An ORTEP representation of the seven-coordinate complex is provided in Figure 1. Oxidative addition of the aryl bromide bond affords a five-membered metallacycle with a W–C bond distance[8] of 2.219 (16) Å. The metallacycle is nearly planar with the largest deviation from the least-squares plane of the five atoms being 0.032 Å. The geometry around tungsten can be approximated as a capped octahedron with the carbon of the phenyl group as the capping atom.[9]

In an analogous fashion, the aryl carbon–chlorine bond in **1a** is readily cleaved to afford $W(CO)_3$(**1a**) in 72% yield from $W(CO)_3(PrCN)_3$.[4,5] NMR spectroscopic measurements suggest that $W(CO)_3$(**1a**) is isostructural with $W(CO)_3$(**1b**) with the carbon atom bound to tungsten detected at 168.8 ppm in the $^{13}C\{^1H\}$ NMR spectrum. Monitoring of the reaction mixture by infrared spectroscopy reveals that the oxidative addition is complete in less than 15 min with the metal carbonyl infrared bands observed at 2016 (m), 1941 (s), and 1911 (m) cm^{-1}. Initial interaction of the ligand **1a** with $W(CO)_3(RCN)_3$ results in formation of an intermediate species identified as $W(CO)_3(RCN)$(**1a**) by infrared spectroscopy (ν_{CO} = 1906 (s), 1790 (s) cm^{-1}) in which **1a** is bound only through the imine nitrogen atoms (see Scheme I). Oxidative addition with loss of the remaining nitrile ligand occurs as the rate-determining step. Qualitatively, the overall rate of reaction increases in the series in the anticipated order $X = Cl < Br < I$.[1] Kinetic studies designed to quantify this ordering and determine the possible role of an aryl halide coordination complex[10] as an intermediate are underway. This can be contrasted with the behavior of $W(CO)_3(PrCN)_3$ in neat chlorobenzene in which case no reaction is detected after 1 day at room temperature.

We have also investigated the chemistry of the closely related ligand **2**. Addition of 1 equiv of **2** to a CH_2Cl_2 solution of $W(CO)_3(PrCN)_3$ results in immediate formation of a deep blue solution from which $W(CO)_3(PrCN)$(**2**) can be isolated in 46% yield. Metal carbonyl bands are observed at 1918 (s) and 1814 (m) cm^{-1} in CH_2Cl_2 solution, and integration of the ^1H NMR in CD_3CN reveals the presence of 1 equiv of PrCN per $W(CO)_3(PrCN)$(**2**). The nitrile group is very labile and readily replaced by CO within minutes at room temperature to afford deep purple $W(CO)_4$(**2**) characterized by metal carbonyl bands at 2009 (m), 1905 (s), and 1852 (m) cm^{-1} and a symmetrical bonding of **2** as evidenced by ^1H NMR.[11] On storage at room temperature, CH_2Cl_2 solutions of $W(CO)_3(PrCN)$(**2**) scavenge adventitious CO to form $W(CO)_4$(**2**) in a reaction accelerated by exposure to the atmosphere. We have not observed any evidence of oxidative addition of ligand **2** in this system nor in the related molybdenum complexes.[12]

Infrared spectra of the intermediate species $W(CO)_3(PrCN)$(**1a**) and the complex $W(CO)_3(PrCN)$(**2**) suggest that **1** is a poorer π-acceptor[13] than **2**, affording a more basic metal center which would favor oxidative addition. However, we suggest that structural differences between the two ligands are largely responsible for their divergent reactivity. Note that the imine double bond (1.31 (2) Å) in the metallacycle **1** is essentially unchanged from that of the uncoordinated arm of the ligand (1.29 (2) Å). The metallacycle derived from **2** would be strained because of the longer C–N single bond (1.468 (6) Å).[12] In addition, the sp^2 carbon in **1** allows for conjugation of the C=N with the phenyl ring of the metallacycle in $W(CO)_3$(**1**). Aryl carbon–halogen bonds can be readily cleaved by an oxidative addition pathway when appended to tungsten(0) by a suitably designed ligand. However, subtle changes in the ligand framework evidently have a dramatic effect on the propensity for oxidative addition in these systems.

Acknowledgment. T.G.R. is the recipient of a Distinguished New Faculty Grant from the Camille & Henry Dreyfus Foundation Inc. We are grateful for support from the University of Utah Research Committee for a Faculty Starter (Summer) Grant and the donors of the Petroleum Research Fund, administered by the American Chemical Society. High-field NMR spectrometers employed in this work were obtained through departmental grants from the National Science Foundation.

Registry No. **1a**, 81512-53-0; $W(CO)_3$(**1a**, 109744-50-5; $W(CO)_3(PrCN)$(**1a**), 109744-51-6; **1b**, 108791-83-9; $W(CO)_3$(**1b**), 109764-45-6; **1c**, 109721-19-9; **2**, 109721-20-2; $W(CO)_3(PrCn)$(**2**), 109744-52-7; $W(CO)_4$(**2**), 109744-53-8; $W(CO)_3(EtCN)_3$, 83732-33-6; $W(CO)_3(PrCN)_3$, 83732-34-7; chlorobenzene, 108-90-7.

Supplementary Material Available: Figures containing an ORTEP representation of $W(CO)_3$(**1b**), proton NMR spectra of $W(CO)_3$(**1b**), and a carbon APT spectrum of $W(CO)_3$(**1b**) and experimental section containing the preparation and spectroscopic characterization of compounds along with crystallographic data including tables of NMR data, bond distances and angles, and final positional and thermal parameters (23 pages); a listing of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

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(7) Crystal data for $W(CO)_3$(**1b**): $WBr_2O_3N_2C_{16}H_{14}$, yellow, monoclinic, $P2_1/c$, a = 8.224 (2) Å, b = 7.732 (1) Å, c = 31.321 (11) Å, β = 96.03 (3)°, V = 1980.4 $Å^3$, Z = 4, Mo Kα, of 3723 reflections collected at ambient temperature (Syntex P1, $4° < 2\theta < 48°$) were unique of which 2510 had $F_o \geq 3\sigma(F_o)$ and were used in the solution (Patterson) and refinement. Final refinement included all non-hydrogen atoms as anisotropic and hydrogen atoms as idealized isotropic contributions. For 244 parameters, R = 0.064 and R_w = 0.086, GOF = 3.1, and highest peak in the final map of 4.6 e $Å^{-3}$ approximately 1.2 Å from W.

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Structure of (*t*-Bu$_2$PH)(CO)$_2$Fe(μ-CO)(μ-*t*-Bu$_2$P)Rh(COD)-(*Fe*–*Rh*): Corrigendum[1]

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Summary: The crystal structure of the title compound, $C_{27}H_{49}FeO_3P_2Rh$, was described (*Organometallics* **1987**, *6*, 506–512) as monoclinic, space group *Cc*, with Z = 8. It is properly described as orthorhombic, space group *Fdd*2, with a' = 60.334 Å, b' = 22.720 Å, c' = 8.735 Å, and Z = 16, whereupon the two molecules of the *Cc* asymmetric unit are seen to be equivalent by symmetry.

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(1) Contribution No. 7614 from the Arthur Noyes Laboratory of Chemical Physics. Work supported in part by NIH Grant GM-16966.

0276-7333/87/2306-1996$01.50/0

Table I. Atom Coordinates (Space Group *Fdd*2)

	x	*y*	*z*
Rh	0.0379	0.1374	0.8777
Fe	0.0661	0.0678	1.0192
P(1,3)	0.0744	0.1559	0.9058
P(2,4)	0.0589	–0.0277	1.0777
O(1,4)	0.0451	0.0168	0.7384
O(2,5)	0.1126	0.0563	1.0954
O(3,6)	0.0444	0.1205	1.2846
C(1)	0.0519	0.0460	0.8369
C(2)	0.0939	0.0605	1.0606
C(3)	0.0520	0.1000	1.1765
C(4)	0.0790	–0.0845	1.0047
C(5,7)	0.0992	–0.0940	1.1142
C(6)	0.0890	–0.0630	0.8480
C(7,5)	0.0666	–0.1440	0.9719
C(8)	0.0504	–0.0455	1.2788
C(9,10)	0.0672	–0.0185	1.3942
C(10,9)	0.0475	–0.1140	1.3165
C(11)	0.0268	–0.0185	1.3052
C(12)	0.0814	–0.2210	1.0368
C(13,15)	0.0585	0.2430	1.1115
C(14)	0.0971	0.2005	1.1696
C(15,13)	0.0920	0.2735	0.9555
C(16)	0.0944	0.1570	0.7361
C(17,19)	0.0900	0.0995	0.6386
C(18)	0.0908	0.2095	0.6252
C(19,17)	0.1190	0.1550	0.7895
C(20)	0.0262	0.2145	0.7572
C(21)	0.0272	0.1665	0.6540
C(22)	0.0068	0.1320	0.6038
C(23)	–0.0032	0.0895	0.7092
C(24)	0.0045	0.0900	0.8750
C(25)	0.0025	0.1370	0.9690
C(26)	–0.0082	0.1955	0.9318
C(27)	0.0042	0.2355	0.8358

The crystal structure of the title compound, $C_{27}H_{49}FeO_3P_2Rh$, was described[2] as monoclinic, space group *Cc*, with a = 8.735 (2) Å, b = 22.720 (3) Å, c = 30.485 (4) Å, β = 98.28 (2)°, and Z = 8. It is properly described as orthorhombic, space group *Fdd*2. The vectors (-1,0,-2), (0,1,0), and (1,0,0) describe a face-centered cell with a' = 60.334 Å, b' = 22.720 Å, c' = 8.735 Å, β' = 90.04° → 90° ($\alpha' = \gamma'$ = 90°), and Z = 16; the corresponding coordinate transformations are $x' = -{}^1/_2z + 0.0494$, $y' = y + {}^1/_8$, and $z' = x - {}^1/_2z$. After applying these transformations to the coordinates in Table II of ref 2 and appropriately averaging over the two independent molecules in *Cc*, we obtain the coordinates in Table I; the average coordinate shift involved in the averaging was less than 1.0σ. The process was somewhat complicated because the coordinates in Table II, ref 2, do not correspond to discrete molecules (several atoms must be moved to other asymmetric units).

The statement[2] that "the Rh atom ... has a roughly square-planar coordination" is incorrect in its context: the constellation of cited atoms Rh, P(1,3), C(1), and the midpoints M (C(20) and C(21)) and M′ (C(23) and C(24)) of the two double bonds of the COD ligand is perhaps more nearly tetrahedral than planar (the dihedral angle between the planes P–Rh–C and M–Rh–M′ is 61°). The six "bond" angles are 80, 107, 163, 123, 99, and 88° (in the order P–Rh–C(1), P–Rh–M, P–Rh–M′, etc.), while the perpendicular displacements from the least-squares plane range from 0.30 to 0.73 Å. However, atoms Rh, Fe (instead of C(1)), P(1,3), M, and M′ *are* (slightly twisted) coplanar, with respective deviations 0.03, –0.25, 0.27, –0.23, and 0.17 Å from their least-squares plane and rough twofold symmetry (angles 107 and 112° at P(1,3)–Rh–M and Fe–Rh–M′). Atom C(1), which in any case[2] is only weakly bonded to Rh, lies –1.68 Å off the plane.

The sets of out-of-plane deviations in footnote 17, ref 2, are entirely different not only from the set found here (but not quoted) for the corresponding averaged atoms but also from each other, and this last in spite of the approximate structural identity of the two molecules already noted on p 507, column 2, of ref 2, and the actual equivalence demonstrated here. The two planes of ref 2 apparently were derived directly from the published coordinates and hence involve atoms in various molecules—and not the same selection of atoms (equivalent by symmetries of *Cc*) for the two.

No other substantial changes in the description of the structure need to be made other than to note that there is only one molecule in the asymmetric unit, so that all the molecules are structurally equivalent.

Registry No. (t-Bu_2PH)$(CO)_2Fe$(μ-CO)(μ-t-Bu_2P)Rh(COD), 106681-53-2.

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On the Existence of Methylborylene. An ab Initio Investigation of the CBH_3 Potential Energy Surface

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Summary: Methylborylene, CH_3–B:, is a minimum on the potential energy surface. Although CH_2=BH is 24.3 kcal/mol more stable (MP4/SDTQ/6-311G**//6-31G*), the 1,2-H shift barrier is indicated to be 25.0 kcal/mol. As higher levels of theory are not expected to reduce this value appreciably, it should be possible to observe methylborylene under appropriate experimental conditions. This contrasts with the carbene analogue CH_3–CH:, which is predicted to rearrange to ethylene without any appreciable barrier. Similarly, the boron-substituted singlet carbene H_2B—CH:, although stabilized by π-delocalization (H_2B^-=CH^+), is not indicated to be a stable species when electron correlation corrections are taken into consideration. Rearrangement into CH_2=BH, the simplest compound with a C=B double bond, is predicted to occur without activation. The entire triplet CBH_3 potential energy surface is indicated to lie above the singlet surface. The singlet–triplet energy separation in BH (31.8 kcal/mol at the highest level of theory) is increased by 11.8 kcal/mol in CH_3B due to methyl substitution.

In the presence of C_8K (intercalated potassium–graphite), methylboron dibromide, CH_3BBr_2, reacts with acetylenes and with olefins to give a variety of organoboron compounds with intriguing structures.[1-3] Some of these

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