

η^5 -Imidazolato Complexes of Ruthenium

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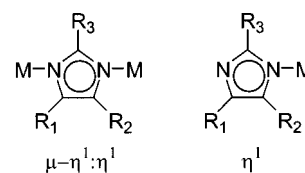
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Summary: The imidazolato complexes $[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{C}_3\text{HN}_2)]_3$, $\text{Cp}^*\text{Ru}(\eta^5\text{-Ph}_2\text{C}_3\text{HN}_2)$, and $\text{Cp}^*\text{Ru}(\eta^5\text{-Me}_2\text{C}_3\text{HN}_2)$ have been prepared and characterized. The latter complexes represent the first structural documentation of the η^5 -imidazolato ligand coordination mode to any metal. $[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{C}_3\text{HN}_2)]_3$ converts to $\text{Cp}^*\text{Ru}(\eta^5\text{-Ph}_2\text{C}_3\text{HN}_2)$ upon heating in tetrahydrofuran, demonstrating that the η^5 -imidazolato ligand is thermodynamically preferred over the $\mu\text{-}\eta^1\text{:}\eta^1$ -ligand in the $\text{Cp}^*\text{Ru(II)}$ system.

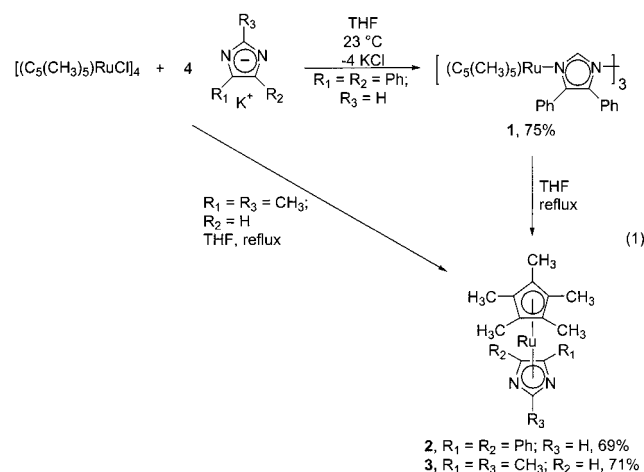
Transition metal complexes containing imidazolato ligands are well known.¹ Interest in metal complexes with these ligands has been driven by their structural resemblance to histidine groups in the metal-binding sites of certain proteins.^{2,3} The most common coordination mode of imidazolato ligands is $\mu\text{-}\eta^1\text{:}\eta^1$, although η^1 coordination has been observed (Chart 1).^{4,5} Other coordination modes are presently unknown. Herein we report the synthesis, structure, and properties of a series of ruthenium(II) complexes containing $\mu\text{-}\eta^1\text{:}\eta^1$ - and η^5 -imidazolato ligands. The latter complexes represent the first structural documentation of the η^5 -imidazolato ligand coordination mode to any metal. A complex containing a $\mu\text{-}\eta^1\text{:}\eta^1$ -imidazolato ligand has been isolated and characterized. Unexpectedly, it converts to the η^5 -

Chart 1



imidazolato complex upon heating. Such facile conversion of the $\mu\text{-}\eta^1\text{:}\eta^1$ ligand to the η^5 ligand suggests that the latter coordination mode may be observed in other low-valent metal complexes and that such interactions may be relevant to biological systems.

Treatment of $[(\text{C}_5(\text{CH}_3)_5)\text{RuCl}]_4$ ⁶ with 4,5-diphenylimidazolotopotassium in tetrahydrofuran at ambient temperature for 18 h afforded the trimeric 4,5-diphenylimidazolato complex **1** as a dark red solid after workup (eq 1).⁷ The trimeric structure of **1** was established



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(7) A 100 mL Schlenk flask was charged with $[\text{Cp}^*\text{RuCl}]_4$ (0.250 g, 0.229 mmol) and tetrahydrofuran (25 mL). A solution of 4,5-diphenylimidazolotopotassium was prepared by mixing 4,5-diphenylimidazole (0.202 g, 0.916 mmol) and potassium hydride (0.037 g, 0.916 mmol) in tetrahydrofuran (35 mL). After stirring for 18 h at ambient temperature, this solution was added by cannula to the ruthenium reactant. After being stirred for 18 h at ambient temperature the resultant solution was filtered through a 2 cm pad of Celite on a coarse glass frit. The volatile components were removed under reduced pressure to afford **1** as a spectroscopically pure dark red crystalline solid (0.313 g, 75%). An analytical sample was crystallized from hexane at -20°C : mp $177\text{--}179^\circ\text{C}$; IR (Nujol, cm^{-1}) 3051 (w), 1599 (s), 1501 (s), 1259 (w), 1153 (m), 1070 (m), 1028 (m), 974 (w), 909 (w), 762 (s), 697 (s), 666 (w); ^1H NMR (benzene- d_6 , δ) 7.98 (s, 1 H, $\text{Ph}_2\text{Im C-H}$), 6.92 (dd, $J = 5$ Hz, $J = 2$ Hz, 6 H, m- and p- $\text{C}_6\text{H}_2\text{H}_2\text{H}$), 6.43 (dd, $J = 7$ Hz, $J = 2$ Hz, 4 H, o- $\text{C}_6\text{H}_2\text{H}_2\text{H}$), 1.56 (s, 15 H, $\text{C}_5(\text{CH}_3)_5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , ppm) 144.12 (s, $\text{Ph}_2\text{Im C-H}$), 139.31 (s, $\text{Ph}_2\text{Im C}$), 137.81 (s, ipso C of Ph group), 129.49 (s, ortho C-H of Ph group), 126.02 (s, meta C-H of Ph group), 125.94 (s, para C-H of Ph group), 72.40 (s, $\text{C}_5(\text{CH}_3)_5$), 10.21 (s, $\text{C}_5(\text{CH}_3)_5$). Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{Ru}$: C, 65.91; H, 5.75; N, 6.15. Found: C, 65.55; H, 5.94; N, 6.16.

by X-ray crystallographic analysis.⁸ In addition, the imidazolate ring C–H unit of **1** resonated at δ 7.98 in the ^1H NMR and at 144.12 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. These shifts, relative to the values observed for 4,5-diphenylimidazole (^1H NMR δ 8.02; $^{13}\text{C}\{^1\text{H}\}$ NMR 148.69 ppm), do not suggest η^5 -coordination of the imidazolate ligand, but are consistent with the observed $\mu\text{-}\eta^1\text{:}\eta^1$ coordination mode. Refluxing of **1** for 18 h in tetrahydrofuran or treatment of $[(\text{C}_5(\text{CH}_3)_5)\text{RuCl}]_4$ with 4,5-diphenylpyrazolotopassium in refluxing tetrahydrofuran for 18 h afforded $(\eta^5\text{-4,5-diphenylimidazolato})(\eta^5\text{-pentamethylcyclopentadienyl})\text{ruthenium}$ (**2**) as a brown crystalline solid after workup.⁹ Adoption of the η^5 coordination mode in **2** was suggested by the upfield shifts of the imidazolate ring CH unit (^1H NMR δ 6.45; $^{13}\text{C}\{^1\text{H}\}$ NMR 109.35 ppm), relative to **1**. As described below, the X-ray crystal structure of **2** confirmed the presence of the η^5 -imidazolate ligand. Treatment of $[(\text{C}_5(\text{CH}_3)_5)\text{RuCl}]_4$ with 2,4-dimethylimidazolatopotassium in tetrahydrofuran at ambient temperature afforded low (<50%) yields of $(\eta^5\text{-2,4-dimethylimidazolato})(\eta^5\text{-pentamethylcyclopentadienyl})\text{ruthenium}$ (**3**), apparently due to the low solubility of the potassium reagent.¹⁰ There was no evidence for a $\mu\text{-}\eta^1\text{:}\eta^1$ complex similar to **1** in the crude reaction mixture, apparently due to steric congestion caused by the methyl group in the 2-position of the imidazolate ligand. However, conducting the reaction in refluxing tetrahydrofuran for 2 h afforded **3** in 73% yield as a light brown solid after workup. The presence of a $\eta^5\text{-2,4-dimethylimidazolate}$ ligand in **3** was

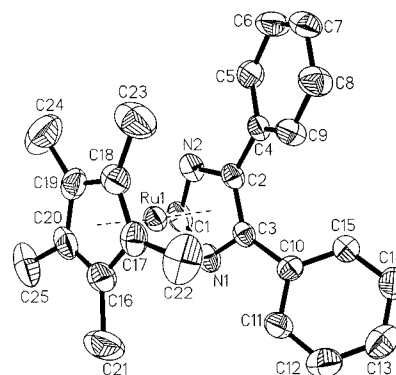


Figure 1. Perspective view of $((\text{C}_6\text{H}_5)_2\text{C}_3\text{HN}_2)(\text{C}_5(\text{CH}_3)_5)\text{-Ru}$ (**2**) with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru–C(1) 2.164(4), Ru–C(2) 2.186(3), Ru–C(3) 2.209(3), Ru–N(1) 2.239(3), Ru–N(2) 2.221(3), Ru–C(16) 2.169(4), Ru–C(17) 2.160(4), Ru–C(18) 2.152(4), Ru–C(19) 2.151(4), Ru–C(20) 2.174(4), Ru– $\text{C}_5(\text{CH}_3)_5(\text{centroid})$ 1.794(3), Ru– $(\text{C}_6\text{H}_5)_2\text{C}_3\text{-HN}_2(\text{centroid})$ 1.861(3), $\text{C}_5(\text{CH}_3)_5(\text{centroid})\text{-Ru-}(\text{C}_6\text{H}_5)_2\text{C}_3\text{-HN}_2(\text{centroid})$ 178.1(1).

suggested by the upfield shifts of the imidazolate ring CH unit (^1H NMR δ 5.42; $^{13}\text{C}\{^1\text{H}\}$ NMR 96.15 ppm), relative to **1**, and was confirmed by an X-ray crystal structure determination.⁸

Figure 1 shows a perspective view of **2**, along with selected bond lengths and angles.⁸ Complex **2** exists in a pseudo-metallocene structure, with the five-membered rings being twisted $12.8(1)^\circ$ from the eclipsed conformation. The ruthenium–carbon bond lengths associated with the pentamethylcyclopentadienyl ligand range from 2.151 to 2.174 Å. Within the imidazolate ligand, the ruthenium–carbon bond lengths range between 2.164 and 2.209 Å, while the ruthenium–nitrogen bond lengths are 2.221(3) and 2.239(3) Å. Accordingly, the ruthenium–carbon bond lengths to the pentamethylcyclopentadienyl ligand are shorter than the related values for the imidazolate ligand. The differential bonding of ruthenium to the two π -bonded ligands is further illustrated by the ruthenium–pentamethylcyclopentadienyl (centroid) and ruthenium–imidazolate (centroid) distances of 1.794(3) and 1.861(3) Å, respectively. The two π -bonded ligands in **2** are essentially coplanar, with a pentamethylcyclopentadienyl (centroid)–ruthenium–imidazolate (centroid) angle of $178.1(1)^\circ$.

Complexes **2** and **3** exhibit irreversible oxidations at 0.750 and 0.736 V, respectively, by cyclic voltammetry in acetonitrile.¹¹ These values are slightly more positive than the analogous values for pentamethylruthenocene ($E_{1/2} = 0.54$ V) and the ruthenium pyrazolato complexes $(\text{C}_5(\text{CH}_3)_5)(3,5\text{-R}_2\text{pz})\text{Ru}$ ($\text{R} = \text{CH}_3$ (0.631 V), tBu (0.600 V), Ph (0.702 V))¹² and indicate that the imidazolate ligands are less electron donating than a cyclopentadienyl ligand and are even slightly less donating than isomeric pyrazolato ligands.

The major finding described herein is documentation of η^5 -imidazolate ligand coordination to ruthenium in **2** and **3**. This is the first example of this bonding mode

(8) Crystal data for **2**: crystals grown from hexane at -20°C , $\text{C}_{25}\text{H}_{26}\text{N}_2\text{Ru}$, triclinic, group $P\bar{1}$, $a = 7.5054(6)$ Å, $b = 9.7217(7)$ Å, $c = 15.8937(11)$ Å, $V = 1048.31(13)$ Å³, $Z = 2$, $T = 295(2)$ K, $D_{\text{calc}} = 1.443$ g cm⁻³, $R(F) = 4.54\%$ for 4648 observed reflections ($2.68^\circ \leq 2\theta \leq 56.58^\circ$). All non-hydrogen atoms in **2** were refined with anisotropic displacement parameters. Full data for the X-ray crystal structure determination of **2** are included in the Supporting Information. The X-ray crystal structures of **1** and **3** were also determined. The poor crystal quality of **1** prohibits a detailed structure report; however, the identity of the compound was unambiguously determined. Complex **3** exhibits a sandwich structure similar to that of **2**. Complete details will be reported in a later full paper.

(9) A 100 mL Schlenk flask was charged with $[\text{Cp}^*\text{RuCl}]_4$ (0.250 g, 0.229 mmol) and tetrahydrofuran (35 mL). To this mixture was added a solution of 4,5-diphenylimidazalatopotassium (prepared by mixing 4,5-diphenylimidazole (0.202 g, 0.916 mmol) and potassium hydride (0.037 g, 0.916 mmol) in tetrahydrofuran (35 mL)). The combined solutions were refluxed for 18 h. Upon cooling, the brown solution was filtered through a 2 cm pad of Celite on a coarse glass frit. The volatile components were removed under reduced pressure to afford **2** as a brown powder (0.287 g, 69%). Brown crystals were grown by crystallization from hexane at -20°C : mp $151\text{--}153^\circ\text{C}$; IR (Nujol, cm⁻¹) 3033 (w), 1600 (m), 1502 (m), 1422 (m), 1220 (m), 1189 (w), 1114 (w), 1067 (m), 1025 (m), 948 (m), 903 (w), 761 (s), 695 (s), 670 (m), 657 (s); ^1H NMR (benzene- d_6 , δ) 7.82 (dd, $J = 8.0$ Hz, $J = 1.5$ Hz, 4 H, $\text{o-C}_6\text{H}_4\text{H}_2$), 7.12 (tt, $J = 7.5$ Hz, $J = 1.5$ Hz, 4 H, $\text{m-C}_6\text{H}_4\text{H}_2$), 7.04 (tt, $J = 7.5$ Hz, $J = 1.7$ Hz, 2 H, $\text{p-C}_6\text{H}_4\text{H}_2$), 6.45 (s, 1 H, $\text{Ph}_2\text{Im C-H}$), 1.53 (s, 15 H, $\text{C}_5(\text{CH}_3)_5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , ppm) 134.08 (s, ipso C of Ph group), 129.25 (s, ortho C-H of Ph group), 128.13 (s, meta C-H of Ph group), 127.61 (s, para C-H of Ph group), 110.12 (s, $\text{Ph}_2\text{Im C}$), 109.35 (s, $\text{Ph}_2\text{Im C-H}$), 85.26 (s, $\text{C}_5(\text{CH}_3)_5$), 10.53 (s, $\text{C}_5(\text{CH}_3)_5$). Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{Ru}$: C, 65.91; H, 5.75; N, 6.15. Found: C, 65.50; H, 5.90; N, 6.39.

(10) In a manner similar to the preparation of **2**, $[\text{Cp}^*\text{RuCl}]_4$ (0.500 g, 0.459 mmol), 2,4-dimethylimidazole (0.177 g, 1.839 mmol), and potassium hydride (0.074 g, 1.839 mmol) in tetrahydrofuran (70 mL) were combined to afford **3** as a brown powder (0.445 g, 73%). Crystals suitable for single-crystal X-ray diffraction were grown by sublimation at 70°C (0.1 mmHg): mp $83\text{--}84^\circ\text{C}$; IR (Nujol, cm⁻¹) 3054 (w), 1599 (s), 1545 (w), 1500 (s), 1260 (w), 1154 (m), 1070 (w), 1029 (m), 991 (w), 975 (m), 909 (w), 978 (w), 762 (s), 714 (m), 696 (s), 667 (m), 590 (w); ^1H NMR (benzene- d_6 , δ) 5.42 (s, 1 H, $\text{Me}_2\text{Im C-H}$), 2.36 (s, 3 H, $\text{Me}_2\text{Im CH}_3$), 1.91 (s, 3 H, $\text{Me}_2\text{Im CH}_3$), 1.68 (s, 15 H, $\text{C}_5(\text{CH}_3)_5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , ppm) 121.53 (s, $\text{Me}_2\text{Im C-CH}_3$), 109.36 (s, $\text{Me}_2\text{Im C-CH}_3$), 96.15 (s, $\text{Me}_2\text{Im ring C-H}$), 84.31 (s, $\text{C}_5(\text{CH}_3)_5$), 15.08 (s, $\text{Me}_2\text{Im CH}_3$), 12.37 (s, $\text{Me}_2\text{Im CH}_3$), 10.96 (s, $\text{C}_5(\text{CH}_3)_5$). Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{N}_2\text{-Ru}$: C, 54.36; H, 6.69; N, 8.45. Found: C, 53.93; H, 6.73; N, 8.18.

(11) The cyclic voltammetry experiments were conducted in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate under the conditions previously described in ref 12.

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to any metal.¹³ The previous lack of complexes with η^5 -imidazolato ligands is particularly surprising, since **1** converts quantitatively to **2** upon heating, indicating that the η^5 -imidazolato ligand is thermodynamically preferred over the μ - η^1 : η^1 -imidazolato coordination mode. The facile conversion of **1** to **2** argues that η^5 -imidazolato ligand coordination may be possible in other low-valent metal complexes. Additionally, similar μ - η^1 : η^1 - to η^5 -imidazolato isomerizations may be thermodynamically favorable in at least some of the many known mid to late transition metal complexes containing μ - η^1 : η^1 -imidazolato ligands.¹⁴ This raises the intriguing possibility that η^5 coordination of histidine-derived ligands can occur in metalloenzymes and that such ligation may play a role in catalytic activity.^{2,3} In addition to the above issues, Fu and co-workers have recently demonstrated that azaferrocenes and azaruthenocenes can

function as nucleophilic catalysts in a variety of organic transformations.¹⁴ Presumably the lone pairs of electrons on the nitrogen atoms of **2** and **3** retain substantial basicity, and complexes containing η^5 -imidazolato ligands may serve as similar nucleophilic catalysts.

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Supporting Information Available: Synthetic procedures, analytical and spectroscopic data for **1–3**, tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) For unsuccessful attempts to prepare η^5 -imidazolato complexes of iron, see: Seel, F.; Sperber, V. *Angew. Chem., Int. Ed. Engl.* **1968**, 7, 70. Seel, F.; Sperber, V. *J. Organomet. Chem.* **1968**, 14, 405.

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