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Stable Cationic Dimethyl(hydrido)platinum(IV) Complex

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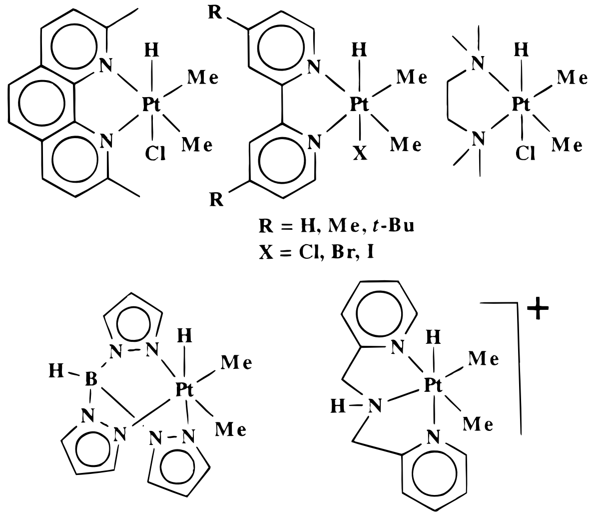
The complex [$PtMe_2$(9N3)], **1**, 9N3 = 1,4,7-triazacyclononane, undergoes protonation by triflic acid and, reversibly, even by methanol to form the cationic complex [$PtHMe_2$(9N3)]$^+$, **2**, which is thermally stable up to 190 °C in the solid state as the triflate salt. Oxidation of **1** or **2** by H_2O_2 or by H_2O/O_2 gives the hydroxy complex [Pt(OH)Me_2(9N3)]$^+$, which can be reversibly protonated to the aqua complex [Pt(OH_2)Me_2(9N3)]$^{2+}$.

Introduction

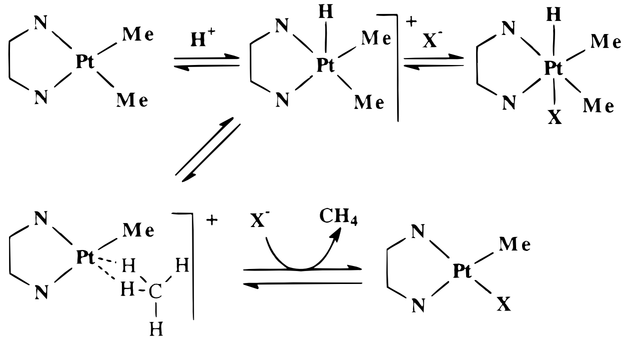
Transition metal alkyl(hydride) complexes are important intermediates in many catalytic processes, ranging from homogeneous hydrogenation of unsaturated organic compounds to the functionalization of alkanes. In particular, the activation of alkanes by platinum(II) complexes is believed to occur by C−H oxidative addition to give alkyl(hydrido)platinum(IV) intermediates, and so there has been intense interest in the synthesis and properties of such complexes.[1−8]

Alkyl(hydrido)platinum(IV) complexes were first proposed as reaction intermediates in the protonolysis of methylplatinum(II) bonds,[3] but the first examples were directly detected relatively recently.[4] These complexes contained bidentate nitrogen-donor ligands and included examples such as [Pt(H)XMe_2(NN)] (X = Cl, Br, I; NN = 2,9-dimethyl-1,10-phenanthroline, 2,2′-bipyridine, or its derivatives, and tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) (Chart 1). They were identified by NMR techniques at low temperature, but decomposed easily at room temperature by reductive elimination to give RH and the corresponding platinum(II) complex [PtXR(NN)].

Chart 1. Some Dimethyl(hydrido)platinum(IV) Complexes



Scheme I[a]



[a]NN = diimine or diamine ligand, X = anionic ligand.

The mechanism for the reductive elimination is believed to involve the dissociation of the ligand trans to the hydride to form a cationic, 5-coordinate intermediate [$PtHR_2$(NN)]$^+$, which then undergoes reductive elimination of RH as illustrated in Scheme 1.[1,4] Hence, it was deduced that if the methyl(hydrido)platinum(IV) complex contained no easily dissociated ligand, the complexes should be thermally stable. This was shown to be the case as demonstrated by the thermally stable complexes [$PtHMe_3$(bu_2bpy)] (bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine)[5] and [$PtHMe_2${$(pz)_3BH$−N,N′,N″}] ([$(pz)_3BH$]$^-$ = tripyrazol-1-ylborate, Chart 1), which is stable in toluene solution and decomposes only at 140 °C;[6] the derivative from tris(3,5-dimethylpyrazolyl)borate was stable in the solid state up to 190 °C.[6a] The

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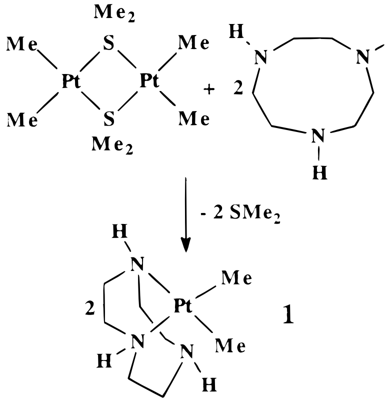
tripyrazolylborate ligand is anionic and has a strong preference for binding as a *fac*-tridentate ligand, and both factors should serve to stabilize platinum(IV) with respect to platinum(II).[6] The more flexible, neutral tridentate ligand bis(2-pyridylmethyl)amine (BPMA) gives the cationic complex $[PtHMe_2(BPMA)]^+$, which has intermediate thermal stability and decomposes to give methane and $[PtMe(BPMA)]^+$ over a period of about 1 day at room temperature.[7] The BPMA ligand is coordinated in a bidentate fashion in the platinum(II) complex $[PtMe_2(BPMA)]$, as a *fac*-tridentate ligand in $[PtHMe_2(BPMA)]^+$, and as a *mer*-tridentate ligand in $[PtMe(BPMA)]^+$, and so it was not obvious if the lower thermal stability of $[PtHMe_2(BPMA)]^+$ compared to $[PtHMe_2\{(pz)_3BH\}]$ was a result of the greater ligand flexibility of BPMA or of the positive charge in $[PtHMe_2(BPMA)]^+$. This prompted the present study of the related chemistry using the neutral ligand 9N3 = 1,4,7-triazacyclononane. Since this ligand, like $HBpz_3^-$, has a strong tendency to bind as a *fac*-tridentate ligand,[9] it should give a thermally stable complex $[PtHMe_2(9N3)]^+$ if this is the stability-determining factor, but the complex should be less stable, like $[PtHMe_2(BPMA)]^+$, if the charge is the more important factor. This paper reports the results of this study, including some unexpected complications resulting from air oxidation.

Results and Discussion

Synthesis and Characterization of a Stable Dimethyl(hydrido)platinum(IV) Complex Cation. The platinum(II) complex $[PtMe_2(9N3)]$, **1**, was prepared by displacement of the weakly bound Me_2S ligands in $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ by the ligand 1,4,7-triazacyclononane (9N3) in dry toluene under a nitrogen atmosphere (eq 1). Complex **1** is a white solid that is thermally stable when stored in inert atmosphere but which is decomposed over a period of days by reaction with moist air. The complex is moderately soluble in organic solvents such as acetone, methanol, or dichloromethane. In the ^1H NMR spectrum, complex **1** gives a methylplatinum resonance at $\delta = 0.18$ with satellites due to the coupling $^2J(PtH) = 91$ Hz, a value typical of square-planar platinum(II) complexes.[4-8] It is therefore deduced that the 9N3 ligand is bidentate in **1**. At −40 °C, the NCH_2 protons of the 9N3 ligand give rise to six resonances as expected for the proposed structure, but these resonances are significantly broader at room temperature, perhaps due to the onset of a fluxional process involving exchange between free and coordinated N-donors. The methylplatinum resonance was well resolved at all temperatures. The NH resonances were not resolved.



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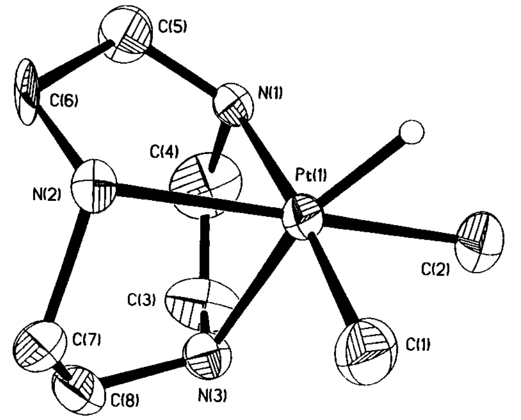

Figure 1. View of the molecular structure of the cationic complex **2**. Disorder at C(6) and C(7) is not shown, and the only hydrogen atom shown is the PtH atom, whose position was not refined and which is shown as a sphere of arbitrary radius.

A solution of complex **1** in dry methanol under a nitrogen atmosphere reacted with triflic acid (CF_3SO_3H) to form a yellow solution, from which the dimethyl(hydrido)platinum(IV) complex $[PtHMe_2(9N3)][CF_3SO_3]$, **2**, could be precipitated as a white solid by addition of dry diethyl ether. In the solid state, **2** was stable for at least 2 months at room temperature when exposed to the moist air atmosphere, as determined by ^1H NMR. Thermogravimetric analysis under nitrogen atmosphere showed that complex **2** does not begin to decompose until 197 °C, and it is stable for at least 2 h when held at a constant temperature of 155 °C. Thus, complex **2** is among the most thermally stable methyl(hydrido)metal complexes known,[5,6,8] and it is clear that it is the presence of the strongly bound *fac*-tridentate ligand that leads to thermal stability, whether the product is neutral or cationic.[6-8] In addition, since the 9N3 ligand is not bulky, it is now clear that steric blocking is not necessary in thermally stable complexes of this kind.[6]

The ^1H NMR spectrum of complex **2** in acetone-d_6 displayed a single methylplatinum resonance at $\delta = 0.63$ with a coupling constant $^2J(PtH) = 69$ Hz, in the range expected for a platinum(IV) complex.[4,6] The hydride resonance was observed at $\delta = -19.46$, with coupling $^1J(PtH) = 1332$ Hz, similar to values in related complexes.[4-8] The 9N3 ligand gave resonances at $\delta = 5.75$ [1H] and 5.28 [2H] due to the NH protons and two broad multiplets at $\delta = 3.17$ and 3.55 due to the CH_2 protons of the ligand. According to symmetry, there should be six CH_2 resonances, but there is accidental overlap, and only two equal intensity peaks, assigned to *exo* and *endo* protons respectively, are resolved. The infrared spectrum showed the Pt−H stretching vibration at 2224 cm^{-1}.

The proposed structure for **2** was confirmed by an X-ray structure determination. The molecular structure is shown in Figure 1, and crystal data and selected bond lengths and angles are given in Tables1 and 2. The hydride ligand was tentatively located in the structure determination, but it could not be refined; its position is shown in Figure 1, but the bond parameters are

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Table 1. Crystal Data and Structure Refinement for 2

formula, fw	$C_9H_{19}F_3N_3O_3PtS$, 501.42
temp	294(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	P2(1)/n
cell dimens	$a = 10.0462(2)$ Å $b = 15.8421(6)$ Å $c = 10.5005(4)$ Å $\beta = 95.245(1)°$
volume, Z	1664.2(1) $Å^3$, 4
density (calcd)	2.001 Mg/m^3
abs coeff	8.595 mm^{-1}
$F(000)$	956
θ range	2.33−22.49°
no. of reflns collected	8395
no. of ind reflns	2128 [R(int) = 0.1024]
no. of data/restraints/params	2119/0/231
goodness-of-fit on F^2	1.106
final R indices [$I > 2\sigma(I)$]	R1 = 0.0496, wR2 = 0.1222
R indices (all data)	R1 = 0.0559, wR2 = 0.1318

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 2

Pt(1)−C(1)	1.98(2)
Pt(1)−C(2)	2.059(14)
Pt(1)−N(1)	2.142(12)
Pt(1)−N(2)	2.157(8)
Pt(1)−N(3)	2.170(8)
C(1)−Pt(1)−C(2)	87.2(7)
C(1)−Pt(1)−N(1)	175.1(5)
C(2)−Pt(1)−N(1)	95.1(6)
C(1)−Pt(1)−N(2)	97.0(6)
C(2)−Pt(1)−N(2)	174.9(6)
N(1)−Pt(1)−N(2)	80.5(3)
C(1)−Pt(1)−N(3)	95.4(5)
C(2)−Pt(1)−N(3)	96.0(5)
N(1)−Pt(1)−N(3)	80.1(3)
N(2)−Pt(1)−N(3)	80.8(4)

unreliable and are not discussed. The structure shows the expected distorted octahedral stereochemistry at platinum, with the 9N3 ligand coordinated in the *fac*-tridentate fashion and with the two methyl groups and the hydride in the other three positions. The distance PtN(3) = 2.17(1) Å, for the nitrogen trans to hydride, appears longer than PtN(1) = 2.14(1) Å and PtN(2) = 2.16(1) Å, for the nitrogen atoms trans to methyl, consistent with the higher trans-influence of hydride,[6] but the difference is barely statistically significant. Two of the three NH groups are involved in hydrogen bonding to bridging triflate anions, and this leads to formation of unusual one-dimensional chains as shown in Figure 2.

Acid−Base Properties of Complex 2 and H/D Exchange Reactions. The NMR spectrum of a solution of **2** in acetone-d_6 changed slowly with time. In particular, the hydride (and NH) resonance decreased in intensity over a period of several days and eventually disappeared, while remaining peaks were unchanged. The IR spectrum of a sample of **2** isolated after extended storage in acetone-d_6 showed ν(PtD) = 1599 cm^{-1}, and so it is clear that the reaction involves H−D exchange at the hydride to give $[PtDMe_2(9N3)]^+$, **2***. The IR spectrum also showed that H−D exchange occurred in the NH groups when **2** was dissolved in acetone-d_6 or methanol-d_4, since the product isolated from solution showed ν(ND) = 2419 cm^{-1}. However, even in samples stored for weeks at room temperature, there was no evidence for incorporation of deuterium into the methylplatinum groups, indicating that reversible formation of a methane complex does not occur.[1,4,7] The H−D exchange reaction at the hydride position was reversible, as shown by dissolving $[PtDMe_2(9N3)]^+[CF_3SO_3]^-$ in acetone and showing by ^1H NMR that the hydride was slowly reformed.

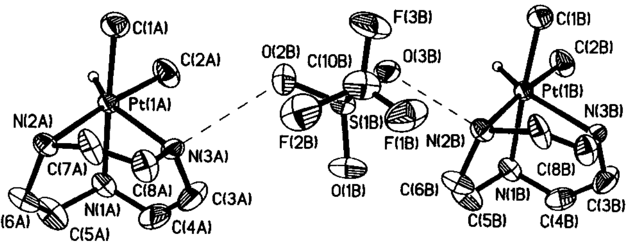
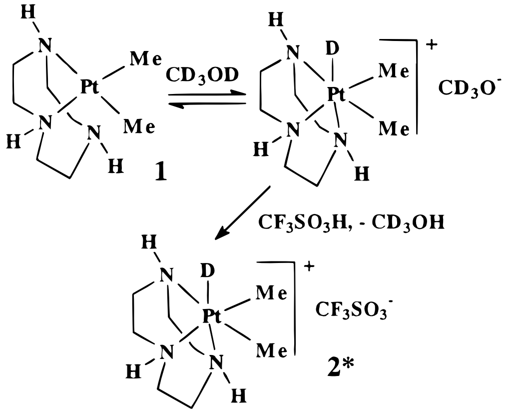


Figure 2. View of the hydrogen bonding between the triflate anion and the NH groups of complex **2**, leading to a linear chain structure. There is disorder in the position of the F atoms of the triflate group that is not illustrated. The H-bonding distances O(2)···N(3) = 2.94(3) Å and O(3)···N(2) = 2.91(3) Å.

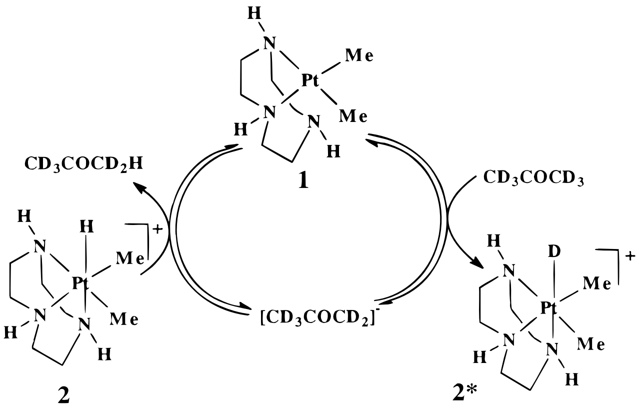
Scheme 2



Complex **1** is a rather strong base, as shown by the following observations. Dissolution of **1** in methanol-d_4 gave a solution containing only $[PtDMe_2(9N3)]^+[CD_3O]^-$, as deduced by the NMR spectrum. In particular, the observation of the methylplatinum resonance at δ = 0.60 with $^2J(PtH)$ = 69 Hz shows clearly that oxidation to platinum(IV) had occurred and the parameters are essentially the same as those of **2** in acetone-d_6. However, evaporation of the solution gave back the starting complex **1**, identified by its NMR spectrum in acetone-d_6. Thus, there is an easy equilibrium in methanol; at low concentration (complex **1** has only moderate solubility) the equilibrium favors **2,** but as the solution is concentrated, **1** is reformed. Addition of excess pyridine to a solution of **2** in acetone-d_6 did not cause deprotonation to reform **1**, whereas addition of excess sodium hydroxide did. Hence, in neutral or acidic solution, it is likely that deprotonation of **2** to form **1** will be unfavorable. These data are incorporated into the reaction sequence shown in Scheme 2. As expected, dissolution of **1** in methanol-d_4 followed by addition of triflic acid gave the cation $[PtDMe_2(9N3)]^+$, showing no hydride resonance in the ^1H NMR spectrum.

There are two likely mechanisms for the H−D exchange reactions of **2** and **2***. One involves reversible deprotonation to give **1,** and the other involves reversible protonation to yield a short-lived dihydrogen (HD)

Scheme 3

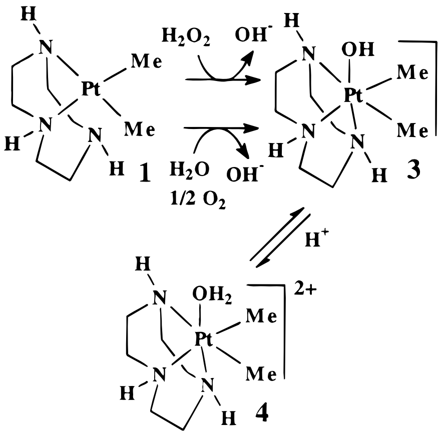


complex $[PtMe_2(HD)(9N3)]^{2+}$. A comparison was made of the rates of H/D exchange of solutions of **2** in acetone-d_6 either alone, with added triflic acid, with added pyridine, or with a catalytic amount of the platinum(II) precursor **1**. As monitored by ^1H NMR, the first three solutions all reacted slowly, each giving about 20% reaction after 1 day, but the solution containing **1** underwent complete H/D exchange within minutes at room temperature. Added **1** is equivalent to adding a strong base (see above), and so it is clear that the easiest route to H/D exchange involves reversible deprotonation to give **1,** as shown in Scheme 3. Note that a direct proton transfer between complexes **1** and **2** may occur,[5] but it does not lead to H/D exchange.

Complications Caused by Air Oxidation. Complex **2** can be prepared in pure form in methanol solution, but earlier attempts at its synthesis in other solvents were only partly successful. For example, the reaction of **1** with acids, including triflic acid, CF_3CO_2H, and $H[BF_4]$, in THF gave a mixture of **2** and a second complex. If a stoichiometric amount of acid was used, the second complex **3** was characterized by a methylplatinum resonance at $\delta = 1.03$, $^2J(PtH) = 68$ Hz, but if excess acid was used, the second complex **4** was characterized by a methylplatinum resonance at $\delta = 1.30$, $^2J(PtH) = 65$ Hz. Neither of these complexes gave a hydride resonance in the ^1H NMR spectrum. The concentrations of these secondary products were lower if the THF was rigorously dry and if the reactions were carried out under dry nitrogen, but it was very difficult to avoid their formation as minor impurities.

Complex **3** could be prepared independently and in spectroscopically pure form by reaction of **1** with hydrogen peroxide, and it is characterized as the hydroxo complex $[PtMe_2(OH)(9N3)]OH$ (Scheme 4). Complex **3** was hygroscopic, and so it was difficult to obtain in analytically pure form, but it reacted with excess triflic acid to give complex **4**, which was characterized as the aqua complex $[PtMe_2(OH_2)(9N3)][CF_3SO_3]_2$. This protonation was very easily reversible, as shown by the formation of complex **3**, identified by its ^1H NMR spectrum, on reaction of **4** with 1 equiv of KOH. Complex **4** was also formed rapidly and in spectroscopically pure form by reaction of **1** in THF solution with water and triflic acid under an atmosphere of air. In this reaction, it is clear that oxygen is a reagent, since the similar reaction under nitrogen atmosphere gave the hydride **2** as major product.

Scheme 4



Complex **4** can be formed by reaction of a solution of **2**, as the triflate salt, with hydrogen peroxide and triflic acid, but the reaction is slow, requiring 5 days to go to completion. The reaction of **1** with hydrogen peroxide and triflic acid to give **4** is much faster and is certainly complete within an hour under similar conditions. Clearly, the reaction of **1** with hydrogen peroxide to give **3** or **4** does not occur by a mechanism in which the hydride **2** is formed and then oxidized, but **4** must be formed by direct reaction of hydrogen peroxide with **1**. Similarly, the hydride **2** is only slowly decomposed (over a period of weeks) to **4** by reaction with oxygen and excess acid, so the rapid formation of **4** by reaction of **1** with H_2O/O_2 cannot involve the intermediate formation of **2**.

There have been several independent studies of the oxidation of platinum(II) complexes using alcohols, water, hydrogen peroxide, oxygen, or combinations of these reagents, as illustrated in eqs 2−5, but it has proved difficult to determine the detailed mechanisms involved.[9−12] The oxidation of $[PtMe_2(bipy)]$ by hydrogen peroxide (eq 2) is simple in stoichiometry but probably more complex mechanistically,[12] and the oxidation of the same compound by alcohols is now known to require a co-oxidant such as O_2 (eq 3).[10] On the other hand, the oxidation of $[PtMe_2(HBpz_3)]^-$ by water occurs without a co-oxidant according to eq 4, $N_3 = HBpz_3$, forming hydrogen as a byproduct.[11] An interesting example involving the 9N3 ligand, which involves oxidation of a platinum(II) complex by O_2 to form a binuclear bis(peroxide) complex, is shown in eq 5.[9] It was proposed that the reaction occurred by way of a short-lived monodentate peroxoplatinum(IV) intermediate, which then displaced a dimethyl sulfoxide (dmso) ligand from another molecule to yield the isolated product (eq 5). A similar intermediate could form by reaction of complex

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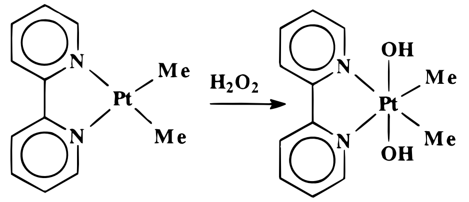

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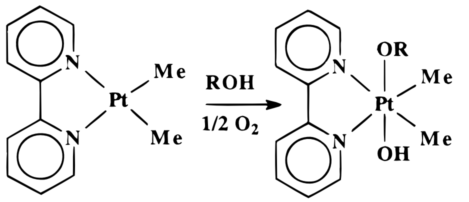

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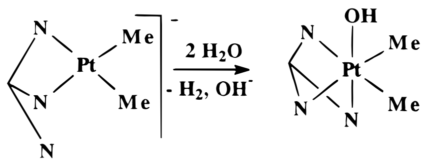

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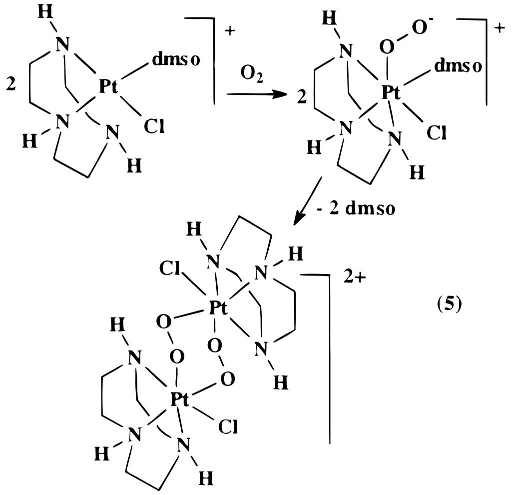
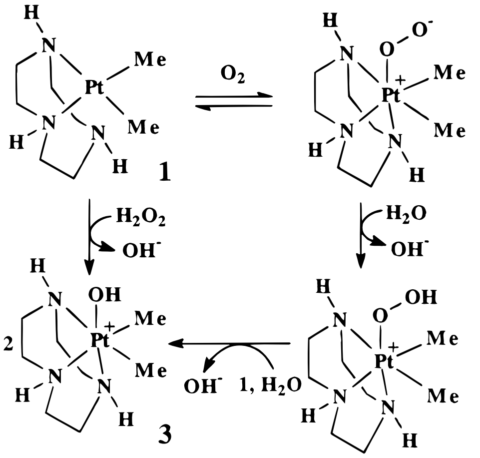


(5)

1 with oxygen (Scheme 5), but the first-formed intermediate contains no easily displaced ligand in this case and is likely to undergo reversible protonation by water to give a hydroperoxide complex $[PtMe_2(OOH)(9N3)]^+$. The simplest way to form **3** from this would be to displace hydroperoxide by hydroxide (the hydroperoxide would then oxidize a second equivalent of **1**, see Scheme 5). However, this ligand substitution involving a Pt−O bond trans to nitrogen at platinum(IV) is likely to be slow, and it is more likely that a bimolecular reaction occurs with **1** to cleave the O−O bond, as shown in Scheme 5. No methoxoplatinum(IV) complexes were detected when the oxidation occurred in methanol solvent (compare eq 3),[10] consistent with the proposed mechanism. However, more complex mechanisms, including radical chain processes,[10] cannot be discounted.

It is not clear how the slow conversion of **2** to **3** or **4** occurs. It might occur by deprotonation of **2** to give **1** (in an equilibrium that is very unfavorable), followed by reaction of **1** with oxygen or hydrogen peroxide, as suggested for the analogous tripyrazolylborate complexes.[11] However, it is not possible to eliminate an alternative mechanism involving slow direct attack by the oxidant at the PtH group of **2**. In none of the reactions forming **3** or **4**, when carried out in sealed NMR tubes, was it possible to detect dihydrogen as a product by its ^{1}H NMR spectrum. Another mechanism might involve one-electron oxidation of **2** by the oxidant to give transient $[PtHMe_2(9N3)]^{2+}$, but by analogy with chemistry of $[RhMe_3(9N3)]$,[13] this would be expected to lead to reductive elimination of methane or ethane and so is improbable.

Scheme 5



Experimental Section

NMR spectra were recorded by using Varian Gemini 300 or 200 MHz spectrometers, and chemical shifts are reported relative to TMS. Elemental analysis were carried out by Guelph Chemical Laboratories Ltd. Diethyl ether and toluene were dried over sodium under nitrogen, while methanol was dried over magnesium under nitrogen. All reactions were carried out under N_2, either using Schlenk techniques or in a drybox. The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ was prepared according to the literature method.[14]

$[PtMe_2(9N3)]$. In a Schlenk flask under N_2, $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (240 mg, 0.418 mmol) and 9N3 (104 mg, 0.805 mmol) were dissolved in dry toluene, and the solution was stirred for 2 h. A white precipitate formed. The solvent was removed by syringe, and the product was washed with dry toluene (3 × 10 mL) and then dried under vacuum. Yield: 203.1 mg, 71%. Anal. Calcd for $C_8H_{21}N_3Pt$: C, 27.11; H, 5.98; N 11.86. Found: C, 26.29; H, 6.05; N, 11.16. NMR (acetone-d_6): $\delta(^1H) = 4.05$ [m, 2H, CH_2]; 3.19 [m, 2H, CH_2]; 3.17 [m, 2H, CH_2]; 2.96 [m, 2H, CH_2]; 2.87 [m, 2H, CH_2]; 2.65 [m, 2H, CH_2]; 0.18 [s, 6H, $^2J(PtH) = 91$ Hz, Pt−Me].

$[PtHMe_2(9N3)][CF_3SO_3]$. To a suspension of $[PtMe_2(9N3)]$ (42.2 mg, 0.119 mmol) in dry methanol (1.5 mL) was added CF_3SO_3H (11.5 μL, 0.139 mmol) to give a pale yellow solution.The mixture was stirred for 3 min, and then dry diethyl ether (35 mL) was added to precipitate the product as a white solid. The solvent was removed by syringe, and the product was dried under vacuum. Yield: 32.9 mg, 55%. Decomp at 197 °C. Anal. Calcd for $C_9H_{22}N_3F_3O_3SPt$: C, 21.40; H, 4.40; N, 8.33. Found: C, 21.56; H, 4.20; N, 8.20%. NMR (acetone-d_6): δ (^{1}H) = 5.75 [br, 2H, NH]; 5.28 [br, 1H, NH]; 3.17 [m, 6H, CH_2]; 3.35 [m, 6H, CH_2]; 0.63 [s, 6H, $^2J(PtH) = 70$ Hz, Pt-Me]; −19.46 [s, 1H, $^1J(PtH) = 1339$ Hz, PtH]. δ (^{13}C) = 51.94 [s, CH_2]; 50.52 [s, CH_2]; 50.03 [s, CH_2]; −21.70 [s, $^1J(PtC) = 608$ Hz, Pt−Me]. IR (Nujol): $\nu_{Pt-H} = 2224$ cm^{-1}, $\nu_{N-H} = 3251$ cm^{-1}.

H−D Exchange Reaction. A sample of $\mathbf{2}^+CF_3SO_3^-$ in acetone-d_6 was stored for 1 week, during which time the resonances due to the PtH and NH protons decreased in intensity, while the other peaks in the ^{1}H NMR spectrum were unchanged. The sample was evaporated, and the IR spectrum

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(13) Fooladi, A.; Tilset, M. *Inorg. Chem.* **1997**, *36*, 6021.

(14) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.

of the product **2*** was recorded. IR (Nujol): ν(ND) = 2419 (ms); ν(PtD) = 1599 (ms) cm^{-1}. Only very weak peaks due to ν(NH) and ν(PtH) were observed. The reaction was reversed on dissolution of **2*** in acetone. Similar H−D exchange occurred in CD_3OD solution.

[Pt(OH)Me$_2$(9N3)]OH. To a suspension of [PtMe$_2$(9N3)] (13 mg, 0.037 mmol) in acetone-d_6 (0.5 mL) in an NMR tube was added H_2O_2 (30 μL, 0.29 mmol) by microsyringe. The tube was shaken, and a colorless solution was formed rapidly. The solution was allowed to react for 1 h before the NMR spectrum was obtained. ^{1}H NMR (acetone-d_6): $\delta = 1.03$ [s, 6H, ^2J(PtH) = 68 Hz, PtMe]; 3−3.5 [br m, 12H, CH$_2$]; 5.75 [br, 2H, NH]; 7.15 [br, 1H, NH]. The hydroxo proton resonance was not resolved.

[Pt(OH$_2$)Me$_2$(9N3)][CF$_3$SO$_3$]$_2$. To a suspension of [PtMe$_2$(9N3)] (10 mg, 0.028 mmol) in acetone-d_6 (0.5 mL) in an NMR tube was added a large excess of H_2O_2 (20 μL, 0.20 mmol) and CF_3SO_3H (0.03 mmol) by microsyringe. The tube was shaken, and a pale yellow solution was formed. The solution was allowed to react for 2 h. before the NMR spectrum was obtained. ^{1}H NMR (acetone-d_6): $\delta = 1.30$ [s, 6H, ^2J(PtH) = 65 Hz, PtMe]; 3.13 [br, 4H, CH$_2$]; 3.42 [br, 6H, CH$_2$]; 3.60 [br, 2H, CH$_2$]; 6.25 [br, 2H, NH]; 8.25 [br, 1H, NH]. Note that under these conditions a broad, intense OH resonance is observed due to excess H_2O_2/H_2O at $\delta = 4.4$.

Preparative reactions were carried out by suspending [PtMe$_2$(9N3)] (60 mg, 0.17 mmol) in acetone (3 mL) and adding H_2O_2 (100 μL, 0.98 mmol) and triflic acid (15 μL, 0.17 mmol). The solution was stirred for 3 h. $MgSO_4$ was added to remove free water, and the mixture was stirred for 10 min. The solution was filtered, and dry pentane (40 mL) was added to precipitate the product as a white solid. The solvent was removed by syringe, and the product was dried under vacuum. Yield: 11.3 mg, 10%. Anal. Calcd for $C_{10}H_{23}N_3F_6O_7S_2Pt$: C, 17.9; H, 3.5; N, 6.3. Found: C, 19.1; H, 3.9; N, 6.4 (the poor analysis is due to a small impurity of **3**, as the triflate salt, formed by deprotonation during the workup). ^{1}H NMR (acetone-d_6): $\delta = 1.27$ [s, ^2J(PtH) = 65 Hz, PtMe]; 3.20, 3.40, 3.60 [br, CH$_2$]; 6.14 [br, NH]; 7.65 [br, NH]. The expected resonance from the aqua ligand was not resolved.

Structure Determination. Crystals of **2** were grown from a saturated solution of acetone-d_6, and a crystal (size 0.33 × 0.25 × 0.16 mm) was mounted in a glass capillary. Crystal data and refinement parameters for **2** are listed in Table 1, and selected interatomic distances and angles are listed in Table 2. Data were collected by using a Nonius Kappa-CCD system. Unit cell parameters were calculated from reflections obtained from 10 consecutive data images collected at ϕ intervals of 1° using DENZO (Nonius, 1998). One full hemisphere of data was collected by incremental ϕ scans of 1° followed by 1° ω scans to capture cusp data (Nonius COLLECT, 1998). An analysis of systematic absences and intensity statistics indicated the monoclinic space group $P2_1/n$, and this was borne out by successful refinement of the structure. Data were scaled using SCALEPACK (Nonius, 1997), and empirical absorption corrections were applied using redundant data and XPREP (Shelxtl 5.03). Full-matrix least-squares refinement on F^2 was performed after solving using Patterson methods and the solution package SHELXTL 5.03 (Sheldrick, G. M., Madison, WI). Anisotropic thermal parameters were applied to all non-hydrogen atoms. There was disorder in the atoms C6, C7, and the F atoms, and all were successfully modeled with 50% disorder. In the final difference map, an electron density peak was found in the area where the PtH ligand was expected, but attempted refinement was unsuccessful. The largest residual peak was found to be associated with Pt1 (1.350 e Å^{-3}).

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of **2** and crystal data for **1**, PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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