Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

Ruthenium Carbene, Alkenyl and Alkynyl Complexes Containing Pendant Uracil Groups: an Investigation into the Formation of Alkenyl-phosphonio Complexes.

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1. Simulation of the variable temperature $^{31}P\{^{1}H\}$ NMR spectra of 6c[OTf].

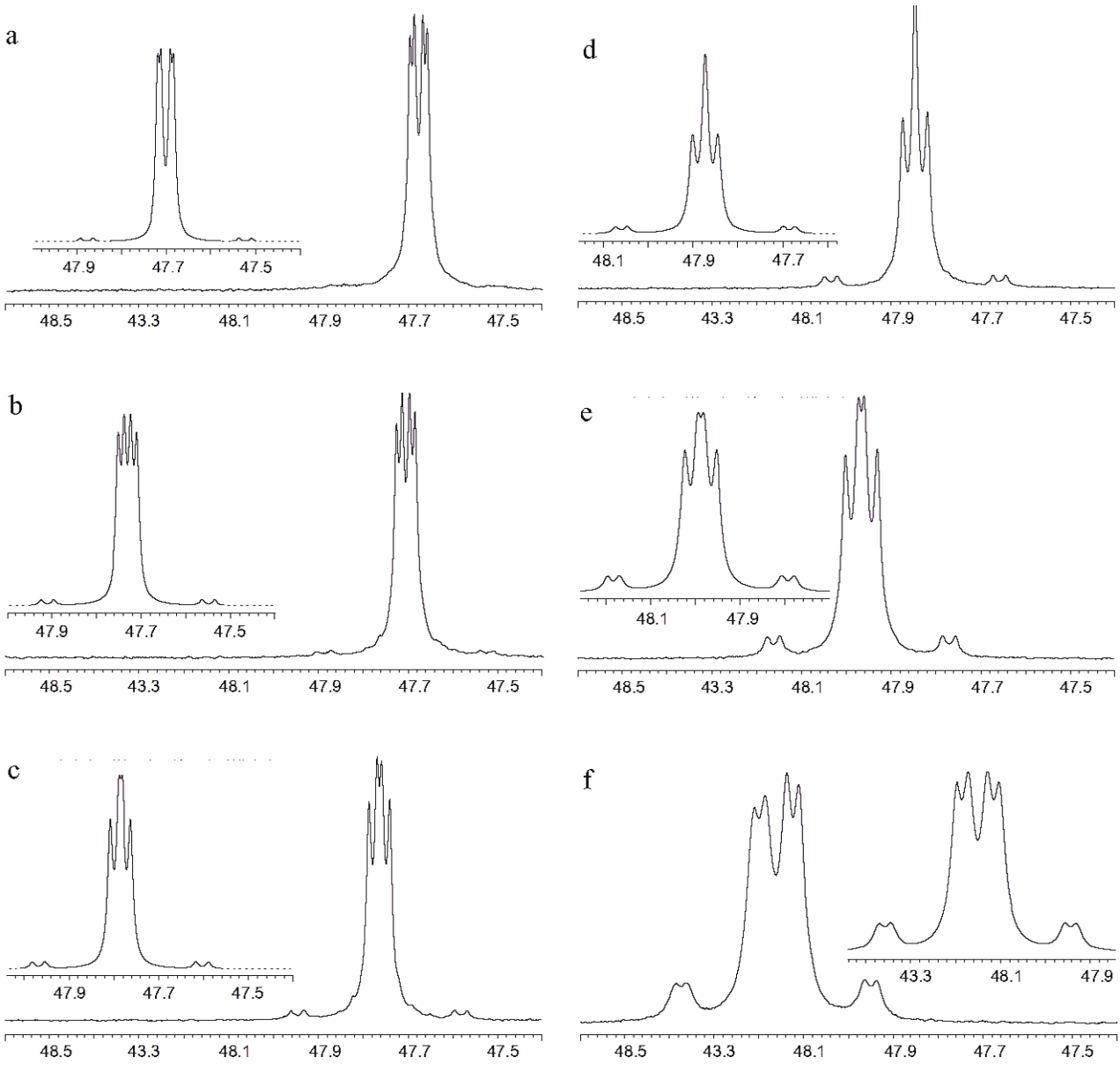

Figure S-1: Actual and Simulated (inserts) Variable Temperature $^{31}P\{^{1}H\}$ NMR spectra of **6c**[OTf] showing the ruthenium-bound PPh_3 groups only. Temperatures: a) 300 K, b) 275 K c) 255 K d) 235 K, e) 215 K f) 195 K

Temperature	P_A	P_B
300 K	δ 47.72	δ 47.67
275 K	δ 47.76	δ 47.69
255 K	δ 47.82	δ 47.74
235 K	δ 47.92	δ 47.82
215 K	δ 48.05	δ 47.93
195 K	δ 48.23	δ 48.05

Table S-1: Simulated chemical shifts for the NMR spectra shown in Figure 1. P_A and P_B are arbitrary labels. The coupling constants $^{2}J_{PP}$ and $^{4}J_{PP}$ were kept constant throughout at 35.0 Hz and 5.4 Hz respectively.

2. Variable Temperature ^{1}H NMR spectrum of 6a[OTf]

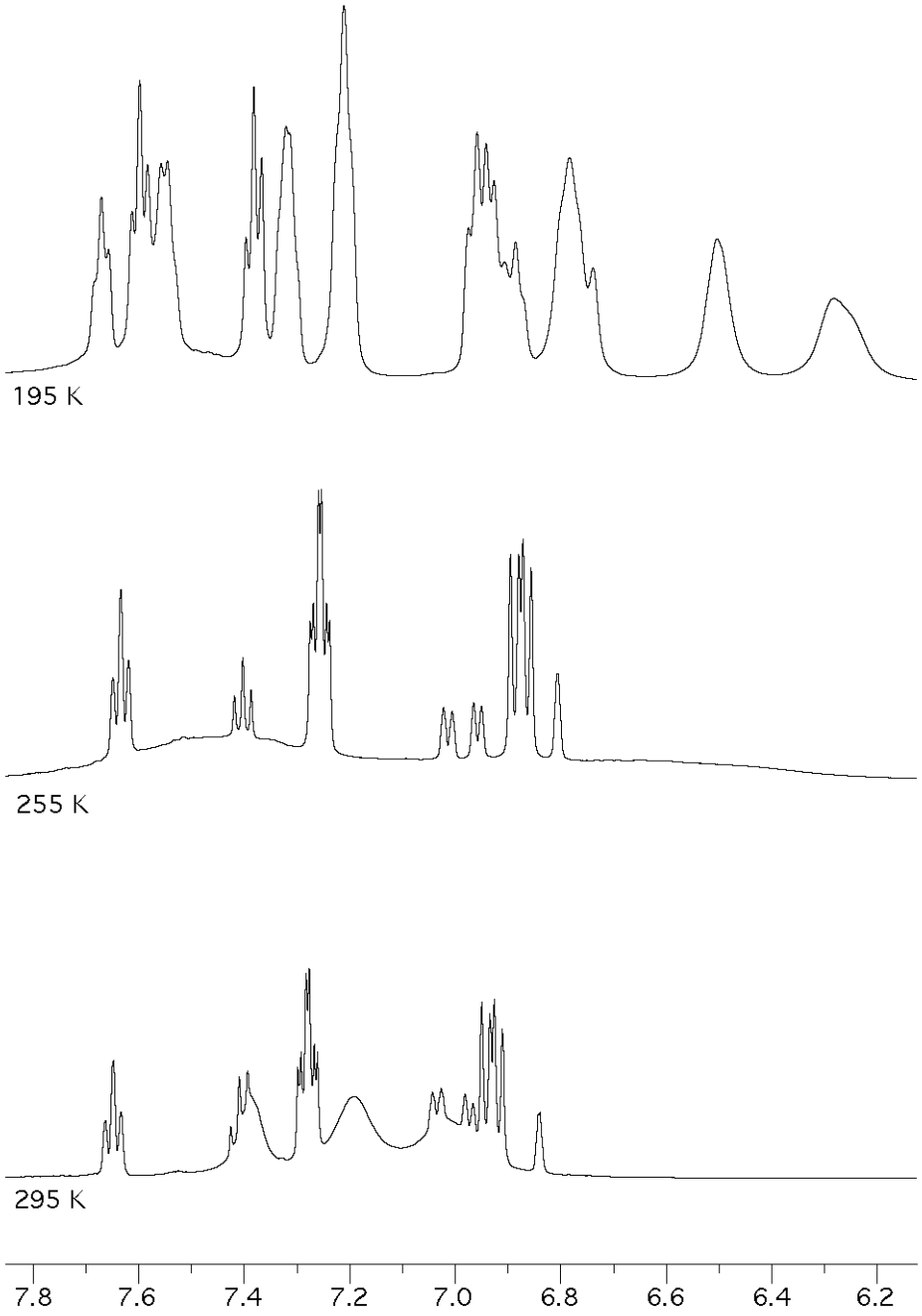

Figure S-2 Variable Temperature ^{1}H NMR spectrum of **6a**[OTf]: phenyl region only.

3. Selective $^{1}H\{^{31}P\}$ experimeints on [6a]OTf

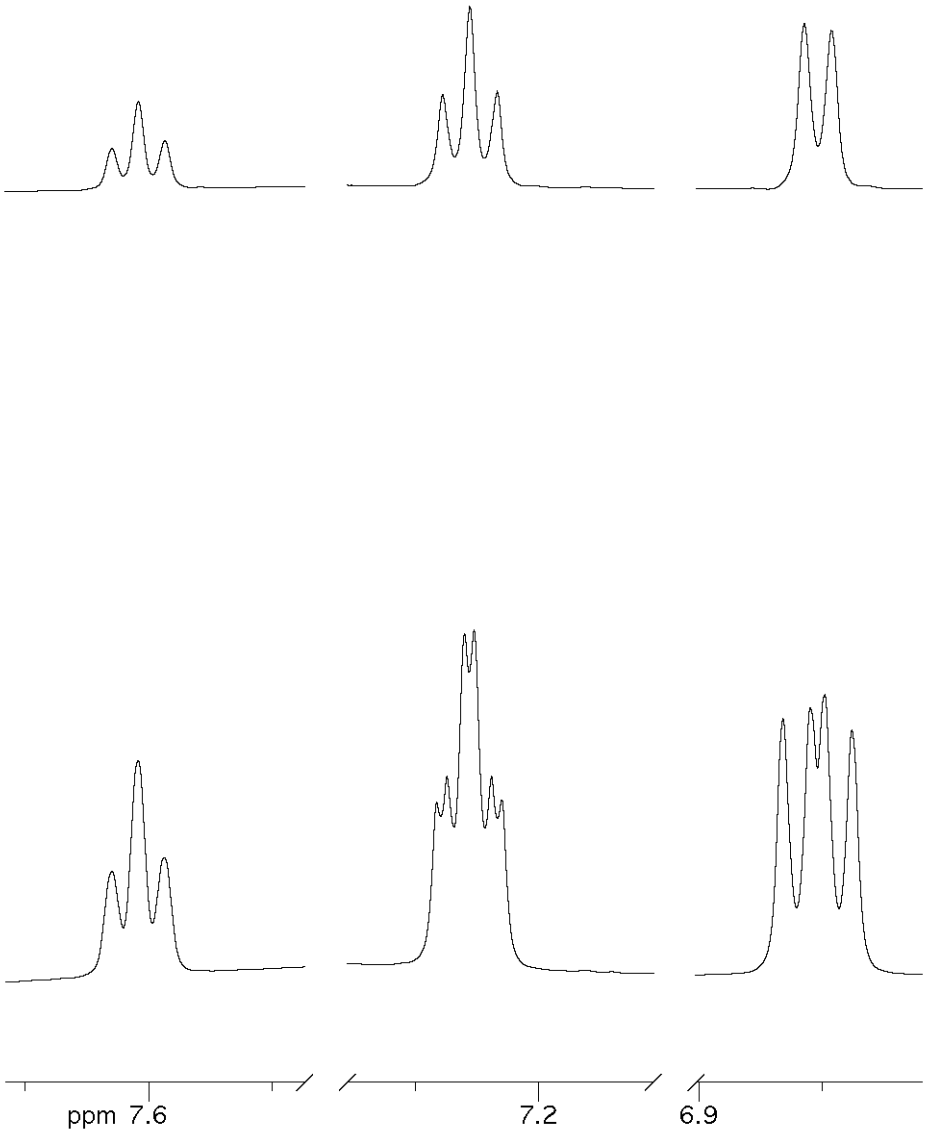

Figure S-3: Aromatic region of 700 MHz ^{1}H NMR (bottom) and $^{1}H\{^{31}P\}$ (top) spectra of **8c**[OTf] at 260 K. The $^{31}P\{^{1}H\}$ NMR spectrum is selectively decoupled at 17 ppm, indicating that the resonances observed are due to the phenyl groups on the phosphine bonded to the vinyl ligand in **6c**[OTf]. As shown these resonances are essentially temperature invariant, demonstrating that the ruthenium-coordinated PPh_3 groups are undergoing restricted rotation.

4. Single crystal X-ray structure of 3c[OTf]0.75CH_2Cl_2:0.25Et_2O

Slow diffusion of diethyl ether into a CH_2Cl_2 solution of **3c**[OTf] resulted in the formation of single crystals of the complex suitable for study by X-ray diffraction. The compound crystallised in the monoclinic space group $P2_1/n$ as the mixed CH_2Cl_2:diethyl ether solvate in a 75:25 ratio.

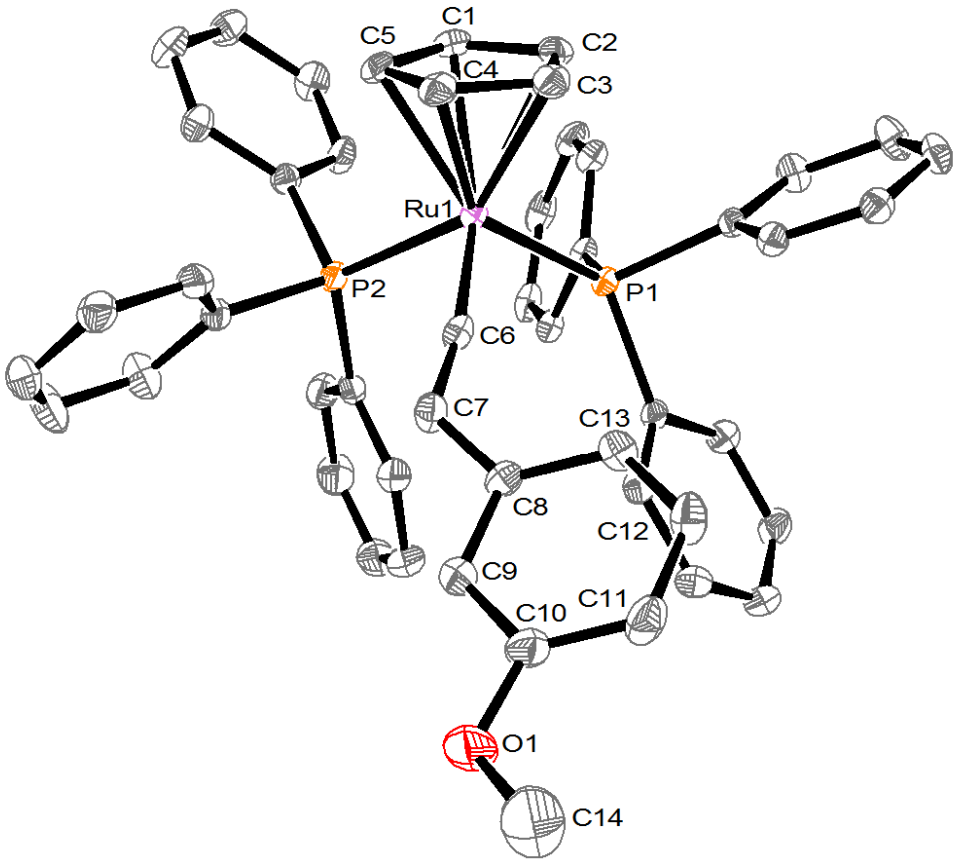

Figure S-4 ORTEP representation of the cation of complex **3c**[OTf], thermal ellipsoids set at the 50 % probability level and all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (º). C(1)-Ru(1) 2.2824(19), C(2)-Ru(1) 2.3045(19), C(3)-Ru(1) 2.2738(19), C(4)-Ru(1) 2.2516(19), C(5)-Ru(1) 2.2303(18), C(6)-Ru(1) 1.8405(19), C(6)-C(7) 1.322(3), C(7)-C(8) 1.467(3), P(1)-Ru(1) 2.3493(5), P(2)-Ru(1) 2.3372(5), C(6)-Ru(1)-P(1) 98.43(6), C(6)-Ru(1)-P(2) 89.10(6), P(2)-Ru(1)-P(1) 97.522(18).

Empirical formula	C52.75 H47 Cl1.50 F3 O4.25 P2 Ru S
Formula weight	1054.15
Temperature	110(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 12.3192(10) Å
	b = 12.4402(10) Å
	c = 31.194(3) Å
	α= 90°.
	β= 94.150(2)°.
	γ = 90°.
Volume	4768.1(7) $Å^3$
Z	4
Density (calculated)	1.468 Mg/m^3
Absorption coefficient	0.582 mm^{-1}
F(000)	2160
Crystal size	0.21 x 0.12 x 0.09 mm^3
Theta range for data collection	1.31 to 28.32°.
Index ranges	-16<=h<=16, -16<=k<=16, -41<=l<=41
Reflections collected	48327
Independent reflections	11871 [R(int) = 0.0386]
Completeness to theta = 28.32°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.950 and 0.843
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11871 / 4 / 635
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0334, wR2 = 0.0767
R indices (all data)	R1 = 0.0447, wR2 = 0.0810
Largest diff. peak and hole	0.660 and -0.523 $e.Å^{-3}$

Table S-2 Crystallographic Data for **3c**[OTf]0.75CH_2Cl_2:0.25Et_2O.