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# The reaction of trimethylsilyldiazomethane with complexes of the type [PtX(CH$_3$)(diphosphine)] (X = Cl, Br, I). Some observations on β-hydrogen migrations in PtCHRCH$_3$ species and organoplatinum(II)-catalysts for alkene formation from trimethylsilyldiazomethane

**Paola Bergamini,***[a] **Emiliana Costa,**[b] **Christian Ganter,**[b] **A. Guy Orpen**[b] **and Paul G. Pringle***[b]

[a] *Dipartimento di Chimica dell'Università di Ferrara e Centro di Studio su Fotoreattività e Catalisi del CNR, via L. Borsari 46, 44100 Ferrara, Italy*
[b] *School of Chemistry, University of Bristol, Cantocks Close, Bristol, UK BS8 1TS*

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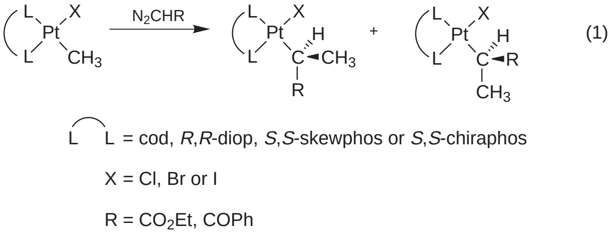
Treatment of [PtX(CH$_3$)(diphos)] **1** {X = Cl, Br, I; diphos = (*4R*,*5R*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (diop), (*2S*,*4S*)-2,4-bis(diphenylphosphino)pentane (skewphos), (*2S*,*3S*)-2,3-bis(diphenylphosphino)-butane (chiraphos)} with N$_2$CHSiMe$_3$ gives two series of products: "α-products", [PtX(CH$_2$SiMe$_3$)(diphos)] **2** and "β-products" [PtX(CH$_2$CH$_2$SiMe$_3$)(diphos)] **3**. Which product is formed and their stability depends on the ancillary ligands X and diphos. Treatment of [PtCl(CH$_3$)(diop)] **1a** with an excess of N$_2$CHSiMe$_3$ gives the α-product [PtCl(CH$_2$SiMe$_3$)(diop)] **2a** in high yield. The structure of **2a** was confirmed by X-ray crystallography. Under similar conditions [PtCl(CH$_3$)(skewphos)] **1d** reacts with an excess of N$_2$CHSiMe$_3$ to give the β-product [PtCl(CH$_2$CH$_2$SiMe$_3$)(skewphos)] **3d** as shown unambiguously by a combination of $^1$H-COSY and $^{31}$P NMR spectroscopy. It is established that the reaction sequence is **1** ⟶ **3** ⟶ **2** and the conversion of **3** ⟶ **2** is *via* a β-hydrogen migration and elimination of CH$_2$=CHSiMe$_3$. The stability of **3** with respect to β-hydrogen elimination is in the order Cl > Br > I and chiraphos > skewphos > diop; a mechanism is proposed based on five-coordinate platinum(II) intermediates to rationalize these trends. The reactions of [PtX(CH$_3$)(diphos)] with N$_2$CHSiMe$_3$ and N$_2$CHCOOEt are contrasted and it is concluded that in PtCHRMe species, a SiMe$_3$ group facilitates β-hydrogen migration while a CO$_2$Et group retards β-hydrogen migration. The complexes **2** are catalysts for the conversion of N$_2$CHSiMe$_3$ to Me$_3$SiCH=CHSiMe$_3$.

## Introduction

The formation of a C–C bond at a metal centre and β-hydrogen elimination are two of the most important steps in many transition metal complex catalysed processes.[1] We and others have previously shown that carbenes generated from diazocarbonyls insert into Pt–CH$_3$ bonds [eqn. (1)] to give branched alkylplatinum(II) species which are remarkably kinetically stable with respect to β-hydrogen transfer.[2,3] Moreover carbene insertions into the Pt–CH$_3$ bonds in optically active complexes of the type [PtX(CH$_3$)(diphos)] occurred with modest diastereoselectivity and no epimerisation at the α-carbon was observed.[2] We wanted to investigate whether the bulky, electron rich carbene CHSiMe$_3$ would insert into Pt–CH$_3$ with greater diastereoselectivity. However we report here that when trimethylsilyldiazomethane is the reagent, Pt–CH$_3$ insertion is followed by rapid β-hydrogen migration. The significance of these observations to the mechanism of β-hydrogen migration in PtCHRCH$_3$ species is discussed.



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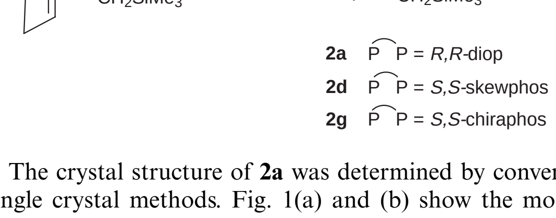
## Results and discussion

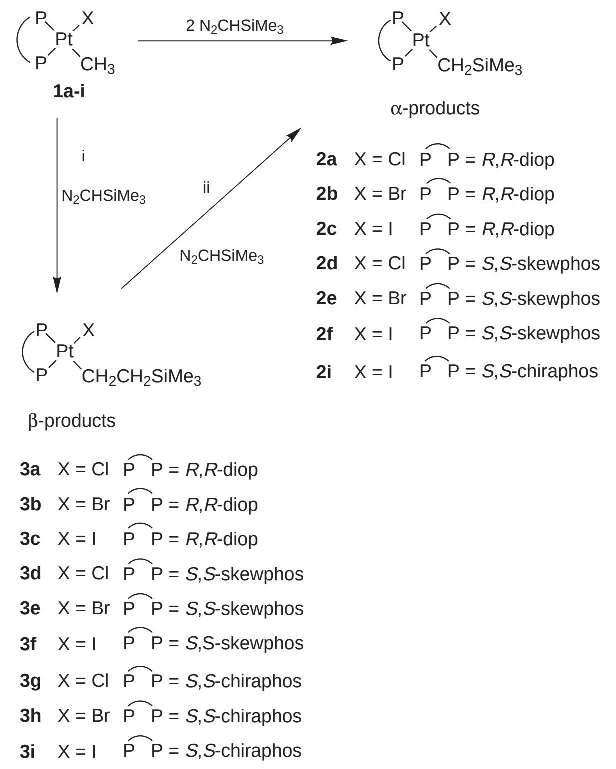
Treatment of [PtCl(CH$_3$)(*R*,*R*-diop)] **1a** [*R*,*R*-diop = (4*R*,5*R*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane] with more than two equivalents of N$_2$CHSiMe$_3$ in CH$_2$Cl$_2$ gave exclusively [PtCl(CH$_2$SiMe$_3$)(*R*,*R*-diop)] **2a** (see Scheme 1) as shown by a combination of elemental analysis, IR, $^{31}$P, $^1$H NMR spectroscopy (see Experimental section and Table 1 for the data) and X-ray crystallography (see below). Moreover treatment of [PtCl(CH$_2$SiMe$_3$)(cod)][4] with *R*,*R*-diop also gave the complex **2a** [eqn. (2)] as shown by $^{31}$P NMR spectroscopy.



(2)

The crystal structure of **2a** was determined by conventional single crystal methods. Fig. 1(a) and (b) show the molecular structures of the two independent molecules of complex **2a** present in the crystal and Table 2 gives important structural parameters for these molecules. The structure determination unambiguously confirms the absolute configuration shown. As expected the platinum is square planar with small deviations from ideal coordination geometry and the Pt–P distances reflect the higher *trans* influence of the $CH_2SiMe_3$ group compared with chloride. As shown in the torsion angle data given in Table 2, there is considerable variation in the conformation of the *R*,*R*-diop ligand (and of the $CH_2SiMe_3$ ligand) in the two independent molecules.

Treatment of $[PtCl(CH_3)(S,S\text{-skewphos})]$ **1d** [*S*,*S*-skewphos = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane] with an excess of $N_2CHSiMe_3$ gave (after 15 min) a new species quantitatively which has been isolated and assigned the structure **3d** (see Scheme 1) on the basis of elemental analysis, $^{31}P$ NMR, $^{13}C$ DEPT, $^1H$ and particularly $^1H$-COSY NMR, (see Table 1 and Experimental section for the data).



**Scheme 1**

**Table 1** $^{31}P$ NMR data[a]

| Compound | $\delta(P_A)$ | $^1J(PtP_A)$ | $\delta(P_B)$ | $^1J(PtP_B)$ | $^2J(P_AP_B)$ |
|---|---|---|---|---|---|
| **2a** | 5.5 | 4329 | 8.5 | 1745 | 14 |
| **2b** | 5.7 | 4323 | 5.6 | 1763 | 14 |
| **2c** | 3.2 | 4157 | 0.6 | 1799 | 15 |
| **2d** | 16.2 | 4224 | 15.6 | 1730 | 23 |
| **2e** | 16.0 | 4222 | 13.7 | 1746 | 22 |
| **2f** | 13.2 | 4064 | 9.5 | 1765 | 24 |
| **2g** | 45.0 | 4152 | 42.5 | 1780 | 13 |
| **2i** | 41.3 | 4040 | 42.2 | 1769 | 22 |
| **3a** | 7.7 | 4684 | 8.3 | 1492 | 12 |
| **3b** | 8.0 | 4676 | 6.3 | 1528 | 12 |
| **3c** | 4.5 | 4473 | 1.3 | 1567 | 12 |
| **3d** | 18.4 | 4545 | 15.2 | 1466 | 22 |
| **3e** | 18.5 | 4545 | 14.2 | 1493 | 22 |
| **3f** | 14.7 | 4361 | 10.5 | 1518 | 12 |
| **3g** | 44.4 | 4520 | 44.6 | 1504 | 10 |
| **3h** | 45.1 | 4516 | 44.4 | 1509 | 12 |
| **3i** | 42.7 | 4355 | 42.2 | 1511 | 12 |

[a] Spectra (81 MHz) measured in MeCN at 21 °C; chemical shifts ($\delta$) in ppm (±0.1) to high frequency of 85% $H_3PO_4$. Coupling constants ($J$) in Hz (±3). $P_A$ is trans to the halogen and $P_B$ is trans to the carbon.

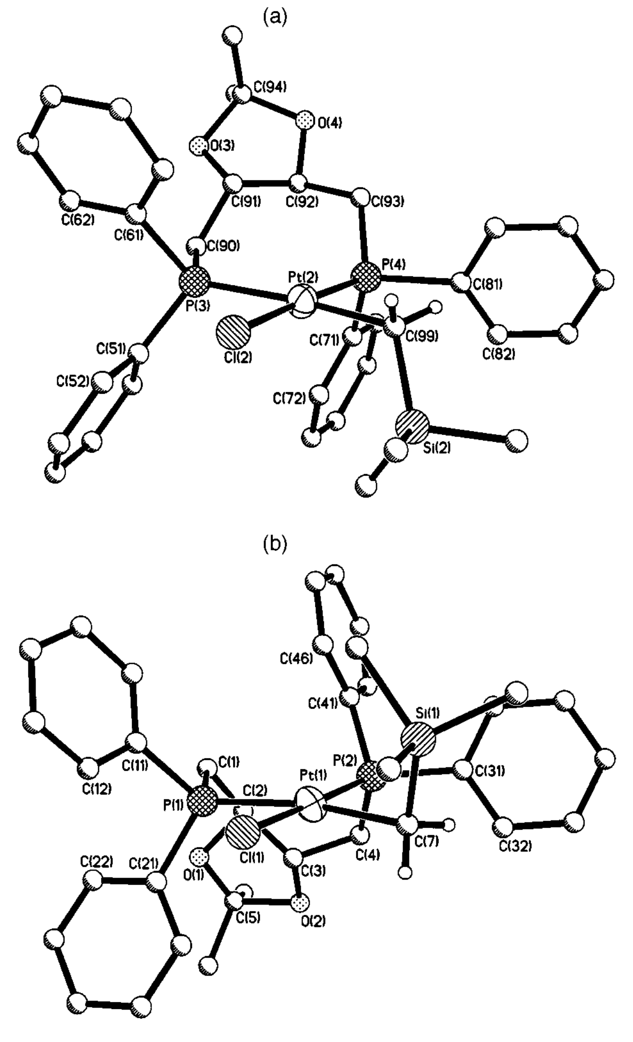


**Fig. 1** (a) Molecular structure of first independent molecule of **2a** showing labelling scheme, all hydrogen atoms have been omitted for clarity. (b) Molecular structure of second independent molecule of **2a** showing labelling scheme, all hydrogen atoms have been omitted for clarity.

**Table 2** Selected bond distances (Å), angles (°) and torsion angles (°) from the crystal structure of **2a**

| | | | | | |
|---|---|---|---|---|---|
| Pt–P(1) (*trans* to C) | 2.36(2) | 2.321(13) | Pt–C | 2.18(4) | 2.09(3) |
| Pt–P(2) (*trans* to Cl) | 2.215(11) | 2.242(13) | Pt–Cl | 2.371(13) | 2.366(10) |
| $C–Pt–P_{cis}$ | 93.5(12) | 92.8(8) | C–Pt–Cl | 83.6(12) | 83.6(8) |
| $C–Pt–P_{trans}$ | 168.6(12) | 169.5(8) | $P_{trans}–Pt–Cl$ | 175.9(5) | 176.3(5) |
| P–Pt–P | 96.2(5) | 97.7(5) | $P_{cis}–Pt–Cl$ | 87.0(4) | 86.0(5) |
| Cl–Pt–C–Si | −71.3 | 71.1 | $Pt–P_{trans\ to\ C}–C–C$ | 70.0 | −57.0 |
| (P)C–C–C–C(P) | −82.0 | −89.6 | $Pt–P_{cis\ to\ C}–C–C$ | 39.7 | −77.4 |
| $P_{trans\ to\ C}–C–C–C$ | −24.6 | 107.8 | $P–Pt–P_{trans\ to\ C}–C$ | −8.6 | −6.4 |
| $P_{cis\ to\ C}–C–C–C$ | 66.6 | 61.6 | $P–Pt–P_{cis\ to\ C}–C$ | −58.7 | 60.2 |

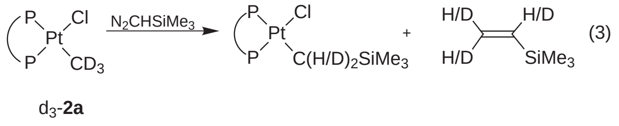
Thus there is apparently a sharp contrast in the products **2a**, with a $SiMe_3$ group on the α-carbon (an "α-product") and **3d**, with a $SiMe_3$ group on the β-carbon (a "β-product") formed by addition of an excess of $Me_3SiCHN_2$ to [$PtCl(CH_3)$(*R*,*R*-diop)] and [$PtCl(CH_3)$(*S*,*S*-skewphos)] respectively. However further study by $^{31}P$ NMR spectroscopy revealed that if 1 equivalent of $Me_3SiCHN_2$ is added to [$PtCl(CH_3)$(*R*,*R*-diop)] **1a**, a complex having $^{31}P$ parameters similar to **3d** is observed (Table 1) in the mixture of species present and is assigned the structure **3a**; this β-product **3a** appears stable in $CDCl_3$ for at least 24 h. After 2 h treatment of [$PtCl(CH_3)$-(*S*,*S*-skewphos)] **1d** with an excess of $Me_3SiCHN_2$, a small amount of a second species with the same $^{31}P$ NMR parameters as **2d** [generated *via* the route shown in eqn. (2)] was observed (Table 1). Therefore it is apparent that **1a** and **1d** with an excess of $Me_3SiCHN_2$ undergo the following sequence of transformations: $Pt–CH_3 \longrightarrow Pt–CH_2CH_2SiMe_3 \longrightarrow PtCH_2SiMe_3$ (see Scheme 1).

The same pattern is seen for the reactions of the complexes [$PtX(CH_3)$(*R*,*R*-diop)] (X = Br **1b** or I **1c**) and [$PtX(CH_3)$-(*S*,*S*-skewphos)] (X = Br **1e** or I **1f**) with $Me_3SiCHN_2$. Thus $^{31}P$ NMR spectra show that upon treatment of **1a**–**f** with 1 equivalent of $Me_3SiCHN_2$ the β-products, assigned structures **3a**–**f** on the basis of the similarity of their $^1J(PtP)$ values (Table 1), are formed which are stable in the absence of an excess of $Me_3SiCHN_2$. When an excess of $Me_3SiCHN_2$ is used, the α-products, assigned structures **2a**–**f** again on the basis of the similarity of their $^1J(PtP)$ values, are formed (Table 1). In these reactions, with the exception of **2a** and **3d** (see above), the products were not isolated.

It was noticed that the chloro complexes undergo the second step in Scheme 1 (**3** $\longrightarrow$ **2**) more slowly than their bromo and iodo analogues. The six-membered chelate (skewphos) complexes also undergo the second step more slowly than the seven-membered chelate (diop) analogues which prompted us to investigate whether there was a trend in reactivity with chelate ring size. Thus the reactions of the five-membered chelate complexes **1g**–**i** [chiraphos, (2*S*,3*S*)-2,3-bis(diphenylphosphino)ethane] with $Me_3SiCHN_2$ were followed by $^{31}P$ NMR spectroscopy and it was revealed that the reactions were slower than **1a**–**f** and, with **1g** and **1h**, the only products observed (even after 20 h in the presence of an excess of $Me_3SiCHN_2$) were the β-products **3g** and **3h**, *i.e.* the second step in Scheme 2 with the five-membered chelates was not observed; **2g** has been generated *via* the route shown in eqn. (2). With the iodo complex **1i**, a species assigned to the α-product **2i** (identified from its $^{31}P$ parameters only, see Table 1) was detected when an excess of $N_2CHSiMe_3$ was used, consistent with the greater tendency of the iodo complexes to form the α products.

A mechanism to explain the formation of **2a**–**f** and **3a**–**i** from the corresponding **1a**–**i** and $N_2CHSiMe_3$ is proposed in Scheme 2. Insertion of the $CHSiMe_3$ into the $Pt–CH_3$ bond of **1a**–**i** (step i) to give the transient species **A** (the mechanism for insertions of this type we have previously discussed in detail[2]) is followed by β-hydrogen migration (step ii) to give a five-coordinate hydridoplatinum(II) species **B**.[5] A β-hydrogen migration to the substituted alkenyl carbon (step iii) would give the observed β-products **3a**–**i**. Alternatively, dissociation of vinyltrimethylsilane from **B** (step iv) would give the four-coordinate hydrido species **C** which would then rapidly insert more $CHSiMe_3$ (step v) to give the observed α-products **2a**–**f**.

Further insight into the reactions discussed above was gained from observations made with the deuterium-labelled complex d$_3$-**1a**. Monitoring the reaction of d$_3$-**1a** with 2 equivalents of $N_2CHSiMe_3$ in $CHCl_3$ by $^2H$ NMR spectroscopy revealed that vinyltrimethylsilane was the only detected organic product and that the deuterium was distributed over all three alkenyl sites equally (3 equally intense singlets at $\delta$ 6.18, 5.93 and 5.67 in agreement with the $^1H$ shifts measured for a genuine sample of $CH_2{=}CHSiMe_3$); a deuterium resonance at $\delta$ 0.51 was also detected and assigned to the α-methylene of the trimethylsilylmethyl ligand [see eqn. (3)]. Scheme 3 shows how this



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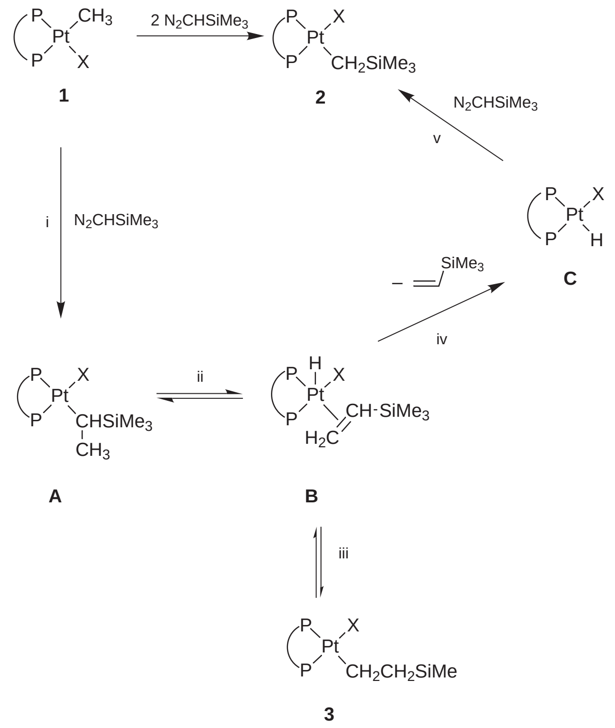
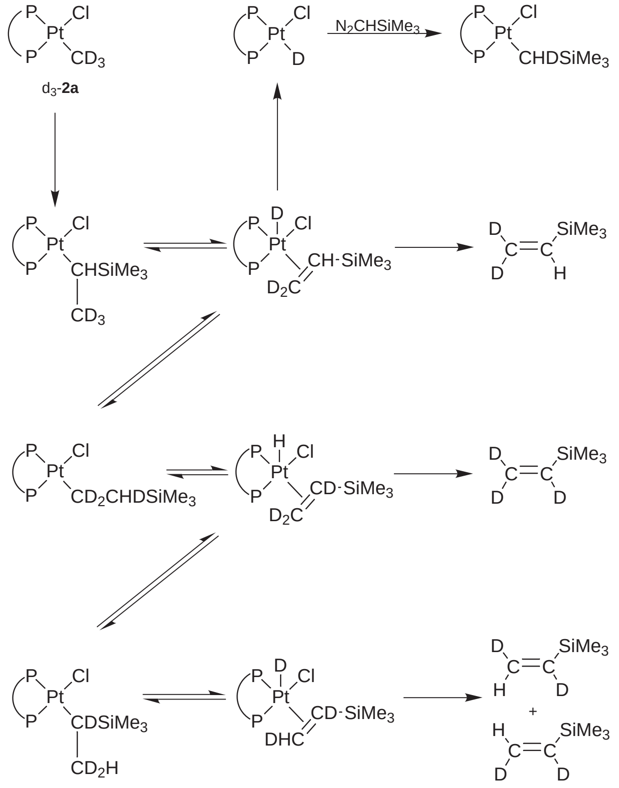


Scheme 2

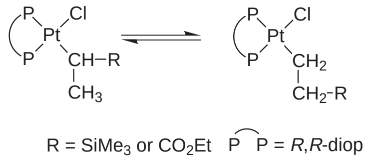


Scheme 3

scrambling of the deuterium can be rationalised by invoking a series of β-hydrogen migrations. These results are consistent with the β-hydrogen migrations from **B** (steps ii and iii in Scheme 2) being reversible and occurring rapidly relative to the alkene elimination from **B** (step iv in Scheme 2).

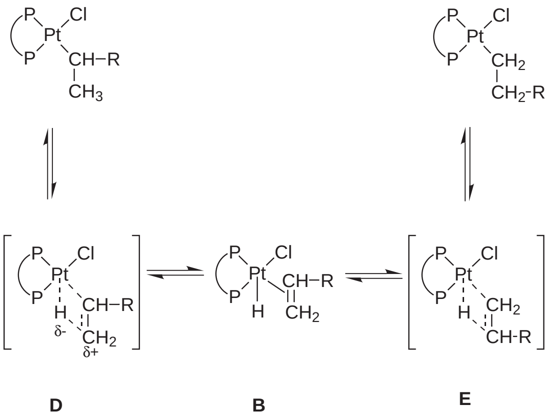
The deuteriation studies show that the complexes [PtX(CHMeSiMe$_3$)(diphos)] and [PtX(CH$_2$CH$_2$SiMe$_3$)(diphos)] can interconvert rapidly *via* β-hydrogen migrations.

It is of interest to consider how the substituents R may influence the thermodynamics and kinetics of the systems shown in eqn. (4). We have never observed species containing the branched alkyl Pt–CHMeSiMe$_3$ nor species containing the linear alkyl Pt–CH$_2$CH$_2$CO$_2$Et and therefore we are not able to determine whether the instability is kinetic or thermodynamic. Young *et al.*[6] have recently shown that the Pt–C bond in [PtCl(CH$_2$SiMe$_3$)(PMe$_3$)$_2$] is anomalously weak and moreover have reported that $^1J$(PtP) for the *trans* phosphorus is inversely correlated with the Pt–alkyl bond strength. Our $^1J$(PtP) data (Table 1) are consistent with the Pt–CH$_2$SiMe$_3$ bonds being weaker than the Pt–CH$_2$CH$_2$SiMe$_3$ bonds. Therefore one of the thermodynamic driving forces for the transformation of Pt–CHMeSiMe$_3$ into Pt–CH$_2$CH$_2$SiMe$_3$ [eqn. (4)] is the greater Pt–C bond strength. Furthermore it has been shown[7] that for steric and electronic reasons, primary alkyl metal complexes MCH$_2$R generally contain stronger M-C bonds than secondary alkyl metal complexes MCHR$_2$ and thus when R is the bulky SiMe$_3$ group it is not surprising that the linear Pt–CH$_2$CH$_2$SiMe$_3$ species is the only one observed. The stability of the branched species PtCHMeCO$_2$Et may be due in part to the stabilisation of the δ− charge on the α-carbon by the electronegative CO$_2$Et.



(4)

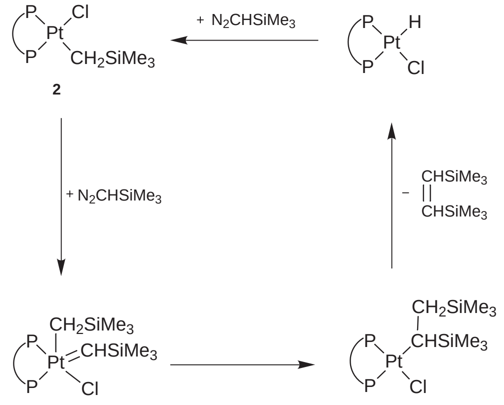
The greater kinetic lability of the Pt–CHMeSiMe$_3$ species than the Pt–CHMeCO$_2$Me species can be rationalised by consideration of the associative mechanism proposed in Scheme 4 which is consistent with previously reported[5,8,9] mechanisms for β-hydrogen migration in alkylplatinum(II) complexes; in coordinating solvents such as methanol, dissociation of halide or phosphine to give three-coordinate platinum(II) species as intermediates in β-hydrogen elimination have also been proposed[9] but since our reactions were carried out in CDCl$_3$, we have not considered this possibility further. Species **D** and **E** are transition states en route to the five-coordinate intermediate **B**. From previous work,[5] we would predict that intermediate **B** would be more stable when R = CO$_2$Et since this yields the better π-acceptor alkene ligand. However we suggest that the lower activation energy observed when R = SiMe$_3$ than when R = CO$_2$Et is a consequence of two factors: (i) the lower stability of the PtCHRMe species when R = SiMe$_3$ (see above) and (ii) the stabilization of the developing $\delta+$ on the carbon β to the SiMe$_3$ group in **D** by hyperconjugation.[10]



Scheme 4

From the mechanism presented in Scheme 4, it might also be expected that ancillary ligands which can stabilise the five-coordinate species **B** would promote the conversion of **3** ⟶ **2**. It is known[11] that the stability of trigonal bipyramidal platinum(II) complexes PtX$_2$L$_3$ increases in the order Cl < Br < I and thus if **B** is trigonal bipyramidal, this would explain why our bromo and iodo complexes favour the formation of **2** more than the chloro analogues. Moreover the strain caused by the 120° angle in the diphosphine chelates in **B** would decrease in the order chiraphos (five-membered) > skewphos (six-membered) > diop (seven-membered) consistent with the preference of the diop complexes to form **2**.

The conversion of N$_2$CHSiMe$_3$ to Me$_3$SiCH=CHSiMe$_3$ is catalysed by complexes of type **2**. Hence addition of N$_2$CHSiMe$_3$ to a solution of **2a** (0.1 equivalent) in CDCl$_3$ led to evolution of N$_2$ and formation of *trans* alkene (as shown by $^1$H NMR). The catalysis turnover was slow: *ca.* 2 h$^{-1}$ with **2a** and *ca.* 1 h$^{-1}$ with complexes **2d** and **2g** [generated according to eqn. (2)]. The rate of the catalysis with **2a** was similar in CD$_3$CN and furthermore, when the cationic species [Pt(NCMe)(CH$_2$SiMe$_3$)(diop)]O$_3$SCF$_3$ was generated *in situ* and used as the catalyst, only trace amounts of Me$_3$SiCH=CHSiMe$_3$ were detected among the many products that formed very rapidly. Hence we favour the mechanism shown in Scheme 5 involving uncharged intermediates.



Scheme 5

In conclusion we have shown that the rate of β-hydrogen migration in [PtX(CHRCH$_3$)(diphos)] is a function of the stereoelectronic effects of R. When R = SiMe$_3$, β-hydrogen migration is facilitated while for R = CO$_2$Et, β-hydrogen migration is effectively arrested at ambient temperatures.

## Experimental

All reactions were carried out in air at *ca.* 20 °C. The phosphines and Me$_3$SiCHN$_2$ solution were used as purchased from Aldrich. The complexes [PtX(CH$_3$)L$_2$] (L$_2$ = *R*,*R*-diop, *S*,*S*-skewphos, *R*,*R*-chiraphos)[2] and [PtCl(CH$_2$SiMe$_3$)(cod)][4] were made as previously described. $^{31}$P-{$^1$H} (81 MHz), $^{13}$C-{$^1$H} (50 MHz), and $^1$H (200 MHz) spectra were measured using a Bruker AM200 spectrometer at 22 °C.

### Preparation of [PtCl(CH$_2$SiMe$_3$)(*R*,*R*-diop)] 2a from [PtCl(CH$_3$)(*R*,*R*-diop)]

The complex [PtCl(CH$_3$)(*R*,*R*-diop)] (230 mg, 0.30 mmol) was dissolved in CH$_2$Cl$_2$ or CHCl$_3$ (3 cm$^3$) and vigorously stirred while Me$_3$SiCHN$_2$ (0.45 cm$^3$ of a 2 M solution in n-hexane, 0.90 mmol) was added. The mixture was stirred for 2 h and then the solvent removed under reduced pressure to give a white solid which was triturated with diethyl ether (2 $cm^3$) and then filtered off to give 208 mg (80%) of product. Elemental analysis (calculated for $C_{35}H_{43}ClO_2P_2PtSi$): C, 51.00 (51.55); H, 5.45 (5.25%); $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ −0.20 [s, 9H, $Si(CH_3)_3$]; 0.4–0.7 (complex multiplets, 2H, diastereotopic $PtCH_2Si$); 1.12 (s, 3H, $CH_3$), 1.14 (s, 3H, $CH_3$), other diop resonances are complex multiplets centred at the following shifts: $\delta$ 2.28 (1H), 2.74 (1H), 2.91 (1H), 3.23 (1H), 3.81 (2H) 3.90 (1H) and 7.6–8.0 (20H); $^{13}$C NMR (50 MHz, $CDCl_3$, assignments from DEPT): $\delta$ 4.5 [$Si(CH_3)_3$]; 17.3 [d, $J$(PC) 88.8, $J$(PtC) 632, $PtCH_2Si$]; 27.3 (s, $CH_3$ of diop); 30.7 [d, $J$(PC) 23.5, $CH_2P$]; 33.4 [d, $J$(PC) 37.3 Hz, $CH_2P$]; 128–135 (complex multiplets); IR (CsI disc) $\nu$(PtCl) at 280 $cm^{-1}$. Crystals for the X-ray crystallography were obtained by slow diffusion of $Et_2O$ into a $CH_2Cl_2$ solution of **2a**.

### Preparation of [PtCl($CH_2SiMe_3$)(*R*,*R*-diop)] 2a from [PtCl($CH_2SiMe_3$)(cod)]

To a stirred solution of the complex [PtCl($CH_2SiMe_3$)(cod)] (40 mg, 0.094 mmol) in $CH_2Cl_2$ (1 $cm^3$) was added a solution of diop (47 mg, 0.094 mmol) in $CH_2Cl_2$ (2 $cm^3$) dropwise over 5 min *via* a syringe. After 15 min, the solvent was removed under reduced pressure and then the residue triturated with $Et_2O$ (3 $cm^3$) to give the product **2a** (60 mg, 78%) as a fluffy white solid. The $^{31}$P and $^1$H NMR spectra were identical to the product **2a** obtained above. The complexes [PtCl($CH_2SiMe_3$)(skewphos)] **2d** and [PtCl($CH_2SiMe_3$)(chiraphos)] **2g** were made similarly from the appropriate diphosphine in *ca.* 80% yields.

### Preparation of [PtCl($CH_2CH_2SiMe_3$)(*S*,*S*-skewphos)] 3d

The complex [PtCl($CH_3$)(*R*,*R*-skewphos)] (60 mg, 0.088 mmol) was dissolved in $CH_2Cl_2$ (1 $cm^3$) which had been previously stirred over $NaHCO_3$ for 10 h to remove traces of acid. $Me_3SiCHN_2$ (0.175 $cm^3$ of a 2 M solution in n-hexane, 0.35 mmol) was added. The mixture was stirred for 1 h and then the solvent removed under reduced pressure to give a white solid which was triturated with n-pentane (2 $cm^3$) and then filtered off to give 52 mg (80%) of product. Elemental analysis (calculated for $C_{34}H_{43}ClP_2PtSi$): C, 52.85 (52.90); H, 5.60 (5.40%); $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ −0.40 [s, 9H, $Si(CH_3)_3$]; 0.15 (1H), 0.55 (1H), 1.0 (2H) (complex multiplets, assigned to two of the four $PtCH_2CH_2Si$ protons based on the observation of cross-peaks in the COSY spectrum) other skewphos resonances are centred at the following shifts: $\delta$ 0.98 and 1.05 (2 overlapping dd, 7.1, 13.0 Hz, 6H, $CH_3$), 2.88 (1H), 2.72 (1H), 1.86 (2H), and 7.2–8.0 (20H); $^{13}$C NMR (50 MHz, $CDCl_3$, assignments from DEPT): $\delta$ −1.3 [$Si(CH_3)_3$]; 24.0 [d, $J$(PC) 98.0 Hz, $J$(PtC) not resolved, $Pt\mathit{C}H_2CH_2Si$]; 23.3 (s, $PtCH_2\mathit{C}H_2Si$); other skewphos signals at 36.8 (s), 17.8 (s), 19.4 (s), 26–28 (complex multiplets), 126–137 (complex multiplets).

### NMR characterisation of the other complexes

The other complexes were characterised in solution by $^{31}$P NMR spectroscopy only and assigned their structures as α-products (**2**) or β-products (**3**) by comparison of their $^1J$(PtP) values with those for **2a**, **2d**, **2g** and **3d** (see Table 1). In a typical experiment 0.025 mmol of complex was dissolved in $CDCl_3$ (0.4 $cm^3$) and then 12.6 $cm^3$ of $Me_3SiCHN_2$ in hexane (2 M, 0.025 mmol) added. When the nitrogen evolution had subsided the $^{31}$P NMR spectrum was recorded. More $Me_3SiCHN_2$ (typically 0.1 mmol) was then added and the spectrum recorded at appropriate intervals over 24 h.

### Catalysis of alkene formation from $N_2CHSiMe_3$

A solution of **2a** in $CDCl_3$ (100 μL, 0.20 M, 0.02 mmol) was added to a solution of $Me_3SiCHN_2$ in hexane (100 μL, 2 M, 0.20 mmol) diluted with $CDCl_3$ (0.4 $cm^3$). Nitrogen evolution was observed and the formation of *trans*-$Me_3SiCH{=}CHSiMe_3$ monitored by $^1$H NMR spectroscopy ($\delta_H$ 6.60) after 10, 50, 90, 120 min and 24 h. The $^{31}$P NMR spectrum showed that **2a** was the only detected P-containing species present after 24 h. Similar experiments with **2d** and **2g** in $CDCl_3$ and **2a** in $CD_3CN$ were also carried out.

### Structure determination of [PtCl($CH_2SiMe_3$)(*R*,*R*-diop)] 2a

Crystal data for [PtCl($CH_2SiMe_3$)*R*,*R*-diop)] **2a**, $C_{35}H_{43}ClO_2P_2PtSi$, $M = 852.76$, monoclinic, space group $P2_1$ (no. 4), $a = 15.026(4)$, $b = 14.802(6)$, $c = 16.712(7)$ Å, $\beta = 104.43(3)°$, $V = 4026(4)$ Å$^3$, $Z = 4$, $D_x = 1.658$ Mg m$^{-3}$, $T = 293$ K, $\mu$(Mo-K$_\alpha$) = 4.123 mm$^{-1}$, 6262 reflections collected, 6178 unique ($R_{int}$ 0.048) all used in refinement, $\theta \le 22.5°$. $R_1 = 0.064$, $wR_2$ 0.113. Phenyl rings were constrained to idealised geometry and all silicon and carbon atoms assigned isotropic displacement parameters. The absolute structure was confirmed by refinement of the Flack parameter [$x = 0.05(3)$].[12]

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