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Phosphido-Bridged Tungsten-Iridium and Iron-Iridium 1,5-Cyclooctadiene Complexes

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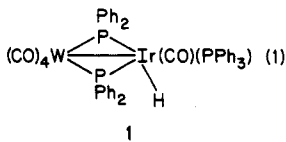
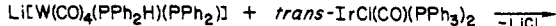
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The new heterobimetallic complexes $(\text{CO})_4\text{M}(\mu\text{-PPh}_2)_2\text{IrH}(\text{COD})$ (COD = 1,5-cyclooctadiene; 2, M = W; 3, M = Mo; 4, M = Cr) have been prepared by the reaction of $[\text{Ir}(\mu\text{-Cl})(\text{COD})]_2$ with the corresponding $\text{Li}[\text{M}(\text{CO})_4(\text{PPh}_2\text{H})(\text{PPh}_2)]$ reagent. The methyl complex $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{IrCH}_3(\text{COD})$ (5) derives from a modification of the above syntheses. These complexes have been spectroscopically characterized with 2 fully defined by an X-ray diffraction study: $P2_1$, $a = 11.260$ (3) Å, $b = 15.221$ (4) Å, $c = 11.756$ (3) Å, $\beta = 111.80$ (2)°, $V = 1870.8$ (8) Å³, $Z = 2$, $R = 0.0418$, $R_w = 0.0407$. The W and Ir atoms are bridged by the two $\mu\text{-PPh}_2$ ligands with the W further coordinated by four CO's and the Ir by a hydride and the COD ligand. The $\text{WIr}(\mu\text{-P})_2$ core of the molecule is planar, and the W-Ir distance of 2.893 (1) Å implies a metal-metal bond between these atoms. The Fe-Ir complex $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{IrH}(\text{COD})$ (7) was prepared by an analogous reaction using $\text{Li}[\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})(\text{PPh}_2)]$. From this complex derives the chloro derivative $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{IrCl}(\text{COD})$ (8), which has been crystallographically characterized: $P2_1/n$, $a = 11.438$ (2) Å, $b = 25.149$ (3) Å, $c = 11.750$ (2) Å, $\beta = 108.85$ (1)°, $V = 3198.7$ (9) Å³, $Z = 4$, $R = 0.0379$, $R_w = 0.0394$. The Fe and Ir atoms are bridged by the two $\mu\text{-PPh}_2$ ligands with the Fe further coordinated by three CO's and the Ir by a chloride and the COD ligand. The $\text{FeIr}(\mu\text{-P})_2$ core of the molecule is bent, and the Fe-Ir distance of 2.703 (1) Å implies a metal-metal bond between these atoms. The COD ligand of the W-Ir complex 2 can be replaced by two CO's at 1000 psi pressure and 100 °C to give $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{IrH}(\text{CO})_4$ (6). Likewise, the Fe-Ir complex 7 reacts with CO + PPh_3 to give the known compound $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{IrH}(\text{CO})(\text{PPh}_3)$, but under much milder conditions than the reactions of 2 with CO. These results show an influence of the adjacent metal W or Fe on the reactivity of the Ir center.

Heterobimetallic complexes which link together metals with substantially different chemical properties are inherently interesting since they may lead to unusual bifunctional activation of organic substrates. Particularly appealing in this regard are complexes which combine metals from the left of the transition series (groups 4-6) with Rh and Ir, because of the catalytic relevance of these latter metals and the facility with which they undergo oxidative-addition and reductive-elimination reactions. In an earlier study we prepared the bis(phosphido)bridged W-Ir complex 1 (eq 1), and this gave a novel set of bi-



metallic acyl-hydride and carbene-hydride derivatives.¹ However, complex 1 showed little reactivity at the Ir center. For example, it did not react with H₂ or CO nor with ethylene. We have sought to alter the Ir end of molecules like 1 to increase their reactivity. One logical approach is to replace the CO and PPh_3 ligands by olefin ligands which should be more easily substituted or removable via hydrogenation. Herein we describe a series of such bimetallic complexes which link $\text{Ir}(\text{R})(\text{COD})$ (COD = 1,5-cyclooctadiene; R = H, CH₃, Cl) to $\text{M}(\text{CO})_x$ (M = Cr, Mo, W, Fe) fragments via bridging phosphido ligands and present a brief exploration of their derivative chemistry. An interesting aspect of this study concerns the significant reactivity differences at the Ir end of the molecule when the adjacent metal is changed from W to

(1) Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* 1984, 3, 782.

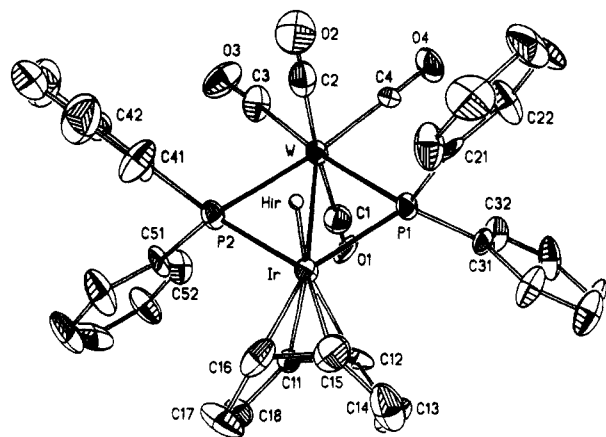
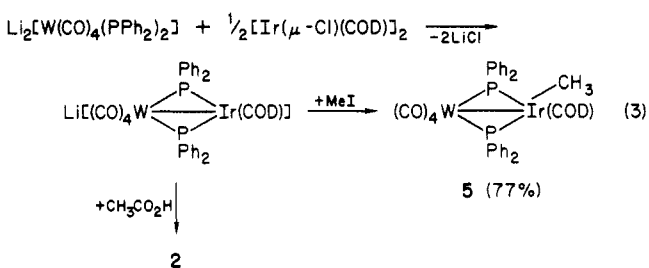
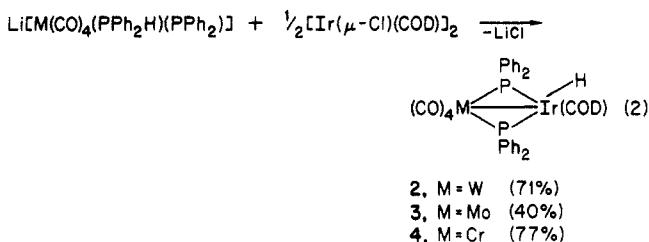


Figure 1. An Ortep drawing of $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{Ir}(\text{H})(\text{COD})$ (2). Thermal ellipsoids are drawn at the 40% probability level.

Fe. Also described are X-ray diffraction studies of $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{IrH}(\text{COD})$ and $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{IrCl}(\text{COD})$. These complexes have significantly different core geometries due to the different coordination requirements of the W and Fe atoms.

Results

Preparation and Characterization of $(\text{CO})_4\text{M}(\mu\text{-PPh}_2)_2\text{Ir}(\text{R})(\text{COD})$ Complexes. We have previously demonstrated the preparation of phosphido-bridged binuclear complexes by the "bridged-assisted" synthetic method² using the reaction of (diphenylphosphido)carbonylmetalates with metal chlorides, e.g., eq 1.³ This synthetic chemistry is easily extended to prepare complexes with COD ligands by using the reagent $[\text{Ir}(\mu\text{-Cl})(\text{COD})]_2$ (eq 2 and 3). The necessary phosphido reagents



for these reactions were generated in situ by addition of 1 or 2 equiv of *n*-BuLi to the corresponding $\text{M}(\text{CO})_4(\text{PPh}_2\text{H})_2$ precursor complex.¹ The intermediate complex $[(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{Ir}(\text{COD})]^-$ shown in eq 3 has not been characterized, but its conversion into 2 and 5 is consistent with its indicated formulation. Complexes 2 through 5 have been characterized by their spectroscopic data (Table I and Experimental Section) with 2 also defined by an

Table I. ^{31}P and ^1H NMR Data^{a-c}

compd	^{31}P , δ	$J(^{31}\text{P}-^{183}\text{W})$, Hz	^1H , δ	$J(^1\text{H}-^{31}\text{P})$, Hz
2	157.6 (s)	159.5	7.9 (dm, 8 H), 7.0 (m, 12 H), 4.5 (br s, 2 H), 3.0 (br s, 2 H), 2.3 (br m, 2 H), 1.8 (br m, 6 H)	40
3	182.6 (s)		-17.0 (t, 1 H), 7.9 (dm, 8 H), 6.9 (br m, 12 H), 4.5 (br s, 2 H), 3.0 (br s, 2 H), 2.3 (br m, 4 H), 1.2 (br m, 5.5 H)	15.3 39
4	202.9 (s)		-17.0 (t, 1 H), 7.9 (dm, 8 H), 7.0 (m, 12 H), 4.5 (br s, 2 H), 3.1 (br s, 2 H), 2.4 (br m, 2 H), 1.3 (br m, 6 H)	16.0 33
5	170.7 (s)	179.1	-17.0 (t, 1 H), 8.1 (dm, 8 H), 7.0 (m, 12 H), 3.8 (br s, 2 H), 2.8 (br s, 2 H), 2.4 (br m, 2 H), 1.5 (br m, 6 H)	16.0 35
6	138.0 (s)		-0.8 (t, 3 H), 7.7 (dm, 8 H), 7.3 (m, 12 H)	9.0 38
7	99.8 (s)		-13.7 (t, 1 H), 7.4 (dm, 8 H), 6.8 (m, 12 H), 4.6 (br s, 2 H), 3.6 (br s, 2 H), 2.2 (br m, 8 H)	16.0 22
8	82.3 (s)		-11.8 (t, 1 H), 7.7 (br m, 8 H), 6.7 (m, 12 H), 5.1 (br s, 2 H), 4.4 (br s, 2 H), 3.2 (br m, 2 H), 1.8 (br m, 6 H)	8.3

^a ^{31}P NMR solvents: C_6D_6 (2, 5); $(\text{CD}_3)_2\text{CO}$ (3, 4); CDCl_3 (6-8).
^b ^1H NMR solvents: C_6D_6 (2-5, 7, 8); CDCl_3 (6).

X-ray diffraction study (Figure 1). Each complex shows the expected parent ion in its mass spectrum, and IR and NMR data are consistent with the structures drawn. For illustration, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 2 (Table I) shows a single resonance at δ 157.6 assigned to the equivalent $\mu\text{-PPh}_2$ ligands. The downfield position of this resonance implies the presence of a WIr bond,^{2,4} consistent with the determined structure ($\text{W}-\text{Ir} = 2.893$ (1) Å). The ^1H NMR spectrum of 2 shows a hydride resonance at δ -17.0 ($J_{\text{H-P}} = 16.0$ Hz), as well as resonances for the $\mu\text{-PPh}_2$ phenyl substituents and for the 1,5-cyclooctadiene ligand. The methyl complex 5 shows a methyl resonance at δ -0.8 (t) in its ^1H NMR spectrum.

Carbonylation of 2 To Give $(\text{CO})_4\text{W}(\text{PPh}_2)_2\text{Ir}(\text{H})(\text{CO})_2$ (6). Attempts to remove the COD ligands in complexes 2-5 by hydrogenation or carbonylation at elevated pressures up to 1000 psi at room temperature were unsuccessful. However, heating a hexane solution of 2 at 110 °C under 1000 psi pressure gave the new compound 6 in

(2) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1990; Chapter 40.

(3) Rosenberg, S.; Whittle, R. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* 1984, 106, 5934.

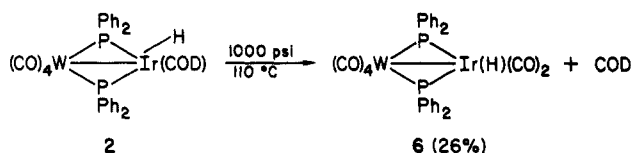
(4) (a) Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* 1980, 19, 186. (b) Carty, A. J.; Maclaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* 1981, 204, C27. (c) Garrou, P. E. *Chem. Rev.* 1981, 81, 229. (d) Johansson, G.; Stetzer, O. *Chem. Ber.* 1977, 110, 3438. (e) Carty, A. J. *Adv. Chem. Ser.* 1982, No. 196, 163.

Table II. Crystallographic Details for $(\text{CO})_4\text{W}(\mu\text{-PPH}_2)_2\text{IrH}(\text{COD})$ (2) and $(\text{CO})_3\text{Fe}(\mu\text{-PPH}_2)_2\text{IrCl}(\text{COD})$ (8)

	2	8
formula	$\text{C}_{36}\text{H}_{33}\text{O}_4\text{P}_2\text{IrW}\cdot\text{C}_3\text{H}_6\text{O}$	$\text{C}_{35}\text{H}_{32}\text{ClFeIrP}_2\text{O}_3$
cryst system	monoclinic	monoclinic
space group	$P2_1$	$P2_1/n$
crystal size	$0.21 \times 0.31 \times 0.36$	$0.21 \times 0.33 \times 0.39$
a , Å	11.260 (3)	11.438 (2)
b , Å	15.221 (4)	25.149 (3)
c , Å	11.756 (3)	11.750 (2)
β , Å	111.80 (2)	108.85 (1)
V , Å ³	1870.8 (8)	3198.7 (9)
Z	2	4
$d(\text{calcd})$, g cm ⁻³	1.82	1.76
μ , cm ⁻¹	71.4	50.8
max/min transm	0.406/0.115	0.256/0.123
diffractometer		Nicolet R3
radiation		Mo $K\alpha$ ($\lambda = 0.71073$ Å)
monochromator		graphite crystal
temp, °C		23
scan technique		ω , full profile
scan speed, deg min ⁻¹	var, 4-20	var, 6-20
2θ scan range, deg	4-45	4-48
data collected	$\pm h, k, l$	$\pm h, k, l$
unique data	2556 (2702 collected)	5020 (5431 collected)
unique data with $F_o \geq 3\sigma(F_o)$	2422 ($F_o \geq 3\sigma(F_o)$)	4230 ($F_o \geq 4\sigma(F_o)$)
data/parameters	5.7	12.4
standard reflectns	3/97 (no decay)	3/97 (no decay)
g^a	0.0008	0.0008
$R_F, R_{wF}, \text{GOF}^a$	0.0418, 0.0407, 1.612	0.0379, 0.0394, 1.16
mean shift, esd max, final cycle	0.060	0.049
highest peak, final diff map, e Å ³	1.13	1.15

$$^a w^{-1} = \sigma^2(F_o) + |g|(F_o)^2; R_F = \sum[|F_o| - |F_c|] / \sum|F_o|; R_{wF} = [\sum w^{1/2}(|F_o| - |F_c|)] / \sum w^{1/2}|F_o|.$$

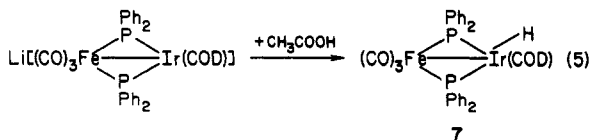
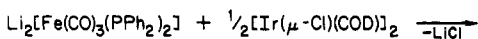
which the COD ligand has been replaced by two carbonyl ligands (eq 4). Complex 6 was isolated in modest yield



(4)

and was spectroscopically characterized. Its mass spectrum showed the expected parent ion, and resonances characteristic of the $\mu\text{-PPH}_2$ and hydride ligands are apparent in its NMR spectrum (Table I). The downfield chemical shift of the equivalent $\mu\text{-PPH}_2$ ligands implies a metal-metal bond in 6.⁴

Preparation of $(\text{CO})_3\text{Fe}(\mu\text{-PPH}_2)_2\text{Ir}(\text{H})(\text{COD})$ (7) and Its Conversion to $(\text{CO})_3\text{Fe}(\mu\text{-PPH}_2)_2\text{Ir}(\text{Cl})(\text{COD})$ (8). Phosphidometalates derived from $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$ have been shown to also work well in these "bridge-assisted" synthetic reactions,^{5,6} as is true in the present study since reaction of $\text{Li}_2[\text{Fe}(\text{CO})_3(\text{PPh}_2)_2]$ with $[\text{Ir}(\mu\text{-Cl})(\text{COD})]_2$ followed by protonation gives the Fe-Ir complex 7 (eq 5). NMR data indicate that complex 7 is

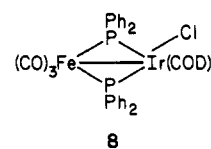


formed in greater than 90% yield, but we have been repeatedly frustrated in attempts to isolate it in pure form.

(5) (a) Targos, T. S.; Rosen, P. P.; Whittle, R. R.; Geoffroy, G. L. *Inorg. Chem.* 1985, 24, 1375. (b) Rosenberg, S.; Lockledge, S. P.; Geoffroy, G. L., submitted for publication.

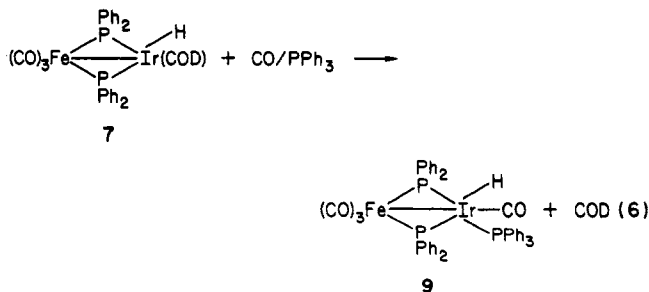
(6) Shulman, P., unpublished results.

It is persistently contaminated with the chloride complex 8, but the mechanism of the formation of this complex is



unknown. Complex 8 has been crystallographically characterized (Figure 2), and spectroscopic data for both 7 and 8 are consistent with the indicated formulations. Both complexes show downfield $\mu\text{-PPH}_2$ ³¹P NMR resonances indicative of the presence of metal-metal bonds, and the presence of the hydride ligand in 7 is indicated by its hydride ¹H NMR resonance at $\delta -11.8$ (t).

Conversion of 7 into $(\text{CO})_3\text{Fe}(\mu\text{-PPH}_2)_2\text{Ir}(\text{H})(\text{CO})(\text{PPh}_3)$ (9). In contrast to the harsh conditions required to replace the COD ligand in 2 by CO, complex 7 reacts with CO under 80 psi 1:1 CO/H₂ pressure at 22 °C in the presence of 1 equiv of PPh₃ to give the known complex 9⁶ (eq 6). Complex 9 was previously prepared by the direct



reaction of $[\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})(\text{PPh}_2)]^-$ with *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (eq 7).⁶

X-ray Diffraction Studies of $(\text{CO})_4\text{W}(\mu\text{-PPH}_2)_2\text{Ir}(\text{H})(\text{COD})$ (2) and $(\text{CO})_3\text{Fe}(\mu\text{-PPH}_2)_2\text{Ir}(\text{Cl})(\text{COD})$ (8). Pertinent crystallographic data for 2 and 8 are listed in

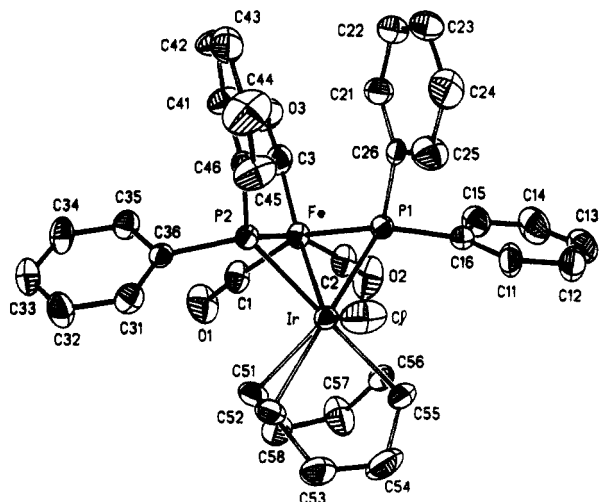


Figure 2. An Ortep drawing of $(\text{CO})_3\text{Fe}(\mu\text{-PPH}_2)_2\text{IrCl}(\text{COD})$ (8). Thermal ellipsoids are drawn at the 40% probability level.

Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{Å}^2 \times 10^3$) for $(\text{CO})_4\text{W}(\mu\text{-PPH}_2)_2\text{Ir}(\text{H})(\text{COD})$ (2)

atom	x	y	z	U_{iso}^a
Ir	2332 (1)	5000	5623 (1)	28 (1)
H(Ir)	812 (19)	5008 (92)	4876 (83)	1 (29)
W	1861 (1)	6771 (1)	4667 (1)	28 (1)
P(1)	1661 (5)	6117 (4)	6539 (4)	31 (2)
P(2)	2246 (5)	5389 (4)	3692 (5)	35 (2)
C(1)	3745 (24)	7054 (14)	5628 (21)	46 (6)
C(2)	-67 (25)	6487 (14)	3840 (20)	51 (10)
C(3)	1895 (25)	7408 (15)	3178 (20)	51 (10)
C(4)	1474 (17)	7909 (12)	5274 (16)	35 (7)
O(1)	4762 (14)	7257 (11)	6080 (11)	54 (6)
O(2)	-1148 (16)	6383 (13)	3368 (16)	77 (8)
O(3)	1979 (17)	7752 (14)	2334 (15)	81 (9)
O(4)	1206 (18)	8574 (10)	5602 (15)	77 (9)
C(11)	4531 (16)	4849 (12)	6204 (15)	28 (4)
C(12)	4268 (18)	5074 (13)	7186 (19)	49 (9)
C(13)	4371 (26)	4445 (19)	8221 (21)	76 (12)
C(14)	3195 (30)	3846 (16)	7946 (26)	81 (16)
C(15)	2310 (25)	3839 (16)	6681 (21)	62 (11)
C(16)	2563 (21)	3577 (16)	5684 (18)	55 (9)
C(17)	3823 (23)	3221 (16)	5733 (29)	73 (12)
C(18)	4828 (25)	3957 (16)	5905 (21)	62 (11)
C(21)	72 (17)	6090 (13)	6620 (14)	30 (7)
C(22)	-370 (22)	6825 (15)	7026 (21)	61 (11)
C(23)	-1586 (20)	6842 (19)	7087 (23)	69 (11)
C(24)	-2386 (27)	6108 (20)	6728 (28)	82 (15)
C(25)	-1895 (20)	5391 (21)	6387 (23)	75 (12)
C(26)	-726 (21)	5376 (17)	6258 (19)	59 (10)
C(31)	2557 (20)	6560 (12)	8042 (16)	36 (8)
C(32)	3295 (20)	7325 (13)	8288 (18)	42 (9)
C(33)	3907 (24)	7620 (15)	9431 (20)	58 (11)
C(34)	3958 (23)	7137 (17)	10437 (18)	59 (10)
C(35)	3291 (23)	6387 (19)	10268 (20)	63 (12)
C(36)	2633 (22)	6075 (18)	9100 (18)	58 (10)
C(41)	911 (21)	4978 (17)	2300 (15)	51 (9)
C(42)	826 (19)	5309 (13)	1194 (17)	41 (5)
C(43)	-156 (29)	5030 (28)	113 (27)	97 (15)
C(44)	-995 (32)	4370 (21)	169 (29)	88 (16)
C(45)	-883 (30)	4073 (21)	1300 (27)	90 (15)
C(46)	78 (22)	4373 (17)	2325 (19)	61 (10)
C(51)	3613 (21)	5243 (13)	3236 (17)	45 (9)
C(52)	4594 (20)	5883 (16)	3514 (21)	50 (10)
C(53)	5725 (22)	5717 (16)	3304 (26)	63 (12)
C(54)	5858 (24)	4966 (22)	2769 (26)	80 (14)
C(55)	4916 (30)	4363 (18)	2431 (27)	80 (15)
C(56)	3755 (29)	4507 (15)	2654 (25)	77 (15)
O ^b	3184 (21)	2586 (23)	1044 (22)	149 (16)
C(91) ^b	3007 (38)	1394 (28)	-192 (41)	151 (27)
C(92) ^b	2554 (33)	2212 (27)	220 (29)	89 (16)
C(93) ^b	1290 (32)	2476 (26)	-529 (31)	119 (20)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^b Acetone solvate.

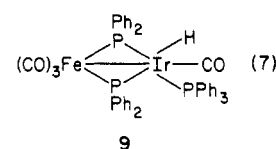
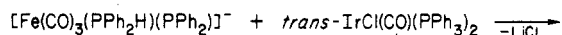
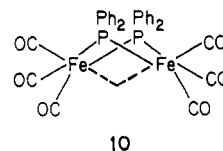


Table II, and Tables III–VI give the atomic positional parameters and selected bond distances and angles. Ortep drawings of 2 and 8 are respectively shown in Figures 1 and 2. In each case the two metal atoms are bridged by two $\mu\text{-PPH}_2$ ligands, and the metal–metal distances of 2.893 (1) (2) and 2.703 (1) Å (8) are consistent with single bonds between these atoms. For 2 this distance compares well with other W–Ir distances: $\text{Cp}_2\text{W}_2\text{Ir}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)_2$, W–Ir = 2.723 (2), 2.852 (2) Å;^{7a} $\text{CpWIr}_3(\text{CO})_{11}$, W–Ir = 2.815 (1), 2.792 (1), 2.864 (1) Å;^{7b} $\text{WIrH}(\mu\text{-PPH}_2)_2(\text{CO})_5(\text{PPh}_3)$, W–Ir = 2.8764 (6) Å;² $\text{WIrH}(\mu\text{-PPH}_2)_2(\text{C}(\text{OCH}_3)\text{Ph})(\text{CO})_4(\text{PPh}_3)$, W–Ir = 2.858 (1) Å.¹ The Fe–Ir distance of 2.703 (1) Å in complex 8 compares well with corresponding distances in $(\text{C}_5\text{Me}_5)\text{IrFe}_2(\text{CO})_9$ (Fe–Ir = 2.6987 (7), 2.616 Å)⁸ but is significantly shorter than the 2.960 (1) Å Fe–Ir distance in $\text{FeIr}(\mu\text{-PPH}_2)(\text{CO})_5(\text{PPh}_3)_2$ in which the metal–metal bond is clearly of the donor–acceptor type.⁹

Although the formulations of 2 and 8 are seemingly quite similar, their overall geometries as determined by the X-ray diffraction studies are markedly different. The W–Ir($\mu\text{-P}$)₂ core of 2 is essentially planar with a [P2–Ir–P1]–[P2–W–P1] dihedral angle of 14.8°. In contrast, the Fe–Ir($\mu\text{-P}$)₂ core of 8 is bent with a [P1–Ir–P2]–[P1–Fe–P2] dihedral angle of 78.8°. Furthermore, the coordination geometries at the Ir centers in the two complexes are different even though the coordination numbers are the same. In the W–Ir complex 2 the Ir center has a trigonal-bipyramidal geometry whereas it is square-pyramidal in the Fe–Ir complex 8. Also, the tungsten center in 2 is octahedrally coordinated whereas the Fe center in 8 has a square-pyramidal coordination geometry.

As a consequence of the different geometries, the metal–metal bonding in the two complexes must be quite different. The Fe–Ir complex 8 with square-pyramidal coordination at both metals has a structure very similar to that of $\text{Fe}_2(\mu\text{-PPH}_2)_2(\text{CO})_6$ (10).¹⁰ In the latter com-



pound a bent metal–metal bond was invoked to fill the sixth octahedral coordination site on each metal. Stated another way, the bent structure is adopted in order to allow for the metal–metal interaction to occur.¹⁰

In contrast, the metal–metal bonding in the W–Ir complex 2 must be quite different. The tungsten center of 2 is already octahedrally coordinated without the metal–metal bond. Thus there is no driving force to generate a bent structure. Instead, the planar structure is adopted,

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(9) Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Morrison, E. D.; Duttera, M. R.; DeBrosse, C. W.; Whittle, R. R.; Geoffrey, G. L. *Organometallics* 1983, 2, 846.

(10) Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* 1982, 104, 6550.

Table IV. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{\AA}^2 \times 10^3$) for $(\text{CO})_3\text{Fe}(\mu\text{-PPH}_2)_2\text{IrCl}(\text{COD})$ (8)

atom	x	y	z	U_{iso}^a
Ir	2931.5 (2)	681.7 (1)	2.287.4 (2)	32 (1)
Fe	2368 (1)	1724 (1)	1894 (1)	35 (1)
P(1)	3179 (2)	1212 (1)	781 (2)	32 (1)
P(2)	4000 (2)	1393 (1)	3367 (2)	32 (1)
O1	4633 (2)	80 (1)	2378 (3)	71 (1)
O(1)	1008 (5)	1875 (3)	3587 (6)	79 (3)
O(2)	-49 (5)	1739 (3)	31 (6)	83 (3)
O(3)	3180 (7)	2819 (3)	1834 (7)	86 (3)
C(1)	1581 (7)	1819 (3)	2966 (7)	49 (3)
C(2)	918 (7)	1732 (2)	725 (7)	50 (3)
C(3)	2878 (7)	2392 (3)	1830 (7)	53 (3)
C(11)	2731 (4)	546 (2)	-1208 (4)	56 (3)
C(12)	2232 (4)	408 (2)	-2419 (4)	72 (4)
C(13)	1401 (4)	749 (2)	-3218 (4)	85 (5)
C(14)	1068 (4)	1228 (2)	-2808 (4)	79 (4)
C(15)	1567 (4)	1366 (2)	-1597 (4)	58 (3)
C(16)	2399 (4)	1025 (2)	-797 (4)	40 (3)
C(21)	5015 (4)	1899 (2)	587 (4)	48 (3)
C(22)	6128 (4)	2027 (2)	406 (4)	61 (3)
C(23)	6926 (4)	1625 (2)	303 (4)	68 (4)
C(24)	6610 (4)	1093 (2)	380 (4)	75 (4)
C(25)	5497 (4)	964 (2)	561 (4)	64 (4)
C(26)	4699 (4)	1367 (2)	664 (4)	33 (2)
C(31)	4451 (4)	1145 (1)	5791 (4)	45 (3)
C(32)	4581 (4)	1266 (1)	6984 (4)	57 (3)
C(33)	4338 (4)	1780 (1)	7295 (4)	56 (3)
C(34)	3964 (4)	2172 (1)	6412 (4)	54 (3)
C(35)	3833 (4)	2051 (1)	5219 (4)	44 (3)
C(36)	4077 (4)	1537 (1)	4908 (4)	34 (2)
C(41)	6013 (4)	2061 (2)	3518 (5)	55 (3)
C(42)	7260 (4)	2167 (2)	3719 (5)	76 (4)
C(43)	8107 (4)	1750 (2)	3924 (5)	72 (4)
C(44)	7707 (4)	1227 (2)	3928 (5)	90 (5)
C(45)	6459 (4)	1120 (2)	3727 (5)	65 (4)
C(46)	5612 (4)	1537 (2)	3522 (5)	35 (2)
C(51)	1917 (7)	568 (3)	3636 (7)	48 (3)
C(52)	2708 (7)	145 (3)	3733 (6)	51 (3)
C(53)	2306 (9)	-410 (3)	3240 (8)	68 (4)
C(54)	1765 (12)	-465 (4)	1955 (9)	99 (5)
C(55)	1811 (7)	21 (3)	1194 (7)	51 (3)
C(56)	1045 (6)	446 (3)	1080 (7)	50 (3)
C(57)	70 (8)	513 (5)	1709 (8)	86 (5)
C(58)	527 (7)	521 (4)	3036 (8)	66 (4)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

as found for many bis(phosphido)-bridged compounds containing $\text{M}(\text{CO})_4$ fragments with $\text{M} = \text{Cr}, \text{Mo}, \text{or } \text{W}$.^{6a,11} Yet the metal-metal distance and the requirements of the 18e rule indicate the presence of a W-Ir bond in 2. Although assignment of oxidation states in polynuclear complexes such as these is risky, the most likely formulation of 2 is with W(0) and Ir(3+) centers.¹ The metal-metal bond would then be a donor-acceptor bond with W donating electron density to Ir via one of its filled $d\pi$ orbitals that points along the W-Ir axis.

The important conclusion that can be drawn from the structural comparison of 2 and 8 is that the coordination and metal-metal bonding preference for one metal (Fe, W) markedly influences the coordination geometry adopted by an adjacent metal (Ir) in a binuclear complex. As the structures of 2 (W-Ir) and 8 (Fe-Ir) illustrate, whether the Ir center has a square-pyramidal (8) or a trigonal-bipyramidal (2) coordination is dictated by the metal-metal

Table V. Selected Bond Distances and Angles for $(\text{CO})_4\text{W}(\mu\text{-PPH}_2)_2\text{Ir}(\text{H})(\text{COD})$ (2)

Bond Distances (\AA)			
W-Ir	2.893 (1)	Ir-C(11)	2.32 (2)
W-P(1)	2.501 (6)	Ir-C(12)	2.27 (2)
W-P(2)	5.209 (6)	Ir-C(15)	2.17 (2)
W-C(1)	2.05 (2)	Ir-C(16)	2.18 (2)
W-C(2)	2.07 (2)	C(11)-C(12)	1.34 (3)
W-C(3)	2.01 (2)	C(12)-C(13)	1.52 (3)
W-C(4)	1.98 (2)	C(13)-C(14)	1.54 (4)
C-O(av)	1.14 (2)	C(14)-C(15)	1.45 (3)
Ir-P(1)	2.286 (6)	C(15)-C(16)	1.36 (4)
Ir-P(2)	2.313 (6)	C(16)-C(17)	1.50 (4)
		C(17)-C(18)	1.55 (2)
		C(11)-C(18)	1.47 (3)
Bond Angles (deg)			
W-P(1)-Ir	74.2 (2)	C(2)-W-C(4)	91 (1)
W-P(2)-Ir	73.6 (2)	C(3)-W-C(4)	88 (1)
P(1)-W-P(2)	99.0 (2)	C(21)-P(1)-C(31)	99 (1)
P(1)-Ir-P(2)	111.8 (2)	C(41)-P(2)-C(51)	101 (1)
Ir-W-P(1)	49.5 (1)	C(11)-C(12)-C(13)	124 (2)
Ir-W-P(2)	50.1 (1)	C(12)-C(13)-C(14)	114 (2)
W-Ir-P(1)	56.3 (1)	C(13)-C(14)-C(15)	115 (3)
W-Ir-P(2)	56.3 (1)	C(14)-C(15)-C(16)	127 (3)
W-Ir-h(2)	77 (5)	C(15)-Cn16-C(17)	125 (2)
C(1)-W-C(2)	175 (1)	C(16)-C(17)-C(18)	112 (2)
C(1)-W-C(3)	92 (1)	C(17)-C(18)-C(11)	119 (2)
C(1)-W-C(4)	87 (1)	C(18)-C(11)-C(12)	126 (2)
C(2)-W-C(3)	93 (1)	W-C-O(av)	176 (1)

Table VI. Selected Bond Distances and Angles for $(\text{CO})_3\text{Fe}(\mu\text{-PPH}_2)_2\text{IrCl}(\text{COD})$ (8)

(a) Bond Distances (\AA)			
Ir-Fe	2.703 (1)	Fe-P(1)	2.240 (2)
Ir-P(1)	2.305 (2)	Fe-P(2)	2.255 (2)
Ir-P(2)	2.303 (2)	Fe-C(1)	1.785 (9)
Ir-Cl	2.440 (2)	Fe-C(2)	1.779 (6)
Ir-C(51)	2.264 (9)	Fe-C(3)	1.788 (9)
Ir-C(52)	2.248 (8)	C(1)-O(1)	1.14 (1)
Ir-C(55)	2.235 (7)	C(2)-O(2)	1.14 (1)
Ir-C(56)	2.245 (6)	C(3)-O(3)	1.13 (1)
(b) Bond Angles (deg)			
Ir-P(1)-Fe	73.0 (1)	P(1)-Ir-Cl	95.6 (1)
Ir-P(2)-Fe	72.7 (0)	P(2)-Ir-Cl	100.6 (1)
Ir-Fe-P(1)	54.6 (0)	C(1)-Fe-C(2)	89.2 (4)
Ir-Fe-P(2)	54.5 (0)	C(1)-Fe-C(3)	98.6 (4)
Fe-Ir-P(1)	52.4 (1)	C(2)-Fe-C(3)	101.1 (3)
Fe-Ir-P(2)	52.8 (0)	Fe-C(1)-O(1)	175.4 (6)
P(1)-Fe-P(2)	80.8 (1)	Fe-C(2)-O(2)	175.6 (8)
P(1)-Ir-P(2)	78.4 (1)	Fe-C(3)-O(3)	176.7 (9)
Fe-Ir-Cl	138.7 (1)		

bonding and coordination needs of the adjacent metal.

Discussion

One of the objectives of this study was to determine if the reactivity at the Ir end of molecules of the type $(\text{CO})_x\text{M}(\mu\text{-PPH}_2)_2\text{Ir}(\text{R})(\text{CO})(\text{PPh}_3)$ could be enhanced by replacing the CO and PPh_3 ligands by 1,5-cyclooctadiene. The latter ligand was anticipated to be readily removed by hydrogenation to generate an unsaturated Ir center. We have found that the desired bimetallic M-Ir(COD) complexes 2-5 with $\text{M} = \text{W}, \text{Mo}, \text{and } \text{Cr}$ are easily synthesized, but the COD ligand is not easily removed in these compounds. No reaction occurred when the complexes were stirred under high pressures of H_2 at 22 °C in both the presence and the absence of CO. It was possible to displace the COD ligand in 2 with CO, but only by heating to 110 °C under a CO pressure of 1000 psi. In no instance have we observed hydrogenation of the COD ligand in this family of complexes, apparently because of the lack of reactivity of the Ir center with H_2 . This relative inertness

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may be attributed to a +3 oxidation state for the Ir center. As noted above, assignment of oxidation states to individual metals in bimetallic complexes is often ambiguous, but the most reasonable formulation of complexes 2–4 is with W(0) and Ir(3+) centers.¹ Oxidative addition of H₂ to an Ir(3+) center is not a likely process, and this must surely limit the chemistry available to these complexes.

In contrast to the results mentioned above, the COD ligand in the Fe–Ir complex 7 was easily displaced by CO and PPh₃ at 22 °C under 80 psi 1:1 H₂/CO to give complex 9. Recall that the WIr complex 2 required 100 °C and 1000 psi of CO for the analogous reaction to occur. Thus, changing the adjacent metal fragment from W(CO)₄ to Fe(CO)₃ causes a significant increase in reactivity of the Ir center. The mechanisms of these displacement reactions are unknown and may be different for the two complexes. One reasonable mechanism involves formation of an open coordination site for CO or PPh₃ addition by prior cleavage of the metal–metal bond. Loss of the COD ligand and reformation of the metal–metal bond could then occur to give the observed products. As noted above in the discussion of the crystal structures of 2 and 8, replacing a (CO)₄W fragment with (CO)₃Fe causes a significant change in the nature of the metal–metal bonding. We suggest that it is this difference that accounts for the different reactivity of 2–5 as compared to 7. If all of these complexes are formulated as having (CO)_xM⁰ fragments bound to an Ir(3+) center via a donor–acceptor bond, this bond must be much weaker in the Fe–Ir complexes 7 and 8 than it is in the Cr, Mo, and W complexes 2–5. Overall, the major conclusion to be drawn from this study is that the nature of an adjacent metal (Fe, W) has a marked influence on both the chemistry and the coordination geometry of the iridium center.

Experimental Section

W(CO)₄(PPh₂H)₂,^{1,12} Mo(CO)₄(PPh₂H)₂,¹³ Cr(CO)₄(PPh₂H)₂,^{13,14} and [Ir(μ-Cl)(COD)]₂¹⁵ were prepared by the literature methods. Glacial CH₃COOH, *n*-BuLi, and MeI (Aldrich) were purchased and used as received without further purification. Unless otherwise specified, all operations were performed under a prepurified N₂ atmosphere by using rigorously dried and deoxygenated solvents and standard Schlenk techniques. The spectroscopic instruments employed in this research have been previously described¹ except that in this study some IR spectra were recorded on an IBM IR-32 FT/IR spectrometer. Field desorption mass spectra were recorded by Robert Hale at the Tennessee Eastman Co., Kingsport, TN. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Synthesis of (CO)₄W(μ-PPh₂H)₂IrH(COD) (2). **Method A.** MeLi (0.520 mL of a 1.2 M solution in tetrahydrofuran (THF)) was added to a THF (10-mL) solution of W(CO)₄(PPh₂H)₂ (408 mg, 0.710 mmol) and stirred for 5 min to generate Li[W(CO)₄(PPh₂H)(PPh₂H)] in situ. This orange solution was added via cannula to an orange THF (20-mL) solution of [Ir(μ-Cl)(COD)]₂ (200 mg, 0.298 mmol). After being stirred for 5 min, the purple solution was reduced to a brown oil by rotary evaporation. This oil was supported onto 1.5 g of SiO₂ by rotary evaporation of a CH₂Cl₂ solution. This SiO₂ was loaded at the top of a 12 in. × 3/4 in. glass SiO₂ chromatography column. Elution with 20% CH₂Cl₂/hexane afforded a small yellow band containing mostly W(CO)₆(PPh₂H) followed by an orange band of 2. Removal of solvent from this band followed by recrystallization from acetone

and vacuum drying for 4 h afforded air-stable orange microcrystals of an acetone solvate of 2 in 66% yield (381 mg, 0.393 mmol). Anal. Calcd for C₃₆H₃₆IrO₅P₂W: C, 45.66; H, 3.80. Found: C, 45.45; H, 4.09. MS (FD): *m/e* 967 (M⁺). IR (CH₂Cl₂): ν_{CO} 2041 (s), 1958 (s), 1912 (s) cm⁻¹.

Method B. *n*-BuLi (0.380 mL of a 1.6 M hexane solution) was added to a 20-mL THF solution of W(CO)₄(PPh₂H)₂ (204 mg, 0.305 mmol) and the mixture stirred for 5 min to generate Li₂[W(CO)₄(PPh₂H)₂] in situ. This orange solution was transferred via cannula to an orange THF (20-mL) solution of [Ir(μ-Cl)(COD)]₂ (104 mg, 0.156 mmol). The resultant purple solution was stirred for 5 min, and then 100 μL of glacial acetic acid was added. After being stirred for 10 min, this brown solution was reduced to a brown oil by rotary evaporation, and chromatography on SiO₂ in the manner described above afforded complex 2 in 71% yield (209 mg, 0.220 mmol).

Synthesis of (CO)₄Mo(μ-PPh₂H)₂IrH(COD) (3). Following method A above, complex 3 was isolated as air-stable orange microcrystals in 40% yield (102 mg, 0.116 mmol) from Mo(CO)₄(PPh₂H)₂ (171 mg, 0.295 mmol), MeLi (250 μL of a 1.2 M THF solution), and [Ir(μ-Cl)(COD)]₂ (99 mg, 0.148 mmol). Anal. Calcd for C₃₆H₃₃IrMoO₄P₂·CH₂Cl₂: C, 45.91; H, 3.62. Found: C, 45.93; H, 3.73. MS (FD): *m/e* 882 (M⁺). IR (CH₂Cl₂): ν_{CO} 2043 (s), 1966 (vs), 1960 (s), 1919 (vs) cm⁻¹.

Synthesis of (CO)₄Cr(μ-PPh₂H)₂IrH(COD) (4). Following method A above complex 4 was isolated as air-stable orange microcrystals in 77% yield (183 mg, 0.219 mmol) from Cr(CO)₄(PPh₂H)₂ (154 mg, 0.287 mmol), MeLi (250 μL of a 1.2 M THF solution), and [Ir(μ-Cl)(COD)]₂ (95 mg, 0.142 mmol). Anal. Calcd for C₃₆H₃₃CrIrO₄P₂·CH₂Cl₂: C, 48.20; H, 4.35. Found: C, 48.62; H, 4.35. IR (hexane): ν_{CO} 2029 (m), 1954 (s), 1945 (m), 1916 (s) cm⁻¹. MS (FD): *m/e* 836 (M⁺).

Synthesis of (CO)₄W(μ-PPh₂H)₂Ir(CH₃)(COD) (5). Substituting MeI for CH₃COOH in the method B preparation of 2 gave complex 5 in 68% yield as orange microcrystals (110 mg, 0.112 mmol) from *n*-BuLi (200 mL of a 1.6 M hexane solution) and [Ir(μ-Cl)(COD)]₂ (102 mg, 0.115 mmol). Anal. Calcd for C₃₇H₃₃IrO₄P₂W·CH₂Cl₂: C, 42.74; H, 3.47. Found: C, 43.22; H, 3.04. IR (CH₂Cl₂): 2033 (s), 1944 (s), 1912 (s) cm⁻¹. MS (FD): *m/e* 981 (M⁺).

Attempted Hydrogenation of Complexes 2–5. Solutions of complexes 2–5 were placed in a 100-mL Parr reactor and charged to 1000 psi of H₂ or 1000 psi of 1:1 H₂/CO and stirred for 12 h, but the starting complexes were recovered unchanged upon opening the reactor.

Synthesis of (CO)₄W(μ-PPh₂H)₂Ir(H)(CO)₂ (6). A 100-mL Parr reactor was loaded with complex 2 (310 mg, 0.320 mmol), 70 mL of hexane, and a magnetic stir bar and then charged to 1000 psi with carbon monoxide. The reactor was placed in an oil bath and heated at 100 °C for 24 h. After being cooled and vented to the atmosphere, the orange solution was rotary evaporated to give an orange solid. Chromatography in the manner described in the method A preparation of 2 using a hexane eluent afforded three small faint yellow bands followed by a large orange band. Removal of solvent from the orange fraction afforded complex 6 as an air-stable orange solid in 26% yield (75 mg, 0.82 mmol). Anal. Calcd for C₃₀H₂₀O₆P₂WIr: C, 39.34; H, 2.21. Found: C, 39.29; H, 2.31. IR (hexane): ν_{CO} 2054 (vs), 2033 (s), 1997 (s), 1966 (s), 1941 (s) cm⁻¹. MS (FD): *m/e* 915 (M⁺).

Synthesis of (CO)₃Fe(μ-PPh₂H)₂Ir(H)(COD) (7) and (CO)₃Fe(μ-PPh₂H)₂Ir(Cl)(COD) (8). Following method B above complex 7 was isolated in >90% crude yield before chromatography as a brown solid from Fe(CO)₅(PPh₂H)₂ (502 mg, 0.988 mmol), *n*-BuLi (1.3 mL of a 1.6 M hexane solution), and [Ir(μ-Cl)(COD)] (329 mg, 0.49 mmol). It was spectroscopically characterized (ν_{CO} (hexane) 2008 (vs), 1958 (m), 1948 (vs) cm⁻¹), but all attempts to purify the sample by chromatography led to the isolation of a mixture of 7 and (CO)₃Fe(μ-PPh₂H)₂Ir(Cl)(COD) (8). 8: IR (hexane): ν_{CO} 2031 vs, 1975 m, 1966 s cm⁻¹. MS (FD): *m/e* 810 (M⁺ - Cl).

Reaction of 7 with CO + PPh₃. A Fischer-Porter glass pressure bottle was charged with complex 7 (101 mg, 0.124 mmol),

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(13) Treichel, P. M.; Wong, W. K. *Inorg. Chim. Acta* **1979**, *33*, 171.

(14) We find it easiest to prepare the Cr(CO)₄(norbornadiene) precursor to this compound via the route given for the W analogue: King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *11*, 1837.

(15) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

PPh₃ (36 mg, 0.137 mmol), and 20 mL of toluene and pressurized to 80 psi with CO. After the mixture was stirred for 23 h, the bottle was vented to the atmosphere and the solution was reduced to a yellow brown oil by rotary evaporation as a MeOH azeotrope. Chromatography in the manner described in method B above using a 50:50 CH₂Cl₂/hexane eluant afforded a yellow band followed by a second larger yellow band. Removal of solvent from the first band afforded complex **8** in 8% yield (8 mg, 0.099). Removal of solvent from the second fraction afforded the known complex **9**⁶ as an air-stable yellow compound in 24% yield (30 mg, 0.030 mmol). IR (CH₂Cl₂): ν_{CO} 2035 (s), 2026 (m), 2004 (m), 1973 (m), 1952 (s) cm⁻¹.

X-ray Diffraction Studies of 2 and 8. Orange cylindrically shaped crystals of **2** and **8**, respectively obtained by recrystallization from acetone and CH₂Cl₂, were mounted on fine glass fibers and coated with urethane varnish to provide a barrier to the atmosphere. Preliminary photographs of **2** showed that the crystal possessed 2/*m* Laue symmetry. From systematic absences in the diffraction data (0*k*0, *k* = 2*n* + 1), the space group was either *P*2₁ or *P*2₁/*m*. Preliminary photographs of **8** and systematic absences uniquely identified the space group as *P*2₁/*n*. Unit-cell dimensions of both were obtained from the angular settings of 25 high-angle reflections including Friedel sets to judge optical alignment. Diffraction data were processed by using a learned profile routine to improve the accuracy in the measurements of weak reflections. In addition to corrections for *Lp* effects, empirical (ψ-scan) absorption corrections were applied to both sets of diffraction data. Pertinent crystal and intensity data are listed in Table II. All programs and scattering factors were obtained from the SHELXTL (version 4.1) and P3 program packages (Nicolet Corp., Madison, WI). Further details of the diffraction procedures are given in ref 16.

On the basis of the *E* statistics ($|E^2 - 1| = 0.76$) of **2** and the results of merging 150 redundant reflections, *R*(*I*) = 0.08, an initial assumption that the correct space group was the noncentrosymmetric alternative, *P*2₁, was made and later proved correct by the successful solution (direct methods, Solv) and chemically reasonable refinement of the structure. Although the structure contains near-mirror-plane symmetry, defined by W, Ir, Cl, C1, and C2, its alignment is not consistent with *P*2₁/*m* symmetry. The structure was solved by heavy-atom methods which provided the metal atom locations. Subsequent difference Fourier syntheses provided the locations of the remaining non-hydrogen atoms.

Following anisotropic refinement of the non-hydrogen atoms, a difference map revealed both the location of the hydride ligand on Ir and the presence of a molecule of acetone solvate. The remaining hydrogen atoms were placed in idealized locations (*d*(C-H) = 0.96 Å, *U* = 1.2*U* of the attached C), but not refined. The final refinement cycles included H(Ir) with an isotropic temperature factor and a constrained H-Ir distance of 1.61 (1) Å. The enantiomorph reported gave a significantly lower *R*_w value than its coordinate inverted structure (0.0418 vs. 0.0432). Table III lists the atomic coordinates, and Table IV summarizes selected bond distances and angles. Additional crystallographic information is available in the supplementary material.

The structure of **8** was solved by direct methods (Solv) which revealed the Ir, Fe, Cl, and P atom locations. The remainder of the non-hydrogen atoms were located in subsequent difference Fourier syntheses. The model used in the final refinement by a blocked-cascade routine included all non-hydrogen atoms as anisotropic contributions and hydrogen atoms as idealized (*d*(C-H) = 0.96 Å) isotropic, but unrefined contributions. The carbon atoms of the phenyl rings were constrained as rigid hexagons, *d*(C-C) = 1.395 Å. Final atomic coordinates are given in Table V, and Table VI gives selected bond distances and angles. Additional crystallographic information is available in the supplementary material.

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Registry No. **2**, 101471-42-5; **3**, 101492-13-1; **4**, 101471-43-6; **5**, 101471-44-7; **6**, 101471-45-8; **7**, 101471-46-9; **8**, 101471-47-0; **9**, 101471-48-1; W(CO)₄(PPh₂H)₂, 70505-43-0; [Ir(μ-Cl)(COD)]₂, 12112-67-3; Mo(CO)₄(PPh₂H)₂, 18399-63-8; Cr(CO)₄(PPh₂H)₂, 38433-41-9; Fe(CO)₃(PPh₂H)₂, 18399-67-2; W, 7440-33-7; Mo, 7439-98-7; Cr, 7440-47-3; Fe, 7439-89-6; Ir, 7439-88-5.

Supplementary Material Available: Tables of structure factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for **2** and **8** (48 pages). Ordering information is given on any current masthead page.

(16) Rheingold, A. L.; Sullivan, P. J. *Organometallics* 1983, 2, 327.