J|A|C|S
COMMUNICATIONS

Published on Web 05/16/2002

Syntheses and Skeletal Transformations of NCNH- and NCN-Bridged Tetrairidium(III) Cages

Yoshiaki Tanabe, Shigeki Kuwata,† and Youichi Ishii*,‡

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

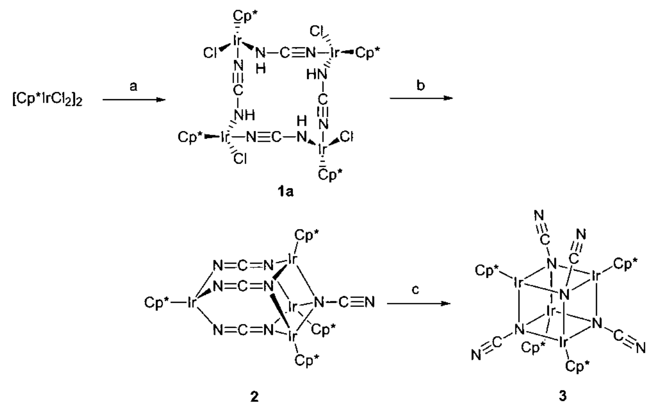
Received October 30, 2001

Polynuclear transition-metal complexes with nitrogen-based bridging ligands such as nitrido, imido, cyano, and azido have recently been attracting considerable attention not only because of their structural diversity but also in connection with their unique physicochemical properties including semiconductivity and magnetism.[1] Although cyanamides ($NCNR_2$)[2] and their deprotonated forms, cyanamide ($NCNR^-$)[3] and cyanoimide or carbodiimide (NCN^{2-})[4] anions, have been known to behave as potential bridging ligands in dinuclear complexes, their use in the synthesis of complexes with higher nuclearity still remains to be exploited.[5,6] Here we describe the synthesis of an NCNH-bridged macrocyclic tetrairidium complex and its skeletal transformations into NCN-bridged cuboidal complexes.

When the dinuclear iridium complex $[Cp^*IrCl_2]_2$ ($Cp^* = \eta^5$-C_5Me_5) was treated with 2 equiv of sodium hydrogencyanamide at room temperature, the NCNH-bridged tetrairidium complex $[Cp^*IrCl(\mu_2$-NCNH-$N,N')]_4$ (**1a**) was obtained in 86% yield (Scheme 1). Complex **1a** exhibits one strong IR absorption at 2211 cm^{-1} assignable to the asymmetric stretching vibration of the NCNH moiety, while the IR absorption at 3221 cm^{-1} and the ^{1}H NMR signal at δ 3.57 are assignable to the NH group. These observations suggest that **1a** has a highly symmetrical structure composed of Cp*IrCl(NCNH) units. The $^{13}C\{^1H\}$ NMR signals at δ 10.2 (Me), 85.7 (Cp* ring carbons), and 129.6 (NCNH) also support the symmetrical structure of **1a**.

The molecular structure of $[Cp^*IrI(\mu_2$-NCNH-$N,N')]_4{\cdot}C_7H_8$ (**1b**$\cdot C_7H_8$), which is readily obtained by the halogen exchange of **1a** with excess sodium iodide in 51% yield, has been established by X-ray crystallography.[7] As depicted in Figure 1, the complex has a characteristic 16-membered macrocyclic structure with an approximate S_4 symmetry. Each iridium center adopts a three-legged piano-stool structure, where the Ir−NH and Ir−N bond distances are 2.12 (mean) and 2.03 (mean) Å, respectively. The C−NH and C−N bond distances at 1.31 (mean) and 1.14 (mean) Å, respectively, as well as the essentially linear Ir−N−C (168° (mean)) and N−C−NH (174° (mean)) arrangements suggest that the NCNH bridge is better described as a hydrogencyanamido(1−) ligand ($N{\equiv}C{-}NH^-$) rather than a hydrogencarbodiimido(1−) ligand ($N^-{=}C{=}NH$).[3a−c,e,f] Although a few NCNH-bridged dinuclear complexes have been reported in the literature,[3a,f] the 16-membered $(M$-$NCNH)_4$ tetranuclear complex is unprecedented. Related metallacyclic structures have only been found in polymeric dicyanamide salts $M[N(CN)_2]_2$ (M = Mn, Fe, Co, Ni, Cu)[6a,e,f] and tetrameric silyl- or germylcarbodiimides $(R_2ENCN)_4$ (E = Si, Ge).[8]

Scheme 1 [a]



[a] Reagents and conditions: (a) 2 Na(NCNH), rt; (b) 4 NEt_3, rt; (c) *p*-xylene, reflux.

Treatment of the tetrairidium macrocycle **1a** with 4 equiv of triethylamine at room temperature led to the formation of the "C_3-elongated cubane-like" tetrairidium complex $[Cp^*Ir(\mu_3$-NCN-$N,N,N')_3(IrCp^*)_3(\mu_3$-NCN-$N,N,N)]$ (**2**) in 44% yield as the major product. For complex **2**, neither NMR signals nor IR absorptions assignable to NH groups are observed, while each of the ^{1}H NMR resonance due to the Cp* protons (δ 1.53, 1.58) and the $^{13}C\{^1H\}$ NMR signals of the Me (δ 9.6, 9.0), Cp* ring (δ 83.9, 82.5), and NCN carbons (δ 131.5, 144.6) appears as a pair of peaks with the intensity ratio of 1:3. These data indicate that complex **2** consists of two distinct types of Cp*Ir and NCN units in the ratio of 1:3. The IR absorptions at 2043 (m) and 2105 (s) cm^{-1} assignable to the NCN stretching vibrations are also in agreement with the formulation.

The molecular structure of $\mathbf{2}{\cdot}0.5C_7H_8$ has unambiguously been determined by an X-ray analysis (Figure 1).[9] Three linear NCN ligands (N−C−N, 176.6° (mean)) lying in parallel with each other bridge the four iridium centers with a μ_3-$\kappa N,\kappa N,\kappa N'$ coordination mode. Within these bridges, all the N−C bond distances and the Ir−N−C bond angles fall in the range of 1.20−1.26 Å and 118.8−125.3°, respectively. On the basis of these metric features, the three NCN ligands are regarded to adopt the carbodiimido(2−) structure ($N^-{=}C{=}N^-$) as the dominant canonical form. The fourth NCN ligand caps three iridium atoms with a μ_3-$\kappa N,\kappa N,\kappa N$ coordination mode, where the N(7)−C(4) and N(8)−C(4) bond distances at 1.305(7) and 1.177(7) Å, respectively, indicate that this NCN ligand can be described as cyanoimido(2−) ($N{\equiv}C{-}N^{2-}$). As a whole, the $Ir_4(NCN)_4$ core forms an elongated cubane-like skeleton with an approximate C_{3v} symmetry, one of the iridium corners (Ir(1))

* To whom correspondence should be addressed. E-mail: ishii@chem.chuo-u.ac.jp
† Present address: Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan.
‡ Present address: Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan.

10.1021/ja017436e CCC: $22.00

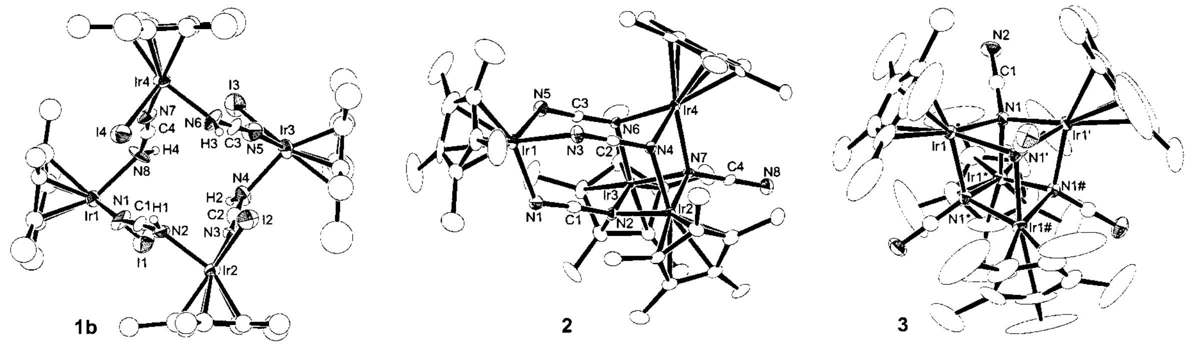


Figure 1. ORTEP drawings of **1b** (left), **2** (middle), and **3** (right) with thermal ellipsoids drawn at the 30% (for **1b** and **3**) or 50% (for **2**) probability level.

being separated by the three μ_3-NCN-*N*,*N*,*N*′ bridges. It should be pointed out that complexes containing a μ_3-NCN ligand are very rare; only the μ_3-κN,κN,$\kappa N'$ coordination mode has been found in a trinuclear gold complex $[\{(Ph_3P)Au\}_2NCN\{Au(PPh_3)\}][BF_4]$.[5c]

When the "elongated cubane" complex **2** was heated in refluxing *p*-xylene, the regular cubane-type complex [Cp*Ir(μ_3-NCN-*N*,*N*,*N*)]$_4$ (**3**) was obtained in 71% yield. The IR spectrum of **3** shows one absorption at 2110 cm^{-1} assignable to the NCN stretching vibration. The ^{1}H and ^{13}C{^{1}H} NMR spectra exhibit only one set of Cp* and NCN signals (^{1}H NMR: δ 1.44; ^{13}C{^{1}H} NMR: δ 8.1 (C_5*Me*$_5$), 84.4 (*C*$_5$Me$_5$), 129.7 (NCN)). These observations suggest a highly symmetric structure of **3**, which has further been determined by an X-ray analysis (Figure 1).[10] The molecule has a crystallographic D_{2d} symmetry. Each of the four linear NCN ligands caps three iridium centers with a μ_3-κN,κN,κN coordination mode, where the N(1)−C(1) and N(2)−C(1) bond distances are 1.28(1) and 1.21(1) Å, respectively. The long interatomic distances between the iridium atoms (3.3670(6) and 3.3909(6) Å) exclude any metal−metal bonding interaction. Complex **3** represents the first example of the cyanoimido(2−)-bridged cubane, although some M_4N_4 cubane-type cores have recently been synthesized and received considerable interest.[11]

In conclusion, we have synthesized a series of NCNH- and NCN-bridged tetrairidium complexes **1**−**3** and revealed their novel skeletal transformations from macrocycle **1** to cubane **3** via "elongated cubane" **2**. Although we must await further investigation to elucidate the reaction mechanisms for these conversions, the present study has demonstrated that NCNH$^-$ and NCN^{2-} anions work as versatile and potential bridging units to construct new polymetallic systems. Studies on the physicochemical properties of **1**−**3** are also in progress.

Acknowledgment. We thank the Ministry of Education, Culture, Sports, Science and Technology, Japan, for a Grant-in-Aid and Rigaku Corporation for the X-ray diffraction analysis of **2**·0.5C_7H_8. Y.T. also thanks the JSPS Research Fellowships for Young Scientists.

Supporting Information Available: Experimental and spectroscopic details and tables of crystallographic data, positional and thermal parameters, bond distances and angles, and thermal ellipsoid figures for complexes **1b**·C_7H_8, **2**·0.5C_7H_8, and **3** (PDF). X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955−978. (b) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239−482. (c) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283−391. (d) Ribas, J.; Escuer, A.; Monfort, M.; Vicente, R.; Cortés, R.; Lezama, L.; Rojo, T. *Coord. Chem. Rev.* **1999**, *193*−*195*, 1027−1068.

(2) (a) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Marchant, N. S. *Polyhedron* **1984**, *3*, 1033−1035. (b) Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. *Organometallics* **1987**, *6*, 1073−1080. (c) Begley, M. J.; Hubberstey, P.; Walton, P. H. *J. Chem. Soc., Dalton Trans.* **1995**, 957−962. (d) Bera, J. K.; Nethaji, M.; Samuelson, A. G. *Inorg. Chem.* **1999**, *38*, 1725−1735.

(3) (a) Chaudhuri, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *J. Chem. Soc., Chem. Commun.* **1985**, 265−266. (b) Brader, M. L.; Ainscough, E. W.; Baker, E. N.; Brodie, A. M.; Ingham, S. L. *J. Chem. Soc., Dalton Trans.* **1990**, 2785−2792. (c) Ainscough, E. W.; Baker, E. N.; Brader, M. L.; Brodie, A. M.; Ingham, S. L.; Waters, J. M.; Hanna, J. V.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1991**, 1243−1249. (d) Haag, P.; Lechler, R.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 112−116. (e) Ainscough, E. W.; Brodie, A. M.; Cresswell, R. J.; Turnbull, J. C.; Waters, J. M. *Croat. Chem. Acta* **1999**, *72*, 377−394. (f) Meyer, F.; Hyla-Krypsin, I.; Kaifer, E.; Kircher, P. *Eur. J. Inorg. Chem.* **2000**, 771−781. (g) Fabre, P.-L.; Galibert, A. M.; Soula, B.; Dahan, F.; Castan, P. *J. Chem. Soc., Dalton Trans.* **2001**, 1529−1536. (h) Crutchley, R. J. *Coord. Chem. Rev.* **2001**, *219*−*221*, 125−155.

(4) (a) Beck, W.; Bock, H.; Schlodder, R. *Z. Naturforsch.* **1974**, *B29*, 75−79. (b) Mindiola, D. J.; Tsai, Y.-C.; Hara, R.; Chen, Q.; Meyer, K.; Cummins, C. C. *Chem. Commun.* **2001**, 125−126. (c) Cao, R.; Tatsumi, K. Presented at the 79th CSJ National Meeting, Kobe, Japan, March 2001; Paper 1PA101.

(5) (a) Krogmann, K.; Mattes, R. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 1046. (b) Reischmann, R.; Hausen, H.-D.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 123−133. (c) Schneider, W.; Angermaier, K,; Schmidbaur, H. *Z. Naturforsch.* **1996**, *B51*, 801−805.

(6) Inorganic polymers with these ligands have been investigated: (a) Kohout, J.; Jäger, L.; Hvastijová, M.; Kožíšek, J. *J. Coord. Chem.* **2000**, *51*, 169−218. (b) Becker, M.; Nuss, J.; Jansen, M. *Z. Naturforsch.* **2000**, *B55*, 383−385. (c) Zusai, K.; Katayama, T.; Ishida, T.; Nogami, T. *Mol. Cryst. Liq. Cryst. Sci. Technol.* **2000**, *A343*, 121−126. (d) Becker, M.; Jansen, M. *Acta Crystallogr.* **2001**, *C57*, 347−348. (e) Miller, J. S.; Manson, J. L. *Acc. Chem. Res.* **2001**, *34*, 563−570. (f) Batten, S. R. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 107−114.

(7) Selected spectral data for **1b** are as follows. ^{1}H NMR (C_6D_6): δ 1.62 (s, 60H, Me), 3.48 (s, 4H, NH). ^{13}C{^{1}H} NMR (C_6D_6): δ 10.6 (s, C_5*Me*$_5$), 86.7 (s, *C*$_5$Me$_5$), 126.5 (s, NCN). IR (KBr, cm^{-1}): 3271 (w), 2218 (s, NCN). Crystallographic data for **1b**·C_7H_8: orthorhombic, space group $P2_12_12_1$, orange, a = 13.654(9) Å, b = 13.776(8) Å, c = 32.91(1) Å, V = 6189(5) Å^3, Z = 4, T = 21 °C, $R(R_w)$ = 0.050 (0.050) for 3791 reflections [$I > 3\ \sigma(I)$], GOF = 1.37.

(8) (a) Obermeyer, A.; Kienzle, A.; Weidlein, J.; Riedel, R.; Simon, A. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1357−1363. (b) Dahrouch, M.; Rivière-Baudet, M.; Satgé, J.; Mauzac, M.; Cardin, C. J.; Thorpe, J. H. *Organometallics* **1998**, *17*, 623−629.

(9) Crystallographic data for **2**·0.5C_7H_8: triclinic, space group $P\bar{1}$, yellow, a = 11.8609(6) Å, b = 13.632(1) Å, c = 17.707(1) Å, α = 110.448(2)°, β = 91.827(4)°, γ = 115.614(2)°, V = 2361.6(3) Å^3, Z = 2, T = −150 °C, $R(R_w)$ = 0.030 (0.038) for 9169 reflections [$I > 3\ \sigma(I)$], GOF = 1.80.

(10) Crystallographic data for **3**: tetragonal, space group $I\bar{4}2m$, orange, a = 11.967(2) Å, c = 15.248(5) Å, V = 2183.7(6) Å^3, Z = 2, T = 21 °C, R (R_w) = 0.025 (0.032) for 1268 reflections [$I > 3\ \sigma(I)$], GOF = 0.98.

(11) (a) Mai, H.-J.; Meyer zu Köcker, R.; Wocadlo, S.; Massa, W.; Dehnicke, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1235−1236. (b) Halcrow, M. A.; Sun, J.-S.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1995**, *34*, 4167−4177. (c) Gómez-Sal, P.; Martín, A.; Mena, M.; Yélamos, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2185−2186. (d) Abernethy, C. D.; Bottomley, F.; Decken, A.; Cameron, T. S. *Organometallics* **1996**, *15*, 1758−1759. (e) Sarasa, J. P.; Poblet, J. M.; Bénard, M. *Organometallics* **2000**, *19*, 2264−2272. (f) Link, H.; Decker, A.; Fenske, D. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1567−1574. (g) Verma, A. K.; Nazif, T. N.; Achim, C.; Lee, S. C. *J. Am. Chem. Soc.* **2000**, *122*, 11013−11014. (h) Krieger, M.; Gould, R. O.; Harms, K.; Greiner, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2001**, *627*, 747−754. (i) Freitag, K.; Gracia, J.; Martín, A.; Mena, M.; Poblet, J.-M.; Sarasa, J. P.; Yélamos, C. *Chem.*−*Eur. J.* **2001**, *7*, 3644−3651.

JA017436E