

Are $J(\text{Si-H})$ NMR Coupling Constants Really a Probe for the Existence of Nonclassical H-Si Interactions?

Stuart R. Dubberley,[†] Stanislav K. Ignatov,[‡] Nicholas H. Rees,[†] Alexei G. Razuvaev,[‡]
Philip Mountford,^{*,†} and Georgii I. Nikonov^{*,§}

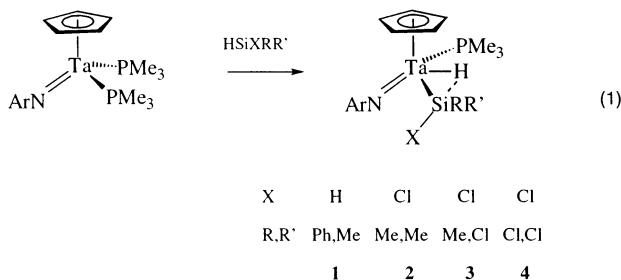
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK, University of Nizhnii Novgorod, 23, Gagarin Avenue, Nizhnii Novgorod 603600, Russia, and Department of Chemistry, Moscow State University, Vorob'evy Gory, 119899 Moscow, Russia

Received July 30, 2002; E-mail: nikonov@org.chem.msu.su

Recently, a great deal of progress has been made in studying complexes with nonclassical interligand interactions.¹ In the field of silane Si-H bond σ -complexes $L_nM(\eta^2\text{-H-SiR}_3)$ the most common means for probing the H-Si bonding is by measurement of $^1J(\text{Si-H})$ coupling constants, with magnitudes higher than 20 Hz being attributed to the presence of a direct H-Si interaction.^{1c,d} Usually electron-donating groups at the silicon atom effect higher $^1J(\text{Si-H})$ values and, by implication, stronger Si-H interactions, whereas electron-withdrawing groups render a deeper degree of Si-H bond oxidative addition and hence a comparatively diminished $^1J(\text{Si-H})$.^{1a-d}

Here we report ^{29}Si NMR and DFT studies of a series of silylhyrido complexes of Ta, having nonclassical M-H...Si-X interligand hypervalent interactions (IHIs).^{2,3} For the first time we have observed a correlation between the magnitude of $J(\text{Si-H})$ values and the identity of the substituent X which is *opposite* to that one found for silane σ -complexes. Moreover, DFT calculations of model systems showed that an increase in $J(\text{Si-H})$ does not necessarily correspond to the strengthening of the Si-H interaction.

Complexes of the type $\text{Cp}(\text{ArN})\text{Ta}(\text{PMe}_3)(\text{H})(\text{SiR}_3)$ (**1-4**) (Ar = 2,6- $\text{C}_6\text{H}_3\text{iPr}_2$; SiR_3 = SiMePhH (**1**), SiMe₂Cl (**2**), SiMeCl₂ (**3**), SiCl₃ (**4**)) were prepared in 50–70% isolated yields by the oxidative addition of silanes HSiR_3 to $\text{Cp}(\text{ArN})\text{Ta}(\text{PMe}_3)_2$ (eq 1) and characterized by NMR and IR spectra and by X-ray diffraction studies of **2**³ and **3**.⁴



The molecular structure of **3** (Figure 1) strongly resembles the previously reported structure of **2**³, with the chlorine Cl(2), and hydride atoms lying trans to each other (mean deviation from the TaSiClH plane = 0.03 Å). In complexes with IHI such an orientation allows for the overlap of the M-H bond orbital and the (Si-Cl)* antibonding orbital which leads to the electron density transfer from the former to the latter and elongation of the Si-Cl bond.² Importantly, the “in-plane” chlorine forms a Si-Cl(2) bond of 2.117 (2) Å which is significantly longer ($\Delta = 0.053(4)$ Å) than

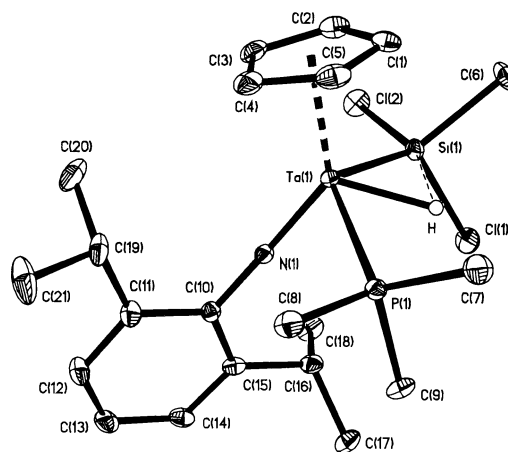


Figure 1. Molecular structure of **3**. Displacement ellipsoids (non-H atoms) are shown at 50% probability level. Hydrogens bonded to carbon atoms are omitted for clarity.

the bond to the “out-of-plane” chlorine (Si-Cl(1) = 2.064(3) Å). The Si-Cl bonds in transition metal silyls are normally elongated relative to the parent silanes due to the operation of Bent’s rule.^{2a,5} Since in **3** this factor contributes equally to both the Si-Cl(1) and Si-Cl(2) bond lengths, the relative lengthening of the latter by 0.053(4) Å manifests the presence of IHI. This is the first time that a direct comparison of two types of different Si-Cl bonds, one interacting with the hydride and the other noninteracting, is possible at the same silicon center. It is also noteworthy that there is no experimental difference in the Ta-Si bond lengths in **2** (2.574(1) Å) and **3** (2.569(2) Å; $\Delta = 0.005(2)$ Å) despite the presence of two electron-withdrawing Cl substituents on Si in the latter. This suggests that contribution of IHI to any expected shortening of the Ta-Si bond² in **3** is much less than that in **2**. This conclusion is further supported by the DFT study.

The ^{29}Si NMR spectra of **1-4** show a remarkable trend in that the magnitude of the $J(\text{H-Si})$ coupling constant sequentially *increases* from 14 Hz in **1** to 33 Hz in **2** and 40 Hz in **3** to 50 Hz in **4** as the number of chlorine groups on silicon increases. This trend is *opposite* to that observed for normal Si-H bond σ -complexes^{1c} and could be at first glance considered as evidence for strengthening of the Si-H interaction on going from **1** to **4**. However, how the strength of the Si-H IHI should change upon increasing chlorination of the SiR_3 groups is not a priori clear because the electronic origin of this type of nonclassical bonding is different from the more common σ -bond complexation.^{2a} On one hand, increasing n in $\text{SiR}_{3-n}\text{Cl}_n$ would be expected to shorten the Ta-Si bond due to an increase in Bent’s rule effects and thus bring the silicon and hydride atoms into closer contact. On the other hand,

[†] Oxford.

[‡] University of Nizhnii Novgorod.

[§] Moscow State University.

Table 1. Selected Results of DFT Calculations for Cp(MeN)Ta(PMe₃)(H)(SiH_{3-n}Cl_n) (*n* = 0–3) (Bond Lengths in Å)

Bond	SiXR ₂			
	SiH ₃ (5)	SiClH ₂ (6) ^a	SiClHCl(7) ^b	SiCl ₃ (8)
Ta–H	1.810	1.828	1.819 [1.95(7)]	1.810
Ta–Si	2.606	2.556 [2.574(1)]	2.545 [2.569(2)]	2.547
Ta–P	2.531	2.540 [2.550(1)]	2.538 [2.522(2)]	2.538
Si–H ^c	2.288	2.062	2.115 [2.15(7)]	2.174
Si–Cl ^d		2.236 [2.177(2)]	2.208 [2.117(2)]	2.189
Si–Cl ^e			2.184 [2.064(3)]	2.174, 2.167

^a Experimental values for **2** in brackets, the hydride atom was located from the difference map but not refined. ^b Experimental values for **3** in brackets. ^c Ta-bound hydride. ^d In-plane chlorine trans to hydride. ^e Out-of-plane chlorine(s)

Table 2. Changes in Atom-Weighted Bond Orders (BO) and Wiberg Indices (WI) in a Series Cp(MeN)Ta(PMe₃)(H)(SiH_{3-n}Cl_n) (*n* = 0–3)

bond		SiXR ₂			
		SiH ₃ (5)	SiClH ₂ (6)	SiClHCl(7)	SiCl ₃ (8)
Ta–H ^a	BO	0.4942	0.4668	0.4723	0.4798
	WI	0.6376	0.5881	0.6028	0.6168
Ta–Si	BO	0.6044	0.6467	0.6500	0.6690
	WI	0.7581	0.7684	0.7547	0.7396
Si–H ^a	BO	0.1872	0.2792	0.2622	0.2458
	WI	0.1350	0.2095	0.1831	0.1608
Si–X ^b	BO	0.7393	0.5621	0.6073	0.6500
	WI	0.9135	0.7090	0.7495	0.7830
Si–R ₁	BO	0.7516 ^c	0.7487 ^c	0.6272 ^d	0.6668 ^d
	WI	0.9365 ^c	0.9083 ^c	0.7874 ^d	0.8115 ^d
Si–R ₂	BO	0.7512 ^c	0.7480 ^c	0.7427 ^c	0.6613 ^d
	WI	0.9410 ^c	0.9119 ^c	0.8812 ^c	0.8077 ^d

^a H – hydride interacting both with Ta and Si. ^b X – substituent at silicon trans to hydride H, X = H in the case of SiH₃ and X = Cl in the case of chlorosilyls. ^c R = H. ^d R = Cl.

however, a larger *n* causes greater electron deficiency at silicon, which would be accompanied by orbital contraction, and this could result in a decrease of orbital overlap between the Si and H atoms. In addition, the increase in the electron-withdrawing ability of the SiR_{3-n}Cl_n group would make the Ta–H bond less basic.⁶

This matter has been clarified by means of DFT calculations⁷ of a series of model complexes with the formula Cp(MeN)Ta(PMe₃)(H)(SiH_{3-n}Cl_n) (*n* = 0–3, compounds **5**–**8**, respectively). Selected results of the calculations are given in Table 1. The most important result of the calculations is that instead of a monotonic change in values of the parameters on going from *n* = 0 to *n* = 3 due to Bent's rule, the compound Cp(MeN)Ta(PMe₃)(H)(SiH₂Cl) (**6**) exhibits extreme values. Thus, on going from Cp(MeN)Ta(PMe₃)(H)(SiH₃) (**5**) to **6** the Si–H distance first decreases (stronger Si–H interaction), as predicted, from 2.288 to 2.064 Å and then increases to 2.115 Å in **7** and 2.174 Å in **8**, while the Ta–H bonds first elongates (weaker Ta–H interaction) and then contracts again, indicating the strongest IHI is found for **6**. This is further supported by the largest values of the bond orders and Wiberg indices⁸ for the Si–H contact in **6**, accompanied by the lowest values for the Ta–H bonds (Table 2). The apparently anomalous changing of these and other parameters, however, is totally consistent with the theory of IHI and establishes that **6** has the strongest H–Si bonding. The weaker IHI found in **7** (model for **3**) compared to that in **6** (model for **2**) allows us to understand why the Ta–Si bond in **3** is only marginally shortened in comparison with that in **2**: in **3** the expected

contraction of the Ta–Si bond due to IHI decreases, whereas contraction due to Bent's rule effect increases, and the two opposite trends compensate each other.

Therefore, the increase in the magnitude of *J*(H–Si) upon going from **2** to **4** is not paralleled by a strengthening of the interligand interaction. Other factors, such as possible increase of the through two-bond Si–Ta–H magnetic interactions due to increasing silicon 3s character in the Ta–Si bond, should be considered to account for this behavior.

In conclusion, we have observed for the first time⁹ a reverse correlation between the number of electron-withdrawing substituents at silicon and the silicon hydride coupling constants in transition metal silyl hydride complexes and established that, contrarily to expectation, an increase in the magnitude of *J*(H–Si) does not necessarily correspond to stronger bonding interaction between these two ligands.

Acknowledgment. This work was supported by Royal Society (London) through a joint research grant to G.I.N. and P.M.. Also, G.I.N. is grateful to INTAS for a YS INTAS fellowship. S.K.I. and A.G.R. thank RFBR for financial support (project 00-03-32094).

Supporting Information Available: Experimental details and characterization data (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Kubas, G. J. *Metal Dihydrogen and σ -Bond Complexes*; Kluwer Academic/Plenum: New York, 2001. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (c) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151. (d) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (e) Nikonov, G. I. *J. Organomet. Chem.* **2001**, *635*, 24. (f) Nikonov, G. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 3355.
- (2) (a) Nikonov, G. I.; Kuzmina, L. G.; Vyboishchikov, S. F.; Lemenovskii, D. A.; Howard, J. A. K. *Chem.-Eur. J.* **1999**, *5*, 2497. (b) Bakmutov, V. I.; Howard, J. A. K.; Keen, D. A.; Kuzmina, L. G.; Leech, M. A.; Nikonov, G. I.; Vorontsov, E. V.; Wilson, C. C. *Dalton Trans.* **2000**, 1631.
- (3) Nikonov, G. I.; Mountford, P.; Ignatov, S. K.; Green, J. C.; Cooke, P. A.; Leech, M. A.; Kuzmina, L. G.; Razuvaev, A. G.; Rees, N. H.; Blake, A. J.; Howard, J. A. K.; Lemenovskii, D. A. *Dalton Trans.* **2001**, 2903.
- (4) X-ray analysis of **3**: C₂₁H₃₅Cl₂NPSiTa, *M_r* = 612.41, orthorhombic, space group *Pbcu*, *a* = 16.331(3) Å, *b* = 17.298(4) Å, *c* = 17.968(4) Å, *V* = 5075.9(18) Å³, *Z* = 8, ρ_{calcd} = 1.603 g cm⁻³, *R* = 0.035, *R_w* = 0.095.
- (5) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.
- (6) Basicity of the hydride is a prerequisite of IHI.²
- (7) All calculations were carried out with the Gaussian 98 program package (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998) using density functional theory applying Becke's 1988 nonlocal exchange functional in conjunction with Perdew's correlation functional, commonly aliased as BP86. The compound basis set was used for the calculation consisted of the 6-31G(d) basis set for the silicon, phosphorus and nitrogen atoms, 6-31G for the carbon atoms and the silyl hydrogens, and the 3-21G basis set for the hydrogen atoms of Cp ring and methyl groups. The basis set augmented by the *p*-polarization function (6-31G(d,p) basis set) was used for the hydride H atom. The Hay–Wadt VDZ effective core potentials (ECP) and the corresponding VDZ basis sets were used for the tantalum atom, and the "Stuttgart" quasi-relativistic ECP were used for the atom Cl in this model. For more details and references see ref 3.
- (8) Wiberg K. B. *Tetrahedron* **1968**, *24*, 1024.
- (9) F. R. Lemke has recently made a similar observation (private communication).

JA027935V