Notes

Tetrametallic Copper and Gold Derivatives of a Cyano-Iridium-Diiron-Monocarborane Cluster

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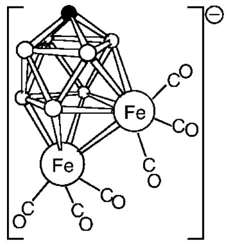
*Summary: The cyano-iridium-diiron complex $[N(PPh_3)_2][8,10\text{-}\{Ir(\mu\text{-}PPh_2)(CN)(Ph)(PPh_3)\}\text{-}8\text{-}(\mu\text{-}H)\text{-}6,6,6,10,10\text{-}(CO)_5\text{-}closo\text{-}6,10,1\text{-}Fe_2CB_7H_7]$ (**3**) has been synthesized by reaction of a THF solution of $[8,10\text{-}\{Ir(\mu\text{-}PPh_2)(Ph)(CO)(PPh_3)\}\text{-}8\text{-}(\mu\text{-}H)\text{-}6,6,6,10,10\text{-}(CO)_5\text{-}closo\text{-}6,10,1\text{-}Fe_2CB_7H_7]$ (**2**) with $[NEt_4]CN$ in the presence of Me_3NO, followed by metathesis with $[N(PPh_3)_2]Cl$. Compound **3** in CH_2Cl_2 with $[CuCl(PPh_3)]_4$ or $[AuCl(PPh_3)]$, in the presence of $TlPF_6$, yields $[8,10\text{-}\{Ir(\mu\text{-}PPh_2)(Ph)\{(CN)M(PPh_3)_n\}(PPh_3)\}\text{-}8\text{-}(\mu\text{-}H)\text{-}6,6,6,10,10\text{-}(CO)_5\text{-}closo\text{-}6,10,1\text{-}Fe_2CB_7H_7]$ ($M = Cu$, $n = 2$ (**4**) or $M = Au$, $n = 1$ (**5**), respectively). The structures of **4** and **5** have been established by X-ray diffraction experiments.*

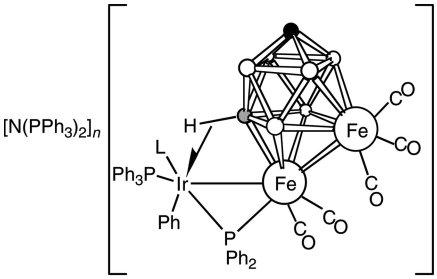
Chart 1



1

○ BH ● CH

Chart 2



	n	L
2	0	CO
3	1	CN
4	0	CN{Cu(PPh$_3$)$_2$}
5	0	CN{Au(PPh$_3$)}

● CH ○ BH ● B

Introduction

As part of our ongoing studies[1] on metal complexes of monocarbon carborane ligands, we have recently reported the synthesis of the anionic 10-vertex diferramonocarborane $[6,6,6,\text{-}10,10,10\text{-}(CO)_6\text{-}closo\text{-}6,10,1\text{-}Fe_2CB_7H_8]^-$ (**1**; Chart 1)[2] and its reactions with transition metal cations to give neutral, heterotrimetallic[2,3] complexes. Such reactions take advantage of the fact that metal-monocarborane complexes very often bear at least one unit of negative charge[1] and therefore are susceptible to further attack by electrophiles that include cationic metal fragments. However, a monoanionic complex such as **1**, upon reaction with a transition element monocation, for example, $\{Ir(CO)(PPh_3)_2\}^+$, affords *neutral* products such as $[8,10\text{-}\{Ir(\mu\text{-}PPh_2)(Ph)(CO)(PPh_3)\}\text{-}8\text{-}(\mu\text{-}H)\text{-}6,6,6,10,10\text{-}(CO)_5\text{-}closo\text{-}6,10,1\text{-}Fe_2CB_7H_7]$ (**2**; see Chart 2)[3] that generally are resistant to attachment of a further cationic metal fragment. To overcome this, we are exploring ways of “reactivating” these neutral species such as **2** to accept another metal center, one aspect of which we report here.

The carbonyl ligands in an anionic species such as **1** are typically difficult to replace by chemical means, whereas conversion of **1** to a neutral complex like **2** renders these ligands more susceptible to substitution.[1–3] Thus, treatment of a THF (tetrahydrofuran) solution of **2** with $[NEt_4]CN$, in the presence of Me_3NO to facilitate CO removal, followed by cation metathesis using $[N(PPh_3)_2]Cl$, affords the salt $[N(PPh_3)_2][8,10\text{-}\{Ir(\mu\text{-}PPh_2)(CN)(Ph)(PPh_3)\}\text{-}8\text{-}(\mu\text{-}H)\text{-}6,6,6,10,10\text{-}(CO)_5\text{-}closo\text{-}6,10,1\text{-}Fe_2CB_7H_7]$ (**3**; see Chart 2). This replacement of a *neutral* CO ligand by the CN^- *anion* afforded an anionic species that we hoped would add a fourth metal center by introduction of a suitable cationic synthon. Cyanide groups are also well established as bridging moieties in the formation of high-nuclearity species.[4]

In the IR spectrum of compound **3**, a weak CN stretching band appears at $\nu_{max} = 2100\ cm^{-1}$, along with CO stretching

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[1] (a) McGrath, T. D.; Stone, F. G. A. *J. Organomet. Chem.* **2004**, *689*, 3891. (b) McGrath, T. D.; Stone, F. G. A. *Adv. Organomet. Chem.* **2005**, *53*, 1.

[2] Franken, A.; McGrath, T. D.; Stone, F. G. A. *Organometallics* **2005**, *24*, 5157.

[3] Franken, A.; McGrath, T. D.; Stone, F. G. A. *J. Am. Chem. Soc.* **2006**, *128*, 16169.

[4] Contakes, S. M.; Klausmeyer, K. K.; Rauchfuss, T. B. *Inorg. Synth.* **2004**, *34*, 166.

10.1021/om700801j CCC: $40.75

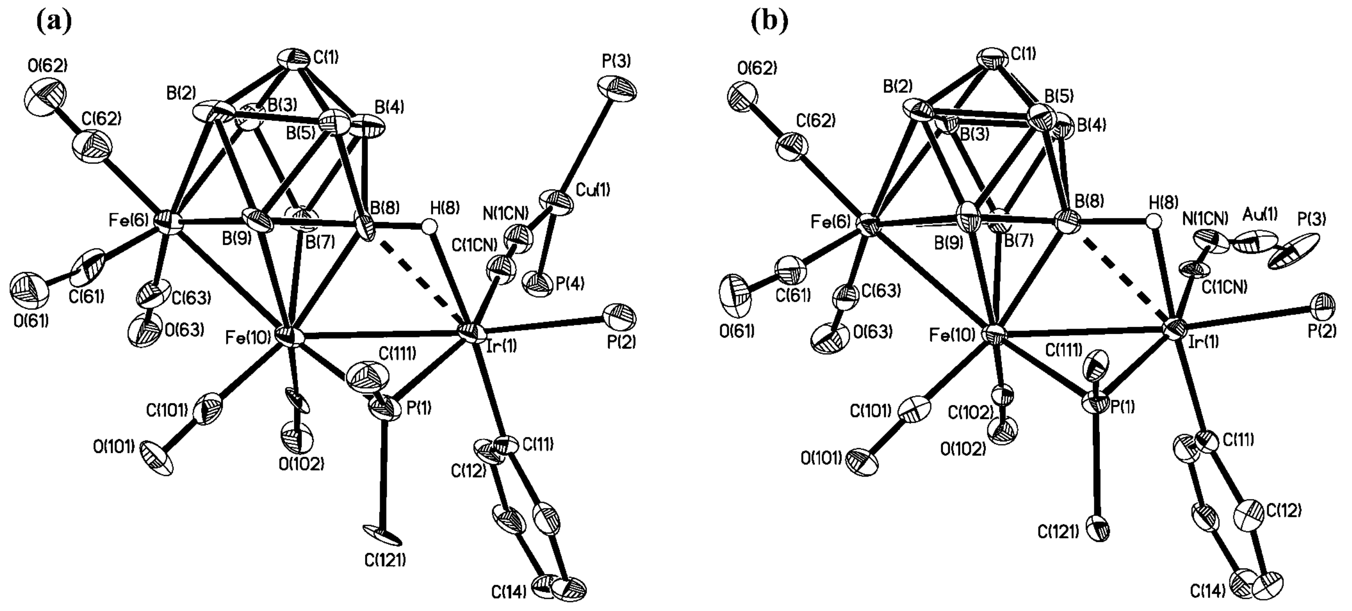

Figure 1. Structures of (a) compound **4** and (b) compound **5**. Thermal ellipsoids are drawn with 40% probability. For clarity, only the H atom involved in the B-H$\rightharpoonup$Ir unit is shown, all but the *ipso* C atoms of the μ-PPh_2 phenyl rings are omitted, and the phenyl rings of PPh_3 ligands are omitted. Selected distances (Å) and angles (deg) are as follows. For **4**: Fe(6)−Fe(10) 2.581(3), Fe(10)−Ir(1) 2.767(2), Fe(10)−P(1) 2.258(4), Ir(1)···B(8) 2.336(16), Ir(1)−H(8) 1.82(12), Ir(1)−C(1CN) 2.015(13), Ir(1)−C(11) 2.092(13), Ir(1)−P(1) 2.267(3), Ir(1)−P(2) 2.285(4), C(1CN)−N(1CN) 1.180(15), N(1CN)−Cu(1) 1.897(11), Cu(1)−P(3) 2.243(4), Cu(1)−P(4) 2.276(4); Fe(6)−Fe(10)−Ir(1) 135.00(8), Ir(1)−C(1CN)−N(1CN) 177.0(11), C(1CN)−N(1CN)−Cu(1) 172.0(11), N(1CN)−Cu(1)−P(3) 123.9(3), N(1CN)−Cu(1)−P(4) 114.9(3), P(3)−Cu(1)−P(4) 121.15(16), C(1CN)−Ir(1)−P(1) 159.1(4). For **5**: Fe(6)−Fe(10) 2.5842(15), Fe(10)−Ir(1) 2.7630(13), Fe(10)−P(1) 2.270(2), Ir(1)···B(8) 2.349(8), Ir(1)−H(8) 1.84(6), Ir(1)−C(1CN) 2.008(7), Ir(1)−C(11) 2.097(7), Ir(1)−P(1) 2.2871(19), Ir(1)−P(2) 2.2952(19), C(1CN)−N(1CN) 1.155(8), N(1CN)−Au(1) 2.016(6), Au(1)−P(3) 2.239(2); Fe(6)−Fe(10)−Ir(1) 136.05(4), Ir(1)−C(1CN)−N(1CN) 174.1(7), C(1CN)−N(1CN)−Au(1) 155.5(6), N(1CN)−Au(1)−P(3) 175.09(17), C(1CN)−Ir(1)−P(1) 158.6(2).

bands at 2031, 1976, and 1927 cm^{-1}, respectively. The latter are, as expected, generally lower in frequency than those for neutral compound **2**, where the highest frequency band is at $\nu_{max} = 2050$ cm^{-1}.[2] The $^{11}B\{^1H\}$ NMR data for **3** are very similar to those of the precursor **2** and do not merit further discussion. In contrast, the $^{31}P\{^1H\}$ NMR resonances for **3** are rather different from those for **2**. In addition to the peak for the cation, the μ-PPh_2 unit gives rise to a signal at δ 110.0 (cf. δ 137.1 in **2**) and the Ir-PPh_3 group to one at δ 31.6 (cf. δ 19.9 in **2**), suggesting that CO substitution had occurred at the iridium center. This was further substantiated by the $^{13}C\{^1H\}$ NMR spectrum, where a doublet is seen at δ 142.1 (J(PC) = 40 Hz) that may be assigned to the CN group, and no signal attributable to an Ir-CO ligand (which resonates at δ 178.1 in **2**). Moreover, the Ir-bound CO ligand in **2** is *transoid* to the μ-PPh_2 unit (the C−Ir−P angle is 158.56(12)°, and J(PC) is 99 Hz),[3] and the observation of strong P−C coupling for the CN group in **3** would further be consistent with this ligand having replaced the Ir-bound CO in **2**. The size of the P−C coupling constant is also indicative of the cyanide unit being C-bonded (rather than N-bonded) to the iridium center. Unfortunately single crystals of **3** suitable for an X-ray diffraction study were not available to establish definitively the site of CN substitution, but the structures determined for compounds **4** and **5** do confirm this formulation for **3**.

As noted above, it was of interest to determine whether the anion of **3** would react with appropriate cationic metal reagents to give compounds containing *four* metal centers. Thus, solutions of **3** in CH_2Cl_2 were treated with a mixture of $TlPF_6$ and either $[CuCl(PPh_3)]_4$ or $[AuCl(PPh_3)]$. These copper- and gold-phosphine reagents are among the synthons that we have found most commonly will form heterobimetallic products from anionic metallacarboranes,[1] and these reactions did indeed give neutral, tetrametallic complexes, namely, $[8,10\text{-}\{Ir(\mu\text{-}PPh_2)(Ph)\{(CN)M(PPh_3)_n\}(PPh_3)\}\text{-}8\text{-}(\mu\text{-}H)\text{-}6,6,6,10,10\text{-}(CO)_5\text{-}\mathit{closo}\text{-}6,10,1\text{-}Fe_2CB_7H_7]$ (M = Cu, n = 2 (**4**); M = Au, n = 1 (**5**)) (see Chart 2). Both products were fully characterized by analytical and spectroscopic means and by X-ray diffraction structural studies. The results of the latter experiments are presented in Figure 1.

Each of compounds **4** and **5** is seen to retain the core structure of the parent compound **2**, except that overall the CO ligand formerly bound to the Ir center in **2** has been replaced by a $\{(CN)M(PPh_3)_n\}$ moiety (M = Cu, n = 2; M = Au, n = 1); the Ir(1)−C(1CN)−N(1CN) angle is close to linear in each case, as is to be expected. However, the coordination environments of the Cu and Au atoms themselves are rather different. The principal difference is that the copper center is three-coordinate, bearing two PPh_3 ligands in addition to the bond with the cyanide, whereas the gold atom is only two-coordinate and is bonded to only a single PPh_3 group plus the cyanide. Thus, the angles (N−Cu−P or P−Cu−P) at copper are all close to 120° (range 114.9(3)−123.9(3)°) and the N−Au−P angle is almost linear (175.09(17)°). Such differences are not unexpected given the known preference for gold to adopt a two-coordinate geometry and for copper to tend toward three- or four-coordination.[5] The origin of the "additional" phosphine in **4** is presumed to be scavenging from the copper reagent. One other notable variation between the structures of **4** and **5** are differences in the C−N−M angles: whereas C(1CN)−N(1CN)−Cu(1) is almost linear (172.0(11)°), the C(1CN)−N(1CN)−Au(1) angle is rather bent (155.5(6)°). This is not unusual, however:

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(5) (a) Evan, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *232*, 171. (b) Hamilton, E. J. M.; Welch, A. J. *Polyhedron* **1991**, *10*, 471. (c) Carvajal, M. A.; Novoa, J. J.; Alvarez, S. *J. Am. Chem. Soc.* **2004**, *126*, 1465.

in compounds where cyanide ligands bridge between copper and another metal center,[6] the C−N−Cu angle varies between between 110° and 180°, and in the two structurally characterized complexes containing cyanide bridges to gold,[7] the C−N−Au angles range from around 145° to 175°. In the present case, we attribute the differences between **4** and **5** to the steric demands of two versus one PPh_3 ligand.

Spectroscopic parameters for compounds **4** and **5** are broadly similar to each other and also resemble those for the precursors **2** and **3**, except for the obvious differences such as signals due to the added $\{M(PPh_3)_n\}$ units. The latter give rise to peaks in the expected ranges in the ^1H and $^{13}C\{^1H\}$ NMR spectra and to a broad resonance at δ −2.3 in the $^{31}P\{^1H\}$ NMR spectrum of **4** and a broad singlet (δ 30.2) in the corresponding spectrum for **5**. These last spectra also show the chemical shift of the μ-PPh_2 group to be slightly affected by coordination of the $\{M(PPh_3)_n\}$ units, with resonances around δ 118 for **4** and **5**, albeit only around 8 ppm downfield of the signal for **3**. Similarly, the C≡N stretching frequency is significantly increased, by some 30 cm^{-1}, upon formation of **4** and **5**, perhaps suggesting some C···N antibonding character associated with the N lone pair orbital in **3**.

In conclusion, we have successfully demonstrated one possible method of "reactivating" a neutral (poly)metallic complex to accept an additional cationic metal fragment, namely, by replacing a neutral donor such as CO with an anionic ligand such as CN^-. The anionic species so formed (**3**) was able to accept transition metal cations, forming the tetrametallic complexes **4** and **5**. Although in the present case this did not result in the formation of further metal−metal bonds, the principle has nevertheless been demonstrated, and we are actively exploring this and related avenues in the synthesis of ever larger complexes and higher nuclearity clusters.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using Schlenk line techniques. Solvents were stored over and distilled from appropriate drying agents under nitrogen prior to use. Petroleum ether here refers to that fraction of boiling point 40–60 °C. Chromatography columns (typically ca. 18 cm in length and ca. 2 cm in diameter) were packed with silica gel (Acros, 60–200 mesh). Filtration through Celite typically employed a plug ca. 5 cm long and ca. 2 cm in diameter. Infrared spectra were recorded from CH_2Cl_2 solutions; all spectra showed a broad, medium-intensity band at ca. 2500–2550 cm^{-1} due to B-H absorptions. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA) on crystalline or microcrystalline samples that had been dried overnight in vacuo. On occasion residual solvent remained after drying, its presence and approximate proportion confirmed by integrated ^1H NMR spectroscopy, and this was factored into the calculated microanalysis data. NMR spectra were recorded from CD_2Cl_2 solutions at ambient temperatures and at the following frequencies (MHz): ^1H, 360.1; ^{13}C, 90.6; ^{11}B, 115.5; and ^{31}P, 145.8. Chemical shifts (δ, expressed in ppm) are referenced to $SiMe_4$ (^1H, ^{13}C), external $BF_3 \cdot Et_2O$ (^{11}B), and external 85% H_3PO_4 (^{31}P); and coupling constants (J) are in hertz. Compound **2**,[3] $[CuCl(PPh_3)]_4$,[8] and $[AuCl(PPh_3)]$[9] were prepared according to the literature; all other materials were used as received.

Preparation of $[N(PPh_3)_2][8,10\text{-}\{Ir(\mu\text{-}PPh_2)(CN)(Ph)(PPh_3)\}\text{-}8\text{-}(\mu\text{-}H)\text{-}6,6,6,10,10\text{-}(CO)_5\text{-}\mathit{closo}\text{-}6,10,1\text{-}Fe_2CB_7H_7]$ (3). Compound **2** (0.27 g, 0.25 mmol) and $[NEt_4]CN$ (ca. 0.08 g, 0.5 mmol) were dissolved in THF (20 mL), a solution of Me_3NO (ca. 0.04 g, 0.5 mmol) in CH_2Cl_2 (10 mL) was added dropwise, and the mixture was stirred at ambient temperature for 1 h. Solid $[N(PPh_3)_2]Cl$ (0.29 g, 0.5 mmol) was added, and after stirring a further 1 h the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2 (4 mL), and the extract filtered (Celite) and applied to a chromatography column. Elution with CH_2Cl_2/THF (9:1) gave a red fraction that yielded red microcrystals of **3** (0.19 g, 46%), after removal of solvent in vacuo. Anal. Calcd for $C_{87}H_{84}B_7Fe_2IrN_2O_7P_4$ (**3**·2THF): C, 59.0; H, 4.8; N, 1.6. Found: C, 59.4; H, 4.5; N, 1.9. IR (cm^{-1}): ν_{max}(C≡N) 2100 w; ν_{max}(CO) 2031 s, 1976 s, 1927 w. ^1H NMR: δ 7.63–7.24 (m, 60H, Ph), 6.45 (br s, 1H, cage CH), −9.54 (br, 1H, B-H⇀Ir). $^{13}C\{^1H\}$ NMR: δ 220.9 (d, J(PC) = 46, CO), 213.3 (CO), 142.1 (d, J(PC) = 40, CN), 134.5–126.5 (Ph), 96.3 (br, cage C). $^{11}B\{^1H\}$ NMR: δ 34.8 (1B, B(8)), 14.0 (1B), 9.2 (2B), −11.0 (1B), −12.9 (2B). $^{31}P\{^1H\}$ NMR: δ 110.0 (d, J(PP) = 11, μ-PPh_2), 31.6 (d, $IrPPh_3$), 21.2 (s, $N(PPh_3)_2$).

Preparation of $[8,10\text{-}\{Ir(\mu\text{-}PPh_2)(Ph)\{(CN)M(PPh_3)_n\}(PPh_3)\}\text{-}8\text{-}(\mu\text{-}H)\text{-}6,6,6,10,10\text{-}(CO)_5\text{-}\mathit{closo}\text{-}6,10,1\text{-}Fe_2CB_7H_7]$ (M = Cu, n = 2 (4); M = Au, n = 1 (5)). (i) A mixture containing compound **3** (0.20 g, 0.12 mmol), $[CuCl(PPh_3)]_4$ (ca. 0.09 g, 0.06 mmol), and $TlPF_6$ (ca. 0.05 g, 0.14 mmol) in CH_2Cl_2 (20 mL) was stirred at ambient temperature for 1 h. Solvent was removed in vacuo, the residue was extracted with CH_2Cl_2 (3 mL), and the extract was filtered (Celite) and applied to a chromatography column. Elution with CH_2Cl_2/petroleum ether (4:1) gave an orange fraction that yielded orange microcrystals of **4** (0.13 g, 63%), after removal of solvent in vacuo. Anal. Calcd for $C_{80}H_{70}B_7Cl_2CuFe_2IrNO_5P_4$ (**4**·CH_2Cl_2): C, 54.5; H, 4.0; N, 0.8. Found: C, 54.8; H, 4.2; N, 1.0. IR (cm^{-1}): ν_{max}(C≡N) 2133 w; ν_{max}(CO) 2038 s, 1982 s, 1933 w. ^1H NMR: δ 7.51–6.96 (m, 60H, Ph), 6.48 (br s, 1H, cage CH), −9.61 (br, 1H, B-H⇀Ir). $^{13}C\{^1H\}$ NMR: δ 217.4 (d, J(PC) = 12, CO), 212.4 (CO), 142.1 (d, J(PC) = 32, CN), 134.1–127.5 (Ph), 99.2 (br, cage C). $^{11}B\{^1H\}$ NMR: δ 34.4 (1B, B(8)), 13.0 (1B), 9.7 (2B), −11.5 (1B), −12.7 (2B). $^{31}P\{^1H\}$ NMR: δ 117.2 (br, μ-PPh_2), 30.0 (br, $IrPPh_3$), −2.3 (br, $CuPPh_3$).

(ii) Similarly, compound **3** (0.20 g, 0.12 mmol), $[AuCl(PPh_3)]$ (ca. 0.07 g, 0.14 mmol), and $TlPF_6$ (ca. 0.05 g, 0.14 mmol) afforded orange microcrystals of **5** (0.13 g, 68%). Anal. Calcd for $C_{61}H_{53}AuB_7Fe_2IrNO_5P_3$: C, 47.3; H, 3.5; N, 0.9. Found: C, 46.9; H, 3.6; N, 0.8. IR (cm^{-1}): ν_{max}(C≡N) 2132 w; ν_{max}(CO) 2038 s, 1981 s, 1932 w. ^1H NMR: δ 7.56–7.07 (m, 45H, Ph), 6.55 (br s, 1H, cage CH), −9.63 (br, 1H, B-H⇀Ir). $^{13}C\{^1H\}$ NMR: δ 223.2 (d, J(PC) = 13, CO), 212.2 (CO), 143.8 (d, J(PC) = 38, CN), 134.3–127.4 (Ph), 98.5 (br, cage C). $^{11}B\{^1H\}$ NMR: δ 34.6 (1B, B(8)), 13.9 (1B), 9.8 (2B), −10.9 (1B), −12.8 (2B). $^{31}P\{^1H\}$ NMR: δ 118.6 (d, J(PP) = 10, μ-PPh_2), 30.2 (br s, $AuPPh_3$), 29.1 (d, $IrPPh_3$).

X-Ray Crystallographic Structure Determinations. For both determinations: Bruker-Nonius X8 APEX CCD area-detector diffractometer, Mo Kα X-radiation (λ = 0.7103 Å), T = 110(2) K. Several sets of narrow data frames were collected at different values of θ, for various initial values of φ and ω, using 0.5° increments of φ or ω. Data frames were integrated using SAINT;[10] the substantial redundancy in data allowed an empirical absorption correction (SADABS)[10] to be applied, based on multiple measurements of equivalent reflections. Both structures

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(6) (a) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 388. (b) Bruno, I.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr.* **2002**, *B58*, 389.

(7) (a) Brown, N. C.; Carpenter, G. B.; Connelly, N. G.; Crossley, J. G.; Martin, A.; Orpen, A. G.; Rieger, A. L.; Rieger, P. H.; Worth, G. H. *J. Chem. Soc., Dalton Trans.* **1996**, 3977. (b) Mohamed, A. A.; Abdou, H. E.; Fackler, J. P. *Inorg. Chem.* **2006**, *45*, 11.

(8) Jardine, F. H.; Rule, J.; Vohra, G. A. *J. Chem. Soc. A* **1970**, 238.

(9) Bruce, M. I.; Nicholson, B. K.; Bin Shawkataly, O. *Inorg. Synth.* **1989**, *26*, 325.

(10) *APEX 2*, version 1.0; Bruker AXS: Madison, WI, 2003–2004.

were solved using conventional direct methods and refined by full-matrix least-squares on all F^2 data using SHELXTL version 6.12,[11] with anisotropic thermal parameters assigned to all non-H atoms. The locations of the cage-carbon atoms were verified by examination of the appropriate internuclear distances and the magnitudes of their isotropic thermal displacement parameters. Similarly, differentiation of the cyanide C and N atoms was by comparison of their isotropic thermal parameters: the present models with the cyanide C terminus bonded to iridium afforded a more satisfactory refinement. All hydrogen atoms were set riding on their parent atom with fixed isotropic thermal parameters defined as $U_{\mathrm{iso}}(\mathrm{H}) = 1.2 \times U_{\mathrm{iso}}(\mathrm{parent})$, with the exception that the H atom involved in the B-H$\rightharpoonup$Ir group in each case was allowed positional refinement. The asymmetric fraction for **5** contained one molecule of CH_2Cl_2 as solvate; in the same crystals the Au-bound PPh_3 ligand was disordered in two of the Ph rings, treated (for each ring) as two parts with refining complementary occupancies (approximate ratios 51:49 and 52:48 at convergence).

Crystal Data. For **4**: formula = $C_{79}H_{68}B_7CuFe_2IrNO_5P_4$, fw = 1678.33, monoclinic, $P2_1/c$, a = 16.490(3) Å, b = 19.830(3) Å, c = 24.010(3) Å, β = 98.589(6)°, V = 7762.8(19) Å^3, Z = 4, ρ_{calcd} = 1.436 g cm^{-3}, μ(Mo Kα) = 2.477 mm^{-1}, 57 240 reflections collected, 14 042 independent (R_{int} = 0.2024), wR_2 = 0.2052, R_1 = 0.1988 (all data), wR_2 = 0.1566, R_1 = 0.0758 ($F > 4\sigma(F)$). For **5**·CH_2Cl_2: formula = $C_{62}H_{55}AuB_7Cl_2Fe_2IrNO_5P_3$, fw = 1634.42, triclinic, $P\bar{1}$, a = 15.358(5) Å, b = 15.787(5) Å, c = 15.948(6) Å, α = 85.577(9)°, β = 64.734(9)°, γ = 66.820(9)°, V = 3195.2(19) Å^3, Z = 2, ρ_{calcd} = 1.699 g cm^{-3}, μ(Mo Kα) = 5.016 mm^{-1}, 41 128 reflections collected, 14 395 independent (R_{int} = 0.0718), wR_2 = 0.1056, R_1 = 0.0918 (all data), wR_2 = 0.0891, R_1 = 0.0491 ($F > 4\sigma(F)$).

Supporting Information Available: Full details of the crystal structure analyses in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] *SHELXTL*, version 6.12; Bruker AXS: Madison, WI, 2001.