

Formation of Ruthenium–Aminocarbene Complexes from Aldimines and Aminals

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Specific pyridine-based aldimines and aminals act as chelating ligands towards the RuCpL and RuTpL (Tp = hydrido trispyrazolylborate) fragments giving κ^2N,N' -coordinated cyclic imine complexes. Under particular conditions, as elucidated in this paper, these complexes rearrange into cyclic aminocarbene complexes. Thus, the reaction of [RuCp(L)(CH₃CN)₂](PF₆) (L = CH₃CN, PMe₃, SbPh₃) with 1 equiv. of py–N=CHR [R = Ph (phenyl), Fc (ferrocenyl), Np (naphthyl)] affords the cyclic aminocarbene complexes [RuCp(L)(=C(R)NH–py)]PF₆, whereas when L = PPh₃, PiPr₃, and CO the reaction stops at the stage of the imine complex [RuCp(L)(κ^2N,N' –py–N=CHR)]PF₆. Analogously, [RuTp–

(COD)Cl] (COD = 1,5-cyclooctadiene) also reacts readily with the imines py–N=CHR (R = Ph, pMeOC₆H₄, Np) at elevated temperatures to yield the aminocarbene complexes [RuTp{=C(R)NH–py}Cl]. This process may open a new synthetic route for obtaining carbene complexes. The mechanism of the imine–aminocarbene conversion was analyzed by DFT/B3LYP calculations. Accordingly, the operation of a direct 1,2 hydrogen shift can be ruled out; the reaction seems to involve hydrido iminoacyl intermediates resulting from C–H bond activation and deprotonation/protonation steps. © Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003

Introduction

It is highly fascinating to witness the vast and diversified varieties of rearrangements within and between molecules ligated to a transition metal center. In a recent communication,^[1] we reported the conversion of an aldimine to an amino carbene (Scheme 1, top). This conversion is analogous to the rearrangement of a coordinated olefin to a carbene (Scheme 1, bottom).^[2] Both of these processes involve a formal 1,2 hydrogen shift whose intimate mechanism remains unknown. For the olefin–carbene conversion, the presence of a heteroatom X featuring a strong π -donor group is of crucial importance. In fact, if X = H, alkyl, or aryl, the reverse process is more favorable.^[3]

In a previous report,^[1] we reacted the complex [RuCp(L)(CH₃CN)₂](PF₆), where L = CH₃CN, PMe₃, PPh₃, or CO, with (*E*)-*N*-(phenylmethylene)-2-pyridine amine (py–N=CHPh). The outcome of the reaction varied with the nature of the co-ligand L. Whereas [RuCp(L){=C–

(Ph)NH–py}]PF₆ was obtained when CH₃CN and PMe₃ were employed, the reaction stops at the stage of the imine complex [RuCp(L)(κ^2N,N' –py–N=CHR)]PF₆ with L = PPh₃ and CO. Similarly, [RuTp(COD)Cl] (Tp = hydrido trispyrazolylborate, COD = 1,5-cyclooctadiene) reacts readily with py–N=CHPh at elevated temperatures to give the aminocarbene complex [RuTp{=C(Ph)NH–py}Cl].

Our goal was to extend the scope of the above reactions to better understand the reasons for the intriguing imine–aminocarbene conversion. Towards this goal, we have used other imines with the general structure py–N=CHR, viz. R = ferrocenyl (Fc) and naphthyl (Np), and also py–CH₂–N=CHPh. Furthermore, we also used pyridine-based aminals which are known to be capable of forming amino carbenes by C–N and N–H bond cleavage and amine elimination.^[4,5] We have included also PiPr₃ and SbPh₃ as co-ligands to see whether the ligand size changes the reaction outcome. Finally, DFT/B3LYP calculations were performed to back up the mechanistic suggestions.

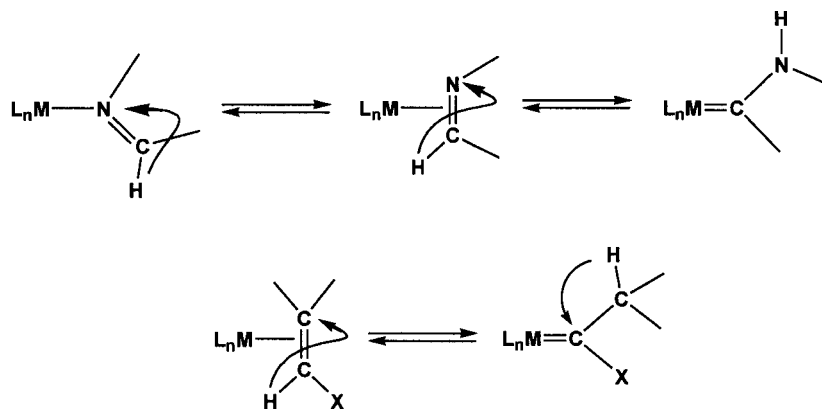
Results and Discussion

Synthesis and Characterization

Treatment of [RuCp(L)(CH₃CN)₂](PF₆) [L = CH₃CN (**1**), PMe₃ (**2a**)] with 1 equiv. of py–N=CHR [R = Ph (phenyl), Fc (ferrocenyl), Np (naphthyl)] afforded the aminocarbene

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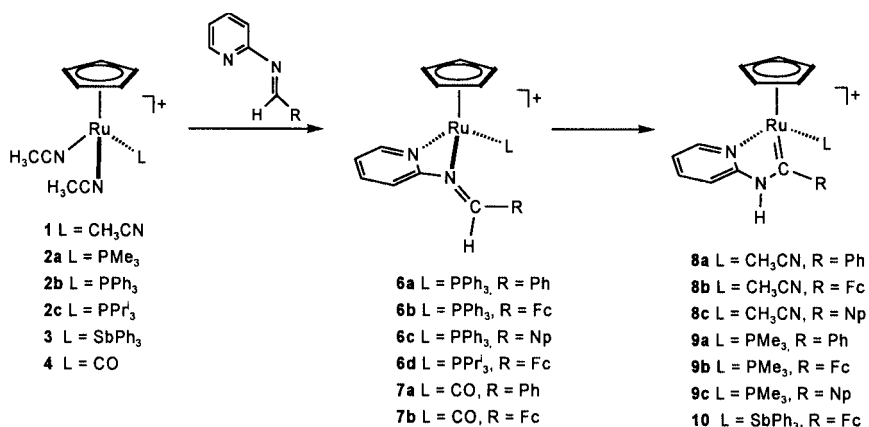


Scheme 1

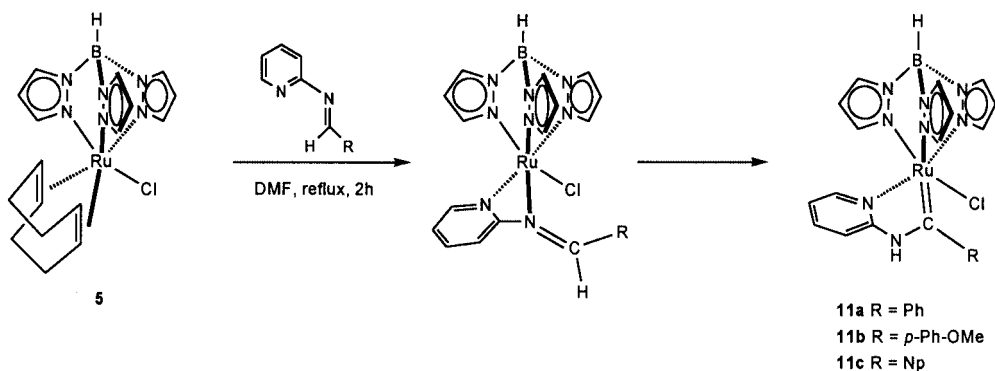
complexes $[\text{RuCp}(\text{L})\{\text{C}(\text{R})\text{NH-py}\}]\text{PF}_6$ (**8a–c**, **9a–c**) in high yields (Scheme 2). A similar transformation between $[\text{RuCp}(\text{SbPh}_3)(\text{CH}_3\text{CN})_2]\text{PF}_6$ (**3**) and py-N=CHFc leads to the aminocarbene complex $[\text{RuCp}(\text{SbPh}_3)\{\text{C}(\text{Fc})\text{NH-py}\}]\text{PF}_6$ (**10**). Analogously, $[\text{RuTp}(\text{COD})\text{Cl}]$ (**5**) also readily reacts with the imines py-N=CHR ($\text{R} = \text{Ph}$, $p\text{-MeOC}_6\text{H}_4$, Np) at elevated temperatures to yield the aminocarbene complexes $[\text{RuTp}\{\text{C}(\text{R})\text{NH-py}\}\text{Cl}]$ (**11a–c**) (Scheme 3). The ferrocenyl-based imine py-N=CHFc was not stable under the reaction conditions. We note that no carbene complexes were obtained from **1–3** by reaction with monodentate aldimines RN=CHR' ($\text{R} = \text{Ph}$, $i\text{Pr}$; $\text{R}' = \text{Ph}$, $i\text{Pr}$).

All of the carbene complexes formed are air-stable, in both solution and in the solid state, with the exception of **8a–c**, and were characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and elemental analysis. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **8–10**, the carbene moiety is identified by downfield signals in the range of $\delta = 263.2$ to 281.4 ppm. Other spectral changes accompanying the transformation to aminocarbene complexes include a characteristic broad resonance between $\delta = 11.8$ and 13.2 ppm assignable to the NH proton.

The solid-state structure of **11a** was determined by single-crystal X-ray diffraction. An ORTEP diagram is depicted in Figure 1 with some bond lengths reported in the caption.



Scheme 2



Scheme 3

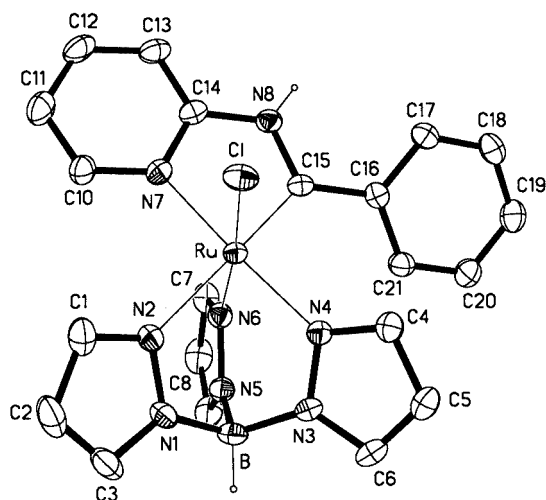


Figure 1. Structural view of **11a** showing 20% thermal ellipsoids (aromatic H atoms omitted); selected bond lengths (Å) and angles (°): Ru–N(2) 2.210(3), Ru–N(4) 2.074(3), Ru–N(6) 2.048(3), Ru–N(7) 2.046(3), Ru–Cl 2.414(1), Ru–C(15) 1.915(3), C(15)–Ru–N(7) 79.7(1), C(15)–Ru–N(6) 92.8(1), C(15)–Ru–N(4) 92.2(1), C(15)–Ru–N(2) 176.6(1), C(15)–Ru–Cl 94.1(1)

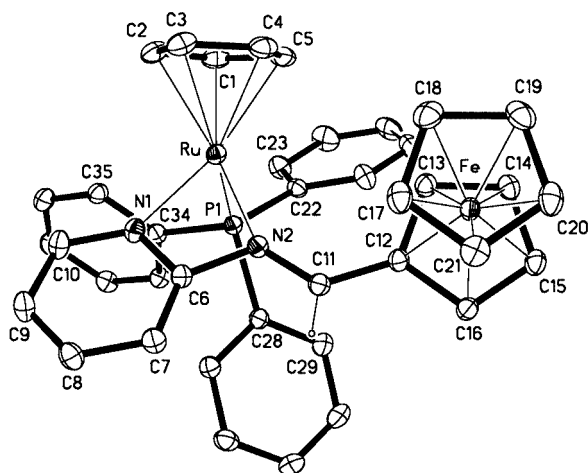


Figure 2. Structural view of **6b**·(CH₃)₂CO showing 40% thermal ellipsoids [aromatic H atoms, PF₆[−] and (CH₃)₂CO omitted for clarity]; selected bond lengths (Å) and angles (°): Ru–C(1–5)_{av} 2.186(2), Ru–P(1) 2.310(1), Ru–N(1) 2.104(1), Ru–N(2) 2.168(1), N(2)–C(11) 1.294(2), N(1)–Ru–N(2) 62.2(1)

The coordination geometry is distorted octahedral with all angles at ruthenium between 79 and 98° and 172 and 176°. The two Ru–N(Tp) bond lengths cis to the carbene moiety are significantly shorter [Ru–N(4) = 2.074(3) Å, Ru–N(6) = 2.048(3) Å] than that trans to the carbene moiety [Ru–N(2) = 2.210(3) Å]. The Ru–N(py) and Ru–Cl bond lengths are 2.046(3) and 2.414(1) Å. The Ru–C(15) bond length is 1.915(3) Å, which is similar to that in other heteroatom-stabilized ruthenium carbene complexes (cf. 1.959(1) Å in **9a**^[1]). The C(15)–Ru–N(7) angle is 79.1(1)°.

If the ligand L in [RuCp(L)(CH₃CN)₂]PF₆ is relatively bulky, such as PPh₃ or P*i*Pr₃, or if it is a relatively strong π acceptor, as in the case of CO, the reaction with py–N=CHR does not result in the formation of aminocarbene

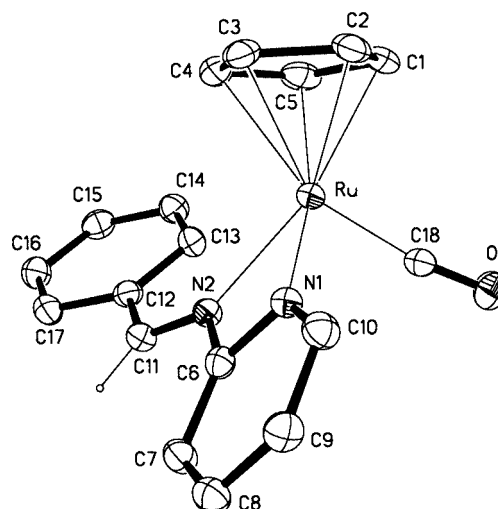


Figure 3. Structural view of **7a** showing 50% thermal ellipsoids (aromatic H atoms and PF₆[−] ions omitted for clarity); selected bond lengths (Å) and angles (°): Ru–C(1–5)_{av} 2.201(2), Ru–C(18) 1.876(2), Ru–N(1) 2.125(2), Ru–N(2) 2.167(2), N(2)–C(11) 1.288(3), C(18)–O 1.144(2), N(1)–Ru–N(2) 62.8(1), Ru–C(18)–O 171.6(1)

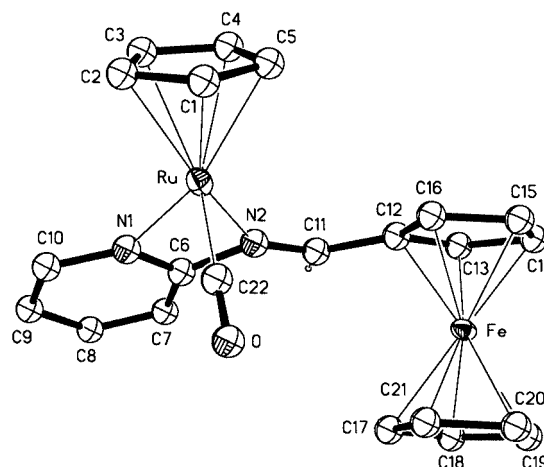
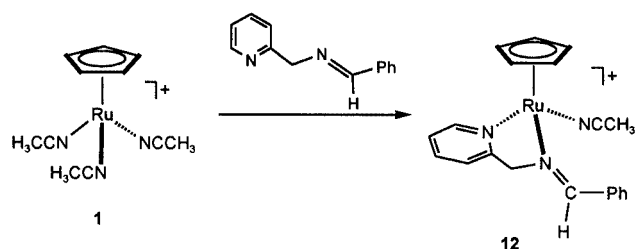


Figure 4. Structural view of **7b** showing 50% thermal ellipsoids (aromatic H atoms and PF₆[−] ions omitted for clarity); selected bond lengths (Å) and angles (°): Ru–C(1–5)_{av} 2.174(11), Ru–C(22) 1.846(10), Ru–N(1) 2.080(9), Ru–N(2) 2.133(8), N(2)–C(11) 1.267(11), C(22)–O 1.139(11), N(1)–Ru–N(2) 60.3(3), Ru–C(22)–O 176.1(11)

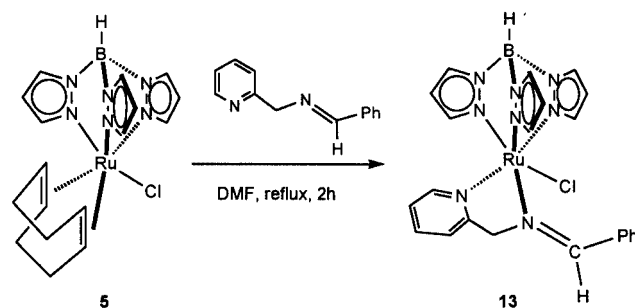
complexes. Instead, and in keeping with previous results,^[1] the complexes [RuCp(L)(κ^2 N,N'-py–N=CHR)]PF₆ (**6a–d**, **7a,b**) are obtained according to Scheme 2. In view of the strained four-membered N–Ru–N–C ring system, it is noteworthy that no rearrangement to carbene complexes is observed, even at elevated temperature for 24 h. Complexes **6** and **7** were characterized by NMR spectroscopy and elemental analysis. In addition, the structures of **6b**, **7a**, and **7b** were determined by X-ray crystallography and are presented in Figure 2, Figure 3 and Figure 4. The overall structures are very similar and they can be described as three-legged piano stool conformations with the two N atoms of the imine ligand and the PPh₃ and CO ligands, respectively, as the legs. The N–Ru–N angles in **6b**, **7a**, and **7b** are

62.2(1), 62.8(1), and 60.3(3)°, respectively. The four-membered N–Ru–N–C ring system is essentially planar with torsion angles of 2.5(1), –2.1(1), and –1.4(5)°.

Notwithstanding these stable structures, the relief of the strain of the four-membered N–Ru–N–C ring might be a factor that favors the rearrangement of the $\kappa^2\text{NN}$ imine into the aminocarbene complex. In fact, the imine complex derived from $\text{py-CH}_2\text{-N=CHR}$, rather than py-N=CHR , that features a five-membered N–Ru–N–C–C ring instead of a four-membered one, does not convert into the aminocarbene, even if kept for long times at elevated temperatures. This lack of reactivity is the case for $[\text{RuCp}(\text{CH}_3\text{CN})(\kappa^2\text{N,N'}\text{-py-CH}_2\text{-N=CHPh})]\text{PF}_6$ (**12**) and $[\text{RuTp}(\kappa^2\text{N,N'}\text{-py-CH}_2\text{-N=CHPh})\text{Cl}]$ (**13**) that are obtained from **1** and **5**, respectively (Schemes 4 and 5). A structural view of **12** is given in Figure 5 with selected bond lengths reported in the caption. This complex can be described in terms of a three-legged piano stool conformation



Scheme 4



Scheme 5

with the two N atoms of the imine ligand and the N atom of the CH_3CN ligand as the legs. It is worth noting that the N–Ru–N angle [77.8(1)°] is considerably larger than those in **6b**, **7a**, and **7b**.

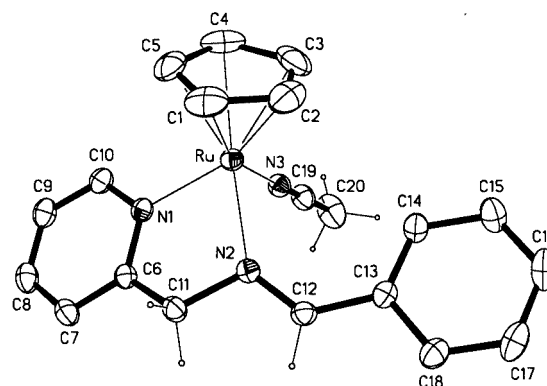
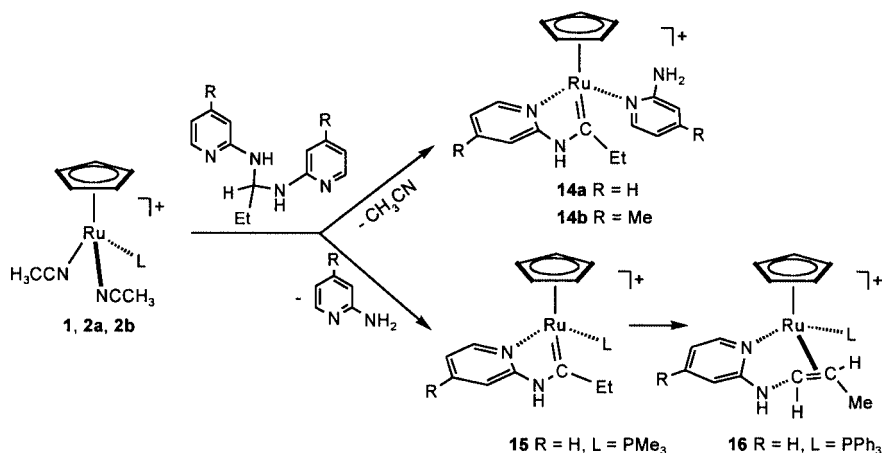


Figure 5. Structural view of **12** showing 50% thermal ellipsoids (aromatic H atoms and PF_6^- ions omitted for clarity); selected bond lengths (Å) and angles (°): Ru–C(1–5)_{av} 2.153(3), Ru–N(1) 2.104(1), Ru–N(2) 2.117(1), Ru–N(3) 2.077(1), N(1)–Ru–N(2) 77.8(1), Ru–N(3)–C(19) 178.9(3)

The generality of cyclic aminocarbene construction is further implied by the finding that amins also react with the RuCpL and RuTpL fragments to form the corresponding aminocarbene complexes. In these reactions, the amina at first obviously transforms back into the starting aldimines and amines. Thus, **1** and **2** react with *N,N'*-bis(2-pyridyl)-1,1-propanediamine [py-NHCH(Et)NH-py] and *N,N'*-bis(2-picoly)-1,1-propanediamine [$\text{pyMe-NHCH(Et)NH-pyMe}$] to form $[\text{RuCp}(\text{py-NH}_2)\{\text{C}(\text{NH-py})\text{Et}\}]\text{PF}_6$ (**14a**), $[\text{RuCp}(\text{pyMe-NH}_2)\{\text{C}(\text{NH-pyMe})\text{Et}\}]\text{PF}_6$ (**14b**), and $[\text{RuCp}(\text{PMe}_3)(\text{C}(\text{NH-py})\text{Et})]\text{PF}_6$ (**15**) in high yields (Scheme 6). Interestingly, with **2b** the reaction does not stop at the aminocarbene stage, but proceeds further to give the olefin complex **16**. Such a mode of rearrangement is a common decomposition pathway of electron-deficient carbene complexes.^[3] A structural view of **16**, determined



Scheme 6

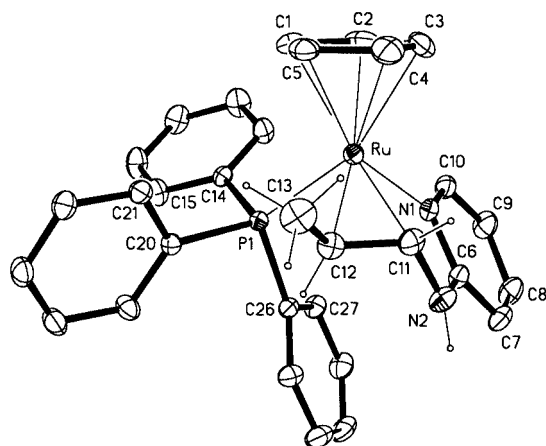
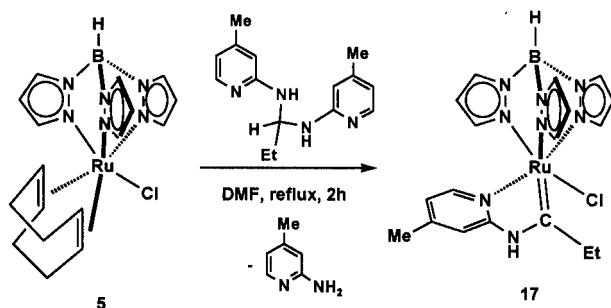


Figure 6. Structural view of **16** showing 20% thermal ellipsoids (aromatic H atoms and PF_6^- ions omitted for clarity); selected bond lengths (Å) and angles ($^\circ$): $\text{Ru}-\text{C}(1-5)_{\text{av}}$ 2.224(4), $\text{Ru}-\text{P}(1)$ 2.348(1), $\text{Ru}-\text{N}(1)$ 2.122(1), $\text{Ru}-\text{C}(11)$ 2.171(3), $\text{Ru}-\text{C}(12)$ 1.272(3), $\text{C}(11)-\text{C}(12)$ 1.383(5), $\text{N}(1)-\text{Ru}-\text{C}(11)$ 76.1(1)



Scheme 7

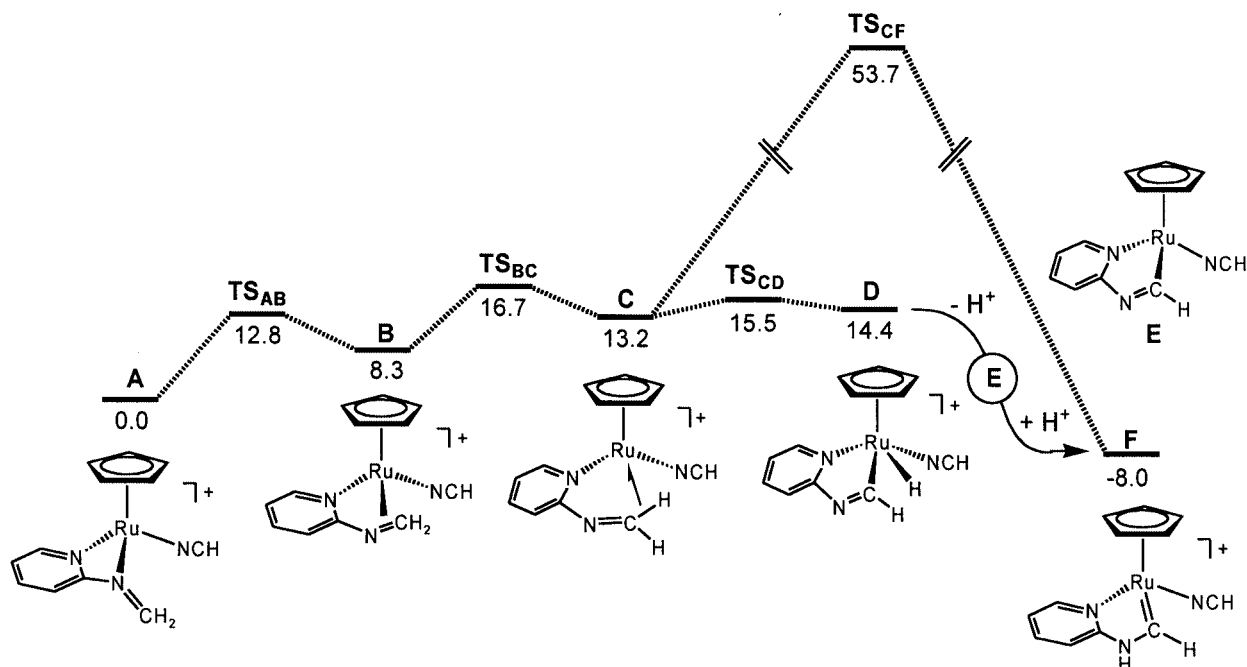
by X-ray crystallography, is shown in Figure 6 with selected bond lengths reported in the caption. Similarly, $[\text{RuTp}(\text{COD})\text{Cl}]$ (**5**) reacts with pyMe-NHCH(Et)NH_2

pyMe to give $[\text{RuTp}\{\text{C}(\text{NH-pyMe})\text{Et}\}\text{Cl}]$ (**17**) as shown in Scheme 7. These reactions involve both C–H and C–N activation steps, which thereby release a 2-aminopyridine molecule. It may be pertinent to note that **2b** does not react with $\text{py-N}=\text{CHPh}$ to form an aminocarbene complex or a rearrangement product thereof.

Mechanistic Aspects

In the absence of detectable intermediate products on the way from the $\kappa^2\text{NN}$ -imine to the aminocarbene complexes, we performed DFT (B3LYP) calculations using $\text{py-N}=\text{CH}_2$ and HCN as model ligands. Along these lines, several key intermediates can be proposed and these are depicted in Scheme 8 (energy in kcal/mol). The overall reaction is exothermic by 8.0 kcal/mol. The reliability of the computational method (details in the Exp. Sect.) is supported by the good agreement between the calculated geometries of **A** and **F** (Figure 7) with the X-ray structures for the related complexes (**6a**, **6b**, **7a**, **7b**, and **9a**).

At first, the imine moiety of the $\kappa^2\text{N,N'}$ - $\text{py-N}=\text{CH}_2$ complex **A** becomes side-on coordinated (**B**). The endothermic nature of this step (8.3 kcal/mol) points to the preference for end-on coordination, although the activation barrier is relatively low (12.8 kcal/mol). Next, an agostic C–H bond is formed (**C**) that is energetically unfavorable by 4.9 kcal/mol. In proceeding from **A** to **C**, a rotation about the $-\text{N}=\text{CH}_2$ bond takes place that moves the substituent (hydrogen in the model system) from a syn position to an anti one, with respect to the metal center. Subsequent C–H bond activation leads eventually to the hydrido iminoacyl intermediate **D**.^[6–8] This process is slightly endothermic by 1.2 kcal/mol and has a small activation barrier (2.3 kcal/mol). Such types of intermediates have been suggested recently for the reaction of $[\text{RuHCl}(\text{P}(\text{Pr}_3)_2)_2]$ also



Scheme 8

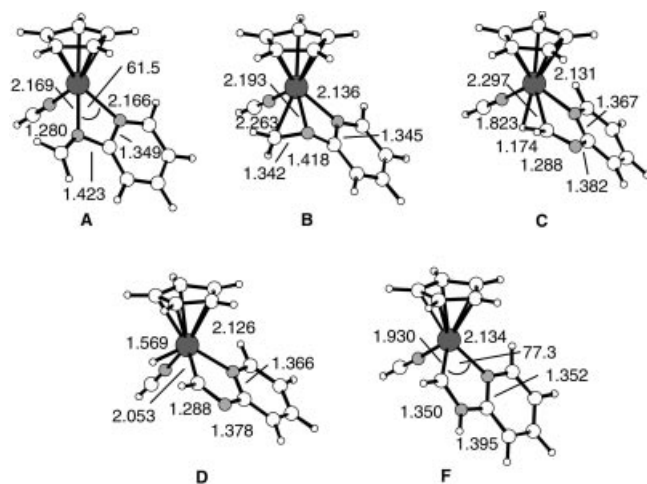


Figure 7. Optimized B3LYP geometries of the equilibrium structures **A**, **B**, **C**, **D**, and **F** (distances in Å and angles in deg)

with imines, in which case, however, isocyanides are formed and not aminocarbenes.^[9]

It appears that the step from **C** to **D** involving C–H activation/oxidative addition, is particularly crucial to the overall imine-to-aminocarbene transformation. The reactivity of the imine complex is arguably lessened in the case of sterically demanding co-ligands like PPh₃ in **2b** and P*i*Pr₃ in **2c**. Note that the cone angle^[10] increases in the order CH₃CN < PMe₃ < SbPh₃ < PPh₃ < P*i*Pr₃. Alternatively, the presence of a strongly π -accepting co-ligand, such as CO, in **4** may prevent the oxidative addition step. The structures of the entities **A**–**F** as well as the corresponding transition states **TS_{AB}**–**TS_{CF}** are shown in Figure 7 and Figure 8.

The mechanism that is least clear is that for the onward reaction from **D** to **F**. According to our DFT calculations, a direct 1,2 hydrogen shift has a barrier as high as 53.7 kcal/mol and, thus, it is safe to exclude it. Alternative possibilities include the intermediacy of a neutral imino acyl complex **E** or, more appealingly, deprotonation/protonation assisted by adventitious water, counterion, or solvent. We favor a hydrogen-transfer pathway based on the implication of water as depicted in Scheme 9. Such a process, though in need of verification, would be consistent with the proton-transfer catalysis of water molecules arranged in cyclic aggregates that have been suggested, for example, for the de-

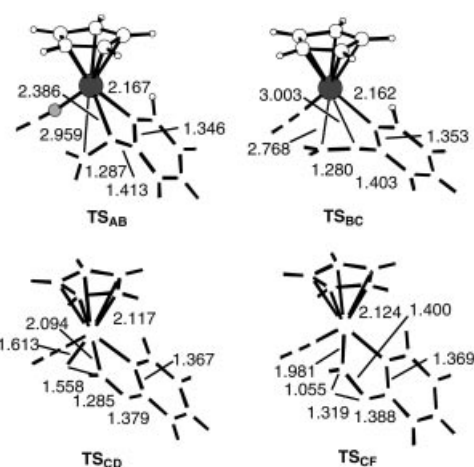


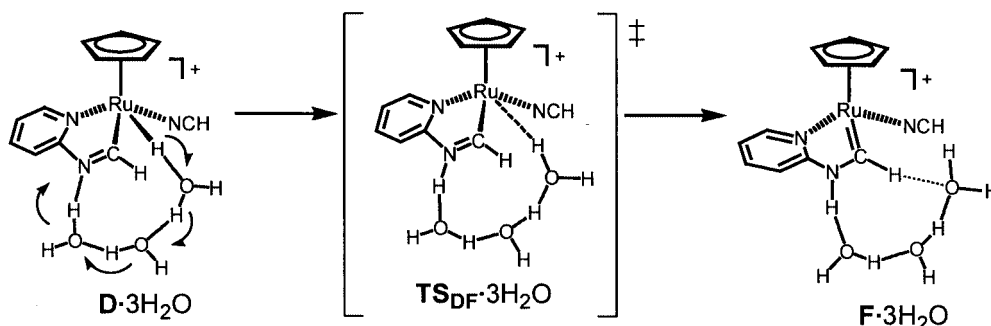
Figure 8. Optimized B3LYP geometries of the transition states **TS_{AB}**, **TS_{BC}**, **TS_{CD}**, and **TS_{CF}** (distances in Å)

hydration of carbonic acid^[11] or the hydration of sulfur trioxide.^[12]

Conclusion

The factors that contribute to the present imine-to-aminocarbene rearrangement are summarized as follows. (i) The reaction is chelate assisted with the presence of the pyridine moiety being essential for the coordination of the imine to the metal center. (ii) In the four-membered N–Ru–N–C ring, the chelated imine ligand is under steric strain. (iii) The five-membered ring system N–Ru–C–N–C, arising from the rearrangement, interacts with the planar pyridine ring and can be considered as a 10- π -electron metallacycle that benefits from aromatic stabilization. (iv) Heteroatom stabilization seems to be an important factor too. (v) The co-ligand L should not be too bulky and only a moderate π acceptor.

The reaction of pyridine-based aldimines and amins with both RuCp and RuTp complexes could furnish alternative and simple preparation methods for special carbene complexes without the use, for example, of diazoalkanes.



Scheme 9

Experimental Section

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.^[13] The deuterated solvents were purchased from Aldrich and dried over 4-Å molecular sieves. [RuCp(CH₃CN)₃]PF₆ (**1**),^[14] [RuCp-(PMe₃)(CH₃CN)₂]PF₆ (**2a**), [RuCp(PPh₃)(CH₃CN)₂]PF₆ (**2b**), and [RuCp(PiPr₃)(CH₃CN)₂]PF₆ (**2c**),^[15] [RuCp(SbPh₃)(CH₃CN)₂]PF₆ (**3**),^[16] [RuCp(CO)(CH₃CN)₂]PF₆ (**4**) and [RuTp(COD)Cl] (**5**),^[17] [RuCp(PPh₃)(κ²N,N'-py-N=CHPh)]PF₆ (**6a**), [RuCp(CO)-(κ²N,N'-py-N=CHPh)]PF₆ (**7a**), [RuCp(CH₃CN){=C(Ph)NH-py}]PF₆ (**8a**), [RuCp(PMe₃){=C(Ph)NH-py}]PF₆ (**9a**), [RuTp-{=C(Ph)NH-py}Cl] (**11a**), [RuCp(py-NH₂){=C(NH-py)Et}]PF₆ (**12a**), [RuCp(PMe₃){=C(NH-py)Et}]PF₆ (**13**), and [RuCp(PPh₃)(py-NH-η²-CH=CHMe)]PF₆ (**14**)^[1] were prepared according to literature procedures. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Bruker AVANCE-250 spectrometer and were referenced to SiMe₄ and H₃PO₄ (85%), respectively. ¹H and ¹³C{¹H} NMR signal assignments were confirmed by ¹H-COSY, 135-DEPT, and HMQC(¹H-¹³C) experiments.

[RuCp(PPh₃)(κ²N,N'-py-N=CHFc)]PF₆ (6b**):** (*E*)-*N*-(Ferrocenylmethylene)-2-pyridineamine (py-N=CHFc) (44 mg, 0.152 mmol) was added to a solution of **2b** (100 mg, 0.152 mmol) in CH₂Cl₂ (5 mL). After the mixture was stirred at room temperature for 9 h, the solvent was evaporated under vacuum and the resulting red solid was collected on a glass frit and washed twice with diethyl ether (10 mL). Yield: 105 mg (80%). C₃₉H₃₄F₆FeN₂P₂Ru (863.57): calcd. C 54.24, H 3.97; found C 54.29; H 4.04. ¹H NMR ([D₆]acetone, 20 °C): δ = 9.20 (s, 1 H, N=CHFc), 8.52 (d, *J*_{H,H} = 4.42 Hz, 1 H, py⁶), 7.77 (vt, *J*_{H,H} = 7.84 Hz, 1 H, py⁴), 7.55–7.15 (m, 17 H, PPh₃, py³, py⁵), 5.26–5.17 (m, 1 H, FeCp^s), 5.06–4.99 (m, 1 H, FeCp^s), 4.97–4.87 (m, 2 H, FeCp^s), 4.69 (s, 5 H, RuCp), 4.26 (s, 5 H, FeCp) ppm. ¹³C{¹H} NMR ([D₆]acetone, 20 °C): δ = 169.7 (1C, py⁶), 164.5 (1C, py²), 151.9 (*J*_{C,P} = 1.4 Hz, 1C, N=CHFc), 138.1 (1C, py⁴), 133.7 (*J*_{C,P} = 40.6 Hz, 3C, Ph¹), 133.3 (*J*_{C,P} = 11.0 Hz, 6C, Ph^{2,6}), 130.1 (*J*_{C,P} = 2.2 Hz, 3C, Ph⁴), 128.5 (*J*_{C,P} = 9.9 Hz, 6C, Ph^{3,5}), 123.9 (1C, py³), 109.2 (1C, py⁵), 75.8 (1C, FeCp^{s1}), 74.8 (1C, FeCp^s), 74.7 (1C, FeCp^s), 74.5 (5C, RuCp), 74.5 (1C, FeCp^s), 71.9 (1C, FeCp^s), 70.2 (5C, FeCp) ppm. ³¹P{¹H} NMR ([D₆]acetone, 20 °C): δ = 49.7 (PPh₃), -144.2 (*J*_{PF} = 719.5 Hz, PF₆) ppm.

[RuCp(PPh₃)(κ²N,N'-py-N=CHNp)]PF₆ (6c**):** An NMR tube was charged with **2b** (50 mg, 0.080 mmol) and *N*-(naphthylmethylene)-2-pyridine amine (py-N=CHNp) (23 mg, 0.080 mmol), and when they were dissolved in [D₆]acetone (0.5 mL), the color changed from yellow to dark red. After 12 h at room temperature NMR spectra were taken indicating quantitative formation of **6c**. ¹H NMR ([D₆]acetone, 20 °C): δ = 10.24 (s, 1 H, N=CHNp), 9.27 (d, *J*_{H,H} = 7.31 Hz, 1 H, py⁶), 8.64 (td, *J*_{H,H1} = 5.28, *J*_{H,H2} = 0.80 Hz, 1 H, py⁴), 8.15–7.99 (m, 1 H, py³), 7.90–7.80 (m, 1 H, py⁵), 7.78–7.58 (m, 7 H, Np), 7.47–7.16 (m, 15 H, PPh₃), 4.76 (d, *J*_{H,H} = 0.16 Hz, 5 H, RuCp) ppm. ¹³C{¹H} NMR ([D₆]acetone, 20 °C): δ = 162.9 (1C, py⁶), 164.0 (1C, py²), 152.1 (1C, N=CHNp), 138.4 (1C, py⁴), 136.9, 135.5, 134.0 (3C, Np), 133.3 (*J*_{C,P} = 41.5 Hz, 3C, Ph¹), 133.2 (*J*_{C,P} = 11.5 Hz, 6C, Ph^{2,6}), 132.3 (1C, Np), 130.2 (*J*_{C,P} = 2.2 Hz, 3C, Ph⁴), 129.3, 128.7 (2C, Np), 128.5 (*J*_{C,P} = 9.9 Hz, 6C, Ph^{3,5}), 128.0, 127.1, 125.6, 124.8 (4C, Np), 122.2 (1C, py³), 110.2 (1C, py⁵), 75.3 (*J*_{C,P} = 2.1 Hz, 5C, RuCp) ppm. ³¹P{¹H} NMR ([D₆]acetone, 20 °C): δ = 49.7 (PPh₃), -144.1 (*J*_{PF} = 719.5 Hz, PF₆) ppm.

[RuCp(PiPr₃)(κ²N,N'-py-N=CHFc)]PF₆ (6d**):** This compound was prepared analogously to **6b** by using **2c** (50 mg, 0.090 mmol) and py-N=CHFc (26 mg, 0.090 mmol) as the starting materials. Yield: 49 mg (71%). C₃₀H₄₀F₆FeN₂P₂Ru (761.52): calcd. C 47.32, H 5.29; found C 47.41, H 5.33. ¹H NMR ([D₆]acetone, 20 °C): δ = 9.64 (s, 1 H, N=CHFc), 8.64 (d, *J*_{H,H1} = 5.03 Hz, 1 H, py⁶), 7.96 (t, *J*_{H,H} = 7.99 Hz, 1 H, py⁴), 7.66 (d, *J*_{H,H} = 8.45 Hz, 1 H, py³), 7.41 (dd, *J*_{H,H1} = 7.54, *J*_{H,H2} = 5.25 Hz, 1 H, py⁵), 5.31–5.22 (m, 1 H, FeCp^s), 5.09–5.01 (m, 1 H, FeCp^s), 5.00–4.90 (m, 2 H, FeCp^s), 4.72 (s, 5 H, RuCp), 4.45 (s, 5 H, FeCp), 2.26 (m, *J*_{PH} = 7.27 Hz, 3 H, CH), 1.14 (ddd, *J*_{H,H1} = 12.90, *J*_{H,H2} = 7.20, *J*_{H,H3} = 2.43 Hz, 18 H, CH₃) ppm. ¹³C{¹H} NMR ([D₆]acetone, 20 °C): δ = 170.1 (1C, py⁶), 165.5 (1C, py²), 153.0 (1C, N=CHFc), 138.5 (1C, py⁴), 124.1 (1C, py³), 108.5 (1C, py⁵), 76.0 (1C, FeCp^{s1}), 74.9 (1C, FeCp^s), 74.6 (1C, FeCp^s), 73.2 (1C, FeCp^s), 72.9 (1C, FeCp^s), 71.7 (*J*_{C,P} = 1.35 Hz, 5C, RuCp), 70.4 (5C, FeCp), 26.8 (*J*_{C,P} = 18.9 Hz, 3C, P[CH(CH₃)₂]₃), 19.5 [6C, P[CH(CH₃)₂]₃] ppm. ³¹P{¹H} NMR ([D₆]acetone, 20 °C): δ = 52.2 (PiPr₃), -144.1 (*J*_{PF} = 708.1 Hz, PF₆).

[RuCp(CO)(κ²N,N'-py-N=CHFc)]PF₆ (7b**):** This compound was prepared analogously to **6b** by using **4** (50 mg, 0.090 mmol) and py-N=CHFc (26 mg, 0.090 mmol) as the starting materials. Yield: 132 mg (89%). C₂₂H₁₉F₆FeN₂OPRu (629.29): calcd. C 41.99, H 3.04; found C 41.87; H 3.10. ¹H NMR ([D₆]acetone, 20 °C): δ = 9.67 (s, 1 H, N=CHFc), 8.53 (d, *J*_{H,H} = 5.18 Hz, 1 H, py⁶), 8.14 (dt, *J*_{H,H1} = 8.14, *J*_{H,H2} = 1.27 Hz, 1 H, py⁴), 7.80 (d, *J*_{H,H} = 8.38 Hz, 1 H, py³), 7.52 (dd, *J*_{H,H1} = 7.54, *J*_{H,H2} = 5.41 Hz, 1 H, py⁵), 5.38 (s, 5 H, RuCp), 5.14–4.92 (m, 4 H, FeCp^s), 4.47 (s, 5 H, FeCp) ppm. ¹³C{¹H} NMR ([D₆]acetone, 20 °C): δ = 200.7 (1C, CO), 171.0 (1C, py⁶), 166.0 (1C, py²), 152.7 (1C, N=CHFc), 140.4 (1C, py⁴), 124.2 (1C, py³), 109.9 (1C, py⁵), 81.9 (1C, FeCp^s), 81.1 (5C, RuCp), 76.4 (1C, FeCp^s), 76.3 (1C, FeCp^s), 75.7 (1C, FeCp^s), 74.6 (1C, FeCp^{s1}), 71.0 (5C, FeCp) ppm.

[RuCp(CH₃CN)(=C(Fe)NH-py)]PF₆ (8b**):** Compound py-N=CHFc (133 mg, 0.461 mmol) was added to a solution of **1** (200 mg, 0.461 mmol) in CH₂Cl₂ (7 mL). After the mixture was stirred at room temperature for 24 h, the solvent was evaporated under vacuum and the resulting purple solid was collected on a glass frit and washed twice with diethyl ether (10 mL). Yield: 152 mg (85%). C₂₃H₂₂F₆FeN₃PRu (642.33): calcd. C 43.01, H 3.45; found C 43.11; H 3.47. ¹H NMR ([D₆]acetone, 20 °C): δ = 11.90 (br. s, 1 H, NH), 9.10 (d, *J*_{H,H} = 5.63 Hz, 1 H, py⁶), 7.95 (ddd, *J*_{H,H1} = 8.45, *J*_{H,H2} = 7.23, *J*_{H,H3} = 1.37 Hz, 1 H, py⁴), 7.72 (dd, *J*_{H,H1} = 8.38, *J*_{H,H2} = 0.83 Hz, 1 H, py³), 7.22 (ddd, *J*_{H,H1} = 7.23, *J*_{H,H2} = 5.86, *J*_{H,H3} = 1.29 Hz, 1 H, py⁵), 5.28–5.18 (m, 1 H, FeCp^s), 5.16–5.10 (m, 1 H, FeCp^s), 4.86 (s, 5 H, RuCp), 4.84–4.78 (m, 2 H, FeCp^s), 4.30 (s, 5 H, FeCp), 2.34 (s, 3 H, CH₃CN) ppm. ¹³C{¹H} NMR ([D₆]acetone, 20 °C): δ = 264.6 (1C, Ru=C), 159.0 (1C, py²), 155.8 (1C, py⁶), 138.7 (1C, py⁴), 127.2 (1C, CH₃CN), 119.7 (1C, py³), 112.3 (1C, py⁵), 87.9 (1C, FeCp^{s1}), 80.7 (5C, RuCp), 75.1 (1C, FeCp^s), 74.2 (1C, FeCp^s), 73.8 (1C, FeCp^s), 70.3 (5C, FeCp), 68.2 (1C, FeCp^s), 3.1 (1C, CH₃CN) ppm.

[RuCp(CH₃CN)(=C(Np)NH-py)]PF₆ (8c**):** This compound was prepared analogously to **8b** by using **1** (100 mg, 0.230 mmol) and py-N=CHNp (64 mg, 0.276 mmol) as the starting materials. Yield: 111 mg (83%). C₂₃H₂₀F₆N₃PRu (584.47): calcd. C 47.27, H 3.45; found C 47.33; H 3.40. ¹H NMR ([D₆]acetone, 20 °C): δ = 12.86 (s, 1 H, NH), 9.21 (ddd, *J*_{H,H1} = 5.73, *J*_{H,H2} = 1.54, *J*_{H,H3} = 0.75 Hz, 1 H, py⁶), 8.14–7.99 (m, 4 H, Np, py⁴), 7.94–7.85 (m, 1 H, Np), 7.78–7.69 (m, 2 H, Np), 7.67 (d, *J*_{H,H} = 8.06 Hz, 1 H, py³), 7.63–7.53 (m, 1 H, Np), 7.41 (ddd, *J*_{H,H1} = 7.31, *J*_{H,H2} = 5.80, *J*_{H,H3} = 1.38 Hz, 1 H, py⁵), 4.74 (s, 5 H, RuCp), 2.47 (s, 3 H,

CH₃CN) ppm. ¹³C{¹H} NMR ([D₆]acetone, 20 °C): δ = 269.5 (1C, Ru=C), 158.4 (1C, py²), 155.7 (1C, py⁶), 138.9 (1C, py⁴), 136.9, 135.1, 133.7, 129.8, 128.9, 128.6, 128.4, 126.5, 125.3, 125.1 (10C, Np), 124.6 (1C, CH₃CN), 120.5 (1C, py³), 113.2 (1C, py⁵), 82.1 (5C, RuCp), 2.9 (1C, CH₃CN) ppm.

[RuCp(PMe₃)₃=C(Fe)NH-py]PF₆ (9b): This compound was prepared analogously to **8b** by using **2a** (50 mg, 0.107 mmol) and py-N=CHFc (31 mg, 0.107 mmol) as the starting materials. Yield: 68 mg (94%). C₂₄H₂₈F₆FeN₂P₂Ru (677.36): calcd. C 42.56, H 4.17; found C 42.61; H 4.19. ¹H NMR ([D₆]acetone, 20 °C): δ = 11.89 (br. s, 1 H, NH), 8.97 (dd, *J*_{H,H1} = 5.94, *J*_{H,H2} = 0.69 Hz, 1 H, py⁶), 7.88 (m, 1 H, py⁴), 7.76 (d, *J*_{H,H} = 8.07 Hz, 1 H, py³), 7.12 (ddd, *J*_{H,H1} = 7.16, *J*_{H,H2} = 5.79, *J*_{H,H3} = 1.37 Hz, 1 H, py⁵), 5.20 (d, *J*_{PH} = 0.30 Hz, 5 H, RuCp), 5.15–5.05 (m, 1 H, FeCp^s), 4.94–4.87 (m, 1 H, FeCp^s), 4.83–4.74 (m, 2 H, FeCp^s), 4.33 (s, 5 H, FeCp), 1.09 (d, *J*_{PH} = 9.90 Hz, 9 H, PMe₃) ppm. ¹³C{¹H} NMR ([D₆]acetone, 20 °C): δ = 263.2 (*J*_{C,P} = 12.1 Hz, 1C, Ru=C), 157.9 (1C, py⁶), 155.7 (*J*_{C,P} = 1.9 Hz, 1C, py²), 137.5 (1C, py⁴), 119.2 (1C, py³), 113.0 (1C, py⁵), 88.0 (1C, FeCp^{s1}), 83.0 (5C, RuCp), 76.8 (1C, FeCp^s), 73.7 (1C, FeCp^s), 73.0 (1C, FeCp^s), 70.6 (5C, FeCp), 66.9 (1C, FeCp^s), 17.5 (*J*_{C,P} = 31.8 Hz, 3C, PMe₃) ppm. ³¹P{¹H} NMR ([D₆]acetone, 20 °C): δ = 6.2 (PMe₃), –144.2 (¹*J*_{PF} = 708.4 Hz, PF₆) ppm.

[RuCp(PMe₃)₃=C(Np)NH-py]PF₆ (9c): This compound was prepared analogously to **8b** by using **2a** (50 mg, 0.107 mmol) and py-N=CHNp (25 mg, 0.107 mmol) as the starting materials. Yield: 59 mg (91%). C₂₄H₁₇F₆N₂P₂Ru (610.42): calcd. C 47.22, H 2.81; found C 47.17; H 2.78. ¹H NMR ([D₆]acetone, 20 °C): δ = 12.66 (br. s, 1 H, NH), 9.08 (d, *J*_{H,H} = 5.79 Hz, 1 H, py⁶), 8.20–7.47 (m, 9 H, Np, py⁴, py³), 7.32 (ddd, *J*_{H,H1} = 7.23, *J*_{H,H2} = 5.86, *J*_{H,H3} = 1.37 Hz, 1 H, py⁵), 4.94 (d, *J*_{PH} = 0.30 Hz, 5 H, RuCp), 1.34 (d, *J*_{PH} = 9.90 Hz, 9 H, PMe₃) ppm. ¹³C{¹H} NMR ([D₆]acetone, 20 °C): δ = 268.8 (*J*_{C,P} = 9.7 Hz, 1C, Ru=C), 157.6 (1C, py²), 155.8 (1C, py⁶), 147.4 (1C, Np), 137.8 (1C, py⁴), 133.7 (1C, Np), 129.4 (1C, Np), 128.5 (2C, Np), 126.9 (1C, Np), 126.7 (1C, Np^a), 126.5 (1C, Np), 125.3 (2C, Np), 119.9 (1C, py³), 113.6 (1C, py⁵), 84.1 (5C, RuCp), 17.5 (*J*_{C,P} = 32.3 Hz, 3C, PMe₃) ppm. ³¹P{¹H} NMR ([D₆]acetone, 20 °C): δ = 5.4 (PMe₃), –144.2 (¹*J*_{PF} = 719.5 Hz, PF₆) ppm.

[RuCp(SbPh₃)₃=C(Fe)NH-py]PF₆ (10): This compound was prepared analogously to **6b** by using **3** (80 mg, 0.107 mmol) and py-N=CHFc (31 mg, 0.107 mmol) as the starting materials. Yield: 89 mg (87%). C₃₉H₃₄F₆FeN₂PSbRu (954.35): calcd. C 49.08, H 3.59; found C 49.12, H 3.62. ¹H NMR ([D₆]acetone, 20 °C): δ = 11.76 (br. s, 1 H, NH), 9.19 (d, *J*_{H,H} = 5.18 Hz, 1 H, py⁶), 7.67 (dt, *J*_{H,H1} = 7.73, *J*_{H,H2} = 0.91 Hz, 1 H, py⁴), 7.53–7.12 (m, 16 H, SbPh₃, py³), 6.98 (ddd, *J*_{H,H1} = 6.62, *J*_{H,H2} = 6.24, *J*_{H,H3} = 0.46 Hz, 1 H, py⁵), 5.36 (s, 5 H, RuCp), 5.07–4.94 (m, 2 H, FeCp^s), 4.86–4.73 (m, 2 H, FeCp^s), 4.27 (s, 5 H, FeCp) ppm. ¹³C{¹H} NMR ([D₆]acetone, 20 °C): δ = 263.4 (1C, Ru=C), 157.4 (1C, py²), 155.9 (1C, py⁶), 135.2 (1C, py⁴), 134.9 (6C, Ph^{3,5}), 132.2 (3C, Ph¹), 130.2 (3C, Ph⁴), 129.3 (6C, Ph^{3,5}), 118.6 (1C, py³), 113.0 (1C, py⁵), 87.6 (1C, FeCp^{s1}), 79.3 (5C, RuCp), 76.5 (1C, FeCp^s), 74.3 (1C, FeCp^s), 73.7 (1C, FeCp^s), 70.2 (5C, FeCp), 67.1 (1C, FeCp^s) ppm.

[RuTp{C(C₆H₄OMe)_p}-py]Cl (11b): A solution of **5** (100 mg, 0.218 mmol) and *N*-(*p*-methoxyphenylmethylene)-2-pyridineamine (py-N=CHC₆H₄OMe) (92.5 mg, 0.436 mmol) in DMF (4 mL) was heated under reflux for 2.5 h. After evaporation of the solvent under reduced pressure, the brown product was washed with pentane (2 × 5 mL), and dried under vacuum. Yield: 94.4 mg (77%).

C₂₂H₂₂BN₈ClORu (561.81): calcd. C 47.04, H 3.95; found C, 47.11, H 3.89. ¹H NMR ([D₆]DMSO, 20 °C): δ = 13.17 (s, 1 H, NH), 8.33 (d, *J*_{H,H} = 5.5 Hz, 1 H, py⁶), 8.11 (br. s, 1 H, Tp), 8.05 (d, *J*_{H,H} = 2.2 Hz, 1 H, Tp), 7.89 (d, *J*_{H,H} = 2.4 Hz, 1 H, Tp), 7.85 (d, *J*_{H,H} = 2.2 Hz, 1 H, Tp), 7.83–7.68 (m, 2 H, py^{3,4}), 7.16 (t, *J*_{H,H} = 6.3 Hz, 1 H, py⁵), 6.77 (s, 4 H, Ph), 6.64 (br. s, 1 H, Tp), 6.50 (vt, 1 H, *J*_{H,H} = 1.8 Hz, Tp), 6.00 (vt, 1 H, *J*_{H,H} = 2.0 Hz, Tp), 5.94 (vt, 1 H, *J*_{H,H} = 2.1 Hz, Tp), 5.88 (d, *J*_{H,H} = 1.6 Hz, 1 H, Tp), 3.71 (s, 3 H, OCH₃) ppm. ¹³C{¹H} NMR ([D₆]DMSO, 20 °C): δ = 276.9 (1C, Ru=C), 161.1 (1C, py²), 160.7 (1C, Ph⁴), 151.2 (1C, py⁶), 149.6 (1C, Ph¹), 146.2 (1C, Tp), 143.0 (1C, Tp), 142.4 (1C, Tp), 137.2 (1C, Tp), 137.1 (1C, py⁴), 135.8 (1C, Tp), 135.5 (1C, Tp), 128.0 (2C, Ph^{3,5}), 115.3 (1C, py⁵), 113.8 (1C, Ph^{2,6}), 112.3 (1C, py³), 106.8 (2C, Tp), 105.9 (1C, Tp), 56.1 (1C, OCH₃) ppm.

[RuTp{C(Np)NH-py}Cl] (11c): This compound was prepared analogously to **11b** by using **5** (100 mg, 0.218 mmol) and py-N=CHNp (61 mg, 0.262 mmol) as the starting materials. Yield: 87.9 mg (69%). C₂₅H₂₂BN₈ClRu (581.84): calcd. C 51.61, H 3.81; found C 51.57, H 3.78. ¹H NMR (CDCl₃, 20 °C): δ = 12.30 (s, 1 H, NH), 8.85–5.66 (m, 21 H, py^{2–6}, Np, Tp) ppm. ¹³C{¹H} NMR (CDCl₃, 20 °C): δ = 281.4 (1C, Ru=C), 159.7 (1C, py²), 151.0 (1C, py⁶), 142.2 (1C, Tp), 141.1 (1C, Tp), 136.9 (1C, py⁴), 136.2 (1C, Tp), 135.7 (1C, Tp), 135.4 (1C, Tp), 134.6 (1C, Tp), 129.1–124.8 (m, 10C, Np), 118.7 (1C, py⁵), 105.9 (1C, py³), 105.9 (3C, Tp) ppm.

[RuCp(CH₃CN)(κ²N,N'-py-CH₂-N=CHPh)PF₆ (12): This compound was prepared analogously to **6b** by using **1** (100 mg, 0.230 mmol) and *N*-(phenylmethylene)-2-picolyamine (py-CH₂-N=CHPh) (50 mg, 0.253 mmol) as the starting materials. Yield: 90 mg (74%). C₂₀H₂₀F₆N₃PRu (548.44): calcd. C 43.80, H 3.68; found C 43.85, H 3.71. ¹H NMR ([D₆]acetone, 20 °C): δ = 9.19 (d, *J*_{H,H} = 5.05 Hz, 1 H, py⁶), 9.11 (d, *J*_{H,H} = 1.26 Hz, 1 H, N=CHPh), 8.50–8.48 (m, 2 H, py⁴, Ph), 7.98 (dt, *J*_{H,H1} = 7.78, *J*_{H,H2} = 1.53 Hz, 1 H, py³), 7.68–7.56 (m, 4 H, Ph), 7.44 (vt, 1 H, *J*_{H,H} = 6.56 Hz, py⁵), 5.62 (d, 1 H, *J*_{H,H1} = 17.69 Hz, CH₂), 5.43 (d, *J*_{H,H} = 17.69 Hz, 1 H, CH₂), 4.28 (s, 5 H, Cp), 2.19 (s, 3 H, CH₃CN) ppm. ¹³C{¹H} NMR ([D₆]acetone, 20 °C): δ = 173.0 (1C, py⁶), 160.5 (1C, py²), 155.2 (1C, N=CHPh), 137.7 (1C, py⁴), 134.3 (1C, Ph¹), 132.5 (1C, Ph⁴), 130.2 (2C, Ph^{2,6}), 128.8 (2C, Ph^{3,5}), 125.9 (1C, CH₃CN), 124.3 (1C, py³), 120.6 (1C, py⁵), 74.6 (1C, CH₂), 70.5 (5C, Cp), 2.7 (1C, CH₃CN) ppm.

[RuTp(κ²N,N'-py-CH₂-N=CHPh)Cl] (13): This compound was prepared analogously to **11b** by using **5** (100 mg, 0.218 mmol) and py-CH₂-N=CHPh (47 mg, 0.240 mmol) as the starting materials. Yield: 87.9 mg (64%). C₂₂H₂₂BN₈ClRu (545.81): calcd. C 48.41, H 4.06; found C 48.49, H 4.13. ¹H NMR (CDCl₃, 20 °C): δ = 9.05 (s, 1 H, N=CH), 8.12 (d, *J*_{H,H} = 5.8 Hz, 1 H, py⁶), 7.89 (d, *J*_{H,H} = 2.4 Hz, 1 H, Tp), 7.83 (d, *J*_{H,H} = 1.9 Hz, 1 H, Tp), 7.73 (d, *J*_{H,H} = 2.2 Hz, 1 H, Tp), 7.61 (d, *J*_{H,H} = 1.4 Hz, 1 H, Tp), 7.57 (d, *J*_{H,H} = 2.2 Hz, 1 H, Tp), 7.4–7.37 (m, 3 H, Ph), 7.33 (d, *J*_{H,H} = 2.1 Hz, 1 H, Tp), 7.23–7.13 (m, 2 H, Ph), 7.02 (t, *J*_{H,H} = 7.6 Hz, 1 H, py⁴), 6.74 (t, *J*_{H,H} = 7.5 Hz, 1 H, py⁵), 6.61 (d, *J*_{H,H} = 14.9 Hz, 1 H, CH₂), 6.44 (d, *J*_{H,H} = 7.9 Hz, 1 H, py³), 6.26 (vt, *J*_{H,H} = 2.1 Hz, 1 H, Tp), 6.03 (vt, *J*_{H,H} = 2.1 Hz, 1 H, Tp), 5.67 (vt, *J*_{H,H} = 2.0 Hz, 1 H, Tp), 5.23 (d, *J*_{H,H} = 16.0 Hz, 1 H, CH₂) ppm. ¹³C{¹H} NMR (CDCl₃, 20 °C): δ = 171.4 (1C, N=CHPh), 162.4 (1C, py²), 153.6 (1C, py⁶), 145.1 (1C, Tp), 144.3 (1C, Tp), 141.7 (1C, Tp), 136.6 (1C, Tp), 135.4 (1C, Tp), 134.9 (1C, Tp), 134.4 (1C, py⁴), 133.7 (1C, Ph¹), 130.0 (1C, Ph⁴), 128.2 (2C, Ph^{2,6}), 128.0 (2C, Ph^{3,5}), 123.2 (1C, py⁵), 119.2 (1C, py³), 106.8 (1C, Tp), 106.6 (1C, Tp), 106.2 (1C, Tp), 75.2 (1C, CH₂) ppm.

[RuCp(pyMe-NH₂)₃=C(NH-pyMe)Et]PF₆ (14b): A solution of **1** (100 mg, 0.230 mmol) and *N,N'*-bis(2-picoly)-1,1-propanediamine

Table 1. Details for the crystal structure determinations of complexes **6b**·(CH₃)₂CO, **7a**, **7b**, **11a**, **12**, and **16**

	6b ·(CH ₃) ₂ CO	7a	7b	11a	12	16
Empirical formula	C ₄₂ H ₄₀ F ₆ FeN ₂ OP ₂ Ru	C ₁₈ H ₁₅ F ₆ N ₂ OPRu	C ₂₂ H ₁₉ F ₆ FeN ₂ OPRu	C ₂₁ H ₂₀ BClN ₈ Ru	C ₂₀ H ₂₀ F ₆ N ₃ PRu	C ₃₁ H ₃₀ F ₆ N ₂ P ₂ Ru
Formula mass	921.62	521.36	629.28	531.78	548.43	707.58
Crystal size, mm	0.45 × 0.35 × 0.10	0.75 × 0.07 × 0.05	0.40 × 0.06 × 0.06	0.32 × 0.22 × 0.18	0.64 × 0.20 × 0.12	0.70 × 0.04 × 0.02
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> , Å	11.035(1)	10.485(1)	10.820(7)	27.131(7)	10.167(2)	13.469(2)
<i>b</i> , Å	14.187(2)	13.966(2)	13.369(9)	11.152(3)	11.840(2)	15.052(3)
<i>c</i> , Å	14.450(2)	12.698(2)	30.38(2)	15.546(4)	18.149(3)	14.808(3)
α , deg	74.574(3)					
β , deg	70.554(3)	90.338(3)	93.17(2)	106.24(1)	96.803(3)	100.60(1)
γ , deg	67.939(3)					
<i>V</i> , Å ³	1951.2(4)	1859.2(4)	4387(5)	4516(2)	2169.3(6)	2950.7(9)
<i>Z</i>	2	4	8	8	4	4
$\rho_{\text{calcd.}}$, g cm ^{−3}	1.569	1.863	1.905	1.564	1.679	1.593
<i>T</i> , K	173(2)	123(2)	123(2)	297(2)	183(2)	297(2)
μ , mm ^{−1} (Mo- <i>K</i> α)	0.906	1.000	1.493	0.839	0.859	0.703
<i>F</i> (000)	936	1032	2496	2144	1096	1432
Absorption corr.	multi scan	multi scan	none	multi scan	multi scan	multi scan
θ_{max} , deg.	30	30	25	25	30	30
No. of reflections measd.	24939	12429	23139	22327	30388	40569
No. of unique reflections	10853	5172	7627	3937	6244	8421
no. of reflections <i>I</i> > 2 σ (<i>I</i>)	9168	3956	4022	3140	5260	6841
No. of params	515	262	367	289	295	379
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] ^[a]	0.031	0.028	0.080	0.033	0.032	0.045
<i>R</i> ₁ (all data)	0.041	0.047	0.162	0.048	0.041	0.058
<i>wR</i> ₂ (all data)	0.082	0.062	0.219	0.092	0.091	0.134
Diff. Four. peaks, min./max., e [−] Å ^{−3}	−0.63/0.83	−0.42/0.56	−1.09 /1.86	−0.55/0.92	−0.86/0.85	−0.74/1.51

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

[pyMe–NHCH(Et)NH–pyMe] (59 mg, 0.20 mmol) in CH₂Cl₂ (8 mL) was stirred at room temperature for 3 h. The volume of the solution was then reduced to about 1 mL. Upon addition of diethyl ether, a brick-red solid was obtained that was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 98 mg (75%). C₂₀H₂₅F₆N₄PRu (567.48): calcd. C 42.33, H 4.44; found C 43.27, H 4.40. ¹H NMR ([D₆]acetone, 20 °C): δ = 12.70 (br. s, 1 H, NH), 9.15 (d, *J*_{H,H} = 6.00 Hz, 1 H, py), 8.16 (d, *J*_{H,H} = 6.16 Hz, 1 H, py), 7.39 (m, 1 H, py), 7.15 (d, *J*_{H,H} = 5.53 Hz, 1 H, py), 6.49 (m, 1 H, py), 6.30 (br. s, 2 H, NH₂), 6.19 (d, *J*_{H,H} = 5.05 Hz, 1 H, py), 4.98 (s, 5 H, Cp), 4.07 (m, *J*_{H,H} = 7.27 Hz, 1 H, CH₂), 3.87 (m, *J*_{H,H} = 7.31 Hz, 1 H, CH₂), 2.43 (s, 3 H, py–Me), 2.08 (s, 3 H, py–Me), 1.43 (t, *J*_{H,H} = 7.50 Hz, 3 H, CH₃) ppm. ¹³C{¹H} NMR ([D₆]acetone, 20 °C): δ = 276.6 (1C, Ru=C), 162.6 (1C, py^q), 158.6 (1C, py^q), 154.7 (1C, py), 151.5 (1C, py), 150.5 (1C, py^q), 150.0 (1C, py^q), 121.5 (1C, py), 115.1 (1C, py), 112.4 (1C, py), 109.9 (1C, py), 82.1 (5C, Cp), 45.5 (1C, CH₂CH₃), 20.5 (1C, py–Me), 20.0 (1C, py–Me), 12.2 (1C, CH₂CH₃) ppm.

[RuTp{C(NH–pyMe)Et}Cl] (**17**): This compound was prepared analogously to **11b** by using **5** (100 mg, 0.218 mmol) and pyMe–NHCH(Et)NH–pyMe (72.5 mg, 0.283 mmol) as the starting materials. Yield: 65.6 mg (61%). C₁₈H₂₂BN₈ClRu (497.76): calcd. C 43.43, H 4.46; found C 43.39, H 4.49. ¹H NMR ([D₆]DMSO, 20 °C): δ = 13.06 (s, 1 H, NH), 8.15 (d, *J*_{H,H} = 5.8 Hz, 1 H, py^q), 8.06 (d, *J*_{H,H} = 1.7 Hz, 1 H, Tp), 7.98 (d, *J*_{H,H} = 2.2 Hz, 1 H, Tp), 7.87 (d, *J*_{H,H} = 2.2 Hz, 1 H, Tp), 7.82–7.70 (m, 2 H, 2Tp), 7.44 (s, 1 H, py³), 6.98 (dd, *J*₁ = 6.0, *J*₂ = 1.3 Hz, 1 H, py⁵), 6.45 (vt, *J*_{H,H} = 2.0 Hz, 1 H, Tp), 6.28 (vt, *J*_{H,H} = 2.0 Hz, 1 H, Tp), 5.88 (vt, *J*_{H,H} = 2.1 Hz, 1 H, Tp), 5.79 (d, *J*_{H,H} = 1.9 Hz, 1 H, Tp),

3.47–3.15 (m, 2 H, CH₂), 2.07 (s, 3 H, py–Me), 0.77 (t, *J*_{H,H} = 7.7 Hz, 3 H, CH₃) ppm. ¹³C{¹H} NMR ([D₆]DMSO, 20 °C): δ = 290.3 (1C, Ru=C), 160.0 (1C, py²), 150.7 (1C, py⁶), 148.5 (1C, py⁴), 145.1 (1C, Tp), 142.7 (1C, Tp), 141.6 (1C, Tp), 136.6 (1C, Tp), 135.7 (1C, Tp), 135.6 (1C, Tp), 120.7 (1C, py⁵), 111.9 (1C, py³), 106.6 (1C, Tp), 106.5 (1C, Tp), 106.3 (1C, Tp), 39.6 (1C, CH₂), 21.5 (1C, CH₃–CH₂), 10.9 (1C, py–Me) ppm.

Crystallographic Structure Determinations: Crystals of **6b**·(CH₃)₂CO, **7a**, **7b**, **11a**, **12**, and **16** were obtained by vapor diffusion of Et₂O into either CH₂Cl₂ or acetone solutions. Crystal data and experimental details are given in Table 1. All X-ray data were collected on a Bruker Smart CCD area detector diffractometer (graphite-monochromated Mo-*K* α radiation, λ = 0.71073 Å, 0.3° ω -scan frames covering either hemispheres (**7a**, **7b**) or complete spheres of the reciprocal space, Bruker Kryoflex cooling unit). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied (multi-scan method with the program SADABS^[18]). All structures were solved by direct methods using the program SHELXS-97.^[19] Structure refinements on F² were carried out with program SHELXL-97.^[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding on the atoms to which they were bonded. Critical hydrogen atoms were refined in positional parameters without such restraints.

CCDC-200230 to -200235 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cam-

bridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details: All calculations were performed using the Gaussian98 software package on the Silicon Graphics Origin 2000 of the Vienna University of Technology.^[21] The geometry and energy of the model complexes and the transition states were optimized at the B3LYP level^[22] with the Stuttgart/Dresden ECP (SDD) basis set^[23] to describe the electrons of the ruthenium atom. For the C, N, and H atoms the 6-31g** basis set was employed.^[24] A vibrational analysis was performed to confirm that the structures of the model compounds have no imaginary frequencies. The transition-state structure was relaxed after applying a small perturbation to ensure that it is connected to the corresponding reactant and product. A vibrational analysis was also performed to confirm that it has only one imaginary frequency. The geometries were optimized without constraints (C_1 symmetry).

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