Ruthenium Complexes Bearing η^5-Pyrazolato Ligands

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Pyrazolato ligands have an extensive coordination chemistry among the middle to late transition metals and either exhibit η^1-bonding to a single metal or act as bridging ligands between two metals.[1] We and others have recently demonstrated that η^2-pyrazolato ligand coordination is common in the early transition metals[2,3] and is feasible among complexes of the groups 1 and 2 metals.[4,5] Among the larger lanthanide and actinide ions, η^2-pyrazolato ligand coordination is most frequently observed[6] and an unusual μ-η^2:η^2-coordination mode has been recently documented.[7] Conspicuously absent from the literature are complexes bearing η^5-pyrazolato ligands, although the possibility of this coordination mode has been suggested in several reviews.[1] The lack of complexes bearing η^5-pyrazolato ligands is surprising, since complexes with η^5-pyrrolyl ligands are well-known for metals across the periodic table.[8] In the course of exploring pyrazolato complexes of the early transition metals, we became interested in investigating the possibility of η^5-pyrazolato ligand coordination. Herein we report the synthesis, structure, and properties of a series of ruthenium(II) complexes bearing η^5-pyrazolato ligands. This is the first documentation of this coordination mode in any metal. Molecular orbital calculations have been carried out on a model ruthenium(II) pyrazolato complex. The theoretical results demonstrate that η^5-pyrazolato ligands employ orbitals similar to those of η^5-cyclopentadienyl ligands to bond to ruthenium(II) centers, which implies that η^5-pyrazolato ligand coordination should be feasible in many metals.

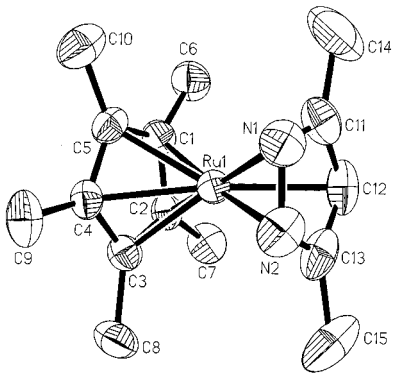
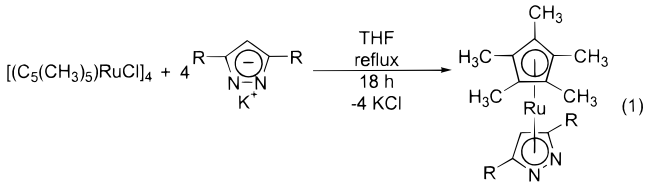


Figure 1. Perspective view of $((CH_3)_2C_3HN_2)(C_5(CH_3)_5)Ru$ (**1**) with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru−C(1) 2.145(3), Ru−C(2) 2.145(3), Ru−C(3) 2.152(3), Ru−C(4) 2.177(3), Ru−C(5) 2.171(3), Ru−C(11) 2.182(3), Ru−C(12) 2.205(3), Ru−C(13) 2.178(4), Ru−N(1) 2.178(3), Ru−N(2) 2.174(3), Ru−$C_5(CH_3)_5$(centroid) 1.785(3), Ru−$(CH_3)_2C_3HN_2$(centroid) 1.837(3), $C_5(CH_3)_5$(centroid)−Ru−$(CH_3)_2C_3HN_2$(centroid) 177.31(13).

Treatment of $[(C_5(CH_3)_5)RuCl]_4$[9] with 3,5-dimethylpyrazolatopotassium,[4] 3,5-diphenylpyrazolato(tetrahydrofuran)potassium,[4] or 3,5-di-*tert*-butylpyrazolatopotassium[4] in tetrahydrofuran afforded (η^5-3,5-dimethylpyrazolato)(η^5-pentamethylcyclopentadienyl)-ruthenium(II) (**1**, 71%), (η^5-3,5-di-*tert*-butylpyrazolato)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (**2**, 72%), or (η^5-3,5-diphenylpyrazolato)(η^5-pentamethylcyclopentadienyl)-ruthenium(II) (**3**, 71%), as dark green, pale yellow, or dark brown crystalline solids, respectively (eq 1).[10] Complexes **1**−**3** were



1, R = CH_3, 71%
2, R = $C(CH_3)_3$, 72%
3, R = C_6H_5, 71%

characterized by spectral and analytical methods, and the molecular structure of **1** was determined by X-ray crystallography. The presence of π-bound pyrazolato ligands was strongly suggested by the positions of the pyrazolato ring hydrogen resonances in the ^{1}H NMR spectra (**1**, δ 4.39; **2**, δ 4.72; **3**, δ 5.59) and of the hydrogen-substituted carbon resonances in the $^{13}C\{^1H\}$ NMR spectra (**1**, 79.29 ppm; **2**, 71.23 ppm, **3**, 72.24 ppm). For comparison, early transition metal complexes bearing η^2-pyrazolato ligands show resonances for the pyrazolato ring hydrogen in the ^{1}H NMR spectra between δ 5.94−6.60 and for the hydrogen-substituted ring carbon in the $^{13}C\{^1H\}$ NMR between 106 and 113 ppm.[2] Complexes **1**−**3** exhibit irreversible oxidations at 0.631, 0.600, and 0.702 V, respectively, by cyclic voltammetry in acetonitrile.[11] These values are slightly more positive than the analogous value for pentamethylruthenocene ($E^{1/2}$ = 0.54 V),[12] and indicate that the pyrazolato ligands are less electron-donating

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(11) The cyclic voltammetry experiments were conducted with a BAS-100 electrochemical analyzer using a glassy carbon working electrode and a Ag/AgCl reference electrode. The solvent was acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate. The sweep rate was 100 mV/s. The reported potential values are for irreversible oxidations. The oxidation potentials are relative to an internal ferrocene standard ($E°$ = 0.31 V): Gagne, R. R.; Koval, C. H.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

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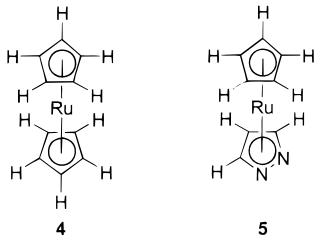
than a cyclopentadienyl ligand. The X-ray crystal structure of **1** was determined.[13] Figure 1 shows a perspective view of the molecule, along with selected bond lengths and angles. Complex **1** exists in a pseudo-metallocene structure, with the five-membered rings being twisted 24.3(2)° from the eclipsed conformation. The ruthenium−carbon bond lengths associated with the pentamethylcyclopentadienyl ligand range between 2.145 and 2.177 Å. Within the pyrazolato ligand, the ruthenium−carbon bond lengths range between 2.182 and 2.205 Å, while the ruthenium−nitrogen bond lengths are 2.174(3) and 2.177(3) Å. Accordingly, the ruthenium−carbon bond lengths to the pentamethylcyclopentadienyl ligand are shorter than the related values for the pyrazolato ligand. The differential bonding of ruthenium to the two π-bonded ligands is further illustrated by the ruthenium−pentamethylcyclopentadienyl (centroid) and ruthenium−pyrazolato (centroid) distances of 1.785(3) and 1.837(3) Å, respectively. The two π-bonded ligands in **1** are essentially coplanar, with a pentamethylcyclopentadienyl (centroid)−ruthenium−pyrazolato (centroid) angle of 177.31(13)°. The dihedral angles between the planes of the five-membered rings and the methyl substituents average 1.5(3)° for the pentamethylcyclopentadienyl ligand and 2.6(4)° for the 3,5-dimethylpyrazolato ligand.

To understand the bonding between the pyrazolato ligands and ruthenium(II), ab initio calculations were carried out at the B3LYP/LANL2DZ level of theory on ruthenocene (**4**) and the model complex (η^5-pyrazolato)(η^5-cyclopentadienyl)ruthenium(II) (**5**).[14] The calculations on **5** show the cyclopentadienyl and



4 **5**

pyrazolato ligands to be η^5-coordinated and coplanar (centroid−Ru−centroid angle 178.8°), like the results of the structural analysis for **1**. This particular level of theory overestimates the ruthenium−carbon and ruthenium−nitrogen bond lengths by ca. 0.1 Å. However, the difference in the bond lengths between the pyrazolato and cyclopentadienyl centroids (0.08 Å in **5**) is similar to the value observed in **1** (0.052 Å). In **4**, the carbon p-orbitals bond equally strongly to ruthenium. However, in **5** the pyrazolato nitrogen p-orbitals do not participate as strongly as the carbon p-orbitals in the bonding to ruthenium (Figure 2a). Although the lower lying, symmetric combination of the nitrogen lone pairs is fairly distinct (Figure 2b), the higher lying, antisymmetric combination mixes with a number of metal and ligand orbitals of the proper symmetry.

The experimental and theoretical results establish that η^5-coordination of pyrazolato ligands is easily achieved. A previous attempt to prepare pyrazolato analogues of ferrocene did not yield isolable compounds.[15] This report has probably discouraged

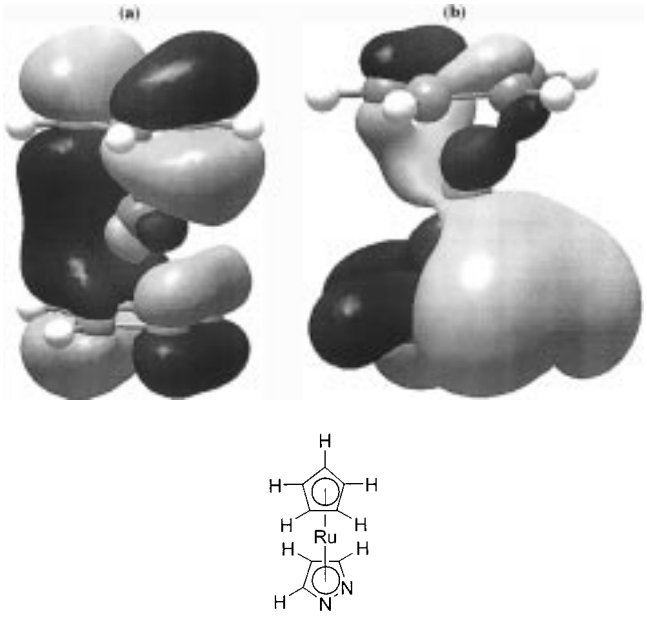


Figure 2. Two of the occupied orbitals of **5**, emphasizing (a) an orbital involved in π-bonding to the ruthenium atom, and (b) the orbital containing the symmetric combination of the nitrogen lone pairs.

further investigation of complexes bearing π-pyrazolato ligands. The successful syntheses of **1**−**3** probably originates from kinetic stabilization due to the bulky $(C_5(CH_3)_5)$Ru(II) fragment and the substituents in the 3- and 5-positions of the pyrazolato ligands. Interestingly, we have been unable to prepare (η^5-pyrazolato)(η^5-pentamethylcyclopentadienyl)ruthenium(II) as a pure compound, supporting the idea that subsitution at the 3- and 5-positions is crucial to the stability to **1**−**3**. In this vein, bulky groups in the 2- and 5-positions of pyrrolyl ligands have been shown to confer kinetic stability to complexes bearing η^5-pyrrolyl ligands.[8] The calculations demonstrate that the overlap between the pyrazolato p-orbitals and the ruthenium d-orbitals is not as extensive as in ruthenocene. Consistent with this prediction, the oxidation potentials of **1**−**3** are 0.09−0.16 V more positive than that of pentamethylruthenocene and the molecular structure of **1** shows longer bond lengths to the pyrazolato ligand atoms than to the pentamethylcyclopentadienyl ligand carbons. On the basis of our results, it is likely that η^5-pyrazolato ligand coordination will be feasible in many metal complexes, particularly low-valent mid to late transition metal complexes. Furthermore, anions of related nitrogen-rich five-membered heterocycles should also be capable of π-coordination to many metal centers. Unique characteristics of the η^5-pyrazolato ligand include its electron-withdrawing character relative to that of the cyclopentadienyl ligand, as well as the presence of basic lone pairs on the nitrogen atoms. Such characteristics should lead to a rich and varied reaction chemistry in complexes bearing η^5-pyrazolato ligands.[16,17] We are continuing to explore the chemistry of **1**−**3** and related complexes. These studies will be reported in due course.

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Supporting Information Available: Synthetic procedures, analytical and spectroscopic data for **1**−**3**, and tables of positional parameters for **4** and **5** (PDF) and X-ray crystallographic file for **1**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. JA990109A

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(17) Initial reactivity studies have demonstrated that **1** can be mercurated and forms an adduct with boron trifluoride. Reactivity studies of **1**−**3** are ongoing.