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Synthesis and Reactivity of 16-Electron Pentamethylcyclopentadienyl–Ruthenium(II) Complexes with Bis(imidazolin-2-imine) Ligands

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The 1,2-bis(imidazolin-2-imino)ethane ligands BL^{Me} and BL^{iPr} were prepared, in which the ability of the imidazolium moiety to effectively stabilize a positive charge leads to highly basic ligands with a strong electron-donating capacity. This feature is illustrated by the isolation of very stable half-sandwich 16-electron ruthenium complexes of the type $[(\eta^5\text{-}C_5Me_5)Ru(BL^R)]^+$ (**1**, R = Me; **2**, R = *i*Pr), which even resist coordination of the chloride counterion. Their inertness towards hard, π-basic ligands does not prevent these complexes from displaying high reactivity towards soft σ-donor/π-acceptor ligands such as CO and isocyanides, and the complexes $[\mathbf{1}\cdot CO]CF_3SO_3$ and $[\mathbf{1}\cdot CNXy]CF_3SO_3$ (XyNC = 2,6-dimethylphenyl isocyanide) can be isolated. These complexes exhibit CO and CN stretching vibrations at 1886 and 1991 cm^{-1}, respectively, which reveals the electron richness and strong π-electron releasing capability of the ruthenium–imine moiety.

Introduction

Coordinatively unsaturated organometallic complexes play a fundamental role as intermediates in homogeneous transition-metal-catalyzed reactions, and their occurrence is rationalized by the 16- and 18-electron rule proposed by Tolman.[1] Numerous examples have been prepared to date, and their electronic and magnetic properties have been studied.[2] Various factors can be responsible for the stabilization of these species, amongst which the introduction of π-donor ligands such as alkoxides, alkylthiolates, amides, or halides can be successfully employed for the creation of π-stabilized unsaturation.[2,3] Accordingly, the stabilization of 16-electron half-sandwich ruthenium complexes of the type $[(\eta^5\text{-}C_5Me_5)Ru(PR_3)X]$ (X = OR, NHR, Cl, Br, I) can be achieved by electron donation from the heteroatomic anionic ligand.[4] Similarly, ligand π-coordination has been suggested to exist in highly reactive ruthenium–amidinate complexes such as $[(\eta^5\text{-}C_5Me_5)Ru\{i\text{PrNC(Me)N}i\text{Pr}\}]$.[5] In contrast, the cationic 16-electron tmeda complex $[(\eta^5\text{-}C_5Me_5)Ru(Me_2NCH_2CH_2NMe_2)]^+$ can be isolated despite the lack of nitrogen-to-metal π-donation. This complex, however, can only be stabilized by the use of the noncoordinating $[B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]^-$ (BAr'_4) counteranion.[6] The same holds true for the rare 16-electron phosphane complexes $[(\eta^5\text{-}C_5Me_5)Ru(PP)]BAr'_4$ [PP = $(PEt_3)_2$, $i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{P}i\text{Pr}_2$].[7]

Results and Discussion

We present herein the neutral 1,2-bis(imidazolin-2-imino)ethane ligands BL^{Me} and BL^{iPr} and their ability to form 16-electron half-sandwich ruthenium complexes of unprecedented stability. BL^R (R = Me, *i*Pr) are obtained in high yield as air-stable off-white solids from the reaction of the readily available imidazolin-2-imines[8] $Imine^{Me}$ and $Imine^{iPr}$ with 1,2-ethyleneditosylate followed by deprotonation with KO*t*Bu.[9,10] The reaction of BL^{Me} and BL^{iPr} with $[(\eta^5\text{-}C_5Me_5)RuCl]_4$[11] in thf affords the violet-colored complexes $[(\eta^5\text{-}C_5Me_5)Ru(BL^{Me})]Cl$, [**1**]Cl, and $[(\eta^5\text{-}C_5Me_5)Ru(BL^{iPr})]Cl$, [**2**]Cl, in which the chloride counteranions can be easily exchanged for the triflate anion (Scheme 1). Crystals of [**1**]OTf·thf suitable for X-ray diffraction analysis could be obtained from a thf/hexane solution. The unit cell is composed of noninteracting cations **1** and triflate anions, and the shortest Ru–O and Ru–F distances are 5.65 and 6.87 Å, respectively. Any interaction between the cations and the thf solvent molecules can also be excluded as the shortest $Ru\text{–}O_{thf}$ separation is 5.97 Å. In addition, there is no indication of any agostic interaction between the ruthenium center and the C–H bonds of the diimine ligand. The cationic half-sandwich complex exhibits a two-legged piano stool geometry with the $\eta^5\text{-}C_5Me_5$ and the η^2-diimine ligands adopting a pseudotrigonal planar coordination sphere around the ruthenium atom (Figure 1). The Ct–Ru–N1–N2 dihedral angle (Ct = centroid of the Cp

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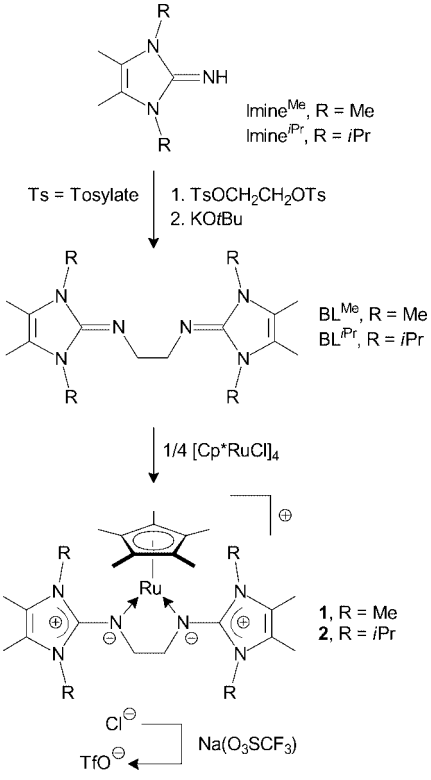
ring) is 179.6°, and the sum of the N1–Ru–N2 angle [76.71(6)°] and the two Ct–Ru–N angles is 360.0°. Accordingly, cation **1** can be regarded as being almost perfectly C_{2v}-symmetric.



Scheme 1.

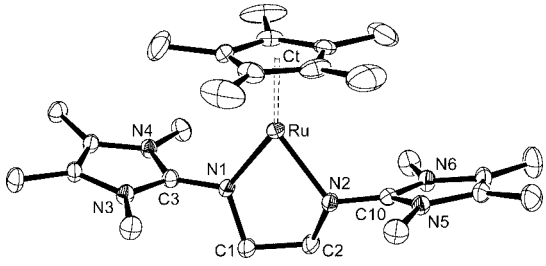


Figure 1. ORTEP diagram of the cation in [**1**]OTf with thermal displacement parameters drawn at 50% probability.[18] The Cp* ligand is disordered over two positions; only one position is shown. Selected bond lengths [Å] and angles [°]: Ru–N1 2.060(2), Ru–N2 2.073(2), Ru–C(Cp*) 2.103(4)–2.194(4), N1–C3 1.349(2), N2–C10 1.345(2); N1–Ru–N2 76.71(6).

The Ru–N distances of 2.060(2) and 2.073(2) Å are significantly shorter than those in the related complex [(η^5-C_5Me_5)Ru(tmeda)]BAr′$_4$ [2.183(7), 2.180(6) Å],[6a] and they fall in the same range as the Ru–N bond length observed for the amidinate complex [(η^5-C_5Me_5)Ru{iPrNC(Me)-NiPr}] [2.073(3) Å].[5a] Even shorter Ru–N distances are found in neutral bimetallic Cp*Ru complexes containing a highly π-basic diamide ligand.[12] The short Ru–N bonds in **1** are in agreement with a strong electron-releasing capability of the BL^{Me} ligand, which is implied by the ylidic resonance structure shown in Scheme 1. Charge separation in coordinated BL^{Me} can be also clearly deduced from the observation of perpendicularly oriented imidazole moieties with respect to the Ru–N–N coordination plane (dihedral angles = 86.0 and 82.6°). This orientation rules out the possibility of π-interaction between the exocyclic nitrogen atoms and the imidazole rings, leading to elongated C–N distances [N1–C3 = 1.349(2) Å and N2–C10 = 1.345(2) Å], much longer than expected for a N–C(sp^2) double bond (1.28 Å) and almost in the range of a N–C(sp^2) single bond (1.38 Å).[13]

The molecular structure of cation **2** in [**2**]OTf·thf, which displays crystallographic mirror symmetry, is shown in Figure 2. Inspection of the crystal packing reveals the absence of any relevant intermolecular contact between the cation and the triflate and the thf molecules. In comparison to **1**, however, the coordination sphere around the ruthenium atom is slightly distorted from a pseudotrigonal planar arrangement. The Ct–Ru–N1–N1a dihedral angle is 168.0°, and the sum of the N1–Ru–N1a angle [77.56(9)°] and the Ct–Ru–N angles is 358.8°. This distortion is associated with a slippage of the NCH_2CH_2N moiety of the diimine ligand to one side of the molecule, opening the opposite side of the ruthenium coordination sphere for two intramolecular C7–H7···Ru contacts of 2.88 Å. This rather long distance excludes the presence of a strong agostic interaction,[7,14] but could imply intramolecular hydrogen bonds of the X–H···M type.[15,16] The Ru–N/N1a bond length in **2** is 2.076(2) Å, which is slightly longer than the corresponding distances found in **1**.

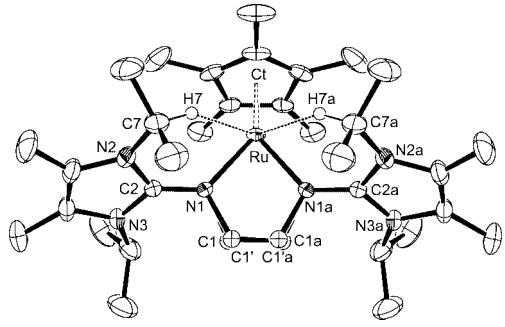


Figure 2. ORTEP diagram of the cation in [**2**]OTf with thermal displacement parameters drawn at 50% probability.[18] The ethylene bridge is disordered. Selected bond lengths [Å] and angles [°]: Ru–N1 2.076(2), Ru–C(Cp*) 2.120(2)–2.156(2), N1–C2 1.340(2); N1–Ru–N1a 77.50(8).

In agreement with the presence of 16-electron species in the solid state, the cations in [**1**]OTf and [**2**]OTf also exhibit C_{2v} symmetry in solution according to their ^{1}H and ^{13}C NMR spectra in [D_6]acetone. For instance, the ^{1}H NMR spectrum of [**1**]OTf shows one singlet for the NCH_2CH_2N moiety together with three singlets for the three different types of methyl groups. In contrast, two doublets are observed in the ^{1}H NMR spectrum of [**2**]OTf for the diastereotopic isopropyl methyl groups, indicating a hindered rotation of the imidazoline moieties around the N1–C2 axis at r.t. on the NMR timescale. Furthermore, the nature of the counterion does not have any impact on the chemical

shifts, and the ^1H and ^{13}C NMR spectra recorded for [**1**]Cl and [**2**]Cl are identical with those observed for the corresponding triflates. Low-temperature NMR spectroscopic studies of the chloride complexes in [D_6]acetone solution do not reveal any significant changes, suggesting negligible ruthenium–chloride interaction or a rapid dynamic behavior even at –90 °C (see NMR spectra in the Supporting Information). Low solubility impeded NMR measurements in less polar solvents such as [D_8]toluene. Ultimately, the solid-state structure of [**2**]Cl·0.75thf shows an asymmetric unit, which is composed of four independent cations **2**, four chloride anions, and three thf molecules (Figure 3). The shortest Ru–Cl distance is 5.89 Å, excluding any interaction and providing final proof of the stability of these unsaturated 16-electron complexes. The geometries at the ruthenium centers and the Ru–N distances are very similar to the parameters observed in [**2**]OTf·thf with the exception of Ru···H interactions, which were not observed.

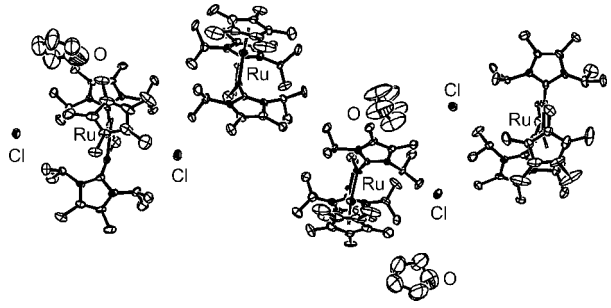


Figure 3. ORTEP diagram of the asymmetric unit of [**2**]Cl·0.75thf with thermal displacement parameters drawn at 50% probability.[18,19]

It should be noted that dynamic behavior in solution was reported for the related complex [(η^5-C_5Me_5)RuCl(tmeda)], for which the solid-state structure shows that the chloride atom is attached to the ruthenium center with an unusually long Ru–Cl distance of 2.5116(9) Å.[17] To compare this complex, which contains a hard σ-donor diamine ligand, with our Cp*Ru–diimine complexes, we performed DFT (density functional theory) calculations to determine their heterolytic gas phase Ru–Cl bond dissociation enthalpies.[18] For [**1**]Cl and [**2**]Cl, the enthalpies required to split the chloride ion from the corresponding complex cations are 295.0 and 294.4 kJ/mol, respectively, whereas for the tmeda complex, a significantly higher value of 413.8 kJ/mol was obtained, indicating a much stronger Ru–Cl interaction. These results suggest that the large difference of almost 120 kJ/mol between the gas phase dissociation enthalpies accounts for the observed strong dissociation of the Cp*Ru–diimine complexes in solution, where anion and cation solvation supports straightforward heterolytic Ru–Cl bond cleavage.

On the basis of structural and theoretical results, it can be assumed that the unusual stability of cationic complexes **1** and **2** stems from the strong π-electron releasing capability of the diimine ligands BL^{Me} and BL^{iPr}. Indeed, cyclic voltammetric studies on [**1**]OTf and [**2**]OTf in acetonitrile afford very negative redox potentials of $E°$ = –588 mV and $E°$ = –569 mV versus the ferrocene/ferrocenium couple.[20] These potentials are much lower than usually observed for a reversible one-electron Ru^{II}/Ru^{III} oxidation process in cyclopentadienyl–ruthenium complexes.[21] In contrast, it is not surprising that the values reported for *neutral* 16-electron Cp*Ru–amidinate complexes obviously fall in an even more negative range.[5d] The reactivity of [**1**]OTf towards carbon monoxide and 2,6-dimethylphenyl isocyanide (XyNC) gives further evidence for the electron richness of the metal center. Treatment of thf solutions of [**1**]OTf with CO gas or 1 equiv. of XyNC at ambient temperature yields the complexes [**1**·CO]OTf and [**1**·CNXy]OTf as a yellow or red crystalline solid, respectively. In the IR spectra, the CO and CN stretching vibrations are at 1886 and 1991 cm^{-1}, which is strongly shifted to lower wavenumbers in comparison to the free, uncoordinated ligands. In general, significantly higher values were reported for other cationic complexes of the type [Cp*Ru(N∩N)CO]$^+$, for examle $\tilde{\nu}_{CO}$ = 1959 and 1963 cm^{-1} for N∩N = RN=CH–CH=NR (R = *i*Pr, Mes),[22] $\tilde{\nu}_{CO}$ = 1963 cm^{-1} for N∩N = bipy,[23] $\tilde{\nu}_{CO}$ = 1948 cm^{-1} for N∩N = phenanthroline,[24] and $\tilde{\nu}_{CO}$ = 1931 cm^{-1} for N∩N = $Me_2NCH_2CH_2NH_2$.[25] Remarkably, the CO stretching frequency in [**1**·CO]OTf is even slightly lower than the values reported for the amidinate complexes [(η^5-C_5Me_5)Ru{*i*PrNC(Me)N*i*Pr}CO] ($\tilde{\nu}_{CO}$ = 1901 cm^{-1}) and [(η^5-C_5Me_5)Ru{*t*BuNC(Ph)N*t*Bu}CO] ($\tilde{\nu}_{CO}$ = 1888 cm^{-1}).[5a]

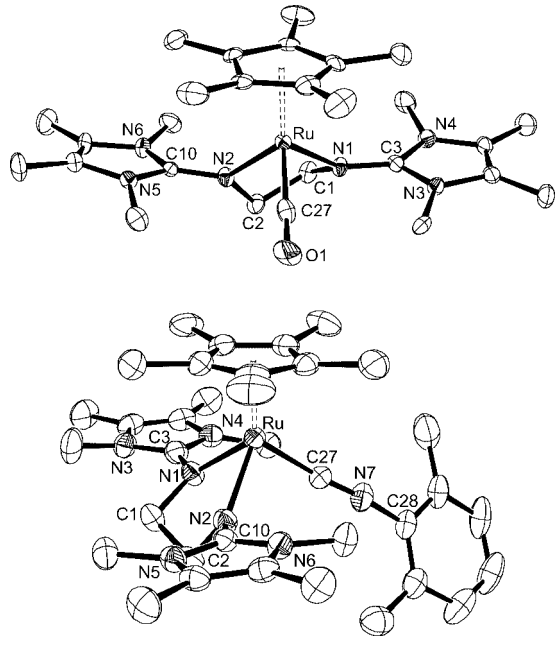


Figure 4. ORTEP diagram of the cations in [**1**·CO]OTf (top) and [**1**·CNXy]OTf (bottom) with thermal displacement parameters drawn at 50% probability.[18] Selected bond lengths [Å] and angles [°] in [**1**·CO]$^+$/[**1**·CNXy]$^+$: Ru–N1 2.165(3)/2.185(3), Ru–N2 2.145(3)/2.153(2), Ru–C27 1.831(4)/1.907(3), Ru–C(Cp*) 2.192(3)–2.272(4)/2.194(3)–2.233(3), N1–C3 1.323(4)/1.331(4), N2–C10 1.319(5)/1.335(4), C27–O1 1.162(5), C27–N7 1.179(4); N1–Ru–N2 77.38(12)/77.94(9), Ru–C27–O1 172.0(4), Ru–C27–N7 175.6(3), C27–N7–C28 174.8(4).

The molecular structures of the cations in [**1**·CO]OTf and [**1**·CNXy]OTf are shown in Figure 4. Both complexes exhibit a three-legged piano stool geometry with elongated Ru–N bonds in comparison to the structure of **1**. The ruthenium–carbon bonds are short [Ru–CO 1.831(4) Å, Ru–CN 1.907(3) Å], confirming strong metal-to-ligand π-back-donation. For instance, the Ru–C distance in [**1**·CO]OTf is significantly shorter than the distances observed for related cationic complexes of the type $[Cp^*Ru(N^{\frown}N)CO]^+$,[26] and it falls in the same range as the bond length observed for the neutral amidinate complex $[(\eta^5\text{-}C_5Me_5)Ru\{t\text{BuNC(Ph)-N}t\text{Bu}\}CO]$.[5a]

Conclusions

In this contribution, we have presented 16-electron ruthenium half-sandwich complexes of unusual stability, which can be ascribed to the strong π-basic nature of the novel bis(imidazolin-2-imine) ligands BL^{Me} and BL^{iPr}, leading to a weak propensity of the Ru atom to coordinate other π-basic ligands such as chloride. In contrast, strong binding of σ-donor/π-acceptor ligands such as CO or isocyanides can be observed. This behavior makes these highly stabilized, yet reactive 16-electron complexes suitable systems for the activation of small molecules such as N_2 and H_2 and promising candidates for catalytic applications. These investigations are currently in progress in our laboratory.

Supporting Information (see footnote on the first page of this article): Preparation of the compounds, selected NMR spectra, cyclic voltammetric traces, crystal data, computational details, presentations of the calculated molecular structures together with Cartesian coordinates of their atomic positions.

Acknowledgments

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[18] Details of the electronic structure calculations and of the X-ray crystal structure determinations and presentations of the calculated molecular structures can be found in the Supporting Information. CCDC-646821 to -646825 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.
[19] The crystal of [**2**]Cl was not of high quality. The structure is noncentrosymmetric and contains four independent formula units, but a variety of programs failed to indicate any higher symmetry. All ethylene bridges fail to refine satisfactorily, which may indicate disorder problems. We are attempting to obtain a more reliable dataset, but the current data definitely establish that there is no coordination of chloride to ruthenium.
[20] The potentials were measured at a scan rate of 100 mV/s against a Ag/AgCl reference electrode (3 M KCl). The ferrocene/ferrocenium couple displays a reversible cyclic voltammetric trace with a redox potential $E° = +476$ mV under these conditions; the values given in the text are referenced to $E°(Fc/Fc^+) = 0$ mV.
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