2008 *Organometallics* **2005,** *24,* 2008−2011

Synthesis and Characterization of Cationic Rhodium Complexes with Stable Silylenes

Eva Neumann and Andreas Pfaltz*

Department of Chemistry, University of Basel, St. Johanns-Ring 19,
CH- 4056 Basel, Switzerland

Received January 5, 2005

*Summary: Two cationic rhodium(I)−tetrasilylene complexes, [Rh(SitBuNHC=CHNtBu)$_4$]BAr$_F$ (**4**; BAr$_F$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) and [Rh(SitBuNH$_2$C=CH$_2$NtBu)$_4$]BAr$_F$ (**5**), were prepared from [Rh(cod)$_2$]BAr$_F$ and 1,3-di-tert-butyl-2,3-dihydro-1H-1,3,2-diazasilol-2-ylidene (**1**) or its saturated analogue **2**, respectively (Figure 1). The two complexes were characterized by X-ray analysis and NMR spectroscopy. The crystal structures revealed a square-planar coordination geometry for both complexes. Only tetrakis(silylene) complexes were formed, even in the presence of less than 4 equiv of silylene.*

Introduction

Figure 1. Stable N-heterocyclic silylenes **1** and **2**.

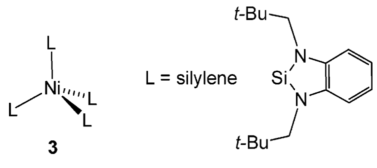


Figure 2. Tetrahedral silylene−nickel complex **3**.

N-heterocyclic carbenes (NHC) have emerged as a versatile class of ligands for homogeneous catalysis.[1] Accordingly, a wide variety of NHC−metal complexes have been prepared and investigated as catalysts. In contrast, analogous silylene metal complexes have received much less attention. The first stable silylene **1** (Figure 1), a silicon analogue of an NHC, was reported by Denk et al. in 1994,[2] and since then, various transition-metal complexes of silylenes of this type[3−6] have been prepared.[7,8] Ni(cod)$_2$ was shown to form the homoleptic tris(silylene) complex [Ni(**1**)$_3$],[9] whereas the tetrakis(silylene)−nickel complex **3** was obtained by starting from a *N,N′*-dineopentyl-substituted silylene (Figure 2).[10,11] The crystal structure of complex **3** showed a tetrahedral arrangement of the four silylene ligands. The tris(silylene)− and tetrakis(silylene)−palladium complexes [Pd(**1**)$_3$] and [Pd(**2**)$_4$], as well as dinuclear silylene-bridged compounds, were formed using [Pd(PPh$_3$)$_3$] and [Pd(cod)(CH$_3$)$_2$] as precursors.[12,13] However, no crystal structures were reported for these homoleptic complexes.

The potential of stable silylenes as ligands in catalysis remains to be explored. Recently, Fürstner et al. successfully used a mixed dinuclear (silylene)(phosphine)palladium(0) complex, in which a heterocyclic silylene acts as a bridging ligand, to catalyze the Suzuki coupling of arylboronic acids with bromoarenes.[13] However, the nature of the actual catalytically active species in this reaction is not known.

Although rhodium plays an important role in homogeneous catalysis, no complexes of this metal with η^1-bound N-heterocyclic silylenes are known. Here, we report the syntheses and crystal structures of two homoleptic square-planar cationic rhodium(I)−silylene complexes.

Results and Discussion

For the synthesis of silylene complexes, [Rh(cod)$_2$]BAr$_F$ (BAr$_F$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) was used as a precursor. This crystalline salt was readily prepared, using a modified procedure reported for the preparation of the analogous tetrafluoroborate (Scheme 1).[14] When a red slurry of [Rh(cod)$_2$]BAr$_F$ was treated with 4 equiv of silylene **1** in hexane for 14 h at room temperature, an orange suspension of the cationic tetrakis(silylene) complex **4** was formed.

---

* To whom correspondence should be addressed. E-mail: andreas.pfaltz@unibas.ch.

[1] Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

[2] Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691.

[3] West, R.; Denk, M. *Pure Appl. Chem.* **1996**, *68*, 785.

[4] Haaf, M.; Schmedake, T. A.; Paradise, B. J.; West, R. *Can. J. Chem.* **2000**, *78*, 1526.

[5] Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaser, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1931.

[6] Heinicke, J.; Oprea, A.; Kindermann, M. K.; Karpati, T.; Nyulaszi, L.; Veszpremi, T. *Chem. Eur. J.* **1998**, *4*, 541.

[7] (a) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704. (b) Hill, N. J.; West, R. *J. Org. Chem.* **2004**, *689*, 4165−4183.

[8] (a) Gehrhus, B.; Lappert, M. F. *J. Organomet. Chem.* **2001**, *617−618*, 209. (b) Dysard, J. M.; Tilley, T. D. *Organometallics* **2000**, *19*, 4726. (c) Cai, X.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Can. J. Chem.* **2000**, *78*, 1484−1490 (d) Evans, W. J.; Perotti, J. M.; Ziller, J. W.; Moser, D. F.; West, R. *Organometallics* **2003**, *22*, 1160−1163. (e) Amoroso, D.; Haaf, M.; Yap, G. P. A.; West, R.; Fogg, D. E. *Organometallics* **2002**, *21*, 534−540.

[9] Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Powell, D.; West, R. *Organometallics* **2000**, *19*, 3263.

[10] Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *Organometallics* **1998**, *17*, 5599.

[11] Avent, A. G.; Gerhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *J. Organomet. Chem.* **2003**, *686*, 321−331.

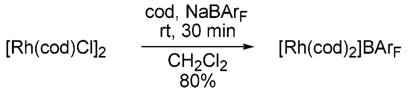
[12] Herrmann, W. A.; Harter, P.; Gstöttmayr, C. W. K.; Bielert, F.; Seeboth, N.; Sirsch, P. *J. Organomet. Chem.* **2002**, *649*, 141.

[13] Fürstner, A.; Krause, H.; Lehmann, C. W. *Chem. Commun.* **2001**, 2372.

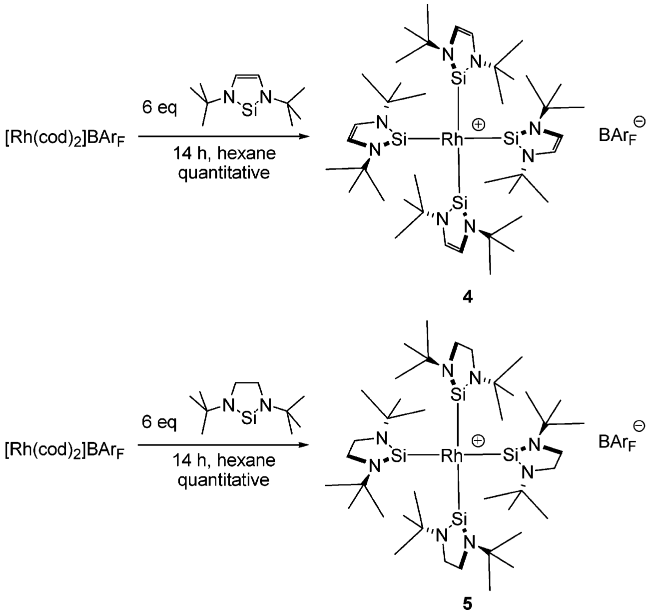
[14] Schenck, T. G.; Milne, C. T. C.; Sawyer, J. F.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2338.

10.1021/om050010e CCC: $30.25

Scheme 1. Synthesis of $[Rh(cod)_2]BAr_F$



Scheme 2. Synthesis of Complexes 4 and 5



The extremely air-sensitive product **4** was obtained in quantitative yield as an orange powder, which could be crystallized from dichloromethane–hexane. The analogous complex **5** was prepared in the same manner from silylene **2** (Scheme 2).[4]

Attempts to synthesize mixed bis(silylene)(cod)Rh complexes by replacement of just one 1,5-cyclooctadiene moiety were unsuccesssful. The homoleptic tetrakis-(silylene)complexes **4** and **5** were the only products observed, even when less than 4 equiv of silylene was used. In acetonitrile as solvent, $[Rh(cod)(CH_3CN)_2]$-BAr_F[15] was formed as an intermediate, but again only the homoleptic silylene complexes **4** and **5** were observed, together with a number of unidentified side products. In this respect, the reactivity of the silylenes **1** and **2** differs from that of analogous N-heterocyclic carbenes. Only partial ligand exchange leading to Rh-(cod)(NHC)X complexes could be achieved, when an excess of carbene was reacted with $Rh_2(cod)_2X_2$.[16] Thus, it seems more difficult to form tetrakis(NHC) complexes, probably due to steric strain resulting from the shorter Rh–C compared to Rh–Si bonds.

Complexes **4** and **5** crystallized from dichloromethane/hexane as orange and yellow plates, respectively, which were subjected to X-ray crystallographic analysis. ORTEP representations of the crystal structures are depicted in Figures 3 and 4; crystallographic data and selected structural parameters are given in Tables 1 and 2. Both complexes are centrosymmetric and show a windmill-shaped, square-planar arrangement of the four silylene ligands. The three-coordinate silicon atoms adopt an almost perfectly planar geometry, with the sum of bond angles being 360.6° (**4**) and 360.0° (**5**). Rh–Si distances are between 2.29 and 2.32 Å for both complexes. As expected, the Rh–Si bonds are somewhat shorter than in silyl–Rh complexes (2.32–2.38 Å) or bridged μ-$(R_2Si)Rh_2$ complexes (2.34–2.36 Å). [17,18]

Table 1. Crystallographic Data[a]

	4	5
empirical formula	$C_{40}H_{80}N_8RhSi_4$, $C_{32}H_{12}BF_{24}$	$C_{40}H_{88}N_8RhSi_4$, $C_{32}H_{12}BF_{24}$
formula wt	1751.59	1759.65
temp (K)	173K	173K
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*
unit cell dimens		
a (Å)	21.827(2)	20.9469(6)
b (Å)	19.811(2)	20.6092(6)
c (Å)	19.503(2)	19.3746(4)
β (deg)	108.762(8)	103.192(2)
unit cell vol (Å^3)	7985 (2)	8143.3 (4)
Z	4	4
calcd density (g cm^{-3})	1.457	1.435
abs coeff μ (mm^{-1})	0.376	0.369
F(000)	3608	3640
cryst size (mm)	0.23 × 0.32 × 0.4	0.3 × 0.4 × 0.5
limiting indices (measd)	$h, \pm 30; k, \pm 29; l, \pm 27$	$h, \pm 29; k, \pm 28; l, \pm 27$
no. of collected/unique rflns	91 539/11 663 ($R_{int} = 0.06$)	88 079/11 880 ($R_{int} = 0.08$)
θ range for data collecn (deg)	1.424–30.039	1.405–30.024
completeness to θ_{max}	0.998	0.997
no. of data/params	6679 ($I > 3\sigma(I)$)/553	6019 ($I > 3\sigma(I)$)/552
goodness of fit on *F*	1.1384	1.026
R	3.92	5.04
R_w	4.12	5.28

[a] Cambridge Crystallographic Database deposition numbers CCDC 255531 and 255532.

Si–N bond distances and N–Si–N angles of the free silylenes change very little upon coordination to Rh (**1**, 1.75 Å, 89.0°; **4**, 1.73–1.74 Å, 91.0–91.3°).[2] No other examples of square-planar tetrakis(silylene) complexes were found in the literature. The only somewhat related silylene complexes, for which crystal structures were reported, are the above-mentioned tetrahedral [Ni-(silylene)$_4$] (**3**) and square-planar mixed *trans*-bis(chlorosilyl)bis(silylene)palladium(II) and -platinum(II) complexes.[9,10]

The solution structures of complexes **4** and **5**, analyzed by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy in tetrahydrofuran-d_8 and diethyl ether-d_{10}, were consistent with the crystal structures. The metal to silylene ratio, determined by integration of the silylene and the BAr_F protons, was 1:4. No ESI-MS spectra could be obtained due to the high sensitivity of the complexes.

Experimental Section

All manipulations were conducted under nitrogen or argon, using vacuum line or glovebox techniques. Dichloromethane was dried over CaH_2 and distilled under a argon atmosphere. Deuterated solvents were degassed using three *freeze–pump–thaw* cycles and stored over activated molecular sieves (4 Å). Hexane was used as purchased from Fluka (absolute over molecular sieves). $NaBAr_F$[20] and silylenes **1**[21] and **2**[4] were

---

(15) According to: Green, M.; Kuc, T. A.; Taylor, S. H. *J. Chem. Soc., Chem. Commun.* **1970**, *22*, 1553.

(16) (a) Herrmann, W. A.; Goossen, L. J.; Artus, G. R. J.; Köcher, C. *Organometallics* **1997**, *16*, 2472. (b) Köcher, C.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *532*, 261.

(17) (a) Aizenberg, M. J.; Elsevier, C. J.; Milstein, D. *J. Organomet. Chem.* **1998**, *551*, 81. (b) Thorn, D. L.; Harlow, R. L. *Inorg. Chem.* **1990**, *29*, 2017.

(18) Rosenberg, L.; Fryzuk, M. D.; Rettig, S. J. *Organometallics* **1999**, *18*, 958 (Supporting Information).

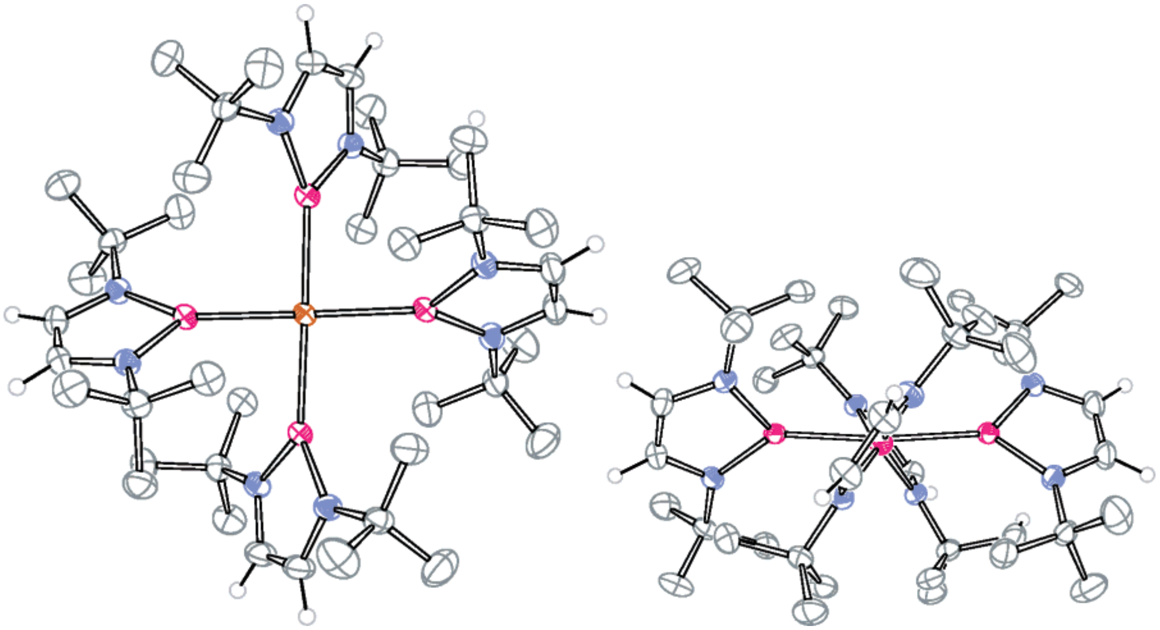


Figure 3. ORTEP representation of the cation moiety of complex **4** in top view (left) and side view (right). The BAr$_F$ anion and most of the protons, except ring protons, are omitted for clarity.

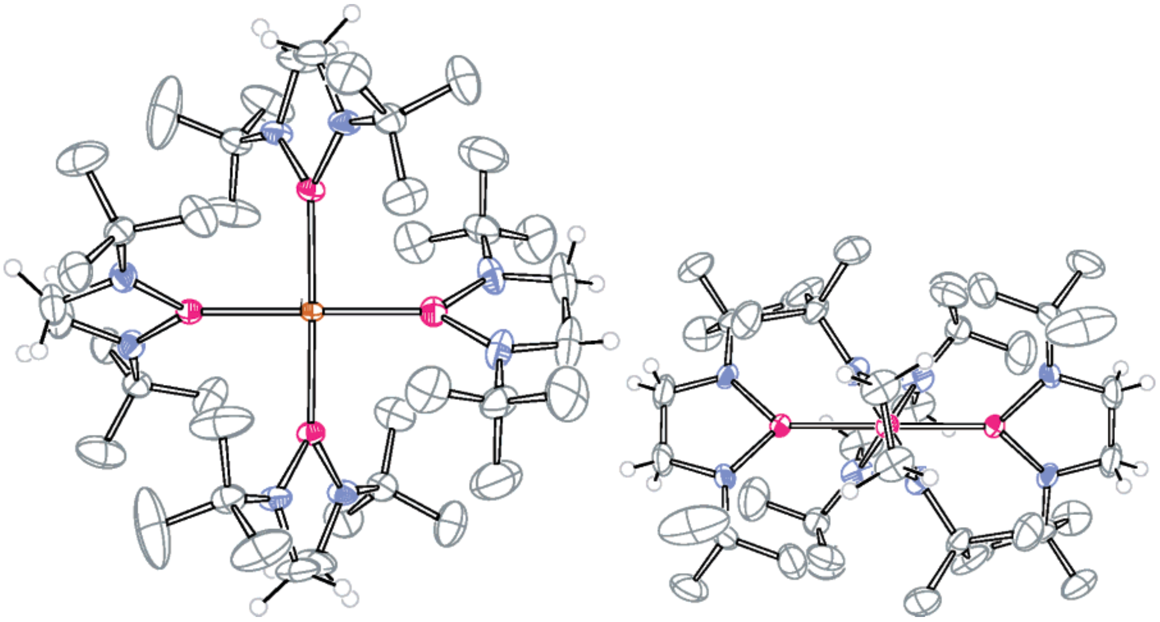


Figure 4. ORTEP representation of the cation moiety of complex **5** in top view (left) and side view (right). The BAr$_F$ anion and most protons except ring protons are omitted for clarity.

prepared as previously described. [Rh(cod)Cl]$_2$ was purchased from Strem. 1,5-Cyclooctadiene was purchased from Fluka and distilled prior to use.

NMR spectra were recorded on Bruker Advance 400 and 500 MHz NMR spectrometers equipped with BBO broadband probe heads. References were 5.32 ppm (^{1}H NMR) and 53.8 ppm (^{13}C NMR) for CH_2Cl_2 and 3.58 (1.73) ppm (^{1}H NMR) and 67.4 (25.3) ppm (^{13}C NMR) for THF. IR spectra were measured on a Perkin-Elmer 1600 series FTIR spectrometer. KBr was thoroughly dried under high vacuum, and samples were prepared in the glovebox. Microanalytical data were obtained using Leco CHN-900 analyzers. X-ray structural data were collected on a KappaCCD four-cycle diffractometer at 173 K.

[Rh(cod)$_2$]BAr$_F$ was prepared using a modified literature synthesis of [Rh(cod)$_2$]BF$_4$.[14] To a solution of [Rh(cod)Cl]$_2$ (100 mg, 0.2 mmol) in CH_2Cl_2 (3 mL) was added solid NaBAr$_F$ (363 mg, 0.41 mmol). Addition of 1,5-cyclooctadiene (75 μL, 0.6 mmol) to the orange reaction mixture resulted in immediate formation of a dark red suspension, which was stirred for 30 min at room temperature and then filtered through a plug of Celite. Evaporation of the volatiles afforded 387 mg of the product (81% yield). The dark red solid was recrystallized from CH_2Cl_2/hexane to give 320 mg of dark red needles (67% yield). ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K; δ (ppm)): 2.42 (s, 8H, cod), 5.11 (s, 4H, cod), 7.54 (s, BAr$_F$ para CH), 7.69 (s, BAr$_F$ ortho CH). ^{13}C NMR (125 MHz, CD_2Cl_2; δ (ppm)): 29.9, 108.0 (d, $^1J_{C-Rh} = 7.7$ Hz), 117.9 (BAr$_F$, para CH), 125.0 (q, CF$_3$, $^1J_{F-C}$

---

(19) (a) Moser, D.; Bosse, T.; Olson, J.; Moser, J.-L.; Guzei, I. A.; West, R. *J. Am. Chem. Soc.* **2002**, *124*, 4186. (b) Su, M.-D. *J. Am. Chem. Soc.* **2003**, *125*, 1714.

(20) Reger, D. L.; Wright, T. D.; Little, C. A.; Lamba, J. J. S.; Smith, M. D. *Inorg. Chem.* **2001**, *40*, 3810.

(21) Haaf, M.; Schmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolte, A. J.; Denk, M.; West, R. *J. Am. Chem. Soc.* **1998**, *120*, 12714.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4 and 5

	4	5
Rh1−Si1	2.3104(8)	2.2988(8)
Rh1−Si2	2.2922(8)	2.289(2)
Rh1−Si3		2.316(2)
Si1−N1	1.735(2)	1.714(3)
Si1−N2	1.736(2)	1.712(3)
Si2−N3	1.734(2)	1.711(3)
Si2−N4	1.735(2)	
Si1−Rh1−Si1′	94.63(4)	178.83(6)
Si1−Rh1−Si2	173.86(2)	90.59(3)
Si1−Rh1−Si2′	86.72(2)	
Si1′-Rh1−Si2	86.72(2)	90.59(3)
Si1′-Rh1−Si2′	173.86 (2)	
Si2−Rh1−Si2′	92.57(4)	
Si1−Rh1−Si3		89.41(3)
Si1′-Rh1−Si3		89.41(3)
Si2−Rh1−Si3		179.995
N1−Si1−N2	91.0(2)	94.1(2)
N3−Si2−N4	91.3(2)	
N3−Si2−N3′		94.1(2)
N4−Si3−N4′		94.2(2)
Rh1−Si1−N1	131.60(9)	132.2(1)
Rh1−Si1−N2	137.05(8)	133.7(2)
Rh1−Si2−N3	138.32(8)	132.9(2)
Rh1−Si2−N4	129.85(8)	
Rh1−Si3−N4		132.9(1)

[a] Both compounds show C_2 symmetry. While in **3** two of the silicon atoms lie on the C_2 axes, all silicon atoms are in general positions in compound **2**. Therefore, the number of Rh−Si distances and the number of Si−Rh−Si, N−Si−N, and Rh−Si−N angles differ in both cases. The symmetry-generated atoms are marked with a prime (′).

= 272 Hz), 129.0 (BAr$_\mathrm{F}$ ipso to CF$_3$), 135.1 (BAr$_\mathrm{F}$ ortho CH), not observed (q, BAr$_\mathrm{F}$ ipso to B, $^1J_{\mathrm{B-C}}$ = 50 Hz). IR (KBr; ν (cm^{-1})): 2936.5 (m), 1896.7 (m), 2845.4 (w), 1612.4 (m), 1432.7 (w), 1358.7 (s), 1280.9 (s), 1121.1 (s$_\mathrm{br}$), 986.5 (w), 889.1 (m), 836.3 (m), 780.1 (w), 711.8 (m), 674.1 (m). MS (FAB; *m/z*): 319 (M$^+$) 100%, 211 (M$^+$ − cod) 42.2%. Anal. Calcd (found): C, 48.76 (48.62); H, 3.07 (3.07). Mp: 175 °C dec.

Complex 4. [Rh(cod)$_2$]BAr$_\mathrm{F}$ (98 mg, 0.075 mmol) was weighed into a Schlenk tube suspended in hexane (2 mL). Addition of solid silylene **1** (60 mg, 0.306 mmol) afforded an orange suspension after stirring for 14 h. The resulting solid was separated by filtration and washed three times with small amounts of hexane. After drying under high vacuum, the product was obtained in quantitative yield (based on ^{1}H NMR) as a light orange powder, which showed essentially the same NMR spectrum as the recrystallized material. The extreme air sensitivity of the powdery compound results in fuming and immediate decomposition when in contact with air. The product was recrystallized from CH$_2$Cl$_2$/hexane to afford dark orange crystals. ^{1}H NMR (500 MHz, THF-d_8; δ (ppm)): 1.5 (s, 72H, *tert*-butyl), 6.83 (s, 8H, C*H*=C*H*), 7.6 (s, 4H, BAr$_\mathrm{F}$ para CH), 7.76 (t, 8H, BAr$_\mathrm{F}$ ortho CH, $^4J_{\mathrm{H-F}}$ = 2.5 Hz). ^{13}C NMR (125 MHz, THF-d_8; δ (ppm)): 30.1 (C(*CH$_3$*)$_3$), 55.8 (*C*(CH$_3$)$_3$), 117.2 (BAr$_\mathrm{F}$, para CH), 120.8 (*C*H=*C*H), 124.5 (q, CF$_3$, $^1J_{\mathrm{F-C}}$ = 272 Hz), 129.0 (BAr$_\mathrm{F}$ ipso to CF$_3$), 134.6 (BAr$_\mathrm{F}$ ortho CH), 161.8 (q, BAr$_\mathrm{F}$ ipso to B, $^1J_{\mathrm{B-C}}$ = 50 Hz). ^{29}Si NMR (99 MHz, THF-d_8; δ (ppm)): δ 95.6 ($^1J_{\mathrm{Si-Rh}}$ = 82.5 Hz). IR (KBr; ν (cm^{-1})): 2977 (s), 1611 (w), 1466 (m), 1396 (w), 1356 (m), 1279 (s), 1207 (m), 1123 (s, br), 1000 (w), 885 (m), 839 (m), 809 (w), 738 (m), 713 (m), 659 (s). Anal. Calcd (found): C, 49.37 (49.31); H, 5.29 (5.15); N, 6.40 (6.30). Mp: 200 °C dec.

Complex 5. The complex was synthesized as described above, starting from 98 mg (0.075 mmol) of [Rh(cod)$_2$]BAr$_\mathrm{F}$ and 60 mg (0.3 mmol) of **2**. From the resulting bright yellow suspension complex **5** was obtained in quantitative yield (based on ^{1}H NMR) as a yellow powder, which was recrystallized from CH$_2$Cl$_2$/hexane to give light orange crystals. ^{1}H NMR (250 MHz, THF-d_8; δ (ppm)): 1.38 (s, 72H, *tert*-butyl), 3.28 (m, 16H, C*H$_2$*C*H$_2$*), 7.55 (s, 4H, para BAr$_\mathrm{F}$), 7.72 (m, 8H, ortho BAr$_\mathrm{F}$). ^{13}C NMR (125 MHz, THF-d_8; δ (ppm)): 32.0 (C(*CH$_3$*)$_3$), 46.6 (*C*H$_2$*C*H$_2$), 54.1 (*C*(CH$_3$)$_3$), 117.4 (BAr$_\mathrm{F}$, para CH), 124.0 (q, CF$_3$, $^1J_{\mathrm{F-C}}$ = 272 Hz), 128.8 (BAr$_\mathrm{F}$ ipso to CF$_3$), 134.7 (BAr$_\mathrm{F}$ ortho CH), 161.8 (q, BAr$_\mathrm{F}$ ipso to B, $^1J_{\mathrm{B-C}}$ = 50 Hz). ^{29}Si NMR (99 MHz, THF-d_8; δ (ppm)): δ 134.5 ($^1J_{\mathrm{Si-Rh}}$ = 76.6 Hz). IR (KBr; ν (cm^{-1})): 2976 (m), 1611 (w), 1474 (m), 1396 (w), 1355 (m), 1279 (s), 1126 (s, br), 1036 (w), 973 (m), 887 (m), 838 (m), 803 (w), 744 (w), 713 (m), 682 (m). Anal. Calcd (found): C, 49.15 (48.74); H, 5.73 (5.57); N, 6.37 (6.13). Mp: ∼195 °C dec.

Acknowledgment. We thank Markus Neuburger for recording the crystal structures and for his assiduous help with the refinement.

Supporting Information Available: CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050010E