Notes

Stability of the *trans*-Bis(H···Si) Structure in the Complex $RuH_2(PCy_3)_2(\kappa\text{-}\eta^2\text{-}H\cdots SiMe_2\text{-}o\text{-}C_6H_4\text{-}SiMe_2\cdots H)$, Studied by Density Functional Theory

Man-Fai Fan and Zhenyang Lin*

Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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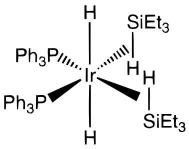
Summary: The complex $RuH_2(PCy_3)_2(trans\text{-}\kappa\text{-}\eta^2\text{-}H\cdots SiMe_2\text{-}o\text{-}C_6H_4\text{-}SiMe_2\cdots H)$ *exhibits a number of intriguing structural features, in particular the apparent trans configuration of the two H···Si units, the nearly collinear axial trans-H−Ru−H bonds, and the adoption of a near-*C_{2v} *symmetry. Theoretical studies indicate that, in the experimental structure, the drastic distortion of the two H···Si units avoids the competition for σ*-back-donation while strengthening both the axial Ru−H and the Ru−Si bonds through a favorable orbital interaction with the metal d-orbitals. Such distortion is enhanced by the presence of chelation which forces a small Si−Ru−Si angle. The H···Si interaction distance is 1.842 Å, and the density Laplacian plot* $(-\nabla^2\rho)$ *reveals that the extent of H···Si interaction is quite weak, with little sign of competition for the metal-to-ligand back-donation. Comparisons with the unchelated model complex* $RuH_2(PH_3)_2(H\cdots SiH_3)_2$ *show that the chelation causes a weaker H···Si interaction, with an H···Si distance of the unchelated complex of ∼1.750 Å.*

The observation of interligand H···Si distances of less than ∼2.0 Å in transition-metal hydrido silyl complexes and the unusually high H−Si coupling constants (50−100 Hz) in ^1H NMR spectroscopy have led to the formulation of η^2-silane complexes similar to the more familiar "nonclassical" η^2-H_2 complexes. Such η^2-(H···Si) complexes are generally considered as intermediates of the important process of hydrosilation, and a number of review papers have appeared.[1] The class of "nonclassical" η^2-silane complexes $MCpL_2(H\cdots SiR_3)$, where M is a group 6 or 7 metal, has been extensively studied both experimentally and theoretically, and it was found that the H···Si σ-bond behaves much like π-acceptors CO and PR_3 in a Dewar−Chatt-like bonding−back-bonding manner, with the metal-to-ligand σ*- or π*-back-donation dominating the bonding picture.[1−3]

Since the characterization of the first unsubstituted η^2-$H\cdots SiH_3$ complex *cis*-Mo(CO)(depe)$_2$(η^2-$H\cdots SiH_3$),[4] the structural peculiarities of η^2-(H···Si) coordination have become more apparent. Several of our previous theoretical studies[5] of such η^2-(H···Si) complexes with early-to-middle transition-metal series have concluded that the H···Si bond is a rather strong σ*-acceptor ligand comparable to the widely recognized π-acceptor ligands such as CO and PR_3. Also, the H···Si complexes examined theoretically thus far have H···Si "bond" lengths of ∼1.65−1.85 Å, which are significantly longer than the uncoordinated $H-SiH_3$ bond (1.48 Å). The formation of such "elongated" complexes is facilitated by the readiness of the Si center to be hypervalent with an electronegative ligand, which is the terminal M−H ligand adjacent to SiR_3.[6] We have recently shown that weak polarizing H···Si interactions are present even at an H···Si distance of up to ∼2.2 Å.[5c]

It is thus interesting to investigate the possibility of complexes having more than one η^2-(H···Si) coordination. The iridium bis(hydrido-silyl) complex $[Ir(PPh_3)_2H_2(\eta^2\text{-}H\cdots SiEt_3)_2](SbF_6)$ (**1**) was reported by Crabtree in 1995 and was proposed to have *cis*-bis(η^2-silane) coordination on the basis of NMR data.[7] Recently, another chelated complex, $RuH_2(PCy_3)_2(\kappa\text{-}\eta^2\text{-}H\cdots SiMe_2\text{-}o\text{-}C_6H_4-SiMe_2\cdots H)$ (**2**), was shown by X-ray crystallography to possess a near-C_{2v} symmetry, consisting of an approximately collinear axial H−Ru−H bond, with the two



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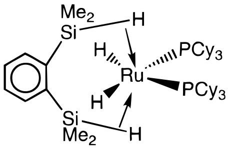

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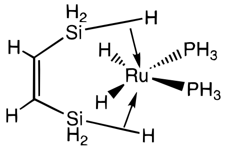
P and two H_{eq} atoms lying on the same plane.[8] The most interesting feature is the apparent *trans*-bis(H···Si) coordination. These structural features are intriguing because, if the complex is considered as having “classical” (i.e. noninteracting) H and SiR_3 ligands, and the complex is thus considered to be 8-coordinate, the square-antiprism structure should be possible. In another extreme, if the H···Si unit is considered to be a fully “nonclassical” 2e σ-donor, the parallel *trans* orientation of the two coordinated H···Si units would cause severe competition of the metal d-orbital for back-donation, similar to the hypothetical *trans* isomer of the complex $Mo(CO)(depe)_2(\eta^2\text{-}H\cdots SiH_3)$.[5a] These intriguing characteristics led us to undertake a theoretical study to provide some insight into the driving forces behind the stability of the apparently *trans*-bis(H···Si) coordination. Among the various possible factors we will investigate are (1) the strength and nature of the H···Si interactions in the experimental structure, (2) the possible role of *o*-phenylene chelation in stabilizing the unusual C_{2v} structure, and (3) the driving forces behind the characteristic distortion of the two *trans*-(H···Si) units.



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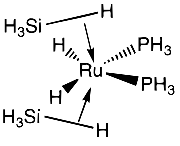

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Density functional theory (DFT) calculations on the model complex **3** and some related structures have been carried out at the B3LYP level of theory. This level of theory has been shown to reproduce well several “nonclassical” (metal−silane and metal−dihydrogen) structures.[5b,9] The atoms Ru, Si, and P were described by the effective core potentials (ECPs) of Wadt and Hay with a double-ζ valence basis set,[10] and the standard 6−31g basis sets were used for H and C. The atoms in direct bonding with the Ru center were augmented with polarization functions, namely, the standard p-polarization function (i.e. 6−31g**) for the terminal hydride ligands and the d-polarization functions of Huzinaga for P and Si.[11] To reproduce the experimentally observed structure, geometry optimization was performed with an overall C_{2v} symmetry, with the C_2 axis bisecting the P−Ru−P angle and a symmetry plane containing the P−Ru−P triangle. The *o*-phenylene group (*o*-C_6H_4) linking the two Si atoms was simplified to −CH=CH−, and the organic substituents of Si and P were replaced by hydrogens for theoretical simplicity. The stability of the C_{2v} model structure was examined through calculation of the harmonic normal vibration modes of the B3LYP-optimized structure and an unconstrained (C_1 symmetry) geometry optimization of the model complex **3**. The unchelated analogue **4** was also optimized at both C_{2v} and C_1 symmetries to study the possible effect of chelation on the stability of the experimental C_{2v} structure. The extent of the Ru d→(H···Si) σ^*-back-donation was studied with a natural bond orbital (NBO) analysis[12] and the features of the Laplacian of the valence electron density ($-\nabla^2\rho$).[13] Laplacian plots of valence electron density only have been frequently used and been proven to be particularly useful in understanding metal−ligand interactions in transition-metal complexes.[14] All the above calculations were performed with the Gaussian94 software package[15] on a Silicon Graphics Indigo[2] workstation. Calculation of the density Laplacian ($-\nabla^2\rho$) was performed with the MOPLOT package[16] on the basis of the calculated B3LYP electron density of the optimized structure.

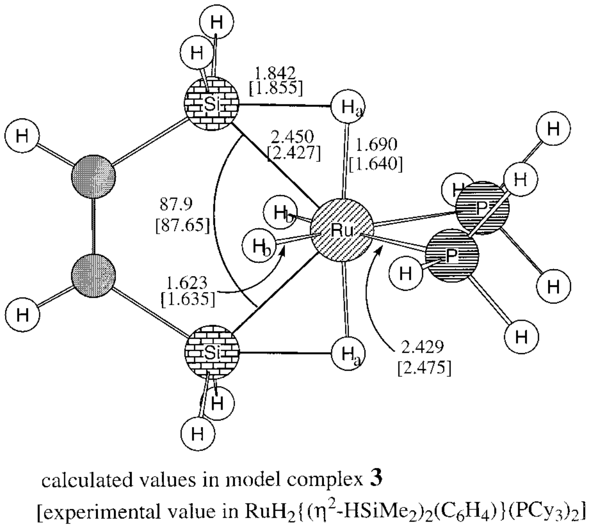

Figure 1. B3LYP-optimized structure of **3**, showing two *trans*-η^2-H···Si coordinations to the Ru center.

The important structural parameters of the B3LYP-optimized geometry of **3** with overall C_{2v} symmetry are summarized in Figure 1. The calculated $Ru-H_{ax}$ and Ru−Si bond lengths and the $H_{ax}-Ru-H_{ax}$ and Si−Ru−Si bond angles are in good agreement with experiment. While the calculated bond angles involving the phosphines and the H_{eq}’s appear to deviate from the experimental values (95 vs 109° in experiment), a similar geometry optimization at the B3LYP level with the two PH_3’s replaced by PMe_3’s (while maintaining an overall C_{2v} symmetry) gives a larger P−Ru−P angle of 99.2°, in closer agreement with experiment, and the axial bonds are little affected by the phosphine substitution.

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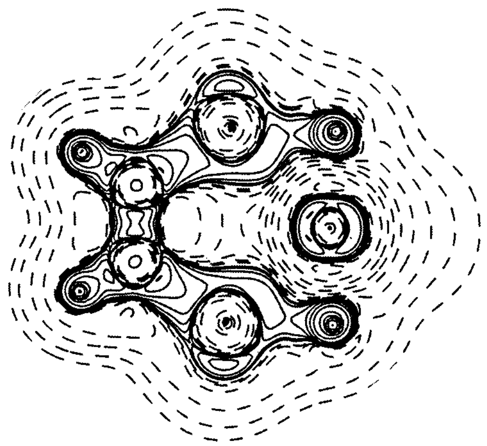


Figure 2. Density Laplacian plot of **3** on the Ru$-$H$_{ax}$$-$Si plane, showing the local density concentrations lying along the Ru$-$Si and Ru$-$H$_{ax}$ bonds and the strong polarizing H···Si interaction.

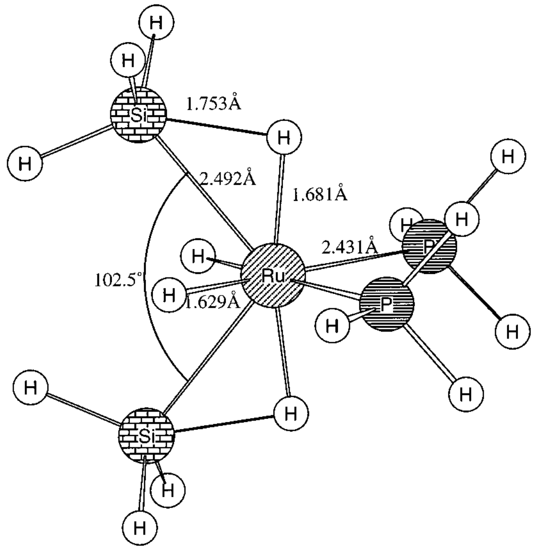


Figure 3. B3LYP-optimized structure of **4**, showing distortion of the two coordinated H···Si units similar to that for the chelated model **3**.

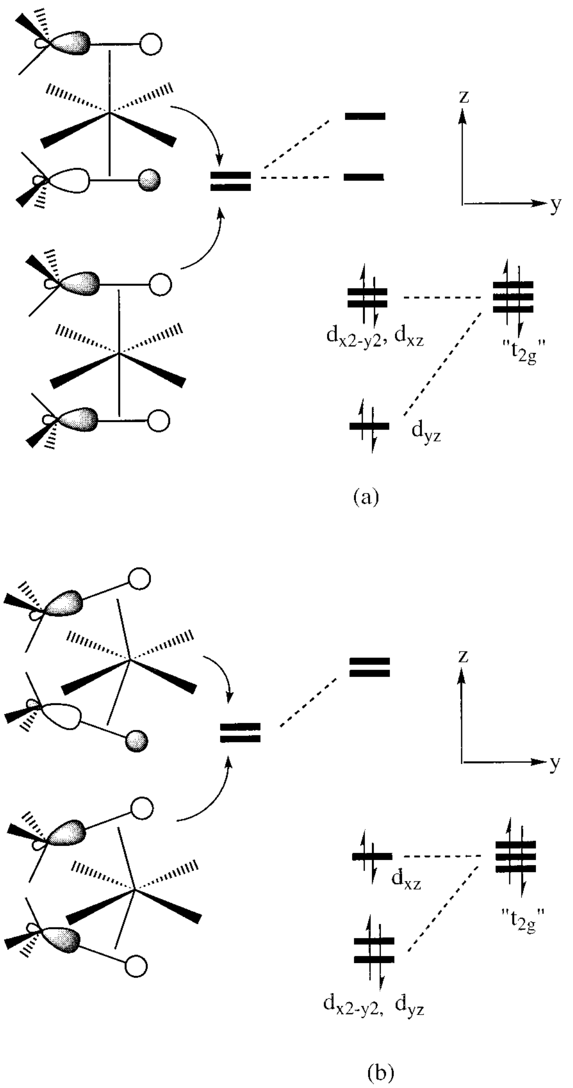
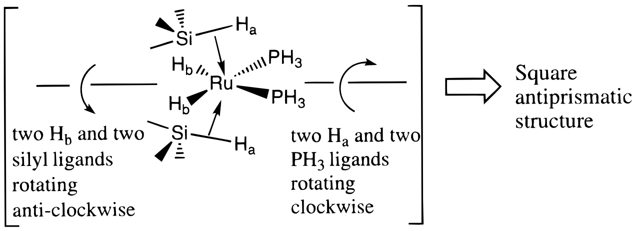


Figure 4. Qualitative MO interaction diagrams illustrating (a) the competition of the two H···Si "σ-bonds" for metal back-donation and (b) the stabilization caused by the distortion.

The nature of the *trans*-bis(H···Si) coordination has been studied through an analysis of the Laplacian of the valence electron density ($-\nabla^2\rho$),[13] and the plot for the model complex **3** on the plane defined by the Ru center and the two coordinated Si atoms is shown in Figure 2. Prominent direct covalent Ru$-$Si and Ru$-$H$_{ax}$ bonds are observed (as indicated by local density concentrations lying along the Ru$-$Si and Ru$-$H$_{ax}$ bonds), with significantly curved and weakened H$_{ax}$···Si "bonds" in comparison to that found in our previous theoretical study[5a] of the complex *cis*-Mo(CO)(depe)$_2$-(H···SiH$_3$), suggesting a far more significant degree of Ru$\rightarrow$(H···Si) σ* back-donation. Natural bonding orbital (NBO) analysis shows an occupation number of the H$-$Si valence bond orbital of ~1.5, confirming that the H···Si σ*-orbital is significantly occupied. Structurally, the calculated H···Si interaction distance of 1.842 Å is within the range of "stretched" η^2-silane complexes (1.65$-$2.00 Å), as studied experimentally and theoretically in most "nonclassical" hydrido-silyl complexes.[1,5]

To examine the possible role of chelation of the two H···Si units on stabilizing the C_{2v} structure, calculations of the unchelated model complex **4** have also been performed. The optimized structure of **4** is shown in Figure 3 with important structural parameters. Notably, **4** shows a distortion of the two H···Si coordination units similar to that in **3** even without the constraint of the *o*-phenylene chelation, and the corresponding bond lengths and angles are rather similar, except for the Si$-$Ru$-$Si angle (which in **3** is obviously constrained by the chelation). Both the NBO and density Laplacian analyses indicate more or less the same extent of σ*-back-donation and similar bonding of the Ru$-$H$_{ax}$$-$Si triangle.

It may be speculated that, as evident from the facile fluxionality of **2**,[8] the stable square-antiprism 8-coordinate isomer **2′** might exist as a stable structure in an equilibrium with the C_{2v} structure **2** in solution (see **5**). Parallel geometry optimizations with C_1 symmetry were performed without any symmetry or structural constraints for both model complexes **3** and **4**. Relaxing the symmetry constraints does not produce a new structure for complex **3**. For the unchelated complex **4**, however, a distorted structure **4′** in which the two coordinated Si- - -H units deviate from the same plane was located.



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4′ is 1.6 kcal/mol more stable than **4** and is an intermediate structure between **4** and a square antiprism (see **5**). Frequency analysis of the chelated model complex **3** indicates the presence of three imaginary (negative frequency) vibration modes between −20 and −70 cm^{-1}, which correspond to motions of the PH_3 ligands due to the C_{2v} symmetry constraints. For the unchelated model complex **4**, however, the A_2-mode vibration to give **4′** is also found. These results suggest that the chelating environment and the steric bulk of the experimental PCy_3 ligands may prevent free distortion of the C_{2v} structure for complex **2**.

Given the stability of the C_{2v} structure of the chelated complex **2** (or **3**), the observed structural features of **2** can be rationalized by a qualitative molecular orbital interaction scheme, as shown in Figure 4. In an "idealized" 6-coordinate situation, where the two H···Si "ligands" act as simple 2e σ-donors, the metal d_{yz} orbital interacts simultaneously with the two *trans*-σ*-orbitals, causing severe competition of metal-to-ligand σ*-back-donation (Figure 4a). After the distortion, the resulting nearly *trans*-dihydride configuration enables the metal d_{yz} and $d_{x^2-y^2}$ orbitals to be utilized in favorable MO interactions with the H···Si σ*-orbitals (Figure 4b). Such an interaction is seen to be cooperative rather than competitive, as expected from the structural features alone. The two stabilized orbitals are actually located as the second and fourth highest occupied MOs in the calculated SCF molecular orbitals while the HOMO involves mainly the d_{xz} metal orbital, which is not affected by the distortion.

In summary, the *trans*-bis(η^2-H···Si) structure of complex **2** reflects the inherent stabilization of the complex through a particular distorted coordination of the two *trans*-(H···Si) units. The prominent H···Si interactions are similar in nature to other examples of η^2-silane complexes, and the stability of the unusual C_{2v} symmetry is governed by a subtle balance of electronic, structural, and steric factors. We believe this study will provide a clue to the structure and fluxionality of the analogous iridium complex **1** and an impetus for further investigations of bis(H···Si) coordination.

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Supporting Information Available: Tables giving the coordinates, Mulliken charges, and total energies for model complexes **3**, **4**, **4′**, and an analogue of **3** with the two PH_3's replaced by PMe_3 (4 pages). Ordering information is given on any current masthead page.

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