"Unsymmetrical" Diruthenium Amidinates in Which the μ_2-Amidinate Bridge Is Perpendicular to the Ru−Ru Axis: Synthesis and Reactions of Derivatives of $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-amidinate})Ru(\eta^5\text{-}C_5H_5)]^+$

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New diruthenium complexes, of which two organoruthenium species, $(\eta^5\text{-}C_5Me_5)Ru$ and $(\eta^5\text{-}C_5H_5)Ru$, are linked by a bridging amidinate ligand, were synthesized and characterized. Treatment of $(\eta^5\text{-}C_5Me_5)Ru(\eta\text{-amidinate})$ [amidinate: ^{i}PrN=C(Me)N^{i}Pr] with $[(\eta^5\text{-}C_5H_5)Ru(\eta\text{-NCMe})_3]^+PF_6^-$ resulted in formation of a cationic diruthenium amidinate, $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-amidinate})Ru(\eta^5\text{-}C_5H_5)(\eta\text{-NCMe})]^+PF_6^-$ (**4**), which was converted to $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-amidinate})Ru(\eta^5\text{-}C_5H_5)X$ [X = Cl (**5a**), Br (**5b**)] by treatment with the halide anion. The molecular structures and spectroscopic data of **4** and **5a** including their solution dynamics are compared with their bis-pentamethylcyclopentadienyl homologues, $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-amidinate})Ru(\eta^5\text{-}C_5Me_5)(\eta\text{-NCMe})]^+PF_6^-$ and $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-amidinate})Ru(\eta^5\text{-}C_5H_5)Cl$. Treatment of **5a** with $TlBF_4$ produced a diruthenium complex, $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-amidinate})Ru(\eta^5\text{-}C_5H_5)]^+BF_4^-$ (**6**), bearing 34 valence electrons, which was isolated and characterized by spectroscopy. The coordinatively unsaturated nature of **6** was evidenced by facile reactions with two-electron-donor ligands, NCMe, PMe_3, ^{t}BuNC, and CO. The coordinatively unsaturated complex **6** and its precursors, **4** and **5**, exhibited catalytic activity toward cyclization of *N*-tosyl-*N*-allyltrichloroacetamide, which was compared with the corresponding bis-pentamethylcyclopentadienyl homologues.

Introduction

Multinuclear transition metal complexes have received considerable attention because of potential cooperative reactivity of the metals in the cluster core with organic substrates, which may lead to the discovery of new catalyses.[1] Dinuclear compounds are one of the smallest classes of multimetallic complexes, and a great deal of work has been carried out on their preparation, structures, physical properties, and reactions.[2,3] One of the strategies to synthesize new dinuclear complexes is the design of appropriate ligands that bridge over dual metals to stabilize the dinuclear framework.[2,3] Bridging amidinate ligands are one of the best investigated ligands;[4−8] in particular, Cotton and co-workers synthesized a series of complexes in which two nitrogen atoms in the amidinate ligand are located parallel to the metal−metal axis and reported many unique aspects of their chemistry.[6] In our continuing studies on ruthenium amidinate chemistry,[5a,b] we recently discovered a new coordination mode of dinuclear metal amidinates; the molecular structure of $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^i$PrN=C(Me)N^{i}Pr)Ru$(\eta^5\text{-}C_5Me_5)X$ (**1**; X = Cl, Br) revealed that the amidinate ligand is perpendicularly arranged to the Ru−Ru axis, and π-coordination of the amidinate

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ligand to one of the ruthenium atoms contributes to stabilization of the dinuclear structure.[8c] An interesting feature of this complex is generation of a coordinatively unsaturated species from **1** by counteranion exchange: a 34-electron complex, $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^i PrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5Me_5)]^+Y^-$ (**2**; Y = PF_6, BF_4, TPFPB), can be isolated, characterized, and subjected to studies on its unique reactivity with two-electron-donor ligands and molecular hydrogen.[8b] High reactivity of this coordinatively unsaturated species actually provided its efficient catalysis for atom-transfer radical cyclization of *N*-allyl trichloroacetamides to trichlorinated γ-lactams.[8a]

Studies on the reactive dinuclear ruthenium amidinates **1** and **2** prompted us to synthesize other dinuclear metal complexes bearing "perpendicularly coordinated" bridging amidinate ligands. Preparation of **1** is accomplished by treatment of $[(\eta^5\text{-}C_5Me_5)RuX]_4$[9] with a mononuclear coordinatively unsaturated ruthenium amidinate, $(\eta^5\text{-}C_5Me_5)Ru(\eta\text{-}^i PrN{=}C(Me)N^iPr)$ (**3**).[8c] This indicates that exploration of appropriate organometallic species capable of reacting with **3** may provide us a novel dinuclear complex in which two different metal moieties are bridged by a μ-amidinate ligand. A candidate of a possible substitute of $[(\eta^5\text{-}C_5Me_5)RuX]_4$ is a transition metal complex that has easily replaceable ligands by "$(\eta^5\text{-}C_5Me_5)Ru(\eta\text{-}^i PrN{=}C(Me)N^iPr)$" species. In ruthenium chemistry, $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_3]PF_6$[10] has been extensively studied as a good precursor of a variety of $(\eta^5\text{-}C_5H_5)$-substituted ruthenium complexes, in which coordinated NCMe molecules are highly reactive toward ligand substitution.[11] In this paper, we wish to report the first successful example of this exploration that treatment of **3** with $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_3]^+PF_6^-$ provides an "unsymmetrical" dinuclear ruthenium amidinate, $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^i PrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5H_5)(\eta\text{-}NCMe)]^+PF_6^-$ (**4**). Starting from this new complex, halogeno-derivatives $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^i PrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5H_5)(X)$ (X = Cl, Br) (**5**) are synthesized, from which a coordinatively unsaturated species, $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^i PrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5H_5)]^+BF_4^-$ (**6**), can be generated. As noted above, it is well known the importance of coordinatively unsaturated species in homogeneous catalysis,[12,13] and the catalytic activity of **6** toward cyclization of *N*-allyl trichloroacetamides has been investigated in comparison with that of **2**.

Results and Discussion

Preparation of a Cationic Acetonitrile Complex. Treatment of **3** with an equimolar amount of $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_3]^+PF_6^-$ in THF at room temperature resulted in formation of a new compound, which was isolated as brown crystals after recrystallization. The following data suggest this product to be the desired diruthenium complex **4** (isolated yield from **3** was 73%). A peak assignable to $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^i PrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5H_5)(\eta\text{-}NCMe)]^+$ was detected by ESI mass spectroscopy (M^+ = 545.10). ^1H and ^{13}C NMR spectra showed signals due to one C_5Me_5, one C_5H_5, one $^i PrN{=}C(Me)N^iPr$, and one coordinated acetonitrile. The dinuclear structure is evidenced by a ^{13}C resonance due to the coordinated amidinate carbon, $^i PrN{=}\mathit{C}(Me)N^iPr$, appearing at δ 126.6, which is 20−40 ppm higher than mononuclear ruthenium amidinates. The assignments from the spectroscopy are supported by X-ray structure determination, which provided the molecular structure shown in Figure 1 (left).

For comparison, a bis-$(\eta^5\text{-}C_5Me_5)$ analogue of this acetonitrile complex, $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^i PrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5Me_5)(\eta\text{-}NCMe)]^+PF_6^-$ (**7**), was prepared and characterized. Treatment of **2** (Y = PF_6) with excess amounts of acetonitrile was followed by removal of the solvent to give **7** in quantitative yield. The ESI mass spectrum showed a peak due to $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^i PrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5Me_5)(\eta\text{-}NCMe)]^+$ (M = 615.18). Since this complex showed dynamic behavior as described later, the ^1H and ^{13}C NMR spectra were measured at −70 °C, suggesting that the molecule contains one $\mu\text{-}^i PrN{=}C(Me)N^iPr$, one NCMe, and two magnetically inequivalent $\eta^5\text{-}C_5Me_5$ ligands. A signal assignable to the coordinated amidinate carbon appearing at δ 124.4 in ^{13}C NMR at 25 °C indicates that this carbon is coordinated to the ruthenium center; this is good evidence for the dinuclear structure of **7**. Crystallography of **7** provided the molecular structure shown in Figure 1 (right).

Structural features of the "unsymmetrical diruthenium amidinate" **4** in comparison with its bis-Cp* homologue **7** are summarized as follows: The molecular

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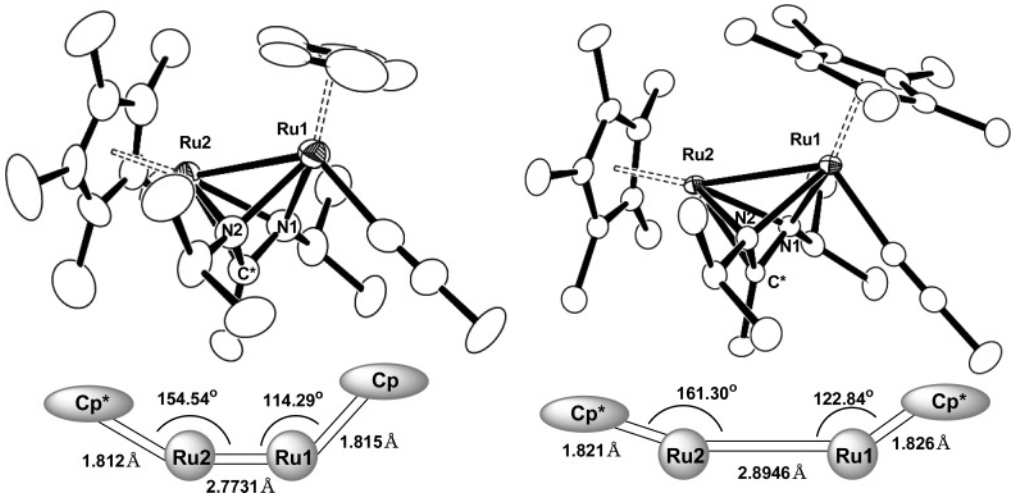
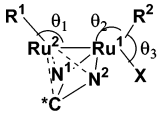


Figure 1. Molecular structures of **4** (left) and **7** (right) with representative bond distances and angles.

Table 1. Representative Bond Distances (Å) and Angles (deg) of Diruthenium Amidinates



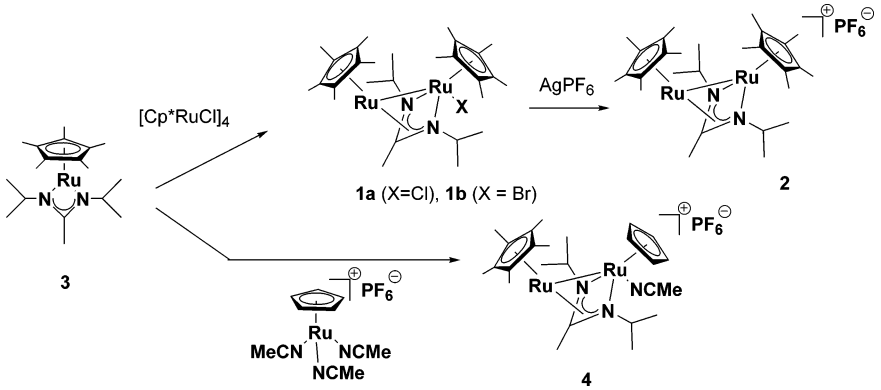
R^1 = center of Cp*
R^2 = center of Cp or Cp*
X = NCMe, Cl, Br, PMe_3, CN^tBu

	1a	1b[5a]	4	5a	7	8
Ru^1-Ru^2	2.8427(7)	2.8561(4)	2.7731(7)	2.7535(4)	2.8946(3)	2.7517(7)
Ru^1-X	2.458(1)	2.6152(5)	2.081(6)	2.4391(8)	2.096(3)	2.341(2)
Ru^2-R^1	1.832	1.846	1.810	1.817	1.821	1.811
Ru^1-R^2	1.819	1.821	1.805	1.803	1.826	1.830
q_1	159.71	159.75	154.54	154.13	161.30	153.99
q_2	121.87	120.79	114.29	114.75	122.84	109.59
q_3	117.02	116.97	120.46	120.29	118.70	116.86
Ru^1-N^1	2.142(6)	2.140(3)	2.133(5)	2.116(2)	2.143(2)	2.134(5)
Ru^1-N^2	2.125(6)	2.154(3)	2.125(5)	2.133(2)	2.144(2)	2.144(5)
Ru^2-N^1	2.106(4)	2.104(3)	2.104(5)	2.117(2)	2.099(2)	2.119(5)
Ru^2-N^2	2.099(4)	2.109(3)	2.130(5)	2.113(2)	2.106(2)	2.115(5)
Ru^2-C^*	2.110(5)	2.108(4)	2.138(6)	2.147(3)	2.103(3)	2.110(6)

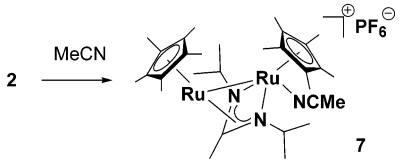
structure of **7** is very similar to that of **1**, the structure of which has already been reported previously,[8c] except that acetonitrile is coordinated to the ruthenium center with a Ru−N bond length of 2.096(3) Å instead of a bromine atom (Ru−Br = 2.6152(5) Å). There are many similarities in the molecular structures of **4** and **7**: the bridging amidinate ligand is located perpendicular to the Ru−Ru axis, and there are two Ru−N σ-bonds in the coordination mode of one Ru atom to the amidinate ligand, whereas the other ruthenium atom is bound to the face of the amidinate ligand in a η^3-fashion. Two isomers should exist for **4**; in one isomer, the Cp*Ru moiety is bonded to the face of the amidinate ligand, whereas the CpRu fragment is bound to it in the other. We carefully checked the possible existence of two isomers, but found that only the isomer shown in the ORTEP drawing was detected. An important difference in the bond distances of **4** from **7** is the Ru−Ru bond [2.7731(7) Å], which is shorter than that of **7** by approximately 0.12 Å. The Ru−Ru distances generally observed for diruthenium complexes are in the range 2.71−2.90 Å. We consider that the Ru−Ru distance of **4** is more normal than that of **7** and that steric hindrance between two bulky Cp* ligands elongates the Ru−Ru bond of **7** compared with its Cp*Cp homologue **4**. A comparison of the representative bond distances and angles with those of the compounds previously reported is summarized in Table 1. Each center of two cyclopentadienyl rings and two ruthenium atoms are on the same plane, and three angles θ_1, θ_2, and θ_3 are defined as shown in the table. It is apparent that steric repulsion between two sterically bulky Cp* ligands in **7** results in rather large θ_1 and θ_2 angles.

^{1}H and ^{13}C NMR spectra of **4** at room temperature and those of **7** at −70 °C are in accord with those deduced from the crystal structure as described above. As reported previously,[8b] a coordinatively unsaturated diruthenium amidinate species, $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^i PrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5Me_5)]^+$ (**2**), showed characteristic dynamic behavior in solution; π-coordination of the bridging amidinate ligand to one Ru center is switched to the other Ru in the low-energy barrier (ca. 3.3 kcal/mol by DFT calculation[5d]), leading to "swinging" of the amidinate ligand. Dissociation of the acetonitrile ligand in both **4** and **7** could give rise to generation of a coordinatively unsaturated species **2** and its Cp*Cp homologue, respectively, leading to exchange of the π-coordination site of the bridging amidinate ligand (Scheme 3). Such dynamic behavior in solution was actually observed by variable-temperature ^{1}H NMR spectra of **7**. At −70 °C, sharp signals due to two C_5Me_5 ligands, one bridging amidinate (^{i}Pr, CMe) and one NCMe, appeared separately. They coalesced at −5 °C and became a broad singlet at 15 °C, and a sharp doublet was observed above 35 °C. These spectral changes indicate reversible dissociation of the acetonitrile ligand from **7** accompanied by "swinging" of the amidinate ligand. Although similar dynamic behavior

Scheme 1



Scheme 2



could be induced by dissociation of the coordinated acetonitrile from **4** in solution, there was no change of the ^{1}H NMR spectra in the temperature range −25 to 45 °C (in CD_2Cl_2) or from rt to 70 °C (in $C_2D_4Cl_2$). Since rapid exchange of the coordinated CH_3CN to CD_3CN was observed in the ^{1}H NMR in a CD_3CN solution of **4**, reversible dissociation of the acetonitrile ligand of **4** in solution itself takes place. This can be rationalized by assuming that there is a significant difference in energy between the two possible isomers of **4**, and the dissociation of acetonitrile from **4** does not accompany the swinging of the bridging amidinate ligand to form the isomer that was not detected by spectroscopy.[14]

Preparation of Neutral Halogeno Complexes. It is known that conversion of cationic ruthenium acetonitrile complexes to neutral halogeno analogues has been achieved by their treatment with halogen anions.[13f] Treatment of **4** with excess amounts of NH_4Cl, LiCl, or LiBr resulted in formation of (η^5-C_5Me_5)Ru(μ-^{i}PrN═C(Me)N^{i}Pr)Ru(η^5-C_5H_5)X [X = Cl (**5a**), Br (**5b**)] (100% conversion, 50−90% isolated yields). Spectroscopic features of these complexes are similar to those of **4** except that there is no signal due to the coordinated acetonitrile ligand. In fact, ^{1}H and ^{13}C NMR spectra showed two singlets corresponding to η^5-C_5Me_5 and η^5-C_5H_5 ligands and peaks due to the one set of a bridging amidinate ligand. The structure deduced from the spectroscopy is coincident with the crystal structure of **5a** as shown in Figure 2. For comparison, crystallography of the bis-Cp* homologue **1a** was performed. The bond distances and angles of **5a** and **1a** are similar to those of **4** and **7**, respectively; for example, the Ru−Ru bond distance is 2.7535(4) Å for **5a**, whereas it is 2.8427(7) Å for **1a**. The two angles, θ_1 and θ_2, of **5a** and **1a** are similar to those of **4** and **7**, respectively. As described previously,[8a] a halide of the bis-Cp* complex **1a** and **1b** reversibly dissociates in solution. Variable-temperature ^{1}H NMR studies of **5a** and **5b**, which might show evidence of dissociation of the halide, revealed no line broadening in CD_2Cl_2 up to 40 °C or in $C_2D_4Cl_2$ at rt to 70 °C.

Reactions of "Unsymmetrically Substituted" μ_2-Amidinate Complexes. A special feature of diruthenium amidinate chemistry of the bis-Cp* complex **1** is facile formation of isolable cationic coordinatively unsaturated species **2** by exchange of its halogen ligand by weakly coordinating anions. Although we examined formation of a coordinatively unsaturated Cp−Cp* homologue, [(η^5-C_5Me_5)Ru(μ-^{i}PrN═C(Me)N^{i}Pr)Ru(η^5-C_5Me_5)]$^+$ (**6**) from either **4** or **5**, it was found to be more difficult than we expected. No reaction occurred in attempted thermal removal of coordinated acetonitrile from **4** at 140 °C in a vacuum.[13f] Treatment of **5a** with $AgPF_6$, LiTPFPB, and $NaBF_4$ in CD_2Cl_2 resulted in complete recovery of the starting material. Preparation of **6** (counteranion = BF_4) was finally accomplished by reaction of **5a** with $TlBF_4$ in CD_2Cl_2 at room temperature. This reaction produced a solution containing an air- and moisture-sensitive compound with an intense violet color, which is typical for coordinatively unsaturated ruthenium complexes. The coordinatively unsaturated nature of **6** was proved by treatment of this solution with CH_3CN, which instantly formed **4**. ESI mass measurement of the isolated complex in THF revealed a parent peak due to [(η^5-C_5Me_5)Ru(μ-^{i}PrN═C(Me)-N^{i}Pr)Ru(η^5-C_5H_5)]$^+$ without showing any other signals. ^{1}H and ^{13}C NMR spectra in CD_2Cl_2 showed two singlets due to the Cp* (δ_H 1.65, δ_C 10.0, 84.6) and Cp (δ_H 4.38, δ_C 68.6) and signals due to the bridging amidinate. Chemical shifts of these peaks are different from those of **4**, **5a**, and **5b** in the same solvent; in particular, the peak due to the central carbon of the amidinate ligand appeared at δ 116.9. Although a single crystal suitable for X-ray structure determination was unfortunately not available,[15] these spectroscopic data and the reactions with acetonitrile and other two-electron-donor ligands described below strongly suggest successful formation of **6**.

Treatment of **6** with PMe_3, ^{t}BuNC, or CO in CD_2Cl_2 instantly formed the corresponding adducts at room

(14) EHMO calculations of a model compound, [(η^5-C_5Me_5)Ru-(μ_2-NHCH═NH)Ru (η^5-C_5H_5)]$^+$, suggests that the isomer in which the Cp* ligand is bound to the face of the amidinate ligand is more stable in total energy than the other.

(15) In attempted preparation of a single crystal of **6**, a crystal of [(η^5-C_5Me_5)Ru(μ_2-^{i}PrNC(Me)═N^{i}Pr)(η^5-C_5H_5)Ru(μ-Cl)Ru(η^5-C_5H_5)(μ_2-^{i}-PrNC(Me)═N^{i}Pr)Ru(η^5-C_5Me_5)]$^+$ (A) was accidentally formed. The data are not sufficient for detailed discussion of bond distances and angles (R = 0.087 [$I > 2\sigma(I)$]), but enough to discuss the atom connectivity and the molecular structure. Since A is not seen in the solution of **6**, we consider that only a tiny amount of A, which is not detectable by NMR, is crystallized out from the solution. However, this is supporting evidence for the formation of **6**, which is allowed to react with **5a** to give A.

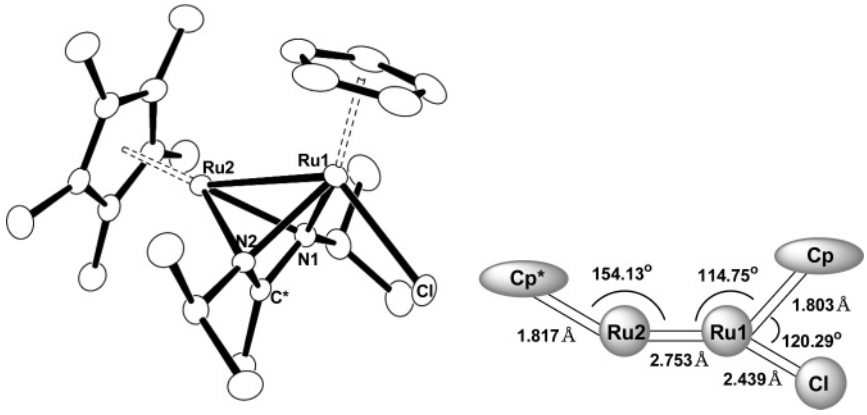
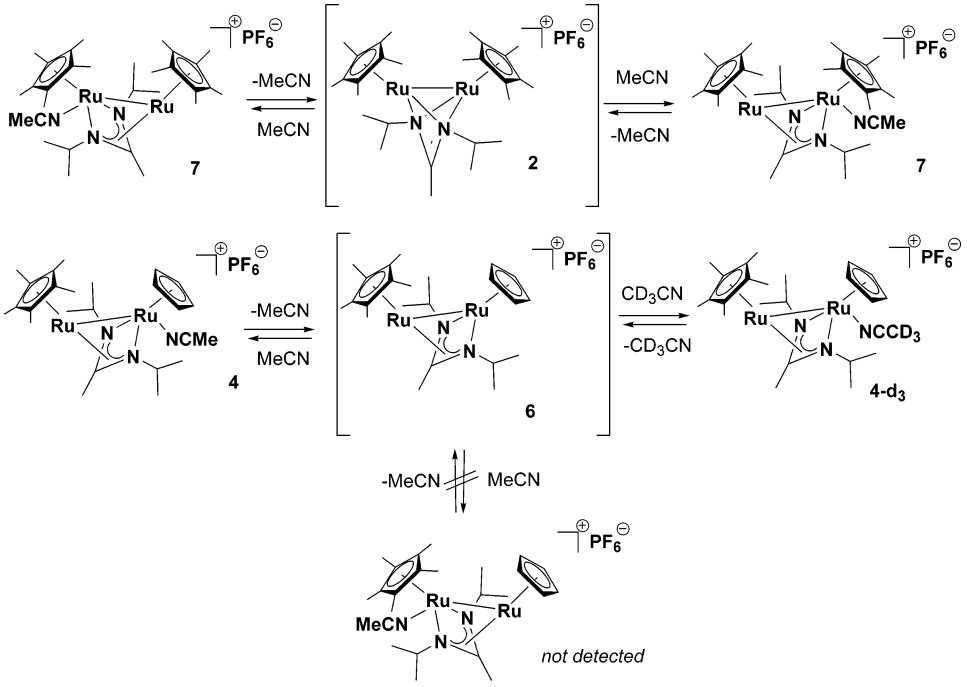


Figure 2. Molecular structures of **5a** with representative bond distances and angles.

Scheme 3



temperature. The reaction of **6** with PMe_3 gave $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^iPrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5Me_5)(\eta\text{-}PMe_3)]^+BF_4^-$ (**8**) quantitatively. The same compound was alternatively synthesized by exchange of coordinated MeCN of **4** by PMe_3. The parent mass peak ($M^+ = 621.15$) was observed by ESI spectrum in THF, and ^1H, ^{13}C, and ^{31}P NMR spectra are consistent with those deduced from the structure of **8**, which was determined by an X-ray diffraction study. As shown in Figure 3, the ORTEP drawing of **8** shows an analogous structure to **4** and **5a**, in which PMe_3 is coordinated with the ruthenium atom bound to the Cp ligand. Bond distances and angles are also similar to those of **4** and **5a**. Treatment of **6** with 1 equiv of ^{t}BuNC resulted in formation of the adduct $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^iPrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5Me_5)(\eta\text{-}CN^tBu)]^+BF_4^-$ (**9**). Interestingly, ESI mass measurement suggested formation of **9** as a single product; however, ^1H and ^{13}C NMR spectra suggested a 5:1 mixture of two products. At present, we consider from careful H−H, C−H COSY, and NOE experiments that **9** is a mixture of two isomers, **9a** and **9b** shown in Scheme 5. As described above, the isomer analogous to **9b** potentially exists in all of the Cp−Cp* complexes, **4**, **5a**, **5b**, and **8**. In contrast to the reaction of **4** with PMe_3, **9** was not formed by attempted ligand replacement of **4** by ^{t}BuNC. The reaction of **6** with CO also took place instantly to give a complicated mixture of products, which were difficult to separate and assign. The ESI mass spectrum of this mixture showed two major peaks corresponding to $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^iPrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5H_5)(\eta\text{-}CO)_2]^+$ ($M = 601.09$) and $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^iPrN{=}C(Me)N^iPr)Ru(\eta^5\text{-}C_5H_5)(\eta\text{-}CO)]^+$ ($M = 573.10$). As reported previously, reaction of coordinatively unsaturated diruthenium amidinate **2** with CO resulted in formation of the adduct of **2** accompanied by cluster fragmentation. The reaction of **6** with CO presumably proceeded in similar reaction pathways, i.e., adduct formation to give $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^iPrN{=}C(Me)N^iPr)(\eta\text{-}CO)]^+BF_4^-$ followed by cluster fragmentation to form $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}^iPrN{=}C(Me)N^iPr)(\eta\text{-}CO)]^+BF_4^-$ and $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}^iPrN{=}C(Me)N^iPr)(\eta\text{-}CO)]^+BF_4^-$.

Catalysis. Coordinatively unsaturated species are often postulated as key intermediates of the catalytic cycle in homogeneous catalysis. Our recent work has demonstrated that coordinatively unsaturated diruth-

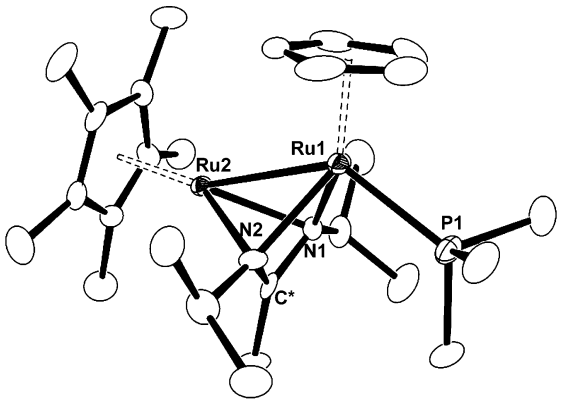
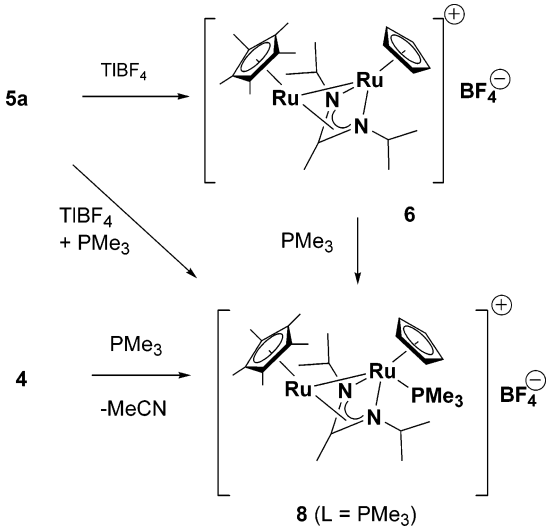
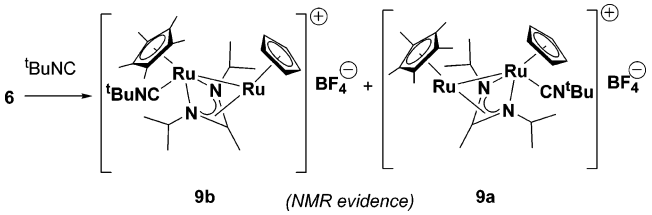


Figure 3. Molecular structure of **8**.

Scheme 4



Scheme 5



enium amidinate **2**, which can also be generated in situ by treatment of air-stable **1** with weakly coordinating anions, is a good catalyst for atom-transfer radical cyclization of *N*-allyl trichloroacetamides.[8a] Similar catalysis of the Cp*−Cp homologues of **1** and **2** was investigated by a series of experiments summarized in Table 3. *N*-Allyl-*N*-tosyltrichloroacetamide (**10**) was used as the substrate,[16,17] and four types of catalysts (or combination of a catalyst precursor with an activator) were examined: (a) isolated coordinatively unsaturated complexes (**2** and **6**), (b) halide precursors (**1a**, **1b**, **5a**, and **5b**), (c) the halide precursors + weakly coordinating anions as the activator, (d) acetonitrile complexes (**4** and **7**). Cyclic voltammograms of **2** and **6** in THF showed a quasi-reversible one-electron oxidation wave (**2**; E_{pa} = +0.26 V, E_{pc} = +0.35 V, **6**; E_{pa} = +0.32 V, E_{pc} = +0.45 V vs Ag/Ag^+ at the scan rate of 0.1 V/s) due to the Ru(II)/Ru(III) oxidation process. Since the oxidation potential of **6** is slightly higher than that of **2**, it was expected that **6** could be a somewhat inefficient catalyst for the cyclization of **10**. However, the results showed that **6** had another problem as the catalyst. The reactions using (a) revealed that **6** showed catalytic activity at the initial stage but deactivated quickly. The reactions using (b), (c), and (d) showed that the Cp*−Cp catalysts are apparently less efficient than the bis-Cp* homologues;[18] this is attributed to the properties of **6**, little of which is produced either from the halide precursor by anion exchange or from the acetonitrile complex by the dissociation of the coordinated acetonitrile. Quick deactivation also contributes to the catalyst inefficiency. Rather, these experiments revealed the special properties of the bis-Cp* complexes as the catalyst, which are first recognized by the present study, in which the catalytic activity was compared with their Cp*−Cp homologues. Replacement of the Cp* ligand by the less electron-donating Cp group makes the Ru−X or Ru^+−(η-NCMe) bond stronger; this prevents the generation of **6** from **4** or **5a**. The sterically less bulky as well as less electron-donating Cp ligand cannot stabilize the coordinatively unsaturated **6** effectively, thus causing the quick deactivation. In other words, two Cp* ligands, which effectively stabilize **2**, are more important for catalysis than we expected.

Conclusion

As reported earlier, the diruthenium amidinates **1** and **2** and their derivatives are the first example of complexes bearing a bridging amidinate ligand located perpendicular to the Ru−Ru axis. In this article are reported the second examples of diruthenium compounds bearing the "perpendicularly" coordinated μ_2-amidinate ligand, which constructs a rigid bimetallic framework by coordination of two Ru−N σ-bonds to one Ru atom and facial π-allyl-like coordination. Of interest is the generality of this new coordination mode, and the present reaction has opened the way of synthesizing dinuclear complexes having two different ruthenium moieties bound to a "perpendicular" μ_2-amidinate ligand. In other words, the reaction of coordinatively unsaturated ruthenium amidinate **1** with precursors of coordinatively unsaturated metal species other than $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ and $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_3]^+$ possibly provides a synthetic route to new bimetallic amidinates including heterobimetallic compounds. Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-amidinate})Ru(\eta^5\text{-}C_5H_5)]^+$ and $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-amidinate})Ru(\eta^5\text{-}C_5H_5)(L)]^+$, where L is a two-electron-donor ligand, has made possible their comparison in molecular structures, spectral data, solu-

(16) Reviews for radical cyclization chemistry: (a) Clark. A. *J. Chem. Soc. Rev.* **2002**, *31*, 1. (b) Giese, B.; Kopping, B.; Göbel, T.; Dickhaut, J.; Thoma, G.; Kulicke, K. J.; Trach, F. *Organic Reactions*; Wiley-VCH: New York, 1996. (c) Iqubal, J.; Bhatia, K.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519.

(17) Representative examples for transition metal catalyzed lactam synthesis: (a) Bryans, J. S.; Chessum, N. E. A.; Huther, N.; Parsons, A. F.; Ghelfi, F. *Tetrahedron* **2003**, *59*, 6221. (b) Clark, A. J.; Battle, G. M.; Bridge, A. *Tetrahedron Lett.* **2001**, *42*, 1999. (c) Bryans, J. S.; Chessum, N. E. A.; Huther, N.; Parsons, A. F.; Ghelfi, F. *Tetrahedron Lett*. **2001**, *42*, 2901. (d) Ishibashi, H.; Uemura, N.; Nakatani, H.; Okazaki, M.; Sato, T.; Nakamura, N.; Ikeda, M. *J. Org. Chem.* **1993**, *58*, 2360. (e) Nagashima, H.; Ozaki, N.; Ishii, M.; Seki, K.; Washiyama, M.; Itoh, K. *J. Org. Chem.* **1993**, *58*, 464. (f) See also ref 8c.

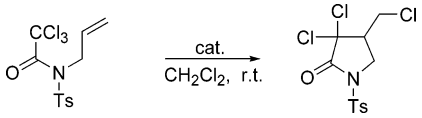
(18) For special features of the Cp* ligand compared with the Cp group: Jutzi, P. *Comments Inorg. Chem.* **1987**, *6*, 123.

Table 2. Crystallographic Data

	1a	4	5a	7	8
empirical formula	$C_{28}H_{47}N_2Ru_2Cl$	$C_{25}H_{40}N_3Ru_2PF_6$	$C_{23}H_{37}N_2Ru_2Cl$	$C_{30}H_{50}N_3Ru_2PF_6$	$C_{26}H_{46}N_2Ru_2P_2F_6$
cryst size (mm)	0.22 × 0.20 × 0.03	0.18 × 0.13 × 0.08	0.30 × 0.30 × 0.10	0.40 × 0.20 × 0.10	0.15 × 0.12 × 0.10
fw	649.29	729.72	579.15	799.85	764.73
temp, K	123(2)	123(2)	123(2)	123(2)	123(2)
radiation	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)	Mo Kα (0.71069Å)	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)
cryst syst	trigonal	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	$R\bar{3}$	$P2_12_12_1$	$P2_1/c$	$Pbcn$	$P2_1/n$
unit cell params	17.670(7)	11.8755(3)	11.324(3)	27.89(1)	11.098(2)
a (Å)	17.670(7)	12.2789(3)	13.828(5)	16.67(1)	17.656(2)
b (Å)	47.99(2)	40.576(1)	15.581(4)	14.429(7)	17.454(2)
c (Å)	90	90	90	90	90
α (deg)	90	90	92.14(1)	90	91.3437(8)
β (deg)	120.00	90	90	90	90
γ (deg)	12975.2(91)	5872.7(7)	2438(1)	6706(6)	3419.1(8)
V (Å^3)	18	8	4	8	4
Z					
ρ_{calc} (g cm^{-3})	1.496	1.651	1.578	1.584	1.651
abs coeff, mm^{-1}	1.158	1.141	1.360	1.006	1.187
F(000)	6012.00	2944.00	1176.00	3264.00	1720.00
θ range (deg)	3.2 to 27.5	3.0 to 27.5	3.0 to 27.4	3.1 to 27.5	3.0 to 27.5
indep reflns	6573 [R(int) = 0.044]	13 404 [R(int) = 0.075]	5544 [R(int) = 0.039]	7692 [R(int) = 0.052]	7748 [R(int) = 0.045]
reflns observed	6559 (>2σ)	11 154 (>2σ)	4575 (>2σ)	7679 (>2σ)	7737 (>2σ)
refinement method	full-matrix least-squares on F^2				
data/restraints/ params	6573/0/345	13 404/0/748	5544/0/291	7692/0/430	7748/0/413
goodness-of-fit on F^2	1.000	1.000	1.006	1.000	1.002
final R indices [I>2σ(I)]	R_1 = 0.0650[a] wR_2 = 0.1500[b]	R_1 = 0.0490[a] wR_2 = 0.1020[b]	R_1 = 0.0280[a] wR_2 = 0.0730[b]	R_1 = 0.0270[a] wR_2 = 0.0500[b]	R_1 = 0.0660[a] wR_2 = 0.1920[b]
R indices (all data)	0.0840	0.0660	0.0380	0.0630	0.090
larg diff peak and hole, e Å^{-3}	1.83 and −1.31	1.92 and −1.50	0.68 and −0.70	1.01 and −0.94	3.11 and −1.99

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

Table 3. Catalytic Cyclization of an *N*-Allyltrichloroacetamide[a]



entry	catalyst (mol %)	time (h)	conv (%)[b]	yield (%)[c]
1[d]	**2**	0.5	99	94
2	**6**	4	12	10
3	**7**	4	52	49
4	**4**	4	trace	
5[d]	**1a** + $NaPF_6$	0.5	>99	>99
6	**5a** + $NaPF_6$	4	32	30
7	**5a** + $TlPF_6$	4	10	

[a] Reactions were carried out in the presence of 10 mol % of the Ru_2 catalyst or a 1:1 mixture of the Ru_2 catalyst and activator ($NaPF_6$ or $TlPF_6$). [b] Determined by ^{1}H NMR using a residual proton peak of the NMR solvent as the internal standard. [c] Isolated yield after column chromatography. [d] Reported in ref 8a.

tion dynamics, and catalysis with the bis-Cp* homologues. Particular features are (1) the Cp−Cp* complexes have a shorter Ru−Ru bond than the bis-Cp* complex, (2) dynamic behavior due to the swinging of the bridging amidinate ligand is not observed, (3) the halogen abstraction from (η^5-C_5Me_5)Ru(μ_2-amidinate)-Ru(η^5-C_5H_5)(Cl) is more difficult than the bis-Cp* homologue, and (4) catalytic activity of the Cp−Cp* complexes for cyclization of *N*-tosyl-*N*-allyltrichloroacetamides is seen but is lower than that of the bis-Cp* homologue. These results are rather interesting in leading us to the conclusion that the bis-Cp* complexes have special structural features, solution dynamics, reactions, and catalysis to which two bulky and electron-donating Cp* ligands contribute.

Experimental Section

General Procedures. Manipulation of air- and moisture-sensitive organometallic compounds was carried out under a dry argon atmosphere using standard Schlenk tube techniques associated with a high-vacuum line. All solvents were distilled over appropriate drying reagents prior to use (toluene, pentane, Et_2O, THF; Ph_2CO/Na, MeCN, CH_2Cl_2; CaH_2, acetone; MS 4A). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL Lambda 600 or a Lambda 400 spectrometer at ambient temperature unless otherwise noted. ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts (δ values) were given in ppm relative to the solvent signal (^{1}H, ^{13}C) or standard resonances (^{31}P; external 85% H_3PO_4). IR spectra were recorded on a JASCO FT/IR-550 spectrometer. Melting points were measured on a Yanaco micro melting point apparatus. ESI mass spectra were recorded on a JEOL JMS-T100CS apparatus. Elemental analyses were performed by the Elemental Analysis Center, Faculty of Science, Kyushu University. Photolysis was performed by a Xe lamp (USHIO Inc. UM-453B-A). Starting materials, (η^5-C_5Me_5)Ru(μ-amidinate) (**3**)[5i] and [(η^5-C_5H_5)Ru(NCMe)$_3$]$^+PF_6^-$,[10] were synthesized by the method reported in the literature.

Preparation of [(η^5-C_5Me_5)Ru(μ-amidinate)Ru(η^5-C_5H_5)-(η-NCMe)]$^+PF_6^-$ (4). In a 20 mL Schlenk tube were placed (η^5-C_5Me_5)Ru(μ-amidinate) (**3**) (70 mg, 0.186 mmol) and [(η^5-C_5H_5)Ru(NCMe)$_3$]$^+PF_6^-$ (81 mg, 0.186 mmol). Then, THF (10 mL) was added, and the resulting brown solution was stirred at room temperature for 30 min. The solvent was removed in vacuo, and the residue was recrystallized from a mixture of dichloromethane and pentane at room temperature to give **4** as brown crystals (135 mg, 0.136 mmol, 73%). Mp: 151 °C (dec). Mass (M^+ − MeCN) (ESI) = 545.10. Exact mass (ESI-TOF) calcd for $^{12}C_{23}{}^1H_{37}{}^{14}N_2{}^{102}Ru_2$: 545.1044. Found: 545.1044. Anal. Calcd for $C_{25}H_{40}N_3Ru_2PF_6$: C, 41.15; H, 5.53; N, 5.76. Found: C, 40.89; H, 5.47; N, 5.63. ^{1}H NMR (600 MHz, CD_2Cl_2, rt): δ 1.04 and 1.06 (d, J = 6.2 Hz, CHMe_2), 1.68 (s, C_5Me_5), 2.00 (s, NC(Me)N of amidinate), 2.42 (s, NCMe),

2.84 (sept, J = 6.2 Hz, C*H*Me$_2$), 4.53 (s, C$_5$*H*$_5$). ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, rt): δ 3.9 (NC*Me*), 10.2 (C$_5$*Me*$_5$), 15.8 (NC(*Me*)N of amidinate), 22.2 and 25.4 (CH*Me*$_2$), 52.6 (*C*HMe$_2$), 68.7 (*C*$_5$H$_5$), 84.8 (*C*$_5$Me$_5$), 126.6 (N*C*N of amidinate), 129.0 (N*C*Me). IR (KBr): ν (cm^{-1}) = 2978 (s), 2911 (s), 2859 (s).

Preparation of [(η^5-C$_5$Me$_5$)Ru(μ-amidinate)Ru(η^5-C$_5$Me$_5$)(η-NCMe)]$^+$PF$_6^-$ (7). In a 20 mL Schlenk tube, **2** (50 mg, 0.066 mmol) was dissolved in acetonitrile (5 mL). The resulting red solution was stirred at room temperature for 5 min. The solvent was removed in vacuo, and the residue was recrystallized from a mixture of dichloromethane and pentane at room temperature to give **7** (48 mg, 0.060 mmol, 91%) as red crystals. Mp: 132 °C (dec). This complex is not very stable in solution presumably due to the reversible formation of unstable **6**. Although a single crystal for the X-ray study was fortunately obtained, recrystallization of **7** to prepare samples suitable for elemental analysis produced some amounts of impurities hardly separable from **7**. This was presumably due to decomposition of the formed **6**. Mass (M$^+$ − MeCN) (ESI) = 615.18. Exact mass (ESI-TOF): calcd for $^{12}C_{28}{}^1H_{47}{}^{14}N_2{}^{102}Ru_2$: 615.1826. Found: 615.1830. ^{1}H NMR (400 MHz, CD_2Cl_2, rt): δ 1.20 (br, CH*Me*$_2$), 1.74 (s, C$_5$*Me*$_5$), 1.83 (s, NC(*Me*)N of amidinate), 2.30 (br, NC*Me*), 3.01 (sept, J = 6.3 Hz, C*H*Me$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, rt): δ 3.6 (br, NC*Me*), 12.1 (br, C$_5$*Me*$_5$), 24.0 (br, CH*Me*$_2$), 14.8 (NC(*Me*)N of amidinate), 54.4 (*C*HMe$_2$), 84.9 (*C*$_5$Me$_5$), 121.4 (N*C*N of amidinate), 124.4 (N*C*Me). IR (KBr): ν (cm^{-1}) = 2977 (s), 2905 (s).

Preparation of (η^5-C$_5$Me$_5$)Ru(μ-amidinate)Ru(η^5-C$_5$H$_5$)(Cl) (5a). In a 20 mL Schlenk tube were placed **4** (52 mg, 0.071 mmol) and NH_4Cl (20 mg, 0.374 mmol). Then, dichloromethane (10 mL) was added, and the resulting orange solution was stirred at room temperature for 1 h. The solvent was removed in vacuo, and the residue was redissolved in dichloromethane (3 mL). On addition of Et_2O (15 mL), a white precipitate of NH_4PF_6 was formed and removed by filtration. Removal of solvents gave **5a** (35 mg, 0.060 mmol, 85%). Mp: 185 °C (dec). Anal. Calcd for $C_{23}H_{37}N_2Ru_2Cl$: C, 47.69; H, 6.44; N, 4.84. Found: C, 47.33; H, 6.34; N, 4.77. ^{1}H NMR (400 MHz, CD_2Cl_2, rt): δ 1.10 and 1.18 (d, J = 6.2 Hz, CH*Me*$_2$), 1.66 (s, C$_5$*Me*$_5$), 1.98 (s, NC(*Me*)N of amidinate), 2.88 (sept, J = 6.2 Hz, C*H*Me$_2$), 4.34 (s, C$_5$*H*$_5$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, rt): δ 10.2 (C$_5$*Me*$_5$), 16.4 (NC(*Me*)N of amidinate), 22.0 and 25.7 (CH*Me*$_2$), 53.2 (*C*HMe$_2$), 68.6 (*C*$_5$H$_5$), 83.2 (*C*$_5$Me$_5$), 125.6 (N*C*N of amidinate). IR (KBr): ν (cm^{-1}) = 2979(s), 2894 (s).

Preparation of (η^5-C$_5$Me$_5$)Ru(μ-amidinate)Ru(η^5-C$_5$H$_5$)(Br) (5b). In a 20 mL Schlenk tube were placed **5a** (30 mg, 0.052 mmol) and LiBr (45 mg, 0.518 mmol). Then, dichloromethane (5 mL) was added, and the resulting orange solution was stirred at room temperature for 1 h. The solvent was removed in vacuo, and the residue was redissolved in dichloromethane (3 mL) and washed with water (10 mL). Concentration of the combined extracts afforded **5b** (28 mg, 0.045 mmol, 86%). The same compound was alternatively prepared by treatment of **4** with LiBr by a similar procedure. Mp: 133 °C (dec). Anal. Calcd for $C_{23}H_{37}N_2Ru_2Br$: C, 44.29; H, 5.98; N, 4.49. Found: C, 44.34; H, 6.03; N, 4.52. ^{1}H NMR (400 MHz, acetone, rt): δ 1.07 and 1.20 (d, J = 6.3 Hz, CH*Me*$_2$), 1.69 (s, C$_5$*Me*$_5$), 1.99 (s, NC(*Me*)N of amidinate), 2.90 (sept, J = 6.3 Hz, C*H*Me$_2$), 4.36 (s, C$_5$*H*$_5$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, rt): δ 10.0 (C$_5$*Me*$_5$), 16.7 (NC(*Me*)N of amidinate), 22.8 and 26.2 (CH*Me*$_2$), 53.7 (*C*HMe$_2$), 68.6 (*C*$_5$H$_5$), 83.6 (*C*$_5$Me$_5$), 126.4 (N*C*N of amidinate). IR (KBr): ν (cm^{-1}) = 2973(s), 2897(s).

Preparation of a [(η^5-C$_5$Me$_5$)Ru(μ-amidinate)Ru(η^5-C$_5$H$_5$)]$^+$BF$_4^-$ (6). In a 20 mL Schlenk tube were placed **5a** (50 mg, 0.086 mmol) and $TlBF_4$ (94 mg, 0.43 mmol). Then, dichloromethane (5 mL) was added, and the resulting orange solution was stirred at room temperature for 1 h. After removal of TlCl by filtration, the filtrate was concentrated in vacuo to give **6** (32 mg, 0.051 mmol, 60%). Mp: 179 °C (dec). Because of extreme air and moisture sensitivity of **6**, attempted elemental analysis gave unsatisfactory results. Mass (M$^+$) (ESI) = 545.10. Exact mass (ESI-TOF): calcd for $^{12}C_{23}{}^1H_{37}{}^{14}N_2{}^{102}Ru_2$: 545.1044. Found: 545.1038. ^{1}H NMR (400 MHz, CD_2Cl_2, rt): δ 1.09 and 1.22 (d, J = 6.1 Hz, CH*Me*$_2$), 1.65 (s, C$_5$*Me*$_5$), 1.88 (s, NC(*Me*)N of amidinate), 2.94 (sept, J = 6.1 Hz, C*H*Me$_2$), 4.38 (s, C$_5$*H*$_5$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, rt): δ 10.0 (C$_5$*Me*$_5$), 15.7 (NC(*Me*)N of amidinate), 22.0 and 25.3 (CH*Me*$_2$), 52.4 (*C*HMe$_2$), 68.6 (*C*$_5$H$_5$), 84.6 (*C*$_5$Me$_5$), 116.9 (N*C*N of amidinate). IR (KBr): ν (cm^{-1}) = 2967(s), 2902(s).

Preparation of [(η^5-C$_5$Me$_5$)Ru(μ-amidinate)Ru(η^5-C$_5$H$_5$)(η-PMe$_3$)]$^+$PF$_6^-$ (8). In a 20 mL Schlenk tube were placed **4** (20 mg, 0.027 mmol) and PMe$_3$ (5 μL, 0.041 mmol). Then, dichloromethane (5 mL) was added, and the resulting orange solution was stirred at room temperature for 1 h. Concentration of the resulting solution gave **8** (20 mg, 0.026 mmol, 97%). The same compound was alternatively prepared by treatment of **6** with PMe$_3$ in CH_2Cl_2. Mp: 153 °C (dec). Mass (M$^+$ − PMe$_3$) (ESI) = 621.15. Exact mass (ESI-TOF) calcd for $^{12}C_{26}{}^1H_{46}{}^{14}N_2{}^{31}P_1{}^{102}Ru_2$: 621.14856. Found: 621.15020. ^{1}H NMR (400 MHz, CD_2Cl_2, rt): δ 0.69 and 1.00 (d, J = 6.0 Hz, CH*Me*$_2$), 1.69 (s, C$_5$*Me*$_5$), 1.75 (d, J_{P-H} = 8.8 Hz, P*Me*$_3$), 2.16 (s, NC(*Me*)N of amidinate), 2.77 (sept, J = 6.0 Hz, C*H*Me$_2$), 4.67 (s, C$_5$*H*$_5$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, rt): δ 9.7 (C$_5$*Me*$_5$), 16.9 (NC(*Me*)N of amidinate), 22.4 (d, J_{C-P} = 28.8 Hz, P*Me*$_3$), 23.4 and 26.1 (CH*Me*$_2$), 53.1 (*C*HMe$_2$), 69.6 (*C*$_5$H$_5$), 85.4 (*C*$_5$Me$_5$), 113.2 (N*C*N of amidinate). ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, rt): δ −12.3. IR (KBr): ν (cm^{-1}) = 2979(s), 2922(s).

Preparation of [(η^5-C$_5$Me$_5$)Ru(μ-amidinate)Ru(η-CN^{t}Bu)(η^5-C$_5$H$_5$)]$^+$PF$_6^-$ (9). In a NMR tube were placed **6** (12 mg, 0.019 mmol) and CN^{t}Bu (4 μL, 0.035 mmol). Then, CD_2Cl_2 (0.5 mL) was added, and the resulting orange solution was stirred at room temperature for 10 h. Concentration of the resulting solution in vacuo afforded **9** as a mixture of two isomers (13 mg, 0.018 mmol, 95%). Mass (M$^+$ − CN^{t}Bu) (ESI) = 628.18. Exact mass (ESI-TOF) calcd for $^{12}C_{28}{}^1H_{46}{}^{14}N_3{}^{31}P_1{}^{102}Ru_2$: 628.1779. Found: 628.1787. Major isomer: ^{1}H NMR (600 MHz, CD_2Cl_2, rt): δ 1.06 and 1.10 (d, J = 6.1 Hz, CH*Me*$_2$), 1.57 (s, CN^t*Bu*), 1.90 (s, C$_5$*Me*$_5$), 2.11 (s, NC(*Me*)N of amidinate), 3.16 (sept, J = 6.1 Hz, C*H*Me$_2$), 4.69 (s, C$_5$*H*$_5$). ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, rt): δ 13.3 (C$_5$*Me*$_5$), 17.0 (NC(*Me*)N of amidinate), 23.9 and 26.8 (CH*Me*$_2$), 55.4 (*C*HMe$_2$), 74.5 (*C*$_5$H$_5$), 89.2 (*C*$_5$Me$_5$), 122.6 (N*C*N of amidinate). Minor isomer: ^{1}H NMR (600 MHz, CD_2Cl_2, rt): δ 0.74 and 1.06 (d, J = 6.1 Hz, CH*Me*$_2$), 1.57 (s, CN^t*Bu*), 1.74 (s, C$_5$*Me*$_5$), 1.96 (s, NC(*Me*)N of amidinate), 2.72 (sept, J = 6.1 Hz, C*H*Me$_2$), 4.77 (s, C$_5$*H*$_5$). ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, rt): δ 10.3 (C$_5$*Me*$_5$), 15.7 (NC(*Me*)N of amidinate), 22.9 and 25.1 (CH*Me*$_2$), 52.4 (*C*HMe$_2$), 71.3 (*C*$_5$H$_5$), 85.7 (*C*$_5$Me$_5$), 124.4 (N*C*N of amidinate). IR (KBr): ν (cm^{-1}) = 2138(s). The NMR assignment was unequivocally carried out by H−H and C−H COSY experiments as shown in the Supporting Information.

Reaction of 4 with CO. A 5 mm ϕ NMR tube containing a solution of **6** [10 mg, 0.014 mmol in CD_2Cl_2 (0.5 mL)] was filled with CO (1 atm) and sealed. The resulting orange solution was shaken frequently at room temperature for 6 h, during which ^{1}H NMR was periodically measured. Concentration of the resulting solution in vacuo afforded a mixture of the carbonyl complexes, the ESI mass spectra of which suggested formation of [Cp*CpRu$_2$(μ-amidinate)(CO)]PF$_6$ and [Cp*CpRu$_2$(μ-amidinate)(CO)$_2$]PF$_6$. Mass (ESI) of the mixture: M$^+$[{Cp*CpRu$_2$(μ-amidinate)(CO)}$^+$] = 573.10, M$^+$-[{Cp*CpRu$_2$(μ-amidinate)(CO)$_2$}$^+$] = 601.09. Exact mass (ESI-TOF) calcd for a peak corresponding to $^{12}C_{24}{}^1H_{37}{}^{14}N_2{}^{16}O_1{}^{102}Ru_2$: 573.0993. Found: 573.0992, and that to $^{12}C_{25}{}^1H_{37}{}^{14}N_2{}^{16}O_2{}^{102}Ru_2$: 601.0942. Found: 601.0938. IR (KBr): (mixture) ν_{CO} (cm^{-1}) = 1946(s), 1811(s).

Catalytic Cyclization of *N*-Allyl-*N*-tosyltrichloroacetamide. The general procedure is as follows: In a 20 mL

Schlenk tube were placed a catalyst (0.01 mmol) or a mixture of catalyst precursor and activator (0.01 mmol each) and *N*-allyl-*N*-tosyltrichloroacetamide (35.7 mg, 0.10 mmol). Then, dichloromethane (0.75 mL) was added, and the mixture was stirred at room temperature for 0.5−4 h under an argon atmosphere. The resulting mixture was filtered through a pad of Celite, and the filtrate was concentrated. ^{1}H NMR of the crude product was measured in CD_2Cl_2 to estimate the conversion of the starting material. Chromatographic purification by silica gel eluting with a mixture of hexane and ether gave the desired product.

X-ray Data Collection and Reduction. Single crystals of **1a**, **4**, **5a**, **7**, and **8** were grown from CH_2Cl_2/pentane. X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). The data were collected at 123(2) K using ω scans in the θ range of $3.2° \le \theta \le 27.5°$ (**1a**), $3.0° \le \theta \le 27.5°$ (**4**), $3.0° \le \theta \le 27.4°$ (**5a**), $3.1° \le \theta \le 27.5°$ (**7**), and $3.0° \le \theta \le 27.5°$ (**8**). Data were collected and processed using CrystalClear (Rigaku) on a Pentium computer. The data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom Patterson methods[19] for **1a** and **8** and by direct methods[20] for **4**, **5a**, and **7**, and expanded using Fourier techniques.[21] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 6559 observed reflections and 345 variable parameters for **1a**, 11 154 observed reflections and 748 variable parameters for **4**, 4575 observed reflections and 291 variable parameters for **5a**, 7679 observed reflections and 430 variable parameters for **7**, and 7737 observed reflections and 413 variable parameters for **8**. Neutral atom scattering factors were taken from Cromer and Waber.[22] All calculations were performed using the CrystalStructure[23,24] crystallographic software package. Details of final refinement are summarized in Table 2, and the numbering scheme employed is shown in Figures 1, 2, and 3, which were drawn with ORTEP with 50% probability ellipsoids. Detailed data as well as the bond distances and angles are shown in the Supporting Information.

Electrochemical Measurements. Cyclic voltammetric studies were carried out using a BAS 50B/W electrochemical analyzer in a glove box filled with purified nitrogen. The measurement was performed at room temperature using a ruthenium complex (0.0015 mmol) in THF (5 mL) containing Bu_4NPF_6 (0.1 M) as a supporting electrolyte. A three-electrode cell was used, which was equipped with a platinum disk working electrode, a platinum wire counter electrode, and a silver reference electrode comprised of a silver wire in contact with $AgNO_3$ (0.01 M) and Bu_4NPF_6 (0.2 M) in acetonitrile.

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Supporting Information Available: Variable-temperature NMR data (**4**, **7**), ^{1}H and ^{13}C NMR data (**6**, **8**, **9**), ^{13}C NMR and ESI mass data for the products of the reaction of **4** with CO, ESI mass spectra of the compounds **4**, **7**, **8**, and **9**, cyclic voltammograms of **2** and **6**, and details of crystallographic studies (**4**, **7**, **5a**, **1a**, **8**). This material is available free of charge via the Internet at http://pubs.acs.org.

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