Synthesis and Reactivity of $Ru(PPh_3)_3(CO)HF$ and the N-Heterocyclic Carbene Derivatives $Ru(NHC)(PPh_3)_2(CO)HF$

Steven P. Reade,[†] Devendrababu Nama,[‡] Mary F. Mahon,[†] Paul S. Pregosin,*[,‡] and Michael K. Whittlesey*[,†]

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K., and Laboratory of Inorganic Chemistry, ETHZ, Honggerberg, CH-8093 Zurich, Switzerland

Received February 22, 2007

The reaction of $Ru(PPh_3)_3(CO)H_2$ with excess $Et_3N{\cdot}3HF$ at elevated temperature affords the hydride fluoride complex $Ru(PPh_3)_3(CO)HF$ (**1**). This reacts with a series of N-heterocyclic carbenes (NHCs) at ambient temperature to form the mono-NHC products $Ru(NHC)(PPh_3)_2(CO)HF$ (NHC = IMe_4 (**2**), IEt_2Me_2 (**3**), ICy (**4**), $I^iPr_2Me_2$ (**5**)). Complexes **2**−**4** convert from the trans- to cis-phosphine isomers in solution over weeks (relative rates **2** > **3** ≫ **4**), while **5** undergoes both isomerization and disproportionation to yield *cis*-$Ru(I^iPr_2Me_2)(PPh_3)_2(CO)HF$ (**6**), **1**, and $Ru(I^iPr_2Me_2)_2(PPh_3)(CO)HF$ (**7**) in a matter of hours. The molecular structures of compounds **1**−**4** have been determined by X-ray crystallography.

Introduction

Fluoride complexes of the platinum group metals constitute a largely neglected class of compounds, which have long been considered as being too unstable and/or too reactive to be of any value. This is primarily because of the supposed incompatibility between the soft late-metal center and the small, hard, electronegative fluoride ligand.[1] However, the development over the last 5−10 years of more widely applicable synthetic routes allowing fluoride to be introduced into the coordination sphere of a metal (e.g., AgF metathesis,[2] C−F bond activation,[3−5] development of mild HF sources such as $Et_3N{\cdot}3HF$,[2,6] and oxidative addition of XeF_2[7,8]) has made M−F complexes more common. Consequently, a better understanding of the fundamental bonding interactions that can help to stabilize M−F complexes has also developed,[9,10] such that there are now a range of synthetic and catalytic applications.[4,7,11]

In the majority of M−F complexes, one or more tertiary phosphines are present as ancillary ligands, although not always in an innocent capacity.[12] For some time, we have been interested in determining how stability and reactivity are affected upon replacing PR_3 by an N-heterocyclic carbene (NHC), given that NHCs are significantly better σ-donor ligands.[13] Having recently established that NHC ruthenium hydride chloride complexes show patterns of reactivity comparatively different

* To whom correspondence should be addressed. E-mail: chsmkw@bath.ac.uk (M.K.W.).

[†] University of Bath.

[‡] ETHZ.

(1) (a) Doherty, N.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553. (b) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425. (c) Clark, H. C. S.; Holloway, J. H. In *Advanced Inorganic Fluorides: Synthesis, Characterization and Applications*; Nakajima, T., Žemva, B., Tressaud, A., Eds.; Elsevier: Amsterdam, 2000; p 51. (d) Grushin, V. V. *Chem. Eur. J.* **2002**, *8*, 1006.

(2) Grushin, V. V.; Marshall, W. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4476.

(3) (a) Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 264. (b) Anderson, C. M.; Crespo, M.; Ferguson, G.; Lough, A. J.; Puddephatt, R. J. *Organometallics* **1992**, *11*, 1177. (c) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373. (d) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber.-Recl.* **1997**, *130*, 145. (e) Richmond, T. G. *Top. Organomet. Chem.* **1999**, *3*, 243. (f) Archibald, S. J.; Braun, T.; Gaunt, J. A.; Hobson, J. E.; Perutz, R. N. *Dalton Trans.* **2000**, 2013. (g) Braun, T.; Cronin, L.; Higgitt, C. L.; McGrady, J. E.; Perutz, R. N.; Reinhold, M. *New J. Chem.* **2001**, *25*, 19. (h) Braun, T.; Noveski, D.; Neumann, B.; Stammler, H.-G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2745. (i) Ferrando-Miguel, G.; Gerard, H.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **2002**, *41*, 6440. (j) Reinhold, M.; McGrady, J. E.; Perutz, R. N. *J. Am. Chem. Soc.* **2004**, *126*, 5268. (k) Burling, S.; Elliott, P. I. P.; Jasim, N. A.; Lindup, R. J.; McKenna, J.; Perutz, R. N.; Archibald, S. J.; Whitwood, A. C. *Dalton Trans.* **2005**, 3686. (l) Torrens, H. *Coord. Chem. Rev.* **2005**, *249*, 1975. (m) Braun, T.; Perutz, R. N. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, U.K., 2006; Vol. 1, Chapter 1.26, p 725.

(4) (a) Braun, T.; Foxon, S. P.; Perutz, R. N.; Walton, P. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3326. (b) Braun, T.; Perutz, R. N. *Chem. Commun.* **2002**, 2749.

(5) Kirkham, M. S.; Mahon, M. F.; Whittlesey, M. K. *Chem. Commun.* **2001**, 813.

(6) (a) Whittlesey, M. K.; Perutz, R. N.; Greener, B.; Moore, M. F. *Chem. Commun.* **1997**, 187. (b) Fraser, S. L.; Antipin, M. Yu.; Khroustalyov, V. N.; Grushin, V. V. *J. Am. Chem. Soc.* **1997**, *119*, 4769. (c) Marshall, W. J.; Grushin, V. V. *Organometallics* **2004**, *23*, 3343. (d) Grushin, V. V.; Marshall, W. J. *J. Am. Chem. Soc.* **2004**, *126*, 3068. (e) Noveski, D.; Braun, T.; Krückemeier, S. *J. Fluorine Chem.* **2004**, *125*, 959.

(7) Holloway, J. H.; Hope, E. G. *J. Fluorine Chem.* **1996**, *76*, 209.

(8) (a) Blake, A. J.; Cockman, R. W.; Ebsworth, E. A. V.; Holloway, J. H. *J. Chem. Soc., Chem. Commun.* **1988**, 529. (b) Brewer, S. A.; Holloway, J. H.; Hope, E. G. *J. Chem. Soc., Dalton Trans.* **1994**, 1067. (c) Brewer, S. A.; Coleman, K. S.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Russell, D. R.; Watson, P. G. *J. Chem. Soc., Dalton Trans.* **1995**, 1073. (d) Coleman, K. S.; Holloway, J. H.; Hope, E. G. *J. Chem. Soc., Dalton Trans.* **1997**, 1713. (e) Coleman, K. S.; Holloway, J. H.; Hope, E. G.; Langer, J. *J. Chem. Soc., Dalton Trans.* **1997**, 4555. (f) Yahav, A.; Goldberg, I.; Vigalok, A. *J. Am. Chem. Soc.* **2003**, *125*, 13634. (g) Yahav, A.; Goldberg, I.; Vigalok, A. *Inorg. Chem.* **2005**, *44*, 1547.

(9) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

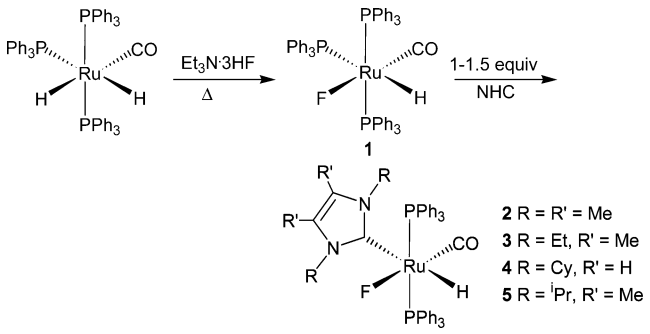
(10) (a) Mezzetti, A.; Becker, C. *Helv. Chim. Acta* **2002**, *85*, 2686. (b) Becker, C.; Kieltsch, I.; Broggini, D.; Mezzetti, A. *Inorg. Chem.* **2003**, *42*, 8417.

(11) (a) Grushin, V. V. *Angew. Chem., Int. Ed.* **1998**, *37*, 994. (b) Ishii, Y.; Chatani, N.; Yorimitsu, S.; Murai, S. *Chem. Lett.* **1998**, 157. (c) Barthazy, P.; Hintermann, L.; Stoop, R. M.; Wörle, M.; Mezzetti, A.; Togni, A. *Helv. Chim. Acta* **1999**, *82*, 2448. (d) Barthazy, P.; Stoop, R. M.; Wörle, M.; Togni, A.; Mezzetti, A. *Organometallics* **2000**, *19*, 2844. (e) Braun, T.; Perutz, R. N.; Sladek, M. I. *Chem. Commun.* **2001**, 2254. (f) Sladek, M. I.; Braun, T.; Neumann, B.; Stammler, H.-G. *Dalton Trans.* **2002**, 297. (g) Kuhl, S.; Schneider, R.; Fort, Y. *Adv. Synth. Catal.* **2003**, *345*, 241.

(12) (a) Blum, O.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1991**, 258. (b) den Reijer, C. J.; Wörle, M.; Pregosin, P. S. *Organometallics* **2000**, *19*, 309. (c) Jasim, N. A.; Perutz, R. N.; Whitwood, A. C.; Braun, T.; Izundu, J.; Neumann, B.; Rothfeld, S.; Stammler, H.-G. *Organometallics* **2004**, *23*, 6140. (d) Macgregor, S. A.; Roe, D. C.; Marshall, W. J.; Bloch, K. M.; Bakhmutov, V. I.; Grushin, V. V. *J. Am. Chem. Soc.* **2005**, *127*, 15304.

10.1021/om070164p CCC: $37.00
Publication on Web 06/07/2007

Scheme 1



from those of the related RuH_2 compounds,[14] we decided to investigate the synthesis and properties of the hydride fluoride analogues. We now report the preparation of the *N*-Me-, *N*-Et-, *N*-Cy-, and *N*-^{i}Pr-substituted carbene complexes Ru(NHC)-(PPh$_3$)$_2$(CO)HF, which are formed upon addition of the free NHCs to the previously unknown tris(phosphine) hydride fluoride complex Ru(PPh$_3$)$_3$(CO)HF. Hitherto, there have been just four fully characterized late M−F complexes containing NHC ligands reported: one by ourselves (Ru),[15,16] one by Sadighi (Au),[17] and two by Radius and co-workers (Ni).[18] Herein, we describe the first indication that the reactivity of M−F species can be significantly altered by different N-substituents on the carbene.

Results and Discussion

Formation, Structural Characterization, and Reactivity of Ru(PPh$_3$)$_3$(CO)HF. When a THF solution of Ru(PPh$_3$)$_3$-(CO)H$_2$ was heated at 85 °C in the presence of 3 equiv of Et$_3$N·3HF, a red solution was rapidly formed, which upon workup allowed isolation of the hydride fluoride complex Ru(PPh$_3$)$_3$-(CO)HF (**1**).[19] This is formed as a white, air-sensitive crystalline solid, which is only moderately soluble in toluene, benzene, or THF. The proton NMR spectrum of **1** (benzene-d_6) revealed the presence of a single hydride resonance at δ −5.05, with coupling to one trans (J_{HP} = 112.5 Hz) and two cis phosphorus nuclei (J_{HP} = 25.2 Hz), which correlates with the geometry shown in Scheme 1. The ^{31}P{^{1}H} NMR spectrum consists of an A$_2$X pattern, while the Ru−F signal appeared as a quartet at δ −385.1 (J_{FP} = 23.5 Hz) in the ^{19}F NMR spectrum.[20] This low-frequency ^{19}F position is consistent with a fluoride ligand bound to a saturated ruthenium center.[21] Although no coupling between the hydride and fluoride resonances was observable, their combined presence in the same molecule was confirmed by ^{1}H−^{19}F HMBC correlation spectroscopy. The compound displayed a single carbonyl IR absorption band at 1917 cm^{-1}, lower than the values for the related hydride chloride species Ru(PPh$_3$)$_3$(CO)HCl (1920 cm^{-1})[22] and Ru(P-P)(PPh$_3$)(CO)HCl (dppm/dppp/dppb/dppf, 1920 cm^{-1}; dppe, 1925 cm^{-1})[23] or the hydride bromide derivative Ru(PPh$_3$)$_3$(CO)HBr (1950 cm^{-1}).[24]

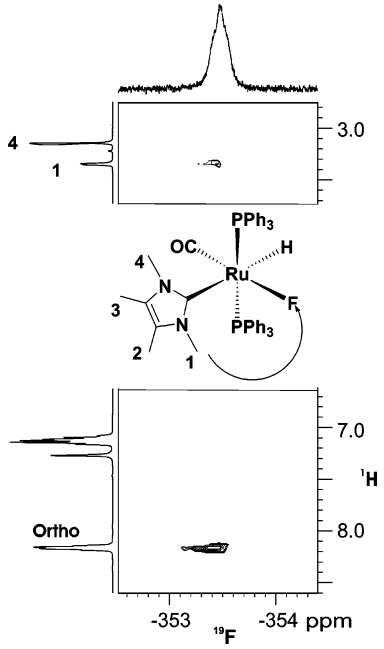


Figure 1. ^{1}H−^{19}F HOESY spectrum of complex **2** showing a selective NOE contact to one NHC methyl group as well as the ortho protons of the triphenylphosphine (benzene-d_6, 400 MHz, 298 K).

Complex **1** proved to be inert upon exposure to either H_2 or ethene but reacted with CO in benzene at room temperature to afford a white precipitate of Ru(PPh$_3$)$_2$(CO)$_2$HF.[25] The relatively high frequency hydride resonance (δ −2.58) is in agreement with the presence of a trans carbonyl ligand. The ^{19}F NMR spectrum showed a broad singlet for the Ru−F signal, although shifted >30 ppm to lower frequency than that for **1**.

Synthesis and Characterization of Ru(NHC)(PPh$_3$)$_2$(CO)-HF (NHC = IMe$_4$, IEt$_2$Me$_2$, ICy, I^{i}Pr$_2$Me$_2$). Addition of ca. 1.5 equiv of the NHC ligands IMe$_4$, IEt$_2$Me$_2$, ICy, and I^{i}Pr$_2$-Me$_2$ to toluene suspensions of **1** led to the formation of colorless, solid-free solutions of the mono-NHC complexes Ru(NHC)-(PPh$_3$)$_2$(CO)HF (NHC = IMe$_4$ (**2**), IEt$_2$Me$_2$ (**3**), ICy (**4**), I^{i}Pr$_2$-Me$_2$ (**5**)) within the space of approximately 5 min. In all cases, except for **4**, the complexes precipitated as white solids within a period of 10−15 min.[26] Crystals of **2**−**4** were isolated from benzene/hexane solutions and proved suitable for a single-crystal

(13) (a) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815. (b) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2006. (c) Glorius, F. A. *Top. Organomet. Chem.* **2007**, *21*, 1.

(14) Burling, S.; Kociok-Köhn, G.; Mahon, M. F.; Whittlesey, M. K.; Williams, J. M. J. *Organometallics* **2005**, *24*, 5868. See also ref 26.

(15) Chatwin, S. L.; Davidson, M. G.; Doherty, C.; Donald, S. M.; Jazzar, R. F. R.; Macgregor, S. A.; McIntyre, G. J.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2006**, *25*, 99.

(16) An interaction between ruthenium and an *o*-fluorine substituent in the fluorinated NHC 1,3-bis(2,6-difluorophenyl)imidazol-2-ylidene has recently been reported: Ritter, T.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 11768.

(17) Laitar, D. S.; Müller, T. G.; Gray, T. G.; Sadighi, J. P. *Organometallics* **2005**, *24*, 4503.

(18) (a) Schaub, T.; Radius, U. *Chem. Eur. J.* **2005**, *11*, 5024. (b) Schaub, T.; Backes, M.; Radius, U. *J. Am. Chem. Soc.* **2006**, *128*, 15964.

(19) The reaction of the dihydride complex with anhydrous HF yields the cationic fluoride-bridged dimer [{Ru(PPh$_3$)$_2$(CO)}$_2$(μ-F)$_3$]$^+$.[8e]

(20) The ^{19}F NMR resonances of **1**−**5** in benzene-d_6 varied in appearance, ranging from broad, unresolved singlets to well-resolved quartets. We thank an anonymous reviewer, who suggested that the broadening may arise from hydrogen bonding to adventitious water or HF and that addition of dry CsF can scavenge such impurities. Indeed, we find that, upon addition of CsF to samples of **2** and **3**, broad ^{19}F resonances are sharpened to quartets, allowing J_{FP} coupling constants of 23.0 Hz to be determined in both cases.

(21) Huang, D. J.; Koren, P. R.; Folting, K.; Davidson, E. R.; Caulton, K. G. *J. Am. Chem. Soc.* **2000**, *122*, 8916.

(22) Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 2947.

(23) Santos, A.; López, J.; Montoya, J.; Noheda, P.; Romero, A.; Echavarren, A. M. *Organometallics* **1994**, *13*, 3605.

(24) Sánchez-Delgado, R. A.; Thewalt, U.; Valencia, N.; Andriollo, A.; Márquez-Silva, R.-L.; Puga, J.; Schöllhorn, H.; Klein, H.-P.; Fontal, B. *Inorg. Chem.* **1986**, *25*, 1097.

(25) The analogous complex Ru(P^{t}Bu$_2$Me)$_2$(CO)$_2$HF has been reported by Caulton and co-workers and found to have a high-frequency hydride chemical shift: Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1994**, *13*, 1476.

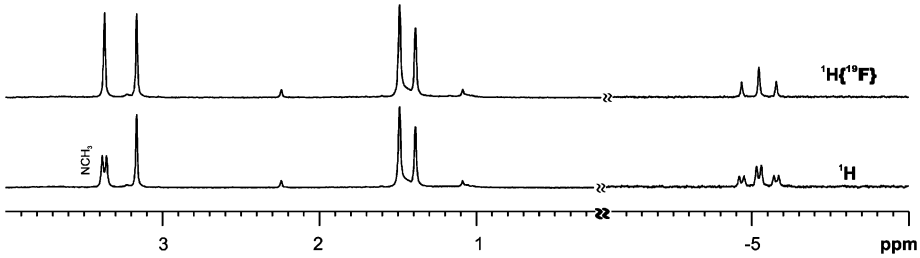


Figure 2. Section of the ^1H (lower trace) and $^1H\{^{19}F\}$ (upper trace) NMR spectra of complex **2** (d_8-THF, 200 MHz, 298 K).

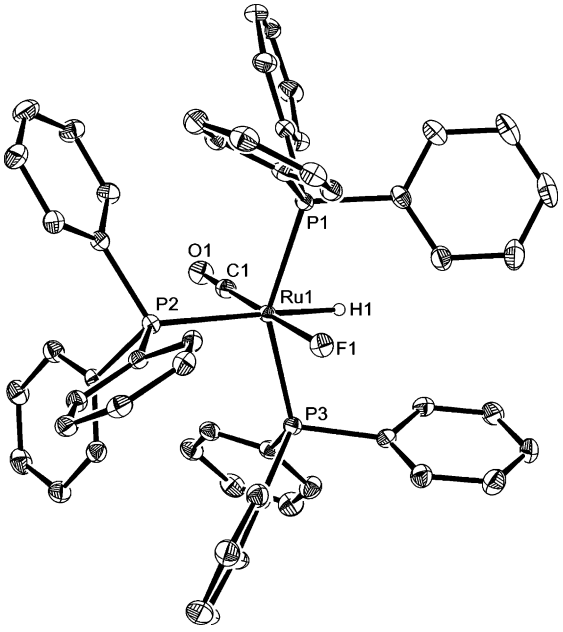


Figure 3. Molecular structure of **1**. Thermal ellipsoids are represented at the 30% probability level. Carbon-bound hydrogen atoms and solvent have been omitted for clarity. Selected distances (Å) and angles (deg): Ru(1)−P(1) = 2.3608(5), Ru(1)−P(2) = 2.4422(5), Ru(1)−P(3) = 2.3462(5), Ru(1)−C(1) = 1.819(3), Ru(1)−F(1) = 2.0986(15); P(1)−Ru(1)−P(3) = 150.13(2), F(1)−Ru(1)−C(1) = 177.94(11).

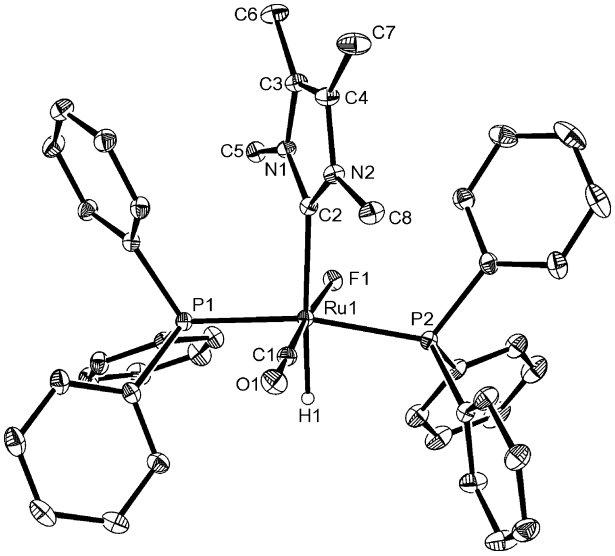


Figure 4. Molecular structure of **2**. Thermal ellipsoids are represented at the 30% probability level. Carbon-bound hydrogen atoms and disordered solvent have been omitted for clarity. Selected distances (Å) and angles (deg): Ru(1)−P(2) = 2.3434(4), Ru(1)−P(2) = 2.3499(4), Ru(1)−C(1) = 1.8144(16), Ru(1)−C(2) = 2.1702(16), Ru(1)−F(1) = 2.0887(9); P(1)−Ru(1)−P(2) = 164.189-(15), F(1)−Ru(1)−C(1) = 175.62(6).

X-ray study. Isolation of X-ray-quality crystals of **5** was precluded by its solution reactivity, which is discussed further below.

Proton NMR spectroscopy revealed hydride resonances between δ −5 and −6 for **2**−**5** in benzene-d_6, each with a doublet of triplets multiplicity resulting from coupling to both ^{19}F and ^{31}P. The high-frequency hydride position combined with the J_{HP} values (see Experimental Section) implies incorporation of the NHC ligand trans to hydride (Scheme 1).

Restricted rotation about the M−C_{NHC} bond was established in all cases by ^1H NMR spectroscopy. Thus, complex **2** shows four nonequivalent carbene methyl resonances. The N−C_{NHC}−N plane is not parallel to the P−Ru−P axis, and consequently, one of the two *N*-methyl resonances is closer to the Ru−F group. As a consequence, the 2-D $^{19}F-^1H$ HOESY spectrum affords a selective NOE contact from the fluoride ligand to this methyl group (Figure 1). As each *N*-Me resonance shows a selective NOESY cross-peak to its proximate *C*-Me partner, all four of the methyl signals can be fully assigned. Interestingly, there is a selective, through-space interaction from the ^{19}F spin to the proximate methyl group, which was confirmed via selective $^1H\{^{19}F\}$ decoupling (Figure 2). No exchange peaks were observed in the phase-sensitive proton 2-D NOESY map, indicative of a significant barrier to Ru−C_{NHC} rotation. The $^{31}P\{^1H\}$ spectrum of **2** shows a singlet at δ 44.8, while the ^{19}F resonance is observed as a broad multiplet at δ −353.3.[20]

X-ray Crystal Structures of 1−4. The solid-state structures of **1**−**4** were determined by X-ray crystallography and are shown in Figures 3−6. A distorted-octahedral geometry at the ruthenium center is observed in all cases with the two trans phosphines tilted toward the hydride (P−Ru−P: **1**, 150.13-(2)°: **2**, 164.19(2)°; **3**, 168.21(4)°: **4**, 161.94(3)°), a feature also common to the structure of $Ru(PPh_3)_3(CO)H_2$.[27] As expected, the structures contain fluoride ligands trans to the CO groups, enhancing push−pull stabilization.[9] Unfortunately, carbonyl/fluoride disorder precludes determination of accurate Ru−F distances in **3** and **4**. However, in the absence of such disorder it is noteworthy that the Ru−F bond distance in **2** (2.0887(9) Å) is somewhat shorter than the comparable distance in **1** (2.0986(15) Å), although they both lie in the range reported for the related complexes $Ru(PPh_3)_2(CO)_2F_2$ (2.011(4) Å),[8c] Ru-(dmpe)$_2$F(FHF) (2.101(3) Å),[5] $Ru(P^tBu_2Me)_2(CO)(=CF_2)HF$ (2.065(1) Å),[21] and $Ru(IMes)_2(CO)HF$ (2.019(5) Å).[15] The orientation of the phosphine ligands relative to the carbene is similar in structures **2**−**4**, such that the NHC ring is sandwiched by one phenyl ring from each triphenylphosphine, as shown in

(26) This behavior contrasts markedly with that of the hydride chloride analogue $Ru(PPh_3)_3(CO)HCl$, which we have recently shown reacts with $I^iPr_2Me_2$ in a very different way: Burling, S.; Mahon, M. F.; Powell, R. E.; Whittlesey, M. K.; Williams, J. M. J. *J. Am. Chem. Soc.* **2006**, *128*, 13702.

(27) Junk, P. C.; Steed, J. W. *J. Organomet. Chem.* **1999**, *587*, 191.

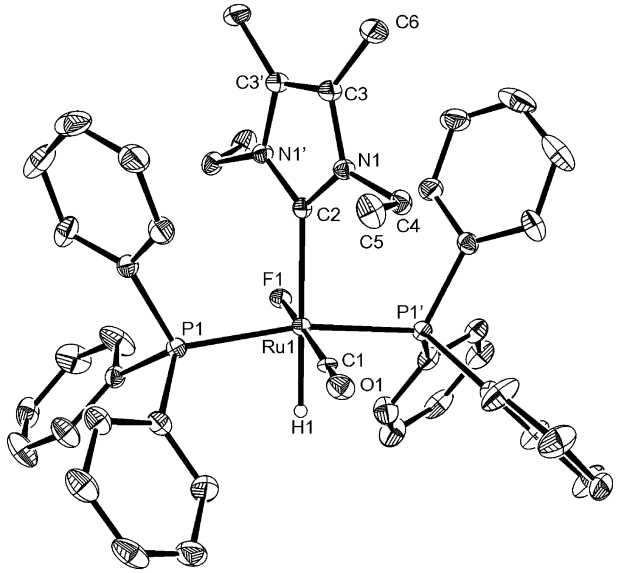


Figure 5. Molecular structure of **3**. Thermal ellipsoids are represented at the 30% probability level. Carbon-bound hydrogen atoms and disordered components have been omitted for clarity. Atoms labeled with a prime are related to those in the asymmetric unit by the symmetry operation $-x, y, {}^1/_2 - z$. Selected distances (Å) and angles (deg): Ru(1)−P(1) = 2.3540(7), Ru(1)−P(1′) = 2.3540(7), Ru(1)−C(1) = 1.944(5), Ru(1)−C(2) = 2.196(4), Ru(1)−F(1) = 1.976(5); P(1)−Ru(1)−P(1′) = 168.21(4), F(1)−Ru(1)−C(1) = 174.7(8).

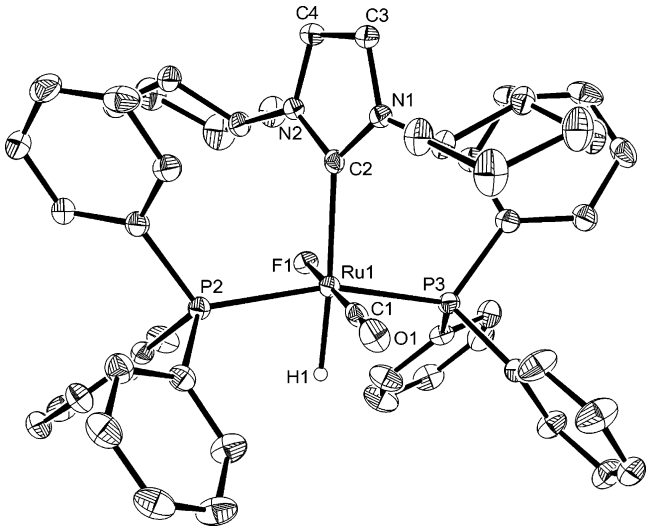


Figure 6. Molecular structure of **4**. Thermal ellipsoids are represented at the 30% probability level. Carbon-bound hydrogen atoms and the minor disordered component have been omitted for clarity. Selected distances (Å) and angles (deg): Ru(1)−P(2) = 2.3534(8), Ru(1)−P(3) = 2.3497(8), Ru(1)−C(1) = 1.851(5), Ru(1)−C(2) = 2.192(3), Ru(1)−F(1) = 2.021(2); P(2)−Ru(1)−P(3) = 161.94(3), F(1)−Ru(1)−C(1) = 176.9(4).

Figure 7 for Ru(IMe$_4$)(PPh$_3$)$_2$(CO)HF (**2**). Closest distances from the mean NHC ring plane to carbon atoms in the each flanking arene are 3.01 and 3.04 Å in **2**, 3.11 and 3.11 Å in **3**, and 3.17 and 3.21 Å in **4.** These data broadly reflect the steric trend of the carbene substituents in each case, while also suggesting the presence of $\pi-\pi$ interactions in all three compounds.

Reactivity of 2−4. Slow, but clean, isomerization of **2**−**4** to their corresponding cis-phosphine isomers was seen in THF-d_8 at ambient temperature over a period of 1−2 weeks (Scheme 2).[28] Thus, in the case of **2**, depletion of the triplet Ru−H resonance was accompanied by the formation of a doublet of doublet of doublets hydride signal at δ −6.40, with characteristic trans and cis values of J_{HP} (128.8, 27.1 Hz). Heteronuclear correlation experiments facilitated the assignment of two phosphorus resonances at δ 42.0 and 23.1 and a broad ^{19}F signal (−343.1 ppm) to the cis-phosphine product. Qualitatively, the rate of isomerization decreased in the order **2** > **3** ≫ **4**.

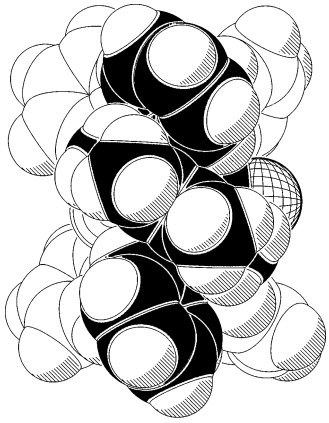
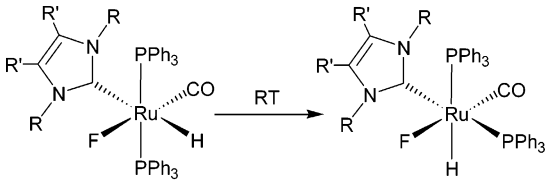


Figure 7. Space-filling plot of **2**, viewed along the C3−Ru1−C4 bisector, to illustrate the solid-state structural sandwiching of the NHC moiety by one phenyl group from each triphenylphosphine ligand. Relevant carbon atoms are highlighted in black.

Scheme 2



2 (R = R' = Me)
3 (R = Et, R' = Me)
4 (R = Cy, R' = H)

We have indirect evidence that the isomerization process is initiated by loss of PPh$_3$. Thus, **2** reacted with IMe$_4$ and CO at room temperature to give the bis(carbene) and dicarbonyl complexes Ru(IMe$_4$)$_2$(PPh$_3$)(CO)HF (^{1}H, δ −5.58, dd, J_{HP} = 27.4 Hz, J_{HF} = 6.0) and Ru(IMe$_4$)(PPh$_3$)(CO)$_2$HF (^{1}H, δ −2.65, dd, J_{HP} = 23.5, J_{HF} = 8.2 Hz), respectively (Ru(IMe$_4$)(PPh$_3$)(CO)$_2$-HF reacted further with CO to give Ru(IMe$_4$)(PPh$_3$)(CO)$_3$ as the ultimate reaction product). Phosphine loss was also found upon dissolution of **3** in pyridine, which gave the mono-(phosphine) complex Ru(IEt$_2$Me$_2$)(PPh$_3$)(CO)(py)HF (^{1}H, δ −11.47, br d, J_{HP} = 22.6 Hz; ^{31}P{^{1}H}, δ 46.8, d, J_{PF} = 23.6 Hz; ^{19}F, δ −289.1, d, J_{PF} = 23.0 Hz). Efforts to observe direct phosphine exchange proved unsuccessful, as there was no incorporation of P(*p*-tolyl)$_3$ found when the isomerization of **2** was run in THF-d_8 with 10 equiv of free phosphine added.

Reactivity of 5. The *N*-^{i}Pr complex **5** proved to be more unstable in solution than complexes **2**−**4**, degrading over a period of only hours via both isomerization and disproportionation. At early times, **5** displayed signals similar to those seen for **2**: the hydride appeared (benzene-d_6) as a doublet of triplets

(28) While **2** and **3** (**4** was not investigated) isomerized in benzene as well as THF, the reactions were not as clean and were always accompanied by variable amounts (5−20% by ^{1}H NMR) of species showing a triplet hydride resonance at ca. δ −15. There were no corresponding Ru−F resonances in the ^{19}F NMR spectra, prompting us to suggest that these species are hydrolysis products resulting from reaction of Ru−F with traces of water on glassware or cannula or in the solvent.

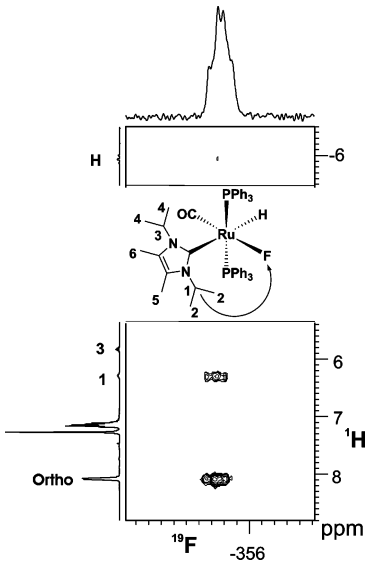


Figure 8. $^{1}H-^{19}F$ HOESY spectrum of complex **5** showing a selective NOE contact to one of the two isopropyl methine protons and the ortho protons of the triphenylphosphine (benzene-d_6, 400 MHz, 298 K).

(δ −5.94, J_{PH} = 25.6, J_{HF} = 4.8 Hz), the $^{31}P\{^{1}H\}$ spectrum showed equivalent P atoms at δ 40.5 (J_{PF} = 27.6 Hz), and the Ru−F resonance was observed at δ −355.6 as a poorly resolved multiplet. The two *N*-^{i}Pr (and *C*-Me) groups are nonequivalent, and again, the 2-D $^{19}F-^{1}H$ HOESY spectrum showed a selective contact to one of the two ^{i}Pr methine protons at δ 6.29 (Figure 8), thereby facilitating the assignment of all of the aliphatic protons.

^{1}H NMR spectroscopy (THF-d_8) as a function of time revealed facile depletion of the triplet hydride signal for **5** and the formation of three new groups of resonances (Figure 9) that can be assigned to **1**, complex **6**, which is the cis-phosphine isomer of **5**, and the bis-NHC complex **7** (Scheme 3). After several hours, the relative intensities of the four Ru species are ca. 1:1:3:4 for **5**, **6**, **1**, and **7**, respectively: i.e., **5** and **6** have become the minor components. Phase sensitive 2-D NOESY spectroscopy reveals that none of these complexes are in equilibrium on the NMR time scale (Figure 10). The cis-phosphine hydride fluoride **6** gives broad NMR resonances at 298 K, although cooling below 283 K (Figure 11) gives the expected coupling of the hydride signal to two inequivalent phosphine ligands (splitting by Ru−F is hard to resolve).

The major components, complexes **1** and **7**, arise from a disproportionation reaction. The bis-I^{i}Pr$_2$Me$_2$ complex, **7**, revealed a sharp doublet of doublets for its hydride resonance at δ −7.57, with the two bond interactions, 28.3 and 7.5 Hz, assigned to J_{HP} and J_{HF}, respectively. Complex **7** displayed a sharp doublet at 44.6 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum (J_{PF} = 41.4 Hz) and a broad ^{19}F signal at ca. δ −344. A $^{13}C\{^{1}H\}-^{1}H$ HMBC correlation from the hydride resonance (Figure 12) shows three high-frequency ^{13}C signals at ca. δ 184, 192 (carbenic carbons), and 204 (CO) consistent with the two NHC ligands in **7** being inequivalent.

Summary

The new hydride fluoride complex Ru(PPh$_3$)$_3$(CO)HF, which can be prepared by reaction of Ru(PPh$_3$)$_3$(CO)H$_2$ with Et$_3$N·3HF, reacts readily with the N-heterocyclic carbenes IMe$_4$, IEt$_2$Me$_2$, ICy, and I^{i}Pr$_2$Me$_2$ to afford the new fluoro NHC complexes Ru(NHC)(PPh$_3$)$_2$(CO)HF in yields of ca. 60%. The subsequent stability of these species proves to be highly dependent on the N substituents, with the isopropyl derivative undergoing rapid isomerization and disproportionation in solution in a matter of hours. Such a process may have implications in catalytic reactions involving, for example, large phosphine or phosphite ligands and NHCs.

With respect to the more general properties of late-metal fluoride complexes, we note that there is no evidence for the

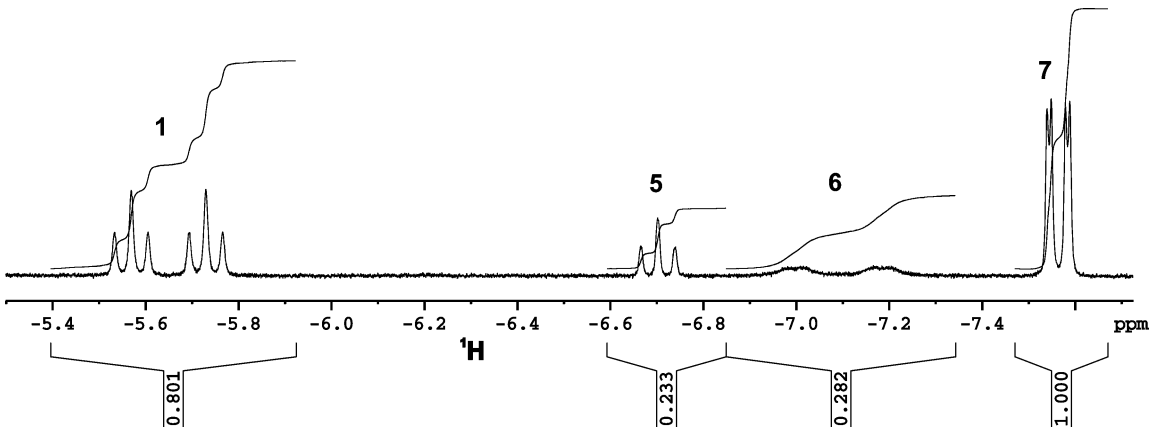
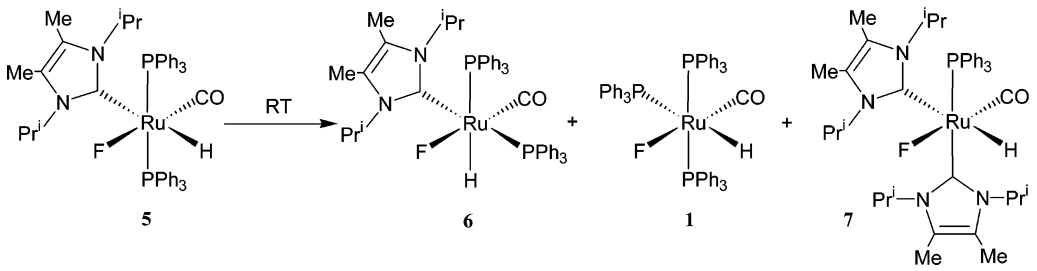


Figure 9. ^{1}H NMR spectrum of complex **5** after several hours showing the four Ru-species **5**, **6**, **1**, and **7** in the ratio ca. 1/1/3/4 (THF-d_8, 700 MHz, 298 K).

Scheme 3



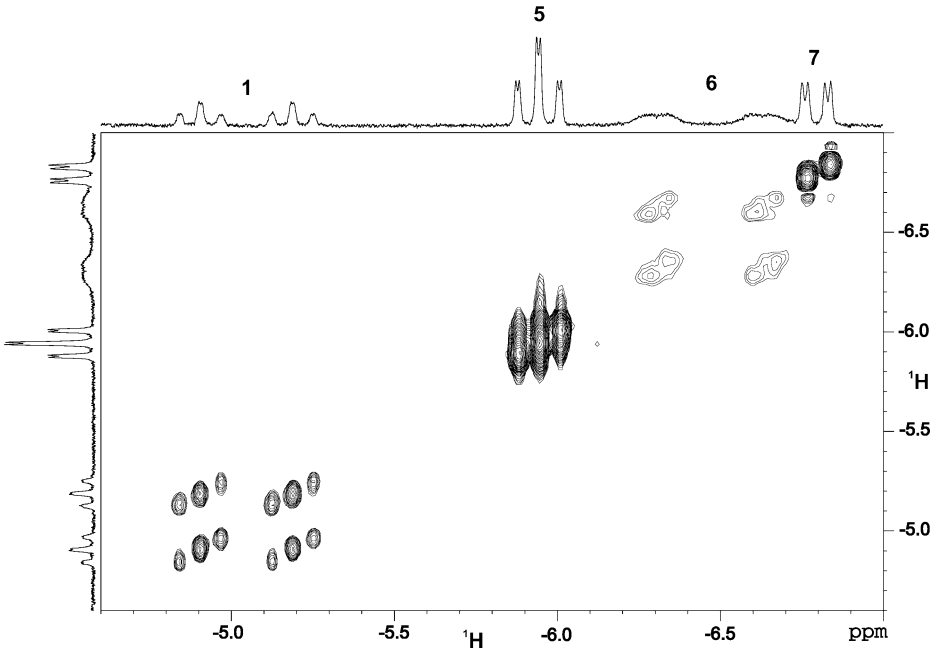


Figure 10. Section of the hydride region of the phase-sensitive NOESY spectrum after isomerization and disproportionation of **5**, which reveals the lack of exchange between **1**, **6**, and **7** (benzene-d_6, 400 NMR, 298 K).

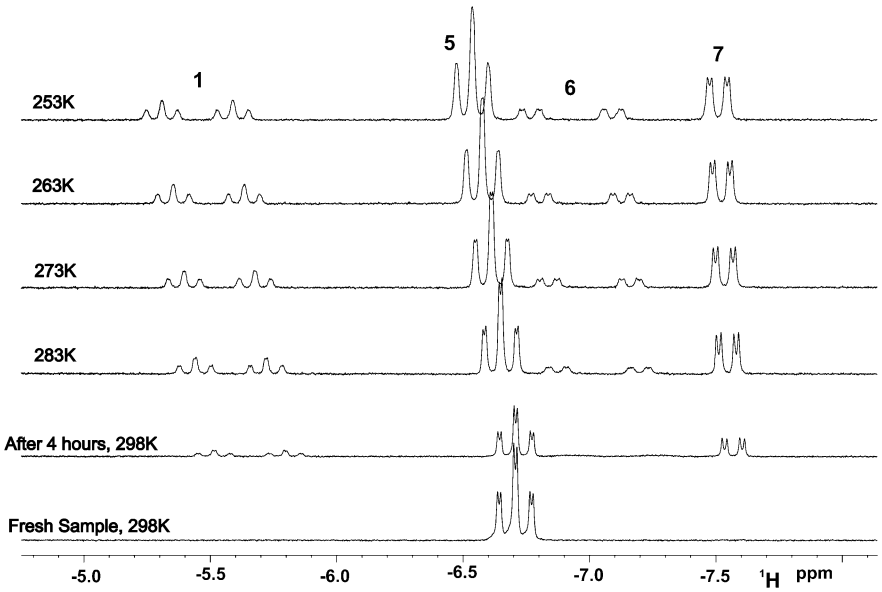


Figure 11. Variable-temperature NMR spectra of complex **6**, showing the eight line pattern below 283 K (THF-d_8, 400 MHz).

formation of "H−F" type complexes, such as described by Grushin,[6b,29] Perutz,[4a,6a,30] and others.[5,31] This is likely to be due to the "hard" ruthenium atom in the $[Ru(L)(PPh_3)_2(CO)]^{2+}$ fragment (L = NHC, PPh_3) which favors F^- over "H−F" or F−H−F$^-$.[10b] In $Ru(PPh_3)_3(CO)HF$ and $Ru(NHC)(PPh_3)_2(CO)$-HF, the fluoride ligand remains firmly bound to the ruthenium, despite the presence of a cis-hydride atom.

Experimental Section

General Comments. All manipulations were carried out under argon using standard Schlenk or glovebox techniques under an atmosphere of argon. Solvents were purified using an MBraun SPS solvent system (toluene, Et_2O) or Innovative Technologies solvent system (THF) or were purified under a nitrogen atmosphere from sodium benzophenone ketyl (benzene, hexane) or Mg/I_2 (ethanol). NMR solvents (Aldrich) were vacuum-transferred from potassium (benzene-d_6, THF-d_8). $Ru(PPh_3)_3(CO)H_2$,[32] IMe_4, IEt_2Me_2, ICy, and $I^iPr_2Me_2$[33,34] were prepared via literature methods. $Et_3N{\cdot}3HF$ (Aldrich) was used as received.

NMR spectra were recorded on Bruker Avance 400 and 500 MHz (Bath) and DPX 200, 400, 500, and 700 MHz NMR spectrometers

(29) (a) Pilon, M. C.; Grushin, V. V. *Organometallics* **1998**, *17*, 1774. (b) Roe, D. C.; Marshall, W. J.; Davidson, F.; Soper, P. D.; Grushin, V. V. *Organometallics* **2000**, *19*, 4575.

(30) (a) Jasim, N. A.; Perutz, R. N. *J. Am. Chem. Soc.* **2000**, *122*, 8685. (b) Jasim, N. A.; Perutz, R. N.; Foxon, S. P.; Walton, P. H. *Dalton Trans.* **2001**, 1676.

(31) (a) Coulson, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3111. (b) Murphy, V. J.; Hascall, T.; Chen, J. Y.; Parkin, G. *J. Am. Chem. Soc.* **1996**, *118*, 7428. (c) Murphy, V. J.; Rabinovich, D.; Hascall, T.; Klooster, W. T.; Koetzle, T. F.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 4372. (d) Gil-Rubio, J.; Weberndörfer, B.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1999**, 1437. (e) Vicente, J.; Gil-Rubio, J.; Bautista, D.; Sironi, A.; Masciocchi, N. *Inorg. Chem.* **2004**, *43*, 5665.

(32) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.

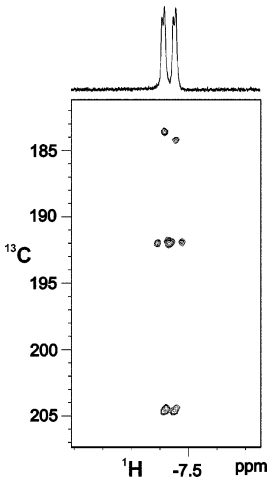


Figure 12. Section of the $^{1}H-^{13}C\{^{1}H\}$ HMBC spectrum of **7** at ambient temperature, showing correlations to each of the two nonequivalent carbene carbons and the carbonyl carbon (THF-d_8, 700 MHz).

(ETHZ), at 298 K unless otherwise stated, and referenced to benzene (^{1}H, δ 7.15; ^{13}C, δ 128.0) or THF (δ 3.58). $^{31}P\{^{1}H\}$ NMR chemical shifts were referenced externally to 85% H_3PO_4 (δ 0.0). 2D experiments (^{1}H COSY, $^{1}H-X$ (X = ^{13}C, ^{31}P) HMQC/HMBC, NOESY) were performed using standard Bruker pulse sequences. $^{19}F-^{1}H$ HOESY experiments were acquired using the standard four-pulse sequence and carried out using a doubly tuned TXI probe. IR spectra were recorded as Nujol mulls on a Nicolet Nexus FTIR spectrometer.

Ru(PPh$_3$)$_3$(CO)HF (1). A solution of Ru(PPh$_3$)$_3$(CO)H$_2$ (1.3 g, 1.4 mmol) and Et$_3$N·3HF (0.69 g, 4.3 mmol) in THF (40 mL) was heated at 85 °C for 5.5 h, cooled to room temperature, and concentrated under vacuum, and Et$_2$O (30 mL) was added to precipitate a pink/cream solid. This was washed with Et$_2$O (3 × 20 mL) and dried in vacuo overnight to yield Ru(PPh$_3$)$_3$(CO)HF as a white solid. Yield: 0.7 g (53%). Crystals suitable for X-ray crystallography were obtained upon layering a THF solution with hexane. Despite repeated attempts, we were unable to achieve acceptable microanalysis results for **1**, with the % C value always low. ^{1}H NMR (benzene-d_6, 400 MHz, 298 K): δ 7.5−7.2 (m, 17H, PC_6H_5), 6.9−6.6 (m, 28H, PC_6H_5), −5.05 (dt, J_{HP} = 112.5 Hz, J_{HP} = 25.2 Hz, 1H, Ru−H). $^{31}P\{^{1}H\}$ NMR: δ 39.5 (m), 18.7 (m). $^{13}C\{^{1}H\}$ NMR: δ 206.3 (dt, J_{CF} = 65.0 Hz, J_{CP} = 13.6 Hz, Ru−*C*O), 137.5 (d, J_{CP} = 26.0 Hz, PC_6H_5), 136.9 (virtual triplet ('vt'), J_{CP} = 20.9 Hz, PC_6H_5), 135.1 (m, PC_6H_5), 129.5 (s, PC_6H_5), 129.1 (s, PC_6H_5), 128.5 (s, PC_6H_5). ^{19}F NMR: δ −385.1 (q, J_{FP} = 23.5 Hz). IR (cm^{-1}): 1917 (ν_{CO}). ESI-TOF MS: [M − HF − PPh$_3$ + H]$^+$ *m*/*z* 655.0891 (theoretical *m*/*z* 655.0898).

Ru(IMe$_4$)(PPh$_3$)$_2$(CO)HF (2). Ru(PPh$_3$)$_3$(CO)HF (0.20 g, 0.21 mmol) and IMe$_4$ (0.038 g, 0.31 mmol) were dissolved in toluene (10 mL) and the solution stirred at room temperature for 1 h. The suspension was filtered by cannula, and the remaining white solid was washed with hexane (3 × 7 mL) and toluene (5 mL) to afford Ru(IMe$_4$)(PPh$_3$)$_2$(CO)HF as a white solid. Yield: 0.10 g (60%). Anal. Found (calcd) for $C_{44}H_{43}N_2OP_2FRu$: C, 66.26 (66.24); H, 5.80 (5.43); N, 3.16 (3.51). ^{1}H NMR (benzene-d_6, 400 MHz, 298 K): δ 8.05 (m, 12H, PC_6H_5), 7.05−6.99 (m, 18H, PC_6H_5), 3.04 (br s, 3H, NCH_3), 3.24 (br s, 3H, NCH_3), 1.37 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), −5.19 (dt, J_{HP} = 22.5 Hz, J_{HF} = 4.4 Hz, 1H, Ru−H). $^{31}P\{^{1}H\}$ NMR: δ 44.8. $^{13}C\{^{1}H\}$ NMR: δ 208.3 (dt, J_{CF} = 64.0 Hz, J_{CP} = 13.7 Hz, Ru−*C*O), 188.9 (Ru−*C*, br t), 136.9 ('vt', J_{CP} = 20.4 Hz, PC_6H_5), 127.0−135.0 (PC_6H_5), 125.8 (s, *C*CH$_3$=CCH$_3$), 125.1 (s, CCH$_3$=*C*CH$_3$), 35.8 (s, N*C*H$_3$), 30.3 (s, NC*H*$_3$), 9.4 (s, *C*H$_3$), 8.9 (s, *C*H$_3$). ^{19}F NMR: δ −353.3 (br s). IR (cm^{-1}): 1888 (ν_{CO}). ESI-TOF MS: [M − HF + H]$^+$ *m*/*z* 779.1894 (theoretical *m*/*z* 779.1900).

Ru(IEt$_2$Me$_2$)(PPh$_3$)$_2$(CO)HF (3). Ru(PPh$_3$)$_3$(CO)HF (0.166 g, 0.18 mmol) and IEt$_2$Me$_2$ (0.041 g, 0.27 mmol) were dissolved in toluene (8 mL) and stirred at ambient temperature for 1 h, by which time a white precipitate of Ru(IEt$_2$Me$_2$)(PPh$_3$)$_2$(CO)HF had formed. Yield: 0.090 g (61%). Anal. Found (calcd) for $C_{46}H_{47}N_2OP_2FRu$: C, 66.68 (66.89); H, 5.87 (5.74); N, 3.48 (3.39). ^{1}H NMR (benzene-d_6, 400 MHz, 298 K): δ 8.07−8.00 (m, 12H, PC_6H_5), 7.10−6.98 (m, 18H, PC_6H_5), 3.73 (q, J_{HH} = 7.1 Hz, 2H, NCH_2), 3.68 (br m, 2H, NCH_2), 1.58 (s, 3H, NCH_2CH_3), 1.43 (s, 3H, NCH_2CH_3), 0.94 (t, J_{HH} = 7.1 Hz, 3H, CH_3) 0.78 (t, J_{HH} = 7.1 Hz, 3H, CH_3), −6.07 (dt, J_{HP} = 22.5 Hz, J_{HF} = 4.4 Hz, 1H, Ru−H). $^{31}P\{^{1}H\}$ NMR: δ 42.8 (d, J_{PF} = 25.8 Hz). ^{19}F NMR: δ −363.0 (br s). IR (cm^{-1}): 1891 (ν_{CO}). ESI-TOF MS: [M − HF + H]$^+$ *m*/*z* 807.2201 (theoretical *m*/*z* 807.2214).

Ru(ICy)(PPh$_3$)$_2$(CO)HF (4). Ru(PPh$_3$)$_3$(CO)HF (0.20 g, 0.21 mmol) and ICy (0.060 g, 0.26 mmol) were dissolved in toluene (10 mL), and the reaction mixture was stirred at room temperature for 1 h. Reduction of the volume and addition of hexane afforded white crystals of Ru(ICy)(PPh$_3$)$_2$(CO)HF. Yield: 0.12 g (60%). Anal. Found (calcd) for $C_{52}H_{55}N_2OP_2FRu$: C, 68.41 (68.93); H, 6.24 (6.12); N, 2.96 (3.09). ^{1}H NMR (benzene-d_6, 400 MHz, 298 K): δ 7.94 (m, 12H, PC_6H_5), 7.16−7.02 (m, 18H, PC_6H_5), 6.65 (d, J_{HH} = 2.2 Hz, 1H, NC*H*), 6.57 (d, J_{HH} = 2.2 Hz, 1H, NC*H*), 5.10 (br m, 1H, C*H*-Cy), 4.83 (m, 1H, C*H*-Cy), 1.73 (m, 2H, CH_2-Cy) 1.44−0.80 (m, CH_2-Cy), −5.46 (dt, J_{HP} = 25.2 Hz, J_{HF} = 4.4 Hz, Ru−H, 1H). $^{31}P\{^{1}H\}$ NMR: δ 40.5 (d, J_{PF} = 27.5 Hz). ^{19}F NMR: δ −366.6 (t, J_{FP} = 27.5 Hz). IR (cm^{-1}): 1912 (ν_{CO}). ESI-TOF MS: [M − HF + H]$^+$ *m*/*z* 887.2862 (theoretical *m*/*z* 887.2842).

Ru(I^{i}Pr$_2$Me$_2$)(PPh$_3$)$_2$(CO)HF (5). Ru(PPh$_3$)$_3$(CO)HF (0.2 g, 0.21 mmol) and I^{i}Pr$_2$Me$_2$ (0.057 g, 0.32 mmol) were dissolved in toluene (7 mL), and the mixture was stirred at ambient temperature for 1 h. The solution was filtered by cannula and the resulting white solid washed with hexane (3 × 7 mL) and toluene (5 mL), yielding Ru(I^{i}Pr$_2$Me$_2$)(PPh$_3$)$_2$(CO)HF as a white solid. Yield: 0.11 g (60%). The facile disproportionation/isomerization reaction of **5** prevented microanalysis from being determined. ^{1}H NMR (benzene-d_6, 400 MHz, 298 K): δ 8.05−7.93 (m, 12H, PC_6H_5), 7.10−6.89 (m, 18H, PC_6H_5), 6.29 (br sept, J_{HH} = 7.1, 1H, NC*H*), 5.71 (sept, J_{HH} = 7.1, 1H, NC*H*), 1.84 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 1.02 (d, J_{HH} = 7.1, 6H, NCH(CH_3)$_2$), 0.75 (d, J_{HH} = 7.1, 6H, NCH(CH_3)$_2$), −5.94 (dt, J_{HP} = 25.6 Hz, J_{HF} = 4.8 Hz, Ru−H, 1H). $^{31}P\{^{1}H\}$ NMR: δ 40.5 (d, J_{PF} = 27.6 Hz). ^{19}F NMR: δ −355.6 (br m). IR (cm^{-1}): 1900 (ν_{CO}). ESI-TOF MS: [M − HF + H]$^+$ *m*/*z* 835.2537 (theoretical *m*/*z* 835.2528).

Mass Spectrometry. A micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik GmbH) was used; this was coupled to an Agilent 1200 LC system (Agilent Technologies). Rather than any chromatographic separation taking place, the LC system was used as an autosampler and sample introduction mechanism only. A 10 μL sample was injected into a 30/70 flow of water/acetonitrile at 0.3 mL/min in the mass spectrometer. The nebulizing gas used was N_2, applied at a pressure of 1 bar. The drying gas was also N_2, supplied at a flow rate of 8 L/min and a temperature of 200 °C. Positive ion mode was used with a corresponding capillary voltage of −4000 V. Only full scan data were acquired. Samples were prepared under inert-atmosphere conditions in an MBraun glovebox by dissolving 1 mg of compound in 1 mL of CH_3CN, and then diluting 1 μL of the mixture to 1 mL. For each acquisition 10 uL of 5 mM sodium formate was injected after the sample as a calibrant over the mass range *m*/*z* 50−1500, using the high precision calibration (HPC) algorithm. Data acquisition and automated processing were controlled via Compass OpenAccess 1.2 software (Bruker Daltonik GmbH). The data for

(33) Kühn, N.; Kratz, T. *Synthesis* **1993**, 561.
(34) Nolan, S. P. Personal communication.

Table 1. Crystal Data and Structure Refinement Details for Compounds 1−4

	1	2	3	4
empirical formula	$C_{59}H_{54}FO_2P_3Ru$	$C_{47}H_{46}FN_2OP_2Ru$	$C_{46}H_{47}FN_2OP_2Ru$	$C_{52}H_{55}FN_2OP_2Ru$
formula wt	1008.00	836.87	825.87	905.99
T/K	150(2)	150(2)	150(2)	150(2)
wavelength	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	*Pn*	*C2/c*	*C2/c*	$P2_1/n$
a/Å	12.9570(2)	14.6000(1)	23.5920(5)	9.1570(1)
b/Å	12.4210(2)	22.8140(2)	9.9650(2)	23.8970(4)
c/Å	15.1290(2)	24.3010(2)	18.0880(5)	20.5620(3)
α/deg	90	90	90	90
β/deg	96.749(1)	96.007(1)	112.962(1)	92.436(1)
γ/deg	90	90	90	90
U/Å^3	2417.97(6)	8049.84(11)	3915.44(16)	4495.41(11)
Z	2	8	4	4
D_c/g cm^{-3}	1.384	1.381	1.401	1.339
μ/mm^{-1}	0.471	0.512	0.525	0.464
F(000)	1044	3464	1712	1888
cryst size/mm	0.30 × 0.25 × 0.20	0.38 × 0.30 × 0.05	0.20 × 0.10 × 0.10	0.15 × 0.10 × 0.05
min, max θ for data collecn/deg	3.95, 27.49	3.53, 34.95	3.57, 27.47	3.79, 25.03
index ranges	$-16 \le h \le 16$; $-16 \le k \le 16$; $-19 \le l \le 19$	$-23 \le h \le 23$; $-36 \le k \le 36$; $-39 \le l \le 39$	$-30 \le h \le 30$; $-12 \le k \le 12$; $-23 \le l \le 23$	$-10 \le h \le 10$; $-25 \le k \le 28$; $-24 \le l \le 24$
no. of rflns collected	50 166	94 781	23 475	35 757
no. of indep rflns, R_{int}	10 639, 0.0341	17 581, 0.0513	4448, 0.0499	7755, 0.0753
no. of obsd rflns (>2σ)	9833	13824	3874	6130
abs cor	multiscan	multiscan	multiscan	multiscan
max, min transmission	0.91, 0.88	0.97, 0.94	0.90, 0.86	0.96, 0.91
no. of data/restraints/params	10 639/3/600	17 581/13/490	4448/3/260	7755/9/549
goodness of fit on F^2	1.035	1.062	1.253	1.022
final *R*1, w*R*2 ($I > 2\sigma(I)$)	0.0254, 0.0581	0.0391, 0.0783	0.0428, 0.0917	0.0404, 0.0792
final *R*1, w*R*2 (all data)	0.0303, 0.0604	0.0604, 0.0855	0.0544, 0.0949	0.0600, 0.0869
largest diff peak, hole/e Å^{-3}	0.678, −0.505	1.014, −0.700	0.364, −0.594	0.621, −0.990
abs structure param	−0.054(14)			

compounds **2**−**5** show a consistent loss of HF from the expected formula, with compound **1** also undergoing loss of PPh_3. The observed mass and isotope pattern perfectly matched the corresponding theoretical values, as calculated from the expected elemental formula with a loss of HF. These calculations were carried out using the data processing software DataAnalysis 3.4 (Bruker Daltonik GmbH).

X-ray Crystallography. Single crystals of **1**−**4** were analyzed at 150(2) K using graphite-monochromated Mo Kα radiation and a Nonius Kappa CCD diffractometer. Data collection and refinement details are summarized in Table 1. The structures were solved using SHELXS-97[35] and refined using SHELXL-97.[35] In **1,** the asymmetric unit was seen to contain one solvent THF molecule in addition to one complex molecule. In addition to one molecule of the carbene complex, the asymmetric unit in **2** was also seen to contain half of a benzene molecule (disordered over two sites). These disordered moieties are located proximate to a crystallographic 2-fold rotation axis which serves to generate the remaining solvent fragments. The asymmetric unit in **3** consists of half of one molecule, the remaining portion being generated via a 2-fold crystallographic rotation axis on which C2, H1, and Ru1 are located. The carbonyl and fluoride ligands also exhibited 1/1 disorder in this structure, which was modeled in the refinement. Similarly, 78/22 disorder between the fluoride and carbonyl ligands was successfully modeled in **4**, subject to the Ru−F, Ru−C_{CO}, and C≡O distances being restrained to be similar in both partial fragments. The hydrides in all four structures were located and refined at a distance of 1.6 Å from the central ruthenium atoms.

Crystallographic data for **1**−**4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 632303 (**1**), 644339 (**2**), 644338 (**3**), and 634671 (**4**). Copies of these data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (+44) 1223 336033, e-mail deposit@ccdc.cam.ac.uk).

Acknowledgment. We thank Drs. Anneke Lubben and John Lowe for mass spectrometry and NMR support, respectively. We acknowledge Johnson Matthey plc for the loan of hydrated $RuCl_3$. Financial support was provided via a Doctoral Training Award (to S.P.R. at the University of Bath), the Swiss National Science Foundation, and the ETHZ.

Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070164P

(35) Sheldrick, G. M. *Acta Crystallogr.* **1990**, 467−473, A46. Sheldrick, G. M. SHELXL-97, a Computer Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.