Preparation, Structure, and Reactivities of Amido-Bridged Dinuclear Rhodium(III) and Rhodium(II) Complexes

Hiroyuki Matsuzaka,* Teruo Kamura, Ko Ariga, Yuko Watanabe, Takashi Okubo, Tomohiko Ishii, Masahiro Yamashita, Mitsuru Kondo,† and Susumu Kitagawa†

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Minami-osawa, Hachioji, Tokyo 192-0397, Japan

Received October 21, 1999

*Summary: Reaction of [Cp*RhX(μ$_2$-X)]$_2$ (**2a**, X = Cl; **2b**, X = Br) with (LiNH)$_2$C$_{10}$H$_6$-1,8 gave the novel amido-bridged dinuclear Rh(III) complex [Cp*Rh{(μ$_2$-NH)$_2$C$_{10}$H$_6$-1,8}(μ$_2$-X)RhCp*]X (**3a**, X = Cl; **3b**, X = Br), which further converted to the Rh(II) complex Cp*Rh{(μ$_2$-NH)$_2$C$_{10}$H$_6$-1,8}RhCp* (**4**) by Na/Hg reduction. Treatment of **4** with benzyl bromides produced **3b** and the corresponding bibenzyl derivatives, whereas protonation of **4** with CF$_3$CO$_2$H afforded [Cp*Rh{(μ$_2$-NH)$_2$C$_{10}$H$_6$-1,8}(μ$_2$-H)RhCp*]O$_2$CCF$_3$ (**5**). Complex **2a** also reacted with 2 equiv of LiNHC$_6$H$_4$R-p to yield [Cp*Rh(μ$_2$-NHC$_6$H$_4$R-p)$_3$RhCp*]Cl (**6**·Cl: **6a**, R = Me; **6b**, R = H; **6c**, R = Cl).*

In contrast to the extensive studies on the amido complexes of early transition elements, those of the late transition metals have been much less developed.[1] We have recently shown that the Ir(III) complex [Cp*IrCl-(μ$_2$-Cl)]$_2$ (**1**, Cp* = η^5-C$_5$Me$_5$) is an excellent precursor of a new family of this class of compounds and a series of amido-bridged diiridium complexes were readily obtained from **1** upon treatment with lithium arylamide.[2] These findings prompted us to extend this chemistry to the dinuclear rhodium system. Here we wish to describe the preparation, structure, and reactivities of arylamido-bridged dirhodium complexes.[3,4,5]

Reaction of [Cp*RhX(μ$_2$-X)]$_2$ (**2a**, X = Cl; **2b**, X = Br) with 1 equiv of (LiNH)$_2$C$_{10}$H$_6$-1,8 at −90 °C to room temperature produces [Cp*Rh{(μ$_2$-NH)$_2$C$_{10}$H$_6$-1,8}(μ$_2$-X)RhCp*]X (**3a**, X = Cl; **3b**, X = Br) in moderate yield (Scheme 1).[6] Complex **3** was isolated as an orange microcrystalline solid and spectroscopically characterized,[6] with **3b** being further defined by X-ray crystallography.[7] The ^{1}H NMR spectrum of **3b** shows signals due to Cp* and NH protons at δ 1.17 and 4.85, respectively, together with three sets of resonances due to the naphthyl group. The electronic conductivity of **3** in chloroform (31−36 S cm^2 mol^{-1}) compares well to that of a chloroform solution of [Bu$^n_4$N]BF$_4$ (23 S cm^2 mol^{-1}). These features suggest the triply bridged structure of **3** shown in Scheme 1, which has been unequivocally confirmed by the X-ray diffraction analysis of **3b**. Although the quality of the crystal structure is low,[7] an ORTEP drawing of a cationic portion of **3b**, shown in Figure 1, clearly indicates a dinuclear structure in which the two Cp*Rh units are triply bridged by the diamidonaphthalene and the Br ligands. Two Cp* moieties are almost parallel (dihedral angle 4.61°) and are in the eclipsed conformation. The intramolecular distance between the two Rh atoms (3.04 Å) indicates the absence

† Present address: Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan.

(1) (a) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1. (b) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (c) Lappert, M. F.; Power, P. P.; Sangerand, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, U.K., 1980. (d) Driver, M. S.; Harwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 4708 and references therein. (e) Anwander, R. *Top. Curr. Chem.* **1996**, *179*, 33.

(2) Matsuzaka, H.; Ariga, K.; Kase, H.; Kamura, T.; Kondo, M.; Kitagawa, S.; Yamasaki, M. *Organometallics* **1997**, *16*, 4514.

(3) Mononuclear amido complexes of Rh: (a) Cetinkaya, B.; Lappert, M. F.; Torroni, S. *J. Chem. Soc., Chem. Commun.* **1979**, 843. (b) Watt, G. W.; Grum, J. K. *J. Am. Chem. Soc.* **1965**, *87*, 5366. (c) Watt, G. W.; Crum, J. K.; Summers, J. T. *J. Am. Chem. Soc.* **1965**, *87*, 4641. (d) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1986**, *5*, 2469. (e) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 682. (f) Fryzuk, M. D. MacNeil, P. A. *J. Am. Chem. Soc.* **1985**, *107*, 6708. (g) Fryzuk, M. D.; MacNeil, P. A.; Ball, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6414. (h) Fryzuk, M. D.; MacNeil, P. A.; McManus, N. T. *Organometallics* **1987**, *6*, 882. (i) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 355. (j) Organ, G. J.; Cooper, M. K.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1984**, 2377. (k) Espinet, P.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 1542. (l) Mashima, K.; Abe, T.; Tani, K. *Chem. Lett.* **1998**, 1201.

(4) Dinuclear amido complexes of Rh: (a) Fernández, M. J.; Moderego, J.; Oro, L. A.; Apreda, M.-C.; Cano, F. H.; Foces-Foces, C. *J. Chem. Soc., Dalton Trans.* **1989**, 1249. (b) Oro, L. A.; Fernández, M. J.; Modrego, J.; Foces-Foces, C.; Cano, F. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 913. (c) Connelly, N. G.; Loyns, A.; Fernández, M. J.; Modrego, J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1989**, 683. (d) Fernández, M. J.; Moderego, J.; Lahoz, F. J.; López, J. A.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1989**, 2587. (e) Oro, L. A.; Fernández, M. J.; Moderego, J.; Lopec, J. M. *J. Organomet. Chem.* **1985**, *287*, 409. (f) Fernandez, M. J.; Modrego, J.; Oro, L. A.; Apreda, M.-C.; Cano, F. H.; Foces-Foces, C. *Inorg. Chim. Acta* **1989**, *157*, 161. (g) Ge, Y.-W.; Sharp, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 3667. (h) Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2339. (i) Kolel-Veetile, M. K.; Rahim, M.; Edwards, J.; Rheingold, A. L.; Ahmed, K. *Inorg. Chem.* **1992**, *31*, 3877. (j) Ge, Y.-W.; Sharp, P. R. *Organometallics* **1988**, *7*, 2334. (k) Sharp, P. R.; Ge, Y.-W. *J. Am. Chem. Soc.* **1987**, *109*, 3796. (l) Retboll, M.; Ishii, Y.; Hidai, M. *Chem. Lett.* **1998**, 1217. (m) Brunet, J.-J.; Daran, J.-C.; Neibecker, D.; Rosenberg, L. *J. Organomet. Chem.* **1997**, *538*, 251.

(5) Several dirhodium complexes with a (μ$_2$-NH)$_2$C$_{10}$H$_6$-1,8 ligand have been reported.[4a−f] For the structurally related dirhodium complex Rh$_2$(PPh$_3$)$_4$(μ$_2$-NHPh)$_2$, see ref 4m.

(6) **3a**: yield 44%. ^{1}H NMR (CDCl$_3$): δ 7.82 (d, 2H, *J* = 7.3 Hz, aryl), 7.49 (d, 2H, *J* = 7.8 Hz, aryl), 7.34 (dd, 2H, *J* = 7.8, 7.3 Hz, aryl), 5.01 (br s, 2H, NH), 1.14 (s, 30H, Cp*). Anal. Calcd for C$_{30}$H$_{38}$Cl$_2$N$_2$Rh$_2$·CH$_2$Cl$_2$: C, 47.23; H, 4.51; N, 3.55. Found: C, 47.61; H, 4.92; N, 3.88. **3b**: yield 41%. ^{1}H NMR (CDCl$_3$): δ 7.79 (d, 2H, *J* = 7.4 Hz, aryl), 7.50 (d, 2H, *J* = 8.0 Hz, aryl), 7.34 (dd, 2H, *J* = 8.0, 7.4 Hz, aryl), 4.85 (br s, 2H, NH), 1.17 (s, 30H, Cp*). Anal. Calcd for C$_{30}$H$_{38}$Br$_2$N$_2$Rh$_2$·CH$_2$Cl$_2$: C, 42.45; H, 4.60; N, 3.19. Found: C, 42.23; H, 4.50; N, 3.16.

(7) Crystal data for C$_{32}$H$_{42}$Br$_2$Cl$_4$N$_2$Rh$_2$: *P*2$_1$/*c* (monoclinic), *a* = 11.731(1) Å, *b* = 18.690(7) Å, *c* = 17.042(2) Å, β = 95.505(9)°, *V* = 3719(1) Å^3, *Z* = 4, *D* = 1.718 g cm^{-3}; graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å); *R* (*R*$_w$) = 9.0% (10.1%) and GOF = 3.91 for 4928 reflections (*I* > 3σ(*I*)) collected with 5.0 < 2θ < 51.3° at 298 K.

10.1021/om990844v CCC: $19.00
Publication on Web 01/04/2000

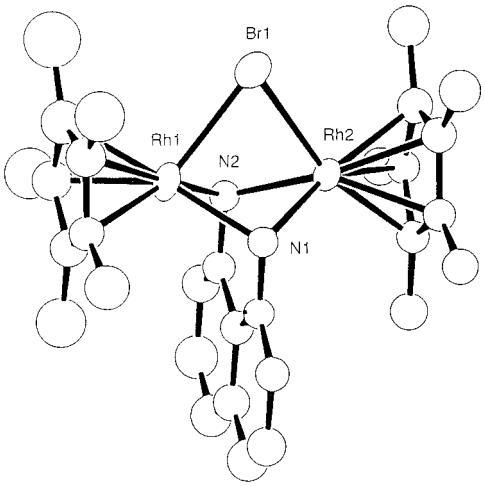
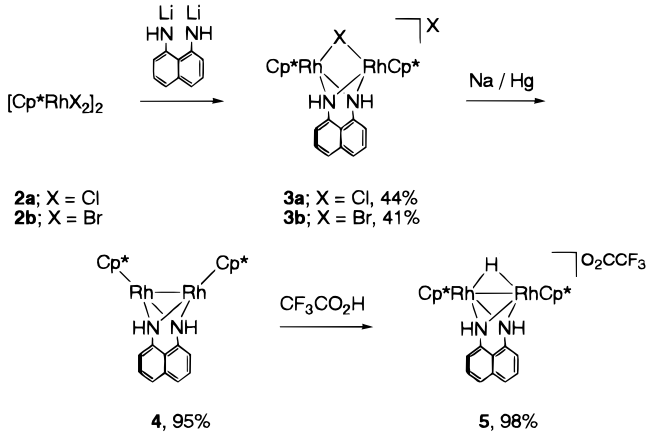


Figure 1. ORTEP drawing of the cationic part of **3b.** Selected bond distances (Å) and angles (deg) are as follows: Rh(1)···Rh(2), 3.04(2); Rh(1)−N(1), 2.124(10); Rh(1)−N(2), 2.126(10); Rh(1)−Br(1), 2.566(2); Rh(2)−N(1), 2.12(1); Rh(2)−N(2), 2.128(10); Rh(2)−Br(1), 2.574(2); N(1)−Rh(1)−N(2), 72.7(4); N(1)−Rh(1)−Br(1), 82.3(3); N(2)−Rh(1)−Br(1), 83.4(3); N(1)−Rh(2)−N(2), 72.7(4); N(1)−Rh(2)−Br(1), 82.1(3); N(2)−Rh(2)−Br(1), 83.2(3); Rh(1)−N(1)−Rh(2), 91.5(4); Rh(1)−N(2)−Rh(2), 91.3(4); Rh(1)−Br(1)−Rh(2), 72.58(6).

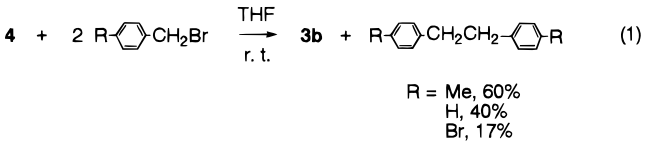
Scheme 1



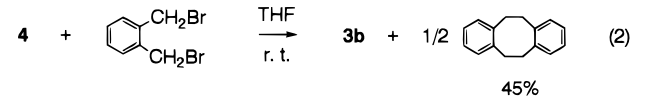
of a metal−metal bonding interaction. In the crystal lattice, each bromide anion bridges amido groups of the neighboring molecules via the weak hydrogen bond to form a one-dimensional chain along the *c* axis.[8]

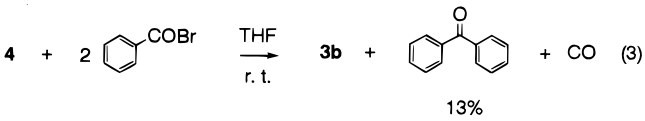
Reduction of **3** with Na/Hg readily proceeds to give the dinuclear Rh(II) complex Cp*Rh{(μ_2-NH)$_2$C$_{10}$H$_6$-1,8}RhCp* (**4**, Scheme 1; >95%), which was isolated as a dark red crystalline solid and spectroscopically characterized.[9] The ^{1}H NMR spectrum of **4** exhibits a resonance for the Cp* protons at δ 1.74 ppm, which appears significantly downfield compared to that observed for **3** (vide supra). The diamagnetic nature of **4** indicates the existence of a metal−metal bond between the two Rh(II) centers. These spectral features compare well with those of the crystallographically defined diiridium complex Cp*Ir{(μ_2-NH)$_2$C$_{10}$H$_6$-1,8}IrCp* [2] and suggest an analogous dinuclear structure.

To examine the reactivities of **4** with electrophiles, its reactions with several organic bromides and CF$_3$CO$_2$H were investigated. Complex **4** reacts with benzyl bromides to yield **3b** and the corresponding bibenzyls in moderate yield (eq 1). A similar coupling reaction of



benzyl bromide was recently reported to proceed in the presence of the thiolato-bridged diruthenium complex Cp*Ru(μ_2-SPr^i)$_2$RuCp*, in which the intermediate Cp*Ru(CH$_2$Ph)(μ_2-SPr^i)$_2$RuBrCp* was isolated.[10] In the present case, no such species could be detected, even at low temperature (−90 °C) with a limited amount of benzyl bromides employed. Treatment of **4** with 1,2-bis(bromomethyl)benzene does not afford benzocyclobutane but produces 1,5-dibenzocyclooctane (eq 2).[11] Decarbonylative coupling of benzoyl bromide readily proceeds in the presence of **4** to give benzophenone (eq 3). Complex





4 also smoothly and quantitatively reacts with CF$_3$CO$_2$H to yield the hydrido complex [Cp*Rh{(μ_2-NH)$_2$C$_{10}$H$_6$-1,8}(μ_2-H)RhCp*]O$_2$CCF$_3$ (**5**), which was obtained as red plates and spectroscopically characterized (Scheme 1).[12] The ^{1}H NMR spectrum of **5** shows a characteristic resonance at δ −10.78 (t, $^1J_{Rh-H}$ = 27 Hz) due to the μ_2-hydride, in addition to the signals of Cp* and naphthyl protons.

(8) Distances between weakly hydrogen-bonded atoms (Å): N(1)−Br(2), 3.41(1); N(2*)−Br(2), 3.416(9).

(9) Yield: 1.08 g, 95%. ^{1}H NMR (C$_6$D$_6$): δ 7.36 (d, 2H, J = 8.3 Hz, aryl), 7.09 (dd, 2H, J = 8.3, 7.2 Hz, aryl), 6.82 (d, 2H, J = 7.2 Hz, aryl), 3.34 (br s, 2H, NH), 1.71 (s, 30H, Cp*). Anal. Calcd for C$_{30}$H$_{38}$N$_2$Rh$_2$: C, 56.97; H, 6.06; N, 4.43. Found: C, 55.72; H, 6.01; N, 4.46.

(10) Takahashi, A.; Mizobe, Y.; Matsuzaka, H.; Dev, S.; Hidai, M. *J. Organomet. Chem.* **1993**, *456*, 243.

(11) The Ni(0) complex mediated formation of dibenzocyclooctane from 1,2-bis(bromomethyl)benzene has been reported: Hipler, B.; Uhlig, E. *J. Organomet. Chem.* **1980**, *199*, C27.

(12) Yield: 98%. ^{1}H NMR (CDCl$_3$): δ 7.51(d, 2H, J = 7.5 Hz, aryl), 7.45 (d, 2H, aryl, J = 7.5 Hz), 7.22 (dd, 2H, J = 7.5 Hz, aryl), 4.48 (br s, 2H, NH), 1.58 (s, 30H, Cp*), −10.78 (t, J_{Rh-H} = 28 Hz, Rh−H−Rh).

(13) **6a**: yield 30%. ^{1}H NMR (CDCl$_3$): δ 7.92−6.98 (m, 12H, aryl), 5.12, 4.23, 2.44 (br s, 1H each, NH), 2.33, 2.30, 2.29 (s, 3H each, C$_6$H$_4$*Me*), 1.15 (s, 30H, Cp*). Anal. Calcd for C$_{41}$H$_{54}$ClN$_3$Rh$_2$·$^1/_2$CH$_2$Cl$_2$: C, 57.12; H, 6.35; N, 4.82. Found: C, 57.56; H, 6.44; N, 4.86. **6b**·Cl: yield 31%. ^{1}H NMR (CDCl$_3$): δ 8.06−6.90 (m, 15H, aryl), 5.28, 4.50, 2.53 (br s, 1H each, NH), 1.15 (s, 30H, Cp*). Anal. Calcd for C$_{38}$H$_{48}$ClN$_3$Rh$_2$·$^1/_2$CHCl$_3$: C, 54.55; H, 5.77; N, 4.96. Found: C, 54.86; H, 5.92; N, 4.75. **6c**·Cl: yield 42%. ^{1}H NMR (CDCl$_3$): δ 8.01−6.82 (m, 12H, aryl), 5.40, 4.55, 2.32 (br s, 1H each, NH), 1.19 (s, 30H, Cp*). Anal. Calcd for C$_{38}$H$_{48}$Cl$_4$N$_3$Rh$_2$·CH$_2$Cl$_2$: C, 47.98; H, 4.35; N, 4.30. Found: C, 48.07; H, 5.13; N, 4.50.

(14) This is in sharp contrast to what is observed for the previously reported diiridium system,[2] in which treatment of **1** with 3 equiv of the same LiNHC$_6$H$_4$R-*p* produced an amido-bridged diiridium complex similar to **6**·Cl in high yield.

(15) Crystal data for C$_{40}$H$_{47}$Cl$_{10}$N$_3$Rh$_2$O$_4$: $P2_12_12_1$ (orthorhombic), a = 18.009(4) Å, b = 18.901(4) Å, c = 14.450(2) Å, V = 4918(1) Å^3, Z = 4, D = 1.613 g cm^{-3}; graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å); R (R_w) = 9.3% (10.6%) and GOF = 1.42 for 1682 reflections ($I > 3\sigma(I)$) collected with 5.0 < 2θ < 55.5° at 298 K.

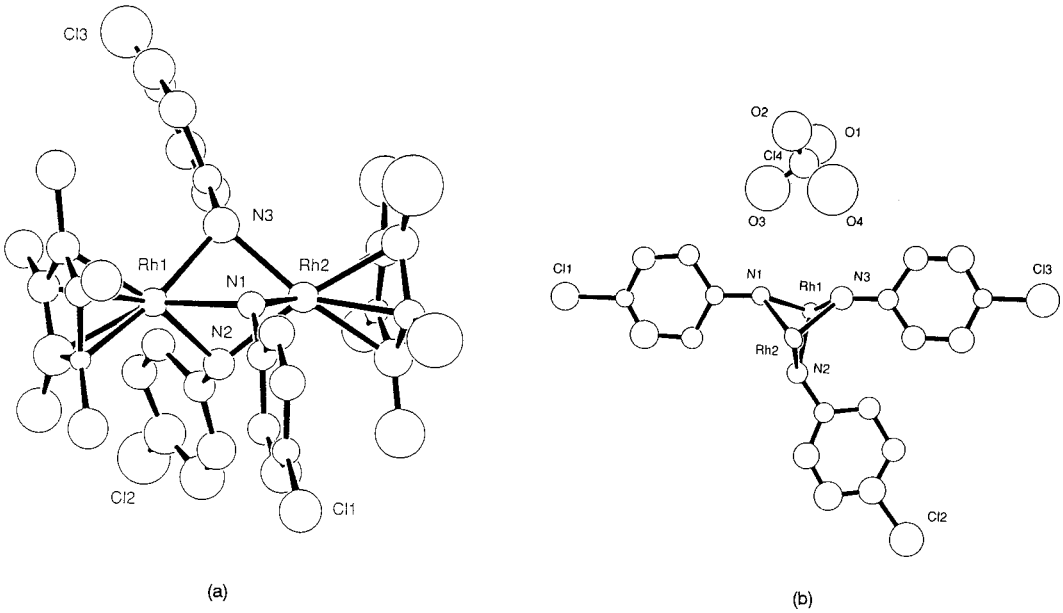
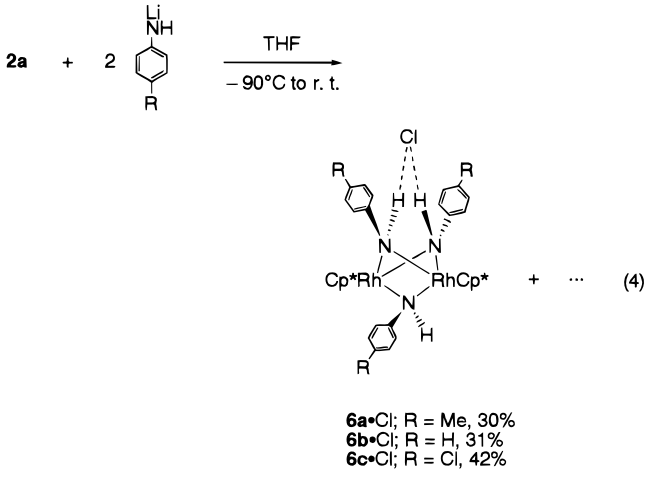


Figure 2. ORTEP drawings of **6c**·ClO_4: (a) view of the cationic part; (b) view almost along the Rh···Rh axis (Cp* groups are omitted for clarity). Selected bond distances (Å) and angles (deg) are as follows: Rh(1)···Rh(2), 3.00(2); Rh(1)−N(1), 2.17(3); Rh(1)−N(2), 2.12(3); Rh(1)−N(3), 2.13(4); Rh(2)−N(1), 2.10(3); Rh(2)−N(2), 2.10(3); Rh(2)−N(3), 2.12(4); N(1)−Rh(1)−N(2), 74(1); N(1)−Rh(1)−N(3), 70(1); N(2)−Rh(1)−N(3), 79(1); N(1)−Rh(2)−N(3), 76(1); N(1)−Rh(2)−N(3), 71(1); N(2)−Rh(2)−N(3), 80(1); Rh(1)−N(1)−Rh(2), 89(1); Rh(1)−N(2)−Rh(2), 90(1); Rh(1)−N(3)−Rh(2), 90(1).

On the other hand, **2a** reacts with *2 equiv* of $LiNHC_6H_4R$-*p* at −80 °C to room temperature to give $[Cp^*Rh(\mu_2\text{-}NHC_6H_4R\text{-}p)_3RhCp^*]Cl$ (**6**·Cl: **6a**, R = Me; **6b**, R = H; **6c**, R = Cl) in moderate yield (eq 4).[13] The



6a•Cl; R = Me, 30%
6b•Cl; R = H, 31%
6c•Cl; R = Cl, 42%

amount of the lithium amide employed is critical for the isolation of **6**·Cl. Thus, treatment of **2a** with 3 equiv of $LiNHC_6H_4R$-*p* led only to intractable materials.[14] The ^1H NMR spectrum of **6c**·ClO_4 indicates inequivalent NH protons whose three distinct resonances appear at δ 3.31, 2.73, and 2.46, whereas the Cp* protons appear as a singlet at δ 1.13. These spectral features are fully consistent with its crystal structure.[15,16] An ORTEP drawing of the cationic part of **6c**·ClO_4 is given in Figure 2, in which two Cp*Rh fragments are bridged by three amido ligands. Two of the three μ_2-NHC_6H_4Cl-*p* groups are hydrogen-bonded to the perchlorate anion, which lies in the outer coordination sphere and is not bound to the metal (Figure 2b).[17] The two Cp* moieties are almost parallel (dihedral angle 5.63°) and are in a staggered conformation. The intramolecular distance between the two Rh atoms is 3.08(1) Å, indicating the absence of a metal−metal bond interaction.

Further studies are in progress on the preparation of the amido-bridged polynuclear noble metal complexes as well as on their reactivities.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 10640549, Priority Areas No. 284-11120246 and 401-10149104) from The Ministry of Education, Science, Sports and Culture of Japan.

Supporting Information Available: Text giving experimental details on the preparation of **3**−**5**, **6**·Cl, and **6c**·ClO_4 and reactions of **4** with organic bromides, tables giving details of the X-ray structure determinations, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **3b** and **6c**·ClO_4, ORTEP drawings of the cationic part of **3b** and **6c**·ClO_4 with complete atom-numbering schemes, and a packing diagram of **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990844V

(16) For related structurally defined dinuclear Rh complexes having the $[Cp^*Rh(\mu_2\text{-}X)_3RhCp^*]^+$ core, see the following. X = Cl: (a) Valderrama, M.; Scotti, M.; Campos, P.; Sariego, R.; Peters, K.; von Schnering, H. G.; Werner, H. *New J. Chem.* **1988**, *12*, 633. (b) Umakoshi, K.; Murata, K.; Yamashita, S.; Isobe, K. *Inorg. Chim. Acta* **1991**, *190*, 185; X = SR: (c) Garcia, J. J.; Torrens, H.; Adams, H.; Bailey, N. A.; Shacklady, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1993**, 1529. (d) Hou, Z.; Ozawa, Y.; Isobe, K. *Chem. Lett.* **1990**, 1863.

(17) Distances between the hydrogen-bonded atoms (Å): N(1)−O(3), 3.27(7); N(2)−O(4), 3.34(8).