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Synthesis and Characterization of Tetrakis(carbene)ruthenium(II) Complexes Featuring an $[Ru(NHC)_4]^{2+}$ Core

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The synthesis of different ruthenium(II) complexes with an $[Ru(NHC)_4]^{2+}$ (NHC = N-heterocyclic carbene) core is reported. The reaction of $[(\eta^6\text{-}C_6H_4Me\textit{i}Pr)RuCl(\mu\text{-}Cl)]_2$ with 1 equiv. of the NHC $\textit{i}Pr_2Im$ in thf leads to the clean formation of $[(\eta^6\text{-}C_6H_4Me\textit{i}Pr)Ru(\textit{i}Pr_2Im)Cl_2]$ (**1**), but use of an excess of the carbene at higher temperatures affords side products such as $[Ru(\textit{i}Pr_2Im)_4H]Cl$ (**9**). Complexes of the type $[Ru(R_2Im)_4Cl_2]$ [R = Me (**2**), *n*Pr (**3**), Me*i*Pr (**6**)] were synthesized by the reaction of $[Ru(PPh_3)_3Cl_2]$ with Me_2Im, $\textit{n}Pr_2Im$, and Me*i*PrIm. Compound **6** was isolated as a mixture of isomers that differ in the relative orientation of the asymmetrically substituted NHC ligand with respect to the Ru–Cl vector. Replacement of the chlorido ligands in **2** and **3** with acetonitrile leads to the formation of $[Ru(R_2Im)_4(CH_3CN)]Cl_2$ [R = Me (**4**), *n*Pr (**5**)]. At higher temperatures, complex **6** eliminates HCl under C–H activation of one of the NHC ligand *i*Pr groups to give the cyclometallation product **7**. The reaction of $[Ru(PPh_3)_3Cl_2]$ with $\textit{i}Pr_2Im$ afforded the cyclometallation product $[Ru(\textit{i}Pr_2Im)_3\{\textit{i}Pr(C_3H_6)Im\}Cl]$ (**8**) or the hydrido complex $[Ru(\textit{i}Pr_2Im)_4(H)]Cl$ (**9**) as the main product depending on the reaction conditions. The complexes **1**, **3**, **4**, and **7** as well as two isomers of **6** were structurally characterized.

Introduction

The last two decades have witnessed a rapid increase in the use of N-heterocyclic carbenes (NHCs) as supporting ligands in transition metal homogeneous catalysis.[1] As with phosphanes, NHCs promise control of metal center reactivity through a variation in the nature of the ligand substituents. In this respect, (NHC)ruthenium complexes and their application in metathesis reactions have played a pivotal role in the elevation of NHC ligands to the ubiquitous position that they now occupy in organometallic chemistry and catalysis.[2] A large amount of (NHC)ruthenium chemistry published in the literature still aims towards the improvement of metathesis catalysts; however, NHC-stabilized ruthenium half-sandwich complexes are also a focus of interest.[3] In the course of our ongoing work on nickel complexes stabilized with 1,3-dialkylimidazolin-2-ylidene ligands (R_2Im, see Figure 1),[4] we became interested in small molecule activation using complexes of the type $[Ru(R_2Im)_4Cl_2]$, a class of compounds introduced for imidazolidin-2-ylidene ligands by Lappert and coworkers.[5] Recent publications on complexes of the type $[Ru(NHC)_4(H)]^+$ by the Whittlesey group[6] and by Wolf et al.[7] prompted us to disclose our own results in this area. Herein we report the synthesis and characterization of novel tetrakis(carbene)chlorido complexes of the type *trans*-$[Ru(NHC)_4Cl_2]$ (see Figure 1) and derivatives thereof.

Results and Discussion

We have previously reported in some detail the synthesis of $[Ni(R_2Im)_2]$ precursors and applications of the $[Ni(R_2Im)_2]$ complex fragment in stoichiometric and catalytic reactions.[4] To expand this type of chemistry, we envisioned that precursors of complex fragments of the type

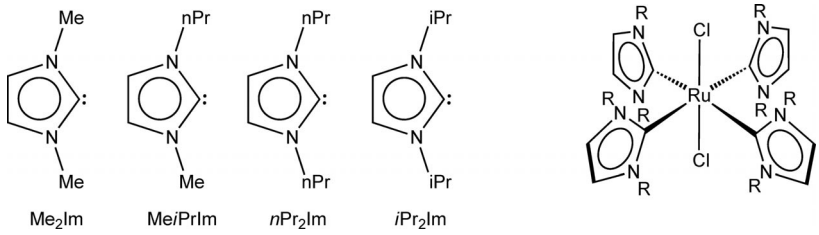

Figure 1. Ligands used for the attempted synthesis of ruthenium complexes of the type *trans*-$[RuCl_2(NHC)_4]$.

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[CpM(R_2Im)] (M = Co, Rh, Ir) and [(arene)M′(R_2Im)] (M′ = Fe, Ru, Os) might be of interest to us. (Carbene)ruthenium complexes of the type [(*p*-cymene)Ru(NHC)X_2] have been studied, but to the best of our knowledge no reduction chemistry of these complexes has been reported.[8] Therefore, we aimed towards the synthesis of [(η^6-C_6H_4Me*i*Pr)-Ru(*i*Pr_2Im)Cl_2], which was prepared according to procedures reported earlier for similar compounds.[8] The reaction of [(η^6-C_6H_4Me*i*Pr)RuCl(μ-Cl)]$_2$ with 1 equiv. of the NHC in thf cleanly forms [(η^6-C_6H_4Me*i*Pr)Ru(*i*Pr_2Im)Cl_2] (**1**) as an orange powder, which was characterized by X-ray diffraction on single crystals obtained from a concentrated dme solution of the compound at room temperature (see Figure 2).

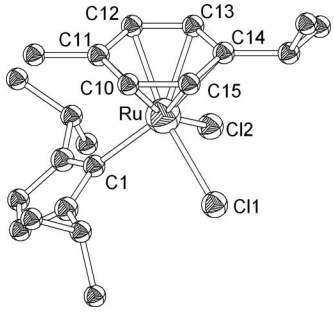


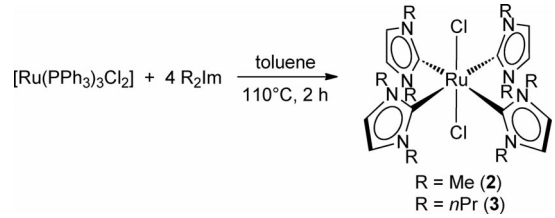
Figure 2. Thermal ellipsoid drawing of the molecular structure of **1** (thermal ellipsoids at 40% probability; H atoms omitted for clarity). Selected bond lengths [pm] and angles [°]: Ru–$ar_{centroid}$ 1.699(6), Ru–C(1) 208.9(5), Ru–C(10) 220.4(6), Ru–C(11) 223.8(5), Ru–C(12) 220.3(6), Ru–C(13) 218.9(5), Ru–C(14) 227.1(5), Ru–C(15) 218.4(6), Ru–Cl(1) 242.90(14), Ru–Cl(2) 242.43(13); C(1)–Ru–Cl(1) 88.69(15), C(1)–Ru–Cl(2) 90.28(14).

Complex **1** crystallizes in the orthorhombic space group *Pbca* with one molecular formula in the asymmetric unit. The molecular structure reveals a pseudooctahedral mononuclear ruthenium(II) compound, with the arene ligand, the carbene ligand, and two chlorido ligands in the coordination sphere of the ruthenium atom. The Ru–C(1) bond length of 208.9(5) pm is close to the Ru–$C_{carbene}$ distance reported for [(η^6-C_6H_4Me*i*Pr)Ru(Cy_2Im)Cl_2] (209.3 pm) by Hermann and co-workers[8a] and similar to distances found in molecular structures of complexes [(η^6-C_6H_4Me*i*Pr)-Ru(NHC)Cl_2] published by others.[8l,8m,8q,8v] It has been demonstrated that NHC-stabilized (cymene)ruthenium complexes are useful catalysts for different kinds of reactions including the cyclopropanation of olefins, ring-closing olefin metathesis, ring-opening metathesis polymerization, and cycloisomerization reactions as well as the oligomerization of alkynes.[8]

Despite the straightforward synthesis of **1**, we recognized a violet byproduct in small amounts from the reaction of [(η^6-C_6H_4Me*i*Pr)RuCl(μ-Cl)]$_2$ with the NHC, especially when a larger excess of *i*Pr_2Im was used and higher temperatures were applied. This side product was almost insoluble in thf, and its ^{1}H NMR spectrum revealed no resonances for the arene ring, but contained signals that were assigned to coordinated carbene ligands. This compound was later characterized as [Ru(*i*Pr_2Im)$_4$H]Cl (vide infra), but at that time we could not detect a resonance for the hydrido ligand, and no proof was obtained for the presence of a ruthenium hydride from IR spectroscopy. However, all data available including a preliminary X-ray structure on low-quality crystals of this complex led to the formulation of a complex with four NHC ligands coordinated to the ruthenium atom, similar to ruthenium complexes reported by Lappert's group with imidazolidin-2-ylidenes.[5] Since 16-electron complexes $[ML_4X]^+$ (M = Fe, Ru, Os; L = neutral two-electron donor ligand) are in general very interesting fragments for binding and activation of small molecules, we decided to systematically investigate the synthesis of complexes of the type [Ru(R_2Im)$_4Cl_2$] with different alkyl-substituted NHCs, which are shown in Figure 1. Early experimental results using different Ru^{II} precursors have shown that in principle a variety of these precursors could be used to synthesize this compound, but that the use of [Ru-(PPh_3)$_3Cl_2$][9] provides a very convenient entry into this type of chemistry.

Reaction of [Ru(PPh_3)$_3Cl_2$] with *n*-Alkyl-Substituted Imidazolin-2-ylidenes, Me_2Im and *n*Pr_2Im

The treatment of [Ru(PPh_3)$_3Cl_2$] with 4 equiv. of Me_2Im and *n*Pr_2Im afforded the yellow complexes [Ru(Me_2Im)$_4Cl_2$] (**2**) and [Ru(*n*Pr_2Im)$_4Cl_2$] (**3**) cleanly (Scheme 1). Wolf and co-workers recently reported the synthesis of the closely related complex [Ru(Me_2ImMe_2)$_4Cl_2$] (Me_2ImMe_2 = 1,3,4,5-tetramethylimidazolin-2-ylidene) starting from [$RuCl_2$-(cod)]$_x$ and the corresponding NHC.[7] In this publication the authors mentioned some problems with the purification of [Ru(Me_2ImMe_2)$_4Cl_2$] if [Ru(PPh_3)$_3Cl_2$] was used as a starting material. In our case, the reaction of Me_2Im with [Ru(PPh_3)$_3Cl_2$] proceeds quantitatively, and after washing no further purification steps are required. The use of [(η^6-C_6H_4Me*i*Pr)RuCl(μ-Cl)]$_2$ instead of [Ru(PPh_3)$_3Cl_2$] as starting material leads to the same compounds, albeit in lower yields. The yellow complexes **2** and **3** have been isolated in excellent yields, and their compositions have been confirmed by elemental analysis. In the EI mass spectra, the peaks for the molecular ions (**2**: *m*/*z* = 556.0; **3**: *m*/*z* = 780.1) were detected, as well as peaks for the consecutive cleavage of one or two carbene ligands under EI-MS conditions.



Scheme 1. Synthesis of **2** and **3**.

The NMR spectroscopy of complex **2** was hampered due to its insolubility in common solvents such as benzene, toluene, dichloromethane, and ethers, which might be indicative of an ionic form of this complex in solution, [Ru(Me_2Im)$_4$-Cl]Cl or [Ru(Me_2Im)$_4$]Cl_2, whereas for **3** we observed rea-

sonable solubility in toluene, thf, and dichloromethane. The ^{1}H NMR spectrum recorded in [D$_6$]acetone reveals a singlet at δ = 7.13 ppm for the protons of the backbone and a sharp triplet at δ = 0.66 ppm for the *n*Pr methyl group, which suggests equivalence of the NHC ligands on the NMR time scale. The diastereotopic *n*Pr methylene protons give rise to four sets of resonances at δ = 1.62, 1.73, 2.94, and 4.41 ppm (integration shows four protons for each multiplet). On the basis of ^{1}H/^{1}H correlation spectra, we assigned the multiplets at δ = 2.94 and 4.41 ppm to the methylene group bonded to the nitrogen atoms of the imidazole ring and the multiplets at δ = 1.62 and 1.73 ppm to the diastereotopic protons of the central methylene group of the *n*Pr substituent. This splitting of the resonances can be observed up to a temperature of 90 °C. In the ^{13}C NMR spectrum of **3** only one set of signals was observed for the NHC ligands, with a resonance for the carbene carbon atom at δ = 191.1 ppm. Single crystals of **3** were grown from saturated thf solutions of **3** at –40 °C. The molecular structure of **3** is depicted in Figure 3; it is an octahedral dichloridoruthenium(II) complex, which is stabilized by four NHC ligands.

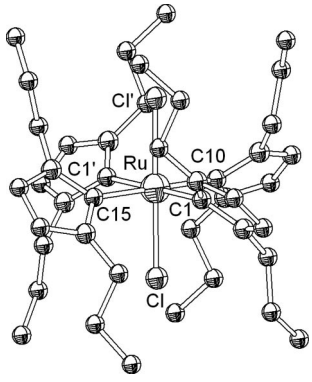


Figure 3. Thermal ellipsoid drawing of the molecular structure of **3** (thermal ellipsoids at 40% probability; H atoms omitted for clarity). Selected bond lengths [pm] and angles [°]: Ru–Cl 247.6(1), Ru–C(1) 210.7(2), Ru–C(10) 210.1(3), Ru–C(15) 211.0(3); C(1)–Ru–C(1)′ 178.03(14), C(1)–Ru–C(10) 90.99(7), C(1)–Ru–C(15) 89.01(7), C(10)–Ru–C(15) 180.0, C(1)–Ru–Cl′ 89.95(7), C(1)′–Ru–Cl′ 90.08(7), C(1)–Ru–Cl 90.08(7), C(1)′–Ru–Cl 89.94(7), C(15)–Ru–Cl 90.703(16), C(10)–Ru–Cl 89.297(16), Cl′–Ru–Cl 178.59(3), C(10)–Ru–Cl′ 89.297(16), C(15)–Ru–Cl′ 90.703(16). Symmetry transformations used to generate equivalent atoms: –*x*, *y*, –*z* + 1/2.

Complex **3** crystallizes in the monoclinic space group *C*2/*c* with half of the molecule and a thf solvent molecule in the asymmetric unit. The two-fold rotation axis contains the atoms C10, Ru, and C15. The ruthenium atom is octahedrally coordinated to four NHC ligands and two chlorido ligands *trans* to each other. The Ru–Cl [247.6(1) pm] and Ru–C$_{carbene}$ [210.7(2), 210.1(3), 211.0(3) pm] distances are unexceptional. The Ru–C bonds, however, are slightly elongated compared to the Ru–C$_{carbene}$ distance found in **1**. In the solid state the NHC ligands are arranged in a paddle-wheel orientation with respect to the Ru–Cl vector, which explains the observation of different sets of resonances for the diastereotopic methylene protons of the *n*Pr substituent in the ^{1}H NMR spectrum. Short H···Cl contacts between 254.82(2) and 262.34(2) pm are observed, especially for one set of the hydrogen atoms of the methylene group attached to the nitrogen atom.

Although complex **2** is insoluble in most organic solvents, it is soluble in acetonitrile. By using acetonitrile as a solvent, compounds **2** and **3** dissolve with the quantitative formation of the ionic acetonitrile adducts [Ru(R$_2$Im)$_4$(NCMe)$_2$]Cl$_2$ [R = Me (**4**), *n*Pr (**5**)], which were isolated as colorless solids. Complex **4** is sufficiently soluble in [D$_3$]acetonitrile to further clarify the nature of **2**. ^{1}H and ^{13}C NMR spectra of **4** reveal one set of resonances for the NHC ligands. The ^{1}H NMR spectrum of **4** recorded in CD$_2$Cl$_2$ featured a singlet at δ = 3.22 ppm for the methyl protons, a singlet at δ = 7.21 ppm for the protons of the imidazole backbone, and a singlet for the coordinated acetonitrile ligand at δ = 2.47 ppm. The IR spectrum of the acetonitrile adduct **4** reveals a weak band at 2248 cm^{-1} for the C–N stretch in the solid state, which is slightly shifted compared to uncoordinated acetonitrile.

Colorless crystals of [Ru(Me$_2$Im)$_4$(NCMe)$_2$]Cl$_2$ (**4**) were obtained from a saturated solution of **4** in a mixture of acetonitrile and toluene at –40 °C. The chloride atoms, as well as additional solvent molecules, occupy general positions in the lattice, and the structure of the complex cation of **4** is shown in Figure 4.

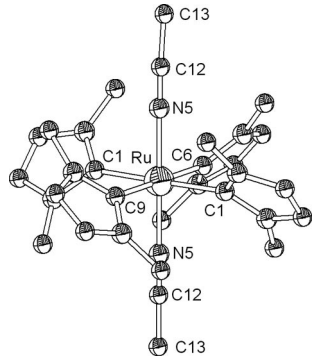


Figure 4. Thermal ellipsoid drawing of the molecular structure of the complex cation of **4** (thermal ellipsoids at 40% probability; H atoms omitted for clarity). Selected bond lengths [pm] and angles [°]: Ru–C(1) 210.4(4), Ru–C(1)′ 210.4(4), Ru–C(6) 211.0(6), Ru–C(9) 211.9(6), Ru–N(5) 202.1(3), Ru–N(5)′ 202.1(3); C(1)–Ru–C(1)′ 178.1(3), C(1)–Ru–C(6) 89.05(13), C(1)–Ru–C(9) 90.95(13), C(1)–Ru–N(5) 89.72(15), C(1)–Ru–N(5)′ 90.28(15), C(1)′–Ru–C(6) 89.05(13), C(1)′–Ru–C(9) 90.95(13), C(1)′–Ru–N(5) 90.28(15), C(6)–Ru–C(9) 180.000(1), C(6)–Ru–N(5) 90.01(11), C(6)–Ru–N(5)′ 90.01(11), C(9)–Ru–N(5) 89.99(11), C(9)–Ru–N(5)′ 89.99(11), N(5)–Ru–N(5)′ 180.0(2), C(12)–N(5)–Ru 178.2(4). Symmetry transformations used to generate equivalent atoms: –*x* + 1, *y*, –*z* + 1/2.

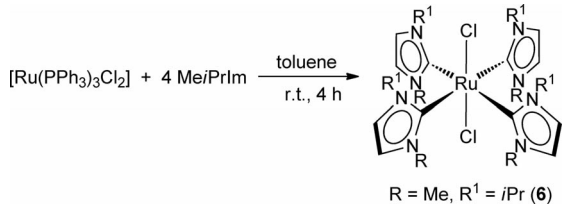
The complex cation has an octahedral coordination geometry at the ruthenium atom. The N-donors of MeCN occupy mutually *trans* coordination sites, and the four NHC carbene carbon atoms form an equatorial plane. The

ruthenium–nitrogen distances of 202.1(3) pm are similar to those observed for the cationic complexes [Ru{1,2-bis(2,2′-bipyridyl-6-yl)ethane}$(CH_3CN)_2]^{2+}$ (201.8 pm) and [Ru(phen-NH-phen)$(CH_3CN)_2]^{2+}$ (202.6 pm) {phen-NH-phen = bis[1,10-(phenanthrolin-2-yl)amine]}.[10] The Ru–$C_{carbene}$ distances range between 210.4(4) and 211.9(6) pm and are the same as those observed for complex **3**.

The colorless acetonitrile adduct [Ru(*n*Pr_2Im)$_4$-$(NCMe)_2]Cl_2$ (**5**) was also prepared quantitatively by dissolving compound **3** in acetonitrile, but it was not possible to isolate **5** in a pure form. Under standard vacuum conditions the coordinated acetonitrile molecules are eliminated to regenerate **3**. We attribute this behavior to the increasing steric demand of the NHC ligand coordinated to the ruthenium atom going from Me_2Im to *n*Pr_2Im. However, [D_6]-**5** was characterized by ^{1}H and ^{13}C NMR spectroscopy by dissolving **3** in CD_3CN. The spectrum is significantly different to that of **3** in [D_6]acetone. The replacement of two chlorido ligands with neutral acetonitrile donor ligands leads to a shift of the resonances of the *n*Pr substituents in the ^{1}H NMR spectrum. The methylene groups attached to the nitrogen atoms give rise to two multiplets at δ = 3.19 and 3.42 ppm, which are significantly shifted. The differences in the chemical shifts of these resonances of the diastereotopic protons, $\Delta\delta$, is much larger for **3** ($\Delta\delta$ = 1.47 ppm) than for **5** ($\Delta\delta$ = 0.23 ppm). We attribute this behavior to a much weaker interaction of the sidearm of the NHC ligand with the axial ligands (Cl^- vs. MeCN). This finding is further supported by the fact that the other methylene protons give rise to just one (not two) set of resonances in the ^{1}H NMR spectrum. A white powder containing **5** was formed from the reaction of **3** with acetonitrile after precipitating with toluene. This powder contains the monoacetonitrile adduct [Ru(*n*Pr_2Im)$_4$$(CH_3CN)]Cl_2$ as the main component, and this complex clearly shows NMR features of an asymmetrically substituted compound with an [Ru(*n*Pr_2Im)$_4$] core in solution.

Reaction of [Ru(PPh_3)$_3$$Cl_2$] with the Mixed *n*-Alkyl-Substituted Imidazolin-2-ylidene Me*i*PrIm

[Ru(PPh_3)$_3$$Cl_2$] reacts cleanly with 4 equiv. of Me_2Im and *n*Pr_2Im to give [Ru(Me_2Im)$_4$$Cl_2$] (**2**) and [Ru(*n*$Pr_2$Im)$_4$$Cl_2$] (**3**), respectively; however, for an investigation of the chemistry of these compounds two major drawbacks have been identified: complex **2** is insoluble in common organic solvents, whereas **3** is soluble, but the NMR spectra of mixtures of this compound with other species were complicated to interpret. To avoid these drawbacks we were interested in preparing similar complexes with *i*Pr groups attached to the nitrogen atom in the hope of increasing the solubility of the complexes. However, since the molecular structures reported so far revealed a crowded ligand sphere at the metal atom, we decided to use the two-fold *i*Pr-substituted NHC *i*Pr_2Im as well as the mixed methyl-isopropyl-substituted NHC Me*i*PrIm. After 4 h at room temperature, treatment of [Ru(PPh_3)$_3$$Cl_2$] with 4 equiv. of Me*i*PrIm in toluene leads to a red solution, which contains different isomers of [Ru(Me*i*PrIm)$_4$$Cl_2$] (**6**), one of which has been structurally characterized (see Scheme 2 and Figure 6).



Scheme 2. Synthesis of **6**.

The difference between the isomers lies in the relative alignment of the asymmetrically substituted NHC ligand with respect to the Ru–Cl vector (vide infra). Attempts to isolate any of the isomers in their pure form failed so far. However, we have identified one major isomer from this reaction, presumably the "up,down,up,down" isomer. The methyl groups of the coordinated NHC of this isomer point alternately in different directions relative to the plane through Ru and the NHC carbene carbon atoms (or the Ru–Cl vector). This complex displays a ^{1}H NMR spectrum with one set of peaks for the methyl and isopropyl substituents and the backbone with the correct integration ratio. In addition to these resonances, the NMR spectra usually contain signals for at least three other compounds, and the ratio of these depends on the reaction conditions. So far we have seen no clear correlation between the reaction conditions employed and the different isomers of **6** formed. The isomeric ratio of mixtures of the four isomers can be changed by stirring solutions of **6** at room temperature. For example, after one week in thf the amount of the main isomer increases to 78%. The same isomer was identified as the main product after more than 20 reactions performed under a variety of different reaction conditions. The ^{1}H NMR spectrum of the major product features two doublets at δ = 0.9 and 1.36 ppm for the isopropyl methyl hydrogen atoms, a septet at δ = 5.67 ppm for the isopropyl methine hydrogen atoms, and a singlet at δ = 3.56 ppm for the four hydrogen atoms of the methyl group attached to the NHC nitrogen atom. Due to overlapping signals and more complicated splitting of signals of the other likely isomers, we could not unambiguously assign all resonances to the different compounds. However, the region between δ = 3.00 and 4.00 ppm in the ^{1}H NMR spectrum is the most valuable to identify these other isomers in solution, as the resonances here are well separated. Seven singlets at δ = 3.56, 3.59, 3.60, 3.61, 3.63, 3.64, and 3.65 ppm were detected in this region, and we propose assignment of these resonances to the four isomers as follows: δ = 3.56 ppm is assigned to the "up,down,up,down" isomer **6a**, δ = 3.63 ppm to the "up,up,up,up" isomer **6b**, δ = 3.64 ppm to the "up,up,down,down" isomer **6c**, and δ = 3.59, 3.60, 3.61, and 3.65 ppm to the "up,up,up,down" isomer **6d**. Simple steric arguments support the suggestion that the major isomer **6a** is the "up,down,up,down" isomer. The splitting of the methyl resonances of **6d** into four sets of signals is a

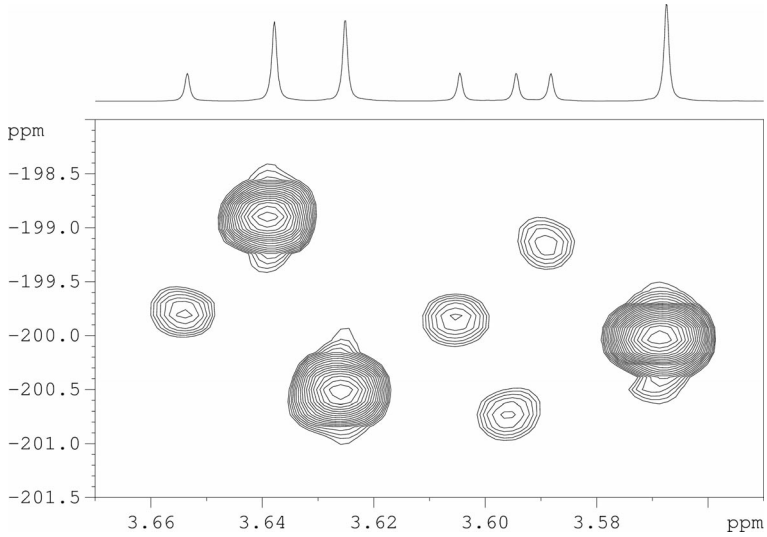


Figure 5. ^{15}N ^{1}H HMBC NMR spectrum of the isomer mixture in the range between δ = 3.67 and 3.55 ppm (^{1}H) and δ = –201.5 and –198.0 ppm (^{15}N).

result of the paddle-wheel orientation of the ligands in these compounds (see also Figure 6), which leads to a different orientation of the two methyl groups of the mutually *trans*-orientated "up" ligands with respect to the "down" ligand. The result of a $^{15}N/^{1}H$ heteronuclear multiple-bond correlation (HMBC) NMR experiment on the isomeric mixture in the range between δ = 3.67 and 3.55 ppm (^{1}H) and δ = –201.5 and –198.0 ppm (^{15}N) is shown in Figure 5. This spectrum reveals one ^{15}N cross peak at δ = –200.1, –200.6, and –199.0 ppm for each of the three isomers **6a**, **6b**, and **6c**, respectively. For each of the four singlets of **6d** at δ = 3.59, 3.60, 3.61, and 3.65 ppm four ^{15}N cross peaks were obtained at δ = –199.3, –200.8, –199.89, and –199.90 ppm.

All isomers show good solubility in toluene and in more polar solvents such as thf and dichloromethane, but we were not able to isolate the individual isomers in bulk. However, we succeeded in performing X-ray analyses on selected crystals of the "up,up,up,up" isomer **6b**. These crystals were grown either by layering a toluene solution with hexane (toluene/hexane, 1:1) or from ethereal solutions at –40 °C. The molecular structure of this compound is given in Figure 6.

Compound **6b** crystallizes in two different phases, the monoclinic space group *C*2/*c* (not shown) and the orthorhombic space group *Pna*2$_1$ (see Figure 6). In both cases molecular structures of "up,up,up,up" isomers of complex **6** were refined. On the molecular level, both structures show the same chemical constitution, i.e. the ruthenium atom is octahedrally coordinated to two chlorido and four NHC ligands, which are arranged in a paddle-wheel orientation. In both phases two different isomers of **6b** have been observed. The difference between these isomers lies in the relative orientation of the NHC ligands. With respect to the NHC methyl group orientation at the Ru–Cl vector, the NHC ligands of the molecule depicted in Figure 6 are oriented to form a left-handed helix resulting in the isomer Λ-"up,up,up,up"-[Ru(Me*i*PrIm)$_4$Cl$_2$], whereas other molecules in the unit cell are the enantiomers Δ-"up,up,up,up"-[Ru(Me*i*PrIm)$_4$Cl$_2$], in which the ligand set forms a right-handed helix (not shown).

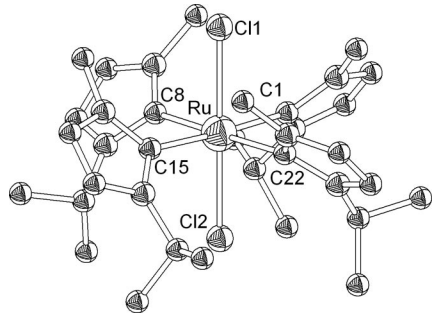
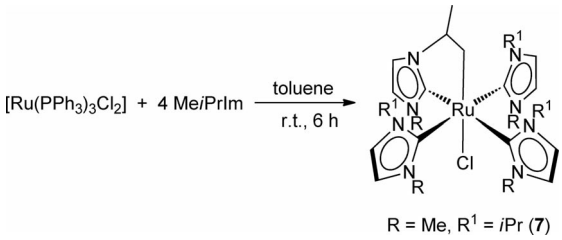


Figure 6. Thermal ellipsoid drawing of the molecular structure of **6b** in *Pna*2$_1$ (thermal ellipsoids at 40% probability; H atoms omitted for clarity). Selected bond lengths [pm] and angles [°]: Ru–Cl(1) 249.5(1), Ru–Cl(2) 246.9(1), Ru–C(1) 212.0(2), Ru–C(8) 210.9(2), Ru–C(15) 212.3(2), Ru–C(22) 212.2(2); C(1)–Ru–Cl(1) 89.53(7), C(1)–Ru–Cl(2) 90.48(7), C(1)–Ru–C(8) 89.45(10), C(1)–Ru–C(15) 177.10(10), C(1)–Ru–C(22) 89.15(10), C(8)–Ru–Cl(1) 90.67(7), C(8)–Ru–Cl(2) 90.55(7), C(8)–Ru–C(15) 89.75(9), C(8)–Ru–C(22) 178.55(10), C(15)–Ru–Cl(1) 87.69(6), C(15)–Ru–Cl(2) 92.32(6), C(15)–Ru–C(22) 91.66(9), C(22)–Ru–Cl(1) 89.71(7), C(22)–Ru–Cl(2) 89.07(7), Cl(1)–Ru–Cl(2) 178.78(2).

During attempts to investigate the isomerization of **6** in boiling toluene, we observed a color change in the solutions. At elevated temperatures, **6** eliminates HCl through C–H activation of one of the NHC ligand *i*Pr groups to give cyclometallation products (see Scheme 3). Similar results have been obtained from reactions of [Ru(PPh$_3$)$_3$Cl$_2$] with 4 equiv. of *i*PrMeIm in toluene at 120 °C for 6 h. After cooling the reaction mixture to room temperature, a product was precipitated by addition of hexane, which could not be extensively characterized. In the EI mass spectra of this product a peak at *m*/*z* = 632.3 was observed, which is in accord with [Ru(Me*i*PrIm)$_4$Cl$_2$]HCl, but a satisfactory elemental analysis of this material was not obtained. We were

unable to interpret the NMR spectra due to the large number of isomers formed. Compound **6** was synthesized only in isomer mixtures of four compounds, and in the case of an HCl elimination reaction from these complexes at least eight isomers have to be considered. Thus, we decided not to pursue this reaction further. However, layering a toluene solution of the reaction mixture with hexanes led to some crystals suitable for X-ray diffraction. The result of the X-ray analysis is given in Figure 7 and at least confirms HCl elimination from one of the isomers (presumably from the "up,up,up,down" isomer) of **6**.



Scheme 3. Synthesis of compound **7**.

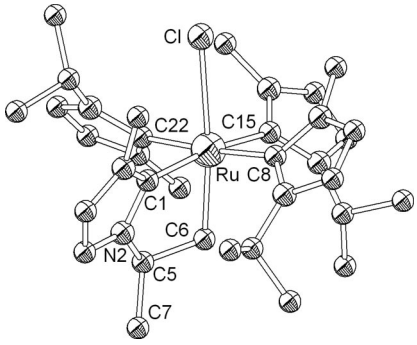
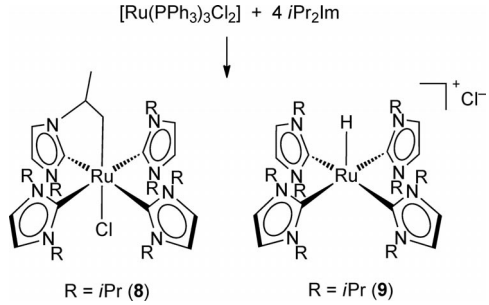


Figure 7. Thermal ellipsoid drawing of the molecular structure of the HCl elimination product **7** (thermal ellipsoids at 40% probability; H atoms omitted for clarity). Selected bond lengths [pm] and angles [°]: Ru–C(1) 205.3(2), Ru–C(6) 212.5(2), Ru–C(8) 210.8(2), Ru–C(15) 210.3(2), Ru–C(22) 211.9(2), Ru–Cl 275.3(1), C(5)–C(6) 153.8(3), C(5)–C(7) 152.7(3); C(1)–Ru–C(6) 77.25(9), C(1)–Ru–C(8) 92.52(9), C(1)–Ru–C(15) 170.11(9), C(1)–Ru–C(22) 88.93(10), C(1)–Ru–Cl 95.10(6), C(6)–Ru–C(8) 96.96(9), C(6)–Ru–C(15) 92.96(9), C(6)–Ru–C(22) 87.11(9), C(6)–Ru–Cl 172.24(6), C(8)–Ru–C(15) 89.99(10), C(8)–Ru–C(22) 175.89(9), C(8)–Ru–Cl 84.53(7), C(15)–Ru–C(22) 89.22(10), C(15)–Ru–Cl 94.66(7), C(22)–Ru–Cl 91.51(7), C(5)–C(6)–Ru 109.71(14).

The molecular structure of compound **7** clearly reveals that one of the methyl groups of the *i*Pr substituents was C–H-activated under HCl elimination from [Ru(Me-*i*PrIm)$_4$Cl$_2$]. The Ru–C(6) distance of 212.5(2) pm is in the range typically observed for ruthenium–carbon single bonds. Several C–H activation reactions of NHC substituents at the ruthenium atom have been described in the literature,[7,11] and the molecular structure of **7** clearly demonstrates the viability of cyclometallation reactions under HCl elimination in complexes with an [Ru(NHC)$_4$] core.

Reaction of [Ru(PPh$_3$)$_3$Cl$_2$] with *i*Pr$_2$Im

The reaction of [Ru(PPh$_3$)$_3$Cl$_2$] with *i*Pr$_2$Im leads to mixtures of different products, depending on the conditions employed. A dichlorido complex [Ru(*i*Pr$_2$Im)$_4$Cl$_2$] similar to the complexes described above with the sterically less hindered NHCs was not observed. The mixtures obtained consist of a deep blue C–H activation product, [Ru(*i*Pr$_2$Im)$_3$-{*i*Pr(C$_3$H$_6$)Im}Cl] (**8**), which is formally the HCl elimination product of the dichlorido complex [Ru(*i*Pr$_2$Im)$_4$Cl$_2$], of a violet hydrido-chlorido complex [Ru(*i*Pr$_2$Im)$_4$(H)]Cl (**9**), and as a third component of the imidazolium salt *i*Pr$_2$Im·HCl in various amounts (Scheme 4).



Scheme 4. Reaction of [Ru(PPh$_3$)$_3$Cl$_2$] with *i*Pr$_2$Im.

The reaction of [Ru(PPh$_3$)$_3$Cl$_2$] with *i*Pr$_2$Im in a stoichiometric ratio of 1:6 in toluene at room temperature leads to a blue precipitate after a reaction time of 14 h, which contains **8** and an imidazolium salt *i*Pr$_2$Im·HCl and a brown solution, consisting of PPh$_3$ and minor amounts of the reaction products. Both compounds **8** and *i*Pr$_2$Im·HCl have similar solubilities in organic solvents, but separation of the reaction products may be achieved by a procedure, which includes deprotonation of the imidazolium salt with KO*t*Bu, dissolution of the NHC and *t*BuOH in hexane and extraction of the [Ru(*i*Pr$_2$Im)$_3$(*i*Pr{C$_3$H$_6$}Im)Cl]/KCl mixture into thf.

Due to the low symmetry of the complex, each methyl and methine group of **8** gives rise to one set of resonances in the ^{1}H NMR spectrum. Eight doublets are observed for each backbone proton between δ = 7.08 and 6.85 ppm. Furthermore, the ^{1}H NMR spectrum of **8** features seven septets for the isopropyl methine protons between δ = 5.51 and 2.97 ppm, a multiplet at δ = 2.47 ppm for the methine proton next to the activated CH$_2$ group, and two multiplets at δ = 1.27 and 1.44 ppm for the protons of the methylene group attached to the ruthenium center. For the isopropyl methyl groups of **8**, 15 doublets were observed between δ = 1.47 and 0.69 ppm. The CH$_2$ carbon atom gives rise to a signal at δ = 1.08 ppm in the ^{13}C NMR spectrum. The assignment of the ^{1}H and ^{13}C NMR specta were assisted by DEPT-135, ^{1}H,^{1}H COSY, and ^{1}H,^{13}C heteronuclear single quantum coherence NMR experiments.

Raising the reaction temperature to 100 °C leads to an acceleration of the formation of **8** – the reaction is complete after 3 h – but also to the formation of **9** as a new product. Similar results have been obtained by using other ruthenium(II) starting materials such as [Ru(C$_6$Me$_6$)Cl$_2$] and [Ru-

(cod)Cl_2], which might be of some importance to catalytic transformations by using Ru^{II} compounds and an excess of NHC ligands. Longer reaction times at higher temperatures led to increased formation of **9**. Procedures for the synthesis of similar chlorido-hydrido complexes with an [$Ru(NHC)_4$] core starting from different compounds have been published recently by the groups of Whittlesey and Wolf.[6,7] If the reaction of 1 equiv. of [$Ru(PPh_3)_3Cl_2$] with 6 equiv. of *i*Pr_2Im is performed in xylene at 140 °C, a violet powder consisting of [Ru(*i*Pr_2Im)$_4$H]Cl and 2 equiv. of *i*Pr_2ImHCl are isolated. Separation of the chlorido-hydrido complex can be achieved by using a similar procedure as described above for the isolation of **8**.

The ^{1}H NMR spectrum of **9** features four doublets at δ = 0.56, 0.67, 1.20, and 1.27 ppm for the isopropyl methyl groups, two septets at δ = 4.19 and 5.18 ppm for the isopropyl methine protons, two doublets at δ = 6.96 and 6.97 ppm for the backbone protons and, most significantly, a high-field-shifted resonance at δ = –40.92 ppm for the hydrido ligand. Similar hydrido resonances at low frequencies for complexes of the type [$Ru(NHC)_4(H)$][$BArF_4$] have been reported by Whittlesey and co-workers.[6b] The assignment of the resonances for **9** was supported by ^{1}H,^{1}H NOESY spectroscopy. Despite several attempts, we were unable to obtain crystals of **7** and **8** suitable for X-ray diffraction.

Conclusions

We have shown that complexes with an $[Ru(NHC)_4]^{2+}$ core can be synthesized from a variety of Ru^{II} precursors, in particular by the reaction of [(η^6-C_6H_4Me*i*Pr)RuCl(μ-Cl)]$_2$ and [$Ru(PPh_3)_3Cl_2$] and different alkyl-substituted 1,3-dialkylimidazolin-2-ylidenes, Me_2Im, *n*Pr_2Im, Me*i*PrIm, and *i*Pr_2Im. In the cases of Me_2Im, *n*Pr_2Im, and Me*i*PrIm, the reaction with [$Ru(PPh_3)_3Cl_2$] leads to dichlorido complexes [$Ru(NHC)_4Cl_2$] [NHC = Me_2Im (**2**), *n*Pr_2Im (**3**), Me*i*PrIm (**6**)]. The chlorido ligands in these molecules are only weakly bound and can be replaced by small donor molecules, exemplified by the reaction of **2** and **3** with acetonitrile, to form complexes of the type [$Ru(R_2Im)_4(CH_3CN)$]-Cl_2 [R = Me (**4**), *n*Pr (**5**)]. Compound **6** was isolated as a mixture of isomers due to the asymmetric substitution pattern of Me*i*PrIm. The difference between the isomers observed lies in the relative alignment of the asymmetrically substituted NHC ligand with respect to the Ru–Cl vector. At high temperatures, **6** eliminates HCl through C–H activation of one of the NHC *i*Pr groups to give cyclometallation products. One of the isomers formed (**7**) was structurally characterized. In the case of the reaction of [Ru-(PPh_3)$_3Cl_2$] with the sterically more demanding 1,3-diisopropylimidazolin-2-ylidene ligand (*i*Pr_2Im), a dichlorido complex of the type [$Ru(NHC)_4Cl_2$] was not observed. Depending on the reaction conditions, the cyclometallation product [Ru(*i*Pr_2Im)$_3${*i*Pr(C_3H_6)Im}Cl] (**8**) or the hydrido complex [Ru(*i*Pr_2Im)$_4$H]Cl (**9**) was formed, accompanied by large amounts of the imidazolium chloride (*i*Pr_2Im·HCl). We speculate that both, intramolecular C–H activation processes of the ligand and intermolecular C–H activation processes of the solvent molecules, play a dominant role in the formation of the hydrido complex. When the high-temperature synthesis leading to **9** was performed in C_6D_6, identical chemical shifts were obtained for the NHC ligands, but the characteristic hydrido resonance at δ = –40.9 ppm for **9** was almost absent. To summarize, the reaction of [$Ru(PPh_3)_3$-Cl_2] with different alkyl-substituted 1,3-dialkylimidazolin-2-ylidenes provides a convenient entry point into the chemistry of complexes featuring an [$Ru(NHC)_4$] core. Moreover, these results are also of importance for the interpretation of catalytic processes, for which the precatalysts are formed in situ from an Ru^{II} precursor and NHC ligands at high temperatures, especially when an excess of the NHC is employed.

Experimental Section

General: All reactions and subsequent manipulations involving organometallic reagents were performed under argon by using standard Schlenk techniques. Elemental analyses were performed with an Elementar vario micro cube. NMR spectra were recorded with Bruker Avance 400 and Avance DMX 600 spectrometers at 298 K. ^{13}C NMR spectra are broad-band proton-decoupled (^{13}C{^{1}H}). Standard DEPT-135 experiments were recorded to distinguish CH_3- and CH-type carbon atoms from C- or CH_2-type carbon atoms in the ^{13}C NMR spectra; NMR spectroscopic data are reported relative to tetramethylsilane. Coupling constants are quoted in Hz. Residual solvent peaks used as internal standards were as follows: $CDCl_3$: δ = 7.24 ppm (^{1}H); C_6D_6: δ = 7.15 ppm; CD_3CN: δ = 1.94 ppm; $(CD_3)_2CO$: δ = 2.05 ppm (^{1}H); natural-abundance carbon signal: CD_3CN: δ = 1.2 ppm; $(CD_3)_2CO$: δ = 30.8 ppm; $CDCl_3$: δ = 77.0 ppm; C_6D_6: δ = 128.0 ppm (^{13}C). IR spectra were recorded with a Bruker Vertex 70 FTIR spectrometer as KBr pellets or with a Nicolet 380 FTIR spectrometer as solids by using an ATR unit. [$Ru(PPh_3)_3Cl_2$],[9] [(η^6-C_6H_4Me*i*Pr)RuCl(μ-Cl)]$_2$,[12] and the NHCs[4b] were prepared according to literature procedures. All other reagents were purchased from commercial sources and purifiedaccording to standard techniques.

Synthesis of [(η^6-C_6H_4Me*i*Pr)Ru(Im*i*Pr)Cl_2] (1): At room temperature, *i*Pr_2Im (0.60 mL, 3.90 mol) was added slowly to a suspension of [(η^6-C_6H_4Me*i*Pr)RuCl(μ-Cl)]$_2$ (1.20 g, 1.96 mmol) in thf (40 mL). The reaction mixture was stirred at room temperature for 5 h, and the resulting red-brown precipitate was collected by filtration, washed with two portions of diethyl ether (20 mL) and pentane (20 mL), and dried in vacuo. The product was obtained as an orange powder (1.10 g, 61%). Crystals suitable for X-ray diffraction were grown from saturated dme solutions of **1** at room temperature. $C_{19}H_{30}Cl_2N_2Ru$ (458.08): calcd. C 49.78, H 6.60, N 6.22; found C 49.62, H 6.83, N 6.12. ^{1}H NMR ($CDCl_3$): δ = 1.35 [d, J = 6.94 Hz, 6 H, ArCH(CH_3)$_2$], 1.47 [d, $^3J_{HH}$ = 6.7 Hz, 12 H, CH(CH_3)$_2$], 2.13 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, ArC*H*), 5.20 (d, $^3J_{HH}$ = 6.0 Hz, 2 H, Ar*H*), 5.37 [sept, $^3J_{HH}$ = 6.7 Hz, 8 H, C*H*(CH_3)$_2$], 5.51 (d, $^3J_{HH}$ = 6.0 Hz, 2 H, Ar*H*), 7.12 (s, 8 H, C*H*=C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.7 (Ar*C*H_3), 22.8 [CH(*C*H_3)$_2$], 25.1 [ArCH(*C*H_3)$_2$], 30.9 [Ar*C*H(CH_3)$_2$], 52.1 [*C*H(CH_3)$_2$], 83.4 (Ar*C*H), 85.3 (Ar*C*H), 106.6 (Ar*C*CH_3), 119.0 (N*CC*N), 149.5 (Ar-*Ci*Pr), 201.9 (N*C*N) ppm. EI-MS: *m*/*z* (%) = 422.2(9) [M – Cl]$^+$, 383.3 (16) [M – Cl – *i*Pr – 2 Me]$^+$.

Synthesis of [Ru(Me$_2$Im)$_4$Cl$_2$] (2): At room temperature, Me$_2$Im (0.80 mL, 8.40 mmol) was added slowly to a suspension of [Ru(PPh$_3$)$_3$Cl$_2$] (2.00 g, 2.09 mmol) in toluene (40 mL). The reaction mixture was heated to 100 °C for 30 min. The color of the precipitate changed from brown to bright yellow. The precipitate was collected by filtration, washed with two portions of toluene (20 mL) and hexane (20 mL), and dried in vacuo. The product was obtained quantitatively as a yellow powder (1.16 g). $C_{20}H_{32}Cl_2N_8Ru$ (556.5): calcd. C 43.16, H 5.80, N 20.13; found C 43.03, H 5.71, N 19.85. EI-MS: *m*/*z* (%) = 556.0 (5) [M]$^+$, 460.0 (21) [M – Me$_2$Im]$^+$, 364.0 (32) [M – 2 Me$_2$Im]$^+$.

Synthesis of [Ru(*n*Pr$_2$Im)$_4$Cl$_2$] (3): At room temperature, *n*Pr$_2$Im (1.90 mL, 1.50 mmol) was added slowly to a suspension of [Ru(PPh$_3$)$_3$Cl$_2$] (3.00 g, 3.13 mmol) in toluene (50 mL). The reaction mixture was heated to 100 °C for 2 h with formation of an orange-red solution and a red oil. All volatile material was removed in vacuo, and the residue was suspended in hexane (40 mL). The undissolved yellow material was collected by filtration, washed with hexane (20 mL), and dried in vacuo. The product was obtained as a yellow powder (2.00 g, 82%). Crystals were obtained from saturated thf solutions of **3** at –40 °C. $C_{36}H_{64}Cl_2N_8Ru$ (780.9): calcd. C 55.37, H 8.26, N 14.35; found C 54.94, H 8.08, N 13.73. ^{1}H NMR [(CD$_3$)$_2$CO]: δ = 0.66 (t, $^3J_{HH}$ = 7.3 Hz, 24 H, CH_3), 1.62 (m, 8 H, CH_2CH$_3$), 1.73 (m, 8 H, CH_2CH$_3$), 2.94 (dt, 8 H, NCH_2), 4.41 (dt, 8 H, NCH_2), 7.13 (s, 8 H, NC*H*C*H*N) ppm. ^{13}C NMR [(CD$_3$)$_2$CO]: δ = 12.4 (*C*H$_3$), 26.6 (*C*H$_2$CH$_3$), 52.1 (N*C*H$_2$), 121.3 (N*CC*N), 191.1 (N*C*N) ppm. EI-MS: *m*/*z* (%) = 780.1 (2) [M]$^+$, 628.0 (33) [M – *n*Pr$_2$Im]$^+$, 476.0 (45) [M – 2 *n*Pr$_2$Im]$^+$.

Synthesis of [Ru(Me$_2$Im)$_4$(CH$_3$CN)$_2$]$^{2+}$Cl$_2^-$ (4): To a clear solution of [Ru(Me$_2$Im)$_4$Cl$_2$] (55.0 mg,0.10 mmol) in acetonitrile (10 mL) was added toluene (10 mL) to form a colorless precipitate. The colorless solid was collected by filtration and washed with toluene. Single crystals were obtained from a saturated solution of **4** in acetonitrile at –20 °C. Formation of **4** was quantitative according to NMR spectroscopy. Isolated yield: 25.0 mg (39%). $C_{24}H_{38}Cl_2N_{10}Ru$ (638.6): calcd. C 45.14, H 6.00, N 21.93; found C 45.12, H 6.04, N 22.16. IR (KBr): $\tilde{\nu}$ = 2248 (m, ν_{CN}) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ = 2.74 (s, 6 H, CNCH_3), 3.22 (s, 24 H, NCH_3), 7.21 (s, 8 H, NC*H*C*H*C) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ = 5.8 (s, CN*C*H$_3$), 37.4 (s, N*C*H$_3$), 124.0 (s, N*CC*N), 186.2 (N*C*N) ppm; a resonance for *C*NCH$_3$ was not observed. EI-MS: *m*/*z* (%) = 461.0 (5) [Ru(ImMe)$_3$Cl$_2$]$^+$, 364.0 (25) [RuCl$_2$(ImMe)$_2$]$^+$, 96.1 (100) [ImMe]$^+$, 41.0 (52) [MeCN]$^+$.

Synthesis of [Ru(*n*Pr$_2$Im)$_4$(CH$_3$CN)$_2$]$^{2+}$Cl$_2^-$ (5): Compound **5** can be prepared quantitatively by dissolving **3** in acetonitrile. However, its isolation was hampered due to its instability under standard vacuum conditions (coordinated acetonitrile eliminates with regeneration of **3**). Acetonitrile adducts of **3** with the monoacetonitrile adduct [Ru(*n*Pr$_2$Im)$_4$(CH$_3$CN)]Cl$_2$ as the main component were synthesized according to the following procedure: Compound **3** (100 mg, 0.12 mmol) was dissolved in acetonitrile (5 mL), and toluene (5 mL) was added to form a colorless precipitate. The colorless solid was collected by filtration, washed with toluene, and dried in a stream of nitrogen. Yield: 61 mg (60%). [Ru(*n*Pr$_2$Im)$_4$(CH$_3$CN)$_2$]-Cl$_2$ (**5**): ^{1}H NMR (CD$_3$CN): δ = 0.76 (t, $^3J_{HH}$ = 7.4 Hz, 24 H, CH_3), 1.63 (m, 16 H, CH_2CH$_3$), 3.19 (m, 8 H, NCH_2), 3.42 (m, 8 H, NCH_2), 7.34 (s, 8 H, NC*H*C*H*N) ppm. ^{13}C NMR (CD$_3$CN): δ = 5.3 (NC*C*H$_3$), 11.6 (*C*H$_3$), 24.9 (*C*H$_2$CH$_3$), 51.7 (N*C*H$_2$), 121.1 (N*CC*N), 185.3 (CH$_3$*C*N), 191.8 (N*C*N) ppm. [Ru(*n*Pr$_2$Im)$_4$-(CH$_3$CN)]Cl$_2$: ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.72 (t, $^3J_{HH}$ = 7.4 Hz, 12 H, CH_3), 0.78 (t, $^3J_{HH}$ = 7.4 Hz, 12 H, CH_3), 1.68 (m, 16 H, CH_2CH$_3$), 2.33 (s, 3 H,CNC$_3$), 2.87 (m, 4 H, NCH_2), 3.20 (m, 4 H, NCH_2), 3.43 (m, 4 H, NCH_2), 4.30 (m, 4 H, NCH_2), 7.07 (d, $^3J_{HH}$ = 2.5 Hz, 4 H, NC*H*CHN), 7.09 (d, $^3J_{HH}$ = 2.5 Hz, 4 H, NC*H*CHN) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ = 6.1 (NC*C*H$_3$), 11.0 (*C*H$_3$), 11.7 (*C*H$_3$), 24.9 (*C*H$_2$CH$_3$), 25.2 (*C*H$_2$CH$_3$), 50.8 (N*C*H$_2$), 51.2 (N*C*H$_2$), 120.4 (N*CC*N), 121.8 (N*CC*N), 191.1 (N*C*N) ppm; CD$_3$*C*N resonance not observed. IR (ATR): $\tilde{\nu}$ = 2209 (m, ν_{CN}) cm^{-1}.

Synthesis of [Ru(Me*i*PrIm)$_4$Cl$_2$] (6): At room temperature, Me*i*PrIm (0.25 mL, 2.00 mmol) was added slowly to a suspension of [Ru(PPh$_3$)$_3$Cl$_2$] (480 mg, 0.50 mmol) in toluene (20 mL). The reaction mixture was stirred at room temperature for 4 h, which resulted in the formation of a red solution. Hexane (20 mL) was added to the solution, and storage at –20 °C overnight caused precipitation of **6**. The precipitate was collected by filtration, washed twice with hexane (5 mL), and dried in vacuo. Yield: 210 mg (0.31 mmol, 62%). Crystals were obtained by layering a toluene solution of **6** with hexane (1:1) and from diethyl ether solutions of **6** at –40 °C. According to NMR spectroscopy, different isomers of **6** were formed in various amounts depending on the exact reaction conditions employed. CHN analysis was performed on the crude isomer mixture of **6**. The NMR parameters of the main isomer are given below. $C_{28}H_{48}Cl_2N_8Ru$ (668.2): calcd. C 50.29, H 7.23, N 16.76; found C 50.21, H 7.24, N 16.27. ^{1}H NMR (C$_6$D$_6$): δ = 0.90 (d, ^3J = 6.8 Hz, 3 H, *i*Pr CH_3), 1.36 (d, $^3J_{HH}$ = 6.4 Hz, 3 H, *i*Pr CH_3), 3.56 (s, 3 H, NCH_3), 5.67 (sept, 1 H, *i*Pr C*H*), 6.43 (d, $^3J_{HH}$ = 1.9 Hz, 1 H, NC*H*CHN), 6.65 (d, $^3J_{HH}$ = 2.0 Hz, 1 H, NCHC*H*N) ppm. ^{13}C NMR (C$_6$D$_6$): δ = 22.1 (*i*Pr *C*H$_3$), 27.7 (*i*Pr *C*H$_3$), 39.2 (N*C*H$_3$), 50.6 (*i*Pr *C*H), 116.0 (N*C*HCHN), 122.8 (N*C*HCHN), 197.7 (N*C*N) ppm.

Synthesis of [Ru(*i*Pr$_2$Im)$_3${*i*Pr(C$_3$H$_6$)Im}Cl] (8): At room temperature, *i*Pr$_2$Im (0.32 mL, 2.00 mmol) was added slowly to a brown suspension of [Ru(PPh$_3$)$_3$Cl$_2$] (480 mg, 0.50 mmol) in toluene (20 mL). The reaction mixture was stirred at room temperature for 14 h, which resulted in the formation of a blue precipitate. Undissolved material was collected by filtration, washed with three portions of toluene (5 mL) and two portions of hexane (5 mL), and dried in vacuo. The product contained **8** and the imidazolium salt *i*Pr$_2$Im·HCl in a 1:2 mixture. Yield: 410 mg (73% based on Ru). Separation of pure **8** can be achieved by using a similar procedure as described for complex **9**, albeit yields are very low. **8**: $C_{36}H_{63}ClN_8Ru{\cdot}2iPr_2ImHCl$ (1120.4): calcd. C 57.81, H 8.72, N 14.98; found C 58.33, H 8.61, N 14.81. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.69–1.47 (m, 45 H, *i*Pr), 1.27–1.44 (m, 2 H, CH_2Ru), 2.47 (m, 1 H, C*H*CH$_2$Ru), 2.47 (sept, 1 H, *i*PrC), 2.97 (sept, 1 H, *i*PrC), 3.75 (sept, 1 H, *i*PrC), 3.98 (sept, 1 H, *i*PrC), 4.45 (sept, 1 H, *i*PrC), 4.68 (sept, 1 H, *i*PrC), 4.79 (sept, 1 H, *i*PrC), 5.51 (sept, 1 H, *i*PrC), 6.85 (d, $^3J_{HH}$ = 2.3 Hz, 1 H, NC*H*CHN), 6.94 (d, $^3J_{HH}$ = 2.3 Hz, 1 H, NC*H*CHN), 6.95 (d, $^3J_{HH}$ = 2.3 Hz, 1 H, NC*H*CHN), 6.98 (d, $^3J_{HH}$ = 2.3 Hz, 1 H, NC*H*CHN), 6.99 (d, $^3J_{HH}$ = 2.3 Hz, 1 H, NC*H*CHN), 7.02 (d, $^3J_{HH}$ = 2.3 Hz, 1 H, NC*H*CHN), 7.05 (d, $^3J_{HH}$ = 2.3 Hz, 1 H, NC*H*CHN), 7.07 (d, $^3J_{HH}$ = 2.3 Hz, 1 H, NC*H*CHN) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ = 1.08 (Ru*C*H$_2$), 19.85 (*i*Pr *C*H$_3$), 22.55 (*i*Pr *C*H$_3$), 22.59 (*i*Pr *C*H$_3$), 22.65 (*i*Pr *C*H$_3$), 22.70 (*i*Pr *C*H$_3$), 22.74 (*i*Pr *C*H$_3$), 23.29 (*i*Pr *C*H$_3$), 23.31 (*i*Pr *C*H$_3$), 23.32 (*i*Pr *C*H$_3$), 23.75 (*i*Pr *C*H$_3$), 23.85 (*i*Pr *C*H$_3$), 23.98 (*i*Pr *C*H$_3$), 24.77 (*i*Pr *C*H$_3$), 24.91 (*i*Pr *C*H$_3$), 25.41 (*i*Pr *C*H$_3$), 49.01 (*i*Pr *C*H), 50.93 (*i*Pr *C*H), 51.16 (*i*Pr *C*H), 51.51 (*i*Pr *C*H), 51.56 (*i*Pr *C*H), 51.87 (*i*Pr *C*H), 52.80 (*i*Pr *C*H), 62.23 [*C*H(CH$_3$)CH$_2$Ru], 115.09 (N*C*HCHN), 116.34 (N*C*HCHN), 116.64 (N*C*HCHN), 116.72 (N*C*HCHN),117.25 (N*C*HCHN), 117.72 (N*C*HCHN), 118.08 (N*C*HCHN), 118.38 (N*C*HCHN), 193.16 (N*C*N), 194.43 (N*C*N), 199.13 (N*C*N), 200.08 (N*C*N) ppm.

Synthesis of [Ru(*i*Pr$_2$Im)$_4$(H)]$^+$Cl$^-$ (9): At room temperature, *i*Pr$_2$Im (0.48 mL, 3.00 mmol) was added slowly to a suspension of [Ru(PPh$_3$)$_3$Cl$_2$] (480 mg, 0.50 mmol) in xylene (20 mL). The reaction mixture was stirred at 120 °C for 4 d, which resulted in the formation of a violet precipitate. The reaction mixture was cooled to room temperature, and the insoluble material was collected by filtration, washed with three portions of toluene (5 mL) and two portions of hexane (5 mL), and dried in vacuo. The product contained **9** and the imidazolium salt *i*Pr$_2$Im·HCl in a 1:2 mixture. The components of this mixture could not be separated by simple extraction procedures. However, the imidazolium salt can be removed from the mixture by using the following method: the mixture was stirred with a stoichiometric amount of KO*t*Bu in thf overnight. All insoluble material was collected by filtration, washed with thf, and dried in vacuo. The resulting powder was extracted with CH_2Cl_2, and all volatile material was removed from the filtrate. Yield: 203 mg (54%). $C_{36}H_{65}ClN_8Ru$ (745.9): calcd. C 57.92, H 8.78, N 15.01; found C 58.09, H 8.54, N 14.38. ^{1}H NMR (CD_2Cl_2): δ = –40.92 (s, 1 H, Ru*H*) 0.56 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, 4-*H*$_3$), 0.67 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, 4′-*H*$_3$), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, 3-*H*$_3$), 1.27 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, 3′-*H*$_3$), 4.19 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, 2′-*H*), 5.18 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, 2-*H*), 6.96 (d, $^3J_{HH}$ = 2.2 Hz, 4 H, 1′-*H*), 6.97 (d, $^3J_{HH}$ = 2.2 Hz, 4 H, 1-*H*) ppm. ^{13}C NMR (CD_2Cl_2): δ = 22.58 (*i*Pr *C*H$_3$), 22.61 (*i*Pr *C*H$_3$), 23.04 (*i*Pr *C*H$_3$), 23.52 (*i*Pr *C*H$_3$), 50.59 (*i*Pr *C*H), 52.18 (*i*Pr *C*H), 116.26 (N*C*HCHN), 116.93 (N*C*HCHN), 197.74 (N*C*N) ppm.

Table 1. X-ray data collection and processing parameters.

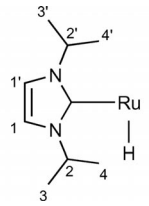
	1	**3**	**4**
Empirical formula	$C_{19}H_{30}Cl_2N_2Ru$	$C_{44}H_{80}Cl_2N_8O_2Ru$	$C_{32}H_{50}Cl_2N_{14}Ru$
Formula mass	458.42	925.13	802.83
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	*C*2/*c*	*C*2/*c*
a [Å]	16.8343(8)	20.8941(17)	14.536(3)
b [Å]	13.9418(8)	15.6112(19)	22.166(3)
c [Å]	17.5227(12)	15.7060(11)	18.541(3)
α [°]	90	90	90
β [°]	90	104.368(8)	135.89(2)
γ [°]	90	90	90
V [Å^3]	4112.6(4)	4962.8(8)	4158.1(12)
Z	8	4	4
$D_{calcd.}$ [g cm^{-1}]	1.481	1.238	1.282
μ [mm^{-1}]	1.026	0.465	0.545
Total no. of reflections	18969	18771	13091
No. of independent reflections	3392	4516	3908
No. of observed reflections[a]	2481	3429	2551
R_{int}	0.0838	0.0361	0.1057
No. of parameters	230	263	230
Goof	1.055	1.029	1.012
Final R[b]/wR_2[c]	0.0454/0.0990	0.0362/0.0921	0.0527/0.0924

[a] Reflections with I > 2σ(*I*). [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. X-ray data collection and processing parameters.

	6b	**6b**	**7**
Empirical formula	$C_{28}H_{48}Cl_2N_8Ru$	$C_{32}H_{58}Cl_2N_8ORu$	$C_{35}H_{55}ClN_8Ru$
Formula mass	668.71	742.83	724.39
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	*C*2/*c*	*Pna*2$_1$	*P*2$_1$/*c*
a [Å]	10.9560(12)	11.496(2)	9.0328(12)
b [Å]	14.9120(14)	29.666(6)	32.510(4)
c [Å]	21.6270(19)	11.039(2)	15.113(3)
α [°]	90	90	90
β [°]	113.260(12)	90	122.918(13)
γ [°]	90	90	90
V [Å^3]	3246.1(5)	3764.9(13)	3725.5(10)
Z	4	4	4
$D_{calcd.}$ [g cm^{-1}]	1.368	1.311	1.292
μ [mm^{-1}]	0.678	0.594	0.527
Total no. of reflections	22948	40726	46933
No. of independent reflections	22948	8969	8826
No. of observed reflections[a]	3860	8307	7466
R_{int}	0.0475	0.1034	0.0672
No. of parameters	184	411	418
Goof	1.140	1.054	1.033
Final R[b]/wR_2[c]	0.0447/0.1171	0.0367/0.0860	0.0398/0.1038

[a] Reflections with $I > 2\sigma(I)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.



Crystal Structure Determination of 1, 3, 4, 6a, 6b, and 7: Crystal-data collection and processing parameters are given in Tables 1 and 2. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a STOE IPDS I image-plate diffractometer (Mo-K_α radiation; $\lambda = 0.71073$ Å). Data were collected at 203 K (**1**, **3**, **4**) or at 173 K (**6a**, **6b**, **7**), equivalent reflections were merged and the images were processed with the STOE IPDS or CCD software package. Corrections for Lorentz-polarization effects and absorption were performed, and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions. Extinction corrections were applied as required. Crystallographic calculations were performed by using SHELXS-97 and SHELXL-97.[13] CCDC-793035 (**1**), -793036 (**3**), -793037 (**4**), -793038 (**6a**), -793039 (**6b**), -793040 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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