Cp*(^{i}Pr$_3$P)Ru(Cl)(η^2-HSiClMe$_2$): the first complex with simultaneous Si–H and RuCl···SiCl inter-ligand interactions†

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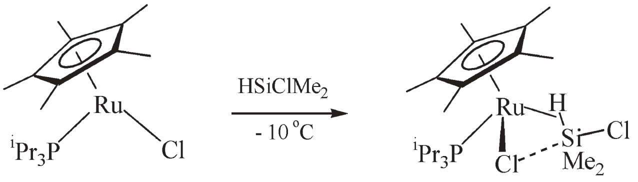
The addition of HSiMe$_2$Cl to the unsaturated compound Cp*(^{i}Pr$_3$P)RuCl gives an unstable adduct which, according to NMR ($J_{H\text{–}Si}$ = 33.5 Hz), X-ray crystal structure and DFT evidence, is a silane σ-complex Cp*(^{i}Pr$_3$P)Ru(Cl)(η^2-HSiMe$_2$Cl) supported by an unprecedented, simultaneous inter-ligand RuCl···SiCl hypervalent interaction between the chloride ligand on ruthenium and the SiMe$_2$Cl group.

Non-classical inter-ligand interactions are formed by electron-deficient agostic and σ-complexes[1] and electron-rich hypervalent interactions (IHI).[2] Both of these types have been found for silyl groups,[3,4] and we have recently shown how both IHIs and silane σ-complexes can be stabilised in the same Cp$_2$/PMe$_3$ ligand environment in titanocenes, depending on the substituents of the SiR$_3$ group.[5] Complexes with several σ-bond ligands (H$_2$ and HSiR$_3$) are long known,[1,6] but no examples with simultaneous interactions of both different types at the same metal centre have been documented so far. Here we report the synthesis and X-ray crystal structure of the complex Cp*(^{i}Pr$_3$P)Ru(Cl)(η^2-HSiMe$_2$Cl) which contains a stretched silane ligand, hypervalently interacting with the chloride ligand on ruthenium.

Complexes of type Cp*(^{i}Pr$_3$P)Ru(Cl)(SiR$_3$)(H) (R$_3$ = Cl$_2$Me **1**, Cl$_3$ **2**, PhH$_2$ **3**, Ph(SiPhH$_2$)H), prepared by the reaction of Cp*(^{i}Pr$_3$P)RuCl with silanes, have previously been reported as classical on the basis of their stability at room temperature and small Si–H coupling constants (<20 Hz[3a]).[7,8] In contrast, secondary silanes do not give stable adducts.[9] We have found that complexes Cp*(R$_3$P)Ru(Cl)(HSiR$_3$) (R$_3$ = PhH$_2$ **3**, SiClMe$_2$ **4**, SiPhMe$_2$ **5**) have very different stabilities. While the reaction of Cp*(^{i}Pr$_3$P)RuCl with excess H$_3$SiPh readily affords **3** along with some Cp*(^{i}Pr$_3$P)Ru(SiH$_2$Ph)(H)$_2$, in the case of HSiClMe$_2$ and HSiPhMe$_2$ at room temperature the equilibrium is shifted towards Cp*(^{i}Pr$_3$P)RuCl and free silane. However, the adduct **4** forms at −10 °C (eqn. (1)), whereas **5** is observed only at −90 °C. The ^{1}H NMR spectrum of **4** at −40 °C revealed a hydride signal at −9.65 ppm, flanked by ^{29}Si satellites with a coupling constant $J_{H\text{–}Si}$ = 33.5 Hz, suggesting the presence of a Si–H σ-interaction. No ^{29}Si satellites could be seen for **3** at room temperature but a clear $J_{H\text{–}Si}$ coupling constant of 30 Hz was measured at −10 °C. For **5**, $J_{H\text{–}Si}$ = 32 Hz at −90 °C. Surprisingly, both values are slightly lower than in **4**, in spite of the presence of more electron-donating R-groups at Si in **5**. The formulation of **3–5** as σ-complexes is not surprising, if it is taken into account that: (i) in Cp*(R$_3$P)Ru(Cl)(SiR$_3$)(H) the Ru atom is in the high formal oxidation state IV,[1] (ii) an electron-withdrawing chloride ligand is present[1] and (iii) that σ-complexes occur for the isolable compounds [Cp*(Me$_3$P)$_2$Ru(η^2-HSiCl$_3$)]$^+$ and Cp*(Ph^{i}Pr$_2$P)Ru(Cl)(η^2-H$_2$).[10,11]



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(1)

The variation of $\nu_{Ru\text{–}H}$ in the IR spectra of compounds **1–4** with the nature of SiR$_3$ group provides further support for the non-classical nature of **4**. Namely, the Ru–H stretch shifts to shorter wave numbers along the series **2**: 2120 cm^{-1} > **1**: 2096 cm^{-1} > **3**: 2000–2050 cm^{-1} > **4**: 1916 cm^{-1}. Although IR spectroscopy has been less popular than NMR spectroscopy as a means for characterising silane σ-complexes, a red shift of the M–H stretch indicates the formation of such a complex.[3d] For comparison, in the classical compound Cp*(pyr$_3$P)RuH$_2$(SiPhMe$_2$)[12] the Ru–H stretches are observed at much larger wave numbers (2085 and 2055 cm^{-1} *vs.* 1916 cm^{-1} in **4**).

In accord with the spectroscopic evidence of a σ-complex, the X-ray structure‡ of **4** (Fig. 1) revealed an elongated Ru–Si bond of 2.3982(7) Å compared to the 2.2950(5)–2.364 Å range found in related chlorosilyl complexes of ruthenium[7] and marginally shorter than in classical Cp*(pyr$_3$P)RuH$_2$(SiPhMe$_2$) (2.4213(7) Å)[12] which has only donor groups at Si. In addition to the short Si···H contact of 2.05 Å, which is probably subject to the uncertainty of the hydride's location from the X-ray study, there is a short Si···Cl contact of 3.014 Å between the silyl and chloride ligands (the sum of the van der Waals radii is 3.81Å).[13] The Cl–Ru–Si–Cl torsion angle of 179.5° is close to 180° and the Cl–Si–Cl angle is 165.61°, signifying the relative *trans* disposition of the two Cl groups. There appears to be a donation from the Ru-bound chloride lone pair to the $\sigma^*_{Si\text{–}Cl}$ antibonding orbital of the silane, leading to a hypervalent silicon centre and the elongation of the Si–Cl(2) bond to 2.155(1) Å, a value beyond the range 2.094–2.149 Å typical of classical chlorosilyl complexes.[7,14] However, the IHI of the type Ru–H···Si–Cl is missing in **4** since the Si-bound chlorine and hydride are not in a *trans* disposition.[3d,4,5] In comparison, shorter Si–Cl (2.144 Å) and Si–Ru (2.364 Å) bonds are found in the

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† Electronic Supplementary Information (ESI) available: Details of the preparation of **4** and DFT calculations of **7–10**. See http://www.rsc.org/suppdata/cc/b5/b500679a/

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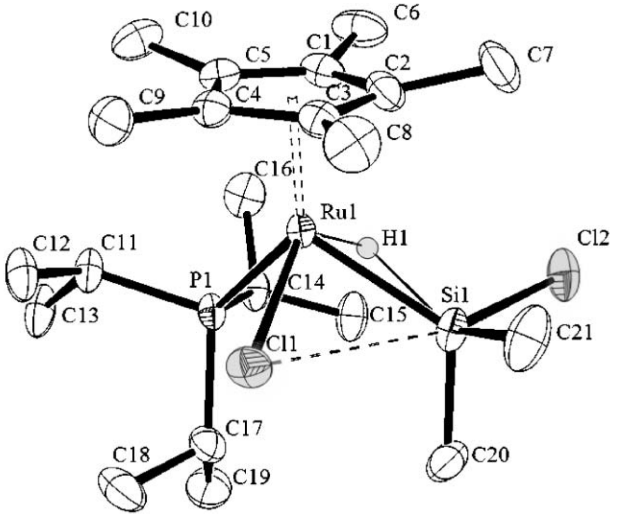


Fig. 1 Molecular structure of complex **4**. Selected bond lengths (Å) and angles (°): Ru(1)–Si(1) 2.3982(7), Ru(1)–P(2) 2.3813(6), Ru(1)–Cl(1) 2.4129(6), Si(1)–Cl(2) 2.155(1), Si(1)–C(20) 1.872(3), Si(1)–C(21) 1.885(3), Si(1)–Cl(1) 3.014(1), Ru(1)–H(1) 1.53(3), Si(1)–H(1) 2.05(3); Si(1)–Ru(1)–P(1) 103.36(2), Si(1)–Ru(1)–Cl(1) 77.59(2), Cl(1)–Si(1)–C(20) 88.85(1), Cl(1)–Si(1)–C(21) 87.62(1), Cl(1)–Si(1)–Ru(1) 51.42(1), Cl(1)–Si(1)–H(1) 85.3(10), Cl(2)–Si(1)–H(1) 81.2(10), Cl(2)–Si(1)–Ru(1) 114.20(3), Cl(2)–Si(1)–C(20) 101.04(12), Cl(2)–Si(1)–C(21) 100.08(10), Ru(1)–Si(1)–C(20) 119.84(10), Ru(1)–Si(1)–C(21) 115.37(10), Cl(2)–Si(1)–Cl(1) 165.61(3).

Table 1 DFT-calculated bond lengths (Å), bond angles (°) and $J_{H–Si}$ (Hz) for model complexes **7–10**

	7	**8**[a]	**8′**	**9**	**10**[b]
Ru–H	1.613	1.604 [1.53]	1.602	1.603	1.598 [1.485]
Ru–Cl(1)	2.455	2.451 [2.413]	2.444	2.444	2.433 [2.416]
Ru–P	2.301	2.308 [2.381]	2.314	2.315	2.325 [2.323]
Ru–Si	2.474	2.427 [2.398]	2.426	2.388	2.361 [2.311]
Si···H	1.991	2.072 [2.054]	2.076	2.104	2.156 [2.092]
Si–Cl(2)[c]	—	2.168 [2.155]	—	2.148	2.129 [2.094]
Si–Cl	—	—	2.149	2.128	2.104/2.107
Si···Cl(1)	3.183	3.040 [3.014]	3.219	3.047	3.110 [3.102]
Cl(1)···Si–Cl(2)	—	161.4 [165.6]	97.8	162.4	162.0 [166.4]
$J_{calcd\ Si–H}$	−23.0 [32][d]	−19.5 [33.5][d]	−17.3	−4.7 [19][d]	−0.4 [<6][d]

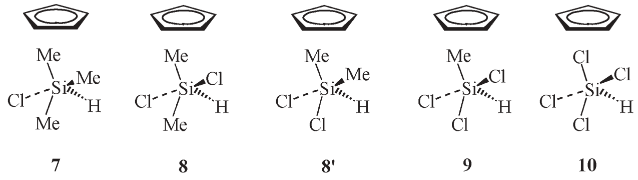
[a] X-ray data for **4** in brackets. [b] X-ray data for $Cp^*(^iPr_2MeP)Ru(Cl)(SiCl_3)(H)$ in brackets. [c] The atom Cl(2) on Si is *trans* to the chloride ligand Cl(1). [d] $J_{obs\ Si–H}$ for **5**, **4**, **1** and **2** in brackets.

classical complex $Cp^*(Ph_3P)RuH_2(SiClMe_2)$.[14] It is also informative to compare the X-ray structure of **4** to that of closely related compound $Cp^*(Me^iPr_2P)Ru(Cl)(SiCl_3)(H)$ **6**.[7] The latter of these complexes is at a more advanced stage in the oxidative addition of the Si–H bond to the ruthenium, and has a shorter Ru–Si bond of 2.3152 (8) Å due to the presence of three electron-withdrawing chlorine groups on the silicon. In spite of this, the observed RuCl···Si distance of 3.111(1) Å in **6** is 0.097 Å longer than in **4**. This difference stems from a more acute Cl(1)–Ru–Si bond angle in **4** (**4**: 77.59(2)° *vs.* **6**: 82.26(3)°), clearly demonstrating the attraction in **4** between the chloride and silyl groups. Before this work, such an interaction between a chloride ligand and a main-group element was reported only for stannyl complexes in the form of MCl···SnCl inter-ligand bonding.[15]

To shed more light on the bonding arrangements in **1–6**, we used DFT§ to calculate a series of model complexes $Cp(Me_3P)Ru(Cl)(SiCl_nMe_{3-n})(H)$ (n = 0: **7**, 1: **8**, 2: **9**, 3: **10**) and a rotamer of **8**, the complex **8′**, with a methyl group *trans* to the chloride ligand (Scheme 1). It can be seen from Table 1 that progressive substitution of the Me groups at Si in **7** for chlorine atoms leads to a shortening of the Ru–H and Ru–Si bonds and an increase in the Si–H separation due to increased back-donation from the metal to the σ*(Si–H) antibonding orbital.[1] Noteworthily, the RuCl···Si contact distance decreases from **7** to **8** and then increases again from **8** to **10** as the Ru–Si bond shortens, whereas the rotation of the silyl in **8** to give **8′** results in an abrupt elongation of this contact and a decrease in the Si–Cl(2) bond length from 2.168 Å to 2.149 Å. Overall, the rotamer **8′** is 2.5 kcal mol^{-1} less stable than **8**. The rotation of the $SiMe_2Cl$ group alone leads only to a negligible change in steric hindrance, since the second methyl group in both forms is directed towards the Cp ring. Furthermore, in accordance with the presence of the hypervalent interaction RuCl···Si–Cl, in complexes **7** and **9**, the Si–Cl bond *trans* to the chloride on Ru is longer than the Si–Cl bond *trans* to the Cp ring.

The progressive weakening of the Si–H interaction from **7** to **10** is mirrored by the decrease in absolute value of the calculated $J_{H–Si}$ (Table 1). The smaller absolute values of calculated $J_{H–Si}$ possibly reflect a greater degree of oxidative addition in model complexes **9** and **10**. Importantly, the sign of the coupling constant has been calculated† to be negative. The sign rather than the absolute value of $J_{H–Si}$ has been recently suggested to be a more rigorous criterion for the presence of a direct Si–H intercation.[5]

The large values of the Mayer bond orders[15] (MBO, Table 2) and the overlap-weighted natural bond orders† unambiguously establish the presence of Si···H and Si···Cl interactions. The MBOs confirm the decrease in the Si···H interaction concurrent with the strengthening of the Ru–Si and Ru–H bonds from **7** to **10**. The rotation of the $SiMe_2Cl$ ligand in **8** to give **8′** results in a somewhat more advanced Si–H addition and the loss of the hypervalent interaction Si···Cl(1) (the MBO for the Si···Cl(1) interaction decreases from 0.131 to 0.074, whereas the Si–Cl(2) bond strengthens from 0.876 to 0.915). Altogether, these data suggest the presence of simultaneous σ Si···H and hypervalent RuCl···Si–Cl interactions. The latter interaction is the strongest in complex **8**, the model of real compound **4**. In complex **10**, the model of real compound **2**, both interactions are weak.



Scheme 1 Model complexes **7–10** drawn as Newman projections down the Si–Ru bond, so that the Ru atom is eclipsed and hence not visible.

Table 2 Mayer bond orders for **7–10**, calculated from the DFT density matrix

	7	**8**	**8′**	**9**	**10**
Ru–H	0.684	0.701	0.711	0.708	0.722
Ru–Cl(1)[a]	0.707	0.691	0.734	0.718	0.757
Ru–P	0.806	0.805	0.796	0.791	0.781
Ru–Si	0.619	0.653	0.690	0.694	0.730
Si···H	0.172	0.157	0.149	0.143	0.125
Si–Cl(2)	—	0.876	0.915	0.919	0.962
Si–Cl′	—	—	—	0.983	1.013/1.028
Si···Cl(1)	0.095	0.131	0.074	0.122	0.101

[a] Chloride ligand Cl(1) is in a *trans* position with respect to the atom Cl(2).

σ-Complexes with secondary Si–H interactions[6] related to the *cis*-effect[1] have previously been reported and can alternatively be viewed as containing the distorted $(R_3SiH_2)^-$ moiety.[2] In **4**, two different types of inter-ligand interactions occur simultaneously at the same metal centre—the residual σ-Si–H interaction and the unprecedented Cl···Si–Cl hypervalent interaction. The relative stabilities of **3**, **4** and **5** show that the presence of the RuCl···Si–Cl interaction can stabilise the adduct, even for a tertiary silane. Interestingly, the values of J_{H-Si} in **3–5** are very similar, in spite of the very different nature of their SiR_3 groups. Electron-withdrawing groups tend to decrease J_{H-Si} in σ-complexes because of the increased back-donation from the metal onto the antibonding orbital σ^*_{Si-H}.[1,3] Such an unusual trend in complexes **3–5** can be accounted for by steric factors. Namely, the increased repulsion of the larger tertiary silanes from the bulky Cp* ligand impedes the oxidative addition of the Si–H bond.

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Notes and references

‡ Selected X-ray data for **4**: $C_{27}H_{50}ClMoN_2P_2Si$, M_r = 526.58, monoclinic, space group $P2_1/c$, a = 10.9544(3), b = 15.0911(4), c = 15.4986(4) Å, β = 99.898(1)°, V = 2524.00(12) Å^3, Z = 4, T = 123.0(2) K, μ = 0.948 mm^{-1}, ρ_{calcd} = 1.386 g cm^{-3}, R = 0.0339, R_w = 0.0797 for 6694 unique reflections with 239 variables. CCDC 261259. See http://www.rsc.org/suppdata/cc/b5/b500679a/ for crystallographic data in CIF or other electronic format.

§ DFT calculations: All calculations were carried out using the Gaussian-03 package[16] applying Becke's exchange functional[18] in combination with Perdew's correlation functional (B-P86)[19] and the Perdew–Burke–Ernzerhof exchange and correlation functionals (PBE-PBE).[20] The calculations were performed using the "Stuttgart" 28 electron effective core potential[21] on the ruthenium atom, with a corresponding triple-ζ valence basis set augmented by one diffuse *p* function (contraction scheme {31111/411/311}). On other atoms, the standard 6–31G** basis set was employed. Full geometry optimization for all the molecular structures was performed. The ^1H–^{29}Si spin–spin coupling constants for complexes **7–10** were calculated at B3LYP level using an extended basis set within the Gauge-Including Atomic Orbitals (GIAO) approach[22] using the Gaussian-03 program.[17] Natural bond orbital analysis was performed using the NBO 3.1 program,[23] incorporated in the Gaussian-03 package. The Kohn–Sham orbitals resulting from the DFT calculations were employed.

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