Control of Si–C Bond Cleavage at Carbon α to Phosphorus. Suppression of Facile Protodesilylation of $PPh_2CH_2SiMe_2H$ by Complexation through Phosphorus to Ruthenium and the *X*-Ray Crystal and Molecular Structure of [Ru(η^6-*p*-cymene)Cl_2($PPh_2CH_2SiMe_2OH$)]

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Facile cleavage of the Si–C bond α to P in $Ph_2PCH_2SiMe_2H$ which is induced by HY (Y = OH, OMe, or Cl) is suppressed on complexation at Ru in [Ru(η^6-cym)Cl_2($PPh_2CH_2SiMe_2H$)] (cym = *p*-cymene); instead the latter reacts where Y = OH to afford the silanol complex [Ru(η^6-cym)Cl_2($PPh_2CH_2SiMe_2OH$)] which has been structurally characterized by *X*-ray diffraction.

Designing synthetic strategy around organosilicon chemistry[1,2] relies on control of silicon–carbon bond-cleavage reactions. Facile silyl-group cleavage from a carbon atom α to phosphorus has recently been reported by Eaborn and coworkers,[3] who have suggested that initial protonation at P is followed by nucleophilic attack at Si to generate an ylidic intermediate *via* silyl loss, *i.e.* steps which are reminiscent of the protodesilylation of arylsilanes[4] and the fracture of the Si–C bond in ylides[5] like $Me_3P{=}CHSiMe_3$ respectively. We offer a new perspective on such mechanistic arguments, which follows from a fundamental disparity between the reactivity of the phosphino(silyl)methane[6] $PPh_2CH_2SiMe_2H$ (**1**) in its uncomplexed state and as a ligand in the transition-metal derivative [Ru(η^6-cym)Cl_2L] (**2**) [cym = *p*-cymene, L = (**1**)]. Thus while compound (**1**) is desilylated even by traces of water, complex (**2**) undergoes Si–H bond hydrolysis to afford a stable product [Ru(η^6-cym)Cl_2($PPh_2CH_2SiMe_2OH$)] (**3**) which has been structurally characterized using *X*-ray diffraction.

Preparative routes to phosphinoalkylsilanes including compound (**1**) and its analogue $PPh_2(CH_2)_2SiMe_2H$ (**4**) have been described elsewhere.[6] Further examination of the properties of these molecules has revealed that the methane derivative (**1**) rapidly and completely reverts to its precursor[6] $PMePh_2$ in the presence of protic reagents like H_2O, HCl, or MeOH. By contrast the corresponding ethane (**4**) is stable under similar conditions. Protodesilylation of compound (**1**) according to equation (1) was characterized by use of *in situ* ^1H n.m.r. spectroscopy: the silyl products[7] $SiMe_2HY$ are those expected to be generated by nucleophilic attack at Si, while with ^2H_2O the isotopomer $P(CH_2{}^2H)Ph_2$ was formed exclusively. Compounds (**1**) and (**4**) behaved similarly on treatment with MeI,

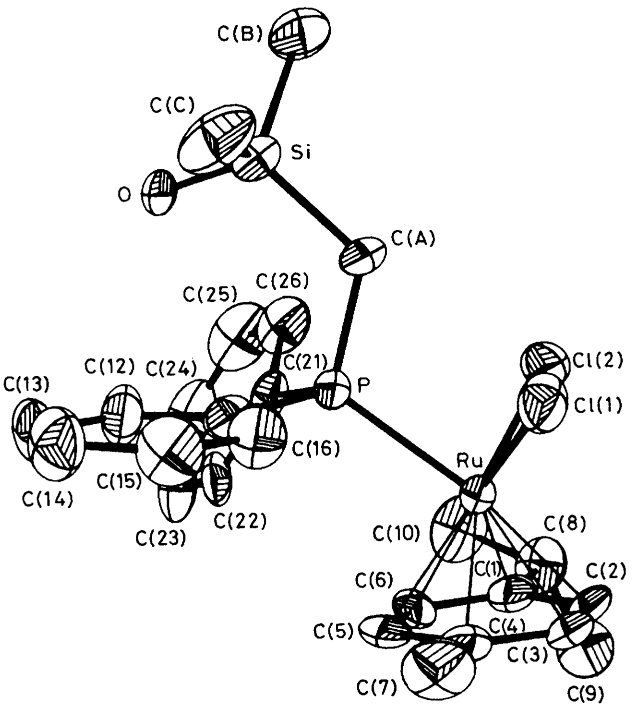

Figure 1. Molecular geometry of compound (**3**). Selected bond distances and angles: Ru–Cl(1), 2.407(3); Ru–Cl(2), 2.410(3); Ru–P, 2.353(3); P–C(A), 1.820(12); C(A)–Si, 1.866(12); Si–O, 1.591(8); Si–C(B), 1.878(15); Si–C(C), 1.861(16) Å. P–Ru–Cl(1), 87.2(1); P–Ru–Cl(2), 84.2(1); Cl(1)–Ru–Cl(2), 88.2(1); P–C(A)–Si, 121.2(7); C(A)–Si–O, 110.2(7); C(B)–Si–O, 105.5(6); C(C)–Si–O, 109.2(7); C(B)–Si–C(C), 111.2(8)°.

however, with quantitative conversion to the phosphonium species $[PPh_2Me(CH_2)_nSiMe_2H]I$ (n = 1 or 2).

$$\underset{(\mathbf{1})}{PPh_2CH_2SiMe_2H} + HY \rightarrow PPh_2Me + SiMe_2HY \qquad (1)$$

$$Y = OH, Cl, \text{ or } OMe$$

Addition of the silane (**1**) to a solution in dry tetrahydrofuran (THF) of the binuclear species $[Ru(\eta^6\text{-cym})Cl_2]_2$ led to immediate precipitation of an orange complex. This product was identified as $[Ru(\eta^6\text{-cym})Cl_2(PPh_2CH_2SiMe_2H)]$ (**2**) from its ^1H n.m.r. spectrum, which as well as cym and Ph resonances showed signals attributable to a $SiMe_2H$ group,† and by its i.r. spectrum which included a strong absorption due to ν(Si–H) (2120 cm^{-1}). Refrigeration (−20 °C) of a solution in acetone of compound (**2**) led to very slow (~120 days) deposition of ruby-red crystals: an *X*-ray crystal structure determination‡ established that substitution at Si had taken place affording the silanol derivative $[Ru(\eta^6\text{-cym})Cl_2(PPh_2CH_2SiMe_2OH)]$ (**3**) of (**2**), the molecular geometry of which is shown in Figure 1. The silane : silanol transformation (**2**) : (**3**) is slow in wet solvents and may conveniently be monitored by using either ^1H or ^{31}P n.m.r. spectroscopy: solvolysis by MeOH is even slower but by contrast gaseous HCl induces immediate chlorination, equation (2).

$$\underset{(\mathbf{2})}{[Ru(\eta^6\text{-cym})Cl_2(PPh_2CH_2SiMe_2H)]} \xrightarrow{HY} \underset{(\mathbf{3}\text{: } Y = OH)}{[Ru(\eta^6\text{-cym})Cl_2(PPh_2CH_2SiMe_2Y)]} \qquad (2)$$

A comparison between equations (1) and (2) reinforces the mechanistic proposition[3] referred to initially: elimination of lone-pair availability at P by electron donation to Ru leads to suppression of Si–C bond cleavage in a way which may be useful in controlling such reactions, and substitution at Si is indeed slow in the stabilized P–C–Si configuration. Compound (**3**), which is formed from (**2**) by hydrolysis at Si, is structurally unremarkable except for the widening of the P–C–Si angle to 121.2°, an effect which we assume is sterically induced. There is no evidence for intra- or inter-molecular bonding contacts with the silanol function although both were evident in the structure[8] of the related complex $[Ru(PPh_2CH_2SiMe_2OH)(CO)_2(CO_2CF_3)_2\cdot Et_2O]$. Ring-opening of the latter occurs[9] with pyridine, leading to 'dangling' silanol co-ordination at Ru^{II} closely resembling that displayed in (**3**).

$$\underset{(\mathbf{4})}{PPh_2(CH_2)_2SiMe_2H}$$

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† Compound (**2**): ^1H n.m.r., δ −0.43 (d, Si*Me*$_2$H), 3.45 (septet, SiMe$_2$*H*, *J* 3.5 Hz), 0.71 (d, CH*Me*$_2$), 2.45 (septet, C*H*Me$_2$, *J* 7.2 Hz). ^{31}P n.m.r., δ −117 p.p.m. Satisfactory microanalytical data were obtained for this complex and also for compound (**3**).

‡ *Crystal data* for (**3**): $C_{25}H_{33}RuCl_2PSiO$, M = 579.6, space group $P2_1/c$, a = 10.2580(7), b = 14.2058(8), c = 18.055(1) Å, β = 98.592(5)°, U = 2601.50(8) Å^3, Z = 4, D_c = 1.48 g cm^{-3}; Enraf–Nonius CAD4 diffractometer, Mo-K_α radiation (λ = 0.71069 Å), μ = 6.32 cm^{-1}; 2349 observed reflections refined to a conventional R = 0.044 (R_w = 0.049). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

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