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Preliminary Communication

The reactions of Me_3SiCHN_2 with $[PtX_2(S,S\text{-skewphos})]$: highly diastereoselective carbene insertions into Pt–Cl bonds, and Me_3SiCHN_2 as a CH_2N_2 equivalent

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Abstract

$[PtCl_2(S,S\text{-skewphos})]$ reacts with Me_3SiCHN_2 in dry CH_2Cl_2 to give $[PtCl(S\text{-}CHClSiMe_3)(S,S\text{-skewphos})]$ in high yield, but in the presence of water $[Pt(CH_2Cl)_2(S,S\text{-skewphos})]$ is formed. Treatment of $[PtCl(S\text{-}CHClSiMe_3)(S,S\text{-skewphos})]$ with NaI gives $[PtI(CHISiMe_3)(S,S\text{-skewphos})]$ as a 1:1 mixture of diastereoisomers.

Chloromethyl complexes are important precursors for other functionalised organometallic complexes [1], and chloromethylplatinum complexes have been used for stoichiometric [2] and catalytic [3] C–C bond forming reactions. We have previously shown [4] that diazocarbonyl compounds react with complexes of the type $[PtCl_2L_2]$ (L_2 = cyclooctadiene or a diphosphine) to give substituted chloromethylplatinum(II) complexes containing an asymmetric carbon atom α to the platinum, and that this reaction is moderately diastereoselective when L_2 is a chiral diphosphine. We now report the reaction between the readily available Me_3SiCHN_2 and $[PtCl_2(S,S\text{-skewphos})]$ which, in the absence of water, gives $[PtCl(S\text{-}CHClSiMe_3)(S,S\text{-skewphos})]$ (**1a**) with high diastereoselectivity but in the presence of water gives $[Pt(CH_2Cl)_2(S,S\text{-skewphos})]$ (**5a**) quantitatively.

Treatment of $[PtX_2(cod)]$ (X = Cl, Br or I) with an excess of Me_3SiCHN_2 gave the monoinsertion products $[PtX(CHXSiMe_3)(cod)]$ [5*] in 80–90% yields (Scheme 1) as shown by a combination of elemental analysis and ^1H and ^{13}C NMR spectroscopy. Substitution of the cod ligands by the optically active diphosphine $(2S,4S)\text{-}Ph_2PCHMeCH_2CHMePPh_2$ (S,S-skewphos) gave the corresponding $[PtX(CHXSiMe_3)(S,S\text{-skewphos})]$ as 1:1 mixtures of diastereoisomers **1a** and **1b**, **2a** and **2b**, **3a** and **3b** [6*].

When $[PtCl_2(S,S\text{-skewphos})]$ in $CHCl_3$ was treated with a hexane solution of Me_3SiCHN_2, the same mixture of diastereoisomers **1a** and **1b** was formed (Scheme 1) but in a ratio of *ca.* 15:1, as shown by integration of the ^{31}P NMR signals. Crystals of the major isomer were grown from CH_2Cl_2/Et_2O and X-ray crystal structure analysis [7*] revealed (see Fig. 1) that the configuration about the α-carbon is *S*. As for $[PtCl(R\text{-}CHClCO_2Et)(R,R\text{-diop})]$ [4] the conformation adopted by the chiral alkyl has the α-hydrogen near the coordination plane of the platinum (torsion angle P(2)–Pt–C(1)–H(1a) = 7°). This orientation allows the larger Cl and $SiMe_3$ substituents at C_α to avoid the crowded Pt coordination plane. The skewphos six membered ring adopts a flattened chair conformation in the solid state. The bulky substituent on C_α ($SiMe_3$) lies in the least crowded site between the pseudo-equatorial phenyl groups (*cf.* Cl(2) which is closer to the pseudo-axial phenyl groups).

In contrast to the diastereoselectivity shown in the reaction of the dichloro complex above, when $[PtX_2(S,S\text{-skewphos})]$ (X = Br or I) was treated with Me_3SiCHN_2 in $CDCl_3$, the products were essentially 1:1 mixtures of diastereoisomers **2a**, **2b** and **3a**, **3b**. The same 1:1 ratio of **3a** and **3b** is obtained as the ultimate product of the reaction between NaI and **1a** in MeCN (Scheme 2), showing that nucleophilic substitution of chloride by iodide has lead to complete racemization at the α-carbon. An intermediate was observed in this reaction to which we assign the structure **4** on the basis of its ^{31}P NMR parameters [6*]. The iodide substitution reaction (Scheme 2) is much faster in MeCN than in the less polar solvent $CDCl_3$. The

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* Reference number with asterisk indicates a note in the list of references.

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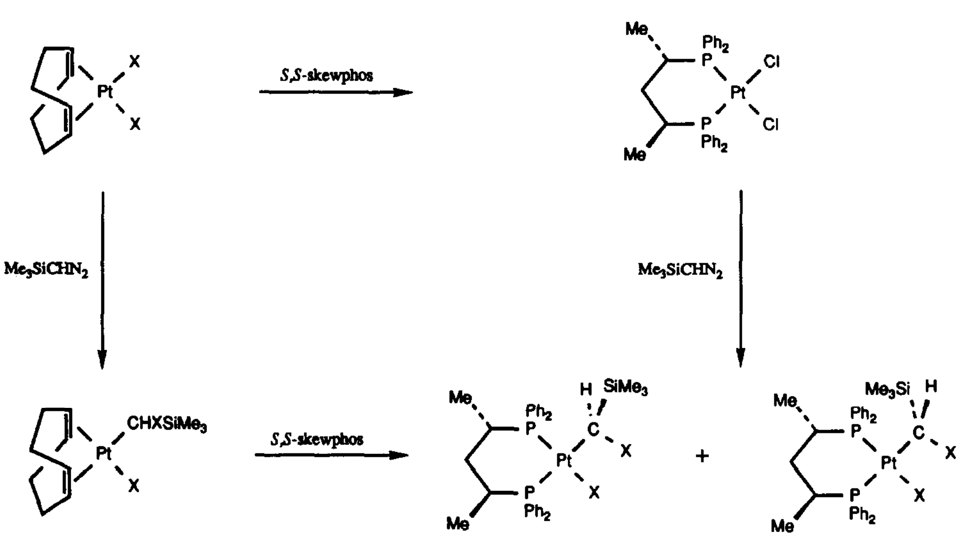
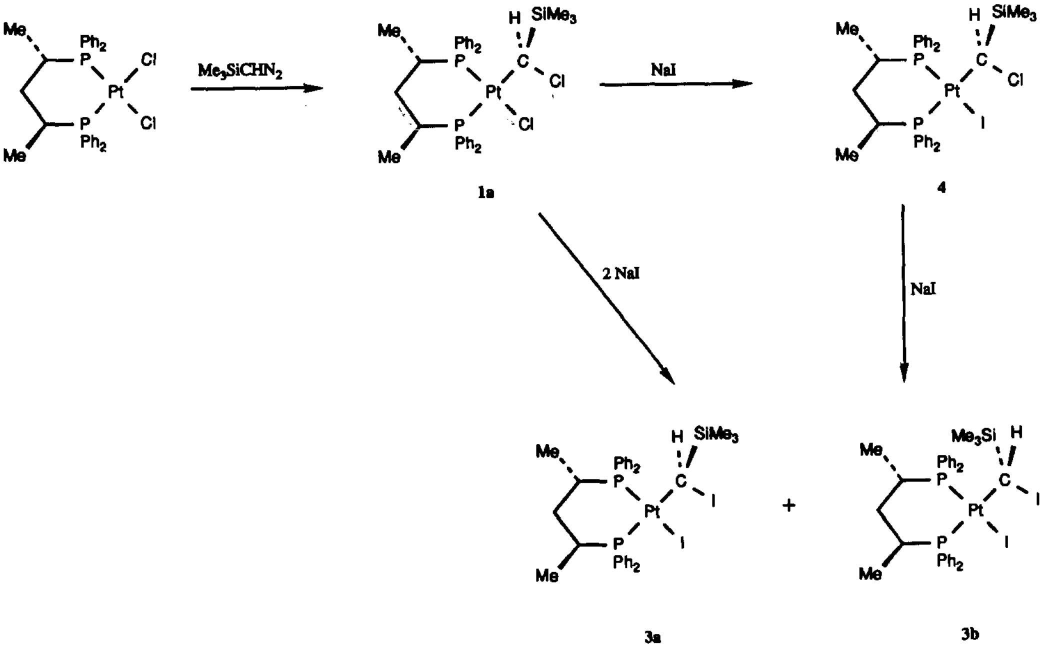


1a X = Cl 1b X = Cl
2a X = Br 2b X = Br
3a X = I 3b X = I

Scheme 1.

observed racemization and the accelerating effect of the more polar solvent are both consistent with a dissociative mechanism for halide substitution at C_α though we cannot exclude the possibility that the products **3a** and **3b** interconvert under the reaction conditions.

The reactions of Me_3SiCHN_2 with $[PtX_2(S,S\text{-skewphos})]$ are sensitive to the amount of water present in the dichloromethane solvent. For example when the reaction of $[PtCl_2(S,S\text{-skewphos})]$ with Me_3SiCHN_2 is carried out in dry CH_2Cl_2 the products of monoinsertion, **1a,b**, are formed exclusively. However when



Scheme 2.

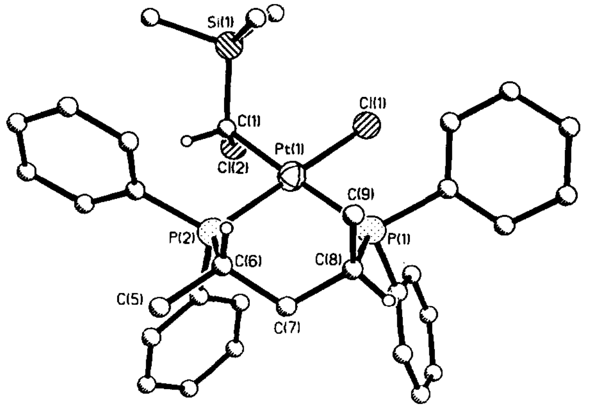


Fig. 1. Molecular structure of **1a** showing atom labelling scheme. All methyl and phenyl group hydrogens are omitted for clarity. Important molecular dimensions include: bond lengths (Å) Pt(1)–Cl(1) 2.360(4), Pt(1)–P(1) 2.318(4), Pt(1)–P(2) 2.232(4), Pt(1)–C(1) 2.104(12); bond angles (°) P(1)–Pt(1)–P(2) 94.0(1), Cl(1)–Pt(1)–C(1) 88.4(4).

CH_2Cl_2 saturated with water is used, **1a,b** are formed more rapidly, and a new species is also detected, which becomes the exclusive product when the reaction is carried out in a 3:2:1 mixture of CH_2Cl_2:acetone:water. This second product is assigned structure $[Pt(CH_2Cl)_2(S,S\text{-skewphos})]$ (**5a**) on the basis of the symmetrical ^{31}P NMR spectra and an X-ray crystal structure [8*] of the isolated complex **5a** (see Fig. 2). The bromo (**5b**) and iodo (**5c**) analogues have been made under similar conditions. In these reactions Me_3SiCHN_2 is behaving as a CH_2N_2 equivalent [9].

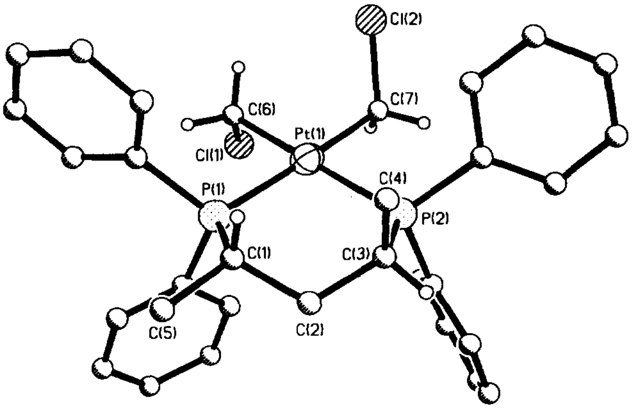
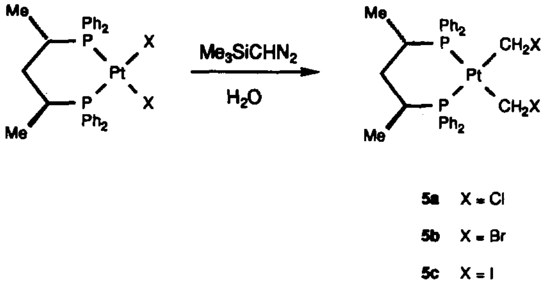


Fig. 2. Molecular structure of **5a** showing atom labelling scheme. All methyl and phenyl group hydrogens are omitted for clarity. Important molecular dimensions include: bond lengths (Å) Pt(1)–P(1) 2.285(3), Pt(1)–P(2) 2.278(3), Pt(1)–C(6) 2.109(10), Pt(1)–C(7) 2.096(14); bond angles (°) P(1)–Pt(1)–P(2) 95.8(1), C(6)–Pt(1)–C(7) 85.9(4).

Further work is in progress to uncover the mechanism of these desilylation reactions (eqn. (1)).



(1)

Acknowledgements

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5 The chloro complex $[PtCl(CHClSiMe_3)(cod)]$ was recently mentioned in the following article: G. Ferguson, J.F. Gallagher, A.J. McAlees, R. McCrindle, J. Philips and G.J.B. Williams, *J. Organomet. Chem.*, *430* (1992) C23.

6 All isolated new compounds have been characterised by elemental analyses, IR, ^1H, ^{31}P and ^{13}C NMR spectroscopy. The ^{31}P NMR data for **1**–**5**:
1a $\delta(P_A)$ 13.3, $^1J(PtP_A)$ 4116, $\delta(P_B)$ 14.1, $^1J(PtP_B)$ 1719, $^2J(P_AP_B)$ 24; **1b** $\delta(P_A)$ 14.4, $^1J(PtP_A)$ 4128, $\delta(P_B)$ 10.7, $^1J(PtP_B)$ 1660, $^2J(P_AP_B)$ 24; **2a** $\delta(P_A)$ 12.8, $^1J(PtP_A)$ 4066, $\delta(P_B)$ 12.1, $^1J(PtP_B)$ 1760, $^2J(P_AP_B)$ 23; **2b** $\delta(P_A)$ 13.7, $^1J(PtP_A)$ 4074, $\delta(P_B)$ 8.7, $^1J(PtP_B)$ 1707, $^2J(P_AP_B)$ 24; **3a** $\delta(P_A)$ 10.1, $^1J(PtP_A)$ 3904, $\delta(P_B)$ 6.3, $^1J(PtP_B)$ 1823, $^2J(P_AP_B)$ 24; **3b** $\delta(P_A)$ 9.4, $^1J(PtP_A)$ 3894, $\delta(P_B)$ 4.5, $^1J(PtP_B)$ 1799, $^2J(P_AP_B)$ 24; **4** $\delta(P_A)$ 10.3, $^1J(PtP_A)$ 3942, $\delta(P_B)$ 7.8, $^1J(PtP_B)$ 1757, $^2J(P_AP_B)$ 24; **5a** $\delta(P_A)$ 10.3, $^1J(PtP_A)$ 1850; **5b** $\delta(P_A)$ 13.2, $^1J(PtP_A)$ 1877; **5c** $\delta(P_A)$ 11.9, $^1J(PtP_A)$ 1938.

7 Crystal data for **1a**: $C_{33}H_{40}Cl_2P_2PtSi$, $M_r = 792.7$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 11.152(5)$, $b = 16.102(4)$, $c = 19.021(5)$ Å, $U = 3415(2)$ Å^3, $Z = 4$, $D_x = 1.54$ g cm^{-3}, $\bar{\lambda} = 0.71073$ Å, μ(Mo-Kα) = 44.1 cm^{-1}, $F(000) = 1576$, $T = 295$ K. Data were collected on a Siemens P3m diffractometer for a unique octant of reciprocal space with $4 < 2\theta < 50°$. The structure was solved by direct methods and full-matrix least-squares refinement (186 pa-

rameters) converged to final residual indices $R = 0.044$, $wR = 0.046$, $S = 1.22$ using 2528 absorption and extinction corrected data for which $I > 2\sigma(I)$. Hydrogen atoms were placed in idealised positions (C–H 0.96 Å). The absolute configuration shown in Fig. 1 was confirmed by refinement (Rogers' $\eta = 1.06(4)$).

8 Crystal data for **5a**: $C_{31}H_{34}Cl_2P_2Pt$, $M_r = 734.5$, monoclinic, space group $P2_1$ (No. 4), $a = 8.784(2)$, $b = 16.808(4)$, $c = 10.814(2)$ Å, $\beta = 109.27(2)°$, $U = 1507.3(6)$ Å^3, $Z = 2$, $D_x = 1.62$ g cm^{-3}, $\bar{\lambda} = 0.71073$ Å, μ(Mo-Kα) $= 49.6$ cm^{-1}, $F(000) = 724$, $T = 295$ K. Data were collected on a Siemens P3m diffractometer for a unique quadrant of reciprocal space with $4 < 2\theta < 50°$. The structure was solved by Patterson methods and refined by full-matrix least-squares refinement (325 parameters) converged to final residual indices $R = 0.029$, $wR = 0.036$, $S = 0.96$ using 2449 absorption corrected data for which $I > 2\sigma(I)$. Hydrogen atoms were placed in idealised positions (C–H 0.96 Å). The absolute configuration shown in Fig. 2 was confirmed by refinement (Rogers' $\eta = 0.94(5)$).

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