(1)	93.4(4)	C(3)−Pt−N(2)	97.4(4)
C(1)−Pt−N(2)	97.1(4)	C(3)−Pt−O(1)	90.0(4)
C(1)−Pt−O(1)	177.1(3)	N(1)−Pt−N(2)	75.0(2)
C(2)−Pt−C(3)	87.7(4)	N(1)−Pt−O(1)	89.0(2)
C(2)−Pt−N(1)	99.9(3)	N(2)−Pt−O(1)	85.2(2)
C(2)−Pt−N(2)	174.1(3)		

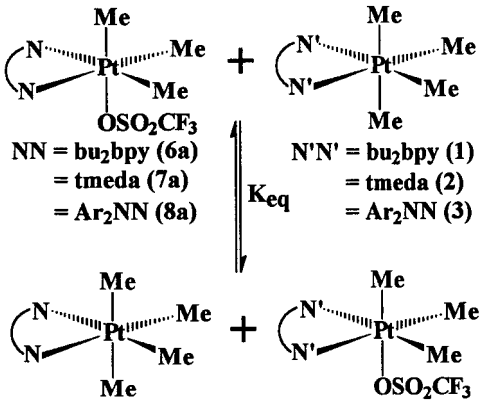
exception being the N(1)−Pt−N(2) bond angles [both 75.0°(2)] which depart significantly from the ideal 90° octahedral angle, due to the restricted bite of the NN chelating ligand.[5b,14] The lengths of the Pt−C(3) and Pt−C(4) bonds of both structures do not differ significantly [ranging from 2.030(4) to 2.060(9) Å] and are of typical magnitude for a methylplatinum(IV) ligand trans to an imine N.[5b,14] The Pt−C(1) bond lengths for the methylplatinum ligands trans to O of both complexes are very similar [2.021(5) (**8a**), 2.052(10) (**8b**·acetone)], and very similar to those for the methylplatinum ligands trans to N (see earlier). This similarity is somewhat surprising since, based on the magnitude of ^2J(PtH) obtained from the ^{1}H NMR spectra of **8a** and **8b** [ca. 67 Hz (trans to N), ca. 82 Hz (trans to O), Table 1], a shorter Pt−C bond length would be expected for the Pt−Me ligands trans to O. The Pt−O bond length for **8a** [2.276(3) Å] is slightly longer than that for **8b**·acetone [2.207(7) Å], with both being of typical magnitude for a Pt(IV)−O bond trans to a methyl ligand.[9a] For complex **8b**·acetone, the presence of a coordinated H_2O ligand (giving a cationic complex), and not a OH ligand (giving a neutral complex), is supported by two results, namely, the successful location of both of the hydrogen atoms of the H_2O ligand and the presence of the SO_3CF_3 anion in the unit cell.

Methyl Ligand Exchange Reactions. The methyl ligand exchange reactions between the electron-rich complexes [$PtMe_4$(NN)] [NN = bu_2bpy (**1**), tmeda (**2**), Ar_2NN (**3**)] and the electrophilic complexes *fac*-[$PtMe_3$-(SO_3CF_3)(NN)] [NN = bu_2bpy (**6a**), tmeda (**7a**), Ar_2NN (**8a**)] are shown in Scheme 6.

The reaction of [$PtMe_4(bu_2bpy)$] (**1**) and *fac*-[$PtMe_3(SO_3$-$CF_3)$(tmeda)] (**7a**) in acetone-d_6 solution results in the immediate formation of an equilibrium mixture between the reactants and [$PtMe_4$(tmeda)] (**2**) and *fac*-[$PtMe_3(SO_3$-$CF_3)(bu_2bpy)$] (**6a**). The same equilibrium mixture is obtained by reacting complexes **2** and **6a** (Scheme 6). The equilibrium highly favors complexes **1** and **7a** with $K_{eq} = [\mathbf{2}][\mathbf{6a}]/[\mathbf{1}][\mathbf{7a}] = 3 \times 10^{-2}$ (Scheme 6). The reaction of *fac*-[$PtMe_3(SO_3CF_3)(Ar_2NN)$] (**8a**) and [$PtMe_4$(NN)] [NN = bu_2bpy (**1**), tmeda (**2**)] immediately proceeded to completion (by ^{1}H NMR) to give 1 equiv of [$PtMe_4(Ar_2$-NN)] (**3**) and 1 equiv of *fac*-[$PtMe_3(SO_3CF_3)$(NN)] [NN = bu_2bpy (**6a**), tmeda (**7a**)] (Scheme 6). In agreement, mixtures of complex **3** and either complex **6a** or **7a** gave no reaction (by ^{1}H NMR).

(14) Levy, C. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 2108.

Scheme 6



It is proposed that the reactions proceed by initial dissociation of the SO_3CF_3 ligand of *fac*-[$PtMe_3(SO_3CF_3)$(NN)] to give the electrophilic five-coordinate intermediate [$PtMe_3(NN)]^+$, which then attacks one of the highly nucleophilic mutually trans methylplatinum ligands of [$PtMe_4$(N′N′)] to give *fac*-[$PtMe_3(SO_3CF_3)$(N′N′)] and [$PtMe_4$(NN)]. This methyl ligand transfer step is analogous to the S_E2 mechanism established for the cleavage of a methylplatinum bond of [$PtMe_4$(NN)] (NN = 2,2′-bipyridine, 1,10-phenanthroline) by electrophilic reagents such as H^+ and SO_2.[6a,d] The presence of the weakly coordinating triflate ligand in complexes **6a**, **7a**, and **8a** is essential. For example, the analogous trifluoroacetato complexes, *fac*-[$PtMe_3(O_2CCF_3)$(NN)] (where O_2CCF_3 is a better ligand for platinum than SO_3CF_3), do not react easily with [$PtMe_4$(NN)]. The presence of the highly nucleophilic, mutually trans methylplatinum ligands of complexes **1**−**3** is also critical. For example, the methylplatinum ligands that are trans to μ-H in the complex [$Pt_2(\mu$-H)$Me_6(bu_2bpy)_2]SO_3CF_3$ [which show reactivity intermediate between those in [$PtMe_4$(LL)] and those in the less reactive *fac*-[$PtMe_3$X(LL)] (X = halide)] give no reaction with **6a**, **7a**, or **8a**.[5]

The reactions shown in Scheme 6 favor [$PtMe_4$(NN)] (and hence disfavor *fac*-[$PtMe_3(SO_3CF_3)$(NN)]) in the same order as the π-accepting properties of the NN ligand, i.e., $Ar_2NN \gg bu_2bpy >$ tmeda.[15] The complexes with better π-accepting NN ligands are better able to stabilize the tetramethylplatinum unit having the strongest σ-donor methyl ligands.

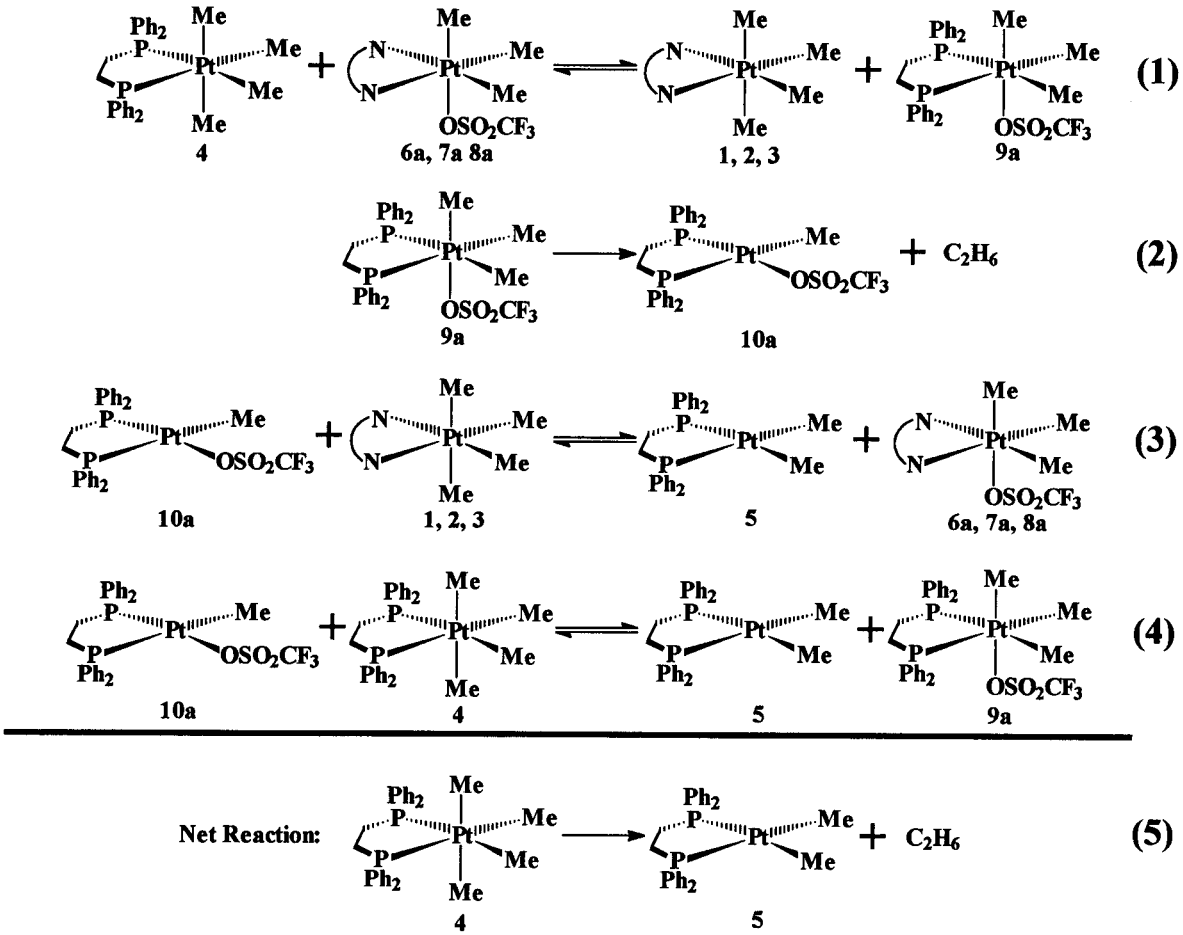
In an attempt to study the effect of changing the chelating ligand from a N donor to a P donor on the reactions in Scheme 6, [$PtMe_4$(dppe)] (**4**) was reacted with a stoichiometric amount of *fac*-[$PtMe_3(SO_3CF_3)$(NN)] [NN = bu_2bpy (**6a**), tmeda (**7a**), Ar_2NN (**8a**)] in acetone-d_6 solution to give 1 equiv each of [$PtMe_2$(dppe)] (**5**), ethane, and *fac*-[$PtMe_3(SO_3CF_3)$(NN)]. The reaction is truly catalytic in *fac*-[$PtMe_3(SO_3CF_3)$(NN)] and is very fast. For example, the reaction reaches completion (by ^{1}H and $^{31}P\{^1H\}$ NMR) within ca. 60 min with ca. 5 mol % catalyst and within seconds when reacted stoichiometrically.

The proposed mechanism for this reaction is shown in Scheme 7. Monitoring the reaction at room temperature by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy shows only the presence of the catalyst (complex **6a**, **7a**, or **8a**), **4**, **5**, and ethane (δ = 0.82 in acetone-d_6); no intermediates were detected at room temperature. No CH_4 or C_2H_4 was detected (by ^{1}H NMR). The reaction of eq 1 involves electrophilic methyl ligand abstraction from $PtMe_4$(dppe)] (**4**) by *fac*-[$PtMe_3(SO_3CF_3)$(NN)] [NN = bu_2bpy (**6a**), tmeda (**7a**), Ar_2NN (**8a**)] to yield [$PtMe_4$(NN)] [NN = bu_2bpy (**1**), tmeda (**2**), Ar_2NN (**3**)] and *fac*-[$PtMe_3(SO_3CF_3)$(dppe)] (**9a**). The complexes [$PtMe_4$(NN)] and *fac*-[$PtMe_3(SO_3CF_3)$(dppe)] (which could not be detected at room temperature) were detected and fully characterized upon monitoring the stoichiometric reaction by low-temperature (−70 °C) ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy (Table 1, see earlier). Stoichiometric reactions performed at room temperature could not be monitored by NMR since they are too rapid and catalytic reactions employ a concentration of catalyst (and hence a concentration of intermediates) too low to detect by NMR. Complex **4** then undergoes rapid C−C bond reductive elimination to give [$PtMe(SO_3CF_3)$(dppe)] (**10a**) and C_2H_6 (eq 2). Equations 3 and 4 involve methyl ligand transfer from either [$PtMe_4$(NN)] (**1**, **2**, or **3**) or [$PtMe_4$(dppe)] (**4**) to the electrophile [$PtMe(SO_3CF_3)$(dppe)] (**10a**), giving the product [$PtMe_2$(dppe)] (**5**) and regenerating *fac*-[$PtMe_3(SO_3CF_3)$(NN)] (**6a**, **7a**, or **8a**) or *fac*-[$PtMe_3(SO_3CF_3)$(dppe)] (**9a**), respectively. The possibility was considered that these methyl transfer reactions might proceed by a nucleophilic, redox mechanism as shown in Scheme 1, but the highly electrophilic properties of the platinum(II) species[9] and the electron-rich nature of the tetramethylplatinum(IV) species[6] disfavor this mechanism. Independent experiments show that the reactions of both eqs 3 and 4 occur easily, since mixtures of complex **10a** and complex **1**, **2**, **3**, or **4** in acetone-d_6 rapidly react to give **5** and **6a**, **7a**, **8a**, or **9a**, respectively. The net reaction is thus the reductive elimination of C_2H_6 from [$PtMe_4$(dppe)] (**4**) to give [$PtMe_2$(dppe)] (**5**) (eq 5). The occurrence of redox reactions analogous to those in Scheme 1 such as *fac*-[$PtMe_3(SO_3CF_3)$(LL)] + [$PtMe_2$(dppe)] ⇄ [$PtMe_2$(LL)] + [$PtMe_3(SO_3CF_3)$(dppe)] can be ruled out, as mixtures of [$PtMe_2$(dppe)] (**5**) and *fac*-[$PtMe_3(SO_3CF_3)$(NN)] show no reaction even after several days in solution (LL = NN, dppe; NN = bu_2bpy, tmeda, Ar_2NN). This observed absence of reaction is not simply a highly unfavorable equilibrium, as a mixture of **5** and *fac*-[$Pt(CD_3)_3(SO_3CF_3)(bu_2bpy)$] (**6a***) showed no intermolecular Pt−CH_3 for Pt−CD_3 scrambling (by ^{1}H NMR) even after several days in solution. The instability of *fac*-[$PtMe_3(SO_3CF_3)$(dppe)] (**9a**) toward reductive elimination (see earlier) did not allow an analogous reaction between **5** and [$Pt(CD_3)_3(SO_3CF_3)$(dppe)] (**9a***) to be performed.

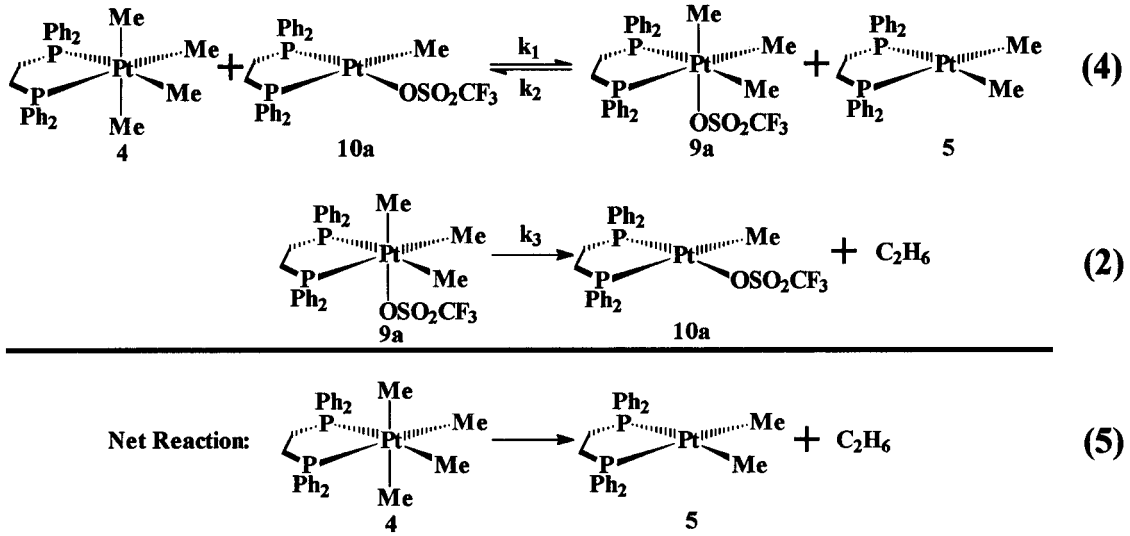
Tetramethylplatinum(IV) complexes are generally very stable to reductive elimination, evolving ethane only at elevated temperatures, and thus the unprecedented room-temperature reductive elimination presented here is remarkable.[6b] For example, thermogravimetric analysis (TGA) reveals that $PtMe_4$(dppe)] (**4**) decomposes only at ca. 110 °C in the solid state. Presumably it is the easy reductive elimination of C_2H_6 from complex **9a** that enables the catalytic decomposition of **4** to take place. Since the complexes *fac*-[$PtMe_3(SO_3CF_3)$(NN)] [NN = bu_2bpy (**6a**), tmeda (**7a**), Ar_2NN (**8a**)] are stable to reductive elimination (see earlier), no catalysis is observed in the reactions shown in Scheme 6.

(15) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

Scheme 7



Scheme 8



If the mechanism in Scheme 7 is correct, complex **10a** alone should be a suitable catalyst for the decomposition of **4** via eq 4 and eq 2 only, greatly simplifying the proposed mechanism (Scheme 8). This prediction was upheld, as treatment of **4** with either **10a** or $HOSO_2CF_3$ {which generates **10a** in situ via the protonation product of **4**, *fac*-[$PtMe_3(SO_3CF_3)$(dppe)] (eq 2)} in acetone-d_6 solution gave rapid catalytic production of [$PtMe_2$(dppe)] and C_2H_6. Only ca. 10 mol % of $HOSO_2CF_3$ was needed for the reaction to be complete within ca. 60 min. The kinetics of the reaction of [$PtMe_4$(dppe)] (**4**) with [$PtMe(SO_3CF_3)$(dppe)] (**10a**) (Scheme 8) in acetone-d_6 were studied by $^{31}P\{^1H\}$ NMR spectroscopy at 22 °C. A typical set of spectra was shown in the preliminary communication; under kinetic conditions, only resonances due to [$PtMe_4$(dppe)] and [$PtMe_2$(dppe)] were observed since the concentration of **10a** was too low to allow its resonances to be observed.[5c]

Figure 2a shows a graph of the concentration of [$PtMe_4$(dppe)] (**4**) versus time as it reacts according to

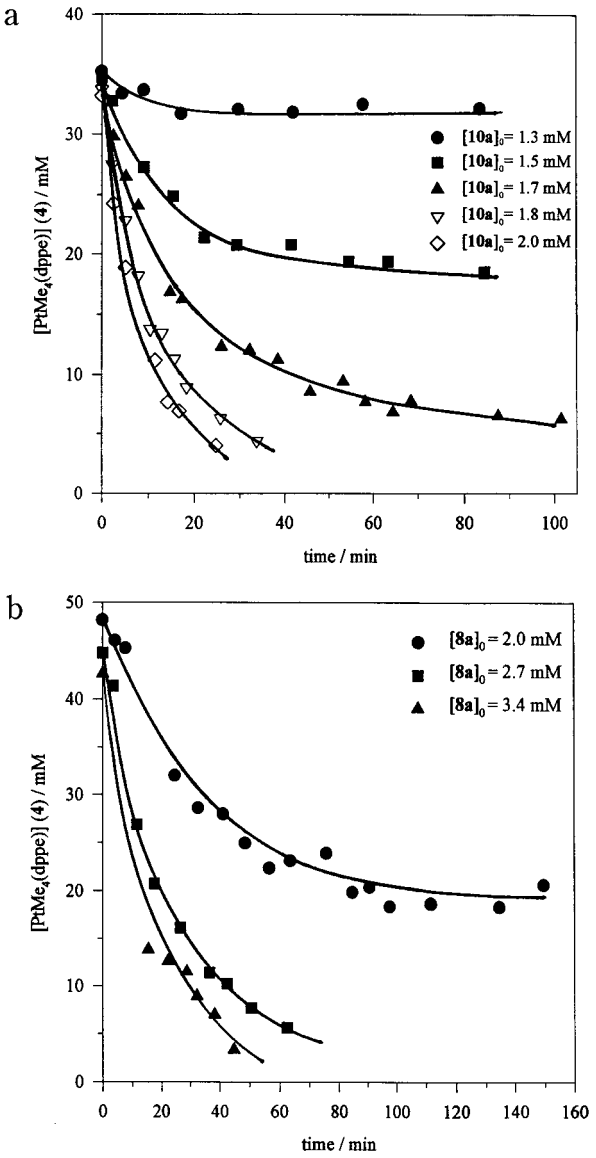


Figure 2. Graphs of the concentration of $[PtMe_4(dppe)]$ (**4**) versus time for eq 5 (acetone-d_6, 22 °C) using various initial concentrations of catalyst as measured by $^{31}P\{^1H\}$ NMR spectroscopy. (a) Catalyst = $[PtMe(SO_3CF_3)(dppe)]$ (**10a**). (b) Catalyst = *fac*-$[PtMe_3(SO_3CF_3)(Ar_2NN)]$ (**8a**). In all cases $t = 0$ is the time of initial mixing.

eq 5, as a function of the initial concentration of $[PtMe(SO_3CF_3)(dppe)]$ (**10a**) and shows that the rates of reaction increase with increasing initial catalyst concentration. The same qualitative dependence on initial catalyst concentration was observed in a similar experiment using *fac*-$[PtMe_3(SO_3CF_3)(Ar_2NN)]$ (**8a**) as the catalyst (Figure 2b, Scheme 7). The data presented in Figure 2 are reproducible.

Although Figure 2 clearly establishes the catalytic effect, attempts to simulate the kinetic curves, for example using equations based on either the steady-state approximation for the intermediate *fac*-$[PtMe_3(SO_3CF_3)(dppe)]$ (**9a**) shown in Scheme 8 or on the assumption that the reaction of eq 4 constitutes a rapid equilibrium, were unsuccessful.[16] The following observations are relevant to understanding this problem. Monitoring the reaction of **4** with a stoichiometric amount of **10a** in acetone-d_6 at −70 °C by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy revealed that **9a** (and **9b**) was present at detectable and varying concentration ranging from ca. 10−20% of total platinum concentration at intermediate stages of reaction. Furthermore, this low-temperature NMR experiment revealed that the ratio [**9a**][**5**]/[**4**][**10a**] did not remain constant throughout the course of the reaction. Hence, it is not possible to make the steady-state approximation for [**9a**] nor to assume a rapid equilibrium between **9a** + **5** and **10a** + **4** at least under these conditions. Stoichiometric reactions performed at room temperature could not be monitored by NMR since they are too rapid and catalytic reactions (Figure 2) employ a concentration of catalyst (and hence a concentration of intermediates) too low to detect by NMR. To establish whether eq 4 is reversible, a H/D scrambling experiment was performed. If eq 4 is rapidly reversible, it would be expected that the reaction of $[Pt(CD_3)_4(dppe)]$ (**4***) with $[Pt(CH_3)SO_3CF_3(dppe)]$ (**10a**) would give statistical CH_3 for CD_3 scrambling among the methylplatinum ligands of all the complexes in Scheme 8. However, monitoring the stoichiometric reaction of **4*** with **10a** by low-temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (−70 °C, see Experimental Section) showed no evolution of either C_2H_6 or CD_3CH_3 and no incorporation of $Pt-CH_3$ ligands into either **4*** or **9a***, suggesting that the reverse reaction of eq 4 is insignificant. Nevertheless, attempts to fit the data in Figure 2a to the rate expression obtained if $k_2 = 0$, or indeed by making no assumptions about relative rates, were also unsuccessful. Another problem with Scheme 8 is that it is somewhat oversimplified and does not consider the aquation reactions of complexes **9a** and **10a** (giving **9b** and **10b**, respectively). Presumably $[PtMe(OH_2)(dppe)]SO_3CF_3$ (**10b**) and *fac*-$[PtMe_3(OH_2)(dppe)]SO_3CF_3$ (**9b**) undergo similar methyl transfer and reductive elimination reactions, respectively, to the corresponding triflato complexes and should thus be included in the proposed mechanism shown in Schemes 7 and 8. The curves shown in Figure 2 are most readily interpreted in terms of the mechanism of Scheme 8, with the complications outlined above but also with the complication of slow catalyst decomposition during the reaction, this having its greatest effect at lowest catalyst concentrations when the reactions are slow. Under these conditions, it can be seen that the reactions begin as expected but then slow and may fail to reach completion. In other words, the catalysts have a limited active lifetime.

Conclusions

In conclusion, electrophilic platinum(II) and platinum(IV) complexes react with electron-rich tetramethylplatinum(IV) complexes to provide the first examples of the transfer of a nucleophilic methylplatinum(IV) ligand to an electrophilic transition-metal complex. These reactions occur very rapidly at room temperature and are highly dependent on the electronic properties of both the complexes involved. Electrophilic methyl ligand abstraction from $[PtMe_4(dppe)]$ to give the five-coordinate species $[PtMe_3(dppe)]^+$ is followed by rapid reductive elimination to give C_2H_6 and $[PtMe_2(dppe)]$. This observation has led to the successful catalysis of

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the reductive elimination of ethane from [$PtMe_4$(dppe)]. The mechanism proposed is supported by the detection of intermediates by low-temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and by isotopic labeling experiments. This work gives strong support to the theory that C−H and C−C bond reductive elimination reactions from organoplatinum(IV) complexes occur after initial ligand dissociation and provides further insight into the fundamentally important area of alkane activation/formation reactions.

Experimental Section

General Procedures. All reagents were synthesized under a N_2 atmosphere using standard Schlenk techniques, unless otherwise stated. All solvents were freshly distilled, dried and degassed prior to use. NMR spectra were recorded using a Varian Gemini spectrometer (^1H at 300.10 MHz, ^{19}F at 282.32 MHz, $^{31}P\{^1H\}$ at 121.44 MHz). Chemical shifts are reported in ppm with respect to TMS (^1H), $CFCl_3$ (^{19}F), or H_3PO_4/D_2O (^{31}P). The ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra are referenced to the residual protons of the deuterated solvents or to $CFCl_3$ or H_3PO_4/D_2O contained in a coaxial insert, respectively. The temperature of the NMR spectrometer probe was calibrated using the supplied MeOH calibration routine (Varian), and all temperatures reported have been corrected. Dry CD_2Cl_2 and acetone-d_6 were distilled on a vacuum line from P_2O_5 or molecular sieves respectively onto the complex in flame-dried NMR tubes, which were then flame-sealed when rigorously dry conditions are specified. Otherwise, freshly opened vials of the NMR solvent were used without further purification, and samples were prepared in a drybox. Elemental analyses were determined by Guelph Chemical Laboratories, Canada. Thermogravimetric (TGA) studies were performed using a Perkin-Elmer TGA 7 Thermogravimetric Analyzer equipped with a Perkin-Elmer TAC 7/DX Thermal Analysis Controller. Samples for TGA analysis were heated in platinum pans under a N_2 atmosphere in the range 20−1000 °C at a rate of 20 °C/min.

The reagents Ar_2NN,[15,17] [$PtMe_4$(bu_2bpy)] (**1**),[5b] [$PtMe_4$(dppe)] (**4**),[6e] [$PtMe_2$(bu_2bpy)],[18] [$PtMe_2$(tmeda)],[13,19] [$PtMe_2$(Ar_2NN)],[13,20] [$PtMe_2$(dppe)] (**5**),[13] *fac*-[$PtMe_3(SO_3CF_3)$(bu_2bpy)] (**6a**),[5b] [$Pt_2Me_8(\mu\text{-}SMe_2)_2$],[6e] *fac*-[$PtMe_3(O_2CCF_3)$($bu_2bpy$)],[5b] and [$Pt_2(\mu\text{-}H)Me_6(bu_2bpy)_2$]$SO_3CF_3$[5b] were synthesized according to literature procedures.

Kinetics Experiments. All stock solutions were prepared in a Vacuum Atmospheres drybox. The reactions were performed at 22 °C in acetone-d_6 and were monitored mainly by $^{31}P\{^1H\}$ NMR spectroscopy using a known amount of OP(OMe)$_3$ as an internal integration standard. The [$PtMe_4$(dppe)] (**4**) stock solution was filtered through Celite filter-aid prior to use, eliminating any undissolved [$PtMe_4$(dppe)]. Integrations from the $^{31}P\{^1H\}$ NMR spectra agreed well with those obtained from ^1H NMR spectra acquired periodically throughout the experiment.

H/D Exchange Experiments between 4* and 10a. Complexes **4*** and **10a** were combined in a 5 mm NMR tube charged with acetone-d_6 at −78 °C, shaken, and immediately inserted into the precooled (−70 °C) spectrometer probe. Monitoring the reaction by ^1H NMR spectroscopy revealed no resonances at the typical chemical shifts of C_2H_6 or the methylplatinum ligands of either **4** or **9**. An isotope effect on the $^{31}P\{^1H\}$ NMR chemical shifts for both **5** and **10a** was observed with resonances occurring at progressively lower frequency with increased deuteration. Only single resonances for both **4** and **9** (assigned to the perdeuterated complexes **4*** and **9***, respectively) were observed, fully consistent with the proposed absence of Pt−CH_3 for Pt−CD_3 exchange in eq 4.

Preparation of Complexes. [$PtMe_4$(tmeda)] (2). A mixture of [$Pt_2Me_8(\mu\text{-}SMe_2)_2$] (0.10 g, 0.157 mmol) and tmeda (100 μL, 0.46 mmol) in diethyl ether (25.0 mL) was stirred for 2 h under a N_2 atmosphere. The solvent was removed from the solution in vacuo to give a white powder. Yield: 0.105 g (90%). Anal. Calcd for $C_{10}H_{28}N_2Pt$: C, 32.3; H, 7.6; N, 7.5. Found: C, 32.5; H, 7.7; N, 7.1. ^1H NMR in acetone-d_6: δ = 2.72 [s, 4H, ^3J(PtH) = 6.8 Hz, tmeda−CH_2], 2.46 [s, 12H, ^3J(PtH) = 12.5 Hz, tmeda−Me], 0.53 [s, 6H, ^2J(PtH) = 73.1 Hz, Pt−Me (trans to tmeda)], −0.31 [s, 6H, ^2J(PtH) = 41.0 Hz, Pt−Me (trans to Me)].

[$PtMe_4$(Ar_2NN)] (3). This complex can be generated in situ either by the reaction of [$Pt_2Me_8(\mu\text{-}SMe_2)_2$] with 2 equiv of Ar_2NN or by the reaction of [$PtMe_4$(NN)] [NN = bu_2bpy (**1**), tmeda (**2**)] with *fac*-[$PtMe_3(SO_3CF_3)$(Ar_2NN)] (see text). Complex **3** could not be isolated since decomposition ensues after ca. 30 min in solution. ^1H NMR in acetone-d_6: δ = 9.14 [s, 2H, ^3J(PtH) = 31.0 Hz, imine], 7.32 [m, 6H, phenyl], 3.22 [septet, 4H, ^3J(HH) = 7.0 Hz, ^{i}Pr−H], 1.29 [d, 12H, ^3J(HH) = 7.0 Hz, ^{i}Pr−Me], 1.08 [d, 12H, ^3J(HH) = 7.0 Hz, ^{i}Pr−Me], 0.59 [s, 6H, ^2J(PtH) = 73.4 Hz, Pt−Me trans to Ar_2NN], −0.08 [s, 6H, ^2J(PtH) = 43.9 Hz, mutually trans Pt−Me].

***fac*-[$PtMe_3(SO_3CF_3)$(tmeda)] (7a).** To a suspension of [$PtMe_2$(tmeda)] (0.75 g, 2.19 mmol) in diethyl ether (25.0 mL) was added $MeOSO_2CF_3$ (0.400 mL, 3.53 mmol). After stirring the solution under a N_2 atmosphere for 18 h, the solvent was removed in vacuo to give a very hygroscopic, off-white powder. Yield: 1.10 g (99%). Anal. Calcd for $C_{10}H_{25}F_3N_2O_3PtS$: C, 23.8; H, 5.0; N, 5.5. Found: C, 23.5; H, 4.6; N, 5.5. ^1H NMR in acetone-d_6 (22 °C): δ = 2.98 [br m, 4H, tmeda−CH_2], 2.66 [br m, 6H, tmeda−Me], 2.55 [br m, 6H, tmeda−Me], 0.96 [br s, 9H, ^2J(PtH) = 72.0 Hz, Pt−Me]. ^{19}F NMR in acetone-d_6 (22 °C): δ = −79 (s). ^1H NMR in CD_2Cl_2 (22 °C): 2.80 [br m, 4H, tmeda−CH_2], 2.62 [br m, 6H, tmeda−Me], 2.40 [br m, 6H, tmeda−Me], 0.90 [br s, 9H, ^2J(PtH) = 66.0 Hz, Pt−Me]. ^{19}F NMR in CD_2Cl_2 (22 °C): δ = −79 (s).

***fac*-[$PtMe_3(SO_3CF_3)$(Ar_2NN)] (8a).** To a solution of [$PtMe_2$(Ar_2NN)] (0.20 g, 0.33 mmol) in diethyl ether (25.0 mL) was added $MeOSO_2CF_3$ (0.100 mL, 0.88 mmol). After stirring the solution under a N_2 atmosphere for 3 h, the solvent was removed in vacuo to give a hygroscopic, orange powder. Yield: 0.24 g (94%). Anal. Calcd for $C_{30}H_{45}F_3N_2O_3PtS$: C, 47.0; H, 5.9; N, 3.7. Found C, 46.7; H, 5.8; N, 3.5. ^1H NMR in acetone-d_6 (22 °C): δ = 9.48 [s, 2H, ^3J(PtH) = 25.2 Hz, imine], 7.42 [m, 6H, phenyl], 2.92 [septet, 4H, ^3J(HH) = 6.8 Hz, ^{i}Pr−H], 1.32 [d, 12H, ^3J(HH) = 6.8 Hz, ^{i}Pr−Me], 1.15 [d, 12H, ^3J(HH) = 6.9 Hz, ^{i}Pr−Me], 1.05 [br s, 9H, ^2J(PtH) = 74.2 Hz, Pt−Me]. ^{19}F NMR in acetone-d_6 (22 °C): δ = −79 (s). ^1H NMR in CD_2Cl_2 (22 °C): δ = 8.82 [s, 2H, ^3J(PtH) = 21.0 Hz, imine], 7.4 [m, 6H, phenyl], 2.96 [septet, 4H, ^3J(HH) = 7 Hz, ^{i}Pr−H], 1.36 [d, 12H, ^3J(HH) = 7.0 Hz, ^{i}Pr−Me], 1.18 [d, 12H, ^3J(HH) = 7.0 Hz, ^{i}Pr−Me], 1.05 [br s, 9H, ^2J(PtH) = 70.0 Hz, Pt−Me]. ^{19}F NMR in CD_2Cl_2 (22 °C): δ = −79 (s).

***fac*-[$PtMe_3(SO_3CF_3)$(dppe)] (9a).** This complex can be generated in situ at −70 °C either by treatment of an NMR solution (acetone-d_6) of [$PtMe_2$(dppe)] with 1 equiv of $MeOSO_2CF_3$ or by treatment of an NMR solution (acetone-d_6) of [$PtMe_4$(dppe)] (**4**) with either *fac*-[$PtMe_3(SO_3CF_3)$(NN)] (**6a**−**8a**) or [$PtMe(SO_3CF_3)$(dppe)] (**10a**) (see text). Rapid reductive elimination of C_2H_6 from *fac*-[$PtMe_3(SO_3CF_3)$(dppe)] (**9a**) to afford [$PtMe(SO_3CF_3)$(dppe)] (**10a**) precludes the synthesis and isolation of **9a** (see text). ^1H NMR of *fac*-[$PtMe_3(SO_3CF_3)$(dppe)] (**9a**) in acetone-d_6 (−70 °C): δ = 1.22 [br t, 6H, ^2J(PtH) = ca. 55 Hz, ^3J(PH) + ^3J(P′H) = ca. 5 Hz, Pt−Me trans to dppe], 0.25 [br t, 3H, ^2J(PtH) = ca. 75 Hz, ^3J(PH) = ca. 5 Hz, Pt−Me trans to SO_3CF_3]. $^{31}P\{^1H\}$ NMR of *fac*-[$PtMe_3(SO_3CF_3)$(dppe)] (**9a**)

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Table 4. Crystal Data and Structure Refinement for 8a and 8b

	8a	8b
empirical formula	$C_{30}H_{45}F_3N_2O_3PtS$	$C_{33}H_{53}F_3N_2O_5PtS$
fw	765.83	841.92
temp	298(2) K	298(2) K
wavelength	0.710 73 Å	0.710 73 Å
cryst syst	monoclinic	triclinic
space group	$P2(1)/n$	$P\bar{1}$
unit cell dimens	$a = 12.3957(2)$ Å	$a = 10.1436(3)$ Å
	$b = 14.3533(1)$ Å	$b = 10.4667(3)$ Å
	$c = 19.1125(1)$ Å	$c = 21.4047(6)$ Å
	$\alpha = 90°$	$\alpha = 100.704(1)°$
	$\beta = 91.9760(10)°$	$\beta = 101.342(1)°$
	$\gamma = 90°$	$\gamma = 96.004(1)°$
volume, Z	3398.46(6) Å^3, 4	2165.8(1) Å^3, 2
density (calcd)	1.497 Mg/m^3	1.291 Mg/m^3
abs coeff	4.237 mm^{-1}	3.334 mm^{-1}
$F(000)$	1536	852
no. of data/restraints/params	5935/0/362	5478/0/409
goodness-of-fit on F^2	1.051	1.001
final R indices [$I > 2\sigma(I)$]	R1 = 0.0278	R1 = 0.0475
	wR2 = 0.0683	wR2 = 0.1271
R indices (all data)	R1 = 0.0353	R1 = 0.0575
	wR2 = 0.0718	wR2 = 0.1559

in acetone-d_6: $\delta = 25.5$ [s, ^1J(PtP) = 1120 Hz, dppe]. ^{19}F NMR in of *fac*-[PtMe$_3$(SO$_3$CF$_3$)(dppe)] (**9a**) acetone-d_6 (−70 °C): $\delta = -76$ (s). At −70 °C, in acetone-d_6 complex **9a** is in equilibrium with its aquation isomer, *fac*-[PtMe$_3$(OH$_2$)(dppe)]SO$_3$CF$_3$ (**9b**) (see text). ^{1}H NMR of *fac*-[PtMe$_3$(OH$_2$)(dppe)]SO$_3$CF$_3$ (**9b**) in acetone-d_6 (−70 °C): $\delta = 1.23$ [br t, 6H, ^2J(PtH) = ca. 55 Hz, ^3J(PH) + ^3J(P′H) = ca. 5 Hz, Pt−Me trans to dppe], 0.02 [br t, 3H, ^2J(PtH) = ca. 75 Hz, ^3J(PH) = ca. 5 Hz, Pt−Me trans to SO$_3$CF$_3$]. ^{31}P{^{1}H} NMR of *fac*-[PtMe$_3$(OH$_2$)(dppe)]SO$_3$CF$_3$ (**9b**) in acetone-d_6: $\delta = 20.5$ [s, ^1J(PtP) = 1115 Hz]. ^{19}F NMR of *fac*-[PtMe$_3$(OH$_2$)(dppe)]SO$_3$CF$_3$ (**9b**) in acetone-d_6 (−70 °C): $\delta = -75$ (s).

[PtMe(SO$_3$CF$_3$)(dppe)] (10a). To a solution of [PtMe$_2$(dppe)] (**5**) (0.50 g, 0.80 mmol) in diethyl ether (25.0 mL) was added MeOSO$_2$CF$_3$ (0.150 mL, 1.32 mmol). After stirring the solution under a N_2 atmosphere for 18 h, the solvent was removed in vacuo to give a white powder. Yield: 0.58 g (96%). Due to the hygroscopic nature of **10a** (and thus the subsequent formation of **10b**, see text), reproducible microanalyses could not be obtained. ^{1}H NMR in acetone-d_6: $\delta = 7.6-7.9$ [m, 20H dppe−phenyl], 2.85 [m, 2H, dppe−CH$_2$], 2.60 [m, 2H, dppe−CH$_2$], 0.38 [br dd, 3H, ^2J(PtH) = ca. 48 Hz, ^3J(P^{a}H) = 1.5 Hz, ^3J(P^{b}H) = 7.5 Hz, Pt−Me]. ^{31}P{^{1}H} NMR in acetone-d_6: $\delta =$ 36.0 [br s, 1P, ^1J(PtP) = 4646 Hz, P trans to SO$_3$CF$_3$]; 56.0 [br s, 1P, ^1J(PtP) = 1853 Hz, P trans to Me].

Crystal Structure Analyses of *fac*-[PtMe$_3$(SO$_3$CF$_3$)-(Ar$_2$NN)], 8a, and *fac*-[PtMe$_3$(OH$_2$)(Ar$_2$NN)]SO$_3$CF$_3$·acetone, 8b. Crystals of **8a** and **8b** of size 0.2 × 0.2 × 0.2 mm in each case were mounted on glass fibers. Data were collected by using a Siemens P4 diffractometer fitted with a CCD detector. Structures were solved by direct methods and refined by full-matrix least-squares on F^2. The crystal and refinement data are given in Table 4.

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

Supporting Information Available: Tables of positional and thermal parameters of the non-hydrogen atoms, bond distances and angles, and hydrogen atom coordinates for **8a** and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9809419