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Redistribution of Methyl Groups between Silicon Centers in Bis(silyl)tungsten Complexes: Silyl Silylene Complex Intermediates as the Source of Interligand Reactivity

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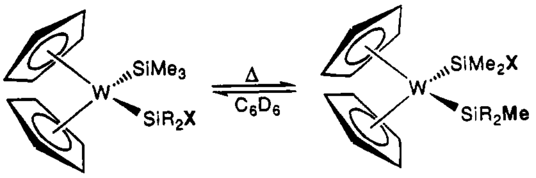
Summary: The bis(silyl) complexes $Cp_2W(SiMe_3)(SiR_2X)$ *(R = i-Pr,* CH_3*,* CD_3*, X = Cl,* OSO_2CF_3*) isomerize thermally to bis(silyls)* $Cp_2W(SiMe_2X)(SiR_2Me)$*, with rates strongly dependent on the nature of R and X, solvent polarity, and the presence of strong Lewis acid catalysts such as* $B(C_6F_5)_3$*. A mechanism is proposed in which an electrophilic cationic silyl(silylene)tungstenocene intermediate is formed by dissociation of* X^-*, followed by migration of a methyl group to the electrophilic silylene center, and finally reassociation of* X^- *to the other silicon to complete the process.*

The ability of transition metal complexes to catalyze the redistribution or disproportionation of groups in organosilicon compounds has been known for many years.[2] However, mechanistic details of the inherently interesting Si—C bond formation and cleavage processes were largely unknown. Recently, intriguing indications that silane redistribution may involve direct transfer of an alkyl group between silyl and silylene centers have come from the studies of Pannell[3] and Ogino[4] and Turner[5] on the photolysis of di- and oligosilyl complexes, $CpFe(CO)_2(Si_xR_y)$. In this report we describe the facile migration under thermal conditions of alkyl groups between adjacent silicon centers in tungsten bis(silyl) complexes of the formula $Cp_2W(SiMe_3)(SiR_2X)$ and present evidence that the redistribution proceeds by direct migration of alkyl groups between silicon centers in the key intermediate, a cationic silyl silylene complex intermediate formed by dissociation of X^-.

Thermolysis of the bis(silyl) complexes $Cp_2W(SiMe_3)(SiR_2X)$[6-8] (R = *i*-Pr, CD_3; X = Cl, OSO_2CF_3) yields equilibrium amounts of the isomeric complexes $Cp_2W(SiMe_2X)(SiR_2Me)$ as indicated in eq 1.[9] Both the rate and equilibrium position is strongly dependent on the nature of X^- and the size of the substituent R. For example, thermolysis of $Cp_2W(SiMe_3)(Si(i\text{-}Pr)_2Cl)$ (**1a**) at 160 °C in benzene-d_6 slowly results in a 1:6 equilibrium mixture of **1a** and $Cp_2W(SiMe_2Cl)(Si(i\text{-}Pr)_2Me)$ (**2a**). The half-life of this redistribution process is ca. 8 days. The same equilibrium distribution is also achieved from the thermolysis of pure **2a**. In contrast, the triflate derivative, $Cp_2W(SiMe_3)(Si(i\text{-}Pr)_2OTf)$ (**1b**, OTf = OSO_2CF_3), undergoes complete rearrangement to $Cp_2W(SiMe_2OTf)(Si(i\text{-}Pr)_2Me)$ (**2b**) in less than 24 h at 25 °C. The degenerate redistribution of methyl groups is also observed in the less hindered system, $Cp_2W(SiMe_3)(Si(CD_3)_2X)$ (X = Cl, **3a**; OTf, **3b**), albeit at much slower rates than the *i*-Pr complexes. The thermolysis of **3a** ultimately leads to a statistical (3:2) distribution of the CH_3 groups between the $SiMe_3$ and $SiMe_2$ sites, which can be conveniently monitored by ^1H NMR. Equilibrium is attained after 12 d at 170 °C for **3a**, whereas the triflate analog **3b** requires only 4 d at 50 °C.



(1)

That the migrations of the CD_3 groups in **3a**,**b** are *intra*molecular in nature is clearly established by the mass spectra of the complexes following thermolysis, which exhibit only parent ion patterns corresponding to compounds containing two CD_3 groups. On the other hand, the X^-groups scramble *inter*molecularly and faster than the intramolecular methyl migrations. For example, **1a** reacts with **3b** to yield **1b** and **3a** faster than CD_3 scrambling in **3a** or **3b**.

There is also a strong solvent dependence on the rate of methyl migration. The kinetics of methyl scrambling of **3b** (45 °C) monitored by ^1H NMR follows a first-order approach to equilibrium, and the observed rate constant increases with solvent polarity and dielectric constant[10] in the following order: C_6D_{12} (1) < C_6D_6 (7) ≪ CD_2Cl_2

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[7] The triflate derivatives were prepared from the chlorides by reaction with Me_3SiOTf.[8]

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[9] The rearranged isomers have all been isolated and fully characterized by multinuclear NMR and elemental analysis; see the supplementary material. In addition, **2a**,**b** have been structurally characterized by single crystal X-ray diffraction studies: Pestana, D. C.; Koloski, T. S.; Carroll, P. J.; Berry, D. H. Manuscript in preparation.

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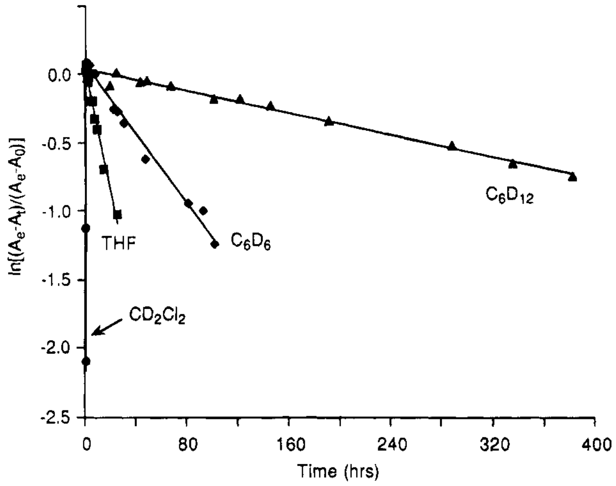


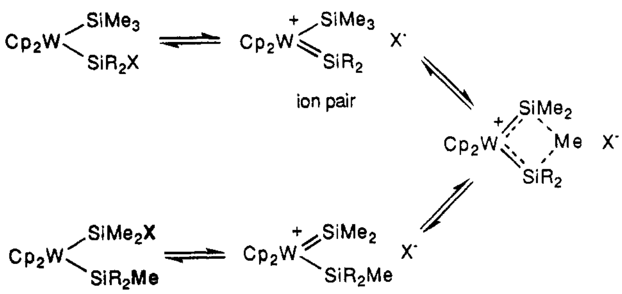
Figure 1. Plot of approach to equilibrium of methyl redistribution in **3b** at 45 °C.

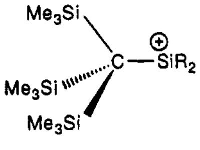
(1330) (Figure 1). The rate in THF-d_8 was also measured and found to be intermediate between C_6D_6 and CD_2Cl_2 ($k_{rel} = 23$), but this value is somewhat suspect, as the THF solvent polymerized to a gel during the course of the run.

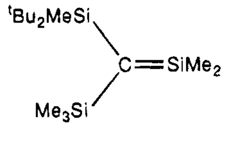
The net transformation in eq 1 involves exchange of methyl and X^- between adjacent silyl centers; thus, the simplest possible mechanism would be a dyotropic rearrangement in which the symmetrical transition state contains methyl and X^- groups bridging two pentacoordinate silicons. Although a similar process has been suggested by Corriu for the redistribution of hydridosilicates,[11] a dyotropic rearrangement seems unlikely in the present case. The more hindered doubly bridging transition state leads to slower redistribution of bulkier hydridosilicates, whereas the bulky *i*-Pr derivatives **1a,b** rearrange much faster than the corresponding methyl compounds **3**. Furthermore, the dyotropic rearrangement would involve an essentially nonpolar transition state and thus would not be expected to exhibit the observed solvent dependence on the rate.

Related 1,3-migrations of groups between silicon centers have been previously shown to occur readily when one of the silicons is extremely electron deficient, as in a silyl cation or a silaolefin. Eaborn and coworkers[12] have extensively studied the reactions of trisyl compounds $(Me_3Si)_3C(SiR_2X)$ with halide abstracting agents and found rapid intramolecular exchange of Me and R groups prior to trapping of the transient silyl cation. Similarly, Wiberg has observed that 1,3-methyl migration is extremely facile in silene complexes of the general formula $(R_3Si)_2C{=}SiR_2$. In a particularly dramatic example, it was reported that the ^1H NMR spectrum of $(t\text{-}Bu_2MeSi)(SiMe_3)C{=}SiMe_2$ at 30 °C exhibits a *single* resonance for the three Si–Me environments due to rapid migration of methyl groups between three- and two-coordinate silicon centers, even though the X-ray structure of this silene features a normal, localized silicon–carbon double bond.[13]

Scheme 1







Similar to the trisyl and silene systems shown above, the tungsten bis(silyl) complexes contain an Si–E–Si moiety and might be expected to undergo facile 1,3-methyl migrations if sufficient electrophilic character is generated at one of the silicon centers. This can most easily be achieved by dissociation of X^- to form the tungsten-substituted silyl cation, which with π-backbonding would be more reasonably described as a silylene complex ($W{=}SiR_2$) with the positive charge delocalized onto the metal.[6,9] The formation of a polar species such as an ion pair prior to methyl migration would be consistent with the observed solvent effects on the rate. Furthermore, there is good precedent for the dissociation of triflate ion from $M{-}SiR_2{-}OTf$ complexes in particular. Tilley and co-workers have reported that $Cp^*(PMe_3)_2RuSiPh_2OTf$ is ca. 17 times more conducting in solution than the chloride derivative and demonstrated that metathesis of the triflate with noncoordinating anions yields stable cationic silylene complexes.[14] Gladysz and Lee have also reported evidence for the dissociation in solution of triflate from $Cp_2(NO)(PPh_3)Re(ER_2OTf)$ (E = Si, Ge).[15]

The most consistent mechanism with the experimental data for the methyl group transfer is depicted in Scheme 1. The electrophilic silyl silylene intermediate is generated by initial dissociation of X^-. The symmetrical transition state (or intermediate) is then generated by bridging a methyl group. Complete transfer to the second silicon would result in a new silyl silylene complex intermediate, and association of X^- completes the process. In addition to accounting for the solvent effects, this mechanism is also consistent with the observed *intra*molecular scrambling of methyl groups and *inter*molecular scrambling of X^-.

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Note that following the formation of the silyl silylene complex intermediate, the mechanism is similar to that proposed for the photochemical rearrangement of iron and manganese di- and oligosilyl complexes.[3,4] This mechanism was first proposed in 1986 by Pannell and co-workers,[3a] and the Pannell group also concluded that electron deficiency at silicon accelerates the migrations.[3c] The proposed bridging methyl species in the scheme is analogous to the complexes recently isolated and structurally characterized by Ogino, Tobita, and co-workers which contain a methoxy group bridging two silicon centers.[4c,d] Interestingly, Tilley has recently found that the stable silylene complexes $[Cp^*(PMe_3)_2Ru{=}SiR_2]^+$ abstract alkyl groups from ruthenium silyls to yield net *inter*molecular redistribution.[16] The lack of intermolecular redistribution of alkyl groups in the present instance presumably reflects the inability of the silylene complex intermediate, which is only present in low concentrations, to undergo bimolecular reactions.

Consistent with the proposed mechanism involving initial X^- dissociation, addition of catalytic amounts of Lewis acids such as $B(C_6F_5)_3$ leads to enormous increases in the rates of methyl group scrambling. For example, treatment of **1a** with <5% $B(C_6F_5)_3$ in benzene lead to complete redistribution to **2a** in <3 min at 25 °C, compared with days at 160 °C in the absence of borane. Similarly, scrambling of **3a** requires 12 d at 170 °C but is complete in <30 min at 25 °C with catalytic amounts of $B(C_6F_5)_3$. Attempts to isolate the expected cationic silylene complex, $[Cp_2W(SiMe_3)({=}SiR_2)]^+[XB(C_6F_5)_3]^-$, from the reactions with stoichiometric borane have been unsuccessful to date, due the instability of the product.

The reactivity observed for complexes **1** and **3** appears to be a fairly unusual instance in which migration of groups between different ligands in a complex occurs directly ligand to ligand, without first moving to the metal center. However, the metal assists the transfer by facilitating X^- dissociation and generation of the requisite electrophilic silicon center. Further elucidation of the redistribution process and attempts to isolate intermediates from the borane reactions are in progress.

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Supplementary Material Available: Text giving details of the syntheses and a table of NMR data for **1b**, **2a**,**b**, and **3b** (3 pages). Ordering information is given on any current masthead page.

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