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View from the bridge: a pseudo-Jahn–Teller approach to transition metal hydrosilane complexes†

Martin J. Paterson,[a] Nicholas P. Chatterton[b] and G. Sean McGrady[c]

[a] *Department of Chemistry, Imperial College London, Exhibition Road, London, UK SW7 2AZ*
[b] *Departement de Recherche Fondamentale sur la Matière Condensée, CEA-Grenoble, 38054 Grenoble, Cedex 09, France*
[c] *Department of Chemistry, University of New Brunswick, Fredericton NB, Canada E3B 6E2. E-mail: smcgrady@unb.ca*

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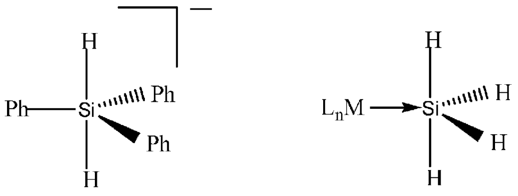
The model complex [Cp(CO)$_2$Mn(SiH$_4$)] has been studied by time-dependent DFT methods: hence, it is shown to be unstable with respect to a pseudo-Jahn–Teller distortion which brings an equatorial Si–H moiety into contact with the Mn centre.

Instability in high-symmetry molecular configurations with non-degenerate ground states has traditionally been treated by valence bond (VB) methods, employing concepts such as localized electron pairs and VSEPR theory. More recent molecular orbital (MO) methods have taken a different approach, considering this instability to arise from a pseudo-Jahn–Teller (pJT) interaction, in which a low-lying excited state can mix in to the ground state by distortion of the system to lower symmetry.[1] Such a pJT approach has been employed successfully to predict and rationalise a range of low-symmetry phenomena in several areas of inorganic chemistry. These span such diverse topics as structural distortions in the solid state,[2] molecular fluxionality[3] and electron delocalisation in mixed-valence compounds.[4] A pJT approach is often illuminating in offering an alternative view of a situation which is inadequately explained by simple VB considerations. This is particularly true in the non-classical realm of organometallic chemistry, and the deficiencies of such an approach have been specifically noted for hydrosilane complexes,[5] as well as for the related phenomenon of agostic bonding.[6] Thus, while a VB analysis may lead to the correct structural conclusions, greater insight can be gained into the electronic processes at work by examining also why alternative structures are disfavoured. In this paper, we explore the bonding in a model transition metal (TM) hydrosilane complex using a pJT approach, which reveals how the complex is stabilised by distortion which permits an M–H–Si bridging interaction to develop.

The nature of the interaction between η^2-coordinated hydrosilanes and TM centres has been the subject of considerable debate since [Cp′(CO)$_2$Mn(η^2-HSiHPh$_2$)] (**1**) [Cp′ = (η^5-C$_5$H$_4$Me)] was isolated over three decades ago.[7] These hydrosilane complexes are typically prepared photochemically: time-resolved infrared spectroscopic studies by Harris *et al.* have shown interaction between the Si–H bonds of silanes and the unsaturated photofragment [Cp(CO)$_2$Mn] to occur within a few picoseconds of its generation.[8] The Si–H bonds in these complexes are lengthened by *ca.* 20% on coordination to around 1.8 Å, with $J_{\mathrm{Si,H}}$ values being reduced to around one-third of the values in the free silane.[9] Both of these parameters imply a situation where oxidative addition of the Si–H bond has been arrested at an intermediate stage. An adapted version of the Dewar–Chatt–Duncanson (DCD) model[10] is usually used to treat the bonding in these species.[11] However, although the DCD approach is adequate for simple types of σ-bond complex such as molecular H$_2$ systems, hydrosilane complexes present a rather sterner challenge. Here, factors such as the proclivity of Si to engage in hypervalent interactions also play an important role.[12] Nikonov and co-workers have isolated a series of hydrosilane complexes displaying 'interligand hypervalent interactions' (IHIs) between adjacent silyl and hydride ligands.[13] Although oxidative addition of the Si–H moiety is formally complete in these systems, they display short Si···H contacts and relatively high $J_{\mathrm{Si,H}}$ values: electron donation is presumed to occur from the basic hydride ligand into a σ* orbital on the geminal silyl ligand. Sabo-Etienne *et al.* have identified similar secondary Si···H interactions in the solid state, which manifest themselves in sterically unfavourable ligand dispositions about a TM centre.[14]

The coordination environment at the Si atom in hydrosilane complexes is invariably a distorted trigonal bipyramid (TBP).[9] For example, [Cp′(CO)$_2$Mn(η^2-HSiFPh$_2$)] (**2**) displays an H–Mn–Si–F torsional angle of 174.1°,[15] revealing the F atom to lie in the same plane as the Mn–Si–H moiety. Distortion from a regular TBP involves migration of the H atom towards the Mn centre ($\angle$H–Si–F = 148.8(2)° in **2**). Such a silicon-centered view of hydrosilane complexes permits us to compare their structures with conventional hypervalent species like [H$_2$SiPh$_3$]$^-$ (**3**),[16] in which the Si atom displays a regular TBP coordination environment; as well as with hypothetical complexes of the form [L$_n$MSiH$_4$] (**4**) in which a dative σ-bond is formed between Mn and Si, as shown in Chart 1. In fact, a complex of the type **4** was invoked by Nikonov to describe the extreme case of negligible ligand-to-metal donation but complete metal-to-ligand back-donation.[17]



3 **4**

Chart 1

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† Electronic supplementary information (ESI) available: atomic coordinates (B3LYP/6-31++G** level) for [Cp(CO)$_2$Mn(SiH$_4$)] at the TBP constrained and fully optimised geometries. See http://www.rsc.org/suppdata/nj/b4/b412371a/

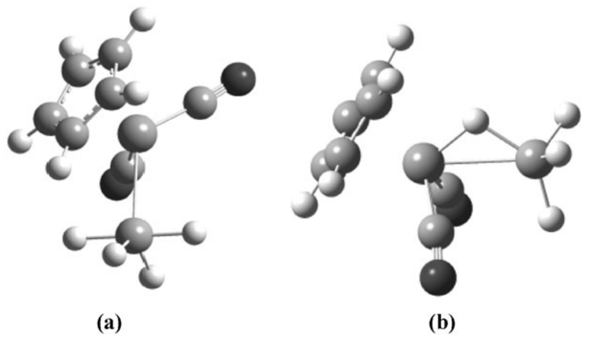

Fig. 1 Optimised B3LYP/6-31++G(d,p) geometries of [Cp(CO)$_2$Mn(SiH$_4$)] (5): (a) all geometrical parameters optimised with Si constrained to TBP coordination, and (b) in the full space of coordinates, corresponding to the minimum energy structure.

In the light of this rich bonding motif displayed by silicon in its TM complexes, we decided to investigate the bonding in a model hydrosilane complex without any preconceptions. Accordingly, we have used DFT calculations to explore the electronic changes occurring when the model system [Cp(CO)$_2$Mn(SiH$_4$)] (**5**) [Cp = (η^5-C$_5$H$_5$)] relaxes to its minimum energy from a enforced regular TBP geometry at Si.

The geometry of [Cp(CO)$_2$Mn(SiH$_4$)] (**5**) was optimised using the Gaussian program suite.[18] The popular B3LYP exchange/correlation functional[19] was used in conjunction with a 6-31++G(d,p) basis set. The structure was optimised in the full space of nuclear coordinates and in the constrained TBP space, in which the Si atom was restricted to TBP coordination; *i.e.* $\angle$H$_{eq}$–Si–H$_{eq}$ = 120° and $\angle$H$_{eq}$–Si–H$_{ax}$ = 90°. The fully optimised structure was confirmed as a minimum on the potential energy surface by computing the analytical Hessian matrix and by observing that all eigenvalues were positive. Time-dependent density functional theory (TD-DFT) computations were performed at both the fully optimised structure and the TBP constrained structure. In this way, the manifold of low-lying electronic states was obtained for each geometry. By examining the dominant single particle-hole states using the canonical Kohn–Sham orbitals, we were able to correlate the states along the coordinate connecting the two structures.

The geometries of [Cp(CO)$_2$Mn(SiH$_4$)] (**5**) resulting from the DFT calculations are shown in Fig. 1. Fig. 1(a) shows the structure with the Si centre constrained to TBP coordination, while Fig. 1(b) displays the minimum energy structure in the full space of coordinates. The main geometrical change on going from (a) to (b) is the migration of an equatorial hydrogen atom along the Si–Mn bond to take up a bridging position. Indeed, structure optimisation starting from geometry (a) follows a gradient leading to the minimum (b) which involves only the motion of this H atom, with concomitant slight rotation of the Mn ligand sphere. Hence, the results of our computations can be interpreted in terms of a pJT interaction at the TBP geometry. The pJT effect is often considered as a lowering of the energy of the HOMO induced by mixing with the LUMO. The interaction then depends on the HOMO–LUMO energy gap and on the symmetry of these orbitals and the vibrational coordinate which links them.[20] However, the pJT effect is more properly considered as a vibronic interaction of all close-lying electronic states.[3,21,22] (see ref. 21 for a proper CASSCF based state description of the pJT effect). Unfortunately, large TM complexes necessitate a more approximate treatment of the excited electronic states.

We have used time-dependent density functional theory (TD-DFT) to compute and characterise the various low-lying excited states at both geometries shown in Fig. 1. At the constrained TBP geometry (a) there are three very low-lying excited states, at energies of 1.136, 1.247 and 1.505 eV above the ground state. These three excited states can all interact vibronically with the ground state, but the next one at 3.034 eV is too high in energy. The single particle–hole states contributing to these three excited states involve occupancy of the LUMO (see the configuration numbers on the left of Fig. 2(b), where c_i^j is the weight of the configuration with orbital j occupied in place of orbital (i). Thus, the formalism used here reduces to a HOMO–LUMO interaction when only a subset of excited states is considered. Indeed, the first excited state at 1.136 eV has the HOMO–LUMO excitation as the configuration with the largest weight (0.449). At the TBP geometry, the orbitals involved in the ground and excited states are shown schematically in Fig. 2(a). These orbitals are delocalised over all six atomic centres in the MnSiH$_4$ moiety. They have the

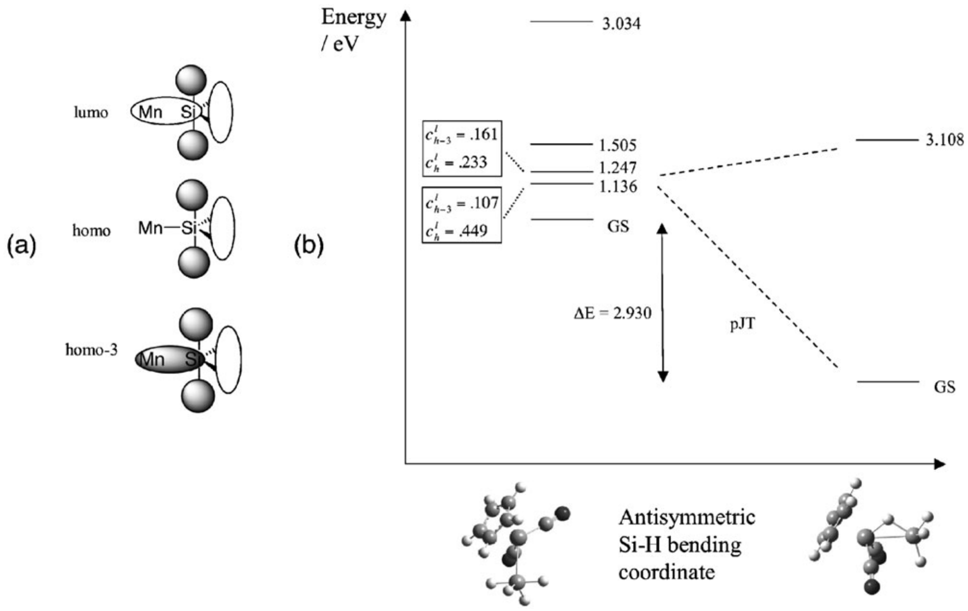

Fig. 2 (a) Primary orbitals involved in the lowest excited states of [Cp(CO)$_2$Mn(SiH$_4$)] (5) at the TBP geometry, (for simplicity only the Si–H bonding phase is shown), and (b) state correlation diagram showing the pJT distortion from TBP to fully relaxed structure. Orbital configuration numbers for the two lowest excited states are given to the left. The coordinate from left to the right in this plot is an antisymmetric Si–H$_{eq}$ bending vibration which stabilises the LUMO (occupied in the three lowest excited states at the TBP geometry).

same axial–equatorial nodal structure, but differ in their bonding character with respect to the Mn–Si σ-bond. HOMO-3 is antibonding between the two equatorial Si–H bonds and the Mn–Si σ-bond, whereas the HOMO is non-bonding and the LUMO is bonding with respect to the same centres. The LUMO also contains significant Si–H antibonding character. Thus, while a bonding interaction between the Mn–Si σ-bond and the closer Si–H_{ax} moieties is precluded in the LUMO, this is not the case for the distal Si–H_{eq} bonds.[23] The two lowest lying excited states involve excitations from the HOMO-3 and the HOMO to the LUMO. These exited states thus impart Mn–H_{eq}–Si bonding character to the molecule. The coordinate which permits the HOMO–LUMO interaction is the antisymmetric bending vibration of the two Si–H_{eq} ligands. At the true energetic minimum, the lowest excited state lies 3.108 eV above the ground state. Thus, a lowering of the ground state energy by 2.93 eV along the Si–H–Mn coordinate is accompanied by an increase in the energy of the lowest excited states. The corresponding Si–H_{eq} antibonding orbital (correlating with the TBP LUMO) is the HOMO-2 at the fully optimised minimum.

In summary, the constrained structure of **5** in Fig. 1(a) represents a donor–acceptor complex between the Lewis acid SiH_4 and the Lewis base [Cp(CO)$_2$Mn]. We have shown such a situation to be unstable with respect to a pJT distortion which brings an equatorial Si–H moiety towards the Mn centre. Such a situation contrasts with $[H_2SiPh_3]^-$ **3**, for which we have carried out analogous TD-DFT calculations. These show the TBP geometry to be the minimum energy structure, with a HOMO–LUMO gap of 3.81 eV, and an excited state gap of 3.57 eV.

References

1 I. B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds. Introduction to the Theory*, Wiley, New York, 1996.
2 J. K. Burdett, *Molecular Shapes*, Wiley, New York, 1980.
3 I. B. Bersuker, *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry*, Plenum, New York, 1984.
4 I. B. Bersuker and S. A. Borshch, in *Advances in Chemical Physics*, eds. I. Prigogine and S. A. Rice, Wiley, New York, 1992, **Vol. 81**.
5 D. L. Lichtenberger, *Organometallics*, 2003, **22**, 1599.
6 W. Scherer and G. S. McGrady, *Angew. Chem., Int. Ed.*, 2004, **43**, 1782.
7 W. Jetz and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 4.
8 H. Yang, K. T. Kotz, M. C. Asplund, M. J. Wilkens and C. B. Harris, *Acc. Chem. Res.*, 1999, **32**, 551.
9 U. Schubert, *Adv. Organomet. Chem.*, 1990, **30**, 151.
10 (*a*) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939; (*b*) M. J. S. Dewar, *Bull. Soc. Chim.*, 1951, **18**, C79.
11 (*a*) M.-F. Fan, G. Jia and Z. Lin, *J. Am. Chem. Soc.*, 1996, **118**, 9915; (*b*) M.-F. Fan and Z. Lin, *Organometallics*, 1997, **16**, 494; (*c*) M.-F. Fan and Z. Lin, *Organometallics*, 1999, **18**, 286.
12 R. H. Crabtree and D. G. Hamilton, *Adv. Organomet. Chem.*, 1988, **28**, 299.
13 See for example: G. I. Nikonov, L. G. Kuzima and J. A. K. Howard, *J. Chem. Soc., Dalton Trans.*, 2002, 3037.
14 (*a*) K. Hussein, C. J. Marsden, J.-C. Barthelat, V. Rodriguez, S. Conejero, S. Sabo-Etienne, B. Donnadieu and B. Chaudret, *Chem. Commun.*, 1999, 1315; (*b*) F. Delpech, S. Sabo-Etienne, J.-C. Daran, B. Chaudret, K. Hussein, C. J. Marsden and J.-C. Barthelat, *J. Am. Chem. Soc.*, 1999, **121**, 6668.
15 U. Schubert, K. Ackermann and B. Worle, *J. Am. Chem. Soc.*, 1982, **104**, 7378.
16 M. J. Bearpark, G. S. McGrady, P. D. Prince and J. W. Steed, *J. Am. Chem. Soc.*, 2001, **123**, 7736.
17 G. I. Nikonov, *Organometallics*, 2003, **22**, 1597.
18 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian Development Version (Revision B.07)*, Gaussian, Inc., Pittsburgh, PA, 2003.
19 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1293.
20 T. A. Albright, J. K. Burdett and M.-H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, 1985.
21 M. J. Bearpark, L. Blancafort and M. A. Robb, *Mol. Phys.*, 2002, **100**, 1753.
22 I. B. Bersuker, *Chem. Rev.*, 2001, **101**, 1067.
23 Although The Mn···H_{eq} distance (3.6 Å) is greater than the Mn···H_{ax} one (3.1 Å), the difference is not large.