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Migrations in a Polysilyl Complex of Rhodium. Trapping of an Apparent Silylene Intermediate and Observation of Reversible Si−Si Bond Reductive Elimination

Gregory P. Mitchell and T. Don Tilley*

Department of Chemistry, University of California, Berkeley, California 94720-1460

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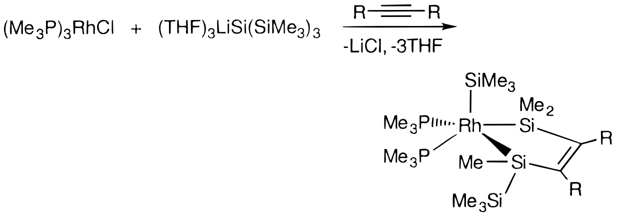
*Summary: Reaction of $(Me_3P)_3RhCl$ with $(THF)_3LiSi(SiMe_3)_3$ in the presence of 2-butyne or diphenylacetylene generates $(Me_3P)_2(Me_3Si)\overline{RhSiMe_2C(R){=}C(R)Si}Me(SiMe_3)$ (**1**, R = Me; **2**, R = Ph). These complexes undergo a fluxional process which exchanges the $SiMe_3$ groups, apparently by Si−Si bond reductive elimination/oxidative addition.*

Organosilicon[1] and transition-metal silicon[2,3] chemistry are replete with examples of intramolecular 1,2- and 1,3-migrations. For transition-metal systems, such migrations are often envisioned as proceeding via discrete, intermediate silylene complexes.[3] We have recently provided some support for such scenarios, by isolating and characterizing the first examples of $L_nM{=}SiR_2$ species.[4] However, despite compelling circumstantial evidence that silylene complexes mediate migrations in metal−silicon systems,[2,3] this has yet to be confirmed by direct observation. Of course, silylene complexes formed by 1,2- and/or 1,3-migrations may be difficult to observe simply because of their highly reactive and transient nature. Thus, the current situation warrants serious consideration of alternative mechanisms, such as ones involving concerted "double migrations" or dyotropic shifts.[5] Recently we reported the observation of apparent 1,2- and 1,3-migrations in the isomerization of the coordinatively unsaturated rhodium and iridium polysilyl complexes $(Me_3P)_3M{-}Si(SiMe_3)_3$ (M = Rh, Ir) to $(Me_3P)_3M{-}SiMe_2SiMe(SiMe_3)_2$ derivatives. The latter complexes are thermally unstable, and the iridium species cleanly decomposes to $(Me_3P)_3(H)\overline{IrSiMe_2SiMe(SiMe_3)SiMe_2C}H_2$ via cyclometalation.[6] Here we report further observations on the migration chemistry associated with this system, which have resulted from attempts to trap intermediates in the above rearrangements.

Since alkynes are known to trap silylene groups which have been extruded by transition-metal complexes,[2a,b,7] we examined the reaction of $(Me_3P)_3RhCl$[8] with $(THF)_3LiSi(SiMe_3)_3$[9] in the presence of 1 equiv of 2-butyne. In pentane this reaction produces a yellow-orange solution, from which complex **1** was isolated in 72% yield (eq 1).[10,11] The analogous reaction with diphenylacetylene produced compound **2**. Crystals of **1** contain enantio-



(1)

1, R = Me
2, R = Ph

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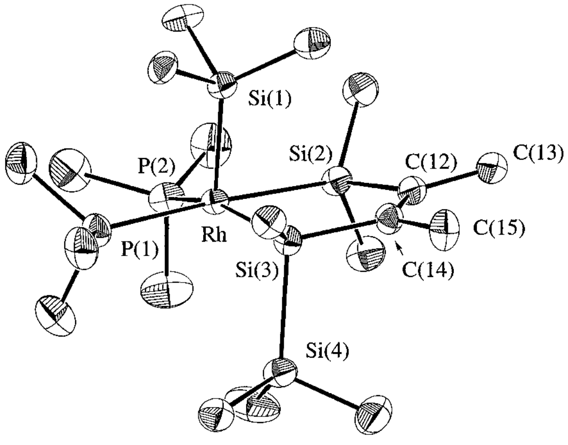
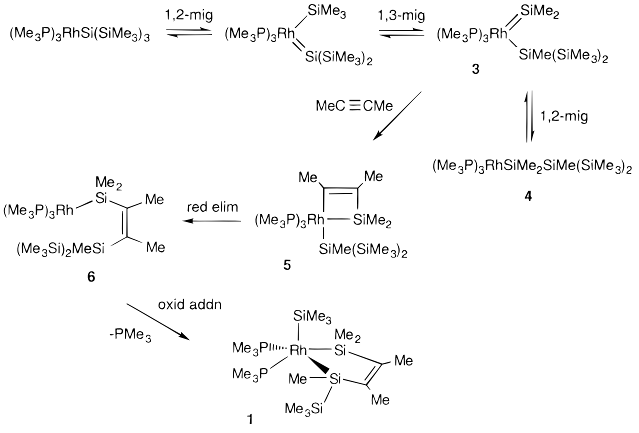


Figure 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (deg): Rh−Si(1) = 2.309(2), Rh−Si(2) = 2.406(2), Rh−Si(3) = 2.346(2), Rh−P(1) = 2.382(2), Rh−P(2) = 2.410(2), Si(3)−Si(4) = 1.877(7), C(12)−C(14) = 1.361(10); P(1)−Rh−P(2) = 92.64(7), P(1)−Rh−Si(1) = 94.75(8), P(1)−Rh−Si(3) = 97.87(7), P(2)−Rh−Si(1) = 112.98(7), P(2)−Rh−Si(2) = 89.06(7), Si(1)−Rh−Si(2) = 87.97(7), Si(1)−Rh−Si(3) = 85.15(7), Si(2)−Rh−Si(3) = 79.33(7), Si(2)−C(12)−C(14) = 115.5(5), Si(2)−C(12)−C(13) = 120.6(5), Si(3)−C(14)−C(12) = 117.2(6), Si(3)−C(14)−C(15) = 121.7(7).

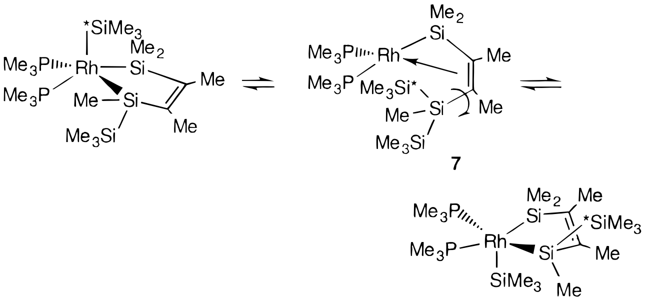
meric pairs related by an inversion center, and the molecular geometry (Figure 1)[12] may be described as an approximate square-based pyramid, with the trimethylsilyl ligand occupying the apical position. The five-membered ring is only slightly puckered, such that the angle between the $RhSi_2$ plane and the C_2Si_2 least-squares plane is 170°. Only the diastereomer shown in eq 1 is observed in this reaction, presumably because the other isomer would experience excessive nonbonded repulsions between trimethylsilyl groups.

A possible mechanism for the formation of **1** is given in Scheme 1. The rhodium silyl complex which is undoubtedly formed initially, $(Me_3P)_3RhSi(SiMe_3)_3$, appears to undergo facile 1,2- and 1,3-migration processes that in the absence of added alkyne give **4**.[6] Presumably, 2-butyne traps the silyl−silylene complex **3**, per-

Scheme 1



haps by 2 + 2 cycloaddition to give the transient metallasilacyclobutene complex **5**. Reductive elimination of a Si−C bond in **5** would give the rhodium silyl **6**, which, via loss of a PMe_3 ligand and oxidative addition of a Si−Si bond, would be converted to the final product **1**. No intermediates were observed during the formation of **1** at −70 °C, as determined by ^1H and ^{31}P NMR spectroscopy. Interestingly, **1** is also formed by the direct addition of 2-butyne to **4** (generated in solution[6]), indicating that **4** is in equilibrium with the silyl−silylene complex **3**.



(2)

Metallacycles **1** and **2** exhibit fluxional behavior in solution. Thus, at room temperature, the ^1H NMR spectrum of **1** displays only single resonances for the $SiMe_3$ and $SiMe_2$ groups (benzene-d_6 solution). Cooling of a toluene-d_8 solution of **1** allows observation of decoalescence behavior ($T_c = -30$ °C; $\Delta G^{\ddagger} = 11(1)$ kcal mol^{-1}) and resolution of inequivalent $SiMe_3$ and $SiMe_2$ resonances.[10] We propose that this fluxionality derives from a Si−Si bond reductive elimination/oxidative addition cycle, as shown in eq 2. Rotation about a Si−C bond in the intermediate vinylsilyl complex **7** would

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(10) Selected data for **1**: ^1H NMR (benzene-d_6, 400 MHz, 25 °C) δ 0.23 (br s, 18 H, $SiMe_3$), 0.58 (br s, 6 H, $RhSiMe_2$), 0.85 (d, $^3J_{HRh} = 4$ Hz, 3 H, RhSi*Me*$SiMe_3$), 0.97 (d, $^2J_{HP} = 7$ Hz, 9 H, PMe_3), 1.08 (d, $^2J_{HP} = 7$ Hz, 9 H, PMe_3), 2.05 (s, 3 H, CMe), 2.08 (s, 3 H, CMe); ^1H NMR (toluene-d_8, 400 MHz, −70 °C) δ 0.22 (s, 9 H, $SiMe_3$), 0.37 (s, 9H, $SiMe_3$), 0.53 (br s, 3 H, $RhSiMe_2$), 0.83 (br s, 3 H, $RhSiMe_2$), 0.88 (d, $^2J_{HP} = 7$ Hz, 9 H, PMe_3), 0.94 (d, $^3J_{HRh} = 4$ Hz, 3 H, RhSi*Me*$SiMe_3$), 1.00 (d, $^2J_{HP} = 7$ Hz, 9 H, PMe_3), 2.17 (s, 3 H, CMe), 2.22 (s, 3 H, CMe); $^{31}P\{^1H\}$ NMR (benzene-d_6, 162.0 MHz, 25 °C) δ −28.50 (m). Anal. Calcd for $RhP_2Si_4C_{19}H_{51}$: C, 40.98; H, 9.23. Found: C, 40.72; H, 9.01. Selected data for **2**: ^1H NMR (benzene-d_6, 400 MHz, 25 °C), δ 0.39 (br s, 18 H, $SiMe_3$), 0.61 (br s, 6 H, $RhSiMe_2$), 0.78 (d, $^3J_{HRh} =$ 3 Hz, 3 H, RhSi*Me*$SiMe_3$), 0.94 (d, $^2J_{HP} = 7$ Hz, 9 H, PMe_3), 1.07 (d, $^2J_{HP} = 7$ Hz, 9 H, PMe_3), 6.88 (m, Ph), 7.10 (m, Ph), 7.24 (m, Ph), 7.30 (m, Ph); $^{31}P\{^1H\}$ NMR (benzene-d_6, 162.0 MHz, 25 °C) δ −29.55 (m). Anal. Calcd for $RhP_2Si_4C_{29}H_{55}$: C, 51.15; H, 8.14. Found: C, 50.75; H, 8.40. Selected data for **8**: ^1H NMR (benzene-d_6, 400 MHz, 25 °C) δ 0.55 (s, 27 H, $SiMe_3$), 1.14 (br s, 27 H, PMe_3); $^{31}P\{^1H\}$ NMR (benzene-d_6, 162.0 MHz, 25 °C) δ −22.20 (m). Anal. Calcd for $RhGeP_3Si_3C_{18}H_{54}$: C, 39.52; H, 9.95. Found: C, 39.20; H, 10.31. Selected data for **9**: ^1H NMR (benzene-d_6, 400 MHz, 25 °C) δ −11.4 (dt, H, $^2J_{HP} =$ 160 Hz, $^2J_{HP} = 20$ Hz, IrH), −0.64 (m, 1 H, $IrCH_2$), −0.55 (m, 1 H, $IrCH_2$), 0.55 (s, 3 H, SiMe), 0.59 (s, 9 H, $SiMe_3$), 0.63 (s, 9 H, $SiMe_3$), 0.68 (s, 3 H, SiMe), 1.11 (d, $^2J_{HP} = 8$ Hz, PMe_3), 1.27 (d, $^2J_{HP} = 8$ Hz, PMe_3), 1.30 (d, $^2J_{HP} = 8$ Hz, PMe_3); $^{31}P\{^1H\}$ NMR (benzene-d_6, 162.0 MHz, 25 °C) δ −63.55 (m, 2 overlapping resonances, 2 P), −54.90 (m, 1 P). Anal. Calcd for $IrGeP_3Si_3C_{18}H_{54}$: C, 30.33; H, 7.64. Found: C, 30.20; H, 7.90.

(11) Compound **1** was prepared by adding a solution of $(THF)_3LiSi(SiMe_3)_3$ (0.385 g, 0.818 mmol) in 15 mL of pentane to a solution of $(Me_3P)_3RhCl$ (0.300 g, 0.818 mmol) and 2-butyne (100 μL, 1.3 mmol) in 15 mL of pentane. After removal of solvent, the product was extracted into pentane and then crystallized from that solvent in 72% yield. For compound **8**, a solution of $(Me_3P)_3RhCl$ (0.300 g, 0.818 mmol) in 20 mL of pentane was added to a solution of $(THF)_3LiGe(SiMe_3)_3$ (0.421 g, 0.818 mmol) in 15 mL of pentane. The mixture immediately became deep red, and it was stirred for 30 min before the volatile materials were removed under pressure. The product was extracted into pentane and then crystallized by concentration and cooling of this solution (isolated yield 85%) to afford black, air-sensitive crystals.

(12) Crystal data for **1**: $RhP_2Si_4C_{19}H_{51}$, fw 556.81, orange prisms, triclinic, $P\bar{1}$, $a = 9.706(3)$ Å, $b = 10.011(3)$ Å, $c = 15.603(5)$ Å, $\alpha = 78.53(1)°$, $\beta = 88.76(2)°$, $\gamma = 78.38(1)°$, $V = 1455.0(7)$ Å^3, $Z = 2$, μ(Mo Kα) = 18.51 cm^{-1}, $T = 155$ K. Of 4115 empirically absorption corrected data ($2\theta_{max} = 51.1°$), 3797 were independent and observed. $R(F) =$ 6.6%; $R(wF) = 7.7\%$.

allow addition of a second Si−Si bond and exchange of the $SiMe_3$ groups. The observed fluxionality therefore lends some support to the latter part of the mechanism outlined in Scheme 1. Addition of excess PMe_3 to **1** did not result in trapping of the proposed vinylsilyl complex **6** and had no effect on the rate of the fluxional process.

With the hope that a germylene complex analogous to $(Me_3P)_3(Me_3Si)Rh{=}Si(SiMe_3)_2$ might be more stable and therefore observable, we attempted to generate such a species by the reaction of $(Me_3P)_3RhCl$ with $(THF)_3LiGe(SiMe_3)_3$[13] in pentane. Surprisingly, this reaction gave the deep red complex $(Me_3P)_3RhGe(SiMe_3)_3$ (**8**), isolated in 85% yield.[10,11] Complex **8** is stable at room temperature but gradually decomposes at 70 °C over 2−3 h to a mixture of products, including several hydride complexes. It does not react with 1 equiv of 2-butyne at room temperature over 2.5 h. In a similar manner, reaction of $(THF)_3LiGe(SiMe_3)_3$ with "$(Me_3P)_3IrCl$" (generated in situ by addition of PMe_3 to $[(COE)_2IrCl]_2$)[14] produces the cyclometalated product *fac*-$(Me_3P)_3\overline{Ir(H)Ge(SiMe_3)_2SiMe_2C}H_2$ (**9**), isolated as colorless crystals in 29% yield.[10] Thus, no convincing evidence for migration chemistry was observed in either germyl complex.

The results described above provide further evidence for the participation of 1,2- and 1,3-migrations in metal silyl complexes. This migration chemistry results in the dramatic rearrangement of a polysilyl complex to give a novel tris(silyl)rhodium derivative. Currently it appears that silylene intermediates are involved, but it is impossible at this time to definitively rule out other mechanistic possibilities. Also of interest is the reversible Si−Si bond oxidative addition/reductive elimination equilibrium observed for **1** (eq 2). Given the rarity of both steps,[2] the facility of this process is quite remarkable. As indicated in eq 2, this intramolecular process may be assisted by formation of an intermediate η^3-silaallyl structure (**7**). Apparently, an alternative C−H activation in this intermediate would produce an excessively strained chelate ring. We are continuing to explore this system in search of new information.

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Supporting Information Available: Text giving experimental procedures and characterization data for compounds and tables of crystal, data collection, and refinement parameters, atomic coordinates, bond distances and angles, and anisotropic displacement parameters (21 pages). Ordering information is given on any current masthead page.

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