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Core Expansion Reactions of Cyanamido/Carbodiimido-Bridged Polynuclear Iridium Complexes

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Core expansion reactions of di- and tetrairidium complexes [Cp*Ir(μ_2-NCN-*N*,*N*)]$_2$ (**1**; Cp* = η^5-C_5Me_5), [Cp*Ir(μ_3-NCN-*N*,*N*,*N*)]$_4$ (**2**), and phosphine derivatives of **1** have been investigated, and it has been revealed that cyanamido ligands in these complexes can change their coordination modes flexibly on reactions with a second transition metal complex. Treatment of diiridium complex **1** with [Cp*IrCl$_2$]$_2$ gives the tetrairidium complex [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N′*)$_2$(IrCp*Cl$_2$)$_2$] (**6**) with μ_3-κN,κN,$\kappa N'$ cyanoimido(2-) ligands. On the other hand, the reaction of **1** with [PdCl(η^3-C_3H_5)]$_2$ affords the NCN-bridged Ir$_2$Pd$_4$ hexanuclear complex [(Cp*IrCl)$_2$(μ_4-NCN-*N*,*N*,*N′*,*N′*)$_2${Pd$_2$(μ-Cl)(η^3-C_3H_5)$_2$}$_2$] (**7**) and Ir$_4$Pd$_4$ octanuclear complex [(Cp*Ir)$_4$(μ_4-NCN-*N*,*N*,*N*,*N′*)$_4${PdCl(η^3-C_3H_5)}$_4$] (**8**). The NCN-bridges in **7** provide the first example of the crystallographically determined μ_4-κN,κN,$\kappa N'$,$\kappa N'$ carbodiimido(2-) ligand. Complex **8** with μ_4-κN,κN,κN,$\kappa N'$ cyanoimido(2-) ligands can also be synthesized selectively by the reaction of the parent cubane complex **2** with [PdCl(η^3-C_3H_5)]$_2$. Diphosphine derivative of **1**, [{Cp*Ir(μ_2-NCN)}$_2$(μ-dppm)] (**4**; dppm = $Ph_2PCH_2PPh_2$), behaves differently on reactions with [PdCl(η^3-C_3H_5)]$_2$ and [MCl(cod)]$_2$ (cod = cycloocta-1,5-diene) to form the NCN-bridged Ir$_2$M$_2$ (M = Pd, Rh, Ir) tetranuclear complexes [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N′*)$_2${PdCl(η^3-C_3H_5)}$_2$(μ-dppm)] (**9**) and [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N′*)$_2${MCl(cod)}$_2$(μ-dppm)] (**11a**, M = Rh; **11b,** M = Ir), respectively. The molecular structures for **6**, **7**, **8**, **11a**, and **11b** have been determined by single-crystal X-ray analyses.

Introduction

Much current research interest has been focused on the chemistry of multinuclear complexes constructed with bridging N_3^- and CN^- ligands because these small unsaturated anions give rise to a variety of intriguing three-dimensional structures with advanced functions such as molecular magnets, molecular boxes, and gas storage.[1] Although the cyanamide anions (NCN^{2-} and $NCNH^-$) have structures closely related to N_3^- and CN^-, coordination chemistry of cyanamido-bridged complexes has been developed much less extensively.[2−4] However, owing to the resonance between cyanoimido/amido ($N{\equiv}C{-}N^{2-}$/$N{\equiv}C{-}NH^-$) and carbodi-

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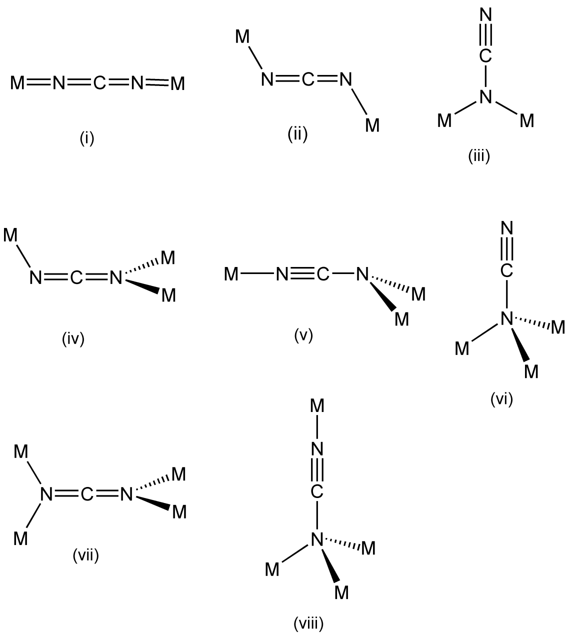

Figure 1. Bridging coordination modes of the NCN^{2-} ligand. (i) μ_2-κN,$\kappa N'$ (linear),[2d,e] (ii) μ_2-κN,$\kappa N'$ (bent),[2e] (iii) μ_2-κN,κN,[6b] (iv) μ_3-κN,κN,$\kappa N'$ (carbodiimido(2-)),[2c,6a,c] (v) μ_3-κN,κN,$\kappa N'$ (cyanoimido(2-)), (vi) μ_3-κN,κN,κN,[6] (vii) μ_4-κN,κN,$\kappa N'$,$\kappa N'$, (viii) μ_4-κN,κN,κN,$\kappa N'$.[6d]

imido ($^{-}$N=C=N^{-}/$^{-}$N=C=NH) structures, the cyanamide anions can adopt a variety of coordination modes ranging from terminal to μ_4 as shown in Figure 1.[5] The cyanamide-carbodiimide resonance also leads to their exceptionally soft nature as an imide/amide anion, which enables the cyanamido ligand to form stable complexes with both early and late transition metals. In addition, the sterically small rod-like structures of the cyanamido anions are considered to be advantageous on incorporation into sterically congested polymetallic systems.

These promising features of the cyanamido ligands prompted us to explore the synthetic chemistry of cyanamido-bridged polynuclear complexes. In fact, we have recently revealed that several unique cyanamido-bridged multinuclear structures can be constructed quite effectively.[6] For example, di- and tetrairidium complexes such as [Cp*Ir(μ_2-NCN-N,N)]$_2$ (**1**, Cp* = η^5-C$_5$Me$_5$))[6b] and [Cp*Ir(μ_3-NCN-N,N,N)]$_4$ (**2**),[6a] as well as triruthenium complexes such as [(Cp*Ru)$_3$(μ_3-NCN-N,N,N)$_2$]$^-$,[6b] were synthesized, and their reactivities including the skeletal transformations and heterometallic cluster formations have been disclosed. In particular, the metal-bound nitrogen atoms of the cyanamido ligands in complex **1**, which are sp^3-hybridized, can coordinate to a cationic transition metal fragment ML$^+$ to form the NCN-capped heterotrinuclear complexes [(Cp*Ir)$_2$(ML)(μ_3-NCN-N,N,N)$_2$]$^+$ (ML = Pd(η^3-C$_3$H$_5$) (**3a**); Rh(cod) (**3b**, cod = cycloocta-1,5-diene); RuCp (Cp = η^5-C$_5$H$_5$)). In the present study, we have turned our attention to the donor ability of the sp-hybridized terminal nitrogen atoms in complexes **1**, **2**, and phosphine derivatives of **1** ([{Cp*Ir(μ_2-NCN-N,N)}$_2$(μ-dppm)] (**4**, dppm = Ph$_2$PCH$_2$PPh$_2$) and [{Cp*Ir(μ_2-NCN-N,N)}$_2$(PMe$_3$)] (**5**)) which can be viewed as metallonitriles and revealed some core expansion reactions leading to the formation of heterobimetallic tetra-, hexa-, and octanuclear complexes including the first example of a structurally characterized μ_4-NCN-κN,κN,$\kappa N'$,$\kappa N'$ complex.

Experimental Section

General Considerations. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise specified. Complexes **1**,[6b] **2**,[6a] **4**,[6b] **5**,[6b] [Cp*IrCl$_2$]$_2$,[7] [PdCl(η^3-C$_3$H$_5$)]$_2$,[8] [IrCl(cod)]$_2$,[9] and [RhCl(cod)]$_2$[9] were prepared according to the literature methods. CH$_2$Cl$_2$, C$_2$H$_4$Cl$_2$ (1,2-dichloroethane), and MeOH were dried and distilled over P$_4$O$_{10}$ (CH$_2$Cl$_2$, C$_2$H$_4$Cl$_2$) and Mg (MeOH) and degassed before use. Other solvents (dehydrated-grade, Aldrich) and reagents including Na$_2$NCN (MP Biomedicals Inc.) were commercially obtained and used without further purification. ^{1}H (500 MHz) and ^{31}P{^{1}H} (202 MHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer. IR spectra were recorded on a JASCO FT/IR-410 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyzer. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by ^{1}H NMR spectroscopy.

Synthesis of [(Cp*Ir)$_2$(μ_3-NCN-N,N,N')$_2$(IrCp*Cl$_2$)$_2$] (6). Method 1. Complex **1** (40.1 mg, 0.055 mmol) and [Cp*IrCl$_2$]$_2$ (44.2 mg, 0.055 mmol) were dissolved in toluene (4 mL) and stirred for 21 h at room temperature. The resulting reddish purple suspension was dried up in vacuo, and the resulting reddish purple powder was extracted with C$_2$H$_4$Cl$_2$. Slow addition of hexane to the concentrated extract afforded [(Cp*Ir)$_2$(μ_3-NCN-N,N,N')$_2$(IrCp*Cl$_2$)$_2$]·2C$_2$H$_4$Cl$_2$ (**6**·2C$_2$H$_4$Cl$_2$) as reddish purple crystals.[10] The crystals gave off a part of C$_2$H$_4$Cl$_2$ molecules when dried up in vacuo to afford a reddish purple powder with the empirical formula **6**·0.5C$_2$H$_4$Cl$_2$ (71.6 mg, 0.045 mmol, 83% yield). ^{1}H NMR (CDCl$_3$): δ 1.93 (s, 30H, Cp*), 1.65 (s, 30H, Cp*). IR (KBr, cm^{-1}): 2162 (s, ν_{NCN}). Anal. Calcd for C$_{43}$H$_{62}$Cl$_5$Ir$_4$N$_4$ (**6**·0.5C$_2$H$_4$Cl$_2$): C, 32.66; H, 3.95; N, 3.54. Found: C, 32.33; H, 3.98; N, 3.53. Crystals of **6** suitable for X-ray diffraction study were obtained by further recrystallization from CH$_2$Cl$_2$-MeOH-hexane.

Method 2. [Cp*IrCl$_2$]$_2$ (42.5 mg, 0.053 mmol) and Na$_2$NCN (4.6 mg, 0.053 mmol) were slurried in THF and stirred overnight. The initial orange solution gradually changed to a reddish purple suspension. The resulting mixture was dried up in vacuo and extracted with C$_2$H$_4$Cl$_2$. Slow addition of hexane to the concentrated extract afforded **6**·2C$_2$H$_4$Cl$_2$ as reddish purple crystals, which was collected by filtration and dried up in vacuo to afford **6**·0.5C$_2$H$_4$Cl$_2$ (35.0 mg, 0.022 mmol, 83% yield).

Reaction of 1 with [PdCl(η^3-C$_3$H$_5$)]$_2$. Complex **1** (17.1 mg, 0.023 mmol) and [PdCl(η^3-C$_3$H$_5$)]$_2$ (18.0 mg, 0.049 mmol) were

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(10) The composition of this material was confirmed by a preliminary X-ray study.

dissolved in THF, and the mixture was stirred for 13 h at room temperature. The resulting red suspension was dried up in vacuo to afford a yellow powder. The ^{1}H NMR analysis of the crude material indicated that [(Cp*IrCl)$_2$(μ_4-NCN-*N*,*N*,*N*′,*N*′)$_2${Pd$_2$(μ-Cl)(η^3-C$_3$H$_5$)$_2$}$_2$] (**7**) and [(Cp*Ir)$_4$(μ_4-NCN-*N*,*N*,*N*,*N*′)$_4${PdCl(η^3-C$_3$H$_5$)}$_4$] (**8**) were formed in the ratio of 12:1. This powder was extracted with CH$_2$Cl$_2$, and addition of hexane to the concentrated extract gave a mixture of **7** and **8** as orange crystals (16.6 mg, 56% total yield, **7**/**8** = 7:4). **7**: ^{1}H NMR (CDCl$_3$): δ 5.45 (m, 4H, C$_3$H$_5$), 4.11 (br, 8H, C$_3$H$_5$), 3.03 (d, *J* = 12.0 Hz, 8H, C$_3$H$_5$), 1.90 (s, 30H, Cp*). IR (KBr, cm^{-1}): 2014 (s, ν_{NCN}). Analytically pure samples of **7** could not be obtained even by repeated recrystallization because of contamination of **8**.

Synthesis of 8 from 2. Complex **2** (32.9 mg, 0.022 mmol) and [PdCl(η^3-C$_3$H$_5$)]$_2$ (17.9 mg, 0.049 mmol) were dissolved in CH$_2$Cl$_2$ and stirred for 14 h at room temperature. The resulting orange solution was dried up in vacuo and extracted with CH$_2$Cl$_2$. Slow addition of hexane to the concentrated extract afforded **8**·6CH$_2$Cl$_2$ as orange crystals. The crystals gave off CH$_2$Cl$_2$ molecules when dried in vacuo to afford an orange powder of **8** (48.2 mg, 0.022 mmol, 98% yield). The single crystal of **8**·6CH$_2$Cl$_2$ used in the X-ray study was obtained by further recrystallization from CH$_2$Cl$_2$-hexane at −20 °C. ^{1}H NMR (CDCl$_3$): δ 5.46 (m, 4H, C$_3$H$_5$), 4.11 (br, 8H, C$_3$H$_5$), 3.04 (br d, *J* = 12.0 Hz, 8H, C$_3$H$_5$), 1.55 (s, 60H, Cp*). IR (KBr, cm^{-1}): 2152 (s, ν_{NCN}). Anal. Calcd for C$_{56}$H$_{80}$Cl$_4$Ir$_4$N$_8$Pd$_4$: C, 30.55; H, 3.66; N, 5.09. Found: C, 30.16; H, 3.82; N, 4.78.

Reaction of 2 with [Pd(η^3-C$_3$H$_5$)(acetone)$_n$](OTf). To a CH$_2$Cl$_2$ solution (2 mL) of complex **2** (31.6 mg, 0.021 mmol) was added an acetone solution of [Pd(η^3-C$_3$H$_5$)(acetone)$_n$](OTf) (OTf = OSO$_2$CF$_3$) prepared in situ from [PdCl(η^3-C$_3$H$_5$)]$_2$ (15.8 mg, 0.043 mmol) and silver triflate (22.1 mg, 0.086 mmol) in acetone (4 mL), and the mixture was stirred for 13 h at room temperature. The resulting dark red solution was dried up in vacuo, and the residual dark red solid was extracted with CH$_2$Cl$_2$. The extract was evaporated and recrystallized from MeOH-ether to yield red crystals of [(Cp*Ir)$_2${Pd(η^3-C$_3$H$_5$)}(μ_3-NCN-*N*,*N*,*N*)$_2$](OTf) (**3a**OTf) (31.4 mg, 0.030 mmol, 71% yield), whose spectral data are identical with those reported previously.[6b]

Synthesis of [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N*′)$_2${PdCl(η^3-C$_3$H$_5$)}$_2$(μ-dppm)] (9). Complex **4** (18.2 mg, 0.016 mmol) and [PdCl(η^3-C$_3$H$_5$)]$_2$ (7.1 mg, 0.019 mmol) were dissolved in benzene, and the mixture was stirred at room temperature until the yellow solution turned orange (overnight). The resulting solution was evaporated to dryness, and the residual orange powder was extracted with CH$_2$Cl$_2$. Slow addition of hexane to the concentrated extract afforded orange crystals, which were collected by filtration and dried in vacuo to give [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N*′)$_2${PdCl(η^3-C$_3$H$_5$)}$_2$(μ-dppm)]·CH$_2$Cl$_2$ (**9**·CH$_2$Cl$_2$) as an orange solid. The crystals gave off CH$_2$Cl$_2$ molecules when dried in vacuo to afford **9** (19.6 mg, 0.013 mmol, 81% yield). ^{1}H NMR (CDCl$_3$): δ 7.46−7.31 (m, 20H, Ph), 5.46−5.32 (m, 2H, C$_3$H$_5$), 3.96 (d, *J* = 12.0 Hz, 2H, C$_3$H$_5$), 3.75 (d, *J* = 11.5 Hz, 2H, C$_3$H$_5$), 3.73 (br, 2H, CH$_2$ of dppm), 2.93 (d, *J* = 12.0 Hz, 2H, C$_3$H$_5$), 2.75 (d, *J* = 11.5 Hz, 2H, C$_3$H$_5$), 1.45 (s, 30H, Cp*). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 8.40 (s, dppm). IR (KBr, cm^{-1}): 2095 (s, ν_{NCN}). Anal. Calcd for C$_{53}$H$_{62}$Cl$_2$Ir$_2$N$_4$P$_2$Pd$_2$: C, 42.86; H, 4.21; N, 3.77. Found: C, 42.82; H, 4.21; N, 3.65.

Synthesis of [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N*′)$_2${PdCl(η^3-C$_3$H$_5$)}$_2$(PMe$_3$)] (10). To a CH$_2$Cl$_2$ solution of **1** (32.3 mg, 0.044 mmol) was added PMe$_3$ (1.0 M solution in THF, 45 μL, 0.045 mmol). The reaction mixture was evaporated, and complex **5** thus formed was extracted with benzene (6 mL). [PdCl(η^3-C$_3$H$_5$)]$_2$ (24.1 mg, 0.066 mmol) was added to the benzene solution, and the mixture was stirred overnight at room temperature. The resulting purple solution was evaporated to dryness, and the residue was extracted with CH$_2$Cl$_2$. Slow addition of toluene (0.5 mL) and hexane (15 mL) to the extract afforded [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N*′)$_2${PdCl(η^3-C$_3$H$_5$)}$_2$(PMe$_3$)] (**10**) as purple crystals (9.7 mg, 8.2 μmol, 19% yield). ^{1}H NMR (CDCl$_3$): δ 5.31 (br, 2H, C$_3$H$_5$), 3.89 (br, 2H, C$_3$H$_5$), 3.76 (br, 2H, C$_3$H$_5$), 2.85 (d, *J* = 11.5 Hz, 2H, C$_3$H$_5$), 2.73 (d, *J* = 11.5 Hz, 2H, C$_3$H$_5$), 1.79 (s, 15H, Cp*), 1.68 (s, 15H, Cp*), 1.64 (d, *J* = 11.0 Hz, 9H, PMe$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −22.3 (s, PMe$_3$). IR (KBr, cm^{-1}): 2113 (s, ν_{NCN}). Anal. Calcd for C$_{31}$H$_{49}$Cl$_2$Ir$_2$N$_4$PPd$_2$: C, 31.64; H, 4.20; N, 4.76. Found: C, 31.40; H, 4.15; N, 4.59.

Synthesis of [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N*′)$_2${RhCl(cod)}$_2$(μ-dppm)] (11a). Complex **4** (17.3 mg, 0.015 mmol) and [RhCl(cod)]$_2$ (8.0 mg, 0.016 mmol) were dissolved in benzene, and the mixture was stirred for 13 h at room temperature. The resulting solution was evaporated to dryness, and the residual orange powder was extracted with C$_2$H$_4$Cl$_2$. Slow addition of hexane to the concentrated extract afforded [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N*′)$_2${RhCl(cod)}$_2$(μ-dppm)]·C$_2$H$_4$Cl$_2$ (**11a**·C$_2$H$_4$Cl$_2$) as orange crystals (21.3 mg, 0.012 mmol, 81% yield). ^{1}H NMR (CDCl$_3$): δ 7.47−7.27 (m, 20H, Ph), 4.37 (br, 4H, cod), 4.01 (br, 4H, cod), 3.71 (br, 2H, CH$_2$ of dppm), 2.49, 2.42 (m, 4H each, cod), 1.75 (m, 8H, cod), 1.43 (s, 30H, Cp*). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 7.36 (s, dppm). IR (KBr, cm^{-1}): 2077 (s, ν_{NCN}). Anal. Calcd for C$_{65}$H$_{80}$Cl$_4$Ir$_2$N$_4$P$_2$Rh$_2$ (**11a**·C$_2$H$_4$Cl$_2$): C, 45.62; H, 4.71; N, 3.27. Found: C, 45.68; H, 4.75; N, 3.29.

Synthesis of [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N*′)$_2${IrCl(cod)}$_2$(μ-dppm)] (11b). This compound was prepared from complex **4** (20.4 mg, 0.018 mmol) and [IrCl(cod)]$_2$ (12.8 mg, 0.019 mmol) in a manner analogous to that described for **11a**. Recrystallization from C$_2$H$_4$Cl$_2$-hexane gave orange crystals of [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N*′)$_2${IrCl(cod)}$_2$(μ-dppm)]·C$_2$H$_4$Cl$_2$ (**11b**·C$_2$H$_4$Cl$_2$) (27.9 mg, 0.015 mmol, 81% yield). ^{1}H NMR (CDCl$_3$): δ 7.42−7.28 (m, 20H, Ph), 4.06 (m, 4H, cod), 3.73 (m, 4H, cod), 3.68 (br, 2H, CH$_2$ of dppm), 2.32, 2.23 (m, 4H each, cod), 1.56 (br, 8H, cod), 1.43 (s, 30H, Cp*). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 6.62 (s, dppm). IR (KBr, cm^{-1}): 2084 (s, ν_{NCN}). Anal. Calcd for C$_{65}$H$_{80}$Cl$_4$Ir$_4$N$_4$P$_2$ (**11b**·C$_2$H$_4$Cl$_2$): C, 41.31; H, 4.27; N, 2.96. Found: C, 41.07; H, 4.30; N, 2.61.

X-ray Diffraction Studies. Diffraction data for **6**, **7**, **8**·6CH$_2$Cl$_2$, **11a**·C$_2$H$_4$Cl$_2$, and **11b**·C$_2$H$_4$Cl$_2$ were collected on a Rigaku Mercury CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) at −150 °C for the 2θ range of 5−55° (Table 1). Intensity data were corrected for Lorenz-polarization effects and for empirical (REQAB[11] for **6**, **7**, **11a**·C$_2$H$_4$Cl$_2$) and numerical (NUMABS[12] for **8**·6CH$_2$Cl$_2$, **11b**·C$_2$H$_4$Cl$_2$) absorptions. All calculations were performed using the CrystalStructure[13] crystallographic software package except for refinements, which were performed using SHELXL-97.[14] The positions of non-hydrogen atoms were determined by direct methods (SHELXS-97[14] for **6** and **8**·6CH$_2$Cl$_2$; SIR-97[15] for **11a**·C$_2$H$_4$Cl$_2$) or heavy atom Patterson methods (SHELXS-97[14] for **7**; PATTY[16] for

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Table 1. X-ray Crystallographic Data for, **6**, **7**, **8**·$6CH_2Cl_2$, **11a**·$C_2H_4Cl_2$, and **11b**·$C_2H_4Cl_2$

	6	**7**	**8**·$6CH_2Cl_2$	**11a**·$C_2H_4Cl_2$	**11b**·$C_2H_4Cl_2$
chemical formula	$C_{42}H_{60}Cl_4Ir_4N_4$	$C_{34}H_{50}Cl_4Ir_2N_4Pd_4$	$C_{62}H_{92}Cl_{16}Ir_4N_8Pd_4$	$C_{65}H_{80}Cl_4Ir_2N_4P_2Rh_2$	$C_{65}H_{80}Cl_4Ir_4N_4P_2$
fw	1531.65	1466.65	2711.19	1711.38	1890.01
crystal dimension	0.40 × 0.15 × 0.05	0.25 × 0.12 × 0.10	0.40 × 0.30 × 0.30	0.40 × 0.20 × 0.10	0.60 × 0.20 × 0.10
crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a, Å	35.337(6)	10.596(2)	15.590(4)	10.165(2)	10.145(3)
b, Å	7.3127(11)	10.775(2)	31.156(8)	17.775(4)	17.805(5)
c, Å	23.656(4)	11.100(2)	17.291(5)	17.886(3)	17.870(5)
α, deg	90	70.804(10)	90	95.766(3)	95.918(2)
β, deg	130.4845(13)	60.313(7)	104.481(2)	98.457(3)	98.423(4)
γ, deg	90	78.821(11)	90	102.319(3)	102.416(4)
V, Å^3	4649.3(13)	1039.0(3)	8132(4)	3093.5(12)	3087.9(14)
Z	4	1	4	2	2
ρ_{calced}, g cm^{-3}	2.188	2.344	2.214	1.837	2.033
$F(000)$	2864	680	5136	1680	1808
μ, cm^{-1}	117.075	83.781	79.681	50.913	88.847
no. reflections measured	17238	7803	26411	23762	23368
no. unique reflections	5300	4574	8349	11054	11053
R_{int}	0.046	0.027	0.052	0.045	0.054
no. parameters refined	245	227	434	713	713
$R1$ ($I > 2\sigma(I)$)[a]	0.0410	0.0313	0.0534	0.0417	0.0502
$wR2$ (all data)[b]	0.0991	0.0775	0.1267	0.1015	0.1283
GOF [c]	1.111	1.062	1.095	1.063	1.062

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2F_o^2 + (aP)^2 + bP]$ (a = 0.0457 (**6**), 0.0354 (7), 0.0561 (**8**), 0.0556 (**11a**), 0.0754 (**11b**); b = 55.6694 (**6**), 1.8314 (**7**), 237.7419 (**8**), 8.2683 (**11a**), 9.2589 (**11b**); $P = (\max(F_o^2,0) + 2F_c^2)/3$. [c] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(N_{\mathrm{obs}} - N_{\mathrm{params}})]^{1/2}$.

11b·$C_2H_4Cl_2$) and subsequent Fourier syntheses (DIRDIF-99).[17] All the non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters, while all the hydrogen atoms except for those attached to disordered fragments were placed at the calculated positions with fixed isotropic parameters. The η^3-C_3H_5 ligand bound to the Pd(2) atom in **7** and one of the CH_2Cl_2 molecules in **8**·$6CH_2Cl_2$ were found to be disordered with the occupancies of 0.50:0.50 and 0.60:0.40, respectively, and the hydrogen atoms of these fragments were not placed.

Results and Discussion

NCN-Bridged Tetrairidium Complex 6. When complex **1** was allowed to react with 1 equiv of $[Cp^*IrCl_2]_2$ in toluene at room temperature, the tetrairidium complex $[(Cp^*Ir)_2(\mu_3$-NCN-$N,N,N')_2(IrCp^*Cl_2)_2]\cdot 0.5C_2H_4Cl_2$ (**6**·$0.5C_2H_4Cl_2$) was obtained in 83% yield (Scheme 1). The ^{1}H NMR spectrum of complex **6** exhibits two singlets assignable to the Cp* protons in the intensity ratio of 1:1, while the IR spectrum of **6** shows one strong ν_{NCN} band at 2162 cm^{-1}, which is about 70 cm^{-1} higher in wavenumber than that of **1** (2093 cm^{-1}). The molecular structure of **6** was unambiguously established by X-ray crystallography (Figure 2, Table 2). The molecule has a crystallographic C_2 axis passing through the center of the Ir_2N_2 core. The Cp^*IrCl_2 fragments introduced are connected to the terminal nitrogen atoms of the respective NCN ligands with a μ_3-$\kappa N,\kappa N,\kappa N'$ coordination mode. The N(1)−C(1) and N(2)−C(1) bond distances at 1.310(15) and 1.165(15) Å, respectively, as well as the essentially linear Ir(2)−N(2)−C(1) bond angle (160.3(6)°) indicate that the NCN-bridges in **6** can be described as cyanoimido(2-) ligands. In agreement with this, the sum of the bond angles around the N(1) atom (332°) confirms its sp^3 nature. It should be mentioned that all the known μ_3-$\kappa N,\kappa N,\kappa N'$ type NCN-bridges have been regarded to possess a carbodiimido(2-) structure,[2c,6a,c] and therefore complex **6** provides the first example of the μ_3-$\kappa N,\kappa N,\kappa N'$ cyanoimido(2-) bridge.[18] On the other hand, the structure of the Ir_2N_2 core is little affected by the peripheral coordination of Cp^*IrCl_2 moieties and shows metric features similar to those of related imido complexes such as $[Cp^*Ir(\mu_2\text{-NR})_2]$ (R = Ph, cyclopentyl).[19] The Ir(1)−Ir(1)* distance at 2.8670(3) Å is slightly longer than that of **1** (2.8179(9) Å)[6b] but still suggests the presence of a metal−metal bonding interaction, and the Ir_2N_2 core is puckered with a N(1)−Ir(1)−Ir(1)*−N(1)* torsion angle of 120.0(4)°.

It is also interesting to note that the reaction site of **1** toward a Lewis acidic metal species is controlled by the nature of the reactant. As mentioned briefly in the introduction, **1** reacts with a cationic palladium species $[Pd(\eta^3\text{-}C_3H_5)(\mathrm{acetone})_n](\mathrm{OTf})$, which essentially acts as a formal 12e fragment $[Pd(\eta^3\text{-}C_3H_5)]^+$, to form the heterotrinuclear cluster **3a**. In this reaction the metal-bound nitrogen atoms behave as the donor sites.[6b] In contrast, in the case of **6**, the less coordinatively unsaturated (16e) Cp^*IrCl_2 fragment is selectively bound to the terminal nitrogen atom in **1**.

Since **1** is prepared from the 1:2 reaction of $[Cp^*IrCl_2]_2$ with Na_2NCN,[6b] it is expected that **6** is obtained directly from a 1:1 reaction of these starting materials. Indeed, $[Cp^*IrCl_2]_2$ smoothly reacted with an equimolar amount of Na_2NCN to give **6** in 83% yield. This result indicates that **6** may be viewed as an intermediate for the conversion of

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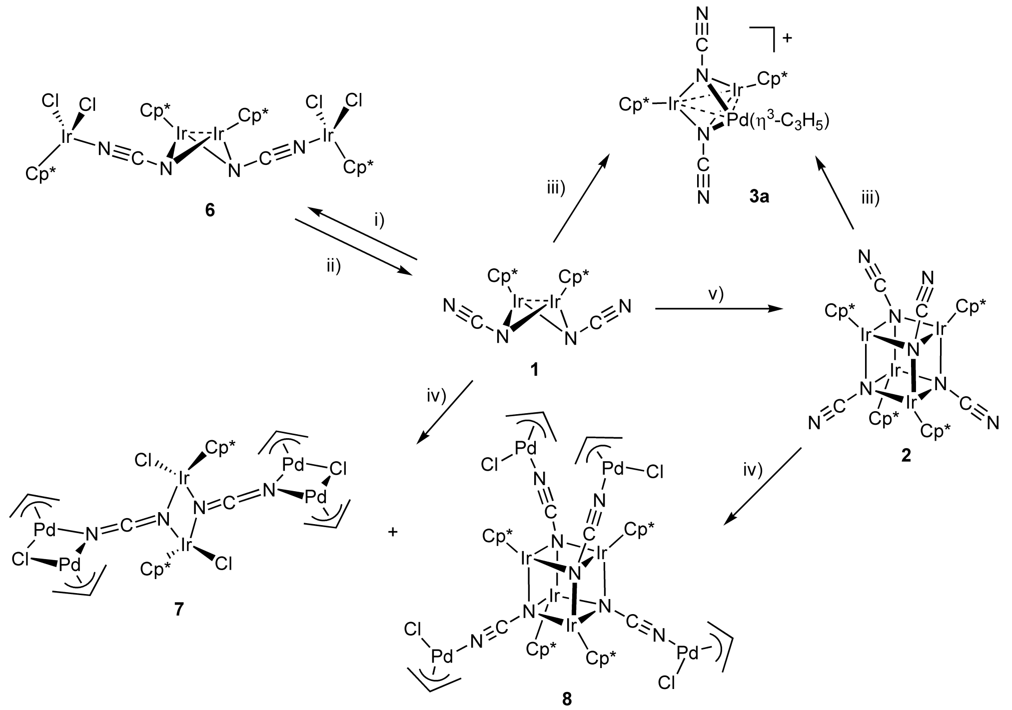
Scheme 1[a]



[a] Reagents or conditions: i) $[Cp^*IrCl_2]_2$, ii) Na_2NCN, iii) $[Pd(\eta^3\text{-}C_3H_5(acetone)_n]^+$, iv) $2[PdCl(\eta^3\text{-}C_3H_5)]_2$, v) 80 °C, 1-PrOH.

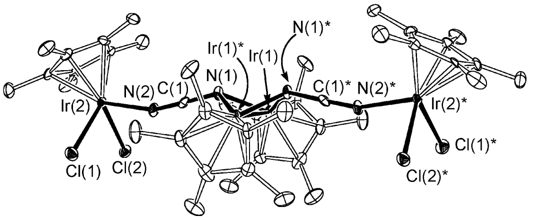


Figure 2. Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawing of **6** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **6**[a]

Ir(1)−Ir(1)*	2.8670(3)	Ir(1)−N(1)	2.030(9)
Ir(1)−N(1)*	2.021(5)	Ir(2)−N(2)	2.060(10)
N(1)−C(1)	1.310(15)	N(2)−C(1)	1.165(15)
N(1)−Ir(1)−N(1)*	75.4(3)	Ir(1)−N(1)−Ir(1)*	90.1(3)
Ir(1)−N(1)−C(1)	121.2(4)	Ir(1)*−N(1)−C(1)	121.1(5)
Ir(2)−N(2)−C(1)	160.3(6)	N(1)−C(1)−N(2)	178.8(7)

[a] Symmetry code: $-x$, y, $-z + 1/2$.

$[Cp^*IrCl_2]_2$ into **1**. It has also been confirmed that **6** is quantitatively converted into **1** on reaction with Na_2NCN in CH_2Cl_2.

NCN-bridged Ir_2Pd_4 and Ir_4Pd_4 Complexes 7 and 8. Considering the difference between the reactivities of Cp^*IrCl_2 and $[Pd(\eta^3\text{-}C_3H_5)]^+$ fragments toward **1**, we next investigated the reaction with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (Scheme 1). Treatment of **1** with 2 equiv of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ in THF at room temperature resulted in the formation of a mixture of the Ir_2Pd_4 hexanuclear complex $[(Cp^*IrCl)_2(\mu_4\text{-NCN-}N,N,N',N')_2\{Pd_2(\mu\text{-Cl})(\eta^3\text{-}C_3H_5)_2\}_2]$ (**7**) and the Ir_4Pd_4 octanuclear complex $[(Cp^*Ir)_4(\mu_4\text{-NCN-}N,N,N,N')_4\{PdCl(\eta^3\text{-}C_3H_5)\}_4]$ (**8**) in the ratio of 12:1 (Scheme 1). Although separation of **7** and **8** was unsuccessful because of slow conversion of **7** to **8** during recrystallization, both products could be fully characterized by spectroscopy as well as X-ray crystallography.

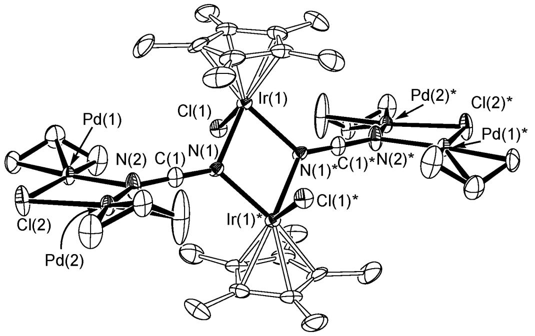


Figure 3. ORTEP drawing of **7** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

The ^1H NMR spectrum of **7** indicates that it consists of Cp*Ir and $Pd(\eta^3\text{-}C_3H_5)$ units in the ratio of 1:2, while the IR spectrum shows a strong ν_{NCN} band at 2014 cm^{-1}, which is about 80 cm^{-1} lower in wavenumber than that of **1** (2093 cm^{-1}). The latter observation is diagnostic of the structural change of the NCN-bridge from cyanoimido(2-) to carbodiimido(2-). The molecular structure of **7** has been determined by an X-ray study (Figure 3, Table 3). The molecule has a crystallographic inversion center. In accordance with the spectroscopic analysis, complex **7** is an Ir_2Pd_4 hexanuclear complex where two monocationic $Pd_2(\mu\text{-Cl})(\eta^3\text{-}C_3H_5)_2$ units are attached to the terminal nitrogen atoms of the respective cyanamido ligands in **1**, and the diiridium core is coordinated by two chloro ligands with trans geometry to compensate the change of the charge distribution caused by the deformation of the cyanamido ligands. The coordinative saturation of the iridium centers results in the elongation of the Ir···Ir

Table 3. Selected Bond Distances (Å) and Angles (deg) for **7**[a]

Ir(1)−N(1)	2.116(4)	Ir(1)−N(1)*	2.122(4)
Pd(1)−Cl(2)	2.422(2)	Pd(1)−N(2)	2.088(7)
Pd(2)−Cl(2)	2.415(2)	Pd(2)−N(2)	2.087(7)
N(1)−C(1)	1.216(6)	N(2)−C(1)	1.222(7)
N(1)−Ir(1)−N(1)*	74.20(16)	Cl(2)−Pd(1)−N(2)	84.27(18)
Cl(2)−Pd(2)−N(2)	84.4(2)	Pd(1)−Cl(2)−Pd(2)	86.29(5)
Ir(1)−N(1)−Ir(1)*	105.80(18)	Ir(1)−N(1)−C(1)	126.4(3)
Ir(1)−N(1)*−C(1)	127.8(3)	Pd(1)−N(2)−Pd(2)	104.8(2)
Pd(1)−N(2)−C(1)	126.3(6)	Pd(2)−N(2)−C(1)	128.3(7)
N(1)−C(1)−N(2)	179.2(7)		

[a] Symmetry code: −*x*, −*y* + 1, −*z* + 1.

separation up to 3.3802(2)Å. The Ir_2N_2 and Pd_2ClN squares are nearly planar (N(1)−Ir(1)−Ir(1)*−N(1)* torsion angle, 180.0(3)°; Cl(2)−Pd(1)−Pd(2)−N(2) torsion angle, 175.3(2)°) and arranged twisted to each other with the dihedral angle of 65.1°. The N−C bond distances are almost the same (N(1)−C(1), 1.216(6); N(2)−C(1), 1.222(7) Å), and the Pd−N−C and Ir−N−C bond angles fall in the range of 126.3−128.3°. The sum of the bond angles around the N(1) and N(3) atoms are 359−360°; the planar geometry of these nitrogen atoms indicates their sp^2 character. All these metric features support the description of the NCN-bridges as carbodiimido(2-) ligands. It is worth mentioning that μ_4-$\kappa N,\kappa N,\kappa N',\kappa N'$ coordination mode of the cyanamido ligand is very rare; to the best of our knowledge, complex **7** provides the first example of structurally characterized cyanamido complexes of this type.[20] A related structure has been proposed only for one of the tautomeric structures of the tetranuclear gold complex $[\{Au(PPh_3)\}_4(\mu_4\text{-NCN})]^{2+}$.[2c]

On the other hand, complex **8** shows a stretching vibration assignable to the NCN moiety at 2152 cm^{-1} in the IR spectra, which is about 60 and 40 cm^{-1} higher in wavenumber than that of **1** and **2** (2110 cm^{-1}), respectively, and suggests the presence of cyanoimido(2-) type NCN-bridges. The ^1H NMR spectrum of **8** indicates that complex **8** consists of Cp*Ir and $Pd(\eta^3\text{-}C_3H_5)$ units in the ratio of 1:1. The molecular structure of $\mathbf{8}\cdot 6CH_2Cl_2$ has been established by an X-ray analysis (Figure 4, Table 4). As depicted in Figure 4, **8** is an Ir_4Pd_4 octanuclear complex in which four $PdCl(\eta^3\text{-}C_3H_5)$ fragments are ligated to the terminal nitrogen atoms of the NCN ligands in cubane cluster **2**. The molecule has a crystallographic C_2 axis passing through the cubane core. The long Ir···Ir interatomic distances (3.377−3.442 Å) exclude any metal−metal bonding interaction within the Ir_4N_4 moiety, which is consistent with the 72e structure of this core. The unsymmetrical (Ir)N−C and (Pd)N−C bond distances at 1.32 and 1.16 Å (mean), respectively, and the almost linear Pd−N−C bond angles (175° (mean)) confirm that the cyanamido ligands in **8** can be described as cyanoimido(2-) with the μ_4-$\kappa N,\kappa N,\kappa N,\kappa N'$ coordination mode. This coordination mode has rarely been found in molecular cyanamido complexes;[21] related structures have been found only in the Ru_3B complex $(PPN)[(Cp^*Ru)_3(\mu_3\text{-NCN})\{(\mu_4\text{-NCN})(BEt_3)\}]$ (PPN = $(Ph_3P)_2N^+$) and Ru_3Au complex $[(Cp^*Ru)_3(\mu_3\text{-NCN})\{(\mu_4\text{-NCN})(AuPPh_3)\}]$, though in the latter case considerable π-electron delocalization over the μ_4-NCN ligand was observed.[6d]

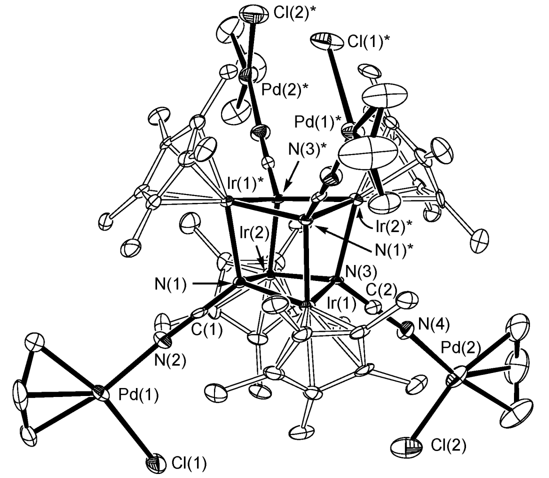


Figure 4. ORTEP drawing of **8** with thermal ellipsoids drawn at 50% probability level. Solvating CH_2Cl_2 molecules and hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $\mathbf{8}\cdot 6CH_2Cl_2$[a]

Ir(1)−N(1)	2.161(8)	Ir(1)−N(1)*	2.157(6)
Ir(1)−N(3)	2.154(7)	Ir(2)−N(1)	2.163(7)
Ir(2)−N(3)	2.175(7)	Ir(2)−N(3)*	2.180(6)
Pd(1)−N(2)	2.062(8)	Pd(2)−N(4)	2.072(8)
N(1)−C(1)	1.317(11)	N(2)−C(1)	1.156(12)
N(3)−C(2)	1.313(12)	N(4)−C(2)	1.162(12)
N(1)−Ir(1)−N(1)*	74.6(2)	N(1)−Ir(1)−N(3)	73.5(2)
N(1)*−Ir(1)−N(3)	75.3(2)	N(1)−Ir(2)−N(3)	73.0(2)
N(1)−Ir(2)−N(3)*	74.7(2)	N(3)−Ir(2)−N(3)*	75.0(2)
Ir(1)−N(1)−Ir(1)*	103.2(2)	Ir(1)−N(1)−Ir(2)	105.5(3)
Ir(1)−N(1)−C(1)	113.9(6)	Ir(1)*−N(1)−Ir(2)	102.8(2)
Ir(1)*−N(1)−C(1)	115.5(5)	Ir(2)−N(1)−C(1)	114.5(5)
Pd(1)−N(2)−C(1)	175.8(7)	Ir(1)−N(3)−Ir(2)	105.3(3)
Ir(1)−N(3)−Ir(2)*	102.4(2)	Ir(1)−N(3)−C(2)	115.2(6)
Ir(2)−N(3)−Ir(2)*	102.7(3)	Ir(2)−N(3)−C(2)	115.2(5)
Ir(2)*−N(3)−C(2)	114.4(5)	Pd(2)−N(4)−C(2)	173.8(7)
N(1)−C(1)−N(2)	178.7(8)	N(3)−C(2)−N(4)	178.7(9)

[a] −*x* + 1, *y*, −*z* + 1/2 + 1.

It would be reasonable to presume that the $Ir_4(NCN)_4$ core of **8** is formed by dimerization of the $Ir_2(NCN)_2$ core of **1**. We have previously disclosed that **1** is kinetically stable at room temperature but dimerizes to give **2** at 80 °C in 1-propanol.[6b] Since the conversion of **1** to **8** takes place under ambient conditions, a palladium species such as $[PdCl(\eta^3\text{-}C_3H_5)]$ is considered to act as a promoter for the dimerization. However, we must await further investigation to clarify the mechanism of this process. It is also expected that complex **8** is obtained more conveniently and selectively from **2**. In fact, treatment of **2** with 2.2 equiv of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ in CH_2Cl_2 at room temperature afforded **8** quantitatively.

On the other hand, **2** was transformed selectively into the trinuclear complex **3a** on reaction with $[Pd(\eta^3\text{-}C_3H_5)(acetone)_n]^+$ cation in 71% isolated yield. In this case, the cubane core of **2** is split into two diiridium fragments at least in a formal sense, which is the reverse process of the formation of **2** and **8**. The interconversion between a M_2N_2-type dinuclear species and a M_4N_4-type cubane cluster has

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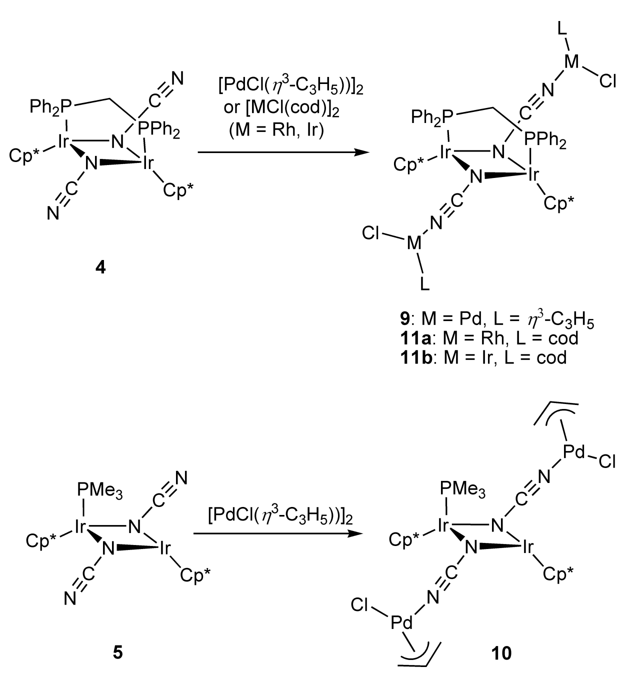
(20) Related metal−NCN structures have been characterized crystallographically only in inorganic cyanamide salts such as $Sm_2(NCN)_3$[5a] and Zn(NCN): Becker, M.; Jansen, M. *Acta Crystallogr. C* **2001**, *57*, 347–348.

(21) Related metal−NCN structures have also been found in a few inorganic cyanamide salts such as $Cu_4(NCN)_2NH_3$: Liu, X.; Müller, P.; Dronskowski, R. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1071–1074.

Scheme 2



scarcely been reported in the literature;[22] it has recently been described that the alkylimido-bridged diiron complex [FeCl(μ_2-N^{t}Bu)(NH$_2$^{t}Bu)]$_2$ undergoes reductive dimerization to form the cubane complex [FeCl(μ_3-N^{t}Bu)]$_4$$^-$, while the fission of the cubane core has not been observed.[23] Furthermore, although dimerization of sulfido-bridged dinuclear complexes to form M$_4$S$_4$ cubane complexes have been reported with a variety of transition metals,[24] the reverse reaction has not been developed. The NCN-bridged iridium complexes including **1** and **2** provide a unique system where both assembly and fission of multimetallic complexes are controlled by the nature of the reactant metal species.

NCN-Bridged Ir$_2$M$_2$ Complexes 9−11 (M = Pd, Rh, Ir). In the reaction of **1** with [PdCl(η^3-C$_3$H$_5$)]$_2$ giving **7**, the coordination of chloro ligands to the 32e Ir$_2$ core plays an important role in forming the μ_4-κN,κN,$\kappa N'$,$\kappa N'$ type NCN bridge. To gain further insight into this coordination behavior, reactivities of complexes **4** and **5** with [PdCl(η^3-C$_3$H$_5$)]$_2$ were examined (Scheme 2). Complexes **4** and **5** have a 36e and a 34e Ir$_2$ core, respectively, and are anticipated to have lower tendency to bind chloro ligands or to dimerize to form the cubane core. As expected, the reaction of **4** with 1 equiv of [PdCl(η^3-C$_3$H$_5$)]$_2$ in benzene at room temperature gave the Ir$_2$Pd$_2$ complex [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N′*)$_2${PdCl(η^3-C$_3$H$_5$)}$_2$-(μ-dppm)] (**9**) as the sole product in 81% yield (Scheme 2).

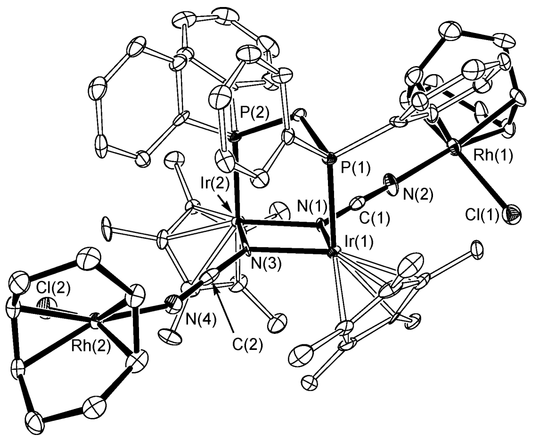


Figure 5. ORTEP drawing of **11a** with thermal ellipsoids drawn at 50% probability level. Solvating C$_2$H$_4$Cl$_2$ and hydrogen atoms are omitted for clarity.

The IR spectrum of **9** shows one strong ν_{NCN} band at 2095 cm^{-1}, which is about 50 cm^{-1} higher in wavenumber than that of **4** (2048 cm^{-1}),[6b] suggesting that the coordination of palladium takes place with maintenance of the cyanoimido(2-) structure as observed with **6**. The ^{1}H NMR spectrum exhibits a set of signals attributable to the two Cp*, two η^3-C$_3$H$_5$, and one dppm ligands. These spectral features are in full agreement with the formulation. The molecular structure was further confirmed by a preliminary X-ray study, although the low quality of the crystals prevented full refinement of the structure.[25]

Complex **5** reacted similarly with [PdCl(η^3-C$_3$H$_5$)]$_2$ to form [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N′*)$_2${PdCl(η^3-C$_3$H$_5$)}$_2$(PMe$_3$)] (**10**) in moderate yield. Again, a ν_{NCN} band is observed at 2113 cm^{-1} in the IR spectrum of **10**, which is about 60 cm^{-1} higher in wavenumber than that of **5** (2063 cm^{-1}) and diagnostic of the μ_3-κN,κN,$\kappa N'$ type cyanoimido(2-) ligands. The structure of **10** was also confirmed by a preliminary X-ray study.[26]

Although only preliminary X-ray structures were available for **9** and **10**, related Ir$_2$M$_2$ (M = Rh, Ir) were synthesized from **4** and structurally characterized.[27] Thus, the reaction of **4** with 1 equiv of [RhCl(cod)]$_2$ in benzene at room temperature gave the NCN-bridged Ir$_2$Rh$_2$ tetranuclear complex [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N′*)$_2${RhCl(cod)}$_2$(μ-dppm)] (**11a**) in 81% yield. All spectral features of **11a** including the ν_{NCN} absorption at 2077 cm^{-1} are comparable to those of **9** and **10**. Similar reaction with [IrCl(cod)]$_2$ afforded [(Cp*Ir)$_2$(μ_3-NCN-*N*,*N*,*N′*)$_2${IrCl(cod)}$_2$(μ-dppm)] (**11b**) in good yield, which exhibits a ν_{NCN} band at 2084 cm^{-1}.

The molecular structures of **11a**·C$_2$H$_4$Cl$_2$ and **11b**·C$_2$H$_4$Cl$_2$ have been established by X-ray diffraction studies (Figure 5, Table 5). The crystals of these compounds are isomorphous and only the molecular structure of **11a** is shown in Figure 5. In complexes **11a** and **11b**, like in

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[22] Allan, R. E.; Beswick, M. A.; Cromhout, N. L.; Paver, M. A.; Raithby, P. R.; Steiner, A.; Trevithick, M.; Wright, D. S. *Chem. Commun.* **1996**, 1501–1502.

[23] Duncan, J. S.; Zdilla, M. J.; Lee, S. C. *Inorg. Chem.* **2007**, *46*, 1071–1080.

[24] (a) Dobbs, D. A.; Bergman, R. G. *Inorg. Chem.* **1994**, *33*, 5329–5336. (b) Herberhold, M.; Jin, G.-X.; Milius, W. *Chem. Ber.* **1995**, *128*, 557–560. (c) Feng, Q.; Krautscheid, H.; Rauchfuss, T. B.; Skaugset, A. E.; Venturelli, A. *Organometallics* **1995**, *14*, 297–304. (d) Tang, Z.; Nomura, Y.; Ishii, Y.; Mizobe, Y.; Hidai, M. *Inorg. Chim. Acta* **1998**, *267*, 73–79. (e) Kuwata, S.; Andou, M.; Hashizume, K.; Mizobe, Y.; Hidai, M. *Organometallics* **1998**, *17*, 3429–3436. (f) Kabashima, S.; Kuwata, S.; Hidai, M. *J. Am. Chem. Soc.* **1999**, *121*, 7837–7845.

[25] Cell parameters for **9**·CH$_2$Cl$_2$: $a = 19.32(3)$ Å, $b = 13.181(14)$ Å, $c = 22.07(3)$ Å, $\beta = 102.75(2)°$, $V = 5482(13)$ Å^3; monoclinic, space group $P2_1/c$, R ($I > 3\sigma(I)$) = 0.055.

[26] Cell parameters for **10**: $a = 12.35(2)$ Å, $b = 18.94(2)$ Å, $c = 17.23(2)$ Å, $\beta = 107.53(3)°$, $V = 3750(10)$ Å^3; monoclinic, space group $P2_1/c$, R ($I > 3\sigma(I)$) = 0.061.

[27] Reaction of complex **1** with 1 equiv of [RhCl(cod)]$_2$ resulted in the formation of the NCN-bridged heterotrinuclear complex [(Cp*Ir)$_2$-{Rh(cod)}(μ_3-NCN-*N*,*N*,*N*)$_2$][RhCl$_2$(cod)] (**3b**[RhCl$_2$(cod)]).[6b]

Table 5. Selected Bond Distances (Å) and Angles (deg) for **11a**·$C_2H_4Cl_2$

Ir(1)−N(1)	2.110(5)	Ir(1)−N(3)	2.118(4)
Ir(2)−N(1)	2.103(4)	Ir(2)−N(3)	2.125(4)
Rh(1)−N(2)	2.051(5)	Rh(2)−N(4)	2.056(5)
N(1)−C(1)	1.271(7)	N(2)−C(1)	1.177(8)
N(3)−C(2)	1.278(7)	N(4)−C(2)	1.189(8)
N(1)−Ir(1)−N(3)	72.52(17)	N(1)−Ir(2)−N(3)	72.51(18)
Ir(1)−N(1)−Ir(2)	108.0(2)	Ir(1)−N(1)−C(1)	121.3(3)
Ir(2)−N(1)−C(1)	128.0(4)	Rh(1)−N(2)−C(1)	166.7(5)
Ir(1)−N(3)−Ir(2)	106.9(2)	Ir(1)−N(3)−C(2)	124.4(4)
Ir(2)−N(3)−C(2)	125.2(3)	Rh(2)−N(4)−C(2)	157.3(5)
N(1)−C(1)−N(2)	178.3(8)	N(3)−C(2)−N(4)	178.5(8)

complex **6**, each cyanamido ligand is coordinated by an MCl(cod) unit at the terminal nitrogen atom with essentially linear M−N−C angles (**11a**, 162°; **11b**, 164° (mean)). The apparent difference between the (Ir_2)N−C and (M)N−C bond distances (**11a**, 1.27 and 1.18 Å; **11b**, 1.26 and 1.18 Å (mean)) also confirms the description of the NCN-bridges as cyanoimido(2-) ligands. These observations with complexes **4** and **5** clearly indicate that the coordination behavior of metal fragments at the terminal nitrogen atoms of the cyanamido ligands in the $Ir_2(\mu\text{-NCN})_2$ type complexes is strongly coupled with the electronic nature of the Ir_2 core.

Conclusion

In this study we have demonstrated syntheses and characterization of novel tetra-, hexa-, and octanuclear heterobimetallic cyanamido complexes by utilizing the coordination ability of the terminal nitrogen atoms of the NCN ligands in **1**, **2**, **4**, and **5**. In these core expansion reactions, the μ_2-κN,κN and μ_3-κN,κN,κN cyanoimido(2-) ligands in the starting complexes were found to change their coordination modes depending both on the nature of the metal fragment introduced and on the electronic situation of the Ir_2 core, and unique coordination modes of NCN-bridges such as μ_3-κN,κN,$\kappa N'$ (cyanoimido(2-)), μ_4-κN,κN,$\kappa N'$,$\kappa N'$ (carbodiimido(2-)) and μ_4-κN,κN,κN,$\kappa N'$ (cyanoimido(2-)) were characterized in the products. Splitting of the cubane-type tetrairidium core was also observed in the reaction of **2** and $[PdCl(\eta^3\text{-}C_3H_5)]_2$. These results exemplify that the cyanamido ligand can act as a flexible and versatile building block for heterobimetallic clusters. Further studies on the reactivities of the new cyanamido clusters obtained here are now in progress.

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Supporting Information Available: Crystallographic data for **6**, **7**, **8**·$6CH_2Cl_2$, **11a**·$C_2H_4Cl_2$, and **11b**·$C_2H_4Cl_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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