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Neutron and X-ray Diffraction Studies and DFT Calculations of Asymmetric Bis(silyl) Niobocene Hydrides

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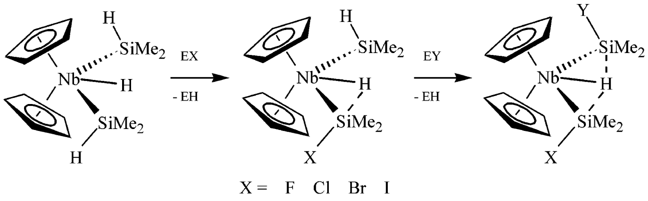
*Summary: The first asymmetric bis(silyl) niobocene hydrides Cp$_2$Nb(SiHMe$_2$)H(SiXMe$_2$) (**2**: X = F (**a**), Cl (**b**), Br (**c**), I (**d**)), having interligand interactions Nb−H···Si−X, were prepared by selective halogenation of the Si−H bond in Cp$_2$Nb(SiHMe$_2$)$_2$H. X-ray studies of **2b,c** and a combined X-ray/neutron diffraction study of **2b** establish a slightly stronger interaction of the niobium-bound hydride with the halosilyl ligand.*

The class of complexes having nonclassical interactions between a hydride and silyl ligands[1] has been recently enlarged by examples with multicenter H−Si bonding.[2] Interactions of one silyl group with two,[3] three,[4] and four hydrides[5] were reported by the groups of Sabo-Etienne, Roper, and Lemke. Some of us have been studying the phenomenon of interligand hypervalent interactions (IHI)[6,7] M−H···Si−X and found that in the symmetrical bis(silyl) complexes Cp$_2$Nb(SiXMe$_2$)$_2$H (**1a**−**d**; X = F, Cl, Br, I) two silicon atoms interact with one hydride located in the center of the symmetry plane of niobocene. It is of interest to investigate the asymmetric compound Cp$_2$Nb(SiYMe$_2$)H(SiXMe$_2$), since one could expect that the nonequivalent silyl groups will interact with the hydride differently, resulting in *competitive IHI* and giving rise to the problem of accurate location of the hydride ligand in the symmetry plane of the metallocene fragment. Group 5 metallocenes with three different substituents have been reported only very recently.[8]

Scheme 1. Synthetic Strategy for Asymmetric Bis(silyl) Niobocenes



3 **2** **a** **b** **c** **d**

The compounds Cp$_2$Nb(SiYMe$_2$)H(SiXMe$_2$) can be prepared, in principle, by stepwise electrophilic Si−H bond activation[6a,c] via the so far unknown asymmetric complexes Cp$_2$Nb(SiHMe$_2$)H(SiXMe$_2$) (**2**). The latter compounds can be envisaged to result from *selective Si−H bond activations* in Cp$_2$Nb(SiHMe$_2$)$_2$H (**3**) (Scheme 1). Here we report the preparation and X-ray structures of the first asymmetric complexes **2** and a neutron diffraction structure of **2b**, allowing for the accurate location of the hydride. DFT studies have also been performed to elucidate the nature of the Si−H interactions.

A wide variety of reagents have been screened to achieve the selective halogenation of **3**, the best results

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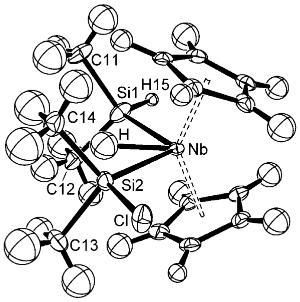

Figure 1. Molecular plot of **2b** as obtained from combined neutron/X-ray diffraction analysis (ellipsoids are plotted at 50% probability). The SiMe$_2$H is rotationally disordered such that the “H(15) site” has partial occupancies of 0.75 for H(15) and 0.25 for the methyl carbon C(15).

of which are reported here. Generally, the selectivity of fluorination is low, and the best yield of **2a** after purification was 27% for Ph$_3$CPF$_6$. Unfortunately, the X-ray structure[9] of **2a** is severely disordered in the position of the fluorine atom, due to the closeness of the sizes of the hydride and fluoride groups, which strongly disturbs the molecular parameters. Complexes **2b**−**d** were prepared in high yield under the action of 1 equiv of Me$_3$SnX (X = Cl, Br) and [NHMe$_2$Ph]I, respectively. The Nb−H bond stretch ν(Nb−H) decreases from 1728 cm^{-1} in **2a** to 1695 cm^{-1} in **2d**, suggesting weakening of the bond.

The molecular structure of **2b** (Figure 1) was determined by combined X-ray and neutron diffraction (ND) refinement.[10] The X-ray structure of **2c** strongly resembles that of **2b** and is deposited in the Supporting Information. As expected, the Nb−Si bond lengths for the SiHMe$_2$ (2.6528(5) Å) and SiClMe$_2$ (2.5961(5) Å) groups in **2b** are significantly different. The Si−Cl bond of 2.1829(7) Å is slightly longer than in the previously studied complexes Cp$_2$Nb(SiClMe$_2$)$_2$H[6a] (**1b**, 2.163(1) Å), Cp$_2$Nb(SiClMe$_2$)H$_2$[6a] (2.170(2) Å), and Cp(ArN)Ta(PMe$_3$)(H)(SiClMe$_2$)[7] (2.177(2) Å) with IHI and is 8.1% longer than in organic chlorosilanes, suggesting increased interligand interaction. IHI consists of electron density transfer from the basic M−H bond orbital onto the Si−X* antibonding orbital (if X lies trans to H) and results in a relatively long Si−X bond, a shortened M−Si bond, an elongated M−H bond, and a short Si−H contact.[6a,7] Contrary to expectations, the present ND study reveals that the hydride is located exactly symmetrically between the two silicon centers (Si(1)−Nb−H = Si(2)−Nb−H = 52.9(6)°). Although the statistical significance is weak, because of the shorter Nb−SiClMe$_2$ bond length, the hydride appears to lie closer to the SiClMe$_2$ group than to the SiHMe$_2$ ligand (2.085(17) versus 2.126(17) Å), resulting in a stronger interaction with the chlorosilyl center. Also in accord with the presence of IHI is the small Si(1)−Nb(1)−Si(2) bond angle of 105.853(19)° (104.27(5)° in **1b**[6a]), in comparison to the angle in the classical compounds Cp$_2$Nb(SiPhMe$_2$)$_2$H (110.81(5)°)[6a] and Cp$_2$Ta(SiHMe$_2$)$_2$H (109.90(7)°).[11] The Nb−H bond length of 1.804(17) Å[12] is close to the ND value of 1.816(8) Å determined in **1b**[6b] and is only marginally elongated relative to the Ta−H bonds found by ND studies in Cp$_2$Ta(SiHMe$_2$)$_2$H[11] (1.785(15) Å) and Cp$_2$TaH$_3$ (1.771(9) Å, average).[13]

Table 1. Selected DFT Calculated Bond Lengths (Å) for 2a−d and 3

bond	**3**, X = H	**2a**, X = F	**2b**, X = Cl	**2c**, X = Br	**2d**, X = I
Nb−SiX	2.670	2.636	2.629	2.627	2.628
Nb−SiH	2.670	2.673	2.675	2.676	2.679
Si-X	1.521	1.681	2.194	2.386	2.617
Si−H[a]	1.521	1.519	1.518	1.518	1.518
Nb−H	1.787	1.793	1.795	1.796	1.797
HSi−H[b]	2.189	2.247	2.229	2.239	2.251
XSi−H[b]	2.187	2.092	2.095	2.087	2.063

[a] Si bound hydride. [b] Nb-bound hydride.

The Si−Br bond length in **2c** is significantly longer than that in Cp$_2$Nb(SiBrMe$_2$)$_2$H[6a] (2.378(2) versus 2.349(2) Å) and 11% longer than in bromosilanes. The shorter H···SiBrMe$_2$ contact of 2.07(3) Å in comparison to the H···SiHMe$_2$ distance (2.16(3) Å), and the increased Si(1)−Nb(1)−Si(2) bond angle of 107.27(7))° (103.37(7)° in Cp$_2$Nb(SiBrMe$_2$)$_2$H) confirm the stronger interaction of the hydride with the bromosilyl group.

Modern quantum-mechanical calculations provide an independent means for understanding the structure and bonding of the hydride complexes.[14] In this work complexes **2a**−**d** and **3** were calculated by the DFT method.[15] Apart from the somewhat overestimated Nb−Si bond lengths, which also lead to the slightly longer Si···H contacts (Table 1), there is a very good agreement between the calculated and observed structures. In agreement with increasing IHI, the Nb−H bond in **2a**−**d** elongates and becomes weaker (the Wiberg bond indices (WI) and NBO bond orders (BO)[9] decrease; Table 2) down the halogen group, whereas the Nb−Si bond proceeds via a shallow minimum, as in **1a**−**d**.[6] Confirming this trend, the XMe$_2$Si···H contact decreases and strengthens from X = Cl to X = I, whereas the HMe$_2$Si···H distance in **3** is longer than any XMe$_2$Si···H contact (X = halogen). Therefore, the Si···H distances in the asymmetric bis(silyls) do not follow a simple electronegativity trend. The unexpected finding of this

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[9] See the Supporting Information for more details and references.

[10] Crystal data for **3b**: C$_{14}$H$_{24}$ClNbSi$_2$, M_r = 376.87, monoclinic, space group $P2_1/c$ (No. 14), a = 16.3876(4) Å, b = 8.5767(3) Å, c = 14.5354(4) Å, β = 93.627(2)°, V = 1702.96(9) Å^3, Z = 4, ρ_{calcd} = 1.470 g cm^{-3}. X-ray analysis: 4109 reflections, R = 0.027, R_w = 0.034. Neutron diffraction study: the data were collected at IPNS (Argonne) by the time-of-flight Laue method, 826 reflections, crystal size 2 × 2 × 0.5 mm^3, R = 0.112, R_w = 0.082. The inclusion of X-ray data was necessary to complement the neutron analysis. Use of a combined set of data has resulted in the stable refinement of all atoms and a satisfactory agreement of the observed and calculated data. Full details of the neutron data collection and the joint X-ray/neutron refinement are given in the Supporting Information.

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[12] This value nicely confirms the well-known trend that the M−H bond length decreases from left to right across the periodic table. For the second period elements the accurate ND values are Nb−H = 1.804(17) Å, Mo−H = 1.737(5) Å, Ru−H = 1.611(7) Å, and Rh−H = 1.566(3) Å: Bau, R.; Drabnis, M. H. *Inorg. Chim. Acta* **1997**, *259*, 27.

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[15] Calculations were performed using the GAUSSIAN98 series of programs. Density functional theory (DFT) was used, with the BP86 functional. Effective core potentials (ECP) and their associated double-ξ LANL2DZ basis sets were used for the niobium, silicon, chlorine, bromine, and iodine atoms supplemented by a set of d-polarization functions in the case of Si, Cl, Br, and I. The 6-31G(d,p) basis set was employed for the H atom directly bonded to the metal and the F atom, while a 6-31G basis set was used for the rest of the atoms in the system. The topological properties of the electron density were investigated using the XAIM 1.0 program.[9]

Table 2. Wiberg (WI) and NBO (BO) Bond Indices in 2a−d and 3

bond		**3**, X = H	**2a**, X = F	**2b**, X = Cl	**2c**, X = Br	**2d**, X = I
Nb−H	BO	0.4539	0.4479	0.4425	0.4413	0.4389
	WI	0.5590	0.5469	0.5416	0.5387	0.5344
XSi−H[a]	BO	0.2341	0.2753	0.2824	0.2876	0.2971
	WI	0.1565	0.1833	0.1868	0.1913	0.1992
HSi−H[a]	BO	0.2332	0.2089	0.2141	0.2109	0.2060
	WI	0.1558	0.1392	0.1427	0.1406	0.1369
Si−X	BO	0.7675	0.5191	0.6940	0.7079	0.7132
	WI	0.8848	0.5409	0.7450	0.7900	0.8255
Nb−SiX	BO	0.5221	0.5596	0.5647	0.5679	0.5691
	WI	0.6373	0.6175	0.6513	0.6588	0.6641
Nb−SiH	BO	0.5223	0.5226	0.5199	0.5188	0.5189
	WI	0.6378	0.6467	0.6413	0.6404	0.6419

[a] Nb-bound hydride.

study is that the Si···H contact of 2.092 Å in the fluoro derivative **2a** is between the values found for **2b** and **2c**. Despite this, the calculated WIs and BOs[9] also show that the XMe$_2$Si···H interaction becomes stronger monotonically down the halogen group. The special position of **2a** is also seen from the fact that the HMe$_2$Si···H bond length (and strength) goes via an extremum on **2b**. This result can be accounted for in terms of a significant contribution of the *electrostatic* dipole−dipole interaction[16] between the negatively charged hydride and positively charged silicon centers in **2a**, which alongside IHI contributes to the Si···H bonding. Obviously, the importance of this term decreases down the halogen group, in accordance with the decreasing electronegativity of the halogen attached to the silicon atom, whereas the strength of *covalent* IHI increases in the opposite direction.[6a] The AIM study[17] of the electron density of **2a**−**d** confirms this conclusion. Although, as in the symmetric analogues **1**,[6a] the bond critical points[17] for the Si···H contacts have not been found, the Laplacian of the charge density distribution shows that the concentration of the charge density of the hydride is polarized toward the Si(X) atom. The decrease of charge density on the Nb−H bond critical points ($\rho(\mathbf{r}_c)$) and increase of the corresponding Laplacians ($\nabla^2\rho(\mathbf{r}_c)$) in **2a**−**d** confirm electron density depletion, whereas the increase of $\rho(\mathbf{r}_c)$ for the Si−X bonds accompanied by the decrease of $\nabla^2\rho(\mathbf{r}_c)$ from −0.0664 to −0.1169 shows that the Si−X bond accumulates this electron density, in accordance with IHI increasing down the group.

In conclusion, we have developed synthetic routes to the asymmetric bis(silyl) niobocene hydrides Cp$_2$Nb(SiHMe$_2$)H(SiXMe$_2$) (X = F, Cl, Br, I) and determined by a combined ND, X-ray, and DFT study that the Si···H interaction is stronger with the halosilyl ligand.

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Supporting Information Available: Text, tables and figures giving experimental details and characterization data for the new compounds, details of the ND study of **2b**, and computational details; X-ray data for **2a**−**c** are available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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