

Control of Si–C Bond Cleavage at Carbon α to Phosphorus. Suppression of Facile Protodesilylation of $\text{PPh}_2\text{CH}_2\text{SiMe}_2\text{H}$ by Complexation through Phosphorus to Ruthenium and the X-Ray Crystal and Molecular Structure of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2(\text{PPh}_2\text{CH}_2\text{SiMe}_2\text{OH})]$

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Facile cleavage of the Si–C bond α to P in $\text{Ph}_2\text{PCH}_2\text{SiMe}_2\text{H}$ which is induced by HY (Y = OH, OMe, or Cl) is suppressed on complexation at Ru in $[\text{Ru}(\eta^6\text{-cym})\text{Cl}_2(\text{PPh}_2\text{CH}_2\text{SiMe}_2\text{H})]$ (cym = *p*-cymene); instead the latter reacts where Y = OH to afford the silanol complex $[\text{Ru}(\eta^6\text{-cym})\text{Cl}_2(\text{PPh}_2\text{CH}_2\text{SiMe}_2\text{OH})]$ 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 arylsilanes⁴ and the fracture of the Si–C bond in ylides⁵ like $\text{Me}_3\text{P}=\text{CHSiMe}_3$ respectively. We offer a new perspective on such mechanistic arguments, which follows from a fundamental disparity between the reactivity of the phosphino(silyl)methane⁶ $\text{PPh}_2\text{CH}_2\text{SiMe}_2\text{H}$ (**1**) in its uncomplexed state and as a ligand in the transition-metal derivative $[\text{Ru}(\eta^6\text{-cym})\text{Cl}_2\text{L}]$ (**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 $[\text{Ru}(\eta^6\text{-cym})\text{Cl}_2(\text{PPh}_2\text{CH}_2\text{SiMe}_2\text{OH})]$ (**3**) which has been structurally characterized using X-ray diffraction.

Preparative routes to phosphinoalkylsilanes including compound (**1**) and its analogue $\text{PPh}_2(\text{CH}_2)_2\text{SiMe}_2\text{H}$ (**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 precursor⁶ 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 products⁷ SiMe_2HY are those expected to be generated by nucleophilic attack at Si, while with $^2\text{H}_2\text{O}$ the isotopomer $\text{P}(\text{CH}_2^2\text{H})\text{Ph}_2$ was formed exclusively. Compounds (**1**) and (**4**) behaved similarly on treatment with MeI,

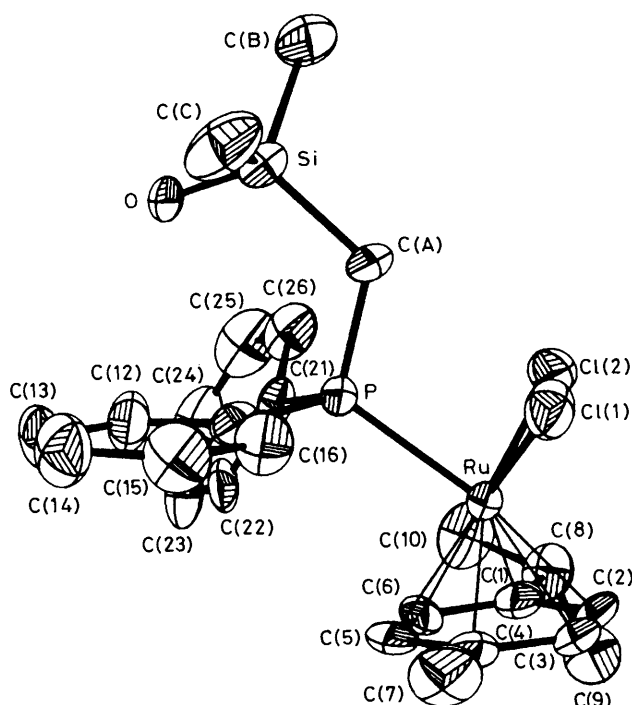
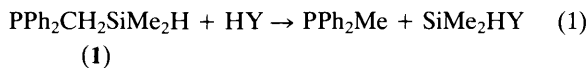


Figure 1. Molecular geometry of compound (3). Selected bond distances and angles: Ru-Cl(1), 2.407(3); Ru-Cl(2), 2.410(3); Ru-P, 2.353(3); P-C(A), 1.820(12); C(A)-Si, 1.866(12); Si-O, 1.591(8); Si-C(B), 1.878(15); Si-C(C), 1.861(16) Å. P-Ru-Cl(1), 87.2(1); P-Ru-Cl(2), 84.2(1); Cl(1)-Ru-Cl(2), 88.2(1); 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 $[\text{PPh}_2\text{Me}(\text{CH}_2)_n\text{SiMe}_2\text{H}]^+$ ($n = 1$ or 2).



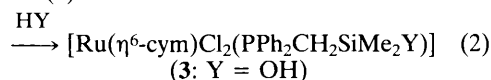
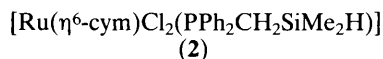
Y = OH, Cl, or OMe

Addition of the silane (1) to a solution in dry tetrahydrofuran (THF) of the binuclear species $[\text{Ru}(\eta^6\text{-cym})\text{Cl}_2]_2$ led to immediate precipitation of an orange complex. This product was identified as $[\text{Ru}(\eta^6\text{-cym})\text{Cl}_2(\text{PPh}_2\text{CH}_2\text{SiMe}_2\text{H})]$ (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 $\nu(\text{Si-H})$ (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

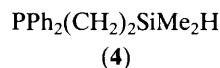
[†] Compound (2): ^1H n.m.r., δ -0.43 (d, SiMe_2H), 3.45 (septet, SiMe_2H , J 3.5 Hz), 0.71 (d, CHMe_2), 2.45 (septet, CHMe_2 , J 7.2 Hz). ^{31}P n.m.r., δ -117 p.p.m. Satisfactory microanalytical data were obtained for this complex and also for compound (3).

[‡] Crystal data for (3): $\text{C}_{25}\text{H}_{33}\text{RuCl}_2\text{PSiO}$, $M = 579.6$, space group $P2_1/c$, $a = 10.2580(7)$, $b = 14.2058(8)$, $c = 18.055(1)$ Å, $\beta = 98.592(5)^\circ$, $U = 2601.50(8)$ Å³, $Z = 4$, $D_c = 1.48\text{ g cm}^{-3}$; Enraf-Nonius CAD4 diffractometer, Mo- K_α radiation ($\lambda = 0.71069$ Å), $\mu = 6.32\text{ cm}^{-1}$; 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.

place affording the silanol derivative $[\text{Ru}(\eta^6\text{-cym})\text{Cl}_2(\text{PPh}_2\text{CH}_2\text{SiMe}_2\text{OH})]$ (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).



A comparison between equations (1) and (2) reinforces the mechanistic proposition³ 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 structure⁸ of the related complex $[\text{Ru}(\text{PPh}_2\text{CH}_2\text{SiMe}_2\text{OH})(\text{CO})_2(\text{CO}_2\text{CF}_3)_2 \cdot \text{Et}_2\text{O}]$. Ring-opening of the latter occurs⁹ with pyridine, leading to 'dangling' silanol co-ordination at Ru^{II} closely resembling that displayed in (3).



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