Ruthenium Silyl Complexes from the Reaction of Chlorosilanes with an Amphoteric Ruthenium Hydride. Evidence for an Agostic Ru−H−Si Intermediate

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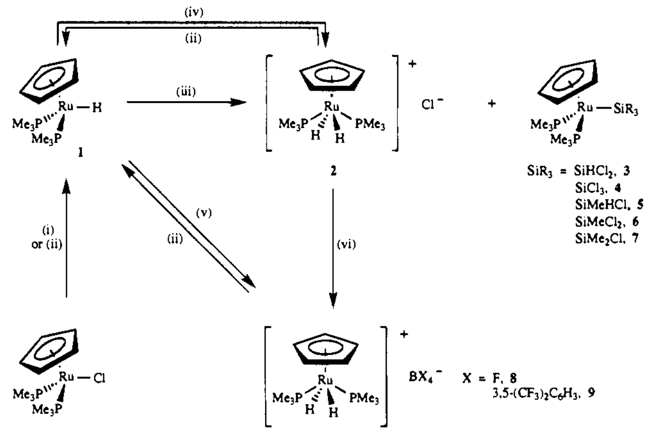
Functionalized transition metal silyl complexes, $L_nMSiR_{3-n}X_n$ (n = 1−3; X = H, halogen), and their chemistry have been an area of active investigation.[1,2] Nucleophilic and radical exchange reactions can generate new metal silyl complexes, whereas hydride or halide abstraction reactions can generate cationic metal silylene or silylyne complexes. Common synthetic routes to metal silyl complexes involve "alkali halide elimination" (*i.e.*, a metal anion reacting with a halosilane or a metal halide reacting with a silyl anion) and the oxidative addition of a Si−X bond (generally Si−H) to a low-valent metal center. The formation of metal silyl complexes with HCl elimination, by the reaction of a metal chloride with a hydrosilane or the reaction of a metal hydride with a chlorosilane, has been used only to a limited extent.[3−5] Reported herein is an example of a metal hydride, $Cp(Me_3P)_2RuH$ (**1**), reacting with chlorosilanes to form metal silyl complexes $Cp(Me_3P)_2RuSiR_3$ (SiR_3 = $SiHCl_2$ (**3**), $SiCl_3$ (**4**), SiMeHCl (**5**), $SiMeCl_2$ (**6**), and $SiMe_2Cl$ (**7**)) by HCl elimination. A nucleophilic exchange mechanism for this reaction involving a unique cationic ruthenium silyl hydride, containing a Ru−H−Si interaction, is proposed to account for these results.

The electron-rich ruthenium hydride **1**[6] reacts with a variety of electron-deficient chlorosilanes in methylene chloride at room temperature to yield the ruthenium dihydride $[Cp(Me_3P)_2Ru(H)_2]Cl$ (**2**) and the corresponding ruthenium silyl complexes **3**−**7**[7] as described in Scheme 1. Dihydride **2** was isolated as a white air-sensitive solid in >90% yields, while silyl complexes **3**−**7** were isolated as yellow air- and water-sensitive solids in 60−85% yields. Protonation of **1** with HX (X = Cl, BF_4, and $B(3,5-(CF_3)_2C_6H_3)_4$[8]) in Et_2O yields dihydrides **2**, **8**, and **9**, respectively, in nearly quantitative yields (Scheme 1).[9] When the formation of **3**−**7** was monitored by ^1H NMR spectroscopy, **1** was observed to react with each chlorosilane in a 2:1 molar ratio, with the quantitative formation of dihydride **2** and the corresponding silyl complex; no other ruthenium- or silicon-containing products were observed.[10] The spectroscopic properties of silyl complexes **3**−**7** exhibit several interesting trends. A general decrease in $^2J_{SiP}$ is observed as electronegative Cl substituents on silicon are replaced by less electronegative H and Me (**4**, $^2J_{SiP}$ = 43.6 Hz; **3**, $^2J_{SiP}$ = 36.2 Hz; **6**, $^2J_{SiP}$ = 35.4 Hz; **5**, $^2J_{SiP}$ = 30.5 Hz; **7**, $^2J_{SiP}$ = 30.2 Hz), consistent with Bent's rule.[11] In the hydrosilyl complexes, a decrease in $^1J_{SiH}$ [**3** (199.6 Hz) > **5** (163.6 Hz)] as well as a decrease in ν(Si−H) [**3** (2073 cm^{-1}) > **5** (2026 cm^{-1})] is observed when a Cl is replaced by a Me.[12]

Scheme 1. Formation of Ruthenium Hydride, Dihydride, and Silyl Complexes[a]



[a] Reaction conditions: (i) excess $LiAlH_4$ in Et_2O; (ii) excess KOMe in refluxing MeOH; (iii) 0.5 equiv of R_3SiCl in CH_2Cl_2; (iv) HCl in Et_2O; (v) $[H(OEt_2)_n][BX_4]$ (n = 1, 2) in CH_2Cl_2 or Et_2O; (vi) excess $NaBF_4$ in MeOH.

Table 1. Relative Reactivity of Chlorosilanes with $Cp(Me_3P)_2RuH$ (**1**)

chlorosilane	relative reactivity with **1**[a]	$\Delta\theta$,[b] deg	$\sum\chi_i$[c]
$HSiCl_3$	3.0	−27	52.7
$SiCl_4$	1.0	0	59.2
$MeHSiCl_2$	1.4×10^{-3}	−39	40.5
$MeSiCl_3$	1.2×10^{-5}	−12	47.0
Me_2SiCl_2	1.2×10^{-6}	−24	34.8

[a] Chlorosilane reactivities were normalized to the reactivity of $SiCl_4$.[7] [b] Steric difference around silicon relative to $SiCl_4$. $\Delta\theta = \sum\theta(SiRR'Cl_2) - \sum\theta(SiCl_4)$, based on Tolman's cone angles for H, Cl, and Me (θ = 75°, 102°, and 90°, respectively).[20] [c] Summation of Tolman's χ_i electronic parameters for the four substituents on silicon: H, Cl, and Me (χ_i = 8.3, 14.8, and 2.6, respectively).[20]

Hydride **1** appears to exhibit amphoteric qualities in its reactions with chlorosilanes, acting formally as an acid by losing H^+ upon forming silyl complexes **3**−**7** and as a base by accepting H^+ to form dihydride **2**. The reactivity of **1** with the chlorosilanes was examined by competition experiments, the results of which are listed in Table 1. The relative reactivities of the various chlorosilanes with **1** cover *6 orders of magnitude*, with $HSiCl_3$ being the most reactive and Me_2SiCl_2 the least reactive. The electronic nature of the chlorosilane, not sterics, appears to be the controlling factor in this reaction. The electron-deficient $HSiCl_3$ and $SiCl_4$ are very reactive; they will even react (complete in <5 min) with **1** in Et_2O at −78 °C. Replacing a Cl with a Me group decreases the electron deficiency and the reactivity of the chlorosilane such that, in an NMR experiment, the reaction of Me_2SiCl_2 (35 mM) with **1** (70 mM) in CD_2Cl_2 was ~50% complete in 3 h. A secondary effect is also observed upon replacing a Cl with a H, resulting in an increased reactivity with **1** (*i.e.* $HSiCl_3$ > $SiCl_4$ and $MeHSiCl_2$ > $MeSiCl_3$). Furthermore, there appears to be a

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[1] Tilley, T. D. In *The Silicon−Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1991; pp 245−307.

[2] Tilley, T. D. In *The Silicon−Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley & Sons: New York, 1991; pp 309−364.

[3] Chatt, J.; Eaborn, C.; Ibekwe, S. D.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 1343−1351.

[4] Isaacs, E. E.; Graham, W. A. G. *Can. J. Chem.* **1975**, *53*, 975−978.

[5] Grobe, J.; Walter, A. *J. Organomet. Chem.* **1977**, *140*, 325−348.

[6] Mayer, J. M.; Calabrese, J. C. *Organometallics* **1984**, *3*, 1292−1298.

[7] Experimental details as well as spectroscopic and analytical data for **1**−**10** are provided in the supplementary material.

[8] Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920−3922.

[9] The spectroscopic properties of the dihydride fragment $[Cp(Me_3P)_2RuH_2]^+$ are consistent with a classical configuration. ^1H NMR (CD_2Cl_2): δ −9.9 (t, $^2J_{PH}$ = 29 Hz, 2H, RuH) for **2**, **8**, and **9**. Also, T_1 measurements (400 MHz in CD_2Cl_2) for **8** gave a value of 9.4 s at 293 K, which decreases to 2.0 s at 208 K for the dihydride resonance.

[10] Halosilanes which did not react with hydride **1** included Me_3SiCl, Me_2SiHCl, $(Me_3Si)_3SiBr$, Ph_3SiCl, Bu^tSiCl_3, $Bu^t_2SiCl_2$, $(C_5Me_5)SiCl_3$, and $(C_5Me_5)SiMeCl_2$. Slow reactions (several days) were observed between **1** and Ph_2SiCl_2 or $(C_5Me_5)SiHCl_2$ in the NMR tube, but these reactions were complicated by the reaction of **1** with CD_2Cl_2, which produces $Cp(Me_3P)_2RuCl$ and CD_2HCl.

[11] Bent, H. A. *Chem. Rev.* **1961**, *61*, 276−311.

[12] Similar spectroscopic trends and correlations to Bent's rule have been observed by Malisch and co-workers for silyl complexes of chromium, molybdenum, tungsten, manganese, and iron.[21−23]

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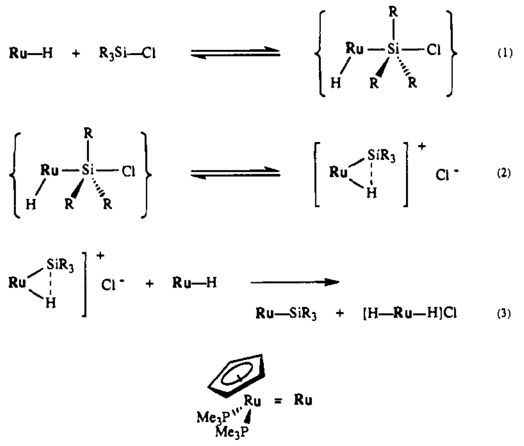
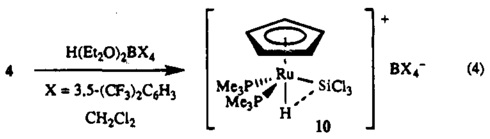
Scheme 2. Proposed Nucleophilic Exchange Reaction Mechanism



lower limit of $\Sigma\chi_i \sim 30$ (Table 1) for chlorosilanes containing Cl, H, or Me substituents, since Me_2HSiCl ($\Sigma\chi_i = 28.3$) and Me_3SiCl ($\Sigma\chi_i = 22.6$) do not react with **1**.

A mechanism for the reaction of **1** with chlorosilanes based on a nucleophilic exchange reaction is proposed in Scheme 2. A chlorosilane undergoes a nucleophilic attack by **1** to give a pentacoordinate silicon[13-16] intermediate (eq 1) which, upon loss of chloride, produces a cationic ruthenium silyl hydride (eq 2). Deprotonation of the cationic ruthenium silyl hydride with **1** yields the dihydride **2** and a ruthenium silyl complex (eq 3). The first example of a cationic metal silyl hydride $[Cp(Me_3P)_2RuH(SiCl_3)][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (**10**) was independently prepared by protonation of **4** with $[H(Et_2O)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ in CH_2Cl_2 (eq 4). Complex **10** was isolated as a tan air- and water-sensitive solid in 88% yield.[7] The hydride proton of **10** appears as a triplet at δ −9.87 ($^2J_{PH} = 11$ Hz) in the ^1H NMR spectrum with ^{29}Si satellites ($^2J_{SiH} = 48$ Hz). In the DEPT ^{29}Si NMR spectrum, only a doublet is observed at δ 30.60, with $^2J_{SiH} = 49$ Hz and no observable $^2J_{SiP}$. The small $^2J_{PH}$ value, compared to those of **2**, **8**, and **9** ($^2J_{PH} = 29$ Hz), suggests a weakened Ru−H interaction. Furthermore, the large $^2J_{SiH}$ value is consistent with an agostic interaction between the RuH and the Si center and is within the $^2J_{SiH}$ range ($^2J_{SiH} = 38-69$ Hz) observed for neutral manganese silyl hydrides containing agostic Mn−H−Si interactions.[17-19] Complex **10** is readily deprotonated by **1** to regenerate silyl **4** and yield dihydride **9**, analogous to the proposed final step in Scheme 2 (eq 3). Attempts to protonate silyl complexes **3**−**7** with HX, where X^- is a nucleophile like Cl^- or F^- (from BF_4^-), generally result in Ru−Si bond cleavage to form dihydride **2** or **8** and the corresponding silane R_3SiX. This Ru−Si bond cleavage represents the reverse of eqs 1 and 2 in Scheme 2.



Electron-rich hydride **1** readily reacts with electron-deficient chlorosilanes to form ruthenium silyl complexes and a classical cationic ruthenium dihydride. The mechanism of this reaction is consistent with a nucleophilic exchange reaction involving a cationic ruthenium silyl hydride intermediate containing an agostic Ru−H−Si interaction. Further investigations into the structure and reactivity of the unique cationic ruthenium silyl hydride are currently underway.

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Supplementary Material Available: Details of experimental procedures and the spectroscopic and analytical data for complexes **1**−**10** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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