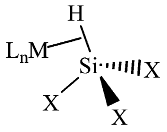
Organometallics **2003,** *22,* 1597−1598

Correspondence

The Puzzle of Cp(CO)$_2$Mn(HSiCl$_3$): Classical or Nonclassical?



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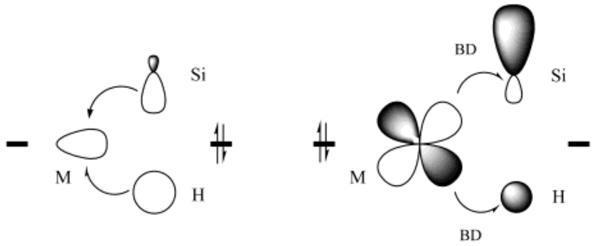
Sir: The phenomenon of silane σ-bond complexation (**1**) has long been known and underpins our fundamental knowledge about transition-metal-mediated transformations of silanes.[1] Bonding in such species is usually described in terms of the Dewar−Chatt−Duncanson (DCD) model (Scheme 1) as donation of an (Si−H) bonding orbital onto a vacant metal orbital supported by partial back-donation (BD) from a filled metal d orbital into the (Si−H) antibonding orbital, resulting in residual Si−H bonding.[1a,b] It is commonly believed that the extent of BD, depending on the nature of the metal, supporting ligands, and substituents on the silicon atom, dictates the degree of oxidative addition of the Si−H bond.[1a,c,2] NMR spectroscopy is considered to be the most powerful means for the identification and characterization of silane σ-complexes. Thus, genuine silane σ-complexes exhibit large silicon−hydrogen coupling constants J(Si−H) of 50−70 Hz, whereas a J(Si−H) value below 20 Hz is believed to signify the presence of a classical silyl hydride complex.[1c,d] There is, however, a remarkable exception to this rule: the compound (C$_5$H$_4$Me)(CO)$_2$Mn(HSiCl$_3$) (**2**) exhibits a J(Si−H) value of 54.8 Hz but according to a photoelectron spectroscopy (PES) study and Fenske−Hall calculations is better described as a Mn(III) silyl hydrido species.[2] Schubert mentioned that this high value of J(Si−H) could be due to a large Si 3s orbital character in the Mn−Si bond,[1c] suggesting a large through-two-bond coupling constant, although this argument fails to explain why the very related complex Cp(CO)Fe(H)(SiCl$_3$)$_2$ has a J(Si−H) value of only 20 Hz.[3] Lichtenberger attributed the large J(Si−H) value in **2** to a nonbonding coupling due to the “inherently narrow angle between the d_{yz} and d_{z^2} metal hybrides, which holds the Si and H atoms in close proximity”,[2b] i.e., to a “nonbonding magnetic interaction” as found in bicyclopentanes and related compounds.[4] Corey and Braddock-Wilking pointed out that “if this is actually the case, some caution interpreting NMR data as a criterion for agostic interactions may be necessary”.[1d] Another problem of this explanation is that it fails to rationalize the low value of J(Si−H) in Cp(CO)Fe(H)(SiCl$_3$)$_2$. Indeed, if a “nonbonding interaction” is present in **2**, then one would expect that Cp(CO)Fe(H)(SiCl$_3$)$_2$, having the bulkier SiCl$_3$ in place of carbonyl and the smaller Fe in place of Mn, would have sterically more enhanced proximity of the hydride and silyl ligands and hence a larger J(Si−H) value, which is not the case. The story, however, took an unexpected turn when Lin et al. performed MP2 and DFT calculations on Cp(CO)$_2$Mn(HSiCl$_3$) (model for **2**) and Cp(CO)$_2$Mn(HSiFH$_2$) (model for the nonclassical complex Cp(CO)$_2$Mn(HSiFPh$_2$) studied by neutron diffraction, ^{29}Si NMR, and PES) and found that *both compounds* have short Si−H bond lengths; i.e., they are nonclassical.[5]

Scheme 1



These apparently contradictory results of NMR, PES, and computational studies bring about a question as to what is the right description of the bonding situation in **2** and which method gives the “wrong” result. Our answer is that **2** is nonclassical but, surprisingly, all three studies are right. Moreover, the qualitative DCD model is still valid.

Let us consider what happens when one goes from the nonclassical complex (C$_5$H$_4$Me)(CO)$_2$Mn(HSiPh$_3$) (having a Mn(I) center according to the PES study[2a] and a J(Si−H) value of 63.5 Hz;[1c] the Si−H distance for the similar complex (C$_5$H$_5$)(CO)$_2$Mn(HSiHPh$_2$) is 1.76(4) Å according to an X-ray study[1c]) to **2**. Putting electronegative chlorine substituents on Si in HSiCl$_3$ brings about a rehybridization of the silicon center: namely, more Si 3s character goes to the bond with the hydride and more 3p character to the chlorines (Bent’s rule).[6,7] Such a replacement lowers the energy of *both* the (Si−H) bonding and (Si−H)* antibonding orbitals, leading to

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[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.

[2] (a) Lichtenberger, D. L.; Rai-Chaundhuri, A. *J. Am. Chem. Soc.* **1990**, *112*, 2492. (b) Lichtenberger, D. L.; Rai-Chaundhuri, A. *J. Am. Chem. Soc.* **1989**, *111*, 3583.

[3] Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1159.

[4] Bartfield, M.; Della, E. W.; Pigou, P. E.; Walters, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 3549.

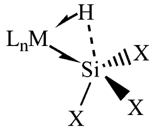
[5] Choi, S. H.; Feng, J. W.; Lin, Z. Y. *Organometallics* **2000**, *19*, 2051.

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

[7] Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

10.1021/om020694f CCC: $25.00

several consequences. (i) As mentioned above, the back-donation into the antibonding orbital (Si−H)*, mainly localized on silicon, increases, resulting in shorter and stronger M−Si bonding as observed in X-ray studies and calculations. (ii) This increased back-donation from the metal should be accompanied by *decreased direct donation from the Si−H bond* to the metal because the (Si−H) bonding orbital is lower in energy, thus resulting in *effective electron density transfer* from the metal onto silane, as observed by the PES study.[2b] (iii) Since the J(Si−H) value of 370 Hz in free $HSiCl_3$ is significantly larger than in silanes $HSiR_3$ (R = alkyl, aryl; J(Si−H) < 200 Hz), one can expect that, if any bonding between H and Si in a $HSiCl_3$ complex remains, the J(Si−H) value for the *same degree of oxidative addition* of the Si−H bond to the metal should be higher than the coupling constant in a complex of $HSiR_3$ (R = alkyl, aryl). This means that comparable values of coupling constants can be found for both the $L_nM(HSiCl_3)$ and $L_nM(HSiR_3)$ (R = alkyl, aryl) complexes, even though the former can have a greater degree of Si−H oxidative addition. Therefore, the cooperative effect of factors i and ii should lead to the features experimentally observed in the PES study of **2**, whereas decreased Si−H donation to the metal should compensate increased back-donation and thus lead to some residual Si−H bonding and formation of the nonclassical silane complex $Cp(CO)_2Mn(HSiCl_3)$, as observed in Lin's calculations. This bonding situation can be described as shown in **3**. Large Si 3s character in the residual Si−H bond results in a rather large *one-bond* J(Si−H) value, although the degree of oxidative addition of the Si−H bond in **2** may be in fact higher than in other silane complexes $Cp(CO)_2Mn(HSiR_3)$.



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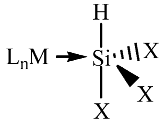
Finally, it is interesting to note the difference between the second-row elements E (such as carbon, E = C) and their heavier analogues (Si, Ge, Sn). In terms of a simple two-orbital interaction MO diagram increased population of the antibonding level (E−H)* causes rupture of the E−H bond.[7] However, this is not necessarily the case for E = Si, Ge, Sn because of the propensity of these elements to be hypervalent. For example, in the extreme case of negligible (Si−H)→M donation but complete BD from the metal into the (Si−H)* antibonding orbital in a silane complex, the Si−H bond will not break; rather, a hypervalent silicon species such as **4** will be formed.



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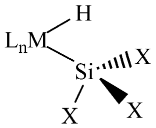
Complex **4** can be viewed as a donor−acceptor complex of the Lewis acid $HSiX_3$ with the Lewis base L_nM and will *be indistinguishable by PES* from the oxidative addition product $L_nM(H)(SiX_3)$ (**5**), as both will exhibit electron depletion of the metal center and electron density transfer to the silicon center, exactly what was observed for **2**.[2a] The bonding situation as in **4** can be approached in a highly electropositive metal complex (ideally the left-hand side of the transition series) supported by electron-donating ligands, such as phosphines and cyclopentadienyls, and strengthened by a low oxidation state. Corresponding hydride compounds have strong hydridic character. A related situation was observed in the form of interligand hypervalent interactions in hydride derivatives of niobocene and Cp−imido complexes of Ta with functionalized silyl ligands (**6**).[8,9]



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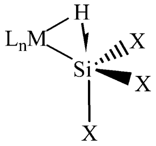

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Received August 23, 2002

OM020694F

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[9] 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.