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Some binding modes of 2-aminopyridine to ruthenium(II) fragments

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The bonding modes of 2-aminopyridine (apy) (1 equiv.) with some ruthenium(II) fragments were studied. In the reaction with $[RuCp(CH_3CN)_3]^+$ (**1**) one acetonitrile ligand is replaced with apy being κ^1(N-pyridine) bonded. This complex is very air-sensitive transforming into dinuclear $[RuCp(\mu^3\text{-dapy})]_2^{2+}$ where dapy is deprotonated apy. On the other hand, $[RuCl_2(PPh_3)_3]$ exchanges one phosphine ligand for apy which is coordinated in the κ^2N,N' mode. Similar to **1**, the complexes $[RuCp(CH_3CN)_2L]^+$(L = PMe_3, PPh_3 or CO), also react with apy to give $[RuCp(CH_3CN)(L)(\kappa^1N\text{-apy})]^+$. These compounds were reacted with HC≡CPh with appreciable differences depending on L. While with L = CH_3CN no clean reaction took place, with L = PMe_3 an η^3-allyl carbene is formed with release of apy. With L = PPh_3 or CO, dapy stabilizes a Fischer carbene through chelation. Finally, if **1** is reacted with 2-*N*,*N*-dimethylaminopyridine (dmapy), all acetonitriles are displaced in favor of η^6-coordinated dmapy.

Introduction

The use of chelating ligands which form four-membered and thus strained ring systems is a promising route for creating vacant coordination sites in transition metal complexes where substrates can be attached for further conversions. One such an example is 2-aminopyridine (apy) (Chart 1, **A**) which is able to undergo facile opening of the strained M–N–C–N ring at the M–NH_2 bond allowing, for instance, coordination of alkynes to yield vinylidene and cyclic aminocarbenes.[1,2] Because of lesser strain five-membered rings are typically more favored.[3] This is also effected by bridging two metal centers, with or without an additional metal–metal bond (**B**, **B′**).[1,4] Interestingly, complexes with κ^2N,N' four-membered ring systems with apy have so far been hypothesized only as putative intermediates, while complexes containing a deprotonated apy are very common.[5,6] Chelate formation, however, is not the only way conceivable for binding apy to a metal fragment. Some possible structural types of the coordination modes of apy are summarized in Chart 1.

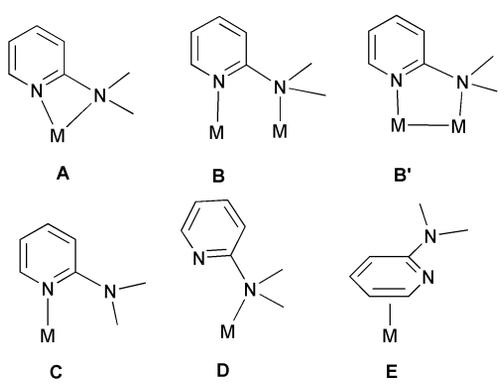

Chart 1

N(κ^1)-bonding (**C**) occurs typically *via* the pyridine nitrogen and happens particularly if the metal fragment is reluctant to accept six electrons resulting from π coordination. A typical example is provided by some planar platinum(II) complexes.[7] On the other hand, N(κ^1)-bonding *via* the weaker amine nitrogen (**D**) is rather exceptional and may occur only if coordination at the pyridine N-donor site is not feasible for steric reasons. Finally, while π-pyridine complexes are known for parent pyridine and some of its derivatives,[8,9] those of apy (**E**) to our knowledge remain still unknown.

In the context of these varied bonding properties of apy, we investigate in the present work the ways in which apy interacts with $[RuCp(CH_3CN)_3]PF_6$ (**1**) as the starting material and derivatives thereof in which one acetonitrile ligand is replaced with PMe_3 (**2a**), PPh_3 (**2b**) or CO (**3**). In addition, $[RuCl_2(PPh_3)_3]$ is investigated. This topic, while interesting by itself, may aid in better understanding the behavior of apy complexes in catalytic conversions. It may be worthwhile to emphasize the distinct chemical nature of the three nitrogen atoms involved, *viz*. the sp-N of CH_3CN, the sp^2-N of pyridine and the sp^3/sp^2-N of the amine group.

Results and discussion

Treatment of **1** with apy (1 equiv.) results in the formation of $[RuCp(\kappa^1N\text{-apy})(CH_3CN)_2]PF_6$ (**5a**) in 76% isolated yield, which from ^{1}H and $^{13}C\{^1H\}$ NMR and elemental data is clearly κ^1N(py) bound rather than κ^2N,N' (Scheme 1). This complex is very air-sensitive both in solution and in the solid state (see below). The finding that only one apy ligand is attached is noteworthy since in using parent pyridine under otherwise the same conditions, mixtures of $[RuCp(py)_n(CH_3CN)_{3-n}]^+$ (n = 1–3) are obtained. On the other hand, the mono-pyridine complex could be isolated using 2-methylpyridine (and others).[10] As claimed by Fish *et al*., this indicates that steric crowding around nitrogen impedes N-bonding. In fact, with 2,4,6-trimethylpyridine only the π-bonded complex is provided. Similarly, $[RuCp(2\text{-Mepy})(CH_3CN)_2]^+$ is prone to release the acetonitriles to give, in an N to π rearrangement, $[RuCp(\eta^6\text{-2-Mepy})]^+$.

This feature is also observed in the present work. Thus, if **1** is reacted with the bulkier 2-*N*,*N*-dimethylaminopyridine (dmapy), $[RuCp(\eta^6\text{-dmapy})]PF_6$ (**9**) is obtained (Scheme 2). The formulation was verified by a combination of elemental analysis, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. Furthermore, a single-crystal X-ray analysis revealed the structure which is illustrated in Fig. 1 with selected bond distances reported in the figure legend. To the best of our knowledge, this appears to be the first structurally characterized example of a ruthenium complex featuring an η^6-coordinated pyridine (and apy) ligand. In view of the literature[11,12] it did not come as a surprise that the η^6-coordinated dmapy ligand is not planar but displays a

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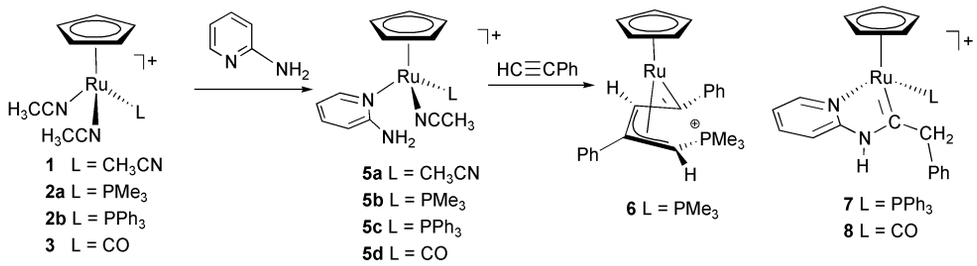


Scheme 1

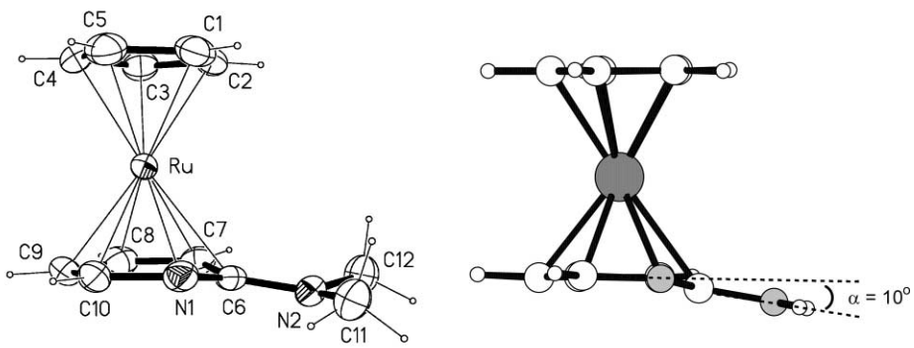
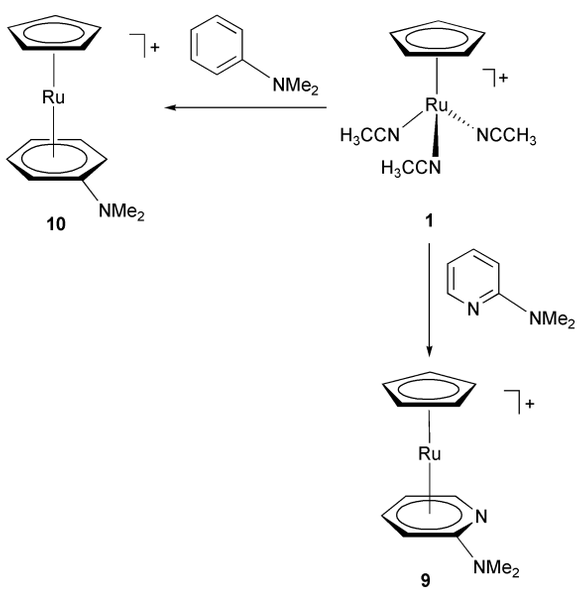


Fig. 1 (Left) Structural view of $[RuCp(\eta^6\text{-dmapy})]PF_6$ (**9**) showing 50% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths (Å): Ru–C(1–5)$_{av}$ 2.179(2), Ru–C(6) 2.350(2), Ru–C(7) 2.202(2), Ru–C(8) 2.195(2), Ru–C(9) 2.214(2), Ru–C(10) 2.179(2), Ru–N(1) 2.228(2), C(6)–C(7) 1.430(3), C(6)–N(1) 1.382(2), C(6)–N(2) 1.335(2), C(10)–N(1) 1.377(3), C(11)–N(2) 1.454(3), C(12)–N(2) 1.460(3). (Right) Optimized DFT/B3LYP geometry of $[RuCp(\eta^6\text{-}NC_5H_4NH_2)]^+$.



Scheme 2

significant shift of the *ipso*-carbon bearing the NMe_2 substituent out of the mean aromatic plane away from the CpRu fragment by 0.181(3) Å equivalent to 15° folding of the ring (angle between the planar part of the pyridine ligand and the N(1)–C(7)–C(6)–N(2) plane is 11.5(2)°, see Fig. 1). A reasonable explanation is that the surplus of π electron density arising from the π-donor substituent NR_2 becomes less intense by this kind of distortion. For comparison purposes, we also prepared the analogous ruthenium *N*,*N*-dimethylaniline complex $[RuCp(\eta^6\text{-}C_6H_5NMe_2)]PF_6$ (**10**) according to Scheme 2. The structure as determined by X-ray crystallography, is shown in Fig. 2. It also reveals a pronounced folding of the arene ring with C6 bent away from the RuCp unit by 0.125(3)° equivalent to a 10° folding of the ring (angle between the planar part of the phenyl ligand and C(7)–C(11)–C(6)–N(1) plane measures 6.4(2)°, see Fig. 2). Additional support for the supposition that the bending in this case is purely electronic in nature and not a packing effect stems from DFT/B3LYP calculations on the model complexes $[RuCp(\eta^6\text{-}NC_5H_4NH_2)]^+$ and $[RuCp(\eta^6\text{-}C_6H_5NH_2)]^+$. The optimized structures of these complexes are shown in Figs. 1 and 2. In agreement with the X-ray structural data, both the $\eta^6\text{-}NC_5H_4NH_2$ and $\eta^6\text{-}C_6H_5NH_2$ rings were calculated to be bent, by about 10 and 8°, respectively, in excellent agreement with experimental data.

To study the effect of co-ligands we also reacted apy with $[RuCp(CH_3CN)_2L]PF_6$, where L = PMe_3 (**2a**), PPh_3, (**2b**) or CO (**3**). In all these cases we obtained the complexes $[RuCp(CH_3CN)(L)(\kappa^1N\text{-apy})]^+$ (**5b**–**d**) in high yields, in full conformity with **1** (Scheme 1). Dramatic differences, however, are observed upon the onward reaction with the alkyne HC≡CPh. While with **5a** no clean reaction took place with a complex mixture of organic products found, with **5b** the known η^3-allyl carbene complex $[RuCp(=C(Ph)(\eta^3\text{-}CHC(Ph)CHPMe_3)]PF_6$ (**6**) was obtained following release of apy (Scheme 1). Mechanistic aspects of this conversion have been discussed previously.[13] With **5c** and **5d**, on the other hand, the cyclic amino carbenes $[RuCp(PPh_3)(=C(CH_2)PhNH\text{-}py)]PF_6$ (**7**) and $[RuCp(CO)(=C(CH_2)PhNHpy)]PF_6$ (**8**) were afforded in 78 and 84% isolated yields, respectively. Thus, apy remains in the complex and upon deprotonation stabilizes a Fischer carbene through chelation. Despite the fact that no vinylidene intermediates could be observed, such species are most likely key intermediates on the way to aminocarbene complexes as outlined already recently.[1,14]

The carbene complexes are air-stable both in solution and in the solid state and were characterized by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis. In the $^{13}C\{^1H\}$ NMR spectra of **7** and **8** the carbene moiety is identified by downfield signals at 275.7 and 275.9 ppm.[14] Other spectral changes accompanying the transformation to amino carbene complexes include, for **7**, a characteristic broad resonance at 12.09 ppm assignable to the NH proton. For **8**, we were unable to locate the NH proton.

As mentioned above, **5a** is not air-stable. Upon exposure to air, the yellow solution of **5a** in acetone rapidly turned dark green. NMR monitoring revealed the formation of a diamagnetic species which after work-up was isolated in 84% yield

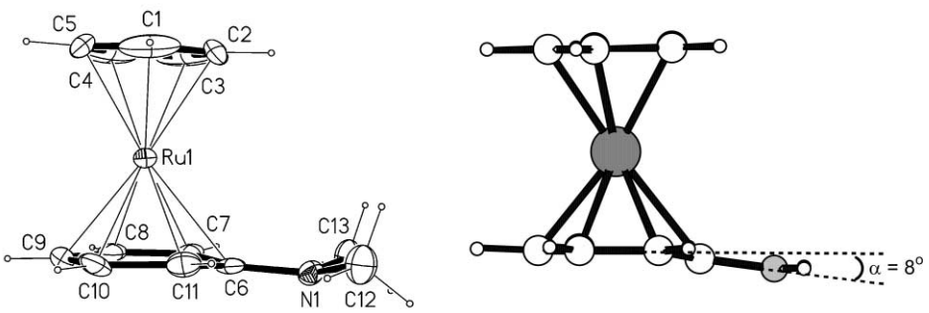
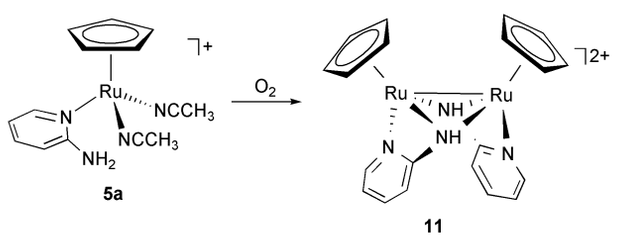


Fig. 2 (Left) Structural view of $[RuCp(\eta^6\text{-}C_6H_5NMe_2)]PF_6$ (**10**) showing 50% thermal ellipsoids (only the first of the two crystallographically independent complexes is displayed; PF_6^- omitted for clarity). Selected bond lengths (Å): Ru–C(1–5)$_{av}$ 2.167(7), Ru–C(6) 2.344(4), Ru–C(7) 2.215(5), Ru–C(8) 2.194(6), Ru–C(9) 2.221(5), Ru–C(10) 2.212(6), Ru–C(11) 2.223(5), C(6)–N(1) 1.368(6), C(12)–N(1) 1.460(7), C(13)–N(1) 1.446(7), C(6)–C(7) 1.414(8), C(6)–C(11) 1.444(7), C(7)–C(8) 1.402(8), C(8)–C(9) 1.389(9), C(9)–C(10) 1.417(10), C(10)–C(11) 1.425(8). (Right) Optimized DFT/B3LYP geometry of $[RuCp(\eta^6\text{-}C_6H_5NH_2)]^+$.

as the dinuclear complex $[RuCp(\mu_3\text{-dapy})]_2(PF_6)_2$ (**11**) as shown in Scheme 3 (dapy = deprotonated apy). Support for this formulation comes from elemental analysis as well as from ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. In the ^{1}H NMR spectrum the hydrogen atoms of the Cp ring were downfield shifted to 6.01 ppm indicative of an oxidation state higher than +II. The NH proton gives rise to a characteristic low-field shifted signal at 11.75 ppm. Similarly, in the $^{13}C\{^1H\}$ NMR spectrum the ring carbon atoms of the Cp ligand were found to be downfield shifted appearing as a singlet at 91.0 ppm. Based on these findings and the diamagnetic nature of **11**, the Ru(II) metal center was apparently oxidized to Ru(III) forming a binuclear species with a metal–metal bond. The single-crystal X-ray crystallographic analysis of **11** depicted in Fig. 3 confirms the dimeric nature of this compound.

Selected bond distances and angles are reported in the figure legend. The Cp ligands are in mutual *cis* configuration. The apy ligand has been deprotonated and acts both as a κ^2N,N' chelating and a μ_3-bridging ligand. The core of the dinuclear complex consists of a four-membered Ru–N–Ru–N ring. The N(2)–Ru(1)–N(4) and N(2)–Ru(2)–N(4) angles are 93.4(1) and 93.2(1)°, respectively. The Ru(1)–Ru(2) distance of 2.652(1) Å clearly indicates the presence of a metal–metal single bond.[15] The two dapy ligands form a four-membered ring system with N(1)–Ru(1)–N(2) and N(3)–Ru(2)–N(4) angles of 63.9(1)°. The two bridging NH groups of the complex form straight N–H ··· F hydrogen bonds to one F atom of the two crystallographically independent PF_6^- octahedra (N ··· F = 2.941(2) and 3.052(2) Å).

Finally, we have reacted apy (1 equiv.) with $[RuCl_2(PPh_3)_3]$ (**4**). In this case an orange complex $[RuCl_2(PPh_3)_2(\kappa^2N,N'\text{-apy})]$ (**12**) was formed. This complex appears to be the first isolated and fully characterized complex containing a κ^2N,N'-coordinated apy ligand. While the NMR spectra are unremarkable, crystals suitable for a single-crystal X-ray diffraction study could be grown and the results confirm the κ^2N,N' coordination mode of apy. An ORTEP plot of the Ru complex of the solvate **12**·$CHCl_3$ is shown in Fig. 4 with selected bond distances and angles given in the figure legend. The crystals of **12**·$CHCl_3$ contain discrete $[RuCl_2(PPh_3)_2(\kappa^2N,N'\text{-apy})]$ units



Scheme 3

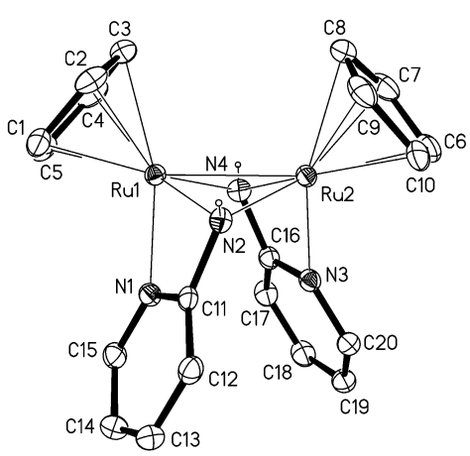


Fig. 3 Structural view of $[RuCp(\mu_3\text{-dapy})]_2(PF_6)_2$ (**11**) (50% ellipsoids; PF_6^- and aromatic H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ru(1)–C(1–5)$_{av}$ 2.197(2), Ru(2)–C(6–10)$_{av}$ 2.203(2), Ru(1)–Ru(2) 2.652(1), Ru(1)–N(1) 2.105(2), Ru(1)–N(2) 2.071(2), Ru(2)–N(3) 2.091(2), Ru(2)–N(4) 2.087(2); N(1)–Ru(1)–N(2) 63.9(1), N(3)–Ru(2)–N(4) 63.9(1), Ru(1)–N(2)–Ru(2) 79.9(1), Ru(1)–N(4)–Ru(2) 79.3(1), N(2)–Ru(1)–N(4) 93.4(1), N(2)–Ru(2)–N(4) 93.2(1).

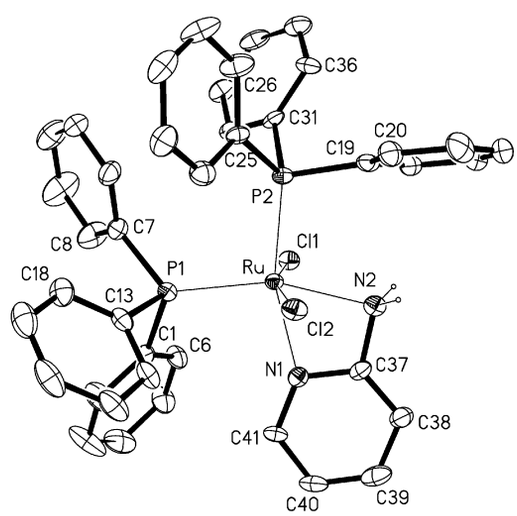


Fig. 4 Structural view of $[RuCl_2(PPh_3)_2(\kappa^2N,N'\text{-apy})]\cdot CHCl_3$ (**12**·$CHCl_3$) (40% ellipsoids; aromatic H atoms and solvent omitted for clarity). Selected bond lengths (Å) and angles (°): Ru–P(1) 2.287(2), Ru–P(2) 2.296(2), Ru–Cl(1) 2.423(1), Ru–Cl(2) 2.412(1), Ru–N(1) 2.151(4), Ru–N(2) 2.212(4); Cl(1)–Ru–Cl(2) 162.3(1), N(1)–Ru–N(2) 62.3(2), P(1)–Ru–P(2) 100.1(6), N(2)–Ru–Cl(1) 82.8(1), N(2)–Ru–Cl(2) 79.7(1).

with the metal in a severely distorted octahedral environment featuring *trans* chloro ligands. The Cl(1)–Ru–Cl(2) angle is 162.3(1)°. The apy ligand forms a distorted four-membered ring system with a N(1)–Ru–N(2) angle of 62.3(2)°. The two PPh_3 ligands are inequivalent, one being *trans* to N(py) and one *trans* to $N(NH_2)$ of the apy ligand. This appears to be the first example of a complex showing this particular bonding mode of apy without needing any specific precautions. This result lends further support to a recent suggestion[16] that the ruthenium complex-controlled catalytic N-mono and N,N-dialkylation of apy with alcohols proceeds *via* κ^2N,N'-apy ligated species.

Conclusion

The diverse bonding modes available make 2-aminopyridine a highly fascinating ligand in transition metal chemistry. The presence of the amino group in the *ortho* position not only introduces chelating ability but beyond this delicately modifies the relative stabilities of nitrogen(N)-bonded and π-bonded pyridines. The π-donor property of the amine group tends to increase the electron availability in the aromatic ring, thereby providing a driving force for π-complexation, and furthermore enhances the donor strength of the pyridine nitrogen. Bulky substituents sterically hinder the nitrogen nonbonding electrons from coordination. In this contribution, we have prepared and structurally characterized, for the first time, complexes containing a κ^2N,N'- and η^6-coordinated apy ligands, respectively.

Experimental

General

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[17] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[RuCp(CH_3CN)_3]PF_6$ (**1**),[18] $[RuCp(PMe_3)(CH_3CN)_2]PF_6$ (**2a**),[19] $[RuCp(PPh_3)(CH_3CN)_2]PF_6$ (**2b**),[19] $[RuCp(CO)(CH_3CN)_2]PF_6$ (**3**)[18] and $[RuCl_2(PPh_3)_3]$ (**4**)[20] were prepared according to the literature. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE-250 spectrometer and were referenced to $SiMe_4$ and H_3PO_4 (85%), respectively. ^1H and $^{13}C\{^1H\}$ NMR signal assignments were confirmed by ^1H-COSY, DEPT-135 and HMQC(^1H–^{13}C) experiments.

Syntheses

$[RuCp(\kappa^1N\text{-apy})(CH_3CN)_2]PF_6$ (5a). To a solution of **1** (200 mg, 0.461 mmol) in CH_3NO_2 (5 mL) 2-aminopyridine (apy) (44 mg, 0.461 mmol) was added. After the mixture was stirred at room temperature for 4 h, the solvent was removed under vacuum and the resulting yellow solid was collected on a glass frit and washed twice with diethyl ether (10 mL). Yield: 171 mg (76%). Found: C 34.42; H 3.59. $C_{14}H_{17}F_6N_4PRu$ requires C, 34.50; H, 3.52%. ^1H NMR (δ, CD_2Cl_2, 20 °C): 8.24 (dd, J_{HH1} = 5.94, J_{HH2} = 1.37 Hz, 1H, py^6), 7.46 (ddd, J_{HH1} = 8.45, J_{HH2} = 6.93, J_{HH3} = 1.60 Hz, 1H, py^4), 6.71 (d, J_{HH} = 8.22 Hz, 1H, py^3), 6.60 (ddd, J_{HH1} = 6.85, J_{HH2} = 6.24, J_{HH3} = 0.91 Hz, 1H, py^5), 5.64 (s, 2H, NH_2), 4.40 (s, 5H, Cp), 2.42 (s, 6H, $NCCH_3$). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 161.0 (1C, py^2), 152.0 (1C, py^6), 138.0 (1C, py^4), 126.5 (2C, $NCCH_3$), 113.4 (1C, py^3), 110.2 (1C, py^5), 68.7 (5C, Cp), 3.8 (2C, $NCCH_3$).

$[RuCp(PMe_3)(\kappa^1N\text{-apy})(CH_3CN)]PF_6$ (5b). This compound was prepared analogously to **5a** using **2a** (200 mg, 0.426 mmol) and apy (41 mg, 0.426 mmol) as the starting materials. Yield: 158 mg (71%). Found: C 34.58; H 4.40. $C_{15}H_{23}F_6N_3P_2Ru$ requires C, 34.49; H, 4.44%. ^1H NMR (δ, acetone-d_6, 20 °C): 8.47 (d, J_{HH} = 6.12 Hz, 1H, py^6), 7.50 (ddd, J_{HH1} = 8.32, J_{HH2} = 7.17, J_{HH3} = 1.43 Hz, 1H, py^4), 6.80 (d, J_{HH} = 8.03 Hz, 1H, py^3), 6.55 (ddd, J_{HH1} = 6.88, J_{HH2} = 6.50, J_{HH3} = 0.76 Hz, 1H, py^5), 6.12 (s, 2H, NH_2), 4.62 (s, 5H, Cp), 2.66 (d, J_{HH} = 1.53 Hz, 3H, $NCCH_3$), 1.49 (d, J_{HH} = 1.53 Hz, 9H, PMe_3). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 161.2 (1C, py^2), 152.0 (1C, py^6), 137.9 (1C, py^4), 128.0 (J_{CP} = 9.7 Hz, 1C, $NCCH_3$), 113.7 (1C, py^3), 109.8 (1C, py^5), 74.3 (J_{CP} = 2.3 Hz, 5C, Cp), 17.8 (J_{CP} = 28.0 Hz, 3C, PMe_3), 4.2 (1C, $NCCH_3$). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 4.9 (PMe_3), −144.3 ($^1J_{PF}$ = 707.7 Hz, PF_6).

$[RuCp(PPh_3)(CH_3CN)(\kappa^1N\text{-apy})]PF_6$ (5c). This compound was prepared analogously to **5a** using **2b** (200 mg, 0.305 mmol) and apy (29 mg, 0.305 mmol) as the starting materials. Yield: 189 mg (87%). Found: C, 50.68; H, 4.19. $C_{30}H_{29}F_6N_3P_2Ru$ requires C, 50.85; H, 4.12%. ^1H NMR (δ, acetone-d_6, 20 °C): 8.31 (d, J_{HH} = 5.79 Hz, 1H, py^6), 7.59–7.03 (m, 16H, PPh_3, py^4), 6.54 (d, J_{HH} = 8.53 Hz, 1H, py^3), 6.37 (t, J_{HH} = 5.94 Hz, 1H, py^5), 6.11 (s, 2H, NH_2), 4.66 (s, 5H, Cp), 2.11 (d, J_{HH} = 1.53 Hz, 3H, $NCCH_3$). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 161.8 (1C, py^2), 152.9 (1C, py^6), 137.7 (1C, py^4), 134.2 (J_{CP} = 40.6 Hz, 3C, Ph^1), 133.2 (J_{CP} = 10.6 Hz, 6C, $Ph^{2,6}$), 131.8 (J_{CP} = 9.7 Hz, 1C, $NCCH_3$), 130.0 (J_{CP} = 2.2 Hz, 3C, Ph^4), 128.5 (J_{CP} = 9.3 Hz, 6C, $Ph^{3,5}$), 113.0 (1C, py^3), 110.0 (1C, py^5), 75.9 (J_{CP} = 2.2 Hz, 5C, Cp), 2.8 (1C, $NCCH_3$). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 49.1 (PPh_3), −144.2 ($^1J_{PF}$ = 707.8 Hz, PF_6).

$[RuCp(CO)(\kappa^1N\text{-apy})(CH_3CN)]PF_6$ (5d). This compound was prepared analogously to **5a** using **3** (100 mg, 0.237 mmol) and apy (23 mg, 0.237 mmol) as the starting materials. Yield: 89 mg (87%). Found: C 33.01; H 2.87. $C_{13}H_{14}F_6N_3OPRu$ requires C, 32.92; H, 2.97%. ^1H NMR (δ, acetone-d_6, 20 °C): 8.26 (dd, J_{HH1} = 6.12, J_{HH2} = 1.04 Hz, 1H, py^6), 7.54 (ddd, J_{HH1} = 8.57, J_{HH2} = 7.06, J_{HH3} = 1.60 Hz, 1H, py^4), 6.77 (d, J_{HH} = 8.48 Hz, 1H, py^3), 6.60 (ddd, J_{HH1} = 6.88, J_{HH2} = 6.31, J_{HH3} = 0.94 Hz, 1H, py^5), 5.23 (s, 5H, RuCp), 6.15 (s, 2H, NH_2), 2.44 (s, 3H, $NCCH_3$). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 202.0 (1C, CO), 162.9 (1C, py^2), 154.3 (1C, py^6), 140.2 (1C, py^4), 131.0 (1C, $NCCH_3$), 115.0 (1C, py^3), 112.0 (1C, py^5), 83.5 (s, 5C, RuCp), 3.7 (s, 1C, $NCCH_3$).

$[RuCp(=C(Ph)(\eta^3\text{-}CHC(Ph)CHPMe_3)]PF_6$ (6). To a solution of **5b** (50 mg, 0.096 mmol) in acetone (4 mL) HC≡CPh (10.5 μL, 0.096 mmol) was added. After the mixture was stirred at room temperature for 4 h, the solvent was removed under vacuum and the resulting dark-red solid was collected on a glass frit and washed twice with diethyl ether (10 mL). Yield: 47 mg (83%). The NMR data are in agreement with those of an authentic sample reported in the literature.[21]

$[RuCp(PPh_3)(=C(CH_2)PhNHpy)]PF_6$ (7). To a solution of **5c** (80 mg, 0.119 mmol) in CH_2Cl_2 (4 mL) HC≡CPh (13.1 μL, 0.119 mmol) was added. After the mixture was stirred at room temperature for 4 h, the solvent was removed under vacuum and the resulting brown solid was collected on a glass frit and washed twice with diethyl ether (10 mL). Yield: 73 mg (78%). Found: C 55.98; H 4.22. $C_{36}H_{32}F_6N_2P_2Ru$ requires C, 56.18; H, 4.19%. ^1H NMR (δ, acetone-d_6, 20 °C): 12.09 (br s, 1H, NH), 9.14 (d, J_{HH} = 5.79 Hz, 1H, py^6), 7.82–7.07 (m, 21H, PPh_3, Ph, py^4), 6.99 (ddd, J_{HH1} = 7.31, J_{HH2} = 5.94, J_{HH3} = 1.37 Hz, 1H, py^5), 6.85 (d, J_{HH} = 8.53 Hz, 1H, py^3), 4.99 (d, J_{HH} = 0.30 Hz, 5H, RuCp), 5.04 (d, J_{HH} = 16.1 Hz, 1H, CH_2), 4.57 (d, J_{HH} = 15.8 Hz, 1H, CH_2). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 275.7 (J_{CP} = 10.8 Hz, 1C, =C), 156.7 (1C, py^2), 155.2 (J_{CP} = 1.84 Hz, 1C, py^6), 137.1 (1C, py^4), 136.1 (1C, Ph^1), 133.0 (J_{CP} = 11.5 Hz, 6C, $PPh_3^{2,6}$), 131.8 (J_{CP} = 46.5 Hz, 3C, PPh_3^1), 130.4 (J_{CP} = 2.0 Hz, 3C, PPh_3^4), 129.9 (2C, $Ph^{2,6}$), 129.0 (2C, $Ph^{3,5}$), 128.5 (J_{CP} = 10.1 Hz, 6C, $PPh_3^{3,5}$), 128.5 (1C, Ph^4), 119.8 (1C, py^3), 114.0 (1C, py^5), 83.7 (J_{CP} = 1.4 Hz, 5C, RuCp), 56.6

Table 1 Crystallographic data for **9**, **10**, **11** and **12**·$CHCl_3$

	9	**10**	**11**	**12**·$CHCl_3$
Formula	$C_{12}H_{15}F_6N_2PRu$	$C_{13}H_{16}F_6NPRu$	$C_{20}H_{20}F_{12}N_4P_2Ru_2$	$C_{42}H_{37}Cl_5N_2P_2Ru$
M_w	433.30	432.31	808.48	910.00
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)	$Pbca$ (no. 61)
a/Å	9.654(1)	7.082(1)	9.166(1)	11.215(2)
b/Å	12.595(2)	20.162(4)	10.224(1)	22.814(3)
c/Å	12.390(2)	10.718(2)	15.354(2)	31.409(4)
α/°			88.201(3)	
β/°	101.505(2)	100.217(3)	84.110(3)	
γ/°			64.720(3)	
V/Å^3	1476.4(3)	1506.1(5)	1294.1(3)	8036(2)
Z	4	4	2	8
T/K	173(2)	123(2)	123(2)	173(2)
μ(Mo-Kα)/mm^{-1}	1.232	1.205	1.397	0.836
θ_{max}/°	30	30	30	25
Total rflns.	15003	22481	9552	35553
Indep. rflns.	4228	8520	6540	7073
Parameters	210	401	370	412
R_{int}	0.020	0.040	0.011	0.135
R_1 (all data)	0.030	0.057	0.024	0.110
wR_2 (all data)	0.063	0.108	0.052	0.132

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

(1C, CH_2). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 53.8 (PPh_3), −144.2 ($^1J_{PF}$ = 717.0 Hz, PF_6).

[RuCp(CO)(=C(CH$_2$)PhNHpy)]PF$_6$ (8). This compound was prepared analogously to **7** using **5d** (80 mg, 0.169 mmol) and HC≡CPh (18.5 μL, 0.169 mmol) as the starting materials. Yield: 76 mg (84%). Found: C 46.58; H 3.23. $C_{19}H_{17}F_6N_2OPRu$ requires C, 46.62; H, 3.20%. ^1H NMR (δ, CD_3NO_2, 20 °C): 8.75 (d, J_{HH} = 5.79 Hz, 1H, py^6), 8.04 (t, J_{HH} = 7.46 Hz, 1H, py^4), 7.74 (d, J_{HH} = 8.22 Hz, 1H, py^3), 7.50–7.24 (m, 6H, py^5, Ph), 5.31 (s, 5H, RuCp), 5.17 (d, J_{HH} = 13.7 Hz, 1H, CH_2), 4.82 (d, J_{HH} = 12.2 Hz, 1H, CH_2). $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20 °C): 275.9 (1C, =C), 196.4 (1C, CO), 156.7 (1C, py^2), 156.2 (1C, py^6), 140.3 (1C, py^4), 134.9 (1C, Ph^1), 130.0 (2C, Ph^{2,6}), 129.0 (2C, Ph^{3,5}), 127.7 (1C, Ph^4), 121.9 (1C, py^3), 115.2 (1C, py^5), 85.7 (5C, RuCp), 73.2 (1C, CH_2).

[RuCp(η^6-dmapy)]PF$_6$ (9). To a solution of **1** (200 mg, 0.461 mmol) in CH_2Cl_2 (5 mL) 2-*N*,*N*-dimethylaminopyridine (dmapy) (57.2 μL, 0.461 mmol) was added. After the mixture was stirred at room temperature for 4 h, the solvent was removed under vacuum and the resulting white solid was collected on a glass frit and washed twice with diethyl ether (10 mL). Yield: 162 mg (81%). Found: C 33.31; H 3.39. $C_{12}H_{15}F_6N_2PRu$ requires C, 33.23; H, 3.46%. ^1H NMR (δ, acetone-d_6, 20 °C): 6.99 (t, 1H, py^6), 6.39–6.22 (m, 3H, py), 5.51 (s, 5H, Cp), 3.07 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 136.7 (1C, py^2), 99.1 (1C, py^6), 87.5 (1C, py^4), 81.2 (1C, py^3), 79.6 (5C, Cp), 63.4 (1C, py^5), 36.9 (2C, NMe_2).

[RuCp(η^6-C$_6$H$_5$NMe$_2$)]PF$_6$ (10). This compound was prepared analogously to **9** using **1** (100 mg, 0.230 mmol) and *N*,*N*-dimethylaniline (29.2 μL, 0.230 mmol) as the starting materials. Yield: 90 mg (90%). Found: C 36.15; H 3.77. $C_{13}H_{16}F_6NPRu$ requires C, 36.12; H, 3.73%. ^1H NMR (δ, acetone-d_6, 20 °C): 6.11–5.88 (m, 5H, Ph), 5.40 (s, 5H, Cp), 2.94 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 127.6 (1C, Ph^1), 83.4 (2C, Ph^{2,6}), 80.6 (1C, Ph^4), 78.0 (5C, Cp), 68.0 (2C, Ph^{3,5}), 39.2 (2C, NMe_2).

[RuCp(μ$_3$-dapy)]$_2$(PF$_6$)$_2$ (11). To a solution of **1** (300 mg, 0.691 mmol) in acetone (10 mL) apy (66 μL, 0.691 mmol) was added. After the mixture was stirred at room temperature for 10 min, air was bubbled through the solution for 5 min, whereupon the colour changed from yellow to dark green. After stirring for 10 h the solvent was removed under vacuum, the resulting green solid was collected on a glass frit and washed twice with pentane (10 mL). Yield: 235 mg (84%). Found: C 29.64; H 2.56. $C_{20}H_{20}F_{12}N_4P_2Ru_2$ requires C, 29.71; H, 2.49%. ^1H NMR (δ, acetone-d_6, 20 °C): 11.75 (br s, 2H, NH), 7.85 (dt, J_{HH1} = 8.03, J_{HH2} = 1.91 Hz, 2H, py^6), 7.59 (dd, J_{HH} = 4.78, J_{HH2} = 0.57 Hz, 2H, py^4), 7.12 (d, J_{HH} = 8.03 Hz, 2H, py^3), 6.87 (ddd, J_{HH1} = 7.36, J_{HH2} = 5.26, J_{HH3} = 0.48 Hz, 2H, py^5), 6.01 (s, 10H, Cp). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 172.1 (2C, py^2), 151.7 (2C, py^6), 140.7 (2C, py^4), 120.3 (2C, py^3), 118.0 (2C, py^5), 91.0 (10C, Cp).

[RuCl$_2$(PPh$_3$)$_2$(κ^2*N*,*N*′-apy)] (12). A solution of **4** (300 mg, 0.313 mmol) and apy (30 mg, 0.313 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 4 h. After removal of the solvent under reduced pressure, the orange product was washed three times with diethyl ether (45 mL), and dried under vacuum. Yield: 190 mg (77%). Found: C, 62.32; H, 4.52. $C_{41}H_{36}Cl_2N_2P_2Ru$ requires C, 62.28; H, 4.59%. ^1H NMR (δ, DMSO-d_6, 20 °C): 7.54–6.67 (m, 34H, PPh_3, py), 3.89 (s, 2H, NH_2). $^{13}C\{^1H\}$ NMR (δ, dmso-d_6, 20 °C): 160.2 (1C, py^2), 148.1 (1C, py^6), 137.4 (1C, py^4), 135.5 (J_{CP} = 9.2 Hz, 6C, Ph^4), 133.7 (J_{CP} = 44.1 Hz, 6C, Ph^1), 133.7 (J_{CP} = 19.8 Hz, 12C, Ph^{2,6}), 129.3 (J_{CP} = 17.0 Hz, 12C, Ph^{3,5}), 112.2 (1C, py^3), 108.4 (1C, py^5). $^{31}P\{^1H\}$ NMR (δ, DMSO-d_6, 20 °C): 49.9 (PPh_3).

Computational details

All calculations were performed using the Gaussian98 software package on the Silicon Graphics Origin 2000 of the Vienna University of Technology.[22] The geometry and energy of the model complexes and the transition states were optimized at the B3LYP level[23] with the Stuttgart/Dresden ECP (SDD) basis set[24] to describe the electrons of the Ru atom. For the H, C and N atoms the 6-31g** basis set was employed.[25] A vibrational analysis was performed to confirm that the structures of the model compounds have no imaginary frequency. The geometries were optimized without constraints (C_1 symmetry).

X-Ray crystallography

Crystals of **9**, **10** and **11** were obtained by diffusion of diethyl ether into acetone solutions, whereas crystals of **12**·$CHCl_3$ were obtained by diffusion of Et_2O into a $CHCl_3$ solution. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Bruker Smart CCD area

detector diffractometer (graphite monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, 0.3° ω scan frames, Bruker Kryoflex cooling unit). Corrections for crystal decay and for absorption were applied.[26] The structures were solved by direct methods using the program SHELXS97.[27] Structure refinement on F^2 was carried out with program SHELXL97.[27] All non-hydrogen atoms were refined anisotropically. Most hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Some crucial hydrogen atoms were refined in x, y and z. Compound **10** contains two crystallographically different, but stereochemically similar formula moieties in the asymmetric unit of a definitely acentric unit cell. In **12**·$CHCl_3$ the solvent is disordered, the composition is idealized, and the solvent was taken into account with procedure SQEEZE of program PLATON;[28] two N–H ··· Cl(Ru) hydrogen bonds with N ··· Cl = 3.374(5) Å link each two Ru complexes in pairs.

CCDC reference numbers 205216–205219.

See http://www.rsc.org/suppdata/DT/b3/b302416d/ for crystallographic data in CIF or other electronic format.

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