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Silane(silyl) and Bis(silyl)hydrido Manganese Complexes with Different Mn···H···Si Interaction: Observation of Gradual Si–H Bond Activation on the Metal Center

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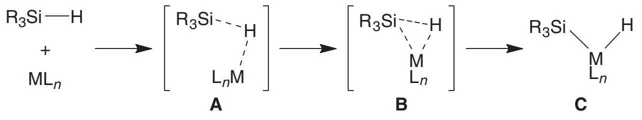
Three manganese–carbonyl complexes having a xanthene-based silane(silyl) or bis(silyl) chelate ligand were synthesized and characterized. The single-crystal X-ray analysis of these complexes demonstrated that an Si–H bond is sequentially activated on the metal according to ligand substitution of CO with xanthene-oxygen or η^6-toluene.

The Si–H bond activation of hydrosilanes induced by transition-metal complexes is an attractive process for its broad application to the synthesis of organosilicon compounds (e.g., hydrosilylation).[1] Generally, it is proposed that this bond activation can be achieved by interaction of the Si–H σ bond with a coordinatively unsaturated metal center.[1] A possible reaction mechanism of the Si–H activation suggested by Schubert and co-workers based on their comprehensive study (Scheme 1) involves the generation of silane complexes **A** and **B**, both having a 3c–2e M–H–Si bond, as key intermediates.[2] Thus, coordination of the hydrogen of a silane Si–H bond to the coordinatively unsaturated metal center in a complex ML_n can lead to the formation of **A** bearing an $\eta^1(H)$-silane ligand, and then the coordination mode of the silane ligand in **A** can change to an η^2-mode to give complex **B** that has stronger M···Si interaction compared with that in **A**. Finally, **B** can be converted either into a hydrido(silyl) complex **C** via complete oxidative addition or into other types of intermediate via σ-CAM mechanism,[3] etc. Therefore, to understand the detailed reaction mechanism of the Si–H activation, it is indispensable to experimentally elucidate how bonding interaction between a metal and an Si–H bond (M···H···Si interaction) can gradually change at some different stages of the process. This elucidation can also provide useful geometric parameters of M···H···Si interaction for supposing possible structures of intermediates in the theoretical study on the Si–H activation.

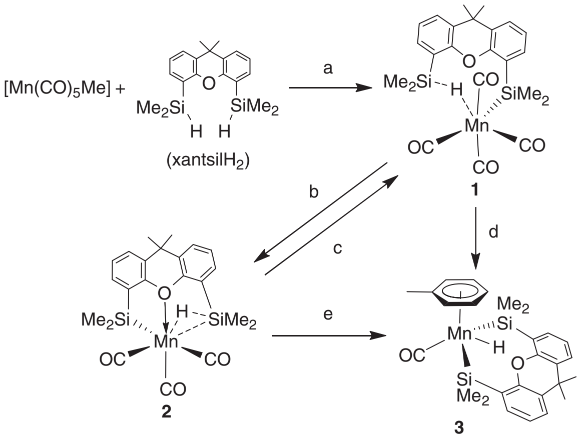
In this contribution, we report synthesis and structure determination of three manganese–carbonyl complexes **1**–**3** with a xanthene-based silane(silyl) or bis(silyl) chelate ligand, i.e., xantsil(H) or xantsil [xantsil: (9,9-dimethylxanthene-4,5-diyl)-bis(dimethylsilyl)].[4] Crystal structure analysis revealed that complexes **1**–**3** have substantially different Mn···H···Si(xantsil) interaction in the coordination sphere. By decreasing the number of CO ligands on Mn, the Mn···Si interaction is strengthened while the Si···H interaction is weakened. This stepwise observation of a change of Mn···H···Si interaction at three different stages in the Si–H activation is the most important point of this work.



Scheme 1. A possible reaction sequence in silane Si–H bond activation promoted by a coordinatively unsaturated metal complex ML_n.[2]

Three manganese complexes **1**–**3** were all synthesized photochemically (Scheme 2).[5] Photoirradiation of a 1:1 mixture of $[Mn(CO)_5Me]$ and bis(silane) xantsilH_2 in pentane for 0.5 h gave silane(silyl) complex [Mn{xantsil(H)}$(CO)_4$] (**1**) as yellow crystals in 43% yield. A possible formation mechanism of **1** involves photoinduced dissociation of a carbonyl ligand in $[Mn(CO)_5Me]$, oxidative addition of an Si–H bond of xantsilH_2, methane elimination, and intramolecular coordination of the other Si–H bond in the resulting xantsil(H) ligand to Mn. Further irradiation of **1** in pentane for 3 h led to dissociation of one carbonyl ligand in **1** followed by coordination of xanthene-oxygen to Mn to give tricarbonyl(silane)(silyl) complex [Mn{xantsil(H)}$(CO)_3$] (**2**) as yellow crystals in 53% yield. This CO dissociation reaction is reversible: Reaction of **2** in C_6D_6 with a CO atmosphere for 22 h at room temperature resulted in disappearance of **2** to afford **1** in 89% NMR yield. On the other hand, irradiation of a toluene solution of **1** for a longer period (9 h) afforded η^6-toluene complex [Mn(xantsil)(H)(η^6-toluene)-(CO)] (**3**) in 69% yield through dissociation of three carbonyl ligands. Complex **3** also formed by photoreaction of a toluene solution of **2** for 9 h in 50% yield. This indicates that complex **2** is an intermediate of the photoinduced conversion of **1** to **3**.

The single-crystal X-ray analysis revealed that **1** has an octahedral structure composed of a silane(silyl) bidentate chelate ligand [xantsil(H)] and four carbonyl ligands (Figure 1).[5] The



Scheme 2. Synthesis of silane(silyl) and bis(silyl)hydrido manganese complexes **1**–**3**. Conditions: (a) $h\nu$ ($\lambda > 300$ nm), pentane, 0.5 h, ca. 5 °C, −CO, −MeH; (b) $h\nu$ ($\lambda > 300$ nm), pentane, 3 h, ca. 5 °C, −CO; (c) +CO (1 atm), C_6D_6, 22 h, r.t.; (d) $h\nu$ ($\lambda > 300$ nm), toluene, 9 h, ca. 5 °C, −3CO; (e) $h\nu$ ($\lambda > 300$ nm), toluene, 9 h, ca. 8 °C, −2CO.

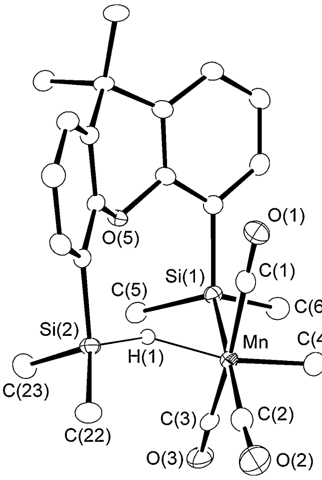


Figure 1. Crystal structure of **1**. Selected interatomic distances (Å) and angles (°): Mn–Si(1) 2.4702(9), Mn···Si(2) 2.9646(9), Mn–H(1) 1.71(4), Si(2)–H(1) 1.53(4), Si(1)–Mn–Si(2) 96.50(3), Mn–H(1)–Si(2) 132(2).

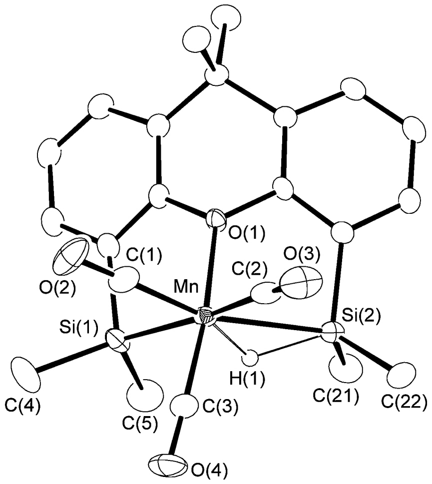


Figure 2. Crystal structure of **2**. Selected interatomic distances (Å) and angles (°): Mn–Si(1) 2.3942(5), Mn···Si(2) 2.6174(5), Mn–O(1) 2.1344(10), Mn–H(1) 1.61(2), Si(2)–H(1) 1.60(2), Si(1)–Mn–Si(2) 107.444(17), Mn–H(1)–Si(2) 109.6(14).

coordination mode of the xantsil(H) ligand that consists of a silane and a silyl ligand is unprecedented for metal–xantsil complexes.[4] This is also the first example of a silane(silyl)-manganese complex. The silane silicon Si(2) and silyl silicon Si(1) atoms are located at mutually cis positions. The Mn–Si(1) distance [2.4702(9) Å] is in the range typical of usual manganese–silyl bonds (2.319–2.564 Å).[1] On the other hand, the Mn···Si(2) distance [2.9646(9) Å] is much longer than those of known (η^2-silane)manganese complexes [2.254(1)–2.461(7) Å][1,2] and is also longer than the sum (2.50 Å) of the covalent radii[6] of low spin manganese (1.39 Å) and silicon (1.11 Å). Hydrogen H(1), which was found on the difference Fourier map and refined, bridges between Mn and Si(2) with a large Mn–H(1)–Si(2) bond angle [132(2)°] to form a 3c–2e Mn–H–Si bond [Mn–H(1): 1.71(4) and Si(2)–H(1): 1.53(4) Å]. These geometric features imply that the silane ligand in **1** is coordinated to Mn in an $\eta^1(H)$-mode. A few related $\eta^1(H)$-silane ligands are known:[7] For instance, Tilley and co-workers reported an (η^1-silane)iron complex [(MeQn$_2$SiH)Fe{N(SiMe$_3$)$_2$}$_2$] (Qn: 8-quinolyl), where the Fe···Si distance is 3.06(2) Å and the Fe–H–Si angle is 128.6(7)°.[7b] Thus, **1** can be regarded as an Si–H agostic complex, in which the weakly coordinated η^1-silane ligand is held on the metal probably by the chelate effect.[8] The negligible interaction between Mn and Si(2) in **1** is attributable to both electronic and steric effects. The electronic effect is based on the relatively electron-deficient Mn(I) center of the [Mn(CO)$_4$] fragment that causes the weak π-back donation to the silane ligand.[9] On the other hand, the steric factor is based on the steric repulsion between the xantsil(H) ligand and the [Mn(CO)$_4$] fragment. This is reflected on some interatomic distances between carbon atoms in SiMe groups and a CO ligand, i.e., C(2)···C(22) [3.143(5) Å] and C(5)···C(23) [3.703(5) Å], which are much shorter than the sum (3.7 Å) of the van der Waals radii of carbon (1.7 Å)[10a] and the methyl group (2.0 Å),[10b] and twice the radius (4.0 Å) of the methyl group, respectively.

The X-ray crystal structure analysis of complex **2** clearly shows that **2** carries a tridentate xantsil(H) ligand with an η^2-Si–H coordination and adopts an octahedral geometry (Figure 2).[5] The xanthene oxygen is coordinated to the Mn center: The Mn–O(1) distance [2.1344(10) Å] is comparable with the Mn–O(THF) distance [2.100(4) Å] in [Mn(CO)$_3$(THF)(μ-Cl)]$_2$.[11] The Mn–Si(1) bond length [2.3942(5) Å] is normal for an Mn–Si(silyl) single bond although it is shorter than that of **1** [2.4702(9) Å]. The Mn···Si(2) distance [2.6174(5) Å] of the 3c–2e Mn–H–Si bond is considerably shorter than the Mn···Si(2) distance of **1** [2.9646(9) Å] by ca. 0.35 Å but is still longer than the Mn–Si distances of known (η^2-silane)manganese complexes [2.254(1)–2.461(7) Å].[1,2] Hydrogen H(1) bridges between Mn and Si(2) with a narrower Mn–H(1)–Si(2) angle [109.6(14)°] compared with that of **1** [132(2)°]. The change of the coordination mode of the silane ligand from η^1 in **1** to η^2 in **2** is attributable in part to the increase of electron richness of the Mn center by substitution of one CO ligand with xanthene-oxygen, which leads to a stronger π-back donation from manganese to the Si–H bond.[9] The decrease of the steric repulsion in **2** can also contribute to the stronger π-back donation. Thus, some closest interatomic distances between carbon atoms in SiMe groups and CO ligands, i.e., C(1)···C(4) [3.237(3) Å] and C(2)···C(22) [3.177(3) Å], are longer than the corresponding distances in **1** [C(2)···C(22): 3.143(5) Å and C(4)···C(6): 3.128(5) Å] even after shortening of the Mn···Si(2) distance.

X-ray analysis shows that **3** can be best described as a bis(silyl)hydrido complex with a four-legged piano stool geometry composed of an η^6-toluene, a CO, a hydrido, and a xantsil ligand (Figure 3).[5] The Si–H bond of the xantsil(H) ligand in **1** is almost cleaved in **3** through substitution of three CO ligands with an η^6-toluene ligand. Two Mn–Si bond lengths [Mn–Si(1): 2.4026(7) and Mn–Si(2): 2.4069(7) Å] are nearly identical and are similar to that of the Mn–Si(silyl) bond in **2** [2.3942(5) Å]. Hydrogen H(1) is located between two silicon atoms of the xantsil ligand. The two Si···H(1) interatomic distances of **3** [Si(1)···H(1): 1.88(3) Å and Si(2)···H(1): 1.97(3) Å] are almost the same and are longer than the Si–H distances of the silane ligand in **1** [1.53(4) Å] and **2** [1.60(2) Å],

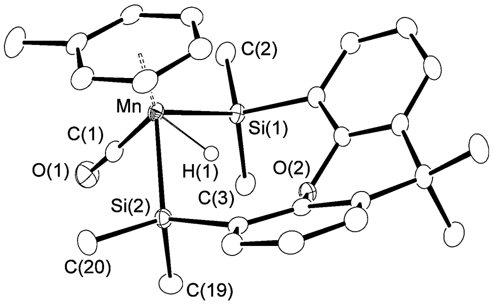


Figure 3. Crystal structure of **3**. Selected interatomic distances (Å) and angles (°): Mn–Si(1) 2.4026(7), Mn–Si(2) 2.4069(7), Mn–H(1) 1.45(3), Si(1)···H(1) 1.88(3), Si(2)···H(1) 1.97(3), Si(1)–Mn–Si(2) 103.37(3), Mn–H(1)–Si(1) 91.6(15), Mn–H(1)–Si(2) 88.1(15).

and are similar to the Si···H distances (1.9–2.1 Å) of hydrido(silyl) complexes with significant silyl–hydrido interaction.[12] Thus, the Si···H(1) interaction in **3** is extremely weakened compared with that in the silane ligand of **1** and **2**. This is mainly because the number of electron-accepting CO ligands is decreased to only one, and an electron-donating η^6-toluene ligand is coordinated instead. This leads to a more electron-rich metal center and thus makes the back donation to the σ^* orbital of the Si–H bonds stronger.

The NMR spectroscopic analysis of **1** and **2** in C_6D_6 at room temperature demonstrates their dynamic property. The ^{1}H NMR spectrum of **1** exhibits only one singlet signal assignable to its four SiMe groups at δ 0.79. In the ^{1}H NMR spectrum of **2**, two sets of the signals of SiMe and 9-CMe groups are observed at δ 0.53 and 1.08 (for SiMe) and δ 1.02 and 1.26 (for 9-CMe). Each of the ^{29}Si{^{1}H} NMR spectra of **1** and **2** shows only one signal at δ 3.0 (**1**) and 23.1 (**2**), indicating that two silicon atoms in **1** and **2** are equivalent on the NMR time scale. These observations suggest that the dynamic behavior in **1** and **2** involves migration of the hydrogen atom in the 3c–2e Mn–H–Si bond between two silicon atoms. A similar hydrogen migration was observed in an (η^1-silane){tris(silyl)}rhodium complex [Rh(o-$Me_2SiC_6H_4SiMe_2$)(η^1-o-$HSiMe_2C_6H_4SiMe_2$)(PPh_3)] reported by Nagashima and co-workers.[7c] Low-temperature NMR spectroscopic measurements for **1** and **2** in toluene-d_8 indicate that the dynamic behavior is fast on the NMR time scale. The ^{1}H NMR spectrum (800 MHz) of **1** at −90 °C in toluene-d_8 shows only one slightly broadened SiMe signal at δ 0.81 ($\Delta\nu_{1/2} = 5.2$ Hz) and broadened 9-CMe signal at δ 1.34 ($\Delta\nu_{1/2} = 11$ Hz). The ^{1}H NMR spectrum (800 MHz) of **2** at −60 °C in toluene-d_8 shows two broad SiMe signals at δ 0.47 ($\Delta\nu_{1/2} = 15$ Hz), 1.11 ($\Delta\nu_{1/2} = 17$ Hz) and two broad 9-CMe signals at δ 1.01 ($\Delta\nu_{1/2} = 19$ Hz), 1.19 ($\Delta\nu_{1/2} = 18$ Hz).[13] The ^{29}Si{^{1}H} NMR spectra of **1** and **2** at −90 °C exhibit only one signal at δ 1.9 (**1**) and 22.7 (**2**).

To elucidate the degree of Mn···H···Si interaction of **1** and **2** in solution, the Si–H coupling constant (J_{SiH}) was determined by NMR spectroscopy. The ^{1}H NMR spectrum of **2** shows a singlet at δ −5.21 assignable to the hydrogen of the 3c–2e Mn–H–Si bond with ^{29}Si satellites (J_{SiH} = ca. 49 Hz). This J_{SiH} value is in the range (38–65.4 Hz) of the values for complexes [Cp′Mn(CO)L(η^2-H–SiHPh$_2$)] (Cp′: C_5H_4Me, C_5Me_5; L: CO, isocyanide, phosphine).[2] On the other hand, the ^{1}H NMR spectrum of **1** in C_6D_6 at room temperature shows a broad singlet (δ −11.95) for the hydrogen of the 3c–2e Mn–H–Si bond, where ^{29}Si satellites are not observed. Therefore, the J_{SiH} value (46 Hz) of **1** was determined by a ^{29}Si NMR spectrum with proton coupling that showed a doublet of octets at 3.1 ppm. The coupling constant of **1** is smaller than those of η^1-silane complexes (79 Hz for an iridium complex[7a] and 112 Hz for a rhodium complex[7c]) and is comparable with that of **2** (ca. 49 Hz). This suggests that, in solution, the Si–H bond of the silane ligand in **1** is significantly weakened by the extensive dynamic behavior of **1**.

In summary, a series of manganese complexes **1**–**3** with a xanthene-based silane(silyl) or bis(silyl) chelate ligand were synthesized and structurally determined. Gradual activation of the Si–H bond in the xantsil(H) moiety with the change of ligands on a metal center was directly observed in the crystal structures of **1**–**3**. In solution, dynamic behaviors of **1** and **2** involving fast migration of the hydrogen in the 3c–2e Mn–H–Si bond were observed by NMR spectroscopy.

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