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Ruthenium(II) and iron(II) complexes of *N*-pyridyl substituted imidazolin-2-ylidenes

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ABSTRACT

N-mesityl-*N*′-pyridyl-imidazolium chloride **1a** and the corresponding bromide salt **1b** have been deprotonated with NaH in THF giving the free N-heterocyclic carbene *N*-mesityl-*N*′-pyridyl-imidazolin-2-ylidene **2** in 80% yield (starting from **1a**). Imidazolium salt **1a** reacts with $RuCl_3 \cdot xH_2O$ to give a racemic mixture of dinuclear di-μ-chloro bridged ruthenium complexes $[(\kappa^2\text{-}\mathbf{2})_2Ru(\mu\text{-}Cl)_2Ru(\kappa^2\text{-}\mathbf{2})_2]^{2+}$ $[\mathbf{3a}]^{2+}$. The carbene carbon atoms as well as the halides are arranged in *cis*-positions to each other whereas the nitrogen atoms adopt a *trans*-configuration. The di-μ-bromo bridged derivative $[(\kappa^2\text{-}\mathbf{2})_2Ru(\mu\text{-}Br)_2Ru(\kappa^2\text{-}\mathbf{2})_2]^{2+}$ $[\mathbf{3b}]^{2+}$ was obtained from $RuCl_3 \cdot xH_2O$ and **1b**. The bridging halide ligands can be removed by the reaction with silver or sodium salts of bidentate Lewis acids. Complex $[\mathbf{3a}]^{2+}$ reacts with silver pyridylcarboxylate to give a racemic mixture of the mononuclear complex $[\mathbf{4}]^+$. Reaction of $[\mathbf{3a}]^{2+}$ with the sodium salt of L-proline resulted in a diastereomeric mixture of complexes $[\mathbf{5}]^+$. The free N-heterocyclic carbene **2** reacts with $[FeCl_2(PPh_3)_2]$ to give after anion exchange with $NaBPh_4$ *cis*/*cis*/*trans* coordinated $[Fe(\kappa^2\text{-}\mathbf{2})_2(MeCN)_2](BPh_4)_2$ $[\mathbf{6}](BPh_4)_2$. The molecular structures of $[\mathbf{3b}](PF_6)_2$, $[\mathbf{4}]PF_6$ and $[\mathbf{6}](BPh_4)_2 \cdot H_2O$ are reported.

1. Introduction

The utilization of N-heterocyclic carbenes (NHCs) [1] as ligands in organometallic chemistry has attracted considerable attention in recent years. NHCs do not only form stable complexes with transition metals in high or low oxidation states, but are increasingly employed as spectator ligands in novel catalysts [2]. We have studied benzannulated N-heterocyclic carbenes [3] and their metal complexes [4]. Of particular interest are NHC ligands which are functionalized with donor groups at the nitrogen atoms of the heterocycle. Such ligands are capable of forming a stable $M–C_{carbene}$ and a labile M-donor bond. A number of complexes with donor-functionalized [5] and pincer-type [5b,6] benzimidazolin-2-ylidene ligands are known.

Recent reports describe imidazolin-2-ylidenes which are N-substituted by nitrogen-donors. Among these are *N*-(α-picolyl) [7] and *N*-(2-pyridyl) [7b–f,8] substituted NHCs as well as pincer-ligands derived from N-substituted imidazolin-2-ylidenes [9]. A large number of Ag^I, Pd^{II}, Ir^I, Rh^I, Ni^{II}, Cu^I and Ru^{II} complexes with these ligands exhibiting diverse structural motifs have been described. All of these have in common that the carbene carbon atom is coordinated to the metal center while the additional nitrogen donor might or might not coordinate. Di- and polynuclear complexes with donor-functionalized carbene ligands are also known [7,8a,d,h,9,10].

We report here on the coordination chemistry of the potentially chelating *N*-pyridyl substituted carbene ligand **2** derived from the imidazolium salts of type **1** (Scheme 1). Both mono and dinuclear ruthenium(II) and mononuclear iron(II) complexes with ligand **2** have been synthesized and characterized by X-ray diffraction studies.

2. Results and discussion

Besides the known *N*-mesityl-*N*′-pyridylimidazolium bromide **1b** [8g], we have prepared the corresponding chloride **1a** from 2-chloropyridine and 1-mesitylimidazole using the method described for the synthesis of **1b**. The ^1H NMR resonance of the NCHN proton in **1a** ($\delta = 11.91$ ppm) is shifted downfield relative to the equivalent resonance in **1b** ($\delta = 11.45$ ppm) [8g]. This observation is consistent with previous results which describe a $N_2C–H\cdots Cl$ hydrogen bond in imidazolium chlorides [11] that seems to be less distinct for the bromides.

Both imidazolium salts **1a** and **1b** can be deprotonated with NaH in THF giving **2**. The free carbene was isolated in 80% yield (from **1a**) (Scheme 1). Formation of **2** is indicated by absence of the signal for the NCHN proton in the ^1H NMR spectrum and the appearance of the characteristic resonance of the carbene carbon atom at $\delta = 219.7$ ppm in the $^{13}C\{^1H\}$ NMR spectrum. Similar

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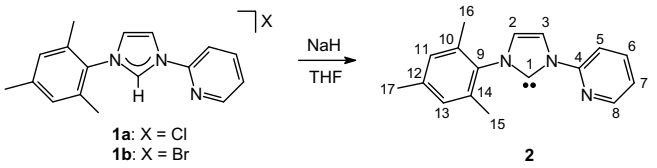


Scheme 1. Synthesis of ligand **2**. The numbering refers to the assignment of the NMR resonances.

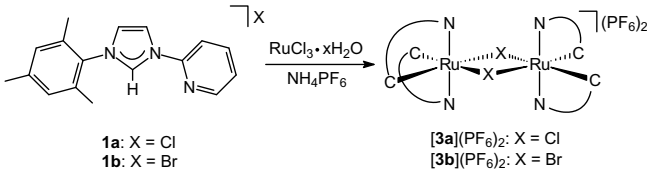
unsymmetrically *N*,*N*′-substituted imidazolin-2-ylidenes have been described by Danopoulos et al. [12].

The reaction of the free carbene **2** with different Ru^{II} precursors under varying reaction conditions applying different stoichiometric ratios of reagents did not lead to uniform products. No discrete ruthenium(II) complexes could be isolated. Mass spectroscopic analysis of the reaction mixture obtained by treatment of the coordinatively unsaturated phosphine complex $[RuCl_2(PPh_3)_3]$ with **2** in varying stoichiometric amounts revealed the formation of the cations $[RuCl(\mathbf{2})_2]^+$ and $[Ru(\mathbf{2})_3]^{2+}$ none of which could be isolated so far. The reaction of **2** with $[RuCl_2(p\text{-cymene})]_2$ led to the mass spectroscopic identification of the same Ru^{II} complexes in addition to the desired complex $[RuCl(p\text{-cymene})(\mathbf{2})]^+$ in the reaction mixture. Again we did not succeed in separating the reaction products. ^1H NMR spectroscopy of the product mixture revealed that the introduction of ligand **2** prevents the free rotation of the *p*-cymene ligand in $[RuCl(p\text{-cymene})(\mathbf{2})]^+$. Four resonances were observed for the aromatic protons of the *p*-cymene ligand in addition to two doublets for the CH_3 groups of the isopropyl substituent [13].

An interesting method for the generation of ruthenium(II) complexes with *N*-pyridyl-functionalized imidazolin-2-ylidenes has been described by Son et al. who reacted $RuCl_3 \cdot xH_2O$ with *N*-methyl-*N*′-pyridylimidazolium iodide to obtain the octahedral tricarbene ruthenium(II) dication [8e]. The analogous reaction of **1a** with $RuCl_3 \cdot xH_2O$ did not yield the mononuclear trischelate but instead the dinuclear complex $[\mathbf{3a}](PF_6)_2$ with two ligands **2** coordinated in the chelating κ^2-mode to each ruthenium(II) center (Scheme 2). We assign this behavior to the larger sterical demand of the *N*-mesityl substituents in **2**.

Carbene complex $[\mathbf{3a}](PF_6)_2$ was identified by $^{13}C\{^1H\}$ NMR spectroscopy showing a resonance at $\delta = 191.3$ ppm which is typical for ruthenium(II) complexes with imidazolin-2-ylidene ligands [14a]. The MALDI mass spectrum (positive ions) shows a signal at ½ of the mass of $[\mathbf{3a}]^{2+}$ which is not due to the dicationic nature of the complex but arises from ruthenium–halogen bond scission and detection of the mononuclear complex cation. While the presence of NHC ligands in $[\mathbf{3a}](PF_6)_2$ was established by spectroscopic methods no information about the stereochemistry of the ligand coordination is available from these data.

Treatment of $RuCl_3 \cdot xH_2O$ with **1b** instead of **1a** results in a mixture of di-μ-chloro and di-μ-bromo diruthenium complex cations $[\mathbf{3a}]^{2+}$ and $[\mathbf{3b}]^{2+}$ (Scheme 2). In spite of the different halogen bridges, the two complex cations give rise to essentially identical NMR spectra. Crystals of $[\mathbf{3b}](PF_6)_2$ suitable for an X-ray diffraction study were grown by diffusion of pentane into a saturated solution



Scheme 2. Synthesis of complexes of type $[\mathbf{3}](PF_6)_2$.

of complexes $[\mathbf{3a}](PF_6)_2/[\mathbf{3b}](PF_6)_2$ in acetone. The structure analysis (Fig. 1) confirms the proposed composition of the complex.

The Ru–C bond distances in the $[\mathbf{3b}]^{2+}$ dication (range 1.951(7)–1.982(6) Å) are remarkably short when compared to other octahedral [8e,14,15] or even pentacoordinated trigonal–bipyramidal Ru^{II} complexes with imidazolin-2-ylidene ligands [16]. We attribute this to the *trans*-position of the carbene ligand to the π-donor bromo ligand.

Compound $[\mathbf{3b}](PF_6)_2$ was observed as pair of Λ,Λ/Δ,Δ enantiomers. The Λ,Δ isomer as well as other possible *cis*/*trans* isomers were not observed. The mesityl and pyridyl rings of two different ligands coordinated to the same metal center are arranged in a coplanar fashion. This face-to-face arrangement in combination with their short separation (3.44 Å) are indicative of π–π interactions [17] between the aromatic rings. Apart from steric factors this π–π interaction is responsible for a restricted rotation of the mesityl rings which leads to two resonances for the *o*-methyl groups ($\delta = 1.90$ and 1.30 ppm) in the ^1H NMR spectrum.

Bidentate *N*,*O*-ligands have been employed successfully in the preparation of ruthenium olefin metathesis catalysts. Samec and Grubbs described an *N*,*O*-prolinate ruthenium benzylidene catalyst which is highly active in the RCM of disubstituted dienes [18]. We demonstrated that a ruthenium benzylidene complex with two *N*,*O*-pyridylcarboxylato ligands shows catalytic RCM activity in protic media [15]. We therefore decided to investigate the cleavage of the dinuclear complex $[\mathbf{3a}]^{2+}$ by anionic *N*,*O*-ligands obtained from silver pyridylcarboxylate and sodium L-prolinate.

Reaction of $[\mathbf{3a}](PF_6)_2$ with two equivalents of silver pyridylcarboxylate in refluxing tetrahydrofurane results in cleavage of

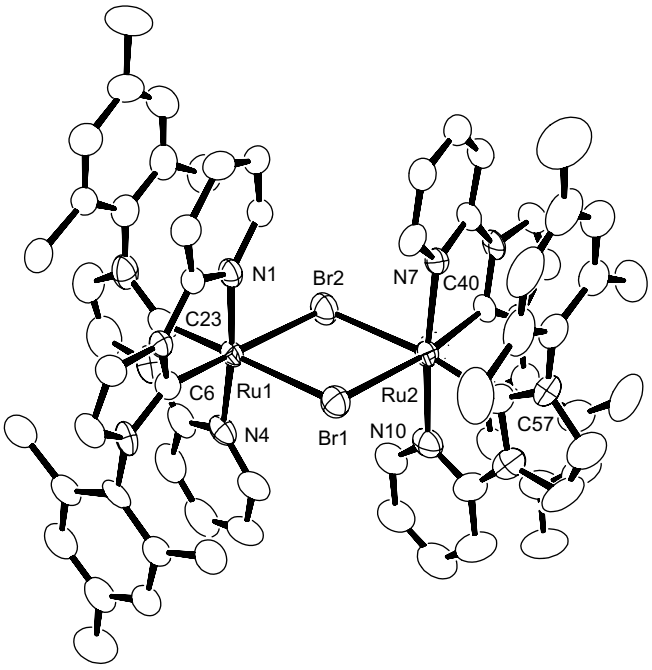


Fig. 1. Molecular structure of the cation $[\mathbf{3b}]^{2+}$ in $[\mathbf{3b}](PF_6)_2$. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–Br1 2.6394(9), Ru1–Br2 2.6468(9), Ru1–N1 2.081(5), Ru1–N4 2.078(5), Ru1–C6 1.982(6), Ru1–C23 1.978(7), Ru2–Br1 2.6365(9), Ru2–Br2 2.6458(9), Ru2–N7 2.097(5), Ru2–N10 2.093(5), Ru2–C40 1.970(6), Ru2–C57 1.951(7); Br1–Ru1–Br2 82.30(3), Br1–Ru1–N1 87.89(13), Br1–Ru1–N4 96.8(2), Br1–Ru1–C6 91.0(2), Br1–Ru1–C23 173.0(2), Br2–Ru1–N1 96.08(13), Br2–Ru1–N4 88.32(13), Br2–Ru1–C6 171.2(2), Br2–Ru1–C23 92.9(2), N1–Ru1–N4 174.0(2), N1–Ru1–C6 77.9(2), N1–Ru1–C23 97.7(2), N4–Ru1–C6 98.2(2), N4–Ru1–C23 77.9(2), C6–Ru1–C23 94.3(3), Br1–Ru2–Br2 82.37(3), Br1–Ru2–N7 96.31(13), Br1–Ru2–N10 88.42(14), Br1–Ru2–C40 171.8(2), Br1–Ru2–C57 92.1(2), Br2–Ru2–N7 87.96(13), Br2–Ru2–N10 96.3(2), Br2–Ru2–C40 91.9(2), Br2–Ru2–C57 170.6(2), N7–Ru2–N10 174.0(2), N7–Ru2–C40 77.6(2), N7–Ru2–C57 97.5(2), N10–Ru2–C40 98.0(2), N10–Ru2–C57 78.6(3), C40–Ru2–C57 94.1(3), Ru1–Br1–Ru2 97.87(3), Ru1–Br2–Ru2 97.45(3).

the dinuclear complex and formation of two equivalents of the mononuclear complex [**4**]PF_6 (Scheme 3). The same reaction was observed with [**3b**]$(PF_6)_2$. Complex [**4**]PF_6 precipitates from the reaction solution together with insoluble silver salts. It can be separated from these by recrystallization from chloroform.

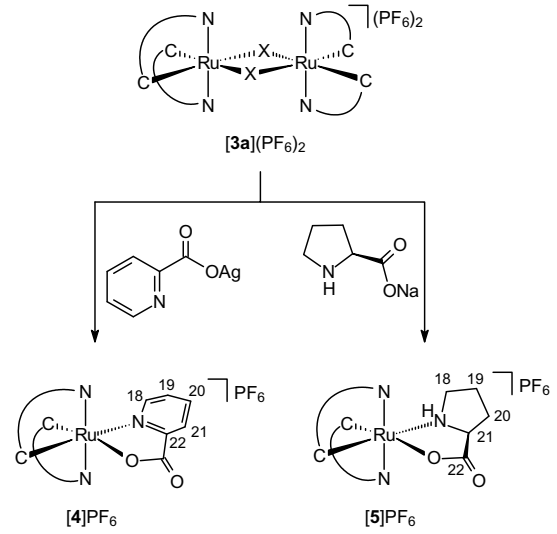
Complex cation [**4**]$^+$ contains two different carbene carbon atoms (*trans* to the oxygen and the nitrogen atoms of the pyridylcarboxylate, respectively). These give rise to two chemically inequivalent carbon atoms observed in the $^{13}C\{^1H\}$ NMR spectrum at $\delta = 197.3$ and 196.7 ppm.

Crystals of [**4**]PF_6 suitable for an X-ray diffraction study were obtained by diffusion of pentane into a solution of the complex in acetone. The structure analysis (Fig. 2) confirms the assumptions made for the composition of [**4**]PF_6. The ruthenium atom is coordinated in a distorted octahedral fashion with small N–Ru–C and O–Ru–N angles (range 76.21(6)–78.21(8)°) observed for the five-membered chelate rings. The Ru–$C_{carbene}$ distances differ slightly (Ru–C1 1.977(2), Ru–C21 1.948(2) Å) with the shorter Ru–C separation observed for the carbene ligand located *trans* to the oxygen atom of the pyridylcarboxylato ligand. Additional geometric parameters for [**4**]$^+$ are similar to equivalent parameters found for [**3b**]$^{2+}$.

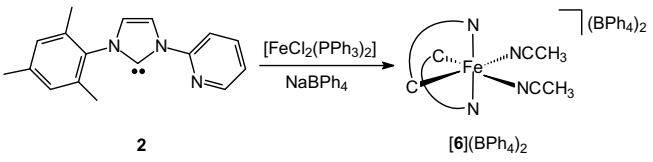
We found that the halogen abstraction from [**3a**]$(PF_6)_2$ does not require the addition of a silver salt or an elevated reaction temperature as applied for the synthesis of [**4**](PF_6). The strong *trans*-effect [4b] of the carbene ligands in [**3a**]$^{2+}$ allows halogen abstraction under cleavage of the dinuclear complex at ambient temperature using sodium L-prolinate. Complex [**3a**]$(PF_6)_2$ reacts with sodium L-prolinate to give a mixture of the diastereomeric complexes [**5**]PF_6. The diastereomers, Δ_L and Λ_L, exhibit distinctly different signals in the NMR spectra. For example, the $^{13}C\{^1H\}$ NMR spectrum exhibits four resonances for the carbene carbon atoms (diastereomer **A**: $\delta = 197.6$ and 195.7 ppm; diastereomer **B**: $\delta = 197.2$ and 195.8 ppm). In addition two resonances were observed for the carboxylato carbon atoms (diastereomer **A**: $\delta = 182.6$ ppm; diastereomer **B**: $\delta = 182.8$ ppm).

In contrast to the non-selective reaction of the free carbene **2** with ruthenium(II) precursors, treatment of $[FeCl_2(PPh_3)_2]$ with **2** in acetonitrile leads after anion exchange to a discrete complex which was isolated and characterized as [**6**]$(BPh_4)_2$ (Scheme 4). The characteristic resonance for the carbene carbon atoms in [**6**]$^{2+}$ was observed in the $^{13}C\{^1H\}$ NMR spectrum at $\delta = 200.2$ ppm while solubility and stability problems have previously prevented recording of the $^{13}C\{^1H\}$ NMR spectra of iron(II) imidazolin-2-ylidene complexes [19]. In addition, the MALDI mass spectrum shows a signal at $m/z = 582$ corresponding to the ion [**6**−2 MeCN]$^+$.

X-ray quality crystals of [**6**]$(BPh_4)_2 \cdot H_2O$ were obtained by slow evaporation of the solvent from an acetonitrile solution of the compound. The structure analysis revealed an iron atom coordi-



Scheme 3. Cleavage of complex [**3a**]$(PF_6)_2$ by Lewis bases. The numbering refers to the assignment of the NMR resonances.



Scheme 4. Synthesis of complex [**6**]$(BPh_4)_2$.

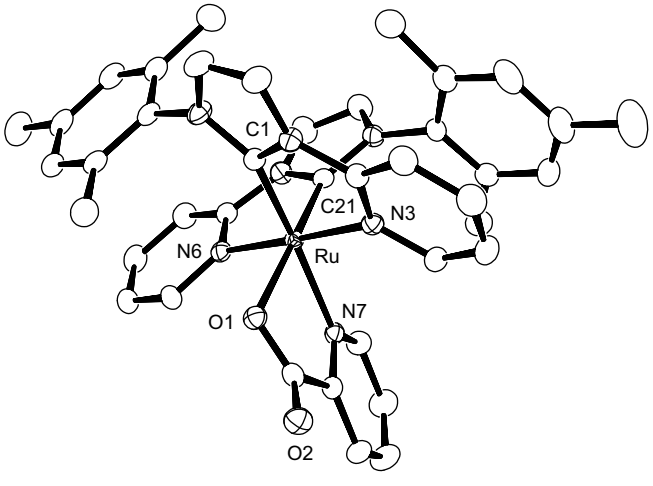


Fig. 2. Molecular structure of the cation [**4**]$^+$ in [**4**](PF_6). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru–O1 2.1585(15), Ru–N3 2.074(2), Ru–N6 2.058(2), Ru–N7 2.124(2), Ru–C1 1.977(2), Ru–C21 1.948(2); O1–Ru–N3 82.80(6), O1–Ru–N6 97.90(7), O1–Ru–N7 76.26(6), O1–Ru–C1 92.55(7), O1–Ru–C21 175.56(7), N3–Ru–N6 178.44(7), N3–Ru–N7 95.14(7), N3–Ru–C1 78.21(8), N3–Ru–C21 101.24(8), N6–Ru–N7 86.38(7), N6–Ru–C1 100.35(8), N6–Ru–C21 78.10(8), N7–Ru–C1 167.73(8), N7–Ru–C21 101.41(8), C1–Ru–C21 90.08(9).

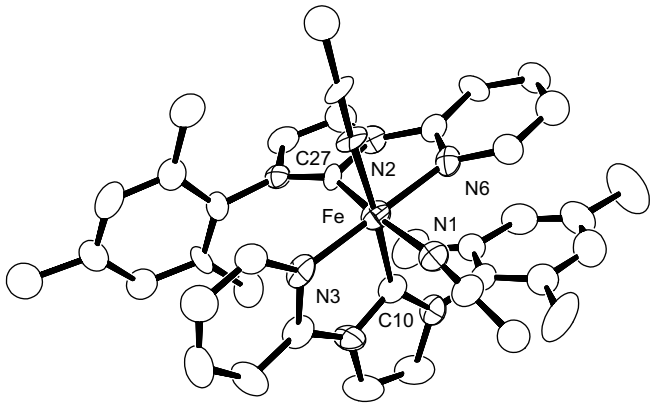


Fig. 3. Molecular structure of the cation [**6**]$^+$ in [**6**]$(BPh_4)_2 \cdot H_2O$. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe–N1 1.980(8), Fe–N2 1.982(8), Fe–N3 1.956(8), Fe–N6 1.963(8), Fe–C10 1.917(10), Fe–C27 1.912(10); N1–Fe–N2 90.6(3), N1–Fe–N3 88.5(3), N1–Fe–N6 93.0(4), N1–Fe–C10 89.0(3), N1–Fe–C27 173.7(5), N2–Fe–N3 93.9(4), N2–Fe–N6 87.3(3), N2–Fe–C10 175.2(5), N2–Fe–C27 92.1(3), N3–Fe–N6 178.0(5), N3–Fe–C10 81.3(6), N3–Fe–C27 96.9(5), N6–Fe–C10 97.4(5), N6–Fe–C27 81.4(5), C10–Fe–C27 88.8(4).

nated in a distorted octahedral fashion (Fig. 3). Both the Λ and Δ isomer coexist in the centrosymmetric unit cell. Short Fe–$C_{carbene}$ bond lengths (1.917(10) and 1.912(10) Å) are found in $[\mathbf{6}]^{2+}$ which are significantly shorter than the equivalent Fe–C separations in octahedral Fe^{III} hexa(imidazolin-2-ylidene) complexes [20]. However, the observed Fe–C bond lengths in $[\mathbf{6}]^{2+}$ compare well with the values found for Fe^{II} imidazolin-2-ylidene complexes [19] and even to those observed for dinitrogen complexes of iron(0) stabilized by a tridentate pincer dicarbene ligand [21].

3. Conclusions

The *N*-pyridyl-*N*′-mesityl substituted imidazolin-2-ylidene **2** has been prepared. Its parent imidazolium salts **1a,b** react with $RuCl_3 \cdot x$-H_2O under formation of dinuclear complexes of type $[Ru(\mathbf{2})_2(\mu\text{-}X)]_2$ (X = Cl, Br). The dinuclear complexes are cleaved by bidentate monoanionic Lewis bases (N–O) to yield monodentate complexes $[Ru(\mathbf{2})_2(N\text{–}O)]PF_6$. Direct reaction of the carbene ligand **2** with $[FeCl_2(PPh_3)_2]$ in acetonitrile yields the iron complex $[Fe(\mathbf{2})_2(NCCH_3)_2](BPh_4)_2$. The mononuclear Ru^{II} and Fe^{II} complexes are promising starting materials for functionalization with an alkylidene ligand which could lead to novel complexes for olefin metathesis.

4. Experimental

4.1. General methods

All reactions were carried out under an argon atmosphere. Solvents were dried and degassed by standard methods. The imidazolium salts **1b** [8g] and $[FeCl_2(PPh_3)_2]$ [22] were prepared according to literature procedures. NMR spectra were recorded on Bruker AC 200 (200 MHz), Bruker Avance I 400 (400 MHz) or Varin Unity Plus 600 (600 MHz) spectrometers. Mass spectra were obtained with a Bruker Reflex IV mass spectrometer.

4.2. Spectroscopic parameters for *1a*

^{1}H NMR (200.1 MHz, $CDCl_3$): δ 11.91 (t, *J* = 1.5 Hz, 1H, H1), 9.37 (d, *J* = 8.4 Hz, 1H, H5), 8.89 (m, 1H, H3), 8.53 (dm, *J* = 4.8 Hz, 1H, H8), 8.12 (m, 1H, H6), 7.48 (dd, *J* = 7.3 Hz, *J* = 4.8 Hz, 1H, H7), 7.30 (m, 1H, H2), 7.05 (s, 2H, H11 and H13), 2.35 (s, 3H, H17), 2.20 (s, 6H, H15 and H16).

4.3. Synthesis of carbene *2*

A suspension of **1a** (1.00 g, 2.90 mmol) and NaH (77 mg, 3.20 mmol) in THF (15 mL) was stirred for 12 h at room temperature. The precipitate was removed by filtration and the solution was brought to dryness *in vacuo*. Yield: 610 mg (2.30 mmol, 80%). For assignment of the resonances see Scheme 1. ^{1}H NMR (599.7 MHz, THF-d_8): δ 8.45 (m, 1H, H5), 8.38 (m, 1H, H8), 8.21 (m, 1H, H3), 7.76 (m, 1H, H6), 7.18 (m, 1H, H7), 7.03 (m, 1H, H2), 6.97 (s, 2H, H11 and H13), 2.32 (s, 3H, H17), 2.05 (s, 6H, H15 and H16). ^{13}C{^{1}H} NMR (150.8 MHz, THF-d_8): δ 219.7 (C1), 154.8 (C4), 148.4 (C8), 139.4 (C9), 138.6 (C6), 137.9 (C12), 135.6 (C10 and C14), 129.3 (C11 and C13), 122.3 (C2), 121.8 (C7), 116.7 (C3), 114.7 (C5), 21.0 (C17), 17.9 (C15 and C16).

4.4. Complex *[3a](PF6)2*

A solution of $RuCl_3 \cdot xH_2O$ (125 mg, 0.60 mmol) and **1a** (360 mg, 1.20 mmol) in ethylene glycole was heated under reflux for 4 h and was after cooling treated with aqueous NH_4PF_6 (500 mg in 5 mL H_2O). A precipitate formed which was separated by filtration and washed with little water. The precipitate was redissolved in dichloromethane. This solution was dried with $MgSO_4$ and then concentrated to 5 mL and added to diethyl ether (70 mL). A yellow precipitate of compound $[\mathbf{3a}](PF_6)_2$ formed which was isolated by filtration and dried *in vacuo*. Yield: 460 mg (0.28 mmol, 95%). For assignment of the resonances see Scheme 1. ^{1}H NMR (400.1 MHz, acetone-d_6): δ 8.41 (d, *J* = 2.3 Hz, 4H, H3), 8.23 (m, 4H, H8), 7.84 (m, 4H, H5), 7.78 (m, 4H, H6), 7.06 (d, *J* = 2.3 Hz, 4H, H2), 6.64 (s, 4H, H13), 6.37 (s, 4H, H11), 6.27 (m, 4H, H7), 2.15 (s, 12H, H17), 1.90 (s, 12H, H15), 1.30 (s, 12H, H16). ^{13}C{^{1}H} NMR (100.6 MHz, acetone-d_6): δ 191.3 (C1), 154.1 (C4), 152.9 (C8), 139.9 (C12), 137.1 (C6), 136.3 (C14), 135.2 (C9), 134.3 (C10), 130.3 (C13), 130.0 (C11), 126.3 (C2), 123.0 (C7), 117.9 (C3), 111.0 (C5), 20.8 (C17), 17.9 (C15), 17.0 (C16). MS (MALDI): *m/z* (%): 663 (100) $[½M]^+$.

4.5. Complex *[4]PF6*

A solution of $[\mathbf{3a}](PF_6)_2$ (280 mg, 0.17 mmol) and silver pyridylcarboxylate (80 mg, 0.35 mmol) in THF (20 mL) was heated under reflux for 8 h. The precipitate was filtered off and dissolved in chloroform. After an additional filtration the solvent was removed *in vacuo*. Yield: 200 mg (0.22 mmol, 65%). For assignment of the resonances see Scheme 3. ^{1}H NMR (400.1 MHz, acetone-d_6): δ 8.50 (d, *J* = 2.4 Hz, 1H, H3), 8.43 (d, *J* = 2.4 Hz, 1H, H3′), 8.09 (m, 1H, H21), 8.07 (m, 1H, H18), 7.98 (m, 1H, H20), 7.87 (m, 2H, H5), 7.81 (m, 3H, H6, H8, H6′), 7.70 (m, 1H, H5′), 7.48 (m, 1H H19), 7.43 (m, 1H, H8′), 7.36 (d, *J* = 2.4 Hz, 1H, H2), 7.34 (d, *J* = 2.4 Hz, 1H, H2′), 6.93 (m, 1H, H7′), 6.86 (m, 2H, H7, H13′), 6.67 (s, 1H, H11), 6.54 (s, 1H, H13), 6.43(s, 1H, H11′), 2.19 (s, 3H, H17′), 2.16 (s, 3H, H17), 2.13 (s, 3H, H15′), 2.10 (s, 3H, H15), 1.60 (s, 3H, H16′), 1.58 (s, 3H, H16). ^{13}C{^{1}H} NMR (100.6 MHz, acetone-d_6): δ 197.3 (C1′), 196.7 (C1), 170.9 (C23), 155.0 (C4′), 154.3 (C22), 153.8 (C4), 152.5 (C18), 150.7 (C8′), 150.2 (C8), 140.0 (C12′), 139.9 (C12), 138.7 (C20), 137.7 (C6′), 137.7 (C14′), 137.5 (C6), 135.7 (C14), 135.7 (C9′), 135.2 (C9), 135.2 (C10), 134.3 (C10′), 130.5 (C13′), 130.1 (C13), 129.8 (C11), 129.5 (C11′), 128.2 (C19), 127.4 (C21), 126.2 (C2), 125.9 (C2′), 122.7 (C7′), 122.3 (C7), 118.1 (C3′), 117.7 (C3), 111.7 (C5′), 111.0 (C5), 20.9 (C17′), 20.8 (C17), 18.8 (C15), 18.0 (C15′), 17.9 (C16′), 17.5 (C16). MS (MALDI): *m/z* (%): 750 (100) $[M]^+$.

4.6. Complex *[5]PF6*

A mixture of L-proline (46 mg, 0.39 mmol) and NaOH (16 mg, 0.40 mmol) in methanol (5 mL) was stirred for 1 h at room temperature. After addition of solid $[\mathbf{3a}](PF_6)_2$ (330 mg, 0.20 mmol) the suspension was left stirring for 4 h. The clear solution was dropped into diethyl ether (100 mL). After filtration, the precipitate was washed with diethyl ether (20 mL) and dried *in vacuo*. Yield: 315 mg (0.36 mmol, 87%). For assignment of the resonances see Scheme 3. Diastereomer A: ^{1}H NMR (400.1 MHz, acetone-d_6): δ 8.70 (H8), 8.43 (H3), 8.40 (H3′), 8.30 (H8′), 7.84 (H6′), 7.83 (H5), 7.78 (H6), 7.78 (H5′), 7.19 (H2′), 7.11 (H2), 7.04 (H7′), 6.80 (H7), 6.77 (H13′), 6.68 (H13), 6.54 (H11), 6.38 (H11′), 5.06 (NH), 3.92 (H21), 2.47 (H18a), 2.19 (H17), 2.12 (H20a), 2.15 (H17′), 2.05 (H15), 2.03 (H15′), 1.65 (H20b), 1.63 (H19a), 1.52 (H16), 1.43 (H16′), 1.18 (H19b), 1.18 (H18b). ^{13}C{^{1}H} NMR (100.6 MHz, acetone-d_6): δ 197.6 (C1′), 195.7 (C1), 182.6 (C22), 154.6 (C4′), 154.4 (C4), 152.6 (C8), 150.1 (C8′), 139.8 (C12), 139.7 (C12′), 137.3 (C6), 137.2 (C6′), 136.9 (C14′), 136.4 (C14), 135.6 (C9), 135.4 (C9′), 134.7 (C10′), 134.3 (C10), 130.5 (C13), 130.3 (C13′), 129.7 (C11), 129.6 (C11′), 125.8 (C2), 125.6 (C2′), 122.3 (C7′), 122.2 (C7), 117.8 (C3), 117.5 (C3′), 111.4 (C5), 111.3 (C5′), 63.1 (C21), 49.7 (C18), 31.4 (C20), 27.4 (C19), 21.0 (C17′), 20.9 (C17), 18.2 (C15), 18.1 (C15′), 17.3 (C16′), 17.3 (C16). Diastereomer B: ^{1}H NMR (400.1 MHz, acetone-d_6): δ 8.50 (H3), 8.37 (H3′), 8.19 (H8), 8.12

Table 1
Crystal data and data collection details for [**3b**]$(PF_6)_2$, [**4**]PF_6 and [**6**]$(BPh_4)_2 \cdot H_2O$

	[**3b**]$(PF_6)_2$	[**4**]PF_6	[**6**]$(BPh_4)_2 \cdot H_2O$
Chemical formula	$C_{68}H_{68}N_{12}Br_2F_{12}P_2Ru$	$C_{40}H_{38}N_7F_6O_2PRu$	$C_{86}H_{82}N_8B_2FeO$
Formula weight (amu)	1705.25	894.81	1321.07
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
Z	4	2	4
T (K)	153(2)	153(2)	293(2)
ρ (g cm^{-3})	1.277	1.525	1.185
μ (mm^{-1})	1.343	0.518	2.029
a (Å)	16.120(3)	11.987(2)	14.0475(7)
b (Å)	20.765(3)	12.182(2)	12.9485(7)
c (Å)	27.564(4)	15.684(3)	42.307(2)
α (°)	90	103.138(3)	90
β (°)	105.937(3)	95.916(3)	105.795(3)
γ (°)	90	116.085(3)	90
V (Å^3)	8872(2)	1948.5(5)	7404.8(6)
λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Cu Kα, 1.54178
Data collected	70094	22505	17355
Unique data	15618	11170	4713
Observed data [$I > 2\sigma(I)$]	9147	9481	3146
R, Rw [$I > 2\sigma(I)$]	0.086, 0.1925	0.0435, 0.0936	0.0667, 0.1632

(H8′), 7.90 (H5), 7.84 (H6), 7.82 (H6′), 7.76 (H5′), 7.17 (H2′), 7.09 (H2), 6.95 (H7′), 6.94 (H7), 6.85 (H13′), 6.73 (H13), 6.50 (H11), 6.39 (H11′), 4.59 (NH), 3.52 (H21), 3.18 (H18a), 2.92 (H18b), 2.20 (H17′), 2.19 (H17), 2.10 (H15′), 2.05 (H20a), 2.02 (H15), 1.92 (H20b), 1.83 (H19a), 1.55 (H19b), 1.48 (H16), 1.40 (H16′). $^{13}C\{^1H\}$ NMR (100.6 MHz, acetone-d_6): δ 197.2 (C1′), 195.8 (C1), 182.8 (C22), 155.4 (C4′), 154.6 (C4), 152.6 (C8), 150.3 (C8′), 139.8 (C12′), 139.8 (C12), 137.7 (C6), 137.3 (C6′), 136.4 (C14), 136.0 (C14′), 135.7 (C9), 135.5 (C9′), 135.0 (C10′), 134.3 (C10), 130.6 (C13), 130.1 (C13′), 129.8 (C11′), 129.8 (C11), 126.3 (C2), 125.9 (C2′), 122.2 (C7′), 122.0 (C7), 117.9 (C3), 117.4 (C3′), 111.6 (C5), 111.5 (C5′), 62.9 (C21), 52.9 (C18), 30.2 (C20), 27.6 (C19), 20.9 (C17′), 20.9 (C17), 18.2 (C15′), 18.2 (C15), 17.4 (C16), 17.3 (C16′). MS (MALDI): m/z (%): 742 (100) $[M]^+$.

4.7. Complex [*6*]$(BPh_4)_2$

To a solution of $[FeCl_2(PPh_3)_2]$ (800 mg, 1.25 mmol) in THF (25 mL) was added a solution of **2** (330 mg, 1.25 mmol) in THF (10 mL) at −78 °C. This mixture was stirred at ambient temperature for 12 h. A precipitate formed during this time which was separated by filtration, washed with diethyl ether (10 mL) and suspended in acetonitrile (10 mL). To this suspension was added a solution of $NaBPh_4$ (427 mg, 1.25 mmol) in acetonitrile (10 mL). After stirring for 12 h, the resulting suspension was filtered and the filtrate was concentrated to 5 mL. Addition of diethyl ether (30 mL) causes precipitation of complex [**6**]$(BPh_4)_2$. Yield: 299 mg (0.45 mmol, 36%). For assignment of the resonances see Scheme 1. ^1H NMR (400.1 MHz, acetonitrile-d_3): δ 8.12 (m, 4H, H3, H8), 7.71 (m, 2H, H6), 7.37 (m, 2H, H5), 7.28 (m, 16H, *o*-H BPh_4), 7.10 (d, J = 2.2 Hz, 1H, H2), 6.99 (m, 16H, *m*-H BPh_4), 6.84 (m, 8H, *p*-H BPh_4), 6.82 (m, 2H, H7), 6.67 (s, 2H, H13), 6.53 (s, 2H, H11), 2.18 (s, 6H, H17), 1.96 (s, 6H, H15), 1.43 (s, 6H, H16). $^{13}C\{^1H\}$ NMR (100.6 MHz, acetonitrile-d_3): δ 200.2 (C1), 164.9 (q, $^1J_{CB}$ = 49.3 Hz, *ipso*-C BPh_4), 155.4 (C4), 154.3 (C8), 140.5 (C12), 139.6 (C6), 136.8 (m, *ortho*-C BPh_4), 136.2 (C9), 134.7 (C14), 134.6 (C10), 130.5 (C13), 130.1 (C11), 129.0 (C2), 126.7 (m, *meta*-C BPh_4), 122.9 (C7), 122.8 (*para*-C BPh_4), 119.5 (C3), 111.5 (C5), 21.0 (C17), 17.7 (C15), 17.5 (C16). MS (MALDI): m/z (%): 582 (100) $[M-2MeCN]^+$.

4.8. Crystal structure determinations

Diffraction data were collected with a Bruker AXS APEX CCD diffractometer. Data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART [23] program package. Structure solutions were found with the SHELXS-97 [24] package using the heavy-atom method and were refined with SHELXL-97 [25] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions. Additional data collection and refinement parameters are given in Table 1.

Appendix A. Supplementary material

CCDC 693197, 693198 and 693199 contains the supplementary crystallographic data for [**3a**]$(PF_6)_2$, [**4**]PF_6 and [**6**]$(BPh_4)_2 \cdot H_2O$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.08.013.

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