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Supplementary Material Available: Tables of fractional atomic coordinates and displacement parameters, anisotropic temperature parameters, and bond distances and angles for complexes 1-3 (13 pages); listings of structure factors for 1-3 (59 pages). Ordering information is given on any current masthead page.

Facile Chelate Assisted Carbon-Halogen Bond Cleavage at Tungsten(0)

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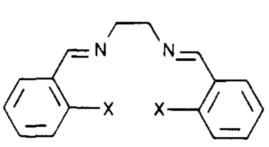
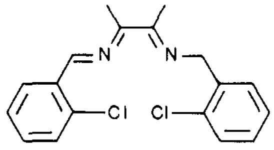
Summary: The aryl carbon-halogen bonds of potentially tetradentate ligands prepared by Schiff base condensation of ethylenediamine and 2-halobenzaldehyde (**1a-c**, X = Cl, Br, I) are readily cleaved by reaction with W(CO)$_3$(RCN)$_3$ to afford seven-coordinate tungsten(II) complexes W(CO)$_3$(**1a-c**). The related ligand 1,4-bis(2-chlorobenzyl)2,3-dimethyl-1,4-diaza-2,3-butadiene (**2**) coordinates to tungsten(0) but does not oxidatively add under similar conditions.

Activation of alkyl and aryl halide bonds can often be accomplished by oxidative addition to low-valent transition-metal centers. This reaction is particularly prevalent for square-planar d^8 complexes of the platinum group metals to afford octahedral d^6 products.[1] We have been exploring the coordination chemistry of a series of potentially tetradentate ligands (**1**, **2**), prepared by Schiff base condensation of appropriately substituted amines and carbonyl compounds, with a variety of transition metals.



1a: X = Cl
b: X = Br
c: X = I



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Herein we report that an aryl halide bond in **1a-c** is readily cleaved upon reaction with tungsten(0) to form seven-coordinate tungsten(II) complexes. Interestingly, the related ligand **2** does not oxidatively add to tungsten(0) under similar conditions. Although oxidative addition to d^6 metal centers has been less frequently studied than for d^8 systems, a number of examples have been reported in the literature.[2] In the case of tungsten, relatively potent electrophiles such as halogens or allyl halides are usually required for oxidative addition to occur under mild conditions.[2c-e]

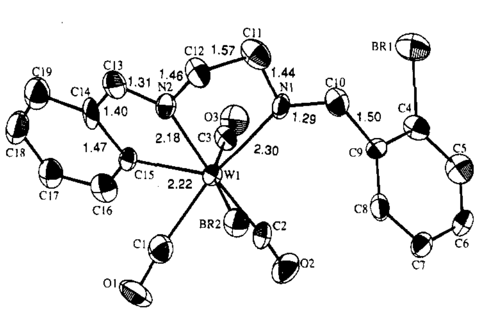
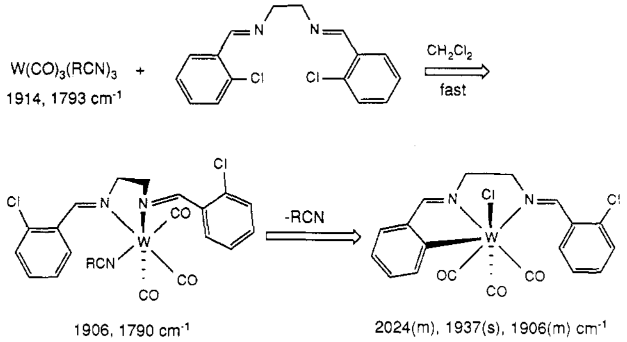


Figure 1. ORTEP representation of W(CO)$_3$(**1b**) including important bond distances (±0.02 Å) involving the metallacycle. Other distances (Å) follow: W1-Br2, 2.651 (2); W1-Cl, 2.02 (2); W1-C2, 2.03 (2); W1-C3, 1.96 (2). Selected bond angles (deg): C3-W1-Br2, 159.5 (5); N2-W1-C2, 174.9 (6); N1-W1-C1, 161.2 (7); N1-W1-N2, 72.2 (5)°; N1-W1-C15, 128.2 (6); N2-W1-C15, 72.8 (6); C3-W1-C15, 68.2 (7)°; C2-W1-C15, 111.1 (6); C1-W1-C15, 67.7 (7); Br2-W1-C15, 132.3 (4).

Scheme I



Addition of 1.0 equiv of **1b** to a CH$_2$Cl$_2$ solution of W(CO)$_3$(EtCN)$_3$[3] under an inert atmosphere at room temperature results in immediate formation of a red solution which subsequently turns yellow as crystals of the product appear. Yellow air-stable crystals were isolated from this solution in 78% yield by addition of Et$_2$O. Analytical[4] and spectroscopic data[5] are consistent with the formulation of the complex as W(CO)$_3$(**1b**) with metal carbonyl bands observed at 2014 (m), 1936 (s), and 1905 (m) cm^{-1} in CH$_2$Cl$_2$ solution. Proton and carbon NMR indicate that that ligand is bound to tungsten in an unsymmetrical fashion. Two distinct imine resonances are observed at 8.862 and 8.718 ppm in the ^{1}H NMR; both are broadened as a consequence of unresolved coupling with the inequivalent methylene protons of the ethylene backbone of the ligand. Tungsten-183 satellites of 8.0 Hz can be observed on the low-field signal when these methylene protons are selectively decoupled. The ^{13}C{^{1}H} spectrum exhibits 19 distinct signals including a quaternary resonance at 167.2 ppm assigned to a phenyl carbon bound to tungsten.[6] The structure of W(CO)$_3$(**1b**) was confirmed by a single-crystal X-ray diffraction study of crystals grown from CH$_2$Cl$_2$/hexane.[7]

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(3) Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692-694.

(4) W(CO)$_3$(**1b**). Anal. Calcd for C$_{19}$H$_{14}$N$_2$Br$_2$O$_3$W: C, 34.47; H, 2.13; N. 4.23. Found: C, 34.44; H, 2.02; N, 4.22. W(CO)$_3$(**1a**). Anal. Calcd for C$_{19}$H$_{14}$N$_2$Cl$_2$O$_3$W: C, 39.82; H, 2.46; N, 4.89. Found: C, 39.83; H, 2.47; N, 4.72. W(CO)$_3$(**1c**). Anal. Calcd for C$_{19}$H$_{14}$N$_2$I$_2$O$_3$W: C, 30.19; H, 1.87; N, 3.71. Found: C, 30.37; H, 1.75; N, 3.64.

(5) Complete spectroscopic data is included as supplementary material.

(6) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 7565-7568.

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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° < 2θ < 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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[11] W(CO)$_4$(**2**). Anal. Calcd for $C_{22}H_{18}N_2Cl_2O_4W$: C, 42.00; H, 2.88; N, 4.45. Found: C, 42.00; H, 2.79; N, 4.37.

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Structure of (t-Bu_2PH)(CO)$_2$Fe(μ-CO)(μ-t-Bu_2P)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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