ORGANOMETALLICS

Silylene-bridged ruthenium dimers via reactions of [(.eta.5-C5Me5)Ru(.mu.-OMe)]2 with silanes. Structure of {[(.eta.5-C5Me5)Ru]2(.mu.-SiPhOMe)(.mu.-OMe)(.mu.-H)}

Brian K. Campion, Richard H. Heyn, and T. Don Tilley

Organometallics, **1992**, 11 (11), 3918-3920• DOI: 10.1021/om00059a070 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

3918 *Organometallics* 1992, *11*, 3918–3920

Silylene-Bridged Ruthenium Dimers via Reactions of $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}OMe)]_2$ with Silanes. Structure of $\{[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)\}$

Brian K. Campion, Richard H. Heyn, and T. Don Tilley*

Department of Chemistry, 0506, University of California at San Diego,
9500 Gilman Drive, La Jolla, California 92093-0506

Received June 4, 1992

Summary: Reaction of the coordinatively unsaturated complex $[Cp^*Ru(\mu\text{-}OMe)]_2$ with Ph_2SiH_2 produces $\{[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)\}$, via substitution of a phenyl group on silicon by methoxide. The structure reveals a Ru–Ru double bond, d(Ru–Ru) = 2.569 (5) Å, which is bridged by the phenyl(methoxy)silylene ligand, a methoxy group, and a hydride ligand (not located). Crystal data: triclinic, a = 11.157 (7) Å, b = 16.336 (8) Å, c = 16.792 (7) Å, α = 74.39 (4)°, β = 88.13 (5)°, γ = 74.71 (5)°, V = 2841 (3) Å^3, Z = 2, and R = 6.69%. The related reaction with $CyMeSiH_2$ (Cy = cyclohexyl) takes a different course, but also proceeds via Si–O bond formation to give CyMeSiH(OMe) and $\{[Cp^*Ru(\mu\text{-}\eta^2\text{-}H\text{-}SiMeCy)]_2(\mu\text{-}H)(H)\}$.

The high lability of silicon compounds in the presence of transition metals can lead to condensation of more than one metal about a bridging silicon ligand.[1] Examples include formation of μ-silylene ligands from secondary silanes[2] or disilanes,[3] μ-$SiR_2(H)$ ligands with α-agostic Si–H–M interactions,[4] μ-$SiR_2(H)$ ligands with M–Si–H–M linkages,[5] and μ-silylyne ligands.[6] Such structures are probably important in a number of metal-mediated reactions of silicon compounds and in related heterogeneous processes on metal surfaces.[7] In pursuit of reactive, "highly metallated" silicon complexes, and coordination complexes of reactive silicon-based species, we have examined reactions of the electron-deficient, methoxy-bridged dimer $[Cp^*Ru(\mu\text{-}OMe)]_2$[8] with secondary silanes. It seemed to us that the silanes might undergo condensation with the ruthenium centers beyond an initial Si–H oxidative addition. These reactions have afforded the complexes $\{[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)\}$ and $\{[Cp^*Ru(\mu\text{-}\eta^2\text{-}H\text{-}SiMeCy)]_2(\mu\text{-}H)(H)\}$ via Si–O bond-forming processes. The formation of $\{[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)\}$ from $[Cp^*Ru(\mu\text{-}OMe)]_2$ and Ph_2SiH_2 involves an interesting substitution of a phenyl group on silicon by methoxide. In general, we find that $[Cp^*Ru(\mu\text{-}OMe)]_2$ is much more reactive toward silanes than the 16-electron complex $Cp^*(PPr^i_3)RuCl$.

Experimental Section

All operations were conducted under anaerobic and anhydrous conditions. Elemental analyses were performed by Mikroanalytishes Labor Pascher. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer. NMR spectra were obtained with a GE QE-300 or a Varian UN-500 instrument. The methoxide $[Cp^*Ru(\mu\text{-}OMe)]_2$ was obtained via a published procedure.[8b]

$\{[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)\}$. To $[Cp^*Ru(\mu\text{-}OMe)]_2$ (0.095 g, 0.17 mmol) in benzene (25 mL) was added Ph_2SiH_2 (67 μL, 0.35 mmol) in 25 mL of benzene. The resulting purple solution was stirred for 30 min, and then the volatiles were removed by vacuum transfer. The residue was extracted into pentane (35 + 10 mL), and concentration and cooling (−40 °C) of this solution gave the product as dark maroon crystals (mp 284–287 °C) in 42% yield (0.045 g). Anal. Calcd for $C_{28}H_{42}O_2SiRu_2$: C, 52.5; H, 6.61. Found: C, 53.1; H, 6.78. IR (benzene-d_6 solution, CaF_2 cell, cm^{-1}): 2978 m, 2945 m, 2892 s, 2780 w, 1478 m br, 1429 m, 1380 m, 1180 w br, 1095 s sh, 1078 s, 1028 s. ^{1}H NMR (300 MHz, benzene-d_6, 23 °C): δ −18.72 (s, 1 H, RuH), 1.63 (s, 30 H, Cp*), 3.72 (s, 3 H, OMe), 3.73 (s, 3 H, OMe), 7.33, 7.45, 8.47 (m, 5 H, SiPh). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, 23 °C): δ 10.94 (Cp*), 53.09 (SiOMe), 70.37 (μ-OMe), 85.48 (Cp*), 127.39, 129.00, 149.25 (SiPh). ^{29}Si NMR (59.6 MHz, benzene-d_6, INEPT, 23 °C): δ 211.12.

For the second isomer (formed slowly in benzene-d_6 solution from the above complex), the following data were determined. ^{1}H NMR (300 MHz, benzene-d_6, 23 °C): δ −18.81 (s, 1 H, RuH), 1.61 (s, 30 H, Cp*), 3.55 (s, 3 H, OMe), 4.07 (s, 3 H, OMe), 7.24, 7.45, 8.43 (m, 5 H, SiPh). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, 23 °C): δ 10.91 (Cp*), 52.60 (SiOMe), 77.39 (μ-OMe), 85.68 (Cp*), 127.38, 128.74, 146.98 (SiPh). ^{29}Si NMR (59.6 MHz, benzene-d_6, INEPT, 23 °C): δ 193.50.

$\{[Cp^*Ru(\mu\text{-}\eta^2\text{-}H\text{-}SiMeCy)]_2(\mu\text{-}H)(H)\}$. To $[Cp^*Ru(\mu\text{-}OMe)]_2$ (0.26 g, 0.46 mmol) was added $CyMeSiH_2$ (220 μL, 1.3 mmol) in benzene (25 mL). After 14 h of stirring, the resulting blood-red solution was evaporated to dryness and extracted with pentane (20 mL). Concentration and cooling (−30 °C) of the pentane solution gave the product as orange-yellow crystals (mp 247–248 °C) in 54% yield. Anal. Calcd for $C_{34}H_{62}Si_2Ru_2$: C, 56.0; H, 8.57. Found: C, 56.0; H, 8.59. IR (Nujol, CsI, cm^{-1}): 2050 w, 1261 m, 1241 m, 1163 w, 1028 s, 992 w, 888 m, 817 w, 780 s, 650 m, 430 w, 350 m br. ^{1}H NMR (300 MHz, benzene-d_6, 23 °C): δ −14.1 (br s, 4 H, RuH), 0.52 (s, 6 H, SiMe), 0.74, 1.35, 1.79, 2.16 (m, 22 H, SiCy), 1.92 (s, 30 H, Cp*). ^{1}H NMR (300 MHz, toluene-d_8, −70 °C): δ −15.81 (s, 1 H, RuH), −13.81 (s, 2 H, SiHRu), −12.94 (s, 1 H, RuH), 0.48 (s, 6 H, SiMe), 0.64, 1.39, 2.01, 2.22 (m, 22 H, SiCy), 1.67 (s, 15 H, Cp*), 2.02 (s, 15 H, Cp*). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, 23 °C): δ 4.96 (SiMe), 12.49 (Cp*), 27.69, 29.42, 31.02, 39.03 (SiCy), 93.25 (Cp*). ^{29}Si{^{1}H} NMR (99.30 MHz, toluene-d_8, 23 °C, DEPT): δ 115.17. The silane CyMeSiH(OMe) was identified as a product by monitoring the reaction in benzene-d_6 by ^{1}H NMR spectroscopy.

X-ray Structure Determination of $\{[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)\}$. A maroon crystal of approximate dimensions 0.25 × 0.25 × 0.40 mm was mounted under nitrogen

---

[1] For recent reviews of transition-metal silicon chemistry, see: (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989, Chapter 24, p 1415. (b) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991, Chapters 9 and 10, pp 245 and 309.

[2] (a) Carré, F. C.; Moreau, J. J. E. *Inorg. Chem.* **1982**, *21*, 3099. (b) Tobita, H.; Kawano, Y.; Shimoi, M.; Ogino, H. *Chem. Lett.* **1987**, 2247. (c) Wang, W. D.; Hommeltoff, S. I.; Eisenberg, R. *Organometallics* **1988**, *7*, 2417. (d) Wang, W. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 1833. (e) McDonald, R.; Cowie, M. *Organometallics* **1990**, *9*, 2468. (f) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917.

[3] (a) Brookes, A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 3469. (b) Kerber, R. C.; Pakkanen, T. *Inorg. Chim. Acta* **1979**, *37*, 61.

[4] (a) Auburn, M.; Ciriano, M.; Howard, J. A. K.; Murray, M.; Pugh, N. J.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 659. (b) Bennett, M. J.; Simpson, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 7156. (c) Suzuki, H.; Takao, T.; Tanaka, M.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 476.

[5] Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059.

[6] (a) Gusbeth, P.; Vahrenkamp, H. *Chem. Ber.* **1985**, *118*, 1143. (b) Kawano, Y.; Tobita, H.; Ogino, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 843.

[7] Clarke, M. P.; Davidson, I. M. T. *J. Organomet. Chem.* **1991**, *408*, 149.

[8] (a) Koelle, U.; Kossakowski, J. *J. Chem. Soc., Chem. Commun.* **1988**, 549. (b) Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712.

0276-7333/92/2311-3918$03.00/0

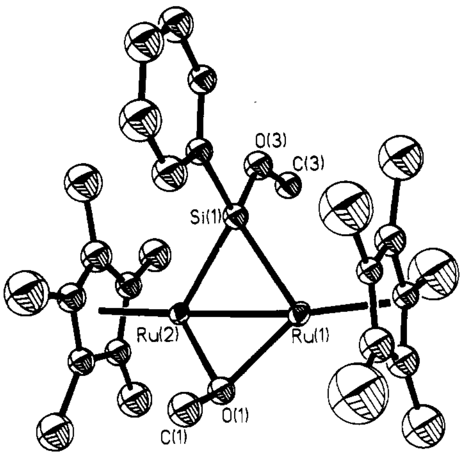
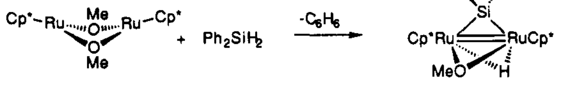


Figure 1. ORTEP view of the molecular structure of $\{[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)\}$.

in a random orientation in a glass capillary and flame-sealed. Centering of 13 reflections from a rotation photograph provided the preliminary unit cell data. Further refinement of the unit cell data was provided by centering of 18 reflections obtained from a preliminary data set ($20° \le 2\theta \le 30°$). The selection of the triclinic cell was confirmed by axial photographs. Data were collected with $\theta/2\theta$ scans ($3° \le 2\theta \le 40°$), at a variable scan speed of 3.0–19.5 min^{-1}, using Mo Kα radiation (λ = 0.71073 Å), on a Siemens R3m/V automated diffractometer equipped with a highly ordered graphite monochromator. Of the 6349 reflections measured, 5285 were independent (R_{int} = 3.48%) and 2063 were considered observed ($F_o > 6\sigma(F)$). The data were corrected for Lorentz and polarization effects, and for a slight decay in the intensity of three check reflections of 1.5%. A semi-empirical absorption correction based on the ψ scan method was employed. The minimum and maximum transmission factors for the correction were 0.7839 and 0.8794, respectively. The structure was solved by direct methods and refined by full-matrix least squares methods. Refinement of a solution in the space group $P1$ did not provide a chemically reasonable structure. Due to a lack of data, only the Ru and Si atoms were refined anisotropically. The Ph rings and the C_5Me_5 rings (inner C atoms) were constrained to be rigid hexagons (d(C–C) = 1.42 Å) and pentagons (d(C–C) = 1.39 Å), respectively. The hydrogen atoms were placed in idealized, calculated positions (d(C–H) = 0.96 Å), with a fixed thermal parameter. R_F = 6.69%, R_{wF} = 8.39%, GOF = 1.42, data/parameter = 8.8:1, largest Δ/σ = 0.152, largest difference peak = 0.85 e Å^{-3}. All calculations made use of the Siemens SHELXTL PLUS computing package (Siemens Analytical X-ray Instruments, Inc., Madison, WI).

Results and Discussion

The methoxy dimer $[Cp^*Ru(\mu\text{-}OMe)]_2$ and excess Ph_2SiH_2 (2 equiv) react in benzene to give a purple solution, from which a dark red crystalline compound can be isolated from pentane. This product was subsequently characterized as the silylene-bridged complex shown in eq 1. The ^1H NMR spectrum of the product revealed that



(1)

a 1:1 ratio of Cp* and methoxy groups was maintained in the product but that the methoxy groups had become inequivalent. A 2:1 ratio of Cp* to phenyl groups was observed as well as a single upfield hydride resonance (δ −18.72) that is consistent with a bridging hydride ligand.[9] The ^{29}Si NMR spectrum for this compound contains a singlet at very low field (δ 211.12), suggesting the presence of a terminal[10] or bridging[11] silylene ligand. Also, the lack of significant J_{SiH} coupling eliminated the possibility of an η^2-Si–H structure.

Table I. Selected Bond Distances (Å) and Angles (deg) for $\{[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)\}$

(a) Bond Distances			
Ru(1)–Ru(2)	2.569 (5)	Ru(4)–O(2)	2.077 (20)
Ru(3)–Ru(4)	2.569 (5)	Si(1)–C(51)	1.910 (24)
Ru(1)–Si(1)	2.309 (10)	Si(2)–C(61)	1.898 (23)
Ru(2)–Si(1)	2.288 (11)	Si(1)–O(3)	1.677 (22)
Ru(3)–Si(2)	2.316 (10)	Si(2)–O(4)	1.677 (22)
Ru(4)–Si(2)	2.309 (12)	O(3)–C(3)	1.394 (40)
Ru(1)–O(1)	2.090 (23)	O(4)–C(4)	1.428 (45)
Ru(2)–O(1)	2.095 (18)	O(1)–C(1)	1.420 (40)
Ru(3)–O(2)	2.096 (28)	O(2)–C(2)	1.482 (41)

(b) Bond Angles			
Ru(1)–O(1)–Ru(2)	75.8 (7)	O(3)–Si(1)–C(51)	97.8 (11)
Ru(3)–O(2)–Ru(4)	76.0 (8)	O(4)–Si(2)–C(61)	98.1 (12)
Ru(1)–Si(1)–Ru(2)	68.0 (3)	O(3)–Si(1)–Ru(1)	122.9 (10)
Ru(3)–Si(2)–Ru(4)	67.5 (3)	O(3)–Si(1)–Ru(2)	120.9 (8)
Ru(1)–O(1)–C(1)	118.8 (19)	O(4)–Si(2)–Ru(3)	123.5 (11)
Ru(2)–O(1)–C(1)	118.1 (21)	O(4)–Si(2)–Ru(4)	123.4 (10)
Ru(3)–O(2)–C(2)	117.1 (20)	C(51)–Si(1)–Ru(1)	124.9 (7)
Ru(4)–O(2)–C(2)	115.8 (19)	C(51)–Si(1)–Ru(2)	123.3 (9)
O(1)–Ru(1)–Si(1)	102.9 (7)	C(61)–Si(2)–Ru(3)	122.8 (7)
O(1)–Ru(2)–Si(1)	103.5 (6)	C(61)–Si(2)–Ru(4)	122.4 (10)
O(2)–Ru(3)–Si(2)	102.9 (7)	Si(1)–O(3)–C(3)	123.9 (19)
O(2)–Ru(4)–Si(2)	103.8 (8)	Si(2)–O(4)–C(4)	126.2 (24)

The molecular structure of $\{[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)\}$ (one of two independent molecules in the crystal) is shown in Figure 1, and relevant geometrical parameters are listed in Table I. The short Ru–Ru distance of 2.569 (5) Å is consistent with the presence of a Ru═Ru double bond. For comparison, the Ru–Ru single bond distance in the silylene-bridged complex $[(CO)_3(Me_3Si)Ru(\mu\text{-}SiMe_2)]_2$ is 2.958 (3) Å.[12] Also the recently reported complexes $\{[Cp^*Ru(\mu\text{-}\eta^2\text{-}H\text{-}SiEt_2)]_2(\mu\text{-}H)(H)\}$ and $[Cp^*Ru(\mu\text{-}H)(\mu\text{-}SiPh_2)]_2$, obtained via addition of secondary silanes to $[Cp^*Ru(\mu\text{-}H)_2]_2$, have single (2.971-Å) and double (2.665-Å) Ru–Ru bond distances, respectively.[4c] The Ru–Si bonds in $\{[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)\}$ are also very short (av 2.31 Å), given the observed range for Ru–Si single bonds in other complexes (2.3–2.5 Å).[1] The bridging hydride ligand was not located in electron density maps. Finally, the Ru–O distances (av 2.09 Å) are similar to values seen for other alkoxy-bridged diruthenium complexes, e.g. $[Cp^*Ru(\mu\text{-}OMe)]_2$ and $[Cp^*(CO)Ru(\mu\text{-}OEt)]_2$.[8b]

The complex $\{[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)\}$ slowly and cleanly isomerizes in benzene-d_6 (60% conversion after 24 h at room temperature) to a new product that displays NMR spectra very similar to those for the starting compound. The ^{29}Si NMR chemical shift for this new product is at δ 193.50. We propose that this isomerization results from rearrangement of the bridging ligands such that the two methoxy groups point in the same direction (eq 2). Related isomerizations involving bridge-to-terminal silylene transformations have been characterized for $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiX^tBu)$ (X = Cl, Br, I, Me) complexes.[13]

Perhaps the most interesting feature of the reaction described above is the phenyl/methoxy substitution that occurs at silicon. Mechanistic details for this rather com-

---

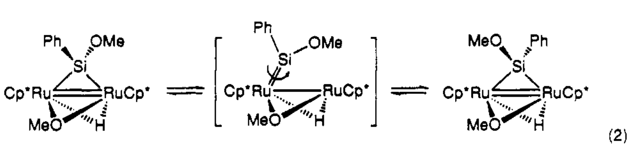
[9] Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

[10] Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801.

[11] Ueno, K.; Hamashima, N.; Shimoi, M.; Ogino, H. *Organometallics* **1991**, *10*, 959.

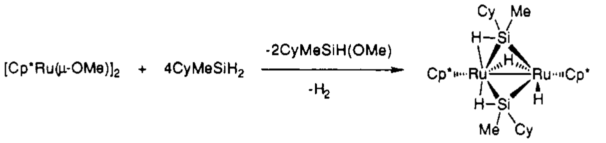
[12] Crozat, M. M.; Watkins, S. F. *J. Chem. Soc., Dalton Trans.* **1972**, 2512.

[13] Tobita, H.; Kawano, Y.; Ogino, H. *Chem. Lett.* **1989**, 2155.



plex transformation are lacking at this time, but it is conceivable that the Si–O bond is formed via oxidative addition of an H–SiHPh$_2$ bond, followed by Si–O reductive elimination to produce Ph$_2$SiHOMe as an intermediate.[14] Cleavage of an SiPh bond has fewer precedents in stoichiometric processes[15] but is observed in transition-metal-catalyzed reactions that redistribute groups on silicon.[16] The key Si–C bond cleavage step could occur via oxidative addition of the Si–C bond or by α-migration of the Ph group from silicon to ruthenium.

Addition of CyMeSiH$_2$ (Cy = cyclohexyl) to [Cp*Ru(μ-OMe)]$_2$ results in formation of a new complex, isolated as orange crystals from pentane, that does not possess methoxy groups. The elemental analysis and NMR spectra are consistent with a stoichiometry of Cp*Ru(SiMeCy)$_2$H$_2$, and the mass spectrum contains a parent ion peak ([M]$^+$ = 730) which indicates that the compound is dimeric. A ν_{RuH} stretching frequency at 2050 cm^{-1} in the infrared spectrum can be assigned to a terminal Ru–H bond. The ^{29}Si{^{1}H} NMR DEPT spectrum contains a single peak at δ 115.17, which is at relatively low field but considerably upfield of the resonance for silylene-bridged {[(η^5-C$_5$Me$_5$)Ru]$_2$(μ-SiPhOMe)(μ-OMe)(μ-H)}. A highly symmetric structure is suggested by the room temperature ^{1}H NMR spectrum, which displays single sets of resonances for the Cp*, SiMeCy, and hydride ligands. However, the very broad single peak at δ −14.1 for the hydride ligands can be attributed to stereochemical nonrigidity at room temperature. Cooling a toluene-d_8 solution of the complex resulted in decoalescence of the hydride resonances at ca. −15 °C, and the ^{1}H NMR spectrum at −70 °C contains two resonances for the Cp* ligands, and three singlets in the hydride region (δ −12.94, −13.81, and −15.81) in a 1:2:1 ratio. The above data are all consistent with the structure shown in eq 3. Also, the NMR spectra for this compound are remarkably similar to the analogous complex {[Cp*Ru(μ-η^2-H-SiEt$_2$)]$_2$(μ-H)(H)}, which was recently characterized by X-ray diffraction.[4c]



The above reactions show that the electron-deficient ruthenium methoxide [Cp*Ru(μ-OMe)]$_2$ can serve as a useful starting material for the synthesis of dinuclear ruthenium–silicon compounds. Furthermore, the facile transfer of an alkoxy group from ruthenium to silicon is demonstrated. Related alkoxy-transfer reactions with mononuclear complexes have been reported. For example, silanes HSiR$_3$ react with *trans*-(PR'$_3$)$_2$(CO)IrOR'' (R' = Me, Ph) to give R$_3$SiOR'' and (PR'$_3$)$_2$(CO)IrH$_2$(SiR$_3$).[17]

Acknowledgment is made to the National Science Foundation for support of this work. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–92), Union Carbide for an Innovation Recognition Program Award (1991–2), and the Mobil Foundation for a financial contribution. We also thank Nora Radu and John Walzer for recording NMR spectra.

Supplementary Material Available: For {[(η^5-C$_5$Me$_5$)Ru]$_2$(μ-SiPhOMe)(μ-OMe)(μ-H)}, tables of crystal data, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates (11 pages). Ordering information is given on any current masthead page.

OM9203183

---

[14] We have recently reported a related sequence that produces a Si–Cl bond: Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* 1992, 1201.

[15] Fernandez, M.-J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* 1984, 2063.

[16] Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* 1981, *19*, 213.

[17] (a) Rappoli, B. J.; Janik, T. S.; Churchill, M. R.; Thompson, J. S.; Atwood, J. D. *Organometallics* 1988, *7*, 1939. (b) Fernandez, M. J.; Esteruelas, M. A.; Oro, L. A.; Apreda, M.-C.; Foces-Foces, C.; Cano, F. H. *Organometallics* 1987, *6*, 1751.

[(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B]$^-$[H(OEt$_2$)$_2$]$^+$: A Convenient Reagent for Generation and Stabilization of Cationic, Highly Electrophilic Organometallic Complexes

M. Brookhart,* B. Grant, and A. F. Volpe, Jr.

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27599

Received June 30, 1992

Summary: A convenient synthesis of the easily handled, crystalline oxonium acid [(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B]$^-$[H(OEt$_2$)$_2$]$^+$ (**1**) is described. The utility of this reagent for generation and stabilization of highly electrophilic cationic transition-metal complexes through protonation reactions is illustrated by the preparation of stable, ether-free salts of [C$_5$Me$_5$(P(OMe)$_3$)CoCH$_2$CH$_2$(μ-H)]$^+$[(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B]$^-$ from C$_5$Me$_5$(P(OMe)$_3$)Co(C$_2$H$_4$). The incorporation of the noncoordinating counterion [(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B]$^-$ in organometallic salts has several advantages relative to [BF$_4$]$^-$ and [PF$_6$]$^-$, including high stability and solubility in relatively nonpolar organic solvents.

I. Introduction

The lack of reactivity and non-nucleophilic character of [BF$_4$]$^-$ and [PF$_6$]$^-$ have led to their widespread use as noncoordinating (or weakly coordinating)[1,2] counterions supporting cationic organometallic complexes. With the

---

[1] For examples of coordinated [BF$_4$]$^-$ and [PF$_6$]$^-$ see: (a) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* 1989, *28*, 2869. (b) Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* 1989, *111*, 6056. (c) Beck, W.; Sunkel, K. *Chem. Rev.* 1988, *88*, 1405.

[2] For descriptions of other noncoordinating counterions see: (a) Shelley, K.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R. *J. Am. Chem. Soc.* 1986, *108*, 3117. (b) Noirot, M. D.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* 1987, *26*, 2216 and references therein.

0276-7333/92/2311-3920$03.00/0