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Unexpected features of stretched Si–H···Mo β-agostic interactions†‡

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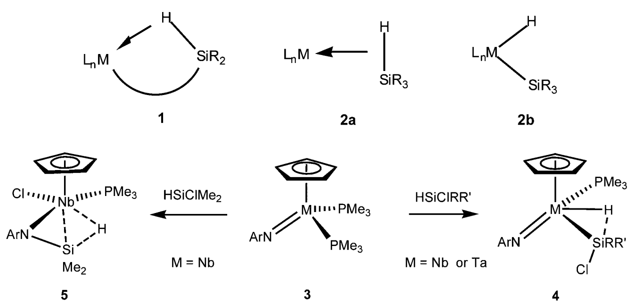
Received (in Cambridge, UK) 1st December 2003, Accepted 12th February 2004
First published as an Advance Article on the web 10th March 2004

Coupling of silanes with the imido group of $(Ar'N)_2Mo(PMe_3)_3$ gives either the silanimine dimer $(ArN–SiHCl)_2$ or Si–H agostic silylamido complexes which do not exhibit the commonly expected correlation between the nature of the substituents on silicon, the degree of Si–H addition and the value of the Si–H coupling constant.

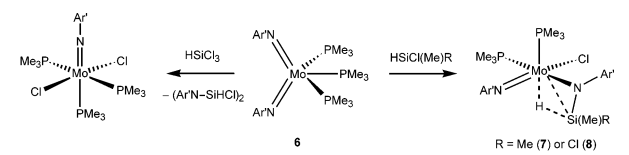
Si–H···M Agostic bonding (schematically represented in **1**) is a relatively recent phenomenon compared to the long-established Si–H bond σ-complexes **2a**.[1–6] Whereas high-order (γ-, δ-) Si–H···M agostic interactions are virtually indistinguishable from σ-bond complexation and can be considered as an intramolecular version of **2a**, much less is known about the bonding in α-[6a,b] and β-Si–H···M agostic species.[2] It is widely accepted[1a,c] that sequential substitution at silicon by electron-withdrawing groups leads to advanced Si–H bond oxidative addition. For σ-bond complexes a *decrease* in Si–H interaction is accompanied by a *decrease* in the magnitude of ^1J(Si–H) from *ca.* 70 Hz in **2a** to below 20 Hz for authentic silyl hydrides **2b**.[1a–d] Considerable importance has been attached to the observed value of ^1J(Si–H) as a means of assessing the extent of Si–H···M interactions.[1c,1d] However, it has very recently been pointed out[7] that Si–H coupling constants measured for species on the **2a**→**2b** reaction coordinate are sensitive to a number of contributions and do not necessarily reflect absolutely the extent of oxidative addition.



We have recently reported that reactions of the d² Group 5 bis(phosphine) imido complexes **3** (Ar = 2,6-diisopropylphenyl) with silanes HSiClRR′ (R, R′ = alkyl and/or Cl) give two types of nonclassical complexes depending on the nature of the metal (Nb, Ta) and R, R′.[8] Complexes **4** (d⁰) feature a M–H···Si interligand hypervalent interaction and **5** (d²) possesses a stretched β-Si–H···Nb agostic interaction. Remarkably for **4** we found that *increased* chlorine substitution at silicon led to an *increase* in ^1J(Si–H) (range 30–50 Hz) but to a *decrease* in Si–H bonding, *i.e.* the *opposite* to that expected for common σ-bond complexes **2a**→**2b**.

The question of how electronegative substituents at silicon affect the strength of Si–H···M interactions, and the associated Si–H coupling constants, in the more widespread agostic complexes of the type **1** has so far remained unprobed. Since this issue cannot be resolved for the complexes **5** (because the reaction of **3** with more chlorinated silanes gives only silyl hydrides **4**) we turned to the related bis(imido) complexes $(RN)_2Mo(PMe_3)_3$ (Cp^- ligand is isolobal to the $(RN)^{2-}$ ligand). Here we present preliminary results of a comprehensive NMR, X-ray and DFT study of stretched β-Si–H agostic complexes of molybdenum, which offer for the first time a unique insight into new and unexpected patterns of Si–H···M agostic interactions.

Reactions of $(Ar'N)_2Mo(PMe_3)_3$ (**6**, Ar′ = 2,6-dimethylphenyl) with the chlorosilanes $HSiClMe_2$ and $HSiMeCl_2$ afforded exclusively the structurally characterised‡ β-agostic Si–H···Mo d² complexes **7** (Fig. 1) and **8**, respectively. The analogous reaction of **6** with $HSiCl_3$ resulted in the unprecedented formation of the silanimine dimer $(Ar'N–SiHCl)_2$[9] and $(Ar'N)MoCl_2(PMe_3)_3$. In none of the reactions are simple d⁰ silyl hydride products analogous to **4** formed.



Complex **7** (R = Me) is an analog of the agostic species **5** and exhibits the same ^1J(Si–H) of 97 Hz. Contrary to expectations based on the trends observed in the previously studied systems,[1] introduction of an electron-withdrawing group in **8** (R = Cl) does not decrease the value of the coupling constant ^1J(Si–H), rather it increases significantly to 129 Hz. Such a trend is normally indicative of a strengthening of the Si–H interaction (shorter Si–H bond) and a corresponding lengthening of the M–Si and M–H bonds.[1] However, examination of the X-ray structures‡ of isomorphous **7** and **8** (selected bond lengths listed in Table 1) does not support this view since they possess virtually identical Mo–H, Si–H and Mo–Si bond distances. Indeed, if anything, there is in fact a marginal shortening of the Mo–Si bond on going from **7** to **8**. In the case of complexes of the type **1** and **2a/b** such a shortening would

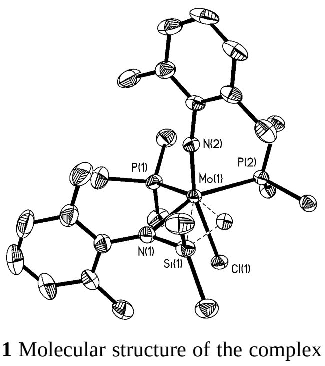


Fig. 1 Molecular structure of the complex **7**.§

DOI: 10.1039/b315517j

† Dedicated to Professor Malcolm Green, colleague and mentor, in recognition of his contributions to the chemistry of agostic compounds.
‡ Electronic supplementary information (ESI) available: details of preparations, X-rays studies, DFT calculations and ORTEP Figure for **8**. See http://www.rsc.org/suppdata/cc/b3/b315517j/

Table 1 DFT calculated bond lengths (in Å) for (MeN)(MeNSiMe$_{2-n}$Cl$_n$–H)Mo(Cl)(PMe$_3$)$_2$ (n = 0–2)

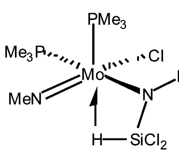
Bond\SiR$_2$	SiMe$_2$ (**9**)^a	SiMeCl (**10**)^a	SiCl$_2$ (**11**)	SiCl$_2$ (**11a**)
Mo–Si	2.673 [2.668(1)]	2.662 [2.657(1)]	2.661	3.093
Mo–N(Si)	2.092 [2.122(3)]	2.112 [2.157(4)]	2.137	2.142
Mo–P^b	2.453 [2.482(2)]	2.443 [2.474(2)]	2.431	2.496
Mo–H	1.953 [1.92(4)]	1.992 [1.93 (4)]	2.085	—
Mo–Cl	2.620 [2.551(1)]	2.613 [2.538(1)]	2.562	2.534
Si–H	1.618 [1.54(4)]	1.589 [1.51(3)]	1.558	1.493
Si–N	1.716 [1.676(4)]	1.684 [1.643(4)]	1.666	1.678

^{a} Experimental values for **7** and **8** in brackets; the Si–H atom was located from difference maps and refined. ^{b} PMe$_3$ *trans* to Mo···H–Si.

normally be rationalized in terms of a more advanced oxidative addition of the H–Si bond to the metal which clearly contradicts the increase in ^1J(Si–H) from **7** to **8**.

To shed more light on these apparently conflicting results we carried out DFT calculations on the model complexes (MeN)(MeNSiMe$_{2-n}$Cl$_n$–H)MoCl(PMe$_3$)$_2$ (n = 0 (**9**), 1 (**10**), 2 (**11**)).‡ The optimized structures for **9** (model for **7**) and **10** (model for **8**) are in good accord with the experimental ones (Table 1). As the number of Cl groups on the silicon atom increases, the Mo–Si bond lengths decrease only slightly and, unexpectedly, become slightly weaker, as evidenced by the decrease in the Wiberg bond indices (WI = 0.1471 for **9**, 0.1445 for **10** and 0.1426 for **11**).[10]‡ Moreover, increased chlorine substitution does not tend towards cleavage of the Si–H bond. In fact, the Si–H bond contracts and strengthens (WI = 0.5830 for **9** *versus* 0.6171 for **10** and 0.6649 for **11**), whereas the Mo–H bond length increases from 1.953 Å to 2.085 Å and weakens (WI = 0.2190, 0.1888, 0.1453 from **9** to **11**). This is also reflected in the Mo–P bond length to the PMe$_3$ *trans* to Mo···H–Si, which becomes shorter and stronger as the Si–H binds less strongly.

An AIM (atoms in molecules) analysis[11] of **9–11** revealed a bifurcated topological structure with a Mo–Si bond critical point (r_c) coalescing with the ring critical point (3,+1), leading to a degenerate critical point structure. As is typical for agostic systems[12] the M–H bond critical point has a large ellipticity, which increases from **9** to **11** (1.547 to 6.880), thus confirming the weakening of the Mo–H bond. In contrast, the Si–H bond strengthens as the number of Cl groups increases, as shown by a significant decrease of the energy density values[11b,c] from −0.3682 to −0.4540 hartree Å^{-3}.‡



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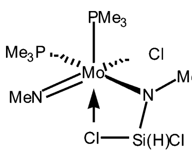

11a

The formation of (Ar′N–SiHCl)$_2$ and (Ar′N)MoCl$_2$(PMe$_3$)$_3$ (rather than a product analogous to compounds **7** and **8** and model **11**) in the reaction with HSiCl$_3$ provides further insight into this system. Optimization of the Si–Cl···Mo bonded structure **11a** (model for a likely intermediate) gave an energy only *ca.* 1 kcal above that of agostic **11**. This is accounted for by the expected increase in Si–H bond strengths on increased Cl substitution at silicon due to increased Si 3s contribution in accordance with the Bent's rule.[13] β-Cl elimination from the real intermediate corresponding to **11a** would ultimately yield the observed products (Ar′N–SiHCl)$_2$ and (Ar′N)MoCl$_2$(PMe$_3$)$_3$.

These surprising results can be rationalized by a Dewar–Chatt–Duncanson (DCD) model (Chart 1) adjusted by Bent's rule.[7b] Sequential substitution of the Me groups on Si for an electron-withdrawing Cl group provides more Si 3s character in the Si–H bond,[13] contracting this bond and making it a worse σ-donor, and thus decreasing the donation component in the DCD scheme. This, and the increased Si 3s character, account for the increase in the Si–H coupling constant from **7** to **8**. On the other hand, introduction of the Cl groups, makes the Si atom more Lewis acidic, thus

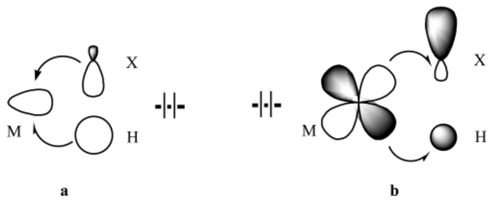

Chart 1 DCD model for the Si–H···M bonding

increasing Mo→(H–Si) σ* back-donation.[1a,1c] These changes affect the Mo–Si and Mo–H interactions unevenly, since the Si–H bonding orbital is more localized on the H atom, whereas the (Si–H) σ* orbital has a bigger contribution from Si.

GIN is grateful to the Royal Society of Chemistry for an International author Award and INTAS for a YS INTAS fellowship. SKI and AGR thank RFBR for financial support (project 03-03-33120). PM and GIN thank the Royal Society (London) for generous support.

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§ CCDC 226162 and 226263. See http://www.rsc.org/suppdata/cc/b3/b315517j/ for crystallographic data in .cif or other electronic format.

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