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Very Strong Trans Effect in Ruthenacyclic Carbamoyl Complexes Leads to Ligand Redistribution in Phosphine Derivatives

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Abstract: The ruthenacyclic carbamoyl complexes $[\text{Ru}(2\text{-NHC}(\text{O})\text{C}_5\text{H}_4\text{N})(\text{CO})_2(\text{X})(\text{NCMe})]$ ($\text{X} = \text{Cl}, \text{Br}$) (**1**) and $[\text{Ru}(2\text{-NHC}(\text{O})\text{C}_5\text{H}_4\text{N})(\text{CO})_2(2\text{-S-Py})]$ (**2**) undergo substitution reactions with organophosphines to afford derivatives which are prone to a redistribution of the phosphine ligand. We have studied these redistribution reactions experimentally and computationally, and proposed an essentially common reaction pathway. The results suggest that the carbamoyl ligand exerts a very strong trans effect.

Keywords: ruthenium; carbamoyl; hydrogenase; phosphine; ligand redistribution; trans effect

1. Introduction

The hydrogenases continue to be of interest because of their relevance to the hydrogen economy, and the most recently discovered [Fe]-hydrogenase (type III hydrogenase) contains a redox-inactive iron cofactor (Figure 1a) [1-7]. A large variety of iron-based model complexes for the metal cofactor have been reported [8-18], including some which mimic the function of the natural enzyme [19-22]. Since ruthenium complexes are known to catalyse a wide variety of reactions that utilise or involve hydrogen or hydrogenation [23-25], we thought that it made sense to also examine ruthenium-based structural mimics such as **1** and **2** (Figure 1b), which we have reported earlier [26-28].

Figure 1. Structure of (a) the active site of [Fe]-hydrogenase, and (b) ruthenacyclic carbamoyl complexes in this study.

In what appeared to be a straightforward study, we looked at the reactivity of the complexes **1/1'** and **2** with phosphine ligands as a general assessment of their chemical reactivity. What we found was that these derivatives were not very stable towards ligand redistribution. This is somewhat surprising as the Ru-P bond is typically fairly strong. The results of our investigations are reported here.

2. Results and discussion

The ruthenacyclic carbamoyl complex **1**, which exists as an ~1:1 mixture of two isomers in solution [26], undergoes rapid substitution of the acetonitrile ligand with triphenylphosphine at ambient temperature to afford the monosubstituted product **3a**. The latter undergoes a redistribution of the phosphine ligand in solution, slowly, to re-form **1** and the disubstituted derivative **4a** (Scheme 1). Adding one equivalent of the phosphine to **3a** gives **4a** only (Figure S6). Similar observations are made with PMe_3 , which gives **3b** and then **4b**, and the chloro analogue **1'** which gives **4a'** with PPh_3 ; complex **1'** also exists as a mixture of two isomers (from its IR spectrum) [26].

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Scheme 1. Formation and ligand redistribution of the phosphine derivatives **3**.

Although a number of studies have shown that ruthenium complexes containing a four-membered metalla-heterocyclic ring are unexpectedly stable [28,29], the complex **2**, which contains a chelating N,S-donor ligand [27], shows similar behaviour as **1** (Scheme 2). Thus, its reactions with one and two equivalents of PMe_3 are instantaneous and give the mono- and di-adducts **3b''** and **4b''**, respectively, via opening of the four-membered metalla-heterocyclic ring at the nitrogen atom; the analogous reaction with $\text{P}(\text{n-Bu})_3$, however, does require more forcing conditions (75°C). On standing in solution, **3b''** is converted to **5**, the mono-substituted phosphine derivative of **2**. On the other hand, it reacts with another equivalent of PMe_3 to afford **4b''**.

Scheme 2. Reaction of complex **2** with organophosphines.

2.1. Crystallographic discussion

The X-ray crystal structural determination of **3b** has been reported previously [28], and those for **3a**, **3b''**, **4a**, **4a'**, **4b''**, **4c''** and **5** are reported here. The ORTEP plots illustrating the molecular structures of **3b''**, **4b''** and **5** are given in Figure 2, and selected bond parameters together with a common atomic labelling scheme for all these complexes are collected in Table 1.

The strong *trans* influence of the carbamoyl group is clearly manifested in the elongated Ru-P bond lengths in the complexes **3** (range: 2.4762(14) - 2.423(3) Å) compared to those for the complexes **4** and **5** (range: 2.3814(13) - 2.2963(10) Å) and the closely related analogues $[\text{RuCl}(\text{CO})(\text{PCy}_3)[\eta^2\text{-(CH}_2\text{-C}_6\text{H}_2\text{Me}_2\text{)-(N}_2\text{C}_3\text{H}_4\text{)(C}_6\text{H}_2\text{Me}_3)]$ and $[\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2]$ (2.306(1)-2.410(1) Å) [30,31]. The Ru-Br bond in **4a** (2.6631(6) Å) is similarly lengthened in comparison with those in **3a** and **3b** (2.5423(8) and 2.5888(4) Å, respectively), and also demonstrates that the carbamoyl has a stronger *trans* influence than the carbonyl ligand [27].

Figure 2. ORTEP plots of **3b''** (top left), **4b''** (top right) and **5** (bottom). All the hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Common atomic labelling scheme and selected bond parameters for complexes **3-5**.

Complex	3a [†]	3b ^{††}	3b ^{‡, #}	4a	4a'	4b [‡]	4c [‡]	5
	X = Br; L = PPh ₃	X = Br; L = PMe ₃	X = SPy; L = PMe ₃	X = Br; L = PPh ₃	X = Cl; L = PPh ₃	X = SPy; L = PMe ₃	X = SPy; L = P ⁿ Bu ₃	X = S; N L = PMe ₃
<i>Bond length (Å)</i>								
Ru-N	2.144(5)	2.121(2)	2.149(7); 2.136(7)	2.151(4)	2.146(3)	2.132(3)	2.144(2)	2.130(3)
Ru-C _{amide}	2.067(6)	2.076(3)	2.050(10); 2.062(10)	2.005(5)	2.008(4)	2.016(4)	2.033(3)	2.008(4)
Ru-X	2.5423(8)	2.5888(4)	2.435(3); 2.447(3)	2.6631(6)	2.5078(10)	2.4981(10)	2.4984(8)	2.5512(10) (X = S); 2.126(3) (X = N)
Ru-L	2.4762(14)	2.4251(8)	2.423(3); 2.432(3)	2.3790(13), 2.3814(13)	2.3710(11), 2.3769(11)	2.3438(11), 2.3481(11)	2.3645(9), 2.3714(9)	2.2963(10)
Ru-C(1)	1.893(7)	1.887(3)	1.879(11); 1.866(11)	1.852(5)	1.844(4)	1.852(4)	1.857(3)	1.834(4)
Ru-C(2)	1.932(7)	1.880(3)	1.878(11); 1.874(10)	-	-	-	-	-
<i>Bond angle (°)</i>								
N-Ru-X	87.50(13)	90.91(7)	81.6(2); 82.6(2)	89.05(11)	87.48(9)	90.33(9)	89.36(7)	91.83(8) (X = S); 87.10(12) (X = N)
N-Ru-L	99.34(14)	96.45(7)	97.0 (2); 97.8(2)	89.05(11)	87.48(9)	90.33(9)	89.36(7)	91.55(9)
L-Ru-X	91.49(4)	88.20(2)	91.90(9); 93.59(9)	87.93(3), 89.95(4)	85.88(4), 88.72(4)	86.15(4), 91.96(4)	87.85(3), 86.23(3)	104.09(3) (X = S); 170.02(9) (X = N)

[†]Exhibits twinning. ^{††}From reference [21]. [#]Two crystallographically independent molecules. SPy = 2-pyridylthiolate.

2.2. Monitoring the ligand redistribution reaction

Monitoring the redistribution of the phosphine ligands in **3a** by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy shows that the resonance due to **3a** (10.4 ppm), and of a small amount of free PPh_3 (-5.0 ppm) [32], decrease in intensities over time and disappear after about 12 h; the resonance for **4a** (32.4 ppm) emerges over that same period of time (Figure 3).

Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (CD_3CN , RT) showing the phosphine ligand redistribution in **3a**.

A similar monitoring by IR spectroscopy shows a slight red-shift in the carbonyl vibrations of **3a** (2058 and 1988 cm^{-1} to 2060 and 1989 cm^{-1}) after 3 h and finally to a mixture of **1** (2062, 1999 and 1989 cm^{-1}) and **4a** (1949 cm^{-1}) after 12 h (Figure S7); another minor species **B** (2044 and 1970 cm^{-1}) is also observed in the final spectrum. A similar study carried out on **3b** shows that it reacts similarly but at a much slower rate (Figure S8), consistent with the expected greater stability of the Ru-PMe_3 bond compared to the Ru-PPh_3 bond. The changes observed with **3b''** are more complex; a species **C** (2032 and 1961 cm^{-1}) appears at 0.5 h but by day 2, another species (2048 and 1982 cm^{-1}) is formed together with a minor amount of **5** (1949 cm^{-1})

(Figure S9). The final spectrum on day 10 shows mainly **5**, and a minor species (2050 and 1984 cm^{-1}) which can be identified as an isomer (*isomer 2*) of **2** in which the S and N atom positions are interchanged [27].

For both **3b** and **3b''**, the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra also suggest the presence of a transient species; standing solutions of these (5 and 10 d, respectively) show new sets of peaks in the ^1H NMR spectra (Figures S10-11), and a ^{31}P resonance (at -9.11 and -7.23 ppm, in **3b** and **3b''**, respectively) (Figures S12-13).

Figure 4. ORTEP plot of **3b** (*isomer 2*). All hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): $\text{Ru-N} = 2.132(4)$, $\text{Ru-C1} = 1.867(5)$, $\text{Ru-C2} = 1.939(5)$, $\text{Ru-C3} = 2.012(5)$, $\text{Ru-Br} = 2.6163(6)$, $\text{Ru-P} = 2.3808(13)$, $\text{N-Ru-Br} = 93.73(10)$, $\text{N-Ru-P} = 89.29(10)$, $\text{Br-Ru-P} = 87.16(4)$.

With careful examination of the spectra, coupled with comparisons made among the three sets of reactions and with values obtained from a computational study (Table S4), we have tentatively identified the CO stretches at 2060 and 1989 cm^{-1} for **3a**, and 2048 and 1982 cm^{-1} for **3b''**, as a second isomer (*isomer 2*) for these complexes. These values are only slightly red-shifted from that of the corresponding *isomer 1*, and are consistent with the

An intriguing aspect concerns the isomerization of **3**. Although it is possible for this to proceed via a non-dissociative pathway such as a Ray-Dutt twist [27], the ligand redistribution observed indicates detachment of the phosphine and hence the

formation of a 16-electron species **A**. In solution, and especially in a coordinating solvent such as MeCN, solvent coordination to form **1** is expected. A dissociative isomerization of **1** and **3** via **A** (or the corresponding **A''** for **3b''**) has been examined computationally (Figures 5 and S14).

Optimization starting from a geometry corresponding to removal of the ligand L from either *isomer 1* or *isomer 2* (of **1** or **3**), or from a trigonal bipyramidal geometry, leads invariably to an approximately square pyramidal geometry for **A** (Figure 6); this geometry has already been observed for the corresponding iron analogue [Fe(2-CH₂C(O)C₅H₃N-6-OMe)(CO)₂(SC₆H₃-2,6-Me₂)] [34]. Presumably, the carbamoyl group exerts a strong *trans* effect and labilises the ligand *trans* to it. The corresponding *trans* influence is apparent in the computed Wiberg bond index for the Ru-P bonds of the complexes **3**; they are smaller for *isomer 1* in which this bond is *trans* to the carbamoyl group (~0.3 and ~0.4, respectively, for the two isomers; Table S5).

Figure 6. Computationally-optimized structure of **A**, together with selected bond parameters.

The free energy changes to **A** approximate to the kinetic barriers for the isomerization and, as depicted, suggests that direct isomerization of **3** is not favourable. This accounts for the presence of **1** in the ligand redistribution of **3a**; isomerization of

the latter proceeds via ligand displacement to form the former. This is also consistent with observations that ligand redistribution in **3b** and **3b''** are significantly slower than **3a**; the barrier, which corresponds to loss of the ligand L, is 64, 101 and 36 kJ mol⁻¹, respectively.

As indicated above, the transient species **B** has been observed for both **3a** and **3b**; its IR spectrum is red shifted from that of **3a** and **3b**, and there is no corresponding resonance in the ³¹P NMR spectrum, suggesting that it does not contain a phosphine ligand. We have tentatively assigned it to a dimeric species with two bridging bromide ligands, *viz.*, [Ru(μ-Br)(2-NHC(O)C₅H₄N)(CO)₂]₂, which may be thought of as having been formed through **A**; the red-shift in the IR values are consistent with that reported earlier for the dimeric compound [Ru(2-NHC(O)C₅H₄N)(SC₆H₄Me)(CO)₂]₂ [26]. Similarly, the transient species **C** observed for **3b''** may be assigned to a dimer of **A''**, *viz.*, [Ru(μ-2-S-C₅H₄N)(2-NHC(O)C₅H₄N)(CO)₂]₂, bridged by two sulphur atoms of the mercaptopyridine ligand; this is similar to that reported for the iron analogue [Fe(μ-2-S-C₅H₃N-6-Me)(COMe)₂(CO)₂]₂ [10].

2.4. Halide abstraction reactions

All the above reactions involve displacement of neutral, 2-electron donor ligands. The complexes **1** can, however, also undergo halide abstraction with silver triflate to form the ionic complexes **6**; subsequent reaction with trimethyl phosphine afford the mono- or di-substituted derivatives **7** and **8** (Scheme 4).

Scheme 4. Halide abstraction in **1/1*** and subsequent reaction with PMe₃.

Both **8** and **8*** have been characterized crystallographically; an ORTEP plot showing the molecular structure of **8***, together with selected bond parameters, is given in Figure 7.

Figure 7. ORTEP plot of the cationic fragment of complex **8***. All the hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Ru–N = 2.170(2), Ru–P1 = 2.4894(8), Ru–P2 = 2.3973(8), Ru–C1 = 1.882(3), Ru–C2 = 1.942(3), Ru–C3 = 2.073(3), C3–Ru–N = 77.70(11), C3–Ru–C1 = 89.45(13), N–Ru–P1 = 103.99(7).

3. Conclusion

In this work, we described the reactivity of two classes of ruthenacyclic carbamoyl complexes with phosphine ligands. The resulting monosubstituted derivatives were found to undergo redistribution of the phosphine ligand and we were able to propose an essentially common reaction pathway for both systems, i.e., via a 16-electron, square pyramidal complex. Examination of the structural parameters of the products, as well as the ligand redistribution pathway, pointed to the very strong *trans* effect/influence of the carbamoyl moiety as the primary factor accounting for the observed reactivity.

4. Experimental

4.1. General procedures

All experiments were performed under an argon atmosphere using standard Schlenk techniques. Chemicals were obtained from Sigma Aldrich and were used as received. The compounds **1**, **2** and **3b** were synthesized following literature procedures [26–28]. Solvents that were used for reactions were distilled over the appropriate drying agents under argon before use. TLC separations were carried out on 20 x 20 cm² plates coated with silica gel 60 F254 from Merck. HRMS were recorded in ESI mode on a Waters UPLC-Q-ToF MS mass spectrometer. ¹H and ¹³C{¹H} NMR spectra were obtained on a JEOL 400 MHz spectrometer at room temperature unless stated otherwise. Chemical shifts for ¹H and ¹³C{¹H} were referenced with respect to the residual resonances of the respective deuterated solvents. Infrared spectra were recorded as acetonitrile solutions, unless stated otherwise, on a Bruker Alpha FT-IR spectrometer in an IR cell with NaCl windows and a path length of 0.1 mm at a resolution of 2 cm^{−1}. Elemental analyses were performed on a PerkinElmer 2400 Series II CHN/O Elemental Analyzer in house.

4.2. Preparation of [RuCl(2-NHC(O)C₅H₄N)(CO)₂(MeCN)] (**1'**)

PhICl₂ (116 mg, 0.42 mmol) was added into a solution of Ru₃(CO)₁₂ (90 mg, 0.14 mmol) in dichloromethane (5 mL) at 0 °C. The resulting mixture was then stirred for 1 h at 0 °C. A sample of 2-aminopyridine (40 mg, 0.42 mmol) was added into the above mixture, and the resulting mixture was left to stir for another 30 min at the same temperature. The mixture was warmed up to room temperature and subsequently left to stir for 3 h at ambient temperature, which gave a white precipitate within few minutes. The white precipitate was separated via filtration and washed with dichloromethane (30 mL) followed by hexane (20 mL). The white residue was then dissolved in acetonitrile (30 mL) and slow evaporation of the solvent at room temperature

yielded white crystalline powder of **1'** (90 mg, 250 μ mol, 60%). IR (acetonitrile, cm^{-1}): ν_{CO} 2061s, 1999m, 1987s; $\nu_{\text{C=O}}$ 1620s. HRMS (m/z): 355.9373, calculated for $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_3\text{Cl}^{102}\text{Ru}$ $[\text{M}+\text{H}]^+$: 355.9376.

4.3. Preparation of $[\text{RuBr}(2\text{-NHC}(\text{O})\text{C}_5\text{H}_3\text{NNH}_2)(\text{CO})_2(\text{MeCN})]$ (**1***)

A solution of $\text{Ru}(\text{CO})_4\text{Br}_2$ (200 mg, 0.53 mmol) and 2,6-diaminopyridine (118 mg, 1.08 mmol) in dichloromethane (30 mL) were stirred for 3 h at room temperature, which gave a white precipitate within few minutes. The white precipitate was separated via filtration and washed with hexane (50 mL) followed by dichloromethane (100 mL). The white residue was then dissolved in acetonitrile (50 mL) and slow evaporation of the solvent at room temperature afforded analytical pure **1*** (150 mg, 360 μ mol, 68%). IR (acetonitrile, cm^{-1}): ν_{CO} 2066s, 2003s; $\nu_{\text{C=O}}$ 1622m. HRMS (m/z): 416.8985, calculated for $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_3\text{Br}^{104}\text{Ru}$ $[\text{M}+\text{H}]^+$: 416.8990.

4.4. Preparation of $[\text{RuBr}(2\text{-NHC}(\text{O})\text{C}_5\text{H}_4\text{N})(\text{CO})_2(\text{PPh}_3)]$ (**3a**)

A sample of PPh_3 (7 mg, 0.03 mmol) in hexane (2 mL) was added into a solution of **1** (10 mg, 0.03 mmol) in acetonitrile (5 mL). The resulting mixture was then kept at ambient temperature for 1 d. Slow evaporation of the solvent afforded **3a** (13 mg, 20 μ mol, 68%) as white crystals. IR (acetonitrile, cm^{-1}): ν_{CO} 2058vs, 1988s, $\nu_{\text{C=O}}$ 1642s. ^1H NMR (400 MHz, CDCl_3): δ 8.91 (d, 1H, $^3J_{\text{HH}} = 6.8$ Hz, 6-H(Py)), 7.85-7.63 (m, 7H, 4-H(Py) and Ph), 7.46-7.40 (m, 9H, Ph), 7.04 (d, 1H, $^3J_{\text{HH}} = 7.0$ Hz, 3-H(Py)), 6.53 (t, 1H, $^3J_{\text{HH}} = 7.3$ Hz, 5-H(Py)) ppm. ^{31}P NMR (400 MHz, CDCl_3): δ 10.41 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ 158.2, 150.5, 140.9, 134.0, 133.9, 133.5, 133.2, 130.6, 128.8, 128.7, 115.8, 110.2 ppm. HRMS (m/z): 622.9545, calculated for $\text{C}_{26}\text{H}_{21}\text{N}_2\text{O}_3\text{PBr}^{104}\text{Ru}$ $[\text{M}+\text{H}]^+$: 622.9527. Anal. Calculated for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_3\text{BrPRu.C}_2\text{H}_3\text{N}$: C 50.84, H 3.50, N 6.35. Found C 51.03, H 2.82, N 6.26.

4.5. Decomposition of $[\text{RuBr}(2\text{-NHC}(\text{O})\text{C}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)_2]$ (**4a**)

A sample of **3a** (20 mg, 0.05 mmol) was stirred for 3 d at ambient temperature in acetonitrile (5 mL). The mixture was then filtered and evaporated the filtrate in vacuum. The residue was separated by column chromatography on silica gel with dichloromethane/ethyl acetate ($v/v = 8/2$) as eluent to afford **4a** (10 mg, 10 μ mol, 45%) as white crystalline powder. IR (acetonitrile, cm^{-1}): ν_{CO} 1949s, $\nu_{\text{C=O}}$ 1633s. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.62 (d, 1H, $^3J_{\text{HH}} = 7.3$ Hz, 6-H(Py)), 7.53-7.45 (m, 12H, Ph), 7.33-7.18 (m, 19H, 4-H(Py) and Ph), 6.40 (d, 1H, $^3J_{\text{HH}} = 8.0$ Hz, 3-H(Py)), 5.88 (t, 1H, $^3J_{\text{HH}} = 6.8$ Hz, 5-H(Py)) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): δ 166.0, 155.2, 149.8, 137.8, 135.1, 134.2, 132.2, 132.5, 129.9, 129.6, 127.8, 127.7, 116.1, 106.5 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3): δ 33.44 ppm. HRMS (m/z): 855.0441, calculated for $\text{C}_{43}\text{H}_{36}\text{N}_2\text{O}_2\text{P}_2\text{Br}^{102}\text{Ru}$ $[\text{M}+\text{H}]^+$: 855.0479.

4.6. Preparation of $[\text{Ru}(2\text{-NHC}(\text{O})\text{C}_5\text{H}_4\text{N})(\text{CO})_2(\text{MeCN})_2]\text{OTf}$ (**6**).

A sample of silver triflate (13 mg, 0.05 mmol) was added into a solution of **1** (18 mg, 0.05 mmol) in acetonitrile (5 mL). The resulting mixture was then stirred for 30 min at ambient temperature. The mixture was filtered, and slow evaporation of the solvent afforded **6** (21 mg, 40 μ mol, 84%) as white powder. IR (acetonitrile, cm^{-1}): ν_{CO} 2083s, 2023s, $\nu_{\text{C=O}}$ 1680s. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 9.83 (br, 1H, NH), 8.44 (d, 1H, $^3J_{\text{HH}} = 5.5$ Hz, 6-H(Py)), 8.03 (t, 1H, $^3J_{\text{HH}} = 7.3$ Hz, 4-H(Py)), 7.28 (d, 1H, $^3J_{\text{HH}} = 8.0$ Hz, 3-H(Py)), 7.22 (t, 1H, $^3J_{\text{HH}} = 6.0$ Hz, 5-H(Py)) ppm. HRMS (m/z): 360.9908, calculated for $\text{C}_{12}\text{H}_{11}\text{N}_4\text{O}_3^{102}\text{Ru}$ $[\text{M}]^+$: 360.9875.

4.7. Preparation of $[\text{Ru}(2\text{-NHC}(\text{O})\text{C}_5\text{H}_4\text{N})(\text{CO})_2(\text{PMe}_3)(\text{NCMe})]\text{OTf}$ (**7**)

A sample of silver triflate (13 mg, 0.05 mmol) was added into a solution of **1** (18 mg, 0.05 mmol) in acetonitrile (5 mL). The resulting mixture was then stirred for 30 min at ambient temperature. The

resulting mixture was then filtered and trimethyl phosphine (2.5 μ L, 0.05 mmol) was added into the filtrate. The resulting mixture was stirred for 1 h at ambient temperature. The solvent was then concentrated to 2 mL under vacuum and left at room temperature, which afforded **7** (22 mg, 40 mmol, 76%) as white powder. IR (acetonitrile, cm^{-1}): ν_{CO} 2074s, 2017s, $\nu_{\text{C=O}}$ 1633s. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 10.00 (br, 1H, NH), 8.33 (d, 1H, $^3J_{\text{HH}} = 6.0$ Hz, 6-H(Py)), 8.03 (t, 1H, $^3J_{\text{HH}} = 8.2$ Hz, 4-H(Py)), 7.33 (d, 1H, $^3J_{\text{HH}} = 7.8$ Hz, 3-H(Py)), 7.18 (t, 1H, $^3J_{\text{HH}} = 6.0$ Hz, 5-H(Py)), 1.85 (d, 1H, $^3J_{\text{PH}} = 8.7$ Hz, Me) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): -23.8 ppm. HRMS (m/z): 396.0035, calculated for $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_3\text{P}^{102}\text{Ru} [\text{M}]^+$: 396.0051.

4.8. Crystallographic studies

Diffraction-quality crystals were grown from acetonitrile (**3a** and **4a'**), dichloromethane/hexane (**3b** (*isomer 2*), **4b''**, **4c''**, **5**, **8** and **8***), methanol (**3b''**), or chloroform/hexane (**4a**), and mounted on quartz fibers. X-ray diffraction data were collected at 103(2) K on a Bruker X8 APEX system, using Cu (**3a** and **3b''**) or Mo (the rest) $\text{K}\alpha$ radiation, with the SMART suite of programs [35]. Data processing and correction were made for Lorentz and polarization effects with SAINT [36], and for adsorption effects with SADABS [37]. Twinning was observed for the crystals of **3a** and **3b''**; the twin laws and cell parameters were determined using the program CELL_NOW [38], and the reflection data processed, and corrections applied using the program TWINABS [39]. All the structural solution and refinement were carried out with the SHELXTL suite of programs [40]. The structures were solved by direct methods to locate the heavy atoms, followed by successive difference maps for the light, non-hydrogen atoms.

Solvates were found in **3a** (MeCN), **3b''** (2xMeOH), **4a** (1.25 CHCl_3 and 0.25 hexane), **4a'** (2 x MeCN), **4b''** (0.2 CH_2Cl_2) and **5** ($\frac{1}{2}$ CH_2Cl_2); with for **4a**, **4b''** and **5** were disordered. Two of the phenyl rings in **4a** were also disordered; each were

modelled with two sites, one with equal occupancies and the other with occupancies summed to unity. Appropriate restraints were placed on all disordered parts. All non-hydrogen atoms were refined with anisotropic displacement parameters in the final model. All the organic hydrogen atoms were placed in calculated positions and refined with a riding model. The crystallographic data are summarized in Tables S6-8.

4.9. Computational studies

The computational studies were carried out using density function theory (DFT), utilizing the hybrid functional of Truhlar and Zhao (M06) [41]. The basis set used was def2TZVP for ruthenium [42], and 6-311+G(2d, p) for the other atoms. The polarized continuum model (PCM) was employed to describe solvated species in acetonitrile. Spin-restricted calculations were used for structural optimization, harmonic frequency calculations and to evaluate zero-point energy (ZPE) corrections. Optimized geometries were characterized as equilibrium structures with all real frequencies. All calculations were performed using the Gaussian 09 suite of programs [43].

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Appendix A. Supplementary data

Experimental and characterisation data for all other derivatives reported, and details of spectroscopic and computational studies. CCDC 1866653-61 and 1872885 contain the supplementary crystallographic data for the structures reported. These are available from the Cambridge Crystallographic Data Centre. Crystallographic tables, and optimized geometry of

computed structures containing supporting information is available free of charge via the internet.

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