J|A|C|S
COMMUNICATIONS

Novel Coordinatively Unsaturated Bimetallic Complexes, $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}^iPrNC(Me){=}N^iPr)Ru(\eta^5\text{-}C_5Me_5)]^+$: A Bridging Amidinate Ligand Perpendicular to the Metal−Metal Axis Effectively Stabilizes the Highly Reactive Cationic Diruthenium Species

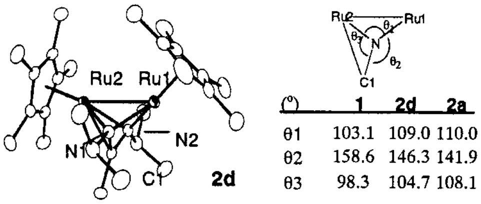
Hideo Kondo, Kouki Matsubara, and Hideo Nagashima*

Institute of Advanced Material Study, Kyushu University, and CREST,
Japan Science and Technology Corporation (JST), Kasuga, Fukuoka 816-8580, Japan

Received August 21, 2001

In our previous paper, we reported a diruthenium complex bearing a bridging amidinate ligand in an unusual bonding mode.[1] Bridging amidinates, of which each nitrogen atom is bound to a different metal center, have been well investigated for their effective stabilization of a wide variety of dinuclear transition metal complexes.[2,3] In these complexes, the bridging amidinate ligand is located parallel to the metal−metal bond.[3] In sharp contrast, the bridging amidinate in our novel complex is perpendicular to the metal−metal axis, in which one ruthenium center bonds with two nitrogen atoms, whereas the other ruthenium atom is bound to the face of the amidinate ligand in the π-allyl-like coordination mode.[1] Of keen interest in this new bonding mode is how effectively the bridging amidinate can stabilize the dinuclear framework. If it is effective, our novel complex would be a good starting point for exploration of various organometallic reactions of the dinuclear systems including catalysis.[4,5] In this paper, we wish to report synthesis of isolable yet highly reactive coordinatively unsaturated diruthenium complexes, $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}^iPrNC(Me){=}N^iPr)Ru(\eta^5\text{-}C_5Me_5)]^+$ (**2a**−**d**) from $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}^iPrNC(Me){=}N^iPr)Ru(Br)(\eta^5\text{-}C_5Me_5)]$ (**1**). Of extreme importance in this outcome is that the "perpendicularly coordinated" bridging amidinate ligand in the new cationic compounds strongly binds the two metal centers even in the reactive coordinatively unsaturated state,[6,7] and thereby addition of two electron donor ligands or bimetallic activation of molecular hydrogen is actually achieved without decomposing the dinuclear framework.

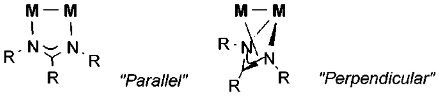
Treatment of **1** with either $AgBF_4$, $AgPF_6$, $AgSbF_6$, or $NaB(C_6F_5)_4$ in CH_2Cl_2 for 1 h afforded the corresponding $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}^iPrNC(Me){=}N^iPr)Ru(\eta^5\text{-}C_5Me_5)]^+(X)^-$ (**2a**−**d**) in 75−99% yield as shown in Scheme 1. The crystal structures of the PF_6 (**2a**)[8] and $B(C_6F_5)_4$ (**2d**)[8] derivatives clearly demonstrate that the counteranions are outside of the coordination sphere. No coordinating solvent was visible. Thus, these compounds are coordinatively unsaturated in the solid states. Representing this, the ORTEP drawing of **2d** is shown in Figure 1. The compounds have a C_s-symmetric structure with a mirror plane including centers of two C_5Me_5 ligands, Ru1, Ru2, and C1 and its adjacent methyl carbon. The Ru1−Ru2 distance in each complex is in the range of 2.91 ± 0.01 Å, indicating the existence of a Ru−Ru single bond. Each of the two Ru atoms is bonded to both of two nitrogen atoms, and there is a relatively long Ru2−C1 bond (2.17−2.19 Å). This coordination mode of the bridging amidinate ligand is similar to **1** having a Ru−Br bond; however, the longer Ru2−C1 bond distance (**1**: Ru2−C1 = 2.104(4) Å)[1] and larger θ_3 angle indicate weaker π-coordination of the bridging amidinate ligand.



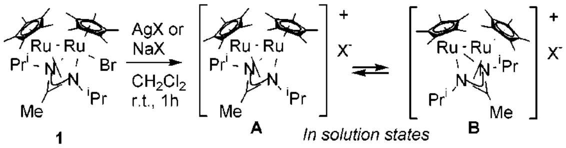
(°)	1	2d	2a
θ1	103.1	109.0	110.0
θ2	158.6	146.3	141.9
θ3	98.3	104.7	108.1

Figure 1. The ORTEP drawings of **2d** with thermal ellipsoids drawn at the 50% probability level. The $B(C_6F_5)_4$ anion is omitted for clarity. θ_1, θ_2, and θ_3 shown in the figure and the table in the inset are torsion angles (deg). Representative bond distances (Å) are as follows. **2d**: Ru1−Ru2 = 2.9198(3), Ru1−N1 = 2.097(3), Ru1−N2 = 2.098(3), Ru2−N1 = 2.101(3), Ru2−N2 = 2.119(3), Ru2−C1 = 2.173(3), N1−C1 = 1.387(4), N2−C1 = 1.387(4).

Chart 1



Scheme 1



2a: X=PF_6; (Yield, 95%)
2b: X=BF_4; (Yield, 75%), **2c**: X=SbF_6; (Yield, 93%)
2d: X=$B(C_6F_5)_4$ (Yield, 99%)

Variable-temperature ^1H NMR spectra of **2a**−**d** in CD_2Cl_2 showed that two C_5Me_5 groups were visible as a sharp singlet, whereas four methyl moieties of the isopropyl substituent of the bridging amidinate group were magnetically equivalent to give a sharp doublet in the temperature range from −80 to 35 °C. This is in sharp contrast to the fact that the C_s-symmetric structure of **1**, which is supported by crystallography, provided two singlets and two doublets due to the C_5Me_5 and methyl moieties of the isopropyl groups in the μ_2-amidinate group. A singlet for C_5Me_5, as well as one doublet for the isopropyl group in the NMR down to −80 °C, indicates rapid motion (time averaged C_{2v} structure) of the amidinate ligand in **2** in solution. In other words, replacement of the coordinating Br atom in **1** by other counteranions resulted in formation of cationic species shown in **A** of Scheme 1, which are interconverted with **B** in CD_2Cl_2. This interconversion is very rapid in the NMR time scale to provide the spectra suggesting formally C_{2v}-symmetric structures.[9]

Isolation of coordinatively unsaturated diruthenium complexes stimulated us to explore reactivity of these compounds with various substrates. The complex **2d** instantly reacted with CO (1 atm) or isonitriles in CH_2Cl_2 to give the corresponding adducts quantitatively. Striking evidence showing the coordinatively unsaturated nature of these complexes is successful oxidative addition of H_2.

10.1021/ja016899h CCC: $22.00

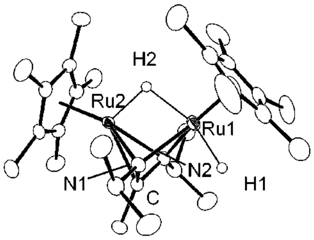
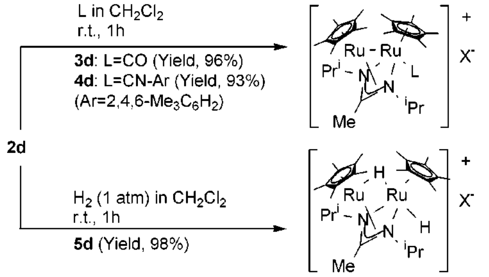


Figure 2. The ORTEP drawing of **5d** with the thermal ellipsoid drawn at the 50% probability level. The $B(C_6F_5)_4$ anion is omitted for clarity. Representative bond distances (Å) are as follows. Ru1−Ru2 = 2.7741(4), Ru1−N1 = 2.105(3), Ru1−N2 = 2.098(3), Ru1−H1 = 1.59(5), Ru1−H2 = 1.86(5), Ru2−H2 = 1.68(5), Ru2−N1 = 2.135(3), Ru2−N2 = 2.144(3), Ru2−C1 = 2.113(3), N1−C1 = 1.380(4), N2−C1 = 1.384(4).

Scheme 2



In a typical example, treatment of **2d** with H_2 (1 atm) in CH_2Cl_2 resulted in rapid color change of the solution from purple to yellow. From the reaction mixture, the corresponding oxidative adduct **5d** was isolated quantitatively. NMR spectra suggest the C_s-symmetric structure of **5d**, showing inequivalent C_5Me_5 groups and two sets of signals due to the isopropyl groups of the bridging amidinate ligand. Two Ru−H peaks were seen as sharp singlets at δ −5.60 and −7.77 ppm. The T_1 value of these two Ru−H signals at 293 K was 4.060 (δ −5.60 ppm) and 2.854 s (δ −7.77 ppm), suggesting that these are not nonclassical hydrides.[10] The IR spectrum of **5d** showed a ν_{Ru-H} absorption at 1956 cm^{-1}. These assignments were supported by ^2H NMR spectra of **5d**-d_2, which was synthesized from **2d** with D_2, showing Ru−D signals at δ −5.44 and −7.72 ppm. The IR spectrum of **5d**-d_2 resulted in the disappearance of the absorption at 1956 cm^{-1} by the isotopic shift. The C_s-symmetric diruthenium dihydride structure was proved by crystallographic analysis of **5d**,[11] in which arrangement of the C_5Me_5 groups and the bridging amidinate are similar to those seen in **2d**. Of particular interest is that one hydride is located at the terminal position, whereas the other bridges the Ru−Ru bond. The terminal hydride is in the trans position to the bridging hydride as shown in Figure 2. The existence of the bridging hydride caused the relatively short Ru−Ru bond (2.7741(4) Å), which is 0.15 Å shorter than that of **2d**.

In summary, we have accomplished the preparation of isolable yet highly reactive "cationic coordinatively unsaturated" diruthenium compounds bearing a bridging amidinate ligand and weakly coordinating counteranions,[12] which is a rare example of dinuclear coordinatively unsaturated compounds.[13] The μ_2-amidinate ligand in the unusual coordination mode compared with other dinuclear transition amidinates plays an essential role in stabilizing the coordinatively unsaturated bimetallic centers, though further investigation is required to clarify how the perpendicular μ_2-amidinate ligand stabilizes the bimetallic moiety in the coordinatively unsaturated state. We believe that these results are an important clue to the development of new reactions and catalysis of diruthenium compounds involving activation of various substrates by coordinatively unsaturated organodiruthenium species, and further investigation on the reactivity of these new compounds is actively in progress.

Acknowledgment. This work was partially supported by the Japan Society for the Promotion of Science (Grants-in-Aid for Scientific Research 10450343, 13540374, 13029090).

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 **2a**, **2d**, **2e**, and **5d** (PDF). A crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Kondo, H.; Yamaguchi, Y.; Nagashima, H. *J. Am. Chem. Soc.* **2001**, *123*, 500−501.

(2) (a) For reviews of amidinate, see: Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219−300. Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403−481. (b) For organoruthenium amidinates, see: Yamaguchi, Y.; Nagashima, H. *Organometallics* **2000**, *19*, 725−727.

(3) For a review on dinuclear organotransition metal amidinates, see: Cotton, F. A. *Inorg. Chem.* **1998**, *37*, 5710−5720.

(4) Recent reviews on metal cluster, see: (a) Süss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41−133. (b) *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; VCH: New York, 1998. (c) *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; VCH: New York, 1999.

(5) For recent progress on reactive diruthenium compounds, see: (a) Haines, R. J. *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 7, pp 625−681. (b) Köelle, U. *Chem. Rev.* **1998**, *98*, 1313−1334. (c) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Fukushima, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13*, 1129−1146. (d) Iwasa, T.; Shimada, H.; Takami, A.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *Inorg. Chem.* **1999**, *38*, 2851−2859. (e) Braun, T.; Laubender, M.; Gevert, O.; Werner, H. *Chem. Ber./Recl.* **1997**, *130*, 559−563.

(6) Since the "perpendicularly" coordinated amidinate ligand is a 7 electron donor to the neutral diruthenium moiety, the total electron count [sum of two Cp* (5e × 2), Br (1e), μ_2-amidinate (7), and Ru−Ru (2e)] of **1** is 36. In contrast, that of **2a**−**2d** is 34, if the ruthenium−ruthenium bond is single. A vacant site for the coordination of the ligand or oxidative addition of H_2 is on the Ru(1) atom.

(7) Recent progress on coordinatively unsaturated mononuclear complexes: (a) Poli, R. *Chem. Rev.* **1996**, *96*, 2135−2204. (b) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25−41. (c) Tenorio, M. J.; Mereiter, K.; Puerta, H. C.; Valerga, P. *J. Am. Chem. Soc.* **2000**, *122*, 11230−11231. (d) Gemel, C.; Huffman, J. C.; Caulton, K. G.; Mauthner, K.; Kirchner, K. *J. Organomet. Chem.* **2000**, *594*, 342−353.

(8) Crystal data for **2a**: monoclinic space group $C2/c$, $a = 31.5792(15)$ Å, $b = 15.1007(5)$ Å, $c = 14.4272(7)$ Å, $\beta = 110.9710(10)°$, $V = 6424.2(5)$ Å^3, $Z = 8$, $R_1 = 0.0401$, $wR_2 = 0.0956$ ($I > 2\sigma(I)$), $R_1 = 0.0579$, $wR_2 = 0.1046$ (all data). **2d**: monoclinic space group $P2_1/c$, $a = 14.1770(5)$ Å, $b = 15.2535(4)$ Å, $c = 23.5483(8)$ Å, $\beta = 92.7110(10)°$, $V = 5086.6(3)$ Å^3, $Z = 4$, $R_1 = 0.0377$, $wR_2 = 0.1070$ ($I > 2\sigma(I)$), $R_1 = 0.0481$, $wR_2 = 0.1221$ (all data). Analytical as well as spectroscopic data of **2a**−**d** are listed in the Supporting Information.

(9) Although a possibility that reversible coordination of the solvent is involved in the interconversion cannot be completely excluded, it was confirmed that there was no sign of coordination of the solvent in the NMR spectra at −80 °C.

(10) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126−4133.

(11) Crystal data for **5d**: monoclinic space group $P2_1/c$, $a = 14.1154(3)$ Å, $b = 15.3888(3)$ Å, $c = 23.4856(7)$ Å, $\beta = 93.4660(9)°$, $V = 5092.2(2)$ Å^3, $Z = 4$, $R_1 = 0.0417$, $wR_2 = 0.1248$ ($I > 2\sigma(I)$), $R_1 = 0.0481$, $wR_2 = 0.1316$ (all data).

(12) It is known that a triflate anion can be coordinated to the transition metal.[14] The crystal structure of the OTf complex, **2e**, which was available by treatment of **1** with AgOTf, showed that the Ru−OTf distance is 2.360 (2) Å, indicating a weak Ru−O bonding interaction, in sharp contrast to the fact that the Ru−counteranion distances are over 3.9 Å in **2a** or **2d**. The Ru−C1 distance in **2e** is 2.126 (3) Å, and θ_1, θ_2, and θ_3 are 106.7, 153.1, and 100.2°, respectively; these values are between those of **1** and **2a**−**d**. The Ru−O bonding interaction is only seen in the solid states, and easily cleaved in solution leading to facile "swing" of the bridging amidinate ligand (VT studies). Furthermore, reaction of **2e** with CO, isonitriles, or H_2 proceeded in a fashion similar to that of **2d** to give the corresponding CO (**3e**), 2,4,6-$Me_3C_6H_2NC$ (**4e**), and dihydride (**5e**) complexes in 87, 95, and 97% yield. The results are summarized in the Supporting Information.

(13) Only one example reported: Matsuzaka, H.; Qü, J.-P.; Ogino, T.; Nishio, M.; Nishibayashi, Y.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Chem. Soc., Dalton Trans.* **1996**, 4307−4312.

(14) For an example of the Ru-η^1-OTf complex, see: Ontko, A. C.; Houlis, J. F.; Schnabel, R. C.; Roddick, D. M. *Organometallics* **1998**, *17*, 5467−5476 and references therein.

JA016899H