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Desilylation and cyclometallation reactions of diphenyl{tris(trimethylsilyl)methyl}phosphine with platinum(II) compounds. Crystal structure of *trans*-$[\overline{\mathrm{PtClPPh_2C(SiMe_3)_2SiMe_2C}}\mathrm{H_2\{PPh_2CH(SiMe_3)_2\}}]$ *

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Abstract

The yellow complex *trans*-$[\mathrm{PtCl_2L_2}]$ ($\mathrm{L = PPh_2CH(SiMe_3)_2}$) has been characterised. An attempt to make a similar complex with the more sterically hindered phosphine $\mathrm{PPh_2C(SiMe_3)_3}$ resulted in the loss of a trimethylsilyl group from one phosphine ligand and activation of a C–H bond in another to give the white complex $\overline{\mathrm{PtClPPh_2C(SiMe_3)_2SiMe_2C}}\mathrm{H_2\{PPh_2CH(SiMe_3)_2\}}$, the structure of which was established by X-ray diffraction.

Introduction

The bulky tris(trimethylsilyl)methyl group has now been attached to a range of metals and non-metals [1,2]. Many of the resulting derivatives show enhanced stability compared with the corresponding unsubstituted methyl compounds, especially in reactions involving nucleophilic attack at the metal or metalloid centre. For example, the compound $\mathrm{RPCl_2}$ ($\mathrm{R = C(SiMe_3)_3}$) reacts only slowly with ethanol [4], and $\mathrm{RSiCl_3}$ does not react even with boiling methanolic silver nitrate [3]. When however the atom next to the group R can be protonated, the trimethylsilyl-substituted methyl derivatives may be less stable than the corresponding unsubstituted compounds since the positive charge promotes nucleophilic attack at silicon.

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[*] Dedicated to Professor F.G.A. Stone on his 65th birthday in recognition of his outstanding contributions to organometallic chemistry.

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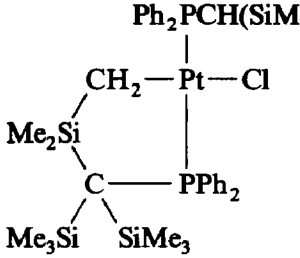
This was first observed in the chemistry of the phosphine $RPPh_2$ (**1b**), which in methanol at room temperature successively loses Me_3Si groups to give the unsubstituted methyl compound $MePPh_2$ [5]. It might be expected that similar cleavage of a trimethylsilyl group could be induced by interactions with Lewis acids other than the proton, for example by complexation with metal ions. Since complexes between phosphines and Pt(II) are particularly well characterised we examined the reactions of the phosphines **1a** and **1b** with the widely used starting material $[PtCl_2(PhCN)_2]$. The complexes *trans*-$PtCl_2L_2$ (**2**) would, if formed, be highly crowded, so that cyclometallation reactions, which are well established [6,7] in the chemistry of platinum and other late transition metals, could also be expected. In the present paper we show that both trimethylsilyl loss and cyclometallation may be observed.

$RPPh_2$
(**1a**) $R = (Me_3Si)_2CH$
(**1b**) $R = (Me_3Si)_3C$

trans-$PtCl_2L_2$
(**2a**) L = (**1a**)
(**2b**) L = (**1b**)



(**3**)

Experimental

^{31}P Chemical shifts are relative to 85% aqueous H_3PO_4.

Reaction of trans-$[PtCl_2(PhCN)_2]$ with $(Me_3Si)_2CHPPh_2$ (1a)

The phosphine $(Me_3Si)_2CHPPh_2$ (0.42 g, 1.27 mmol) was added to *trans*-$[PtCl_2(PhCN)_2]$ (0.30 g, 0.63 mmol) in toluene (20 cm^3) and the yellow brown mixture was heated under reflux for 3 h. A little charcoal was added and after a further 70 min under reflux the mixture was filtered. The filtrate was concentrated to give yellow crystals of *trans*-bis{[bis(trimethylsilyl)methyl]diphenylphosphine}dichloroplatinum (**2a**) M.p. 248–253°C. Found: C, 48.0; H, 6.3. $C_{38}H_{58}Cl_2P_2PtSi_4$ calcd.: C, 47.8; H, 6.1%); $\delta(H)$ ($C_6D_6/CDCl_3$, 1:1) −0.04 (18H, s, $SiMe_3$), 2.77 (1H, t, CH, $J(PH) + J(P'H)$ 15.9 Hz), 7.12, 7.87 ppm (10H, m, Ph); $\delta(P)$ 20.0 ppm, $^1J(PtP)$ 2506 Hz.

Reaction of trans-$[PtCl_2(PhCN)_2]$ with $(Me_3Si)_3CPPh_2$ (1b)

A solution of $(Me_3Si)_3CLi$, made from $(Me_3Si)_3CH$ and MeLi in a mixture of tetrahydrofuran (THF) and ether [5], was added slowly to a solution of Ph_2PCl in THF and the mixture was heated under reflux for 3 h. After removal of solvent the brown residue was extracted with pentane and the pentane was evaporated from the extract to leave a brown solid, which was shown by ^{31}P NMR spectroscopy to be mainly $(Me_3Si)_3CPPh_2$ containing a very small amount of $(Me_3Si)_2CHPPh_2$. A sample of the solid (0.53 g, 1.2 mmol) was added to a refluxing solution of *trans*-$[PtCl_2(PhCN)_2]$ (0.30 g, 0.62 mmol) in toluene (20 cm^3). After 3 h charcoal was added to the brown solution and after a further 0.5 h the solution was filtered and the solvent removed. The brown, spongy residue was washed with pentane to remove traces of the phosphine **1b**, and the remaining solid was dissolved in benzene and the solution passed through a neutral alumina column. The pale yellow eluate was concentrated to deposit a colourless solid. This was recrystallised from benzene–pentane to give crystals (0.06 g), which were shown by X-ray diffraction to be chloro[[bis(trimethylsilyl)methyl]diphenylphosphine][3-diphenylphosphino-2,2,4,4-tetramethyl-3-trimethylsilyl-2,4-disilapentyl-*CP*]platinum (**3**). M.p. 259–261°C. Found: C, 49.6; H, 6.5. $C_{41}H_{65}ClP_2PtSi_5$ calcd.: C, 49.6; H, 6.6%; δ(H) ($C_6D_6/CDCl_3$ 1 : 1) 0.17 (18H, s, $SiMe_3$), 0.19 (18H, s, $SiMe_3$), 0.16 (6H, s, $SiMe_2$), 7.0–7.2, 8.1–8.2, 8.6–8.7 ppm (20H, m, Ph) (signals from the CH and CH_2 protons could not be unambiguously identified); δ(P) 42.7 ppm, dt, ^1J(PtP) 3006, ^2J(PP) 469 Hz, P(1) (Fig. 1); 27.7 ppm ^1J(PtP) 2868 Hz, dt, P(2). The ^{31}P spectrum was like that of *trans*-[$PtCl_2(Bu^n_3P)(Et_3P)$] [8]; it was first order at 145.8 MHz.

Crystal structure determination

Crystal data: $C_{41}H_{65}ClP_2PtSi_5$, $M = 990.9$, monoclinic, space group $P2_1/n$, a 14.550(3), b 14.128(4), c 23.166(3) Å, β 99.74(1)°, $U = 4693.6$ Å^3, $Z = 4$, D_c 1.40 g cm^{-3}, $F(000) = 2024$, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ 32.96 cm^{-1}.

Data were collected on an Enraf-Nonius CAD 4 diffractometer with a crystal of size 0.4 × 0.4 × 0.2 mm. Intensities for h, k, $\pm l$ reflections with $2 < \theta < 25°$ were measured by a $\theta/2\theta$ scan with $\Delta\theta = (0.8 + 0.35 \tan \theta)°$. Two standard reflections monitored every 30 min showed no significant variation. Data were corrected for

Table 1

Fractional atomic coordinates ($\times 10^4$) for (**3**) with estimated standard deviations in parentheses

	x	y	z		x	y	z
Pt	1536.9(2)	2490.9(4)	1261.8(2)	C(17)	−1603(8)	3447(8)	536(5)
Cl	1736(2)	2053(2)	2277(1)	C(18)	−2320(9)	3243(10)	77(6)
P(1)	83(2)	3109(2)	1288(1)	C(19)	−2210(11)	2541(10)	−292(6)
P(2)	3025(2)	2002(2)	1181(1)	C(20)	−1425(10)	2006(9)	−212(5)
Si(1)	2773(2)	1446(2)	−130(1)	C(21)	−701(8)	2163(8)	259(5)
Si(2)	4563(2)	2714(2)	373(2)	C(22)	3884(7)	2485(8)	1779(4)
Si(3)	2522(2)	3485(2)	334(1)	C(23)	3647(8)	3278(8)	2090(5)
Si(4)	−809(3)	1488(3)	1934(2)	C(24)	4281(9)	3656(9)	2536(6)
Si(5)	−1399(2)	3619(3)	2167(2)	C(25)	5139(10)	3230(10)	2712(6)
C(1)	3319(7)	2371(7)	463(4)	C(26)	5371(9)	2412(10)	2440(6)
C(2)	−501(7)	2787(8)	1908(4)	C(27)	4734(8)	2040(9)	1971(5)
C(3)	1378(7)	3021(9)	410(4)	C(28)	2574(6)	4135(6)	−417(3)
C(4)	329(7)	4384(7)	1325(4)	C(29)	2790(9)	4509(8)	858(5)
C(5)	932(8)	4685(8)	1815(4)	C(30)	5520(8)	1863(10)	609(6)
C(6)	1227(9)	5605(9)	1875(5)	C(31)	4627(8)	2941(10)	−418(6)
C(7)	936(9)	6232(9)	1428(6)	C(32)	4975(9)	3831(9)	759(6)
C(8)	338(10)	5949(8)	925(6)	C(33)	1850(9)	686(9)	99(5)
C(9)	44(8)	5011(8)	879(5)	C(34)	3682(9)	623(10)	−345(6)
C(10)	3216(7)	717(7)	1293(4)	C(35)	2182(9)	1965(10)	−838(5)
C(11)	3968(8)	258(8)	1110(5)	C(36)	−191(11)	716(9)	1466(6)
C(12)	4122(9)	−715(8)	1220(5)	C(37)	−483(14)	1063(12)	2708(7)
C(13)	3538(9)	−1188(8)	1517(5)	C(38)	−2060(11)	1268(12)	1691(9)
C(14)	2800(9)	−733(8)	1705(5)	C(39)	−1546(12)	3244(13)	2897(6)
C(15)	2639(8)	206(8)	1587(5)	C(40)	−1047(12)	4898(10)	2248(7)
C(16)	−814(7)	2896(8)	643(4)	C(41)	−2607(10)	3637(15)	1732(8)

Table 2

Intramolecular distances (Å) and angles (°) in **3** with estimated standard deviations in parentheses

a. Bonds

Pt–Cl	2.402(3)	Pt–P(1)	2.299(3)
Pt–P(2)	2.310(3)	Pt–C(3)	2.087(10)
P(1)–C(2)	1.845(11)	P(1)–C(4)	1.835(11)
P(1)–C(16)	1.835(10)	P(2)–C(1)	1.862(11)
P(2)–C(10)	1.848(10)	P(2)–C(22)	1.833(10)
Si(1)–C(1)	1.963(10)	Si(1)–C(33)	1.865(14)
Si(1)–C(34)	1.890(14)	Si(1)–C(35)	1.868(12)
Si(2)–C(1)	1.918(11)	Si(2)–C(30)	1.850(13)
Si(2)–C(31)	1.878(14)	Si(2)–C(32)	1.863(14)
Si(3)–C(1)	1.948(10)	Si(3)–C(3)	1.825(12)
Si(3)–C(28)	1.980(9)	Si(3)–C(29)	1.888(12)
Si(4)–C(2)	1.893(11)	Si(4)–C(36)	1.87(2)
Si(4)–C(37)	1.88(2)	Si(4)–C(38)	1.84(2)
Si(5)–C(2)	1.927(11)	Si(5)–C(39)	1.82(2)
Si(5)–C(40)	1.88(2)	Si(5)–C(41)	1.873(15)

Mean C–C in phenyl rings 1.38(2) Å.

b. Angles

Cl–Pt–P(1)	91.8(1)	Cl–Pt–P(2)	92.4(1)
Cl–Pt–C(3)	173.9(3)	P(1)–Pt–P(2)	174.2(1)
P(1)–Pt–C(3)	86.2(3)	P(2)–Pt–C(3)	89.2(3)
Pt–P(1)–C(2)	118.3(3)	Pt–P(1)–C(4)	101.6(3)
Pt–P(1)–C(16)	116.6(4)	C(2)–P(1)–C(4)	108.6(5)
C(2)–P(1)–C(16)	103.6(5)	C(4)–P(1)–C(16)	107.7(5)
Pt–P(2)–C(1)	110.4(3)	Pt–P(2)–C(10)	113.8(4)
Pt–P(2)–C(22)	110.9(4)	C(1)–P(2)–C(10)	110.4(5)
C(1)–P(2)–C(22)	109.9(5)	C(10)–P(2)–C(22)	101.1(5)
C(1)–Si(1)–C(33)	114.3(5)	C(1)–Si(1)–C(34)	112.1(5)
C(1)–Si(1)–C(35)	115.1(5)	C(33)–Si(1)–C(34)	106.9(6)
C(33)–Si(1)–C(35)	103.2(6)	C(34)–Si(1)–C(35)	104.4(6)
C(1)–Si(2)–C(30)	118.7(5)	C(1)–Si(2)–C(31)	110.6(5)
C(1)–Si(2)–C(32)	113.3(6)	C(30)–Si(2)–C(31)	103.9(6)
C(30)–Si(2)–C(32)	104.1(6)	C(31)–Si(2)–C(32)	105.0(6)
C(1)–Si(3)–C(3)	103.0(5)	C(1)–Si(3)–C(28)	113.5(4)
C(1)–Si(3)–C(29)	117.9(5)	C(3)–Si(3)–C(28)	115.0(4)
C(3)–Si(3)–C(29)	107.8(6)	C(28)–Si(3)–C(29)	100.1(4)
C(2)–Si(4)–C(36)	114.1(6)	C(2)–Si(4)–C(37)	108.5(6)
C(2)–Si(4)–C(38)	112.4(6)	C(36)–Si(4)–C(37)	107.5(7)
C(36)–Si(4)–C(38)	105.8(8)	C(37)–Si(4)–C(38)	108.4(9)
C(2)–Si(5)–C(39)	107.7(7)	C(2)–Si(5)–C(40)	115.5(7)
C(2)–Si(5)–C(41)	117.6(7)	C(39)–Si(5)–C(40)	105.1(8)
C(39)–Si(5)–C(41)	104.9(8)	C(40)–Si(5)–C(41)	104.8(8)
P(2)–C(1)–Si(1)	108.2(5)	P(2)–C(1)–Si(2)	122.1(5)
P(2)–C(1)–Si(3)	98.2(5)	Si(1)–C(1)–Si(2)	111.7(5)
Si(1)–C(1)–Si(3)	105.7(5)	Si(2)–C(1)–Si(3)	109.1(5)
P(1)–C(2)–Si(4)	114.0(6)	P(1)–C(2)–Si(5)	121.2(6)
Si(4)–C(2)–Si(5)	113.9(6)	Pt–C(3)–Si(3)	105.3(4)
P(1)–C(4)–C(5)	115.6(8)	P(1)–C(4)–C(9)	124.6(8)
C(5)–C(4)–C(9)	119(1)	C(4)–C(5)–C(6)	121(1)
C(5)–C(6)–C(7)	119(1)	C(6)–C(7)–C(8)	121(1)
C(7)–C(8)–C(9)	119(1)	C(4)–C(9)–C(8)	121(1)
P(2)–C(10)–C(11)	121.4(8)	P(2)–C(10)–C(15)	119.7(8)

Mean C–C–C angle in phenyl rings 120(1)°.

Lorentz and polarisation effects but not absorption. 5168 reflections with $|F|^2 > \sigma(F^2)$ were used in the structure refinement.

The positions of Pt, P, Cl, Si, and C atoms were found by heavy atom methods and refined by full matrix least squares with anisotropic temperature factors. The methine hydrogen atom of the phosphine ligand was found from a difference map but not refined. The remaining hydrogen atoms were placed at calculated positions (C–H 1.08 Å) and fixed with $B_{iso} = 6.0$ Å^2. Refinement converged at $R = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|) = 0.053$ and $R' = \{[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{1/2} = 0.063$ with $w = 1/\sigma^2(F)$. A final difference map had peaks of up to 2.8 e Å^{-3} near the Pt atom.

A PDP 11/34 computer and the Enraf-Nonius Structure Determination Package were used for the structure solution and refinement. Final atomic coordinates are given in Table 1, and bond lengths and angles in Table 2. Hydrogen atom coordinates and temperature and structure factors are available from the authors.

Results and discussion

The phosphine $(Me_3Si)_2CHPPh_2$ (**1a**) reacts in the usual way with *trans*-$[PtCl_2(PhCN)_2]$ to give the yellow complex **2a**: the *trans*-configuration is confirmed by the ^{31}P NMR data [9]. The more hindered $(Me_3Si)_3CPPh_2$, however, does not give the expected complex **2b**. Instead the product is the white compound **3** (Fig. 1),

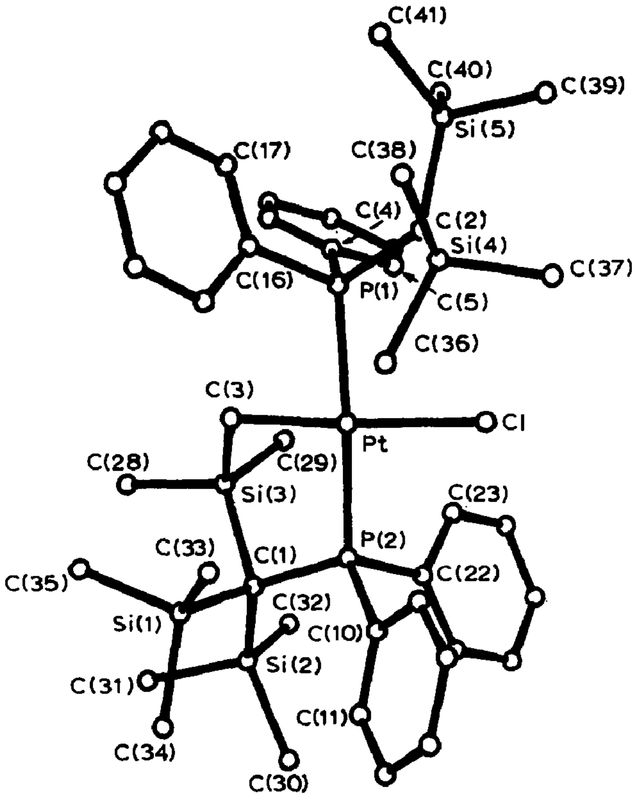


Fig. 1. Molecular structure of $\overline{PtClPPh_2C(SiMe_3)_2SiMe_2C}H_2\{PPh_2CH(SiMe_3)_2\}$ (**3**).

in which a methyl group from one ligand has been metallated and an Me_3Si group has been lost from the other ligand:

$$2\ (Me_3Si)_3CPPh_2 + [PtCl_2(PhCN)_2] \rightarrow$$

$$\underset{(3)}{\overline{PtClPPh_2C(SiMe_3)_2SiMe_2CH_2}}\{PPh_2CH(SiMe_3)_2\} + 2\ PhCN + Me_3SiCl \quad (1)$$

There are precedents for both of these transformations. Metallation of propyl [6], t-butyl [7], and *o*-tolyl groups [6] of phosphine ligands is known to be facilitated by the presence of bulky groups attached to phosphorus. Metallation by manganese of methyl groups attached to silicon in the bidentate phosphine $Ph_2PCH_2SiMe_2CH_2PPh_2$ has also been described [10].

The loss of Me_3Si from the second ligand is similar to that observed when the phosphine is protonated [5]: NMR spectroscopy showed that **3** was formed before the reaction mixture was added to the alumina column, but we cannot be sure whether the breakdown of the $(Me_3Si)_3C$ group results from nucleophilic attack on silicon by chloride formed in the metallation or from traces of moisture in the original reaction mixture. (We have some evidence that it is slow when highly purified starting materials are used.)

The reaction described by eq. 1 is similar to that observed between PBu^t_3 and $PtCl_2$ [11]; in that case also one mole of phosphine is metallated and the other degraded (eq. 2):

$$6\ PBu^t_3 + 3\ PtCl_2 \rightarrow 2\ [\overline{PtClPBu^t_2CMe_2CH_2}\{PBu^t_2H\}] + [PBu^t_3H]_2[PtCl_4] + 2\ CH_2{=}CMe_2 \quad (2)$$

It seems that complexation of the lone pair of a silicon-alkyl-substituted phosphine results in subtle changes in the susceptibility of the bonds to silicon towards nucleophilic attack. Another example is found in the chemistry of $PPh_2CH_2SiMe_2H$. Attack of OH^-, OMe^-, or Cl^- at silicon in the free phosphine results in cleavage of the Si–C bond: in $[Ru(\eta^6\text{-}C_6H_4Me_2)Cl_2(PPh_2CH_2SiMe_2H)]$, however, the Si–H bond is broken [12].

The X-ray study shows that the Pt–Cl, Pt–P, and Pt–C bond lengths in **3** are within experimental error the same as those of the corresponding bonds in *trans*-$[PtMeCl(PMePh_2)_2]$ [13] or *trans*-$[PtCl(CH_2SiMe_3)(PMePh_2)_2]$ [14]. The coordination at platinum is planar, but the P(1)–Pt–Cl and P(2)–Pt–Cl angles are significantly greater and the P(1)–Pt–C angle is significantly less than 90°, presumably as a consequence of the intramolecular strain arising from the bulky ligand and the five-membered ring. In the ligands the Si–C bonds (mean 1.942(10) Å) are longer than the Si–Me bonds (mean 1.87(2) Å), as in $(Me_3Si)_3CPH_2$ [15] and $(Me_3Si)_3CP{=}PC(SiMe_3)_2$ [16,17]. The Ph–P–Ph angles (102.3(5)°) are considerably smaller than tetrahedral.

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