

The reaction of trimethylsilyldiazomethane with complexes of the type [PtX(CH₃)(diphosphine)] (X = Cl, Br, I). Some observations on β-hydrogen migrations in PtCHRCH₃ species and organoplatinum(II)-catalysts for alkene formation from trimethylsilyldiazomethane

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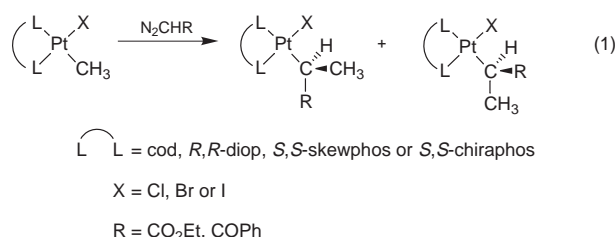
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Treatment of [PtX(CH₃)(diphos)] **1** {X = Cl, Br, I; diphos = (4*R*,5*R*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (diop), (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (skewphos), (2*S*,3*S*)-2,3-bis(diphenylphosphino)-butane (chiraphos)} with N₂CHSiMe₃ gives two series of products: “α-products”, [PtX(CH₂SiMe₃)(diphos)] **2** and “β-products” [PtX(CH₂CH₂SiMe₃)(diphos)] **3**. Which product is formed and their stability depends on the ancillary ligands X and diphos. Treatment of [PtCl(CH₃)(diop)] **1a** with an excess of N₂CHSiMe₃ gives the α-product [PtCl(CH₂SiMe₃)(diop)] **2a** in high yield. The structure of **2a** was confirmed by X-ray crystallography. Under similar conditions [PtCl(CH₃)(skewphos)] **1d** reacts with an excess of N₂CHSiMe₃ to give the β-product [PtCl(CH₂CH₂SiMe₃)(skewphos)] **3d** as shown unambiguously by a combination of ¹H-COSY and ³¹P 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 CH₂=CHSiMe₃. 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(CH₃)(diphos)] with N₂CHSiMe₃ and N₂CHCOOEt are contrasted and it is concluded that in PtCHRMe species, a SiMe₃ group facilitates β-hydrogen migration while a CO₂Et group retards β-hydrogen migration. The complexes **2** are catalysts for the conversion of N₂CHSiMe₃ to Me₃SiCH=CHSiMe₃.

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–CH₃ bonds [eqn. (1)] to give branched alkyl-

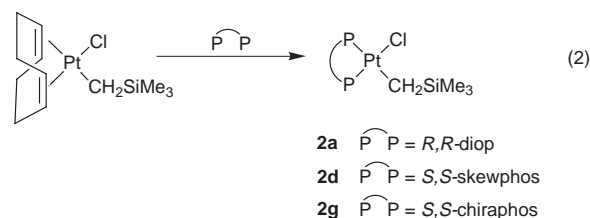


platinum(II) species which are remarkably kinetically stable with respect to β-hydrogen transfer.^{2,3} Moreover carbene insertions into the Pt–CH₃ bonds in optically active complexes of the type [PtX(CH₃)(diphos)] occurred with modest diastereoselectivity and no epimerisation at the α-carbon was observed.² We wanted to investigate whether the bulky, electron rich carbene CHSiMe₃ would insert into Pt–CH₃ with greater diastereoselectivity. However we report here that when trimethylsilyldiazomethane is the reagent, Pt–CH₃ insertion is followed by rapid β-hydrogen migration. The significance of these

observations to the mechanism of β-hydrogen migration in PtCHRCH₃ species is discussed.

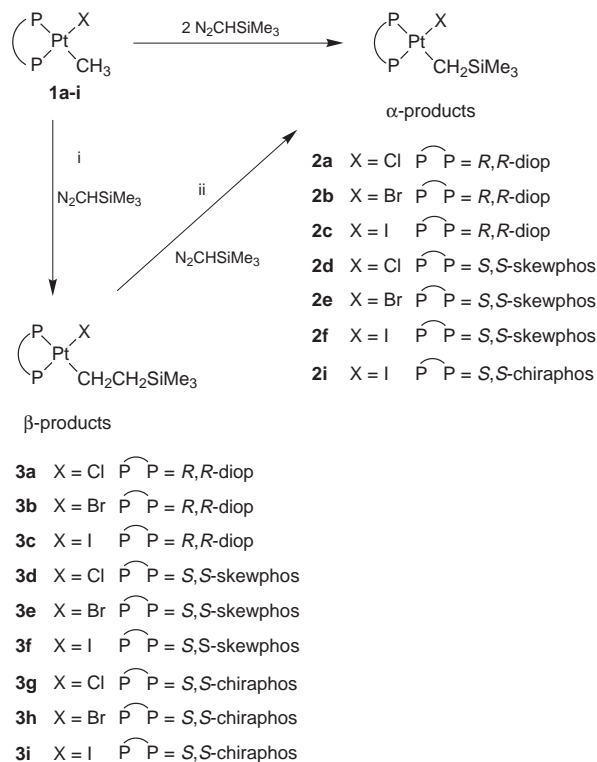
Results and discussion

Treatment of [PtCl(CH₃)(*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 N₂CHSiMe₃ in CH₂Cl₂ gave exclusively [PtCl(CH₂SiMe₃)(*R,R*-diop)] **2a** (see Scheme 1) as shown by a combination of elemental analysis, IR, ³¹P, ¹H NMR spectroscopy (see Experimental section and Table 1 for the data) and X-ray crystallography (see below). Moreover treatment of [PtCl(CH₂SiMe₃)(cod)]⁴ with *R,R*-diop also gave the complex **2a** [eqn. (2)] as shown by ³¹P NMR spectroscopy.



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



Scheme 1

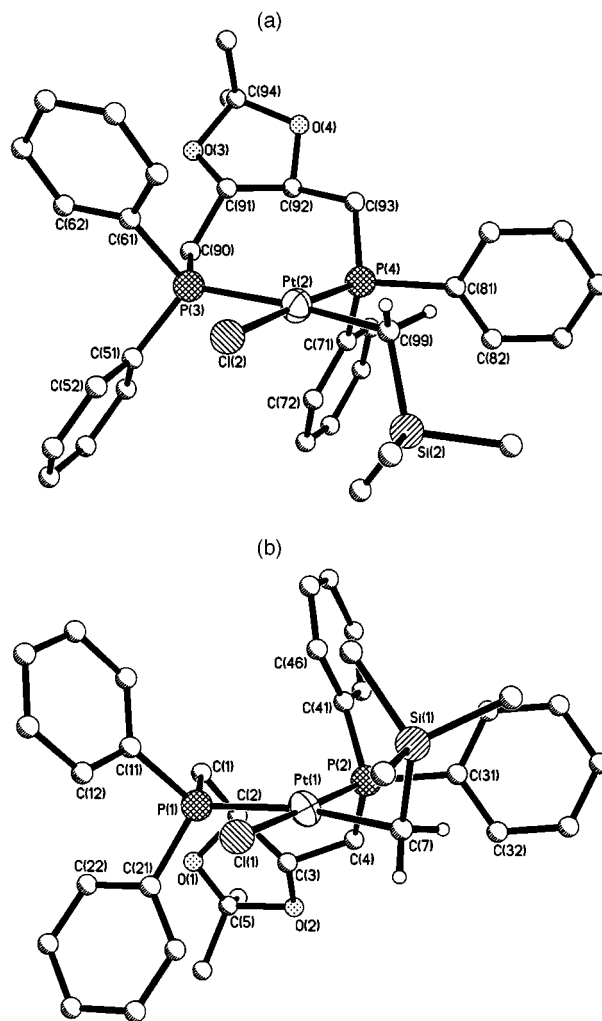
Table 1 ^{31}P NMR data^a

Compound	$\delta(\text{P}_\text{A})$	$^1J(\text{PtP}_\text{A})$	$\delta(\text{P}_\text{B})$	$^1J(\text{PtP}_\text{B})$	$^2J(\text{P}_\text{A}\text{P}_\text{B})$
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 (δ) 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.

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 $[\text{PtCl}(\text{CH}_3)(S,S\text{-skewphos})]$ **1d** [*S,S*-skewphos = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane] with an excess of $\text{N}_2\text{CHSiMe}_3$ 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).



Thus there is apparently a sharp contrast in the products **2a**, with a SiMe₃ group on the α -carbon (an " α -product") and **3d**, with a SiMe₃ group on the β -carbon (a " β -product") formed by addition of an excess of Me₃SiCHN₂ to [PtCl(CH₃)(*R,R*-diop)] and [PtCl(CH₃)(*S,S*-skewphos)] respectively. However further study by ³¹P NMR spectroscopy revealed that if 1 equivalent of Me₃SiCHN₂ is added to [PtCl(CH₃)(*R,R*-diop)] **1a**, a complex having ³¹P 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 CDCl₃ for at least 24 h. After 2 h treatment of [PtCl(CH₃)(*S,S*-skewphos)] **1d** with an excess of Me₃SiCHN₂, a small amount of a second species with the same ³¹P 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 Me₃SiCHN₂ undergo the following sequence of transformations: Pt-CH₃ \longrightarrow Pt-CH₂CH₂SiMe₃ \longrightarrow PtCH₂SiMe₃ (see Scheme 1).

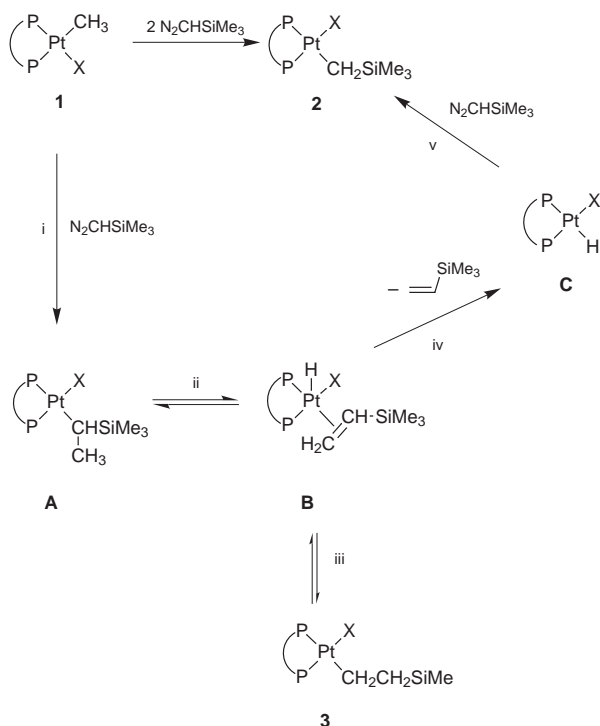
The same pattern is seen for the reactions of the complexes [PtX(CH₃)(*R,R*-diop)] (X = Br **1b** or I **1c**) and [PtX(CH₃)(*S,S*-skewphos)] (X = Br **1e** or I **1f**) with Me₃SiCHN₂. Thus ³¹P NMR spectra show that upon treatment of **1a-f** with 1 equivalent of Me₃SiCHN₂ the β -products, assigned 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 Me₃SiCHN₂. When an excess of Me₃SiCHN₂ 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 Me₃SiCHN₂ were followed by ³¹P NMR spectroscopy and it was revealed that the reactions were slower than **1a-f** and, with **1g** and **1h**, the only products

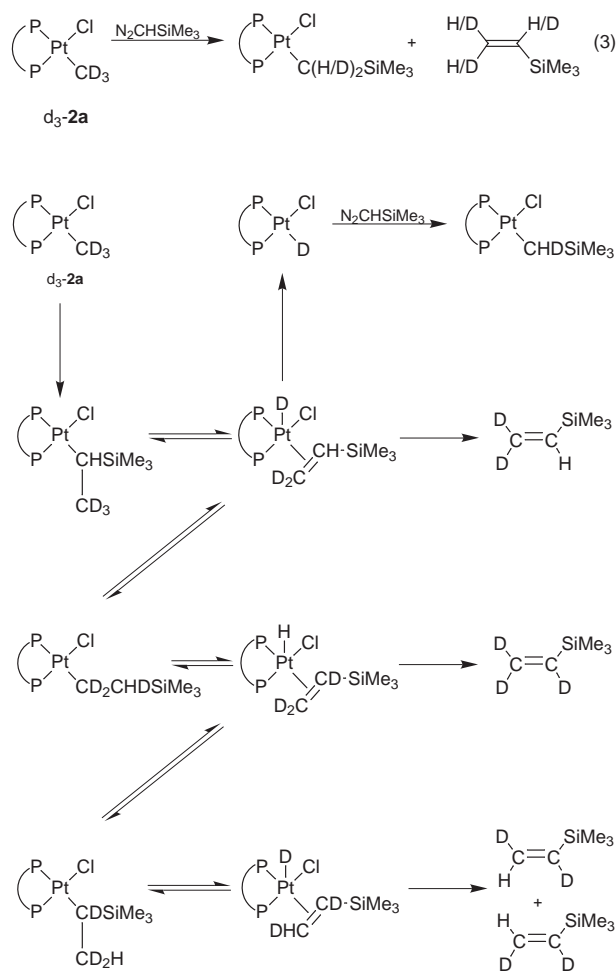
observed (even after 20 h in the presence of an excess of Me₃-SiCHN₂) were the β -products **3g** and **3h**, *i.e.* the second step in Scheme 2 with the five-membered chelates was not observed; **2g** has been generated *via* the route shown in eqn. (2). With the iodo complex **1i**, a species assigned to the α -product **2i** (identified from its ³¹P parameters only, see Table 1) was detected when an excess of N₂CHSiMe₃ 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 N₂CHSiMe₃ is proposed in Scheme 2. Insertion of the CHSiMe₃ into the Pt-CH₃ bond of **1a-i** (step i) to give the transient species **A** (the mechanism for insertions of this type we have previously discussed in detail²) 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 CHSiMe₃ (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 d₃-**1a**. Monitoring the reaction of d₃-**1a** with 2 equivalents of N₂CHSiMe₃ in CHCl₃ 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 δ 6.18, 5.93 and 5.67 in agreement with the ¹H shifts measured for a genuine sample of CH₂=CHSiMe₃); a deuterium resonance at δ 0.51 was also detected and assigned to the α -methylene of the trimethylsilylmethyl ligand [see eqn. (3)]. Scheme 3 shows how this



Scheme 2

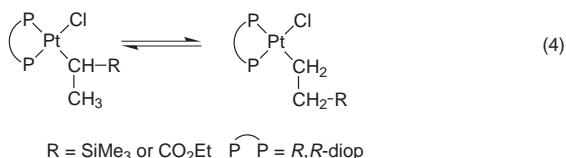


Scheme 3

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).

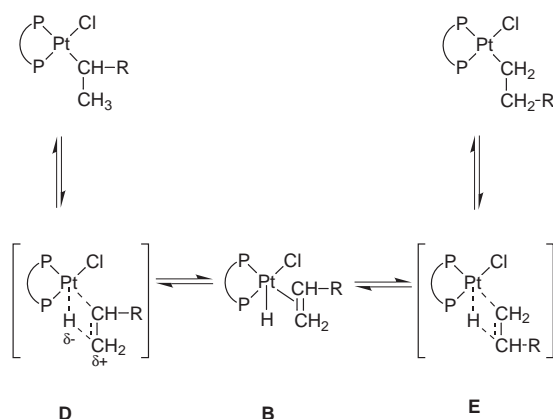
The deuteration studies show that the complexes $[\text{PtX}(\text{CHMeSiMe}_3)(\text{diphos})]$ and $[\text{PtX}(\text{CH}_2\text{CH}_2\text{SiMe}_3)(\text{diphos})]$ can interconvert rapidly *via* β -hydrogen migrations.

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 $\text{Pt-CH}_2\text{CH}_2\text{CO}_2\text{Et}$ 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 $[\text{PtCl}(\text{CH}_2\text{SiMe}_3)(\text{PMe}_3)_2]$ is anomalously weak and moreover have reported that $^1J(\text{PtP})$ for the *trans* phosphorus is inversely correlated with the Pt-alkyl bond strength. Our $^1J(\text{PtP})$ data (Table 1) are consistent with the $\text{Pt-CH}_2\text{SiMe}_3$ bonds being weaker than the $\text{Pt-CH}_2\text{CH}_2\text{SiMe}_3$ bonds. Therefore one of the thermodynamic driving forces for the transformation of Pt-CHMeSiMe_3 into $\text{Pt-CH}_2\text{CH}_2\text{SiMe}_3$ [eqn. (4)] is the greater Pt-C bond strength. Furthermore it has been shown⁷ that for steric and electronic reasons, primary alkyl metal complexes MCH_2R 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 $\text{Pt-CH}_2\text{CH}_2\text{SiMe}_3$ species is the only one observed. The stability of the branched species $\text{PtCHMeCO}_2\text{Et}$ may be due in part to the stabilisation of the δ^- charge on the α -carbon by the electronegative CO_2Et .

The greater kinetic lability of the Pt-CHMeSiMe_3 species than the $\text{Pt-CHMeCO}_2\text{Me}$ species can be rationalised by consideration of the associative mechanism proposed in Scheme 4



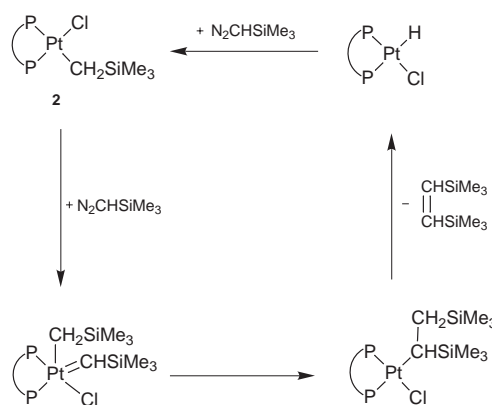
Scheme 4

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 proposed⁹ 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_2Et 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_2Et 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 δ^+ on the carbon β to the SiMe_3 group in **D** by hyperconjugation.¹⁰

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** \rightarrow **2**. It is known¹¹ that the stability of trigonal bipyramidal platinum(II) complexes PtX_2L_3 increases in the order $\text{Cl} < \text{Br} < \text{I}$ 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 $\text{N}_2\text{CHSiMe}_3$ to $\text{Me}_3\text{SiCH=CHSiMe}_3$ is catalysed by complexes of type **2**. Hence addition of $\text{N}_2\text{CHSiMe}_3$ 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 ^1H 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_3CN and furthermore, when the cationic species $[\text{Pt}(\text{NCMe})(\text{CH}_2\text{SiMe}_3)(\text{diop})]\text{O}_3\text{SCF}_3$ was generated *in situ* and used as the catalyst, only trace amounts of $\text{Me}_3\text{SiCH=CHSiMe}_3$ 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 $[\text{PtX}(\text{CHRCH}_3)(\text{diphos})]$ is a function of the stereoelectronic effects of **R**. When **R** = SiMe_3 , β -hydrogen migration is facilitated while for **R** = CO_2Et , β -hydrogen migration is effectively arrested at ambient temperatures.

Experimental

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

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

The complex $[\text{PtCl}(\text{CH}_3)(\text{R,R-diop})]$ (230 mg, 0.30 mmol) was dissolved in CH_2Cl_2 or CHCl_3 (3 cm^3) and vigorously stirred while $\text{Me}_3\text{SiCHN}_2$ (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 cm³) and then filtered off to give 208 mg (80%) of product. Elemental analysis (calculated for C₃₅H₄₃ClO₂P₂PtSi): C, 51.00 (51.55); H, 5.45 (5.25%); ¹H NMR (200 MHz, CDCl₃): δ −0.20 [s, 9H, Si(CH₃)₃]; 0.4–0.7 (complex multiplets, 2H, diastereotopic PtCH₂Si); 1.12 (s, 3H, CH₃), 1.14 (s, 3H, CH₃), other diop resonances are complex multiplets centred at the following shifts: δ 2.28 (1H), 2.74 (1H), 2.91 (1H), 3.23 (1H), 3.81 (2H) 3.90 (1H) and 7.6–8.0 (20H); ¹³C NMR (50 MHz, CDCl₃, assignments from DEPT): δ 4.5 [Si(CH₃)₃]; 17.3 [d, J(PC) 88.8, J(PtC) 632, PtCH₂Si]; 27.3 (s, CH₃ of diop); 30.7 [d, J(PC) 23.5, CH₂P]; 33.4 [d, J(PC) 37.3 Hz, CH₂P]; 128–135 (complex multiplets); IR (CsI disc) ν(PtCl) at 280 cm^{−1}. Crystals for the X-ray crystallography were obtained by slow diffusion of Et₂O into a CH₂Cl₂ solution of **2a**.

Preparation of [PtCl(CH₂SiMe₃)(*R,R*-diop)] **2a** from [PtCl(CH₂SiMe₃)(cod)]

To a stirred solution of the complex [PtCl(CH₂SiMe₃)(cod)] (40 mg, 0.094 mmol) in CH₂Cl₂ (1 cm³) was added a solution of diop (47 mg, 0.094 mmol) in CH₂Cl₂ (2 cm³) dropwise over 5 min *via* a syringe. After 15 min, the solvent was removed under reduced pressure and then the residue triturated with Et₂O (3 cm³) to give the product **2a** (60 mg, 78%) as a fluffy white solid. The ³¹P and ¹H NMR spectra were identical to the product **2a** obtained above. The complexes [PtCl(CH₂SiMe₃)(skewphos)] **2d** and [PtCl(CH₂SiMe₃)(chiraphos)] **2g** were made similarly from the appropriate diphosphine in *ca.* 80% yields.

Preparation of [PtCl(CH₂CH₂SiMe₃)(*S,S*-skewphos)] **3d**

The complex [PtCl(CH₃)(*R,R*-skewphos)] (60 mg, 0.088 mmol) was dissolved in CH₂Cl₂ (1 cm³) which had been previously stirred over NaHCO₃ for 10 h to remove traces of acid. Me₃SiCHN₂ (0.175 cm³ 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 cm³) and then filtered off to give 52 mg (80%) of product. Elemental analysis (calculated for C₃₄H₄₃ClP₂PtSi): C, 52.85 (52.90); H, 5.60 (5.40%); ¹H NMR (200 MHz, CDCl₃): δ −0.40 [s, 9H, Si(CH₃)₃]; 0.15 (1H), 0.55 (1H), 1.0 (2H) (complex multiplets, assigned to two of the four PtCH₂CH₂Si protons based on the observation of cross-peaks in the COSY spectrum) other skewphos resonances are centred at the following shifts: δ 0.98 and 1.05 (2 overlapping dd, 7.1, 13.0 Hz, 6H, CH₃), 2.88 (1H), 2.72 (1H), 1.86 (2H), and 7.2–8.0 (20H); ¹³C NMR (50 MHz, CDCl₃, assignments from DEPT): δ −1.3 [Si(CH₃)₃]; 24.0 [d, J(PC) 98.0 Hz, J(PtC) not resolved, PtCH₂CH₂Si]; 23.3 (s, PtCH₂CH₂Si); 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 ³¹P 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 CDCl₃ (0.4 cm³) and then 12.6 cm³ of Me₃SiCHN₂ in hexane (2 M, 0.025 mmol) added. When the nitrogen evolution had subsided the ³¹P NMR spectrum was recorded. More Me₃SiCHN₂ (typically 0.1 mmol) was then added and the spectrum recorded at appropriate intervals over 24 h.

Catalysis of alkene formation from N₂CHSiMe₃

A solution of **2a** in CDCl₃ (100 μL, 0.20 M, 0.02 mmol) was added to a solution of Me₃SiCHN₂ in hexane (100 μL, 2 M, 0.20 mmol) diluted with CDCl₃ (0.4 cm³). Nitrogen evolution was observed and the formation of *trans*-Me₃SiCH=CHSiMe₃ monitored by ¹H NMR spectroscopy (δ_H 6.60) after 10, 50, 90, 120 min and 24 h. The ³¹P NMR spectrum showed that **2a** was the only detected P-containing species present after 24 h. Similar experiments with **2d** and **2g** in CDCl₃ and **2a** in CD₃CN were also carried out.

Structure determination of [PtCl(CH₂SiMe₃)(*R,R*-diop)] **2a**

Crystal data for [PtCl(CH₂SiMe₃)(*R,R*-diop)] **2a**, C₃₅H₄₃ClO₂P₂PtSi, *M* = 852.76, monoclinic, space group P2₁ (no. 4), *a* = 15.026(4), *b* = 14.802(6), *c* = 16.712(7) Å, β = 104.43(3)°, *V* = 4026(4) Å³, *Z* = 4, *D*_x = 1.658 Mg m^{−3}, *T* = 293 K, μ(Mo-Kα) = 4.123 mm^{−1}, 6262 reflections collected, 6178 unique (*R*_{int} 0.048) all used in refinement, θ ≤ 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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