SUPPORTING INFORMATION

Stoichiometric and Catalytic C-F Bond Activation by the *Trans*-Dihydride NHC Complex $[Ru(IEt_2Me_2)_2(PPh_3)_2H_2]$ (IEt_2Me_2 = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene)

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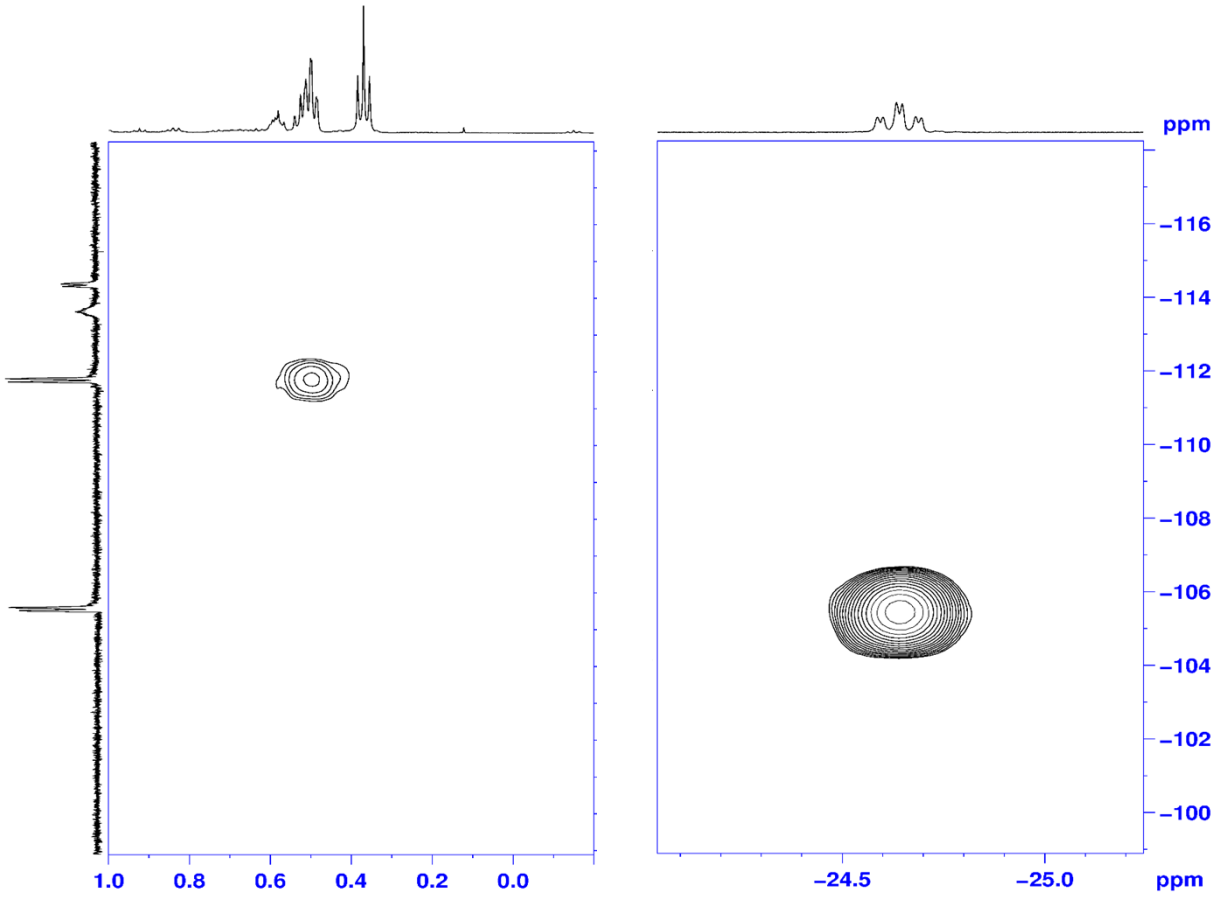

Fig. S-1 Expanded regions from the ^{1}H-^{19}F HMBC spectrum of **4** showing contacts between methyl protons at δ 0.48 and fluorine at δ -112, and between hydride at δ -24.7 and fluorine at δ -105 ppm.

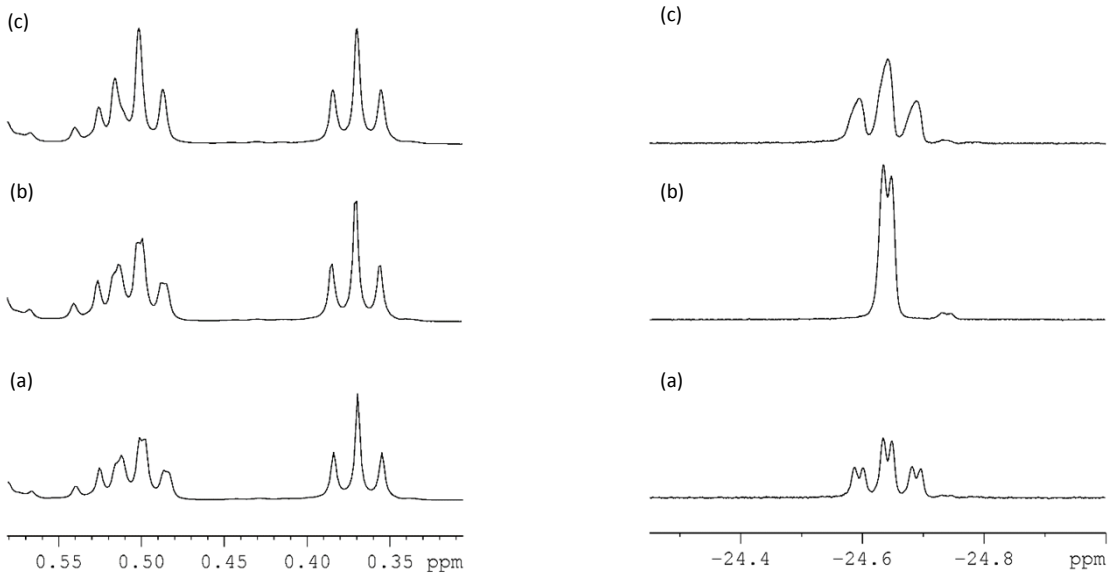

Fig. S-2 Expanded regions of the ^{1}H NMR spectrum of **4** under a variety of multinuclear decoupling conditions. (a) ^{1}H only, (b) $^{1}H\{^{31}P\}$, (c) $^{1}H\{^{19}F\}$.

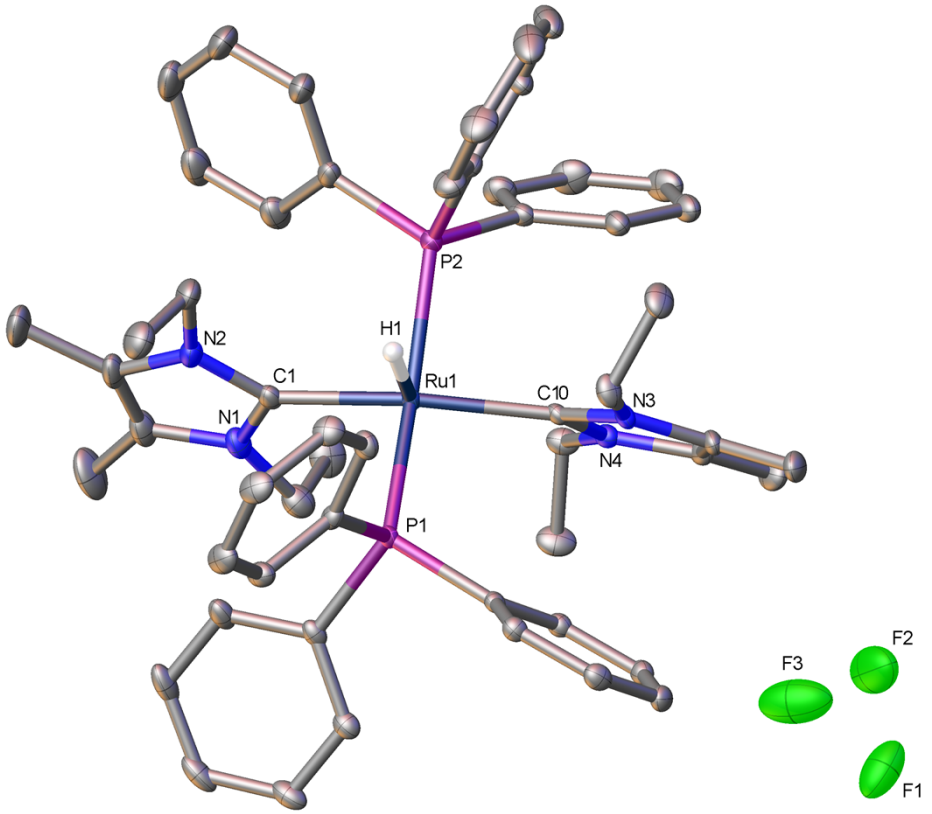

Fig. S-3 Molecular structure of **5**. Hydrogen atoms (with the exception of the hydride ligand) have been omitted for clarity. Ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (º): Ru(1)-C(1) 2.072(3), Ru(1)-C(10) 2.094(2), Ru(1)-P(1) 2.3473(6), Ru(1)-P(2) 2.3219(6), P(1)-Ru(1)-P(2) 161.13(2), C(1)-Ru(1)-P(1) 90.84(7), C(1)-Ru(1)-C(10) 165.39(10).

Table S-1 Crystal data and structure refinement details for compound **5**.

Identification code	**5**
Empirical formula	$C_{62}H_{81}F_3N_4O_2P_2Ru$
Formula weight	1134.36
Temperature/K	150.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.4810(4)
b/Å	15.6824(3)
c/Å	20.8972(4)
α/°	90
β/°	90.399(2)
γ/°	90
Volume/Å^3	5728.7(2)
Z	4
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	0.386
F(000)	2392.0
Crystal size/mm^3	0.5064 × 0.2745 × 0.0819
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.59 to 54.97
Index ranges	$-22 \leq h \leq 22$, $-20 \leq k \leq 17$, $-27 \leq l \leq 25$
Reflections collected	56957
Independent reflections	13111 [R_{int} = 0.0423, R_{sigma} = 0.0412]
Data/restraints/parameters	13111/69/724
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0420, wR_2 = 0.0949
Final R indexes [all data]	R_1 = 0.0614, wR_2 = 0.1046
Largest diff. peak/hole / e Å^{-3}	0.72/-0.63

Notes:

H1 located and refined at a distance of 1.6 Angstroms from Ru1. There are two THF present as guests in the asymmetric unit; that based on O2 was disordered and modelled as being distributed over 2 sites in a 55:45 ratio. C-O and C-C distances in this disordered moiety were treated as being similar to aid convergence. ADP restraints were also included for the same reason.
The 2 hydrogen atoms associated with the 3 fluorines could not be reliably located for refinement and, hence, these were omitted from the refinement.