

Isolable Yet Highly Reactive Cationic Organoruthenium(II) Amidinates, $[\text{Ru}(\eta^6\text{-C}_6\text{R}_6)(\eta\text{-amidinate})]^+\text{X}^-$, Showing Signs of Coordinative Unsaturation: Isolectronic Complexes of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta\text{-amidinate})$

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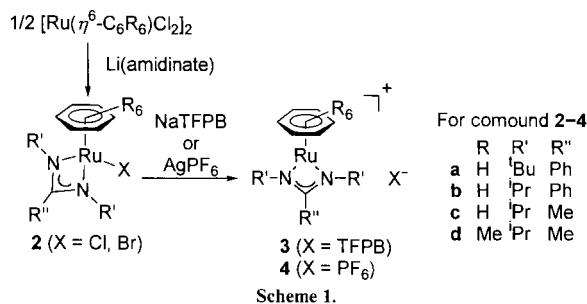
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The coordinatively unsaturated ruthenium(II) complexes $[\text{Ru}(\eta^6\text{-C}_6\text{R}_6)(\eta\text{-amidinate})]^+\text{X}^-$ ($\text{R} = \text{H, Me, X} = \text{TFPB, PF}_6$), being isoelectronic with $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta\text{-amidinate})$, have been isolated and characterized by spectroscopy and crystallography. A weak π -coordination of the amidinate ligands in the solid state was observed by X-ray crystallography. DFT calculations also suggest that such a coordination mode contributes to the stabilization of these complexes. These complexes behave as highly reactive transition metal Lewis acids in the reactions with various two-electron donor ligands.

Coordinatively unsaturated organometallic complexes have been recognized as important intermediates in homogenous catalysis, and their preparation has attracted much attention.¹ In recent years, several stable coordinatively unsaturated ruthenium complexes have been isolated and their reactivity towards various organic substrates has been investigated.² Factors stabilizing these complexes are steric hindrance by bulky ligands,^{2c,d} strong σ -donation of N-ligands,^{2e,f} or π -donation of ligands.^{2b,g-i} We have recently reported the successful isolation of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta\text{-amidinate})$ (**1**) in which the amidinate ligand effectively stabilizes the highly reactive metal center.^{3a} Amidinates usually act as 4-electron σ -donor ligands forming two strong Ru–N bonds, and **1** is thus formally a coordinatively unsaturated 16-electron complex. In fact, the complexes **1** instantly react with various two electron donor ligands or allylic halides.^{3a,b} Although one explanation why the amidinate ligand stabilizes the 16-electron ruthenium species is strong σ -donation of the ligand as seen in Kirchner's complexes,^{2e,f} possible π -coordination of the amidinate ligand as an additional stabilizing factor has been suggested from X-ray structures of **1**, and has been evidenced very recently by the isolation of $\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Br}(\mu_2, \eta\text{-amidinate})$.^{3c} As an extension of these studies, we were interested in the synthesis of isoelectronic cationic complexes, $[\text{Ru}(\eta^6\text{-C}_6\text{R}_6)(\eta\text{-amidinate})]^+$, where coordination of solvents or counter anions is absent. The highly reactive $[\text{Ru}(\eta^6\text{-C}_6\text{R}_6)(\eta\text{-amidinate})]^+\text{X}^-$ [$\text{R} = \text{H, X} = \text{TFPB}$ (**3a**), or $\text{R} = \text{Me, X} = \text{TFPB}$ (**3d**) or PF_6 (**4d**)] (TFPB = [tetrakis{3,5-bis(trifluoromethyl)phenyl}borate]) thus obtained is the first example of a cationic ruthenium-amidinate complex showing signs of coordinative unsaturation.

As shown in Scheme 1, halogeno-precursors **2a–2d** were obtained by the reaction of $[\text{Ru}(\eta^6\text{-C}_6\text{R}_6)\text{Cl}_2]_2$ with Li(amidinate) in THF. These complexes were characterized by spectroscopic methods and X-ray structure determination.^{3d} Anion exchange of **2** with NaTFPB in $\text{C}_6\text{H}_5\text{F}$ or AgPF_6 in CH_2Cl_2 gave the TFPB complexes **3** or PF_6 complexes **4**. The complexes **3a, 3d**, and **4d** having bulky substituents on the amidinate or the arene ligand were isolable in good yields (62–93%) as air and moisture sensitive blue solids.⁴ Less stable **3b** and **3c** were characterized by NMR, but attempted isolation of them has so far been unsuccessful. Preparation of PF_6 homologues

bearing the C_6H_6 ligand (**4a–4c**) led to decomposition of the product, presumably due to facile abstraction of fluorine atoms from the counter anion by the highly electrophilic metal center.



Characterization of the complexes **3a, 3d**, and **4d** was carried out by spectroscopic methods and elemental analyses, which was supported by the X-ray structure determination of **4d**. The ORTEP drawing of **4d** is shown in Figure 1.⁵ This molecular structure indicates that the complex **4d** is monomeric. Neither the counter anion nor the solvent was coordinated.^{6,7} In other words, the complexes **3a, 3d**, and **4d** exist as an ion pair. The cationic ruthenium center should be coordinatively unsaturated, if the formal electron count (amidinate = 4-electron donor) is adopted. Of importance is the distance between the ruthenium atom and the central carbon of the amidinate, 2.431(5) Å, which indicates existence of the bonding interaction; a similar Ru–C distance of coordinatively saturated **2d** is 2.570(10) Å. The shorter Ru–C (center of the amidinate) distance actually provided the folded structure shown in Figure 1, in which a plane consisting of the ruthenium atom and two nitrogen atoms makes an angle of 31.4° with a plane of the amidinate N–C–N moiety. This folded structure of **4d** is similar to that seen in the isoelectronic complexes **1**, suggesting that possible π -coordination of the amidinate ligand could mitigate the coordinatively unsaturated nature of $[\text{Ru}(\eta^6\text{-arene})(\eta\text{-amidinate})]^+$.

Variable temperature NMR studies of $[\text{Ru}(\eta^6\text{-arene})(\eta\text{-amidinate})]^+$ in CD_2Cl_2 , in which the diastereotopic *N*-¹Pr groups of the amidinate ligand is a convenient probe to observe stereochemical change of the complexes, e.g. from a C_{2v} -symmetric structure shown in Scheme 1 to the folded structure in Figure 1, did not afford evidence of π -interaction of the amidinate ligand. Thus, ¹H resonances due to methyl protons of the ¹Pr groups in the amidinate of **3b, 3d**, and **4d** appeared around δ 1.0–1.5 ppm as a single doublet in the temperature range from –90 °C to room temperature, showing that the complex has a C_{2v} symmetric structure. These results indicate that even if there exists the π -interaction of the amidinate in the complexes **3** and **4** in solution, it is weak, reversible, and unable to detect on the NMR time scale. The solution dynamics also suggests that possible coordination of the counter anion or solvent cannot be ruled out in solution. However, that is reversible and cannot be detected by the NMR technique.

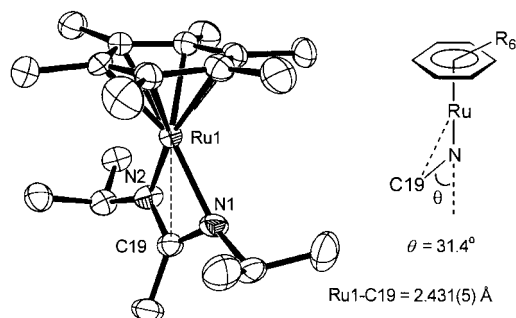
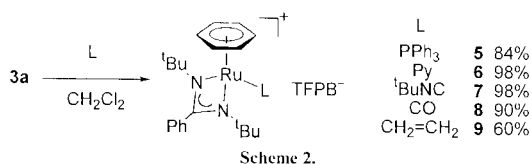


Figure 1. The ORTEP drawing of **4d** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms and the counter anion are omitted for clarity. Representative bond distances (Å) and angles (°) are as follows: Ru1-N1 = 2.058(4), Ru1-N2 = 2.065(4), N1-Ru1-N2 = 64.48(16), N1-C19-N2 = 110.2(4).

The existence of a weak π -coordination of the amidinate ligand is also evident from DFT calculations (B3LYP level) with the model species $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\{\eta\text{-(NH)}_2\text{CH}\}]^+$.⁸ The optimized structure reveals a “folded” amidinate ligand with a bond distance between the ruthenium atom and the central carbon of the amidinate ligand of 2.40 Å. The inversion of the folded C_s symmetric structure proceeds through a planar C_{2v} -symmetric transition state with a very small activation barrier of 3.3 kcal/mol which is easily overcome under experimental conditions in line with the above NMR experiments.

Similar to the complexes **1** the $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\eta\text{-amidinate})]^+$ species are highly reactive towards various two electron donor ligands. For instance, **3a** instantly reacted with PPh_3 , pyridine, $^t\text{BuNC}$, CO, and ethylene in CH_2Cl_2 to give the corresponding adducts $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\eta\text{-amidinate})(\text{L})]^+\text{TFPB}^-$ (**5–9**) in high yields. (Scheme 2) However, the electronic character of the complexes **3** is very different from their isoelectronic complexes **1**. The CO stretching frequency of **8** [ν_{CO} ; 2050 cm^{-1}] is the highest among those of previously reported half-sandwich ruthenium(II) carbonyl complexes.⁹ This is in sharp contrast to the low ν_{CO} of $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\{\eta\text{-(N}^t\text{Bu)}_2\text{CPh}\}(\text{CO})]$ (1888 cm^{-1}).^{3a} Furthermore, rotation of the ethylene ligand about the axis including the ruthenium atom and center of the ethylene in **9** was not frozen even at -100°C in CD_2Cl_2 , while in $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\{\eta\text{-(N}^t\text{Bu)}_2\text{CPh}\}(\eta^2\text{-CH}_2=\text{CH}_2)$ no dynamic behavior of ethylene was observed in $\text{THF-}d_8$ at -60°C .^{3a} The lower rotational barrier of ethylene in **9** than that in $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta\text{-amidinate})(\eta^2\text{-CH}_2=\text{CH}_2)$ indicates a weaker π -back donation of the ruthenium to the ethylene ligand. In sharp contrast to the reversible coordination to **1** having π -donor property, pyridine was irreversibly bound to the cationic metal center of **3a**. These data show that $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\eta\text{-amidinate})]^+$ is a typical transition metal Lewis acid, whereas in sharp contrast, the isoelectronic $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta\text{-amidinate})$ is electron rich and a good π -donor.

In summary, we have achieved the successful isolation and structure elucidation of novel coordinatively unsaturated cationic ruthenium complexes $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\eta\text{-amidinate})]^+\text{X}^-$, which are isoelectronic species to $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta\text{-amidinate})$. The π -coordination of the amidinate ligand as an additional stabilizing factor was indicated by X-ray structure of **4d**, and supported by the DFT calculations. The coordinatively unsaturated nature of the Lewis acidic $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\eta\text{-$



Scheme 2.

amidinate)]⁺ was evidenced by its high reactivity towards various donor ligands. These new results are interesting in comparison with the chemistry of isoelectronic complexes, and further investigation on reactivity of $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\eta\text{-amidinate})]^+$ is currently in progress.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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- 4 In a typical example, **2a** (157 mg, 0.35 mmol) and NaTFPB (311 mg, 0.35 mmol) were dissolved in fluorobenzene (ca. 3 mL) at -40°C . The reaction mixture was allowed to warm to room temperature with stirring for 30 min. The color of the solution changed from reddish brown to dark blue. Insoluble sodium salts were removed by filtration. The resulting dark blue solution was concentrated to ca. 1 mL *in vacuo*, and dry pentane was added. At -35°C , highly air sensitive blue solids of **3a** were precipitated (396 mg, 0.31 mmol, 90%). Anal. Calcd for $\text{C}_{53}\text{H}_{41}\text{N}_2\text{BF}_4\text{Ru}$: C, 49.98; H, 3.24; N, 2.20%. Found: C, 50.50; H, 3.59; N, 2.20%. ¹H NMR of **3a** in CD_2Cl_2 : δ 1.22 (s, 18H; $\text{C}(\text{CH}_3)_3$), 6.13 (s, 6H; C_6H_6), 7.01 (dt, $J = 7.1, 1.8$ Hz, 2H; C_6H_5), 7.38 (t, $J = 7.9$ Hz, 2H; C_6H_5), 7.47 (tt, $J = 7.4, 1.1$ Hz, 1H; C_6H_5), 7.56 (s, 4H; $(\text{CF}_3)_2\text{C}_6\text{H}_3$), 7.73 (t, $J = 2.4$ Hz, 8H; $(\text{CF}_3)_2\text{C}_6\text{H}_3$).
- 5 Crystal data for **4d**: $\text{C}_{20}\text{H}_{35}\text{N}_2\text{F}_4\text{PRu}$; MW = 559.54, triclinic, $a = 11.2702(17)$, $b = 11.638(2)$, $c = 10.0284(14)$ Å, $\alpha = 114.848(8)$, $\beta = 91.205(9)$, $\gamma = 84.317(8)^\circ$, $U = 1187.4(3)$ Å³, $T = 223$ K, space group, $P1$ (No. 2), $Z = 2$, $\mu(\text{Mo K}\alpha) = 0.783$ mm^{-1} , 5086 reflections measured, 5086 unique ($R_{\text{int}} = 0.000$), 4192 observed ($>2\sigma$), final residuals $R_1 = 0.0567$, $wR_2 = 0.1452$ [$I > 2\sigma(I)$]; $R_1 = 0.0759$, $wR_2 = 0.1584$ (all data).
- 6 A possibility that the PF_6^- anion may interact with the ruthenium center in the crystal structure of **4d** is ruled out; even the shortest distance of Ru–F bond, which is 3.59 Å, is much longer than that of the complex, $\text{Ru}(\text{CO})\text{(NO)}(\text{P}^t\text{Bu}_2\text{Me})(\text{BF}_4)$ (2.2984(18) Å)^{7a} or $\text{Ru}_2(\text{O}_2\text{CMe})_4(\text{Py})(\text{BF}_4)$ (2.368(7) Å),^{7b} the counter anion of which coordinates to the metal center.
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- 8 All calculations were performed using the Gaussian 98 software package on the Silicon Graphics Power Challenge of the Vienna University of Technology. The geometry and energy of the model complex and the transition state were optimized at the B3LYP level with the Stuttgart/Dresden ECP (SDD) basis set to describe the electrons of the ruthenium atom. For all other atoms the 6-31G** basis set was employed.
- 9 $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{tmada})(\text{CO})]^+\text{TFPB}^-$,^{2f} 1961 cm^{-1} ; $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PCy}_3)(\text{CO})\text{Cl}$,^{2g} 1908 cm^{-1} ; $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{P}^t\text{Pr}_2\text{Ph})(\text{CO})\text{X}$ (X = I, Br, OR, NHPH),^{2b} 1903–1930 cm^{-1} ; $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{S}_2\text{C}_6\text{H}_4)(\text{CO})$,^{2h} 1965 cm^{-1} .