J. Am. Chem. Soc. 1994, *116*, 6951–6952

6951

Transition-Metal-Mediated Redistribution at Silicon: A Bimolecular Mechanism Involving Silylene Complexes

Steven K. Grumbine[†] and T. Don Tilley[*,‡]

Department of Chemistry
University of California, San Diego
San Diego, California 92093

The recent discovery of base-free transition-metal silylene complexes[1,2] has created the first opportunities to directly examine these elusive species.[3] In particular, a number of mechanistic proposals which feature $L_nM{=}SiR_2$ species as key intermediates[3] can now be tested with reactivity studies. For example, silylene complexes have often been invoked to account for the ability of transition-metal complexes to catalyze redistribution at silicon.[4] For this reaction, mechanistic speculation has centered on intermediate silyl(silylene) complexes of the type $L_nM{=}SiR_2$-(SiR'_3), in which groups at silicon are thought to exchange via 1,2-shifts between the metal and silicon or via 1,3-shifts between silicon centers. Pannell,[5] Ogino,[6] and Turner[7] have reported convincing mechanistic studies which implicate direct 1,3-shifts of R groups between silicon centers in proposed Cp(CO)-Fe=SiR₂(SiR'₃) intermediates generated by the photolysis of Cp(CO)₂FeSiR₂SiR'₃ compounds. Here we report evidence for a new mechanism for metal-mediated redistribution at silicon, involving *intermolecular* exchange of groups between silicon atoms.

During attempts to synthesize silylene complexes of ruthenium, we have encountered various reactions involving the scrambling of substituents at silicon. For example, following our previously devised strategy for the synthesis of cationic ruthenium silylene complexes,[1,8] we treated Cp*(PMe₃)₂RuSi[S(Tol-*p*)](TIPT)₂ (Cp* = η⁵-C₅Me₅, TIPT = -S-2,3,5-ⁱPr₃C₆H₂) with Me₃SiOTf (OTf = OSO₂CF₃) in pentane. As expected, this reaction produced Me₃Si(TIPT) and isolable Cp*(PMe₃)₂RuSi[S(Tol-*p*)](TIPT)(OTf) (24% yield); however, the latter product was

† Current address: Los Alamos National Laboratory, CST-3, Mail Stop C346, Los Alamos, NM 87545.

‡ Permanent address: Department of Chemistry, University of California, Berkeley, CA 94720-1460.

(1) (a) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801. (b) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 358. (c) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 7884. (d) Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 5495–5496.

(2) Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33.

(3) (a) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapter 9 and 10, pp 245 and 309. (b) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415. (c) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37. (d) Zybill, C. *Top. Curr. Chem.* **1991**, *160*, 1. (e) Lickiss, P. D. *Chem. Soc. Rev.* **1992**, 271. (f) Corey, J. In *Advances in Silicon Chemistry*; Larson, G., Ed.; JAI Press, Inc.: Greenwich, CT, 1991; Vol. 1, p 327.

(4) (a) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213. (b) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411. (c) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056. (b) Pannell, K. H.; Rozell, J. M., Jr.; Hernandez, C. *J. Am. Chem. Soc.* **1989**, *111*, 4482. (c) Pannell, K. H.; Wang, L.-J.; Rozell, J. M. *Organometallics* **1989**, *8*, 550. (d) Jones, K. L.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336. (e) Hernandez, C.; Sharma, H. K.; Pannell, K. H. *J. Organomet. Chem.* **1993**, *462*, 259. (f) Pannell, K. H.; Brun, M.-C.; Sharma, H.; Jones, K.; Sharma, S. *Organometallics* **1994**, *13*, 1075.

(6) (a) Tobita, H.; Ueno, K.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2797. (b) Ueno, K.; Tobita, H.; Ogino, H. *Chem. Lett.* **1990**, 369.

(7) Haynes, A.; George, M. W.; Haward, M. T.; Poliakoff, M.; Turner, J. J.; Boag, N. M.; Green, M. *J. Am. Chem. Soc.* **1991**, *113*, 2011.

(8) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673.
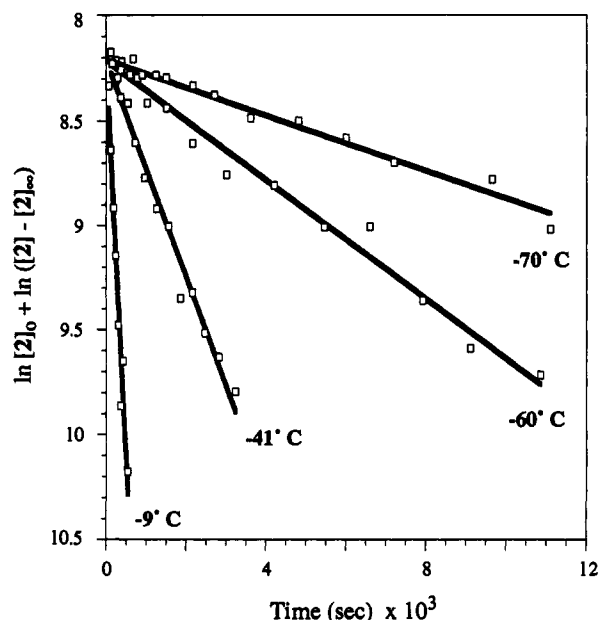
Figure 1. Pseudo-first–second-order plot for the reversible reaction shown in eq 1 with complex 1 in excess (12 equiv, $[\mathbf{1}]_0 = 0.213$ M). Observed forward rate constants:[12] $k(-9\ °C) = 3.2(3) \times 10^{-3}$ s⁻¹; $k(-41\ °C) = 4.4(2) \times 10^{-4}$ s⁻¹; $k(-60\ °C) = 1.21(4) \times 10^{-4}$ s⁻¹; $k(-70\ °C) = 5.1(3) \times 10^{-5}$ s⁻¹.

observed to decompose in benzene-d_6 ($t_{1/2} \approx 1$ day) to two products (1:1 ratio) which could be characterized by NMR spectroscopy as Cp*(PMe₃)₂RuSi[S(Tol-*p*)]₂(TIPT) and Cp*(PMe₃)₂RuSi(TIPT)(OTf)₂.[9] Since silylene complexes have often been invoked to explain redistribution at silicon,[3–7] and since [Cp*(PMe₃)₂-Ru=SiRR′]⁺ silylene derivatives are now accessible as stable entities,[1] we sought to establish possible connections between the observed redistribution chemistry and well-defined silylene complexes.
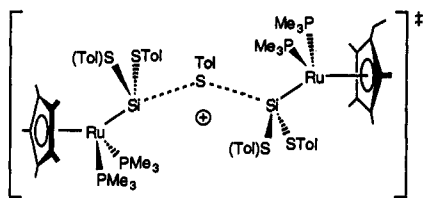
Reaction of the silylene complex [Cp*(PMe₃)₂Ru=Si(SEt)₂]-BPh₄[1a] with Cp*(PMe₃)₂RuSi[S(Tol-*p*)]₃ (**1**)[1a] at −20 °C (1:1, dichloromethane-d_2, 2 h) produces an equilibrium mixture (in ≤10 min) of the redistribution products Cp*(PMe₃)₂Ru=Si-[S(Tol-*p*)]₂⁺ (**3**, 22%),[1a] Cp*(PMe₃)₂Ru—Si(SEt)₂[S(Tol-*p*)] (26%),[10] Cp*(PMe₃)₂Ru=Si(SEt)[S(Tol-*p*)]⁺ (10%),[10] Cp*-(PMe₃)₂Ru—Si(SEt)[S(Tol-*p*)]₂ (9%),[10] Cp*(PMe₃)₂Ru=Si-(SEt)₂⁺ (16%),[1a] and Cp*(PMe₃)₂Ru—Si[S(Tol-*p*)]₃ (17%),[1a] characterized by ¹H and ³¹P NMR spectroscopy. A simpler equilibrium is established in the nearly thermoneutral redistribution of eq 1, in which S(Tol-*p*) groups exchange between the silicon centers of silyl and silylene complexes.[10] The equilibrium


$$(1)$$
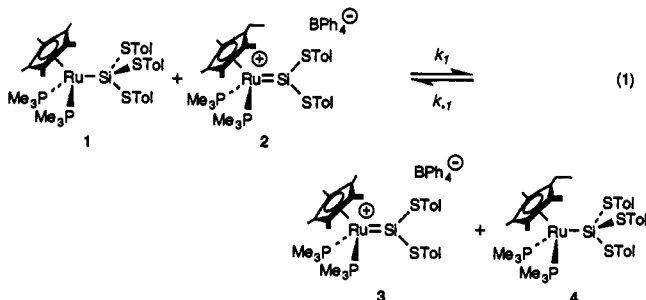
constant in dichloromethane-d_2 was found to be 0.7(2) at both 23 °C and −43 °C (by ³¹P NMR spectroscopy).

The kinetics of substituent exchange for this reversible second-order reaction were monitored by ³¹P NMR spectroscopy at temperatures between −9 °C and −70 °C under pseudo-first-order conditions of excess **1**. Linear plots of $\ln([\mathbf{2}]_0) + \ln([\mathbf{2}] -$

[2]∞) vs time (Figure 1) are consistent with kinetic behavior for a reversible first–second-order reaction[11] and provide the observed forward rate constants.[12] First-order dependence in 1 was confirmed by the linear dependence of the reaction rate on the concentration of 1. An Eyring plot of the data provided the activation parameters $\Delta H^* = 6.8(1)$ kcal/mol and $\Delta S^* = -41(1)$ eu. The very negative entropy of activation suggests a concerted mechanism for thiolate transfer and a highly ordered transition state, as might be expected on the basis of the sterically crowded nature of the reacting silicon centers:

Isolated group-transfer steps of the type described above offer "competition" reactions which may be of use in estimating the relative stabilizing effects of silylene substituents. For example, the silylene complexes $[Cp^*(PMe_3)_2Ru=SiR_2]B(C_6F_5)_4$ (R = O(Tol-p),[13] Me[1d]) rapidly and quantitatively abstract a thiolate group from 1 to produce the silylene 3 (as the $B(C_6F_5)_4^-$ salt) and the corresponding silyl complex (eq 2, L = PMe_3).[10] If the

$$ (2) $$
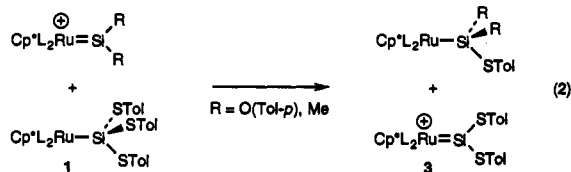
overriding thermodynamic driving force in these reactions is formation of the more stable silylene complex, then the stabilizing influences for the silylene substituents would decrease as S(Tol-p) > O(Tol-p), Me. Further support for this ordering is found in the thermal stability of the silylene complexes in solution and in activation parameters for acetonitrile dissociation from $[Cp^*\text{-}(PMe_3)_2RuSiR_2(NCMe)]^+$ derivatives.[14] Consistently, 3 does not react with $Cp^*(PMe_3)_2RuSi[O(Tol-p)]_3$[10] or $Cp^*(PMe_3)_2$-RuSiMe_3.[10]

The reactions involving transfer of a thiolate group are probably assisted by coordination of a sulfur lone pair to a silylene ligand.

However, methyl group transfer is also quite rapid in this system. At -55 °C, $[Cp^*(PMe_3)_2Ru=SiPh_2]B(C_6F_5)_4$[1d] reacts with $Cp^*(PMe_3)_2RuSiMe_3$ in dichloromethane-d_2 (90% after 35 min) to form $Cp^*(PMe_3)_2RuSiPh_2Me$[8] and $[Cp^*(PMe_3)_2Ru=Si\text{-}Me_2]B(C_6F_5)_4$ (eq 3, L = PMe_3). For comparison, $Cp^*(PMe_3)_2$-

$$ (3) $$

RuSiPh_3[8] does not react with $[Cp^*(PMe_3)_2Ru=SiMe_2]B(C_6F_5)_4$ in dichloromethane-d_2. These results are consistent with the fact that the dimethylsilylene complex is more thermally stable than $[Cp^*(PMe_3)_2Ru=SiPh_2]B(C_6F_5)_4$. In this case, the low kinetic barrier to methyl transfer may result from the high electrophilicity of the reacting silylene silicon center, which is not stabilized by π-donation from a heteroatom substituent. A competition involving different metal centers occurs in the reaction of $Cp^*\text{-}(PMe_3)_2RuSi(SEt)_3$[1a] with $[trans\text{-}(PCy_3)_2(H)Pt=Si(SEt)_2]\text{-}BPh_4$[1c] in dichloromethane-$d_2$ to quantitatively produce $[Cp^*\text{-}(PMe_3)_2Ru=Si(SEt)_2]BPh_4$[1a] and $trans\text{-}(PCy_3)_2(H)PtSi(SEt)_3$[1c] (by ^{1}H and ^{31}P NMR spectroscopy).

In conclusion, we have obtained the first direct evidence for the participation of base-free silylene complexes in reactions that scramble substituents at silicon. These reactions involve intermolecular transfer of substituents, in contrast to previously proposed mechanisms for redistribution at silicon. Such bimolecular transfer reactions could conceivably be involved as steps in metal-catalyzed redistributions. However, for cases involving metal fragments which can bind simultaneously to two silicon atoms, it is evident that intramolecular versions of these exchanges[5-7] will also be quite facile.

Supplementary Material Available: Experimental procedures and kinetics plots (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.

(9) (a) Grumbine, S. K.; Tilley, T. D.; Rheingold, A. L., manuscript in preparation. (b) Grumbine, S. K. Ph.D. Thesis, University of California, San Diego, 1993.

(10) Selected data are as follows. $Cp^*(PMe_3)_2RuSi(SEt)_2[S(Tol-p)]$: $^{31}P\{^1H\}$ NMR $(-20 °C) \delta 3.00$. $Cp^*(PMe_3)_2Ru=Si(SEt)[S(Tol-p)]$: $^{31}P\{^1H\}$ NMR $(-20 °C) \delta -2.53$. $Cp^*(PMe_3)_2RuSi(SEt)[S(Tol-p)]_2$: $^{31}P\{^1H\}$ NMR $(-20 °C) \delta 3.42$. 1: $^{31}P\{^1H\}$ NMR $(23 °C$, dichloromethane-$d_2) \delta 2.23$. 2: (Anal.) C, H; $^{31}P\{^1H\}$ NMR $(23 °C$, dichloromethane-$d_2) \delta -3.17$; $^{29}Si\{^1H\}$ NMR $(23 °C$, dichloromethane-$d_2) \delta 263.05$ (t, $J_{SiP} = 35$ Hz); 3: $^{31}P\{^1H\}$ NMR $(23 °C$, dichloromethane-$d_2) \delta -2.86$.[1a] 4: (Anal.) C, H; $^{31}P\{^1H\}$ NMR $(23 °C$, dichloromethane-$d_2) \delta 1.91$. $Cp^*(PMe_3)_2RuSi[O(Tol-p)]_2[S(Tol-p)]$: $^{31}P\{^1H\}$ NMR $(23 °C$, dichloromethane-$d_2) \delta 5.37$. $Cp^*(PMe_3)_2RuSi-Me_2[S(Tol-p)]$: prepared independently from $Cp^*(PMe_3)_2RuCH_2SiMe_3$ and $HSiMe_2[S(Tol-p)]$ in 88% yield by the method of ref 8; (Anal.) C, H; $^{31}P\{^1H\}$ NMR $(23 °C$, dichloromethane-$d_2) \delta 5.37$. $Cp^*(PMe_3)_2RuSi[O(Tol-p)]_3$: prepared from $Cp^*(PMe_3)_2RuCH_2SiMe_3$ and $HSi[O(Tol-p)]_3$ in 52% yield by the method of ref 8; (Anal.) C, H; $^{31}P\{^1H\}$ NMR $(23 °C$, dichloromethane-$d_2) \delta 7.81$. $Cp^*(PMe_3)_2RuSiMe_3$: prepared from $Cp^*(PMe_3)_2RuSiMe_2OTf$ and MeLi in 65% yield by the method of ref 9; (Anal.) C, H; $^{31}P\{^1H\}$ NMR $(23 °C$, dichloromethane-$d_2) \delta 7.57$.

(11) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; John Wiley and Sons, Inc.: New York, 1981; p 305.

(12) Rate expression for eq 1 under pseudo-first-order conditions of excess 1:

$$ d[2]/dt = -k_{obs}[2] + k_{-1}[3][4] \qquad (k_{obs} = k_1[1]) $$

The integrated rate expression (ref 11) may be written as:

$$ \ln([2]_0) + \ln([2] - [2]_\infty) = - \left\{ \frac{[2] + [2]_\infty}{[2] - [2]_\infty} \right\} k_{obs} t - \ln\{[2]_0([2]_0 - [2]_\infty) + [2]_\infty([2]_0 - [2])\} $$

A plot of $\ln([2]_0) + \ln([2] - [2]_\infty)$ vs time is linear with a slope of $-k_{obs}\{([2]_0 + [2]_\infty)/([2]_0 - [2]_\infty)\}$.

(13) Generated in dichloromethane-d_2 solution from $Cp^*(PMe_3)_2RuSi[O(Tol-p)]_2OTf$ and $LiB(C_6F_5)_4$ (refs 9, 14).

(14) Grumbine, S. K.; Tilley, T. D.; Rheingold, A. L., manuscript in preparation.