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Synthesis and Skeletal Transformation of Cyanamido(2–)- and Cyanamido(1–)-Bridged Ruthenium Complexes with Hexamethylbenzene Ligands

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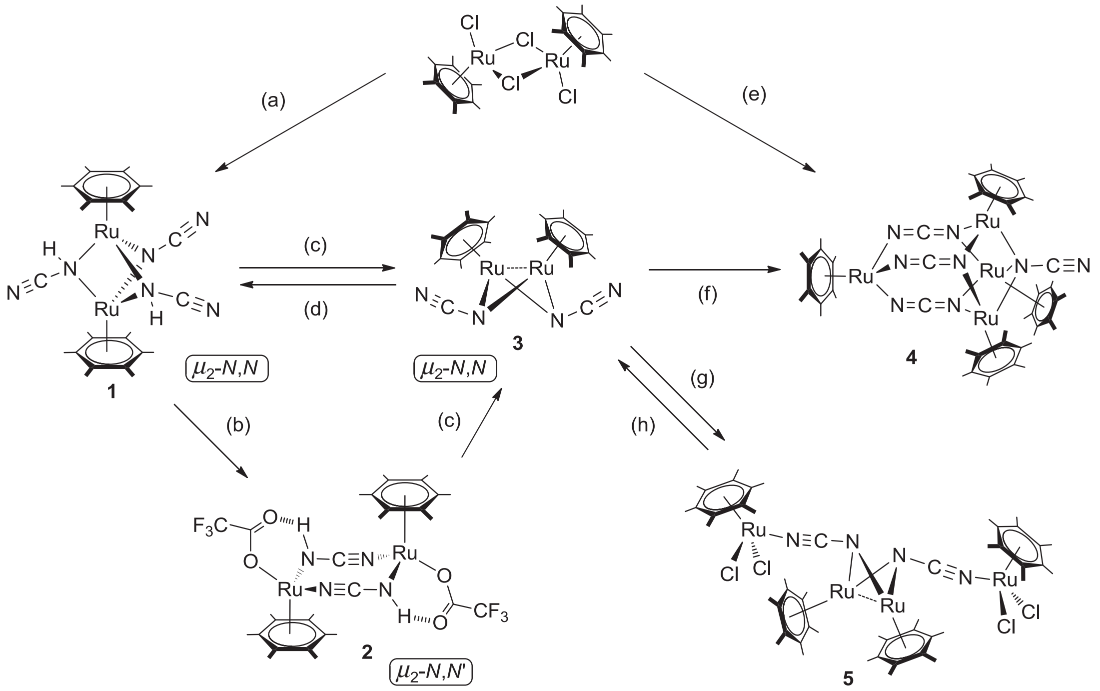
A series of cyanamido-bridged di- and tetraruthenium complexes with η^6-C_6Me_6 ligands have been synthesized, and their interconversion reactions have been investigated. Facile interconversion between the μ_2-$\kappa N,\kappa N$ and μ_2-$\kappa N,\kappa N'$ coordination modes of NCNH ligands at a dimetallic core has been observed for the first time.

In spite of the increasing interests in multinuclear transition metal complexes with nitrogen-based bridging ligands,[1] use of cyanamide anions (NCN^{2-} and $NCNH^-$) in the construction of polymetallic systems remains in the early stage of development.[2–4] Physicochemical properties and reactivities of this series of complexes have been investigated only recently because of the lack of systematic synthetic methods. In our previous study, we have synthesized group 9 (Ir, Rh, and Co) and group 8 (Ru) cyanamido-bridged complexes with ancillary Cp* (Cp*: η^5-C_5Me_5) ligands and revealed their reactivities including unique skeletal transformations.[5] To develop novel coordination structures with cyanamido ligands, we have now examined synthesis of NCN- and NCNH-bridged multinuclear ruthenium complexes with η^6-C_6Me_6 ligands (Scheme 1), which provides the first example of facile interconversion between the μ_2-$\kappa N,\kappa N$ and μ_2-$\kappa N,\kappa N'$ coordination modes of NCNH ligands.

When $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ is allowed to react with 4 equiv of NaNCNH in MeOH or THF at room temperature, the triply bridged dinuclear complex $[\{(\eta^6\text{-}C_6Me_6)Ru(\mu_2\text{-NHCN-}N,N)\}_2(\mu_2\text{-NCN-}N,N)]$ (**1**) is obtained in 78–79% yield.[6] Complex **1** exhibits two IR absorptions at 2196 (m) and 2050 (s) cm^{-1} assignable to the NCN stretching vibrations and only one ^{1}H NMR signal due to the C_6Me_6 protons at δ 2.10 in CD_3OD. The molecular structure of **1**·2MeOH has been determined by a preliminary X-ray diffraction study to confirm that the two ruthenium centers are triply bridged by two NHCN-*N*,*N* and one NCN-*N*,*N* ligands, where the short terminal N–C bond distances (1.05–1.13 Å) clearly indicate that these three bridges can be regarded as cyanamido(1–) or cyanamido(2–) ligands. It should be noted that structurally confirmed complexes with a μ_2-NHCN-*N*,*N* (cyanamido(1–)) ligand have scarcely been reported so far, although there have been known several complexes with μ_2-NCNH-*N*,*N′* (carbodiimido(1–)) type bridges.[3]

Treatment of complex **1** with CF_3COOH in MeOH at room temperature results in the formation of the new NCNH-bridged complex $[(\eta^6\text{-}C_6Me_6)Ru(\mu_2\text{-NHCN-}N,N')(CF_3COO)]_2$ (**2**) in



Scheme 1. Reagents or conditions: (a) NaNCNH (4 equiv), THF or MeOH, rt, 78–79%; (b) CF_3COOH (10 equiv), MeOH, rt, 63%; (c) *t*-BuOK (slight excess), CH_2Cl_2, rt; (d) H_2NCN (slight excess), CH_2Cl_2, rt, 29%; (e) K_2NCN (3 equiv), toluene, 90 °C, 25%; (f) toluene, 100 °C, 42%; (g) $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (0.75 equiv), CH_2Cl_2, rt, 73%; (h) Na_2NCN (excess), CH_2Cl_2, rt, 32%.

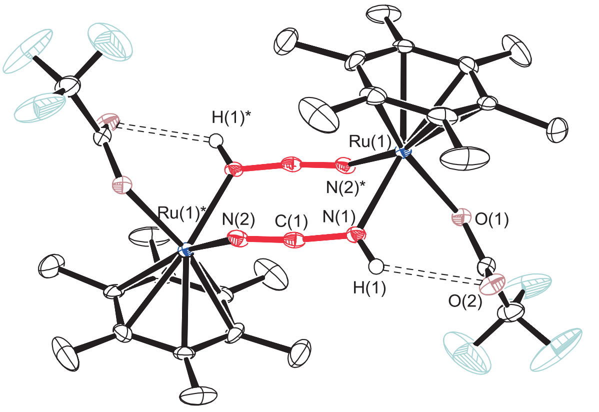


Figure 1. ORTEP drawing of **2** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms (except for H(1) and H(1)*) are omitted for clarity.

63% yield concomitant with the loss of one $NCNH_2$ molecule. The IR (3276 (m), 2134 (s), and 1676 (s) cm^{-1}) and ^1H NMR (δ 1.99) data are in full agreement with the formulation, and the structural details have been unambiguously established by X-ray crystallography (Figure 1). Interestingly, the coordination mode of the NHCN ligands is changed from μ_2-NHCN-*N*,*N* to μ_2-NHCN-*N*,*N′* to form a parallelogramic shaped $[Ru_2(NCN)_2]$ core, although the geometry around the ruthenium centers remains a three-legged piano-stool structure. The HN–C bond distance (1.281(6) Å) is considerably longer than the N–C bond distance (1.173(6) Å), indicating that the NCNH ligand should be regarded as a cyanamido(1–) bridge rather than a corbodiimido(1–). Each carboxylato ligand forms an intramolecular hydrogen bonding with the respective NCNH ligands (O(2)···H(1), 2.41(6) Å). To the best of our knowledge, this reaction provides the first example of structural change between the μ_2-NHCN-*N*,*N* and μ_2-NHCN-*N*,*N′* coordination modes.

On the other hand, reaction of **1** with a strong base, *t*-BuOK, in CH_2Cl_2 also gives rise to formal elimination of $NCNH_2$ to produce the air- and moisture-sensitive deep-blue complex $[(\eta^6\text{-}C_6Me_6)Ru(\mu_2\text{-NCN-}N,N)]_2$ (**3**) in good yield. Deprotonation of a NCNH ligand in **1** should give rise to an anionic diruthenium intermediate, where the dissociation of a $NCNH^-$ anion to form **2** is probably facilitated by the negative charge. The molecular structure of **3** with two μ_2-NCN-*N*,*N* bridges has been determined by a diffraction study and is consistent with its spectral data (IR, 2061 (s) cm^{-1}; ^1H NMR, δ 1.81) (Figure 2). The $[Ru_2N_2]$ core in **3** is strongly puckered with a dihedral angle of 118.3(1)° between the two Ru_2N planes, and the two cyanamido ligands are oriented in a syn stereochemistry. The pyramidalized geometry of the bridging nitrogen atoms suggests that they act as a 2e donor. Consequently, the diruthenium core potentially unsaturated, and in full accordance with this situation, the Ru–Ru distance (2.7892(4) Å) manifests the presence of a metal–metal bonding interaction.[7] Although related ruthenium amido/imido complexes[8] and the isoelectronic diiridium complex $[Cp^*Ir(\mu_2\text{-NCN-}N,N)]_2$[5b] have been reported in the literature, the structural diversity of the cyanamido-bridged $[(\eta^6\text{-}C_6Me_6)Ru]$ complexes is outstanding; three distinct types of diruthenium complexes with cyanamido ligands of different coordination modes are readily accessible.

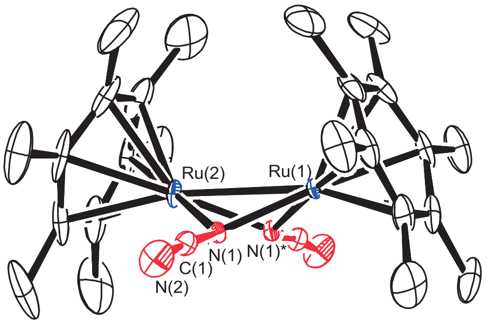


Figure 2. ORTEP drawing of **3** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

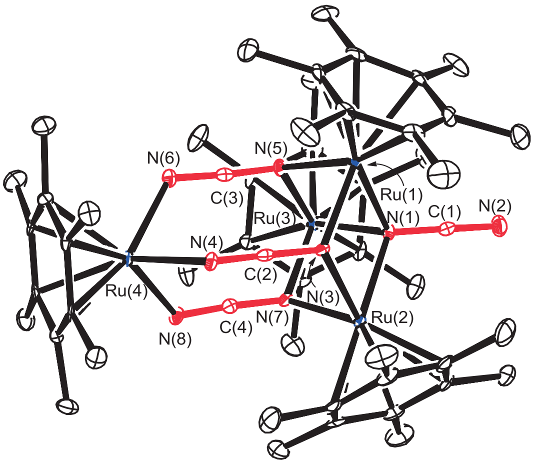


Figure 3. ORTEP drawing of **4**·MeOH with thermal ellipsoids drawn at 50% probability level. Solvating MeOH and hydrogen atoms are omitted for clarity.

Complex **3** can also be generated by treatment of **2** with *t*-BuOK in CH_2Cl_2, although poor solubility of **2** prevents complete conversion. It should be pointed out that the coordination mode of the cyanamido bridge is changed again during this reaction. Interestingly, **3** can be converted back to **1** on reaction with $NCNH_2$ in 29% yield. The ready interconversion of complexes **1**–**3** may be viewed as a unique feature of the cyanamido ligands.

Complex **3** is further utilized as a unit to construct complexes with higher nuclearity. When **3** is heated in toluene for 3 days, dimerization of the Ru_2 core takes place to form the C_3-elongated cubane-like complex $[(\eta^6\text{-}C_6Me_6)Ru(\mu_3\text{-NCN-}N,N,N')_3\{(\eta^6\text{-}C_6Me_6)Ru\}_3(\mu_3\text{-NCN-}N,N,N)]$ (**4**) in 42% yield. Complex **4** shows two IR absorptions at 2074 (m) and 2025 (s) cm^{-1} assignable to the NCN stretching vibrations, and its ^1H NMR spectrum exhibits two signals at δ 2.04 and 1.91 in the intensity ratio of 3:1 assignable to the C_6Me_6 protons. The molecular structure of **4** determined by X-ray crystallography shows that the three NCN ligands lying in parallel with each other bridge the four ruthenium centers with a μ_3-κN,κN,$\kappa N'$ coordination mode, while the fourth adopts a μ_3-κN,κN,κN mode (Figure 3). These NCN bridges can be viewed as carbodiimido(2–) and cyanoimido(2–) ligands, respectively. This result makes a striking contrast with our previous findings

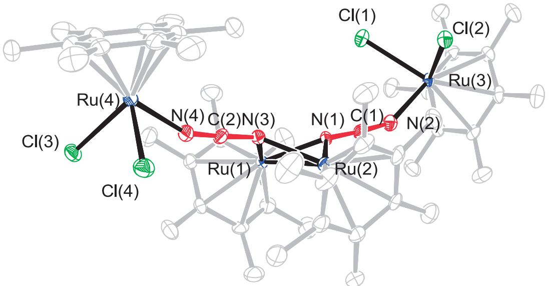


Figure 4. ORTEP drawing of $\mathbf{5}\cdot 4\mathrm{CH_2Cl_2}$ with thermal ellipsoids drawn at 50% probability level. Solvating $\mathrm{CH_2Cl_2}$ and hydrogen atoms are omitted for clarity.

that the thermal dimerization of diiridium complex $[\mathrm{Cp^*Ir}(\mu_2\text{-NCN-}N,N)]_2$ leads to the regular cubane complex $[\mathrm{Cp^*Ir}(\mu_3\text{-NCN-}N,N,N)]_4$.[5b] This difference is presumed to result from the steric size of $\mathrm{C_6Me_6}$ ligands; the more compact cubane core is not suitable for binding four $\mathrm{C_6Me_6}$ ligands. Complex **4** is also synthesized directly by the reaction of $[(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{RuCl_2}]_2$ with $\mathrm{K_2NCN}$ in toluene at 90 °C.

Finally, the reaction of **3** with $[(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{RuCl_2}]_2$ has been revealed to give another tetraruthenium complex $[\{(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{Ru}\}_2\{(\mu_3\text{-NCN-}N,N,N')(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{RuCl_2}\}_2]$ (**5**) as green crystals. A diffraction study of **5** indicates that the $[\mathrm{Ru_2N_2}]$ core in **3** is not largely deformed by the ligation of two $[(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{RuCl_2}]$ units (Figure 4), while the ν(NCN) value of **5** (2108 $\mathrm{cm^{-1}}$) which is 47 $\mathrm{cm^{-1}}$ higher than that of **3** is in agreement with the change of coordination mode from μ_2-NCN-N,N to μ_3-NCN-N,N,N'. As expected, **5** is transformed back to **3** by treatment with $\mathrm{Na_2NCN}$ in $\mathrm{CH_2Cl_2}$.

In conclusion, we have demonstrated that the cyanamido-bridged $[(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{Ru}]$ complexes display remarkable structural diversity and interconvertibility, and structural change between the μ_2-NHCN-N,N and μ_2-NHCN-N,N' coordination modes has been confirmed structurally for the first time. Investigation into further transformation of the cyanamido-bridged complexes are now in progress.

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References and Notes

1 a) J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *193–195*, 1027. b) A. Escuer, G. Aromí, *Eur. J. Inorg. Chem.* **2006**, 4721. c) K. R. Dunbar, R. A. Heintz, *Progress in Inorganic Chemistry*, ed. by K. D. Karlin, John Wiley & Sons, Inc., **1997**, Vol. 45, Chap. 4, pp. 283–391. doi:10.1002/9780470166468.ch4. d) M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scuiller, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier, F. Villain, *Coord. Chem. Rev.* **1999**, *190–192*, 1023. e) L. M. C. Beltran, J. R. Long, *Acc. Chem. Res.* **2005**, *38*, 325. f) K. W. Chapman, P. D. Southon, C. L. Weeks, C. J. Kepert, *Chem. Commun.* **2005**, 3322. g) S. S. Kaye, J. R. Long, *J. Am. Chem. Soc.* **2005**, *127*, 6506. h) J. L. Boyer, M. L. Kuhlman, T. B. Rauchfuss, *Acc. Chem. Res.* **2007**, *40*, 233. i) X.-Y. Wang, Z.-M. Wang, S. Gao, *Chem. Commun.* **2008**, 281.

2 a) W. Beck, H. Beck, R. Schlodder, *Z. Naturforsch., B* **1974**, *29*, 75. b) A. S. Gordetsov, S. V. Zimina, E. Yu. Levakova, N. V. Kulagina, *Zh. Obshch. Khim.* **1997**, *67*, 764. c) W. Schneider, K. Angermainer, H. Schmidbaur, *Z. Naturforsch., B* **1996**, *51*, 801. d) D. J. Mindiola, Y.-C. Tsai, R. Hara, Q. Chen, K. Meyer, C. C. Cummins, *Chem. Commun.* **2001**, 125. e) R. Cao, K. Tatsumi, *Chem. Commun.* **2002**, 2144.

3 a) P. Chaudhuri, K. Wieghardt, B. Nuber, J. Weiss, *J. Chem. Soc., Chem. Commun.* **1985**, 265. b) F. Meyer, I. Hyla-Kryspin, E. Kaifer, P. Kircher, *Eur. J. Inorg. Chem.* **2000**, 771. c) M. Yuan, S. Gao, H.-L. Sun, G. Su, *Inorg. Chem.* **2004**, *43*, 8221. d) A. Escuer, V. McKee, J. Nelson, E. Ruiz, N. Sanz, R. Vicente, *Chem.—Eur. J.* **2004**, *11*, 398. e) M. Yuan, F. Zhao, W. Zhang, F. Pan, Z.-M. Wang, S. Gao, *Chem.—Eur. J.* **2007**, *13*, 2937.

4 For recent reports of mononuclear cyanamido complexes, see: a) M. H. V. Huynh, P. S. White, C. A. Carter, T. J. Meyer, *Angew. Chem., Int. Ed.* **2001**, *40*, 3037. b) S. M. P. R. M. Cunha, M. F. C. G. da Silva, A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.* **2002**, 1791. c) M. H. V. Huynh, T. J. Meyer, R. T. Baker, *J. Am. Chem. Soc.* **2003**, *125*, 2832. d) H. S. Soo, J. S. Figueroa, C. C. Cummins, *J. Am. Chem. Soc.* **2004**, *126*, 11370. e) M. H. V. Huynh, T. J. Meyer, D. L. Jameson, *Inorg. Chem.* **2005**, *44*, 3657. f) S. M. P. R. M. Cunha, M. F. C. G. da Silva, J. J. R. F. da Silva, A. J. L. Pombeiro, *Eur. J. Inorg. Chem.* **2009**, 3966.

5 a) Y. Tanabe, S. Kuwata, Y. Ishii, *J. Am. Chem. Soc.* **2002**, *124*, 6528. b) H. Kajitani, Y. Tanabe, S. Kuwata, M. Iwasaki, Y. Ishii, *Organometallics* **2005**, *24*, 2251. c) K. Takahata, N. Iwadate, H. Kajitani, Y. Tanabe, Y. Ishii, *J. Organomet. Chem.* **2007**, *692*, 208. d) Y. Tanabe, H. Kajitani, M. Iwasaki, Y. Ishii, *Dalton Trans.* **2007**, 4701. e) M. Imaji, Y. Tanabe, Y. Mutoh, Y. Ishii, *Inorg. Chem.* **2009**, *48*, 773.

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7 a) D. W. Engel, K. G. Moodley, L. Subramony, R. J. Haines, *J. Organomet. Chem.* **1988**, *349*, 393. b) H. A. Mirza, J. J. Vittal, R. J. Puddephatt, *Inorg. Chem.* **1993**, *32*, 1327. c) G. M. Ferrence, P. E. Fanwick, C. P. Kubiak, R. J. Haines, *Polyhedron* **1997**, *16*, 1453. d) J. Kuncheria, H. A. Mirza, H. A. Jenkins, J. J. Vittal, R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.* **1998**, 285. e) J. Kuncheria, H. A. Mirza, J. J. Vittal, R. J. Puddephatt, *J. Organomet. Chem.* **2000**, *593–594*, 77.

8 a) R. E. Blake, Jr., R. H. Heyn, T. D. Tilley, *Polyhedron* **1992**, *11*, 709. b) A. K. Burred, A. J. Steedman, *J. Chem. Soc., Chem. Commun.* **1995**, 2109. c) A. K. Burrell, A. J. Steedman, *Organometallics* **1997**, *16*, 1203. d) S. Takemoto, S. Oshio, T. Kobayashi, H. Matsuzaka, M. Hoshi, H. Okimura, M. Yamashita, H. Miyasaka, T. Ishii, M. Yamashita, *Organometallics* **2004**, *23*, 3587. e) S. Takemoto, T. Kobayashi, H. Matsuzaka, *J. Am. Chem. Soc.* **2004**, *126*, 10802. f) H. Kondo, K. Matsubara, H. Nagashima, *J. Am. Chem. Soc.* **2002**, *124*, 534. g) S. Takemoto, H. Morita, K. Kamikawa, H. Matsuzaka, *Chem. Commun.* **2006**, 1328. h) J. M. Hoover, A. DiPasquale, J. M. Mayer, F. E. Michael, *Organometallics* **2007**, *26*, 3297. i) S. Takemoto, T. Kobayashi, T. Ito, A. Inui, K. Karitani, S. Katagiri, Y. Masuhara, H. Matsuzaka, *Organometallics* **2011**, *30*, 2160.