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Competing Metal−π-Acetylene and Metal−σ-(H−Si) Interactions in the Complex $Ti(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}\mathit{trans}\text{-}RC{\equiv}CSiHR_2)$

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Summary: The titanocene−acetylene complex $TiCp_2(\eta^2\text{-}trans\text{-}{}^tBuC{\equiv}CSiHMe_2)$ shows a significant bending of the H−Si bond toward the metal center. Ab initio theoretical calculations are used to clarify the interplay between the coordinated C≡C and H−Si bonds. Analysis of the density Laplacian suggests that the complex is better formulated as having a d^2 metal center. The complex is another elegant example manifesting the strong σ-accepting nature of the H−Si bond.*

Introduction

The coordination of σ and π bonds to transition-metal centers has been an active area of research for many decades, and the study of σ complexes in particular has been driven by the ultimate goal of C-H bond activation.[1] Examples of π complexes include those of ethylene and acetylene,[2] and exemplary σ complexes include those of H_2,[3] C−H (agostic),[4] and H−Si.[5] The bonding in such complexes is usually described by the Dewar−Chatt−Duncanson bonding−back-bonding model,[2,6] unifying the bonding descriptions of terminal π-acceptor, η^2-π, and η^2-σ complexes. The widely studied dihydrogen complexes generally fall into two classes: "nonclassical" with H−H bond lengths approaching that of free H_2 (usually ~0.8 Å) and "classical" with H−H distances over 1.6 Å (although a few examples show an intermediate H−H distance of ~1.3 Å,[3c,d,5c] the bonding in such types of "stretched H_2 complexes" is still not fully understood). This dichotomy is due to the high energy of the H−H σ* orbital, so that populating this orbital breaks the H−H bond readily. In contrast, most of the known "nonclassical" silane complexes have H−Si bond lengths of 1.65−1.85 Å,[5] which are significantly longer than the free silane H−Si bond length of 1.48 Å. It has been demonstrated that such lengthening of the H−Si bond is due to its low-lying σ* orbital, giving the H−Si moiety strong σ*-accepting character.[5c,d]

From the results given above, a truly "nonclassical" H−Si complex can be expected only when there is no back-bonding, i.e., a d^0 system. We are excited by the complex $TiCp_2(\eta^2\text{-}trans\text{-}{}^tBuC{\equiv}CSiHMe_2)$ (**3**), recently synthesized by Rosenthal *et al.*[7a] In one extreme, it could be formulated as a d^0 system if the acetylene is considered to withdraw two electrons from the metal (the metallacyclopropene formulation). Thus, one would expect no back-donation from Ti to the H−Si σ*, and the X-ray-determined H−Si distance of 1.42 Å indeed suggests that the complex is a truly "nonclassical" one. Still, the drastic bending of the H−Si bond toward the metal center, in contrast to the corresponding acetylene complex **4**,[7] which shows *cis* deformations *away* from the metal center, undoubtedly indicates a very strong Ti−(H−Si) interaction. The other extreme of a d^2 metal center for **3** (the π complex formulation) would allow the two metal d electrons to participate in d→σ* back-donation. In addition, if we note that H_2 in "nonclassical" dihydrogen complexes (in which d→σ* back-donation is negligible) is easily displaced,[8] a d^0 metal center for **3** would lead to the apparent dilemma that the Ti−(H−Si) interaction is inherently weak due to the lack of back-bonding. Elucidation of the nature of the Ti−(H−Si) interaction and the electronic configuration of the Ti center is thus very challenging.

In this paper, *ab initio* theoretical calculations are employed to study the interplay between the metal−acetylene and metal−silane interactions of the title compound **3**, with a focus on the structural and electronic effects of the competing metal−acetylene and metal−(H−Si) interactions. The question of whether **3** is a d^0 complex with a truly "nonclassical" Ti−(H−Si) interaction or a d^2 system with a significant Ti d→H−Si σ* back-bonding interaction will be answered.

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Table 1. Selected Structural Data for the Experimental and Various Optimized Structures of 3 (Lengths in Å and Angles in deg)

	exptl	BLYP	B3LYP	MP2
Ti—C(R)	2.162(7)	2.192	2.178	2.133
Ti—C(Si)	2.276(7)	2.375	2.339	2.407
Ti—Si	2.655(2)	2.635	2.617	2.540
Ti—H[a]	1.82(5)	1.875	1.866	1.755
C≡C	1.275(9)	1.298	1.283	1.339
C—Si	1.766(7)	1.792	1.785	1.796
Si—H[a]	1.42(6)	1.660	1.637	1.711
C≡C—Si (inward)	149.5(6)	142.9	144.2	134.6
C≡C—R (outward)	135.2(7)	136.5	138.8	128.4
C—Si—H[a]	98(2)	106.4	105.9	108.4

[a] The significant deviations from experimental results are probably due to the inaccuracy of X-ray locations of H's.

Computational Details

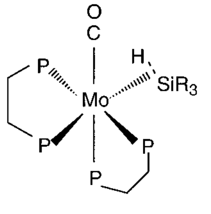
Geometry optimizations of the complex **3** were performed at the density function theory (DFT) and second-order Møller—Plesset perturbation theory (MP2) levels, with the ^{t}Bu and Me groups replaced by H's for theoretical simplicity. The size of the cyclopentadienyl rings and their displacements from Ti were fixed at the experimental averages, as our current focus is only on the competing effect of metal—acetylene and metal—silane interactions. For the DFT levels (BLYP and the SCF-component-augmented B3LYP), all other structural parameters were optimized, while for MP2 an overall C_s symmetry (with the symmetry plane defined by the Ti—acetylene triangle) was also imposed because full geometry optimizations at both the BLYP and B3LYP levels gave an approximate C_s symmetry for the complex (see below). The Cp—Ti—Cp angle was optimized in all cases.

The effective core potential (ECP) of Wadt and Hay[9] with double-ζ valence basis was used for Ti and Si, and the standard 3-21G Gaussian basis set was used for C and H. The acetylene carbons and the hydrogen interacting with the metal center were augmented with standard (d,p) polarization functions (i.e. 3-21G**), and a d polarization function with exponent 0.263 was added to Si.[10]

Ab initio calculations were performed using the Gaussian 94 package[11] on a Silicon Graphics Onyx workstation, and the analysis of valence electron density was done with the MOPLOT package[12] on a Silicon Graphics Indigo2 workstation.

Results and Discussion

In an effort to understand the nature of H—Si σ-bond coordination to transition-metal centers, we have initially carried out *ab initio* calculations on the complex *cis*-Mo(CO)(dppe)$_2$(H—SiR$_3$) (**1**).[13] The *cis* arrangement[14] of the carbonyl and silane is intriguing, because all known H$_2$ complexes with a single CO ligand, in particular *trans*-Mo(CO)(dppe)$_2$(H—H) (**2**) (the corresponding H$_2$ complex of **1**),[15] have *trans* conformations. We have satisfactorily explained that the *cis* preference is due to the strong σ*-accepting ability of the H—Si bond, which has already been recognized in Crabtree's review of σ complexes.[5c] The *cis* arrangement avoids the competition for metal d-electron back-donation between the carbonyl and silane ligands.



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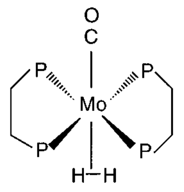

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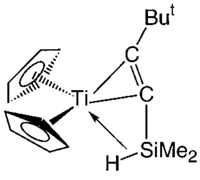

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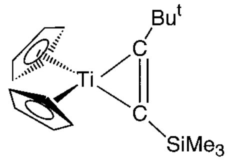

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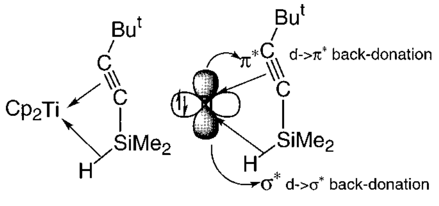

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Ab initio calculations at DFT and MP2 levels were performed on the model system TiCp$_2$(η^2-*trans*-HC≡CSiH$_3$). Important geometrical parameters are listed in Table 1. It is clear that, while the Ti—C(Si) distance is overestimated at various levels (which should not qualitatively affect the discussions below), all qualitative details of the experimental structure are well-reproduced, the agreement of the B3LYP-optimized structure with experiment being particularly good. Specifically, the model system of **3** has both the acetylene and the Si-H bond on the same plane to within theoretical errors, giving an overall C_s symmetry; the Ti—acetylene bonds are highly unsymmetric, with Ti—C(Si) much longer. The significant bending of the H—Si bond toward the metal center is also successfully modeled.

To understand the nature of bonding between the bent-titanocene fragment and the acetylene—(Si—H) ligand in **3**, an analysis of the Laplacian ($-\nabla^2\rho$) of the Hartree—Fock valence electron density[16a] was performed on the plane defined by the Ti—(H—Si) triangle, based on Bader's atoms-in-molecules theory.[16b] Since both the acetylene and H—Si lie on the same plane, the density around C≡C is also shown. In the contour plot

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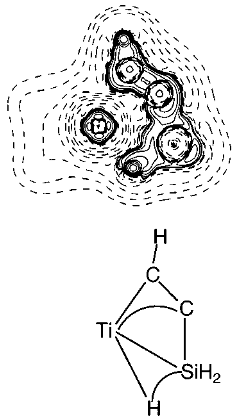

Figure 1. Contour plot of $-\nabla^2\rho$ on the plane Ti—(H—Si). Solid lines represent local electron density concentration ($-\nabla^2\rho > 0$), and dashed lines represent local density depletion ($-\nabla^2\rho < 0$).

of $-\nabla^2\rho$ (Figure 1), two concentrations appear between Ti and C(H), as is usual for a normal covalent bond. The same feature is also observed for Ti—Si, while the bonds Ti—C(Si) and Si—H are weakened significantly. Notably, the H—Si bond path is bent inward to a similar extent as in **1**,[13] showing that the Ti—(H—Si) interaction is rather strong. The Laplacian plot clearly indicates a severe competition between the acetylene and the H—Si moieties, and the direct Ti—Si interaction removes electron density from the Ti—C(Si) bond, thus explaining the rather long Ti—C(Si) bond length as compared with Ti—C(R).

The effect of such competing interactions is clearly manifested by the characteristic bond lengths of the metal-acetylene triangle. A number of *cis*-$TiCp_2$-($RC{\equiv}CSiR'_3$) ($R' \neq H$) complexes, with a silyl group attached to the acetylene but without possible Ti—(H—Si) interactions,[7b,17] show significantly shorter Ti—C bond lengths of ~2.1 Å, compared with that of **3** (Ti—C = 2.162 and 2.276 Å). Their C≡C bond lengths are also slightly longer (1.28—1.31 Å) than that of 1.275 Å in **3**, which has the possibility of a Ti—(H—Si) interaction. This implies that the metal-to-acetylene bonding is significantly weakened by the presence of a Ti—(H—Si) interaction. In other words, the Ti—(Si-H) interaction weakens both the ligand-to-metal σ donation[6b] and the metal-to-ligand π-back-bonding interactions. As for many other metal—silane complexes,[5d,18] the Ti—(Si-H) bonding is dominated by $d \rightarrow \sigma^*$ backdonation, as evidenced by the long Si-H bond length.

The $d \rightarrow \sigma^*$ back-bonding nature of Ti—(Si-H) can be understood by considering the complex **3** as having a d^2 metal center. The d^2-$TiCp_2$ fragment has a low-lying a_1 orbital,[19] which interacts (back-bonds) *simultaneously* with both π^* and σ^* orbitals (see **5**). The Laplacian plot shows that four concentrations appear around the Ti center. This feature can be associated with the "lone pair" a_1 orbital of a bent $TiCp_2$ fragment, indicating a formal d^2 configuration for Ti. In other words, the characteristics of the Laplacian could be derived *mainly* from a spherical core electron density plus the contribution of electron density from electrons occupying one d orbital.[20] It should be noted that alternative interpretations of the Laplacian characteristics are also possible.

The designation of acetylene as a two-electron π-acceptor ligand in this case (see **3**), which results in a formally d^0 configuration, would imply the domination of metal $d \rightarrow \pi^*$ back-bonding by the acetylene. This bonding picture, although a reasonable one, would not be able to account for the existence of a strong Ti—(H—Si) back-bonding interaction as demonstrated above. The theoretical H—Si distance of 1.64—1.71 Å also suggests significant population of the H—Si σ^* orbital.

For transition-metal complexes with multiply bonded ligands (such as oxo, imido, and alkylidene), it is known that two such ligands (both being π acceptors or π donors) will occupy coordination sites such that, if the structural factors allow, competition of the same metal d_π orbital is avoided.[21] It is thus interesting to know how the Ti—(H—Si) interaction can outweigh the unfavorable electronic changes of metal d_π competition and *trans*-deformation of the acetylene. Our calculations suggest that the observed *trans* form of **3** is about 8 kcal mol^{-1} more stable than the *cis* form, which is consistent with the exclusively observed *trans* conformation. This energetic difference further indicates a strong Ti—(H—Si) interaction in the complex.

In conclusion, the complex **3** is better formulated as a d^2 system with comparable back-bonding strengths of the acetylene and H—Si (see **5**), as supported by the characteristics of electron density around the Ti center shown in Figure 1. The competition between the acetylene and the H—Si moiety for coordination to the Ti center is manifested both structurally and electronically. The spectacular structural features of **3** once again confirm the strong σ^*-accepting nature of the H—Si bond.

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