Access to Novel Ruthenium−Amidinate Complexes, (η^6-arene)Ru(η^2-amidinate)X and [Ru(η^2-amidinate)(MeCN)$_4$]$^+$PF$_6^-$ by Photochemical Displacement of the Benzene Ligand in (η^6-C$_6$H$_6$)Ru(η^2-amidinate)X

Taizo Hayashida and Hideo Nagashima*

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

Received March 26, 2002

Novel ruthenium−amidinate complexes, (η^6-C$_6$H$_5$R)Ru(η^2-amidinate)X (R = Me, OMe, F) (**4**) and [Ru(η^2-amidinate)(MeCN)$_4$]$^+$PF$_6^-$ (**5**) are synthesized by photochemical displacement of the benzene ligand in (η^6-C$_6$H$_6$)Ru(η^2-amidinate)X (**3**) by arenes or MeCN. The acetonitrile ligands of **5** are easily replaceable by other σ-donor ligands (L) such as pyridines, phosphines, and isocyanides to afford the corresponding derivatives, [Ru(η^2-amidinate)(MeCN)$_n$(L)$_{4-n}^+$]-PF$_6^-$ (n = 1 or 2).

Introduction

Amidinates are one of the well-investigated pseudoallyl ligands, especially for early transition metals,[1,2] and some of them have lately attracted considerable attention as a substitute of the Cp ligand in metallocene catalysts for olefin polymerization[3] and as a unique bridging ligand for dinuclear complexes.[4] Although a wide variety of transition metal amidinates have been reported, organoruthenium complexes having amidinate ligands are surprisingly rare.[5] We have recently reported the preparation and characterization of a series of organoruthenium amidinates bearing a Cp*,[6a−e] η^6-arene,[6f] or η^4-diene ligand.[6g] In particular, we found that thermally stable but highly reactive 16-electron complexes Cp*Ru(η-amidinate) (**1**) and [(η^6-arene)Ru(η-amidinate)]$^+$X$^-$ (**2**) have an unusual bonding mode of the amidinate ligand, in which π-electrons on the amidinate ligand mitigate the coordinatively unsaturated nature of the ruthenium center.[6a,f] The unique reactivity of these ruthenium amidinates prompted us to explore the synthesis of organoruthenium amidinates with novel structures other than **1** and **2**.

Photochemical substitution of the arene ligand in (η^6-arene)RuX$_2$(PR$_3$) or [(η^6-arene)Ru(η^5-C$_5$R$_5$)]$^+$ and their analogues is an interesting subject in early organometallic photochemistry,[7] leading to practical synthetic methods for several ruthenium complexes.[7,8] In particular, photoirradiation of (η^6-benzene)RuX$_2$(PR$_3$) in aromatic solvents provides access to (η^6-substituted ben-

(1) (a) Baker, R. *Chem. Rev.* **1973**, *73*, 487. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*: University Science Books: Mill Valley, CA, 1987; p 255. (c) Oldham, C. *Prog. Inorg. Chem.* **1968**, *10*, 223. (d) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: San Diego, 1983. (e) Keable, H. R.; Kilner, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1535.

(2) (a) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219. (b) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403.

(3) Recent report for early transition metal amidinates for olefin polymerization. (a) Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 4183. (b) Babcock, J. R.; Incarvito, C.; Rheingold, A. L.; Fettinger, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 5729. (c) Jayaratne, K. C.; Keaton, R. J.; Henningsen, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 10490. (d) Decker, J. M.; Geib, S. J.; Meyer, T. Y. *Organometallics* **1999**, *18*, 4417. (e) Volkis, V.; Shmulinson, M.; Averbuj, C.; Lisovskii, A.; Edelmann, F. T.; Eisen, M. S. *Organometallics* **1998**, *17*, 3155. (f) Averbuj, C.; Tish, E.; Eisen, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 8640. (g) Averbuj, C.; Eisen, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 8755. (h) Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.: Teuben, J. H. *Eur. J. Inorg. Chem.* **1998**, 1867.

(4) (a) Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Inorg. Chim. Acta* **1994**, *224*, 5. (b) Cotton, F. A.; Daniels, L. M.; Maloney, D. J.; Matonic, J. H.; Murillo, C. A. *Polyhedron* **1994**, *13*, 815. (c) Cotton, F. A.; Wojtczak, W. A. *Polyhedron* **1994**, *13*, 1337. (d) Arnold, D. I.; Cotton, F. A.; Maloney, D. J.; Matonic, J. H.; Murillo, C. A. *Polyhedron* **1997**, *16*, 133. (e) Cotton, F. A.; Daniels, L. M.; Matonic, J. H.; Murillo, C. A. *Inorg. Chim. Acta* **1997**, *256*, 277. (f) Cotton, F. A.; Daniels, L. M.; Maloney, D. J.; Matonic, J. H.; Murillo, C. A. *Inorg. Chim. Acta* **1997**, *256*, 283. (g) Cotton, F. A.; Daniels, L. M.; Feng, X.; Maloney, D. J.; Matonic, J. H.; Murillo, C. A. *Inorg. Chim. Acta* **1997**, *256*, 291. (h) Cotton, F. A.; Jordan IV, G. T.; Murillo, C. A.; Su, J. *Polyhedron* **1997**, *16*, 1831.

(5) (a) Robinson, S. D.; Sahajpal, A. *J. Organomet. Chem.* **1976**, *117*, C111. (b) Brown, L. D.; Robinson, S. D.; Sahajpal, A.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 2728. (c) Robinson, S. D.; Sahajpal, A. *J. Organomet. Chem.* **1979**, *164*, C9. (d) Sahajpal, A.; Robinson, S. D. *Inorg. Chem.* **1979**, *18*, 3572. (e) Harris, A. D.; Robinson, S. D.; Sahajpal, A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 1327. (f) Bear, J. L.; Han, B.; Huang, S. *J. Am. Chem. Soc.* **1993**, *115*, 1175.

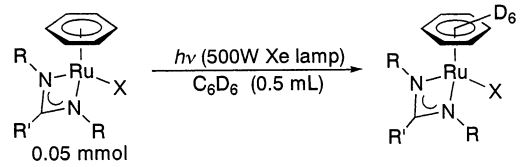
(6) (a) Yamaguchi, Y.; Nagashima, H. *Organometallics* **2000**, *19*, 725. (b) Kondo, H.; Yamaguchi, Y. Nagashima, H. *Chem. Commun.* **2000**, 1075. (c) Kondo, H.; Kageyama, A.; Yamaguchi, Y.; Haga, M.; Kirchner, K.; Nagashima, H. *Bull. Chem. Soc. Jpn.* **2001**, *10*, 1927. (d) Kondo, H.; Nagashima, H. *J. Am. Chem. Soc.* **2001**, *123*, 500. (e) Kondo, H.; Matsubara, K.; Nagashima, H. *J. Am. Chem. Soc.* **2002**, *124*, 534. (f) Hayashida, T.; Yamaguchi, Y.; Kirchner, K.; Nagashima, H. *Chem. Lett.* **2001**, 954. (g) Hayashida, T.; Miyazaki, Y.; Yamaguchi, Y.; Nagashima, Y. *J. Oraganomet. Chem.* **2001**, *634*, 167.

(7) (a) Gill, T. P.; Mann. K. R. *Organometallics* **1982**, *1*, 485. (b) Mann, K. R.; Blough, A. M.; Schrenk, J. L.; Koefod, R. S.; Freedman, D. A.; Matachek, J. R. *Pure Appl. Chem.* **1995**, *67*, 95.

(8) (a) Bennett M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233. (b) Graf, D. D.; Mann. K. R. *Inorg. Chem.* **1997**, *36*, 150. (c) Freedman, D. A.; Evju, J. K.; Pomije, M. K.; Mann, K. R. *Inorg. Chem.* **2001**, *40*, 5711. (d) Gamble, G.; Grutsch, P. A.; Ferraudi, G.; Kutal C. *Inorg. Chem. Acta* **1996**, *247*, 5. (e) Lavallee, R. J.; Kutal, C. *J. Photochem. Photobiol. A: Chem.* **1997**, *103*, 213. (f) Lavallee, R. J.; Kutal, C. *J. Organomet. Chem.* **1998**, *562*, 97. (g) Komatsuzaki, N.; Uno, M.; Kikuchi, H.; Takahashi, S. *Chem. Lett.* **1996**, 677.

10.1021/om020227y CCC: $22.00
Publication on Web 08/16/2002

Table 1. Substituent Effects on Arene Photodisplacement Reactions of 3 in C_6D_6[a]



entry	complex	R	R′	X	time/ h	conversion/ %[b]	selectivity/ %[b]
1	**3a**	^{t}Bu	Ph	Cl	1	82	>99
					6	>99	>99
2	**3b**	tBu	Ph	Br	1	71	>99
					5	>99	>99
3	**3c**	^{i}Pr	Ph	Cl	1	49	58
					5	91	43
4	**3d**	^{i}Pr	Me	Cl	1	78	98
					5	>99	61

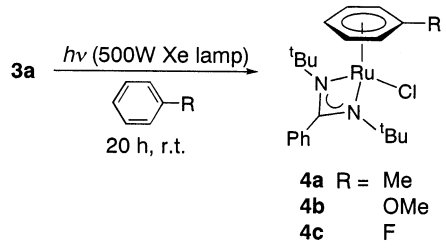
[a] Reaction conditions: the C_6D_6 solution of **3** containing $(CHCl_2)_2$ as an internal standard in an NMR tube sealed under 10^{-3} Torr atmosphere was irradiated by a Xe lamp through a water filter. [b] Calculated by ^{1}H NMR spectra.

zene)$RuX_2(PR_3)$,[8a] whereas that of [(η^6-benzene)Ru(η^5-C_5R_5)]$^+$ in acetonitrile affords [(η^5-C_5R_5)Ru$(MeCN)_3]^+$.[8b−g] Since acetonitrile ligands in metal complexes are generally labile for ligand substitution reaction,[9] the latter acetonitrile complexes, [(η^5-C_5R_5)Ru$(MeCN)_3]^+$, are useful as attractive precursors for a variety of ruthenium complexes[10] or catalysts in organic synthesis[11] by reactions with nitrogen, phosphorus, olefinic, and acetylenic compounds. This prompted us to examine photoassisted replacement of the benzene ligand in (η^6-C_6H_6)Ru(η^2-amidinate)X by substituted benzene or MeCN, which should lead to organoruthenium amidinate with a novel structure. The reaction actually proceeded smoothly to result in efficient preparation of (η^6-C_6H_5R)Ru(η^2-amidinate)X (R = Me, OMe, F) (**4**) and [Ru(η^2-amidinate)-$(MeCN)_4]^+X^-$ [X = PF_6 (**5**), Cl (**5′**)]. Furthermore, the acetonitrile complex **5** is reactive toward various σ-donor ligands (L), leading to novel organoruthenium amidinates, [Ru(η^2-amidinate)$(MeCN)_n(L)_{4-n}]^+X^-$.

Results and Discussion

Photochemical Arene Exchange Reactions. We first investigated the photosensitivity of (η^6-C_6H_6)Ru-(η^2-amidinate)X (X = halogen) (**3a**−**3d**) in C_6D_6 as shown in Table 1. Photoirradiation of a C_6D_6 solution of **3a**−**3d** by a 500 W Xe lamp at room temperature resulted in displacement of the C_6H_6 ligand by a C_6D_6 molecule, which can be monitored by ^{1}H NMR. For instance, the signal intensity of the C_6H_6 ligand at 5.02 ppm on the ^{1}H NMR spectra of **3a** gradually diminished during the photoirradiation, and instead that due to the free C_6H_6 appeared. No sign of H−D exchange in the amidinate ligand was observed. The reaction was over after 5 h, during which no byproduct was observed in the ^{1}H NMR spectra. In the ^{13}C NMR spectrum of the product the C_6D_6 molecule coordinated to the ruthenium is observed at 81.5 ppm as a triplet (J_{CD} = 24.5 Hz), whereas the mass spectrum showing a parent mass peak at *m/e* 451 is in accord with the formation of (η^6-C_6D_6)Ru{η^2-^{t}BuNC(Ph)=N^{t}Bu}Cl (**3a-*d*$_6$**). Halogen atom did not affect the rate or the selectivity of the reaction; photosubstitution of the Br homologue **3b** proceeded without formation of byproducts (Table 1, entry 2). In contrast, the rate and selectivity were affected by the substituents of the amidinate ligands; reactions of **3c** and **3d** were accompanied by side reactions to give the corresponding C_6D_6 complexes in lower yields (Table 1, entries 3 and 4).

Scheme 1



As shown in Scheme 1, the photoirradiation of **3a** in toluene, anisole, and fluorobenzene afforded the corresponding arene complexes (η^6-C_6H_5R)Ru(η^2-amidinate)X {R = Me (**4a**), OMe (**4b**), F (**4c**)} in good yield.[12] Assignment of **4** was performed by ^{1}H and ^{13}C NMR, mass spectra, and elemental analyses, and supported by crystallography of the anisole complex **4b** as shown in Figure 1.[16] Either electron-donating anisole or electron-deficient fluorobenzene reacted with **3a** at a similar rate and with good selectivity.[12]

Photochemical Access to [Ru(η^2-amidinate)-$(MeCN)_4]^+X^-$ [X = PF_6 (5), Cl (5′)]. During the studies described above, we found that photoirradiation of **3a** in PhCN afforded a complicated mixture of products, while dissociation of the benzene ligand was observed in ^{1}H NMR. This can be attributed to coordination of not only the aromatic ring of PhCN but also its nitrile moiety to the intermediate of the photochemical sub-

(9) (a) See ref 1b, pp 199. (b) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1.

(10) For a recent review: Slugovc, C.; Rüba, E.; Schmid, R.; Kirchner, K.; Mereiter, K. *Monatsh. Chem.* **2000**, *131*, 1241.

(11) Recent progress: (a) B. M. Trost, Pinkerton, A. B. *Angew. Chem., Int. Ed.* **2000**, *39*, 360. (b) Trost. B. M.; Machacek. M.; Schnaderbeck, M. J. *Org. Lett.* **2000**, *2*, 1761. (c) Trost, B. M.; Toste, F. D.; Shen, H. *J. Am. Chem. Soc.* **2000**, *122*, 2379. (d) Trost, B. M.; Brown, R. E.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 5877. (e) Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc.* **2000**, *122*, 8081. (f) Trost, B. M.; Pinkerton, A. B.; Kremzow, D. *J. Am. Chem. Soc.* **2000**, *122*, 12007. (g) Trost, B. M.; Shen, H. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2313. (h) Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2001**, *123*, 8862.

(12) Only a few examples have been reported on transition metal complexes bound to fluorobenzenes in the η^6-coordination mode. To our knowledge, fluorobenzene complexes of ruthenium are unknown. Some examples are seen in chromium chemistry;[13] $(FC_6H_5)Cr(CO)_3$ is prepared from $Cr(CO)_6$ only in low yields due to the concomitantly occurring defluorination.[14] In the arene exchange reaction of (arene)-$Cr(CO)_3$[15a] or (arene)$Cr(CO)_2(SiCl_3)_2$,[15b] electron-deficient FC_6H_5 is a weakly coordinated ligand to the chromium atom, being easily replaceable by benzene. Thus, successful exchange of coordinated benzene by fluorobenzene in the present report is not common.

(13) (a) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 3, Chapter 26.2. (b) Michael, J. M. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 5, Chapter 8, and references therein.

(14) Milan, H.; Stefan, T. *J. Organomet. Chem.* **1990**, *393*, 115.

(15) (a) Christopher, A. L. M.; Peter, L. P. *J. Chem. Res. Minipr.* **1979**, 1754. (b) Balaji, R. J.; Kenneth, J. K. *J. Coord. Chem.* **1995**, *34*, 31, and references therein.

(16) Crystal data for **4b**: $C_{22}H_{31}N_2OClRu$; M = 476.01, monoclinic, a = 10.1667(6) Å, b = 17.8999(11) Å, c = 11.9921(7) Å, β = 93.309(2)°, V = 2178.7(2) Å^3, T = 293 K, space group, *Cc* (No. 9), Z = 4, μ(Mo Kα) = 0.856 mm^{-1}, 2489 reflections measured, 2489 unique (R_{int} = 0.000), 2053 observed (>2σ), final residuals R_1 = 0.0413, wR_2 = 0.1021 [I > 2σ(I)]; R_1 = 0.0549, wR_2 = 0.1114 (all data).

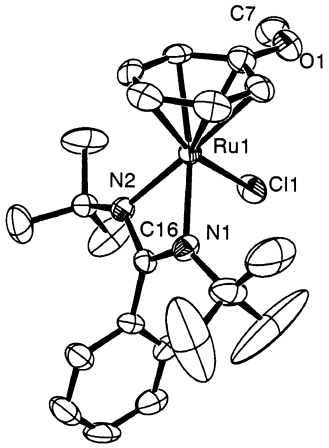


Figure 1. ORTEP drawing of **4b** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Representative bond distances (Å) and angles (deg) are as follows: Ru1−Cl1 = 2.408(2), Ru1−N1 = 2.103(6), Ru1−N2 = 2.115(10), N1−C16 = 1.325(10), N2−C16 = 1.342(9); N1−Ru1−N2 = 61.7(3), N1−C16−N2 = 108.5(7), N1−Ru1−Cl1 = 84.3(2), N2−Ru1−Cl1 = 86.0(3).

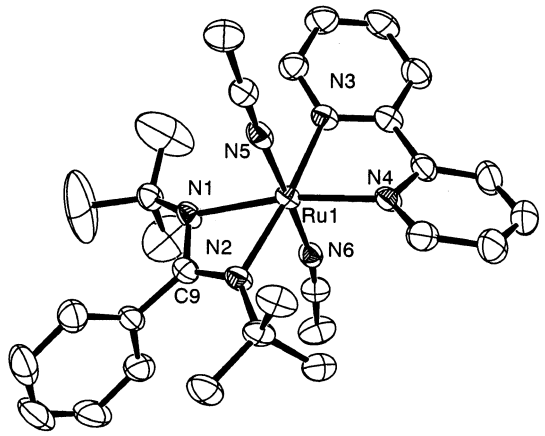
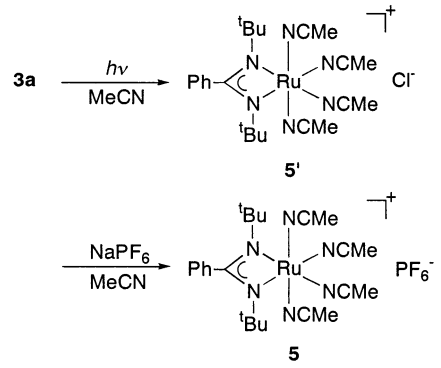


Figure 2. ORTEP drawing of **6** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms and the counteranion are omitted for clarity. Representative bond distances (Å) and angles (deg) are as follows: Ru1−N1 = 2.171(4), Ru1−N2 = 2.103(4), Ru1−N3 = 2.088(4), Ru1−N4 = 2.114(4); N1−Ru1−N2 = 61.48(15), N1−C9−N2 = 110.6(4).

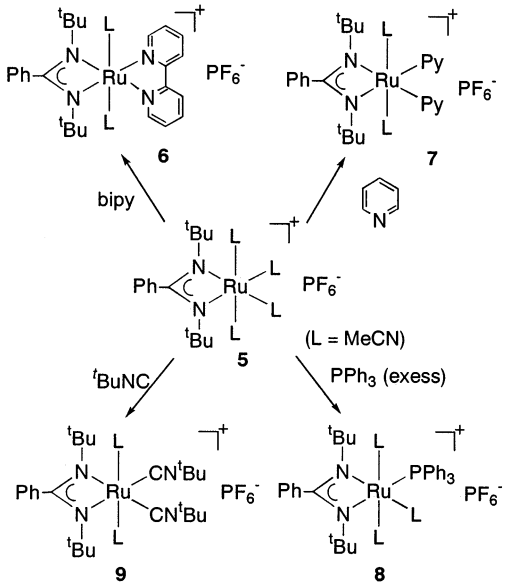
Scheme 2



stitution. Coordination of the nitrile to the intermediates was proved by the result that photoirradiation of **3a** in MeCN afforded the cationic ruthenium−amidinate complex $[Ru(\eta^2\text{-}^t\text{BuNCPh=N}^t\text{Bu})(MeCN)_4]^+Cl^-$ (**5′**) in good yield, as shown in Scheme 2. This complex is highly unstable in both solid and solution states toward air and moisture, but could be assigned by NMR spectroscopy. Anion exchange of **5′** by PF_6^- gave $[Ru(\eta^2\text{-}^t\text{BuNCPh=N}^t\text{Bu})(MeCN)_4]^+PF_6^-$ (**5**), which is stable in MeCN or acetone, but slowly decomposed to give paramagnetic products in chlorinated solvents. Exposure of the MeCN or acetone solution of **5** to air caused instant formation of the paramagnetic complexes.

NMR and mass spectra of **5** suggested similarities in the structure of **5** to that of **5′**. For instance, two ^1H resonances due to the MeCN ligands in acetone-d_6 are seen at 2.57 and 2.67 ppm as singlets in a ratio of 1:1. The integral values of these signals relative to the amidinate ligand suggest the existence of four MeCN ligands, two of them being magnetically equivalent. Two ^{t}Bu groups of the amidinate ligand are magnetically equivalent and observed as a singlet at 1.10 ppm. Similarly, the ^{13}C NMR spectrum of **5** in acetone-d_6 showed the signals due to the MeCN ligands at 3.3 and 3.5 ppm for the methyl carbons and at 123.1 and 124.1 ppm for the nitrile carbons. These results are in accord with the octahedral geometry of **5**, in which of the two

Scheme 3



MeCN ligands are coordinated to the ruthenium at the trans positions of the N atoms of the amidinate ligand, and the other two MeCN ligands are bound to the metal at the axial positions, as illustrated in Scheme 2.

Acetonitrile Complex 5 as a Precursor of New Organoruthenium Amidinates. As described above, the acetonitrile ligand is generally reactive toward ligand substitution. In fact, reaction of **5** with several two-electron-donor ligands resulted in formation of new organoruthenium amidinates, as shown in Scheme 3. Treatment of **5** with bipyridine in acetone afforded $[Ru(\eta^2\text{-amidinate})(MeCN)_2(bipy)]^+PF_6^-$ (**6**) at room temperature. The structure of **6** was assigned by NMR and mass spectroscopy and supported by X-ray crystallography. In the ^1H and ^{13}C NMR spectra of **6** in acetone-d_6, two MeCN ligands (δ_H 2.48 ppm, δ_C 3.2, 123.0 ppm) or two ^{t}Bu groups of the amidinate were magnetically equivalent (δ_H 1.16 ppm, δ_C 34.3, 54.9 ppm). The molecular structure determined by crystallography is illustrated in Figure 2 and reveals that this complex has a distorted octahedral structure and that

the bipyridine ligand coordinates at the trans position of the amidinate ligand.[17] The complex **5** also reacted with pyridine to give a bispyridine complex, $[Ru(\eta^2\text{-amidinate})(MeCN)_2(py)_2]^+PF_6^-$ (**7**). The reaction of **5** with PPh_3 afforded a monophosphine complex $[Ru(\eta^2\text{-amidinate})(MeCN)_3(PPh_3)]^+PF_6^-$ (**8**) in good yield. The existence of the magnetically inequivalent ^{t}Bu groups of the amidinate ligands in the NMR spectrum of **8** suggests that a PPh_3 bonds to the ruthenium atom at the trans position of the nitrogen atoms of amidinate. Further substitution of the MeCN ligand by PPh_3 did not occur even in the presence of an excess amount of PPh_3 and by application of longer reaction time; this could be attributed to steric bulkiness of the PPh_3 ligand, which prevented the introduction of the second PPh_3. The complex $[Ru(\eta^2\text{-amidnate})(MeCN)_2(^tBuNC)_2]^+PF_6^-$ (**9**) was also obtained through the reaction of **5** with excess ^{t}BuNC in acetone. The reaction was slower than that with pyridine or bipyridine, and NMR observation of the initial stage of the reaction showed the formation of the monosubstituted complex $Ru(\eta^2\text{-amidnate})(MeCN)_3(^tBuNC)]^+PF_6^-$ (**9′**) as an intermediate. Complex **5** does not react with tmeda, ^{t}BuCN, olefins (vinyl ethyl ether, cyclooctadiene), arenes (benzene, toluene), or acetylenes (dimethylacetylene, phenyacetylene, 1,6-heptadiyne) even at higher temperature, in contrast to the ability of $[CpRu(MeCN)_3]^+$ to react with these compounds.[10]

Conclusion

As described above, facile access of novel ruthenium−amidinate complexes, $(\eta^6\text{-}C_6H_5R)Ru(\eta^2\text{-amidinate})X$ (**4**) and $[Ru(\eta^2\text{-amidinate})(MeCN)_4]^+X^-$ (**5**), can be accomplished by photochemical displacement of the benzene ligand in **3** by substituted benzene or MeCN. Besides the utility of the present reaction as a synthetic method for these new ruthenium amidinates, high reactivity of **5** toward pyridine, phosphine, and isonitrile ligands opens the way to synthesize $[Ru(\eta^2\text{-amidinate})(MeCN)_n(L)_{4-n}]^+X^-$. We are currently concentrating on a search for new reactions and catalytic applications of **5**.

Experimental Sections

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; Ph_2CO/Na, C_6H_5OMe, CH_2Cl_2; CaH_2, C_6H_5F; P_2O_5, acetone; MS4A). Reagents employed in this research were used without further purification. $(\eta^6\text{-}C_6H_6)Ru(\eta^2\text{-amidinate})X$ were prepared as described in the literature.[6f] ^{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; 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. EI and FAB mass spectra were recorded on a JEOL Mstation JMS-70 apparatus. Elemental analyses were performed by the Elemental Analysis Center, Faculty of Science, Kyushu University. The Xe lamp of USHIO Inc. (500 W, type 50101AA-A) was used for photoreactions of **3**.

The MeCN derivatives, **5**, **6**, **7**, and **9**, are unstable toward air and moisture due to facile liberation of the MeCN ligands, and attempted elemental analyses gave unsatisfactory data. Thus, all of these complexes were characterized by HRMS, and actual charts of ^{1}H and ^{13}C NMR spectra of **5**, **6**, **7**, and **9** are shown in the Supporting Information as the evidence of purity.

NMR Studies on Photoirradiation of 3 in C_6D_6. A dry C_6D_6 solution (0.5 mL) of **3** (0.05 mmol) and $Cl_2CHCHCl_2$ (ca. 5 μL) was degassed and sealed in a NMR tube under reduced pressure (10^{-3} Torr) at −78 °C. The solution was photoirradiated by a 500 W Xe lamp through a water filter. The conversion of **3** and the selectivity of the product were calculated by comparison of the integral values of the ^{1}H NMR signal of **3** or the product with that of $Cl_2CHCHCl_2$.

$(\eta^6\text{-}C_6D_6)Ru\{\eta^2\text{-}^tBuNC(Ph)=N^tBu\}Cl$ (3a-d_6): EI mass $[M^+] = 452$; $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6) δ 34.09 ($C(CH_3)_3$), 55.78 ($C(CH_3)_3$), 81.49 (t, $J_{CD} = 26.4$ Hz; C_6D_6), 126.95 126.97, 128.41, 129.64, 132.06, 139.97 (C_6H_5), 174.50 (NCN).

General Procedure for the Arene Substitution of 3. In a Schlenk tube, a solution (5 mL) of **3a** (0.024 M) in aromatic solvents was irradiated by a Xe lamp with stirring for 20 h at room temperature. After removal of the solvent, the desired product was obtained as an analytically pure form (yield 60−99%).

$(\eta^6\text{-}C_6H_5Me)Ru\{\eta^2\text{-}^tBuNC(Ph)=N^tBu\}Cl$ (4a): yellow solids; mp 219 °C (dec). Anal. Calcd for $C_{22}H_{31}N_2ClRu$: C, 57.44; H, 6.79; N, 6.09. Found: C, 57.39; H, 6.78; N, 6.06. EIMS: $[M^+] = 460$. ^{1}H NMR (400 MHz, C_6D_6): δ 1.25 (s, 18H; $C(CH_3)_3$), 2.12 (s, 3H; $PhCH_3$), 4.74 (d, $J = 5.9$ Hz, 2H; *o*-C_6H_5-Me), 4.84 (t, $J = 5.3$ Hz, 1H; *p*-C_6H_5Me), 5.05 (t, $J = 5.6$ Hz, 2H; *m*-C_6H_5Me), 6.82−7.00 (m, 3H; C_6H_5), 7.09−7.13 (m, 1H; C_6H_5), 7.49 (d, $J = 7.6$ Hz, 1H; C_6H_5). $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 19.56 ($PhCH_3$) 34.14 ($C(CH_3)_3$), 55.57 ($C(CH_3)_3$), 75.97, 81.40, 82.33 98.72 (C_6H_5Me), 126.90 126.93, 128.35, 129.81, 132.13, 140.07 (C_6H_5), 174.31 (NCN).

$(\eta^6\text{-}C_6H_5OMe)Ru\{\eta^2\text{-}^tBuNC(Ph)=N^tBu\}Cl$ (4b): brown solids; mp 206 °C (dec). Anal. Calcd for $C_{22}H_{21}ON_2ClRu$: C, 55.51; H, 6.56; N, 5.88. Found: C, 55.37; H, 6.55; N, 5.78. EIMS: $[M^+] = 476$. ^{1}H NMR (600 MHz, C_6D_6): δ 1.25 (s, 18H; $C(CH_3)_3$), 3.61 (s, 3H; $PhOCH_3$), 4.52 (t, $J = 5.1$ Hz, 1H; *p*-C_6H_5-OMe), 4.68 (d, $J = 5.7$ Hz, 2H; *o*-C_6H_5OMe), 5.20 (t, $J = 5.3$ Hz, 2H; *m*-C_6H_5OMe), 6.86 (t, $J = 7.8$ Hz, 1H; C_6H_5), 6.89−6.97 (m, 1H; C_6H_5), 7.11 (d, $J = 7.1$ Hz, 1H; C_6H_5), 7.49 (d, $J = 7.3$ Hz, 1H; C_6H_5). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 34.01 ($C(CH_3)_3$), 55.65, 55.67 ($C(CH_3)_3$ and $C_6H_5OCH_3$), 62.63, 69.63, 85.51, 135.34 ($C_6H_5OCH_3$), 126.91 126.99, 128.35, 129.74, 132.20, 140.06 (C_6H_5), 173.89 (NCN).

$(\eta^6\text{-}C_6H_5F)Ru\{\eta^2\text{-}^tBuNC(Ph)=N^tBu\}Cl$ (4c): yellow solids; mp 207 (dec). Anal. Calcd for $C_{21}H_{28}N_2FClRu$: C, 54.36; H, 6.08; N, 6.04. Found: C, 54.00; H, 6.06; N, 5.91. EIMS: $[M^+] = 464$. ^{1}H NMR (400 MHz, C_6D_6): δ 1.25 (s, 18H; $C(CH_3)_3$), 4.43 (td, $J_{HH} = 5.9$ Hz, $J_{HF} = 3.9$ Hz, 1H; *p*-C_6H_5F), 4.87 (dd, $J_{HH} = 5.9$ Hz, $J_{HF} = 2.9$ Hz, 2H; *o*-C_6H_5Me), 5.14 (td, $J_{HH} = 5.8$ Hz, $J_{HF} = 2.9$ Hz, 2H; *m*-C_6H_5Me), 6.80−6.96 (m, 3H; C_6H_5), 7.09−7.13 (m, 1H; C_6H_5), 7.44 (d, $J = 7.6$ Hz, 1H; C_6H_5). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 34.03 (d; $J_{CF} = 1.2$ Hz, $C(CH_3)_3$), 55.71 ($C(CH_3)_3$), 65.90 (d; $J_{CF} = 22.3$ Hz, C_6H_5F), 73.24 (C_6H_5F), 87.76 (d; $J_{CF} = 7.0$ Hz, C_6H_5F), 126.90, 127.10, 128.55, 129.65, 132.07 (C_6H_5), 137.00 (d; $J_{CF} = 276.8$ Hz, C_6H_5F), 139.76 (C_6H_5), 174.82 (NCN).

Preparation of $[Ru(\eta^2\text{-}^tBuNC(Ph)=N^tBu)(MeCN)_4]^+PF_6^-$ (5). In a Schlenk tube, a MeCN solution (10 mL) of **3a** (65 mg, 0.15 mmol) was irradiated by a Xe lamp with stirring for 20 h at room temperature. Formation of $[Ru(\eta\text{-}^tBuNC(Ph)=N^tBu)(MeCN)_4]^+Cl^-$ (**5′**) was confirmed by NMR. The ^{1}H NMR data are listed below. The solution was treated with $NaPF_6$ (25 mg,

(17) Crystal data for **6**: $C_{29}H_{37}N_6F_6PRu$; $M = 715.69$, monoclinic, $a = 9.1744(5)$ Å, $b = 13.6993(7)$ Å, $c = 24.8932(17)$ Å, $\beta = 94.3965(10)°$, $V = 2178.7(2)$ Å^3, $T = 293$ K, space group, $P2_1/n$ (No. 14), $Z = 4$, μ(Mo Kα) = 0.620 mm^{-1}, 7047 reflections measured, 7047 unique ($R_{int} = 0.000$), 4931 observed ($>2\sigma$), final residuals $R_1 = 0.0553$, $wR_2 = 0.1460$ [$I > 2\sigma(I)$]; $R_1 = 0.0874$, $wR_2 = 0.1671$ (all data).

0.15 mmol) and stirred for 1 h. Insoluble inorganic salts were removed by filtration. After removal of the solvent, the residue was washed with dry Et_2O and dried in vacuo to give **5** (56 mg, 0.087 mmol, 58%) as white solids. Mp: 181 °C (dec). FABMS: $[M^+] = 497$ (cationic part of **5**). FAB-HRMS: calcd for $C_{23}H_{35}N_6Ru$, 497.1963; found, 497.1973. ^1H NMR (600 MHz, acetone-d_6): δ 0.94 (s, 18H; $C(CH_3)_3$), 2.57 (s, 6H; CH_3CN), 2.67 (s, 6H; CH_3CN), 7.26 (ddd, J = 8.0, 2.0, 1.5 Hz, 2H; C_6H_5), 7.28 (dddd, J = 7.9, 7.3, 1.7, 1.5 Hz, 2H; C_6H_5), 7.34 (tt, J = 7.3, 2.0 Hz, 1H; C_6H_5). $^{13}C\{^1H\}$ NMR (150 MHz, acetone-d_6): δ 3.29, 3.47 (CH_3CN), 33.26 ($C(CH_3)_3$), 54.77 ($C(CH_3)_3$), 123.13, 124.11 (CH_3CN), 127.82, 128.83, 130.93, 140.87 (C_6H_5), 170.47 (NCN).

5′: ^1H NMR (600 MHz, CD_3CN) δ 0.91 (s, 18H; $C(CH_3)_3$), 2.40 (s, 6H; CH_3CN), 2.47 (s, 6H; CH_3CN), 7.21 (ddd, J = 6.1, 1.8, 1.4. Hz, 2H; C_6H_5), 7.26 (tdd, J = 7.5, 1.8, 1.3 Hz, 2H; C_6H_5), 7.35 (tt, J = 7.4, 1.5 Hz, 1H; C_6H_5).

General Procedure for the Ligand Exchange of 5. In a Schlenk tube, an acetone solution (0.023 M) of **5** was treated with the ligand (pyridine, PPh_3; 2 equiv to **5**, bipy; 1 equiv to **5**, and ^{t}BuNC, 5 equiv to **5**) at −78 °C. The mixture was then allowed to warm to room temperature with stirring for 2−10 h. The solvent was removed, and then recrystallization by the CH_2Cl_2/pentane solution for **6**, **7** or wash with Et_2O for **8**, **9** gave the desired product in pure form.

[Ru(η^2-^{t}BuNC(Ph)=N^{t}Bu)(bipy)(MeCN)$_2$]$^+$PF$_6^-$ (6): black crystals (95% yield); mp 192 °C (dec). FAB-MS: $[M^+] = 571$ (cationic part of **6**). FAB-HRMS: calcd for $C_{29}H_{37}N_6Ru$, 517.2123; found, 517.2131. ^1H NMR (600 MHz, acetone-d_6): δ 1.16 (s, 18H; $C(CH_3)_3$), 2.48 (s, 6H; CH_3CN), 7.27−7.35 (m, 5H; C_6H_5), 7.62 (ddd, J = 7.3, 5.9, 1.5 Hz, 2H; bipy), 8.07 (dt, J = 6.0, 1.3 Hz, 2H; bipy), 8.50 (d, J = 8.2 Hz, 2H; bipy), 8.69 (d, J = 5.8 Hz, 2H; bipy). $^{13}C\{^1H\}$ NMR (150 MHz, acetone-d_6): δ 3.22 (CH_3CN), 34.26 ($C(CH_3)_3$), 54.87 ($C(CH_3)_3$), 123.03 (CH_3CN), 123.26, 125.21 (bipy), 127.81, 128.87, 130.95 (C_6H_5), 136.94 (bipy), 142.08 (C_6H_5), 157.62, 160.36 (bipy), 170.78 (NCN).

[Ru(η^2-^{t}BuNC(Ph)=N^{t}Bu)(C$_5$H$_5$N)$_2$(MeCN)$_2$]$^+$PF$_6^-$ (7): bright yellow crystals (84% yield); mp 128 °C (dec). FAB-MS: $[M^+] = 573$ (cationic part of **7**). FAB-HRMS: calcd for $C_{29}H_{39}N_6Ru$, 573.2280; found, 573.2288. ^1H NMR (600 MHz, acetone-d_6): δ 0.79 (s, 18H; $C(CH_3)_3$), 2.96 (s, 6H; CH_3CN), 7.23 (ddd, J = 7.5, 5.1, 0.9 Hz, 4H; C_5H_5N), 7.30−7.34 (m, 2H; C_6H_5), 7.34−7.38 (m, 3H; C_6H_5), 7.68 (tt, J = 7.5, 1.3 Hz, 2H; C_5H_5N), 9.08 (ddd, J = 5.1, 1.5, 0.9 Hz, 4H; C_5H_5N). $^{13}C\{^1H\}$ NMR (150 MHz, acetone-d_6): δ 4.29 (CH_3CN), 33.73 ($C(CH_3)_3$), 54.98 ($C(CH_3)_3$), 124.65 (CH_3CN), 125.40 (C_6H_5N), 127.81, 128.73, 131.35(C_6H_5), 136.04 (C_6H_5N), 141.31 (C_6H_5), 155.1 (C_6H_5N), 171.13 (NCN).

Ru(η^2-^{t}BuNC(Ph)=N^{t}Bu)(PPh$_3$)(MeCN)$_3$]$^+$PF$_6^-$ (8): yellow solids (64% yield); mp 150 °C (dec). FAB-MS: $[M^+] = 718$ (cationic part of **8**). Anal. Calcd for $C_{39}H_{47}N_5PRu$: C, 54.29; H, 5.49; N, 8.12. Found: C, 53.47; H, 5.39; N, 7.95. FAB-HRMS: calcd for $C_{39}H_{47}N_5PRu$, 718.2613; found, 718.2623. ^1H NMR (400 MHz, acetone-d_6): δ 0.71 (s, 9H; $C(CH_3)_3$), 1.13 (s, 9H; $C(CH_3)_3$), 1.87 (d, J_{HP} = 1.0 Hz, 3H; CH_3CN), 2.59 (d, J_{HP} = 0.5 Hz, 6H; CH_3CN), 7.33 (tt, J = 6.9, 1.7 Hz, 2H; C_6H_5), 7.37−7.46 (m, 3H; C_6H_5), 7.47−7.53 (m, 9H; C_6H_5), 7.59−7.70 (m, 6H; C_6H_5). ^{13}C NMR (100 MHz, acetone-d_6): 2.99 (CH_3CN), 3.72 (CH_3CN), 33.83 (d, J_{CP} = 1.2 Hz; $C(CH_3)_3$), 35.16 (d, J_{CP} = 0.8 Hz; $C(CH_3)_3$), 53.37 ($C(CH_3)_3$), 56.41 (d, J_{CP} = 2.9 Hz; $C(CH_3)_3$), 125.32 (CH_3CN), 127, 31 (CH_3CN), 127.62 (C_6H_5), 128.80 (d; J_{CP} = 8.7 Hz; C_6H_5), 129.17 (C_6H_5), 130.37 (d; J_{CP} = 2.1; C_6H_5), 131.88 (C_6H_5), 135.11 (d, J_{CP} = 9.9 Hz; C_6H_5), 135.32 (d, J_{CP} = 9.9 Hz; C_6H_5), 135.51 (d, J_{CP} = 37.9 Hz; C_6H_5), 141.54 (d, J_{CP} = 2.5 Hz; C_6H_5), 175.92 (d, J_{CP} = 2.5 Hz; NCN). $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 50.76 (s; PPh_3), 350.54 (quin, J_{PF} = 708 Hz).

[Ru(η^2-^{t}BuNC(Ph)=N^{t}Bu)(^{t}BuNC)$_2$(MeCN)$_2$]$^+$PF$_6^-$ (9): white solids (88% yield); mp 85 °C (dec). FAB-MS: $[M^+] = 581$ (cationic part of **9**). FAB-HRMS: calcd for $C_{29}H_{47}N_6Ru$, 581.2906; found, 581.2914. ^1H NMR (600 MHz, acetone-d_6): δ 1.01 (s, 18H; $C(CH_3)_3$ of the amidinate), 1.56 (s, 18H; $(CH_3)_3C$ of the isocyanide), 2.63 (s, 6H; CH_3CN), 7.25−7.40 (m, 5H; C_6H_5). ^{13}C NMR (150 MHz, acetone-d_6): δ 3.02 (CH_3CN), 31.20 ($C(CH_3)_3$ of the amidinate), 33.76 ($C(CH_3)_3$ of the isocyanide), 54.17, 58.15 ($C(CH_3)_3$), 123.83 (CH_3CN), 127.88, 129.01, 130.63, 141.33 (C_6H_5), 173.68 (NCN). IR (KBr): ν 2157, 2112 cm^{-1} (NC). The ^{13}C signal of the isocyanide carbon of ^{t}BuNC was not observed.

Acknowledgment. This work was partially supported by the Japan Society for the Promotion of Science (Grants-in-Aid for Scientific Research 10450343, 13540374, 13029090). Help for X-ray analysis by Dr. Kouki Matsubara (Kyushu University) is acknowledged.

Supporting Information Available: ^1H and ^{13}C NMR charts of **5**, **6**, **7**, and **9** and text giving the tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond lengths and angles for **4b** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020227Y