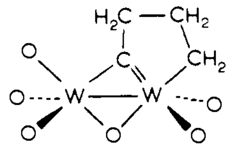

and 165 Hz, implying a gross asymmetry in the alkylidyne bridge, which may formally be assigned to W–C single and double bonds, respectively, as shown in I above. It should be noted that we can find no evidence for the presence of W–H moieties from either ^{1}H NMR spectra or ^{13}C proton-coupled spectra. Thus we believe that the new compound is formed with the liberation of dihydrogen according to eq 1.[10]

$$W_2(O\text{-}i\text{-}Pr)_6 + 2C_2H_4 \rightarrow W_2(\mu\text{-}CCH_2CH_2CH_2)(O\text{-}i\text{-}Pr)_6 + H_2 \quad (1)$$

The new compound has a structural analogy with the previously fully characterized compound $W_2(\mu\text{-}NC(Ph)CHCH)(O\text{-}i\text{-}Pr)_6$ formed by the coupling of C≡C and C≡N ligands at the dinulcear center.[11] A plausible reaction pathway leading to the $W_2(\mu\text{-}CCH_2CH_2CH_2)$ moiety involves (i) C–H activation to generate a hydrido σ,π-vinyl, (ii) conversion to a μ-vinylidene ligand with elimination of H_2 and (iii) coupling of the $\mu\text{-}C{=}CH_2$ ligand with ethylene.

To our knowledge the $W_2(\mu\text{-}CCH_2CH_2CH_2)$ dimetallacycle has not been seen before in organometallic chemistry though there is clearly some analogy with proposed mechanisms for hydrocarbon chain grown on metal surfaces.

Further studies are in progress.[12]

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(10) In the presence of excess ethylene, ethane is formed as evidenced by ^{13}C and ^{1}H NMR spectroscopy employing sealed NMR tubes.

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Preparation, Characterization, and X-ray Crystal Structure of an Acetonitrile-Complexed Ruthenium Silylene

Daniel A. Straus and T. Don Tilley*

Chemistry Department, D-006
University of California at San Diego
La Jolla, California 92093

Arnold L. Rheingold* and Steven J. Geib

Department of Chemistry, University of Delaware
Newark, Delaware 19716

Received April 2, 1987

Silylene complexes ($L_nM{=}SiR_2$) are postulated intermediates in a number of transition-metal-mediated transformations, including Rochow's direct process,[1] catalytic redistribution of silanes,[2] and various silylene-transfer reactions.[3] Unfortunately, such species have been synthetically elusive, despite the well-established existence of congeneric carbene,[4] germylene,[5,6] stannylene,[5,7] and plumbylene[5,6b,c,8] complexes. Although numerous examples of silylene-bridged bimetallic species exist,[9] there are no well-characterized examples of compounds possessing a formal metal–silicon double bond, despite numerous attempts to prepare them.[10] To investigate the chemistry of transition-metal–silicon double bonds, we are attempting to develop synthetic routes to such terminal silylene complexes. Here we report the first synthesis and complete structural characterization of a base-stabilized transition-metal silylene complex.

The synthetic approach described here involves removal of a group bound to silicon with an electrophilic reagent, E^+ (eq 1, $Cp^* = \eta^5\text{-}C_5Me_5$, $L = PMe_3$). This technique has been quite

$$Cp^*L_2Ru{-}SiXR_2 + E^+Y^- \rightarrow [Cp^*L_2Ru{=}SiR_2]^+Y^- + E^+X^- \quad (1)$$

useful in syntheses of carbene complexes[4,11] but has thus far failed to afford the analogous silylenes. In particular, where fluorinated anions (BF_4^-, PF_6^-) have been employed, fluorination of the silyl ligand results.[9b,10a,g] For this reason our efforts have focused on the less-coordinating tetraphenylborate anion. Our choice of an electron-rich metal center should further stabilize an electron-deficient silicon center.

The starting ruthenium silyl complex **2** is prepared by reaction of excess $HSiPh_2Cl$ with the alkyl $Cp^*L_2RuCH_2SiMe_3$[12] (**1**) in toluene at 100 °C (eq 2). This reaction produces mostly the pale

$$\underset{\mathbf{1}}{Cp^*L_2RuCH_2SiMe_3} + (x + 2y)HSiPh_2Cl \xrightarrow[-yPMe_3]{-SiMe_4} x\underset{\mathbf{2}}{Cp^*L_2RuSiPh_2Cl} + y\underset{\mathbf{3}}{Cp^*LRu(SiPh_2Cl)_2H} \quad (2)$$

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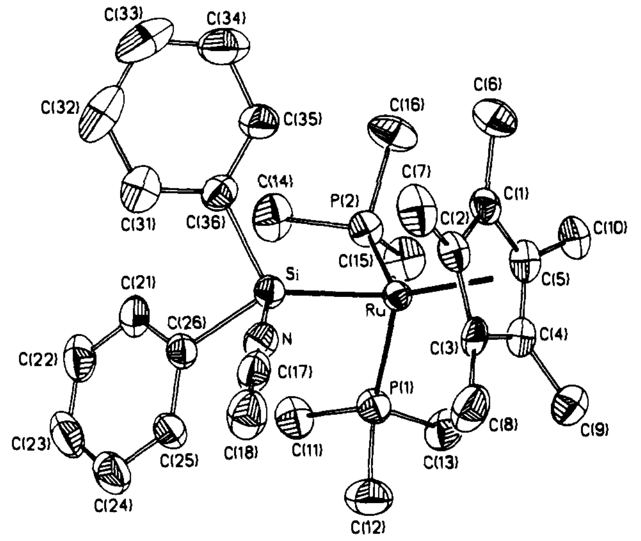
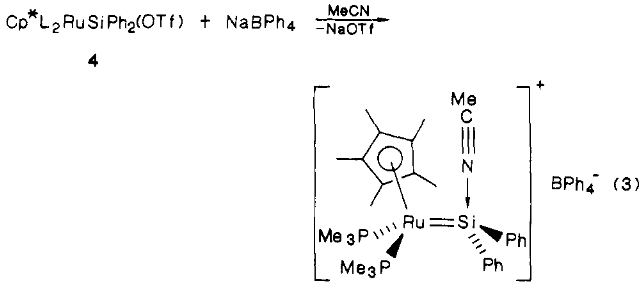


Figure 1. ORTEP view of the cation in $5 \cdot CH_2Cl_2$.

yellow, crystalline Ru(IV) bis silyl **3**, isolated as the cis isomer. Complexes **2** and **3** have been characterized by elemental analyses, IR, and NMR (^1H and ^{13}C).[13] The formation of compounds **2** and **3** undoubtedly involves dissociation of PMe_3 from **1** followed by oxidative addition of silane to ruthenium and elimination of $SiMe_4$. The alkyl **1** activates arenes by a similar mechanism.[14] Compound **3** is driven cleanly to the desired Ru(II) product **2**, a yellow crystalline solid, by reaction with excess (4 equiv) PMe_3 in a sealed tube at 105 °C for 42 h. Reaction of **2** with Me_3SiOTf ($OTf = OSO_2CF_3$) in dichloromethane affords the triflate derivative $Cp^*L_2RuSiPh_2(OTf)$ (**4**) in 89% isolated yield. This yellow, crystalline, benzene-soluble compound appears to possess a covalent Si–O bond, as judged by its solubility in nonpolar aromatic solvents and from infrared data.[13]

In an attempt to exchange the triflate group of **4** for the less-coordinating tetraphenylborate, compound **4** and $NaBPh_4$ were stirred in acetonitrile. Solvent removal and addition of dichloromethane gave separation of a quantitative yield of NaOTf, identified by infrared spectroscopy, and a yellow solution. Concentration and cooling of the dichloromethane solution allowed isolation of the acetonitrile-complexed diphenylsilylene salt **5** as the other reaction product (eq 3). Complex **5**, which crystallizes as a dichloromethane solvate, has been characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography (vide infra).[13] The ν(CN) stretching frequency for **5**, 2395 cm^{-1}, is 135 cm^{-1} greater than that of free acetonitrile, indicating considerable donation of electron density from acetonitrile to the silylene silicon (cf. F_3BNCCH_3 for which $\nu(CN) = 2359$ cm^{-1}).[15]



4

5

(3)

An ORTEP view of the cation in $5 \cdot CH_2Cl_2$ is given in Figure 1.[16] Several features of the structure support the presence of some multiple bonding between Ru and Si. The Ru–Si bond length of 2.328 (2) Å is the shortest Ru–Si distance yet observed and is 0.06 Å shorter than the Ru–Si distance of $Cp^*L_2RuSiPh_2H$ (**6**),[17] 2.387 (1) Å. Other reported Ru–Si distances range between 2.34 and 2.51 Å, with a mean value of 2.44 Å. The Si–N distance of 1.932 (8) Å, which is significantly longer than typical Si–N single bonds to tetrahedral silicon,[18] and distances and angles within the coordinated acetonitrile are consistent with a dative interaction between nitrogen and silicon.[15]

The Si–C distances, 1.916 (8) and 1.930 (6) Å, are somewhat long but within the range of other Si–C(aryl) bonds.[19] This may reflect greater s-character in the bond to electron-rich ruthenium and consequently more p-character in the bonds to other substituents about silicon. This would be consistent with the C(26)–Si–C(36) angle of 102.2 (3)°, which is surprisingly small. These two observations compare with parameters obtained for $(CO)_5Cr{=}Sn\text{-}t\text{-}Bu_2(pyr)$,[7g] which has unusually long Sn–C bonds and a C–Sn–C angle of 109.5 (7)°. Also, rather acute X–Ge–X angles have been found in $(CO)_5Cr{=}Ge(SMes)_2$ (102.4 (2)°)[6a] and in $(CO)_5Cr{=}Ge[CH(SiMe_3)_2]_2$ (102.8 (2)°).[6b] As might be expected for silylene character, the Ru–Si–C angles, 121.2 (2) and 128.2 (2)°, are much larger than the Ru–Si–N angle of 110.9 (2)°, and the C–Si–N angles, 91.3 (3) and 93.8 (3)°, are close to 90°. However, these distortions from tetrahedral coordination about silicon may also be attributed to steric factors. The silicon atom in $5 \cdot CH_2Cl_2$ lies 0.34 Å above the plane defined by Ru, C(26) and C(36). The corresponding value for **6** is 0.51 Å.

Investigation of the reactivity of the cationic, acetonitrile-complexed silylene **5** toward small molecules is in progress. Acetonitrile is displaced from **5** by $LiAlH_4$ in tetrahydrofuran to afford $Cp^*L_2RuSiPh_2H$ (**6**) in 37% yield by ^1H NMR. Diphenylsilyl complex **6** was independently prepared as a pale yellow crystalline solid by reduction of **2** with $LiAlH_4$ in tetrahydrofuran.[13] Proton NMR experiments show that the coordinated acetonitrile in **5** exchanges with free acetonitrile on the NMR time scale in dichloromethane-d_2 solution, suggesting that **5** may be a convenient source of the uncomplexed diphenylsilylene $[Cp^*L_2Ru{=}SiPh_2]^+BPh_4^-$.

Acknowledgment is made to the U.C.S.D. Academic Senate, to the National Science Foundation, and to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, for support of this work under Grant No. AFOSR-85-0228. The U.S. Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation thereon.

Supplementary Material Available: Spectroscopic data for **2–6**, crystal data for **5**, and crystallographic data; tables of bond lengths, bond angles, anisotropic thermal parameters, hydrogen atom coordinates, and positional and thermal parameters for $5 \cdot CH_2Cl_2$ (11 pages); tables of observed and calculated structure factors for $5 \cdot CH_2Cl_2$ (26 pages). Ordering information is given on any current masthead page.

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(13) Data for characterization of **2–6** are included in the Supplementary Material. Selected NMR data for **2**: ^1H NMR (CD_2Cl_2) δ 1.41 (pseudo triplet, 18 H, PMe_3), 1.65 (s, 15 H, C_5Me_5). For **3**: ^1H NMR (CD_2Cl_2) δ −11.60 (d, $J = 3$ Hz, Ru*H*), 1.53 (s, 15 H, C_5Me_5). For **4**: ^1H NMR (CD_2Cl_2) δ 1.42 (pseudo triplet, 18 H, PMe_3), 1.61 (s, 15 H, C_5Me_5). For **5**: ^1H NMR (CD_2Cl_2) δ 1.39 (m, 21 H, $PMe_3 + CH_3CN$), 1.68 (t, $J = 3$ Hz, 15 H, C_5Me_5).

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