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NHC-carbene supported half-sandwich hydridosilyl complexes of ruthenium: the impact of supporting ligands on Si⋯H interligand interactions†

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Reactions of complex [CpRu(pyr)$_3$][PF$_6$] (3) with the NHC carbene IPr (IPr=1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) results in the NHC complex [Cp(IPr)Ru(pyr)$_2$][PF$_6$] (4), which was studied by NMR specroscopy and X-ray diffraction analysis. Reaction of [Cp(IPr)Ru(pyr)$_2$][PF$_6$] (4) with LiAlH$_4$ leads to the trihydride Cp(IPr)RuH$_3$ (5) characterised by spectroscopic methods. Heating of compound 5 with hydrosilanes gives the dihydrido silyl derivatives Cp(IPr)RuH$_2$(SiR$_3$) (6). Systematic X-ray diffraction studies suggest that complexes 6 have stronger interligand Si⋯H interactions than the isolobal phosphine complexes Cp(Pr$^i_3$P)RuH$_2$(SiR$_3$).

Introduction

Half-sandwich complexes of ruthenium find numerous applications in catalysis,[1] and in particular in the hydrosilylation of unsaturated substrates.[2-4] For example, we have previously shown that the phosphine-supported complex [Cp(Pr$^i_3$P)Ru(NCCH$_3$)$_2$]$^+$ is an efficient catalyst for chemoselective hydrosilylation of nitriles, pyridines, amides, and acid chlorides.[4] The key step in any metal-catalysed hydrosilylation is the addition of silane to the metal centre, which has three major outcomes: (a) the formation of a silylhydride species,[5] (b) the formation of a silane σ-complex,[6] and (c) formation of a hydride complex through heterolytic addition to an M-X bond (Chart 1).[7] Therefore, in a separate series of studies we investigated addition of silanes to complexes Cp(R$_3$P)RuH$_3$ to give dihydride silyl derivatives Cp'(R$_3$P)RuH$_2$(SiR$_3$) (Cp'=Cp or Cp*) and investigated the effect of the cyclopentadienyl ring and the phosphine ligand on the extent of interligand interactions between the silyl and hydride ligands.[8] Given the isolobal relationship between NHC carbenes and phosphines and the highly beneficial application of NHCs as phosphine surrogates,[9] we became interested in studying the catalytic and stoichiometric chemistry of NHC-supported half-sandwich complexes of ruthenium. Only a few compounds of this type have been synthesized[10,11] and most of them feature the Cp* (Cp* = pentamethylcyclopentadienyl) spectator group due to the availability of the precursor compound [Cp*RuCl]$_4$.[10] Here we report the synthesis of a new NHC supported trihydride complex of ruthenium and its reactions with silanes to give monosilyl dihydride derivatives, along with a systematic analysis of their X-ray structures and the effect NHC-for-phosphine substitution on the extent of Si-H interligand interactions
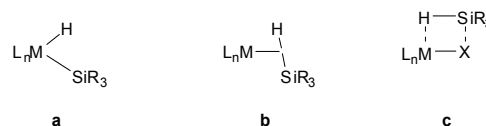

Chart 1 The modes of silane addition to transition metal complexes

Results and discussion

Starting materials. Our preparation of complexes [Cp(Pr$^i_3$P)Ru(NCCH$_3$)$_2$]$^+$[PF$_6$]$^-$ and Cp(Pr$^i_3$P)RuH$_3$ is based on the availability of the tris(nitrile) precursor [CpRu(NCCH$_3$)$_3$]$^+$ (1) and its easy reaction with phosphines to give the target Cp/phosphine derivatives.[12] Previously, Kirchner et al. reported a similar reaction of 1 with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) in THF/toluene (3:2) mixture.[11] However, in our hands this reaction resulted in only low yield of the target carbene complex [Cp(IPr)Ru(NCCH$_3$)$_2$]$^+$[PF$_6$]$^-$ (2). Analysis of the crude reaction mixture by NMR revealed a significant quantity of the imidazolium salt [HIPr]$^+$ and products presumably derived from acetonitrile, suggesting that deprotonation of the coordinated acetonitrile in the cationic compound 1 by basic carbene IPr is the major reaction pathway.

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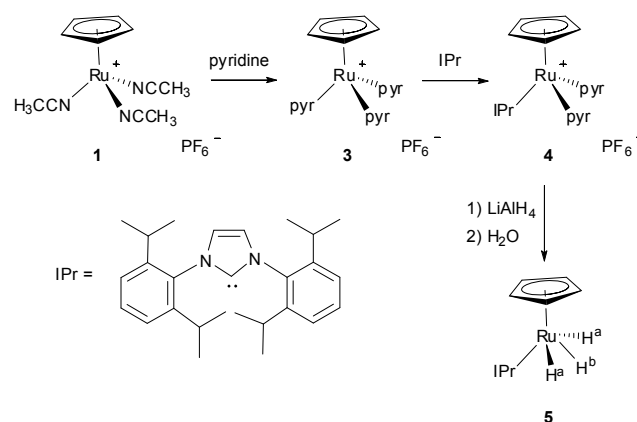
Scheme 1 Preparation of pyridine complexes **3** and **4** and the trihydride **5**.

Previously the increased CH acidity of coordinated nitriles had been observed for related systems.[13] Another by-product evident from NMR was the compound $[CpRu(toluene)]PF_6$ obtained by substitution of nitrile molecules by the solvent (toluene). To circumvent these problems, we prepared the tris(pyridine) derivative $[CpRu(pyr)_3]^+$ (**3**, pyr = pyridine) by dissolving complex **1** in pyridine and removal of volatiles under vacuum (Scheme 1). Interestingly, although pyridine is a better donor than acetonitrile,[14] complex **3** can be reverted into **1** by dissolving in excess acetonitrile. Compound **3** was characterised by ^{1}H and ^{13}C NMR and elemental analysis.

Reaction of complex **3** with IPr in THF or CH_2Cl_2 during 30 min at room temperature led to a high yield (97%) of the NHC carbene complex $[Cp(IPr)Ru(pyr)_2]^+$ (**4**). The coordination of carbene results in a noticeable up-field shift of the Cp signal in the ^{1}H NMR spectrum (in CD_2Cl_2) from 4.19 ppm in **3** to 3.77 pm in **4** and the appearance of signals due to the IPr ligand. X-ray quality crystals of a THF solvate of complex **4** were obtained from THF. The molecular structure of the cationic part is shown in Fig. 1. This is a typical tripodal piano-stool structure having
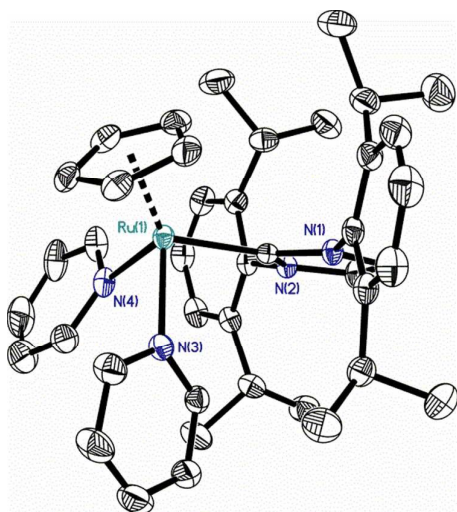
Fig.1 The molecular structure of complex $[Cp(IPr)Ru(pyr)_2][PF_6]$ (**4**). The counter-anion, THF solvate and hydrogen atoms are omitted for clarity.

one carbene and two pyridine legs. The Ru-pyridine distances are 2.1481(17) and 2.1968(18) Å and the Ru-C bond to the IPr ligand is 2.1426(18) Å.

The treatment of complex **4** with $LiAlH_4$ in THF followed by quenching the reaction mixture with water affords the target trihydride $Cp(IPr)RuH_3$ (**5**, Scheme 1). Complex **5** was isolated as a colourless microcrystalline solid after recrystallization from hexane. In the ^{1}H NMR spectrum in C_6D_6 the hydride ligands give rise to an NMR average singlet at -10.67 ppm. The Cp signal is observed at 4.30 ppm, and the carbene backbone HCN signal is found at 6.91 ppm. NMR measurements revealed a large T_1=950 ms (at 194 K) consistent with the description of **5** a classical trihydride complex, and not a η^2-dihydrogen/hydride complex.[15] At this temperature, the hydride ligands become non-equivalent and display a very large coupling constant $J(H^a$-$H^b)$ = 777 Hz, indicating the occurrence of Quantum Mechanical Exchange Coupling.[10e,16] This coupling is intermediate between those observed in related complexes $Cp(Ph_3P)RuH_3$ (900 Hz at 170 K)[17] and $Cp^*(IMes)RuH_3$ (123 Hz at 173 K),[10e] consistent with NHC carbene being a better donor than phosphine.

Preparations of silyl hydride complexes. Heating toluene solution of **5** with silanes to 50°C for 12 h cleanly yields silyl dihydride complexes $Cp(IPr)RuH_2SiR_3$ (**6**, Scheme 2). If the temperature is increased to 70°C, the reaction is completed within 1 h. For comparison, the related reactions of $Cp'(Pr^i_3P)RuH_3$ (Cp' = Cp and Cp*) occur at higher temperatures (>70°C) and are accompanied by side reactions.[8] Another difference is observed for the reaction of $HSiCl_3$ which reacted with $Cp^*(Pr^i_3P)RuH_3$ to give a mixture of $Cp^*(Pr^i_3P)Ru(Cl)(SiCl_3)(H)$ and $Cp^*(Pr^i_3P)RuH_2(SiHCl_2)$ but not $Cp^*(Pr^i_3P)RuH_2(SiCl_3)$. In contrast, heating trihydride **5** in the presence of $HSiCl_3$ furnished the dihydride silyl derivative $Cp(IPr)RuH_2(SiCl_3)$ (**6a**). The silyl complexes **6** were characterised by NMR, IR spectroscopy, and by X-ray studies. In the ^{1}H NMR spectra of **6** the equivalent hydrides give rise to high field singlets in the range -9.59 - -11.25 ppm. In IR, the RuH hydrides display bands at 1985 - 2032 cm^{-1}. The electron-withdrawing groups at the silicon atom cause more low-field NMR signals for the hydride ligands which correlate with the more red-shifted stretches in IR. Thus, the RuH resonance for the trichloride **6a** comes at -9.59 ppm (1985 cm^{-1}) versus -11.25 ppm (2030 cm^{-1}) in the $SiMe_2Ph$ derivative **6f**. The ^{29}Si-^{1}H coupling constants were measured for **6a-b,f** directly from ^{29}Si satellites in ^{1}H NMR and fall in the narrow range 12.0-13.6 Hz. The Si-H couplings of a similar magnitude were previously observed for related compounds $Cp'(Pr^i_3P)RuH_2SiR_3$.[8]

$R_3 =$ Cl$_3$ Cl$_2$Me ClMe$_2$ H$_2$Ph HMePh Me$_2$Ph
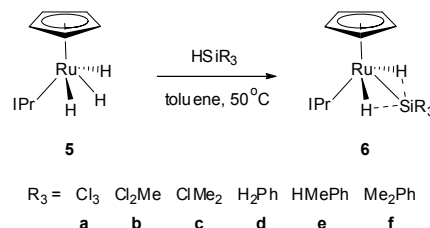   **a**   **b**   **c**   **d**   **e**   **f**

Scheme 2 Preparation of dihydride silyl complexes **6a-f**.

Table 1 Selected molecular parameters (distances in Å, angles in °) for complexes **6**

	6a [a]	**6b**	**6c**	**6d** [c]	**6e**	**6f** [d]
Ru-Si	2.250(1)	2.2951(8)	2.315(1)	2.3276(14)	2.3355(5)	2.354(3)
Si-Cl(trans)	2.100(2) [b]	2.1350(7)	2.174(1)	-	-	-
Ru-H1	1.47(4)	1.51(3)	1.53(3)	1.39(4)	1.63	-
Ru-H2	1.50(6)	1.51(3)	1.55(3)	1.46(5)	1.52	-
Ru-C(IPr)	2.055(4)	2.065(3)	2.043(3)	2.026(4)	2.027(2)	2.053(9)
Si···H	2.02(4)	2.03(3)	2.03(3)	1.76(4)	2.12	-
	2.12(6)		2.05(4)	1.96(5)	2.00	
H1-Ru-H2	110(2)	106.5(9)	106.9(18)	86(2)	105	-
RuH-Si-X(*trans*)	157.2(12)	152.2(7)	151.3(10)	144(2)	-	-
	152.4(17)	152.2(7)				

[a] The structure contains two independent molecules, mean values of geometric parameters are given for them; [b] Average of two bonds (2.104(2) and 2.098(2) Å). The third chloride atom is *trans* to the Cp group and outstands the Si atom at 2.072(2) Å; [c] X=H; [d] The hydride atoms were placed at calculted positions but not refined (see Experimental Part for details).

X-ray studies. Our initial interest in complexes of the type Cp'LRuH$_2$SiR$_3$ (Cp'= cyclopentadienyl ligand; L = a two-electron donor) was driven by the desire to investigate the incidence of Interligand Hypervalent Interactions (IHI) between the silyl and hydride ligands (Chart 2a).[18] Later analysis of the current literature[19] and computational studies of related iron,[20] ruthenium,[21] and rhodium[22] complexes suggested that these systems can be better classified as complexes with multiple interligand Si-H interactions,[19] which in many cases can be conveniently described as complexes of silicate ligands (Chart 2b).[19,23,24] Detailed X-ray studies of phosphine complexes Cp'LRuH$_2$SiR$_3$, i.e. L=PR$_3$,[8] identified the following structural variations: (i) electron-withdrawing groups at silicon (i.e. chlorides) preferably occupy positions *trans* to the hydride ligands, (ii) the Ru-Si bond shortens and (iii) the Si-Cl bond elongates when the Si···H interaction becomes stronger. Systematic variations of phosphine ligands, cyclopentadienyl groups and substituents at silicon allowed for the following conclusions: (i) the Si···H interactions are supported by the presence of electron-withdrawing groups at silicon, such as chlorides, which stabilise the hypervalent silicon centre; (ii) more donating phosphine ligands increase the strength of Si-H interactions, presumably because they make the hydrides more basic and thus better donors, whereas (iii) the increased steric bulk of the cyclopentadienyl ligand, such as in Cp* complexes, weakens this interaction because it prevents the favourable *trans* position of the chloride group relative to the hydride ligand.[8] With these ideas in mind, we became interested to probe the occurrence of Si-H interactions in complexes **6** featuring a strongly donating NHC ligand.
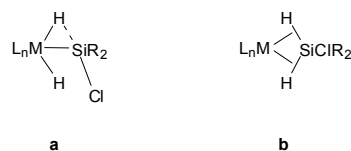
All complexes **6a-f** were studied by X-ray diffraction analysis. The molecular structure of complex **6a** is shown in Fig 2 as an example. Complexes **6b-f** display very similar dihydride silyl structures with the central position of the silyl ligand, so that their structures are given in the Supporting Information. Selected molecular parameters for complexes **6a-f** are garnered in Table 1. Like in related compounds Cp'(R$_3$P)RuH$_2$SiMe$_{3-n}$Cl$_n$ (n=1-3), the chlorosilyl ligands are oriented in such a way that the chloride group is in the *trans* position to the Ru-bound hydride. Thus, in the trichloride **6a** two relevant (Ru)H···Si-Cl angles are 152(2)° and 157(1)°, in the dichloride **6b** two (Ru)H···Si-Cl angles are related by a mirror plane and are both equal to 152.2(7)°, and finally, in the monochloride **6c** the open (Ru)H···Si-Cl bond angle is 151.3(10)°. The Ru-Si bond length progressively increases from 2.250(1) (average for two independent molecules) in **6a** to 2.354(3) in **6f** due to the introduction of more electron-donating substituents at silicon. Noteworthy, in the SiCl$_3$ derivative **6a** the two Si-Cl bonds lying *trans* to hydrides are

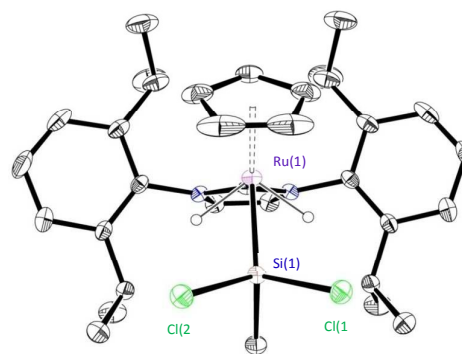**Fig.2** The molecular structure of complex Cp(IPr)RuH$_2$SiMeCl$_2$ (**6b**). There are two independent molecules in the unit cell, only one is shown here. Hydrogen atoms, except the hydrides on ruthenium atom, are omitted for clarity.

a

b

Chart 2 The description of interligand interactions in chlorosilyl complexes (a) in terms of IHI and (b) in terms of silicate coordination

slightly longer than the Si-Cl bond *trans* to the Cp ligand (2.104(2) and 2.098(2) vs 2.072(2) Å), consistent with the involvement of the two former Si-Cl bonds in hypervalent interactions. With the exception of complex **6d**, the RuH¨Si contacts are close to 2 Å and the H-Ru-H bond angles fall in the range 105(1)-109(3)°. In contrast, the complex **6d**, bearing a much smaller SiH$_2$Ph group, shows a highly reduced H-Ru-H bond angle of 86(2)° resulting in much shorter RuH¨Si distances, 1.76(4) and 1.96(5)°. This discrepancy reflects the better ability of small hydride ligands to stabilise a formally six-coordinate silicate centre in **6d**. Most complexes with non-classical interligand Si¨H interactions have the Si-H distance close or shorter than 2 Å, although a few long range interactions are also known.[5,19]

The monochloride complex **6c** was of particular interest to us because it allows for systematic comparison with related phosphine complexes Cp(Pr$^i_3$P)RuH$_2$SiMe$_2$Cl and Cp*(Pr$^i_3$P)RuH$_2$SiMe$_2$Cl previously studied by X-ray analyses.[8] Both CpI compounds show shorter Ru-Si and longer Si-Cl bond lengths than the Cp* complex (Table 2), consistent with the stronger Si-H interactions in the former, which may be related to the favourable *trans* disposition of the hydride and chloride groups allowed by the less bulky Cp ligand.[8c,19] The comparison of the phosphine complex Cp(Pr$^i_3$P)RuH$_2$SiMe$_2$Cl with the NHC complex **6c** reveals further contraction of the Ru-Si distance from 2.3377(7) Å to 2.315(1) Å, respectively, and the concomitant elongation of the Si-Cl bond from 2.153(2) Å to 2.174(1) Å, suggesting that the more donating IPr ligand[25] exerts stronger H¨Si interactions. The latter Si-Cl bond compares well with the elongated distances in hydrido chlorosilyl complexes with Interligand Hypervalent Interactions.[26,27] The rational for these structural trends is that in both the silicate complexes Cp(L)RuH$_2$SiMe$_2$Cl and in compounds with IHI the silicon centre is hypervalent.

Table 2 Selected molecular parameters in complex **6c** and its phosphine analogues.

Parameter	Cp/IPr	Cp/Pr$^i_3$P	Cp*/ Pr$^i_3$P
Ru-Si	2.315(1)	2.3377(7)	2.332(1)
Si-Cl	2.174(1)	2.153(2) [a]	2.126(7)

[a] This Si-Cl distance can be compromised by the rotation disorder of the SiMe$_2$Cl ligand. In the related Cp/Pr$^i_2$PhP complex, the Si-Cl bond is 2.164(1) Å.[8a]

Conclusions

In conclusion, reactions of carbene-supported trihydride Cp(IPr)RuH$_3$ with hydrosilanes afford dihydride silyl derivatives Cp(IPr)RuH$_2$(SiR$_3$) with non-classical Si¨H interligand interactions, which can be described as silicate complexes. X-ray data suggest that the replacement of phosphine ligand in the fragment Cp(Pr$^i_3$P)Ru for the more electron releasing NHC

carbene results in the strengthening of the RuH¨Si interactions.

Experimental

General Methods and Instrumentation

All manipulations were carried out using conventional inert atmosphere glove-box and Schlenk techniques. Solvents were pre-dried by using Grubbs-type purification columns and stored in ampoules equipped with Teflon valve. Deuterated solvents were dried over sodium, potassium, or CaH$_2$ as appropriate, distilled under reduced pressure and stored in Teflon valve ampoules. NMR samples were prepared in New Era tubes equipped with J. Young type Teflon valves. NMR spectra were obtained at room temperature with a Bruker DPX-300 and Bruker DPX-600 instruments ([1]H: 300 and 600 MHz; [13]C: 75.5 and 151 MHz). [1]H and ^{13}C spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer as Nujol mulls between NaCl windows. All data are quoted in wavenumbers (cm^{-1}). Elemental analyses were performed in "ANALEST" laboratories (University of Toronto) or in the analytic laboratory of McMaster University. Complex [CpRu(NCCH$_3$)$_3$]PF$_6$ (**1**) was prepared according to a literature procedure.[28]

[CpRu(pyr)$_3$][PF$_6$] (3)

[CpRu(NCCH$_3$)$_3$] [PF$_6$] (0.250 g, 0.576 mmol) was placed in a Schlenk tube equipped with a magnetic stirring bar. Dry pyridine (20 mL) pre-saturated with N$_2$ was added. The yellow solution was stirred at room temperature for 24 h. Volatiles were removed under vacuum to give 0.310 g of [CpRu(pyr)$_3$][PF$_6$] (**3**) as a dark yellow, air sensitive solid. Yield 98%. ^{1}H NMR (600 MHz, CD$_2$Cl$_2$): δ 4.19 (s, 5 H, Cp), 7.38 (t, *J*(H-H)=7.0 Hz, 6H, py), 7.82 (t, *J*(H-H)=7.8Hz, 3H, py), 8.52 (t, *J*(H-H)=7.0 Hz, 6H, py). ^{13}C NMR (600 MHz, CD$_2$Cl$_2$): δ 53.4 (s, Cp), 125.7 (s, NC**C**C), 137.3 (s, NCC**C**), 154.5 (s, N**C**CC). Anal. Cal. for C$_{20}$H$_{20}$RuN$_3$PF$_6$ (548.43): C, 43.80; H, 3.68; N: 7.66. Found: C, 43.61, H, 4.13; N: 7.54.

[Cp(IPr)Ru(pyr)$_2$][PF$_6$] (4)

To [CpRu(pyr)$_3$][PF$_6$] (**3**) (0.250 g, 0.456 mmol) in 20 mL dichloromethane solution was added IPr NHC (0.174 g, 0.456 mmol). After stirring at room temperature for 1 day, the resulting solution was dried to yield **4** as a brownish-yellow, air sensitive solid (0.380 g, 97 %). This new compound was recrystallised from a THF/hexane (4:1) mixture to give a THF solvate of **4**. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.13 (d, *J*(H-H)=6.9Hz, 12H, CH$_3$), 1.30 (d, *J*(H-H)=7.0Hz,12H, CH$_3$), 2.82 (sept, *J*(H-H)=7.0Hz, 4H, CH in ^{i}Pr), 3.77 (s, 5H, Cp), 7.11 (s, 2H, NC**H** of ^{i}Pr), 7.32-7.46 (m, 6H, C$_6$*H$_3$*), 7.5 (t, *J*(H-H)=6.8 Hz, 4H, *m*-pyr), 7.9 (t, *J*(H-H)=6.8 Hz, 2H, *p*-pyr), 8.5 (d, *J*(H-H)=6.8 Hz, 4H, *o*-pyr). ^{31}P NMR: -145.6 (sept, *J*(P-F) = 709 Hz, PF$_6$). Anal. Cal. for C$_{50}$H$_{67}$RuN$_4$O$_2$PF$_6$ (1002.13) C, 59.93; H, 6.74; N: 5.59. Found: C, 60.74, H, 6.76; N: 5.24.

Cp(IPr)RuH$_3$ (5)

To a solution of **4** (0.200 g, 0.36 mmol) in 2 ml of THF was added LiAlH$_4$ (0.034 g, 0.9 mmol). The resulting mixture was left overnight

at ambient temperature and then was slowly hydrolysed with degassed water. After evaporation of the solvent, the yellow residue was extracted with hexane (3-10 mL). Removal of volatiles and recrystallization at -30°C from hexane solution afforded 0.117 g of **5** in the form of white crystals. Yield: 85% (0.117g). IR (Nujol): v(Ru–H) = 1982 cm^{-1}. ^{1}H NMR (600 MHz, CD$_2$Cl$_2$): δ -10.67 (s, 3H, RuH_3), 1.11 (d J(H-H) = 7.0 Hz, 12 H, CH_3), 1.39 (d, J(H-H)=7.0 Hz, 12 H, CH$_3$), 2.72 (sept, J(H-H)=7.0 Hz, 4H, CH in ^{i}Pr), 4.30 (s, 5 H, Cp), 6.91 (s, 2 H, NCH), 7.32-7.46 (m, 6H, C$_6$H$_3$). ^{13}C NMR (600 MHz, C$_6$D$_6$): δ 25.7 (s, CH$_3$), 23.1 (s, CH$_3$), 28.8 (s, CH(CH$_3$)$_2$), 80 (s, Cp), 122.1 (s, NCH), 123.8 (m-C, C$_6$H$_3$), 129 (p-C, C$_6$H$_3$), 146.0 (Ru-CN$_2$). Anal. Cal. for C$_{32}$H$_{44}$RuN$_2$ (557.78): C, 68.91; H, 7.95; N: 5.02. Found: C, 68.03, H, 7.81; N: 5.01.

Cp(IPr)RuH$_2$(SiCl$_3$) (6a)

To a solution 0.050 g of Cp(IPr)RuH$_3$ in C$_6$D$_6$ was added an equivalent of HSiCl$_3$. The mixture was heated to 50°C overnight. The ^{1}H NMR spectrum showed that Cp(IPr)RuH$_2$(SiCl$_3$) was formed in 82% yield. All solvents were removed under vacuum. Then the product were extracted by hexanes and recrystalised from a mixture of hexane and ether (1:1 ratio). Isolated yield: 57% (0.035 g). IR (Nujol): v(Ru–H) = 1985 cm^{-1}. ^{1}H NMR (600 MHz, C$_6$D$_6$): δ -9.59 (s, 2H, RuH_2), 0.92 (d, J(H-H) = 6.6 Hz, 12H, CH_3), 1.45 (d, J(H-H) = 6.6Hz, 12H, CH_3), 2.82 (sept, J(H-H) = 6.6 Hz, 4H, CH in ^{i}Pr), 4.57 (s, 5H, Cp), 6.51 (s, 2H, NCH), 7.15-7.24 (m, 6H, C$_6$H$_3$). ^{13}C NMR (600 MHz, C$_6$D$_6$): δ 26.3 (s, CH$_3$), 22.9 (s, CH$_3$), 28.6 (CH(CH$_3$)$_2$), 84.5 (s, Cp), 124.7 (NCH), 124.1 (m-C, C$_6$H$_3$), 128.4 (p-C, C$_6$H$_3$), 184.0 (Ru-CN$_2$). ^{29}Si NMR (^{1}H-^{29}Si HSQC): 33.6 (SiCl$_3$). Anal. Cal. for C$_{32}$H$_{43}$RuN$_2$SiCl$_3$ (691.21): C, 55.4; H, 6.27; N: 4.05. Found: C, 53.57, H, 5.98; N: 3.27.

Cp(IPr)RuH$_2$(SiCl$_2$Me) (6b)

To a solution of 0.050 g Cp(IPr)RuH$_3$ in C$_6$D$_6$ was added an equivalent of HSiCl$_2$Me. The mixture was heated to 70°C for 2h. The ^{1}H NMR spectrum showed quantitative formation of Cp(IPr)RuH$_2$(SiCl$_2$Me). All volatiles were removed under vacuum. The product were extracted by hexanes and recrystalised from a mixture of hexane and ether (1:1 ratio). Isolated yield: 88% (0.053 g). IR (Nujol): v(Ru–H) = 1970 cm^{-1}. ^{1}H NMR (600 MHz, C$_6$D$_6$): δ -10.17 (s, 2H, RuH_2), 1.04 (d, J(H-H) = 6.9 Hz, 12H, CH$_3$ of ^{i}Pr), 1.53 (d, J(H-H) = 6.9Hz,12H, of ^{i}Pr), 1.34 (s, 3H, SiCH$_3$), 2.97 (sept, J(H-H) = 6.9Hz, 4H, CH in ^{i}Pr), 4.63 (s, 5H, Cp), 6.64 (s, 2H, NCH), 7.25-7.36 (m, 6H, C$_6$H$_3$). ^{13}C NMR (600MHz, C$_6$D$_6$): δ 26.3 (s, CH$_3$), 22.9 (s, CH$_3$), 24.8 (SiCH$_3$), 28.7 (s, CH(CH$_3$)$_2$), 83.3 (Cp), 124.3 (NCH), 123.9 (m-C, C$_6$H$_3$), 128.4 (p-C, C$_6$H$_3$), 187.3 (Ru-CN$_2$). ^{29}Si NMR (^{1}H-^{29}Si HSQC): 66.7 (SiCl$_2$Me), J(Si-H) = 12.5 Hz. Anal. Cal. for C$_{33}$H$_{46}$RuN$_2$SiCl$_2$ (670.79): C, 59.09; H, 6.91; N: 4.18. Found: C, 58.94, H, 7.09; N: 4.09.

Cp(IPr)RuH$_2$(SiClMe$_2$) (6c)

To a solution of 0.050 g of Cp(IPr)RuH$_3$ in C$_6$D$_6$ was added an equivalent of HSiClMe$_2$. The mixture was heated to 70°C for 2h. The ^{1}H NMR spectrum showed quantitative formation of Cp(IPr)RuH$_2$(SiClMe$_2$). All volatiles were removed under vacuum. The product were extracted by hexanes and recrystalised from a mixture of hexane and ether (1:1 ratio). Isolated yield: 90% (0.053 g). IR (Nujol): v(Ru–H) = 1981cm^{-1}. ^{1}H NMR (600 MHz, C$_6$D$_6$): δ -10.88 (s, 2H, RuH_2), 1.05 (d, J(H-H) = 7.0Hz, 12H, CH$_3$ of ^{i}Pr), 1.51 (d, J(H-H)= 7.0Hz, 12H, CH$_3$ of ^{i}Pr), 1.02 (s, 6H, Si(CH$_3$)$_2$, 2.98 (sept, J(H-H) = 7.0 Hz, 4H, CH of ^{i}Pr), 4.63 (s, 5H, Cp), 6.64 (s, 2H, NCH), 7.26-7.37 (m, 6H, C$_6$H$_3$). ^{13}C NMR (600 MHz, C$_6$D$_6$): δ 26.3 (s, CH$_3$), 22.7 (s, CH$_3$), 18.63 (s, SiCH$_3$) 28.8 (s, CH(CH$_3$)$_2$)$_2$), 82.4 (Cp), 124.1 (NCH),

123.78 (m-C, C$_6$H$_3$), 129.8 (p-C, C$_6$H$_3$), 191.3 (Ru-CN2). ^{29}Si NMR (^{1}H-^{29}Si HSQC): 66.7 (SiClMe$_2$), J(Si-H) = 11.6 Hz. Anal. Cal. for C$_{34}$H$_{49}$RuN$_2$SiCl (650.37): C, 62.79; H, 7.59; N: 4.31. Found: C, 61.76, H, 7.54; N: 4.18.

Cp(IPr)RuH$_2$(H$_2$SiPh) (6d)

To a solution of 0.050 g Cp(IPr)RuH$_3$ in C$_6$D$_6$ was added an equivalent of H$_3$SiPh. The mixture was heated to 70°C for 2h. The ^{1}H NMR spectrum showed that Cp(IPr)RuH$_2$(H$_2$SiPh) was formed in 99% yield. All solvents were removed under vacuum. Then the product were extracted by hexanes and recrystalised from a mixture of hexane and ether (1:1 ratio). Isolated yield: 95% (0.057 g). IR (Nujol): v(Ru–H) = 1992 cm^{-1}. ^{1}H NMR (600 MHz, C$_6$D$_6$): δ -9.59 (s, 2H, RuH$_2$), 0.99 (d, J(H-H)=7.0Hz, 12H, CH$_3$ of ^{i}Pr), 1.37 (d, 12H, CH$_3$ of ^{i}Pr), 2.89 (sept, J(H-H) = 7.0Hz, 4H, CH of ^{i}Pr), 4.44 (s, 5H, Cp), 5.22 (s, 2H, SiH$_2$), 6.56 (s, 2H, NCH), 7.15-7.24 (m, 6H, C$_6$H$_3$), 7.40 (t, J(H-H) = 7.3 Hz, ortho H of SiC$_6$H$_5$), 7.42 (t, J(H-H) = 7.3 Hz, meta H of SiC$_6$H$_5$), 7.82 (t, J(H-H) = 7.3Hz, para H of SiC$_6$H$_5$) . ^{13}C NMR (600 MHz, C$_6$D$_6$): δ 26.1 (s, CH$_3$), 22.5(s, CH$_3$), 29.3 (s, CH of ^{i}Pr), 81.9 (Cp), 124.1 (NCH), 127.2 (m-C, C$_6$H$_3$), 136.1 (p-C, C$_6$H$_3$), 192.4 (Ru-CN$_2$). ^{29}Si NMR (^{1}H-^{29}Si HSQC): -18.8 (SiH$_2$Ph). Anal. Cal. for C$_{38}$H$_{50}$RuN$_2$Si (663.97): C, 68.74; H, 7.59; N: 4.22. Found: C, 67.8, H, 7.46; N: 4.10.

Cp(IPr)RuH$_2$(HSiMePh) (6e)

To a solution of 0.050g Cp(IPr)RuH$_3$ in C$_6$D$_6$ was added an equivalent of H$_2$SiMePh. The mixture was heated to 70°C for 2h. ^{1}H NMR spectrum showed that Cp(IPr)RuH$_2$(SiHMePh) was formed in 99% yield. All solvents were removed under vacuum. Then the product were extracted by hexanes and recrystalised from a mixture of hexane and ether (1:1 ratio). Isolated yield: 78% (0.047 g). IR (Nujol): v(Ru–H) = 2032 cm^{-1}. ^{1}H NMR (600 MHz, C$_6$D$_6$): δ -11.25 (s, 1H, RuH$_2$), -10.81 (s, 1H, RuH$_2$), 1.11 (d, J(H-H) = 7.0Hz, 12H, CH$_3$ of ^{i}Pr), 1.37 (d, J(H-H)=7.0Hz, 6H, CH$_3$ of ^{i}Pr), 1.53 (d, J(H-H) = 7.0Hz, 6H, CH$_3$ of ^{i}Pr), 0.86 (d, J(H-H) = 3.6Hz, 3H, Si(CH$_3$), 2.98 (sept, J(H-H) = 7.0Hz, 2H, CH of ^{i}Pr), 3.10 (sept, J(H-H) = 7.0Hz, 2H, CH of ^{i}Pr), 4.52 (s, 5H, Cp), 5.38 (q, 1H, SiH$MePh$), 6.67 (s, 2H, NCH), 7.22-7.40 (m, 6H, C$_6$H$_3$), 7.36-7.42 (3H, m- and p- of SiC$_6$H$_5$), 7.75 (d, J(H-H) = 3.8Hz 2H, o- SiC$_6$H$_5$). ^{13}C NMR (600 MHz, C$_6$D$_6$): δ 25.7 (s, CH$_3$ of ^{i}Pr), 22.6 (s, CH$_3$ of ^{i}Pr), 7.2 (SiCH$_3$), 28.9 (CH of ^{i}Pr), 81.6 (Cp), 123.7 (NCH), 124.05 (m-C, C$_6$H$_3$), 129.6 (p-C, C$_6$H$_3$), 124.43 (p-C of SiC$_6$H$_5$), 126.8 (m-C of SiC$_6$H$_5$), 135.1 (o-C of SiC$_6$H$_5$), 193.4 (Ru-CN$_2$). ^{29}Si NMR (^{1}H-^{29}Si HSQC): -0.8 (SiHMePh). Anal. Cal. for C$_{39}$H$_{52}$RuN$_2$Si (678.00): C, 69.09; H, 7.73; N: 4.13. Found: C, 71.58, H, 7.55; N: 4.1.

Cp(IPr)RuH$_2$(SiMe$_2$Ph) (6f)

To a solution of 0.050 g Cp(IPr)RuH$_3$ in C$_6$D$_6$ was added an equivalent of HSiMe$_2$Ph. The mixture was heated to 70°C for 2h. The ^{1}H NMR spectrum showed that Cp(IPr)RuH$_2$(SiMe$_2$Ph) was formed in 99% yield. All solvents were removed under vacuum. Then the product were extracted by hexanes and recrystalised from a mixture of hexane and ether (1:1 ratio). Isolated yield: 67% (0.042 g). IR (Nujol): v(Ru–H) = 2030 cm^{-1}. ^{1}H NMR (600 MHz, C$_6$D$_6$): δ -11.25 (s, 2H, RuH$_2$), 1.07 (d, J(H-H) = 7.0 Hz, 12H, CH$_3$ of ^{i}Pr), 1.41 (d, J(H-H) = 7.0Hz, 12H, CH$_3$ of ^{i}Pr), 0.80 (s, 6H, Si(CH$_3$)$_2$, 3.00 (sept, J(H-H) = 7.0 Hz 4H, CH$_3$ of ^{i}Pr), 4.53 (s, 5H, Cp), 6.69 (s, 2H, NCH), 7.28-7.42 (m, 6H, C$_6$H$_3$), 7.36-7.42 (3H, m- and p of SiC$_6$H$_5$), 7.82 (d, 2H, o- of SiC$_6$H$_5$). ^{13}C NMR (600 MHz, C$_6$D$_6$): δ 26.3 (s, CH$_3$ of ^{i}Pr), 22.6 (s, CH$_3$ of ^{i}Pr), 11.7 (s, SiCH$_3$) 28.8 (s, CH$_3$ of ^{i}Pr), 81.7 (Cp), 123.7 (s, NCH), 123.9 (s, m-C, C$_6$H$_3$), 129.46 (s, p-C, C$_6$H$_3$), 126.4 (s, p-C of SiC$_6$H$_5$), 126.7 (s, m-C of SiC$_6$H$_5$), 134.9 (s, o-C of SiC$_6$H$_5$), 194.7 (s, Ru-CN$_2$). ^{29}Si NMR (^{1}H-^{29}Si HSQC): 15.2 (SiCl$_2$Me), J(Si-H) = 13.23Hz. Anal. Cal. for C$_{40}$H$_{54}$RuN$_2$Si (692.03): C, 69.42; H, 7.87; N: 4.05. Found: C, 68.9, H, 7.46; N: 4.04.

Crystal structure determination

Single crystals of **4**, suitable for X-ray diffraction analysis, were grown from THF/hexane (1:1) at -30 °C. Single crystals of complexes **6a-f** were grown from hexane/ether (1:1) solution at -30 °C. The crystals were mounted in a film of perfluoropolyether oil on a glass fibre and transferred to a diffractometer. Intensity data for **6a**, **6c**, and **6d** were collected on a Bruker SMART 1K diffractometer and for **4** and **6b**, **6e**, **6f** on a Bruker AXS KAPPA machine, using MoKα radiation (0.71073 Å). Absorption corrections based on measurements of equivalent reflections were applied. All structures were solved by direct methods[29] and refined by full matrix least-squares on F^2[30,31] with anisotropic thermal parameters for all non-hydrogen atoms. For compounds **4**, **6a**, **6b**, **6c**, and **6d** all non-hydride hydrogen atoms were placed in calculated positions and refined using a riding model. The hydride atoms were found from difference Fourier synthesis and refined isotropically. For compound **6e** the hydride atoms were found from difference Fourier synthesis whereas other H atoms were placed in calculated positions and then all H atoms were refined using a riding model. The crystal **6f** was found to be non-merohedrally twinned. The data was processed with CELL_NOW software.[32] Further refinement

resulted in domain ratio 0.82 / 0.18. To prevent "non-positive definite" behaviour all carbon atoms in the structure **6f** were refined using SIMU or RIGU restraints.

Despite compelling independent experimental evidence for the presence of Ru-bound hydrides, the quality of crystallographic data for **6f** was not sufficient to locate the hydride ligands. In order to satisfy the formulation, positions of the hydrides were assigned by applying a rigid fragment model (FRAG/FEND). Thus, the coordinates of the immediate coordination sphere of ruthenium centre were derived from a considerably better quality structure of the closely related compound **6e**, where similar hydride positions were found from the Fourier electron density maps. Once assigned, the hydride atoms for **6f** were refined using riding approximation for the RuH_2 fragment. Other hydrogen atoms were placed in calculated positions and refined using a riding model. The details of X-ray studies are given in Table 3.

Acknowledgements

Table 3 Crystal and structure refinement data for **6a-f**.

	4	6a	6b	6c	6d	6e	6f
Empirical formula	$C_{46}H_{59}F_6N_4OPRu$	$C_{32}H_{43}Cl_3N_2RuSi$ $0.5(C_4H_{10}O)$	$C_{33}H_{42}Cl_2N_2RuSi$	$C_{34}H_{49}ClN_2RuSi$	$C_{38}H_{50}N_2RuSi$	$C_{39}H_{52}N_2RuSi$	$C_{40}H_{54}N_2RuSi$
Formula weight	930.01	728.25	670.78	650.38	663.98	677.98	692.01
colour, habit	orange, block	colourless, block	colourless, block	colourless, block	colourless, block	colourless, block	colourless, block
Crystal size, mm^3	0.10x0.15x0.23	0.14x0.10x0.04	0.12x0.15x0.23	0.36x0.32x0.28	0.16x0.24x0.26	0.10x0.19x0.31	0.10x0.12x0.17
Crystal system	Triclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	P -1	P -1	$Pnma$	$P2_1/n$	P -1	$P2_1/c$	P -1
Unit cell dimensions:							
a, Å	12.0812(3)	11.0661(6)	9.7104(5)	19.0229(7)	10.0980(4)	10.2931(2)	10.4447(12)
b, Å	12.9431(3)	18.8580(10)	19.1394(11)	19.7991(5)	16.7278(6)	16.9562(3)	12.3858(14)
c, Å	14.3806(3)	18.9389(10)	18.2255(10)	19.6305(7)	20.6290(7)	20.9730(4)	15.3320(18)
α, °	98.2779(11)	110.994(2)	90	90	93.744(3)	90	95.821(6)
β, °	99.9999(10)	102.836(2)	90	113.641(4)	94.745(3)	97.4911(11)	99.541(6)
γ, °	90.2522(12)	97.069(2)	90	90	91.931(3)	90	104.375(6)
Volume, $Å^3$	2190.44(9)	3507.4(3)	3387.2(3)	6773.1(4)	3462.6(2)	3629.21(12)	1873.5(4)
Z	2	4	4	8	4	4	2
Density (calcd), g/cm^3	1.410	1.379	1.315	1.276	1.274	1.241	1.227
Absorption coefficient, mm^{-1}	0.460	0.737	0.679	0.601	0.515	0.493	0.479
F(000)	968	1516	1400	2736	1396	1432	732
Temperature, K	200(2)	120(2)	200(2)	123(2)	123(2)	200(2)	200(2)
2θ range for data collection, °	3.76 to 28.35	1.96 to 27.00	1.543 to 28.26	2.98 to 27.50	2.95 to 27.50	1.959 to 28.32	1.716 to 28.79
Reflections collected	25768	15272	51836	15090	15872	31236	29773
Independent reflections	10779 [R(int) = 0.0180]	11291 [R(int) = 0.0422]	3781[R(int) = 0.0222]	10142 [R(int) = 0.0648]	10975 [R(int) = 0.1167]	8998 [R(int) = 0.0205]	14907 [R(int) = 0.1288]
Data / restraints / parameters	10779/0/532	15272 /17/767	4291/0/184	15090/0/718	15872/0/783	8998/0/388	8931/453/398
Goodness-of-fit on F^2	1.028	1.047	0.982	1.068	1.043	1.065	1.216
Final R indices [I>2σ(I)]	R_1 = 0.0371 wR_2 = 0.0960	R_1 = 0.0491, wR_2 = 0.1171	R_1 = 0.0322, wR_2 = 0.0383	R_1 = 0.0527, wR_2 = 0.0936	R_1 = 0.0619, wR_2 = 0.1363	R1 = 0.0302, wR2 = 0.0704	R_1 = 0.1499, wR_2 = 0.3379
R indices (all data)	R_1 = 0.0410 wR_2 = 0.0990	R_1 = 0.0768, wR_2 = 0.1294	R_1 = 0.0708, wR_2 = 0.0754	R_1 = 0.0944, wR_2 = 0.1201	R_1 = 0.0987, wR_2 = 0.1544	R1 = 0.0377, wR2 = 0.0736	R_1 = 0.1858, wR_2 = 0.3605
Largest diff. peak and hole, e.$Å^{-3}$	2.654 and -0.780	2.061 and -1.189	0.478 and -0.552	1.20 and -0.94	1.43 and -0.99	0.532 and -0.326	3.762 and -1.849

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Graphical abstract

stronger than in $^{i}Pr_3P$
complexes
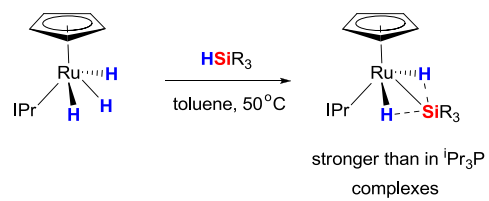
Electron donating NHC carbene ligand IPr exerts stronger RuH···Si interactions in complexes Cp(IPr)RuH$_2$(SiR$_3$) than in related $^{i}Pr_3P$ complexes Cp($^{i}Pr_3P$)RuH$_2$(SiR$_3$).