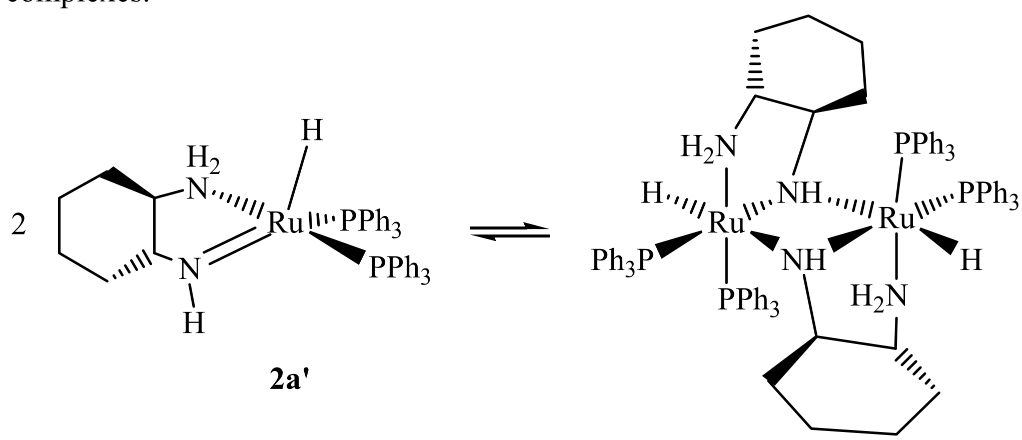
Supporting material for

A Cascade of Dihydride Isomers of Ruthenium. Which One is the Ketone Hydrogenation Catalyst?

*Robert Abbel, Kamaluddin Abdur-Rashid, Michael Faatz, Alen Hadzovic, Alan J. Lough, and Robert H. Morris**

Department of Chemistry, University of Toronto, Toronto, Canada

Possible monomer-dimer equilibrium for the amido-amine complex 2a'. The spectra of complex **2a'** change in a complex way with temperature and this requires further investigation. We tentatively propose that a dynamic monomer-dimer equilibrium is frozen out at –75ºC (eq 1S). Along with the resonance for **2a'** at –20.7 ppm, several triplets or doublet of doublets at –13.4, -13.8, -17.5, -17.8 ppm are observed in the ^{1}H NMR spectrum. Similarly there are overlapping doublet ^{31}P resonances at 62.4, 62.7, 70.3, 73.5, 74.3 along with the resonance due to **2a'** at 72 ppm. These are assigned to dimers such as the one in eq 3, although several other diastereomers are possible. This bridging mode of bidentate amido ligands has been observed for zinc and rhodium complexes.[1]



(1S)

The isomerization of cis,cis-**3a to** cis,trans-**3a.**

Using various concentrations of an isolated and purified mixture of 85 % Δ/Λ-c,c-**3a** and 15% c,t-**3a**, it was possible to study the isomerization of the c,c to c,t by time-resolved NMR spectroscopy (Figure 1S). Simulations provided rate constants for the conversion of c,c-**3a** to c,t-**3a** of 0.017 min^{-1} for a ruthenium concentration of 0.017 M, and 0.042 M during the approach to an equilibrium mixture of about 92 % c,t-**3a** and 8 % Δ/Λ-c,c-**3a** at 20º C.

[1] (a) Bell, N. A.; Moseley, P. T.; Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *36*, 2950. (b) Kramer, R.; Polborn, K.; Robl, C.; Beck, W. *Inorg. Chim. Acta* **1992**, *198*, 415.

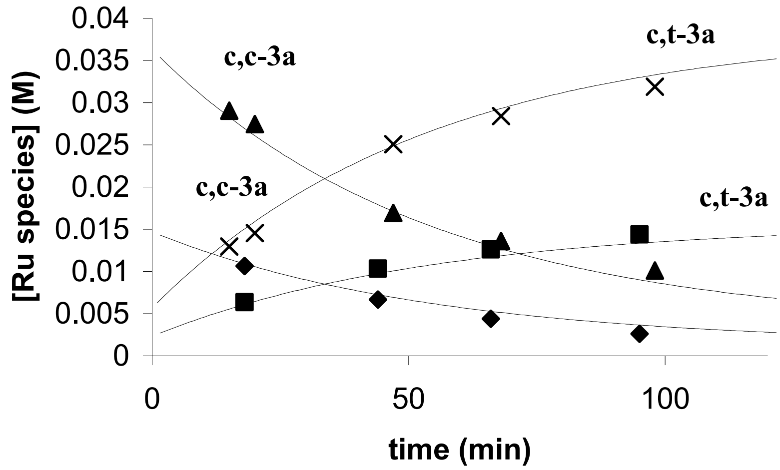


Figure 1S. Change in the concentrations of cis-dihydride isomers as a function of time at 20ºC starting with 0.043 M **3a** (85% c,c-**3a** (▲), 15% c,t-**3a(×))** or with 0.017 M **3a** (85% c,c-3a (♦), 15% c,t-**3a (■)**) in C_6D_6. The lines are calculated on the basis of the rate constants $k_{c,c\text{-}c,t}$= 0.017 min^{-1} and $k_{c,t\text{-}c,c}$ = 0.0015 min^{-1}, K_{eq}(c,t-3a/c,c-3a)= 11.5.

Further evidence for the structure of the diazabutadiene complex 6 in solution.

The proposed structure of **6** is also supported by isotopic labeling and 2-D NMR. $RuHCl(PPh_3)_2(H_2{}^{15}NCH_2CH_2{}^{15}NH_2)$ was produced using 99.5 % ^{15}N-enriched ethylenediamine and this compound was then treated with excess KO^{t}Bu in deuterated benzene under Ar. A two dimensional ^{1}H-^{1}H COSY spectrum reveals that the hydrides in **6** are weakly coupled to each other. The one dimensional ^{1}H NMR spectrum of this mixture shows broadening of both of these signals, indicating a small coupling to the coordinated ^{15}N. The imine hydrogen (CH=N) with the doublet at 5.10 ppm is coupled to the hydrogen on nitrogen (C=NH) with resonances hidden in the aliphatic region at about 1.50 ppm. The cross peaks indicate that the ^{15}NH hydrogen has a doublet of doublets pattern with $^3J_{HH}$ and $^1J_{NH}$ couplings of 6 and 76 Hz, respectively. The latter compares with the one bond ^{1}H-^{15}N couplings found in histidine (90 Hz).[2]

Products of stoichiometric reactions of complexes 3 with acetophenone or benzophenone.

Neither the NMR signals for the free alcohol (1-phenylethanol or diphenylmethanol) nor the amido complexes **2a'** or **2b'**, respectively, are observed when these ketones are reacted with c,c-**3a** and c,c-**3b**, respectively, even though these are the products expected on the basis of Scheme 1 of the article. Instead several hydride-containing complexes are produced. These may be isomeric alkoxide complexes $RuH(OCHPh_2)(diamine)(PPh_3)_2$ or decomposition products resulting from the dehydrogenation of the diamine ligand in the absence of hydrogen gas. Relatives of some of these complexes have been observed in the reactions of the amido complex **2c'**. None of these complexes, apart from one with a broad resonance at approx. –19.2 ppm, in these concentrated C_6D_6 solutions react quickly

[2] Damblon, C.; Prosperi, C.; Lian, L.; Barusov, I.; Soto, R. P.; Galleni, M.; Frère, J.-M.; Roberts, G. C. K. *J. Am. Chem. Soc.* **1999**, *121*, 11575 - 11576.

with 1 atm H_2 to regenerate the c,c-**3** dihydrides. There appears to be another complex with no observable hydride signal that produces most of the c,c-**3** that is regenerated. The lack of a hydride signal may be explained by a rapid association/dissociation reaction of the alcohol product with the amido complexes.

Experimental details for the stoichiometric reactions of 3a and 3b with ketones and 1-phenylethanol. Acetophenone (0.25 mL of 0.2 M solution in C_6D_6) was added to an NMR tube containing the dihydride mixtures in C_6D_6 or toluene-d_8 under Ar. Then the NMR tube was shaken and left to react. The progress of the reaction was monitored by NMR spectroscopy. For the reactions with **3a**, chloroform was added under Ar at the end to kill the hydride complexes and the mixture was poured into hexanes in air to precipitate the Ru compounds as completely as possible and filtered over celite (30 - 80 mesh). The resulting solution was analyzed by chiral GC.

Products from the reaction of c,c-**3a**/c,t-**3a** (80/20) in C_6D_6 with acetophenone under Ar. ^{1}H NMR δ: 8.2-6.8 (m, Ph), 5.0 (br, OCHPhMe), 3.7 (br), 1.17 (br), -13.8 (t, 28 Hz, 10% of total hydride integration), -14.0 (br, 10%), -18.3 (t, 45%, c,t-**3a**), -19.2 (br, 30%). ^{31}P NMR: 74 ppm (br), 72 (vbr, **2a’**), 67 (br), 66 (s, c,t-**3a**).

Products from the reaction of c,c-**3a**/c,t-**3a** (55/45) with 1.5 equiv. rac-1-phenylethanol in C_6D_6 under Ar for 15 min. ^{1}H NMR (hydride region) –7.1 (br, 3%, $RuH_4(PPh_3)_3$), -13.8 (t, 28 Hz, 10%), -18.3 (t, 45%, c,t-**3a**), -18.25 (br, 10%), -20.4 (br, 35%). ^{31}P NMR: 73 (m), 70 (vbr, **2a’**), 74 (br, 15%), 66 (s, c,t-**3a**), 57.7 (s, $RuH_4(PPh_3)_3$).

Products from the reaction of c,c-**3a**/c,t-**3a** in C_6D_6 with benzophenone under Ar: ^{1}H NMR δ: -13.8 (dd, J_{PH} 33, 27), -13.9 (dd, J_{PH} 30, 26), -18.2 (t, J_{PH} 26.7, c,t-**3a**), -19.2 (br t, J_{PH} 27 Hz). ^{31}P NMR: 75.5 (d), 73.8 ppm (d, J_{PP} 33), 72.4 (d), 67.5 (d, J_{PP} 43 Hz), 66.1 (s, c,t-**3a**).

Products from the reaction of c,c-**3b**/c,t-**3b** (80/20) in C_6D_6 with acetophenone under Ar. ^{1}H NMR δ: -7.2 (t, J_{PH} 23 Hz, **6**), -9.5 (br), -13.35 (t), -13.9 (br), -14.5 (t), -17.5 (t), -18.3 (t, c,t-**3b**), -19.7 (t, **2b’**), -19.9 (t, 30, **6**).

Study of the hydrogenation of acetophenone catalyzed by dihydrides 3a in isopropanol. The plots of 1-phenylethanol production versus time in the catalytic hydrogenation reactions are curved (see Fig. 2S). The best method for obtaining reproducible results was the use of the catalyst solution 15 min after its preparation. The rates increase with catalyst concentration and ketone concentration but are approximately independent of hydrogen pressure. Difficulties in reproducibility account for the deviations of the 10 atm and 5 atm runs from the calculated line (Fig. 2S). The pressure independence was verified by measuring the rate first at 5 atm up to 15% conversion and then jumping the pressure to 10 atm and measuring the same rate again up to 25% conversion. Other data are listed in Table 1S. Numerical integration of eq 1 describes a given run at 20º where the total initial concentration of all isomers of **3a** is used but the value of k_1 (approx. 13 $M^{-1}s^{-1}$) varies somewhat from run to run.

$$\text{rate} = \frac{d[\text{alcohol}]}{dt} = k_1[3a]_{initial}[\text{ketone}] \quad (1)$$

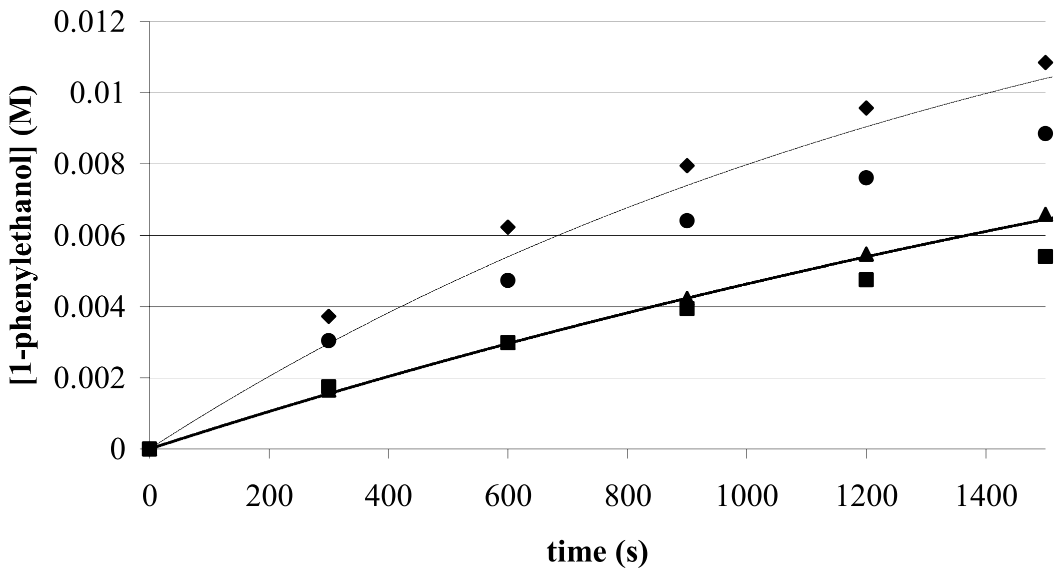


Figure 2S. Plots of the concentration of 1-phenylethanol as a function of time in the hydrogenation of acetophenone in isopropanol with [**3a**] 5.0 x 10^{-5} M (56% c,c-**3a**), 0.0167 M ketone, 5 atm H_2 (diamonds); with 10 atm H_2 (circles); with 0.083 M ketone, 5 atm H_2 (squares); with [**3a**] 2.5 x 10^{-5} M (56% c,c-**3a**), 0.0167 M ketone, 5 atm H_2 (triangles). The solid lines represent the numerical integration of eq 1 with k_1=13 $M^{-1}s^{-1}$. The e.e. range from 56 to 60% (*S*).

The rates are even higher when a base is added and they become sensitive to hydrogen pressure. The complexities of this system would require further extensive investigation.

Table 1S. Comparison of the effect of the solvent, benzene vs isopropanol, on the initial rate of production of alcohol in the hydrogenation of acetophenone at constant hydrogen pressure catalyzed by the mixture of dihydride isomers of **3a**.[a]

Run	Solvent	$[Ru]_{total}$, M	[***c,c*-3a**]$_0$, M	$[H_2]$, M	v_0, Initial rate, Ms^{-1}	v_0/[*c,c*-**3a**] s^{-1}
1	benzene	1.1×10^{-4}	3.6×10^{-5}	0.013	3.4×10^{-6}	9.4×10^{-2}
2	isopropanol	5.0×10^{-5}	2.8×10^{-5}	0.013	1×10^{-5}	0.4
3	isopropanol	2.5×10^{-4}	1.4×10^{-5}	0.013	5×10^{-6}	0.4
4	isopropanol	5.0×10^{-4}	2.8×10^{-5}	0.013	5×10^{-6} [b]	0.2 [b]
5	isopropanol	5.0×10^{-4}	2.8×10^{-5}	0.026	1×10^{-5}	0.4
6	isopropanol	1.0×10^{-5} [c]		0.013	2×10^{-5} [c]	

[a] $[Acetophenone]_0$ = 0.0167 M unless noted; constant $[H_2]$ (5 atm/0.013 M or 10 atm/0.026 M for isopropanol), 293K. The ee of 1-phenylethanol ranged from 61-55% for the benzene runs and 56-60% for the isopropanol runs. [b] $[acetophenone]_0$= 0.083 M. [c] $RuCl_2(PPh_3)_2$(dach); [KOtBu]=1.0×10^{-4} M.

Additional crystallographic data for 1a, 5 and 6 Two diastereomers are observed in the unit cell of crystals of **1a** and **4**. The configuration (and numbering) of the (*R*,*R*)-diamine is kept the same for the two diastereomers while the RuP(1)P(2) part is inverted across a pseudo center of inversion (in fact there is no center of inversion in the P1 space group). For example in **5**, P(1) is *cis* to N(1) in isomer A (the numbering is actually P(1A) and N(1A)) while it is *trans* to N(1) in isomer B.

The X-ray crystal structure of $RuHCl(PPh_3)_2$((*R*,*R*)-dach) (1a). The X-ray structure of complex **1a** (Fig. 3S, Table 2S) verifies the OC-6-43 stereochemistry with hydride trans to chloride. The crystals contain two diastereomeric conformations of **1a**, **A** and **B**; **A** being shown in Fig. 3S. The structures are very similar to that of $RuHCl(PPh_3)_2$(tmen) **1c** (see ref. 27 in the article) including a close NH...Cl contact of 2.7 Å (the axial NH on N(1A) of Fig. 3S), a feature consistent with the facile HCl elimination chemistry displayed by such complexes. Distances RuH…H-N are longer than twice the van der Waals radius of hydrogen (2x1.2 Å) and so hydridic-protonic interactions are either weak or non-existent.

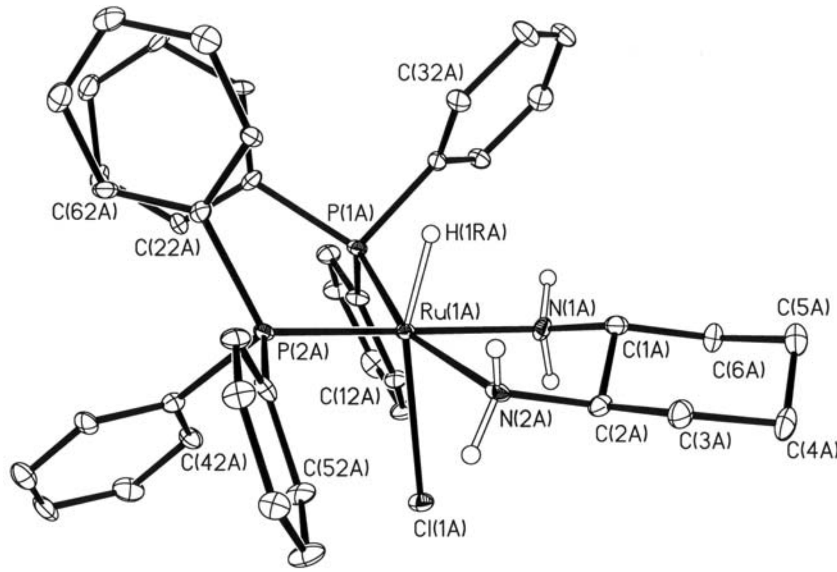


Figure 2S. Structure of isomer **A** of (OC-6-43)-$RuHCl(PPh_3)_2$((*R,R)*-dach)

Additional data for the structures of $RuH(PPh_3)_2(Ph_2PO_2)$((*R*,*R*)-dach) (5) and $Ru_2H_2(PPh_3)_4$(HN=CH-CH=NH) (6). (see Tables 2S, 3S and 4S).

Table 1S. Selected bond distances (Å) and angles (deg.) in complexes 1a and 5[a]

Bond	**1a A**	**1a B**	**5 A**	**5 B**
Ru(1)-H(1R)	1.52(4)	1.56(4)	1.49(4)	1.55(4)
Ru(1)-N(1)	2.060(6)	2.192(6)	2.165(3)	2.183(3)
Ru(1)-N(2)	2.205(6)	2.094(6)	2.190(4)	2.192(3)
Ru(1)-P(1)	2.217(2)	2.209(2)	2.256(1)	2.258(1)
Ru(1)-P(2)	2.136(2)	2.133(2)	2.256(1)	2.245(1)
Ru(1)-X[b]	2.542(2)	2.540(2)	2.295(3)	2.298(3)
O(1)-P(3)			1.508(3)	1.518(3)
P(3)-O(2)			1.497(3)	1.497(3)
O(2)…N(2)			3.016(5)	
O(2)…N(1)				2.944(5)
Angle				
H(1Ru)-Ru(1)-N(1)	84(1)	90(1)	84(1)	94(1)
H(1Ru)-Ru(1)-N(2)	85(1)	100(1)	94(1)	90(1)
H(1Ru)-Ru(1)-P(1)	82(1)	80(1)	87(1)	90(1)
H(1Ru)-Ru(1)-P(2)	92(1)	79(1)	89(1)	79(1)
H(1Ru)-Ru(1)-X[b]	161(1)	171(1)	162(1)	170(1)
N(1)-Ru(1)-N(2)	75.6(2)	77.1(2)	77.9(1)	78.0(1)
N(1)-Ru(1)-P(1)	91.2(2)	162.9(2)	91.41(9)	170.1(1)
N(1)-Ru(1)-P(2)	173.4(2)	97.5(2)	167.3(1)	90.51(9)
N(1)-Ru(1)-X[b]	80.2(2)	81.1(2)	78.5(1)	85.4(1)
N(2)-Ru(1)-P(1)	162.9(2)	90.7(2)	168.99(9)	93.4(1)
N(2)-Ru(1)-P(2)	98.5(2)	174.4(2)	92.31(9)	163.4(1)
N(2)-Ru(1)-X[b]	80.0(2)	79.8(2)	84.6(1)	80.3(1)
P(1)-Ru(1)-P(2)	94.04(7)	94.20(7)	98.64(4)	98.91(4)
P(1)-Ru(1)-X[b]	108.76(7)	108.81(7)	90.76(8)	88.27(8)

P(2)-Ru(1)-X[b]	101.89(7)	100.98(7)	108.90(8)	111.04(7)
O(1)-P(3)-O(2)			118.6(2)	118.0(2)

[a] Two isomers, **A** and **B** are present in the unit cell; the A and B should be added to the atom numbers e.g. P(1A) or P(1B).

[b]X = Cl(1A) or Cl(1B) for **1a**, O(1A) or O(1B) for **5**

Table 2S. Selected bond distances (Å) and angles (deg.) for **6.**

Bond distances			
Ru(1)-H(1Ru)	1.49(3)	Ru(2)-H(2Ru)	1.64(4)
Ru(1)-P(1)	2.2581(8)	Ru(2)-P(3)	2.2660(8)
Ru(1)-P(2)	2.2551(8)	Ru(2)-P(4)	2.2462(9)
Ru(1)-N(1)	2.084(3)	Ru(2)-N(1)	2.208(2)
Ru(1)-N(2)	2.089(3)	Ru(2)-N(2)	2.229(3)
Ru(1)-Ru(2)	2.9735(3)	Ru(2)-C(1)	2.176(3)
C(1)-C(2)	1.394(4)	Ru(2)-C(2)	2.198(3)
N(1)-C(1)	1.395(4)	N(2)-C(2)	1.394(4)
Bond Angles			
H(1Ru)-Ru(1)-P(1)	85(1)	H(2Ru)-Ru(2)-P(3)	90(1)
H(1Ru)-Ru(1)-P(2)	84(1)	H(2Ru)-Ru(2)-P(4)	91(1)
H(1Ru)-Ru(1)-N(1)	98(1)	H(2Ru)-Ru(2)-N(1)	100(1)
H(1Ru)-Ru(1)-N(2)	101(1)	H(2Ru)-Ru(2)-N(2)	103(1)
H(1Ru)-Ru(1)-Ru(2)	136(1)	H(2Ru)-Ru(2)-Ru(1)	73(1)
P(1)-Ru(1)-P(2)	98.11(3)	P(3)-Ru(2)-P(4)	97.78(3)
P(1)-Ru(1)-N(1)	166.40(8)	P(3)-Ru(2)-N(1)	163.00(7)
P(1)-Ru(1)-N(2)	93.69(8)	P(3)-Ru(2)-N(2)	96.78(7)
P(1)-Ru(1)-Ru(2)	122.36(2)	P(3)-Ru(2)-Ru(1)	128.43(2)
P(2)-Ru(1)-N(1)	95.44(8)	P(3)-Ru(2)-N(1)	96.78(7)
P(2)-Ru(1)-N(2)	167.50(8)	P(3)-Ru(2)-N(2)	96.78(7)

P(2)-Ru(1)-Ru(2)	120.41(2)	P(3)-Ru(2)-Ru(1)	128.43(2)
N(1)-Ru(1)-Ru(2)	47.90(7)	N(1)-Ru(2)-Ru(1)	44.45(7)
N(2)-Ru(1)-Ru(2)	48.48(7)	N(2)-Ru(2)-Ru(1)	44.55(7)
N(1)-Ru(1)-N(2)	72.7(1)	N(1)-Ru(2)-N(2)	67.8(1)
Ru(1)-N(1)-C(1)	119.0(2)	Ru(1)-N(2)-C(2)	118.9(2)
N(1)-C(1)-C(2)	112.9(3)	N(2)-C(2)-C(1)	112.6(3)

Table 3S. Summary of crystal data and X-ray parameters for complexes **1a**, **5** and **6**.

	1a	**5**	**6**
Formula	$C_{55}H_{57}ClN_2P_2Ru^a$	$C_{54}H_{55}N_2O_2P_3Ru$	$C_{92}H_{85}N_2P_4Ru^b$
Mr	932.48	957.98	1544.64
Cryst size, mm	0.34 x 0.30 x 0.18	0.15 x 0.12 x 0.10	0.25 x 0.20 x 0.16
Cryst class	triclinic	triclinic	triclinic
Space group	P1	P1	$P\bar{1}$
a, Å	10.8185(2)	11.0741(2)	10.4107(1)
b, Å	13.0054(3)	13.7100(3)	14.1121(2)
c, Å	16.0637(3)	16.8074(3)	27.0744(5)
α, deg	83.061(1)	84.210(1)	97.828(8)
β, deg	77.156(1)	82.089(1)	97.705(1)
γ, deg	81.597(1)	67.678(1)	101.796(1)
V, $Å^3$	2170.78(8)	2334.82(8)	3803.25(1)
Z	2	2	2
T, K	100	150	150
Dcalc, g cm^{-3}	1.427	1.363	1.349
μ(Mo Kα), mm^{-1}	0.537	0.482	0.530
F(000)	972	996	1598

Range θ collected, deg	2.6-30.1	2.86-32.05	2.66-27.48
No. of reflns	38472	38082	51688
No. of ind. reflns	17278	23455	17141
R1[I> 2σ(I)][c]	0.048	0.0352	0.0446
WR2 (all data)[d]	0.129	0.0761	0.110
Goodness of fit	1.017	1.034	1.070
No. of params refined	1141	1124	917
Max peak in final ΔF map, e $Å^{-3}$	0.947	0.485	1.81/-0.90

[a] two C_6H_6 molecules in the unit cell. [b] three C_6H_6 in the unit cell [c] $R1 = \Sigma(F_o-F_c)/\Sigma(F_o)$. [d] $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$