J. Am. Chem. Soc. **1995,** *117,* 10133−10134 10133

Interligand Hypervalent Interaction in the Bis(silyl) Hydride Derivatives of Niobocene

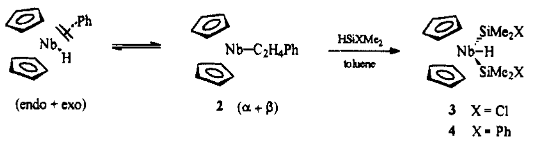
Georgii I. Nikonov,[*,†,‡] Ludmila G. Kuzmina,[§]
Dmitry A. Lemenovskii,[†] and Vasily V. Kotov[†]

Chemistry Department, Moscow State University
Vorob'evy Gory, 119899 Moscow, Russia
Institute of General and Inorganic Chemistry, RAS
Leninsky prosp. 31, 117907 Moscow, Russia

Received March 27, 1995

Recently, there has been an increased interest in the trisubstituted group 5 metallocenes $Cp_2M(ER_m)_nH_{3-n}$ (**1**) bearing different main-group-element substituents ER_m.[1−10] One reason for our interest in this field is the possibility of nonclassical interligand interactions due to the little room in the bisecting plane of the metallocene moiety of **1**. Such interactions are, for example, relevant to the oxidative addition of silanes to transition metals and are believed to play an important role in the σ-bond metathesis mechanism for the dehydrocoupling of primary organosilanes.[11] Buchwald et al. have recently reported that the related titanium complex $Cp_2Ti(SiHPh_2)(H)(PMe_3)$ is better formulated as a σ $H{-}SiHPh_2$ complex.[12] On the basis of a short H−Si contact (1.83 Å) found by the X-ray structure determination of $Cp_2Ta(SiHMe_2)_2H$, Berry et al. discussed the possibility of an analogous ($H{-}SiHMe_2$) interaction.[3a]

Here we report evidence for a new type of nonclassical interligand interaction which was discovered in the bis(silyl hydride niobocene complex $Cp_2Nb(SiClMe_2)_2H$ bearing an electron-withdrawing chloride substituent at silicon. In this compound we found a five-center six-electron Cl···Si···H···Si···Cl bond providing a direct interligand interaction in the coordination sphere of metal.



(endo + exo) **2** (α + β) **3** X = Cl **4** X = Ph (1)

The bis(silyl) complexes **3** and **4** were prepared by a method analogous to that used previously by Green et al. for the synthesis of related bis(stanyl) derivatives.[4] The mechanism of formation of **3** and **4** most likely involves the oxidative addition of silanes to the in situ generated monoalkylniobocene **2** (eq 1).[13] The structures of **3** and **4** were reliably established by ^1H and ^{13}C NMR spectra,[14] which are in accord with the corresponding spectra of tantalum complexes $Cp_2Ta(SiR_3)_2H$ (**5**).[3] The main feature of the ^1H NMR spectra of **3**, **4**, and **5** is that the bis(silyl) hydrides bearing alkyl and aryl substituents at silicon exhibit a downfield-shifted hydride resonance with respect to the corresponding dihydridosilyls, $Cp_2M(H)_2SiR_3$ (−3.23 ppm in **4** versus −4.79 ppm in $Cp_2Nb(H)_2SiPhMe_2$[2]). An opposite trend is observed in the chloro-substituted silyl complexes: −5.01 ppm in $Cp_2Ta(SiClMe_2)_2H$ and −5.15 ppm in **3** versus −4.03 ppm in $Cp_2Ta(H)_2SiClMe_2$.[3a] The upfield shift of a hydride signal is often associated with the formation of a hydride bridge; thus the spectral peculiarities of **3** could be interpreted in terms of some kind of bonding between the hydride and silicon centers. The X-ray structure determinations of **3** and **4** further confirmed this hypothesis.[15]

The molecular structure of **3** is presented in Figure 1. Not surprisingly, complexes **3** and **4** are isostructural and exhibit the typical trisubstituted metallocene geometry. Comparison of these two structures affords strong evidence in favor of a nonclassical interligand interaction in **3**. First of all, there is an apparent asymmetry concerning two silicon atoms in **3**: thus, in **3** the Si(1)−Nb distance of 2.584(5) Å is 0.027 Å shorter than the Si(2)−Nb bond (2.611(5) Å), and both these distances are shorter than the corresponding distances in **4** (2.646(5) and 2.665(4) Å). Hence, the largest difference in the Si−Nb bond lengths in **3** and **4** is 0.081 Å. These values can be compared with the "normal" Si−Nb bond in $Cp_2Nb(C_2H_4)SiMe_3$ (2.669(1) Å)[18] and Si−Ta bonds in the related complexes $Cp_2Ta(H)_2(SiMe_2Ph)$[2] and $Cp_2Ta(H)(SiMe_2H)_2$[3a] of 2.651(4) and 2.629(2) Å (average), respectively. Another important structural feature in **3** is the long Si−Cl distances. Thus, the Si(1)−Cl(1) bond of 2.172(7) Å and Si(2)−Cl(2) bond of 2.155(7) Å are considerably longer than in typical organic chlorosilanes (2.023 Å).[19] These features cannot be explained only on the basis of differences in electronegativity;[20] and another factor is expected to be operative, namely, a nonclassical Cl···Si···H interaction.

Further evidence in favor of an interligand interaction in **3** was inferred from the location of the hydride substituent in **3** and **4**. In **3** the hydride was located from Fourier difference synthesis and refined to a typical Nb−H distance of 1.756 Å.[24]

[†] Moscow University.

[‡] Present address: Chemistry Department, University of Nottingham, Nottingham NG7 2RD, U.K. (until July 1996).

[§] Institute of General and Inorganic Chemistry.

(1) E = B, *n* = 1: Hartwig, J. F.; De Gala, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 3661.

(2) E = Si, *n* = 1: Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701.

(3) E = Si, *n* = 1, 2: (a) Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1991**, *10*, 3648. (b) Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* **1990**, *9*, 2952.

(4) E = Sn, *n* = 1, 2: Green, M. L. H.; Hughes, A. K.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1991**, 1407.

(5) E = P, *n* = 1: (a) Nikonov, G. I.; Lemenovskii, D. A.; Lorberth, J. *Organometallics* **1994**, *13*, 3127. (b) Nikonov, G. I.; Kuzmina, L. G.; Mountford, P.; Lemenovskii, D. A. *Organometallics* **1995**, *14*, 3588.

(6) E = As, *n* = 1: Nikonov, G. I.; Harms, K.; Lorberth, J.; Lemenovskii, D. A. *Inorg. Chem.* **1995**, *34*, 2461.

(7) E = Bi, *n* = 1: Nikonov, G. I. Manuscript in preparation.

(8) E = Sn, *n* = 1: Harris, D. H.; Keppie, S. A.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1653.

(9) E = Sn, *n* = 1: Arkhireeva, T. M.; Bulychev, B. M.; Protsky, A. N.; Soloveichik, G. L.; Bel'sky, V. K. *J. Organomet. Chem.* **1986**, *317*, 33.

(10) E = Si, *n* = 1: Berry, D. H.; Jiang, Q. *J. Am. Chem. Soc.* **1987**, *109*, 6210.

(11) (a) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043. (b) Harrod, J.F.; Ziegler, T.; Tschinke, V. *Organometallics* **1990**, *9*, 897. (c) Britten, J.; Mu, Y.; Harrod, J. F.; Polowin, J.; Baird, M. C.; Samuel, E. *Organometallics* **1993**, *12*, 2672. (d) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22.

(12) Spaltenstein, E.; Palma, P.; Kreutzer, K.; Willoughby, C. A.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 10308.

(13) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134.

(14) These data as well as details of the preparation of **3** and **4** are deposited as supporting information.

(15) Crystal data: both experiments were carried out on a Enraf-Nonius CAD-4 diffractometer at −100 °C using graphite-monochromatized Mo Kα radiation. Structures were solved by direct methods (SHELXS-86) and refined by full-matrix least-squares procedures (SHELXL-93)[16] with anisotropic temperature factors for all the non-H atoms. Hydrogen atoms were found in the difference Fourier synthesis and refined. **3**: $C_{14}H_{23}Cl_2Si_2Nb$, orthorombic, $Pna2_1$, $a = 8.419(9)$ Å, $b = 16.584(4)$ Å, $c = 13.214(5)$ Å, $V = 1845(2)$ Å^3, $Z = 4$, $\mu = 10.6$ cm^{-1}, $D_{calc} = 1.481$ g/cm^{-3}, 4° < θ < 30°, ω scans, $\rho_{max} = 1.498$ e/Å^3, $\rho_{min} = -1.978$ e/Å^3, 2221 unique reflections, 2206 ($F > 4\sigma(F)$) observed reflections, $R = 0.038$ GOF = 1.31, Flack *x* parameter = −0.06(15) (expected values are 0 (within 3 esd's) for correct and +1 for inverted absolute structure.[17] **4**: $C_{26}H_{33}Si_2Nb$, orthorombic, $Pna2_1$, $a = 8.856(7)$ Å, $b = 15.356(9)$ Å, $c = 17.522(8)$ Å, $V = 2383(2)$ Å^3, $R = 0.030$, GOF = 1.04; the full data will be reported elsewhere.

(16) Sheldrick, G. M. *SHELXS-86 Program for Crystal Structure Determination*; Universität Göttingen: 1986; *SHELXL-93, Program for Crystal Structure Refinement*; Universität Göttingen: 1993.

(17) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881.

(18) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 473.

(19) Lukevics, E.; Pudova, O.; Sturkovich, R. In *Molecular Structure of Organosilicon Compounds*; Ellis Horwood Ltd.: New York, 1989.

(20) The bond of Si with more electropositive Nb should have more s character[21] while with more electronegative Cl it has more p character,[22] partially accounting for the short Nb−Si and long Si−Cl bonds. However, in $Cp(CO)Fe(H)(SiCl_3)_2$ the average Si−Cl bond length is only 2.052 Å.[23]

0002-7863/95/1517-10133$09.00/0 © 1995 American Chemical Society

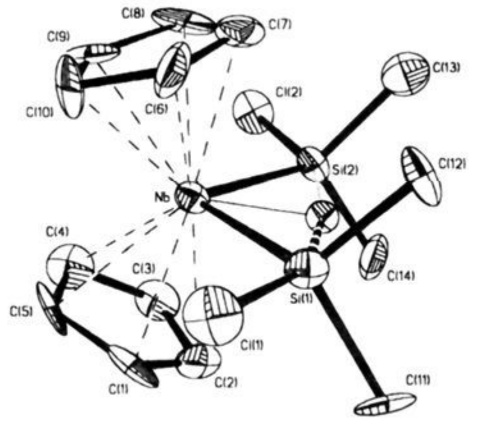


Figure 1. Molecular structure of **3**. Important bond distances (Å) and angles (deg): Nb−Si(1) 2.584(5), Nb−Si(2) 2.611(5), Nb−H 1.756, Si(1)−Cl(1) 2.172(7), Si(2)−Cl(2) 2.155(7), Si(1)−H 1.880, Si(2)−H 2.233, H−Nb−Si(1) 46.7, H−Nb−Si(2) 57.5, Si(1)−Nb−Si(2) 104.26(5), H−Si(1)−C(11) 93.1, H−Si(1)−C(12) 91.8, C(12)−Si(1)−Nb 118.0(6), C(11)−Si(1)−Nb 117.2(6), H−Si(2)−C(13) 91.6, H−Si(2)−C(14) 95.8, C(14)−Si(2)−Nb 118.0(5), C(13)−Si(2)−Nb 115.6(7), H−Si(1)−Cl(1) 157.0, H−Si(2)−Cl(2) 156.4, Cp1−Nb−Cp2 136.5.

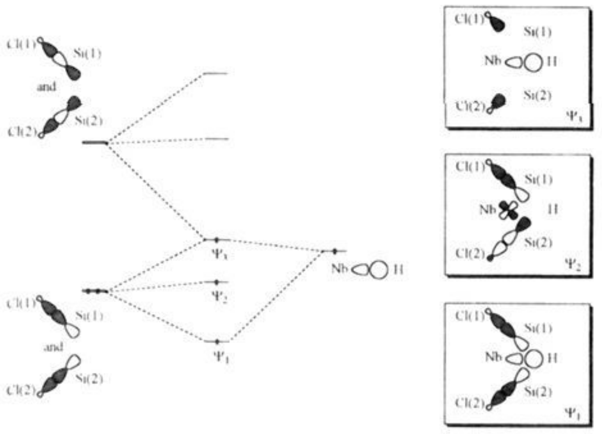


Figure 2. Qualitative MO diagram for the interligand hypervalent bonding in **3** (the symmetrical isomer before the Jahn−Teller distortion is considered).

This final position is essentially asymmetrical with respect to the two silicon atoms, affording a fairly short Si(1)−H contact (1.880 versus 2.233 Å for the Si(2)−H contact) and Si(1)−Nb−H and Si(2)−Nb−H angles of 46.7° and 57.5°, respectively. Both these H−Si contacts are considerably shorter than the sum of van der Waals radii (3.1 Å). In contrast, the hydride in **4** found from the difference map and refined is situated quite symmetrically between the two silicons with a Nb−H distance of 1.713 Å and Si(1)−Nb−H and Si(2)−Nb−H angles both of 55.4°. Despite the acknowledged uncertainties associated with locating hydrogen atoms in heavy atom structures, these findings correlate well with other structural features of these complexes.

Both the short Si−Nb and long Si−Cl distances in **3** can be explained by invoking the possibility of interligand hydride−silyl nonclassical interaction. The location of Si−Cl bonds in the bisecting plane provides an overlap between Si−Cl and Nb−H bonding orbitals. A qualitative MO description is presented in Figure 2. This interaction strongly resembles the 3c−4e hypervalent bonding in hypervalent molecules like PF_5, I_3^-, etc.,[25] but the new important feature is that in **3** it is delocalized over five centers and, thus, can be regarded as a 5c−6e interligand hypervalent bond in the coordination sphere of the niobium center. As in the case of other hypervalent structures, such an interaction causes a rehybridization at the silicon atom: the silicon orbitals taking part in the five-center six-electron Cl···Si···H···Si···Cl bond develop more p character, and thus more s character is left for the bonding with other substituents, thus accounting for the shortening of the Nb−Si bond and the lengthening of the Si−Cl bond in **3**.[26]

Due to the second-order Jahn−Teller effect,[27] one of the Si···H bonds is shorter than the other, accounting for the observed differences in the geometries at the silicon atoms. The equivalence of $SiMe_2Cl$ groups in the low-temperature NMR spectra of **3** is then explained by the tunneling movement of hydride between the two silicon centers.[28] Thus the interligand hypervalent interaction provides bonding between *two lateral silyls* through the *central hydride*. As a result of this, the Si(1)−Nb−Si(2) angle of 104.26(5)° in **3** is considerably smaller than the corresponding angle in the "unperturbed" molecule **4** (110.81(6)°), while even the opposite trend could be expected from pure steric reasons, taking into account the steric hindrance order Ph > Me ≈ Cl. For comparison, the Si(1)−Nb−Si(2) angle (110.81(6)°) in **4** is very close to the Si(1)−Ta−Si(2) angle of 109.9(7)° in the much less hindered $Cp_2Ta(H)(SiMe_2H)_2$.[3a] The hydride−silyl hypervalent bonding should be differentiated from the well-known σ $H-SR_3$ complexes[11,29] where there is an interaction of one silicon atom with one hydride, regarded as M, H, Si three-center bonding.[11,29c,f,g] Another difference in these nonclassical interactions is that in the σ-bond $H-SiR_3$ structures the stronger H−Si interaction is accompanied by a longer M−Si bond length[29d,f] while the opposite situation is observed in **3**.[30]

In summary, we have prepared the first bis(silyl) hydride derivatives of niobocene and found that there is significant nonclassical interaction in $Cp_2Nb(SiClMe_2)_2H$ between H and Si substituents. This interaction has an observable structural effect in **3**, which is especially apparent by comparison of the structures of **3** and **4**. This interaction was rationalized in terms of hypervalent bonding between H and Si centers.

Acknowledgment. The Russian Foundation for Fundamental Investigations is acknowledged for financial support of this work. We thank Prof. A. A. Bagatur'yants for helpful discussions.

Supporting Information Available: Details of preparations and characterization of **3** and **4**, along with tables of positional and thermal parameters for non-hydrogen atoms, hydrogen atom positional parameters, and bond distances and angles for **3** (5 pages); listing of $10F_o$ and $10F_c$ for **3** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA950975X

---

[21] Bancroft, G. M.; Butler, K. D.; Rake, A. T.; Dale, B. *J. Chem. Soc., Dalton Trans.* **1972**, 2025.

[22] Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

[23] Manojlovic-Muir, L.; Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 447.

[24] Wilson, R. D.; Koetzle, T. F.; Hart, D. W.; Kvick, A.; Tripton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1775.

[25] (a) Rundle, R. E. *Rec. Chem. Prog.* **1962**, *23*, 195. (b) Rundle, R. E. *Surv. Prog. Chem.* **1963**, *1*, 83. (c) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54. (d) For review, see: Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

[26] Analogous structural trends were observed in $Cp_2Mo(SnClMe_2)_2$, where interligand hypervalent Cl−Sn−Cl interaction was found: Bel'skii, V. K.; Protskii, A. N.; Bulychev, B. M.; Soloveichik, G. L. *J. Organomet. Chem.* **1985**, *280*, 45.

[27] Pearson, R. G. *Orbital Topology and Elementary Processes*; Wiley: New York, 1976; Chapter 1.

[28] The low-temperature NMR spectra of **3** revealed the equivalence of the $SiMe_2Cl$ group down to −80 °C (no Me group signal splitting), suggesting a facile hydride migration between two silicon centers.

[29] (a) Hart-Davis, A. J.; Graham, W. A. G. *J. Am. Chem. Soc.* **1971**, *93*, 4388. (b) Schubert, U.; Ackermann, K.; Worle, B. *J. Am. Chem. Soc.* **1982**, *104*, 7378. (c) Colomer, E.; Corriu, R. J. P.; Marzin, C.; Vioux, A. *Inorg. Chem.* **1982**, *21*, 368. (d) Carre, F.; Colomer, E.; Corriu, R. J. P.; Vioux, A. *Organometallics* **1984**, *3*, 1272. (e) Schubert, U.; Scholz, G.; Müller, J.; Ackermann, K.; Worle, B.; Stansfield, R. F. D. *J. Organomet. Chem.* **1986**, *306*, 303. (f) Schubert, U.; Müller, J.; Alt, H. G. *Organometallics* **1987**, *6*, 469. (g) Schubert, U.; Bahr, K.; Müller, J. *J. Organomet. Chem.* **1987**, *327*, 357. (h) Raab, H.; Saillard, J.-Y.; Schubert, J.-Y. *J. Organomet. Chem.* **1987**, *330*, 397. (i) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151. (j) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.

[30] The three-center H, Si, M bond is commonly explained in terms of H−Si σ bond orbital donation to a vacant d orbital of metal and some back-bonding from the filled metal d orbital to the σ^* orbital of the H−Si bond.[29h,j] Thus the stronger the Si−H interaction, the longer the Si−M bond length, and vice versa.