

Combined high resolution x-ray and DFT Bader analysis to reveal a proposed Ru-H ... Si interaction in Cp(IPr)Ru(H)₂SiH(Ph)Cl

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Dedicated to M. L. H. Green for his lifelong contribution to Organometallic Chemistry

Abstract

The compound Cp(IPr)Ru(H)₂SiH(Ph)Cl (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) (**1**) was subject to low temperature (30 K), high resolution x-ray structural analysis to obtain a high quality electron density map. This map was subject to a Bader analysis to ascertain the possibility of a Ru-H ... Si interaction. For comparison, DFT calculations employing the well known B3LYP functional in conjunction with a triple zeta basis set was employed. Thus, we not only report the results of a possible Ru-H ... Si interaction but also benchmark the use of the employed level of theory against experimental results.

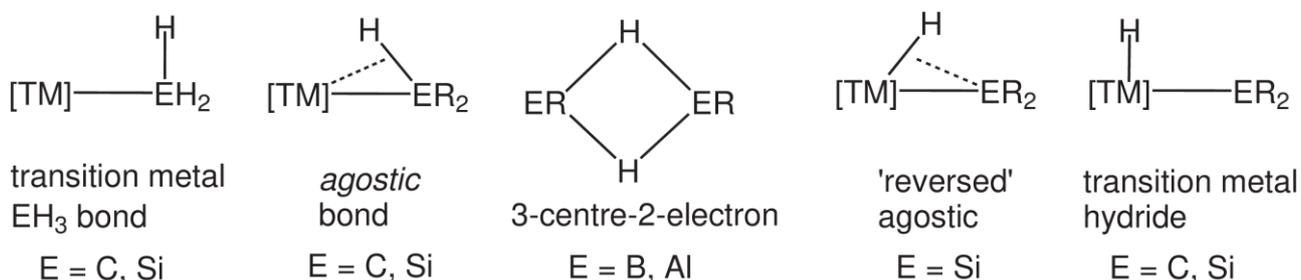
Introduction

The versatile ways for hydrogen, the first element in the periodic table, to form a bond is quite remarkable.[1-3] Despite the lack of lone electron pairs like for example the halogens it is yet interacting with other elements in some unusual manners. For example, it can participate in so called 3-centre-2-electron (3c2e) bonds of the type X-H-E (X = E) where the 2 bonding electrons of one bond are spread over all three elements.[4] A classical example here for X = E is BH₃ which does not exist as such but forms a dimer with itself (B₂H₆). In the case where X is for example a transition metal (TM) and E would be carbon, we have a different scenario. Again, this kind of interaction can be described as a 3c2e bond but, unlike the first example, the electron density is not evenly distributed between the three elements. Instead the C-H bond is donating electron density into a vacant orbital of the TM of suitable shape and energy. This kind of bond has been originally termed 'agostic' but the concept of this type of bonding has been expanded in recent years to term like 'anagostic' or 'pre-agostic'. [1-3, 5, 6]

Agostic bonds are of great importance in organometallic chemistry as it can be seen as a resting state in the hydrogen abstraction reactions for example. We should note that it is not only carbon which does this kind of bonding but silicon, the element below carbon in the periodic table, can show similar properties.

However, a reverse situation can be observed as well where a TM bound hydrogen could interact with suitable Lewis acids like, for example, group 13 elements or silicon as an example of a group 14 element.[7-12] Some examples include the LFe(H)₂BH₂ compound which bears similarities to the B₂H₆ mentioned before.[13] Another example would be the

recently suggested reaction product of a Ru complex with HSiR₃ where the authors note an interaction between the Ru-H and the Si in the solid state.[10-12, 14-19] These various types of interactions are summarised in Scheme 1 which has the agostic interaction on one side of the scale and the reversed agostic interaction on the opposite of the scale with the situation where X = E in the middle of it.



Scheme 1: Range of X-H-E interactions, from TM EH₃ bonds through to TM hydride bonds.

From an electronic perspective, an agostic interaction or agostic bond happens when the C-H bonding orbital is donating electron density into an empty transition metal d-orbital of suitable shape. As a consequence of this, we should observe a bond path in the QTAIM analysis.[20] Thus, a close proximity of a C-H to a TM atom is only a requirement, but not sufficient enough for such an interaction as this interaction might lack of a bond path or the interaction has a similar 'strength' as for example the previously mentioned hydrogen bonds. This was demonstrated by means of DFT calculations on rhodium metal compounds where a ligand H was forced in close proximity to the rhodium atom.[21] Although electron density was donated to a rhodium d-orbital and thus we observed a bond path, the second order perturbation energy in the Natural Bond Orbital (NBO) analysis was similar to the also observed H-Cl interaction in the same molecule.

It should be noted, however, that the absence of a bond path does not necessarily preclude any interactions. In fact, although the archetypical example of an α -agostic interaction between a C-H of a methyl group and Ti is lacking a bond path between the two moieties, this absence was explained by the formation of a 'catastrophic point', that is, the bond critical point is collapsing with the ring critical point and thus annihilates the bond path.[22]

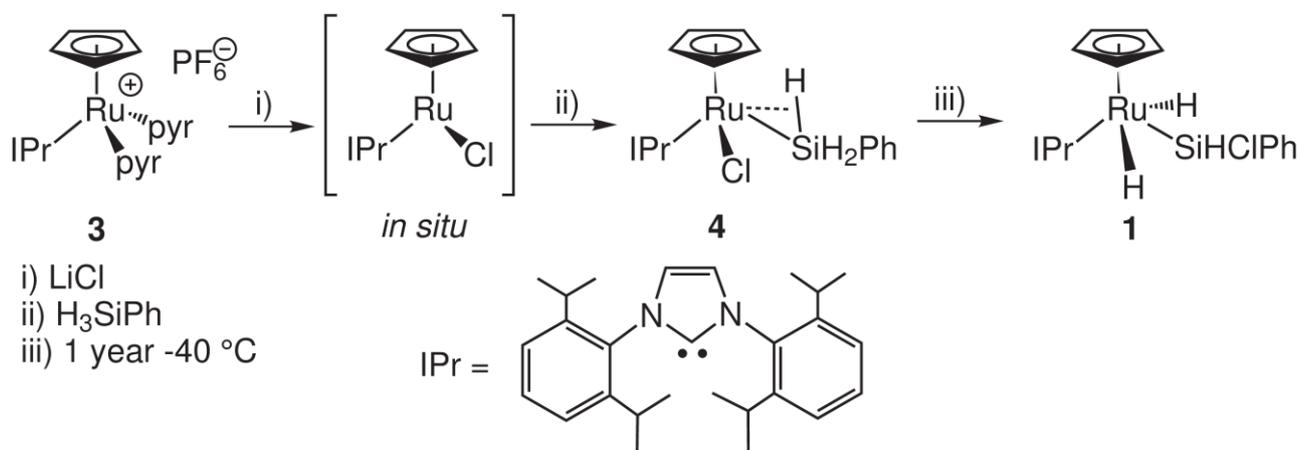
Strictly speaking, x-ray analysis is not sufficient enough to conclude without any doubt the existence of an agostic bond due to the well known problem of determining the exact position of a H next to the much heavier TM. On the other hand, neutron structural analysis will locate the H next to the TM without any doubt. Unfortunately, larger crystals are needed here and these experiments are still not routine.

In a reversed situation where the hydrogen is bound to the TM (X in our scheme) and E would be a Lewis acid like for example Si, we would expect a similar electronic situation. By replacing C with Si, which as vacant d-orbitals, and having the hydrogens bonded to for example Ru, we found examples in the literature which claim to observe a Ru-H ... Si interaction.[13-17]

To this end, we have been interested in the broad area of TM-H-E (Z = C, Si) interactions for some time now.[21, 23, 24] We have recently noticed some nice work from G. Nikonov with a series of compounds having a Ru(H)₂-Si(RR'R'') motif.[15] Here we report the results of a combined low temperature (30 K) x-ray structural determination and DFT calculations at the B3LYP/ecp11 levels of theory of the novel compound Cp(IPr)RuH₂SiClHPh (**1**) (IPr = 1,3-bis(2,6-diisopropylphenyl)). This way we were able to obtain a high precision experimental electron density map which we compare with the one of the computed structures. Thus we obtain a deeper insight into the previously proposed Ru-H ... Si interaction.

Results and discussion

Compound **1** is the result of the reaction of $[\text{Cp}(\text{IPr})\text{Ru}(\text{pyr})_2][\text{PF}_6]$ (**3**) with the silane H_3SiPh via the intermediate $\text{Cp}(\text{IPr})\text{RuCl}$ which is formed *in situ* by the reaction of **3** with LiCl . We propose that the reaction mechanism involves as an initial step the formation of the σ -complex **4** which rearranges over the course of the crystallisation to the final product **1** (Scheme 2)



Scheme 2: Proposed reaction mechanism for the formation of **1**

Crystals suitable for x-ray analysis were grown over the duration of one year at $-40\text{ }^\circ\text{C}$ from a toluene solution layered with hexane.

Structural analysis

The obtained crystals were subject to a high intensity x-ray beam at 30K on beamline I19 at the Diamond research facility (Oxfordshire, United Kingdom). The obtained structure was solved with OLEX2[25] with the hydrogens H1, H2 and H3 being located. All other hydrogens were placed in ideal positions. The so obtained experimental structure along with the computed one are shown in Table 1 together with relevant bond distances and angles. [26]

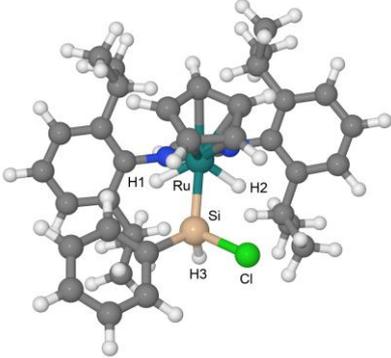
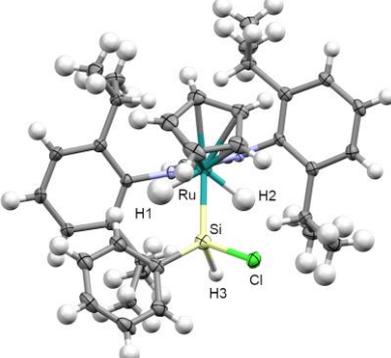
	 Calculated structure of 1-calc at the B3LYP/ecp11 level of theory	 Experimentally obtained structure of 1
d / Å		
Ru-H1	1.600	1.52(5)
Ru-H2	1.584	1.60(4)
Ru-H3	3.293	3.366
Ru-Si	2.335	2.3010(7)
Si-Cl	2.177	2.1137(10)
H1-Si	2.150	2.116
H2-Si	2.195	1.97(4)
H2-Cl	3.014	2.796
H3-Si	1.491	1.54(3)
\angle / °		
H1-Ru-H2	112.79	113(2)
Si-Ru-H1	63.01	63.4(18)
Si-Ru-H2	64.85	57.5(14)
Ru-Si-H3	117.07	121.3(11)
H1-Ru-Si-Cl	-167.23	154.80

Table 1: Experimental and computed structure of **1** together with relevant parameters.

Judging from the reported values in Table 1, the used level of theory is reproducing the structure well within reasonable differences. In particular, the Ru – H and Si – H bonds are well reproduced, bearing in mind the well-known difficulties to observe H next to the more heavier TM by means of x-ray analysis. Thus, we can have some confidence about the obtained electron density map which was subject to a Bader analysis. The only two obvious exceptions seem to be H2, which seems to be closer to the Si in the experimental structure than in the computed one (2.195 vs. 1.97(4)), and the Ru-H distances where the DFT model predicts a reverse bond distance. In the former case, this is also reflected in the difference of the Si-Ru-H2 angle: for the experimental structure we obtain a value of 57.5(14)° vs. 64.85° for the computed one.

The Ru-H distances are a bit more puzzling. Our DFT calculation predicts a Ti-H1 distance of 1.600 (1.52(5) experimentally) and Ti-H2 of 1.584 (1.60(4) experimentally). For comparison, the previously reported structure **2b** reports 1.634 (Ti-H1) and 1.517 (Ti-H2) (cf. Table 2). These values are closer to our theoretical model than to our experimentally observed structure.

There could be three possible explanations for this observation:

- i) the experimental structure located the H in the wrong position due to the well-known problems of locating a hydrogen atom next to the much more heavy transition metal atom
- ii) the used level of theory does not take into consideration dispersion forces and thus gives the wrong location of that hydrogen[27]
- iii) similar to ii) but rather than dispersion forces the used level of theory does not pick up some electronic interactions between the H atom and the Si. This could be for example some spin-orbit coupling which we did not include in our calculations.

As there are a number of examples in the literature where DFT calculations describe the neutron structure very well,[11] we can with some confidence rule out ii) and iii) and we can come to the conclusion that most likely i) is the origin of the observed discrepancy between the observed and computed position of H2.

For comparison, selected bond distances of the compounds Cp(IPr)Ru(H)₂SiR₃ **2** (R = Cl₂Me (**a**); HMePh (**b**)) are reported in Table 2.[15]

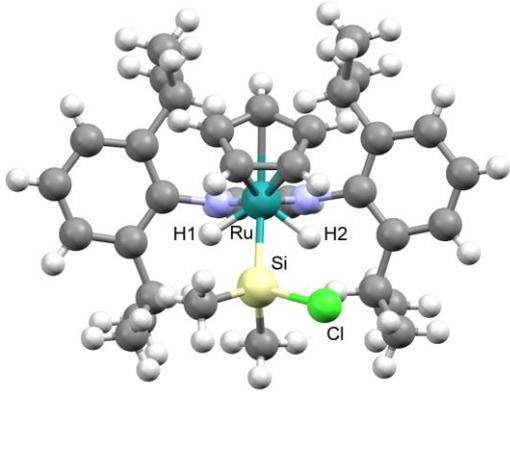
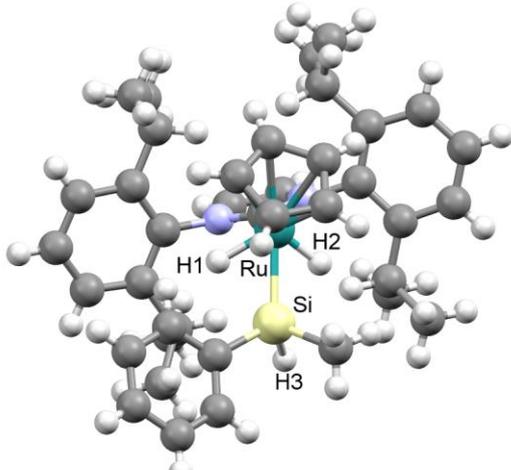
		
	2a	2b
d / Å		
Ru-H1	1.55(3)	1.634
Ru-H2	1.53(3)	1.517
Ru-H3		3.390
Ru-Si	2.3151(10)	2.3355(5)
Si-Cl	2.1736(14)	
H1-Si	2.052	2.115
H2-Si	2.029	2.003
H2-Cl	2.854	
H3-Si		1.529
\angle / °		
H1-Ru-H2	106.9(18)	104.97
Si-Ru-H1	60.4(13)	61.43
Si-Ru-H2	59.6(12)	58.10
Ru-Si-H3		121.16
H1-Ru-Si-Cl		

Table 2: Experimental structures of **2** together with relevant parameters.

Our conclusion is further supported by the Ru-Si and Si-Cl distances. For compound **2b** a Si-Cl bond length of 2.1736(14) Å was reported which is close to 2.177 Å for **1-calc** but different from the 2.1137(10) Å observed for **1**. A more striking difference is found between the Ru-Si bond. The previously reported bond length of 2.3151(10) Å (**2a**) and 2.3355(5) Å (**2b**) agree well with our calculated distance of 2.335 Å but are significantly shorter than the found 2.3010(7) Å for **1**. These values have been observed before in phosphine containing Ru complexes. For example, a shorter values of (2.302(3) Å) was reported for Cp*(Pr₃P)Ru(H)₂(SiHCIMes) and longer values of 2.364(2) Å and 2.4213(7) Å for Cp*(PH₃P)Ru(H)₂(SiClMe₂) and Cp*(pyr₃P)Ru(H)₂(SiPhMe₂), respectively.[17]

It is right now not clear without any doubt what is causing the smaller than calculated Ru-Si distance in **1** compared with other, similar compounds. One possible explanation might be due to the lower temperature the atoms are vibrating less and thus are more oscillating close to the 'ideal' position which should lead to a more compact structure. However, in light that

the calculated structure is assuming a temperature of '0 K', we do not believe this is the sole reason for this observation.

Another interesting point is the torsion angle H1-Ru-Si-C. As it is known from similar compounds, if this angle approaches 180° , a non-classical interaction between the H-Ru bonding orbital with the Si-Cl anti-orbital increases, leading to longer Si-Cl bond. In our case, the angle of -167.23° is close to planarity which would suggest a elongation of the Si-Cl bond. Indeed, the observed value of $2.1137(10)$ Å is close to the previously observed value of $2.117(2)$ Å in the compound $\text{Cp}(\text{ArN})\text{Ta}(\text{PMe}_3)(\text{H})(\text{SiMeCl}_2)$ which are known to show interligand hypervalent interaction (IHI).[17]

Bader analysis of the experimental structure.

The electron density and the Laplacian from the experimentally obtained electron density map were calculated using the program MoPro. For comparison these results are collected in Tables 3 and 4 next to the computed ones.

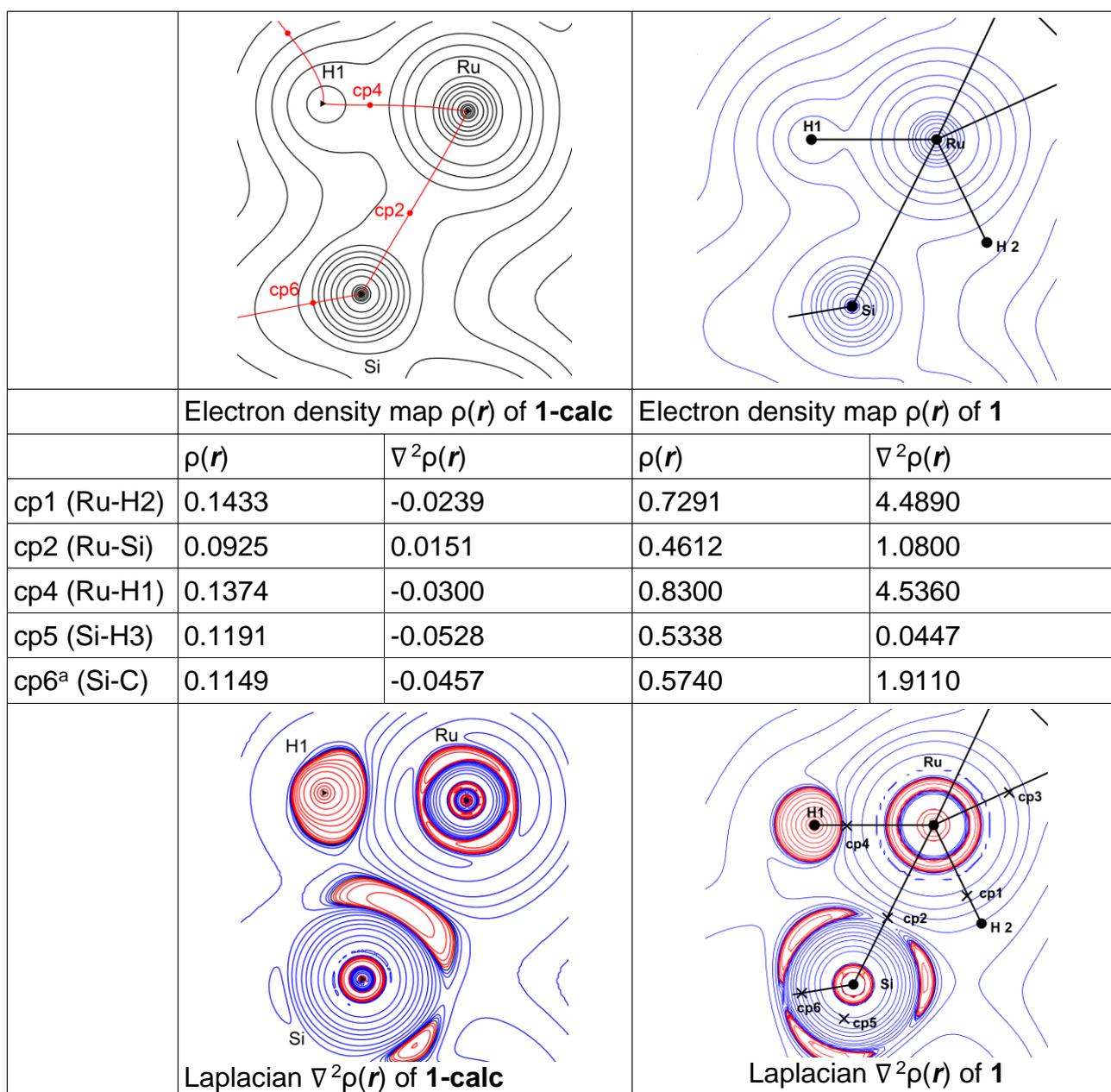
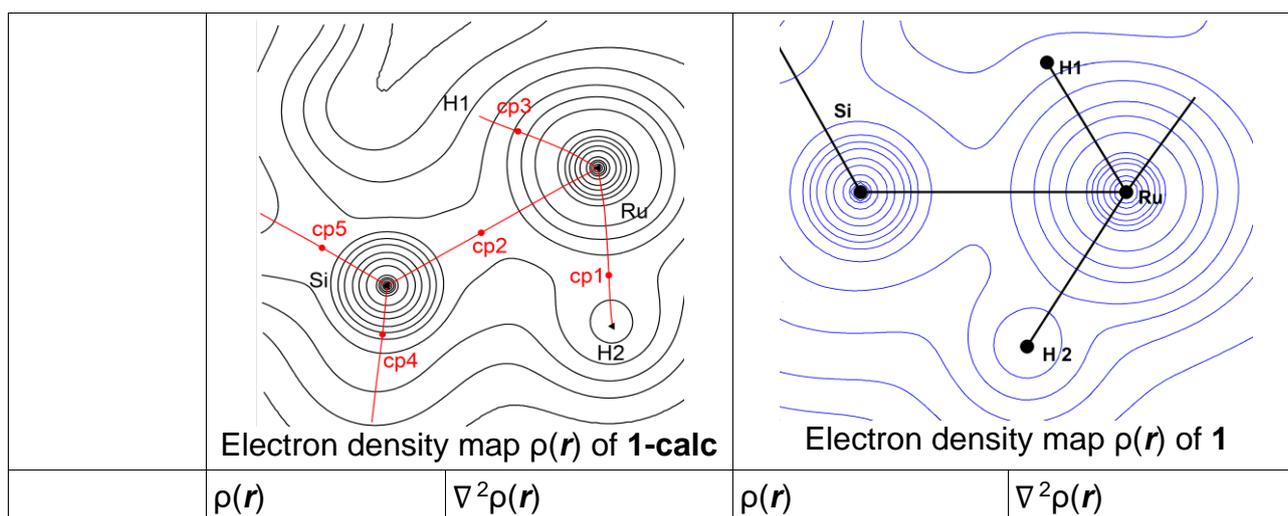


Table 3: Computed and experimentally observed electron density map and the Laplacian of thereof. Plane through Si-Ru-H1

^a) Si-C(*ipso*) bond path.



cp1 (Ru-H2)	0.1433	-0.0239	0.7291	4.4890
cp2 (Ru-Si)	0.0925	0.0151	0.4612	1.0800
cp3 (Ru-H1)	0.1374	-0.0300	0.8300	4.5360
cp4 (Si-H3)	0.1191	-0.0528	0.5338	0.0447
cp5 ^a (Si-C)	0.1149	-0.0457	0.5740	1.9110

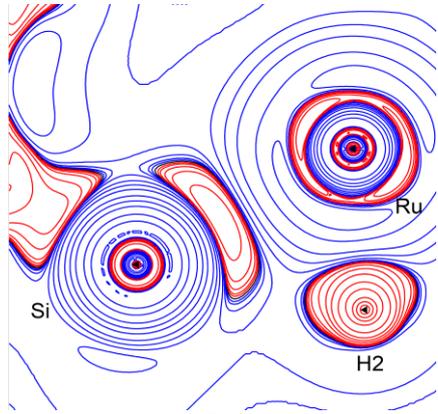
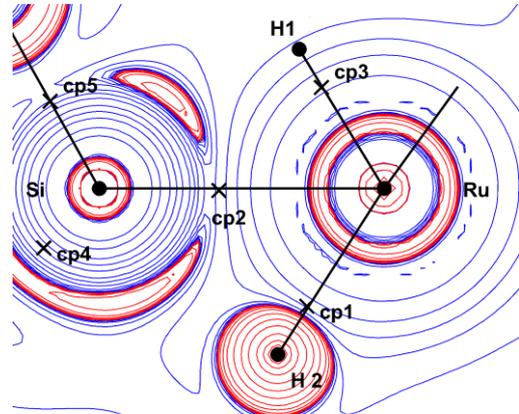
 <p>Laplacian $\nabla^2\rho(r)$ of 1-calc</p>	 <p>Laplacian $\nabla^2\rho(r)$ of 1</p>
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Table 4: Computed and experimentally observed electron density map and the Laplacian of thereof. Plane through Si-Ru-H2.

^a) Si-C(*ipso*) bond path.

In the calculated structure, we do not observe any interaction between H3 and Ru. Furthermore, we do not observe any interaction between the Cl and H2. Instead, we observe a bond path between the Cl atom and one of the hydrogens of a ligand methyl group. For H1, we observe a bond path to one of the *ipso* carbons of one of the aromatic rings in the ligand. The electron density maps of these interactions are supplied in the electronic supplementary information, together with the Laplacian and Virial field function maps as well.

Surprisingly, we do not find any Ru-H interaction with the Si atom for neither H1 nor H2 (cf. Tables 3 and 4 for details) for both the calculated and observed structures. Without the observation of a bond path between either of the Ru-H and Si we cannot observe any interaction in this particular case. Our assumption is further strengthened by inspection of the Laplacian of the electron density map. We do not find any kind of evidence for an interaction between either of the Ru-H atoms with the Si atom. Two possible reasons for this could be envisaged:

- there is no interaction between the Si and either H1 or H2
- there is an interaction but the bond path is collapsed into the ring critical point (catastrophic critical point)

For the latter, some evidence is put forward in the literature. In particular, the well-known agostic titanium compound (dmpe)Ti(Me)Cl₃, which is well known for the α -agostic bond between the CH₂H and the Ti atom does not show a bond path.[22] Here, the common explanation is that the bond path between the C-H bond and the Ti is collapsing and this is indistinguishable with the Ti-C bond ('catastrophic point').[28, 29] The evidence for this is obtained by means of x-ray, neutron and NMR spectroscopy. A similar situation could be envisaged here. Obviously, the collapsing of the bond path is critical to the relative positions of Ru, Si and H. Due to the known problems with the location of H atoms next to TM atoms we feel it would be wrong here to rule out a possible interaction between the Ru-H bond and the Si atom.

Further inspection of Tables 3 and 4 reveals that the electron density at the bond critical

points between both of the Ru-H are very similar (**1-calc**: 0.1374 (H1) and 0.1433 (H2); **1**: 0.8300 (H1) and 0.7291 (H2)), indicating a similarity in bonding. Again, comparing the calculated with the observed electron density we notice the already observed reversed order of the two Ru-H bonded hydrogens: in the calculated structure H2 has the higher electron density whereas in the observed structure it is H1. However, the electron density of the Si-H3 bond is lower, compared with either of the Ru-H bond critical points (**1-calc**: 0.1191; **1**: 0.5338) indicating a weaker Si-H bond compared with the Ru-H bonds. Finally, the electron density for the Ru-Si bond critical point is 0.0925 for **1-calc** and 0.4612 for **1**. Judging of the opposite sign of the Laplacian at the bond critical point for the calculated structure, we can conclude that the Ru-Si bond is also different in its nature, compared with either the Ru-H bonds or the Si-H bond.

Conclusion

We have obtained the low temperature (30 K), high resolution x-ray structure of the novel compound Cp(IPr)Ru(H)₂SiH(Ph)Cl (**1**) which was obtained by a reaction-crystallisation process over the duration of 1 year. The electronic density map of the so obtained structure was subject to a Bader analysis which was compared with a structure obtained by DFT calculation at the B3LYP/ecp11 level of theory. Both obtained electron density maps, and hence the Bader analysis of thereof, are quite similar, with the same being true of the relevant positions of the relevant atoms around the Ru and Si centres. Neither the experimental nor the computational obtained Bader analysis revealed a bond path between the ruthenium H and the silicon atom. This is somewhat surprising as for similar compounds an interaction between these atoms is claimed, mainly on the base of NMR studies. One striking result of our investigation is that both the structural and electronic parameters of H1 and H2 seems to be just the reverse between the calculated and observed structure. Thus, we are currently undertaking some neutron measurements to obtain a more exact location of the Ru-H. This, together with more detailed DFT calculations of this and related compounds will be subject to a more specialised publication.

Experimental Section

Preparation of Cp(IPr)Ru(H)₂(SiHPhCl) (**1**)

All preparations were performed under inert atmosphere as previously described. To the 3 mL THF solution of 0.125 g (0.15 mmol) [Cp(IPr)Ru(pyr)₂][PF₆], 0.006 g (0.15 mmol) of LiCl was added in. The reaction mixture was stirred for 20 min at room temperature under inert atmosphere. The colour of reaction solution turned from yellowish to blue. All volatiles were removed under vacuum, and the crude product was extracted into 5 mL of toluene. The extracted solution of Cp(IPr)RuCl in toluene was cooled down to -40 °C in the freezer and 0.016 g (0.15 mmol, 18.5 μL) H₃SiPh was added. The colour of the resulting mixture turned to yellow. To induce crystallisation, 2 mL of hexane was added on the top of toluene. After one year at -40 °C the final product of Cp(IPr)Ru(H)₂(SiClHPh) was obtained as reddish crystals which were suitable for x-ray analysis.

NMR Measurements.

Solution NMR spectra were recorded on a Bruker NMR spectrometer AVANCE Neo 700 equipped with a Bruker 5 mm ¹⁵N-³¹P/¹⁹F-¹H broadband cryoprobe. Spectra were recorded at 25 °C. Data acquisition and processing were performed using standard Bruker TopSpin software (version 4). ¹H, ¹³C and ²⁹Si chemical shifts are given relative to tetramethylsilane (TMS).

¹H-NMR (700 MHz, benzene-*d*₆, δ/ppm): -10.61 (d, 1H, *J*_{HH} = 5.8 Hz, RuH), 0.97 (d, *J*_{HH} = 6.8 Hz, 6H, CH₃ of *i*-Pr), 0.98 (d, *J*_{HH} = 6.9 Hz, 6H, CH₃ of *i*-Pr), 1.18 (d, *J*_{HH} = 6.8 Hz, 6H,

CH₃ of *i*-Pr), 1.49 (d, $J_{\text{HH}} = 6.8$ Hz, 6H, CH₃ of *i*-Pr), 2.67 (sept, $J_{\text{HH}} = 6.9$ Hz, 2H, CH of *i*-Pr), 2.95 (sept, $J_{\text{HH}} = 6.8$ Hz, 2H, CH of *i*-Pr), 4.52 (s, 5H, Cp), 6.52 (t, $J_{\text{HH}} = 5.4$ Hz, 1H, SiH), 6.55 (s, 2H, NCH), 7.07–7.20 (m, 6H, C₆H₃), 7.24–7.27 (3H, *m*- and *p*- of SiC₆H₅), 7.89 (m, 2H, *o*-SiC₆H₅). Small ²⁹Si satellites were observed at 6.67 and 6.36 ppm for the triplet at 6.52 ppm with a separation of 217.6 Hz corresponding to the ¹J_{SiH} coupling (Figure 1). As expected, the ¹H NMR chemical shifts measured by us for **1** in this work match the majority of those reported for the structurally related compound **6d** in reference [14] (Cp(IPr)RuH₂(SiH₂)Ph, see page 10 in Supporting Information of [14]) with the exception of the SiH₂ (5.22 ppm) and RuH₂ (-11.04 ppm) protons.

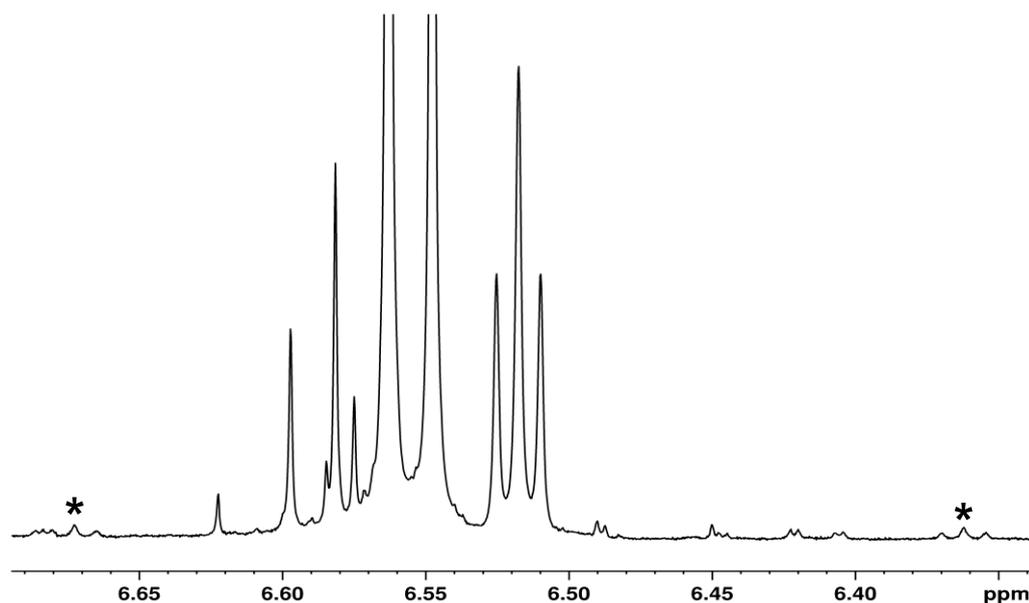


Figure 1. The ¹H NMR spectrum of **1** in C₆D₆ showing ²⁹Si satellites at 6.67 and 6.36 ppm (marked with *) for the triplet at 6.52 ppm assigned to the proton directly bonded to the Si atom.

¹³C-NMR (176 MHz, benzene-*d*₆, δ/ppm): 22.4, 22.5, 25.9 and 26.6 (CH₃ of *i*-Pr); 29.0 and 29.5 (CH of *i*-Pr); 83.3 (Cp); 123.8 (NCH); 124.2–130.2 (CH of C₆H₃, *m*-C and *p*-C of SiC₆H₅); 135.4 (*o*-C of SiC₆H₅); 138.9 (quaternary C of SiC₆H₅); 146.2 and 146.7 (quaternary C of C₆H₃); 192.8 (Ru–CN₂).

²⁹Si NMR (139 MHz, benzene-*d*₆, δ/ppm): 38.7 (¹J_{SiH} = 218 Hz).

DFT calculations:

DFT calculations were conducted using Gaussian09, Rev. D.01.[30] Calculations were performed at the B3LYP level of theory. A mixed basis set consisting of Pople's triple zeta 6-311G(d,p) basis set[31, 32] for all elements but for Ru where the Stuttgart-Dresden electron core potential basis set (keyword SDD) was employed. This mixture of basis set is abbreviated ecp11. Analytical frequency calculation were performed at the obtained structure to ensure a minimum on the potential energy surface (no imaginary frequencies). For the Bader calculation the all electron basis double zeta set DZVP was used for Ru.[33] Bader analysis were performed with the AIM2000 program.[34, 35]

X-ray analysis

The low temperature, high resolution x-ray analysis was performed at the Diamond facility at 30 K. Crystals were mounted on a suitable glass fibre and were cooled with a He stream. (Matthias: you might want to refine that a bit).

The program OLEX2[25] was used to solve the x-ray structure achieving a R factor of **4.48%**. The so obtained high resolution structure was subject to a Bader analysis using the program MoPro.[36, 37]

Acknowledgement

Part of this work was conducted at the Department of Chemistry at the University College London. We greatly acknowledge the use of the teaching cluster 'Sassy' for the calculations. We greatly acknowledge the donation of the crystalline compound from Georgii Nikonov. This work would not have been possible without the help of a number of people. We are greatly in debt to M.L.H. Green and J. Green for their continuous support, inspirations, advice and helpful discussion over the years. We are also thanks P. Mountford for helpful discussions regarding the electronic analysis of this compound. We would like to thank both the staff of the Harwell and Diamond research facility for being very helpful with the facilitation of the experiments.

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this publication and will be subject to an upcoming more specialised publication.

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