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Trimethylsilylplatinum(IV) complexes as reaction intermediates

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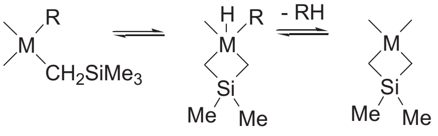
ABSTRACT

The oxidative addition of I_2, $PhCH_2Br$ and MeI with $[Pt(CH_2SiMe_3)_2(DPK)]$, **1**, DPK = di-2-pyridyl ketone, occurred with *trans* stereochemistry to give $[PtI_2(CH_2SiMe_3)_2(DPK)]$, $[PtBr(CH_2Ph)(CH_2SiMe_3)_2(DPK)]$ and $[PtIMe(CH_2SiMe_3)_2(DPK)]$, respectively. Complex **1** reacted with acids HX (X = Cl or CF_3CO_2) to give initially the hydridoplatinum complexes $[PtHX(CH_2SiMe_3)_2(DPK)]$, but these complexes were thermally unstable and decomposed largely by α-silyl migration to give compounds such as $[PtX(SiMe_3)Me_2(DPK)]$, as determined by monitoring the reactions by NMR at low temperature. With excess acid, HX, at room temperature, the products were largely $[PtX_2(DPK)]$, CH_4 and Me_3SiX with Me_4Si as a minor product only. The mechanism of the easy Si–CH_2 bond cleavage is discussed.

1. Introduction

Trimethylsilylmethyl derivatives of transition metals played an important role in developing the present understanding of the nature of the alkyl-transition metal bond [1,2]. The compounds with MCH_2SiMe_3 groups contain no β-hydrogen atom and so they are stabilized with respect to the most common mechanism of decomposition, namely the β-hydride elimination reaction [1,2]. The trimethylsilylmethyl complexes, and related compounds which have no β-hydrogen atom, must therefore decompose by other mechanisms, and there are well-defined examples of decomposition through γ-hydride elimination to give a metallasilacyclobutane [Eq. (1)] [3–7], β-methyl migration to give a methyl derivative [Eq. (2)] [8,9], α-hydride elimination to give an alkylidene complex [Eq. (3)] [10,11], or α-trimethylsilyl migration to give a trimethylsilyl derivative [Eq. (4)] [12–17]. In many cases the reactions are facilitated by the presence of a second group R, which may be an alkyl, hydride or halide ligand, and the C–H or C–Si bond activation step may involve oxidative addition or metathesis (Eqs. (1)–(4)) [1–17].



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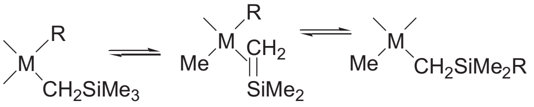

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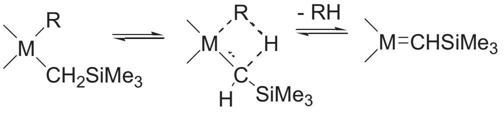

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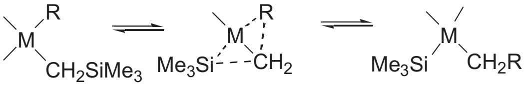

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As part of a project on the mechanism of C–H bond activation at platinum(II) [18–25], the protonolysis of complexes containing $PtCH_2SiMe_3$ groups has been studied [19] and, while this work was in progress, an independent study of related complexes was published [18]. Thus, the protonolysis of trimethylsilylmethyl–platinum(II) bonds in a diimine complex was shown to occur according to Eq. (5) ($R = CF_3CD_2$, S = solvent, $Ar = 3,5\text{-}Me_2C_6H_3$) [18]. No tetramethylsilane, the expected product of simple protonolysis, was formed. Also, there was no deuterium incorporation into the MeSi groups of the product Me_3SiOR, while all possible isotopomers of methane (CH_nD_{4-n}) and methylplatinum groups ($PtCH_nD_{3-n}$) were present (Eq. (5)) [18].

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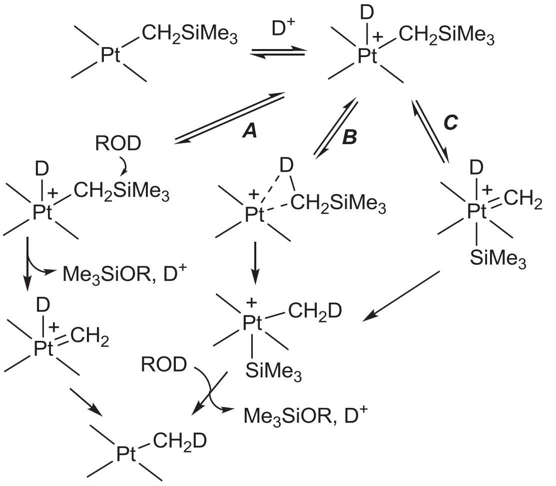
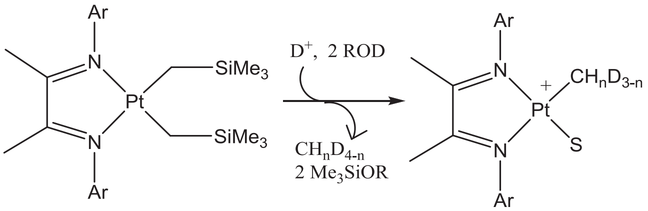


Scheme 1.



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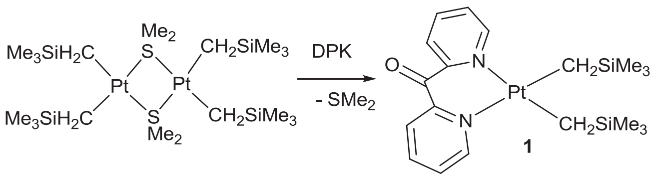
These observations were interpreted in terms of a mechanism (***A***), Scheme 1, which involves nucleophilic attack at silicon to cleave the Si–CH_2 bond in a cationic 16-electron hydridoplatinum(IV) intermediate. It was argued that mechanism (***B***), involving reductive coupling followed by α-migration of the Me_3Si group, would lead to formation of some tetramethylsilane and probably to deuterium incorporation into the methyl groups of the product Me_3SiOR, and that mechanism (***C***), involving earlier α-migration would give a high energy carbene intermediate [18]. There are no well defined platinum(IV) complexes with simple carbene ($Pt{=}CH_2$) groups, though organoplatinum(IV) complexes with stabilized NHC-carbenes are now known [26,27]. Once the product containing the $PtCH_2D$ group is formed, it can undergo H/D exchange with D^+ to give isotopomers containing $PtCH_nD_{3-n}$ groups and then slower cleavage to give isotopomers of methane CH_nD_{4-n} [18].

In an earlier communication, it was noted that intermediates containing $PtSiMe_3$ groups could be detected in analogous reactions of H^+ or D^+ with $[Pt(CH_2SiMe_3)_2(bu_2bipy)]$, bu₂bipy = 4,4′-di-*t*-butyl-2,2′-bipyridine, which appeared inconsistent with mechanism ***A*** in Scheme 1 [19]. This article describes a study of the reactivity of the related complex $[Pt(CH_2SiMe_3)_2(DPK)]$, DPK = di-2-pyridyl ketone. The research connects to a broader theme of Si–C bond activation at transition metal centers [28–30] as well as providing new examples of α-silyl migration of the type illustrated in Eq. (4) [12–17]. Some chemistry of the methylplatinum complex $[PtMe_2(DPK)]$ has been described earlier [25,31,32].

2. Results

2.1. The complex [Pt(CH₂SiMe₃)₂(DPK)], **1**

The complex $[Pt(CH_2SiMe_3)_2(DPK)]$, **1**, was prepared by reaction of the complex $[Pt_2(CH_2SiMe_3)_4(\mu\text{-}SMe_2)_2]$ with di-2-pyridyl ketone (DPK), as shown in Eq. (6). It was readily characterized by its ^1H NMR spectrum, which contained single resonances for the Me_3Si groups [$\delta = -0.19$] and for the $PtCH_2$ groups [$\delta = 0.54$, $^2J(PtH) = 94$ Hz], by comparison to related compounds [18,19].



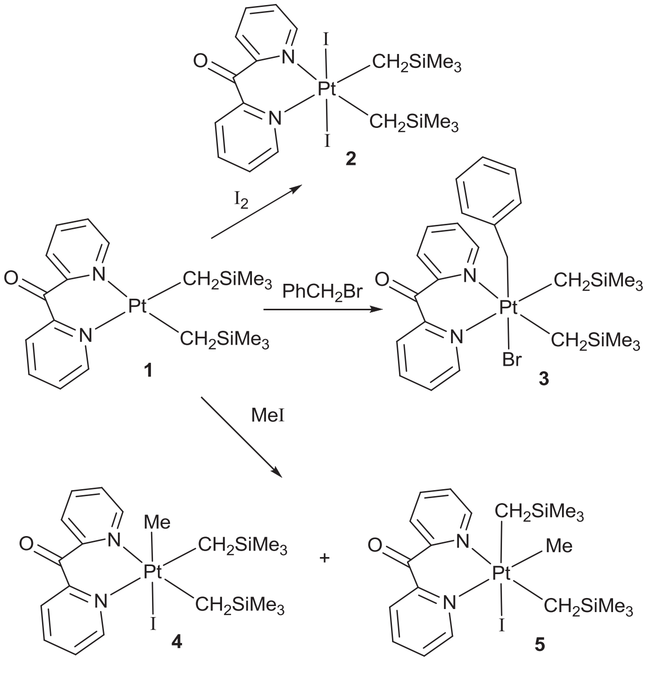
(6)

2.2. Reactions with iodine and alkyl halides

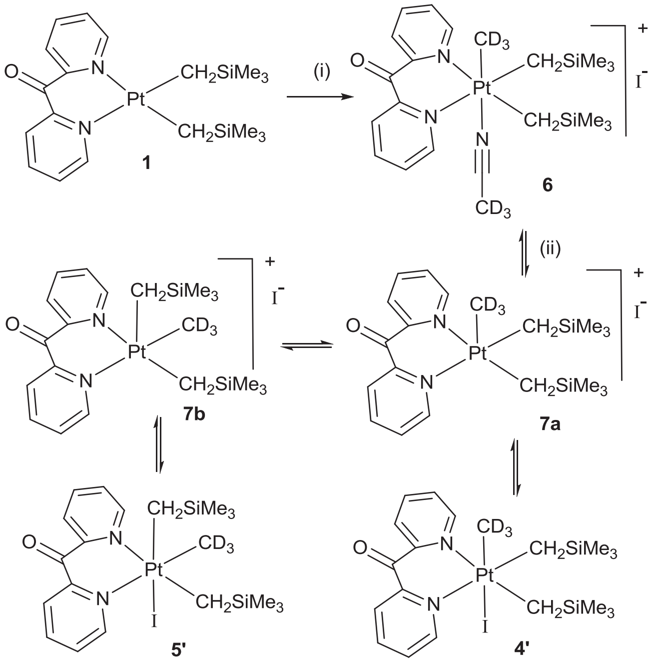
In order to monitor the stereochemistry of oxidative addition to complex **1**, the reactions with iodine, benzyl bromide and methyl iodide were studied (Scheme 2). The reaction with iodine gave the product of *trans* oxidative addition **2** (Scheme 2). Complex **2** has effective C_{2v} symmetry and it, like complex **1**, gave a single resonance in the ^1H NMR spectrum for the Me_3Si groups [$\delta = 0.11$] and for the $PtCH_2$ groups [$\delta = 2.70$, $^2J(PtH) = 86$ Hz].

The reaction of complex **1** with benzyl bromide occurred to give the product of *trans* oxidative addition **3** in about 90% selectivity. Complex **3** has effective C_s symmetry and the ^1H NMR spectrum contained a single resonance for the Me_3Si groups [$\delta = -0.06$] and for the methylene protons of the $PtCH_2Ph$ groups [$\delta = 3.44$, $^2J(PtH) = 88$ Hz]. The methylene protons of the $PtCH_2SiMe_3$ groups are diastereotopic and gave an [AB] multiplet in the ^1H NMR spectrum [$\delta = 1.25$, $^2J(HH) = 14$ Hz, $^2J(PtH) = 84$ Hz; 1.42, $^2J(HH) = 14$ Hz, $^2J(PtH) = 79$ Hz]. A minor product in the initial reaction is likely to be the isomeric complex formed by overall *cis* oxidative addition, but many of the NMR resonances were too weak to allow positive identification. Recrystallization gave complex **3** in pure form.

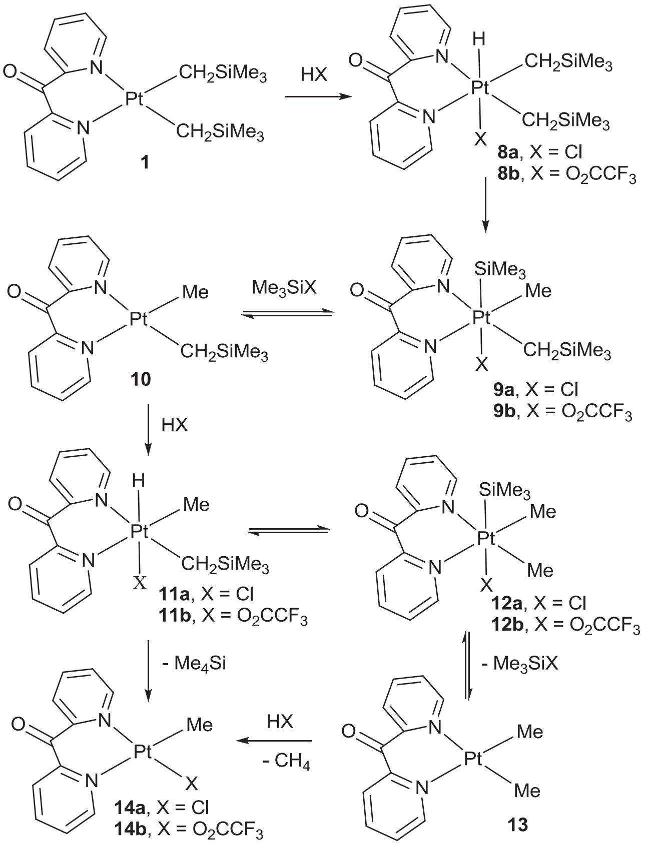
In contrast, the reaction of complex **1** with methyl iodide occurred to give the product of *cis* oxidative addition **5** in about 95% selectivity. Complex **5** has no symmetry so the ^1H NMR spectrum contains two resonances for the Me_3Si protons [$\delta = -0.39$, +0.20] and one for the methylplatinum group [$\delta = 1.71$, $^2J(PtH) = 73$ Hz]. The two Me_3SiCH_2 groups in **5** are non-equivalent and each has diastereotopic methylene protons, so four resonances were



Scheme 2.



Scheme 3. Reagents: (i) CD_3I; (ii) $-CD_3CN$.



Scheme 4.

observed for the $PtCH^aH^bSi$ protons. The minor product was identified as the product of *trans* oxidative addition **4**, identified from its Me_3Si [$\delta = 0.00$] and MePt resonances [$\delta = 0.08$, $^2J(PtH) = 76$ Hz] (see below).

The formation of **5** as major product was unexpected because oxidative addition of alkyl halides to platinum(II) usually occurs with *trans* stereochemistry [31–36], so the reaction of CD_3I with $[Pt(CH_2SiMe_3)_2(DPK)]$, **1**, in CD_3CN or in $(CD_3)_2CO$ solution was monitored by low temperature NMR to search for intermediates. The initial product in CD_3CN at −40 °C was identified as *trans*-$[Pt(CD_3)(CH_2SiMe_3)_2(DPK)(NCCD_3)]I$, **6** (Scheme 3), as expected in an S_N2 mechanism of oxidative addition [37]. The ^1H NMR spectrum contained a single resonance for the Me_3Si group [$\delta = -0.03$] and an [AB] multiplet for the $PtCH_2Si$ protons [$\delta = 1.06$, $^2J(HH) = 14$ Hz, $^2J(PtH) = 84$ Hz; 1.13, $^2J(HH) = 14$ Hz, $^2J(PtH) = 74$ Hz]. At −20 °C, these resonances decayed slowly and new resonances for *trans*-$[PtI(CD_3)(CH_2SiMe_3)_2(DPK)]$, **4′**, were identified. The symmetry is C_s for both **6** and **4′** so the NMR spectra are similar, though with significant differences in chemical shifts. Thus, **4′** gives $\delta(^1H) = 0.06$ for the $SiMe_3$ protons and 1.37, 1.59 for the $PtCH^aH^b$ protons. The final product was identified at 20 °C as *cis*-$[PtI(CD_3)(CH_2SiMe_3)_2(DPK)]$, **5′**, whose NMR spectrum is like **5** but without the methylplatinum resonance. A similar result was obtained in acetone-d_6 solvent, though the cationic intermediate was less stable. These results show that the normal *trans*-oxidative addition occurs but that the kinetic product then undergoes isomerization to the product of *cis* oxidative addition. The isomerization is expected to require a 5-coordinate intermediate, as shown in Scheme 3 [38–40].

2.3. Reaction of $[Pt(CH_2SiMe_3)_2(DPK)]$, 1, with HCl

The reaction of complex **1** with anhydrous HCl in dichloromethane solution occurred to a major extent according to Scheme 4 (X = Cl).

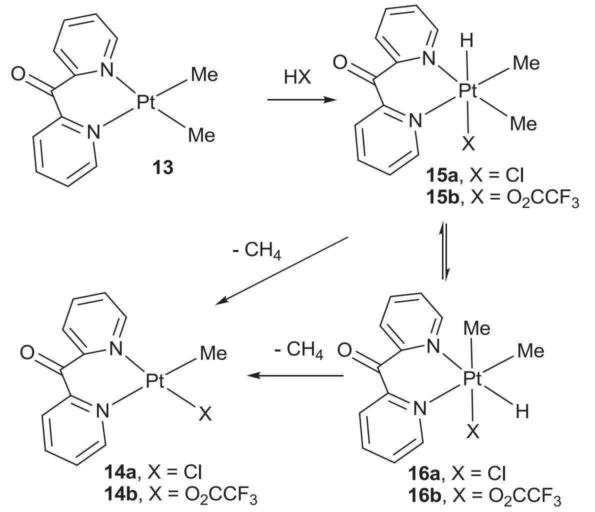
The reaction of complex **1** with one equivalent of HCl at −80 °C gave the complex $[PtHCl(CH_2SiMe_3)_2(DPK)]$, **8a**, as major product. The hydride was characterized by a singlet resonance at $\delta = -20.9$, with $^1J(PtH) = 1595$ Hz [19,41]. The C_s symmetry was indicated by the presence of a single Me_3Si resonance [$\delta = -0.23$] and an [AB] multiplet for the $PtCH_2$ protons [$\delta = 0.50$, $^2J(PtH) = 88$ Hz; 0.83, $^2J(PtH) = 80$ Hz]. At −20 °C, the resonances for **8a** had decayed and the major product was $[PtClMe(SiMe_3)(CH_2SiMe_3)(DPK)]$, **9a**. In the ^1H NMR spectrum, complex **9a** gave a methylplatinum resonance at $\delta = 1.02$, $^2J(PtH) = 61$ Hz, a trimethylsilylplatinum resonance at $\delta = -0.41$, $^3J(PtH) = 18$ Hz, and resonances for the $PtCH_2SiMe_3$ group at $\delta = 0.25$ [Me_3Si] and 0.60, $^2J(PtH) = 85$ Hz; 0.94, $^2J(PtH) = 80$ Hz [$PtCH^aH^b$].

A similar reaction with four equivalents of HCl gave the same initial products as above. However, at −20 °C, resonances assigned to $[PtClMe_2(SiMe_3)(DPK)]$, **12a**, were observed and **12a** became the major product at −5 °C. The C_s symmetry of **12a** was indicated by the presence of a single Me_3SiPt resonance [$\delta = -0.24$, $^3J(PtH) = 18$ Hz,] and a single methylplatinum resonance [$\delta = 1.18$, $^2J(PtH) = 60$ Hz] [19,42]. The formation of complex **12a** was accompanied by formation of Me_3SiCl [$\delta^1H = 0.40$, $\delta^{29}Si = 30$], as well as by smaller amounts of methane [$\delta^1H = 0.24$], Me_4Si [$\delta^1H = 0.00$, $\delta^{29}Si = 0$] and $[PtClMe(DPK)]$, **14a** [$\delta(MePt) = 1.04$, $^2J(PtH) = 77$ Hz]. At room temperature, **14a** had reacted further with HCl to give complete conversion to $[PtCl_2(DPK)]$, with formation of more methane [32]. The methylsilicon products were characterized initially by their ^1H and ^{29}Si chemical shifts and confirmed by "spiking" samples with the authentic compounds [43–45].

When the similar reaction was carried out with DCl, the TMS was formed very largely as Me_3SiCH_2D [$\delta(MeSi) = -0.002$, 9H; $\delta(CH_2D) = -0.02$, 2H, 1:1:1 triplet, $^2J(HD) = 2$ Hz]. No $SiCHD_2$ resonance was detected and the integration of $Me:CH_2D = 9:2$ indicated that no significant amount of $Me_2Si(CH_2D)_2$ was present. A minor amount of Me_4Si was also formed and its ^1H resonance was just resolved at $\delta(MeSi) = 0.00$. No deuterium incorporation into the product Me_3SiCl was detected.

Table 1
Selected NMR data.

Complex	δ($PtCH_2$)	δ(SiMe)	δ(PtH)	δ(PtMe)	δ(Si)
1	0.54 (94)	−0.19			3.0
8a	0.50 (88) 0.83 (80)	−0.23	−20.9 (1595)		2.1
8b	0.22 (88) 0.55 (80)	−0.35	−25.3 (1680)		1.5
9a	0.60 (85) 0.94 (80)	−0.24 0.25		1.02 (60)	6.1 0.2
12a		−0.24 (18)		1.18 (60)	−3.0
12b		−0.17 (20)		1.14 (60)	1.0
15b			−25.8 (1730)	0.86 (70)	



Scheme 5.

*2.4. Reaction of [$Pt(CH_2SiMe_3)_2$(DPK)], **1**, with CF_3CO_2H*

The reaction of complex **1** with trifluoroacetic acid took place in a similar way (Scheme 4, Table 1) but the intermediates were more transient. With three equivalents of CF_3CO_2H in CD_2Cl_2 solution at −80 °C, the hydride complex **8b** was detected. The hydride resonance was at $\delta = -25.3$, with $^1J(PtH) = 1680$ Hz. The C_s symmetry was indicated in the ^1H NMR spectrum by the presence of a single Me_3Si resonance [$\delta = -0.35$] and an [AB] multiplet for the $PtCH_2$ protons [$\delta = 0.22$, $^2J(PtH) = 88$ Hz; 0.55, $^2J(PtH) = 80$ Hz]. The resonances for **8b** decayed slowly even at −80 °C and, by −60 °C, the major product was characterized as **12b** (Scheme 4). In the ^1H NMR spectrum, complex **12b** gave a single Me_3SiPt resonance [$\delta = -0.17$, $^3J(PtH) = 20$ Hz] and a single methylplatinum resonance [$\delta = 1.14$, $^2J(PtH) = 60$ Hz]. As complex **12b** was formed, a resonance for $Me_3SiO_2CCF_3$ [$\delta 1H = 0.34$, $\delta^{29}Si = 34$], as well as by smaller amounts of methane [$\delta = 0.24$], Me_4Si [$\delta = 0.00$] and [$Pt(O_2CCF_3)Me$(DPK)], **14b** [$\delta(MePt) = 1.00$, $^2J(PtH) = 76$ Hz]. With a larger excess (8 equivalents) of trifluoroacetic acid, complex **14b** was the major product even at −80 °C.

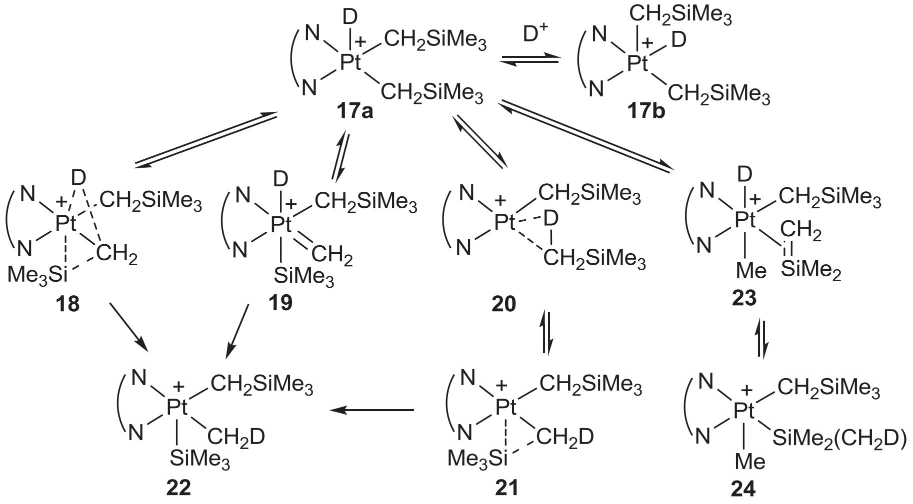
*2.5. Reaction of [$PtMe_2$(DPK)], **13**, with CF_3CO_2H*

The reaction of complex **13** with HCl has been described previously (Scheme 5) [32]. Complex **15a** is sufficiently stable to be isolated at −30 °C but, at higher temperatures, it equilibrates with the product **16a** of *cis* oxidative addition, and then eliminates methane to give **14a**. The hydride intermediates on reaction of **13** with excess CF_3CO_2H are much less stable and they equilibrate much faster. At −80 °C in CD_2Cl_2 solution, the hydrides **15b** and **16b** are both present and at −30 °C the reaction was complete to give methane and **14b** [$\delta(MePt) = 0.82$, $^2J(PtH) = 76$ Hz]. Complex **15b** gives a single methylplatinum resonance [$\delta(MePt) = 0.86$, $^2J(PtH) = 70$ Hz], while complex **16b** gives two [$\delta(MePt) = 1.00$, $^2J(PtH) = 76$ Hz, *trans* to CF_3CO_2; 1.24, $^2J(PtH) = 70$ Hz, *trans* to DPK]. The coupling constant $^1J(PtH)$ is higher for **15b** [$\delta(PtH) = -25.85$, $^1J(PtH) = 1730$ Hz] than for **16b** [$\delta(PtH) = -20.12$, $^1J(PtH) = 1435$ Hz]. These hydride complexes **15b** and **16b** are presumed to be formed as intermediates in the conversion of **13** to **14b** in the reactions of trifluoroacetic acid with complex **1** (Scheme 4), but they were not identified directly in those reactions. It is likely that, under the conditions under which they are formed, they are too shortlived to be characterized directly.

3. Discussion

The reactions of [$Pt(CH_2SiMe_3)_2$(DPK)], **1**, with acids occur in a similar way to those reported earlier for [$Pt(CH_2SiMe_3)_2(bu_2bipy)$] [19]. Overall, the main reaction converts HX + Pt(II)–CH_2SiMe_3 first to Pt(IV)HX(CH_2SiMe_3), then to Pt(IV)XMe($SiMe_3$) and finally to Me_3SiX + Pt(II)Me. A minor reaction (typically *ca.* 10%) converts the intermediate Pt(IV)HX(CH_2SiMe_3) to Me_4Si + Pt(II)X. This minor reaction is absent in the otherwise similar reaction with the diimine stabilizing ligand described by Eq. (5) [18]. Of the mechanisms (Scheme 1) considered in the original report [18], the preferred mechanism ***A*** can be eliminated based on the present work because it does not allow the formation of Me_3Si–Pt bonds at intermediate stages of reaction [19]. Remaining potential mechanisms for the first steps of the reactions are summarized in Scheme 6, based on initial formation of a cationic 16-electron complex **17a**, and some relevant calculated energies using DFT theory for the case with NN = DPK are shown in Fig. 1. There is good precedent for expecting the key rearrangements to occur from the 5-coordinate platinum(IV) intermediates [18–25,38–40]. The potential mechanism involving γ-CH activation analogous to Eq. (1) [3–7] is not considered because it would require a 7-coordinate platinum(VI) intermediate, which would surely lie at very high energy.

Two of the possible mechanisms can be eliminated based on results from isotope labeling or calculated energies. Thus, the mechanism involving initial β-methyl migration to give **23** should be considered based on precedents of Eq. (2) [8,9], but it predicts subsequent deuterium incorporation into the trimethylsilylplatinum group in **24**, and hence into the final product Me_3SiX, which was not observed (note that **24** would be expected to isomerize very easily to the isomer with axial silyl group, analogous to the isotopomer **22**). It has previously been suggested that carbene intermediates such as **19** would be too high in energy to be viable reaction intermediates [18], and this is now supported by the calculations (Fig. 1). Thus, complex **19** is calculated to be 203 kJ mol^{-1} higher in energy than the less stable *cis*-isomer of the hydride derivative, **17b** (Fig. 1). The mechanism involving initial reductive coupling to give the TMS complex **20** is analogous to mechanism ***B*** of Scheme 1 [18]. It was initially rejected because it should lead to formation of TMS and because easy switching of the alkane–platinum interaction between all C–H/C–D bonds of the TMS ligand would be expected to occur and would lead to deuterium incorporation into the product Me_3SiX [18]. In the present work, TMS is formed, albeit as a minor product, and the calculations indicate that **20** is thermodynamically more stable than the precursor **17a** or **17b** and is easily formed from them (Fig. 1). If complex **20** is an intermediate in formation of Me_3SiX, it is necessary that SiC bond activation *via* **21** to give the trimethylsilylplatinum complex **22** should be faster than either displacement of TMS from **20** or switching between coordinated methyl groups of the TMS ligand [18]. The final mechanism involves a concerted reaction in which



Scheme 6.

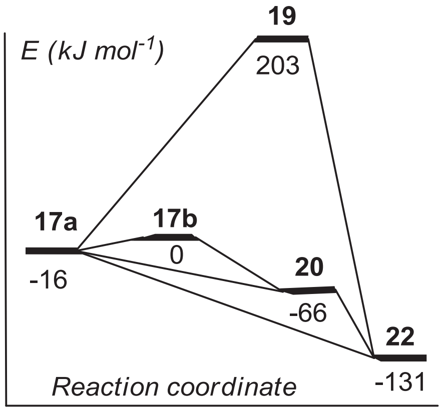
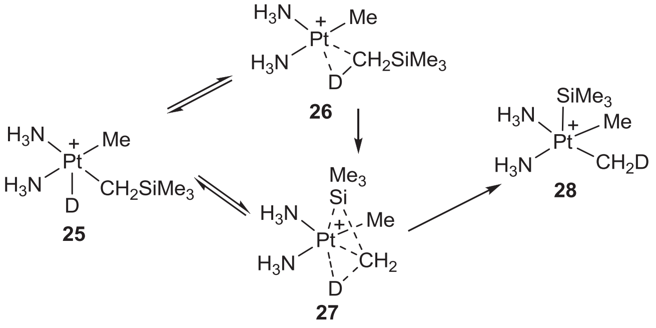


Fig. 1. Relative energies (kJ mol^{-1}, based on **17b** = 0) for some of the complexes in Scheme 6.



Scheme 7.

α-trimethylsilyl migration is accompanied by transfer of the hydride group to the methylene group to give **18** and then the complex **22**. The overall reaction of **17a** or **17b** to give **22** is strongly exothermic, driven by formation of the strong Pt–$SiMe_3$ bond [42], and is therefore irreversible under the mild conditions used. Hence, the mechanism naturally accounts for both the formation of the complexes with Pt–$SiMe_3$ groups and the absence of deuterium in the products Me_3SiX [19].

Calculations have also been carried out with the simpler model system in which two ammine ligands are substituted for DPK, and in which only one trimethylsilylmethyl group is present. The results are summarized in Scheme 7 and Fig. 2.

The reaction can be initiated by easy reductive coupling to give **26** or by silyl migration to give **27**, and **27** is also easily accessible from **26**. Once the Pt–Si bond formation begins, the reaction to give **28** is steeply downhill (Fig. 2) and irreversible under mild conditions. It can be considered that **26** and **27** are η^2- and η^3-TMS complexes, respectively, analogous to the η^2- and η^3-CH_4 complexes which are also of very similar energy [20,22,23], and it is noted that there are several well-characterized SiC σ-complexes which can be considered as analogs of Si–C σ-interaction intermediate complex **27** and which are clearly significant in Si–C bond activation [46,47].

4. Experimental

All syntheses were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques. ^1H and ^{29}Si NMR spectra were recorded by using a Varian Inova 400 spectrometer. The complexes $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, $[Pt_2(CH_2SiMe_3)_4(\mu\text{-}SMe_2)_2]$ and $[PtMe_2(DPK)]$ were prepared according to literature methods [19,31,48]. DFT calculations were carried out using the Becke–Perdew exchange-correlation functional in the Amsterdam Density Functional program [49], including first-order scalar relativistic corrections and standard parameters used in previous studies of organoplatinum compounds [33].

4.1. $[Pt(CH_2SiMe_3)_2(DPK)]$, **1**

To a solution of $[Pt_2(CH_2SiMe_3)_4(\mu\text{-}SMe_2)_2]$ (0.5 g) in Et_2O (50 mL) was added a solution of di-2-pyridyl ketone (DPK, 0.22 g) in Et_2O (10 mL). The mixture was stirred for 2 h and the volume of the solvent was reduced. The product precipitated as a dark red powder, which was filtered, washed with ether and dried under vacuum. Yield: 74%. *Anal.* Calc. for $C_{19}H_{30}N_2OPtSi_2$: C, 41.21; H, 5.46; N, 5.06. Found: C, 40.87; H, 5.25; N, 4.72%. NMR in $(CD_3)_2CO$: $\delta(1H) = -0.19$ [s, 18H, $SiMe_3$]; 0.54 [s, 4H, $^2J(PtH) = 94$ Hz, $PtCH_2$]; 7.78 [m, 2H, H^5]; 8.02 [m, 2H, H^3]; 8.25 [m, 2H, H^4]; 8.88 [m, 2H, $^3J(PtH) = 32$ Hz, H^6]; $\delta(13C) = -10.3$ [s, $PtCH_2$]; 2.8 [s, $SiMe_3$]; 125.5, 129.2, 138.4, 151.0, 155.0 [DPK]; $\delta(29Si) = 3.0$ [s, $SiMe_3$].

4.2. $[PtI_2(CH_2SiMe_3)_2(DPK)]$, **2**

To a solution of $[Pt(CH_2SiMe_3)_2(DPK)]$ (0.10 g) in CH_2Cl_2 (10 mL) was added I_2 (0.048 g). The color of the solution changed from red to deep yellow. After 1 h, the volume of the solution was reduced and the product was precipitated as a yellow powder by addition

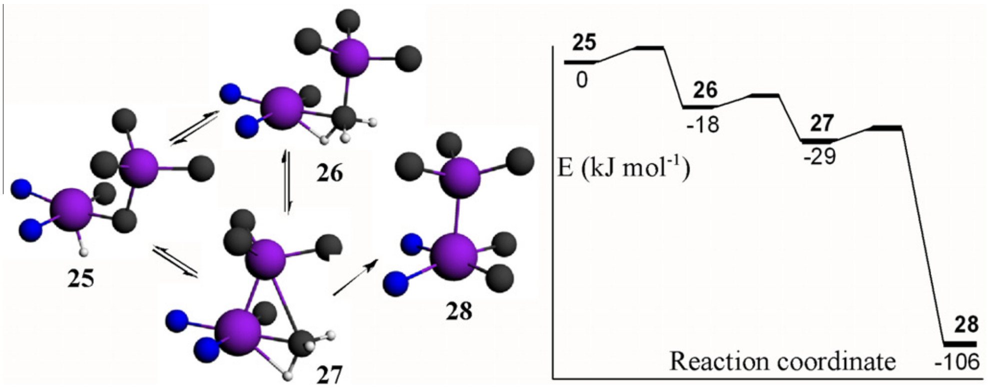


Fig. 2. The calculated structures of intermediate cationic complexes **25**–**27** of Scheme 7 (only H-atoms involved in bonding to platinum are shown for clarity) and their relative energies.

of pentane (10 mL), washed with ether and pentane and dried under vacuum. Yield: 64%. *Anal.* Calc. for $C_{19}H_{30}I_2N_2OPtSi_2$: C, 28.26; H, 3.74; N, 3.47. Found: C, 28.43; H, 3.91; N, 3.54%. NMR in $(CD_3)_2CO$: δ(1H) = 0.11 [s, 18H, $SiMe_3$]; 2.70 [s, 4H, ^2J(PtH) = 86 Hz, $PtCH_2$]; 8.04 [m, 2H, H^5]; 8.37 [m, 2H, H^3]; 8.48 [m, 2H, H^4]; 9.54 [m, 2H, ^3J(PtH) = 20 Hz, H^6].

4.3. [PtBr(CH$_2$Ph)(CH$_2$SiMe$_3$)$_2$(DPK)], **3**

To a solution of [Pt(CH_2SiMe_3)$_2$(DPK)] (0.10 g) in acetone (12 mL) was added $PhCH_2Br$ (0.15 mL). The color of the solution changed from red to pale yellow. After 1 h, the volume of the solution was reduced and the product was precipitated as a yellow powder by addition of pentane (10 mL), washed with ether and pentane and dried under vacuum. Yield: 72%. *Anal.* Calc. for $C_{26}H_{37}BrN_2OPtSi_2$: C, 43.09; H, 5.15; N, 3.87. Found: C, 42.70; H, 4.94; N, 3.71%. NMR in $(CD_3)_2CO$: δ(1H) = −0.06 [s, 18H, $SiMe_3$]; 1.25 [m, 2H, ^2J(HH) = 14 Hz, ^2J(PtH) = 84 Hz, PtC*H*^{a}H^{b}Si]; 1.42 [m, 2H, ^2J(HH) = 14 Hz, ^2J(PtH) = 79 Hz, PtCH^a*H*^{b}Si]; 3.44 [s, ^2J(PtH) = 88 Hz, $PtCH_2Ph$]; 6.66–8.49 [m, 13H, DPK and Ph].

4.4. *cis*-[PtIMe(CH$_2$SiMe$_3$)$_2$(DPK)], **5**

To a solution of [Pt(CH_2SiMe_3)$_2$(DPK)] (0.10 g) in acetone (12 mL) was added MeI (0.15 mL). The color of the solution changed from red to yellow. After 1 h, the volume of the solution was reduced and the product was precipitated as a yellow powder by addition of pentane (10 mL), washed with ether and pentane and dried under vacuum. Yield: 64%. *Anal.* Calc. for $C_{20}H_{33}IN_2OPtSi_2$: C, 34.53; H, 4.78; N, 4.03. Found: C, 35.01; H, 4.89; N, 3.87%. NMR in $(CD_3)_2CO$: δ(1H) = −0.39 [s, 9H, $SiMe_3$]; 0.20 [s, 9H, $SiMe_3$]; 0.92 [m, 1H, ^2J(HH) = 13 Hz, ^2J(PtH) = 88 Hz, PtC*H*^{a}H^b *trans* to I]; 1.07 [m, 1H, ^2J(HH) = 13 Hz, ^2J(PtH) = 88 Hz, PtCH^a*H*^{b} *trans* to I]; 1.25 [m, 1H, ^2J(HH) = 13 Hz, ^2J(PtH) = 80 Hz, PtC*H*^{a}H^b *trans* to N]; 1.37 [m, 1H, ^2J(HH) = 13 Hz, ^2J(PtH) = 92 Hz, PtCH^a*H*^{b} *trans* to N]; 1.71 [s, 3H, ^2J(PtH) = 73 Hz, PtMe]; 7.90–9.40 [m, 8H, DPK]. A trace of the *trans* isomer was detected by resonances at: δ(1H) = 0.00 [s, 18H, $SiMe_3$]; 0.08 [s, 3H, ^2J(PtH) = 76 Hz, PtMe].

4.5. Reaction of CD$_3$I with [Pt(CH$_2$SiMe$_3$)$_2$(DPK)]

To an NMR tube charged with a solution of [Pt(CH_2SiMe_3)$_2$(DPK)] (0.005 g, 0.010 mmol) in CD_3CN (0.5 mL) at −40 °C was added CD_3I (0.10 mmol) by microsyringe. The initial product was identified at −40 °C as *trans*-[Pt(CD_3)(CH_2SiMe_3)$_2$(DPK)-($NCCD_3$)]I. NMR: δ(1H) = −0.03 [s, 18H, $SiMe_3$]; 1.06 [m, 2H, ^2J(HH) = 14 Hz, ^2J(PtH) = 84 Hz, PtC*H*^{a}H^b]; 1.13 [m, 2H, ^2J(HH) = 14 Hz, ^2J(PtH) = 74 Hz, PtCH^a*H*^{b}]; 8.00 [m, 2H, H^5]; 8.29 [m, 2H, H^3]; 8.42 [m, 2H, H^4]; 8.83 [m, 2H, H^6]. At −20 °C, *trans*-[PtI(CD_3)(CH_2SiMe_3)$_2$(DPK)] was also identified. NMR: δ(1H) = 0.06 [s, 18H, $SiMe_3$]; 1.37 [m, 2H, ^2J(HH) = 14 Hz, ^2J(PtH) = 84 Hz, PtC*H*^{a}H^b]; 1.59 [m, 2H, ^2J(HH) = 14 Hz, ^3J(PtH) = 86 Hz, PtCH^a*H*^{b}]; 7.82 [m, 2H, H^5]; 8.21 [m, 2H, H^3]; 8.30 [m, 2H, H^4]; 9.40 [m, 2H, H^6]. The final product was identified at 20 °C as *cis*-[PtI(CD_3)(CH_2SiMe_3)$_2$(DPK)]. δ(1H) = −0.34 [s, 9H, $SiMe_3$]; 0.24 [s, 9H, $SiMe_3$]; 1.01 [m, 1H, ^2J(HH) = 13 Hz, ^2J(PtH) = 88 Hz, PtC*H*^{a}H^b *trans* to I]; 1.17 [m, 1H, ^2J(HH) = 13 Hz, ^2J(PtH) = 88 Hz, PtCH^a*H*^{b} *trans* to I]; 1.32 [m, 1H, ^2J(HH) = 13 Hz, ^3J(PtH) = 80 Hz, PtC*H*^{a}H^b *trans* to N]; 1.47 [m, 1H, ^2J(HH) = 13 Hz, ^2J(PtH) = 92 Hz, PtCH^a*H*^{b} *trans* to N]; 7.86–9.30 [m, 8H, DPK].

4.6. Reaction of CD$_3$I and MeI with [Pt(CH$_2$SiMe$_3$)$_2$(DPK)]

To an NMR tube charged with a solution of [Pt(CH_2SiMe_3)$_2$(DPK)] (0.005 g, 0.010 mmol) in $(CD_3)_2CO$ at −60 °C was added CD_3I (0.10 mmol) by microsyringe. The initial product at −60 °C was identified as mostly *trans*-[Pt(CD_3)(CH_2SiMe_3)$_2$(DPK){OC(CD_3)$_2$}]I. NMR: δ(1H) = −0.12 [s, 18H, $SiMe_3$]; 0.92 [m, 2H, ^2J(HH) = 14 Hz, ^2J(PtH) = 83 Hz, PtC*H*^{a}H^b]; 1.02 [m, 2H, ^2J(HH) = 14 Hz, ^2J(PtH) = 75 Hz, PtCH^a*H*^{b}]; 7.88 [m, 2H, H^5]; 8.25 [m, 2H, H^3]; 8.40 [m, 2H, H^4]; 8.79 [m, 2H, H^6]. At −40 °C, the major product was *trans*-[PtI(CD_3)(CH_2SiMe_3)$_2$(DPK)]. NMR: δ(1H) = −0.02 [s, 18H, $SiMe_3$]; 1.21 [m, 2H, ^2J(HH) = 14 Hz, ^2J(PtH) = 83 Hz, PtC*H*^{a}H^b]; 1.53 [m, 2H, ^2J(HH) = 14 Hz, ^3J(PtH) = 84 Hz, PtCH^a*H*^{b}]; 7.95 [m, 2H, H^5]; 8.21 [m, 2H, H^3]; 8.38 [m, 2H, H^4]; 9.40 [m, 2H, H^6]. The final product was identified at 20 °C as *cis*-[PtI(CD_3)(CH_2SiMe_3)$_2$(DPK)]. δ(1H) = −0.40 [s, 9H, $SiMe_3$]; 0.20 [s, 9H, $SiMe_3$]; 0.99 [m, 1H, ^2J(HH) = 13 Hz, ^2J(PtH) = 86 Hz, PtC*H*^{a}H^b *trans* to I]; 1.09 [m, 1H, ^2J(HH) = 13 Hz, ^2J(PtH) = 87 Hz, PtCH^a*H*^{b} *trans* to I]; 1.25 [m, 1H, ^2J(HH) = 13 Hz, ^3J(PtH) = 80 Hz, PtC*H*^{a}H^b *trans* to N]; 1.35 [m, 1H, ^2J(HH) = 13 Hz, ^2J(PtH) = 92 Hz, PtCH^a*H*^{b} *trans* to N]; 7.86–9.30 [m, 8H, DPK].

A similar reaction was carried out using MeI (12 equivalents) to identify the methylplatinum resonances. *trans*-[PtMe(CH_2SiMe_3)$_2$(DPK){OC(CD_3)$_2$}]I: δ(MePt) = 0.05 [s, 3H, ^2J(PtH) = 79 Hz]; *trans*-[PtIMe(CH_2SiMe_3)$_2$(DPK)]: δ(MePt) = 0.08 [s, 3H, ^2J(PtH) = 76 Hz]; *cis*-[PtIMe(CH_2SiMe_3)$_2$(DPK)]: δ(MePt) = 1.71 [s, 3H, ^2J(PtH) = 73 Hz].

5. Reactions with acids

A typical reaction is described, with details of product identification given in the text. To an NMR tube charged with a solution of [Pt(CH_2SiMe_3)$_2$(DPK)] (0.005 g, 0.010 mmol) in CD_2Cl_2 at −78 °C was added CF_3CO_2H (0.0.03 mmol) by microsyringe. The tube was shaken to ensure mixing, then inserted into the pre-cooled probe of the NMR spectrometer at −80 °C. The NMR spectra were recorded at −80 °C and then at 20 °C intervals to room temperature. Reactions with HCl and DCl were carried out by using standard solutions in CD_2Cl_2.

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