Preparation and Properties of a Ruthenium Complex of a "1-Silaallene"

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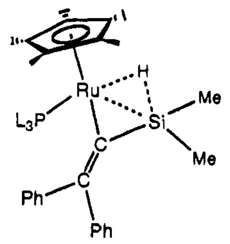
Silenes are normally too reactive to be isolated and characterized if they are not stabilized by appropriately placed bulky substituents[1] or by ligation to a transition metal.[2] Similarly, silaallenes should be at least as unstable as silenes, and indeed, with the single exception of a very highly encumbered example recently reported by West,[3] silaallenes have only been detected as transients.[4] For some years we have been interested in the preparation and properties of highly reactive cumulenes stabilized by ligation to transition metals[5] and thought it would be interesting to attempt to extend this to the preparation of complexes of silaallenes. At this time we report our successful preparation and characterization of **1**, which although not a classical allene can be viewed as an example of a 1-silaallene that is stabilized by both metal ligation and interaction with a metal−hydrogen bond.

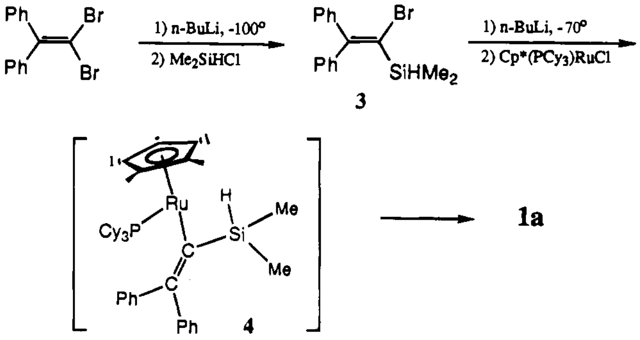


1

a; L = Cy
b; L = Ph, Me, Me

From our successful experience with zirconocene complexes of unstable cumulenes,[5g,h] preparation of a 1-silaallene complex of this metal fragment was initially attempted. Unfortunately, this failed. We were then drawn to Tilley's[2a,b] recent preparation of ruthenium complexes of unencumbered silenes (**2**) and were pleased that his strategy was successful. Preparation of **1a** by this elegant method is outlined in Scheme 1. Treatment of 1,1-dibromo-2,2-diphenylethylene with 1 equiv of *n*-BuLi at −100 °C (maintained at low temperature to prevent rearrangement) followed by addition of 1 equiv of Me$_2$SiHCl at −90 °C gave **3** in 56% isolated yield. Reaction of **3** with 1 equiv of *n*-BuLi in ether at −70 °C followed by 0.7 equiv of Cp*Ru(PCy)$_3$Cl (Cp* = C$_5$Me$_5$) (−60 °C to room temperature over 6 h) gave **1a** (42% from hexane), presumably via **4**.

Scheme 1



Complex **1a** was characterized by multinuclear NMR spectroscopy, mass spectroscopy, elemental analysis,[6] and single-crystal X-ray diffraction.[7] The most characteristic features of the ^{1}H NMR of **1a** are the presence of two nonequivalent methyl groups (δ 0.22 and 0.05 ppm) and the presence of a metal hydride doublet (δ −11.53 ppm; $^2J_{H-P}$ = 11.5 Hz). A pair of ^{29}Si satellites appear at δ −11.42 and −11.64 ppm ($^1J_{H-Si}$ = 66 Hz). The ^{29}Si{^{1}H} NMR exhibits a doublet at δ −81.89 ppm with a coupling constant of 34.7 Hz, which is assigned to the coupling between the ^{29}Si and ^{31}P nuclei. In the ^{1}H-coupled ^{29}Si NMR spectrum, a broad doublet at δ −81.89 ppm was observed with a coupling constant of 66 Hz. This is the same value as the one obtained from the satellites in the ^{1}H NMR spectrum and confirms their origin as coupling with silicon. This coupling constant is in the range (20−70 Hz) reported for a series of manganese η^2-hydrosilane complexes[8a,b] and suggests that only partial transfer of the hydride from silicon to ruthenium has occurred in **1a**. A similar arrested hydrogen transfer has been suggested by Wrighton as a possible explanation for the absence of an Fe−H IR absorption in Cp*(CO)FeH(η^2-CH$_2$=SiMe$_2$).[9] A similar mode of interaction has also been found in a series of zirconocene silaimido complexes,[10] although the degree of bonding of hydrogen to the metal in these complexes is significantly less than that in **1**. Arrested hydrogen

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(1) For stable silenes, see: (a) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229. (b) Wiberg, N.; Wagner, G.; Müller, G.; Roede, J. *J. Organomet. Chem.* **1984**, *271*, 381. (c) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y. M.; Wong Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

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(6) For **1a**: ^{1}H NMR (C$_6$D$_6$) δ 8.60 (d, 2H, J_{H-H} = 7.2 Hz), 7.0−7.4 (m, 8H, *Ph*), 1.66 (s, 15H, C(C*H*$_3$)$_5$), 1.1−1.9 (m, 33H, P*Cy*$_3$), 0.22 (s, 3H, Si-C*H*$_3$), 0.05 (s, 3H, Si-C*H*$_3$), −11.6 (d, 1H, $^2J_{H-P}$ = 11.5 Hz, Ru-*H*); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 175.5 (d, $^2J_{C-P}$ = 10.9 Hz, C1), 152.66, 148.55, 143.04, 128.95, 127.86, 127.17, 125.24, 124.74, 89.96 (d, $^2J_{C-P}$ = 1.8 Hz), 30.78, 29.45 (br), 28.33 (br), 27.15, 11.90, −0.31, −0.50; ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 51.33; ^{29}Si{^{1}H} NMR (C$_6$D$_6$) δ −81.30 (d, $^2J_{Si-P}$ = 34.7 Hz); ^{29}Si NMR (C$_6$D$_6$) δ −81.30 (d of m, $^2J_{Si-H}$ = 66 Hz); MS (FAB) 754 [M$^+$], 515.2 [(M − Me$_2$Si=C=CPh$_2$)$^+$], 474 [(M − PCy$_3$)$^+$]. Anal. Calcd for C$_{44}$H$_{65}$PSiRu·1/2C$_7$H$_8$: C, 71.28; H, 8.69. Found C, 71.25; H, 8.89.

(7) C$_{44}$H$_{65}$PSiRu·1/2C$_7$H$_8$, triclinic, $P\bar{1}$, a = 11.040(2) Å, b = 11.202(3) Å, c = 20.126(5) Å, α = 78.52(2)°, β = 75.40(2)°, γ = 65.45(2)°, V = 2178(1) Å^3, Z = 2, d_{calc} = 1.220 g/cm^{-3}, μ = 4.5 cm^{-1}, 298 K, Siemens R3m/V diffractometer with a graphite monochromator utilizing Mo K$_\alpha$ radiation (λ = 0.710 73 Å), 10 499 reflections were collected (3.0° ≤ 2θ ≤ 55.0°) using the ω scan method. The structure was solved by the heavy atom method and refined in SHELXTL-Plus using full-matrix least-squares methods. The non-H atoms of the complex were treated anisotropically. The positions of the hydrogen atoms were calculated in ideal positions, and their isotropic thermal parameters were fixed, except H1 which was found and refined. The toluene molecule was found to be disordered about centers of inversion. All of the carbon atoms of toluene were refined isotropically with proper value of side occupation factors. R = 4.61, R_w = 4.99, GOF = 1.395, for 5816 reflections with $I > 3\sigma(I)$, largest Δ/σ = 0.001, highest peak = 0.7 e$^-$/Å^3.

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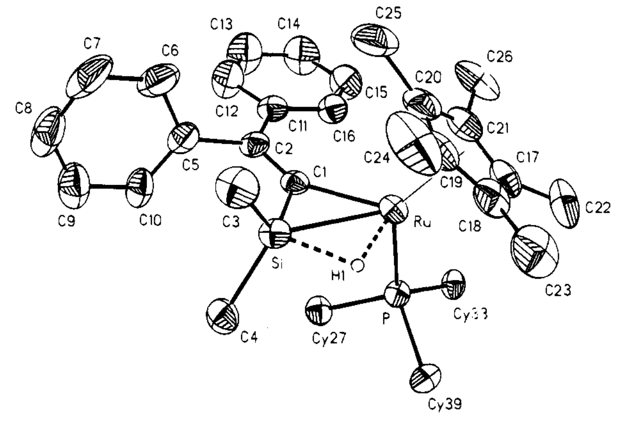
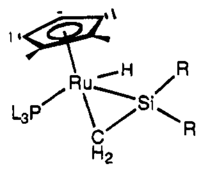


Figure 1. Molecular structure of **1a**, with 40% probability ellipsoids. Phosphine cyclohexyl rings are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **1a**

		Bond Lengths (Å)			
Ru−P	2.3619(12)	Si−C1	1.805(6)	Ru−C1	2.113(4)
Ru−H1	1.58(5)	C1−C2	1.351(6)	Si−C3	1.861(5)
Si−H1	1.70(3)	Ru−Si	2.507(2)	Si−C4	1.878(6)
		Bond Angles (deg)			
P−Ru−Si	98.39(5)	C3−Si−C4	103.8(3)	Ru−C1−Si	79.1(2)
P−Ru−C1	93.37(11)	C2−C1−Ru	150.2(4)	C1−Si−C4	123.5(2)
Si−H1−Ru	100.(2)	H1−Ru−Si	41.9(12)	C1−Si−H1	92.(2)
C1−Si−C3	118.2(3)	Si−Ru−C1	45.0(2)	Ru−Si−H1	38.(2)
C1−Si−Ru	55.84(13)	C2−C1−Si	128.6(4)	H1−Ru−C1	85.0(12)

transfer in **1** was somewhat surprising in view of Tilley's report[2a,b] that hydrogen transfer in **2a** is complete. However,



2
a; L = i-Pr, R = Ph
b; L = Cy, R = Ph
c; L = i-Pr, R = Me
d; L = Cy, R = Me

both silicon hydrogen coupling ($J_{\mathrm{Si-H}}$ = 66 Hz for **1a** vs <20 Hz for **2a**) and X-ray data to be discussed below leave no question about the structure of **1a** and fundamental structural differences between **1a** and **2a**. Finally, the mass spectrum (FAB) of **1a** exhibits a molecular ion peak at 754.3 (m^+) and a peak at 515.2 from loss of the silaallene ligand.

As mentioned above, the structure of **1a** was confirmed by X-ray analysis. A thermal ellipsoids drawing is depicted in Figure 1, and important bond lengths and angles are given in Table 1. The hydride, which was located from a difference Fourier map and refined without any constraints, is bonded almost symmetrically between the Ru and Si atoms [Ru−H1 = 1.58(5) Å, H1−Si = 1.70(3) Å] and clearly confirms the suggested arrested hydrogen transfer structure pictured in **1a**. These bond distances are equal within experimental error to those in the three manganese η^2-hydrosilane complexes reported by Schubert.[8a] Despite the arrested hydrogen transfer structure, the bond length of the coordinated Si=C1 in **1a** [1.805(6) Å] is equal to the corresponding bonds in silene complex **2a** [1.78(2) Å] and in other silene−metal complexes, such as $\mathrm{Cp^*(PMe_3)Ir(\eta^2\text{-}CH_2{=}SiPh_2)}$[2c] [1.810(6) Å] and $\mathrm{Cp_2W(\eta^2\text{-}CH_2{=}SiMe_2)}$[2d] [1.800(8) Å]. In view of significant differences in other bond lengths and angles (vide infra), this is somewhat surprising, although it may simply be coincidental since incomplete hydrogen transfer would be expected to lengthen the C1−Si, bond while the hybridization on the central carbon of the allene moiety should shorten it. As expected, this bond is longer than the corresponding bond in free 1-silaallene[3] [1.704(4) Å] and stable silenes[1] but shorter than normal Si−C(sp^2) single bonds, which appear in the range of 1.85−1.90 Å.[11] The C1−C2 bond length [1.351(6) Å] corresponds to a typical localized carbon−carbon double bond. The Si−C1−C2 angle is 128.6(4)°, which suggests sp^2 hybridization at C1. The Ru−C1 bond length of 2.113(4) Å is significantly shorter than that of the corresponding bond in **2a** [2.25(2) Å] (different hybridization), while the Ru−Si bond is longer [2.507(2) vs 2.382(4) Å], as expected of a three-center two-electron bond. Finally, the Ru−C1−Si angle of **1a** is nearly 7° larger than that in the silene complex **2a** [79.1(2)° vs 71.3(7)°]. Thus, all of the physical data are consistent with significantly different structures for **1a** and the silene complex **2a**.

The chemistries of **1a** and **2**[2a,b] also show significant differences. For example, whereas **2b** decomposes at room temperature (60% in 19 h), **1a** is completely stable when warmed in C_6D_6 at 45 °C for 1 day. Also, unlike **2a**, which was rigorously shown to undergo reversible hydrogen transfer to silicon and also rotation (by an unknown mechanism) of the carbon−silicon bond followed by hydrogen transfer to carbon, **1a** shows no evidence of either. For example, warming **2a** with $\mathrm{PMe_2Ph}$ gives $\mathrm{Cp^*(PMe_2Ph)_2RuSiMePh_2}$, while warming **1a** with the same phosphine showed simple ligand exchange to give 81% of **1b** (from $^1J_{\mathrm{Si-H}}$ = 57 Hz, the bonding apparently has not changed). Similarly, **2a** reacts with CO, while **1a** showed no reaction under similar conditions; heating led to decomposition to multiple products.

All structural and chemical data indicate a substantial difference between **1a** and **2**, and this raises the very interesting question of why the difference. This could be complex, because in addition to the exocyclic methylene in **1a**, the silene and "1-silaallene" complexes for which information is available also differ in ligands both on phosphorus [$\mathrm{PCy_3}$ or $\mathrm{PMe_2Ph}$ vs P(*i*-Pr)$_3$] and on silicon (Me vs Ph). However, although we are currently testing the latter two, we suspect that strain induced by the exocyclic methylene would have the greatest influence on these structural preferences, strain which could be relieved by lengthening the remote metal−silicon bond. This, of course, is accomplished quite nicely by arresting the hydrogen transfer as in **1**.

One interesting chemical property of **1a** is that it catalyzes dimerization of phenylacetylene (head-to-head; 62%) and 1-hexyne (head-to-tail, 57%) to give butenynes. The former gives predominately the *Z* isomer (95:5). Although not particularly efficient as a catalyst, the stereochemistry is somewhat unusual.[12] However, similar stereochemistry, as well as a detailed mechanistic study, was very recently reported for the dimerization of phenylacetylene with $\mathrm{R_3PRu(C{\equiv}CPh)_2}$.[13]

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Supplementary Material Available: Experimental details for the preparation of **1a**, **1b**, and **3**, and tables of crystal structure analysis data for **1a**, including atomic coordinates for all atoms, anisotropic thermal parameters for non-hydrogen atoms, and bond lengths and angles (20 pages); table of observed and calculated structure factors (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(11) Taken from 25 compounds with Si−C(sp^2) bonds listed in the Cambridge Structural Database.

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