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A weak η^1 π-bonding mode for Ru–arene complexes. Nitrile, isonitrile and phosphine derivatives of Ru–phosphino–arene chelating complexes

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It is a pleasure for us to dedicate this paper to Professor François Mathey

Abstract

The synthesis of new derivatives based on a $Ru(Ph_2P–arene)(POHPh_2)$ fragment, possessing nitrile, isonitrile and phosphine ligands, are reported. The new nitrile compounds, e.g. $[Ru(H_2O)(RCN)_2(Ph_2P–\eta^1arene)(POHPh_2)](OTf)_2$, R = Me, *p*-tolyl, reveal a new and unexpected weak η^1 π-bonding mode from a single CH–biaryl arene carbon to the ruthenium atom, as demonstrated by ^{13}C-NMR. The solid-state structures for two examples are reported. In one complex a new Ru–P–O–C=N–H five-membered ring is formed due to the P–OH oxygen attack on the complexed *p*-tolyl nitrile. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: η^1-π-bonding; ^{13}C NMR; Nitrile compounds; Ru–arene complexes; Phosphine ligands

1. Introduction

Arene complexes of Ru(II) have applications as homogeneous catalysts in hydrogenation [1] and C–C coupling reactions [2]. Specifically, Binap has been a successful chiral auxiliary in a number of transformations involving olefinic and ketonic functions [3].

We have recently shown [4–7] that $Ru(OAc)_2$(Binap) can be transformed successively into the complexes **1**–**3** via a series of P–C bond splitting reactions (see Scheme 1). These transformations can be quite facile and result in strongly asymmetric Ru–arene η^6-bonding modes in addition to the new P–O bonds. Indeed, based on X-ray crystallography, there appear to be 'three pairs' of Ru–C(arene) distances, ranging from rather short, ca. 2.1–2.2 Å, up to values between 2.3 and 2.4 Å [6].

We report here eight new derivatives of **1**, involving nitrile, isonitrile and phosphine chemistry, in which the arene has either been partially or fully displaced. The nitrile compounds show an unexpected weak bonding from a single arene carbon to the metal.

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2. Results and discussion

2.1. Characterisation

The complexes **4**–**11** (see Scheme 2) were prepared by reaction of **1** with the appropriate ligand. The complexes have been characterised by NMR and mass spectroscopic methods in combination with elemental analyses and (partly) X-ray diffraction. The arene tris-phosphine complexes **10** and **11** reveal three non-equivalent ^{31}P spins (see Table 1), with the complexed $P(OH)Ph_2$ ligand found at relatively high frequency. The complexed =CH arene carbon signals are readily assigned via C,H-correlations and appear in the region δ = ca. 90–105. The aquo-complexes, **6** and **7** arise due to slow hydrolysis and can be prepared independently by addition of water, whereas the cyclic species **8** develops from nucleophilic attack of the proximate oxygen (of the POH) on a *cis*-complexed *p*-tolyl nitrile. The ^{15}N–^{1}H-COSY of **8** is shown in the inset of Fig. 1. Both the observed ^{15}N chemical shift and protonated N-atom are consistent with a C=NH fragment [8]. Moreover, the new derivative **8** shows the former ^{13}C nitrile resonance at δ = 171.8, indicative of an imine type carbon [9]. There is literature precedence [10] for

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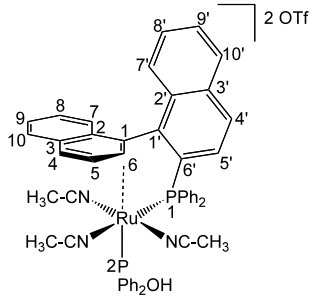
this type of attack at a complexed nitrile. The inclusion of the P-atom in a new five-membered ring results in the expected high frequency shift [11] of its ^{13}P signal to $\delta = 180.1$ from its normal position at $\delta =$ ca. 100–125 [4–6]. The six-coordinate tetrakis isonitrile complex **9** is the most conventional of the series and shows four non-equivalent *t*-butyl groups in addition to signals from the two π-donors, thus supporting its octahedral structure.

On the surface, all of the apparent five-coordinate nitrile complexes **4**–**8**, appear to have structures in which the η^6-arene bonding has been completely displaced, whereas the phosphine and isonitrile derivatives arise from simple substitution of the triflate anion in **10**, and **11** and arene ring plus triflate substitution in **9**. However, the nitrile complexes contain an interesting and unexpected feature as shown by their ^{13}C-NMR data (see Table 1 and Fig. 1). Just one of the (previously η^6-arene) biaryl carbons, C-6, remains situated in a pseudo-sixth coordination position and its ^{13}C position is shifted to $\delta = 105$–112 from that of a 'normal' arene hydrocarbon, which we estimate at ca. $\delta = 127$–130. This interaction, together with a numbering scheme, is shown for complex **4**. This difference in carbon chemical shift is much too large to arise from local anisotropic effects [12]. The adjacent carbon atoms, C-1 and C-5 are found at $\delta =$ ca. 130–140, i.e. in rather routine positions, so that an η^2 description is not suitable for these molecules. The protons on C-6 in **4**–**8**, $\delta = 7.69$–8.27 are also of routine nature.



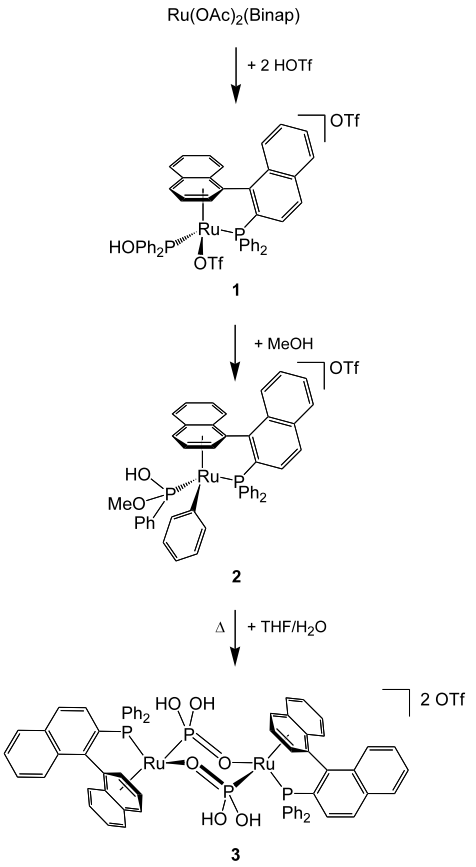
4

One could consider the observed bonding as arising from a 'remote agostic' [13–15], i.e. a weak interaction of the metal with the biaryl C–H bond. However, we do not believe this to be correct based on the normal observed values of both ^1J(C,H) (from the C,H-correlations) and the H-6 proton chemical shifts, both of which seem rather unaffected by the bonding. To exclude the possibility of an agostic interaction from the metal to the C(6)H proton, C,H-correlations of **5**, **6** and **7** at 220 K were measured. The observed $^1J\{^{13}C,^1H\}$ of ca. 161 Hz is unchanged within 1 Hz. The most reasonable explanation involves a weak η^1-bonding mode from a single CH–biaryl arene carbon to the ruthenium atom. A strong interaction might induce larger coordination chemical shifts and shorter bond separations and this brings us to the solid-state.

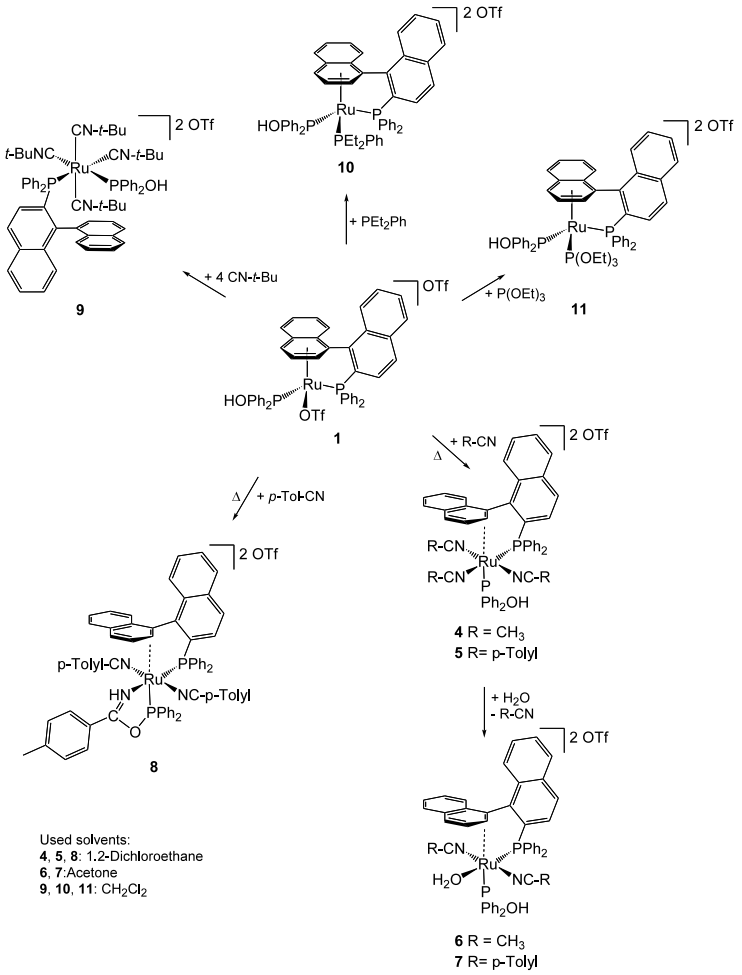
2.2. X-ray diffractions studies

Crystals of the two nitrile-aquo-complexes **6** and **7** were grown from slow diffusion of pentane into an acetone solution and their solid-state structures determined via X-ray diffraction. Figs. 2 and 3 show views of the cations and Table 2 presents a list of bond angles and bond lengths. There is strong disorder in these crystals arising from included solvent and the disordered triflate counterion, so that the *R*-values are not excellent; however, the coordination sphere about the ruthenium is clear.

The immediate ligand environment about ruthenium for **6** and **7** consists of the two P-donors, in *cis* position, two nitrile ligands, in *trans* position, and a complexed water molecule. Complexed water is fairly common and there are a number of structures for ruthenium aquo-complexes reported [16–18]. Carbon C-6 occupies the sixth position in both structures and P-2, possessing the P(OH) group, is in *pseudo-trans* position to this arene carbon. The Ru–C-6 separations, at 2.62 and 2.63 Å, for complexes **6** and **7**, respectively, are clearly too long for a routine σ-bond, but approach the upper end of



Scheme 1.



Scheme 2.

Table 1
^{13}C-, ^{31}P- and ^{1}H-NMR data for **4**–**11**

	4		**5**		**6**		**7**		**8**		**9**		**10**		**11**	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1		139.3		140.6		139.1		140.1		142.6		135.1		118.5		122.3
2		135.0		135.3		134.6		134.7		134.2		132.9		116.4		111.2
3		134.2		134.2		134.0		134.0		134.4		133.4		116.2		115.1
4	8.32	131.6	8.29	131.9	8.14	132.2	8.09	132.2	8.46	132.8	7.65	129.4	8.10	94.7	7.84	92.1
5	8.28	131.8	8.34	131.5	8.02	130.4	8.13	130.7	9.01	131.5	7.10	124.5	6.10	100.4	6.24	104.8
6	7.69	111.8	8.04	111.2	7.78	112.5	7.84	112.2	8.27	105.9	6.59	128.2	6.93	90.4	7.02	96.7
P_1	38.6		35.3		58.3		57.1		40.7		32.2		50.2		53.1	
P_2	124.4		123.1		120.6		116.6		180.1		102.5		116.7		116.0	
P_3													18.6		119.0	

what is known [19] for weak Ru–olefin interactions. The separations from the ruthenium atom to C-5 are both rather long for a bonding interaction, ca. 3.3 Å, consistent with the carbon NMR results. Placing the H-atom on C-6 at ca. 1 Å distance affords Ru···H separations of the order of 2.69–2.70 Å, i.e. there is no reason to invoke a C–H agostic interaction (although a weak one cannot be excluded).

We are not aware of many examples of η^1 Ru–CH bonds; however, Gusev et al. [20] have recently assigned the Ru–CH in **12** as a strong agostic interaction based on the short ca. 2.1 Å M–C separation. Indeed the

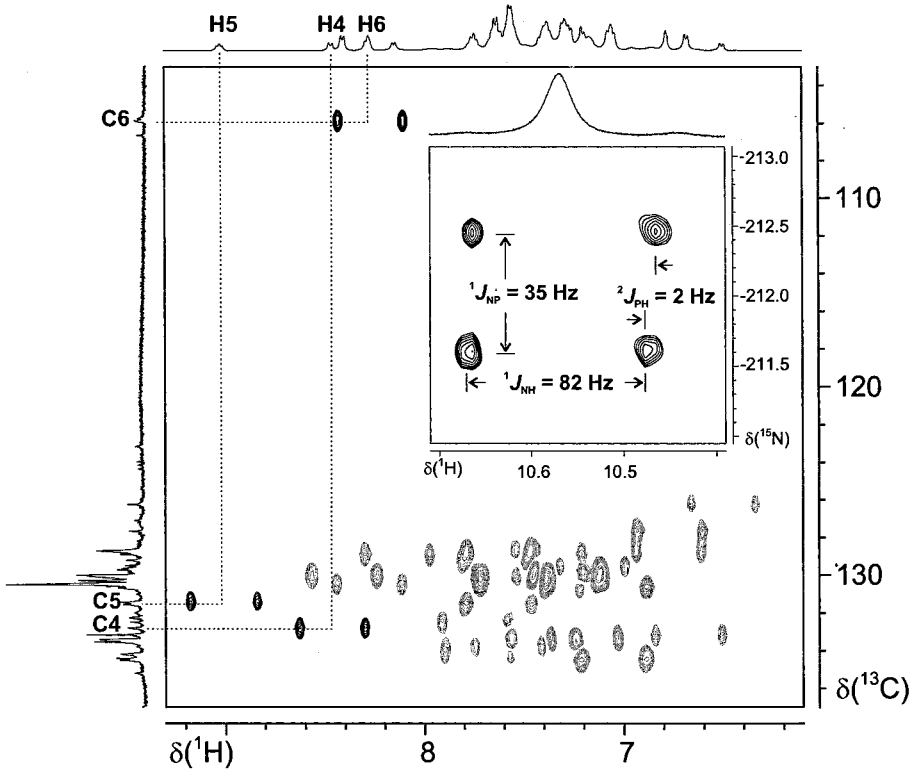
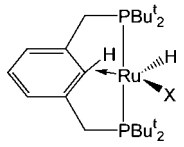


Fig. 1. ^{13}C-,^{1}H-one-bond correlation spectrum showing the three key carbon resonances (dotted lines) in **8** and their appropriate one-bond C, H interactions. The inset gives the one-bond ^{15}N, ^{1}H correlation for **8**, thus simultaneously affording the ^{15}N chemical shift and proving the existence of an NH fragment, which arises from the attack of the POH oxygen on the nitrile carbon ($^{2}J(^{31}P,^{15}N) = 35$ Hz).

reported *high frequency* carbon chemical shift of this Ru–CH carbon, ca. 152 ppm, is consistent with strong M–C σ-bond character. This interaction is obviously different from those found in **4**–**8**.



12

The remaining coordination bond lengths are rather standard [21]. The somewhat longish Ru–O bonds arise due to the *trans* influence of the phosphine P-1 [16] and the observed Ru–P separations differ only slightly, as expected [4–7,22]. The slightly smaller *trans*-N–Ru–N angles, ca. 173–175° presumably reflect the steric bulk of the arene fragment associated with P-1.

3. Conclusion

The Ru(II) centre in the dicationic nitrile complexes **4**–**8** is clearly attempting to reach the more stable 18-electronic configuration. The relatively large arene moiety associated with the tertiary phosphine, P-1, blocks the approach of additional ligands (the syntheses of these nitrile complexes were carried out using a large excess of nitrile). Consequently, this electrophilic metal centre reaches a compromise by weakly binding the closest source of electrons, for **4**–**8**, the C-6 arene carbons, and this is reflected in the appropriate C-13 chemical shifts. There are, of course, well documented [23–26] examples of five-coordinate 16 electron Ru-complexes in which there is no evidence of additional bonding; nevertheless the observed weak, rather novel, bonding represents an interesting alternative.

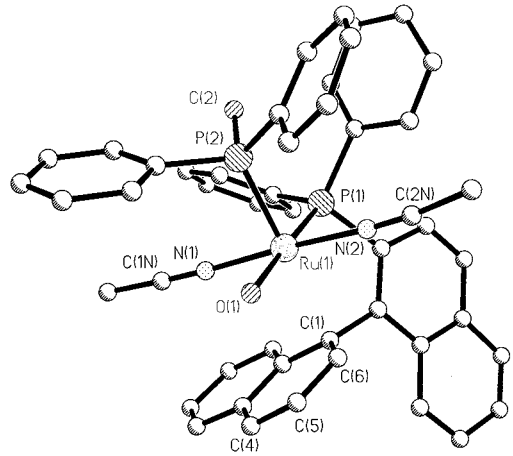


Fig. 2. View of the cation in **6**.

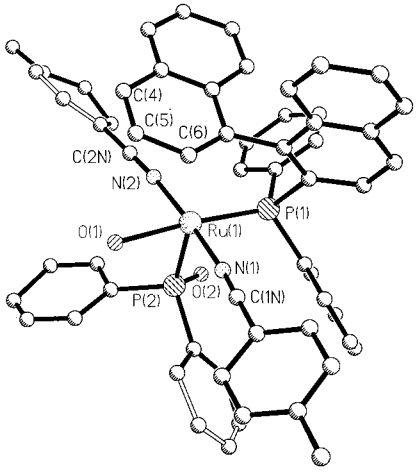


Fig. 3. View of the cation in **7**.

Table 2
Selected bond lengths (Å) and bond angles (°) for **6** and **7**

	6	**7**
Bond lengths		
Ru(1)–N(1)	2.014(6)	2.002(6)
Ru(1)–N(2)	2.006(6)	2.033(6)
Ru(1)–P(1)	2.290(2)	2.282(2)
Ru(1)–P(2)	2.258(2)	2.248(2)
Ru(1)–O(1)	2.199(7)	2.203(5)
Ru(1)–C(6)	2.62	2.63
C(1N)–N(1)	1.125(9)	1.139(10)
C(2N)–N(2)	1.138(9)	1.114(10)
Bond angles		
N(1)–RuN(2)	172.9(3)	175.0(3)
P(1)–Ru–P(2)	93.17(8)	94.08(8)
P(1)–Ru–O(1)	175.0(2)	175.9(1)
P(2)–Ru–O(1)	85.8(2)	85.7(2)
N(1)–Ru–O(1)	85.6(3)	90.3(2)
N(2)–Ru–O(1)	88.2(3)	84.9(2)
P(1)–Ru–N(1)	89.7(2)	93.8(2)
P(2)–Ru–N(1)	94.8(2)	89.3(2)
P(1)–Ru–N(2)	96.6(2)	91.0(2)
P(2)–Ru–N(2)	88.3(2)	91.5(2)

4. Experimental

4.1. X-ray

Air stable, yellow crystals of **6** and **7** were obtained by slow diffusion of C_5H_{12} into a solution of the compound in CH_3COCH_3. A prismatic single crystal was mounted on a glass capillary and a data set covering a hemisphere were collected on a Siemens SMART platform diffractometer equipped with a CCD detector. Data reduction and corrections for Lorentz polarisation and absorption was performed using the programs SAINT [27] and SADABS [28]. The structure was solved by direct methods and refined by full-matrix least-squares (vs. F^2) with the SHELXTL program package [29]. Non-hydrogen atoms were refined anisotropically, hydrogen atoms isotropically (riding model). All crystals were of poor quality; this is reflected in the relatively high R values. The triflate molecules are disordered and were described as rigid groups. In addition, one of the Ph groups at P(2) in compound **6** showed strong disorder. Since a free refinement of this Ph group was not possible, it was also treated as a rigid group. Where refinement with disordered positions did not improve the result of the refinement with non-split positions the group was described as rigid, alternatively the disorder was described via splitting.

Crystal data and structure refinements for **6** and **7** are summarised in Table 3.

All manipulations were carried out under an Ar atmosphere using standard Schlenk techniques. Pentane and Et_2O were distilled from Na–K alloy, CH_2Cl_2 from CaH_2, $C_2H_4Cl_2$ from P_4O_{10} and CH_3COCH_3 dried over molecular sieves. Water was de-oxygenated prior to use; all other chemicals were commercial products and were used as received. NMR spectra were recorded with Bruker DPX-300, Avance 400 and 500 spectrometers. Chemical shifts are given in ppm and coupling constants (J) are given in Hz. Elemental analyses and mass spectroscopic studies were performed at the ETHZ.

4.2. Preparation of **4**

Complex **1** (50 mg, 0.048 mmol) was dissolved in 5 ml $C_2H_4Cl_2$ and MeCN (50 μl, 0.95 mmol) added from a syringe. The solution was stirred in an ampoule at 100 °C for 5 min, then the solvent was removed in

Table 3
Summary of crystal data for complexes **6** and **7**

	6	**7**
Empirical formula	$C_{50}H_{35}F_6N_2O_8P_2RuS_2$	$C_{65}H_{56}F_6N_2O_9P_2RuS_2$
Molecular weight	1132.93	1350.25
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	12.4499(6)	12.2906(18)
b (Å)	18.3455(9)	13.777(2)
c (Å)	23.7919(11)	20.246(3)
α (°)	90	102.07
β (°)	103.2970(10)	90.96(3)
γ (°)	90	109.31839
V (Å^3)	1907.66(9)	3150.3(8)
Z	4	2
Temperature of data collection	r.t.	r.t.
μ (mm^{-1})	0.5091	0.441
Reflections measured	28 054	23 119
Unique reflections	12 765	10 804
R_{int}	0.0594	0.0791
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.1300$; $wR_2 = 0.3461$	$R_1 = 0.1020$; $wR_2 = 0.1828$

vacuo and the remaining residue washed two times with C_5H_{12} to afford **4** as pale yellow solid. Yield: 52 mg, 94%.

^{1}H-NMR (d_6-acetone, 500 MHz): $\delta = 10.15$ (d, br, O*H*, 1H), 8.32 (d, $^3J_{HH} = 8.4$, H4), 8.28 (m, H5), 8.18 (d, $^3J_{HH} = 8.8$, H4′), 8.13 (d, $^3J_{HH} = 8.1$, H10), 8.11 (d, $^3J_{HH} = 8.1$, H10′), 7.84 (m, 2H), 7.70–7.50 (m, 13H), 7.44 (m, 4H), 7.35 (m, 3H), 7.28 (m, 3H), 6.96 (m, H8), 6.83 (d, $^3J_{HH} = 8.3$, H7), 6.26 (d, $^3J_{HH} = 8.6$, 7′), 2.56 (s, CH_3, 3H), 2.26 (s, CH_3, 3H), 1.57 (s, CH_3, 3H); ^{13}C{^{1}H}-NMR (d_6-acetone, 100 MHz): 144.4 (d, $^2J_{CP} =$ 20, C1′), 139.3 (t, $J_{CP} = 6$, C1), 136.6 (d, $^1J_{CP} = 51$), 135.1 (C3′), 135.0 (d, $J_{CP} = 10$, C2), 134.3, 134.2 (d, $J_{CP} = 10$, C3), 131.8 (C5), 131.7 (d, $^4J_{CP} = 3$), 131.5, 131.4 (d, $^4J_{CP} = 3$), 131.2 (d, $J_{CP} = 11$), 130.6 (d, $J_{CP} =$ 11), 129.8 (C4′), 129.5 (C5′), 129.3, 129.1, 129.0, 128.9 (C10′), 128.6 (C9′), 128.2 (C8′), 127.1 (C8), 126.5 (C7′), 111.8 (d, $J_{CP} = 6$, C6), 4.4 (*C*H$_3$), 3.8 (*C*H$_3$), 2.9(*C*H$_3$); ^{19}F-NMR (d_6-acetone, 282 MHz): -79.23; ^{31}P-NMR (d_6-acetone, 202 MHz): 124.4 (d, $^2J_{PP} = 36$), 48.6 (d, $^2J_{PP} = 36$); mass spectrum (FAB$^+$): 972.6 (MOTf$^+$ − NCCH$_3$), 822.8 (M$^+$ − NCCH$_3$), 740.8 (M$^+$ − (NCCH$_3$)$_3$, 100%), 538.8 (RuBiNap–PPh$_2$); IR (Golden Gate) ν (cm^{-1}): 2359 (vs, N≡C), 2341 (s, N≡C), 2327 (s, N≡C); Anal. Calc. for $C_{52}H_{43}F_6N_3O_7P_2RuS_2$: C, 53.70; H, 3.73; N, 3.61. Found: C, 53.39; H, 3.15; N, 3.15%.

4.3. Preparation of **5**

Complex **1** (40 mg, 0.038 mmol) was dissolved in 3 ml $C_2H_4Cl_2$ and *p*-tolunitrile (30 μl, 0.25 mmol) added from a syringe. The solution was stirred in an ampoule at 100 °C for 5 min during which time the colour changed from orange to yellow. Concentration and addition of C_5H_{12} led to the precipitation of a yellow solid that was washed with C_5H_{12} and dried in vacuo. The product was obtained as light yellow solid. Yield: 46 mg, 88%.

^{1}H-NMR (d_6-acetone, 300 MHz): δ10.61 (d, $^2J_{PH} =$ 15.0, O*H*, 1H), 8.34 (d, $^3J_{HH} = 6.7$, H5), 8.29 (m, H4), 8.21 (d, $^3J_{HH} = 8.8$, H4′), 8.11 (d, $^3J_{HH} = 8.8$, H10′), 8.01 (m, 3H), 7.82 (d, $^3J_{HH} = 8.1$, 2H), 7.75–7.08 (m, 28H), 6.96–6.77 (m, 7H), 6.37 (d, $^3J_{HH} = 7.9$, H7′), 2.52 (s, CH_3, 3H), 2.47 (s, CH_3, 3H), 2.41 (s, CH_3, 3H); ^{13}C{^{1}H}-NMR (d_6-acetone, 100 MHz): 147.4 (tolyl), 147.2 (tolyl), 146.9 (tolyl), 144.5 (d, $^2J_{CP} = 20$, C1′), 140.6 (br, C1), 136.7 (d, $^1J_{CP} = 51$, C6′), 135.3 (C2), 135.2, 135.1 (C3′), 134.3, 134.2 (C3), 133.9, 133.6 (C2′), 131.9 (C4), 131.5 (C5), 131.1, 131.0, 130.8, 130.6, 130.4, 130.0 (C4′), 129.3, 129.1, 128.9 (C10′), 128.7 (C10), 128.5 (C8′), 128.0, 127.4 (C8), 126.4 (C7′), 124.4 (*C*N), 124.1 (*C*N), 123.1 (*C*N), 111.2 (br, C6), 107.1 (*ipso*-tolyl), 106.3 (*ipso*-tolyl), 21.6 (*C*H$_3$), 21.5 (*C*H$_3$); ^{19}F-NMR (d_6-acetone, 282 MHz): -79.20; ^{31}P-NMR (d_6-acetone, 121 MHz): 123.1 (d, $^2J_{PP} = 35$), 47.0 (d, $^2J_{PP} = 35$); mass spectroscopy (FAB$^+$): 1124.4 (M$^+$ − NC*p*-Tolyl + CF_3SO_3), 974.8 (M$^+$ − NC*p*-Tolyl), 740.9 (M$^+$ − (NC*p*-Tolyl)$_3$, 100%), 538.8 (RuBiNap–PPh$_2$); Anal. Calc. for $C_{70}H_{55}F_6N_3O_7P_2RuS_2$: C, 60.43; H, 3.98; N, 3.02. Found: C, 59.78; H, 4.54; N, 2.98%.

4.4. Preparation of **6**

Complex **4** (30 mg, 0.025 mmol) was dissolved in 2 ml CH_3COCH_3 and water (100 μl, 5.56 mmol) was added. The solution was stirred at room temperature (r.t.) for 10 min then concentrated to 1 ml. Treatment with C_5H_{12} precipitates the product which was dried in vacuo. The entire sequence was repeated four times until basically all starting material was gone as monitored by ^{31}P-NMR. Complex **6** was obtained as yellow solid. Yield: 23 mg, 79%.

^{1}H-NMR (d_6-acetone, 300 MHz): 10.04 (br, O*H*, 1H), 8.14 (d, $^3J_{HH} = 8.6$, H4′), 8.09 (d, $^3J_{HH} = 8.3$, H10′), 8.04 (d, $^3J_{HH} = 7.9$, H10), 8.02 (m, H5), 7.85–7.20 (m, 25H), 6.90 (t, $^3J_{HH} = 7.4$, H8), 6.75 (d, $^3J_{HH} =$ 8.1, H7), 6.31 (d, $^3J_{HH} = 8.6$, H7′), 2.22 (s, br, CH_3, 3H), 1.53 (s, br, CH_3, 3H); ^{13}C{^{1}H}-NMR (d_6-acetone, 100 MHz): 144.5 (d, $^2J_{CP} = 18$, C1′), 139.3 (br, C1), 137.3 (d, $^1J_{CP} = 50$, C6′), 135.5, 135.0, 134.9 (C3′), 134.6 (C2), 134.3 (d, $^3J_{CP} = 9$), 134.1 (C3), 133.6, 133.5 (C2′), 132.2 (C4), 131.6, 131.4, 131.3, 131.0, 130.5 (d, $^2J_{CP} =$ 11), 130.4 (C5), 129.9 (*C*N), 129.6, 129.5 (C4′), 129.2 (d, $^2J_{CP} = 3$, C5′), 129.0, 128.9–128.6 (m, br), 128.4, 128.2 (C8′), 127.0 (C8), 126.5 (C7′), 126.4 (br, *C*N), 112.5 (C6), 4.4 (*C*H$_3$), 3.1 (*C*H$_3$); ^{19}F-NMR (d_6-acetone, 282 MHz): -79.25; ^{31}P-NMR (d_6-acetone, 121 MHz): 120.6 (br), 58.3 (br); mass spectroscopy (FAB$^+$): 990.2 (M$^+$ + CF_3SO_3), 972.1 (M$^+$ + CF_3SO_3 − H_2O), 822.6 (M$^+$ − H_2O), 740.8 (M$^+$ − (NCCH$_3$)$_2$, − H_2O, 100%), 539.0 (RuBiNap–PPh$_2$); Anal. Calc. for $C_{50}H_{42}F_6N_2O_8P_2RuS_2$: C, 52.68; H, 3.71; N, 2.46. Found: C, 52.39; H, 3.96; N, 2.51%.

4.5. Preparation of **7**

Complex **5** (20 mg, 0.014 mmol) was dissolved in 2 ml CH_3COCH_3 and water (30 μl, 1.67 mmol) was added. The solution was stirred at r.t. for 10 min then concentrated to 1 ml before treatment with C_5H_{12}. The yellow solid, which precipitated, was washed with C_5H_{12} and dried in vacuo. Compound **7** was obtained as yellow solid. Yield: 17 mg, 94%.

^{1}H-NMR (d_6-acetone, 500 MHz): 10.08 (br, O*H*, 1H), 8.18 (d, $^3J_{HH} = 9.5$, H4), 8.13–8.09 (m, 3H), 7.94 (t, $^3J_{HH} = 8.4$, 2H), 7.84–7.15 (m, 31H), 6.88–6.75 (m, 4H), 2.49 (s, CH_3, 3H), 2.43 (s, CH_3, 3H); ^{13}C{^{1}H}-NMR (d_6-acetone, 100 MHz): 146.7 (tolyl), 146.2 (tolyl), 144.6 (C1′), 140.1 (C1), 137.1, 135.0 (C3′), 134.7 (C2), 134.2 (d, $^2J_{CP} = 9$), 134.0 (C3), 133.4 (d, $^2J_{CP} =$ 11), 133.5 (C2′), 132.2 (C4), 130.7 (C5), 130.4, 130.3, 129.6 (C4′), 128.9 (C5′), 128.7 (C10′), 128.6 (C9), 128.4

(C7), 126.9 (C8), 126.4 (C7′), 123.2 (*C*N), 120.0 (*C*N), 112.2 (C6), 107.4 (*ipso*-tolyl), 106.7 (*ipso*-tolyl), 21.5 (*C*H_3); ^{19}F-NMR (d_6-acetone, 282 MHz): −79.20; ^{31}P-NMR (d_6-acetone, 162 MHz): 116.6 (br), 57.1 (d, $^2J_{PP} = 39$); mass spectroscopy (FAB$^+$): 1142.3 ($M^+ + CF_3SO_3$), 1124.4 ($M^+ + CF_3SO_3 - H_2O$), 974.4 ($M^+ - H_2O$), 740.4 ($M^+ - (NCp\text{-Tolyl})_2 - H_2O$) 100%), 538.5 (RuBiNap–$PPh_2$); Anal. Calc. for $C_{62}H_{50}F_6N_2O_8P_2RuS_2$: C, 57.63; H, 3.90; N, 2.17. Found: C, 57.61; H, 4.02; N, 2.35%.

4.6. Preparation of **8**

Complex **1** (25 mg, 0.024 mmol) was dissolved in 4 ml $C_2H_4Cl_2$ and *p*-tolunitrile (1 ml, 8.45 mmol) added. The solution was stirred in an ampoule at 70 °C for 2 days during which time the colour changed from orange to yellow. Concentration and addition of 10 ml C_5H_{12} led to the precipitation of a yellow solid. This crude product was washed with C_5H_{12}, re-dissolved in CH_2Cl_2, precipitated again with Et_2O and dried in vacuo affording **8** as yellow solid. Yield: 24 mg, 73%.

^{1}H-NMR (d_6-acetone, 500 MHz): 10.59 (br, N*H*, 1H), 9.02 (br, t, $^3J_{HH} = 7.5$, H5), 8.46 (d, $^3J_{HH} = 8.4$, H4), 8.40 (d, $^3J_{HH} = 7.9$, H13, 2H), 8.27 (m, 2H), 8.14 (d, $^3J_{HH} = 7.7$, H10′), 7.74 (m, 2H), 7.65–7.51 (m, 10H), 7.43–7.13 (m, 16H), 7.05 (m, 5H), 6.78 (m, 2H), 6.68 (d, $^3J_{HH} = 8.4$, 2H), 6.50 (d, $^3J_{HH} = 8.6$, H7′), 2.53 (s, C*H*$_3$, 3H), 2.42 (s, C*H*$_3$, 3H), 2.37 (s, C*H*$_3$, 3H); ^{13}C{^{1}H}-NMR (d_6-acetone, 125 MHz): 171.8 (iminoether), 147.1 (*p*-tolyl), 146.5 (C15), 144.4 (d, $^2J_{CP} =$ 21, C1′), 142.6 (br, C1), 137.1 (d, $^1J_{CP} = 49$, C6′), 135.2 (C3′), 134.5, 134.4 (C3), 134.2 (C2), 133.5, 133.4 (C2′), 133.1, 132.8 (C4), 132.5, 132.3, 131.6, 131.5 (C4′), 130.6 (C14), 130.3, 130.1 (br), 129.9 (*C*N), 129.7, 129.6, 129.5, 129.2 (C9′), 128.8 (C10′), 128.7, 127.5 (C8), 127.1 (*C*N), 126.2 (C7′), 123.2 (*ipso*-tolyl), 106.7 (*ipso*-tolyl), 105.9 (br, C6), 105.8 (*ipso*-tolyl), 21.5 (*C*H_3), 21.4 (*C*H_3), 21.2 (*C*H_3); ^{19}F-NMR (d_6-acetone, 282 MHz): −79.16; ^{31}P-NMR (d_6-acetone, 202 MHz): 180.1 (d, $^2J_{PP} = 25$), 40.7 (d, $^2J_{PP} = 25$); ^{15}N-^{1}H-COSY (d_6-acetone, non-enriched, relative to CH_3NO): (d_6-acetone, 40.6 MHz): −212.0 ($^1J_{NH} = 82$, $^2J_{NP} = 2$, $^1J_{NP} = 35$); mass spectroscopy (FAB$^+$): 1241.4 ($M^+ + CF_3SO_3$), 974.4 ($M^+ - NCp$-Tolyl), 858.4 ($M^+ - (NCp\text{-Tolyl})_2$), 740.4 ($M^+ - (NCp\text{-Tolyl})_3$, 100%), 538.4 (RuBiNap–$PPh_2$); Anal. Calc. for $C_{70}H_{55}F_6N_3O_7P_2RuS_2$: C, 60.43; H, 3.98; N, 3.02. Found: C, 60.26; H, 4.03; N, 3.13%.

4.7. Preparation of **9**

Complex **1** (50 mg, 0.048 mmol) was dissolved in 4 ml CH_2Cl_2 and *tert*-butyl isocyanide (24 μl, 0.212 mmol) added. The solution was stirred at r.t. for 2.5 h and then concentrated to 1 ml. Addition of C_5H_{12} led to the precipitation of **9** which, after filtration and washing with C_5H_{12}, was isolated as a white solid. Yield: 61 mg (93%).

^{1}H-NMR (CD_2Cl_2, 400 MHz): 9.80 (d, br, $^2J_{PH} =$ 12.6, 1H, O*H*), 8.29 (dd, $^3J_{HH} = 9.0$, $J_{PH} = 14.9$, H5′), 7.99 (m, 2H), 7.65–7.47 (m, 13H), 7.32 (m, 2H), 7.20–7.10 (m, 8H), 7.02 (t, $J_{HH} = 7.6$, H8), 6.86 (m, 1H), 6.75 (m, 2H), 6.66 (d, $^3J_{HH} = 8.9$, H7′), 6.58 (m, 2H), 1.41 (s, 9H, *t*-Bu), 1.36 (s, 9H, *t*-Bu), 1.34 (s, 9H, *t*-Bu), 1.30 (s, 9H, *t*-Bu); ^{13}C{^{1}H}-NMR (CD_2Cl_2, 100 MHz): 144.0 (C1′), 135.1 (C1), 134.9 (C2′), 134.7 (C3′), 133.4 (C3), 133.3 (d, $J_{CP} = 9.8$), 133.1 (C5′), 132.9 (C2), 132.4 (d, $J_{CP} = 11.8$), 131.6, 130.4 (d, $J_{CP} = 11.0$), 130.2 (d, $J_{CP} =$ 11.0), 129.6, 129.4 (C4), 129.0 (d, $J_{CP} = 10.6$), 129.0 (d, $J_{CP} = 10.4$), 128.6 (C9′), 128.3, 128.2 (C6, C8′), 128.1 (d, $J_{CP} = 11.0$), 127.8 (d, $J_{CP} = 11.8$), 127.7 (C10′), 127.6 (C7′), 126.7 (C7), 126.3 (C8), 126.2 (C9), 124.5 (C5), 60.5, 60.2, 60.0, 30.4, 30.3, 30.0, 29.9; ^{19}F-NMR (CD_2Cl_2, 282 MHz): −79.31; ^{31}P-NMR (CD_2Cl_2, 121 MHz): 102.5 (d, $^2J_{PP} = 28$), 32.2 (d, $^2J_{PP} = 28$); mass spectroscopy (FAB$^+$): 1223 ($M^+ + CF_3SO_3$), 1072.9 (M^+), 989.9 ($M^+ - CN^tBu$; 100%), 635.0 ($Ru(CN^tBu)_4$-PPh_2OH), 551.9 ($Ru(CN^tBu)_3PPh_2OH$); IR (Golden Gate) ν (cm^{-1}): 2221.1 (m, C≡N), 2174 (vs, C≡N); Anal. Calc. for $C_{66}H_{70}F_6N_4O_7P_2RuS_2$: C, 57.76; H, 5.14; N, 4.08. Found: C, 57.57; H, 5.22; N, 4.00%.

4.8. Preparation of **10**

Complex **1** (55 mg, 0.052 mmol) was dissolved in 5 ml CH_2Cl_2 and diethylphenylphosphine (50 μl, 0.412 mmol) added. The solution was stirred at r.t. over night, concentrated and C_5H_{12} added resulting in an orange precipitate. This was washed two times with C_5H_{12} (5 ml) and dried. CH_2Cl_2 (5 ml) and triflic acid (28 μl, 0.315 mmol) were added and the solution stirred for 15 min. The solution was concentrated and Et_2O added resulting in a yellow precipitate which was collected via filtration and washed two times with ether to afford **10** as yellow solid. Yield: 40 mg (63%).

^{1}H-NMR (CD_2Cl_2, 500 MHz): 10.83 (d, $^2J_{PH} = 14.9$, O*H*, 1H), 8.56 (d, $^3J_{HH} = 8.3$, H10), 8.25 (t, $^3J_{HH} = 7.8$, H9), 8.19 (d, $^3J_{HH} = 8.3$, H10′), 8.16 (dd, $^3J_{HH} = 9.0$, $^4J_{PH} = 1.8$, H4′), 8.10 (d, $^3J_{HH} = 7.2$, H4), 8.00 (d, $^3J_{HH} = 8.6$, H7′), 7.88 (t, $^3J_{HH} = 7.5$, H9′), 7.76 (m, H7, H8′), 7.51 (t, $^3J_{HH} = 7.3$), 7.48–7.34 (m, 6H), 7.30–7.24 (m, 5H), 7.20–7.12 (m, 4H), 7.06 (dt, $^3J_{HH} = 7.9$, $^4J_{PH} = 2.4$, 2H), 6.98 (dt, $^3J_{HH} = 7.9$, $^4J_{PH} = 2.0$, 2H), 6.93 (br, H6), 6.74 (dd, $^3J_{HH} = 8.1$, $^3J_{PH} = 12.3$, 2H), 6.66 (d, $^3J_{HH} = 8.6$, H7), 6.53 (dd, $^3J_{HH} = 8.1$, $^3J_{PH} =$ 12.1, 2H), 6.48 (m, 2H), 6.10 (m, br, H5), 2.41 (m, CH_2, 2H), 2.13 (m, CH_2, 1H), 2.00 (m, CH_2, 1H), 0.96 (dt, $^3J_{HH} = 7.5$, $^3J_{PH} = 17.6$, CH_3, 3H), 0.86 (dt, $^3J_{HH} = 7.2$, $^3J_{PH} = 15.6$, CH_3, 3H); ^{13}C{^{1}H}-NMR (CD_2Cl_2, 125 MHz): 145.1 (d, $^1J_{CP} = 52$, C6′), 138.8 (d, $^2J_{CP} = 20$, C1′), 138.0 (d, $^1J_{CP} = 59$), 137.2 (C8), 136.0 (C9), 135.0 (d, $^2J_{CP} = 10$), 134.9 (C3′), 133.2 (d, $^2J_{CP} = 10$), 132.7,

132.4, 132.1 (d, $^3J_{CP} = 7$, C4′), 131.7, 131.5 (C2′), 130.8, 130.6 (C9′), 130.3 (d, $^3J_{CP} = 11$), 130.1 (C10), 129.7 (C8′), 129.6 (C5′), 129.5, 129.3 (d, $^3J_{CP} = 11$), 129.2, 129.1 (C10′), 129.0, 125.8 (C7′), 118.5 (br, C1), 116.4 (br, C2), 116.2 (br, C3), 100.4 (C5), 94.7 (d, $J_{CP} = 7$, C4), 90.4 (m, C5), 22.9 (d, $^1J_{CP} = 27$, CH_2), 22.0 (d, $^1J_{CP} = 27$, CH_2), 10.4 (d, $^2J_{CP} = 4$, CH_3), 9.4 (d, $^2J_{CP} = 8$, CH_3); ^{19}F-NMR (CD_2Cl_2, 282 MHz): −79.4; ^{31}P-NMR (CD_2Cl_2, 262 MHz): 116.7 (t, $J_{PP} = 44$), 50.2 (m), 18.6 (m, $PPhEt_2$); Anal. Calc. for $C_{56}H_{49}F_6O_7P_3RuS_2 \cdot CH_2Cl_2$: C, 53.02; H, 3.98. Found: C, 52.95; H, 4.04%. Mass spectroscopy (FAB^+): 907.1, M^+.

4.9. Preparation of **11**

Complex **1** (32 mg, 0.172 mmol) was dissolved in 5 ml CH_2Cl_2 and triethoxyphosphite (30 μl, 0.172 mmol) added. The solution was stirred at r.t. for 3 h, concentrated and the product precipitated and washed with Et_2O. Compound **11** was obtained as a pale yellow solid. Yield: 29 mg (79%).

^{1}H-NMR (CD_2Cl_2, 500 MHz): 10.26 (br, O*H*, 1H), 8.37 (d, $^3J_{HH} = 8.4$), 8.19 (m, 3H), 7.86 (m, 3H), 7.73 (m, 1H), 7.60 (t, $^3J_{HH} = 7.7$, 1H), 7.54 (t, $^3J_{HH} = 8.3$, 1H), 7.50–7.16 (m, 18H), 7.03 (s, br, 1H), 6.83 (dd, $^3J_{PH} = 12.3$, $^3J_{HH} = 8.3$), 6.69 (d, $^3J_{HH} = 8.8$, 1H), 6.25 (s, br, 1H), 4.05 (m, 3H, CH_2), 3.95 (m, 3H, CH_2), 1.21 (t, $^3J_{HH} = 7.0$, 9H, CH_3); ^{13}C{^{1}H}-NMR (CD_2Cl_2, 125 MHz): 145.6 (d, $^1J_{CP} = 51$, C6′), 138.5 (d, $^2J_{CP} = 19$, C1′), 137.0 (C9), 135.3 (d, $^3J_{CP} = 13$), 132.2 (C8), 135.1 (C3′), 133.2 (d, $^2J_{CP} = 11$), 132.4 (C4′), 131.9, 131.4 (d, $^3J_{CP} = 15$, C2′), 130.8 (C10), 130.7 (d, $^2J_{CP} = 11$), 130.4 (C9′), 130.3 (d, $^2J_{CP} = 11$), 129.9 (C8′), 129.3 (C10′), 129.1 (d, $^3J_{CP} = 12$), 128.8, 128.5 (d, $^3J_{CP} = 11$), 125.6 (C7′), 122.3 (br, C1), 115.1 (br, C3), 111.2 (br, C2), 104.8 (C5), 96.7 (C6), 91.1 (C4), 65.9 (d, $^1J_{CP} = 10$, CH_2), 15.3 (d, $^2J_{CP} = 7$, CH_3); ^{19}F-NMR (CD_2Cl_2, 282 MHz): −79.4; ^{31}P-NMR (CD_2Cl_2, 262 MHz): 119.0 (m, br, $P(OEt_3)$), 116.0 (m, br), 53.1 (m, br); Anal. Calc. for: $C_{52}H_{49}F_6O_{10}P_3RuS_2$: C, 51.79; H, 4.09. Found: C, 51.85; H, 4.29%. Mass spectroscopy (FAB^+): 907.1, M^+.

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