Electronic Supplementary Material (ESI) for Dalton Transactions

$[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_8)][PF_6]$ as a catalyst precursor for the one-pot direct C-H alkenylation of nitrogen heterocycles.

Jason M. Lynam,* Lucy M. Milner, Neetisha S. Mistry, John M. Slattery,* Sally Warrington[a] and Adrian C. Whitwood.

Department of Chemistry, University of York, Heslington, York, YO10 5DD Fax: +44(0)1904322516; Tel: +44(0)1904322534; E-mail: jason.lynam@york.ac.uk, john.slattery@york.ac.uk

Supporting Information

Single Crystal X-ray Diffraction Study on $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_8)][PF_6]$

Crystals of $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_8)][PF_6]$ were obtained from a sample of $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_8)][PF_6]$ dissolved in a mixture of furan and CD_2Cl_2. The asymmetric unit contained two independent $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_8)]^+$ cations and two PF_6^- anions. The related Δ-TRISPHAT salt of the complex has been prepared by Hintermann.[1] The cationic units within the two salts shown essentially identical features, with the Ru-C bonds to the cyclopentadienyl ligands (Ru-C < 2.2 Å) being short than those to the naphthalene. In addition, the naphthalene ligand is asymmetrically coordinated with the Ru-C bonds to the quaternary carbons (typically 2.26-2.27 Å) being longer than those to the hydrogen-substituted carbon atoms (2.19-2.23 Å). In the structure of $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_8)][PF_6]$ there is evidence for π-stacking between the naphthalene of the two cationic units in the asymmetric unit. The neighbouring ligands are essentially co-planar (angle between the planes defined by the two napthatlene ligands 7.64 °) and the shortest intermolecular distances are 3.319(3) [C(2)-C(22)] and 3.331(3) Å [C(6)-C(16)].

Empirical formula	$C_{15}H_{13}F_6PRu$
Formula weight	439.29
Temperature/K	110.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.2345(3)
b/Å	21.0319(10)
c/Å	15.3415(8)
α/°	90.00
β/°	93.266(4)
γ/°	90.00
Volume/Å^3	2974.8(2)
Z	8
ρ_{calc}mg/mm^3	1.962
m/mm^{-1}	1.221
F(000)	1728.0
Crystal size/mm^3	0.3234 × 0.1041 × 0.0726
2Θ range for data collection	5.66 to 64.56°
Index ranges	-13 ≤ h ≤ 13 -30 ≤ k ≤ 30 -21 ≤ l ≤ 22
Reflections collected	28152
Independent reflections	9616[R(int) = 0.0257]
Data/restraints/parameters	9616/0/415
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0285 wR_2 = 0.0626
Final R indexes [all data]	R_1 = 0.0398 wR_2 = 0.0686
Largest diff. peak/hole / e Å^{-3}	0.80/-0.60

Table S1 Crystal data and structure refinement for jml1163

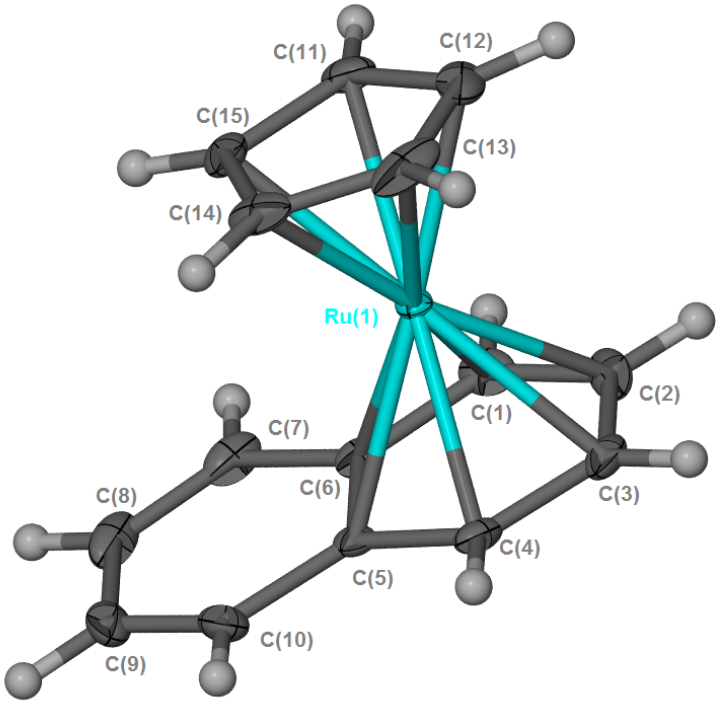

Figure S1 One of the crystallographically-independent [Ru(η^5-C_5H_5)(η^6-$C_{10}H_8$)] cations in the structure of [Ru(η^5-C_5H_5)(η^6-$C_{10}H_8$)][PF_6]. Thermal ellipsoids are shown at the 50 % probability level.

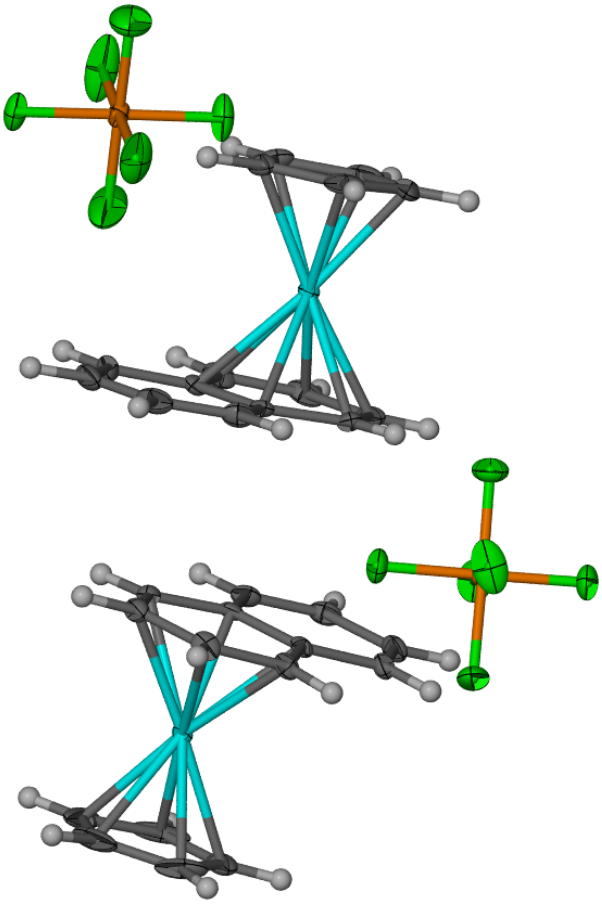

Figure S2 Asymmetric unit of the structure of [Ru(η^5-C_5H_5)(η^6-$C_{10}H_8$)][PF_6]. Thermal ellipsoids are shown at the 50 % probability level.

Ru(1)-C(1)	2.1947(19)	Ru(2)-C(16)	2.2150(18)
Ru(1)-C(2)	2.2138(19)	Ru(2)-C(17)	2.2279(19)
Ru(1)-C(3)	2.2262(19)	Ru(2)-C(18)	2.2182(19)
Ru(1)-C(4)	2.2191(18)	Ru(2)-C(19)	2.2051(18)
Ru(1)-C(5)	2.2714(18)	Ru(2)-C(20)	2.2623(17)
Ru(1)-C(6)	2.2617(18)	Ru(2)-C(21)	2.2653(17)
Ru(1)-C(11)	2.175(2)	Ru(2)-C(26)	2.178(2)
Ru(1)-C(12)	2.162(2)	Ru(2)-C(27)	2.156(2)
Ru(1)-C(13)	2.180(2)	Ru(2)-C(28)	2.163(2)
Ru(1)-C(14)	2.1811(19)	Ru(2)-C(29)	2.170(2)
Ru(1)-C(15)	2.1793(19)	Ru(2)-C(30)	2.172(2)

Table S2 Selected bond lengths (Å) with the crystallographically-independent $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_8)]^+$ cations.

Reference

1. L. Hintermann, L. Xiao, A. l. Labonne and U. Englert, *Organometallics*, 2009, **28**, 5739-5748.