Formation of Ruthenium−Aminocarbene Complexes from Aldimines and Aminals

Christina M. Standfest-Hauser,[a] Kurt Mereiter,[b] Roland Schmid,[a] and Karl Kirchner*[a]

Keywords: Carbenes / Density functional calculations / N ligands / Ruthenium

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 $[RuCp(L)(CH_3CN)_2]PF_6$ (L = CH_3CN, PMe_3, $SbPh_3$) with 1 equiv. of py–N=CHR [R = Ph (phenyl), Fc (ferrocenyl), Np (naphthyl)] affords the cyclic aminocarbene complexes $[RuCp(L)(=C(R)NH–py)]PF_6$, whereas when L = PPh_3, P*i*Pr_3, and CO the reaction stops at the stage of the imine complex $[RuCp(L)(\kappa^2N,N'$-py–N=CHR$)]PF_6$. Analogously, [RuTp(COD)Cl] (COD = 1,5-cyclooctadiene) also reacts readily with the imines py–N=CHR (R = Ph, *p*$MeOC_6H_4$, 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 $[RuCp(L)(CH_3CN)_2]PF_6$, where L = CH_3CN, PMe_3, PPh_3, 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}]PF_6 was obtained when CH_3CN and PMe_3 were employed, the reaction stops at the stage of the imine complex $[RuCp(L)(\kappa^2N,N'$-py−N=CHR$)]PF_6$ with L = PPh_3 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].

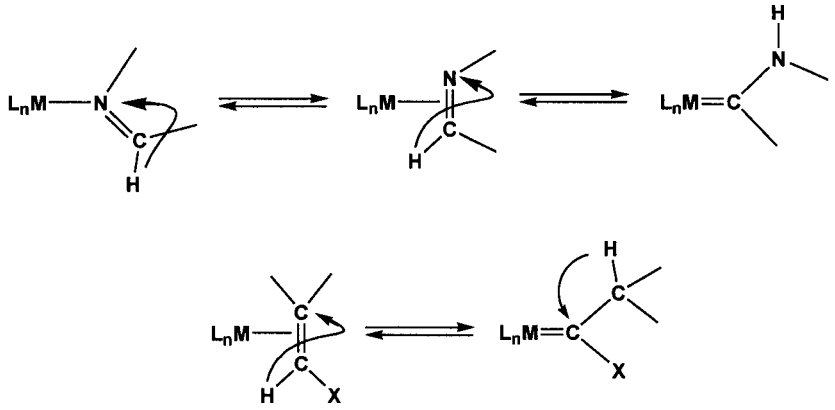
Our goal was to extend the scope of the above reactions to better understand the reasons for the intriguing imine−aminocarbene conversion. Towards this goal, we have used other imines with the general structure py−N=CHR, viz. R = ferrocenyl (Fc) and naphthyl (Np), and also py−CH_2−N=CHPh. Furthermore, 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 P*i*Pr_3 and $SbPh_3$ 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.

[a] Institute of Applied Synthetic Chemistry, Vienna University of Technology,
Getreidemarkt 9, 1060 Vienna, Austria
Fax: (internat.) + 43-1/58801-15499
E-mail: kkirch@mail.zserv.tuwien.ac.at
[b] Institute of Chemical Technologies and Analytics, Vienna University of Technology,
Getreidemarkt 9, 1060 Vienna, Austria

Results and Discussion

Synthesis and Characterization

Treatment of $[RuCp(L)(CH_3CN)_2]PF_6$ [L = CH_3CN (**1**), PMe_3 (**2a**)] with 1 equiv. of py−N=CHR [R = Ph (phenyl), Fc (ferrocenyl), Np (naphthyl)] afforded the aminocarbene

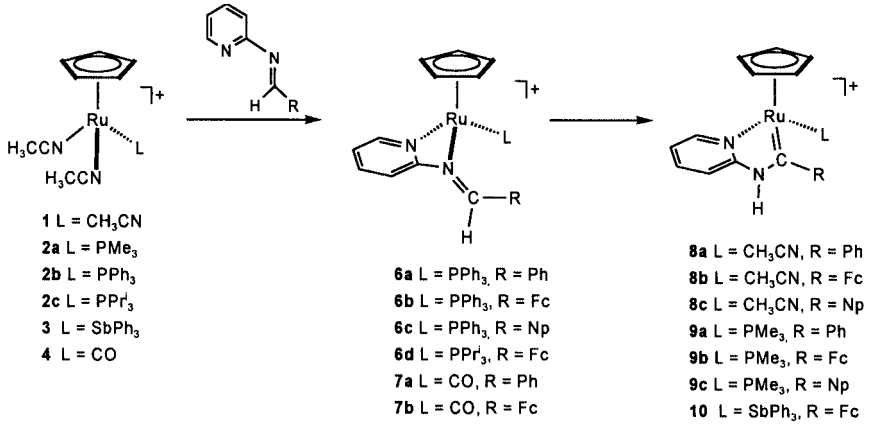


Scheme 1

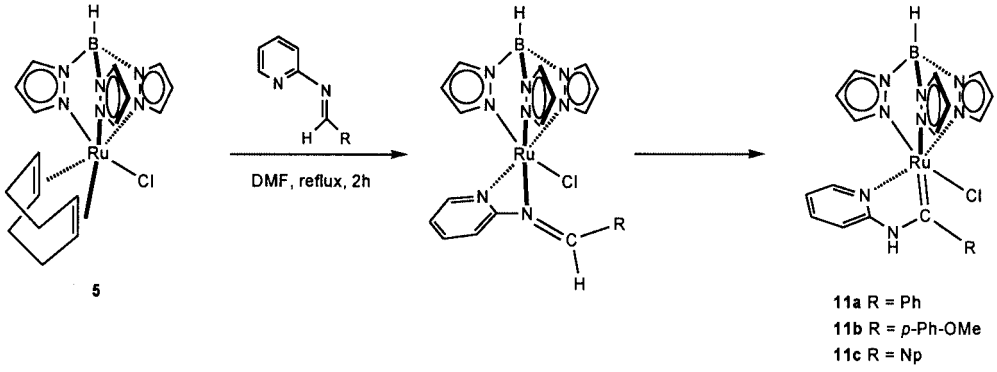
complexes [RuCp(L){=C(R)NH−py}]PF_6 (**8a−c**, **9a−c**) in high yields (Scheme 2). A similar transformation between [RuCp($SbPh_3$)(CH_3CN)$_2$]PF_6 (**3**) and py−N=CHFc leads to the aminocarbene complex [RuCp($SbPh_3$){=C(Fc)-NH−py}]PF_6 (**10**). Analogously, [RuTp(COD)Cl] (**5**) also readily reacts with the imines py−N=CHR (R = Ph, *p*Me-OC_6H_4, Np) at elevated temperatures to yield the aminocarbene complexes [RuTp{=C(R)NH−py}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′ (R = Ph, *i*Pr; R′ = Ph, *i*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, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis. In the $^{13}C\{^1H\}$ NMR spectra of **8−10**, the carbene moiety is identified by downfield signals in the range of δ = 263.2 to 281.4 ppm. Other spectral changes accompanying the transformation to aminocarbene complexes include a characteristic broad resonance between δ = 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

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

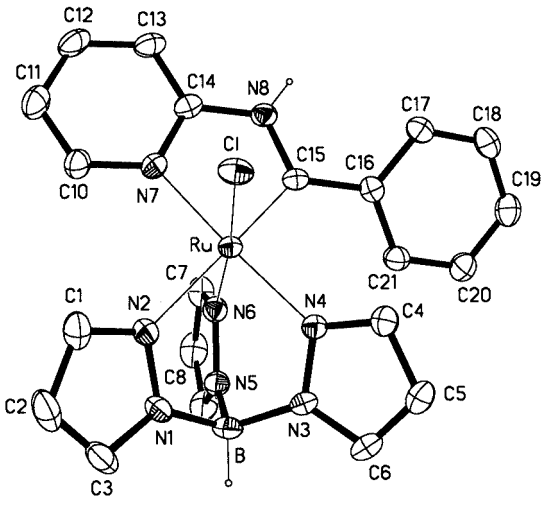


Figure 1. Structural view of **11a** showing 20% thermal ellipsoids (aromatic H atoms omitted); selected bond lengths (Å) and angles (°): Ru−N(2) 2.210(3), Ru−N(4) 2.074(3), Ru−N(6) 2.048(3), Ru−N(7) 2.046(3), Ru−Cl 2.414(1), Ru−C(15) 1.915(3), C(15)−Ru−N(7) 79.7(1), C(15)−Ru−N(6) 92.8(1), C(15)−Ru−N(4)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

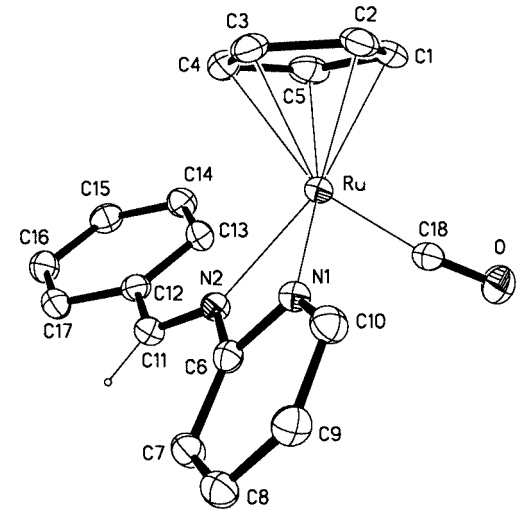


Figure 3. Structural view of **7a** showing 50% thermal ellipsoids (aromatic H atoms and PF_6^- ions omitted for clarity); selected bond lengths (Å) and angles (°): Ru−C(1−5)$_{av}$ 2.201(2), Ru−C(18) 1.876(2), Ru−N(1) 2.125(2), Ru−N(2) 2.167(2), N(2)−C(11) 1.288(3), C(18)−O 1.144(2), N(1)−Ru−N(2) 62.8(1), Ru−C(18)−O 171.6(1)

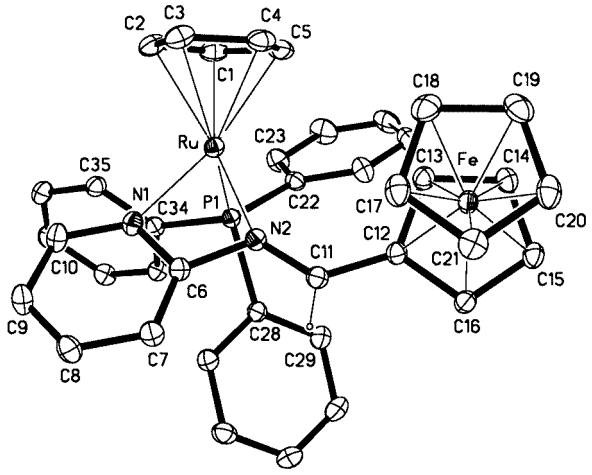


Figure 2. Structural view of **6b**·$(CH_3)_2CO$ showing 40% thermal ellipsoids [aromatic H atoms, PF_6^- and $(CH_3)_2CO$ omitted for clarity]; selected bond lengths (Å) and angles (°): Ru−C(1−5)$_{av}$ 2.186(2), Ru−P(1) 2.310(1), Ru−N(1) 2.104(1), Ru−N(2) 2.168(1), N(2)−C(11) 1.294(2), N(1)−Ru−N(2) 62.2(1)

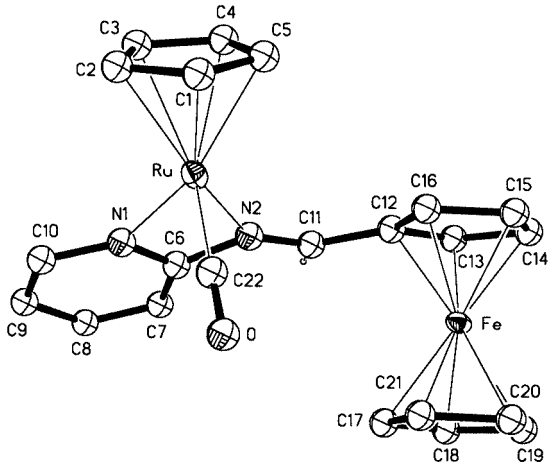


Figure 4. Structural view of **7b** showing 50% thermal ellipsoids (aromatic H atoms and PF_6^- ions omitted for clarity); selected bond lengths (Å) and angles (°): Ru−C(1−5)$_{av}$ 2.174(11), Ru−C(22) 1.846 (10), Ru−N(1) 2.080(9), Ru−N(2) 2.133(8), N(2)−C(11) 1.267(11), C(22)−O 1.139(11), N(1)−Ru−N(2) 60.3(3), Ru−C(22)−O 176.1(11)

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 $[RuCp(L)(CH_3CN)_2]PF_6$ is relatively bulky, such as PPh_3 or P*i*Pr$_3$, 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 complexes. Instead, and in keeping with previous results,[1] the complexes $[RuCp(L)(\kappa^2N,N'\text{-py}-N{=}CHR)]PF_6$ (**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 PPh_3 and CO ligands, respectively, as the legs. The N−Ru−N angles in **6b**, **7a**, and **7b** are

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

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 κ^2NN imine into the aminocarbene complex. In fact, the imine complex derived from py−CH_2−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 [RuCp(CH_3CN)(κ^2*N*,*N*′-py−CH_2−N=CHPh)]PF_6 (**12**) and [RuTp(κ^2*N*,*N*′-py−CH_2−N=CHPh)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 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**.

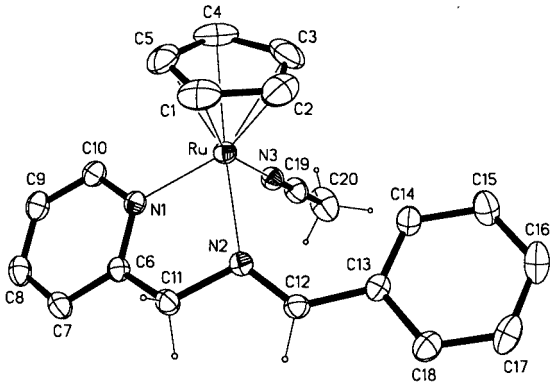
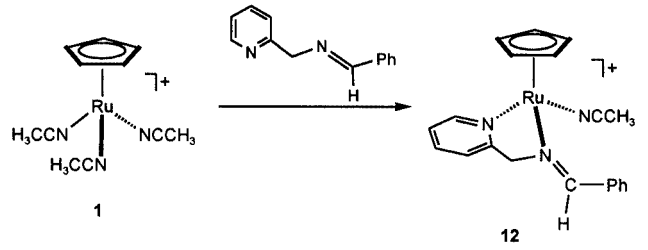
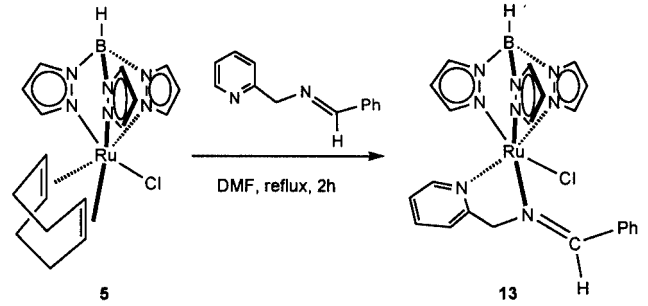


Figure 5. Structural view of **12** showing 50% thermal ellipsoids (aromatic H atoms and PF_6^- ions omitted for clarity); selected bond lengths (Å) and angles (°): Ru−C(1−5)$_{av}$ 2.153(3), Ru−N(1) 2.104(1), Ru−N(2) 2.117(1), Ru−N(3) 2.077(1), N(1)−Ru−N(2) 77.8(1), Ru−N(3)−C(19) 178.9(3)

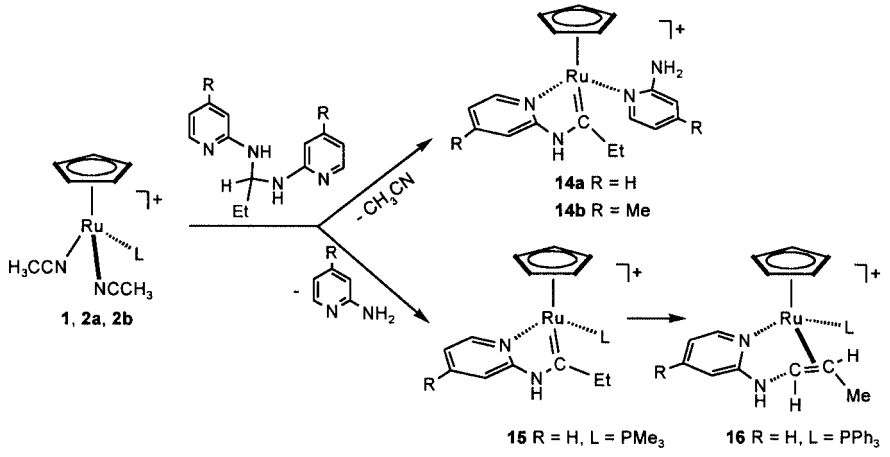


Scheme 4



Scheme 5

The generality of cyclic aminocarbene construction is further implied by the finding that aminals also react with the RuCpL and RuTpL fragments to form the corresponding aminocarbene complexes. In these reactions, the aminal 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-picolyl)-1,1-propanediamine [pyMe-NHCH(Et)-NH−pyMe] to form [RuCp(py−NH_2){=C(NH−py)Et}]-PF_6 (**14a**), [RuCp(pyMe-NH_2){=C(NH−pyMe)Et}]PF_6 (**14b**), and [RuCp(PMe_3)(=C(NH−py)Et]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

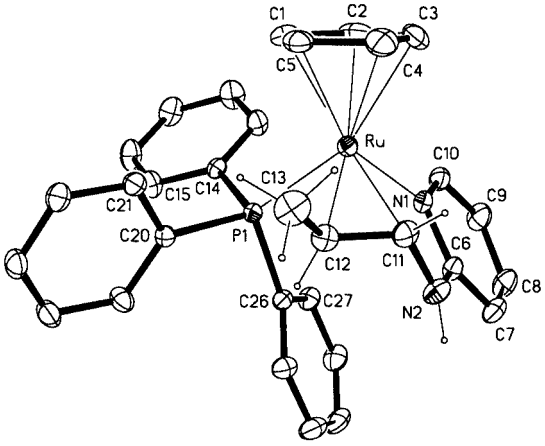
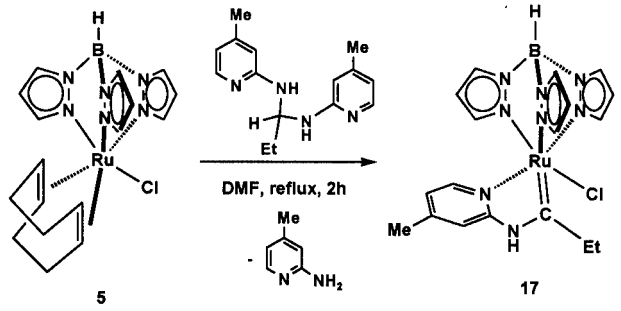


Figure 6. Structural view of **16** showing 20% thermal ellipsoids (aromatic H atoms and PF_6^- ions omitted for clarity); selected bond lengths (Å) and angles (°): Ru−C(1−5)$_{av}$ 2.224(4), Ru−P(1) 2.348(1), Ru−N(1) 2.122(1), Ru−C(11) 2.171(3), Ru−C(12) 1.272(3), C(11)−C(12) 1.383(5), N(1)−Ru−C(11)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



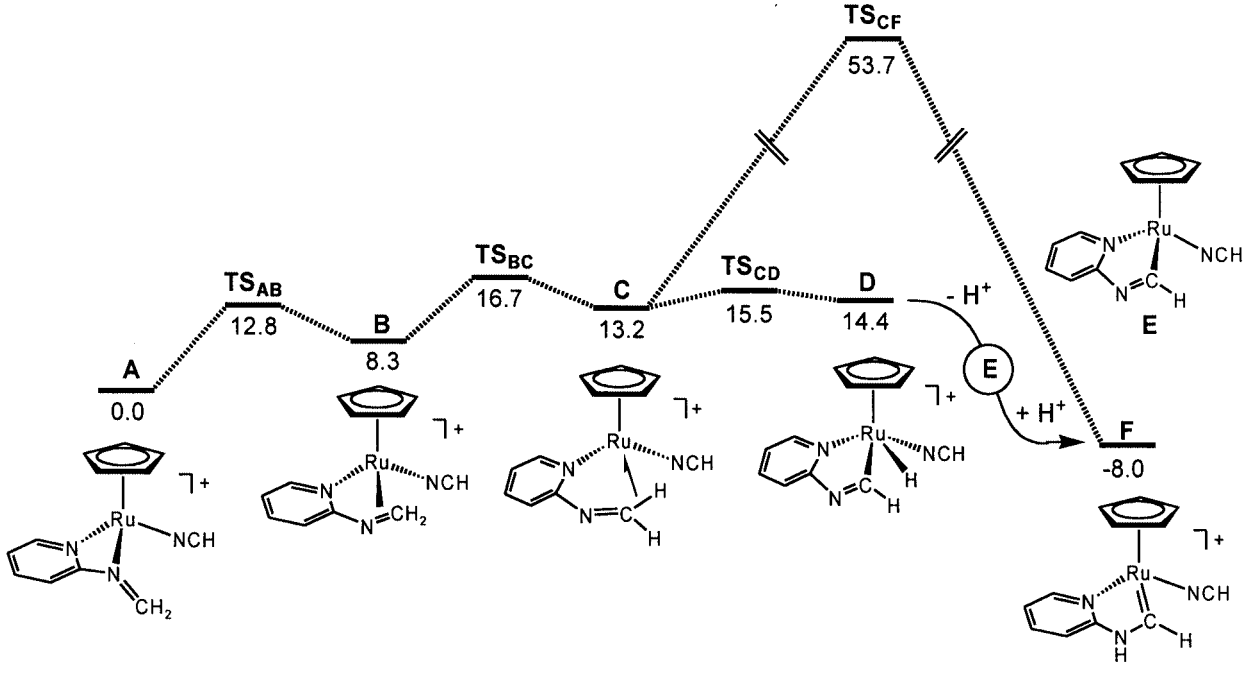
Scheme 7

by X-ray crystallography, is shown in Figure 6 with selected bond lengths reported in the caption. Similarly, [RuTp(COD)Cl] (**5**) reacts with pyMe-NHCH(Et)NH-pyMe to give [RuTp{=C(NH−pyMe)Et}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 py−N=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 κ^2NN-imine to the aminocarbene complexes, we performed DFT (B3LYP) calculations using py−N=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 κ^2N,N'-py−N=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 −N=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 [RuHCl(P*i*Pr$_3$)$_2$]$_2$ also



Scheme 8

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

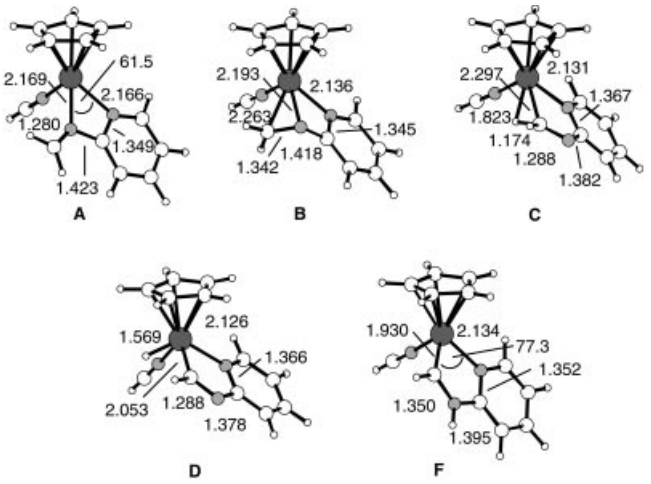


Figure 7. Optimized B3LYP geometries of the equilibrium structures **A**, **B**, **C**, **D**, and **F** (distances in Å and angles in deg)

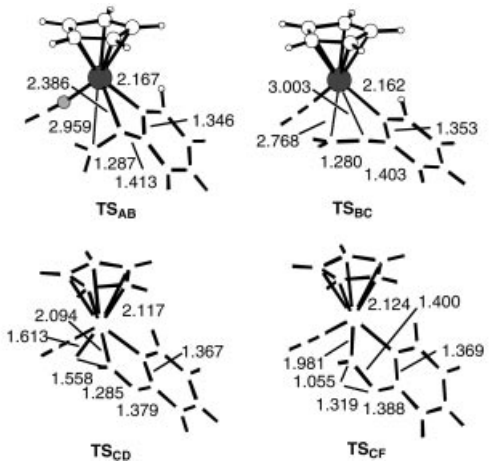


Figure 8. Optimized B3LYP geometries of the transition states TS_{AB}, TS_{BC}, TS_{CD}, and TS_{CF} (distances in Å)

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

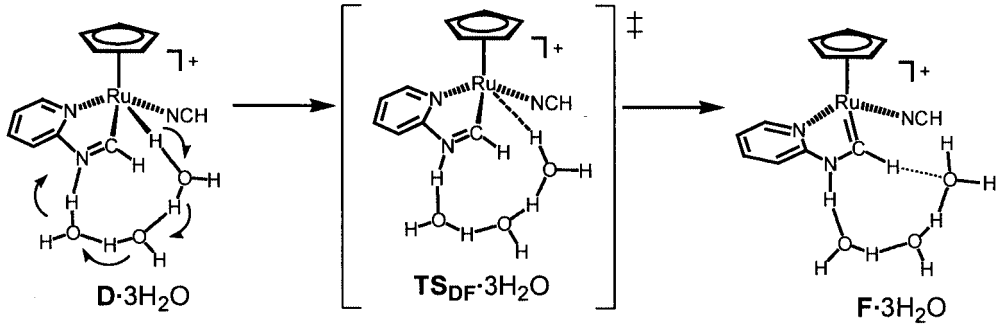
It appears that the step from **C** to **D** involving C−H activation/oxidative addition, is particularly crucial to the overall imine-to-aminocarbene transformation. The reactivity of the imine complex is arguably lessened in the case of sterically demanding co-ligands like PPh_3 in **2b** and P*i*Pr$_3$ in **2c**. Note that the cone angle[10] increases in the order $CH_3CN < PMe_3 < SbPh_3 < PPh_3 < PiPr_3$. 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 dehydration 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 aminals 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

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

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. $[RuCp(CH_3CN)_3]PF_6$ (**1**),[14] $[RuCp(PMe_3)(CH_3CN)_2]PF_6$ (**2a**), $[RuCp(PPh_3)(CH_3CN)_2]PF_6$ (**2b**), and $[RuCp(P\mathit{i}Pr_3)(CH_3CN)_2]PF_6$ (**2c**),[15] $[RuCp(SbPh_3)(CH_3CN)_2]PF_6$ (**3**),[16] $[RuCp(CO)(CH_3CN)_2]PF_6$ (**4**) and $[RuTp(COD)Cl]$ (**5**),[17] $[RuCp(PPh_3)(\kappa^2\mathit{N},\mathit{N}'\text{-py−N=CHPh})]PF_6$ (**6a**), $[RuCp(CO)(\kappa^2\mathit{N},\mathit{N}'\text{-py−N=CHPh})]PF_6$ (**7a**), $[RuCp(CH_3CN)\{=C(Ph)NH-py\}]PF_6$ (**8a**), $[RuCp(PMe_3)\{=C(Ph)NH-py\}]PF_6$ (**9a**), $[RuTp\{=C(Ph)NH-py\}Cl]$ (**11a**), $[RuCp(py-NH_2)\{=C(NH-py\}Et)]PF_6$ (**12a**), $[RuCp(PMe_3)\{=C(NH-py)Et\}]PF_6$ (**13**), and $[RuCp(PPh_3)(py-NH-\eta^2\text{-}CH=CHMe)]PF_6$ (**14**)[1] were prepared according to literature procedures. ^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, 135-DEPT, and HMQC(^1H-^{13}C) experiments.

$[RuCp(PPh_3)(\kappa^2\mathit{N},\mathit{N}'\text{-py−N=CHFc})]PF_6$ (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 CH_2Cl_2 (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%). $C_{39}H_{34}F_6FeN_2P_2Ru$ (863.57): calcd. C 54.24, H 3.97; found C 54.29; H 4.04. ^1H NMR ([D$_6$]acetone, 20 °C): δ = 9.20 (s, 1 H, N=C*H*Fc), 8.52 (d, $J_{H,H}$ = 4.42 Hz, 1 H, py^6), 7.77 (vt, $J_{H,H}$ = 7.84 Hz, 1 H, py^4), 7.55−7.15 (m, 17 H, PPh$_3$, py^3, py^5), 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. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 169.7 (1C, py^6), 164.5 (1C, py^2), 151.9 ($J_{C,P}$ = 1.4 Hz, 1C, N=*C*HFc), 138.1 (1C, py^4), 133.7 ($J_{C,P}$ = 40.6 Hz, 3C, Ph^1), 133.3 ($J_{C,P}$ = 11.0 Hz, 6C, Ph^{2,6}), 130.1 ($J_{C,P}$ = 2.2 Hz, 3C, Ph^4), 128.5 ($J_{C,P}$ = 9.9 Hz, 6C, Ph^{3,5}), 123.9 (1C, py^3), 109.2 (1C, py^5), 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. $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 49.7 (*P*Ph$_3$), −144.2 ($^1J_{PF}$ = 719.5 Hz, *P*F$_6$) ppm.

$[RuCp(PPh_3)(\kappa^2\mathit{N},\mathit{N}'\text{-py−N=CHNp})]PF_6$ (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 [D$_6$]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 ([D$_6$]acetone, 20 °C): δ = 10.24 (s, 1 H, N=C*H*Np), 9.27 (d, $J_{H,H}$ = 7.31 Hz, 1 H, py^6), 8.64 (td, $J_{H,H1}$ = 5.28, $J_{H,H2}$ = 0.80 Hz, 1 H, py^4), 8.15−7.99 (m, 1 H, py^3), 7.90−7.80 (m, 1 H, py^5), 7.78−7.58 (m, 7 H, Np), 7.47−7.16 (m, 15 H, PPh$_3$), 4.76 (d, $J_{H,H}$ = 0.16 Hz, 5 H, RuCp) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 162.9 (1C, py^6), 164.0 (1C, py^2), 152.1 (1C, N=*C*HNp), 138.4 (1C, py^4), 136.9, 135.5, 134.0 (3C, Np), 133.3 ($J_{C,P}$ = 41.5 Hz, 3C, Ph^1), 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, Ph^4), 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, py^3), 110.2 (1C, py^5), 75.3 ($J_{C,P}$ = 2.1 Hz, 5C, RuCp) ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 49.7 (*P*Ph$_3$), −144.1 ($^1J_{PF}$ = 719.5 Hz, *P*F$_6$) ppm.

$[RuCp(P\mathit{i}Pr_3)(\kappa^2\mathit{N},\mathit{N}'\text{-py−N=CHFc})]PF_6$ (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%). $C_{30}H_{40}F_6FeN_2P_2Ru$ (761.52): calcd. C 47.32, H 5.29; found C 47.41, H 5.33. ^1H NMR ([D$_6$]acetone, 20 °C): δ = 9.64 (s, 1 H, N=C*H*Fc), 8.64 (d, $J_{H,H1}$ = 5.03 Hz, 1 H, py^6), 7.96 (t, $J_{H,H}$ = 7.99 Hz, 1 H, py^4), 7.66 (d, $J_{H,H}$ = 8.45 Hz, 1 H, py^3), 7.41 (dd, $J_{H,H1}$ = 7.54, $J_{H,H2}$ = 5.25 Hz, 1 H, py^5), 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, CH$_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 170.1 (1C, py^6), 165.5 (1C, py^2), 153.0 (1C, N=*C*HFc), 138.5 (1C, py^4), 124.1 (1C, py^3), 108.5 (1C, py^5), 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[*C*H(CH$_3$)$_2$]$_3$), 19.5 [6C, P[CH(*C*H$_3$)$_2$]$_3$] ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 52.2 (P*i*Pr$_3$), −144.1 ($^1J_{PF}$ = 708.1 Hz, *P*F$_6$).

$[RuCp(CO)(\kappa^2\mathit{N},\mathit{N}'\text{-py−N=CHFc})]PF_6$ (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%). $C_{22}H_{19}F_6FeN_2OPRu$ (629.29): calcd. C 41.99, H 3.04; found C 41.87; H 3.10. ^1H NMR ([D$_6$]acetone, 20 °C): δ = 9.67 (s, 1 H, N=C*H*Fc), 8.53 (d, $J_{H,H}$ = 5.18 Hz, 1 H, py^6), 8.14 (dt, $J_{H,H1}$ = 8.14, $J_{H,H2}$ = 1.27 Hz, 1 H, py^4), 7.80 (d, $J_{H,H}$ = 8.38 Hz, 1 H, py^3), 7.52 (dd, $J_{H,H1}$ = 7.54, $J_{H,H2}$ = 5.41 Hz, 1 H, py^5), 5.38 (s, 5 H, RuCp), 5.14−4.92 (m, 4 H, FeCp^s), 4.47 (s, 5 H, FeCp) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 200.7 (1C, CO), 171.0 (1C, py^6), 166.0 (1C, py^2), 152.7 (1C, N=*C*HFc), 140.4 (1C, py^4), 124.2 (1C, py^3), 109.9 (1C, py^5), 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.

$[RuCp(CH_3CN)(=C(Fc)NH-py)]PF_6$ (8b): Compound py−N=CHFc (133 mg, 0.461 mmol) was added to a solution of **1** (200 mg, 0.461 mmol) in CH_2Cl_2 (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%). $C_{23}H_{22}F_6FeN_3PRu$ (642.33): calcd. C 43.01, H 3.45; found C 43.11; H 3.47. ^1H NMR ([D$_6$]acetone, 20 °C): δ = 11.90 (br. s, 1 H, NH), 9.10 (d, $J_{H,H}$ = 5.63 Hz, 1 H, py^6), 7.95 (ddd, $J_{H,H1}$ = 8.45, $J_{H,H2}$ = 7.23, $J_{H,H3}$ = 1.37 Hz, 1 H, py^4), 7.72 (dd, $J_{H,H1}$ = 8.38, $J_{H,H2}$ = 0.83 Hz, 1 H, py^3), 7.22 (ddd, $J_{H,H1}$ = 7.23, $J_{H,H2}$ = 5.86, $J_{H,H3}$ = 1.29 Hz, 1 H, py^5), 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, CH$_3$CN) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 264.6 (1C, Ru=*C*), 159.0 (1C, py^2), 155.8 (1C, py^6), 138.7 (1C, py^4), 127.2 (1C, CH$_3$*C*N), 119.7 (1C, py^3), 112.3 (1C, py^5), 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, *C*H$_3$CN) ppm.

$[RuCp(CH_3CN)(=C(Np)NH-py)]PF_6$ (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%). $C_{23}H_{20}F_6N_3PRu$ (584.47): calcd. C 47.27, H 3.45; found C 47.33; H 3.40. ^1H NMR ([D$_6$]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, py^6), 8.14−7.99 (m, 4 H, Np, py^4), 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, py^3), 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, py^5), 4.74 (s, 5 H, RuCp), 2.47 (s, 3 H,

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

CH_3CN) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 269.5 (1C, Ru=*C*), 158.4 (1C, py^2), 155.7 (1C, py^6), 138.9 (1C, py^4), 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, CH_3*C*N), 120.5 (1C, py^3), 113.2 (1C, py^5), 82.1 (5C, RuCp), 2.9 (1C, *C*H$_3$CN) ppm.

[RuCp(PMe$_3$){=C(Fc)NH−py}]PF$_6$ (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%). $C_{24}H_{28}F_6FeN_2P_2Ru$ (677.36): calcd. C 42.56, H 4.17; found C 42.61; H 4.19. ^1H NMR ([D$_6$]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, py^6), 7.88 (m, 1 H, py^4), 7.76 (d, $J_{H,H}$ = 8.07 Hz, 1 H, py^3), 7.12 (ddd, $J_{H,H1}$ = 7.16, $J_{H,H2}$ = 5.79, $J_{H,H3}$ = 1.37 Hz, 1 H, py^5), 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, PMe$_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 263.2 ($J_{C,P}$ = 12.1 Hz, 1C, Ru=*C*), 157.9 (1C, py^6), 155.7 ($J_{C,P}$ = 1.9 Hz, 1C, py^2), 137.5 (1C, py^4), 119.2 (1C, py^3), 113.0 (1C, py^5), 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, PMe$_3$) ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 6.2 (*P*Me$_3$), −144.2 ($^1J_{PF}$ = 708.4 Hz, *P*F$_6$) ppm.

[RuCp(PMe$_3$){=C(Np)NH−py}]PF$_6$ (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%). $C_{24}H_{17}F_6N_2P_2Ru$ (610.42): calcd. C 47.22, H 2.81; found C 47.17; H 2.78. ^1H NMR ([D$_6$]acetone, 20 °C): δ = 12.66 (br. s, 1 H, NH), 9.08 (d, $J_{H,H}$ = 5.79 Hz, 1 H, py^6), 8.20−7.47 (m, 9 H, Np, py^4, py^3), 7.32 (ddd, $J_{H,H1}$ = 7.23, $J_{H,H2}$ = 5.86, $J_{H,H3}$ = 1.37 Hz, 1 H, py^5), 4.94 (d, J_{PH} = 0.30 Hz, 5 H, RuCp), 1.34 (d, J_{PH} = 9.90 Hz, 9 H, PMe$_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 268.8 ($J_{C,P}$ = 9.7 Hz, 1C, Ru=*C*), 157.6 (1C, py^2), 155.8 (1C, py^6), 147.4 (1C, Np), 137.8 (1C, py^4), 133.7 (1C, Np), 129.4 (1C, Np), 128.5 (2C, Np), 126.9 (1C, Np), 126.7 (1C, Np^q), 126.5 (1C, Np), 125.3 (2C, Np), 119.9 (1C, py^3), 113.6 (1C, py^5), 84.1 (5C, RuCp), 17.5 ($J_{C,P}$ = 32.3 Hz, 3C, PMe$_3$) ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 5.4 (*P*Me$_3$), −144.2 ($^1J_{PF}$ = 719.5 Hz, *P*F$_6$) ppm.

[RuCp(SbPh$_3$){=C(Fc)NH−py}]PF$_6$ (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%). $C_{39}H_{34}F_6FeN_2PSbRu$ (954.35): calcd. C 49.08, H 3.59; found C, 49.12, H 3.62. ^1H NMR ([D$_6$]acetone, 20 °C): δ = 11.76 (br. s, 1 H, NH), 9.19 (d, $J_{H,H}$ = 5.18 Hz, 1 H, py^6), 7.67 (dt, $J_{H,H1}$ = 7.73, $J_{H,H2}$ = 0.91 Hz, 1 H, py^4), 7.53−7.12 (m, 16 H, SbPh$_3$, py^3), 6.98 (ddd, $J_{H,H1}$ = 6.62, $J_{H,H2}$ = 6.24, $J_{H,H3}$ = 0.46 Hz, 1 H, py^5), 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. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 263.4 (1C, Ru=*C*), 157.4 (1C, py^2), 155.9 (1C, py^6), 135.2 (1C, py^4), 134.9 (6C, Ph$_3^{2,6}$), 132.2 (3C, Ph$_3^1$), 130.2 (3C, Ph$_3^4$), 129.3 (6C, Ph$_3^{3,5}$), 118.6 (1C, py^3), 113.0 (1C, py^5), 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(C$_6$H$_4$OMe*p*)NH−py)Cl] (11b): A solution of **5** (100 mg, 0.218 mmol) and *N*-(*p*-methoxyphenylmethylene)-2-pyridineamine (py−N=CHC$_6$H$_4$OMe*p*) (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%). $C_{22}H_{22}BN_8ClORu$ (561.81): calcd. C 47.04, H 3.95; found C, 47.11, H 3.89. ^1H NMR ([D$_6$]DMSO, 20 °C): δ = 13.17 (s, 1 H, N*H*), 8.33 (d, $J_{H,H}$ = 5.5 Hz, 1 H, py^6), 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, py^5), 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, OC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 20 °C): δ = 276.9 (1C, Ru=*C*), 161.1 (1C, py^2), 160.7 (1C, Ph^4), 151.2 (1C, py^6), 149.6 (1C, Ph^1), 146.2 (1C, Tp), 143.0 (1C, Tp), 142.4 (1C, Tp), 137.2 (1C, Tp), 137.1 (1C, py^4), 135.8 (1C, Tp), 135.5 (1C, Tp), 128.0 (2C, Ph^{3,5}), 115.3 (1C, py^5), 113.8 (1C, Ph^{2,6}), 112.3 (1C, py^3), 106.8 (2C, Tp), 105.9 (1C, Tp), 56.1 (1C, O*C*H$_3$) 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%). $C_{25}H_{22}BN_8ClRu$ (581.84): calcd. C 51.61, H 3.81; found C 51.57, H 3.78. ^1H NMR ($CDCl_3$, 20 °C): δ = 12.30 (s, 1 H, N*H*), 8.85−5.66 (m, 21 H, py$^{2-6}$, Np, Tp) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ = 281.4 (1C, Ru=*C*), 159.7 (1C, py^2), 151.0 (1C, py^6), 142.2 (1C, Tp), 141.1(1C, Tp), 136.9 (1C, py^4), 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, py^5), 105.9 (1C, py^3), 105.9 (3C, Tp) ppm.

[RuCp(CH$_3$CN)(κ^2*N*,*N*′-py−CH$_2$−N=CHPh)]PF$_6$ (12): This compound was prepared analogously to **6b** by using **1** (100 mg, 0.230 mmol) and *N*-(phenylmethylene)-2-picolylamine (py−CH$_2$−N=CHPh) (50 mg, 0.253 mmol) as the starting materials. Yield: 90 mg (74%). $C_{20}H_{20}F_6N_3PRu$ (548.44): calcd. C 43.80, H 3.68; found C 43.85, H 3.71. ^1H NMR ([D$_6$]acetone, 20 °C): δ = 9.19 (d, $J_{H,H}$ = 5.05 Hz, 1 H, py^6), 9.11 (d, $J_{H,H}$ = 1.26 Hz, 1 H, N=C*H*Ph), 8.50−8.48 (m, 2 H, py^4, Ph), 7.98 (dt, $J_{H,H1}$ = 7.78, $J_{H,H2}$ = 1.53 Hz, 1 H, py^3), 7.68−7.56 (m, 4 H, Ph), 7.44 (vt, 1 H, $J_{H,H}$ = 6.56 Hz, py^5), 5.62 (d, 1 H, $J_{H,H1}$ = 17.69 Hz, CH$_2$), 5.43 (d, $J_{H,H}$ = 17.69 Hz, 1 H, CH$_2$), 4.28 (s, 5 H, Cp), 2.19 (s, 3 H, CH$_3$CN) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 20 °C): δ = 173.0 (1C, py^6), 160.5 (1C, py^2), 155.2 (1C, N=*C*HPh), 137.7 (1C, py^4), 134.3 (1C, Ph^1), 132.5 (1C, Ph^4), 130.2 (2C, Ph^{2,6}), 128.8 (2C, Ph^{3,5}), 125.9 (1C, CH$_3$*C*N), 124.3 (1C, py^3), 120.6 (1C, py^5), 74.6 (1C, CH$_2$), 70.5 (5C, Cp), 2.7 (1C, *C*H$_3$CN) ppm.

[RuTp(κ^2*N*,*N*′-py−CH$_2$−N=CHPh)Cl] (13): This compound was prepared analogously to **11b** by using **5** (100 mg, 0.218 mmol) and py−CH$_2$−N=CHPh (47 mg, 0.240 mmol) as the starting materials. Yield: 87.9 mg (64%). $C_{22}H_{22}BN_8ClRu$ (545.81): calcd. C 48.41, H 4.06; found C 48.49, H 4.13. ^1H NMR ($CDCl_3$, 20 °C): δ = 9.05 (s, 1 H, N=C*H*), 8.12 (d, $J_{H,H}$ = 5.8 Hz, 1 H, py^6), 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, py^4), 6.74 (t, $J_{H,H}$ = 7.5 Hz, 1 H, py^5), 6.61 (d, $J_{H,H}$ = 14.9 Hz, 1 H, C*H*$_2$), 6.44 (d, $J_{H,H}$ = 7.9 Hz, 1 H, py^3), 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, C*H*$_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ = 171.4 (1C, N=*C*HPh), 162.4 (1C, py ^{2}), 153.6 (1C, py ^{6}), 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, py ^{4}), 133.7 (1C, Ph^1), 130.0 (1C, Ph^4), 128.2 (2C, Ph^{2,6}), 128.0 (2C, Ph^{3,5}), 123.2 (1C, py ^{5}), 119.2 (1C, py ^{3}), 106.8 (1C, Tp), 106.6 (1C, Tp), 106.2 (1C, Tp), 75.2 (1C, CH$_2$) ppm.

[RuCp(pyMe-NH$_2$){=C(NH−pyMe)Et}]PF$_6$ (14b): A solution of **1** (100 mg, 0.230 mmol) and *N*,*N*′-bis(2-picolyl)-1,1-propanediamine

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. Details for the crystal structure determinations of complexes **6b**·$(CH_3)_2CO$, **7a**, **7b**, **11a**, **12**, and **16**

	6b·$(CH_3)_2CO$	**7a**	**7b**	**11a**	**12**	**16**
Empirical formula	$C_{42}H_{40}F_6FeN_2OP_2Ru$	$C_{18}H_{15}F_6N_2OPRu$	$C_{22}H_{19}F_6FeN_2OPRu$	$C_{21}H_{20}BClN_8Ru$	$C_{20}H_{20}F_6N_3PRu$	$C_{31}H_{30}F_6N_2P_2Ru$
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	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	11.035(1)	10.485(1)	10.820(7)	27.131(7)	10.167(2)	13.469(2)
b, Å	14.187(2)	13.966(2)	13.369(9)	11.152(3)	11.840(2)	15.052(3)
c, 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)					
V, Å^3	1951.2(4)	1859.2(4)	4387(5)	4516(2)	2169.3(6)	2950.7(9)
Z	2	4	8	8	4	4
$\rho_{calcd.}$, g cm^{-3}	1.569	1.863	1.905	1.564	1.679	1.593
T, K	173(2)	123(2)	123(2)	297(2)	183(2)	297(2)
μ, mm^{-1} (Mo-*Kα*)	0.906	1.000	1.493	0.839	0.859	0.703
F(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 $I > 2\sigma(I)$	9168	3956	4022	3140	5260	6841
No. of params	515	262	367	289	295	379
R_1 $[I > 2\sigma(I)]$[a]	0.031	0.028	0.080	0.033	0.032	0.045
R_1 (all data)	0.041	0.047	0.162	0.048	0.041	0.058
wR_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] $R_1 = \Sigma F_o - F_c / \Sigma F_o$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

[pyMe−NHCH(Et)NH−pyMe] (59 mg, 0.20 mmol) in CH_2Cl_2 (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%). $C_{20}H_{25}F_6N_4PRu$ (567.48): calcd. C 42.33, H 4.44; found C 43.27, H 4.40. ^{1}H NMR ([D$_6$]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, NH_2), 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, CH_2), 3.87 (m, $J_{H,H}$ = 7.31 Hz, 1 H, CH_2), 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, CH_3) ppm. ^{13}C{^{1}H} NMR ([D$_6$]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, *C*H$_2$CH$_3$), 20.5 (1C, py−Me), 20.0 (1C, py−Me), 12.2 (1C, CH$_2$*C*H$_3$) 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%). $C_{18}H_{22}BN_8ClRu$ (497.76): calcd. C 43.43, H 4.46; found C 43.39, H 4.49. ^{1}H NMR ([D$_6$]DMSO, 20 °C): δ = 13.06 (s, 1 H, N*H*), 8.15 (d, $J_{H,H}$ = 5.8 Hz, 1 H, py^6), 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, py^3), 6.98 (dd, J_1 = 6.0, J_2 = 1.3 Hz 1 H, py^5), 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, C*H*$_2$), 2.07 (s, 3 H, py−Me), 0.77 (t, $J_{H,H}$ = 7.7 Hz, 3 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 20 °C): δ = 290.3 (1C, Ru=*C*), 160.0 (1C, py^2), 150.7 (1C, py^6), 148.5 (1C, py^4), 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, py^5), 111.9 (1C, py^3), 106.6 (1C, Tp), 106.5 (1C,Tp), 106.3 (1C, Tp), 39.6 (1C, *C*H$_2$), 21.5 (1C, *C*H$_3$−CH$_2$), 10.9 (1C, py−Me) ppm.

Crystallographic Structure Determinations: Crystals of **6b**·$(CH_3)_2CO$, **7a**, **7b**, **11a**, **12**, and **16** were obtained by vapor diffusion of Et_2O into either CH_2Cl_2 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 F^2 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-

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

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).

Acknowledgments

Financial support by the "Fonds zur Förderung der wissenschaftlichen Forschung" (Project No. P14681-CHE) is gratefully acknowledged. Support from the EC through the COST D17 Action is also acknowledged.

[1] C. M. Standfest-Hauser, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **2002**, *21*, 2001.
[2] [2a] J. N. Coalter, G. J. Spivak, H. Gerard, E. Clot, E. R. Davidson, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1998**, *120*, 9388. [2b] J. N. Coalter, J. C. Bollinger, J. C. Huffman, U. W. Zwanziger, K. G. Caulton, E. R. Davidson, H. Gerard, E. Clot, O. Eisenstein, *New J. Chem.* **2000**, *24*, 9.
[3] [3a] T. Bodnar, A. R. Cutler, *J. Organomet. Chem.* **1981**, *213*, C31. [3b] C. Casey, W. H. Miles, H. Tukada, *J. Am. Chem. Soc.* **1985**, *107*, 2924. [3c] R. S. Bly, R. K. Bly, *J. Chem. Soc., Chem. Commun.* **1986**, 1046.
[4] For the conversion of aminals to aminocarbene ligands on clusters, see: R. D. Adams, *Chem. Rev.* **1989**, *89*, 1703.
[5] For a related acetal rearrangement, see: D. B. Grotjahn, H. C. Lo, *Organometallics* **1996**, *15*, 2860.
[6] A. Ohtaka, N. Kato, H. Kurosawa, *Organometallics* **2002**, *21*, 5464.
[7] For related reactions of this ligand, see: [7a] C. -H Jun, C. W. Moon, D.-Y. Lee, *Chem. Eur. J.* **2002**, *8*, 2422. [7b] J. W. Suggs, *J. Am. Chem. Soc.* **1979**, *101*, 489.
[8] For hydrido-acyl-hydroxycarbene rearrangements, see: [8a] C. P. Casey, C. J. Czerwinski, K. A. Fusie, R. Hayashi, *J. Am. Chem. Soc.* **1997**, *119*, 3971. [8b] D. Steinborn, M. Gerisch, C. Bruhn, J. A. Davies, *Inorg. Chem.* **1999**, *38*, 680.
[9] J. N. Coalter, J. C. Huffman, K. G. Caulton, *Organometallics* **2000**, *19*, 3569.
[10] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.
[11] T. Loerting, C. Tautermann, R. T. Kroemer, I. Kohl, A. Hallbrucker, E. Mayer, K. Liedl, *Angew. Chem. Int. Ed.* **2000**, *39*, 891.
[12] C. A. Pommerening, S. M. Bachrach, L. S. Sunderlin, *J. Phys. Chem. A* **1999**, *103*, 1214.
[13] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd Ed., Pergamon, New York, **1988**.
[14] T. P. Gill, K. R. Mann, *Organometallics* **1982**, *1*, 485.
[15] E. Rüba, W. Simanko, K. Mauthner, K. M. Soldouzi, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1999**, *18*, 3843.
[16] E. Becker, C. Slugovc, E. Rüba, C. Standfest-Hauser, K. Mereiter, R. Schmid, K. Kirchner, *J. Organomet. Chem.* **2002**, *649*, 55.
[17] C. Gemel, G. Trimmel, C. Slugovc, S. Kremel, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1996**, *15*, 3998.
[18] G. M. Sheldrick, *SADABS: Program for Absorption Correction*, University of Göttingen, Germany, **1996**.
[19] G. M. Sheldrick, *SHELXS-97: Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1997**.
[20] G. M. Sheldrick, *SHELXL-97*: *Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.
[21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**. *Gaussian 98*, revision A.7 Gaussian, Inc.: Pittsburgh, PA, **1998**.
[22] [22a] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648. [22b] B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200. [22c] C. Lee, W. Yang, G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[23] [23a] U. Haeusermann, M. Dolg, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *78*, 1211. [23b] W. Kuechle, M. Dolg, H. Stoll, H. Preuss, *J. Chem. Phys.* **1994**, *100*, 7535. [23c] T. Leininger, A. Nicklass, H. Stoll, M. Dolg, P. Schwerdtfeger, *J. Chem. Phys.* **1996**, *105*, 1052.
[24] [24a] A. D. McClean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639. [24b] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650. [24c] A. H. Wachters, *Chem. Phys.* **1970**, *52*, 1033. [24d] P. J. Hay, *J. Chem. Phys.* **1977**, *66*, 4377. [24e] K. Raghavachari, G. W. Trucks, *J. Chem. Phys.* **1989**, *91*, 1062. [24f] R. C. Binning, L. A. Curtiss, *J. Comput. Chem.* **1995**, *103*, 6104. [24g] M. P. McGrath, L. Radom, *J. Chem. Phys.* **1991**, *94*, 511.

Received December 20, 2002

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim