$(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}{}^iPrN{=}C(Me)N^iPr)Ru(X)(\eta^5\text{-}C_5Me_5)$: An Unusual Bonding Mode of μ_2-Amidinate Ligand Providing the First Unequivocal Evidence for Coordinating Ability of π-Conjugate Electrons of the Amidinate Ligands to Transition Metals

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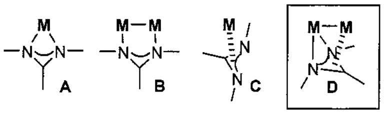
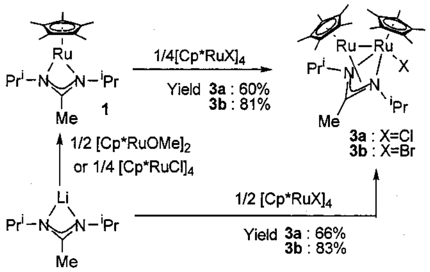
Amidinates have been one of the actively investigated ligands for transition metals in recent years,[1] especially in relation to cyclopentadienyl alternatives in early transition metal complexes.[2,3] It is also important that they are one of the most versatile bridging ligands to stabilize a wide variety of dinuclear transition metal complexes with various orders of M−M bonds.[4,5] In these complexes, amidinate ligands are, in general, bound to the metal centers through two metal−nitrogen σ-bonds, and act as either bidentate or bridging four-electron donors as shown in **A** or **B** in Scheme 1. Although possible coordination of π-electrons in the amidinates has been proposed by Kilner (**C** in Scheme 1),[1a] to the best of our knowledge, there has been no report on the complexes in which amidinates actually behave as π-donor ligands.[6] We have recently reported the synthesis of new ruthenium−aminidate complexes, $(\eta^5\text{-}C_5Me_5)Ru(amidinate)$.[7] Spectroscopic evidence and high reactivity toward two-electron donor ligands[7a] and allylic halides[7b] suggested that these complexes have 16-valence electrons, in which the amidinate ligands act as bidentate four-electron donors as usual. However, short bond distances between the ruthenium atom and central carbon of the amidinate ligand in crystal structures of two of the complexes raised suspicion in our minds that the coordinatively unsaturated nature of the ruthenium center may effectively be mitigated by intramolecular π-coordination of the amidinate ligands. In this paper, we wish to report synthesis and structural determination of novel dinuclear ruthenium complexes, $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}amidinate)Ru(X)(\eta^5\text{-}C_5Me_5)$ [**3a** (X = Cl), **3b** (X = Br)] and their derivatives, providing the first unequivocal evidence that conjugated π-electrons of the amidinate ligands can coordinate to the transition metal species as shown in **D** in Scheme 1.

Scheme 1



Scheme 2



Formation of the complexes **3a** and **3b** was unexpectedly discovered by experiments examining whether highly reactive $(\eta^5\text{-}C_5Me_5)Ru(amidinate)$ (**1**) might be reactive with transition metal fragments. Treatment of **1** with "$(\eta^5\text{-}C_5Me_5)RuX$" species in situ formed from $[(\eta^5\text{-}C_5Me_5)RuX]_4$ (**2a**: X = Cl, **2b**: X = Br)[8] in THF at room temperature afforded a novel diruthenium compound, **3a** or **3b**, as diamagnetic brownish red solid in good yield. Alternatively, **3a** or **3b** can be directly synthesized quantitatively by treatment of 2 equiv of $Li[{}^iPrN{=}C(Me){-}N^iPr]$[7a] with **2a** or **2b**, as shown in Scheme 2. Dinuclear structures of **3a** and **3b** containing two C_5Me_5 groups, one amidinate ligand, one halogen, and two rutheniums were suggested from mass spectra [MH^+ = 649 (**3a**), 694(**3b**)] and elemental analysis.[9] ^1H NMR spectrum of **3a** or **3b** in THF-d_8 at room temperature showed that there are two magnetically inequivalent C_5Me_5 groups and one amidinate moiety, in which two isopropyl groups of the amidinate ligand appeared as a single set of signals consisting of two doublets and one septet. The methyl group bonding with the central carbon of the amidinate ligand was visible as a singlet. These spectral data suggest that there is C_s symmetry in the molecule, of which a mirror plane includes centers of two C_5Me_5 ligands, two Ru atoms, and the central carbon of the amidinate ligand. This C_s symmetric structure was also supported by appearance of nine ^{13}C resonances in the ^{13}C NMR spectrum of **3a** or **3b**. Significant upfield shift of a ^{13}C resonance due to the central carbon of the amidinate ligand (δ 124.2 ppm in **3a**, δ 124.9 ppm in **3b**), which is ~40 ppm higher than that observed in $(\eta^5\text{-}C_5Me_5)Ru(\eta\text{-}amidinate)(L)$ reported earlier,[7a] strongly indicates that there is a bonding interaction between the Ru atom and this carbon.

The molecular structure of **3b** determined by X-ray diffraction study is consistent with that suggested from the above-described spectroscopic data as shown in Figure 1.[10] There is a mirror plane including centers of two C_5Me_5 ligands, Ru1, Ru2, C1 and Br. The Ru1−Ru2 distance (2.8552(4) Å) indicates existence of a Ru−Ru single bond.[5a] Two nitrogen atoms are bound to the Ru1 atom with Ru−N distances of 2.136(3) Å and 2.146(3) Å.

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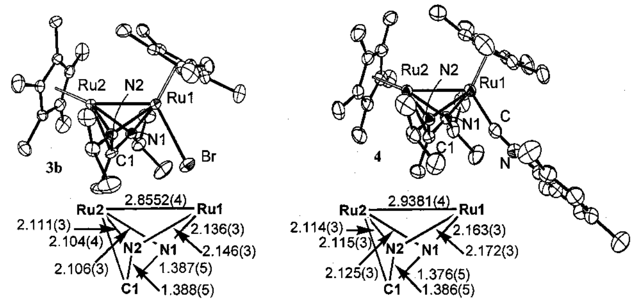
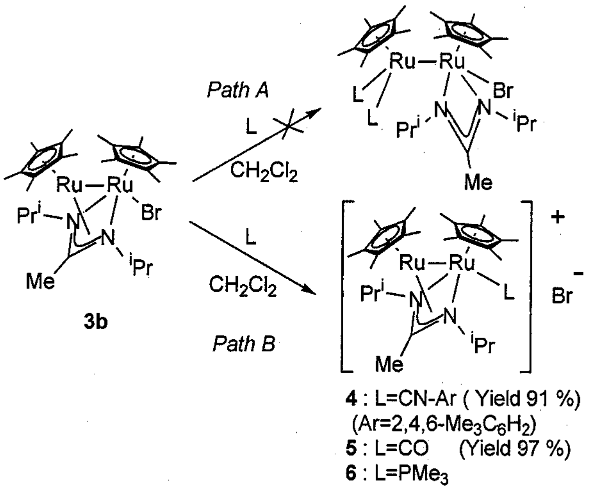


Figure 1. The ORTEP drawings of **3b** (left) and **4** (right) with thermal ellipsoids drawn at the 50% probability level. The Br atom in **4** is omitted for clarity. Figures in the inset are bond lengths (Å).

Scheme 3



Conjugate π-electrons of the amidinate ligand are bonded with the Ru2 atom in the π-allyl coordination mode with Ru2−N1, Ru2−N2, and Ru2−C1 bond distances of 2.106(3), 2.111(3), and 2.104(4) Å, respectively. This π-allyl coordination lengthens N1−C1 (1.387(5) Å) and N2−C1 (1.388(5) Å) bond distances, which are longer than that of (η^5-C_5Me_5)Ru(η-amidinate)(L) by 0.06−0.07 Å[7a] which has no π- coordination of the amidinate ligands.

Although this unusual π-coordination of the amidinate ligand to a ruthenium atom might be weak and easily replaceable by other ligands L (path A in Scheme 3), actual reactions observed were the formation of cationic complexes, [(η^5-C_5Me_5)Ru(μ_2-amidinate)Ru(L)(η^5-C_5Me_5)]$^+$Br$^-$, **4**−**6**, (path B in Scheme 3); this indicates that the π-allyl coodination is unexpectedly robust. Reaction of **3b** with CN−(2,4,6-Me_3−C_6H_2) in CH_2Cl_2 at room temperature gave [(η^5-C_5Me_5)Ru(μ_2-amidinate)Ru(CN−Ar)(η^5-C_5Me_5)]$^+$Br$^-$ (**4**) in good yields. Similar cationic complexes, [(η^5-C_5Me_5)Ru(μ_2-amidinate)Ru(CO)(η^5-C_5Me_5)]$^+$Br$^-$ (**5**) and [(η^5-C_5Me_5)Ru(μ_2-amidinate)Ru(PMe_3)(η^5-C_5Me_5)]$^+$Br$^-$ (**6**) were also synthesized by the reactions of **3b** with CO and PMe_3, respectively. Complete characterization of **4** and **5** was carried out by spectroscopic methods (^{1}H and ^{13}C NMR, IR) and elemental analysis.[11] These spectroscopic data as well as the molecular structure of **4** determined by X-ray analysis (Figure 1)[12] showed that **4** and **5** have μ_2-amidinate ligands which support the Ru−Ru bond by π-allyl coordination. Reaction of **3b** with PMe_3 gave an analogous dinuclear complex **6**; however, coordination of PMe_3 to the ruthenium center was reversible, and **6** was identified by spectroscopy in solution only at low temperatures.[11] Attempted isolation by concentration of the reaction mixture in vacuo resulted in complete regeneration of **3b**.

In summary, we synthesized the first transition metal complexes in which the amidinate ligand, [^{i}PrN═C(Me)−N^{i}Pr]$^-$, acts as a bridging eight-electron donor to stabilize a dinuclear [(η^5-C_5Me)$_5$Ru−Ru(X)(η^5-C_5Me)$_5$]$^+$; this is a new coordination mode of μ^2-amidinate ligand.[4,5,13] In addition to the great interest in these complexes as an intriguing starting point of a novel type of dinuclear ruthenium complexes, of importance is that this result offers indisputable experimental proof of the possible π-coordination of amidinate ligands. We believe that coordination of π-electrons in the amidinate ligands could play a more important role than chemists had expected in stabilizing both mono- and multinuclear transition metal species, which include intermediates or transition states of organometallic reactions; previously proposed effective stabilization of (η^5-C_5Me_5)Ru(η-amidinate) species by intramolecular coordination of π-electrons of the amidinate ligand is one example. Further investigation of the coordinating ability of π-electrons of the amidinate ligands and reaction chemistry starting from **3b** or **3a** is in progress.

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Supporting Information Available: Text giving experimental details and analytical data on new complexes and tables of X-ray structural information, including data collection parameters, positional and thermal parameters, and bond lengths and angles for complexes **3b** and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) **3a**: Anal. Calcd. for $C_{28}H_{47}N_2ClRu_2$: C, 51.80; H, 7.30; N, 4.31. Found: C, 51.73; H, 7.27; N, 4.25. ^{1}H NMR (THF-d_8) δ 1.23 (d, $J = 6.3$ Hz, 6H), 1.31 (d, $J = 6.3$ Hz, 6H,), 1.69 (s, 15H), 1.79 (s, 15H), 1.91 (s, 3H), 3.02 (sep, $J = 6.3$ Hz, 2H). ^{13}C{^{1}H}NMR (THF-d_8) δ 11.4, 13.9, 15.3, 22.7, 26.5, 55.6, 83.7, 84.2, 124.2. Other data for **3a** and full data of **3b** are given in the Supporting Information.

(10) Crystal data for **3b**: monoclinic space group $P2_1/n$, $a = 9.7616(2)$ Å, $b = 15.8832(4)$ Å, $c = 18.6844(3)$ Å, $\beta = 96.2050(10)°$, $V = 2879.96(10)$ Å^3, $Z = 4$, $R1 = 0.0413$, $wR2 = 0.1013$ ($I > 2\sigma(I)$), $R1 = 0.0592$, $wR2 = 0.1065$ (all data).

(11) Spectroscopic as well as analytical data for **4**−**6** are summarized in Supporting Information.

(12) Crystal data for **4**: monoclinic space group $P2_1/n$, $a = 9.5292(5)$ Å, $b = 23.6549(10)$ Å, $c = 17.1336(10)$ Å, $\beta = 103.147(2)°$, $V = 3760.9(3)$ Å^3, $Z = 4$, $R1 = 0.0369$, $wR2 = 0.0939$ ($I > 2\sigma(I)$), $R1 = 0.0410$, $wR2 = 0.0962$ (all data).

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