

Supporting Information

Cp*(Prⁱ₃P)Ru(Cl)(η²-HSiClMe₂): the first complex with simultaneous Si–H and RuCl⋯SiCl interligand interactions

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Experimental Section.

All manipulations were carried out using conventional Schlenk techniques. Solvents were dried over sodium or sodium benzophenone ketyl and distilled into the reaction vessel by high vacuum gas phase transfer. NMR spectra were recorded on a Varian Mercury-νx (¹H, 300 MHz; ¹³C, 75.4 MHz, ³¹P, 120.8 MHz). IR spectrum was obtained from Nujol mull with a FTIR Perkin-Elmer 1600 series spectrometer. Silanes were obtained from Sigma-Aldrich. Cp*(Prⁱ₃P)Ru(Cl) was prepared according to the literature method¹.

Preparation of Cp*(Prⁱ₃P)Ru(Cl)(η²-HSiClMe₂) (4):

The compound Cp*(PⁱPr₃)RuCl (0.050 g, 0.12 mmol) was dissolved in 5 mL of ether and cooled to –30 °C. Cold solution of HSiClMe₂ (0.2 mL, 1.8 mmol) in 1 mL of ether was added, which resulted in an instantaneous colour change from deep blue to light-yellow. The resultant solution was slowly (within a week) concentrated to 1 mL at –30 °C to afford large orange-yellow crystals of **4**.

The sample for the variable temperature NMR studies was prepared by adding HSiMe₂Cl (0.1 mL, 0.9 mmol) to Cp*(Prⁱ₃P)RuCl (20 mL, 0.05 mmol) at room temperature. The formation of **4** starts at –10 °C and is quantitative at –40 °C.

IR (Nujol): $\nu_{\text{Si-H}} = 1916 \text{ cm}^{-1}$. ^1H NMR (300 MHz, -40°C , toluene- d_8): 2.52 (b, 3, $\text{PCH}(\text{CH}_3)_2$), 1.44 (s, 15, $\text{C}_5(\text{CH}_3)_5$), 1.30 (dd, $J(\text{P-H}) = 13.5 \text{ Hz}$, $J(\text{H-H}) = 6.9 \text{ Hz}$, 9, $\text{PCH}(\text{CH}_3)_2$), 1.14 (s, 3, $\text{Si}(\text{CH}_3)$), 1.03 (s, 3, $\text{Si}(\text{CH}_3)$), 0.89 (m, 9, $\text{PCH}(\text{CH}_3)_2$), -9.67 (d, $J(\text{P-H}) = 31.5 \text{ Hz}$, 1, RuH). ^{13}C NMR (toluene- d_8): 98.0 (s, $\text{C}_5(\text{CH}_3)_5$), 22.9 (bs, $\text{PCH}(\text{CH}_3)_2$), 19.9 (s, $\text{PCH}(\text{CH}_3)_2$), 10.7 (s, $\text{C}_5(\text{CH}_3)_5$), 6.2 (s, $\text{Si}(\text{CH}_3)$), 4.0 (s, $\text{Si}(\text{CH}_3)$). ^{31}P NMR (toluene- d_8): 55.2 (s). C,H,N analysis (%): calcd for $\text{C}_{21}\text{H}_{43}\text{Cl}_2\text{PRuSi}$ (526.606): C 47.90, H 8.23; found: C 48.03, H 8.25.

Reaction of $\text{Cp}^*(\text{Pr}^i_3\text{P})\text{Ru}(\text{Cl})$ with H_3SiPh :

An NMR tube was changed with a solution of $\text{Cp}^*(\text{Pr}^i_3\text{P})\text{RuCl}$ in 0.6 mL of toluene- d_8 . About 0.1 mL of H_3SiPh was added by syringe to afford an immediate colour change to yellow. ^1H NMR spectrum at room temperature established the presence of $\text{Cp}^*(\text{Pr}^i_3\text{P})\text{Ru}(\text{Cl})(\eta^2\text{-HSiPhH}_2)$ (**3**) and another hydride compound with a resonance at -11.14 ppm (d, $J(\text{H-H}) = 20 \text{ Hz}$). The spectrum recorded overnight showed the formation of another hydride compound assigned to be $\text{Cp}^*(\text{Pr}^i_3\text{P})\text{RuH}_2(\text{SiH}_2\text{Ph})$ on the basis of its hydride signal at -12.23 ppm (d, $J(\text{P-H}) = 30 \text{ Hz}$) and the Cp^* signal at 1.70 ppm (compare with $\text{Cp}^*(\text{Pr}^i_3\text{P})\text{RuH}_2(\text{SiMe}_2\text{Ph})$: -12.17 (d, $J(\text{P-H}) = 28 \text{ Hz}$, RuH) and 1.62 (s, Cp^*)). The ^1H NMR data for **3** are consistent with the literature data. At -10°C the $J(\text{H-Si})$ of 30 Hz can be resolved from the ^{29}Si satellites of the hydride signal.

DFT calculations:

All calculations were carried out with the Gaussian-03 program package² (Revision C.01) using density functional theory applying Becke's exchange functional³ in combination with Perdew's correlation functional⁴ (B-P86) as well as the Perdew-Burke-Ernzerhof exchange and correlation functionals⁵ (PBE-PBE). The calculations were performed using a "Stuttgart" 28-electron effective core potential⁶ 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 was employed. Full geometry optimizations for all of the molecular

structures were performed. Natural bond orbital analyses (Table 1) were performed with the NBO 3.1 program incorporated in the Gaussian-03 package. For this purpose, the Kohn–Sham orbitals resulting from the DFT calculations were employed.

The ^1H - ^{29}Si spin-spin coupling constants for the complexes under study were calculated within the Gauge-Including Atomic Orbitals (GIAO) approach⁷ using the Gaussian-03 program. Taking into account high sensitivity of magnetic values to the basis set and to the density functional, more extended basis sets were used for the NMR calculations. These correspond to the completely decontracted “IGLO-III” basis set of Kutzelnigg and co-workers⁸. To provide better flexibility in the core region, which is important for coupling constants⁹, it was augmented by one steep *s*-function at silicon and hydrogen. We refer to the resulting basis set as “de-IGLO-III-ext”. The NMR parameters for four free silane molecules that correspond to the silyl ligands in complexes **7–10** at the geometries optimized at PBE–PBE/6-31G** level using two different functionals, PBE–PBE and B3LYP, are given in Table 2.

The calculated ^1H - ^{29}Si coupling constants for the free silanes have a substantially higher absolute value when using B3LYP functional. For example, the calculated $J(\text{H–Si})$ of 369 Hz for HSiCl_3 at the B3LYP level is rather close to the experimental value of 380 Hz.

The calculation of the NMR parameters for the complexes **7–10** was performed at B3LYP level using the “de-IGLO-III-ext” basis set at the silyl and hydride ligands. On other atoms, the original basis used for optimizations was retained.

Crystal structure determination for 4:

Crystals of **4** were grown from ether by cooling the mixture of $\text{Cp}^*\text{Ru}(\text{P}^i\text{Pr}_3)\text{Cl}$ and HSiClMe_2 to $-30\text{ }^\circ\text{C}$. A crystal was coated with perfluoropolyether oil and mounted on a Bruker SMART CCD diffractometer. A set of experimental reflections (14754) was collected at 120 K. The data were corrected for Lorentz and polarization effects. The structure was solved by direct

methods¹¹ and refined by full-matrix least squares procedures.¹² All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except the hydride hydrogen were placed in calculated positions and refined using a “riding” model. The hydride hydrogen was located from Fourier difference synthesis and refined isotropically.

Table 1. Overlap-weighted NAO bond orders calculated from the PBE density matrix using the NBO program^{12,13} invoked from the Gaussian03 package³

	7	8	8'	9	10	SiMe ₃ H	SiMe ₂ HCl
Ru–H	0.413	0.424	0.424	0.428	0.431	—	—
Ru–Cl1	0.325	0.329	0.338	0.337	0.349	—	—
Ru–P	0.520	0.516	0.509	0.510	0.503	—	—
Ru–Si	0.419	0.465	0.470	0.504	0.530	—	—
Si···H	0.340	0.307	0.301	0.289	0.266	0.755	0.755
Si–Cl2	—	0.671	0.693	0.691	0.711	—	0.761
Si–Cl'	—	—	—	0.722	0.745/ 0.744	—	—
Si···Cl1	0.127	0.169	0.121	0.163	0.142	—	—

Cl2 is in the *trans* position with respect to the chloride ligand Cl1.

Table 2. $J(^1\text{H}-^{29}\text{Si})$ coupling constants (Hz) for the free silanes calculated at PBE–PBE/6-31G** geometry

	PBE–PBE		B3LYP	
	de-IGLO-III-ext	6-31G**	de-IGLO-III-ext	6-31G**
SiMe ₃ H	–162.7	–157.4	–179.0	–162.7
SiMe ₂ HCl	–196.9	–188.1	–216.7	–195.1
SiMeHCl ₂	–250.9	–234.9	–275.2	–243.4
SiHCl ₃	–340.1	–309.9	–369.0	–318.3

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