

A Cyanamido-Bridged Diiridium Complex: A Reactive Building Block for Polynuclear Cyanamido Complexes

Hidehito Kajitani,[†] Yoshiaki Tanabe,[‡] Shigeki Kuwata,[§]
Masakazu Iwasaki,^{||} and Youichi Ishii*,[‡]

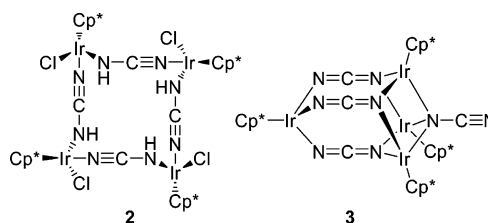
Institute of Industrial Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8505, Japan, Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan, Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan, and Department of Applied Chemistry, Faculty of Engineering, Saitama Institute of Technology, Okabe, Saitama 369-0293, Japan

Received December 25, 2004

Summary: $[\text{Cp}^*\text{IrCl}_2]_2$ reacts with 2 equiv of Na_2NCN to afford the NCN-bridged diiridium complex $[\text{Cp}^*\text{Ir}(\mu_2\text{-NCN-}N,N)]_2$ (**5**), which undergoes further reactions with donor molecules such as CO and phosphines. Complex **5** works as an excellent building block for the synthesis of the NCN-capped heterotrinnuclear complexes $[(\text{Cp}^*\text{Ir})_2(\text{ML})(\mu_3\text{-NCN-}N,N,N)]^+$ ($\text{ML} = \text{Rh}(\text{cod}), \text{CpRu}, \text{Pd}(\eta^3\text{-C}_3\text{H}_5)$) on reactions with cationic group 8–10 metal complexes such as $[\text{Rh}(\text{cod})(\text{acetone})_n]^+$, $[\text{CpRu}(\text{MeCN})_3]^+$, and $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{acetone})_n]^+$, while the dimerization of **5** leads to the cubane-type tetrairidium complex $[\text{Cp}^*\text{Ir}(\mu_3\text{-NCN-}N,N,N)]_4$.

Despite the increasing interest in polynuclear transition-metal complexes with nitrogen-based bridging ligands as advanced materials,¹ use of cyanamide anions (NCN^{2-} and NCNH^-) as bridging ligands for the construction of polynuclear systems remains in the early stages of development.² However, because of their soft, sterically small, and potentially polydentate nature, these anions are expected to provide a new entry for the chemistry of polynuclear complexes. In this context we have shown that the diiridium complex $[\text{Cp}^*\text{IrCl}_2]_2$ (**1**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) reacts with NaNCNH to afford the macrocyclic complex $[\text{Cp}^*\text{IrCl}(\mu_2\text{-NCNH-}N,N')]_4$ (**2**), which is further converted into the C_3 -elongated cubane-like complex $[\text{Cp}^*\text{Ir}(\mu_3\text{-NCN-}N,N,N')_3(\text{IrCp}^*)_3(\mu_3\text{-NCN-}N,N,N)]$ (**3**) (Chart 1) and the regular cubane-type complex $[\text{Cp}^*\text{Ir}(\mu_3\text{-NCN-}N,N,N)]_4$ (**4**).³ Now we have synthesized the NCN-bridged diiridium complex $[\text{Cp}^*\text{Ir}(\mu_2\text{-NCN-}N,N)]_2$ (**5**) and revealed its novel reactivities, including

Chart 1



the dimerization reaction to form **4** as well as the heterotrinnuclear complex formation through the incorporation of a heterometal fragment.

Switching the cyanamide source to react with **1** from NaNCNH to Na_2NCN resulted in a striking change of the reaction product. Thus, when **1** was treated with 2 equiv of Na_2NCN at room temperature, the NCN-bridged diiridium complex **5**, instead of **2**, was obtained as dark red crystals in 47% yield (Scheme 1).⁵ Complex **5** shows one strong IR absorption at 2093 cm^{-1} assignable to the stretching vibration of the NCN moiety, and the ^1H NMR spectrum exhibits only one signal at δ 1.87 assignable to the Cp^* protons. The molecular structure of **5** was determined by X-ray crystallography.⁵ The molecule has a crystallographic C_s symmetry. As depicted in Figure 1, each NCN ligand bridges the iridium centers with a $\mu_2\text{-}\kappa\text{N},\kappa\text{N}$ coordination mode to form the Ir_2N_2 core, which is strongly puckered with a $\text{N}(1)\text{---Ir}(1)\text{---Ir}(2)\text{---N}(1^*)$ torsion angle of $118.0(7)^\circ$. It should be pointed out that complexes with $\mu_2\text{-NCN-}N,N$ ligands have rarely been reported in the literature.⁶ The bond angles around the $\text{N}(1)$ atom (sum 332°) as well as the

* To whom correspondence should be addressed. E-mail: ishii@chem.chuo-u.ac.jp.

[†] The University of Tokyo.

[‡] Chuo University.

[§] Tokyo Institute of Technology.

^{||} Saitama Institute of Technology.

(1) (a) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283–391. (b) Ribas, J.; Escuer, A.; Monfort, M.; Vicente, R.; Cortés, R.; Lezama, L.; Rojo, T. *Coord. Chem. Rev.* **1999**, *193–195*, 1027–1068. (c) Verdager, M.; Bleuzen, A.; Marvaud, V.; Vaissermann, J.; Seuleiman, M.; Desplanches, C.; Scullier, A.; Train, C.; Garde, R.; Gelly, G.; Lomenech, C.; Rosenman, I.; Veillet, P.; Cartier, C.; Villain, F. *Coord. Chem. Rev.* **1999**, *190–192*, 1023–1047.

(2) For recent examples, see: (a) Schneider, W.; Angermaier, K.; Schmidbaur, H. *Z. Naturforsch.* **1996**, *B51*, 801–805. (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. *Chem. Commun.* **2002**, 2144–2145.

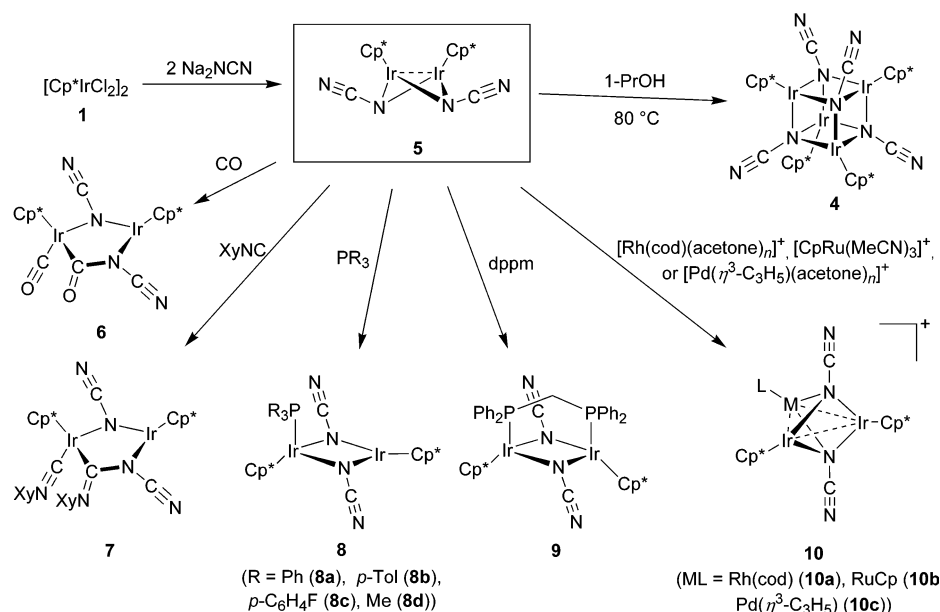
(3) Tanabe, Y.; Kuwata, S.; Ishii, Y. *J. Am. Chem. Soc.* **2002**, *124*, 6528–6529.

(4) Complex **1** (1.0425 g, 1.31 mmol) and Na_2NCN (229.5 mg, 2.67 mmol) were dissolved in methanol (30 mL), and the mixture was stirred for 15 min at room temperature. The resulting dark red solution was dried in vacuo to give a dark red solid, which was dissolved in CH_2Cl_2 –methanol (30:1, 1.0 mL) and the solution passed through a column packed with Al_2O_3 (Merck; eluent 30:1 CH_2Cl_2 –methanol). The first yellow band contains $[\text{Cp}^*\text{Ir}(\mu_3\text{-NCN-}N,N,N')_3(\text{IrCp}^*)_3(\mu_3\text{-NCN-}N,N,N)]$ (**3**),³ while the second dark red band eluted was collected and evaporated to dryness. Recrystallization from CH_2Cl_2 –diethyl ether gave dark red needles of $[\text{Cp}^*\text{Ir}(\mu_3\text{-NCN-}N,N)]_4$ (**4**) (451.6 mg, 47% yield).

(5) Crystallographic data for **5**: $\text{C}_{22}\text{H}_{30}\text{Ir}_2\text{N}_4$, FW = 734.95, orthorhombic, space group $Pnma$, $a = 21.365(6)\text{ Å}$, $b = 15.428(5)\text{ Å}$, $c = 6.697(5)\text{ Å}$, $V = 2207(2)\text{ Å}^3$, $Z = 4$, $T = 21\text{ °C}$, $\rho_{\text{calc}} = 2.211\text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 120.93\text{ cm}^{-1}$, 2519 unique reflections, $R(R_w) = 0.052$ (0.054) for 156 variables and 1731 reflections ($I > 3\sigma(I)$), GOF = 1.001.

(6) Rajca, G.; Weidlein, J. Z. *Anorg. Allg. Chem.* **1986**, *538*, 36–44.

Scheme 1



short N(2)–C(1) bond distance (1.15(3) Å) indicate that the NCN moiety is better described as a cyanamido(2–) ligand rather than a carbodiimido(2–) ligand, and the N(1) atom is sp³ hybridized. On the other hand, the Ir–Ir distance at 2.8179(9) Å is slightly longer than those of the structurally related imido complexes [Cp*Ir(μ₂-

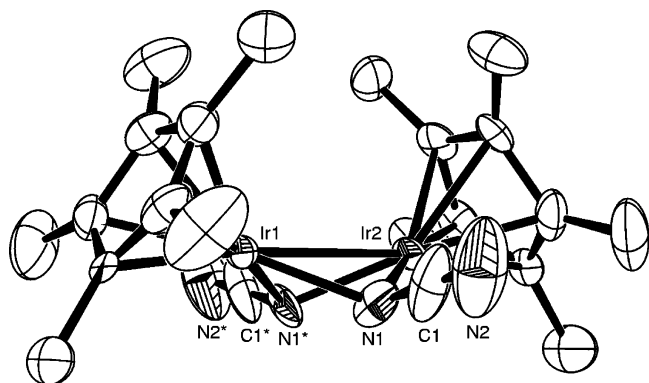


Figure 1. Molecular structure of **5**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

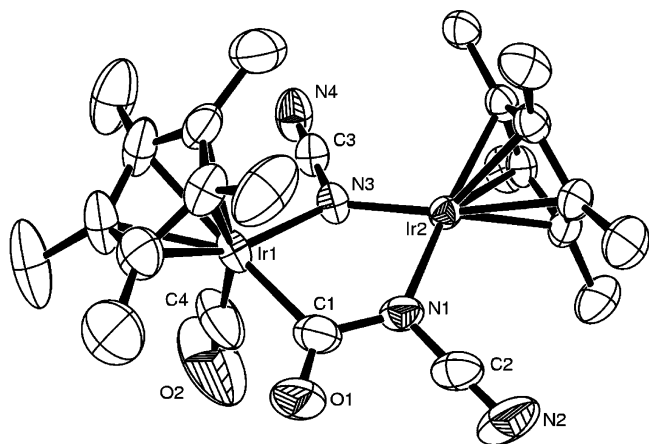


Figure 2. Molecular structure of **6**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

NR)]₂ (R = Ph,⁷ 2.778(1) Å; R = cyclopentyl,⁸ 2.6133(5) Å) but suggests the presence of a metal–metal bonding interaction, which is reflected in the potentially unsaturated nature of the diiridium core.

As expected, complex **5** reacts smoothly with donor molecules. Treatment of **5** with atmospheric CO at room temperature followed by recrystallization under N₂ led to the CO-insertion product [Cp*Ir(CO)(μ₂-NCN-*N,N*)(μ₂-OCNCN)IrCp*] (**6**) in 82% yield (Scheme 1).⁹ The IR spectrum of **6**, showing two strong ν(NCN) bands at 2186 and 2107 cm^{−1} as well as two ν(CO) bands at 2016 and 1615 cm^{−1}, is in full agreement with the formulation. The presence of two distinct iridium centers is also confirmed by the two Cp* signals at δ 1.86 and 1.75 in the ¹H NMR spectrum. The molecular structure of **6** has been unambiguously established by an X-ray analysis (Figure 2).¹⁰ One of the NCN ligands in **5** is coupled with CO¹¹ to form the unprecedented cyanogen isocyanate ligand (NCNCO), and the Ir(1) atom is further coordinated by a CO ligand. The diiridacycle is nearly planar, and the large Ir···Ir separation (3.5687(3) Å) excludes any metal–metal bonding interaction. The related carbodiimido complex [Cp*Ir(CNXy)(μ₂-NCN-*N,N*)(μ₂-XyNCNCN)IrCp*] (**7**) was also obtained from the reaction of **5** with XyNC (Xy = 2,6-dimethylphenyl) (Scheme 1).¹²

(7) Dobbs, D. A.; Bergman, R. G. *Organometallics* **1994**, *13*, 4594–4605.

(8) Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 3771–3778.

(9) The initial products formed under CO, which are tentatively characterized as stereoisomers of [Cp*Ir(CO)(μ₂-NCN-*N,N*)(μ₂-OCNCN)Ir(CO)Cp*] (¹H NMR (CDCl₃): δ 1.88, 1.91, 1.92, 1.94), are not stable under N₂ and are quantitatively transformed into **6** through dissociation of one CO molecule.

(10) Crystallographic data for **6**: C₂₄H₃₀Ir₂N₄O₂, FW = 790.97, triclinic, space group *P*1̄, *a* = 8.888(5) Å, *b* = 11.704(4) Å, *c* = 12.696(4) Å, α = 88.75(3)°, β = 86.05(4)°, γ = 76.30(4)°, *V* = 1280.2(9) Å³, *Z* = 2, *T* = 21 °C, ρ_{calcd} = 2.052 g cm^{−3}, μ(Mo Kα) = 104.40 cm^{−1}, 5779 unique reflections, *R* (*R*_w) = 0.026 (0.026) for 320 variables and 4755 reflections (*I* > 3σ(*I*)), GOF = 1.006.

(11) Ye, C.; Sharp, P. R. *Inorg. Chem.* **1995**, *34*, 55–59.

(12) Spectral data for **7**: ¹H NMR (C₆D₆, δ) 1.42, 1.90 (both s, 15H each, Cp*); IR (KBr, cm^{−1}) 2159 (m, NCN), 2132 (s, NCN), 2090 (s, CN), 1553 (s, CN).

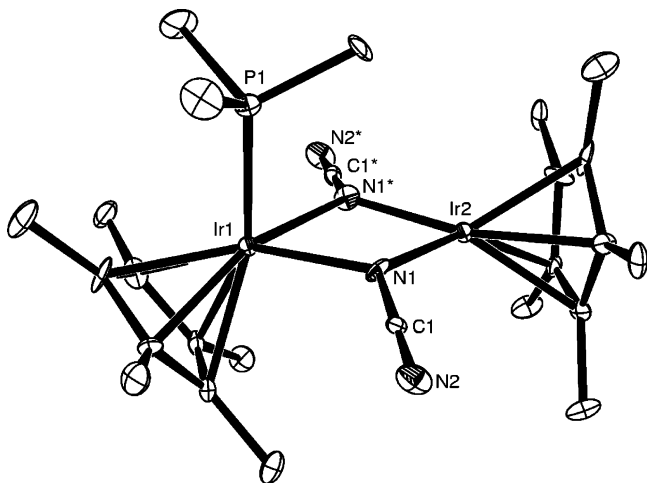


Figure 3. Molecular structure of **8d**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

The reaction of **5** with 1 equiv of PR_3 resulted in the formation of the mono(phosphine) complex $[\text{Cp}^*\text{Ir}(\text{PR}_3)(\mu_2\text{-NCN-}N,N)\text{IrCp}^*]$ (**8a**, $\text{R} = \text{Ph}$; **8b**, $\text{R} = p\text{-Tol}$; **8c**, $\text{R} = p\text{-C}_6\text{H}_4\text{F}$; **8d**, $\text{R} = \text{Me}$) in 34–83% yield (Scheme 1).¹³ No further reaction was observed, even in the presence of an excess amount of PR_3 . In accordance with the formulation, complexes **8** have one strong IR absorption at nearly 2060 cm^{-1} assignable to the NCN stretching vibration, and their ^1H NMR spectra display two Cp^* signals at δ 1.55–1.61 and 1.40–1.46. The molecular structure of **8d** has been established by an X-ray analysis (Figure 3).¹⁴ On coordination of the phosphine ligand, the Ir_2N_2 core is considerably flattened, and the $\text{Ir}\cdots\text{Ir}$ interatomic distance is elongated ($3.2985(5)\text{ \AA}$). The $\text{Ir}(2)\text{--N}(1)$ bond distance ($1.996(7)\text{ \AA}$) is significantly shorter than the $\text{Ir}(1)\text{--N}(1)$ bond distance ($2.113(7)\text{ \AA}$), which indicates some π donation from the NCN ligands to the $\text{Ir}(2)$ atom. Unlike the mono(phosphines), dppm (bis(diphenylphosphino)methane) works as a bidentate ligand to form the coordinatively saturated bis-(phosphine) complex $[(\text{Cp}^*\text{Ir}(\mu_2\text{-NCN-}N,N))_2(\mu\text{-dppm})]\cdot 1.5\text{C}_6\text{H}_6$ (**9** $\cdot 1.5\text{C}_6\text{H}_6$) in 76% yield (Scheme 1), whose molecular structure has also been confirmed crystallographically (ORTEP drawing not shown).¹⁵

Interestingly, the above reaction with phosphines forms a sharp contrast to that of the dimeric phenylimido complex $[\text{Cp}^*\text{Ir}(\mu_2\text{-NPh})_2]$, where one of the imido

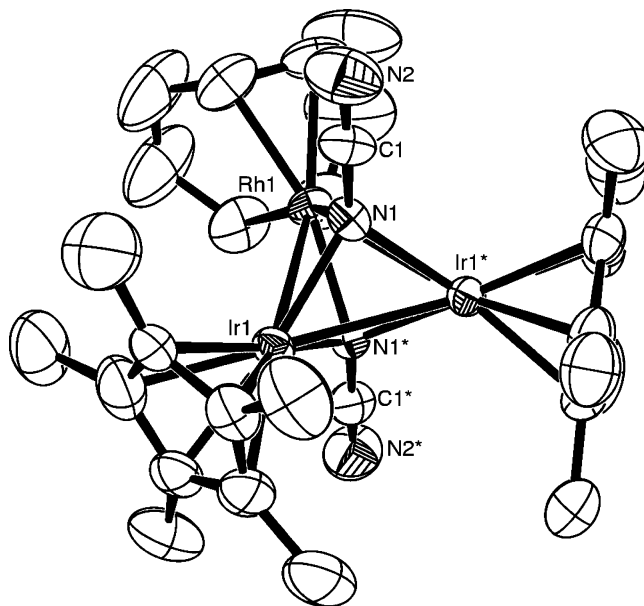


Figure 4. Structure of the cationic part of **10aBPh₄·CH₂Cl₂**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

ligands is eliminated as phosphine imide.⁷ We attribute this difference to the soft character of the cyanamido ligand to form more stable N–metal bonds with late-transition-metal centers; namely, the π -electron conflict between the filled metal $d\pi$ orbitals and the lone pair electrons of the metal-bound nitrogen is greatly weakened by the electron-withdrawing effect of the CN group.

On the other hand, the lone pair electrons of the sp^3 -hybridized bridging nitrogen atoms in **5** are directed outward and are expected to interact with a Lewis acidic metal fragment. Indeed, complex **5** readily reacts with $[\text{Rh}(\text{cod})(\text{acetone})_n](\text{OTf})$ ($\text{cod} = 1,5\text{-cyclooctadiene}$, $\text{OTf} = \text{OSO}_2\text{CF}_3$) to form the heterotrinnuclear complex $[(\text{Cp}^*\text{Ir})_2\{\text{Rh}(\text{cod})\}(\mu_3\text{-NCN-}N,N,N)_2]^+$ (**10a**), which was isolated as the BPh_4 salt **10aBPh₄·CH₂Cl₂** in 87% yield (Scheme 1).¹⁶ Figure 4 depicts the structure of **10a**, which clearly shows that it possesses a triangular Ir_2Rh core capped by two $\mu_3\text{-NCN}$ ligands from both sides.¹⁷ The metric features within the M_3 core are typical of a 48e trinuclear cluster with three M–M bonds. The ^1H NMR spectrum of **10aBPh₄** exhibits signals attributable to the Cp^* (δ 2.03 (30H)) and cod protons (δ 3.90–3.96 (4H), 2.34–2.48 (8H)), and the IR spectrum displays one strong NCN stretching band at 2159 cm^{-1} . Similar reactions of **5** with $[\text{CpRu}(\text{MeCN})_3]^+$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and

(13) Spectral data for **8a**: ^1H NMR (CDCl_3 , δ) 1.40 (d, 15H, $J = 2.0\text{ Hz}$, Cp^*), 1.55 (s, 15H, Cp^*); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ) 18.7 (s); IR (KBr, cm^{-1}) 2064 (s, NCN). Spectral data for **8b**: ^1H NMR (CDCl_3 , δ) 1.40 (d, 15H, $J = 2.0\text{ Hz}$, Cp^*), 1.55 (s, 15H, Cp^*); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ) 17.0 (s); IR (KBr, cm^{-1}) 2060 (s, NCN). Spectral data for **8c**: ^1H NMR (CDCl_3 , δ) 1.42 (d, 15H, $J = 2.0\text{ Hz}$, Cp^*), 1.57 (s, 15H, Cp^*); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ) 18.3 (s); IR (KBr, cm^{-1}) 2065 (s, NCN). Spectral data for **8d**: ^1H NMR (C_6D_6 , δ) 1.46 (s, 15H, Cp^*), 1.61 (s, 15H, Cp^*); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , δ) –23.2 (s); IR (KBr, cm^{-1}) 2062 (s, NCN).

(14) Crystallographic data for **8d**: $\text{C}_{25}\text{H}_{39}\text{Ir}_2\text{N}_4\text{P}$, FW = 811.02, orthorhombic, space group $Pnma$, $a = 19.199(5)\text{ \AA}$, $b = 13.714(5)\text{ \AA}$, $c = 9.781(3)\text{ \AA}$, $V = 2575(1)\text{ \AA}^3$, $Z = 4$, $T = -165\text{ }^\circ\text{C}$, $\rho_{\text{calcd}} = 2.092\text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 104.35\text{ cm}^{-1}$, 3028 unique reflections, $R(R_w) = 0.058$ (0.068) for 184 variables and 2557 reflections ($I > 3\sigma(I)$), GOF = 1.006.

(15) Spectral data for **9**: ^1H NMR (CDCl_3 , δ) 1.45 (s, 30H, Cp^*), 3.84 (t, 2H, $J = 11.4\text{ Hz}$, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ) 7.8 (s); IR (KBr, cm^{-1}) 2049 (s, NCN). Crystallographic data for **9** $\cdot 1.5\text{C}_6\text{H}_6$: $\text{C}_{36}\text{H}_{61}\text{Ir}_2\text{N}_4\text{P}_2$, FW = 1236.51, triclinic, space group $P\bar{1}$, $a = 12.084(4)\text{ \AA}$, $b = 12.105(4)\text{ \AA}$, $c = 19.525(7)\text{ \AA}$, $\alpha = 99.37(1)^\circ$, $\beta = 91.82(1)^\circ$, $\gamma = 118.88(1)^\circ$, $V = 2447(1)\text{ \AA}^3$, $Z = 2$, $T = 21\text{ }^\circ\text{C}$, $\rho_{\text{calcd}} = 1.678\text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 55.55\text{ cm}^{-1}$, 10 868 unique reflections, $R(R_w) = 0.031$ (0.036) for 638 variables and 8788 reflections ($I > 3\sigma(I)$), GOF = 1.004.

(16) To a CH_2Cl_2 solution (30 mL) of **5** (247.8 mg, 0.337 mmol) was added an acetone solution of $[\text{Rh}(\text{cod})(\text{acetone})_n]^+$, which was prepared in situ from $[\text{RhCl}(\text{cod})_2]$ (84.0 mg, 0.170 mmol) and AgOTf (87.0 mg, 0.339 mmol) in acetone (10 mL). The mixture was stirred for 12 h at room temperature, and the resultant dark red solution was dried in vacuo. The residue was dissolved in methanol (30 mL) containing NaBPh_4 (ca. 170 mg, 0.50 mmol). The mixture was stirred for 12 h at room temperature to form a red precipitate, which was collected by filtration, dried in vacuo, and extracted with CH_2Cl_2 . Recrystallization from CH_2Cl_2 –methanol yielded dark red platelike crystals of $[(\text{Cp}^*\text{Ir})_2\{\text{Rh}(\text{cod})\}(\mu_3\text{-NCN-}N,N,N)_2](\text{BPh}_4)\cdot\text{CH}_2\text{Cl}_2$ (**10aBPh₄·CH₂Cl₂**), the CH_2Cl_2 molecule of which was lost by drying in vacuo to give a red powder of **10aBPh₄** (369.3 mg, 0.292 mmol, 87% yield).

(17) Crystallographic data for **10aBPh₄·CH₂Cl₂**: $\text{C}_{55}\text{H}_{64}\text{BCl}_2\text{Ir}_2\text{Rh}$, FW = 1350.20, orthorhombic, space group $Pccn$, $a = 12.680(2)\text{ \AA}$, $b = 12.734(2)\text{ \AA}$, $c = 32.297(4)\text{ \AA}$, $V = 5214(1)\text{ \AA}^3$, $Z = 4$, $T = 21\text{ }^\circ\text{C}$, $\rho_{\text{calcd}} = 1.720\text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 55.59\text{ cm}^{-1}$, 5934 unique reflections, $R(R_w) = 0.051$ (0.052) for 329 variables and 3844 reflections ($I > 3\sigma(I)$), GOF = 1.009.

$[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{acetone})_n]^+$ result in the formation of the heterotrinnuclear complexes $[(\text{Cp}^*\text{Ir})_2(\text{ML})(\mu_3\text{-NCN-}N,N,N)]^+$ (**10b**, ML = RuCp; **10c**, ML = Pd($\eta^3\text{-C}_3\text{H}_5$))¹⁸ (Scheme 1). To the best of our knowledge, **10a–c** provide the first examples of NCN-bridged heteronuclear complexes.

Finally, the dimerization reaction of **5** has been investigated. In 1-propanol at 80 °C, **5** was selectively converted into the cubane-type complex **4**, which was isolated in 75% yield. A preliminary kinetic study was performed by following the reaction by means of ¹H NMR. The reaction obeys second-order kinetics, where the rate constant $k = (1.19 \pm 0.05) \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ at 80 °C. It is interesting to note that the dinuclear complex **5** is thermodynamically less stable than the cubane-type complex **4** but kinetically stable at room temperature. This is in contrast to the related dimerization of the sulfido-bridged diiridium species $[\text{Cp}^*\text{Ir}(\mu_2\text{-S})]_2$, which can be observed only at low temperatures.¹⁹

(18) Spectral data for **10b**BPh₄: ¹H NMR (CD₂Cl₂, δ) 1.88 (s, 30H, Cp*), 4.83 (s, 5H, Cp); IR (KBr, cm⁻¹) 2170 (s, NCN). Spectral data for **10c**OTf: ¹H NMR (CDCl₃, δ) 1.94 (s, 30H, Cp*), 3.26 (d, 2H, $J = 12.3$ Hz, CH₂), 4.19–4.35 (m, 2H, CH₂), 5.85–5.95 (m, 1H, CH); IR (KBr, cm⁻¹) 2145 (s, NCN).

In conclusion, the NCN-bridged dinuclear iridium complex **5** has been synthesized and found to show rich reactivities, including CO insertion, dimerization, and heterotrinnuclear complex formation. These results clearly demonstrate that the NCN²⁻ anion can act as an effective and versatile bridging ligand with a variety of coordination modes to form polynuclear complexes.

Acknowledgment. We thank the Ministry of Education, Culture, Sports, Science and Technology of Japan for a grant-in-aid.

Supporting Information Available: Text giving experimental and spectroscopic details, a table of kinetic data and a figure for the dimerization reaction of **5**, and tables of crystallographic data, positional and thermal parameters, and bond distances and angles and thermal ellipsoid plots for complexes **5**, **6**, **8d**, **9**·1.5C₆H₆, and **10a**BPh₄·CH₂Cl₂; crystallographic data are also available in a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM048978I

(19) (a) Tang, Z.; Nomura, Y.; Ishii, Y.; Mizobe, Y.; Hidai, M. *Inorg. Chim. Acta* **1998**, 267, 73–79. (b) Dobbs, D. A.; Bergman, R. G. *Inorg. Chem.* **1994**, 33, 5329–5336. (c) Herberhold, M.; Jin, G.-X.; Milius, W. *Chem. Ber.* **1995**, 128, 557–560. (d) Feng, Q.; Krautscheid, H.; Rauchfuss, T. B.; Skaugset, A. E.; Venturelli, A. *Organometallics* **1995**, 14, 297–304.