DOI: 10.1002/ejic.200801105

Synthesis and Reactivity of Ru(NHC)(dppp)(CO)H_2 and Ru(NHC)(dppp)(CO)HF Complexes: C–H and C–F Activation

Steven P. Reade,[a] Aaron L. Acton,[a] Mary F. Mahon,[a] Thomas A. Martin,[a] and Michael K. Whittlesey*[a]

Keywords: Carbene ligands / Ruthenium complexes / Hydrido ligands / Fluorido ligands / C–H activation / C–F activation / Nitrogen heterocycles / Cleavage reactions

The hydrido fluorido ruthenium(II) complex [Ru(PPh_3)(dppp)(CO)HF] [**1**, dppp = 1,4-bis(diphenylphosphanyl)propane], which forms upon reaction of [Ru(PPh_3)$_3$(CO)HF] with dppp, reacts with IMes [1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] to give the expected carbene-containing hydrido fluorido complex [Ru(IMes)(dppp)(CO)HF] (**2**), as well as the C–H activated species [Ru(IMes)′(dppp)(CO)H] (**3**). The formation of the latter product results from the reaction of **2** with a base (IMes or Et_3N). Displacement of PPh_3 from [Ru(PPh_3)(dppp)(CO)H_2] by ICy (1,3-dicyclohexylimidazol-2-ylidene) yields [Ru(ICy)(dppp)(CO)H_2] (**7**), which upon reaction with Et_3N·3HF, gives [Ru(ICy)(dppp)(CO)HF] (**8**). Thermolysis of **7** with C_6F_6 at elevated temperature generates **8** and [Ru(ICy)(dppp)(CO)(C_6F_5)H] (**9**). The related fluoroaryl complexes [Ru(ICy)(dppp)(CO)($C_6F_4CF_3$)H] (**10**) and [Ru(ICy)(dppp)(CO)(C_5F_4N)H] (**11**) are formed upon the room temperature C–F activation of $C_6F_5CF_3$ and C_5F_5N by **7**, but also by C–H activation of the partially fluorinated substrates *p*-$C_6F_4HCF_3$ and *p*-C_5F_4HN.

Introduction

N-Heterocyclic carbene (NHC) dihydrido and hydrido halido complexes of the platinum-group metals have proven to be very valuable precursors for the activation of inert bonds.[1] For example, in a number of Rh and Ir NHC complexes, the elimination of either H_2 or HCl generates coordinatively unsaturated species capable of cleaving C–H bonds in the N-substituents of a carbene[2] and at the C-2 and C-4/5 positions of imidazolium salts.[3] Similarly, bond-activation reactions have been described in a number of ruthenium complexes, with examples of intramolecular C–H and C–C cleavage known for RuH_2 species[4–6] and C–H and C–N activation reported for hydrido chlorido compounds.[7]

Chloride turns out to be the most commonly encountered halido ligand, with very few examples known of NHC metal fluorido complexes.[8] We recently reported that the ruthenium NHC hydrido fluorido species [Ru(NHC)(PPh_3)$_2$(CO)HF] [NHC = IMe_4 (1,3,4,5-tetramethylimidazol-2-ylidene), IEt_2Me_2 (1,3-diethyl-4,5-dimethylimidazol-2-ylidene), I*i*Pr_2Me_2 (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) and ICy (1,3-dicyclohexylimidazol-2-ylidene)] could be prepared at room temperature upon substitution of PPh_3 in [Ru(PPh_3)$_3$(CO)HF] by the free carbenes.[9] All four of the carbene complexes proved to be relatively unstable in solution; [Ru(IMe_4)(PPh_3)$_2$(CO)HF], [Ru(IEt_2Me_2)(PPh_3)$_2$(CO)HF] and [Ru(ICy)(PPh_3)$_2$(CO)HF] isomerised within a period of weeks from *trans*- to *cis*-phosphane isomers, while [Ru(I*i*Pr_2Me_2)(PPh_3)$_2$(CO)HF] underwent both isomerisation, as well as disproportionation to [Ru(I*i*Pr_2Me_2)$_2$(PPh_3)(CO)HF] and [Ru(PPh_3)$_3$(CO)HF], within a matter of hours. We reasoned that further studies of hydrido fluorido ruthenium species should incorporate a chelating phosphane ligand in place of the two PPh_3 groups as this should prevent isomerisation/disproportionation, allowing a more detailed investigation of reactivity to be undertaken.

In this paper, we report the preparation and reactivity of *N*-alkyl as well as *N*-aryl carbene complexes of the general formula [Ru(NHC)(P-P)(CO)HF] in which P-P is the bidentate phosphane 1,4-bis(diphenylphosphanyl)propane (dppp). While these compounds do indeed retain their stereochemistry in solution, they prove to be reactive in other ways, with (i) [Ru(IMes)(dppp)(CO)HF] [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] undergoing base induced elimination of HF and subsequent intramolecular C–H activation of the carbene and (ii) [Ru(ICy)(dppp)(CO)HF] taking part in F/H exchange with R_3SiH to afford [Ru(ICy)(dppp)(CO)H_2], which activates C–F and C–H bonds in aromatic fluorocarbons.

[a] Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK
Fax: 44-1225-386231
E-mail: m.k.whittlesey@bath.ac.uk

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

Results and Discussion

The dppp complex [Ru(PPh_3)(dppp)(CO)HF] (**1**) was prepared as a potential precursor to [Ru(NHC)(dppp)(CO)HF] complexes by reaction of [Ru(PPh_3)$_3$(CO)HF] with a slight excess of dppp at 70 °C (Scheme 1). An alternative, but lower yielding route to **1**, involved the addition of Et_3N·HF (TREAT-HF) to [Ru(PPh_3)(dppp)(CO)H_2]. The spectroscopic properties of **1** were found to be similar to those of [Ru(PPh_3)$_3$(CO)HF], with a multiplet hydride resonance observed at δ = –4.18 (cf. δ = –5.05 for [Ru(PPh_3)$_3$(CO)HF]),[9] which through a combination of broadband and selective ^{31}P-decoupling experiments yielded coupling constants of 117.1 (*trans*-$J_{H,P}$), 25.0 (*cis*-$J_{H,P}$), 16.9 (*cis*-$J_{H,P}$) and 4.2 Hz ($J_{H,F}$). The $^{31}P\{^1H\}$ NMR spectrum consisted of an ABX pattern, while the ^{19}F spectrum showed only a low frequency (δ –381) multiplet for the Ru–F resonance.[10,11] The IR carbonyl-stretching frequency of 1900 cm^{-1} is lower than that reported for [Ru(PPh_3)(dppp)(CO)HCl] (1920 cm^{-1}) consistent with fluoride being a stronger π-donor.[12]

The molecular structure of **1** was determined by X-ray crystallography as shown in Figure 1. Selected bond lengths and angles are given in Table 1. The compound displayed a distorted-octahedral geometry with the two, *trans*-phosphanes being tilted towards the hydrido ligand [P(1)–Ru(1)–P(3) 168.09(3)°; P(4)–Ru(2)–P(5) 171.20(3)°].[12,13] The Ru–F bond lengths for the two molecules in the unit cell [2.1005(18), 2.0943(18) Å] are comparable to other hydrido fluorido Ru complexes in the literature[14,15] and in fact identical to the Ru–F distance in [Ru(PPh_3)$_3$(CO)HF][9] (unsurprisingly given that in both cases the π-donor fluorido ligand is *trans* to the π-acceptor CO group).[16]

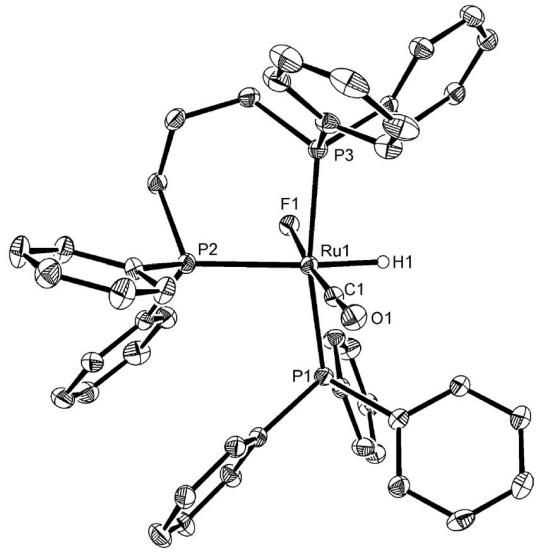
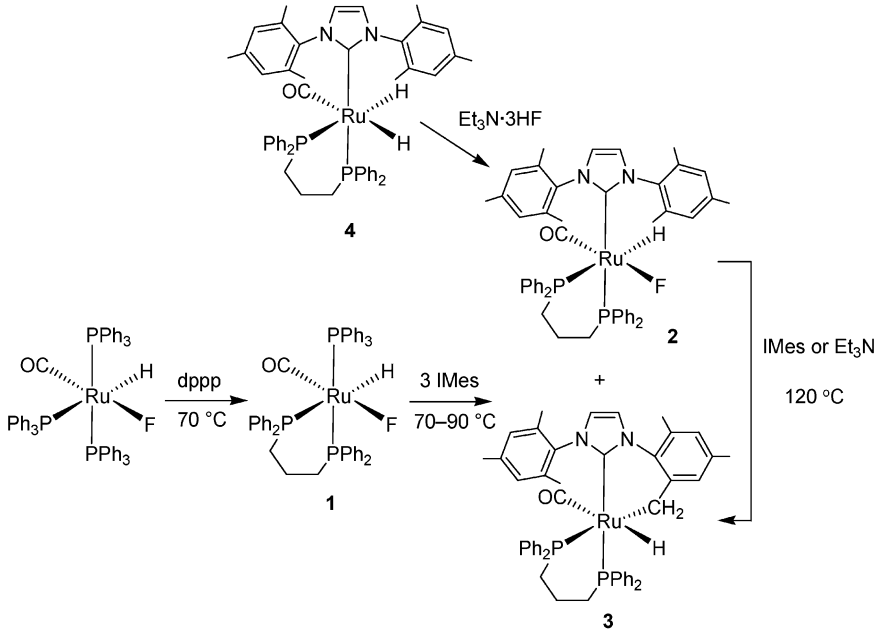


Figure 1. Molecular structure (of one of the molecules in the asymmetric unit) of [Ru(PPh_3)(dppp)(CO)HF] (**1**). Thermal ellipsoids are represented at 30% probability. Hydrogen atoms except Ru–H have been omitted for clarity.

The reaction of **1** with 3 equiv. of IMes at 70–90 °C resulted in the formation of the desired substitution product [Ru(IMes)(dppp)(CO)HF] (**2**), but more surprisingly, also generated [Ru(IMes)′(dppp)(CO)H] (**3**), in which one of the *ortho*-Me groups of a mesityl substituent has undergone C–H activation (Scheme 1). This species was reported by us some time ago upon thermolysis of the dihydrido complex [Ru(IMes)(dppp)(CO)H_2] (**4**) in the presence of an alkene.[5] As the mixture of **2** and **3** proved to be inseparable, an



Scheme 1.

Table 1. Selected bond lengths [Å] and angles [°] for [Ru(PPh_3)(dppp)(CO)HF] (**1**).

Molecule 1			
Ru(1)–C(1)	1.816(4)	Ru(1)–P(2)	2.4354(9)
Ru(1)–F(1)	2.1005(18)	Ru(1)–P(3)	2.3390(9)
Ru(1)–P(1)	2.3622(19)		
P(1)–Ru(1)–P(2)	98.92(3)	P(2)–Ru(1)–P(3)	92.64(3)
P(1)–Ru(1)–P(3)	168.09(3)	C(1)–Ru(1)–F(1)	174.71(12)
Molecule 2			
Ru(2)–C(47)	1.820(4)	Ru(2)–P(6)	2.4396(9)
Ru(2)–F(2)	2.0943(18)	Ru(2)–P(5)	2.3418(9)
Ru(2)–P(4)	2.3752(9)		
P(4)–Ru(2)–P(6)	97.39(3)	P(5)–Ru(2)–P(6)	91.40(3)
P(4)–Ru(2)–P(5)	171.20(3)	C(47)–Ru(2)–F(2)	173.39(12)

Table 2. Selected bond lengths [Å] and angles [°] for [Ru(IMes)(dppp)(CO)HF] (**2**) and [Ru(ICy)(dppp)(CO)HF] (**8**).

	2	**8**
Ru–CO	1.8162(17)	1.801(9)
Ru–C_{NHC}	2.1270(15)	2.130(7)
Ru–F	2.1501(10)	2.121(4)
Ru–$P_{trans\ to\ NHC}$	2.2947(7)	2.328(2)
Ru–$P_{trans\ to\ H}$	2.3537(7)	2.4177(19)
P–Ru–P	92.340(14)	92.11(7)
OC–Ru–P	91.22(5)	96.5(2)
OC–Ru–F	173.76(5)	175.9(3)
C_{NHC}–Ru–F	88.63(5)	89.2(2)
OC–Ru–P	97.09(5)	101.1(2)
C_{NHC}–Ru–P	161.64(4)	165.27(19)
C_{NHC}–Ru–P	102.49(4)	99.16(18)
F–Ru–P	82.59(3)	82.79(12)
F–Ru–P	82.43(3)	82.95(11)

alternative synthetic route to **2** involving reaction of **4** with $Et_3N{\cdot}HF$ was employed. The complex displayed a single hydride resonance at ca. δ –6 with a doublet of doublet of doublets multiplicity. The retention of a large J_{HP} coupling (128 Hz) indicated that the hydride was still *trans* to one end of the dppp ligand. This was verified unambiguously by X-ray crystallography as shown in Figure 2. The bond lengths and angles for **1** and **2** (Table 2) proved to be very similar showing that the incorporation of the carbene ligand had a minimal effect on structure.

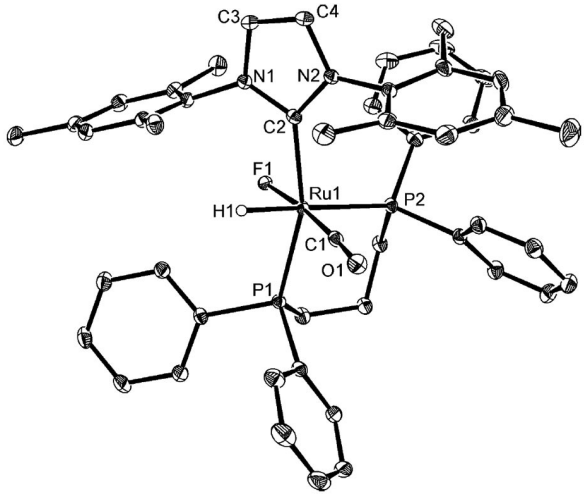
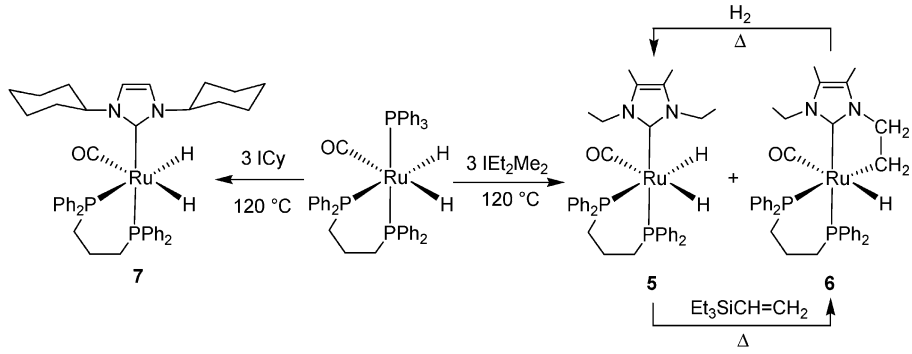


Figure 2. Molecular structure of [Ru(IMes)(dppp)(CO)HF] (**2**). Thermal ellipsoids are represented at 30% probability. Solvent and hydrogen atoms except Ru–H have been omitted for clarity.

The unexpected formation of **3** in the reaction of **1** with IMes was probed in more detail. Loss of HF from **2** followed by intramolecular C–H activation of the IMes ligand in the resulting four coordinate intermediate [Ru(IMes)(dppp)(CO)][6d] would be the most direct route to **3**, although reductive elimination of HF has little literature precedence.[17] Indeed, when **2** was simply heated at 120 °C, there was no formation of **3**, although this complex was formed in near quantitative yield when **2** was heated at 120 °C in the presence of IMes. Thus, the formation of **3** in the initial reaction of **1** with IMes results from the presence of excess carbene; the carbene presumably acts as a base to help remove HF, and indeed, when **2** was heated in the presence of Et_3N, the same transformation took place.

Efforts to prepare other [Ru(NHC)(dppp)$(CO)H_2$] complexes for subsequent reaction with $Et_3N{\cdot}HF$ met with mixed success. NMR spectroscopy provided evidence for the formation of [Ru(IEt_2Me_2)(dppp)$(CO)H_2$] (**5**) upon heating [Ru(PPh_3)(dppp)$(CO)H_2$] with IEt_2Me_2 at elevated temperature, but the compound was always formed as part of a mixture with the C–H activated product [Ru(IEt_2Me_2)′-(dppp)(CO)H] (**6**, Scheme 2). The ratio of **5**/**6** proved to be highly dependent on the reaction conditions; if the reaction was performed under vacuum such that the H_2 released upon formation of the C–H activated species was not retained in solution, then **6** was the sole product, whereas if an argon atmosphere was present (thus helping to retain the H_2 in solution), then a mixture of **5** and **6** was generated. As in earlier studies,[4] complete conversion to **6** was achieved by heating a mixture of the two compounds in the presence of an alkene, while thermolysis of the mixture under 1 atm of H_2 afforded **5**. Both **5** and **6** proved to be extremely soluble in hexane which prevented their full characterisation, and the abandonment of further studies on the reaction of **5** with $Et_3N{\cdot}HF$.

In contrast, the *N*-cyclohexyl carbene ICy (which is far less prone to bond activation)[18] reacted with [Ru(PPh_3)(dppp)$(CO)H_2$] to afford just the dihydrido complex [Ru(ICy)(dppp)$(CO)H_2$] (**7**) (Scheme 2). The NMR spectra of **7** were very similar to those of **4**, suggestive of the same geometry. This was confirmed by an X-ray crystal structure (Figure 3), which revealed a similarly distorted octahedral geometry with a *trans*-C_{NHC}–Ru–P angle of 159.81(7)° (Table 3), close to that found in **4** [158.78(4)°],[4] and also close to the P–Ru–P angle in [Ru(PPh_3)(dppp)$(CO)H_2$] [160.67(9)°].[19] The similarities of the three structures is unsurprising considering that ICy, IMes and PPh_3 have similar steric profiles based on their calculated percentage buried volumes (% V_{bur}).[20] The somewhat shorter Ru–C_{NHC} distance in **7** compared to **4** [1.886(3) Å vs. 1.9054(15) Å] is consistent with ICy being a stronger σ-donor than IMes.[21] Addition of $Et_3N{\cdot}3HF$ to



Scheme 2.

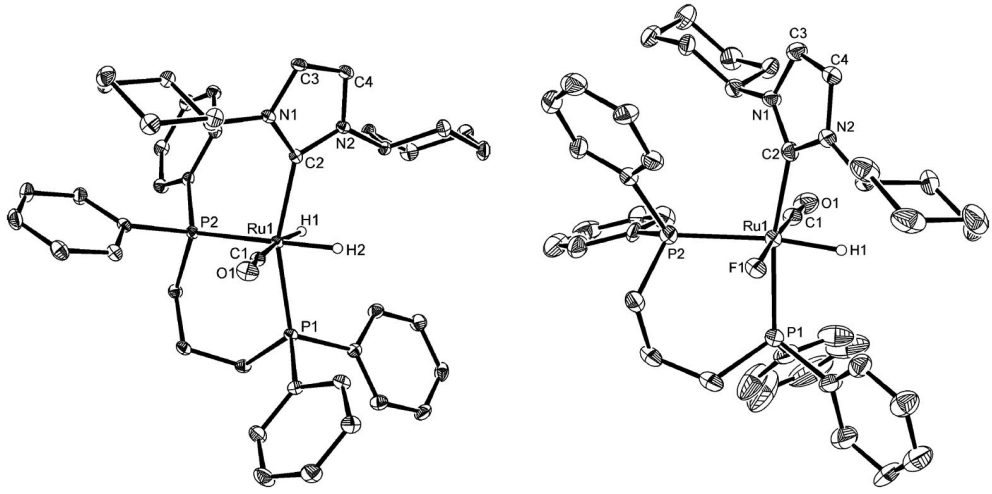


Figure 3. Molecular structures of (left) [Ru(ICy)(dppp)(CO)H_2] (**7**) and (right) one molecule of three in the asymmetric unit of [Ru(ICy)(dppp)(CO)HF] (**8**). Thermal ellipsoids are represented at 30% probability. Hydrogen atoms (except Ru–H) and the solvent in **8** and have been omitted for clarity.

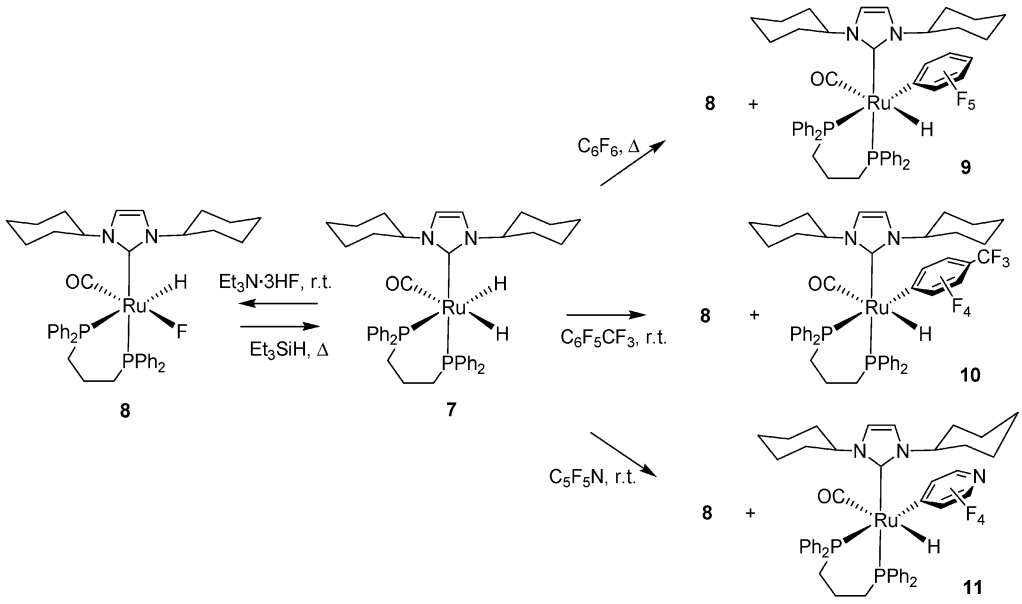
7 resulted in the clean formation of the hydrido fluorido complex [Ru(ICy)(dppp)(CO)HF] (**8**), the crystal structure of which is shown in Figure 3. As seen from the bond lengths and angles given in Table 2, there are only minor differences between the structure of **8** and the IMes analogue **2**.

Table 3. Selected bond lengths [Å] and angles [°] for [Ru(ICy)(dppp)(CO)H_2] (**7**).

Ru(1)–C(1)	1.886(3)	Ru(1)–P(1)	2.2947(7)
Ru(1)–C(2)	2.103(3)	Ru(1)–P(2)	2.3537(7)
C(1)–Ru(1)–C(2)	92.76(10)	C(1)–Ru(1)–P(2)	105.17(8)
P(1)–Ru(1)–P(2)	96.44(2)	C(2)–Ru(1)–P(1)	159.81(7)
C(1)–Ru(1)–P(1)	93.32(8)	C(2)–Ru(1)–P(2)	100.51(7)

On the basis of previous work in which M–F complexes have been reacted with R_3SiH to give metal hydrides,[22,23] **8** was heated with 5 equiv. Et_3SiH at 120 °C and found to undergo quantitative conversion to **7** and Et_3SiF within 3 h (Scheme 3). This interconversion of dihydrido and hydrido fluorido species prompted us to investigate whether C–F bond activation of aromatic fluorocarbons might offer an alternative source of fluoride. Initial experiments with the IMes dihydrido complex **4** were unsatisfactory in this regard as thermolysis in the presence of 10 equiv. of C_6F_6 (even at 120 °C for 12 h) only gave small amounts of **2**. In contrast, when **7** was treated with 10 equiv. C_6F_6 at 120 °C,[24] **8** was formed, but in a 1:1 mixture with the fluoroaryl hydrido species [Ru(ICy)(dppp)(CO)(C_6F_5)H] (**9**) (Scheme 3). The simplest mechanism to account for the two products and their 1:1 ratio involves direct C–F activation of C_6F_6 by a molecule of **7** to give **9** and HF, which then reacts with a second molecule of **7** to yield **8**. Mass balance requires the formation of H_2, which was observed by proton NMR, although over time the hydrogen is used up in the formation of C_6F_5H, which was detected in the ^{19}F NMR spectrum.

Thermolysis of **8** and **9** in the presence of 10 equiv. of Et_3SiH converted **8** back to **7**, but left **9** unchanged. Hence, reaction of **7** with C_6F_6 in the presence of Et_3SiH gave **9** as the single ruthenium containing product. The X-ray crystal structure of the complex (Figure 4, Table 4) revealed a *cis*-Ru(C_6F_5)H arrangement with the pentafluorophenyl ligand *trans* to one end of the dppp. The Ru–C_6F_5 bond length [2.172(3) Å] is significantly shorter than the value of 2.250(4) Å found in [Ru(dmpe)$_2$(C_6F_5)H] [dmpe = 1,2-bis(dimethylphosphanyl)ethane],[25] but in the latter, the



Scheme 3.

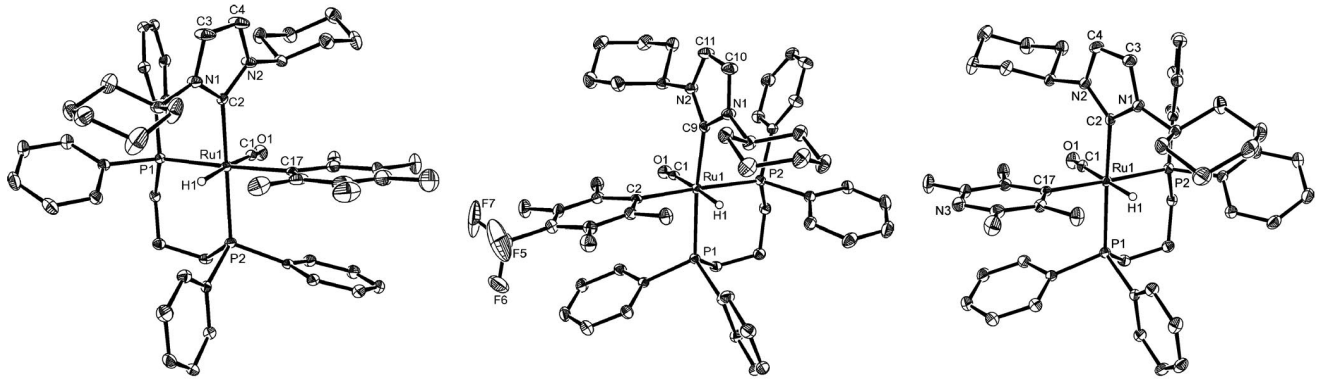


Figure 4. Molecular structures of [Ru(ICy)(dppp)(CO)(C_6F_5)H] (**9**), [Ru(ICy)(dppp)(CO)($C_6F_4CF_3$)H] (**10**) and [Ru(ICy)(dppp)(CO)(C_5F_4N)H] (**11**). Thermal ellipsoids are represented at 30% probability. Solvent in **10** and **11**, the minor disordered fluorines in **10** and hydrogen atoms throughout, except Ru–H, have been omitted for clarity.

Table 4. Selected bond lengths [Å] and angles [°] for [Ru(ICy)(dppp)(CO)(C_6F_5)H] (**9**) [Ru(ICy)(dppp)(CO)($C_6F_4CF_3$)H] (**10**) and [Ru(ICy)(dppp)(CO)(C_5F_4N)H] (**11**).

	9	**10**	**11**
Ru–CO	1.913(3)	1.921(2)	1.909(2)
Ru–C_{NHC}	2.130(3)	2.145(2)	2.127(2)
Ru–C_{aryl}	2.172(10)	2.160(2)	2.149(2)
Ru–$P_{trans\ to\ NHC}$	2.3103(8)	2.3191(6)	2.3326(6)
Ru–$P_{trans\ to\ aryl}$	2.3160(8)	2.3150(6)	2.3197(6)
P–Ru–P	93.77(3)	91.29(2)	93.49(2)
OC–Ru–P	83.75(8)	87.05(7)	82.53(7)
OC–Ru–P	89.95(8)	88.92(7)	91.29(7)
C_{NHC}–Ru–P	92.67(7)	88.49(6)	92.48(6)
C_{NHC}–Ru–P	166.54(7)	168.40(6)	165.75(6)
C_{aryl}–Ru–C_{NHC}	84.99(10)	91.66(8)	86.10(8)
C_{aryl}–Ru–CO	96.16(11)	97.01(9)	96.94(9)
C_{aryl}–Ru–P	177.57(7)	175.80(6)	178.34(6)
C_{aryl}–Ru–P	88.65(7)	87.72(6)	88.08(5)

perfluoroaryl ring is opposite the high *trans* influence hydrido ligand. The steric congestion evident from the molecular structure of **9** (see the space-filling model in Figure 5) was also manifested in the ^{19}F NMR spectrum which displayed five resonances in a 1:1:1:1:1 ratio between –97 and –166 ppm consistent with restricted rotation about the Ru–C_{aryl} bond. In the ^1H NMR spectrum, the hydride resonance appeared as a quartet due to the equivalence of the two *cis*-J_{HP} couplings and the coupling to one of the *o*-F atoms of the C_6F_5 ring.

In contrast to C_6F_6, C–F activation of both $C_6F_5CF_3$ and C_5F_5N took place at room temperature (Scheme 3).[20b] $C_6F_5CF_3$ afforded the hydrido fluorido species **8** along with [Ru(ICy)(dppp)(CO)($C_6F_4CF_3$)H] (**10**), although interestingly, the ratio of the two products varied during the course of the reaction. The quartet hydride signal of **10** was ob-

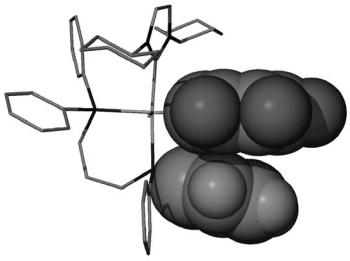


Figure 5. Space filling model of [Ru(ICy)(dppp)(CO)(C_6F_5)H] (**9**), illustrating the potential for π–π interactions.

servable by ^{1}H NMR spectroscopy within 5 min of adding $C_6F_5CF_3$, whereas the hydride signal of **8** only appeared about 10–15 min later. After 45 min, the ratio of **10/8** was still < 1:1 (ca. 1:0.4), indicating that some of the released HF is being trapped (reaction with traces of adventitious water or reaction with the surface of the glassware are the most obvious explanations). When the reaction was run in the presence of a deliberate HF trap in the form of Et_3N (10 equiv.), the ratio of **10/8** was further reduced to 1:0.2. In the case of reaction with pentafluoropyridine, both [Ru(ICy)(dppp)(CO)(C_5F_4N)H] (**11**) and **8** appeared immediately, although the product ratio of ca. 1:0.6 again suggested some side reaction(s) of HF.

The isolation of **10** and **11** was achieved as for **9** by reaction with fluorocarbon in the presence of silane. The X-ray crystal structures of the two compounds (Figure 4) revealed that C–F activation occurs *para* to both the CF_3 and N substituents. There is very little difference between the bond lengths and angles of **9**, **10** or **11** as shown by the metrics presented in Table 4. A common feature of all three structures is that the fluoroaryl ring plane is almost coplanar with the mean-plane subtended by the ruthenium centre, the carbonyl carbon, the α-carbon of the fluoroaryl ring and the phosphorus atom coplanar with the carbonyl (inter-plane angles; 1.25, 8.95 and 2.50° for **9**, **10** and **11**, respectively). Moreover, this conformation is consolidated by offset π–π interactions throughout (Figure 5), between the fluoroaryl ring and a phenyl group attached to the phosphorus *trans* to the carbene (relevant centroid-centroid distances; 3.83, 3.78 and 3.74 Å for **9**, **10** and **11**, respectively).

The high regioselectivity for activation at the *para*-position in $C_6F_5CF_3$ and C_5F_5N is consistent with a reaction mechanism involving either nucleophilic attack or electron transfer.[26] To test the possibility of the latter pathway, the reaction of **7** with $C_6F_5CF_3$ was conducted in the presence of 10 equiv. of the radical trap dihydroanthracene, although perhaps unsurprisingly given earlier reports,[22b,25] this was found to make no difference to either the distribution of products or their rate of formation.

The reactivity of **7** towards partially fluorinated substrates was also investigated and found to vary quite markedly with fluorocarbon. Pentafluorobenzene could only be activated under very forcing conditions (120 °C) and gave a mixture of **8** and **9**, along with a third ruthenium hydride containing product with a chemical shift and multiplicity almost identical to that of **9**. In addition, this species displayed a quintet aryl proton signal at δ = 6.24 and four ^{19}F signals in a 1:1:1:1 ratio at δ = –98.3, –100.7, –141.6 and –142.0 ppm consistent with the tetrafluorophenyl hydride complex [Ru(ICy)(dppp)(CO)(C_6F_4H)H] (this species was also formed upon thermolysis of **7** with 1,4-$C_6F_4H_2$). The formation of **9** and [Ru(ICy)(dppp)(CO)(C_6F_4H)H] indicated that both C–H and C–F activation were taking place, with the latter *para* to the hydrogen substituent. Previous studies on the reactivity of partially fluorinated aromatic molecules with a wide range of transition metal complexes have revealed a wide variation of chemoselectivity. Thus, [(η^5-C_5Me_5)Re(CO)$_3$],[27] [Rh(PEt_3)$_3$H],[28] [Ir(P*i*Pr_3)$_2$H$_5$][29] and [Pt(PCy_3)$_2$][30] are all selective for the C–H bond in both C_6F_5H and C_5F_4HN, while [Ru(dmpe)$_2$H$_2$],[25] [(η^5-C_5Me_5)Rh(PMe_3)H$_2$],[31] [Ni$_2$(I*i*Pr)$_4$(cod)][8e] and [Ni(cod)$_2$/PEt_3][32] all react via C–F cleavage. There are a limited number of examples (e.g. [Rh(PMe_3)$_3$($SiPh_3$)][33] and [(η^5-C_5Me_5)$_2$ZrH$_2$][34]) which react by both C–H and C–F activation. Computational studies comparing the ability of the coordinatively unsaturated fragments [Os(PH_3)$_2$(CO)(C_6H_5)H], [(η^5-C_5H_5)Rh(PH_3)] and [M($H_2PCH_2CH_2PH_2$)] (M = Ni, Pt)[35,36] to undergo oxidative addition of either C–F or C–H bonds indicate that while C–F activation is always thermodynamically more favourable, a lower kinetic barrier usually exists for C–H cleavage.

$C_6F_4HCF_3$ and C_5F_4HN were investigated in the belief that as neither contained *para*-F atoms, they should only be susceptible to C–H activation. While the C–H activation products **10** and **11** were formed as expected upon heating either substrate with **7** to 120 °C, most surprisingly, both reactions also generated **8**, implying that C–F activation was possible at either the *ortho*- or *meta*-C–F positions (there was no evidence for any activation of the CF_3 group in $C_6F_4HCF_3$). However, no hydride signals attributable to the corresponding fluoroaryl hydrido products [Ru(ICy)(dppp)(CO)($C_6F_3HCF_3$)H] and [Ru(ICy)(dppp)(CO)(C_5F_3HN)H] were seen suggesting that either these compounds are not formed or that they are unstable and decompose at the high temperature employed in the reaction. Circumstantial evidence for the latter came upon prolonged heating of a mixture of **8**, **9** and [Ru(ICy)(dppp)(CO)(C_6F_4H)H] at 120 °C for 72 h, which left **8** as the only metal containing species. Further studies are necessary to resolve the fate of the $C_6F_4HCF_3$ and C_5F_4HN after their C–F activation, since we were also unable to detect any significant quantities of free hydrofluorocarbons ($C_6F_3H_2CF_3$, $C_5F_3H_2N$ etc.) in solution by ^{1}H or ^{19}F NMR spectroscopy.

Summary and Conclusions

The NHC hydrido fluorido complexes [Ru(IMes)(dppp)(CO)HF] (**2**) and [Ru(ICy)(dppp)(CO)HF] (**8**), which have been prepared by reaction of the corresponding dihydrido complexes with Et_3N·3HF, contrast to their [Ru(NHC)(PPh_3)$_2$(CO)HF] relatives in that they are stable to isomerisation and disproportionation in solution. Moreover, while the latter are synthesised by room temperature

reaction of the free carbenes with $[Ru(PPh_3)_3(CO)HF]$, reaction of IMes with $[Ru(PPh_3)(dppp)(CO)HF]$ required heat and an excess of carbene, which resulted in a base-induced elimination of HF to give the intramolecular C–H activated complex [Ru(IMes)′(dppp)(CO)H] (**3**) as one of the products. [Ru(ICy)(dppp)(CO)HF] reacted with R_3SiH via F/H exchange to yield the corresponding dihydrido complex $[Ru(ICy)(dppp)(CO)H_2]$ (**7**), which activated the *para*-C–F bonds of the perfluoroaromatic substrates C_6F_6, $C_6F_5CF_3$ and C_5F_5N. Both C–F and C–H activation was observed with the partially fluorinated compounds C_6F_5H, $C_6F_4HCF_3$ and C_5F_4HN. Together with the recent findings from Radius and co-workers,[8a,8d–8f] our results suggest that NHCs have much to offer in the further development of metal fluorido compounds and C–F bond activation.

Experimental Section

General Procedure: All manipulations were carried out under argon using standard Schlenk, high vacuum or glovebox techniques under argon. Solvents were purified using an MBraun SPS solvent system (toluene, Et_2O), Innovative Technologies solvent system (THF, hexane) or under a nitrogen atmosphere from sodium benzophenone ketyl (benzene) or Mg/I_2 (ethanol). NMR solvents (Fluorochem) were vacuum transferred from potassium (C_6D_6, [D_8]toluene). C_6F_6, C_6F_5H, $C_6F_5CF_3$, $C_6F_4HCF_3$, C_5F_5N, C_5F_4HN and Et_3SiH were dried with activated molecular sieves (3 Å) and stored under argon. $[Ru(PPh_3)_3(CO)HF]$,[9] $[Ru(PPh_3)(dppp)(CO)H_2]$,[37] [Ru(IMes)(dppp)(CO)H_2] (**4**),[5] IMes,[38] IEt_2Me_2[39] and ICy[40] were prepared via literature methods. NMR spectra were recorded on Bruker Avance 400 and 500 spectrometers at 25 °C unless otherwise stated, with ^1H and ^{13}C chemical shifts referenced to internal solvent references. $^{31}P\{^1H\}$ NMR chemical shifts were referenced externally to 85% H_3PO_4 (δ = 0.0 ppm), while ^{19}F spectra were referenced to $CFCl_3$ (δ = 0.0 ppm). 2D experiments [^1H COSY, ^1H-X (X = ^{13}C, ^{31}P, ^{19}F) HMQC/HMBC] were performed using standard Bruker pulse sequences. IR spectra were recorded in nujol with a Nicolet Nexus FTIR spectrometer. Elemental analyses were conducted by Elemental Microanalysis Ltd., Okehampton, Devon, UK.

[Ru(PPh$_3$)(dppp)(CO)HF] (1): A suspension of dppp (290 mg, 0.71 mmol) and $[Ru(PPh_3)_3(CO)HF]$ (500 mg, 0.53 mmol) in benzene (150 mL) was placed in an ampoule fitted with a J. Youngs PTFE valve and heated in an oil bath at 70 °C for 25 min. Upon cooling and removal of the solvent, the remaining white solid was washed with hexane (3 × 50 mL) and filtered to remove free PPh_3 and dppp. The remaining solid was dissolved in THF (ca. 20 mL) and layered with pentane, affording a mixture of clear needle like crystals, suitable for X-ray crystallography (0.24 g, 48%). $C_{46}H_{42}OP_3Ru{\cdot}0.5C_5H_{12}$ (840.9): calcd. C 67.74, H 5.63, found C 67.88 , H 5.48. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 8.10 (m, 2 H, PC_6H_5), 7.79 (m, 9 H, PC_6H_5), 7.22–6.78 (m, 24 H, PC_6H_5), 2.61 (m, 1 H, PCH_2), 2.55 (m, 1 H, PCH_2), 2.22 (m, 1 H, PCH_2) 2.00 (m, 1 H, PCH_2), 1.70 (m, 2 H, PCH_2), –4.18 (dddd, $^2J_{H,P}$ = 117.1, $^2J_{H,P}$ = 16.9, $^2J_{H,P}$ = 25.0, $^2J_{H,F}$ = 4.2 Hz, 1 H, Ru-H) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 25 °C): δ = 37.3 (dt, $^2J_{P,P}$ = 291, $^2J_{P,F}$ = $^2J_{P,P}$ = 24 Hz), 28.2 (dt, $^2J_{P,P}$ = 291, $^2J_{P,F}$ = $^2J_{P,P}$ = 19 Hz), 4.1 (dt, $^2J_{P,F}$ = 30, $^2J_{P,P}$ = 23 Hz) ppm. ^{19}F NMR (376 MHz, C_6D_6, 25 °C): δ = –380.7 (m) ppm. IR: $\tilde{\nu}$ = 1900 (s) cm^{-1}.

[Ru(IMes)(dppp)(CO)HF] (2): $Et_3N{\cdot}3HF$ (42.8 mg, 0.27 mmol) and [Ru(IMes)(dppp)(CO)H_2] (**4**) (150 mg, 0.18 mmol) were stirred in benzene (20 mL) at room temperature for 8 h. Anhydrous CsF was then added (202 mg, 1.33 mmol) and the mixture stirred for a further 4 h. After cannula filtration, the filtrate was reduced to dryness to leave a yellow oil. Crystallisation from benzene/hexane afforded colourless crystals of **2** (120 mg, 78%). $C_{49}H_{51}F_1N_2OP_2Ru$ (865.9): calcd. 67.96, H 5.94, N 3.23; found C 68.48, H 6.06, N 3.54 . ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.78 (m, 2 H, PC_6H_5), 7.56 (m, 2 H, PC_6H_5), 7.26 (m, 2 H, PC_6H_5), 7.22–7.05 (m, 11 H, PC_6H_5), 6.93 (s, 2 H, $C_6Me_3H_2$), 6.84 (m, 3 H, PC_6H_5), 6.74 (s, 2 H, $C_6Me_3H_2$), 6.20 (s, 2 H, NCH), 2.68 (m, 1 H, CH_2) 2.44 (s, 6 H, CH_3), 2.39 (m, 1 H, CH_2), 2.29 (s, 6 H, CH_3), 2.04 (m, 1 H, CH_2), 1.92–1.60 (m, 3 H, CH_2), 1.75 (s, 6 H, CH_3), –5.79 (ddd, $^2J_{H,P}$ = 127.6, $^2J_{H,P}$ = 22.0, $^2J_{H,F}$ = 4.9 Hz, 1 H, Ru-H) ppm. $^{31}P\{^1H\}$ (162 MHz, C_6D_6, 25 °C): δ = 28.9 (dd, $^2J_{P,F}$ = 27, $^2J_{P,P}$ = 19 Hz), 3.6 (dd, $^2J_{P,F}$ = 47, $^2J_{P,P}$ = 19 Hz) ppm. ^{19}F (376 MHz, C_6D_6, 25 °C): δ = –365.2 (br. dd, $^2J_{F,P}$ = 47, $^2J_{F,P}$ = 27 Hz, Ru-F) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C): δ = 206.7 (ddd, $^2J_{C,F}$ = 69, $^2J_{C,P}$ = 14, $^2J_{C,P}$ = 8 Hz, Ru-CO), 193.4 (br. m, NCN), 145.5 (dd, $J_{C,P}$ = 13, J = 4 Hz, PC), 142.2 (dd, $J_{C,P}$ = 44, J = 5 Hz, PC), 139.8 (s, NC-$C_6Me_3H_2$), 138.9 (s, CCH_3), 137.9 (s, CCH_3), 136.5 (s, CCH_3), 135.2 (d, $J_{C,P}$ = 13 Hz, PC_6H_5), 134.9 (dd, $J_{C,P}$ = 11, J = 5 Hz, PC_6H_5), 133.5 (dd, $J_{C,P}$ = 10, J = 6 Hz, PC_6H_5), 133.3 (d, $J_{C,P}$ = 10 Hz, PC_6H_5), 129.9 (s, $C_6Me_3H_2$) 129.6 (s, $C_6Me_3H_2$), 129.1 (d, $J_{C,P}$ = 10 Hz, PC_6H_5), 128.9 (d, $J_{C,P}$ = 3 Hz, PC_6H_5), 128.7 (d, $J_{C,P}$ = 29 Hz, PC_6H_5), 128.4 (d, $J_{C,P}$ = 8 Hz, PC_6H_5), 128.3 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 123.8 (s, NCH) 123.8 (s, NCH), 28.4 (dd, $J_{C,P}$ = 20, $J_{C,P}$ = 6 Hz, P*C*H_2), 27.5 (d, $J_{C,P}$ = 19.5 Hz, P*C*H_2), 22.0 (s, *C*H_3), 21.1 (s, PCH_2CH_2), 20.4 (s, CH_3), 18.9 (s, CH_3) ppm. IR: $\tilde{\nu}$ = 1905 (s) cm^{-1}.

[Ru(IEt$_2$Me$_2$)(dppp)(CO)H$_2$] (5): [Ru(PPh$_3$)(dppp)(CO)H_2] (250 mg, 0.31 mmol) and IEt_2Me_2 (142 mg, 0.93 mmol) were combined in a ampoule fitted with a J. Youngs PTFE valve and dissolved in 20 mL of toluene. The solution was heated at 120 °C for 16 h, cooled, freeze-pump-thaw-degassed three times and 1 atm of H_2 added. The reaction mixture was then heated for 4 h at 70 °C to give complete conversion to $[Ru(IEt_2Me_2)(dppp)(CO)H_2]$. Removal of solvent gave a brown oily residue, which was dissolved in hexane (50 mL) and cooled to –20 °C for 7 d to afford **5** as a white powder (26 mg, 12%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 8.35 (m, 2 H, PC_6H_5), 7.94 (m, 2 H, PC_6H_5), 7.74 (m, 2 H, PC_6H_5), 7.29–6.98 (m, 11 H, PC_6H_5), 6.80 (m, 3 H, PC_6H_5), 4.45 (m, 2 H, NCH_2), 4.30–3.19 (br., 2 H, NCH_2), 2.48 (m, 2 H, PCH_2), 2.19 (m, 1 H, PCH_2), 2.01 (m, 1 H, PCH_2), 1.94–1.35 (m, 2 H, PCH_2), 1.45 (s, 6 H, $NCCH_3$), 1.24 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH_2CH_3), –6.43 (br. t, $^2J_{H,P}$ = 29.1 Hz, 1 H, Ru-H), –6.89 (ddd, $^2J_{H,P}$ = 84.9, $^2J_{H,P}$ = 22.0, $^2J_{H,H}$ = 2.8 Hz, 1 H, Ru-H) ppm. $^{31}P\{^1H\}$ (162 MHz, C_6D_6, 25 °C): δ = 43.0 (d, $^2J_{P,P}$ = 23 Hz), 36.2 (d, $^2J_{C,P}$ = 23 Hz) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C): δ = 209.8 (dd, $^2J_{C,P}$ = 9, $^2J_{C,P}$ = 6 Hz, Ru-CO), 187.7 (dd, $^2J_{C,P}$ = 76, $^2J_{C,P}$ = 11 Hz, NCN), 143.5 (dd, $J_{C,P}$ = 44, J = 5 Hz, PC), 143.4 (d, $J_{C,P}$ = 30 Hz, PC), 143.4 (dd, $J_{C,P}$ = 27, J = 3 Hz, PC), 139.4 (d, $J_{C,P}$ = 19 Hz, PC), 135.6 (d, $J_{C,P}$ = 14 Hz, PC_6H_5), 134.9 (d, $J_{C,P}$ = 12 Hz, PC_6H_5), 132.9 (d, $J_{C,P}$ = 11 Hz, PC_6H_5), 130.1 (s, PC_6H_5), 129.2 (d, $J_{C,P}$ = 2 Hz, PC_6H_5), 128.8 (d, $J_{C,P}$ = 6 Hz, PC_6H_5), 128.6 (s, PC_6H_5), 128.5 (s, PC_6H_5), 128.1 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 127.6 (s, PC_6H_5), 127.3 (d, $J_{C,P}$ = 8 Hz, PC_6H_5), 123.5 (s, $NCCH_3$), 123.5 (s, $NCCH_3$), 44.9 (s, NCH_2), 36.3 (dd, $J_{C,P}$ = 26, $J_{C,P}$ = 12 Hz, PCH_2), 35.3 (dd, $J_{C,P}$ = 27, $J_{C,P}$ = 3 Hz, PCH_2), 22.0 (t, $J_{C,P}$ = 4 Hz, PCH_2CH_2), 16.1 (s, CH_2CH_3), 9.9 (s, $NCCH_3$) ppm. IR: $\tilde{\nu}$ = 1913 (s) cm^{-1}.

[Ru(IEt$_2$Me$_2$)′(dppp)(CO)H] (6): A toluene solution (20 mL) of $[Ru(PPh_3)(dppp)(CO)H_2]$ (250 mg, 0.31 mmol) and IEt_2Me_2 (142 mg, 0.93 mmol) was heated at 120 °C for 16 h in an ampoule

fitted with a J. Youngs PTFE valve. The solution was then cooled to room temperature, CH_2=$CHSiMe_3$ (227 μL, 1.55 mmol) added and heated at 120 °C for a further 24 h. Removal of the solvent left an orange/brown residue, which upon extraction with hexane (50 mL) and cooling at –20 °C for 7 d produced **6** as a white powder (18 mg, 8%). ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 8.31 (m, 2 H, PC_6H_5), 7.76 (m, 4 H, PC_6H_5), 7.21 (m, 2 H, PC_6H_5), 7.04 (m, 9 H, PC_6H_5), 6.81 (m, 3 H, PC_6H_5), 4.12 (m, 1 H, NCH_2CH_3), 3.62 (m, 2 H, NCH_2CH_2), 3.15 (m, 1 H, NCH_2CH_3), 2.49 (m, 1 H, PCH_2), 2.42 (m, 1 H, PCH_2), 1.97 (m, 1 H, PCH_2), 1.93 (m, 1 H, PCH_2), 1.67 (m, 1 H, PCH_2), 1.60 (m, 1 H, NCH_2CH_2), 1.43 (s, 3 H, $NCCH_3$), 1.41 (s, 3 H, $NCCH_3$), 1.24 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, NCH_2CH_3), 1.21 (m, 1 H, PCH_2), 0.93 (m, 1 H, NCH_2CH_2), –6.16 (dd, $^2J_{H,P}$ = 101.6, $^2J_{H,P}$ = 17.4 Hz, 1 H, Ru-H) ppm. ^{31}P{^{1}H} (202 MHz, C_6D_6, 25 °C): δ = 38.2 (d, $^2J_{P,P}$ = 23 Hz), 26.4 (d, $^2J_{P,P}$ = 23 Hz) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): δ = 208.7 (dd, $^2J_{C,P}$ = 9, $^2J_{C,P}$ = 7 Hz, Ru-CO), 190.1 (dd, $^2J_{C,P}$ = 82, $^2J_{C,P}$ = 11 Hz, NCN), 143.2 (d, $J_{C,P}$ = 32 Hz, PC), 142.3 (dd, $J_{C,P}$ = 25, J = 4 Hz, PC), 141.1 (d, $J_{C,P}$ = 25 Hz, PC), 140.8 (dd, $J_{C,P}$ = 38, J = 4 Hz, PC), 135.4 (d, $J_{C,P}$ = 13 Hz, PC_6H_5), 134.9 (d, $J_{C,P}$ = 12 Hz, PC_6H_5), 132.9 (d, $J_{C,P}$ = 11 Hz, PC_6H_5), 131.6 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 129.0 (s, $NCCH_3$), 127.8 (s, $NCCH_3$), 127.6 (d, $J_{C,P}$ = 7 Hz, PC_6H_5), 52.8 (dd, $J_{C,P}$ = 7, J = 2 Hz, NCH_2CH_2), 43.9 (s, NCH_2CH_3), 28.9 (dd, $J_{C,P}$ = 23, $J_{C,P}$ = 3 Hz, PCH_2), 27.1 (d, $J_{C,P}$ = 21 Hz, PCH_2), 21.0 (dd, $J_{C,P}$ = 7, $J_{C,P}$ = 3 Hz, PCH_2CH_2), 17.2 (s, NCH_2CH_3), 10.2 (s, $NCCH_3$), 9.3 (s, $NCCH_3$), 9.2 (t, $J_{C,P}$ = 8 Hz, NCH_2CH_2) ppm.

[Ru(ICy)(dppp)(CO)H_2] (7): A toluene suspension (20 mL) of [Ru(PPh_3)(dppp)(CO)H_2] (100 mg, 0.12 mmol) and ICy (86 mg, 0.37 mmol) was placed in an ampoule fitted with a J. Youngs PTFE valve and heated in an oil bath at 120 °C for 16 h. After cooling, removal of the solvent left an orange oil, which when stirred in ethanol (20 mL) precipitated a white solid. The solid was isolated by cannula filtration, washed with hexane (20 mL) and dried under vacuum to yield **7** as a white solid (67 mg, 70%). $C_{43}H_{52}N_2OP_2Ru$ (775.9): calcd. C 66.56, H 6.76, N 3.61; found C 66.32, H 6.86, N 3.57. ^{1}H NMR (400 MHz, $C_6D_5CD_3$, –5 °C): δ = 8.24 (m, 2 H, PC_6H_5), 8.13 (m, 2 H, PC_6H_5), 7.59 (m, 2 H, PC_6H_5), 7.28 (m, 5 H, PC_6H_5), 7.20–6.83 (m, 9 H, PC_6H_5), 6.58 (br. s, 2 H, C_6H_{11}, NCH), 6.32 (s, 1 H, NCH), 4.89 (br. s, 1 H, C_6H_{11}), 2.71–0.59 (m, 25 H, PCH_2, C_6H_{11}), 0.30 (br. s, 1 H, C_6H_{11}), –6.25 (br. t, $^2J_{H,P}$ = 29.1 Hz, 1 H, Ru-H), –7.30 (dd, $^2J_{H,P}$ = 86.7, $^2J_{H,P}$ = 23.5 Hz, 1 H, Ru-H) ppm. ^{31}P{^{1}H} (162 MHz, C_6D_6, 25 °C): δ = 42.9 (d, $^2J_{P,P}$ = 23 Hz), 31.0 (d, $^2J_{P,P}$ = 23 Hz) ppm. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C): δ = 209.3 (dd, $^2J_{C,P}$ = 9, $^2J_{C,P}$ = 6 Hz, Ru-CO), 189.4 (dd, $^2J_{C,P}$ = 75, $^2J_{C,P}$ = 10 Hz, NCN), 147.3 (dd, $J_{C,P}$ = 47, J = 5 Hz, PC_6H_5), 143.7 (dd, $J_{C,P}$ = 24, J = 4 Hz, PC_6H_5), 142.8 (d, $J_{C,P}$ = 31 Hz, PC_6H_5), 138.6 (d, $J_{C,P}$ = 20 Hz, PC_6H_5), 135.3 (d, $J_{C,P}$ = 14 Hz, PC_6H_5), 134.6 (d, $J_{C,P}$ = 12 Hz, PC_6H_5), 133.4 (d, $J_{C,P}$ = 2 Hz, PC_6H_5) 133.1 (d, $J_{C,P}$ = 12 Hz, PC_6H_5), 130.3 (s, PC_6H_5), 129.2 (d, $J_{C,P}$ = 6 Hz, PC_6H_5), 129.1 (s, PC_6H_5), 128.4 (d, $J_{C,P}$ = 17 Hz, PC_6H_5), 128.2 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 128.2 (s, PC_6H_5), 117.3 (s, NCH), 117.1 (s, NCH), 61.1 (s, C_6H_{11}), 59.8 (s, C_6H_{11}), 36.8 (s, C_6H_{11}), 36.7 (d, $J_{C,P}$ = 26 Hz, PCH_2), 25.6 (d, $J_{C,P}$ = 27 Hz, PCH_2), 34.2 (s, C_6H_{11}), 33.9 (s, C_6H_{11}), 33.8 (s, C_6H_{11}), 27.6 (s, C_6H_{11}), 27.2 (s, C_6H_{11}), 27.1 (s, C_6H_{11}), 26.8 (s, C_6H_{11}), 22.1 (s, PCH_2CH_2) ppm. IR: $\tilde{\nu}$ = 1915 (s) cm^{-1}.

[Ru(ICy)(dppp)(CO)HF] (8): Et_3N·3HF (46 mg, 0.28 mmol) was added to a benzene solution (20 mL) of [Ru(ICy)(dppp)(CO)H_2] (**7**) (150 mg, 0.19 mmol) and the mixture stirred at ambient temperature for 8 h. Anhydrous CsF (217 mg, 1.43 mmol) was then added and the mixture stirred for a further 2 h. Filtration by cannula followed by removal of solvent from the filtrate left a brown oil, which upon dissolution in hexane (40 mL) and cooling to –20 °C for 5 d yielded a white solid. This was filtered cold, washed with cold hexane (5 mL) and dried in vacuo to yield [Ru(ICy)(dppp)(CO)HF] (**8**) (52 mg, 34%). Crystals suitable for X-ray crystallography were obtained by slow diffusion of hexane into a concentrated toluene solution of the complex. $C_{43}H_{51}F_1N_2OP_2Ru$ (793.9): calcd. C 65.05, H 6.48, N 3.53; found C 64.62, H 6.65, N 3.26. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 8.20 (m, 2 H, PC_6H_5), 8.06 (m, 2 H, PC_6H_5), 7.60 (m, 4 H, PC_6H_5), 7.27 (m, 2 H, PC_6H_5), 7.17 (m, 4 H, PC_6H_5), 6.91 (m, 3 H, PC_6H_5), 6.70 (m, 3 H, PC_6H_5), 6.73 (s, 1 H, NCH), 6.50 (m, 1 H, C_6H_{11}) 6.31 (s, 1 H, NCH), 4.54 (br. s, 1 H, C_6H_{11}), 3.17 (m, 1 H, PCH_2), 2.98 (m, 1 H, PCH_2) 2.66 (m, 1 H, C_6H_{11}), 2.48 (m, 1 H, C_6H_{11}), 2.40 (m, 1 H, C_6H_{11}), 2.18–0.93 (m, 17 H, PCH_2, C_6H_{11}), 0.77 (m, 3 H, C_6H_{11}), –0.80 (m, 1 H, C_6H_{11}), –5.10 (ddd, $J_{H,P}$ = 128.6, $^2J_{H,P}$ = 20.0, $^2J_{H,F}$ = 6.3 Hz, 1 H, Ru-H) ppm. ^{31}P{^{1}H} (202 MHz, C_6D_6, 25 °C): δ = 30.6 (dd, $^2J_{P,F}$ = 33, $J_{P,P}$ = 26 Hz), 12.8 (dd, $^2J_{P,F}$ = 47, $^2J_{P,P}$ = 26 Hz) ppm. ^{19}F (376 MHz, C_6D_6, 25 °C): δ = –345.7 (br. t, $^2J_{F,P}$ = 39 Hz, RuF) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): δ = 209.4 (ddd, $^2J_{C,F}$ = 68, $^2J_{C,P}$ = 9, $^2J_{C,P}$ = 6 Hz, Ru-CO), 185.7 (dd, $^2J_{C,P}$ = 94, $^2J_{C,P}$ = 9 Hz, NCN), 145.9 (dd, $J_{C,P}$ = 42, J = 7 Hz, PC), 136.6 (d, $J_{C,P}$ = 36 Hz, PC), 136.1 (d, $J_{C,P}$ = 13 Hz, PC_6H_5), 134.1 (d, $J_{C,P}$ = 11 Hz, PC_6H_5), 133.6 (d, $J_{C,P}$ = 11 Hz, PC_6H_5), 132.6 (dd, $J_{C,P}$ = 11, J = 4 Hz, PC_6H_5), 131.0 (s, PC_6H_5), 129.8 (s, PC_6H_5), 129.4 (s, PC_6H_5), 129.0 (s, PC_6H_5), 129.2 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 128.6 (d, $J_{C,P}$ = 10 Hz, PC_6H_5), 128.2 (d, $J_{C,P}$ = 8 Hz, PC_6H_5), 118.4 (s, NCH), 117.0 (s, NCH), 59.9 (d, J = 4 Hz, C_6H_{11}), 59.3 (d, J = 21 Hz C_6H_{11}), 37.7 (s, C_6H_{11}), 35.9 (s, C_6H_{11}), 35.4 (s, C_6H_{11}), 33.6 (s, C_6H_{11}), 28.4 (d, $J_{C,P}$ = 21 Hz, PCH_2), 27.7 (d, $J_{C,P}$ = 21 Hz, PCH_2), 27.5 (s, C_6H_{11}), 27.3 (s, C_6H_{11}), 26.9 (s, C_6H_{11}), 26.7 (s, C_6H_{11}), 26.5 (s, C_6H_{11}), 21.3 (s, PCH_2CH_2) ppm. IR: $\tilde{\nu}$ = 1900 (s) cm^{-1}.

[Ru(ICy)(dppp)(CO)(C_6F_5)H] (9): C_6F_6 (116 μL, 1.01 mmol) and Et_3SiH (160 μL, 1.01 mmol) were added to a toluene solution (10 mL) of **7** (80 mg, 0.10 mmol) and the reaction mixture heated at 120 °C for 16 h. The solvent was removed and the residue washed with hexane to afford **9** as a white powder (74 mg, 76%). $C_{49}H_{51}F_5N_2OP_2Ru$ (941.9): calcd. C 62.4, 5.46, N 2.97; found C 62.85, H 5.72, N 3.01. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 8.28 (m, 2 H, PC_6H_5), 7.79 (m, 2 H, PC_6H_5), 7.27–7.09 (m, 7 H, PC_6H_5), 7.05–6.82 (m, 9 H, PC_6H_5), 6.38 (br. s, 1 H, NCH), 6.28 (br. s, 1 H, NCH), 5.84 (m, 1 H, C_6H_{11}), 5.26 (m, 1 H, C_6H_{11}), 2.63 (m, 2 H, PCH_2), 2.51 (m, 1 H, PCH_2) 2.26 (m, 1 H, C_6H_{11}), 2.08 (m, 1 H, PCH_2), 1.84–0.84 (m, 21 H, PCH_2, C_6H_{11}), –3.89 (q, $^2J_{H,P}$ = $^4J_{H,F}$ = 22.2 Hz, 1 H, Ru-H) ppm. ^{31}P{^{1}H} (162 MHz, C_6D_6, 25 °C): δ = 34.5 (d, $^2J_{P,P}$ = 32 Hz), 31.8 (m) ppm. ^{19}F (376 MHz, C_6D_6, 25 °C): δ = –96.8 (m, 1 F, *o*-F), –99.2 (m, 1 F, *o*-F), –163.8 (m, 1 F, *m*-F), –164.3 (m, 1F, *m*-F), –166.2 (t, $^3J_{F,F}$ = 20.6 Hz, *p*-F) ppm. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C): δ = 205.9 (m, Ru-CO), 184.6 (dd, $^2J_{C,P}$ = 83, $^2J_{C,P}$ = 12 Hz, NCN), 150.7 (dd, J_{CP} = 42, J_{CP} = 7 Hz, PC_6H_5), 148.6 (d, J_{CP} = 36 Hz, PC_6H_5), 142.0 (dd, $J_{C,P}$ = 34, J = 2 Hz, PC_6H_5), 140.8 (dd, $J_{C,P}$ = 40, J = 3 Hz, PC_6H_5), 137.6 (d, $J_{C,P}$ = 33 Hz, PC), 135.7 (d, $J_{C,P}$ = 41 Hz, PC), 135.2 (d, $J_{C,P}$ = 11 Hz, PC_6H_5), 134.9 (d, $J_{C,P}$ = 12 Hz, PC_6H_5), 131.9 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 131.4 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 130.2 (d, $J_{C,P}$ = 25 Hz, PC_6H_5), 128.6 (d, $J_{C,P}$ = 6 Hz, PC_6H_5), 128.4 (d, $J_{C,P}$ = 11 Hz, PC_6H_5), 128.1 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 118.2 (br. s, NCH), 60.2 (s, C_6H_{11}), 59.2 (s, C_6H_{11}), 35.6 (d, J = 8 Hz, C_6H_{11}), 35.3 (s, C_6H_{11}), 34.5 (s, C_6H_{11}), 34.3 (s, C_6H_{11}), 32.5 (dd, $J_{C,P}$ = 28, $J_{C,P}$ = 3 Hz, PCH_2), 32.2 (dd, $J_{C,P}$ = 32, $J_{C,P}$ = 3 Hz, PCH_2), 26.8 (s, C_6H_{11}), 26.7 (s, C_6H_{11}), 26.6 (s, C_6H_{11}), 26.5 (s, C_6H_{11}), 26.5 (s, C_6H_{11}), 26.2 (s, C_6H_{11}), 19.5 (s, PCH_2CH_2) ppm. IR: $\tilde{\nu}$ = 1873 (s) cm^{-1}.

[Ru(ICy)(dppp)(CO)($C_6F_4CF_3$)H] (10): $C_6F_5CF_3$ (46 μL, 0.32 mmol) was added to a toluene solution (10 mL) of [Ru(ICy)(dppp)(CO)H_2] (50 mg, 0.06 mmol) and stirred at ambient temperature for 1 h. Et_3SiH (51 μL, 0.32 mmol) was added to the reaction mixture which was heated at 120 °C for 2 h. The solvent was stripped under vacuum and the residue washed with hexane to afford [Ru(ICy)(dppp)(CO)($C_6F_4CF_3$)H] as a white powder (55 mg, 86%). $C_{50}H_{51}F_7N_2OP_2Ru{\cdot}C_6H_6$ (1070.0): calcd. C 62.8, H 5.37, N 2.62; found C 62.47, H 5.40, N 2.63. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 8.24 (m, 2 H, PC_6H_5), 7.76 (m, 2 H, PC_6H_5), 7.24–7.10 (m, 7 H, PC_6H_5), 6.98–6.82 (m, 9 H, PC_6H_5), 6.34 (d, J_{HH} = 1.78 Hz, 1 H, NCH), 6.23 (d, J_{HH} = 2.09 Hz, 1 H, NC*H*), 5.81 (m, 1 H, C_6H_{11}), 5.22 (m, 1 H, C_6H_{11}), 2.62 (m, 2 H, PCH_2), 2.48 (m, 1 H, PCH_2) 2.24 (m, 1 H, C_6H_{11}), 2.05 (m, 1 H, PCH_2), 1.84–0.76 (m, 21 H, PCH_2, C_6H_{11}), –3.91 (q, $^2J_{H,P}$ = $^4J_{H,F}$ = 22.0 Hz, 1 H, Ru-H) ppm. ^{31}P{^{1}H} (162 MHz, C_6D_6, 25 °C): δ = 34.2 (d, $^2J_{P,P}$ = 33 Hz), 31.3 (m) ppm. ^{19}F (376 MHz, C_6D_6, 25 °C): δ = –55.0 (t, $^4J_{F,F}$ = 21.0 Hz, 3 F, CF_3), –96.4 (m, 1 F, *o*-F), –98.7 (m, 1 F, *o*-F), –144.6 (m, 1 F, *m*-F), –145.3 (m, 1 F, *m*-F) ppm. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C): δ = 205.7 (m, Ru-CO), 183.8 (dd, $^2J_{C,P}$ = 81, $^2J_{C,P}$ = 12 Hz, NCN), 141.7 (d, $J_{C,P}$ = 34 Hz, PC), 140.1 (d, $J_{C,P}$ = 40 Hz, PC), 137.3 (d, $J_{C,P}$ = 33 Hz, PC), 135.1 (d, $J_{C,P}$ = 12 Hz, PC_6H_5), 134.9 (d, $J_{C,P}$ = 12 Hz, PC_6H_5), 131.9 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 131.1 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 130.3 (d, $J_{C,P}$ = 34 Hz, PC_6H_5), 129.2 (d, $J_{C,P}$ = 17 Hz, PC_6H_5), 128.6 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 128.3 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 118.3 (s, NCH), 60.3 (s, C_6H_{11}), 59.3 (s, C_6H_{11}), 35.6 (d, J = 7 Hz, C_6H_{11}), 35.3 (s, C_6H_{11}), 34.4 (s, C_6H_{11}), 34.3 (s, C_6H_{11}), 32.3 (d, $J_{C,P}$ = 29 Hz, PCH_2), 28.7 (d, $J_{C,P}$ = 27 Hz, PCH_2), 26.8 (s, C_6H_{11}), 26.7 (s, C_6H_{11}), 26.6 (s, C_6H_{11}), 26.5 (s, C_6H_{11}), 26.4 (s, C_6H_{11}), 26.1 (s, C_6H_{11}), 19.5 (s, PCH_2CH_2) ppm. IR: $\tilde{\nu}$ = 1879 (s) cm^{-1}.

[Ru(ICy)(dppp)(CO)(C_5F_4N)H] (11): To a toluene solution of [Ru(ICy)(dppp)(CO)H_2] (50 mg, 0.06 mmol) was added C_5F_5N (35 μL, 0.32 mmol). The solution was stirred at room temperature for 1 h before addition of Et_3Si-H (51 μL, 0.32 mmol) and heating at 120 °C for 2 h. The reaction mixture was reduced in vacuo and washed with hexane to yield [Ru(ICy)(dppp)(CO)(C_5F_4N)H] as a white powder (52 mg, 87%). $C_{48}H_{51}F_4N_3OP_2Ru{\cdot}C_6H_6$ (1003.0): calcd. C 64.66, H 5.73, N 4.19; found C 64.72, H 5.78, N 4.19. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 8.30 (m, 2 H, PC_6H_5), 7.76 (m, 3 H, PC_6H_5), 7.28–6.98 (m, 6 H, PC_6H_5), 6.96–6.82 (m, 9 H, PC_6H_5), 6.34 (d, J_{HH} = 1.74 Hz, 1 H, NCH), 6.22 (d, J_{HH} = 1.74 Hz, 1 H, NC*H*), 5.80 (m, 1 H, C_6H_{11}), 5.20 (m, 1 H, C_6H_{11}), 2.61 (m, 2 H, PCH_2), 2.53–0.75 (m, 24 H, PCH_2, C_6H_{11}), –3.87 (q, $^2J_{H,P}$ = $^4J_{H,F}$ = 21.0 Hz, 1 H, Ru-H) ppm. ^{31}P{^{1}H} (202 MHz, C_6D_6, 25 °C): δ = 34.0 (d, $^2J_{P,P}$ = 33 Hz), 30.7 (m) ppm. ^{19}F (376 MHz, C_6D_6, 25 °C): δ = –100.3 (m, 2 F, *m*-F), –103.9 (m, 1 F, *o*-F), 106.7 (m, 1 F, *o*-F) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): δ = 205.6 (m, Ru-CO), 183.5 (dd, $^2J_{C,P}$ = 80, $^2J_{C,P}$ = 12 Hz, NCN), 141.7 (dd, $J_{C,P}$ = 34, $J_{C,P}$ = 2 Hz, PC), 140.0 (dd, $J_{C,P}$ = 40, $J_{C,P}$ = 2 Hz, PC), 137.2 (d, $J_{C,P}$ = 33 Hz, PC), 135.2 (d, $J_{C,P}$ = 12 Hz, PC_6H_5), 134.9 (d, $J_{C,P}$ = 13 Hz, PC_6H_5), 131.9 (d, $J_{C,P}$ = 10 Hz, PC_6H_5), 131.1 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 130.4 (d, $J_{C,P}$ = 43 Hz, PC_6H_5), 129.2 (s, PC_6H_5), 128.8 (d, $J_{C,P}$ = 49 Hz, PC_6H_5), 128.3 (d, $J_{C,P}$ = 9 Hz, PC_6H_5), 118.4 (s, NCH), 60.3 (s, C_6H_{11}), 59.2 (s, C_6H_{11}), 35.7 (d, J = 7 Hz, C_6H_{11}), 35.3 (s, C_6H_{11}), 34.4 (s, C_6H_{11}), 34.3 (s, C_6H_{11}), 32.2 (dd, $J_{C,P}$ = 28, $J_{C,P}$ = 3 Hz, PCH_2),

Table 5. Crystal data and structure refinement for compounds **1**, **2**, **7** and **8**.

Compound	**1**	**2**	**7**	**8**
Empirical formula	$C_{46}H_{42}FOP_3Ru$	$C_{56}H_{59}FN_2OP_2Ru$	$C_{43}H_{52}N_2OP_2Ru$	$C_{44.33}H_{54.11}FN_2OP_2Ru$
Formula weight	823.78	958.06	775.88	813.02
Crystal system	triclinic	triclinic	triclinic	hexagonal
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P6_1$
a [Å]	10.1880(2)	11.7800(1)	9.7350(1)	40.3130(2)
b [Å]	16.7830(3)	12.1130(2)	12.2780(2)	40.3130(2)
c [Å]	23.0560(5)	17.1580(2)	16.9570(3)	14.5800(1)
α [°]	95.101(1)	96.084(1)	79.911(1)	90
β [°]	92.783(1)	97.792(1)	84.049(1)	90
γ [°]	90.684(1)	97.116(1)	69.432(1)	120
U [Å^3]	3921.47(13)	2388.16(5)	1866.32(5) ^{3}	20520.0(2)
Z	4	2	2	18
D_c [g cm^{-3}]	1.395,	1.332	1.381	1.184
μ [mm^{-1}]	0.562	0.441	0.542	0.450
F(000)	1696	1000	812	7650
Crystal size [mm]	0.15 × 0.15 × 0.12	0.35 × 0.22 × 0.15	0.15 × 0.05 × 0.05	0.20 × 0.08 × 0.05
θ min., max. for data collection	3.53, 27.49	3.53, 27.48	3.52, 27.53	3.54, 23.25
Index ranges	–13 ≤ h ≤ 13	–15 ≤ h ≤ 15	–12 ≤ h ≤ 12	–44 ≤ h ≤ 44
	21 ≤ k ≤ 21	15 ≤ k ≤ 15	15 ≤ k ≤ 15	44 ≤ k ≤ 44
	–29 ≤ l ≤ 29	–22 ≤ l ≤ 22	–21 ≤ l ≤ 22	–16 ≤ l ≤ 16
Reflections collected	71302	42981	34683	221677
Independent reflections, R_{int}	17384, 0.0705	10884, 0.0278	8540, 0.0656	19537, 0.1287
Reflections observed (>2σ)	11929	9977	6709	15208
Data completeness	0.965	0.994	0.992	0.995
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
Max., min. transmission	0.94, 0.88	0.92, 0.90	0.97, 0.93	0.98, 0.93
Data/restraints/parameters	17384/2/939	10884/1/577	8540/2/450	19537/13/1387
Goodness-of-fit on F^2	1.057	1.072	1.029	1.025
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0473, 0.0836	0.0279, 0.0679	0.0398, 0.0713	0.0535, 0.1200
Final R_1, wR_2 (all data)	0.0878, 0.0972	0.0320, 0.0709	0.0631, 0.0784	0.0805, 0.1332
Largest diff. peak, hole [e Å^{-3}]	0.515, –0.50	0.691, –0.649	0.448, –0.761	0.984, –0.327
Absolute structure parameter	–	–	–	–0.02(3)

Table 6. Crystal data and structure refinement for compounds **9**, **10** and **11**.

Compound	**9**	**10**	**11**
Empirical formula	$C_{49}H_{51}F_5N_2OP_2Ru$	$C_{56}H_{55}F_7N_2OP_2Ru$	$C_{60}H_{63}F_4N_3OP_2Ru$
Formula weight	941.93	1068.03	1081.14
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	12.4090(3)	13.5440(2)	11.2020(2)
b [Å]	13.8650(3)	13.5560(2)	13.9180(2)
c [Å]	13.9590(3)	15.1060(2)	18.9190(3)
α [°]	83.783(1)	64.739(1)	69.866(1)
β [°]	66.562(1)	87.984(1)	73.345(1)
γ [°]	88.922(1)	81.794(1)	75.351(1)
U [Å^3]	2189.77(9)	2481.57(6)	2613.92(7)
Z	2	2	2
D_c [g cm^{-3}]	1.429	1.429	1.374
μ [mm^{-1}]	0.492	0.449	0.420
F(000)	972	1100	1124
Crystal size [mm]	0.25 × 0.20 × 0.15	0.22 × 0.15 × 0.15	0.25 × 0.20 × 0.10
θ min., max. for data collection	3.51, 27.48	3.84, 27.51	3.77, 27.46
Index ranges	$-16 \le h \le 16$ $18 \le k \le 18$ $-18 \le l \le 18$	$-17 \le h \le 17$ $16 \le k \le 17$ $-19 \le l \le 19$	$-14 \le h \le 14$ $18 \le k \le 18$ $-24 \le l \le 24$
Reflections collected	36187	44147	38269
Independent reflections, R_{int}	9954, 0.0759	11348, 0.0644	11866, 0.0758
Reflections observed (>2σ)	6800	8898	9273
Data completeness	0.994	0.994	0.993
Absorption correction	multi-scan	multi-scan	multi-scan
Max., min. transmission	0.95, 0.83	0.94, 0.87	0.96, 0.83
Data/restraints/parameters	9954/1/545	11348/1/654	11866/1/683
Goodness-of-fit on F^2	1.019	1.024	1.013
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0436, 0.0818	0.0376, 0.0861	0.0387, 0.0875
Final $R1$, $wR2$ (all data)	0.0860, 0.0958	0.0578, 0.0938	0.0604, 0.0970
Largest diff. peak, hole [e Å^{-3}]	1.021, –1.179	0.829, –0.780	0.392, –0.880

28.7 (dd, $J_{C,P}$ = 27, $J_{C,P}$ = 2 Hz PCH_2), 26.8 (s, C_6H_{11}), 26.7 (s, C_6H_{11}), 26.6 (s, C_6H_{11}), 26.5 (s, C_6H_{11}), 26.4 (s, C_6H_{11}), 26.1 (s, C_6H_{11}), 19.4 (s, PCH_2CH_2) ppm. IR: $\tilde{\nu}$ = 1876 (s) cm^{-1}.

X-ray Crystallography: Single crystals of the compounds **1**, **2**, **7**, **8**, **9**, **10** and **11** were analysed at 150 K using a Nonius Kappa CCD diffractometer and Mo(K_α) radiation (λ = 0.71073 Å). The structures were solved using SHELXS-97 and refined using full-matrix least-squares in SHELXL-97.[41] Hydrides were universally located and refined at a distance of 1.6 Å from the metal centre. Convergence was uneventful, with the exception of the following noteworthy points. Data collection details are summarised in Tables 5 and 6. The asymmetric unit in **1** was seen to contain two molecules while, in **2**, the complex crystallised with one molecule of toluene. The crystal of **8** was very small on two dimensions, and diffraction fall-off was evident at higher Bragg angles. Data were consequently collected to a resolution of 0.9 Å. The asymmetric unit was seen to comprise of three molecules of the carbene complex, plus two-thirds of a molecule of hexane. The solvent carbons were treated isotropically, and it was also evident that there was some disorder in this region of the map, which could not be reliably modelled. Restraints were applied within the solvent fragment to assist convergence. The asymmetric unit in **10** was seen to contain one molecule of solvent and one molecule of the carbene complex. Additionally, F5–F7 exhibited 65:35 disorder, which was readily modelled.

Crystallographic data for compounds and have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publications CCDC-708026 (for **1**), -708027 (for **2**), -708028 (for **7**), -708029 (for **8**), -708030 (for **9**), -708031 (for **10**), -708032 (for **11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336033, E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information (see also the footnote on the first page of this article): X-ray crystal structure of [Ru(dppp)$_2$(CO)H]$^+$/[Ru(dppp)$_2$(CO)F]$^+$.[11]

Acknowledgments

Financial support was provided by the EPSRC through a Doctoral Training Award to S. P. R. We thank Johnson Matthey plc for a loan of ruthenium trichloride.

[1] a) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247–2273; b) R. H. Crabtree, *J. Organomet. Chem.* **2005**, *690*, 5451–5457; c) P. L. Arnold, S. Pearson, *Coord. Chem. Rev.* **2007**, *251*, 596–609; d) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172.

[2] a) J. Huang, E. D. Stevens, S. P. Nolan, *Organometallics* **2000**, *19*, 1194–1197; b) R. Dorta, E. D. Stevens, S. P. Nolan, *J. Am. Chem. Soc.* **2004**, *126*, 5054–5055; c) N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 3516–3526; d) N. M. Scott, V. Pons, E. D. Stevens, D. M. Heinekey, S. P. Nolan, *Angew. Chem. Int. Ed.* **2005**, *44*, 2512–2515; e) F. Hanasaka, Y. Tanabe, K. Fujita, R. Yamaguchi, *Organometallics* **2006**, *25*, 826–831; f) Y. Tanabe, F. Hanasaka, K. Fujita, R. Yamaguchi, *Organometallics* **2007**, *26*, 4618–4636.

[3] a) S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *J. Am. Chem. Soc.* **2002**, *124*, 10473–10481; b) A. R. Chianese, A. Kovacevic, B. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 2461–2468; c) M. Viciano, M. Poyatos, M. Sanaú, E. Peris, A. Rossin, G. Ujaque, A. Lledós, *Organometallics* **2006**, *25*, 1120–1134; d) For a recent overview of Rh-NHC chemistry, see: J. M. Praetorius, C. M. Crudden, *Dalton Trans.* **2008**, 4079–4094.

[4] a) R. F. R. Jazzar, S. A. Macgregor, M. F. Mahon, S. P. Richards, M. K. Whittlesey, *J. Am. Chem. Soc.* **2002**, *124*, 4944; b) S. Burling, M. F. Mahon, B. M. Paine, M. K. Whittlesey, J. M. J. Williams, *Organometallics* **2004**, *23*, 4537–4539; c) S. Burling, B. M. Paine, D. Nama, V. S. Brown, M. F. Mahon, T. J. Prior, P. S. Pregosin, M. K. Whittlesey, J. M. J. Williams, *J. Am. Chem. Soc.* **2007**, *129*, 1987–1995.

[5] M. J. Chilvers, R. F. R. Jazzar, M. F. Mahon, M. K. Whittlesey, *Adv. Synth. Catal.* **2003**, *345*, 1111–1114.

[6] a) D. Giunta, M. Hölscher, C. W. Lehmann, R. Mynott, C. Wirtz, W. Leitner, *Adv. Synth. Catal.* **2003**, *345*, 1139–1145; b) R. A. Diggle, S. A. Macgregor, M. K. Whittlesey, *Organometallics* **2004**, *23*, 1857–1865; c) K. A. M. Ampt, S. Burling, S. M. Donald, S. Douglas, S. B. Duckett, S. A. Macgregor, R. N. Perutz, M. K. Whittlesey, *J. Am. Chem. Soc.* **2006**, *128*, 7452–7453; d) R. A. Diggle, S. A. Macgregor, M. K. Whittlesey, *Organometallics* **2008**, *27*, 617–625; e) R. A. Diggle, A. A. Kennedy, S. A. Macgregor, M. K. Whittlesey, *Organometallics* **2008**, *27*, 938–944.

[7] a) K. Abdur-Rashid, T. Fedorkiw, A. J. Lough, R. H. Morris, *Organometallics* **2004**, *23*, 86–94; b) W. Baratta, J. Schütz, E. Herdtweck, W. A. Herrmann, P. Rigo, *J. Organomet. Chem.* **2005**, *690*, 5570–5575; c) S. Burling, M. F. Mahon, R. E. Powell, M. K. Whittlesey, J. M. J. Williams, *J. Am. Chem. Soc.* **2006**, *128*, 13702–13703.

[8] a) D. S. Laitar, P. Müller, T. G. Gray, J. P. Sadighi, *Organometallics* **2005**, *24*, 4503–4505; b) T. Schaub, U. Radius, *Chem. Eur. J.* **2005**, *11*, 5024–5030; c) S. L. Chatwin, M. G. Davidson, C. Doherty, S. M. Donald, R. F. R. Jazzar, S. A. Macgregor, G. J. McIntyre, M. F. Mahon, M. K. Whittlesey, *Organometallics* **2006**, *25*, 99–110; d) T. Schaub, M. Backes, U. Radius, *J. Am. Chem. Soc.* **2006**, *128*, 15964–15965; e) T. Schaub, P. Fischer, A. Steffen, T. Braun, U. Radius, A. Mix, *J. Am. Chem. Soc.* **2008**, *130*, 9304–9317; f) T. Schaub, M. Backes, U. Radius, *Eur. J. Inorg. Chem.* **2008**, *17*, 2680–2690; g) G. B. Nikiforov, H. W. Roesky, P. G. Jones, J. Magull, A. Ringe, R. B. Oswald, *Inorg. Chem.* **2008**, *47*, 2171–2179.

[9] S. P. Reade, D. Nama, M. F. Mahon, P. S. Pregosin, M. K. Whittlesey, *Organometallics* **2007**, *26*, 3484–3491.

[10] The ^{19}F chemical shifts of five- and six-coordinate ruthenium fluorido complexes have been commented on by Caulton and co-workers: D. Huang, P. R. Koren, K. Folting, E. R. Davidson, K. G. Caulton, *J. Am. Chem. Soc.* **2000**, *122*, 8916–8931.

[11] The formation of **1** was often accompanied by minor amounts of *trans*-$[Ru(dppp)_2(CO)H]^+$, which could be formed as the sole reaction product through heating $[Ru(PPh_3)_3(CO)HF]$ with ca. 5 equiv. of dppp. X-ray crystallography revealed a structure which consisted of a 70:30 mix of the hydrido complex *trans*-$[Ru(dppp)_2(CO)H]^+$ and the previously reported fluorido derivative *trans*-$[Ru(dppp)_2(CO)F]^+$.[14] The counter-ion for both cations proved to be the relatively rare $[SiF_5]^-$ anion, which forms upon interaction of HF with surface silica of the glassware.[17b] See Supporting Information for structural details.

[12] A. Santos, J. López, J. Montoya, P. Noheda, A. Romero, A. M. Echavarren, *Organometallics* **1994**, *13*, 3605–3615.

[13] P. C. Junk, J. W. Steed, *J. Organomet. Chem.* **1999**, *587*, 191–194.

[14] P. Barthazy, R. M. Stoop, M. Wörle, A. Togni, A. Mezzetti, *Organometallics* **2000**, *19*, 2844–2852.

[15] a) S. A. Brewer, K. S. Coleman, J. Fawcett, J. H. Holloway, E. G. Hope, D. R. Russell, P. G. Watson, *J. Chem. Soc., Dalton Trans.* **1995**, 1073–1076; b) D. A. J. Harding, E. G. Hope, G. A. Solan, J. Fawcett, *Acta Crystallogr., Sect. C* **2007**, *63*, M383–M384.

[16] a) K. G. Caulton, *New J. Chem.* **1994**, *18*, 25–41; b) A. Mezzetti, C. Becker, *Helv. Chim. Acta* **2002**, *85*, 2686–2703; c) C. Becker, I. Kieltsch, D. Broggini, A. Mezzetti, *Inorg. Chem.* **2003**, *42*, 8417–8429.

[17] It is worth noting that the coordinatively unsaturated complex $[Ir(PtBu_2Ph)_2H_2F]$ will eliminate HF at room temperature upon addition of either just CO or H_2; a) A. C. Cooper, K. Folting, J. C. Huffman, K. G. Caulton, *Organometallics* **1997**, *16*, 505–507; b) A. C. Cooper, J. C. Bollinger, J. C. Huffman, K. G. Caulton, *New J. Chem.* **1998**, *22*, 473–480. The formation of $[Ru(PPh_3)_2(CO)(NO)Cl]$ from treatment of $[Ru(PPh_3)_2(NO)Cl]$ with HC(O)F also necessitates HF elimination during the reaction. G. Doyle, *J. Organomet. Chem.* **1982**, *224*, 355–362.

[18] While neither $[Ru(ICy)(PPh_3)_2(CO)H_2]$ nor $[Ru(ICy)(PPh_3)_2HCl]$ show any activation of the *N*-cyclohexyl groups (S. Burling, G. Kociok-Köhn, M. F. Mahon, M. K. Whittlesey, J. M. J. Williams, *Organometallics* **2005**, *24*, 5868–5878), C–H activation/β-hydrogen migration does take place upon addition of HSO_3CF_3 to $[(\eta^5\text{-}C_5Me_5)Ir(ICy)(CH_3)_2]$ (M. Prinz, M. Grosche, E. Herdtweck, W. A. Herrmann, *Organometallics* **2000**, *19*, 1692–1694).

[19] H. Kawano, R. Tanaka, T. Fujikawa, K. Hiraki, M. Onishi, *Chem. Lett.* **1999**, 401–402.

[20] a) M. S. Viciu, O. Navarro, R. F. Germaneau, R. A. Kelly III, W. J. Sommer, N. Marion, E. D. Stevens, L. Cavallo, S. P. Nolan, *Organometallics* **2004**, *23*, 1629–1635; b) N. M. Scott, S. P. Nolan, *Eur. J. Inorg. Chem.* **2005**, 1815–1828; c) L. Cavallo, A. Correa, C. Costabile, H. Jacobsen, *J. Organomet. Chem.* **2005**, *690*, 5407–5413; d) R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 2485–2495.

[21] This is also borne out by ν(CO) values of 1915 cm^{-1} and 1941 cm^{-1} for **7** and **4**, respectively.

[22] See for example a) K. B. Renkema, U. Wener-Zwanziger, M. D. Pagel, K. G. Caulton, *J. Mol. Catal. A* **2004**, *224*, 125–131; b) J. Vela, J. M. Smith, Y. Yu, N. A. Ketterer, C. J. Flaschenriem, R. J. Lachicotte, P. L. Holland, *J. Am. Chem. Soc.* **2005**, *127*, 7857–7870.

[23] We have recently found that stoichiometric and catalytic activation of C–F bonds can be brought about using $[Ru(NHC)(PPh_3)_2(CO)H_2]$ (NHC = IMes, SIMes, IPr, SIPr) complexes. S. P. Reade, M. F. Mahon, M. K. Whittlesey, *J. Am. Chem. Soc.*, in press.

[24] Reaction occurred at 70 °C, but was significantly slower.

[25] M. K. Whittlesey, R. N. Perutz, M. F. Moore, *Chem. Commun.* **1996**, 787–788.

[26] a) J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, *94*, 373–431; b) T. G. Richmond, *Top. Organomet. Chem.* **1999**, *3*, 243–269; c) H. Torrens, *Coord. Chem. Rev.* **2005**, 1957–1985; d) T. Braun, R. N. Perutz In *Comprehensive Organometallic Chemistry III* (Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Oxford, **2007**, volume 1, pp. 725–758.

[27] F. Godoy, C. L. Higgitt, A. H. Klahn, B. Oelckers, S. Parsons, R. N. Perutz, *J. Chem. Soc., Dalton Trans.* **1999**, 2039–2047.

[28] D. Noveski, T. Braun, B. Neumann, A. Stammler, H.-G. Stammler, *Dalton Trans.* **2004**, 4106–4119.

[29] M. J. Salomon, T. Braun, I. Krossing, *Dalton Trans.* **2008**, 5197–5206.

[30] a) J. Fornies, M. Green, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1977**, 1006–1009; b) N. A. Jasim, R. N. Perutz, A. C. Whitwood, T. Braun, J. Izundu, B. Neumann, S. Rothfeld, H.-G. Stammler, *Organometallics* **2004**, *23*, 6140–6149.

[31] B. L. Edlelbach, W. D. Jones, *J. Am. Chem. Soc.* **1997**, *119*, 7734–7742.

[32] L. Cronin, C. L. Higgitt, R. Karsch, R. N. Perutz, *Organometallics* **1997**, *16*, 4920–4928.
[33] R. J. Lindup, T. B. Marder, R. N. Perutz, A. C. Whitwood, *Chem. Commun.* **2007**, 3664–3666.
[34] B. M. Kraft, W. D. Jones, *J. Organomet. Chem.* **2002**, *658*, 132–140.
[35] R. Bosque, E. Clot, S. Fantacci, F. Maseras, O. Eisenstein, R. N. Perutz, K. B. Renkema, K. G. Caulton, *J. Am. Chem. Soc.* **1998**, *120*, 12634–12640.
[36] M. Rheinhold, J. E. McGrady, R. N. Perutz, *J. Am. Chem. Soc.* **2004**, *126*, 5268–5276.
[37] C. W. Jung, P. E. Garrou, *Organometallics* **1982**, *2*, 658–666.
[38] A. J. Arduengo III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534.
[39] N. Kühn, T. Kratz, *Synthesis* **1993**, 561–562.
[40] S. P. Nolan, personal communication.
[41] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473; G. M. Sheldrick, *SHELXL-97*, a computer program for crystal structure refinement, University of Göttingen, **1997**.

Received: November 12, 2008
Published Online: January 14, 2009

