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# $(\eta^5\text{-}C_5Me_5)Ru(amidinate)$: Highly Reactive Ruthenium Complexes Formally Bearing 16 Valence Electrons Showing Signs of Coordinative Unsaturation

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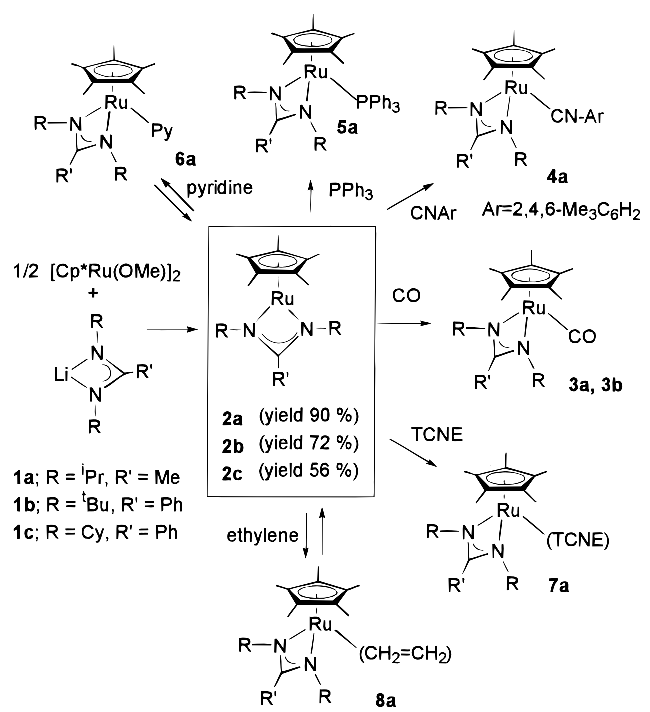
*Summary: Novel coordinatively unsaturated ruthenium complexes, $(\eta^5\text{-}C_5Me_5)Ru(amidinate)$, were synthesized from $[(\eta^5\text{-}C_5Me_5)Ru(OMe)]_2$ and lithium amidinates, which exist as monomers in both solution and solid states and are highly reactive toward two-electron ligands.*

Studies on structures and reactivity of coordinatively unsaturated complexes have received much attention from organometallic chemists in terms of intermediates in transition-metal-catalyzed organic reactions. Introduction of sterically bulky ligands is a method to stabilize compounds having a 16-electron configuration or fewer,[1,2] whereas in complexes having a Ru−X moiety (X = OR, SR) electron donation from the ligand is an alternative method to stabilize the reactive metal center.[3,4] In contrast, $[(\eta^5\text{-}C_5Me_5)Ru(TMEDA)]^+$ was effectively stabilized by the hard $\sigma$-donor character of TMEDA.[5] In this paper, we wish to report novel isolable yet highly reactive ruthenium complexes, $(\eta^5\text{-}C_5Me_5)$-Ru(amidinate). In almost all transition-metal amidinates so far reported,[6] the amidinate ligand generally acts as a bidentate four-electron donor through two metal−nitrogen bonds. In this context, $(\eta^5\text{-}C_5Me_5)$Ru(amidinate) is expected to have 16 valence electrons and to be coordinatively unsaturated.

**Scheme 1**



Treatment of $[(\eta^5\text{-}C_5Me_5)Ru(OMe)]_2$[7a] with 2 equiv of lithium amidinates **1a**−**c** in THF afforded diamagnetic purple solids in good yields, of which spectroscopic data are in accord with $(\eta^5\text{-}C_5Me_5)$Ru(amidinate) (**2a**−**c**) (Scheme 1).[8] The complex **2a** was alternatively formed quantitatively by reaction of 4 equiv of **1a** with $[(\eta^5\text{-}C_5Me_5)RuCl]_4$.[7b] The amidinate complexes are highly sensitive to air and moisture in both solution and solid states, being reactive with various two-electron-donor ligands. For example, **2a**,**b** instantly reacted with CO to give rise to addition of a CO molecule to the ruthenium atom, as shown in Scheme 1. The structure of the carbonyl complexes, which follows the 18-electron rule, was determined by spectral data of **3a**,**b**; this is supported by the crystal structure of **3b**, as shown in Figure 2 (left).[9] The formation of these coordinatively saturated CO complexes provides supporting evidence that the purple solids **2a**−**c** are coordinatively unsaturated $(\eta^5\text{-}C_5Me_5)$Ru(amidinate).

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[1] Ogasawara, M.; Macgregor, S. A.; Streib, W. E.; Folting, K.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1996**, *118*, 10189−10199.

[2] Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278−280.

[3] (a) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25−41. (b) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488−499.

[4] (a) Mashima, K.; Kaneyoshi, H.; Kaneko, S.; Mikami, A.; Tani, K.; Nakamura, A. *Organometallics* **1997**, *16*, 1016−1025. (b) Mashima, K.; Kaneko, S.; Tani, K.; Kaneyoshi, H.; Nakamura, A. *J. Organomet. Chem.* **1997**, *545*−*546*, 345−356.

[5] (a) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 5601−5603. (b) Gemel, C.; Sapunov, V. N.; Mereiter, K.; Ferencic, M.; Schmid, R.; Kirchner, K. *Inorg. Chim. Acta* **1999**, *286*, 114−120.

[6] Review of the amidinate ligands: (a) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219−300. (b) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403−481. To our knowledge, the only example in which the amidinate ligand acts as more than a four-electron donor was seen in a triosmium cluster: Burgess, K.; Holden, H. D.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1983**, 1199−1202.

[7] (a) Koelle, U.; Kossakowski, J. *J. Organomet. Chem.* **1989**, *362*, 383−398. (b) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698−1719.

[8] In a typical example, $[(\eta\text{-}C_5Me_5)Ru(OMe)]_2$ (82 mg, 0.15 mmol) was treated with $Li[MeC(N^iPr)_2]$ (46 mg, 0.31 mmol), which was prepared from MeLi and *N*,*N*′-diisopropylcarbodiimide, in THF at −78 °C, and the mixture was warmed to room temperature. After 1 h, the solvents were removed in vacuo, and the residue was extracted with pentane. Concentration of the extracts gave **2a** as a purple air-sensitive solid (106 mg, 0.28 mmol, 90% yield). Further purification can be achieved by sublimation (50 °C, $10^{-3}$ mmHg). NMR of **2a** in THF-$d_8$: $^1H$, $\delta$ 1.16 (d, $J$ = 6.4 Hz, 12H, $CH(CH_3)_2$), 1.35 (s, 3H, $CCH_3$), 1.71 (s, 15H, $C_5(CH_3)_5$), 3.06 (sep, $J$ = 6.4 Hz, 2H, $CH(CH_3)_2$); $^{13}C$, $\delta$ 10.27, 12.99, 25.43, 48.01, 70.00, 168.08. Other data are given in the Supporting Information.

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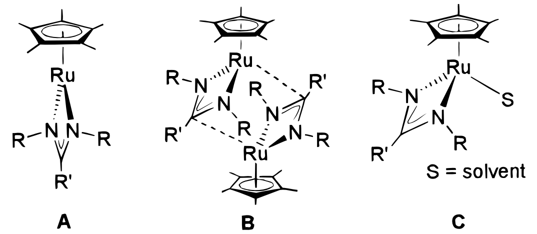

**Figure 1.**

The ($\eta^5$-$C_5Me_5$)Ru(amidinate) complexes are generally reactive with other two-electron-donor ligands. Representative examples are summarized in Scheme 1. Treatment of **2a** with 2,4,6-$Me_3C_6H_2NC$ or $PPh_3$ afforded **4a** or **5a**, respectively, in quantitative yields. A mixture of **2a** and pyridine afforded an $^1H$ NMR spectrum assignable to the pyridine complex **6a** at −90 °C.[10] Reversible and irreversible coordinations were seen in the reactions with olefins. Treatment of **2a** with TCNE afforded the stable complex **7a**. In contrast, formation of the ethylene complex **8a** was evidenced by spectroscopy when a THF solution of **2a** was allowed to stand under an ethylene atmosphere, but **2a** was regenerated quantitatively when ethylene was removed from the reaction mixture under reduced pressure.[11] The $\pi$-acceptor strength of the ligands decreases in the order CO > RNC > $PR_3$ > pyridine,[12] whereas TCNE > ethylene. The above results indicate that better $\pi$-acceptors are tightly coordinated with ($\eta^5$-$C_5Me_5$)Ru(amidinate); in other words, ($\eta^5$-$C_5Me_5$)Ru(amidinate) species is a good donor.[13]

The next question is the structure of ($\eta^5$-$C_5Me_5$)Ru(amidinate) complexes, which showed signs of coordinative unsaturation as described above. A related compound, ($\eta^5$-$C_5Me_5$)Ru(acetylacetonate), formally bearing 16 valence electrons and reactive with several 2-electron donors was reported by Koelle and co-workers, who revealed that this complex existed as a dimer in the solid state and was in equilibrium with a monomer in solution.[14,15] Thus, three possible structures, a monomeric structure having a 16-electron configuration (**A**), a dimer (**B**), and a monomer stabilized by a solvent (**C**), should be considered as the structure of ($\eta^5$-$C_5Me_5$)Ru(amidinate) (Figure 1). $^1H$ and $^{13}C$ NMR resonances derived from methyl groups in the isopropyl moiety of **2a** are good indicators to determine the structure in solution. A partial structure of **A** consisting of the center of the $C_5Me_5$ ligand, the Ru atom, and the amidinate ligand has $C_{2v}$ symmetry, which makes the $^1H$ and $^{13}C$ resonances from the methyl group equivalent. In contrast, this partial structure in **B** and **C** has $C_s$ symmetry, leading to the appearance of two independent methyl signals. In fact, the CO complex **3a** has a structure analogous to that of **C**, showing two inequivalent methyl signals. $^1H$ and $^{13}C$ NMR spectra of **2a** showing only a single methyl signal *in a noncoordinating solvent, methylcyclohexane-*$d_{14}$, from −110 °C to room temperature ruled out the existence of the structure **B** and the possibility that reversible coordination of the solvent was crucial for stabilization of the complex via the structure **C**. Thus, **2a** apparently exists as a monomeric structure such as **A** in hydrocarbon solution. The crystal structure of **2b** provides additional evidence that these complexes exist as monomers without coordination of the solvents, though there is an unprecedented difference in the crystal structures from the structure **A**: the center of the Cp* ring, the Ru atom, and the two nitrogen atoms lie on the same plane, whereas a plane consisting of the Ru atom and two nitrogen atoms makes an angle of 48.9(4)° with a plane of the amidinate N−C−N moiety.[16] The ORTEP drawing is illustrated in Figure 2 (right).

In summary, we have achieved the first successful isolation of ($\eta^5$-$C_5Me_5$)Ru(amidinate) complexes, which exist as monomers in both solution and solid states and are highly reactive with two-electron-donor ligands such as CO and olefins. To our knowledge, this is the first case where amidinate ligands[6] play an important role in effectively stabilizing a coordinatively unsaturated metal center.[17] Further investigation on the structures and reactivity of ($\eta^5$-$C_5Me_5$)Ru(amidinate) is in progress.

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(9) In a typical experimental procedure, **2b** (82 mg, 0.18 mmol) was treated with CO (1 atm) at −78 °C. The mixture was warmed to room temperature. After 30 min, the solvents were removed in vacuo, and the resulting yellow solid was recrystallized from hexane at −20 °C to give **3b** as yellow crystals (45 mg, 0.091 mmol, 45% yield). $^1H$ NMR in THF-$d_8$: $\delta$ 0.90 (s, 18H), 1.77 (s, 15H), 7.17−7.31 (m, 5H). IR (KBr): 1888 $cm^{-1}$. Other data are summarized in the Supporting Information. Crystal data for **3b**: monoclinic, space group $P2_1/n$ (No. 14), $a = 18.958(3)$ Å, $b = 15.336(2)$ Å, $c = 8.775(2)$ Å, $\beta = 90.296(13)°$, $V = 2551.4(8)$ Å$^3$, $Z = 4$; R1 = 0.0520, wR2 = 0.1640 ($I > 2\sigma(I)$); R1 = 0.0993, wR2 = 0.2819 (all data).

(10) At −90 °C in THF-$d_8$, the $^1H$ NMR spectrum of **6a** showed two independent methyl signals derived from the methyl groups of the isopropyl group of the amidinate ligand. Signals assignable to the coordinated pyridine were visible at $\delta$ 7.20 (t), 7.64 (t), and 8.67 (d) (the corresponding signals from uncoordinated pyridine under the same conditions were $\delta$ 7.36, 7.77, and 8.58, respectively). The only signals of uncoordinated pyridine and **2a** were seen at room temperature. At −70 to −20 °C, broadening of the signals was observed. We consider that these spectral features are derived from reversible coordination of pyridine to **2a**, and the details are under study.

(11) $^1H$ NMR resonances of the coordinated ethylene were seen at $\delta$ 2.15 (d, $J = 11.2$ Hz) and 2.65 (d, $J = 11.2$ Hz) at −100 °C in THF-$d_8$. At room temperature, the peak from the coordinated ethylene was visible as a broad singlet at $\delta$ 2.51, due to the rapid rotation of the ethylene ligand.

(12) Elschenbroich, Ch.; Salzer, A. *Organometallics*; VCH: Weinheim, Germany, 1992; p 230.

(13) This is supported by a typically low CO stretching frequency of **3a** or **3b** (1901 $cm^{-1}$ for **3a** and 1888 $cm^{-1}$ for **3b**, cf. ($\eta^5$-$C_5Me_5$)Ru(acac)(CO)[14] 1915 $cm^{-1}$, ($\eta^5$-$C_5Me_5$)Ru($PCy_3$)(CO)Cl[2] 1908 $cm^{-1}$, ($\eta^5$-$C_5Me_5$)Ru($P^iPr_2Ph$)(CO)X (X = I, Br, Cl, OR, NHPh)[3b] 1903−1930 $cm^{-1}$) due to strong back-donation from the ($\eta^5$-$C_5Me_5$)Ru(amidinate) fragment to the CO ligand.

(14) Koelle, U.; Kossakowski, J.; Raabe, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 773−774. The dimeric structure of ($\eta^5$-$C_5Me_5$)Ru(acac) was reported by reinterpretation of the published crystallographic data: Smith, M. E.; Hollander, F. J.; Andersen, R. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1294.

(15) (a) Koelle, U.; Rietmann, C.; Raabe, G. *Organometallics* **1997**, *16*, 3273−3281. (b) Koelle, U. *Chem. Rev.* **1998**, *98*, 1313−1334. Recently Koelle briefly mentioned that a Cp*RuL (L = nitrogen-containing conjugated ligand) may be a monomeric 16e complex (p 1331 in ref 15b).

(16) Crystal data for **2b**: orthorhombic, space group *Pnma* (No. 62), $a = 19.171(3)$ Å, $b = 15.245(3)$ Å, $c = 8.163(3)$ Å, $V = 2385.7(9)$ Å$^3$; $Z = 4$, R1 = 0.0347, wR2 = 0.0920 ($I > 2\sigma(I)$); R1 = 0.0596, wR2 = 0.1074 (all data). The molecular structure of **2c** was monomeric and solvent-free. The angle $\theta$ is 29.7(2)°. See the Supporting Information.

(17) The reason the amidinate ligands can effectively stabilize the coordinatively unsaturated metal center requires further investigation; the amidinate ligands are not bulky enough to protect the reactive metal center and are not hard $\sigma$-donors because of N−C=N conjugation. Weak coordination of $\pi$-electrons on the amidinate ligand may contribute to the stabilization. The folded structures of **2b** and **2c** provided Ru−C (center of the amidinate ligand) distances of 2.336(5) (**2b**) and 2.489(2) Å (**2c**), which are apparently shorter than the corresponding distances in the 18-electron complex **3b** (2.596(6) Å). If the conjugate $\pi$-electrons in the amidinate ligand act as a $\pi$-donor to mitigate the coordinative unsaturation of 16-electron ($\eta$-$C_5Me_5$)Ru(amidinate) species, this additional stabilizing effect would be responsible for the shorter Ru−C bond distances, though it is so weak as to be undetectable by spectroscopy in solution. Although the coordination ability of $\pi$-electrons on the amidinate ligand to transition metals was proposed in a review, clear evidence to suggest it is rare.[6a]

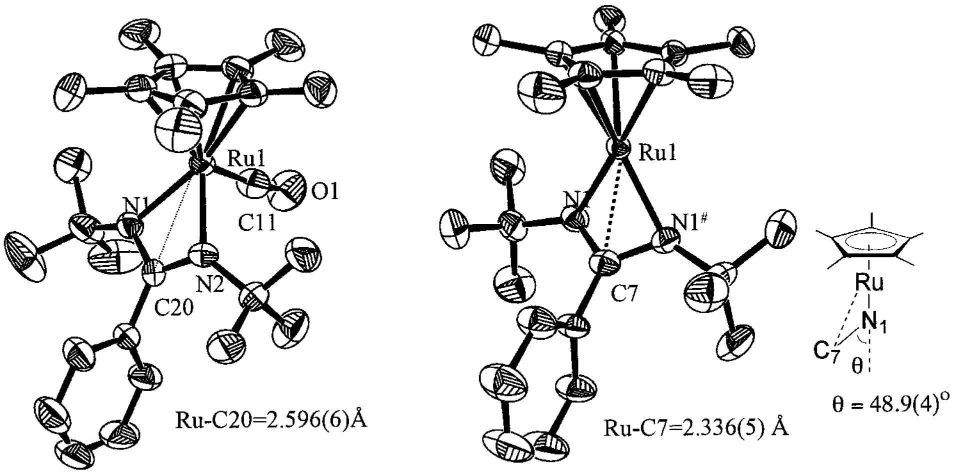

**Figure 2.** ORTEP drawings of the 18-electron complex **3b** (left) and the "16-electron complex" **2b** (right) with thermal ellipsoids drawn at the 50% probability level. Four atoms, Ru1, N1, N2, and C20, lie on the same plane in **3b**. In contrast, **2b** has the "folded" structure, as described in the text. Representative bond distances (Å) and angles (deg) are as follows. **3b**: Ru1−N1 = 2.133(5), Ru1−N2 = 2.135(5), Ru1−C20 = 2.596(6), Ru1−C11 = 1.828(7), N1−C20 = 1.334(8), N2−C20 = 1.319(8); N1−Ru1−N2 = 61.1(2), N1−Ru1−C11 = 96.1(3), N2−Ru1−C11 = 93.9(3), N1−C20−N2 = 109.8(5). **2b**: Ru1−N1(N1#) = 2.073(3), Ru1−C7 = 2.336(5), N1−C7 = 1.347(4); N1−Ru1−N1# = 64.4(2), N1−C7−N1# = 110.1(4).

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**Supporting Information Available:** Text giving experimental details and analytical data on new complexes and tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond lengths and angles for complexes **2b**,**c**, **3b**, and **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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