Notes

Mixed-Metal Cluster Chemistry. 4.[1] Synthesis and X-ray Crystal Structure of $Cp_3W_3Ir_4(\mu\text{-H})(CO)_{12}$

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*Summary: Heating $Cp_2W_2Ir_2(CO)_{10}$ with triphenylamine in refluxing tetrahydrofuran affords $Cp_3W_3Ir_4(\mu\text{-H})(CO)_{12}$ (**1**) in poor yield; an X-ray structural study reveals that the molecule consists of a trigonal bipyramidal $CpW\{Ir(CO)_2\}_4$ unit bicapped by $CpW(CO)_2$ fragments.*

Introduction

Bimetallic clusters with widely differing metals are of interest for a number of reasons, including ligand activation utilizing the polar metal−metal bonds and their use as precursors to bimetallic particles with well-defined stoichiometry. Systematic investigations of the reactivity of such compounds are therefore of considerable interest. Clusters with disparate metals are little investigated, compared to the extensive studies of mixed-metal clusters containing metals from the same or adjacent groups. We recently reported reactivity studies of the tetrahedral cluster $CpWIr_3(CO)_{11}$ (Cp = η^5-C_5H_5) with phosphines, which proceed by way of site-selective ligand substitution,[2,3] and P−C cleavage chemistry of the resultant products.[1] More recently, we have found that analogous reactions of the isostructural cluster $Cp_2W_2Ir_2(CO)_{10}$ with phosphines proceed similarly to afford site-selective products in excellent yield.[4] We have now extended our reactivity studies of $Cp_2W_2Ir_2(CO)_{10}$ to embrace planar nonnucleophilic triphenylamine[5] and obtained $Cp_3W_3Ir_4(\mu\text{-H})(CO)_{12}$, an unusual example of a high-nuclearity (M_n, $n > 6$) mixed-metal cluster.

Results and Discussion

Refluxing $Cp_2W_2Ir_2(CO)_{10}$ with triphenylamine in tetrahydrofuran for 30 h affords the title compound in poor yield among a complex mixture of products, separable with difficulty by thin-layer chromatography; it was conclusively identified as $Cp_3W_3Ir_4(\mu\text{-H})(CO)_{12}$ (**1**) by a combination of NMR spectroscopy and an X-ray structural study.

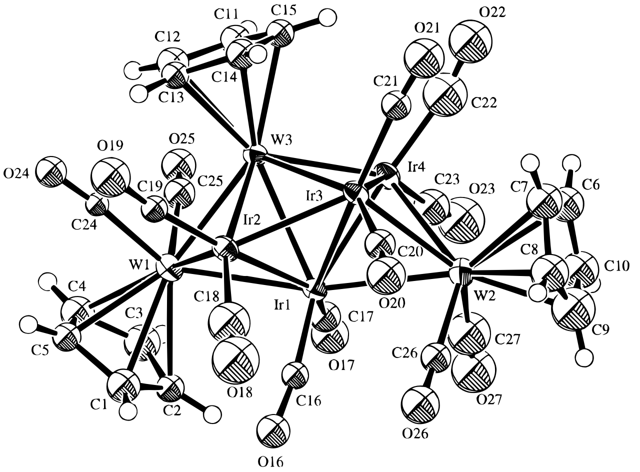

Figure 1. Molecular structure and atomic labeling scheme for $Cp_3W_3Ir_4(\mu\text{-H})(CO)_{12}$ (**1**). Thermal ellipsoids of 50% are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii.

An ORTEP diagram of the crystallographically determined molecular structure of **1** is shown in Figure 1, crystal data are shown in Table 1, and selected bond parameters are listed in Table 2. The seven-vertex cluster **1** is comprised of four iridium and three tungsten atoms arranged as a bicapped trigonal bipyramid. The four iridiums and a tungsten define the central trigonal bipyramidal unit; the iridiums each bear two terminal carbonyl ligands, and the tungsten is coordinated by an η^5-cyclopentadienyl group. The remaining two tungstens occupy capping sites, with both possessing two terminal carbonyl groups and an η^5-cyclopentadienyl ligand. The spectroscopically-identified hydride could not be located crystallographically; potential energy calculations suggest that it is possibly located on W(3)−Ir(4),[6] although this is not the longest M−M vector in the molecule. Structural characterization of a number of tri- and tetranuclear tungsten−iridium clusters have

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[1] Part 3: Waterman, S. M.; Humphrey, M. G.; Tolhurst, V.-A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.*, in press.

[2] Lee, J.; Humphrey, M. G.; Hockless, D. C. R.; Skelton, B. W.; White, A. H. *Organometallics* **1993**, *12*, 3468.

[3] Waterman, S. M.; Humphrey, M. G.; Tolhurst, V.-A.; Skelton, B. W.; White, A. H. *Organometallics* **1996**, *15*, 934.

[4] Waterman, S. M.; Humphrey, M. G.; Lee, J. Unpublished results.

[5] Sobolev, A. N.; Belsky, V. K.; Romm, I. P.; Chernikova, N. Y.; Guryanova, E. N. *Acta Crystallogr.* **1985**, *C41*, 967.

[6] Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

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Table 1. Crystal Structure Data for $Cp_3W_3Ir_4(\mu\text{-}H)(CO)_{12}$ (1)

formula	$C_{27}H_{15}Ir_4O_{12}W_3$
fw	1851.84
space group	$P2_1/c$, monoclinic
cryst dimens (mm)	0.02 × 0.09 × 0.16
scan type	$\omega-2\theta$
a (Å)	16.938(3)
b (Å)	9.124(2)
c (Å)	20.896(3)
β (deg)	106.59(1)
V (Å^3)	3094.7(9)
Z	4
ρ_{calcd} (g cm^{-3})	3.974
F(000)	3212.00
radiation, Å	Mo Kα, 0.710 69
μ, cm^{-1}	283.6
2θ max, deg	50.1
no. of observns	5846
no. of unique data, $I > 3\sigma(I)$	3481
no. of variables	221
R^a ($I > 3\sigma(I)$)	0.048
$R_w{}^b$ ($I > 3\sigma(I)$)	0.044

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = \sqrt{(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)}$.

Table 2. Selected Interatomic Bond Distances (Å) and Angles (deg) for $Cp_3W_3Ir_4(\mu\text{-}H)(CO)_{12}$ (1)

Ir(1)−Ir(2)	2.751(2)	Ir(1)−Ir(3)	2.687(2)
Ir(1)−Ir(4)	2.695(2)	Ir(1)−W(1)	2.864(2)
Ir(1)−W(2)	2.889(2)	Ir(1)−W(3)	2.824(2)
Ir(2)−Ir(3)	2.715(2)	Ir(2)−W(1)	2.832(2)
Ir(2)−W(3)	2.713(2)	Ir(3)−Ir(4)	2.704(2)
Ir(3)−W(2)	2.763(2)	Ir(3)−W(3)	2.682(2)
Ir(4)−W(2)	2.786(2)	Ir(4)−W(3)	2.684(2)
W(1)−W(3)	2.784(2)	W(1)−C(25)	2.01(3)
W(3)···C(25)	2.63(3)	Ir−CO	1.81(3)−1.96(4)
W−CO	1.96(3)−2.01(3)	W−C(Cp)	2.29(3)−2.46(4)
WC−O	1.12(3)−1.14(3)	IrC−O	1.09(3)−1.23(3)

Ir(2)−Ir(1)−Ir(3)	59.88(4)	Ir(2)−Ir(1)−Ir(4)	108.01(6)
Ir(2)−Ir(1)−W(1)	60.52(4)	Ir(2)−Ir(1)−W(2)	113.49(6)
Ir(2)−Ir(1)−W(3)	58.22(4)	Ir(3)−Ir(1) -Ir(4)	60.33(4)
Ir(3)−Ir(1)−W(1)	108.40(6)	Ir(3)−Ir(1)−W(2)	59.28(5)
Ir(3)−Ir(1)−W(3)	58.19(4)	Ir(4)−Ir(1)−W(1)	107.71(6)
Ir(4)−Ir(1)−W(2)	59.74(5)	Ir(4)−Ir(1)−W(3)	58.14(4)
W(1)−Ir(1)−W(2)	165.07(6)	W(1)−Ir(1)−W(3)	58.61(4)
W(2)−Ir(1)−W(3)	106.47(5)	Ir(1)−Ir(2)−Ir(3)	58.89(4)
Ir(1)−Ir(2)−W(1)	61.71(5)	Ir(1)−Ir(2)−W(3)	62.24(5)
Ir(3)−Ir(2)−W(1)	108.57(5)	Ir(3)−Ir(2)−W(3)	59.24(4)
W(1)−Ir(2)−W(3)	60.24(5)	Ir(1)−Ir(3)−Ir(2)	61.24(4)
Ir(1)−Ir(3)−Ir(4)	59.99(4)	Ir(1)−Ir(3)−W(2)	64.00(5)
Ir(1)−Ir(3)−W(3)	63.47(5)	Ir(2)−Ir(3)−Ir(4)	108.82(6)
Ir(2)−Ir(3)−W(2)	118.88(6)	Ir(2)−Ir(3)−W(3)	60.35(4)
Ir(4)−Ir(3)−W(2)	61.25(5)	Ir(4)−Ir(3)−W(3)	59.77(5)
W(2)−Ir(3)−W(3)	114.36(6)	Ir(1)−Ir(4)−Ir(3)	59.69(4)
Ir(1)−Ir(4)−W(2)	63.59(5)	Ir(1)−Ir(4)−W(3)	63.34(4)
Ir(3)−Ir(4)−W(2)	60.41(5)	Ir(3)−Ir(4)−W(3)	59.71(4)
W(2)−Ir(4)−W(3)	113.57(6)	Ir(1)−W(1)−Ir(2)	57.77(4)
Ir(1)−W(1)−W(3)	59.98(4)	Ir(2)−W(1)−W(3)	57.77(4)
Ir(1)−W(2)−Ir(3)	56.72(4)	Ir(1)−W(2)−Ir(4)	56.68(4)
Ir(3)−W(2)−Ir(4)	58.33(5)	Ir(1)−W(3)−Ir(2)	59.55(4)
Ir(1)−W(3)−Ir(3)	58.34(4)	Ir(1)−W(3)−Ir(4)	58.52(4)
Ir(1)−W(3)−W(1)	61.41(5)	Ir(2)−W(3)−Ir(4)	109.48(6)
Ir(2)−W(3)−Ir(3)	60.41(4)	Ir(3)−W(3)−W(1)	110.92(6)
Ir(3)−W(3)−Ir(4)	60.52(5)	Ir(4)−W(3)−W(1)	110.39(6)
Ir(2)−W(3)−W(1)	61.99(5)	W(1)−C(25)−O(25)	161(3)
W(3)−C(25)−O(25)	125(2)	Ir−C−O	168(3)−177(2)
W−C−O	171(2)−177(3)		

been reported;[2,7] the title complex is the largest cluster by far in the W−Ir system. W−Ir distances in **1** (2.682(2)−2.889(2) Å) fall within the range of those previously reported (2.665(2)[7e]−2.9023(9)[2] Å). Similarly, the Ir−Ir distances (2.687(2)−2.751(2) Å) are not unprecedented, with published structures exhibiting values in the range 2.598(1)[7g]−2.814(3)[7g] Å. Interestingly, the shortest W−Ir (2.682(2) Å) and Ir−Ir (2.687(2) Å) distances in **1** involve Ir(3), with a low (5) metal−metal connectivity, while the longest W−Ir (2.889(2) Å) and Ir−Ir (2.751(2) Å) bonds in **1** involve Ir(1), with a high (6) metal−metal connectivity; unlike capped octahedral structures where all metals are bound to 4 or 5 other metals, the core geometry observed here contains a metal with high metal−metal connectivity, and steric considerations may possibly explain bond lengthening associated with Ir(1) (although it is formally a 19 e metal, localized bonding considerations are probably inappropriate). The W−W distance (2.784(2) Å) is rather short; previously reported values span the range 2.991(1)[7a,c]−3.080(1)[7e] Å, with a distance of 2.666(1) Å in $Cp_2W_2Ir\{\mu_3\text{-}\eta^2\text{-}C_2(C_6H_4Me\text{-}4)_2\}(Cl)(CO)_4$ assigned to W═W. For the trinuclear cluster, a W═W double bond gives each metal an 18 electron configuration. In **1**, a W═W would give W(1) 19 e and W(3) 17 e. Although the existence of a dative bond could possibly be invoked to explain the electronic anomaly, and the semibridging CO(25) (see below) also serves to redistribute electron density, it is more likely for a heptametallic cluster that localized bonding arguments are overly simplistic and that the unsaturation is delocalized over the cluster. Other interactions are normal, except W(1)−C(25)−O(25) (161(3)°), the latter possibly indicating some semibridging character; W(3)−C(25) (2.63(3) Å) and W(3)−C(25)−O(25) (125(2)°) are consistent with this idea, as is the presence of a weak low-frequency carbonyl stretch in the IR spectrum (ν_{CO} 1839 cm^{-1}, w) in a similar region to one observed in the precursor $Cp_2W_2Ir_2(CO)_{10}$ (ν_{CO} 1833 cm^{-1}, w), which was also assigned to a crystallographically observed semibridging interaction.[7c]

Complex **1** has a highly unusual bicapped trigonal bipyramidal heptametallic core geometry. Other structurally characterized heptametallic cores incorporating iridium all have the conventional face-capped octahedral geometry and are all homometallic in nature.[8] All but one of the crystallographically authenticated hexametallic cores incorporating iridium possess octahedral core geometries[9] ($(Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta^5\text{-}C_5Me_5)_3$[10] has a "raft" geometry); cluster **1** thus has a new core geometry for iridium that is not related by simple capping to previously characterized core geometries involving this metal.

For heptametallic clusters, there is little (5.5%) energetic difference between the bicapped trigonal bipyramidal and the common capped octahedral core

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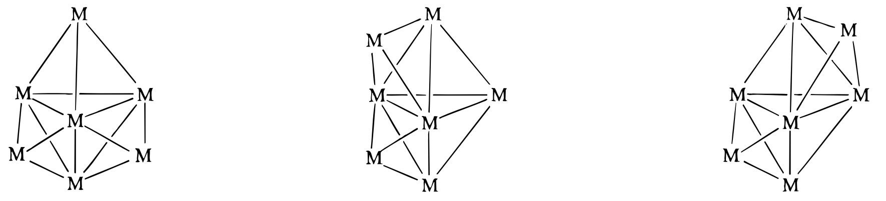
[7] (a) Shapley, J. R.; Hardwick, S. J.; Foose, D. S.; Stucky, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 7383. (b) Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1981**, *20*, 4112. (c) Churchill, M. R.; Bueno, C.; Hutchinson, J. P. *Inorg. Chem.* **1982**, *21*, 1359. (d) Churchill, M. R.; Biondi, L. V.; Shapley, J. R.; McAteer, C. H. *J. Organomet. Chem.* **1985**, *280*, C63. (e) Shapley, J. R.; McAteer, C. H.; Churchill, M. R.; Biondi, L. V. *Organometallics* **1984**, *3*, 1595. (f) Jeffery, J. C.; Ruiz, M. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 1131. (g) Shapley, J. R.; Humphrey, M. G.; McAteer, C. H. In *Selectivity in Catalysis*; Suib, S. L., Davis, M., Eds.; ACS Symposium Series 517; American Chemical Society: Washington, DC, 1993; p 127.

[8] (a) Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 2972. (b) Della Pergola, R.; Garlaschelli, L.; Demartin, F.; Manassero, M.; Masciocchi, N. *J. Organomet. Chem.* **1992**, *436*, 241. (c) Della Pergola, R.; Demartin, F.; Garlaschelli, L.; Manassero, M.; Martinengo, S.; Masciocchi, N.; Sansoni, M. *Organometallics* **1991**, *10*, 2239.



(A)
$Au_3CoRu_3(CO)_{12}(PPh_3)_3$[a] 96 CVE
$Au_3(\mu\text{-}H)Ru_4(CO)_{12}(PPh_3)_3$[b,c] 96 CVE

(B)
No examples

(C)
$[Au_6V(CO)_4(PPh_3)_6]^+$[d] 90 CVE
$[Au_6Pt(CO)(PPh_3)_7]^{2+}$[e] 90 CVE
$[Au_6Co(CO)_2(PPh_3)_6]^+$[f] 90 CVE
$Cp_3W_3Ir_4(\mu\text{-}H)(CO)_{12}$[g] 94 CVE

Figure 2. Bicapped trigonal bipyramidal core isomers and crystallographically verified examples of heptametallic clusters consisting of transition metal core atoms. Key: [a]Ref 12; [b]Ref 11; [c]Ref 13; [d]Ref 14; [e]Ref 15; [f]Ref 16; [g]this work.

geometries,[11] but previous reports of clusters with this core geometry are gold-rich, some markedly so. All reported transition metal clusters with bicapped trigonal bipyramidal cores and the three possible core isomers are summarized in Figure 2.

The PSEPT rule predicted electron count for bicapped trigonal bipyramidal transition metal clusters is 96 CVE (4 × 60(tetrahedra) − 3 × 48(shared faces)). The two clusters of core isomer A are thus electron precise with 96 CVE. No examples of core isomer B are extant. The title cluster is the first transition metal example of isomer C without coinage metals, although three 90 CVE clusters incorporating six gold atoms each have been reported previously, and a number of main group−transition metal cluster examples exist[17] (in each case, the six-coordinate vertex is occupied by a main group atom, emphasizing the unusual nature of **1**). Cluster **1** has 94 CVE (15(3 Cp) + 18(3 W) + 36(4 Ir) + 1(H) + 24(12 CO)). The reason for the formal electron deficiency is not apparent at this stage.

Syntheses of medium- and high-nuclearity clusters continue to attract interest; generally applicable procedures have been summarized.[18] In the present case, the presence of the amine NPh_3 is critical; thermolysis of $Cp_2W_2Ir_2(CO)_{10}$ in its absence affords good yields of $CpWIr_3(CO)_{11}$.[19] Analogous cluster enlargement employing a basic environment in the parent homometallic tetrairidium system has been reported, although heptairidium clusters were not isolated.[9k,20]

The present work provides a further example of anomalous electron counting, highlighting deficiencies in our current understanding of metal clusters. Further chemistry with mixed tungsten−iridium clusters is currently underway.

Experimental Section

General Details. $Cp_2W_2Ir_2(CO)_{10}$ was prepared by the published procedure.[7a] Triphenylamine was obtained commercially (Koch-Light) and used as received. The reaction was performed under an atmosphere of dry nitrogen (high-purity grade, CIG), although no precautions were taken to exclude air during workup. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under an inert atmosphere prior to use. All other solvents were reagent grade and used as received. Petroleum ether refers to a fraction of boiling point 40−70 °C. The progress of the reaction was monitored by analytical thin-layer chromatography (5554 Kieselgel 60 F_{254}, E. Merck), and the products were separated on 20 × 20 cm glass plates coated with 7749 Kieselgel 60 PF_{254} (E. Merck). Infrared spectra were recorded on a Perkin-Elmer FTIR 1600 spectrometer using CaF_2 optics. The ^1H NMR spectrum was recorded on a Varian Gemini 300 spectrometer at 300 MHz, in acetone-d_6 (Aldrich); chemical shifts in ppm are referenced to internal residual acetone.

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(9) (a) Ceriotti, A.; Della Pergola, R.; Garlaschelli, L.; Laschi, F.; Manassero, M.; Masciocchi, N.; Sansoni, M.; Zanello, P. *Inorg. Chem.* **1991**, *30*, 3349. (b) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Sartorelli, U.; Tagliabue, F. *J. Organomet. Chem.* **1982**, *234*, C39. (c) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Malatesta, M. C.; Sartorelli, U. *J. Organomet. Chem.* **1983**, *248*, C17. (d) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Raimondi, C.; Martinengo, S. *J. Organomet. Chem.* **1983**, *243*, C10. (e) Garlaschelli, L.; Malatesta, M. C.; Martinengo, S.; Demartin, F.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1986**, 777. (f) Garlaschelli, L.; Martinengo, S.; Bellon, P. L.; Demartin, F.; Manassero, M.; Chiang, M. Y.; Wei, C.-Y.; Bau, R. *J. Am. Chem. Soc.* **1984**, *106*, 6664. (g) Della Pergola, R.; Garlaschelli, L.; Martinengo, S.; Demartin, F.; Manassero, M.; Masciocchi, N. *J. Chem. Soc., Dalton Trans.* **1988**, 2307. (h) Churchill, M. R.; Bexman, S. A. *Inorg. Chem.* **1974**, *13*, 1418. (i) Della Pergola, R.; Ceriotti, A.; Garlaschelli, L.; Demartin, F.; Manassero, M.; Masciocchi, N.; Sansoni, M. *Inorg. Chem.* **1993**, *32*, 3277. (j) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2345. (k) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Martinengo, S.; Canziani, F. *J. Chem. Soc., Chem. Commun.* **1980**, 903. (l) Della Pergola, R.; Garlaschelli, L.; Martinengo, S.; Demartin, F.; Manassero, M.; Masciocchi, N.; Bau, R.; Zhao, D. *J. Organomet. Chem.* **1990**, *396*, 385. (m) Ceriotti, A.; Della Pergola, R.; Demartin, F.; Garlaschelli, L.; Manassero, M.; Masciocchi, N. *Organometallics* **1992**, *11*, 756. (n) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Garlaschelli, L.; Moret, M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1992**, 1865.

(10) Freeman, M. J.; Miles, A. D.; Murray, M.; Orpen, A. G.; Stone, F. G. A. *Polyhedron* **1984**, *3*, 1093.

(11) Bruce, M. I.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, *252*, 243.

(12) Bruce, M. I.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1982**, 1141.

(13) Bateman, L. W.; Green, M.; Howard, J. A. K.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1982**, 773.

(14) Wurst, K.; Strähle, J.; Beuter, G.; Dell'Amico, D. B.; Calderazzo, F. *Acta Chem. Scand.* **1991**, *45*, 844.

(15) Ito, L. N.; Sweet, J. D.; Mueting, A. M.; Pignolet, L. H.; Schoondergang, M. F. J.; Steggerda, J. J. *Inorg. Chem.* **1989**, *28*, 3696.

(16) Holzer, M.; Strähle, J.; Baum, G.; Fenske, D. *Z. Anorg. Allg. Chem.* **1994**, *620*, 192.

(17) (a) Housecroft, C. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 6420. (b) Housecroft, C. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1332. (c) Chini, P.; Ciani, G.; Martinengo, S.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1979**, 188. (d) Frediani, M.; Bianchi, M.; Salvani, A.; Piacenti, F.; Ianelli, S.; Nardelli, M. *J. Chem. Soc., Dalton Trans.* **1990**, 165. (e) Sunick, D. L.; White, P. S.; Schauer, C. K. *Inorg. Chem.* **1993**, *32*, 5665. (f) Housecroft, C. E.; Shongwe, M. S.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2651. (g) Housecroft, C. E.; Shongwe, M. S.; Rheingold, A. L.; Zanello, P. *J. Organomet. Chem.* **1991**, *408*, 7.

(18) (a) Longoni, G.; Iapalluci, M. C. In *Clusters and Colloids: From Theory to Applications*; Schmid, G., Ed.; VCH: Weinheim, Germany, 1994; p 91. (b) Adams, R. D. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; V. C. H. Publishers: New York, 1990; p 121.

(19) Humphrey, M. G. Unpublished results.

(20) (a) Della Pergola, R.; Cea, F.; Garlaschelli, L.; Masciocchi, N.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1994**, 1501. (b) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Raimondi, C.; Martinengo, S.; Canziani, F. *J. Chem. Soc., Chem. Commun.* **1981**, 528.

Reaction of $Cp_2W_2Ir_2(CO)_{10}$ and NPh_3. A solution of $Cp_2W_2Ir_2(CO)_{10}$ (50.0 mg, 0.0430 mmol) and NPh_3 (10.5 mg, 0.0430 mmol) in THF (15 mL) was refluxed for 30 h. Solvent was removed *in vacuo* to leave a brown residue. Subsequent purification by preparative thin-layer chromatography (7:3 CH_2Cl_2:petroleum ether) resulted in six bands. Bands 1 and 2 were identified as $CpWIr_3(CO)_{11}$ (3.6 mg, 7%) and $Cp_2W_2Ir_2(CO)_{10}$ (19.8 mg, 40%). Bands 4−6 were very minor and have not thus far been characterized. Band 3, R_f 0.51, was crystallized from CH_2Cl_2/octane to afford brown crystals of $Cp_3W_3Ir_4(\mu\text{-}H)(CO)_{12}$ **1** (1.1 mg, 1%). Analytical data for **1** are as follows. IR (c-C_6H_{12}): 2014 vs, 2001 vs, 1985 m, 1969 m, 1946 w, 1940 w, 1839 w cm^{-1}. ^1H NMR (acetone-d_6): δ 5.67 (s) 5H, Cp, 5.60 (s) 5H, Cp, 5.55 (s) 5H, Cp, −6.37 (s) 1H, μ-H. The very small yields of **1** precluded microanalyses. It also proved impossible to obtain a mass spectrum (Australian National University, VG ZAB 2SEQ instrument, 30 kV Cs^+ ions, current 1 mA, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix).

Crystal Structure of 1. An orange platelike crystal of **1** was grown by slow evaporation of a solution in CH_2Cl_2/octane. X-ray data collection was carried out using a Rigaku AFC6S single-crystal diffractometer. Data were collected using the $\omega-2\theta$ scan type at 23.0 °C and were corrected for Lorentz−polarization, absorption (face indexed analytical, transmission factors 0.0944−0.4941), and secondary extinction. The structure was determined by direct methods. The iridiums and tungstens were refined anisotropically; all other non-hydrogen atoms were refined isotropically. Hydrogen atoms were included but not refined. All calculations were performed using teXsan Structure Analysis Software of the Molecular Structure Corp.[21] Relevant data are given in Tables 1 and 2.

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Supporting Information Available: Tables of atomic coordinates and isotropic displacement parameters, anisotropic displacement parameters, interatomic distances, interatomic angles, torsion angles, nonbonded contacts, and selected least-squares planes (40 pages). Ordering information is given on any current masthead page.

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[21] teXsan: *Single Crystal Structure Analysis Software, version 1.6c*; Molecular Structure Corp.: The Woodlands, TX, 1993.