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Reactivity of a Dimethylplatinum(II) Complex with the Bis(2-pyridyl)dimethylsilane Ligand: Easy Silicon−Carbon Bond Activation

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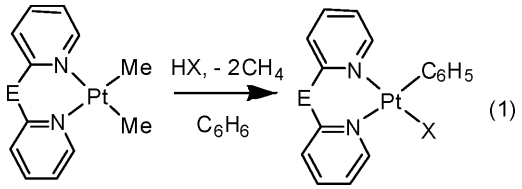
Supporting Information

ABSTRACT: The compound $[PtMe_2(bps)]$ (**1**; bps = bis(2-pyridyl)-dimethylsilane) undergoes easy oxidative addition with bromine, iodine, methyl iodide, or methyl triflate to give $[PtBr_2Me_2(bps)]$, $[PtI_2Me_2(bps)]$, $[PtIMe_3(bps)]$, or $[PtMe_3(OH_2)(bps)][OTf]$, respectively. The complex $[PtIMe_3(bps)]$ is slowly hydrolyzed in solution, with cleavage of the pyridyl−silicon bonds, to give $[PtIMe_3(py)_2]$ and $(Me_2SiO)_n$. In contrast, oxidation of **1** with oxygen/CF_3CH_2OH, hydrogen peroxide, or dibenzoyl peroxide/H_2O occurs with cleavage of a methyl−silicon bond to give $[PtMe(bps)\text{-}\mu\text{-}\{\kappa^3N,N,O\text{-}OSiMe(2\text{-}C_5H_4N)_2PtMe_3\}][CF_3CH_2OB(C_6F_5)_3]$, $[PtMe_3\{\kappa^3N,N,O\text{-}(2\text{-}C_5H_4N)_2SiMeO\}]$, or $[PtMe_3\{\kappa^3N,N,O\text{-}(2\text{-}C_5H_4N)_2SiMeOH\}][PhCOO]$, respectively. Mechanistic studies indicate that this methyl transfer from silicon to platinum occurs after oxidation to platinum(IV) and is induced by hydroxide attack at silicon.

INTRODUCTION

There has been intense interest in carbon−hydrogen bond activation by organoplatinum complexes, in a search for useful catalysts and in order to gain a deeper understanding of reactivity and mechanism in such reactions.[1] Chelating nitrogen-donor ligands are useful in C−H activation reactions of the type shown in eq 1 (E = CH_2, CO, NH), but not all such

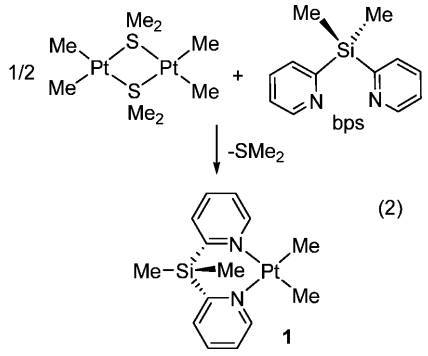


(1)

ligands give good reactivity.[1−3] For example, when the supporting ligand was di-2-pyridylmethane, the product of eq 1 was readily isolated, but when it was 2,2′-bipyridine, the reactions were unsuccessful.[3] It was argued that the twisting of the pyridyl groups out of the square plane of the platinum(II) center when LL = di-2-pyridylmethane, but not when LL = 2,2′-bipyridine, was an important factor in determining reactivity (Figure 1), and therefore that increasing the twist angle should lead to increased reactivity.[3] Introduction of a second methylene bridge in the ligand increases the twist angle (Figure 1), but the seven-membered chelate ring formed by 1,2-bis(2-pyridyl)ethane is not robust, and the easy dissociation of the ligand from platinum makes it unsuitable as a supporting ligand for C−H bond activation.[4] A second way to increase the twist angle is to introduce a larger single atom bridge between the 2-pyridyl groups, and this paper describes the use of a dimethylsilyl bridging group in the ligand bps = $Me_2Si(2\text{-}C_5H_4N)_2$. A preliminary communication showed that the ligand bps does give a larger twist angle (Figure 1) but that the chemistry is complicated by the occurrence of Si−Me bond activation.[5] This paper gives a complete description of the chemistry of the complex $[PtMe_2(bps)]$. The ligand bps has previously been used to form complexes of nickel, palladium, and platinum, some of which are useful for formation of C−C bonds by nickel- or palladium-catalyzed cross coupling.[6]

RESULTS AND DISCUSSION

Synthesis and Structure of $[PtMe_2(bps)]$ (1). The complex $[PtMe_2(bps)]$ (**1**) was prepared as an air-stable solid by the reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$[19] with bps, as shown in eq 2. The ^1H NMR spectrum of complex **1** contained a single



(2)

methylplatinum resonance at δ 0.71, with typical coupling constant $^2J_{PtH}$ = 80 Hz,[2−5] but two methylsilicon resonances at δ 0.77 and 1.11. The nonequivalence of the methylsilicon groups indicates that the ligand adopts a rigid-boat conformation (eq 2).

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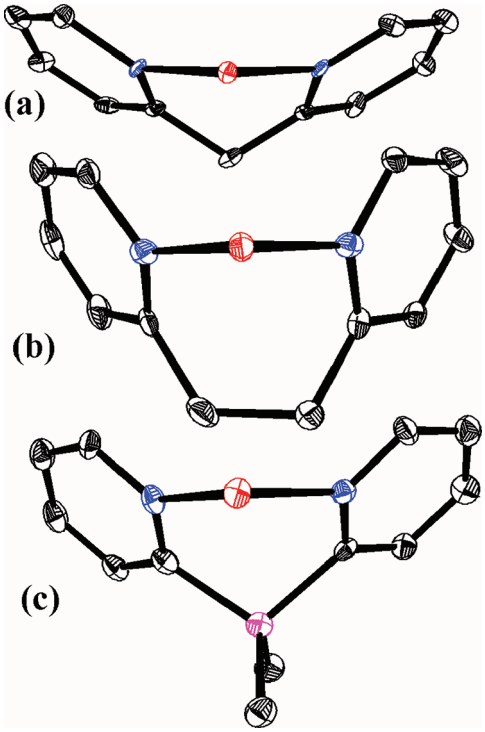


Figure 1. Conformations of bis(pyridine) donors in platinum(II) complexes and mean twist angles of the pyridyl groups from the platinum(II) square plane: (a) $(2\text{-}C_5H_4N)_2CH_2$, 40°; (c) 1,2-$(2\text{-}C_5H_4N)_2C_2H_4$, 70°; $(2\text{-}C_5H_4N)_2SiMe_2$, 53°.

The structure of complex **1** is shown in Figure 2. It confirms that the chelate ring is in the boat conformation, with one

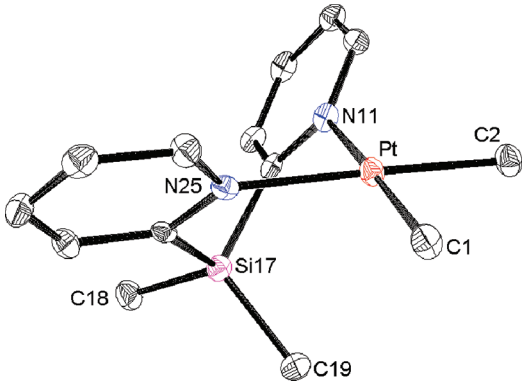
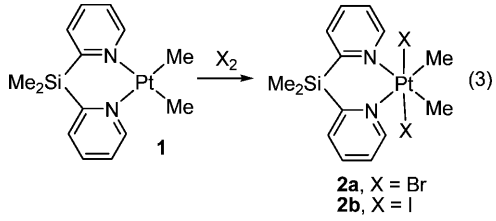


Figure 2. Structure of complex **1**. Selected bond parameters (distances in Å and angles in deg): Pt–C(1), 2.048(8); Pt–C(2), 2.043(8); Pt–N(11), 2.121(7); Pt–N(25), 2.108(7); C(2)–Pt–C(1), 88.3(4); N(25)–Pt–N(11), 90.7(2); C(19)–Si(17)–C(18), 109.7(4); C(16)–Si(17)–C(20), 104.7(4).

methylsilicon group oriented below the square plane of the platinum atom, with Pt···Si(17) = 3.25 Å. The angles about the platinum and silicon atoms are close to the ideal values for square-planar and tetrahedral centers, respectively, and so indicate that there is little strain in the six-membered chelate ring. The pyridyl groups are twisted by an average of 53° out of the square plane of the platinum center.

Oxidative Addition Reactions with Bromine and Iodine. Complex **1** reacted easily with bromine or iodine by trans oxidative addition, to give the products $[PtX_2Me_2(bps)]$ (**2a**, X = Br; **3a**, X = I) according to eq 3. The complexes were characterized by structure determination and by their ^{1}H NMR spectra.



The structures of complexes **2a** and **3a** are shown in Figure 3. Complex **2a** crystallized with some $[PtBr_3Me(bps)]$, with

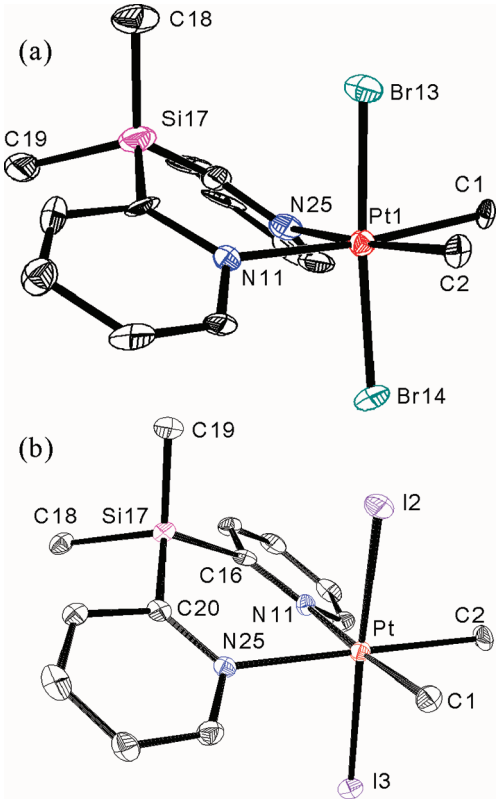


Figure 3. Structures of complexes (a) **2a** and (b) **3a**. Selected bond parameters for **3a** (distances in Å and angles in deg): Pt–C(1), 2.079(8); Pt–C(2), 2.077(8); Pt–N(11), 2.210(6); Pt–N(25), 2.217(6); Pt–I(2), 2.6283(6); Pt–I(3), 2.6523(6); C(2)–Pt–C(1), 85.7(4); N(11)–Pt–N(25), 92.6(2); I(2)–Pt–I(3), 177.16(2); C(19)–Si(17)–C(20), 115.3(4); C(19)–Si(17)–C(16), 114.9(4).

disorder of equatorial methyl and bromide ligands, but **3a** was not disordered; therefore, its bond parameters are more accurately determined.[5] The structures are similar, and the bps ligand is in the boat conformation in each case. The pyridyl groups are twisted out of the Me_2PtN_2 plane by an average value of 40° in **2a** and 43° in **3a**, compared to 53° in complex **1**. The lower twist, and hence flatter boat structure, in the platinum(IV) complexes **2a** and **3a** appears to arise from steric repulsion between bromide or iodide and the adjacent methylsilicon group, aided by longer Pt–N distances than in **1**. The distance Pt···C(19) is 3.52 Å in **1** but 4.80 Å in **3a**, and the angles C(19)–Si(17)–C(20) = 115.3(4)° and C(19)–Si(17)–C(16) = 114.9(4)° in **3a** are significantly distorted

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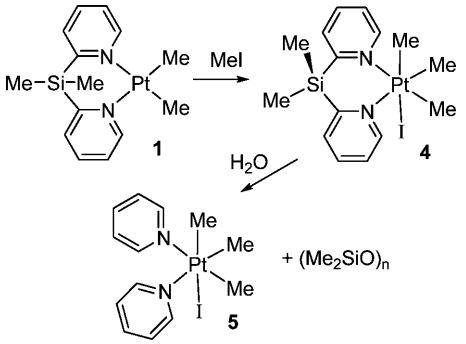
from tetrahedral, in order to relieve the Me···I repulsive interaction. It is clear from Figure 2 that the preferred orientation of the bps ligand in square-planar complexes must distort in order to allow octahedral coordination in platinum(IV) complexes.[6]

The ^{1}H NMR spectrum of complex **3a** gave a single resonance for the two methylplatinum groups at δ 2.31, with the coupling constant $^2J_{PtH}$ = 71 Hz. However, in contrast to complex **1**, the two methylsilicon groups also gave a singlet resonance at δ 0.76. The methylsilicon resonance became broad on cooling to −80 °C but did not split, indicating very much easier inversion of the chelate ring than in the square-planar complex **1**. This easy fluxionality of complex **3a**, which must involve boat inversion, can be understood in terms of the flatter boat structure in comparison to the more rigid complex **1**.

Oxidative Addition of Methyl Iodide or Triflate and Hydrolysis of the bps Ligand. Complex **1** reacted rapidly with methyl iodide to give [PtIMe$_3$(bps)] (**4**), whose structure was readily deduced from its ^{1}H NMR spectrum; it contained two methylplatinum resonances at δ 0.94, with $^2J_{PtH}$ = 72 Hz (Me trans to I) and at δ 1.32, with $^2J_{PtH}$ = 68 Hz (Me trans to N), and two methylsilicon resonances at δ 0.65 and 0.81. In this case, inversion of the Pt(bps) boat conformation does not make the methylsilicon groups equivalent. It is likely that the more stable Pt(bps) boat conformation brings the *syn*-MeSi group closer to the axial methylplatinum rather than to the larger iodoplatinum group, as shown in Scheme 1. Complex **4** could

Scheme 1



be isolated in pure form from the above reaction, but in solution in moist CD_2Cl_2 it was slowly hydrolyzed over a period of several days at room temperature to give the known complex [PtIMe$_3$(C$_5$H$_5$N)$_2$] (**5**)[7] and dimethylsiloxane polymer $(Me_2SiO)_n$, by selective cleavage of the pyridyl–silicon bonds (Scheme 1). The hydrolysis product $(Me_2SiO)_n$ was characterized by a broad methylsilicon resonance in the ^{1}H NMR spectrum at δ 0.1 and by a series of peaks in the ESI-MS corresponding to $(Me_2SiO)_n$.[8] The complex [PtIMe$_3$(C$_5$H$_5$N)$_2$] (**5**) crystallized during attempts to grow crystals of its precursor complex **4** and was structurally characterized (Figure 4). Although complex **5** has been known for many years, its structure has not previously been determined.[7]

The stereochemistry of the initial oxidative addition was determined by monitoring the reaction of complex **1** with CD_3I at low temperature (Figure 5). Addition of CD_3I at −50 °C led to rapid trans oxidative addition to give complex **4a** (Scheme 2, Figure 5a,b), as shown by the absence of the axial methylplatinum (trans to I) resonance of complex **4**. The

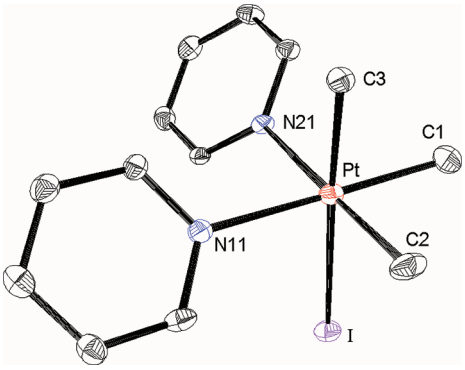


Figure 4. Structure of [PtIMe$_3$(C$_5$H$_5$N)$_2$] (**5**). Selected bond parameters (distances in Å): Pt–C(1), 2.05(1); Pt–C(2), 2.07(1); Pt–N(11), 2.191(7); Pt–N(21), 2.197(7); Pt–I, 2.7917(9) Å.

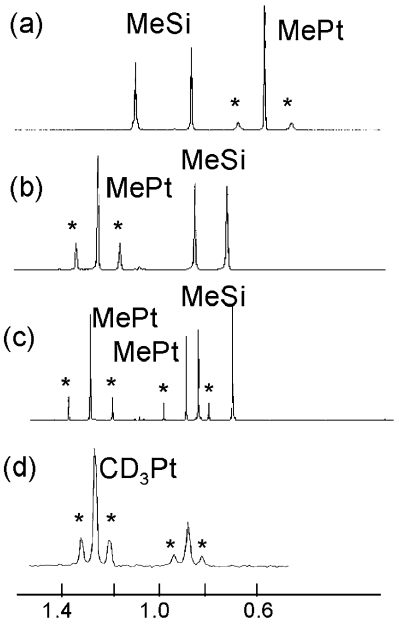


Figure 5. NMR spectra during the reaction of complex **1** with CD_3I in CD_2Cl_2: (a) ^{1}H NMR of complex **1** at −50 °C; (b) ^{1}H NMR of **4′** after addition of CD_3I at −50 °C; (c) ^{1}H NMR of **4a**/**4b** after 1 day at 20 °C; (d) ^{2}H NMR of **4a**/**4b** after 1 day at 20 °C. ^{195}Pt satellite spectra are indicated by *.

scrambling of MePt and CD_3Pt groups was complete in several hours at room temperature to finally give the roughly 2:1 mixture of **4b** and **4a** expected from statistical factors (Figure 5c). The ^{2}H NMR spectrum (Figure 5d) confirmed the assignment and showed that there was no exchange of CD_3Pt and MeSi groups. The scrambling of MePt and CD_3Pt groups is proposed to occur through cationic five-coordinate intermediates ***A*** and ***B*** (Scheme 2).[9,10]

The reaction of methyl triflate with complex **1** in acetone, followed by recrystallization, gave the cationic aqua complex [PtMe$_3$(OH$_2$)(bps)]$^+$ as the triflate salt **6**, whose structure is shown in Figure 6. The Pt(bps) chelate rings are similar in complexes **2**, **3**, and **6**, with the pyridyl groups in **6** twisted out of the C$_2$PtN$_2$ plane by an average of 42° with silicon *syn* to C(1) (Figure 6). The aqua ligand hydrogen bonds to two triflate anions in the dimeric structure, with O(4)···O(1B) = 2.71(1) and O(4)···O(2A) = 2.77(1) Å.

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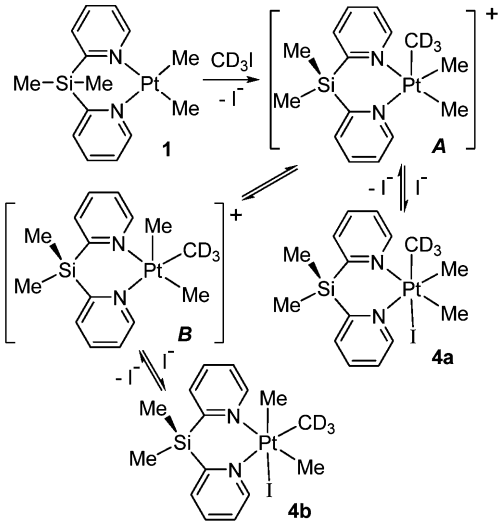
Scheme 2



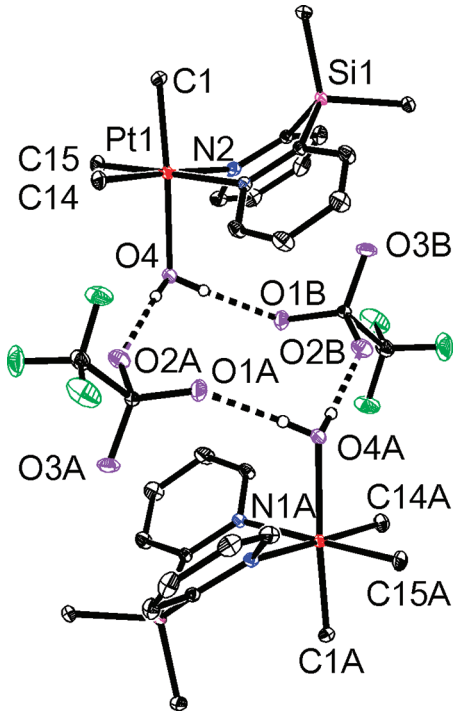


Figure 6. Structure of complex **6**. Selected bond parameters (distances in Å): Pt(1)–C(1), 2.027(2); Pt(1)–C(14), 2.048(2); Pt(1)–C(15), 2.039(2); Pt(1)–N(1), 2.179(2); Pt(1)–N(2), 2.190(2); Pt(1)–O(4), 2.179(2) Å. Hydrogen-bonding distances (in Å): O(4)···O(1), 2.71(1); O(4)···O(2), 2.77(1) Å.

The ^{1}H NMR spectrum of complex **6** in acetone-d_6 at room temperature contained single resonances for the methylplatinum groups at δ 1.21, with $^2J_{PtH}$ = 71 Hz, and for the methylsilicon groups at δ 0.85. Since two MePt and two MeSi resonances are expected for the structure of Figure 6, the complex must be fluxional. At low temperature, each resonance splits to give two major peaks along with some minor poorly resolved ones, as shown in Figure 7. The very easy fluxionality in this case is clearly due to the lability of the potential aqua, acetone, and triflate ligands, which gives easy access to the nonrigid five-coordinate intermediates ***C*** and ***D*** (Scheme 3).[9,10] The free energy of activation is estimated from the Eyring

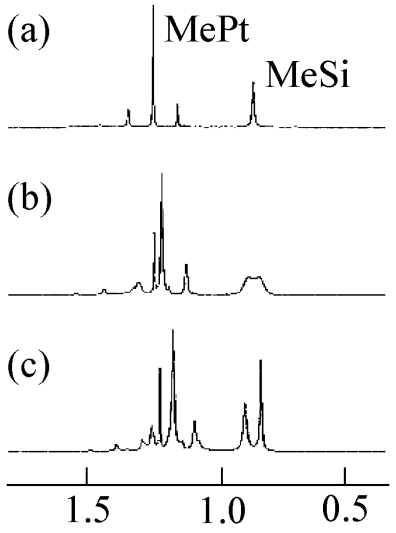
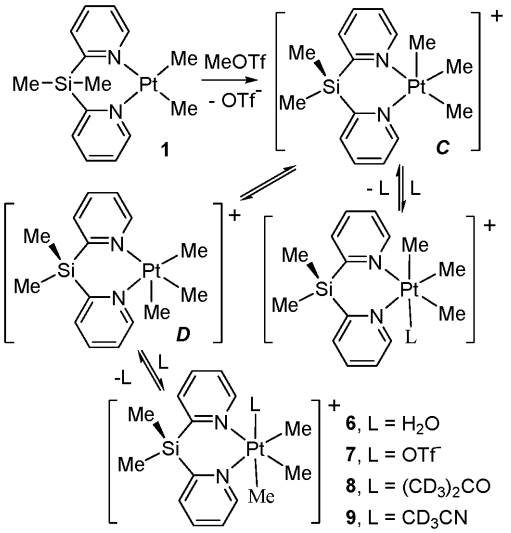


Figure 7. ^{1}H NMR spectra (400 MHz) of complex **6** in acetone-d_6 at (a) 20 °C, (b) −10 °C, and (c) −40 °C.

Scheme 3



equation to be $\Delta G^{\ddagger}$ = 56 kJ mol^{-1}. At low temperature, complex **6** is likely to be the major component, but minor peaks could arise from the triflate complex **7** and the acetone complex **8**, all of which are in rapid equilibrium at room temperature. The ESI-MS of the isolated complex gave a major envelope of peaks centered at m/z 472, as expected for the aqua complex cation, and the corresponding complex prepared from **1**-d_6 and CH_3OTf gave the corresponding peak at m/z 478, as expected for $[PtMe(CD_3)_2(OH_2)(bps)]^+$. If intermolecular methyl group exchange occurred, peaks for all ions $[PtMe_n(CD_3)_{3-n}(OH_2)(bps)]^+$ would be expected, and so the experiment shows that the Me/CD_3 exchange is intramolecular (Scheme 3).[9,10]

The reaction of complex **6** with methyl triflate in CD_3CN solution gave the complex $[PtMe_3(NCCD_3)(bps)]OTf$ (**9**) (Scheme 3), whose ^{1}H NMR spectrum contained two methylplatinum resonances at δ 0.93 (3H, $^2J_{PtH}$ = 76 Hz) and 1.04 (6H, $^2J_{PtH}$ = 66 Hz) and two methylsilicon resonances at δ 0.69 and 0.79, as expected for a rigid structure. Acetonitrile is a better ligand than acetone for platinum, and ligand dissociation from **9** is evidently slow on the NMR time scale.

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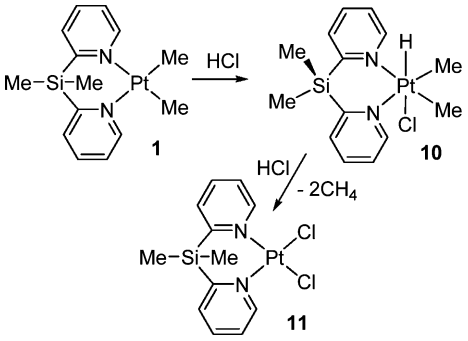
Reactions of Complex 1 with HCl. Complex **1** reacted rapidly with excess HCl at −80 °C to give a transient hydridoplatinum(IV) intermediate, **10**, and then methane and the product of protonolysis of both methylplatinum bonds, [$PtCl_2$(bps)] (**11**) (Scheme 4). Complex **10** was identified in

Scheme 4



the ^{1}H NMR spectrum of the reaction mixture at −80 °C by its hydridoplatinum resonance, which was seen at δ −20.64, with $^1J_{Pt-H}$ = 1593 Hz, with parameters similar to those for several similar complexes.[1−4,11] Complex **10** was short-lived even at low temperature and so could not be fully characterized. The formation of complex **11** is expected to occur through intermediates **10**, [PtClMe(bps)], and [$PtHCl_2$Me(bps)],[1−4] but only **10** was positively identified. Complex **11** existed in a rigid-boat conformation in solution, as shown by the presence of two methylsilicon resonances at δ 0.90 and 1.45 in the ^{1}H NMR spectrum, and in the solid state, as shown by a structure determination (Figure 8). This conformation of the bps ligand is similar to that in complex **1** (Figure 2), with the pyridyl groups twisted out of the square plane of the platinum center by an average of 54°. There is a similarly short contact C(19)−H···Pt = 2.93 Å, which partially blocks one potential axial coordination site. The platinum(II) complex **11** was stable in the presence of HCl in CD_2Cl_2 solution and did not undergo cleavage of the silicon−carbon bonds at room temperature, in contrast to the easy hydrolysis of the pyridyl−carbon bonds in complex **4**. Electrophiles usually give selectivity for aryl−silicon over methyl−silicon bonds, and 2-pyridyl−silicon bonds can be cleaved following initial nucleophilic attack at silicon.[12]

An Unexpected Methyl−Silicon Bond Cleavage Reaction. The reaction of complex **1** with $B(C_6F_5)_3$ in CF_3CH_2OH was carried out in the presence of anisole, with the aim of activating an aromatic C−H bond. However, the reaction was found to occur according to Scheme 5, with the anisole playing no role, to give complex **12**.[5] The reaction had been expected to give initially [PtMe(bps){$CF_3CH_2OB(C_6F_5)_3$}], and the cation [PtMe(bps)]$^+$ was then expected to react with anisole, in a way similar to that shown in eq 1. However, although complex **12** does contain a [$CF_3CH_2OB(C_6F_5)_3$]$^-$ anion and a square-planar platinum(II) center, with the expected [PtMe(bps)]$^+$ fragment, this platinum(II) fragment is connected to an octahedral platinum(IV) center. The platinum(IV) unit can be regarded as [$PtMe_3\{\kappa^3$-*N,N,O*-(2-$C_5H_4N)_2SiMeO\}$], which then acts as a ligand for the platinum(II) fragment, by coordination through the bridging oxygen atom (Figure 9). The sum of the bond angles about this bridging oxygen atom is 358°, indicating that the lone pair of electrons on oxygen is involved in π bonding and so is not stereochemically active. The original κ^2-*N,N*-(2-$C_5H_4N)_2SiMe_2$

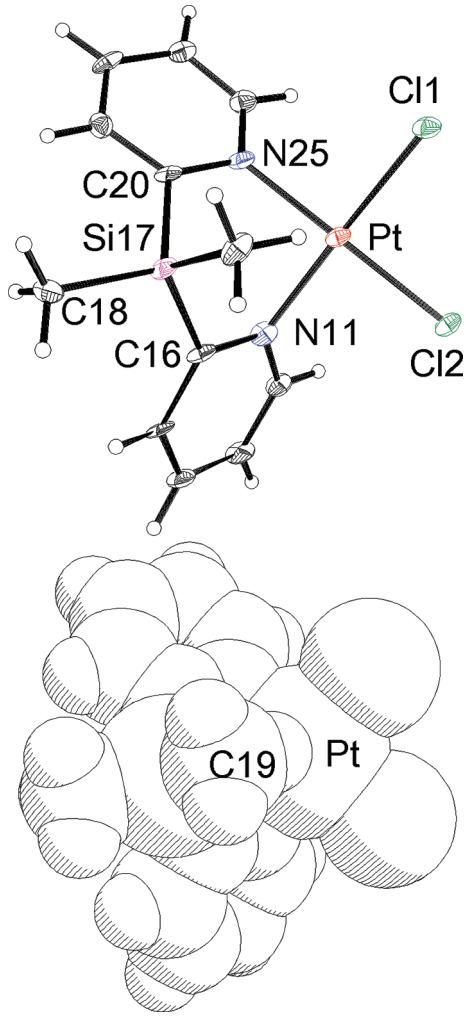
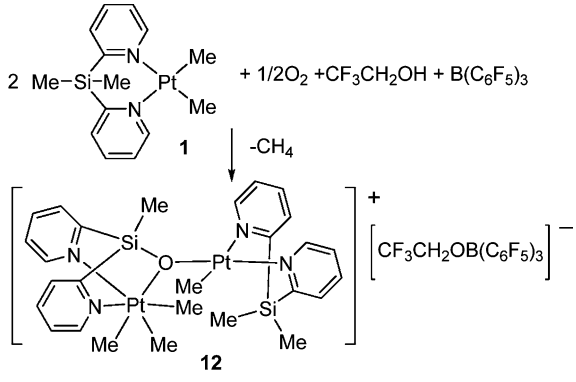


Figure 8. Structure of complex **11**. Selected bond parameters (distances in Å and angles in deg): Pt−Cl(1), 2.294(4); Pt−Cl(2), 2.296(3); Pt−N(11), 2.026(11); Pt−N(25), 2.022(11); Cl(1)−Pt−Cl(2), 90.3(1); N(25)−Pt−N(11), 91.2(5); C(18)−Si(17)−C(19), 112.4(7); C(16)−Si(17)−C(20), 101.4(6). The space-filling model below shows how the syn methylsilicon group lies close to the platinum atom.

ligand in **1** was converted to the κ^3-*N,N,O*-(2-$C_5H_4N)_2SiMeO^-$ ligand in **12**, in a process which formally involves substitution of a methyl by an oxide group at silicon. This was unexpected, given that the 2-pyridylsilicon bond is much more reactive to

Scheme 5



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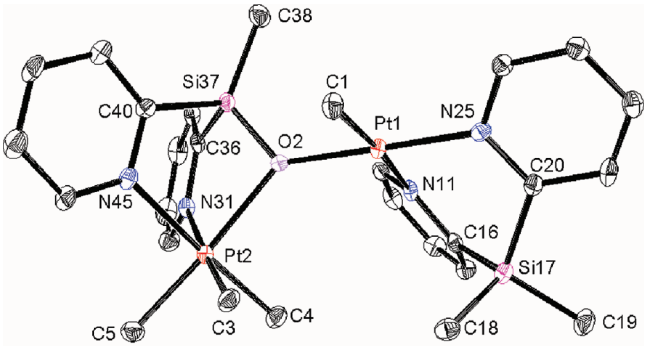


Figure 9. Structure of the cationic component of complex **12**. Selected bond parameters (distances in Å and angles in deg): Pt(1)−N(11), 2.134(6); Pt(1)−N(25), 2.001(6); Pt(1)−O(2), 2.028(5); Pt(1)−C(1), 2.039(8); Pt(2)−N(31), 2.195(6); Pt(2)−N(45), 2.190(6); O(2)−Pt(2), 2.244(5); C(3)−Pt(2), 2.043(8); C(4)−Pt(2), 2.047(8); O(2)−Si(37), 1.632(5); Si(37)−O(2)−Pt(1), 126.3(3); Si(37)−O(2)−Pt(2), 99.8(2); Pt(1)−O(2)−Pt(2), 132.0(2); O(2)−Si(37)−C(38), 119.2(3).

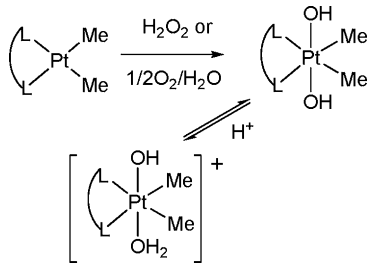
hydrolysis than the methyl−silicon bond in free silanes such as Me_3Si-2-C_5H_4N,[12] as well as in complex **4** (Scheme 1), as described above. The silicon−carbon bond activation evidently occurred under conditions milder than those for many other transition-metal-activated silicon−carbon bond cleavage reactions.[13] It was considered likely that the oxidation to give the platinum(IV) unit in **12**, and the origin of the oxide group, arose from reaction with oxygen (Scheme 5).

The NMR spectra showed that complex **12** was stable in solution. The cation has only C_1 symmetry, and the ^{1}H NMR spectrum contained four methylplatinum and three methylsilicon resonances. Individual assignments were confirmed by recording the NOESY spectrum. Three equal-intensity methylplatinum(IV) resonances occurred at δ 0.15 ($^2J_{Pt-H}$ = 69 Hz), 1.17 ($^2J_{Pt-H}$ = 68 Hz), and 1.23 ($^2J_{Pt-H}$ = 78 Hz), and the methylplatinum(II) resonance occurred at δ 0.64 ($^2J_{Pt-H}$ = 75 Hz). The two methylsilicon resonances of the (bps)Pt^{II} unit occurred at δ 0.95 and 1.63, while the single methylsilicon resonance of the κ^3N,N,O-(2-$C_5H_4N)_2SiMeO^-$ ligand occurred at δ 1.22. If the compound had undergone dissociation in solution, the [$PtMe_3\{\kappa^3N,N,O$-(2-$C_5H_4N)_2SiMeO\}$] unit would give only two methylplatinum resonances in a 2:1 intensity ratio, since it would have C_s symmetry.

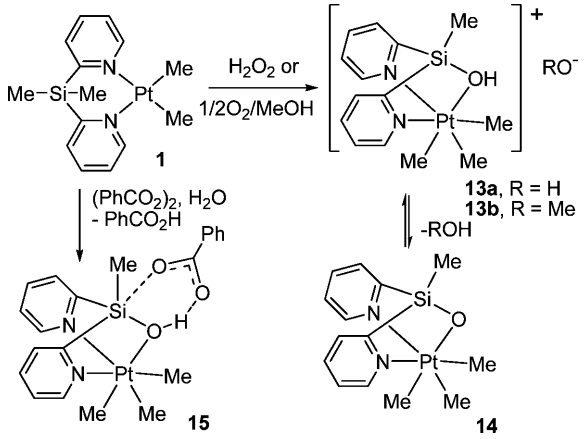
Oxidation of [$PtMe_2$(bps)] with Peroxides and Air. Dimethylplatinum(II) complexes [$PtMe_2$(LL)], containing chelating nitrogen-donor ligands LL, typically react with hydrogen peroxide or with dioxygen in protic media (in the presence of H_2O or ROH) to give platinum(IV) complexes [$PtMe_2(OH)_2$(LL)] or [$PtMe_2$(OH)(OR)(LL)] (Scheme 6), though oxygen is also known to give insertion into a methyl−platinum bond.[14−16] The hydroxoplatinum(IV) complexes are basic, and they take part in strong hydrogen bonding or undergo protonation to give $[PtMe_2(OH)(OH_2)(LL)]^+$.[14,15]

A solution of complex **1** in acetone was stable to air, but a solution in methanol was slowly oxidized over a period of several hours according to Scheme 7. A complex with

Scheme 6



Scheme 7



essentially identical NMR parameters was formed rapidly when complex **1** was treated with hydrogen peroxide in methanol.[5] Although these complexes were formed in high yield in solution, as determined by monitoring the reactions in CD_3OD solution by ^{1}H NMR, attempts to isolate the products occurred with considerable amounts of decomposition. The ^{1}H NMR parameters for products of reactions in CD_3OD are consistent with either structure **13** or **14**. The ESI-MS in methanol contained a peak at m/z 456, corresponding to [$PtMe_3$(HOSiMe(2-$C_5H_4N)_2$)]$^+$, but this does not distinguish between **13** or **14** as the more stable form, since they are likely to be in equilibrium and only the cation will give a peak in the ESI-MS. The corresponding product from the reaction of complex **1** with $^{18}O_2$/MeOH gave the corresponding peak in the ESI-MS at m/z 458, confirming that the oxygen atom was derived from dioxygen and not from methanol. The reaction of complex **1** with dibenzoyl peroxide gave complex **15** (Scheme 7, Figure 10), which was sufficiently stable to be crystallized and so could be characterized more definitively. It gave a peak in the ESI-MS at m/z 456, as expected for the cation [$PtMe_3$(HOSiMe(2-$C_5H_4N)_2$)]$^+$.

The structure of complex **15** (Figure 10) confirms that the methyl transfer from silicon to platinum has occurred to give a trimethylplatinum(IV) complex. An unusual feature of the structure is the tight association of the benzoate group, with the distance Si(1)···O(2A) = 3.07(1) Å indicating a significant secondary bonding interaction between the benzoate anion and silicon, and the distance O(3)···O(1A) = 2.46(1) Å indicating a strong hydrogen bond. The hydrogen atom between O(3) and O(1A) (Figure 10) was tentatively located closer to O(3) than to O(1A), but it could not be refined. A DFT calculation on the simpler acetate complex (Figure 11) supports the presence of an unsymmetrical hydrogen bond with PtO−H = 1.12 Å and CO−H = 1.36 Å, thus supporting the formulation of **15** as being closer to [$PtMe_3\{\kappa^3N,N,O$-(2-$C_5H_4N)_2$SiMeOH}]$^+$[$PhCO_2$]$^-$, a rare example of a silanol complex,[17] than to [$PtMe_3\{\kappa^3N,N,O$-(2-$C_5H_4N)_2$SiMeO}]-[$PhCO_2$H], in each case with a strong hydrogen bond and

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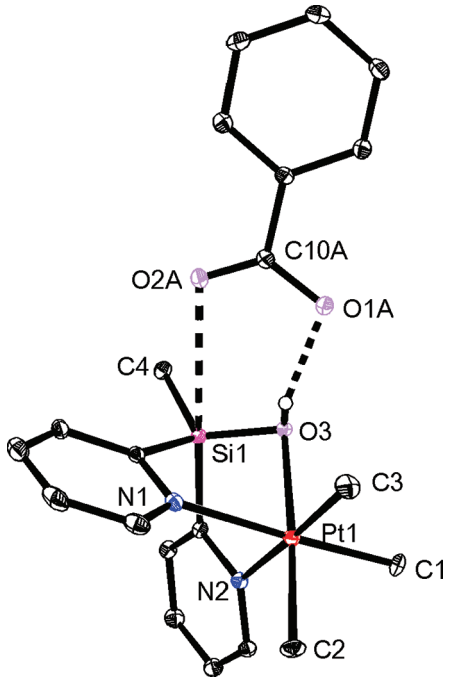


Figure 10. Structure of complex **15**. Selected bond parameters (distances in Å and angles in deg): Pt(1)−C(1), 2.050(5); Pt(1)−C(2), 2.045(4); Pt(1)−C(3), 2.051(5); Pt(1)−N(1), 2.181(4); Pt(1)−N(2), 2.168(4); Pt(1)−O(3), 2.237(3); Si(1)−O(3), 1.623(3); O(3)···O(1A), 2.46(1); Si(1)···O(2A), 3.07(1); Si(1)−O(3)−Pt(1), 99.0(1); O(3)−Si(1)−C(4), 120.7(2).

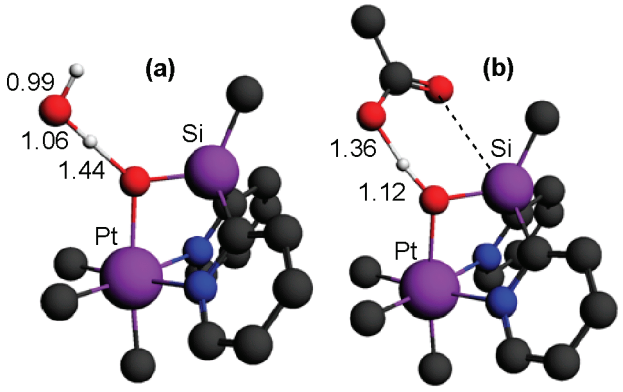


Figure 11. Calculated structures of adducts of complex **14** with (a) H_2O and (b) $MeCO_2H$, including the calculated OH distances.

weaker Si···O secondary bond of the kind likely to be involved in nucleophilic substitution at silicon.[18] In contrast, a DFT calculation suggests the product from hydrogen peroxide oxidation is more reasonably regarded as $[PtMe_3\{\kappa^3N,N,O\text{-}(2\text{-}C_5H_4N)_2SiMeO\}][H_2O]$ than as $[PtMe_3\{\kappa^3N,N,O\text{-}(2\text{-}C_5H_4N)_2SiMeOH\}]^+[OH]^-$, with calculated hydrogen bond distances PtO−H = 1.44 Å and HO−H = 1.06 Å (Figure 11). These formulations are consisted with the expected series of basicity $MeO^- > HO^- > [PtMe_3\{\kappa^3N,N,O\text{-}(2\text{-}C_5H_4N)_2SiMeO\}] > PhCO_2^-$. The low basicity of siloxanes is usually attributed to π-donation from lone pairs on oxygen to σ^* orbitals of the R_3Si unit.[19] The products of oxidation of complex **1** by H_2O_2 or O_2/MeOH are therefore suggested to have structure **14** rather than **13a** or **13b**, respectively (Scheme 7).

The ^1H NMR spectrum, in the region of the MePt and MeSi groups, of the product (**14**) of reaction of H_2O_2 with complex **1** in CD_3OD solution is shown in Figure 12a. There are two

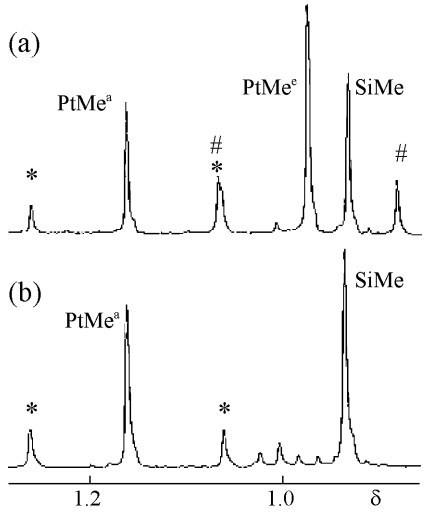
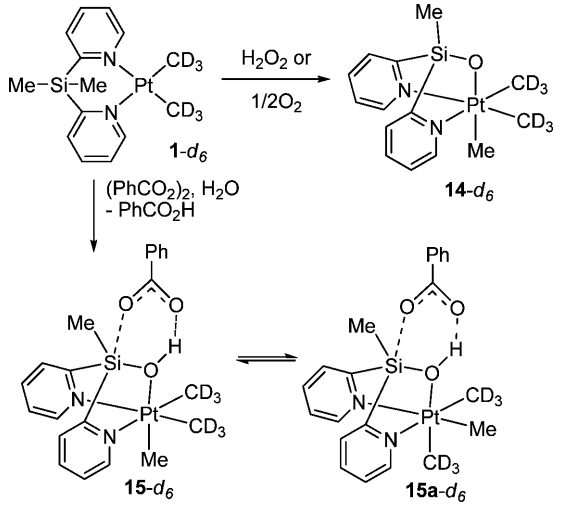


Figure 12. ^1H NMR spectra (400 MHz, CD_3OD) in the methyl region for reactions of hydrogen peroxide with (a) complex **1** and (b) complex **1**-d_6. ^{195}Pt satellite spectra of the axial ($PtMe^a$) and equatorial ($PtMe^e$) methylplatinum protons are shown as * and #, respectively. The low-intensity triplet in (b) at δ 1.0 arises from ether impurity.

methylplatinum resonances at δ 0.98 (6H, $^2J_{PtH}$ = 69 Hz, $PtMe^e$) and 1.15 (3H, $^2J_{PtH}$ = 75 Hz, $PtMe^a$) and only one methylsilicon resonance at δ 0.94 (3H, MeSi), as expected for structure **14** (Scheme 7). A similar reaction with $[Pt(CD_3)_2(bps)]$ (**1**-d_6) gave the corresponding product $[Pt(CD_3)_2Me\{\kappa^3N,N,O\text{-}(2\text{-}C_5H_4N)_2SiMeO\}]$ (**14**-d_6), whose ^1H NMR spectrum is shown in Figure 12b. The equatorial methylplatinum resonance of **14** (Figure 12a) is absent in this spectrum, showing clearly that the methyl group transferred from silicon occupies only the axial position in **14**-d_6, as shown in Scheme 8. The reaction of **1**-d_6 with dibenzoyl peroxide occurred in a similar way to give **15**-d_6 as the kinetic product, but this complex underwent Me/CD_3 exchange over a period of about 2 days to give a 1:2 equilibrium mixture of **15**-d_6 and **15a**-d_6 (Scheme 8). It is likely that this scrambling reaction

Scheme 8



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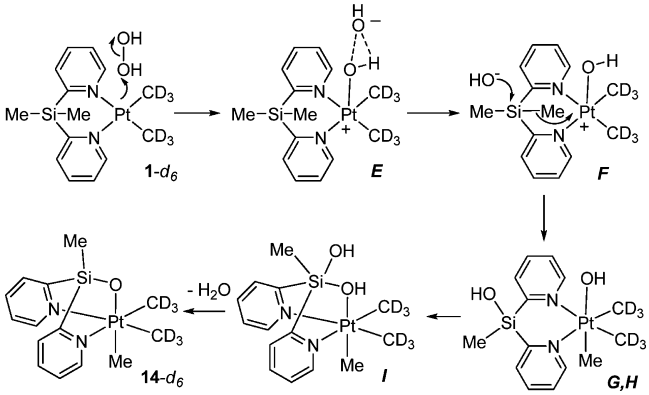
occurs within a five-coordinate intermediate formed by reversible dissociation of the silanol donor. There was no CH_3/CD_3 exchange with the MeSi group, indicating that the methyl group transfer to give **15** is irreversible. The ESI-MS of **14**-d_6 or **15**-d_6 in MeOH each contained a peak at m/z 462, as expected for $[Pt(CD_3)_2Me\{\kappa^3N,N,O\text{-}(2\text{-}C_5H_4N)_2SiMeOH\}]^+$.

The ease of the methyl group transfer to form complexes **14** and **15**, without forming a Pt–Si bond, and the mutually trans positions of the methyl and silanol units in the kinetically controlled products, are unusual features of the reactions of Scheme 8.[13,20] A proposed mechanism is shown in Scheme 9.[5]

Scheme 9



The initial reaction is likely to occur by donation of electrons from the filled $5d_{z^2}$ orbital of the platinum(II) center of complex **1** to the vacant σ^*(O–O) orbital of the hydrogen peroxide (Figure 13), which leads to oxidation of the platinum

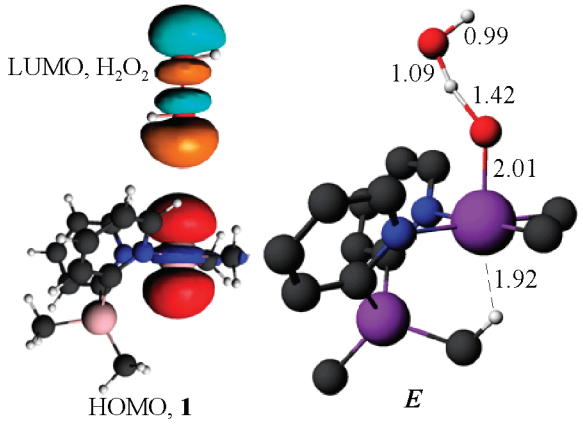


Figure 13. (left) Frontier orbitals, the filled $5d_{z^2}$ orbital of complex **1**, and the vacant σ^*(O–O) orbital of H_2O_2. (right) Calculated structure of ***E*** (Scheme 9), with selected distances.

atom and cleavage of the O–O bond. A DFT calculation predicts that this reaction is favorable and that there will be strong hydrogen bonding between the incipient ion pair $[Pt(OH)Me_2(bipy)]^+OH^-$ (***E***) (Figure 13), whose structure may then also be considered as the aquated oxoplatinum(IV) complex $[Pt(O)Me_2(bipy)]\cdot OH_2$. In solution, a more extensively solvated form is probable, and the theory indicates no significant multiple-bond character in the Pt–O bond of ***E***; thus, it is better considered as $Pt^+\text{-}O^-$ rather than Pt=O.[21] Complex ***E*** is predicted to have a weak SiCH···Pt interaction (Figure 13), which may be considered as an agostic bond, but complete methyl transfer from silicon to platinum is unfavorable because the Si–Me bond is stronger than the Pt–Me bond.[22] Two possible ways for rearrangement of complex ***E*** are shown in Figure 14. The more favorable reaction

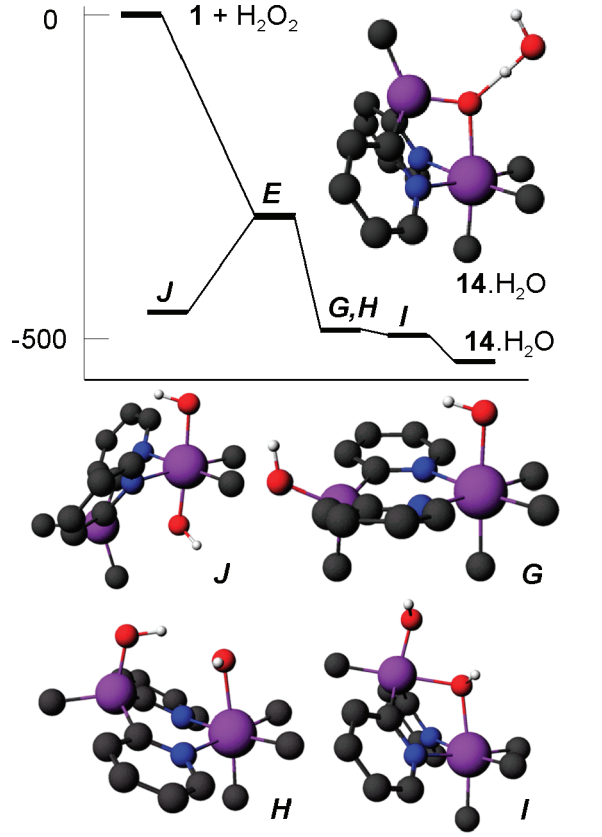


Figure 14. Calculated relative energies and structures of platinum complexes ***J*** and **14**·H_2O and potential reaction intermediates ***E*** and ***G–I***.

occurs by attack by hydroxide at silicon (***F***, Scheme 9) with simultaneous methyl group transfer to platinum to give ***G***. Inversion of the chelate ring can occur to give ***H*** and then the five-coordinate silicon compound ***I***,[23] with final rearrangement gives the product **14**·H_2O (Scheme 9, Figure 14). The hydroxide group might also attack at platinum to give ***J***, the product of simple oxidative addition (Figure 14),[14] in a way similar to that in reactions of complex **1** with halogens (eq 3), but this is calculated to be less favorable and is not observed. The key difference between the reactions of complex **1** with halogens (eq 3) and hydrogen peroxide (Schemes 8 and 9) is the much higher strength of the Si–O bond in comparison to the Pt–O bond, with the hard oxygen-donor ligand which favors attack by hydroxide at silicon rather than platinum.[23] It is noted that this reaction would normally be expected to occur with cleavage of a pyridyl–silicon bond,[12] as in the hydrolysis of complex **4** (Scheme 1), and so the selectivity for cleavage of the methyl–silicon bond must result from electrophilic assistance from the adjacent platinum(IV) center.[24]

■ DISCUSSION AND CONCLUSIONS

The most unusual feature of the chemistry described above is the easy methyl group transfer from silicon to platinum that occurs during some oxidative addition reactions but not others,[5] and it is important to place this chemistry in a broader

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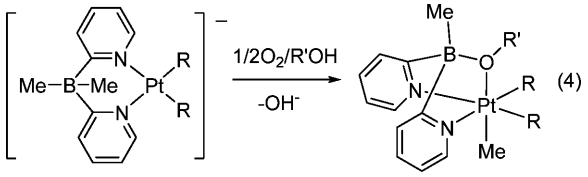
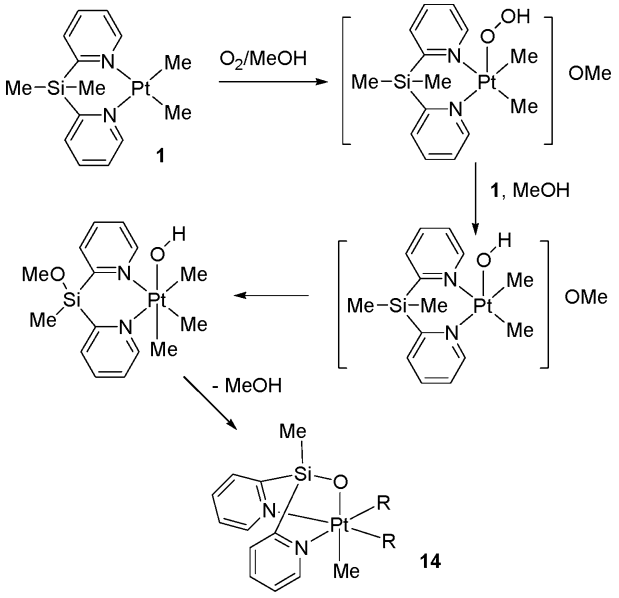
context. A reaction analogous to those discussed above is observed in the methyl transfer from boron to platinum on oxidation of the dimethylbis(2-pyridyl)borate complex shown in eq 4 (R = Me, Ph, R′ = H, Me, Et, *i*-Pr).[24] In the case of the



boron ligand (eq 4), the alkyl transfer may be reversible and, in reactions in alcohol solvents, the alkoxide group remains in the product.[24] However, in the case of the silicon ligand, bps, the methyl transfer is not reversible (Schemes 2 and 3), and the alkoxide group is not observed in the product **14** (Scheme 7). The initial reaction of complex **1** with dibenzoyl peroxide is expected to be $[Pt(O_2CPh)Me_2(bipy)]^+[PhCO_2]^-$, with a coordinated benzoate ligand, but the observed product is complex **15**, which contains no platinum−benzoate group (Figure 10).[5]

The reactions of complex **1** with dioxygen in methanol are expected to occur according to Scheme 10. The initial reaction

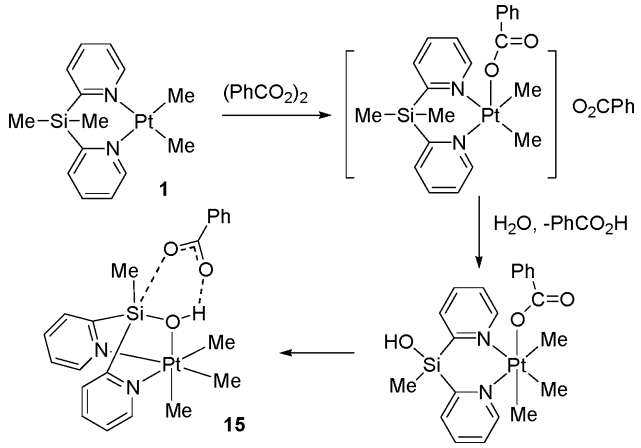
Scheme 10. Proposed Sequence of Reactions To Form Complex 14 by Reaction of 1 with Dioxygen



gives a hydroperoxo complex cation, with methoxide anion, and the hydroperoxo group reacts rapidly with a another 1 equiv of complex **1** to give 2 equiv of a cationic hydroxoplatinum(IV) complex with methoxide anion.[14,15] The methoxide group then attacks at silicon with methyl group transfer to platinum(IV), and finally, the methoxo group is displaced from silicon by the PtOH group to give the product **14** (Scheme 10). The unit of **14** present in the complex **12** (Scheme 5, Figure 9) is presumed to be formed in an analogous way, but with trifluoroethanol in place of methanol.

This mechanism can be compared with the proposed mechanism of reaction with dibenzoyl peroxide, in which the final step involves displacement of benzoate from platinum by the SiOH group (Scheme 11).

Scheme 11. Proposed Sequence of Reactions To Form Complex 15 by Reaction of 1 with $(PhCO_2)_2$



With oxygen-donor ligands, associative substitution at silicon and dissociative substitution at platinum(IV) are both expected to occur easily, and so the thermodynamically preferred product can be formed by displacement of the oxygen-donor ligand from either silicon (Scheme 10) or platinum (Scheme 11). However, substitution at boron is likely to be slow, and so the product is formed by kinetic control in the reaction of eq 4.[12,24]

In the proposed mechanisms of Schemes 9−11, it is important that the methyl group transfer from silicon to platinum is aided by attack of a hard oxygen-donor ligand at silicon rather than at platinum(IV), and this is also likely to be important in intermolecular transfer of alkylsilicon groups to transition metals during stoichiometric or catalytic reactions.[13,22] The only case of oxidative addition using a reagent with an R−O bond without accompanying methyl group transfer was with methyl triflate (Figure 6, Scheme 3). In this case, the methyl group transfer would lead to a tetramethylplatinum(IV) center, with anunfavorable *trans*-Me−Pt−Me linkage.[25] Overall, the reactions described by Vedernikov[24] and in the present work (and preliminary communication)[5] give considerable new insight into how alkyl transfer reactions to platinum(IV) and electrophilic cleavage of alkyl−platinum(IV) bonds can occur.

EXPERIMENTAL SECTION

NMR spectra were recorded by using a Varian Mercury 400 and Varian Inova 400 and 600 spectrometers. Chemical shifts are reported relative to TMS. The ligand bps and the complexes *cis*-/*trans*-$[PtCl_2(SMe_2)_2]$, $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, and $[Pt_2(CD_3)_4(\mu\text{-}SMe_2)_2]$ were prepared according to the literature.[6,26] $^{18}O_2$ (97%) was purchased from Aldrich.

X-ray Structure Determinations. Data were collected at −123 °C using a Nonius Kappa-CCD area detector diffractometer with COLLECT software and with Mo Kα radiation (λ = 0.710 73 Å). The unit cell parameters were calculated and refined from the full data set, and data were refined using the standard software.[27]

DFT Calculations. Calculations were made using the Amsterdam Density Functional program based on the Becke−Perdew functional, with first-order scalar relativistic corrections.[28]

[$PtMe_2$(bps)] (1). To a stirred solution of bis(2-pyridyl)-dimethylsilane (0.75 g, 3.5 mmol) in ether (10 mL) was added $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (1.01 g, 1.75 mmol). The product precipitated from solution as a pale brown solid, which was separated, washed with ether (3 × 2 mL) and pentane (3 × 2 mL), and then dried under high vacuum. Yield: 1.35 g, 88%. NMR in $CDCl_3$: $\delta(^1H)$ 0.71 (s, 6H, $^2J_{PtH}$ =

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80 Hz, PtMe), 0.77 (s, 3H, SiMe), 1.11 (s, 3H, SiMe), 7.21 (t, 2H, $^3J_{HH}$ = 5 Hz, H^5), 7.55 (d, 2H, $^3J_{HH}$ = 7 Hz, H^3), 7.67 (dd, 2H, $^3J_{HH}$ = 5 Hz, 7 Hz, H^4), 8.97 (d, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 25 Hz, H^6); δ(^{13}C) −20.0 (s, PtMe), −3.91 (s, SiMe$_{syn}$), −1.74 (s, SiMe$_{anti}$), 125.4, 130.4, 133.7, 152.4, 163.1 (py). The ^{1}H NMR spectrum was essentially the same at −50 °C. Anal. Calcd for $C_{14}H_{20}N_2PtSi$: C, 38.26; H, 4.59; N, 6.37. Found: C, 38.53; H, 4.85; N, 6.33.

[PtI$_2$Me$_2$(bps)] (3). To a stirred solution of [PtMe$_2$(bps)] (0.200 g, 0.455 mmol) in CH_2Cl_2 (5 mL) was added excess iodine (0.012 g). After 2 h the solvent was removed under vacuum to give the product as a red solid, which was washed with pentane (3 × 3 mL) and ether (3 × 3 mL) and dried under high vacuum. It was crystallized from CH_2Cl_2/pentane. Yield: 0.265 g, 84%. NMR in CD_2Cl_2: δ(^{1}H) 0.81 (s, 6H, SiMe), 2.39 (s, 6H, $^2J_{PtH}$ = 71 Hz, PtMe), 7.42 (dd, 2H, $^3J_{HH}$ = 5 Hz, 7 Hz, H^5), 7.78 (d, 2H, $^3J_{HH}$ = 7 Hz, H^3), 7.86 (t, 2H, $^3J_{HH}$ = 7 Hz, H^4), 9.36 (m, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 22 Hz, H^6). Anal. Calcd for $C_{14}H_{20}I_2N_2PtSi$: C, 24.25; H, 2.91; N, 4.04. Found: C, 23.88; H, 2.77; N, 4.32. The complex [PtBr$_2$Me$_2$(bps)] (**2**) was prepared similarly from [PtMe$_2$(bps)] (0.200 g, 0.455 mmol) and bromine but could not be separated from [PtBr$_3$Me(bps)]. Yield: 0.21 g. NMR for **2** in CD_2Cl_2: δ(^{1}H) 0.82 (s, 6H, SiMe), 1.25 (s, 6H, $^2J_{PtH}$ = 70 Hz, PtMe), 7.33 (dd, 2H, $^3J_{HH}$ = 5 Hz, 7 Hz, H^5), 7.71 (d, 2H, $^3J_{HH}$ = 7 Hz, H^3), 7.77 (t, 2H, $^3J_{HH}$ = 7 Hz, H^4), 9.44 (m, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 17 Hz, H^6). NMR for [PtBr$_3$Me(bps)] in CD_2Cl_2: δ(^{1}H) 0.83 (s, 6H, SiMe), 2.95 (s, 3H, $^2J_{PtH}$ = 68 Hz, PtMe), 7.42−7.95 (m, 6H, H^3−H^5), 9.15 (m, 1H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 38 Hz, H^6 *trans* to Br), 9.89 (m, 1H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 18 Hz, H^6 *trans* to Me).

[PtIMe$_3$(bps)] (4). To a solution of [PtMe$_2$(bps)] (0.100 g, 0.228 mmol) in ether (10 mL) was added MeI (0.042 g, 0.30 mmol). After 30 min the product precipitated as a white solid, which was separated, washed with pentane (3 × 5 mL), and dried under vacuum. Yield: 0.11 g, 82%. NMR in CD_2Cl_2: δ(^{1}H) 0.65 (s, 3H, Si-Me), 0.81 (s, 3H, Si-Me), 0.94 (s, 3H, $^2J_{PtH}$ = 72 Hz, Pt-Me), 1.32 (s, 6H, $^2J_{PtH}$ = 68 Hz, Pt-Me), 7.35 (dd, 2H, $^3J_{HH}$ = 5 Hz, 7 Hz, H^5), 7.79 (d, 2H, $^3J_{HH}$ = 7 Hz, H^3), 7.81 (t, 2H, $^3J_{HH}$ = 7 Hz, H^4), 9.63 (d, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 20 Hz, H^6). Anal. Calcd for $C_{15}H_{23}IN_2PtSi$: C, 30.99; H, 3.99; N, 4.82. Found: C, 31.24; H, 3.72; N, 4.57.

[PtI(CD$_3$)Me$_2$I(bps)] (4-*d*$_3$). To a solution of [PtMe$_2$(bps)] (0.010 g, 0.022 mmol) in acetone-d_6 (1 mL), cooled to −78 °C, was added CD_3I (0.06 mL), and the reaction was monitored by ^{1}H NMR spectroscopy. NMR at −50 °C in acetone-d_6: δ(^{1}H) 0.73 (s, 3H, SiMe), 0.87 (s, 3H, SiMe), 1.29 (s, 6H, $^2J_{PtH}$ = 69 Hz, PtMe), 7.52 (dd, 2H, $^3J_{HH}$ = 5 Hz, 7 Hz, H^5), 7.99 (t, 2H, $^3J_{HH}$ = 7 Hz, H^4), 8.07 (d, 2H, $^3J_{HH}$ = 7 Hz, H^3), 9.62 (d, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 19 Hz, H^6).

[PtIMe$_3$(pyridine)$_2$] (5). This complex was formed by hydrolysis of complex **4** during recrystallization. NMR in CD_2Cl_2: δ(^{1}H) = 1.20 (s, 3H, $^2J_{PtH}$ = 69 Hz, PtMe), 1.44 (s, 6H, $^2J_{PtH}$ = 70 Hz, PtMe), 7.44 (m, 4H, H^m), 7.88 (t, 2H, $^3J_{HH}$ = 7 Hz, H^p), 9.63 (d, 4H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 19 Hz, H^o). The spectrum was identical with that of an authentic sample.[7]

[PtMe$_3$(OH$_2$)(bps)][CF$_3$SO$_3$] (6). To a solution of complex **1** (0.010 g, 0.022 mmol) in acetone-d_6 (1 mL) was added methyl triflate (2.57 μL). NMR at 20 °C: δ(^{1}H) 0.85 (s, 6H, SiMe), 1.21 (s, 9H, $^2J_{PtH}$ = 71 Hz, PtMe), 7.73 (dd, 2H, $^3J_{HH}$ = 6, 7 Hz, H^5), 8.12 (t, 2H, $^3J_{HH}$ = 7 Hz, H^4), 8.23 (d, 2H, $^3J_{HH}$ = 7 Hz, H^3), 9.05 (d, 2H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 18 Hz, H^6). The product was crystallized from acetone/pentane. Yield: 0.009 g, 63%. ESI-MS: *m*/*z* 472; calcd for [PtMe$_3$(OH$_2$)(bps)]$^+$ *m*/*z* 472. Anal. Calcd for $C_{16}H_{25}F_3N_2O_4PtSSi$: C, 30.92; H, 4.05; N, 4.51. Found: C, 30.88; H, 3.84; N, 4.43. The corresponding complex from **1**-d_6 and MeOTf gave ESI-MS *m*/*z* 478 (calcd for [PtMe(CD$_3$)$_2$(OH$_2$)(bps)]$^+$ *m*/*z* 478), with no evidence for other ions [PtMe$_n$(CD$_3$)$_{3-n}$(OH$_2$)(bps)]$^+$ with *n* = 0, 2, 3.

[PtMe$_3$(CD$_3$CN)(bps)][CF$_3$SO$_3$] (9). This was prepared in a similar way but using acetonitrile-d_3 (1 mL) as solvent. NMR at −30 °C: δ(^{1}H) 0.69 (s, 3H, SiMe), 0.79 (s, 3H, SiMe), 0.93 (s, 3H, $^2J_{PtH}$ = 76 Hz, PtMe), 1.04 (s, 6H, $^2J_{PtH}$ = 66 Hz, Pt-Me), 7.58 (dd, 2H, $^3J_{HH}$ = 6 Hz, 7 Hz, H^5), 8.00−8.09 (m, 4H, H^3, H^4), 8.93 (d, 2H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 20 Hz, H^6).

[Pt(H)ClMe$_2$(bps)] (10) and [PtCl$_2$(bps)] (11). To a solution of [PtMe$_2$(bps)] (0.010 g, 0.022 mmol) in CD_2Cl_2 (0.5 mL) in an NMR tube at −80 °C was added a solution of HCl in CD_2Cl_2 (0.5 mL) at −80 °C. The course of the reaction was monitored by NMR. NMR at −80 °C for complex **10**: δ(^{1}H) −20.64 (s, 1H, $^1J_{PtH}$ = 1593 Hz, Pt-H), 0.71 (s, 3H, SiMe), 0.81 (s, 3H, SiMe), 1.11 (s, 6H, $^2J_{PtH}$ = 65 Hz, PtMe), 7.46 (dd, 2H, $^3J_{HH}$ = 5, 8 Hz, H^5), 7.69 (d, 2H, $^3J_{HH}$ = 8 Hz, H^3), 7.96 (t, 2H, $^3J_{HH}$ = 8 Hz, H^4), 9.31 (d, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 18 Hz, H^6), NMR at 20 °C for complex **11**: δ(^{1}H) 0.90 (s, 3H, SiMe), 1.45 (s, 3H, SiMe), 7.39 (dd, 2H, $^3J_{HH}$ = 5, 7 Hz, H^5), 7.61 (d, 2H, $^3J_{HH}$ = 7 Hz, H^3), 7.80 (t, 2H, $^3J_{HH}$ = 7 Hz, H^4), 9.15 (d, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 42 Hz, H^6).

[PtMe(bps)-μ-{OSiMe(2-C$_5$H$_4$N)$_2$PtMe$_3$][CF$_3$CH$_2$OB(C$_6$F$_5$)$_3$] (12). To a solution of [PtMe$_2$(bps)] (0.18 g, 0.45 mmol) in CF_3CH_2OH (5 mL) was added a solution of B(C$_6$F$_5$)$_3$ (0.23 g, 0.45 mmol) in CF_3CH_2OH (5 mL). The mixture was stirred for 2 days, the volume of the solution was reduced to 2 mL, and the mixture was cooled to 0 °C for 2 days to give colorless crystals of the product, which were separated, washed with ether, and dried under high vacuum. Yield: 0.128 g, 37%. NMR in acetone-d_6: δ(^{1}H) 0.15 (s, 3H, $^2J_{PtH}$ = 69 Hz, PtMe), 0.64 (s, 3H, $^2J_{PtH}$ = 75 Hz, PtMe), 0.95 (s, 3H, SiMe), 1.17 (s, 3H, $^2J_{PtH}$ = 68 Hz, PtMe), 1.22 (s, 3H, SiMe), 1.23 (s, 3H, $^2J_{PtH}$ = 78 Hz, PtMe), 1.63 (s, 3H, SiMe), 3.57 (q, 2H, CH_2), 7.01−8.15 (12H, H^3−H^5), 8.49 (d, 1H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 20 Hz, H^6), 8.60 (d, 1H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 20 Hz, H^6), 8.72 (d, 1H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 21 Hz, H^6), 8.96 (d, 1H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 65 Hz, H^6 *trans* to O); δ(^{19}F) −75 (br, 3F, CF_3), −133 (br m, 6F, Ar−F^o), −164 (t, 3F, Ar−F^p), −168 (br, 6F, Ar−F^m). Anal. Calcd for $C_{47}H_{39}BF_{21}N_4O_2Pt_2Si_2$: C, 36.47; H, 2.54; N, 3.62. Found: C, 36.77; H, 2.32; N, 3.62.

[PtMe$_3${κ^3*N*,*N*,*O*-(2-C$_5$H$_4$N)$_2$SiMeO}] (14). To a solution of [PtMe$_2$(bps)] (0.010 g, 0.022 mmol) in CD_3OD (1 mL) was added excess hydrogen peroxide (0.01 mL, 30%). NMR in CD_3OD: δ(^{1}H) 0.94 (s, 3H, SiMe), 0.98 (s, 6H, $^2J_{PtH}$ = 69 Hz, PtMe), 1.15 (s, 3H, $^2J_{PtH}$ = 75 Hz, Pt-Me), 7.43 (dd, 2H, $^3J_{HH}$ = 5 Hz, 7 Hz, H^5), 7.80 (d, 2H, $^3J_{HH}$ = 7 Hz, H^3), 7.86 (t, 2H, $^3J_{HH}$ = 7 Hz, H^4), 8.97 (d, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 20 Hz, H^6). ESI-MS: *m*/*z* 456; calcd for **14** + H$^+$ 456. The complex decomposed on attempted isolation. A compound with identical NMR properties was formed by reaction of [PtMe$_2$(bps)] with O_2 in MeOH for 1 day. ESI-MS: *m*/*z* 456; calcd for **14** + H$^+$ 456; product from $^{18}O_2$ gave *m*/*z* 458.

[PtMe(CD$_3$)$_2${κ^3*N*,*N*,*O*-(2-C$_5$H$_4$N)$_2$SiMeO}] (14-*d*$_6$). This was prepared in a similar way but using [Pt(CD$_3$)$_2$(bps)]. NMR in CD_3OD: δ(^{1}H) 0.94 (s, 3H, SiMe), 1.15 (s, 3H, $^2J_{PtH}$ = 75 Hz, Pt-Me), 7.43 (dd, 2H, $^3J_{HH}$ = 5 Hz, 7 Hz, H^5), 7.80 (d, 2H, $^3J_{HH}$ = 7 Hz, H^3), 7.86 (t, 2H, $^3J_{HH}$ = 7 Hz, H^4), 8.97 (d, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 20 Hz, H^6).

[PtMe$_3${κ^3*N*,*N*,*O*-(2-C$_5$H$_4$N)$_2$SiMeOH}][PhCOO] (15). To a solution of complex **1** (0.050 g, 0.11 mmol) in acetone (10 mL) was added dibenzoyl peroxide (0.030 g, 0.12 mmol). The mixture was stirred for 2 h, and then the volume was reduced to 1 mL and pentane (5 mL) was added to precipitate the product as a white solid, which was separated, washed with ether (3 × 2 mL) and pentane (3 × 2 mL), and dried under high vacuum. Yield: 0.046 g, 73%. NMR in CD_2Cl_2: δ(^{1}H) 1.04 (s, 3H, SiMe), 1.05 (s, 6H, $^2J_{PtH}$ = 70 Hz, PtMe), 1.14 (s, 3H, $^2J_{PtH}$ = 75 Hz, PtMe), 2.12 (s, 1H, O−H), 7.37−7.95 (11H, Ph and H^3−H^5), 8.58 (d, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 20 Hz, H^6). Anal. Calcd for $C_{21}H_{26}N_2O_3PtSi$: C, 43.67; H, 4.54; N, 4.85. Found: C, 43.95; H, 4.42; N, 5.06.

[PtMe(CD$_3$)$_2${κ^3*N*,*N*,*O*-(2-C$_5$H$_4$N)$_2$SiMeOH}][PhCOO] (15-*d*$_6$). To a solution of [Pt(CD$_3$)$_2$(bps)] (0.010 g, 0.022 mmol) in acetone-d_6 (1 mL) was added dibenzoyl peroxide (0.006 g, 0.024 mmol). The solution was transferred to an NMR tube, and the reaction was monitored by recording the ^{1}H NMR spectrum with time. Initially, the relative intensities of the resonances for MeSi (δ 1.04), MePt, trans-N (δ 1.05), and MePt, trans-O (δ 1.14) were 3:(trace):3 but after 2 days at room temperature, the corresponding relative intensities were 3:2:1.

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■ ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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