Electron Distribution, Bonding, and J(Si−H) NMR Coupling Constant in (η^5-C_5H_5)$(CO)_2MnHSiCl_3$: The Molecular Orbital View

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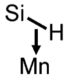
Sir: Among the reactions of hydrosilanes with transition-metal complexes, the oxidative addition of $HSiCl_3$ to the Mn center in $Cp(CO)_2MnHSiCl_3$ has been particularly interesting.[1,2] A key question concerns whether the bonding tends more toward the σ-bond complex **1** or has proceeded substantially to the classical oxidative addition product **2**.[3] The magnitude of the J(Si−H) NMR coupling constant in comparison to that of other metal silyls seems to indicate substantial retention of Si−H bonding as in **1**, whereas the frontier orbital model and the characters obtained from variable photon energy photoelectron spectroscopy[4] clearly indicate nearly complete oxidation of the Mn center to a formal d^4 configuration most consistent with structure **2,** with some residual Si−H interaction remaining, as might be represented by contributions from valence bond drawings **3** or **4**. Nikonov[5] offers a different interpretation of the electronic structure of this molecule. This interpretation favors appreciable retention of Si−H bonding as in **1,** but with substantial donation of metal density to the silyl by means of Mn→Si back-bonding/hypervalent bonding to account for the photoelectron data, as might be represented by valence bond drawings **5** and **6** and similar structures in his correspondence. Part of the puzzle arises from the inadequacy of simple valence bond models to account for the electronic structure of organometallic molecules. For instance, a third possibility is to consider the hydride as bridging between the Mn and Si centers with a three-center−two-electron bond as in **7**. Part of the problem also arises, as pointed out by Schubert in his review,[1] from the need for "a more detailed investigation of the influence of substituents at silicon on the magnitude and sign of the SiMH coupling constants". Modern computational tools[6] are now able to give a better understanding of the coupling constants in metal complexes, and the results show that the original electronic structure and bonding interpretation based on the frontier molecular orbital model and the photoelectron data is correct.



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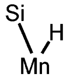

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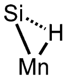

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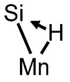

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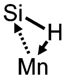

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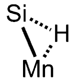

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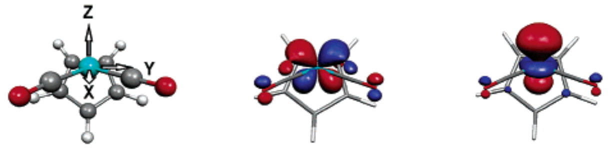
The description of the frontier orbitals of the [Cp$(CO)_2M$] fragment developed by Hoffmann et al. from simple molecular orbital methods has had wide success in explaining and predicting the features of molecules that contain this functional group.[7] The proposal of a different interpretation for $Cp(CO)_2MnHSiCl_3$ prompted us to examine the frontier orbital model and its relationship to the properties of this molecule in more detail with current density functional methods and extensive basis sets.[8] Baerends and Gritsenko point out that Kohn−Sham orbitals "may be expected to be more suitable for use in qualitative molecular orbital theory than either Hartree−Fock or semiempirical orbitals".[9] As it turns out for this system, all three approaches lead to the same description. The HOMO of the $[Cp(CO)_2Mn]$ fragment is the predominantly metal d_{yz} orbital **8**. This orbital is set up for π back-bonding to a ligand that is on the z axis and has a π acceptor orbital in the yz



coordinate axes **8** (HOMO) **9** (LUMO)

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(3) All valence bond representations are with the Mn, Si, and H atoms at the correct relative positions as given in Table 1.

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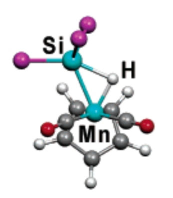
Table 1. Experimental and Calculated Si−H, Mn−H, and Mn−Si Distances (Å) in Cp′(CO)$_2$MnHSiCl$_3$ and Related Molecules[a]

	method	Si−H	Mn−H	Mn−Si
HSiCl$_3$	microwave[19]	1.464		
	calcd	1.478		
Cp′L$_2$MnHSiCl$_3$	X-ray[12]	1.785	1.471[13]	2.254
	calcd	1.823	1.570	2.320
Cp′L$_2$MnHSiFPh$_2$	neutron[20,23]	1.801	1.570	2.351
Cp′LL′MnHSiCl$_3$	calcd	1.833	1.580	2.288
(CO)$_5$MnH	neutron[11]		1.601	
	calcd		1.585	

[a] Abbreviations: Cp′ = η^5-C$_5$H$_4$CH$_3$, L = CO, L′ = PMe$_3$.

plane.[10] The LUMO of the [Cp(CO)$_2$Mn] fragment is the predominantly metal d$_{z^2}$ orbital **9**, and because this orbital has little interaction with the CO and Cp$^-$ ligands, it is set up to be a strong acceptor of electron density from the incoming ligand donor orbital on the *z* axis. The acceptor ability of this orbital is further increased as orbital **8** donates electron density to the ligand. The occupied orbitals that result from interaction of these frontier orbitals of [Cp(CO)$_2$Mn] with HSiCl$_3$ are shown in **10** and **11**. Orbital **10** is an antisymmetric combination of the Mn−Si and Mn−H bonds, localized more toward the Si atom. This orbital is important in the following discussion. Orbital **11** is primarily the rest of the Mn−H bond. These pictures illustrate the dominance of the Mn−Si and Mn−H interactions compared to any residual Si−H interaction. The Cl character in the orbitals occurs because the Cl p orbitals are close in energy to the bond orbital energies, more so for **11** than for **10**.



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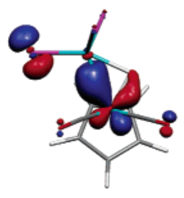

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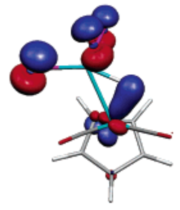

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The Mn−H, Mn−Si, and Si−H interatomic distances in MeCp(CO)$_2$MnHSiCl$_3$ and related molecules are compared with values calculated in this study in Table 1. Schubert has discussed these interatomic distances in relation to the strengths of the Mn−H and Mn−Si interactions.[1] The calculated and experimental Mn−H distances are all within the range of a normal covalent Mn−H bond,[11] except for the very short Mn−H distance from the X-ray diffraction study,[12] where it is known that bond distances involving hydrogen determined by X-ray diffraction are systematically too short.[13] Schubert points out that the Mn−Si bond distance is sensitive to the substituents on Mn and Si and that this distance is the most reliable structural indication of the strength of bonding.[1] The sensitivity of the Mn−Si distance to chemical substitutions is supported by the shorter Mn−Si distance calculated for the molecule where CO is substituted by phosphine (Table 1). It is noted that the experimental Mn−Si distance for MeCp(CO)$_2$MnHSiCl$_3$ is the shortest Mn−Si bond distance known.[14] The calculations underestimate the shortness of this bond, giving a Mn−Si distance 0.07 Å longer than that measured experimentally for MeCp(CO)$_2$MnHSiCl$_3$, a result similar to other DFT calculations.[15]

Table 2. Experimental and Calculated Ionization Energies (eV) and Characters of Cp(CO)$_2$MnHSiCl$_3$

source	ionization	energy	character
PES[4]	1st	8.69	Mn/CO
calcd	HOMO	8.73	90% Mn/CO
PES[4]	3rd	9.32	0−20% Mn
calcd	HOMO-2	9.17	30% d$_{yz}$

In terms of electronic structure, the calculations accurately reproduce the energy and the character of the first ionization as measured by gas-phase photoelectron spectroscopy (Table 2). In agreement with the simple frontier orbital model, the HOMO of Cp(CO)$_2$MnHSiCl$_3$ is the predominantly metal d$_{xz}$ orbital. The orbital **10** that derives from the HOMO of the [Cp(CO)$_2$Mn] fragment (orbital **8**) is stabilized to the HOMO-2 position by bonding and delocalization to HSiCl$_3$. In comparison to the photoelectron data, the calculations appear to slightly underestimate the stabilization and delocalization of the third ionization. The slight underestimation of this bonding interaction by the calculations is consistent with the calculated Mn−Si bond length that is slightly too long. Even with the underestimation of the Mn−Si interaction, the direct H−Si bonding interaction is not a predominant feature in the electronic structure of Cp(CO)$_2$MnHSiCl$_3$. To illustrate, the calculated H−Si bond population in Cp(CO)$_2$MnHSiCl$_3$ is reduced by 75% from the calculated H−Si bond population in HSiCl$_3$.

Experimental and calculated *J*(Si−H) NMR coupling constants[16] are compared in Table 3. The general magnitudes and trends of the coupling values for these systems are modeled well, even though the calculations do not include solvent effects, which have been shown to be important in some systems with metals.[17] For

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[10] Orbital displays created by the program Molekel: Portmann, S.; Lüthi, H. P. *Chimia* **2000**, *54*, 766. Orbitals are shown with surface values of ±0.07, the density **12** is shown with a surface value of 0.08, and the density difference **13** is shown with surface values of ±0.005. In the pictures, the carbonyls are projecting toward the viewer, and the cyclopentadienyl ring is behind and below the metal atom. The coordinate system is defined with the *x* axis bisecting the carbonyls, the *y* axis in the plane of the carbonyls, and the *z* axis pointing toward the vacant coordination site.

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[12] Schubert, U.; Ackermann, K.; Kraft, G.; Woerle, B. *Z. Naturforsch.* **1983**, *38B*, 1488.

[13] Bond distances involving hydrogen are systematically underestimated by X-ray diffraction: Koetzle, T. F. *Trans. Am. Crystallogr. Assoc.* **1997**, *31*, 57.

[14] ConQuest search for all Mn−Si bonds, Cambridge Structure Database, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

[15] Choi, S. H.; Feng, J.; Lin, Z. *Inorg. Chem.* **2000**, *19*, 2051.

[16] For calculation of the *J*(Si−H) coupling constants at the optimized geometries, all-electron relativistic calculations were carried out with core precision set to 6 and the ZORA relativistic model: (a) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597. (b) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101*, 9783. (c) van Lenthe, E.; Ehlers, A. E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943. Only the Fermi contact contributions are reported. Trial calculations showed that inclusion of the spin-dipolar and diamagnetic and paramagnetic orbital contributions only changed the couplings by about 1 Hz.

[17] (a) Autschbach, J. A.; Ziegler, T. *J. Am. Chem. Soc.* **2001**, *123*, 3341. (b) Autschbach, J. A.; Ziegler, T. *J. Am. Chem. Soc.* **2001**, *123*, 5320.

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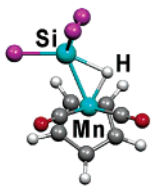
Table 3. Experimental and Calculated J(Si−H) NMR Coupling Constants (Hz)

	NMR	calcd[16]
$HSiCl_3$[21]	370	−338
$(CO)_4Fe(H)(SiCl_3)$[22]	21.7	16
$MeCp(CO)_2MnHSiCl_3$[23,24]	54.8	−38 (−46[a])
$MeCp(CO)(PMe_3)MnHSiCl_3$[23]	20	−22

[a] Value calculated at experimental Mn−Si distance.

$HSiCl_3$ the J(Si−H) coupling value is quite large at over 300 Hz, with the negative sign of the calculated value due to the negative magnetogyric value of Si. The J(Si−H) coupling in $(CO)_4Fe(H)(SiCl_3)$ is on the order of 20 Hz, as is typical for a classical metal hydride silyl, with the sign now positive from the contribution of a two-bond coupling interaction. The J(Si−H) couplings in the Mn complexes are intermediate between these values, being a subtle balance of these two interactions. Considering the value of the experimental coupling constant in $MeCp(CO)_2MnHSiCl_3$ in relation to those of $HSiCl_3$ and $(CO)_4Fe(H)(SiCl_3)$, the extent of weakening of the Si−H bond and formation of a metal hydride silyl is estimated to be 80% complete in $MeCp(CO)_2MnHSiCl_3$. Using the calculated values for the coupling constants, the oxidative addition is estimated to be 85% complete. Both estimates are in excellent agreement with the 75% loss of the Si−H bond population found in the electronic structure calculations and the greater than 80% oxidative addition indicated by the photoelectron spectra. As a note of caution, shortening the Mn−Si distance to the experimental value (Table 1) shifts the calculated coupling constant toward the $HSiCl_3$ value rather than toward the complete oxidative addition value. This underscores the point also made by Nikonov et al. that the coupling constants are a combination of contributions that do not necessarily reflect in detail the extent of oxidative addition.[18] In any event, the orbital descriptions based on NMR coupling constants, photoelectron spectra, and calculations are all in agreement.

Of course any orbital description is an approximation of the electronic structure, but the electron distributions discussed above also can be demonstrated by examination of the total electron density. In principle, the exact total electron density can be obtained from density functional calculations. As shown by the contour of the total electron density in **12**, the Mn−hydride interaction is well formed in comparison to the other bonds in the molecule. Even more revealing is the change in the total density of the molecule from the total densities of the $[Cp(CO)_2Mn]$ and $HSiCl_3$ fragments, as shown in **13**. The surfaces in blue show the regions with depletion of electron density with bond formation, and the surfaces in red show the regions of charge buildup. Density is taken from the predominantly d_{yz} fragment orbital **8** and from the Si−H bond region and is used to build up density in the Mn−H/Mn−Si bond region and the d_{z^2} orbital. The redistribution of charge to optimize the bonding is synergistic, in that a large donation of density from the d_{yz} orbital into the ligand helps promote a large acceptance of electron density into the d_{z^2} orbital.



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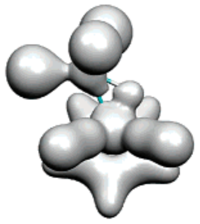
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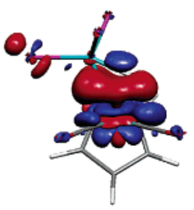
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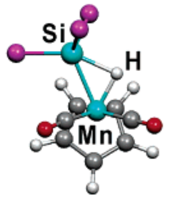
Returning to the valence bond models, the molecular orbitals can be transformed to a set of localized electron pairs for comparison to localized valence bonds. Localized orbital **14** is a well-formed Mn−Si bond. Localized orbital **15** is a well-formed Mn−hydride bond with some polarization toward the Si center. This polarization was not observed in the original Fenske−Hall calculations,[4] which do not include polarization functions on H. The frontier orbitals **8** and **9** of $[Cp(CO)_2Mn]$ available for forming these bonds are primarily the d_{z^2} and d_{yz} orbitals, and the hybrid $(d_{z^2} + d_{yz})$ and $(d_{z^2} - d_{yz})$ orbitals are evident in **14** and **15**. Interestingly, the angle between pure $(d_{z^2} + d_{yz})$ and $(d_{z^2} - d_{yz})$ hybrid orbitals is 49.1°,[4] and the experimental Si−Mn−H angle is 49.9°.[12] In terms of selecting a single valence bond representation, these localized orbitals look most like valence bond representation **4**, with the silyl and hydride ligands located at the optimum coordination sites for the available metal d hybrid orbitals and with donation of hydride density toward the silyl ligand. This might be viewed as an interligand hypervalent interaction (IHI), as described by Nikonov et al. for silyl hydrido complexes of Ta.[18] Valence bond representations **3** and **7** may also be reasonable models of the localized orbitals, depending on personal preference. However, any simple valence bond models of organometallic molecules, depending on how they are interpreted, can be controversial. Caution also must be exercised in the interpretation of NMR coupling constants.[18] The frontier molecular orbital approach, combined with photoelectron measures of energies and electron distributions, provides a description of the electronic structure and



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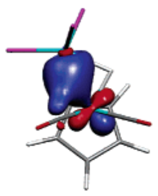
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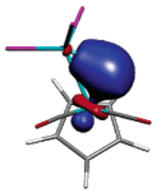
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[21] Measured from ^1H NMR of 20 vol % $HSiCl_3$ in d_6-benzene with a Bruker DRX 500 spectrometer at 25 °C. In $CDCl_3$ the J(Si−H) coupling constant varies from 367 Hz at 22 °C to 369 Hz at −50 °C on a Varian Unity 300 spectrometer.

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[24] For confirmation, we determined this coupling constant to be 57.7 Hz in d_8-toluene at 298 K using the HMQC pulse sequence (Bax, A.; Subramaniam, S. *J. Magn. Reson.* **1986**, *67*, 565).

bonding of $MeCp(CO)_2MnHSiCl_3$ that is supported by presently available electronic structure calculations and is consistent with the known properties of this molecule.

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