Agostic Si–H Interactions

Tandem β-C–H Activation/Si–H Elimination Reactions: Stabilization of C–H Activation Products by β-Agostic Si–H Interactions**

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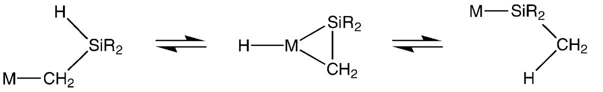
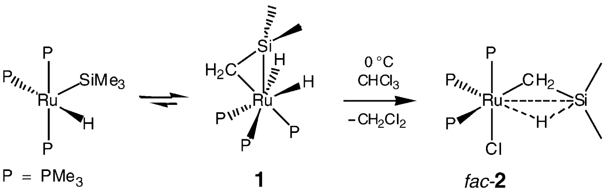
Organometallic complexes of silenes have been postulated and often observed to be intermediates in many C–H, Si–H, Si–C, and Si–Si bond-breaking and bond-forming processes.[1] Many isolated and characterized silene complexes have been synthesized via β-Si–H activation of CH_2SiR_2-H ligands, but this reaction often proceeds further to furnish the metal silyl ($MSiR_2CH_3$) as a more thermodynamically stable product [Eq. (1)].[1a] Interestingly, this preference of breaking SiH/MC and forming CH/MSi bonds is not universal. For instance, the silene complex $[(\eta^5\text{-}C_5Me_5)Ru(P\mathit{i}Pr_3)(\eta^2\text{-}CH_2SiPh_2)H]$, formed via β-Si–H activation, in some cases reacts with hydrosilanes via Si–H instead of C–H reductive elimination, and the selection is triggered by subtle changes in the nature of the incoming silane.[2] Furthermore, selective isotope exchange in osmium and ruthenium silyl complexes suggests that the CH-activation stage of Equation (1) is also reversible.[3] Recent reports of the direct observation of aliphatic β-C–H bond elimination in 16-electron metal silyl complexes by us and by Klei et al.[4] conclusively establish the reversibility of C–H addition/elimination processes in some metal silyl complexes [Eq. (1)]. We now report the first example of conversion from $[M]SiMe_3$ to β-agostic $[M]CH_2SiMe_2$-H species, a total inversion of the usual left-to-right direction of the process in Equation (1).



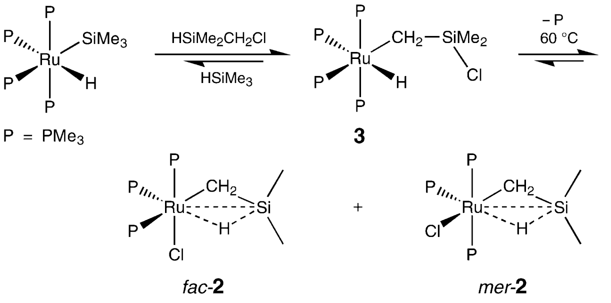
(1)

Treatment of a mixture of the 16-electron $[(Me_3P)_3Ru(SiMe_3)H]$, in equilibrium with the "silene dihydride" complex $[(Me_3P)_3Ru(\eta^2\text{-}CH_2SiMe_2)(H)_2]$ (**1**)[4a,b] with $CHCl_3$ between −40 and 0°C leads to the chlorination of one hydride and the formation of $[(Me_3P)_3Ru(CH_2SiMe_2)(H)Cl]$, *fac*-(**2**) [Eq. (2)], which has been isolated in 86% yield and fully characterized. That this complex is neither a simple η^2-silene hydride nor a η^1-alkyl is evident from strong Si–H scalar coupling ($J(H,Si) = 75$ Hz).[5] A very weak, low-frequency band in the IR spectrum (1615 cm^{-1}; absent in [D_1]*fac*-**2**) is also consistent with an agostic Si···H···Ru, but this assignment is tentative because of the very low intensity of the band.



(2)

A more convenient synthetic route to *fac*-**2** is based on *cis*-$[(Me_3P)_4Ru(CH_2SiMe_2Cl)H]$ (**3**), which in turn can be readily synthesized from $[(Me_3P)_4Ru(SiMe_3)H]$ and $HSiMe_2CH_2Cl$ [Eq. (3)]. Isotopically labeled material, [D_1]*fac*-**2** was synthesized using $DSiMe_2CH_2Cl$. Note that the deuterium atom is only found as Si-D-Ru and no scrambling into C–H positions was observed. The structure of **3** was determined by single-crystal X-ray diffraction to be approximately octahedral, with all bond distances and angles within normal ranges. No evidence for nonclassical Si–Cl···Ru, Si···H–Ru, or Ru–H···Cl interactions was observed in the solid state or in solution



(3)

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(^{1}H NMR: J(H,Si) < 12 Hz; IR: $\tilde{\nu}$(RuH) = 1840 cm^{-1}; Si···H 3.34; Cl···Ru 4.86; H···Cl 4.54 Å).

Thermal (65 °C) or photochemical (350 nm) treatment of **3** in hydrocarbon solvents leads to phosphane loss and formation of *fac*-**2**. Under thermal conditions, *fac*-**2** is in equilibrium with **3**, although the product is strongly favored ($K_{eq} \approx 0.06$ mol L^{-1} at 25 °C). Removal of PMe$_3$ and addition of fresh solvent allows the isolation of **2** nearly quantitatively. In addition, approximately 5 % of the meridional isomer *mer*-(**2**) is also observed [Eq. (3)]. The structure of *mer*-**2** was determined from a pure sample obtained by fractional crystallization (see below). The spectroscopic data is also consistent with the meridional structure, and again, a strong SiH scalar coupling (J(H,Si) = 77.5 Hz) indicates a nonclassical Ru···H···Si linkage.[5] The formation of **3** from HSiMe$_2$CH$_2$Cl and [(Me$_3$P)$_4$Ru(SiMe$_3$)H] and the subsequent conversion of **3** to **2** is an interesting sequence of reactions. Initial exchange of silyl ligands on the metal center by SiH addition and Me$_3$SiH elimination seems likely, given that Me$_3$SiCH$_2$Cl, which lacks the SiH group, does not react after days at ambient temperature. The migration of the chloride ion from carbon to silicon in the synthesis of **3** may involve a dyotropic process as suggested in a similar case for [CpFe(CO)$_2$(SiMe$_2$CH$_2$Cl)].[6] An alternative mechanism involving the oxidative addition of C–Cl and the elimination of Si–Cl cannot be completely excluded, however the intermediate would have to be a yet unknown isomer of **2**, as neither *fac*-**2** nor *mer*-**2** favor the recoordination of PMe$_3$ and the formation of **3**.

The rate of conversion of **3** to **2** is approximately halved in the presence of added [D$_9$]PMe$_3$ (10 equiv), and the labeled phosphane is nonselectively incorporated into both **3** and **2**. This suggests the reaction proceeds via initial PMe$_3$ dissociation, and SiCl oxidative addition would be a likely second step. Interestingly, there are relatively few clear precedents for the oxidative addition of SiCl.[7] It is also noteworthy that the strong Si–Cl bond is maintained in **3**, but cleaved in **2** in preference for Ru–Cl (and agostic Si···H) bonds. It is likely that Cl–Ru π-donation compensates for partial electronic unsaturation in **2**, whereas additional electron donation would contribute nothing to the stability of **3**, an unequivocally 18-electron species.

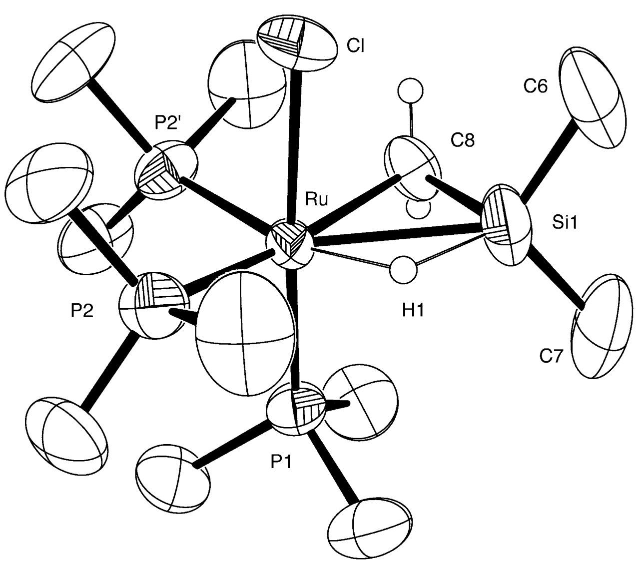

Figure 1. ORTEP diagram of complex *fac*-**2** (30% probability ellipsoids). The second disordered position of the silene fragment is not shown. Selected bond lengths [Å] and angles [°]: Ru-C8 2.307(7), Ru-Si1 2.526(2), Si-C6 1.837(9), Si-C7 1.814(9), Si-C8 1.788(11), Ru-H1 1.550, Si-H1 1.664; Si1-C8-Ru 75.0(3), C8-Si1-Ru 61.9(2).

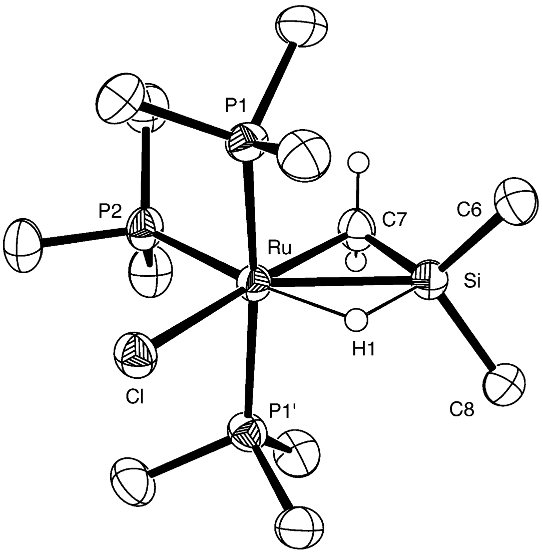

Figure 2. ORTEP diagram of complex *mer*-**2** (30% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ru-C7 2.200(6), Ru-Si 2.468(2), Si-C6 1.878(4), Si-C7 1.790(6), Ru-H1 1.732, Si-H1 1.557; Si-C7-Ru 75.7(2), C7-Si-Ru 59.7(2).

The solid-state structures of *fac*-**2** and *mer*-**2** can both be described as square pyramidal, with three phosphane groups, a Cl atom, and the CH$_2$ group positioned around the ruthenium center, and the agostic Si···H occupying a sixth coordination site (Figure 1 and 2). Disorder of the agostic {CSiH} fragment in *fac*-**2** was successfully modeled (see Experimental Section), and while the heavy-atom positions should be reliable, the location of the hydride is less precise than usual. The Ru–P, Ru–Cl, and Ru–C bond lengths and angles are within normal ranges, but the Ru–Si bond lengths (*fac*-**2**: 2.526(2); *mer*-**2**: 2.468(2) Å) are at the long end of the range for Ru–Si single bonds (approximately 2.3–2.58 Å; 2.39 Å on average).[8] Longer Ru–C and Ru–Si separations in *fac*-**2** than in the *mer* isomer may be due the stronger *trans* influence of phosphane versus Cl on the agostic CSiH ligand, but the crystallographic disorder may also contribute. The hydrides in *fac*-**2** and *mer*-**2** were located in positions bridging the silicon and ruthenium centers (Ru···H/Si···H = 1.550/1.664 Å in *fac*-**2** and 1.732/1.557 Å in *mer*-**2**), consistent with agostic interactions indicated by the spectroscopic evidence. Silane σ-bond complexes can be viewed as products of "arrested" Si–H elimination on the pathway from metal-(silyl)(hydride) complexes to silanes. Analogously, *fac*- and *mer*-**2** can be considered as being frozen during the intramolecular β-Si–H elimination from the ruthenium silene hydride complexes. The Si–C distances (*fac*-**2**: 1.788(11); *mer*-**2**: 1.790(6) Å) are shorter than normal Si–C single bonds (approximately 1.87–1.91 Å),[8] but are comparable to those in metal silene complexes (1.78–1.81 Å).[9] However, the Ru–Si bond lengths in both *fac*- and *mer*-**2** are much longer than in known silene complexes.[9a,b] On the other hand, short Si–C distances are also observed in ruthenium complexes reported by Jones and co-workers ([Cp*(Cy$_3$P)Ru{η^3-HSiMe$_2$-(C=CPh$_2$)}],[5a]) and Sabo-Etienne and co-workers ([(Cy$_3$P)$_2$RuH$_2${η^4-HSiMe$_2$(CH=CHMe)}]).[5b] These β-agostic RuCSiH species also exhibit long Ru–Si and short Si–H bond lengths and can be viewed as an arrested stage of the reductive elimination from 1-silaallene and η^3-silaallyl complexes. Comparison with these compounds strongly supports the view that *fac*- and *mer*-**2** are better described as β-agostic rather than silene complexes. It is tempting to attribute the relative stability of the β-agostic motif entirely to the influence of chloride in **2**, but structural data is not available for **1**. Furthermore, spectroscopic evidence for **1** is consistent with some degree of Si···H interaction. Studies probing the similarities and differences in the structures of **1**, **2**, and substituted derivatives are currently in progress.

The reaction proceeding from [(Me$_3$P)$_3$Ru(H)SiMe$_3$] to **1** and further on to *fac*- and *mer*-**2** is the first example of a [M]SiMe$_3$ to β-agostic [M]CH$_2$SiMe$_2$-H conversion, a reversal of the typical sequence observed in the rearrangement of silaalkyl metal complexes. This reversal is likely the result of SiH coordination to the unsaturated metal center, which would provide greater stabilization than any potential agostic C–H binding in the metal silyl.

Experimental Section

Synthetic procedures and characterization data are included in the Supporting Information.

fac-**2**: 0.32 × 0.30 × 0.24 mm; orthorhombic; *Pnma* (no. 62); $a = 18.7076(3)$, $b = 10.6471(2)$, $c = 10.5218(2)$ Å, $V = 2095.75(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.388$ g cm^{-3}; $2\theta_{max} = 50.7°$; Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å); ∅ oscillations (Rigaku R-AXIS IIc); $T = 200$ K; 12712 reflections, all 2027 unique reflections were used in the refinement; corrected for Lorentz and polarization effects but not for absorption ($\mu = 11.79$ cm^{-1}); solution by direct methods (SIR92); refinement by full-matrix least-squares based on F^2 (SHELXL-93); 137 parameters; hydrogen atoms unrefined (H1 was located); $R_1 = 0.0379$ and $wR_2 = 0.0991$ for 1962 reflections for which $I > 2\sigma(I)$; residual electron density +0.492 and −0.527 e Å^{-3}; the molecule lies on a crystallographic mirror plane perpendicular to the Ru-C8-Si-H1 plane (disordered Si and C8 refined successfully at 50% occupancy). One PMe$_3$ (P2) was rotationally disordered about the Ru–P2 bond (55:45 relative populations).

mer-**2**: 0.44 × 0.22 × 0.12 mm; orthorhombic; *Cmc*2$_1$ (no. 36); $a = 16.2940(4)$, $b = 10.9748(2)$, $c = 11.4191(3)$ Å, $V = 2042.00(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.424$ g cm^{-3}; $2\theta_{max} = 54.96°$; Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å); ∅ oscillations (Rigaku R-AXIS IIc); $T = 200$ K; 8222 reflections, all 2173 unique reflections were used in the refinement; absorption correction by REQAB ($\mu = 11.79$ cm^{-1}, min./max. transmission 0.693/1.000); solution by direct methods (SIR92); refinement by full-matrix least-squares based on F^2 (SHELXL-93); 97 parameters; hydrogen atoms unrefined (H1, H5a, H5b, and H7a were located); $R_1 = 0.0358$ and $wR_2 = 0.0929$ for 2144 reflections for which $I > 2\sigma(I)$; residual electron density +0.814 and −0.855 e Å^{-3}.

CCDC-166039 (*fac*-**2**), CCDC-166037 (*mer*-**2**), and CCDC-166038 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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