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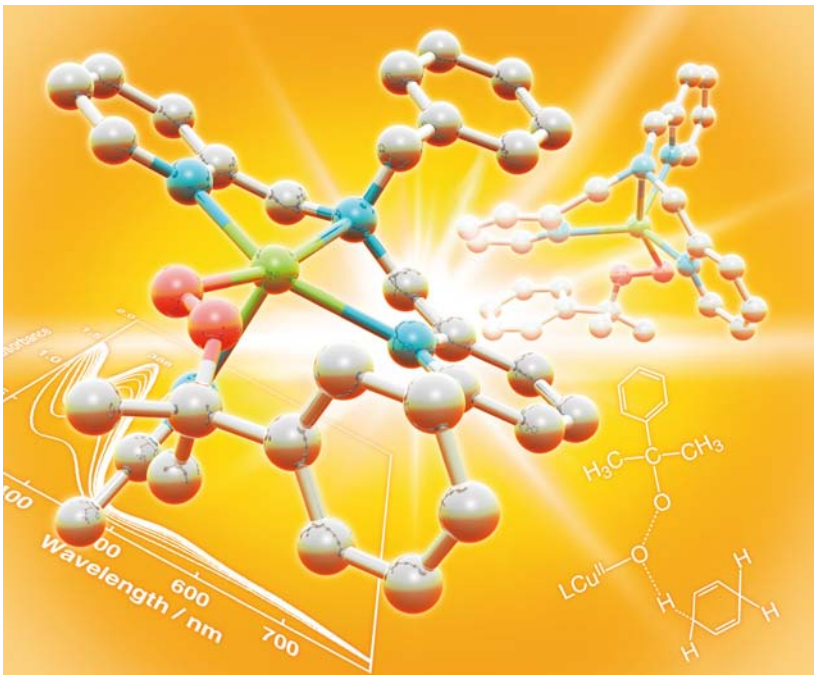

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PAPER

From amine to ruthenaziridine to azaallyl: unusual transformation of di-(2-pyridylmethyl)amine on ruthenium†

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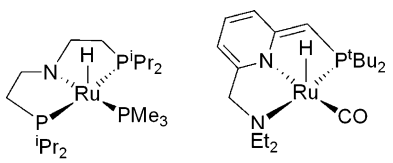
The complexation of di-(2-pyridylmethyl)amine to $RuHCl(PPh_3)_3$ affords the salt [RuH{κ^3*N-fac*-1,3-di-(2-pyridylmethyl)amine}$(PPh_3)_2$]Cl. Reaction with potassium *tert*-butoxide at room temperature yields the unusual ruthenaziridine complex RuH{$\kappa^3 C^{alk}NN^{py}$-1,3-di-(2-pyridylmethyl)amine}$(PPh_3)_2$, where the central nitrogen atom, adjacent alkyl carbon, and pyridine arm coordinate to the metal, leaving the second pyridine arm uncoordinated. Surprisingly, heating of this ruthenaziridine complex with concomitant H_2 formation affords the ruthenium azaallyl complex RuH(κ^3*N*-1,3-di-(2-pyridyl)-2-azaallyl)$(PPh_3)_2$. This is a rare example of a 4d metal complex containing the azaallyl ligand. X-Ray crystal structures and NMR characterization of all three compounds are presented herein.

1 Introduction

Tridentate ligands containing mixed nitrogen and phosphorus donors have recently received much attention, affording tunable and robust ligand systems for late transition metals.[1–7] For example, the highly reactive five-coordinate Ru–PNP complex **A**, which contains a central secondary nitrogen, reversibly reacts with H_2[8] and is a highly active ammonia–borane dehydrogenation catalyst (Scheme 1).[9] Moreover, Ru–PNN complex **B** which contains a central pyridine ring that is dearomatized also reversibly reacts with H_2.[7] It efficiently catalyzes the formation of alcohols into esters[10] and splits water into H_2 and O_2.[11] Ruthenium compounds with tridentate PNP and PNN ligands have also been utilized in the catalytic reduction of ketones.[12–15] The tridentate ligand in these examples is thought to assist in the activation of substrates during bifunctional catalysis.[16–25]



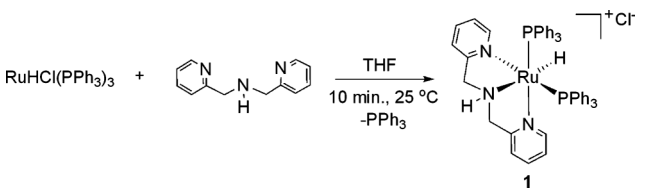
Scheme 1 Examples of ruthenium-based PNP and PNN systems.

Some iron-group complexes containing tridentate nitrogen donor ligands (*NNN*) have been examined for use in catalysis.[26–40] For example, iron complexes of amine-functionalized di-(2-pyridylmethyl)amines have been intensely studied as analogues of active sites of iron-containing oxidases.[41–43] As a simpler starting point, we chose to use the parent compound di-(2-pyridylmethyl)amine, which contains two pendant methylpyridine "arms" and a central secondary amine donor. It is easily synthesized in high yields[44] and is cost-effective, both desirable properties of any ligand system. There are only a few reports of ruthenium compounds containing this ligand.[45–49] We decided to investigate its reactivity with the common ruthenium hydride precursor $RuHCl(PPh_3)_3$ rationalizing that a combination of a secondary amine proton and metal hydride may offer a promising metal–ligand bifunctional system for catalytic transformations, such as H_2 hydrogenation and/or transfer hydrogenation.[13,14,18,20,22–25,50–55]

2 Results and discussion

2.1 Synthesis of ruthenium di-(2-pyridylmethyl)amine and ruthenaziridine complexes

Our investigations began by reacting $RuHCl(PPh_3)_3$ with di-(2-pyridylmethyl)amine, expecting that removal of two phosphines would lead to coordination of the tridentate ligand. However, stirring for several minutes in tetrahydrofuran (THF) afforded the salt [RuH{κ^3*N-fac*-1,3-di-(2-pyridylmethyl)amine}$(PPh_3)_2$]Cl (**1**) in excellent yield (Scheme 2). Complex **1** is freely soluble in protic solvents and was fully characterized by NMR studies in methanol-d_4. This product resulted from the displacement of the chloride anion and removal of only one phosphine. The ^{1}H NMR shows that the NH proton on the di-(2-pyridylmethyl)amine ligand is shifted



Scheme 2 Synthesis of complex **1**.

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significantly downfield (6.2 ppm) compared to the methylene protons (3.8–3.6 ppm). The hydride resonance appears at −14.7 ppm as a triplet ($^2J_{HP}$ = 29 Hz), given the C_s symmetry of the cation.

An X-ray crystal structure of complex **1** was also obtained (Fig. 1, Table 1 and Table 2). In the solid state, **1** adopts a distorted octahedral geometry with the chloride counteranion hydrogen bonded to the amine proton. The bite angles between the central nitrogen atom and pendant pyridine arms are 77.4(2)° and 83.7(2)° for the N1–Ru–N2 and N1–Ru–N3 angles, respectively (Table 1). This is complemented by the larger angle of 95.70(7)° between the phosphine ligands. The Ru–N2 bond is longer for **1** than in the related complexes *trans*,*fac*-[Ru{di-(2-pyridylmethyl)amine}$(CO)_2$Cl][PF_6] and *cis*,*fac*-[Ru{di-(2-pyridylmethyl)amine}$(CO)_2$(MeCN)][PF_6]$_2$ due to the presence of a hydride *trans*- to the central nitrogen atom.[46]

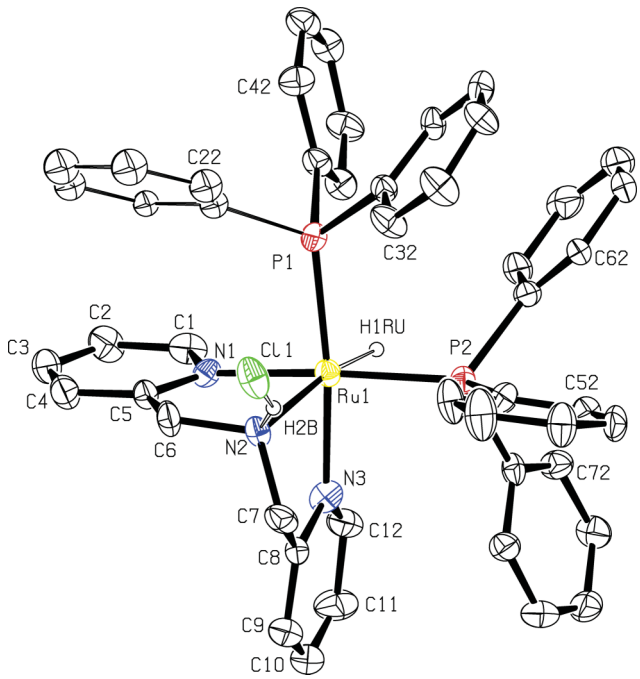


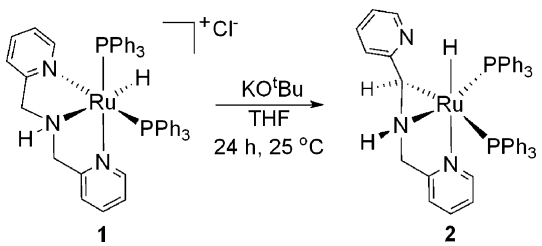
Fig. 1 Molecular structure of **1** depicted with thermal ellipsoids at the 30% probability level. Hydrogen atoms on the aromatic rings and methylene carbons have been omitted for clarity.

When **1** was reacted with one equivalent of potassium *tert*-butoxide, we expected rapid and selective deprotonation of the central nitrogen atom at room temperature to afford RuH{*fac*-1,3-di-(2-pyridylmethyl)amide}$(PPh_3)_2$. However, when monitoring the course of the reaction by NMR spectroscopy, we observed a complex mixture of products as indicated by multiple metal hydride, ligand, and phosphorus signals. The mixture was allowed to stir for 24 h at room temperature and these coalesced into one major product. The ^{1}H NMR spectrum of this product contained a hydride signal coupled to two inequivalent *cis*-phosphines (−15.8 ppm, $^2J_{HP}$ = 29 and 25 Hz). When trying to assign the proton signals in the ^{1}H NMR spectrum, we noticed that one of the protons on the CNC backbone of the ligand, appearing as a broad multiplet, was shifted far downfield (at 5.1 ppm) compared to three other protons, which have well-resolved couplings (at 3.5–3.1 ppm). This is reminiscent of the NH proton in **1**, which was also far downfield with respect to the methylene protons. Indeed,

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1**, **2**, and **3**

Parameter	1	2	3
Ru–H1	1.74(7)	1.63(3)	1.61(3)
Ru–N1	2.128(6)	2.175(3)	2.107(3)
Ru–N2	2.234(5)	2.131(3)	2.055(2)
Ru–N3	2.111(6)	—	2.113(2)
Ru–C7	—	2.121(3)	—
Ru–P1	2.293(2)	2.244(1)	2.3002(7)
Ru–P2	2.284(2)	2.276(1)	2.3081(7)
N2–C6	1.492(8)	1.463(5)	1.335(4)
N2–C7	1.487(8)	1.452(4)	1.334(4)
N1–Ru–N2	77.4(2)	76.7(1)	78.8(1)
N1–Ru–N3	83.7(2)	—	157.1(1)
N2–Ru–N3	77.0(2)	—	78.5(1)
P1–Ru–P2	95.70(7)	103.37(4)	157.96(3)
P2–Ru–N1	172.1(2)	94.39(7)	88.24(7)
P1–Ru–N3	172.6(2)	—	90.84(7)

IR analysis reveals an NH stretching mode at 3271 cm^{-1}. Based on complete 1D/2D NMR spectral characterization and a crystal structure, we determined the compound to be RuH{$\kappa^3 C^{alk} NN^{py}$-1,3-di-(2-pyridylmethyl)amine}$(PPh_3)_2$ which contains an anionic ruthenaziridine moiety and a decoordinated pyridine ring. (**2**, Scheme 3, Fig. 2, Table 1 and Table 2). The methine hydrogen of the alkyl in complex **2** appears at 3.1 ppm.



Scheme 3 Synthesis of **2**.

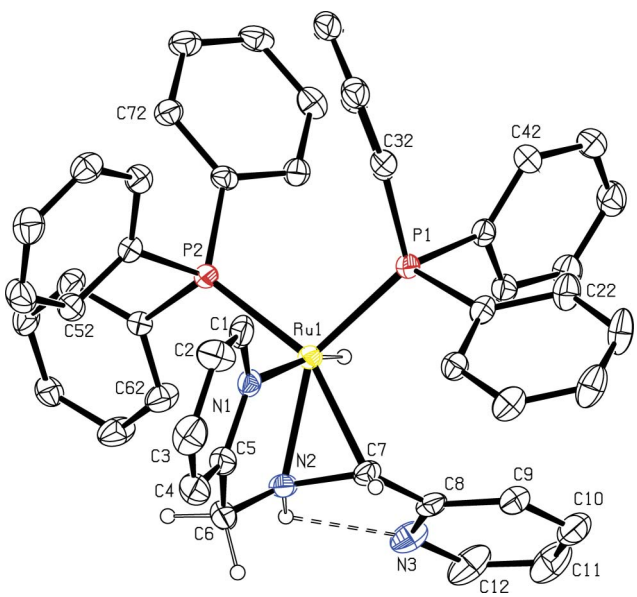


Fig. 2 Molecular structure of **2** depicted with thermal ellipsoids at the 30% probability level. Hydrogen atoms on the aromatic rings have been omitted for clarity.

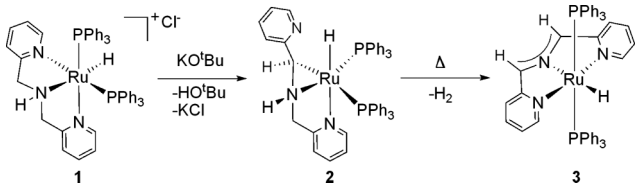
Table 2 X-Ray crystal structure and refinement data for complexes **1**, **2**, and **3**

Compounds	**1**	**2**	**3**
Empirical formula	$C_{48}H_{44}ClN_3P_2Ru$	$C_{48}H_{43}N_3P_2Ru$	$C_{48}H_{41}N_3P_2Ru$
Formula mass	861.32	824.86	822.85
T/K	150(1)	150(1)	150(1)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	11.0768(3)	21.076(4)	11.5061(3)
b/Å	33.850(1)	9.289(2)	11.7305(3)
c/Å	12.4059(2)	20.185(4)	16.1489(3)
α (°)	90	90	88.632(1)
β (°)	91.673(2)	93.48(3)	78.804(1)
γ (°)	90	90	83.233(1)
Volume/Å^3	4649.6(2)	3944(1)	2123.28(9)
Z	4	4	2
Density (calculated/g cm^{-3})	1.230	1.389	1.287
Absorption coefficient (mm^{-1})	0.497	0.517	0.480
F(000)	1776	1704	848
Crystal Size/mm	0.20 × 0.20 × 0.15	0.18 × 0.08 × 0.04	0.30 × 0.13 × 0.03
Theta range for data collection (°)	2.57–25.00	2.58–27.47	2.57–25.12
Reflections collected	29446	38699	15884
Independent reflections	8097 [$R(int)$ = 0.115]	9006 [$R(int)$ = 0.0761]	7369 [$R(int)$ = 0.082]
Completeness to θ = 25.00° (%)	99.0	99.8	97.2
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	0.930, 0.731	0.982, 0.899	0.988, 0.585
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8097/0/471	9006/1/496	7369/0/491
Goodness-of-fit on F^2	0.930	1.020	1.069
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0730	R_1 = 0.0509	R_1 = 0.0407
R indices (all data)	wR_2 = 0.2182	wR_2 = 0.1308	wR_2 = 0.1128

Crystals of **2** were obtained *via* diffusion of pentane into a concentrated solution of benzene. Selected bond lengths and angles are given in Table 1. The complex is severely distorted from an ideal octahedron with large P1–Ru–C7 and P2–Ru–N2 angles of 103.5(1)° and 113.19(8)°, respectively, and a very acute N2–Ru–C7 angle of 39.9(1)°. The hydride ligand is *trans*- to the coordinated pyridine arm. The N2–C7 bond length is 1.452(4) Å, which is indicative of an sp^3-hybridized carbon atom and is comparable with the slightly longer N2–C7 distance of 1.487(8) Å in **1**. The only other two other crystallographically defined compounds that contain the ruthenaziridine motif are prepared by reacting the carbonyl cluster $Ru_3(CO)_{12}$ with 1,4-diazabutadienes (α-diimines).[56,57] The products in these cases were dimers while **2** remains monomeric, possibly due to the steric bulk of the phosphines.

2.2 Synthesis of a ruthenium azaallyl complex

In the preparation of complex **2** by reaction of base with complex **1** at room temperature, a deep emerald green solid also forms in low yield as a by-product. Its presence is signalled by a hydride triplet at −8.6 ppm ($^2J_{HP}$ = 29 Hz) in crude samples of **2**. When ruthenium salt **1** is heated in THF with potassium *tert*-butoxide, an intensely coloured emerald green solution formed, which we thought to be (RuH{*fac*-1,3-di-(pyridylmethyl)amide}(PPh_3)$_2$). The NMR spectrum showed that **2** was replaced by a highly symmetrical molecule containing a triplet at −8.6 ppm ($^2J_{HP}$ = 29 Hz) and a singlet phosphorus peak (proton decoupled) at 50.9 ppm appeared. Surprisingly, it was identified by use of single crystal X-ray diffraction to be a rare azaallyl complex[58–62] with *trans*-PPh_3 ligands (Scheme 4, Fig. 3).



Scheme 4 Summary of the reactivity of complexes **1** and **2**.

Selected metrical parameters for **3** are presented in Table 1. The bite angle between the pyridine nitrogens is 157.96(3)°, while the central Ru–N bond is slightly shorter (Ru–N2 = 2.055(2) Å) than the pyridine Ru–N bonds (Ru–N1 = 2.107(3), Ru–N3 = 2.113(2) Å). The azaallyl N–C bonds are identical (N2–C6 = 1.335(4) Å, N2–C7 = 1.334(4) Å), which suggests delocalization of negative charge about all three atoms. These bond lengths and angles are similar to a previously reported iron 1,3-di-(2-pyridyl)-2-azallyl complex.[60]

The symmetrical structure of **3** explains the triplet pattern of the hydride resonance in the ^{1}H NMR spectrum and the singlet phosphorus peak. Not only was the central amine proton removed from di-(2-pyridylmethyl)amine, but a proton and hydride equivalent were also eliminated to form the tridentate anionic azaallyl ligand. The *trans*- arrangement of the PPh_3 ligands suggests that some ligand rearrangement must have occurred during the formation of **3**, possibly involving phosphine or pyridine arm dissociation.

Initially discovered as a degradation product attached to zinc,[59] the azaallyl ligand has attracted attention more recently due to the intense colours it imparts on a variety of 3d metal precursors. Wolczanski and co-workers have synthesized similar complexes by reacting the lithium dipyridylazaallyl salt with a variety of metals

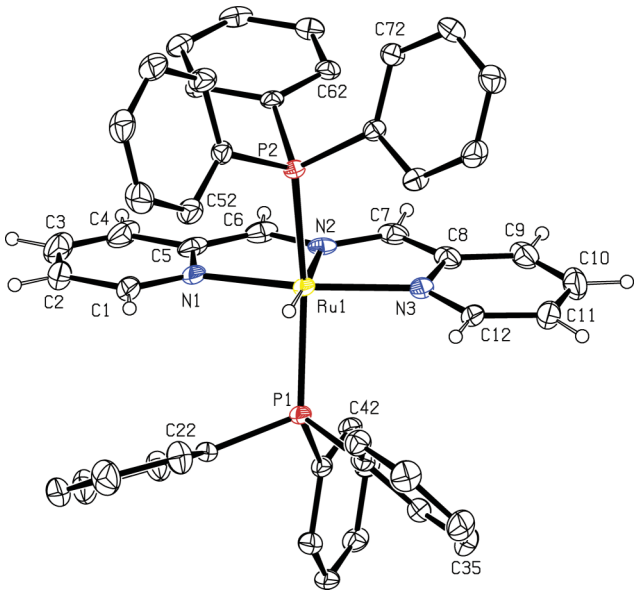
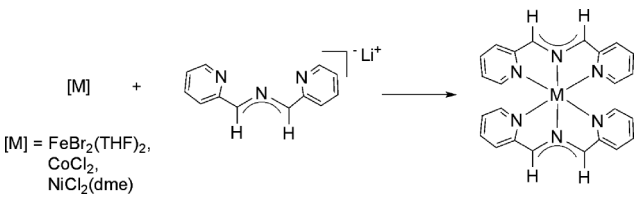


Fig. 3 Molecular structure of **3** depicted with thermal ellipsoids at the 30% probability level. Hydrogen atoms on the phenyl rings have been omitted for clarity.

(Scheme 5).[60,63] These molecules have two intraligand transitions[60] in the visible region with extinction coefficients ranging from 20000–50000 $M^{-1}cm^{-1}$. Azaallyl compound **3** also has two intraligand UV-vis absorption bands, with broad absorbances centered at 697 nm ($\varepsilon = 8500\ M^{-1}cm^{-1}$) and 405 nm ($\varepsilon = 32000\ M^{-1}cm^{-1}$).



Scheme 5 Azaallyl complexes prepared by Wolczanski and co-workers.

There is a minor by-product that forms with **3** which contains a hydride triplet 0.1 ppm upfield and a phosphorus singlet 2 ppm downfield from the signals in **3**, respectively. We were unable to identify or isolate this electronically similar product, but its presence can be minimized if two equivalents of base are used to synthesize complex **3** instead of one.[64]

The azaallyl complex **3** can also be synthesized directly from **2** by refluxing in THF with no added base (Scheme 4). This shows that **2** is indeed a reaction intermediate. However, the azaallyl complex **3** can be synthesized in higher yields and greater purity if two equivalents of base are used when starting from **1** (*vide supra*). Interestingly, the amine proton and hydride of **2** are *cis*- to one another in the solid state (Fig. 2), which suggests that H_2 loss occurs in a bifunctional manner.[54]

3 Conclusion

We have shown that a simple ligand precursor, di-(2-pyridylmethyl)amine, can be manipulated into adopting three different coordination modes. Firstly, the salt [RuH{κ^3*N-fac*-1,3-di-(2-pyridylmethyl)amine}$(PPh_3)_2$]Cl is synthesized where it binds as a neutral tridentate ligand. Upon addition of base, one of the alkyl carbons becomes an anionic two-electron donor and an unusual ruthenaziridine complex (**2**) is formed. Finally, refluxing **1** with base or **2** without base leads to the novel ruthenium hydrido azaallyl complex **3** with concomitant H_2 production. This deprotonation/dehydrogenation reaction pathway is unusual, and mechanistic studies are currently under way.

4 Experimental

4.1 General comments

All experiments were carried out under argon using standard Schlenk and glove box techniques. Tetrahydrofuran (THF) was distilled over Na/benzophenone prior to use. $RuHCl(PPh_3)_3$ was prepared according to a known literature procedure.[65] Di-(2-pyridylmethyl)amine, sublimed potassium *tert*-butoxide, and methanol-d_4 (ampules) were used as received (Aldrich). Air and moisture free benzene-d_6 was prepared by stirring with Na/benzophenone for 2 days, followed by three freeze–pump–thaw cycles and vacuum transfer. All NMR spectroscopic data were collected using a Varian 400 MHz or a Bruker 400 MHz NMR system operating at 400 MHz for ^{1}H, 101 MHz for ^{13}C, or 162 MHz for ^{31}P. All ^{1}H and ^{13}C NMR samples were referenced to their respective residual solvent peaks. Spectroscopic data for ^{31}P NMR were referenced to an external standard of 85% aqueous H_3PO_4 at $\delta = 0.00$. Single-crystal X-ray diffraction data were collected at 150 K using a Nonius Kappa-CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). The CCD data were integrated and scaled using the Denzo-SMN package.[66] The structures were solved and refined using SHELXTL V6.1.[67] Refinement was by full-matrix least-squares on F^2 using all data. All IR spectra were prepared as KBr pellets and carried out on a Perkin-Elmer Spectrum One FT-IR spectrometer. All UV-vis spectra were recorded on a Hewlett-Packard Agilent 8453 UV-vis spectrophotometer. Elemental Analyses were performed on a Perkin–Elmer 2400 CHN elemental analyzer. For compounds **2** and **3** elemental analyses were attempted several times and consistently produced low carbon percentages despite being pure by all other spectroscopic means.

4.2 Synthesis

4.2.1 [RuH{κ^3*N-fac*-1,3-di-(2-pyridylmethyl)amine}$(PPh_3)_2$]-Cl (1). A suspension of $RuHCl(PPh_3)_3$ (1.00 g, 1.08 mmol) in THF (15 mL) was placed in a glass vial charged with a teflon-coated stir bar. Di-(2-pyridylmethyl)amine (237 mg, 1.19 mmol) was added and after 10 min of stirring the solution became cloudy yellow. This was immediately filtered over a medium-pore glass frit and washed with THF (2 × 1 mL). The yellow precipitate on the frit was washed through with methanol (10 mL) and the yellow filtrate was collected. Excess solvent was removed *in vacuo* to afford a bright yellow microcrystalline solid (857 mg, 92%). Crystals suitable for X-ray diffraction were grown *via* slow diffusion of diethyl ether into a concentrated methanol solution at 25 °C. EA: found C 66.4, H 5.3, N 4.9. Calc. for $C_{48}H_{44}N_3P_2ClRu$: C 66.9, H 5.15, N 4.9%. UV-vis: $\lambda_{max}(CH_3CN)$/nm 345 (ε/$M^{-1}cm^{-1}$ 14000). IR: ν_{max}/cm^{-1} 3273 w (NH), 1956 s (RuH). ^{1}H NMR (CD_3OD): δ 8.67 (2H, d, $^3J = 6$ Hz, 6-pyH), 7.33–7.23 (14H, m, 4-pyH and

C_6H_5), 7.09 (6H, m, C_6H_5), 6.95 (12H, m, C_6H_5), 6.89 (2H, d, ^3J = 8 Hz, 3-pyH), 6.61 (2H, m, 5-pyH), 6.16 (1H, m, NH), 3.83 (2H, d, ^2J = 16 Hz, CH_2), 3.64 (2H, dd, ^2J = 16 Hz, CH_2), –14.66 (1H, t, $^2J_{HP}$ = 29 Hz, RuH). ^{13}C $\{^1H\}$ NMR: δ 161.55 (2-pyC), 156.61 (6-pyC), 138–139 (C_6H_5), 137.24 (4-pyC), 135.09 (C_6H_5), 129.76 (C_6H_5), 128.56 (C_6H_5), 124.88 (3-pyC), 122.89 (5-pyC), 63.06 (CH_2). ^{31}P $\{^1H\}$ NMR: δ 67.40 (s, RuP). MS (ESI): found: m/z 826.1961. Calc. for $[C_{48}H_{44}N_3P_2Ru]^+$ 826.2048.

4.2.2 RuH{$\kappa^3C^{alk}NN^{py}$ - 1,3 - di - (2 - pyridylmethyl)amine}-(PPh_3)$_2$ (2). A suspension of **1** (28 mg, 0.033 mmol) in tetrahydrofuran (2 mL) was placed in a glass vial charged with a teflon-coated stir bar. Potassium *tert*-butoxide (4 mg, 0.033 mmol, 0.085 M in THF) was added (excess base is not detrimental). The solution darkened immediately after addition of base and was stirred for 24 h at room temperature, during which the colour changed to green–brown. This green–brown solution was filtered through a pad of Celite, dried *in vacuo*, then redissolved in hexanes (3 mL) and stirred overnight. Finally, the solution was filtered over a medium-pore glass frit and the solid was washed with hexanes (about 3 mL) until the outgoing filtrate was colourless. The remaining solid was dried *in vacuo* to afford a yellow–brown powder (14 mg, 52%). Crystals suitable for X-ray diffraction were grown *via* slow diffusion of pentane into a concentrated benzene solution at 25 °C. EA: found: 63.7, 5.1, 4.9. Calc. for $C_{48}H_{43}N_3P_2Ru$: C 69.9, H 5.25, N 5.1%. IR: ν_{max}/cm^{-1} 3271 w (NH), 1953 s (RuH). ^1H NMR (C_6D_6, *coord* = coordinated, *uncoord* = uncoordinated): δ 8.50 (1H, d, ^2J = 5 Hz, 6-py$H_{uncoord}$), 7.80 (1H, d, ^2J = 5 Hz, 6-pyH_{coord}), 7.55 (12H, m, C_6H_5), 7.02–6.94 (18H, m, C_6H_5), 6.87 (1H, m, 4-py$H_{uncoord}$), 6.58 (1H, m, 5-py$H_{uncoord}$), 6.56 (1H, m, 4-pyH_{coord}), 6.11 (1H, d, ^2J = 7 Hz, 3-pyH_{coord}), 5.94 (1H, d, ^2J = 7 Hz, 3-py$H_{uncoord}$), 5.86 (1H, m, 5-pyH_{coord}), 5.10 (1H, m, NH), 3.42 (1H, dd, ^2J = 16 Hz, CH_2), 3.26 (1H, dd, ^2J = 16 Hz, CH_2), 3.11 (1H, m, CHNH), –15.81 (1H, dd, $^2J_{HP}$ = 29 Hz, $^2J_{HP}$ = 25 Hz, RuH). ^{13}C $\{^1H\}$ NMR: δ 169.65 (2-py$C_{uncoord}$), 158.52 (2-pyC_{coord}), 154.41 (6-pyC_{coord}), 149.26 (6-py$C_{uncoord}$), 143.86–142.71 (C6H5), 134.91 (4-py$C_{uncoord}$), 134.64-133.86 (C_6H_5), 131.57 (4-pyC_{coord}), 127.84 (C_6H_5), 121.97 (5-pyC_{coord}), 120.56 (3-pyC_{coord}), 119.13 (3-py$C_{uncoord}$), 116.27 (5-py$C_{uncoord}$), 59.54 (CHNH), 56.10 (CH_2). ^{31}P $\{^1H\}$ NMR: δ 77.39 (m, RuP), 61.73 (m, RuP). MS (DART): found: m/z 824.2. Calc. for $[C_{48}H_{40}N_3P_2Ru]^+$ (loss of H^-): 824.2.

4.2.3 RuH(κ^3N-1,3-di-(2-pyridyl)-2-azaallyl)(PPh_3)$_2$ (3). A suspension of **1** (28 mg, 0.033 mmol) in THF (2 mL) was placed in a Schlenk flask charged with a teflon-coated stir bar. Potassium *tert*-butoxide (8 mg, 0.067 mmol, 0.085 M in THF) was added. The solution turned dark immediately after addition of base and was heated at 60 °C overnight. The resulting deep emerald green solution was filtered through Celite and dried *in vacuo*. Pentane was added (1 mL), the solution was stirred for 1 h, then filtered over a medium-pore glass frit (the product is soluble in pentane so it must be used sparingly). Solvent was removed *in vacuo* to afford a dark green powder (20 mg 75%). Crystals suitable for X-ray diffraction were grown *via* slow diffusion of pentanes into a concentrated ethereal solution at –30 °C. EA: found: C 68.0, H 5.2, N 5.1. Calc. for $C_{48}H_{41}N_3P_2Ru$: C 70.1, H 5.0, N 5.1%. UV-vis: $\lambda_{max}(C_6H_6)$/nm 697 ($\varepsilon/M^{-1}cm^{-1}$ 8500), 405 (32000). IR: ν_{max}/cm^{-1} 1818 m (RuH). ^1H NMR (C_6D_6): δ 7.87–7.83 (12H, m, C_6H_5), 7.07–6.99 (18H, m, C_6H_5), 6.39 (2H, d, ^2J = 6 Hz, 6-pyH), 6.38 (2H, s, $CH_{azaallyl}$), 6.25 (2H, m, 4-pyH), 5.88 (2H, d, ^2J = 7 Hz, 3-pyH), 5.16 (2H, m, 5-pyH), -8.59 (1H, t, $^2J_{HP}$ = 29 Hz, RuH). ^{13}C $\{^1H\}$ NMR: δ 166.89 (2-pyC), 156.53 (6-pyC), 137.07 (C_6H_5), 134.56 (C_6H_5), 128.75–128.00 (C_6H_5 buried under solvent), 115.58 ($C_{azaallyl}$), 113.82 (5-pyC), 113.67 (3-pyC). ^{31}P $\{^1H\}$ NMR: δ 50.94 (s, RuP). MS (DART): found: m/z 822.2. Calc. for $[C_{48}H_{40}N_3P_2Ru]^+$ (loss of H^-): 822.2.

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