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Dinuclear Ruthenium(II) κ^2-Diamido/η^6-Naphthalene Complexes Featuring a Coordinatively Unsaturated yet Highly π-Basic (η^5-C_5Me_5)Ru Diamide Fragment

Shin Takemoto,[†] Shinya Oshio,[†] Takayuki Shiromoto,[†] and
Hiroyuki Matsuzaka*,[†,‡]

*Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Sakai,
Osaka 599-8531, Japan, and Coordination Chemistry Laboratories, Institute for
Molecular Science, Myodaiji, Okazaki 444-8787, Japan*

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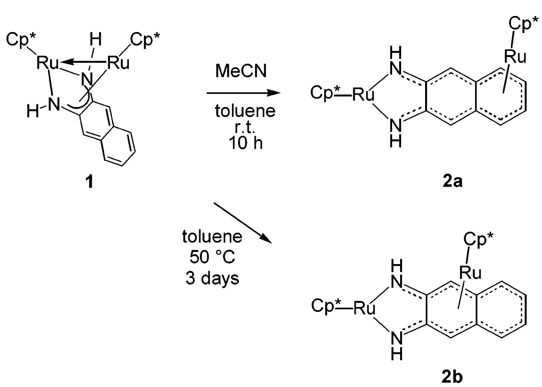
*Summary: Acetonitrile induces a clean isomerization of the amido-bridged diruthenium complex [(Cp*Ru)$_2${μ_2-κ^2:η^4-2,3-naphthalenediamido}] (**1**) into the κ^2:η^6-bonded dinuclear complex [Cp*Ru{μ_2-κ^2:η^6-2,3-naphthalenediamido}RuCp*] (**2a**), featuring a coordinatively unsaturated Cp*Ru terminal diamide fragment. Structural and spectroscopic data of its carbon monoxide and tert-butyl isocyanide adducts indicate that the Cp*Ru diamide fragment can serve as a strong π-base.*

Considerable attention has been focused on the preparation and reactivity of coordinatively unsaturated organotransition-metal complexes, since such species are frequently involved as reactive intermediates in many important organometallic processes. π-Donor derivatives of the Cp*Ru fragments [Cp*RuLX] and [Cp*Ru(μ_2-X)]$_2$ (X = amide,[1,2] alkoxide,[2−4] thiolate,[4−6] amidinate,[7−9] halide[10,11]) have consequently attracted intense interest,[12] in which the anionic π-donor ligands X effectively stabilize the formally 16-valence-electron Ru(II) centers to such an extent that complexes can be isolated, while the coordinatively unsaturated nature of the complexes is manifested by their facile reaction with incoming substrates. Although the chemistry of the Cp*Ru amido complexes is relatively less developed as compared to that of other π-donor derivatives listed above, some recent studies indicated that they may have a rich reaction chemistry.[13−15] During the course of our studies on the amido-bridged dinuclear noble metal complexes, we have recently synthesized the diruthenium 2,3-naphthalenediamido complex **1**, which readily reacts with CO to give a carbamoyl complex.[16] We now report quantitative isomerization of the amido-bridged dimer **1** into the κ^2:η^6-bonded complexes **2a** and **2b** (Scheme 1), which can formally be described as dinuclear zwitterions featuring a 16-electron {Cp*Ru(diamide)}$^-$ fragment.[17,18] The initial reactivity study

Scheme 1



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* To whom correspondence should be addressed. E-mail: matuzaka@ms.cias.osakafu-u.ac.jp.

[†] Osaka Prefecture University.

[‡] Institute for Molecular Science.

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of this system demonstrated that the Cp*Ru diamide fragment readily binds π-acceptor substrates and can serve as a strong π-base.

Addition of excess acetonitrile to a toluene solution of **1** led to clean isomerization of **1** into the κ^2-diamido/η^6-naphthalene complex **2a**, which was formed quantitatively within 10 h at room temperature, isolated as air-sensitive reddish brown needles in 75% yield, and fully characterized by elemental analysis, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and single-crystal X-ray diffraction.[19,20] Similar treatment of a 1:1 mixture of **1** and its Cp′ analogue (Cp′Ru)$_2$[μ_2-2,3-(NH)$_2$C$_{10}$H$_6$] (**1′**; Cp′ = η^5-C$_5$Me$_4$Et) with acetonitrile gave no detectable amount of the crossover products, suggesting that the isomerization is essentially an intramolecular event.[21]

Isomerization of **1** also took place on heating a solution of **1** in hexanes, toluene, or toluene−acetone at 50 °C. Interestingly, these reaction conditions selectively afforded another isomer **2b** (Scheme 1), in which the {Cp*Ru}$^+$ fragment is bound to the inner ring of the naphthalene moiety. Complex **2b** was isolated as red platelike crystals (43%) and has been characterized by analytical, spectroscopic, and crystallographic methods.[22] Once **2b** was formed, it did not afford **2a** when it was stirred in toluene−acetonitrile even at 50 °C. Similarly, complex **2a** remained unchanged on dissolution in toluene and heating at 50 °C for 60 h. We tentatively assume that the isomerization of **1** to **2a** involves some solvent-coordinated intermediates such as [Cp*Ru{κ^2:η^2-μ_2-(NH)$_2$C$_{10}$H$_6$)}RuCp*(MeCN)$_2$],[23] whereas the isomerization to **2b** could proceed without coordination of the solvent molecule.

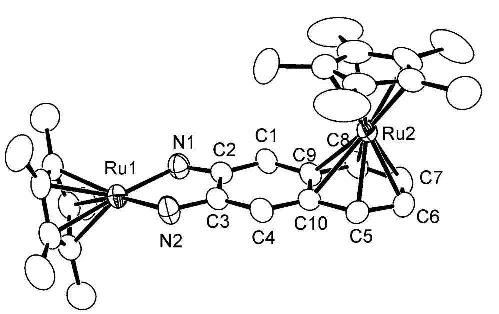
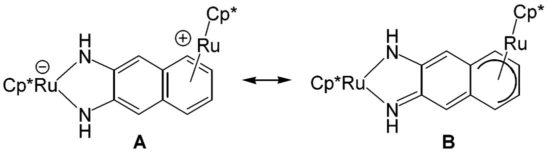


Figure 1. ORTEP drawing of **2a**. Ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ru1−N1, 2.034(3); Ru1−N2, 2.039(3); C2−N1, 1.336(4); C3−N2, 1.335(4); Ru2−C5, 2.219(3); Ru2−C6, 2.208(3); Ru2−C7, 2.207(3); Ru2−C8, 2.220(3); Ru2−C9, 2.364(3); Ru2−C10, 2.380(3).

Chart 1



The molecular structure of **2a** is shown in Figure 1. The molecule features an apparently coordinatively unsaturated Cp*Ru diamide moiety, and the relatively short Ru−N bond lengths (average 2.037 Å) indicate the π-stabilized nature of the formally 16-valence-electron Ru center. The short C−N bond lengths (average 1.336 Å) as compared to those observed for *o*-phenylenediamide complexes (ca. 1.40 Å)[24−26] suggest that the amido nitrogen atoms also form π-bonds with the naphthalene carbon atoms. The π-bound naphthalene ring is η^6-bonded to the Ru2 atom, but the carbon atoms at the ring junction (C9 and C10) exhibit longer Ru2−C distances (average 2.372 Å) than other Ru2−C$_{\text{naphthalene}}$ bond lengths (2.220−2.207 Å). Accordingly, the π-bound ring is slightly puckered along the C5−C8 vector with a dihedral angle of 5.64°. These data suggest that complex **2a** is best described as a hybrid of the zwitterionic κ^2:η^6-naphthalenediamido structure **A** and the neutral κ^2:η^5-iminocyclohexadienylamido structure **B**[20a] (Chart 1). Similar resonance hybridization has been proposed for the recently reported Mn−M (M = Mn, Co, Cd) dinuclear *o*-benzoquinone complexes [(bpy)$_2$M(κ^2:η^4-*o*-benzoquinone)Mn(CO)$_3$][27] and for the Fe(II) η-arylhydrazonyl complex [CpFe{(η-C$_6$H$_5$)N=NCHC$_6$H$_4$-*p*-NMe$_2$}].[28] The structure of **2b**, shown in Figure 2, is analogous to that of **2a**, but the larger deviations in the Ru2−C$_{\text{naphthalene}}$ distances (average 2.424 Å for C2 and

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[19] Preparation of **2a**: to a solution of **1** (1.23 g, 1.95 mmol) in toluene (50 mL) was added acetonitrile (20 mL), and the resulting mixture was stirred at room temperature for 10 h. Concentration of the reaction solution to 25 mL, followed by slow diffusion of hexanes (30 mL), gave **2a** as reddish brown needles. Yield: 915 mg, 75%. Anal. Calcd for C$_{30}$H$_{38}$N$_2$Ru$_2$: C, 57.31; H, 6.09; N, 4.46. Found: C, 56.82; H, 6.07; N, 4.17. ^{1}H NMR (C$_6$D$_6$): δ 7.28 (br s, 2H, NH), 5.92 (s, 2H, aryl), 5.07 (m, 2H, aryl), 4.27 (m, 2H, aryl), 2.17 (s, 15H, Cp*), 1.11 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.8 MHz): δ 164.4, 98.6, 90.7 (aryl), 88.4 (C_5Me$_5$), 79.8, 79.7 (aryl), 71.8 (C_5Me$_5$), 12.9, 9.42 (C$_5$$Me_5$). Crystallographic data for **2a**: C$_{30}$H$_{38}$N$_2$Ru$_2$; M_r = 628.76, triclinic, space group $P\bar{1}$, a = 9.7682(8) Å, b = 11.4013(7) Å, c = 12.4389(12) Å, α = 76.597(5)°, β = 86.581(3)°, γ = 85.825(3)°, V = 1342.71(19) Å^3, Z = 2, T = 296 K, μ(Mo Kα) = 1.145 mm^{-1}, 12 702 reflections measured, 5914 unique (R_{int} = 0.0368), R1 = 0.0360, wR2 = 0.0993, GOF = 1.047.

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[21] Complex **2a** and its Cp′ analogue [Cp′Ru{μ_2-κ^2:η^6-2,3-(NH)$_2$C$_{10}$H$_6$}RuCp′] (**2a′**) were formed in 100% NMR yields.

[22] Preparation of **2b**: a solution of **1** (1.24 g, 1.97 mmol) in toluene/acetone (50/20 mL) was stirred at 50 °C for 3 days. The red solution obtained was concentrated to 15 mL and stored at −30 °C to give **2b** as red platelike crystals. The reaction proceeded similarly when toluene or hexanes was used as solvent. Yield: 528 mg, 43%. Anal. Calcd for C$_{30}$H$_{38}$N$_2$Ru$_2$: C, 57.31; H, 6.09; N, 4.46. Found: C, 57.21; H, 6.08; N, 4.44. ^{1}H NMR (C$_6$D$_6$): δ 6.78 (m, 4H, aryl), 5.64 (br s, 2H, NH), 5.08 (s, 2H, aryl), 2.16 (s, 15H, Cp*), 1.21 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.8 MHz): δ 130.5, 128.6, 123.7, 90.5 (aryl), 83.6, 72.0 (C_5Me$_5$), 70.8 (aryl), 12.7, 8.1 (C$_5$$Me_5$). Crystallographic data for **2b**: C$_{30}$H$_{38}$N$_2$Ru$_2$; M_r = 628.76, monoclinic, space group $P2_1/n$, a = 14.492(6) Å, b = 15.164(6) Å, c = 24.876(8) Å, β = 92.62(3)°, V = 5461(4) Å^3, Z = 8, T = 296 K, μ(Mo Kα) = 1.142 mm^{-1}, 49 888 reflections measured, 12 313 unique (R_{int} = 0.0845), R1 = 0.0782, wR2 = 0.1972, GOF = 1.142.

[23] Solvated species such as [CpRu(NCMe)(η^4-arene)]$^+$ have been proposed as intermediates in the formation of [CpRu(η^6-arene)]$^+$ complexes from [CpRu(NCMe)$_3$]$^+$ and arenes: Koefod, R. S.; Mann, K. R. *J. Am. Chem. Soc.* **1990**, *112*, 7287−7293.

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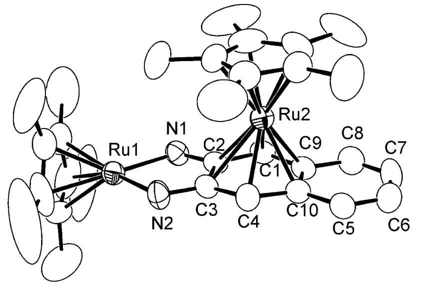
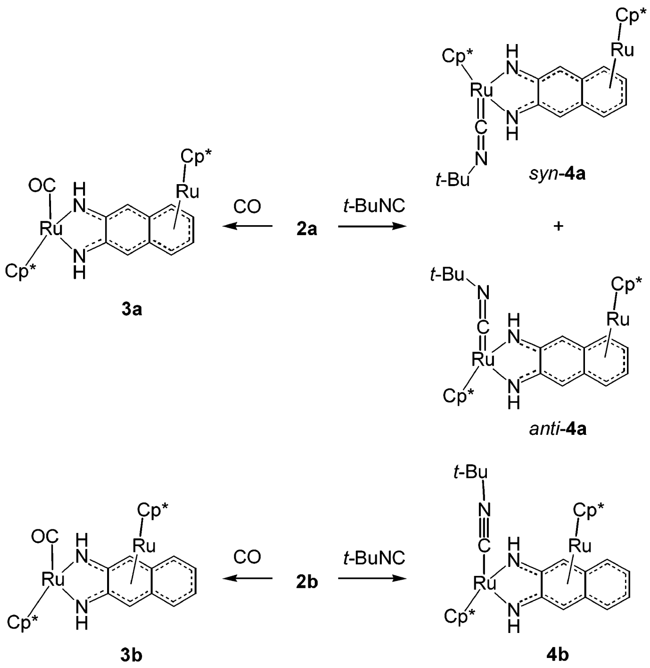


Figure 2. ORTEP drawing of **2b**. Ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ru1–N1, 2.041(6); Ru1–N2, 2.037(6); C2–N1, 1.334(9); C3–N2, 1.332(9); Ru2–C1, 2.218(7); Ru2–C2, 2.427(7); Ru2–C3, 2.432(7); Ru2–C4, 2.226(8); Ru2–C9, 2.216(7); Ru2–C10, 2.222(7).

Scheme 2



C3 vs 2.226–2.208 Å for C1, C4, C9, and C10) and the larger puckering angle of the η^6-bound naphthalene ring (8.51° along the C1–C4 vector) in **2b** as compared to those in **2a** suggest that the contribution from the zwitterionic form **A** is more predominant in **2a** than in **2b**.

Exposure of THF solutions of **2a** and **2b** to atmospheric carbon monoxide led to quantitative formation of the carbonyl adducts **3a** and **3b**, respectively (Scheme 2), both of which were isolated as crystalline materials (**3a**, 91%; **3b**, 43%) and fully defined by elemental analysis, NMR and IR spectroscopy, and X-ray diffraction.[29,30] The infrared spectra of **3a** and **3b** show ν(CO) bands at 1876 and 1888 cm^{-1}, respectively. These values are much lower than those observed for the charge-neutral carbonyl derivatives such as [Cp*Ru(NHPh)(CO)($PPr^i{}_2Ph$)] (1904 cm^{-1})[2] and [Cp*Ru(CO)(amidinates)] (1901–1988 cm^{-1})[9] and may reflect the contribution from the zwitterionic resonance forms, where a negative charge resides on the Cp*Ru diamide fragment.

Addition of *tert*-butyl isocyanide to a THF solution of **2a** led to quantitative formation of a mixture of two isomeric adducts, *syn*-**4a** and *anti*-**4a**,[31–33] whereas complex **2b** exclusively afforded the anti adduct **4b** under similar reaction conditions (Scheme 2).[34] The structures of *syn*-**4a**, *anti*-**4a**, and **4b** have been determined by X-ray crystallography (Figures 3 and 4).[35] Interestingly, the isocyanide ligands in *syn*-**4a** and *anti*-

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(29) Preparation of **3a**: in a 20 mL Schlenk flask, complex **2a** (84 mg, 0.13 mmol) was dissolved in 5 mL of THF. The solution was frozen, and the flask was evacuated. Then, 1 atm of carbon monoxide was flashed into the flask and the mixture was warmed to room temperature with stirring over 15 h. Concentration of the reaction solution to ca. 3 mL, followed by slow diffusion of hexanes (6 mL), gave **3a** as dark orange plates. Yield: 79 mg, 91%. Anal. Calcd for $C_{31}H_{38}N_2ORu_2$: C, 56.69; H, 5.83; N, 4.27. Found: C, 57.09; H, 6.07; N, 3.95. ^{1}H NMR (C_6D_6): δ 5.25 (s, 2H, aryl), 4.71 (m, 2H, aryl), 4.31 (m, 2H, aryl), 4.32 (s, 2H, NH), 1.77 (s, 15H, Cp*), 1.43 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.8 MHz): δ 210.7 (CO), 167.5, 103.5 (aryl), 92.9, 88.2 (C_5Me$_5$), 87.7, 78.6, 76.5 (aryl), 10.3, 9.5 (C$_5$*Me*$_5$). IR (KBr): 1876 cm^{-1} (ν(CO)). Preparation of **3b**: in a 20-mL Schlenk flask, complex **2b** (85 mg, 0.14 mmol) was dissolved in 7 mL of THF. The solution was frozen, and the flask was evacuated. Then, 1 atm of carbon monoxide was flashed into the flask. The reaction mixture was warmed to room temperature and stirred for 5 days. Concentration of the reaction solution to ca. 2 mL, followed by slow diffusion of acetonitrile (8 mL), gave **3b** as an orange solid. Yield: 39 mg, 43%. Crystals suitable for an X-ray diffraction study were grown from benzene/acetonitrile. Anal. Calcd for $C_{31}H_{38}N_2ORu_2$: C, 56.69; H, 5.83; N, 4.27. Found: C, 56.41; H, 6.19; N, 4.46. ^{1}H NMR (C_6D_6): δ 6.77 (m, 4H, aryl), 4.59 (s, 2H, aryl), 2.90 (br s, 2H, NH), 1.66 (s, 15H, Cp*), 1.55 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 213.3 (CO), 141.1, 128.6, 123.0 (aryl), 93.2 (C_5Me$_5$), 90.1 (aryl), 83.4 (C_5Me$_5$), 66.1 (aryl), 10.1, 9.4 (C$_5$*Me*$_5$). IR (KBr): 1888 cm^{-1} (ν(CO)).

(30) Crystallographic data for **3a**: $C_{31}H_{38}N_2ORu_2$; M_r = 656.77, monoclinic, space group *C*2/*c*, $a = 28.9627(19)$ Å, $b = 11.3765(9)$ Å, $c = 18.6104(9)$ Å, $\beta = 114.542(2)°$, $V = 5578.0(6)$ Å^3, $Z = 8$, $T = 296$ K, μ(Mo Kα) = 1.109 mm^{-1}, 26 046 reflections measured, 6360 unique (R_{int} = 0.0333), R1 = 0.0372, wR2 = 0.0984, GOF = 1.045. Crystallographic data for **3b**·C_6H_6: $C_{37}H_{44}N_2ORu_2$; M_r = 734.88, orthorhombic, space group *Pna*2$_1$, $a = 12.874(12)$ Å, $b = 11.863(12)$ Å, $c = 21.582(17)$ Å, $V = 3296(5)$ Å^3, $Z = 4$, $T = 296$ K, μ(Mo Kα) = 0.947 mm^{-1}, 30 525 reflections measured, 7373 unique (R_{int} = 0.0592), R1 = 0.0343, wR2 = 0.0608, GOF = 0.921. ORTEP drawings of **3a** and **3b** are given in the Supporting Information.

(31) Preparation of **4a** (as a mixture of syn and anti isomers): to a solution of **2a** (506 mg, 0.80 mmol) in THF (30 mL) was added *t*-BuNC (200 μL, 2.0 mmol), and the reaction mixture was stirred at room temperature for 4 h. The ^{1}H NMR spectrum of the reaction mixture showed the presence of *syn*-**4a** and *anti*-**4a** in a 1:1 molar ratio. The volatiles were removed in vacuo, and the solid residue was extracted with hexanes (30 mL). The extract was concentrated to ca. 3 mL and stored at −25 °C to give red crystals. The product was obtained as a 1:1 mixture of syn and anti isomers. Yield: 442 mg, 78%. Anal. Calcd for $C_{35}H_{47}N_3Ru_2$: C, 59.05; H, 6.65; N, 5.90. Found: C, 58.98; H, 6.61; N, 6.06. IR (KBr): 1886 cm^{-1} (ν(CN)). ^{1}H NMR data for *syn*-**4a** (C_6D_6): δ 5.21 (s, 2H, aryl), 4.63 (m, 2H, aryl), 4.34 (m, 2H, aryl), 4.69 (br s, 2H, NH), 1.94 (s, 15H, Cp*), 1.50 (s, 15H, Cp*), 1.23 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR data for *syn*-**4a** (C_6D_6): δ 186.9 (*C*NCMe$_3$), 167.3, 105.1 (aryl), 88.2, 87.5 (C_5Me$_5$), 86.9, 77.5, 75.0 (aryl), 55.1 (CN*C*Me$_3$), 32.4 (CNC*Me*$_3$), 10.7, 9.8 (C$_5$*Me*$_5$). ^{1}H NMR data for *anti*-**4a** (C_6D_6): δ 5.17 (s, 2H, aryl), 4.65 (m, 2H, aryl), 4.36 (m, 2H, aryl), 4.67 (br s, 2H, NH), 1.87 (s, 15H, Cp*), 1.65 (s, 15H, Cp*), 1.38 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR data for *anti*-**4a** (C_6D_6): δ 189.3 (*C*NCMe$_3$), 167.1, 105.3 (aryl), 88.5, 87.5 (C_5Me$_5$), 86.5, 77.7, 75.0 (aryl), 54.8 (CN*C*Me$_3$), 32.8 (CNC*Me*$_3$), 10.7, 9.9 (C$_5$*Me*$_5$).

(32) Isolation of *syn*-**4a**: to a solution of **2a** (570 mg, 0.907 mmol) in THF (7 mL) was added *t*-BuNC (266 μL, 2.35 mmol) at room temperature, and the reaction mixture was stirred for 2 h. The volatiles were removed in vacuo, and the residual solid was washed with 50 mL of hexanes to leave 69 mg (11%) of a red solid, whose ^{1}H NMR spectrum showed the presence of a single isomer. The identity of this isomer as *syn*-**4a** was confirmed crystallographically by using single crystals obtained after the solid was recrystallized from hexanes.

(33) Preparation of the single crystals of *anti*-**4a**: to a solution of **2a** (90 mg, 0.14 mmol) in THF (7 mL) was added *t*-BuNC (40 μL, 0.35 mmol) at −80 °C, and the reaction mixture was warmed to room temperature with stirring over 4 h. The ^{1}H NMR spectrum of the reaction mixture showed the presence of *syn*-**4a** and *anti*-**4a** in a 1:2 molar ratio. The volatiles were removed in vacuo, and the solid residue was extracted with hexanes (10 mL). The extract was concentrated to ca. 1 mL and stored at −25 °C to give 64 mg (64%) of a mixture of red microcrystalline solid and relatively large red crystals, which still contains both syn and anti isomers, as judged by ^{1}H NMR. Some pieces of the large crystals were collected manually. The ^{1}H NMR spectrum of the collected crystals showed the presence of a single isomer, which was identified as *anti*-**4a** by X-ray crystallography.

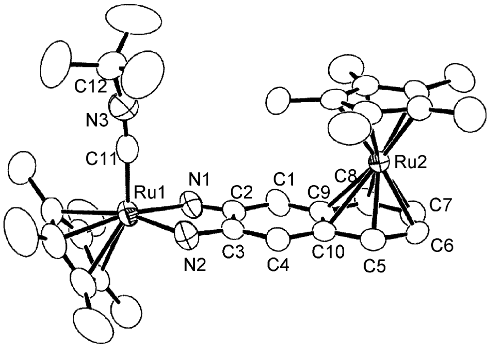

Figure 3. ORTEP drawing of *anti*-**4a**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru1−N1, 2.085(5); Ru1−N2, 2.083(4); Ru1−C11, 1.871(7); C2−N1, 1.329(7); C3−N2, 1.310(7); C11−N3, 1.180(8); C11−N3−C12, 149.4(7).

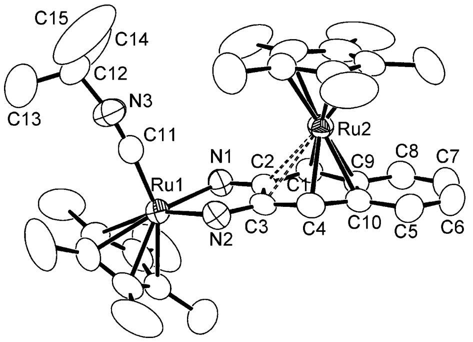

Figure 4. ORTEP drawing of **4b**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru1−N1, 2.110(4); Ru1−N2, 2.107(4); Ru1−C11, 1.892(5); C2−N1, 1.327(6); C3−N2, 1.313(6); C11−N3, 1.165(6); C11−N3−C12, 163.8(6).

4a are significantly bent at nitrogen (C−N−C = 139.2(8)° for *syn*-**4a** and 149.4(7)° for *anti*-**4a**) and exhibit very short Ru−C bond lengths (average 1.856 Å). Such highly reduced terminal isocyanide ligands have been observed in some electron-rich metal complexes[36] but are unprecedented for Ru(II) complexes, which again points to the anionic nature of the Cp*Ru diamide moiety. In accordance with this observation, the IR spectrum of **4a** shows a quite low ν(CN) stretching frequency (1886 cm^{-1} (Nujol)). In sharp contrast, the isocyanide ligand in **4b** shows a larger C−N−C bond angle (163.8(6)°) and longer Ru−C bond lengths (1.892(5) Å) in X-ray crystallography and a higher ν(CN) stretching frequency (1985 cm^{-1}) in the infrared spectrum. Additionally, while the Ru2−(η^6-naphthalene) bonding in *syn*- and *anti*-**4a** are essentially identical with that in **2a**, the π-bound naphthalene ring in **4b** exhibits a significantly larger puckering angle (15.7°) and longer Ru2−C_{ipso} distances (average 2.552 Å) as compared to those in **2b**. Thus, the π-coordinated ring in **4b** can be best described as an η^5-cyclohexadienyl ring, and π-donation from the Cp*Ru diamide fragment is mainly directed to the {(η-naphthalene)RuCp*} unit rather than to the coordinated isocyanide.

In conclusion, we have demonstrated that the amido-bridged diruthenium complex **1** can be selectively transformed into the two isomeric κ^2:η^6-bonded complexes **2a** and **2b** via thermal- or solvent-assisted migration of a Cp*Ru fragment. An interesting feature of the present reaction is the formation of two electronically distinct Ru(II) moieties that can formally be described as $\{Cp^*Ru(\eta^6\text{-arene})\}^+$ and $\{Cp^*Ru(\text{diamide})\}^-$. The spectroscopic and structural data for the CO and *tert*-butyl isocyanide adducts indicate that the anionic diamidoruthenate(II) fragment can serve as a strong π-base. Further investigations into the reactivity of these Ru(II) amido complexes are now in progress.

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Supporting Information Available: Text, tables, and figures giving experimental, spectroscopic, and crystallographic details; full crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) Preparation of **4b**: to a solution of **2b** (92 mg, 0.15 mmol) in THF (10 mL) was added *t*-BuNC (43 μL, 0.38 mmol), and the reaction mixture was stirred at room temperature for 20 h. The volatiles were removed under reduced pressure, and the residual solid was taken up in 10 mL of toluene. Concentration of the toluene solution to 5 mL, slow diffusion of 10 mL of acetonitrile, and storing at −30 °C afforded **4b** as dark brown platelike crystals. Yield: 44 mg, 41%. Anal. Calcd for $C_{35}H_{47}N_3Ru_2$: C, 59.05; H, 6.65; N, 5.90. Found: C, 59.37; H, 6.77; N, 5.86. IR (KBr): 1985 cm^{-1} (ν(CN)). ^1H NMR (C_6D_6): δ 6.85 (m, 2H, aryl), 6.81 (m, 2H, aryl), 4.55 (s, 2H, aryl), 3.12 (br s, 2H, NH), 1.71 (s, 15H, Cp*), 1.62 (s, 15H, Cp*), 1.44 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 186.7 (*C*NCMe$_3$), 144.5, 129.0, 122.2, 90.0 (aryl), 88.3, 82.2 (*C*$_5$Me$_5$), 65.0 (aryl), 54.9 (CN*C*Me$_3$), 32.4 (CNC*Me*$_3$), 10.4, 9.8 (C$_5$*Me*$_5$).

(35) An ORTEP drawing of *syn*-**4a** is given in the Supporting Information. Crystallographic data for *syn*-**4a**: $C_{35}H_{47}N_3Ru_2$; M_r = 711.90, monoclinic, space group $P2_1/c$, a = 12.555(2) Å, b = 16.084(4) Å, c = 16.663(2) Å, β = 97.554(7)°, V = 3335.7(12) Å^3, Z = 4, T = 296 K, μ(Mo Kα) = 0.932 mm^{-1}, 29 752 reflections measured, 7361 unique (R_{int} = 0.2055), R1 = 0.0784, wR2 = 0.1499, GOF = 0.994. Crystallographic data for *anti*-**4a**: $C_{35}H_{47}N_3Ru_2$; M_r = 711.90, monoclinic, space group $P2_1/c$, a = 16.082(7) Å, b = 13.720(5) Å, c = 16.334(6) Å, β = 111.46(3)°, V = 3354(2) Å^3, Z = 4, T = 296 K, μ(Mo Kα) = 0.927 mm^{-1}, 25 674 reflections measured, 6138 unique (R_{int} = 0.0579), R1 = 0.0548, wR2 = 0.1253, GOF = 1.090. Crystallographic data for **4b**: $C_{35}H_{47}N_3Ru_2$; M_r = 711.90, orthorhombic, space group *Pbcn*, a = 20.7065(9) Å, b = 14.4762(8) Å, c = 22.2356(9) Å, V = 6665.2(5) Å^3, Z = 8, T = 296 K, μ(Mo Kα) = 0.933 mm^{-1}, 58 528 reflections measured, 7564 unique (R_{int} = 0.1101), R1 = 0.0519, wR2 = 0.1209, GOF = 0.994.

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