Stability of Methyl Platinum Complexes in Water: The Role of pH and Geometry

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Several water-soluble platinum(II) complexes containing methyl ligands have been prepared, $PtMe_2L_2$ and $Pt(Cl)(Me)L_2$ (L_2 = two P(*m*-$C_6H_4SO_3Na)_3$, TPPTS; (*m*-$C_6H_4SO_3Na)_2PCH_2CH_2P$(*m*-$C_6H_4SO_3Na_2$), DPPETS; (*m*-$C_6H_4SO_3Na)_2PCH_2CH_2CH_2P$(*m*-$C_6H_4SO_3Na)_2$, DPPPTS; or (*m*-$C_6H_4SO_3Na)_2PCH_2CH_2CH_2CH_2P$(*m*-$C_6H_4SO_3Na)_2$, DPPBTS), to establish the stability of the platinum methyl bond in aqueous solution. From pH = 3 to 14 there is no reaction other than ligand substitution of H_2O or OH^- for Cl^-; there is no CH_3OH elimination. At lower pH's protonolysis of the Pt−Me bond occurs, producing CH_4. Dissolving $PtMe_2L_2$ into a solution of HCl at pH = 1 rapidly produces $PtCl_2L_2$ for the bidentate ligands, but *trans*-$Pt(Cl)(Me)L_2$ is observed for the monodentate ligands. *trans*-$PtClMe(TPPTS)_2$ undergoes protonolysis very slowly, indicating an important role for geometry in protonolysis reactions. The protonolysis reactions occur stereospecifically but are sometimes accompanied by *cis*−*trans* isomerization. The *cis* or *trans* thermodynamic preferences, *cis*-$PtCl_2L_2$, *cis*-$PtMe_2L_2$, *cis*-$Pt(OH)(Me)L_2$, *trans*-$Pt(Cl)(Me)L_2$, and *trans*-$Pt(H_2O)(Me)L_2^+$, are not easily explained.

Platinum and palladium complexes are catalysts for many reactions.[1−4] In a number of cases, the product formation involves β-hydride elimination; relatively few involve reductive elimination. A number of reactions such as hydrogenation, hydration, hydroamination, and methane to methanol could involve reductive elimination. Goldberg has shown that reductive elimination can occur from Pt(IV) complexes, with formation of carbon−carbon or carbon−oxygen bonds.[5] Protonolysis reactions of Pt(II) alkyl complexes in CH_3OH have been the subject of a few studies. Reactions of *trans*-$Pt(Me)(X)(PEt_3)_2$ with triflic acid produced methane, possibly through a Pt(IV) hydride. Deuterium labeling showed extensive incorporation into the CH_4.[6] A study of HBF_4 or HCl reaction with *cis*-$PtR_2(PEt_3)_2$ in CH_3OH showed cleavage of one Pt−R (R = Me, Et, etc.) and a slow *cis* to *trans* isomerization.[7] In this protonolysis a 10^4 increase was shown for C_2H_6 elimination over CH_4.[7] Protonolysis studies on platinum(II) alkyls and aryls showed that acid strength was very important, halide sometimes had an effect, steric hindrance occurred, and aryl cleavage was slower than alkyl, but could not distinguish the site of protonolysis.[8] Florinated bidentate phosphines examined by Roddick and co-workers were much less prone to methyl protonolysis.[9] The dimethyl complexes required neat acids and the monomethyl complexes required neat acids at elevated temperatures.[9]

The recent interest in water-soluble organometallic complexes as potential "green" approaches to catalysis raises questions regarding the stability of metal alkyl bonds in aqueous solutions. In this article, we use *cis*-$PtMe_2(TPPTS)_2$, *trans*-$Pt(Cl)(Me)(TPPTS)_2$, $PtMe_2(LL)$, and $Pt(Cl)(Me)(LL)$ (TPPTS = P(*m*-$C_6H_4SO_3Na)_3$, LL = (*m*-$C_6H_4SO_3Na)_2PCH_2CH_2P$(*m*-$C_6H_4SO_3Na)_2$, DPPETS; (*m*-$C_6H_4SO_3Na)_2PCH_2CH_2CH_2P$(*m*-$C_6H_4SO_3Na)_2$, DPPPTS; (*m*-$C_6H_4SO_3Na)PCH_2CH_2CH_2CH_2P$(*m*-$C_6H_4SO_3Na)_2$, DPPBTS) (throughout this article LL is generic for one of the three bidentate ligands and L_2 is generic for two TPPTS ligands or one of the bidentate ligands) to examine the stability of Pt(II)−methyl bonds at pH's from 1 to 14. The geometry also has a significant effect.

Results and Discussion

Synthesis. $Pt(Me)_2L_2$ complexes were prepared by dissolving 1.0 equiv of the selected water-soluble bidentate phosphine or 2 equiv of TPPTS with Pt(1,5-COD)Me_2 in DMSO at room temperature. The NMR characterizations of these complexes are in good agreement

(1) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; John Wiley and Sons: New York, 1992; and references therein.
(2) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*, 2nd ed.; Wiley VCH: New York, 1997.
(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, especially pp 409−416, and references therein.
(4) Tsuji, J. *Synthesis* **1984**, 369.
(5) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576, and references therein.
(6) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (b) Holtcarp, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1997**, *265*, 117.
(7) Romeo, R.; Plutino, M. R.; Elding, L. I. *Inorg. Chem.* **1997**, *36*, 5909.
(8) (a) Romeo, R.; Minniti, D.; Lanza, S. *J. Organomet. Chem.* **1979**, *165*, c36. (b) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U. *Inorg. Chem. Acta* **1986**, *112*, L15. (c) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliata, P.; Calligaro, L.; Belluco, U.; Crociani, B. *Inorg. Chim. Acta* **1985**, *100*, 107.
(9) (a) Bennett, B. L.; Hoerter, J. M.; Houlis, J. F.; Roddick, D. M. *Organometallics* **2000**, *19*, 615. (b) Bennett, B. L.; Birnbaum, J.; Roddick, D. M. *Polyhedron* **1995**, *14*, 187.

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Table 1. Selected ^{1}H, ^{31}P{^{1}H}, and ^{195}Pt NMR Characterization of $PtMe_2L_2$ and Organic Analogues

	^{31}P NMR (D_2O)[a]		^{195}Pt NMR (D_2O)[a]		^{31}P NMR (d_6-DMSO)[a]		^{1}H NMR (D_2O)[a]	
complex	δ(P)	$^1J_{(Pt-P)}$	δ(Pt)[b]	$^1J_{(Pt-P)}$	δ(P)	$^1J_{(Pt-P)}$	$\delta(CH_3)$	$^2J_{(Pt-H)}$
$PtMe_2$(DPPETS)	56.0	1740	−4578	1740			0.22	69.2
$PtMe_2$(DPPE)[13]	45.4	1794					1.08	71.0
$PtMe_2$(DPPPTS)	4.7	1730	−4580	1730	7	1810	0.18	68.4
$PtMe_2$(DPPP)[10]	3.2[c]	1767					0.57	69
$PtEt_2$(DPPP)[11]	3.0[c]	1592			3.2[c]	1790		
$PtMe_2$(DPPBTS)	20.2	1880	−4667	1880	20.7	1880	0.06	67.2
$PtMe_2$(DPPB)[10]	18.8	1847						
cis-$PtMe_2(TPPTS)_2$	30.3	1875	−4676	1875	29.8	1875	0.32	68
cis-$PtMe_2(PPh_3)_2$[12,d]	28	1910					0.29	69.9
cis-$PtMe_2(TPPTS)_2$[6b]	29.4	1880					0.41	68.7

[a] Chemical shifts (δ) are recorded in ppm, and coupling constants (J) are recorded in Hz. [b] Referenced to 0.2 M K_2PtCl_4 in D_2O. [c] NMR spectrum taken in $CDCl_3$. [d] ^{31}P and ^{1}H NMR taken in 3:1 (v:v) CD_2Cl_2/CD_3OD, 253 K.

Table 2. Selected ^{31}P{^{1}H} NMR Characterization for $Pt(Cl)(Me)L_2$ and Their Organic Analogues

	^{31}P NMR (D_2O)[a]		^{31}P NMR (d_6-DMSO)[a]	
complex	δ(P)	$^1J_{(Pt-P)}$[b]	δ(P)	$^1J_{(Pt-P)}$[b]
PtClMe(DPPETS)	49.4 (br)	1738	46.6 (br)	1739
	44.9 (br)	4361	44.9 (br)	4144
PtClMe(DPPE)[13]	43.4[e] (br)	1737	39.0[f] (br)	1765
	42.0 (br)	4224	38.1 (br)	4263
PtClEt(DPPE)[11]	42.9[e] (d)	4478 (<2)	43.4[f] (br)	1737
	42.0 (d)	1558	42.0 (br)	4224
PtClMe(DPPPTS)	7.2 (d)	1630 (22.9)	8.03 (d)	4080 (22.1)
	6.7 (d)	4270	7.47 (d)	1680
PtClMe(DPPP)[15,16]	5.1[e] (d)	4116 (21)	6.02[f] (d)	4187 (22.2)
	3.0 (d)	1644	3.55 (d)	1678
PtClEt(DPPP)[11]	6.8[e] (d)	4418 (18)	5.1[f] (br)	4116
	2.2 (d)	1483	3.0 (br)	1644
PtClMe(DPPBTS)	23.05 (br)	1750	22.3 (d)	4270 (13.5)
	20.53 (br)	4460	20.8 (d)	1750
trans-Pt(Cl)(Me)$(TPPTS)_2$	31.9 (s)	3176	33.3 (s)	3176
cis-Pt(Cl)(Me)$(TPPTS)_2$[g]	22.3 (br)	4635		
	28.8 (br)	1766		
trans-Pt(Cl)(Me)$(TPPTS)_2$[6b]	33.3	3200		
cis-Pt(Cl)(Me)$(PPh_3)_2$[17,h]	22.3	4500		
	27.1	1727		
trans-Pt(Cl)(Me)$(PPh_3)_2$[17,h]	29.6	3147		

[a] Chemical shifts (δ) are recorded in ppm, and coupling constants (J) are recorded in Hz. [b] Coupling constants refer to platinum satellites; numbers in parentheses refer to $^2J_{(P-P)}$ when given. [c] NMR taken in D_2O. [d] NMR taken in d_6-DMSO. [e] NMR taken in $CDCl_3$. [f] NMR taken in CD_2Cl_2. [g] NMR taken in H_2O with a d_6-DMSO insert. [h] Spectra recorded at 36.2 or 162 MHz in $CDCl_3$ at ambient temperature.

with their organic analogues, as shown in Table 1. The $PtMe_2L_2$ complexes have very small $^1J_{Pt-P}$, as previously discussed.[10,13,14]

$PtClMeL_2$ complexes were successfully synthesized in an analogous manner as above, starting with PtCl(1,5-COD)Me. The NMR characterizations of these complexes are also in good agreement with their corresponding organic analogues, as shown in Tables 2 and 3.

The ^{31}P NMR spectrum of PtClMe(DPPBTS) in D_2O resulted in the formation of a minor resonance (30%) along with the resonance for PtClMe(DPPBTS). Upon dissolution into d_6-DMSO, only PtClMe(DPPBTS) is present. This indicates that the minor product present in the D_2O spectrum was $Pt(D_2O)(Me)(DPPBTS)^+$. The formation of an aquo species is also seen in the ^{31}P NMR spectrum of *trans*-Pt(Cl)(Me)$(TPPTS)_2$. Since the minor resonance, in this case, is a singlet, the species present is *trans*-$[Pt(D_2O)(Me)(TPPTS)_2]^+$. The *cis* isomers of these TPPTS complexes are seen in the protonation reactions. The ^{31}P NMR characterization of all these species is located in Table 4.

Reactions. In buffered solutions at pH = 4, 7, and 10 and in 5% NaOH, one of two reactions is observed for $Pt(Cl)(Me)L_2$ (L_2 = 2TPPTS, DPPETS, DPPPTS, or DPPBTS):

$$Pt(Cl)(Me)L_2 + H_2O \rightarrow Pt(Me)(H_2O)L_2^+ + Cl^- \quad (1)$$

$$Pt(Cl)(Me)L_2 + OH^- \rightarrow Pt(OH)(Me)L_2 + Cl^- \quad (2)$$

The exact amounts depend on L_2; the reactions are illustrated by the ^{31}P NMR spectra for L_2 = DPPETS in Figure 1. Figure 1 consists of the ^{31}P NMR spectra of PtClMe(DPPETS) in D_2O, pH 7, pH 10, and 5% NaOH, showing the presence of the different species that exist under the various pH conditions. The species that resonates at 38.0 ppm with $^1J_{(Pt-P)}$ of 3806 Hz in 5 wt % NaOH (4 in Figure 1) has been determined to be Pt(OH)Me(DPPETS) by comparison to its organic analogue Pt(OH)Me(DPPE)[13] (refer to Table 4). The ^{1}H NMR spectrum of PtClMe(DPPETS) in 5% NaOH solution (so only Pt(OH)Me(DPPETS) is present) at 60 °C led to full characterization of the Pt−Me resonance and

(10) Garrow, P. E. *Chem. Rev.* **1981**, *81*, 229.
(11) Slack, D. A.; Baird, M. C. *Inorg. Chim. Acta* **1977**, *24*, 277.
(12) Romeo, R.; Alibrandi, G. *Inorg. Chem.* **1997**, *36*, 4822.
(13) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.
(14) (a) Allen, F. H.; Pidcock, A.; Waterhouse, C. R. *J. Chem. Soc. (A)* **1970**, 2087. (b) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. (A)* **1966**, 1707. (c) Allen, F. H.; Pidcock, A. *J. Chem. Soc. (A)* **1968**, 2700.

Table 3. Selected ^{1}H NMR Characterization of Pt(X)(Me)L_2 and Similar Organic Analogues

	^{1}H NMR (D_2O)[a]				^{1}H NMR (d_6-DMSO)[a]
complex	$\delta(CH_3)$	$^2J_{(Pt-H)}$	$^3J_{(Pcis-H)}$	$^3J_{(Ptrans-H)}$	$\delta(CH_3)$
PtClMe(DPPETS)	0.24 (br)				0.37 (br)
PtClMe(DPPE)[13]	0.51[b] (dd)	53.5	3.5	8.0	
PtClMe(DPPPTS)	0.25 (br)				0.13 (br)
PtClMe(DPPP)	0.79[b] (dd)	59	5.0	7.5	0.44[c,d] (dd)
PtClMe(DPPBTS)	0.26 (br)				0.15 (br)
trans-Pt(Cl)(Me)(TPPTS)$_2$	−0.11 (t)	76			−0.33 (t)
trans-Pt(Cl)(Me)(TPPTS)$_2$[6b]	0.05 (t)	68.7			
trans-Pt(Cl)(Me)(PPh_3)$_2$[18,c]	−0.11	80			
cis-Pt(Cl)(Me)(TPPTS)$_2$[e]	0.46	48	4.4	6.8	
Pt(OH)Me(DPPETS)	0.31 (dd)	50.4	2.6	7.4	
Pt(OH)Me(DPPE)[13]	0.51 (dd)	60.5	3.0	7.1	
Pt(OH)Me(DPPBTS)	0.75 (dd)	55.6	2.8	7.2	
trans-Pt(OH)(Me)(TPPTS)$_2$[f]	−0.61 (br)				
cis-Pt(OH)(Me)(TPPTS)$_2$[f]	0.21 (br)				
cis-Pt(OH)(Me)(PPh_3)$_2$[19,g]	1.10 (dd)	64.6	4.4	7.1	

[a] Chemical shifts (δ) are recorded in ppm, and coupling constants (J) are recorded in Hz. [b] NMR spectrum taken in $CDCl_3$. [c] NMR spectrum taken in CD_2Cl_2. [d] $^2J_{(Pt-H)} = 54$, $^3J_{(Pcis-H)} = 4.5$, and $^3J_{(Ptrans-H)} = 7.8$. [e] NMR taken in water with d_6-DMSO insert. [f] NMR taken in 5% NaOH with d_6-DMSO insert. [g] NMR taken in C_6D_6.

Table 4. Selected ^{31}P{^{1}H} and ^{195}Pt NMR Characterization for Pt(OH)MeL_2, Pt(OH_2)MeL_2^+, and Related Complexes

	^{31}P NMR (d_6-DMSO insert)[a]		^{195}Pt NMR[a]
complex	δ(P)	$^1J_{(Pt-P)}$[b]	δ(Pt)[c]
Pt(OH)Me(DPPETS)[d]	47.9 (d)	1756 (3.4)	−4405 (dd)
	38.0 (d)	3806	
Pt(OH)Me(DPPE)[13,e]	40.5 (br)	1804	
	34.9 (br)	3546	
Pt(OH_2)Me(DPPETS)$^+$[f]	49.2 (br)	1816	
	44.6 (br)	4355	
Pt(OH)Me(DPPPTS)[d]	8.5 (d)	1590 (22.3)	−4377 (dd)
	0.54 (d)	3740	
Pt(OH)(Me)(DPPP)[20,e]	2.1 (d)	1688 (21)	
	−1.1 (d)	3403	
Pt(OH)(Me)(DPPP)[20,g]	3.4 (d)	1636 (19.6)	
	−0.91 (d)	3511	
Pt(OH)(Me)(DPPP)[20,h]	−3.6 (d)	1727 (21)	
	−0.86 (d)	3324	
Pt(OH)(Me)(DPPP)[21,h]	4.9 (d)	1672	
	−0.5 (d)	3468	
Pt(OH)Me(DPPBTS)[d]	27.6 (d)	1710 (12.6)	−4450 (dd)
	10.6 (d)	3890	
trans-Pt(OH)(Me)(TPPTS)$_2$	32.5 (s)	3245	
cis-Pt(OH)(Me)(TPPTS)$_2$	17.4 (d)	4045 (10.2)	
	31.5 (d)	1750	
cis-Pt(OH)(Me)(PPh_3)$_2$[19,h]	18.7 (d)	3608 (10.7)	
	26.9 (d)	1745	
trans-Pt(OH_2)(Me)(TPPTS)$_2^+$	32.9 (s)	3226	
cis-Pt(OH_2)(Me)(TPPTS)$_2^+$	34.6	1822 (12)	
	15.9	4907	

[a] Chemical shifts (δ) are recorded in ppm, and coupling constants (J) are recorded in Hz. [b] Coupling constants refer to platinum satellites; numbers in parentheses refer to $^2J_{(P-P)}$ when given. [c] Referenced to 0.2 M K_2PtCl_4 in D_2O. [d] NMR spectra taken in 5% NaOH. [e] NMR spectra taken in CD_2Cl_2. [f] NMR spectrum taken in pH 10 buffered H_2O. [g] NMR spectrum taken in $CDCl_3$. [h] NMR spectrum taken in C_6D_6.

all of its splitting. Also the ^{1}H NMR spectrum of PtClMe(DPPBTS) in 5% NaOH solution (so only Pt(OH)Me(DPPBTS) is present) at 70 °C led to the same detailed characterization of the methyl ligand. In 5% NaOH solution there was no evidence of phosphine oxidation. At pH = 10, the presence of both PtClMe(DPPETS) and Pt(OH)Me(DPPETS) (3 in Figure 1) is evident.

Similar studies for Pt(Cl)(Me)(DPPPTS) show no reaction except for pH = 10 and 5% NaOH, where Pt(OH)(Me)(DPPTS) is observed, in good spectroscopic agreement with the organic analogue, Pt(OH)(Me)(DPPP).[20,21] The DPPBTS complex, Pt(Cl)(Me)(DPPBTS), undergoes aquation more readily such that Pt(Me)(H_2O)(DPPBTS)$^+$ is observed at pH = 4 and 7. In 5% NaOH only the hydroxy complex is observed.

Dissolution of *trans*-Pt(Cl)(Me)(TPPTS)$_2$ into 5% NaOH at room temperature immediately gives *trans*-Pt(OH)(Me)(TPPTS)$_2$. Over time the *trans* complex isomerizes

(15) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1971.
(16) Kégl, T.; Kollár, L.; Radies, L. *Inorg. Chim. Acta* **1997**, *265*, 249.
(17) Cobley, C. J.; Pringle, P. G. *Inorg. Chim. Acta* **1997**, *265*, 107.
(18) Otto, S.; Roodt, A.; Leipoldt, J. G. *S. Afr. J. Chem.* **1995**, *48*, 114.
(19) Bennett, M. A.; Jin, H.; Li, S.; Rendina, L. M.; Willis, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 8335.
(20) Bennett, M. A.; Rokicki, A.; Puddephatt, R. J. *Inorg. Synth.* **1989**, *25*, 100.
(21) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.

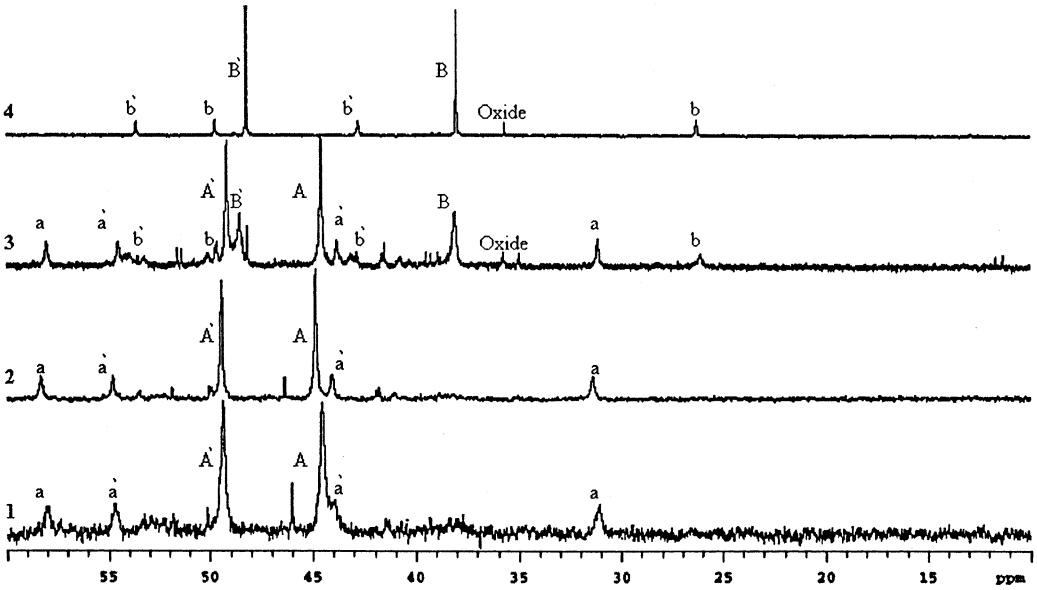

Figure 1. ^{31}P NMR spectra of PtClMe(DPPETS) in D_2O (1), pH 7 (2), pH 10 (3), and 5 wt % NaOH (4). (A) Resonances corresponding to PtClMe(DPPETS). (B) Resonances corresponding to Pt(OH)Me(DPPETS). In all cases, lowercase letters correspond to the distinguishable ^{195}Pt satellites.

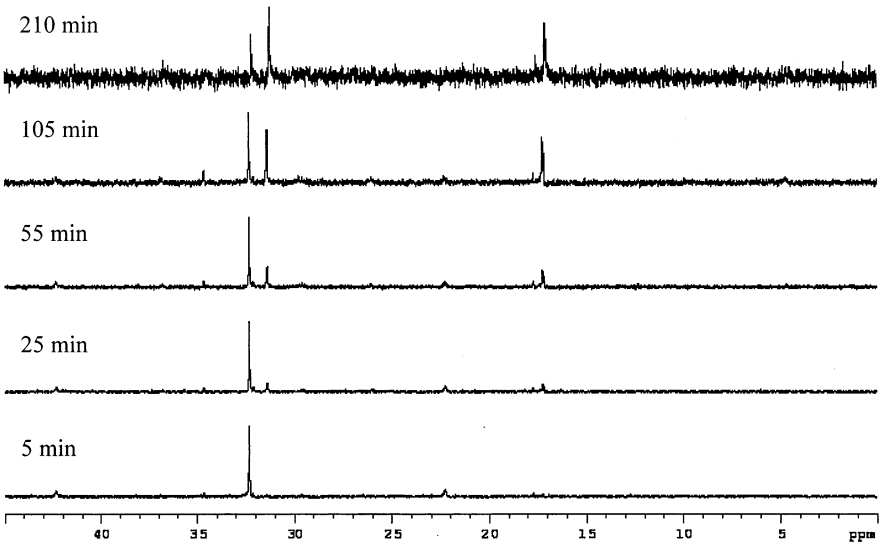

Figure 2. ^{31}P NMR spectra for isomerization of *trans*-Pt(OH)(Me)$(TPPTS)_2$ to the *cis* isomer. The *trans* is a singlet at 32 ppm, and the *cis* has two doublets of 31 and 17 ppm.

to *cis*-Pt(OH)(Me)$(TPPTS)_2$, as shown in Figure 2. At room temperature the isomerization is 50% complete in 60 min and can be accelerated by heat. The characterization of *cis*-Pt(OH)(Me)$(TPPTS)_2$ is in agreement with the characterization of *cis*-Pt(OH)(Me)$(PPh_3)_2$,[19] as shown in Table 4.

The geometrical preferences for these complexes with TPPTS and other monodentate ligands are not readily interpreted. The complexes with two chlorides, two methyls, or a methyl and hydroxide, *cis*-$PtCl_2L_2$, *cis*-$PtMe_2L_2$, and *cis*-Pt(OH)(Me)L_2, are stable as the *cis* isomer, while the *trans* geometry is preferred by *trans*-PtCl(Me)L_2, *trans*-Pt(H_2O)(Me)L_2^+, and from other work *trans*-Pt(Me)$(MeOH)L_2^+$.[12] The rather subtle differences that lead Pt(H_2O)(Me)L_2^+ and Pt(Cl)(Me)L_2 to be thermodynamically stable *trans* while Pt(OH)(Me)L_2 is thermodynamically stable *cis* would benefit from theoretical study.

When $PtMe_2L_2$ is dissolved in triply distilled water, the only complex present as determined by $^{31}P\{^1H\}$ NMR spectroscopy was $PtMe_2L_2$. The pH's of these solutions were observed to be 8.19−8.29. Under conditions ranging from pH = 4−12 only $PtMe_2L_2$ was observed. In no case do we observe MeOH formation from Pt(OH)(Me)L_2, which would be the last step in a platinum(II) system for CH_4 conversion to CH_3OH.[6,22,23] Such an alcohol elimination could also be important in hydration of an alkene.

Protonolysis of the Platinum−Methyl Bond. In contrast to the stability of the Pt−Me bond under basic conditions, methane elimination occurs in acidic condi-

(22) (a) Mylvaganam, K.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **1999**, *121*, 4633. (b) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fuji, H. *Science* **1998**, *280*, 250. (c) Heiberg, H.; Johansson, L.; Gopen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831.

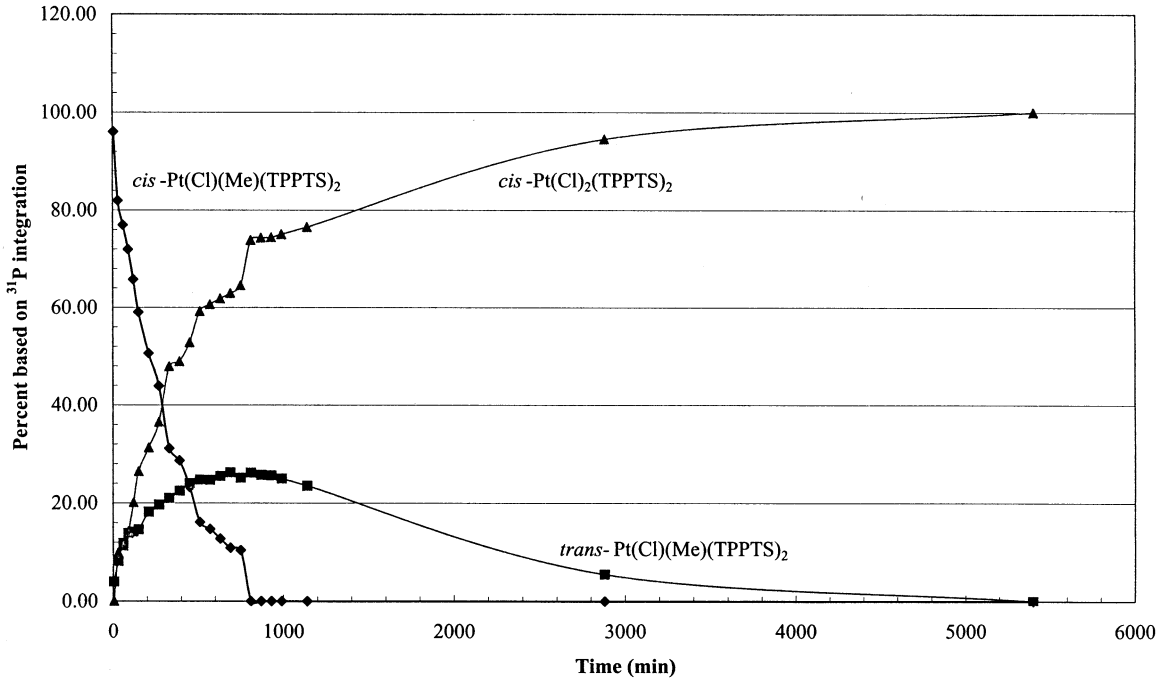

Figure 3. Graph of the amounts of *cis*-Pt(Cl)(Me)(TPPTS)$_2$, *trans*-Pt(Cl)(Me)(TPPTS)$_2$, and *cis*-Pt(Cl)$_2$(TPPTS)$_2$[28] over time based on ^{31}P NMR integration.

tions. Reactions of the bidentate complexes are straightforward and complete in 30 min. When these complexes are reacted with approximately 0.1 M HCl, CH_4 is eliminated and the only species observed by $^{31}P\{^1H\}$ NMR spectroscopy are $PtCl_2(LL)$ complexes. These complexes have been independently synthesized and have identical characterization. The final pH of these solutions was between 0.96 and 1.06. When $PtMe_2(LL)$ complexes were reacted with 10^{-2} M HCl, the species that were observed by $^{31}P\{^1H\}$ NMR spectroscopy were $PtMe(H_2O)(LL)^+$ and PtClMe(LL). Finally, when the complexes $PtMe_2(LL)$ were reacted with approximately 10^{-3} and 10^{-4} M HCl, the only species present as determined by $^{31}P\{^1H\}$ NMR was the starting material (with the broadening of the signals and splitting, products of less than 5% would not be observed). The pH's of the 10^{-3} M HCl solutions with $PtMe_2L_2$ were 7.62−7.92. The pH's of the 10^{-4} M HCl solutions were 7.95−8.26.

In the reactions of 1×10^{-2} M $PtMe_2(LL)$ with 0.1, 10^{-2}, and 10^{-3} M HCl, the presence of CH_4(g) was determined from the individual ^{1}H NMR spectra. The CH_4 elimination accounts for the change of pH in the pH = 2, 3, and 4 reactions. These reactions seem to be stoichiometric in nature. For example, in the 10^{-2} M HCl solution the $[H^+]$ and $PtMe_2L_2$ concentrations are 1:1 and resulted in formation of only 1 equiv of CH_4(g) and 1 equiv of $PtMe(S)L_2$. With L_2 = DPPPTS, the temperature was increased to see if elimination of a second equivalent of CH_4 would occur. Up to 80 °C, no formation of $PtCl_2$(DPPPTS) was apparent from the $^{31}P\{^1H\}$ NMR spectra. At the elevated temperature, the exchange process between PtClMe(DPPPTS) and $PtMe(H_2O)$(DPPPTS)$^+$ was accelerated, leading to broadening of the respective ^{31}P resonances, but cooling to room temperature gave the same sharp signals.

Protonolysis of the TPPTS complexes provides further information on the elimination of CH_4. When *cis*-$PtMe_2$(TPPTS)$_2$ is reacted with 0.10 M HCl, after 30 min *cis*-Pt(Cl)(Me)(TPPTS)$_2$ is dominant with 5% *trans*-Pt(Cl)(Me)(TPPTS)$_2$.

$$\textit{cis}\text{-}PtMe_2L_2' \xrightarrow[-CH_4]{+HCl} \textit{cis}\text{-}Pt(Cl)(Me)L_2' \xrightarrow[-CH_4]{+HCl} \textit{cis}\text{-}PtCl_2L_2' \qquad (3)$$
$$\textit{cis}\text{-}Pt(Cl)(Me)L_2' \rightleftarrows \textit{trans}\text{-}Pt(Cl)(Me)L_2'$$

After 19 h *cis*-$PtCl_2$(TPPTS)$_2$ (70%) and *trans*-Pt(Cl)(Me)(TPPTS)$_2$ (20%) are present; *trans*-Pt(Cl)(Me)(TPPTS)$_2$ is still observable (4%) after 48 h. The pH is 1.03. Similar *cis* to *trans* isomerization of *cis*-Pt(Me)(MeOH)L_2^+ was observed by Romeo and Alibrandi upon protonolysis of *cis*-$PtMe_2L_2$ in MeOH.[12] Using 10^{-2} M HCl produces, primarily, *cis*-$Pt(H_2O)(Me)$(TPPTS)$_2^+$ (55%) and Pt(Cl)(Me)(TPPTS)$_2$ (25%), along with 20% of the *trans* isomers of the two species. Amounts of products at different times are shown in Figure 3.

The observations on *cis*-$PtMe_2$(TPPTS)$_2$ suggest that *trans*-Pt(Cl)(Me)(TPPTS)$_2$ is very slow to undergo protonolysis, so we have examined the direct reaction.

(23) (a) Kushch, L. A.; Lavrushko, V. V.; Misharin, Y. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* **1983**, *7*, 729. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180, and references therein. (c) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235. (d) Prokopchuk, E. M.; Jenkins, H. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 2861. (e) Haskel, A.; Keinan, E. *Organometallics* **1999**, *18*, 4677. (f) Hill, G. S.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 1408. (g) Crumpton, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2000**, *122*, 962. (h) Levy, C. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 35. (i) Hill, G. S.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 8745. (j) Levy, C. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 2108. (k) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209. (l) Gerisch, M.; Bruhn, C.; Vyater, A.; Davies, J. A.; Steinborn, D. *Organometallics* **1998**, *17*, 3101. (m) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845. (n) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684. (o) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946. (p) Williams, B. S.; Holland, A. W.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 252. (q) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 11900.

trans-Pt(Cl)(Me)(TPPTS)$_2$ shows no reaction after 1 h of dissolution in 0.1 M HCl. After 19 h 20% of *cis*-PtCl$_2$-(TPPTS)$_2$ is formed and a trace of *cis*-Pt(Cl)(Me)-(TPPTS)$_2$ is observed; after 48 h 25% of the *trans*-Pt(Cl)(Me)(TPPTS)$_2$ is unreacted, and after 90 h *trans*-Pt(Cl)(Me)(TPPTS)$_2$ is still observed. For higher pH's a similar lack of reactivity toward protonolysis of *trans*-Pt(Cl)(Me)(TPPTS)$_2$ occurs.

Using HBF_4 (0.1 M) as the proton source shows that Cl^- also plays a role; while the first methyl is readily protonated, the second is stable.

$$\mathrm{Pt(Me)_2(TPPTS)_2} + \mathrm{HBF_4} \xrightarrow{\mathrm{H_2O}} \begin{array}{c} \textit{cis}\text{-Pt(H}_2\mathrm{O)(Me)(TPPTS)}_2^{+} \\ \downarrow \\ \textit{trans}\text{-Pt(H}_2\mathrm{O)(Me)(TPPTS)}_2^{+} \end{array} \quad (4)$$

The *cis* complex, Pt(H$_2$O)(Me)(TPPTS)$_2^+$, isomerizes to the *trans* complex, but does not undergo further protonolysis in 2 days. The aquo, methyl complex is stable at room temperature, pH = 1.0, as a 70−30% mixture of *trans* and *cis*, respectively. This is in contrast to Pt-(OH)(Me)(TPPTS), which is stable as the *cis* isomer. The stability of Pt(H$_2$O)(Me)(TPPTS)$_2^+$ toward further protonation, possibly from the positive charge, eliminates protonation of the aquo complex playing a role in protonolysis with HCl.

The protonolysis reactions of platinum methyl complexes provide some observations: (1) protonolysis of the platinum methyl bond requires acidic conditions; (2) the protonolysis is stereospecific, i.e., *cis*-PtMe$_2$(TPPTS)$_2$ gives *cis*-Pt(Cl)(Me)(TPPTS)$_2$; (3) complexes of bidentate ligands where *cis* geometry is maintained eliminate CH_4 more readily; and (4) *cis*-Pt(Cl)(Me)(TPPTS)$_2$ undergoes protonolysis ~10 times more readily than does *trans*-Pt(Cl)(Me)(TPPTS)$_2$. (5) With bidentate florinated phosphine ligands, Roddick and co-workers required elevated temperatures and strong acids to cleave both methyls of PtMe$_2$(LL),[9] while with DPPETS, DPPPTS, and DPPBTS both methyls are readily cleaved at 0.1 M acid and room temperature. This suggests a significant electronic effect on protonolysis by spectator ligands.

Since *cis*-Pt(Cl)(Me)(TPPTS)$_2$ undergoes protonolysis much more readily and appears to be present in about 2% from an equilibrium, it is possible that the mechanism involves *trans* to *cis* interconversion, as shown in reaction 3, although we cannot exclude slow protonolysis on *trans*-Pt(Cl)(Me)(TPPTS)$_2$ and rapid isomerization of *trans*-PtCl$_2$(TPPTS)$_2$. *Cis*−*trans* isomerization of square-planar platinum(II) complexes is well understood and usually occurs rapidly at elevated temperatures. At 60 °C *cis*-PtCl$_2$(TPPTS)$_2$ is formed in 50% yield after 30 min with *trans*-Pt(Cl)(Me)(TPPTS)$_2$ dissolved in 0.10 M HCl. The stability of the Pt−Me bond toward base hydrolysis or protonolysis indicates that platinum may be a poor choice for catalytic reactions that require product elimination from base hydrolysis of an alkyl or protonolysis of an alkyl. However, platinum complexes continue to provide important mechanistic data.

Experimental Section

Materials. Pt(1,5-COD)Me$_2$ was purchased from Strem Chemicals. Water was triply distilled and was purged with nitrogen prior to use. d_6-DMSO, d_4-methanol, and HBF_4 were purchased from Aldrich Chemical Co. Concentrated HCl was purchased from Fisher Scientific. Deuterium oxide was purchased from Isotec Inc. N_2(g) was purchased from Irish Welding Corporation. All materials were used as received without further purification. DPPETS, DPPPTS, DPPBTS,[24] TPPTS,[25] and Pt(Cl)(1,5-COD)Me[26] were synthesized according to published procedures. Elemental analyses were performed by E and R Microanalytical Laboratory, Parisspany, NJ.

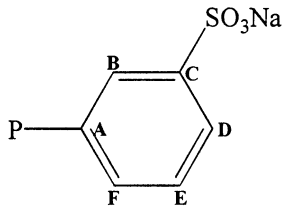

Figure 4. Figure of aryl group to show labeling scheme for C and H atoms.

Solvents. MeOH and DMSO were purchased from Fisher Scientific. $MeNO_2$ was purchased from Aldrich Chemical Co. CH_2Cl_2 and Et_2O were purchased from VWR. All solvents were used without further purification and purged with N_2(g) prior to use.

Buffers. The pH = 4 buffer was composed of a 0.05 M solution of biphthalate. The pH = 7 buffer was composed of a solution of 0.021 M NaH_2PO_4 and 0.029 M Na_2HPO_4. The pH = 10 buffer was composed of a solution of 0.025 M $NaHCO_3$ and 0.025 M Na_2CO_3. All three buffers were purchased from VWR and diluted to the appropriate volume using triply distilled water.

Instrumentation. ^{1}H, ^{31}P, and ^{195}Pt NMR spectra were recorded on a Varian VXR 400 MHz spectrometer. ^{31}P NMR (161.89 MHz) spectra were ^{1}H decoupled and referenced to an external standard of 85% phosphoric acid in D_2O (reference set to 0.00 ppm). ^{195}Pt NMR (85.97 MHz) spectra were referenced to an external standard of 0.2 M K_2PtCl_4 (in 0.4 M KCl/D_2O), which was set to −1627 ppm.[27]

pH measurements were performed using a Fisher Scientific Accumet basic pH meter by Denver Instruments Inc. with a semimicro glass pH electrode with a silver/silver chloride reference electrode. The electrode was calibrated using the pH = 4, 7, and 10 buffers.

Synthesis of PtMe$_2$(LL). Into a small (100 mL) Schlenk flask 150 mg of Pt(1,5-COD)Me$_2$, 1 molar equiv of LL, and a stir bar were added. Then the apparatus was back-filled with N_2(g) three times. Under N_2(g) flow, 5.0 mL of DMSO was added. After all solids had dissolved and were stirred for 5 min, 50 mL of CH_2Cl_2 was added to facilitate precipitation. This crude product was then collected on a fine-grain sintered frit and washed with 2 × 50 mL of CH_2Cl_2. Recrystallization of this from MeOH with $MeNO_2$ yielded the final product. Before being used this was dried under vacuum at 90 °C.

PtMe$_2$(DPPETS) (refer to Figure 4 for labeling scheme). ^{31}P{^{1}H} NMR (D_2O): 50.0 (s, $^1J_{(Pt-P)}$ = 1740). ^{1}H NMR (D_2O): 7.53 (d, J = 9.6, 4H, **D**), 7.41 (d, J = 7.4, 4H, **B**), 7.58 (t, J = 9.0, 4H, **E**), 7.18 (t, J = 7.4, 4H, **F**), 2.12 (br, 4H, PCH_2), 0.22 (t, $^3J_{(P-H)}$ = 6.8, $^2J_{(Pt-H)}$ = 69.2, 6H, PtCH_3). ^{195}Pt NMR (D_2O): −4578(t) ppm, J_{Pt-P} = 1740 Hz. Anal. Calcd for $C_{28}H_{26}Na_4O_2P_2$-

(24) Lucey, D. W.; Atwood, J. D. *Organometallics* **2002**, *21* (12), 2481, and references therein.

(25) (a) Herrmann, W. A.; Kohlpaintner, C. W. *Inorg. Synth.* **1998**, *32*, 14. (b) Bartik, T.; Bartik, B.; Hanson, B. E.; Glass, T.; Bebout, W. *Inorg. Chem.* **1992**, *31*, 2667. (c) Bhanage, B. M.; Divekar, S. S.; Deshparde, R. M.; Chaudhari, R. V. *Org. Proc. Res. Dev.* **2002**, *4* (5), 342.

(26) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

(27) Hollis, S. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3494.

(28) Francisco, L. W.; Moreno, D. A.; Atwood, J. D. *Organometallics* **2001**, *20*, 4237.

PtS_4 or $PtMe_2$(DPPETS): C, 32.60; H, 2.54; Na, 8.91; P, 6.00. Found: C, 32.37; H, 2.49; Na, 8.53; P, 5.82.

$PtMe_2$(DPPPTS) (refer to Figure 4 for labeling scheme). $^{31}P\{^1H\}$ NMR (D_2O): 4.7 (s, $^1J_{(Pt-P)} = 1730$). ^1H NMR (D_2O): 7.78 (d, $J = 7.2$, 4H, **D**), 7.71 (d, $J = 7.6$, 4H, **B**), 7.58 (br, 4H, **E**), 7.42 (t, $J = 7.6$, 4H, **F**), 2.66 (br, 4H, PCH_2), 1.87 (br-t, 2H, PCH_2CH_2), 0.18 (br, $^2J_{(Pt-H)} = 68.4$, 6H, $PtCH_3$). $^{31}P\{^1H\}$ NMR (d_6-DMSO): 7.0 (s, $^1J_{(Pt-P)} = 1810$). ^1H NMR (d_6-DMSO): 7.86 (br, 4H, **D**), 7.64 (br, 4H, **B**), 7.57 (br, 4H, **E**), 7.41 (t, $J = 7.4$, 4H, **F**), 2.60 (br, 4H, PCH_2), 1.63 (br, 2H, PCH_2CH_2), 0.12 (br, $^2J_{(Pt-H)} = 67.6$, 6H, $PtCH_3$). ^{195}Pt NMR: −4580(t) ppm, $J_{Pt-P} = 1730$ Hz. Anal. Calcd for $C_{29}H_{28}Na_4O_{12}P_2PtS_4$ or $PtMe_2$ (DPPPTS): C, 33.31; H, 2.70; Na, 8.79; P, 5.92. Found: C, 33.19; H, 2.82; Na, 8.69; P, 5.82.

$PtMe_2$(DPPBTS) (refer to Figure 4 for labeling scheme). $^{31}P\{^1H\}$ NMR (D_2O): 21.9 (s, $^1J_{(Pt-P)} = 1820$). ^1H NMR (D_2O): 7.42 (d, $J = 8.4$, 4H, **D**), 7.35 (d, $J = 7.6$, 4H, **B**), 7.26 (t, $J = 8.4$, 4H, **E**), 7.08 (t, $J = 7.6$, 4H, **F**), 2.27 (br, 4H, PCH_2), 1.23 (br, 2H, $PCH_2CH_{2\ ax}$), 1.18 (br, 2H, $PCH_2CH_{2\ eq}$), −0.29 (t, $^3J_{(P-H)} = 6.40$, $^2J_{(Pt-P)} = 66.8$, 6H, $PtCH_3$). $^{31}P\{^1H\}$ NMR (d_6-DMSO): 20.7 (s, $^1J_{(Pt-P)} = 1877$). ^1H NMR (d_6-DMSO): 7.82 (d, $J = 6.4$, 4H, **D**), 7.63 (br, 4H, **B**), 7.57 (br, 4H, **E**), 7.42 (br, 4H, **F**), 2.60 (br, 4H, PCH_2), 1.52 (br, 2H, $PCH_2CH_{2\ ax}$), 1.48 (br, 2H, $PCH_2CH_{2\ eq}$), 0.02 (s, $^2J_{(Pt-H)} = 67.6$, 6H, $PtCH_3$). ^{195}Pt NMR (D_2O): −4667 (t, $^1J_{(Pt-P)} = 1820$). Anal. Calcd for $C_{30}H_{30}Na_4O_{12}P_2PtS_4$ or $PtMe_2$(PPPBTS): C, 34.00; H, 2.85; Na, 8.68; P, 5.85. Found: C, 33.82; H, 2.86; Na, 8.54; P, 5.73.

Synthesis of *cis*-$Pt(Me)_2(TPPTS)_2$. Into a 25 mL Schlenk flask were placed 0.2161 g (0.648 mmol) of Pt(1,5-COD)Me_2, 0.8074 g (1.297 mmol) of TPPTS, and a small stir bar. The flask was sealed with a rubber septum, evacuated, and back-filled with N_2 three times, then left under a continuous flow of N_2. To this flask was added 5 mL of degassed DMSO via airtight syringe. The contents of the flask were stirred for 18 h at room temperature. After the allotted time, CH_2Cl_2 was added to the flask to encourage precipitation. The product was collected via vacuum filtration using a medium glass frit. The product was washed with 3 × 50 mL of CH_2Cl_2, followed by 3 × 50 mL of Et_2O, then dried in vacuo at 80 °C for 24 h. Yield = 0.8925 g (96% based on starting Pt complex). ^{195}Pt NMR (D_2O): −4676 (t, $^1J_{Pt-P} = 1875$ Hz, *cis-Pt*$(Me)_2(TPPTS)_2$). $^{31}P\{^1H\}$ NMR (d_6-DMSO): 29.8 (s, $^1J_{Pt-P} = 1875$ Hz, *cis*-Pt$(Me)_2$-(*TPPTS*)$_2$) 98%, 28.1 (s, *OTPPTS*) 2%. ^1H NMR (d_6-DMSO): 7.8−7.2 (m, TPPTS, 24H), 0.19 (m, $^2J_{Pt-H} = 68$ Hz, *cis*-Pt$(CH_3)_2$-$(TPPTS)_2$, 6H). $^{31}P\{^1H\}$ NMR (D_2O): 34.7 (s, *OTPPTS*) 2%, 30.3 (s, $^1J_{Pt-P} = 1875$ Hz, *cis*-Pt$(Me)_2$(*TPPTS*)$_2$) 98%. ^1H NMR (D_2O): 7.8−7.2 (m, TPPTS, 24H), 0.32 (m, $^2J_{Pt-H} = 68$ Hz, *cis*-Pt$(CH_3)(TPPTS)_2$, 6H). Anal. Calcd for $C_{40}H_{36}Na_6O_{19}P_2PtS_7$, $Pt(CH_3)_2(TPPTS)_2$·DMSO: C, 33.36; H, 2.52; Na, 9.58; P, 4.30. Found: C, 32.98; H, 2.43; Na, 9.39; P, 4.14.

Synthesis of PtClMe(LL). Into a small (100 mL) Schlenk flask 150 mg of PtCl(1,5-COD)Me, 1 molar equiv of LL, and a stir bar were added. Then the apparatus was back-filled with N_2(g) three times. Under N_2(g) flow, 5.0 mL of DMSO was added. After all solids had dissolved and were stirred for 5 min, 50 mL of CH_2Cl_2 was added to facilitate precipitation. This crude product was then collected on a fine-grain sintered frit and washed with 2 × 50 mL of CH_2Cl_2. Recrystallization of this from MeOH with $MeNO_2$ yielded the final product. Before being sent out for elemental analysis this was dried under vacuum at 90 °C.

PtClMe(DPPETS). ^1H NMR (D_2O): 8.0−7.5 (16H, *aromatic hydrogens*), 2.42 (br-d, $^3J_{(P-H)} = 28.0$, 2H, PCH_2 *trans* to Cl), 2.25 (br-d, $^3J_{(P-H)} = 24.0$, 2H, PCH_2 *trans* to Me), 0.24 (br, 3H, $PtCH_3$). ^1H NMR (D_2O) at 60 °C: ignoring everything except $PtCH_3$, 0.80 (d, $^3J_{(P-H)} = 4.4$, $^2J_{(Pt-H)} = 44.0$, 3H). $^{31}P\{^1H\}$ NMR (D_2O) VT at 60 °C: 49.4 (s, $^1J_{(Pt-P)} = 1730$, P *trans* to Me), 44.6 (s, $^1J_{(Pt-P)} = 4310$, P *trans* to Cl). ^{195}Pt NMR (D_2O): −4585 (dd, $^1J_{(Pt-P)} = 1720$, $^1J_{(Pt-P)} = 4310$). Anal. Calcd for $C_{27}H_{23}ClNa_4O_{12}P_2PtS_4$ or PtClMe(DPPETS): C, 30.82; H, 2.20; P, 5.89; Cl, 3.37; Na, 8.74. Found: C, 30.58; H, 2.42; P, 5.73; Cl, 3.24; Na, 8.59.

Table 5. Products of $PtMe_2(L_2)$ at Various pH's

L_2	pH[a]	product(s)
DPPETS[b]	6.5 (8.3)	CH_4 (trace), $PtMe_2$(DPPETS)
DPPETS	0.98 (1.06)	CH_4, $PtCl_2$(DPPETS)
DPPETS	2.0 (6.8)	CH_4, Pt(Cl)(Me)(DPPETS), $Pt(Me)(H_2O)(DPPETS)^+$
DPPETS	3.0 (7.8)	CH_4(trace), $PtMe_2$(DPPETS)
DPPETS	4.1 (8.1)	CH_4(trace), $PtMe_2$(DPPETS)
DPPPTS[b]	6.5 (8.3)	$PtMe_2$(DPPPTS)
DPPPTS	0.98 (0.98)	CH_4, $PtCl_2$(DPPPTS)
DPPPTS	2.0 (2.9)	CH_4, Pt(Cl)(Me)(DPPPTS), $PtMe(H_2O)(DPPPTS)^+$
DPPPTS	3.0 (7.9)	CH_4(trace), $PtMe_2$(DPPPTS)
DPPPTS	4.1 (8.3)	CH_4(trace), $PtMe_2$(DPPPTS)
DPPBTS[b]	6.5 (8.2)	$PtMe_2$(DPPBTS)
DPPBTS	0.98 (0.98)	CH_4, $PtCl_2$(DPPBTS)
DPPBTS	2.0 (6.7)	CH_4, Pt(Cl)(Me)(DPPBTS), $PtMe(H_2O)(DPPBTS)^+$
DPPBTS	3.0 (7.6)	CH_4(trace), $PtMe_2$(DPPBTS)
DPPBTS	4.1 (8.0)	CH_4(trace), $PtMe_2$(DPPBTS)
2TPPTS[b]	6.5 (8.4)	$PtMe_2(TPPTS)_2$
2TPPTS[c]	0.98 (1.07)	CH_4, *cis*- and *trans*-Pt(Cl)(Me)$(TPPTS)_2$
2TPPTS	2.0 (6.5)	CH_4, *cis*- and *trans*-Pt(Cl)(Me)$(TPPTS)_2$, *cis*- and *trans*-$Pt(H_2O)(Me)(TPPTS)_2^+$
2TPPTS	3.0 (8.3)	CH_4(trace), $PtMe_2(TPPTS)_2$
2TPPTS	4.1 (8.4)	CH_4(trace), $PtMe_2(TPPTS)_2$

[a] Before addition; after addition is in parentheses. [b] Triply distilled water. [c] After 30 min.

Pt(Cl)(Me)(DPPPTS). $^{31}P\{^1H\}$ NMR (D_2O): 7.2 (d, $^2J_{(P-P)} = 22.9$,$^1J_{(Pt-P)} = 1630$, P *trans* to Me) & 6.7 (d, $^2J_{(P-P)} = 22.9$,$^1J_{(Pt-P)} = 4270$, P *trans* to Cl) 96%, 12.2 (br) and 0.66 (br) minor < 4%. ^1H NMR (D_2O): 7.9−7.5 (16H, *aromatic hydrogens*), 2.85 (br-s, 2H, PCH_2 *trans* to Cl), 2.67 (br-s, 2H, PCH_2 *trans* to Me), 1.92 (br-m, 2H, PCH_2CH_2), 0.25 (m, 3H, $PtCH_3$). ^{195}Pt NMR (D_2O): −4571 (dd, $^1J_{(Pt-P)} = 1630$, $^1J_{(Pt-P)} = 4270$). Anal. Calcd for $C_{28}H_{25}ClNa_4O_{12}P_2PtS_4$ or PtClMe(DPPPTS): C, 31.54; H, 2.36; P, 5.81; Cl, 3.33; Na, 8.62. Found: C, 31.38; H, 2.45; P, 5.63; Cl, 3.21; Na, 8.54.

Pt(Cl)(Me)(DPPBTS). $^{31}P\{^1H\}$ NMR (D_2O): 23.05 (br, $^1J_{(Pt-P)} = 1750$) and 20.53 (br, $^1J_{(Pt-P)} = 4460$) major. ^1H NMR (D_2O): 8.0−7.4 (br-m, 16 H, *aromatic hydrogens*), 2.69 (br, 4H, PCH_2), 1.53 (br, 4H, PCH_2CH_2), 0.26 (br, 3H, $PtCH_3$). ^{195}Pt NMR (D_2O): −4626 (dd, $^1J_{(Pt-P)} = 1750$, $^1J_{(Pt-P)} = 4460$). Anal. Calcd for $C_{29}H_{27}ClNa_4O_{12}P_2PtS_4$ or PtClMe(DPPBTS): C, 32.24; H, 2.52; P, 5.73; Cl, 3.28; Na, 8.51. Found: C, 32.34; H, 2.57; P, 5.41; Cl, 3.40; Na, 8.42.

Synthesis of *trans*-$Pt(Cl)(Me)(TPPTS)_2$. Into a 25 mL Schlenk flask was placed 0.1501 g (0.425 mmol) of Pt(Cl)(1,5-COD)Me, 0.5311 g (0.853 mmol) of TPPTS, and a small stir bar. The flask was sealed with a rubber septum, evacuated, and back-filled with N_2 three times, then the flask was left under a continuous flow of N_2. To the flask was added 5 mL of degassed DMSO via airtight syringe. The contents of the flask were stirred for 18 h at room temperature. After the allotted time, CH_2Cl_2 was added to encourage precipitation. The product was collected via vacuum filtration and washed with 3 × 50 mL of CH_2Cl_2 and 3 × 50 mL of Et_2O and dried in vacuo at 80 °C for 24 h. Yield = 0.5789 g (93.3% based on starting Pt complex). ^{195}Pt NMR (d_6-DMSO): −4662 (t, $^1J_{Pt-P} = 3176$ Hz, *trans-Pt*(Cl)(Me)$(TPPTS)_2$). $^{31}P\{^1H\}$ NMR (d_6-DMSO): 33.3 (s, $^1J_{Pt-P} = 3176$ Hz, *trans*-Pt(Cl)(Me)(*TPPTS*)$_2$) 95%, 26.6 (s, *OTPPTS*) 5%. ^1H NMR (d_6-DMSO): 7.8−7.2 (m, OTPPTS), −0.33 (t, $^2J_{Pt-H} = 76$ Hz, *trans*-Pt(Cl)(CH_3)-$(TPPTS)_2$). $^{31}P\{^1H\}$ NMR (D_2O): 34.7 (s, *OTPPTS*) 4%, 32.9 (s, $^1J_{Pt-P} = 3226$ Hz, *trans*-$[Pt(D_2O)(Me)(TPPTS)_2]^+$) 20%, 31.9 (s, $^1J_{Pt-P} = 3176$ Hz, *trans*-Pt(Cl)(Me)(*TPPTS*)$_2$) 76%. ^1H NMR (D_2O): 7.8−7.2 (m, TPPTS), 0.04 (t, $^2J_{Pt-H} = 73$ Hz, *trans*-$[Pt(D_2O)(CH_3)(TPPTS)_2]^+$), −0.11 (t, $^2J_{Pt-H} = 76$ Hz, *trans*-Pt(Cl)-$(CH_3)(TPPTS)_2$). Anal. Calcd for $C_{39}H_{33}ClNa_6O_{19}P_2PtS_7$, *trans*-

$Pt(Cl)(Me)(TPPTS)_2 \cdot DMSO$: C, 32.07; H, 2.28; Cl, 2.43; Na, 9.44; P, 4.24. Found: C, 31.81; H, 2.20; Cl, 2.56; Na, 9.25; P, 4.02.

Solution Chemistry of $PtMe_2(L_2)$. A clean, dry 2 dram vial was loaded with $(1.08-2.70) \times 10^{-5}$ mol of $PtMe_2(L_2)$. Then, the complex was dissolved in 2.0 mL of 0.105 M HCl, 1.07×10^{-2} M HCl, 9.55×10^{-4} M HCl, 8.1×10^{-5} M HCl, and triply distilled water. The pH of these solutions was then recorded. Finally the NMR spectrum was recorded with a d_6-DMSO insert used as the instrument lock. The products are summarized in Table 5, and the detailed NMR characterizations are provided in the Supporting Information.

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Supporting Information Available: Detailed NMR characterization data and spectra and plots of amounts versus time are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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