Table I. Summary of Kinetic and Product Data for the Reactions of $(OC)_3Mn^-$ with CH_3OH, CH_3OD, CD_3OH, and CD_3OD

neutral substr	product ions	fractn of product ion signal[a]	k_{total},[b] cm^3 $molecule^{-1}$ s^{-1}	calcd rate consts of separate product forming channels[c]
CH_3OH	$(OC)_2Mn(H)(OCH_3)^-$	0.29	$(1.2 \pm 0.1) \times 10^{-10}$	3.5×10^{-11} (k_{OH})
	$(OC)_3Mn(H_2CO)^-$	0.71		8.5×10^{-11} (k_{CH_3})
CH_3OD	$(OC)_2Mn(D)(OCH_3)^-$	0.05	$(1.0 \pm 0.2) \times 10^{-10}$	5.0×10^{-12} (k_{OD})
	$(OC)_3Mn(H_2CO)^-$	0.95		9.5×10^{-11} (k_{CH_3})
CD_3OH	$(OC)_2Mn(H)(OCD_3)^-$	0.54	$(8.4 \pm 0.2) \times 10^{-11}$	4.5×10^{-11} (k_{OH})
	$(OC)_3Mn(D_2CO)^-$	0.46		3.9×10^{-11} (k_{CD_3})
CD_3OD	$(OC)_2Mn(D)(OCD_3)^-$	0.11	$(4.2 \pm 0.2) \times 10^{-11}$	4.6×10^{-12} (k_{OD})
	$(OC)_3Mn(D_2CO)^-$	0.89		3.7×10^{-11} (k_{CD_3})

[a] Errors in these relative integrated product ion signals are ±0.03 from two runs for each substrate molecule. [b] Errors are maximum deviations from the average of two runs for each substrate molecule. Generally, our reproducibility of rate constants is $\leq \pm 10\%$. [c] Obtained by multiplying the average value of k_{total} by the fraction of the product ion ignal for that reaction channel; in units of cm^3 $molecule^{-1}$ s^{-1}.

in methanol to $(OC)_3Mn^-$. The large value for this kinetic isotope effect suggests that the hydroxyl hydrogen is transferred as a proton in a symmetrical Mn···H···O transition state with probably weaker development of the Mn···O bond.[9]

The data clearly establish the two product forming channels in eq 1 as discrete processes involving competitive intermolecular oxidative addition of the H–O and the H–C bonds of CH_3OH to $(OC)_3Mn^-$ yielding the excited isomeric negative ions **1** and **2**, respectively. Multiple bonding

$$\underset{\mathbf{1}}{[(OC)_3Mn(H)(OCH_3)^-]^*} \qquad \underset{\mathbf{2}}{[(OC)_3Mn(H)(CH_2OH)^-]^*}$$

$(Mn{=}OCH_3)$[5] in **1** is expected to yield the excited 18-electron ion which then dissociates a CO ligand to yield the product ion at m/z 143 (eq 1a). Structure **2** is believed to undergo fast intramolecular β-hydrogen migration from oxygen to manganese producing $[(OC)_3Mn(H)_2(H_2CO)^-]^*$ which then reductively eliminates H_2 giving the major product ion at m/z 169 (eq 1b).

The increase in the rate constant for H–C bond oxidative addition of CH_3OH to $(OC)_3Mn^-$ compared to that with secondary CH bonds in alkanes (D^0(2° C–H) ≈ D^0-($HOCH_2$–H))[10] is largely due to the increased number of collisions of $(OC)_3Mn^-$ with CH_3OH since CH_3OH has a significant dipole moment.[11] The doubling of the rate constant k_{OH} for the methanol H–O bond oxidative addition to $(OC)_3Mn^-$ compared to the analogous reaction with H_2O[5] probably is the result of the lower H–O bond dissociation energy ($D^0(CH_3O\text{–}H) = 104 \pm 1$ kcal mol^{-1},[12] $D^0(HO\text{–}H) = 119.3 \pm 0.3$ kcal mol^{-1})[13] and the associated increased acidity ($\Delta H^0_{acid}(CH_3OH) = 379$ kcal mol^{-1}, $\Delta H^0_{acid}(H_2O) = 391$ kcal mol^{-1})[14] of CH_3OH. We believe that it is the similarity of the two separate rate constants for H–C and H–O activation that allows for observation of both reaction channels in the present study. This appears not to be the case with the iridium complex of Bergman et al.[1] and the Lane and Squires $HCr(CO)_3^-$ anion.[2,15]

Acknowledgment. We wish to thank the National Science Foundation for support of this research and Professor Allison and Dr. McElvany for a preprint of their paper.

Registry No. $(OC)_3Mn^-$, 101953-17-7; methanol, 67-56-1.

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[9] Bierbaum et al. (Bierbaum, V. M.; Filley, J.; DePuy, C. H.; Jarrold, M. F.; Bowers, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2818) report $k_H/k_D = 5.5$ for the elimination reaction of H_2N^- with $(C_2H_5)_2O$ ($\rightarrow NH_3 + C_2H_4 + C_2H_5O^-$).

[10] O'Neal, H. E.; Benson, S. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2. $D^0(HOCH_2\text{–}H) = 95.9$ kcal mol^{-1}.

[11] Ion–molecule collision rate constants are calculated by using the *average dipole orientation* theory (Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1); for reactions with $(OC)_3Mn^-$, $k_{ADO}(c\text{-}C_5H_{10}) = 1.0 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{ADO}(CH_3OH) = 1.7 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}.

[12] (a) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rogers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279. (b) Engelking, P. C.; Ellison, G. B.; Lineberger, W. C. *J. Chem. Phys.* **1978**, *69*, 1826 report $\Delta H_f^\circ(CH_3O) = 0.7 \pm 1.0$ kcal mol^{-1}.

[13] "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1971**, *NSRDS-NBS 37*.

[14] Bartmess, J. E.; McIver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2.

[15] Our results from the fast reaction of $(OC)_3Cr^{\bullet-}$ with CH_3OH showed the large oxophilicity of this chromium complex by producing 98% of the complex $(OC)_2Cr(H)(OCH_3)^{\bullet-}$.

Structural Characterization of a Linear [Au···Pt···Au] Complex, $Au_2Pt(CH_2P(S)Ph_2)_4$, and Its Oxidized Linear Metal–Metal Bonded [Au–Pt–Au] Product, $Au_2Pt(CH_2P(S)Ph_2)_4Cl_2$

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Summary: The reaction of the lithiated ylide anion $[Li][CH_2P(S)Ph_2]$ with $Au(C_4H_8S)Cl$ in a 2:1 ratio gives $[Li][Au(CH_2P(S)Ph_2)_2]$, characterized as the $[PPN][Au(CH_2P(S)Ph_2)_2]$ (**1**) salt. The reaction of **1** with *cis*-$Pt(Cl)_2(SEt_2)_2$ in a 2:1 ratio gives the neutral linear trinuclear complex $Au_2Pt(CH_2P(S)Ph_2)_4$ (**2**). The reaction of **1** with K_2PtCl_4 in a 1:1 ratio gives $Au_2Pt(CH_2P(S)Ph_2)_4Cl_2$ (**3**), a novel complex containing linear Cl–Au–Pt–Au–Cl bonding. This same molecular product is obtained (crystallographically identified) upon reaction of **2** with $PhICl_2$. Oxidation of **2** with CCl_4 or with Cl_2 in CCl_4 also gives **3** (identified spectroscopically by NMR) a ong with other yet to be identified species. We report here the X-ray crystal structures. **1**: $[PPN][Au(CH_2P(S)Ph_2)_2]$, $C2/c$ (No. 15), $a = 18.047$ (7) Å, $b = 13.262$ (4) Å, $c = 22.788$ (8) Å, $\beta = 90.91$ (3)°. **2**: $Au_2Pt(CH_2P(S)Ph_2)_4$, $I4$ (No. 82), $a = 17.348$ (17) Å. **3**: $Au_2Pt(CH_2P(S)Ph_2)_4Cl_2 \cdot C_2H_{10}O$, $P2_1/c$ (No. 14), $a = 18.989$ (3) Å, $b = 13.024$ (2) Å, $c = 24.191$ (4) Å, $\beta = 96.08$ (1)°.

The oxidative addition of halogen or other oxidants[1] to

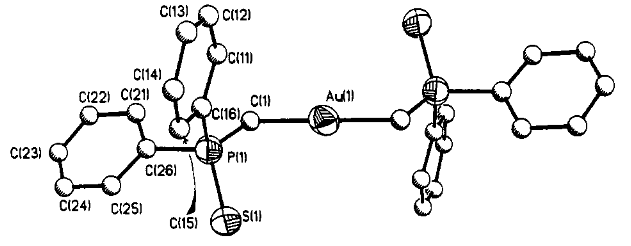


Figure 1. Molecular structure of $[PPN][Au(CH_2P(S)Ph_2)_2]$ (1). The [PPN] counterion and hydrogen atoms are not shown (50% probability displacement ellipsoids; spheres of arbitary size assigned to C atoms for clarity). See Table I for selected bond distances.

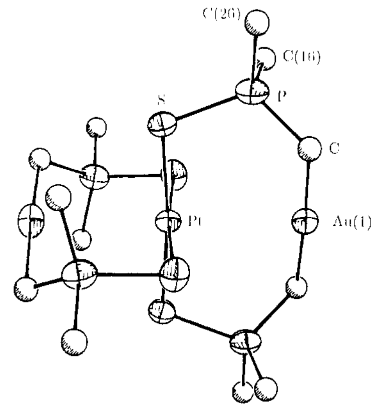
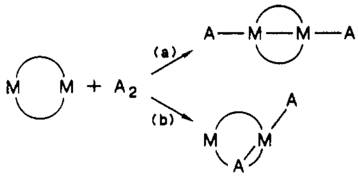


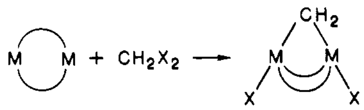
Figure 2. Molecular structure of $Au_2Pt(CH_2P(CH_2P(S)Ph_2)_4$ (2) (50% probability displacement ellipsoids for the metal centers). Phenyl rings are represented by the ipso carbon atom only, for clarity. See Table I for selected bond distances. The molecule has S_4 molecular point group symmetry.

dinuclear ylide complexs of gold(I) and some other dinuclear species[2] can result in the formation of a metal–metal bond and addition at both metal centers (eq 1a). If the



(1)

metal atoms are separated by appropriate bridging ligands, addition can occur at a single center (eq 1b) with no metal–metal bond formation.[3,4] The oxidative addition of methylene dihalides (eq 2) results in the formation of



(2)

a CH_2 bridge. However, this four-electron addition product follows the initial formation[1a] of a XCH_2–Au–Au–X intermediate analogous to the two-electron oxidative addition (eq 1a). With trinuclear species, oxidative addition conceivably could involve only a single center (eq 3b). If the oxidation causes the formation of two new metal–metal bonds, the product can be the symmetrical addition product (eq 3a). Examples of each structure type are known.[4,5] However, we report here the first example of a linear trinuclear complex which demonstrably forms two new metal–metal bonds (eq 3a) upon oxidation with halogens or halogenating reagents. This three-center, two-electron oxidation is of interest in relation to known oxidation of other multinuclear complexes[4,5] and extended linear chain arrays.

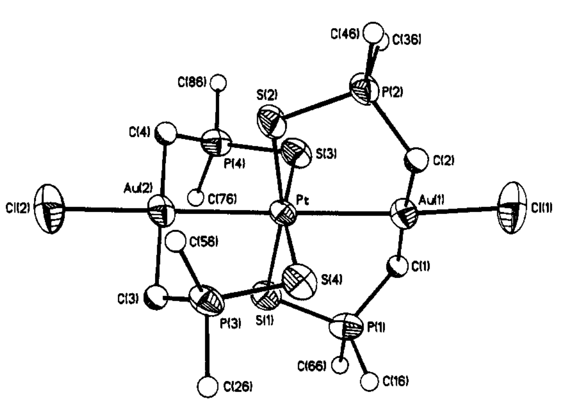
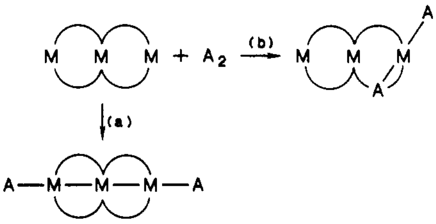


Figure 3. Molecular structure of $Au_2Pt(CH_2P(S)Ph_2)_4Cl_2$ (3) (50% probability displacement ellipsoids shown) for C arbitrary radii used for clarity. Phenyl rings are represented by their ipso carbon atoms; hydrogen atoms are not shown. See Table I for selected bond distances.



(3)

Our studies of dinuclear ylide complexes have included studies of a few complexes[3] of the ylide anion $[CH_2P(S)Ph_2]^{1-}$, methylene thiophosphinate, MTP. Synthesis[6] of

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(6) Synthesis of 1. To 2.0 mmol of $[Li][CH_2(S)PPh_2]$ in dry THF in an inert atmosphere at −10 °C was added 0.32 g (1.0 mmol) of $Au(C_4H_8S)Cl$. After 45 min of stirring, the cooling bath was removed and the reaction slowly equilibrated to room temperature. After 1 h the solvent was reduced in vacuo to approximately one-fourth of its original volume. To this was added an equimolar amount of [PPN][Cl] in a dry THF/methanol solution. After 10 min of stirring a white precipitate, 1, was formed. Cooling of the reaction mixture followed by removal of the THF/LiCl solution gave 0.89 g of 1 (75% yield): ^1H NMR ($CDCl_3$, 22 °C, 200 MHz) $\delta(CH_2)$ 1.516 (J_{HP} = 15.1 Hz). Synthesis of 2. To 40.0 mg (0.034 mmol) of $[PPN][Au(MTP)_2]$ in 5 mL of dry THF in an inert atmosphere at 25 °C was added 7.0 mg (0.017 mmol) of *cis*-$PtCl_2(SEt_2)_2$. After 18 h of stirring the solvent was removed in vacuo, taken up in CH_2Cl_2, and set up for crystallization via ether diffusion. Complex 2 is obtained as dark orange-red crystals: mp 214–215 °C; color change to orange at 180–185 °C. Synthesis of 3. To 20.0 mg (0.017 mmol) of $[PPN][Au(MTP)_2]$, at room temperature under an atmosphere of argon, was added 7 mL of dry CH_2Cl_2, 7.0 mg (0.017 mmol) of K_2PtCl_4, and 0.5 mL of DMSO. After 18 h of reaction the solvent was removed in vacuo at 60 °C. Red crystals of complex 3 were obtained by vapor diffusion of ether into a CH_2Cl_2 solution of the reaction residue.

Table I. Selected Distances in Compounds Studied (Å)

	1	2	3
Au–Pt		3.034 (1)	2.668 (1) and 2.662 (1)
Pt–S		2.346 (5)	2.356 (6)–2.372 (6)
Au–C	2.08 (1)	2.11 (2)	2.09 (2)–2.130 (2)
Au···S	3.849 (2)	3.727 (6) and 3.940 (6)	3.271 (1)–3.801 (1)
Au–Cl			2.452 (8) and 2.443 (7)

the Au^I anion $[Au(CH_2P(S)Ph_2)_2]^{1-}$ and its characterization as the bis(triphenylphosphine)nitrogen(1+) (PPN) salt $[PPN][Au(CH_2P(S)PPh_2)_2]$ (**1**) have enabled us to prepare bimetallic $[Au(MTP)]_2$ (C_i symmetry) and heterobimetallic $AuAg(MTP)_2$ complexes in a rational manner. Under suitable conditions, the trinuclear complex $Au_2Pt(MTP)_4$ (**2**), which in the solid state contains a linear chain arrangement of metal atoms, is formed. Complex **2** can be oxidized[7] to give $Au_2Pt(MTP)_4X_2$ (X = Cl, Br, I) complexes containing new Au–Pt bonds.

Compound **1** can be synthesized[6] in good yield as an air-stable white solid[8] (Figure 1). Its utility as a precursor for mixed-metal multinuclear synthesis arises from several factors, not the least being its anionic nature and the presence of two donor sulfur atoms which can be oriented properly for chelation.

The reaction of **1** with *cis*-$PtCl_2(SEt_2)_2$ gives $Au_2Pt(MTP)_4$ (**2**) as air-stable red-orange crystals[8] (Figure 2). The [Au···Pt···Au] axis of **2** is rigorously linear along the *c* axis with a Au···Pt separation of 3.034 (1) Å. Complex **2** contains two two-coordinate linear C-bound Au(I) centers and one four-coordinate S-bound Pt(II) center. In the solid state, the intermolecular Au···Au distance is 3.246 Å, only slightly longer than the intramolecular Au···Pt distance.

Various reagents can be used to halogenate **2**. When $PhICl_2$ is used as the oxidant[9] in CH_2Cl_2, $Au_2Pt(MTP)_4Cl_2$ is obtained.[7] Other complexes of the type $Au_2Pt(MTP)_4X_2$ (X = Br, I) also have been characterized crystallographically and will be reported elsewhere. The structure (Figure 3) is reported here, crystallized as the diethyl ether (not shown) adduct, formally the oxidative-addition product of Cl_2 with **2**. This product was initially prepared[6] in low yield by reaction of **1** with K_2PtCl_4.

The overall geometry about the three metal centers (nearly linear) in **3** is similar to that of **2**. The Au–Pt bonds, 2.668 (2) and 2.662 (2) Å, are shorter than the Au–Pt bonds reported for the Pt_3Au[10] and Pt_2Au[11] clusters, 2.711–3.026 Å. A Au_2Pt cluster is known[12] which contains an isosceles triangle of metal atoms with a Au–Au bond length of 2.737 (3) Å and Au–Pt bond lengths of 2.601 (4) and 2.600 (3) Å. In the Au–Rh compounds recently reported,[13] the Au–Rh distance is 2.850 Å. $[Pd_3(NCCH_3)_6(PPh_3)_2]^{2+}$, with unsupported[5a] linear [Pd–Pd–Pd] bonds of 2.5921 (5) Å, is the closest structural and electronic relative to **3** which has been characterized previously.[14] The $(Pd_3)^{2+}$ unit contains two more valence electrons and two fewer bonds to the central atom than found in the $(Au_2Pt)^{6+}$ unit of **3**.

There is an overall decrease of about 0.738 Å in the intramolecular Au···Au backbone in going from **2** to **3**. This compression distorts the MTP bridges. As a result, S–Pt–S angles (trans sulfur) are 164.7 (2)° and 164.6 (2)°, approximately 15° out of planarity.

The halogenation described here can be viewed formally (eq 4) as a two-electron oxidation of the $[Au_2Pt]^{4+}$ unit with concomitant (eq 4) formation of two Au–Pt bonds. The

$$[Au^I\cdots Pt^{II}\cdots Au^I]^{4+} \rightarrow [Au^{II}\text{–}Pt^{II}\text{–}Au^{II}]^{6+} + 2e^- \qquad (4)$$

coordination of the ligands about the metal atoms in **2** is unexceptional for Au^I and Pt^{II}. In **3**, the Au^{II} coordination is similar to known metal–metal bonded Au^{II} species.[13] However, the bonding of the six-coordinate Pt^{II} requires further discussion since Pt^{II} species are generally four-coordinate.

A simple model for the metal–metal bonding in **3** can be found in $[H\text{–}H\text{–}H]^-$ with its three-center, four-electron bond. Two electrons in **3** come from the filled $Pt^{II}(5d_{z^2})$ orbital and one each from the σ orbitals of the Au^{II} centers. This model produces a MO description in which two electrons occupy a strongly bonding orbital and two a nonbonding MO, suggesting somewhat diminished Au–Pt single bonds. However, the 5d/6s orbital energy separation in Pt is exceptionally small. Mixing of the Pt 6s and $5d_{z^2}$ orbitals is expected, with a net strengthening of the Pt–Au bonds. Therefore bonding in analogues of **3** should be very sensitive to changes in the central metal atom.

Attempts to synthesize analogues of **2** with different M–M′–M backbones are under investigation. Preliminary studies of the reactions of **2** with alkyl halides and with excess Cl_2 suggest that other products in addition to the dihalogenated trinuclear species are obtained. The complexes $X_2Au\cdots Pt\cdots AuX_2$, X = halide or pseudohalide, certainly seem possible since oxidation of the similar dinuclear Au^I centers to dinuclear Au^{III} has been demonstrated.[3]

Acknowledgment. We acknowledge gratefully the Welch Foundation, the National Science Foundation CHE 8408414 and the Texas A&M Center for Minerals Resources for financial support. Professor George Sheldrick is thanked for his help in solving the structure of **2**. Partial support for G.G. has been received from the Universidad del Valle, Colombia, on leave.

Registry No. **1**, 109638-64-4; **2**, 109638-65-5; **3**, 109638-66-6; $[Li][CH_2(S)PPh_2]$, 60703-90-4; $Au(C_4H_8S)Cl$, 39929-21-0; K_2PtCl_4, 10025-99-7; *cis*-$PtCl_2(SEt_2)_2$, 15442-57-6.

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(7) Oxidation of **2** with $PhICl_2$ in CH_2Cl_2 produces a product with a structure essentially identical with **3** except hexane from crystallization is found in the lattice. Complete refinement (R = 0.0537, R_w = 0.0569 ($P\bar{1}$, No. 2)) of the cell (a = 13.060 (3) Å, b = 14.992 (3) Å, c = 18.618 (5) Å, α = 96.76 (2)°, β = 99.47 (2)°, γ = 105.35 (2)°) shows no significant changes in metal–metal or metal–ligand distances from those of **3**. Chlorination of **2** therefore has been achieved in a very straightforward manner.

(8) Crystallographic data: $C_{62}H_{54}AuP_4S_2N$ (**1**), monoclinic space group $C2/c$ (No. 15), a = 18.049 (7) Å, b = 13.262 (4) Å, c = 22.788 (8) Å, β = 90.91 (3)°, Z = 4, 1986 independent reflections with $I > 3.0\sigma(I)$, R = 0.0517, R_w = 0.0508; $C_{52}H_{48}Au_2PtP_4S_4$ (**2**), tetragonal space group $I\bar{4}$ (No. 82), a = 17.348 (17) Å, c = 9.314 (11) Å, Z = 2, 382 independent reflection with $I > 3.0\sigma(I)$, R = 0.0444, R_w = 0.0496; $C_{52}H_{48}Au_2PtP_4S_4Cl_2\cdot C_2H_{10}O$ (**3**), monoclinic space group $P2_1/c$ (No. 14), a = 18.989 (3) Å, b = 13.024 (2) Å, c = 24.191 (4) Å, β = 96.08 (1)°, Z = 4, 3012 independent reflections $I > 3.0\sigma(I)$, R = 0.0463, R_w = 0.0463. All calculations were performed by using Nicolet SHELXTL crystallographic programs. All data were collected on Nicolet R3m/E four-circle diffractometer at ambient temperature with graphite-monochromated Mo Kα radiation. All data were corrected for Lorentz, decay, polarization, and absorption effects.

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(14) The $[Au\text{–}Pt\text{–}Au]^{6+}$ unit of **3** might also be described to contain $Au^I\text{–}Pt^{IV}\text{–}Au^I$. However, this formulation is less consistent with observed planar four-coordinate geometry observed about each gold center, a geometry typical of $Au^{II}\text{–}Au^{II}$ bonded species.

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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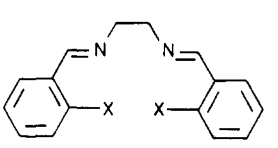
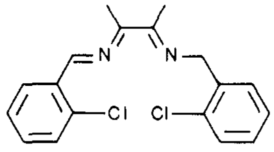
Summary: The aryl carbon–halogen bonds of potentially tetradentate ligands prepared by Schiff base condensation of ethylenediamine and 2-halobenzaldehyde (**1a**–**c**, X = Cl, Br, I) are readily cleaved by reaction with W(CO)$_3$(RCN)$_3$ to afford seven-coordinate tungsten(II) complexes W(CO)$_3$(**1a**–**c**). 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]

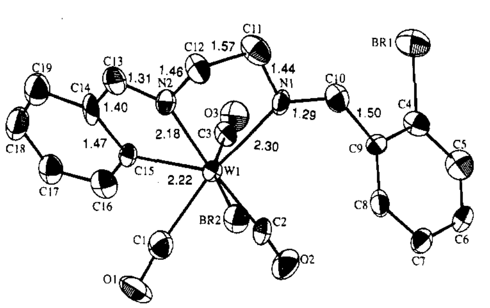
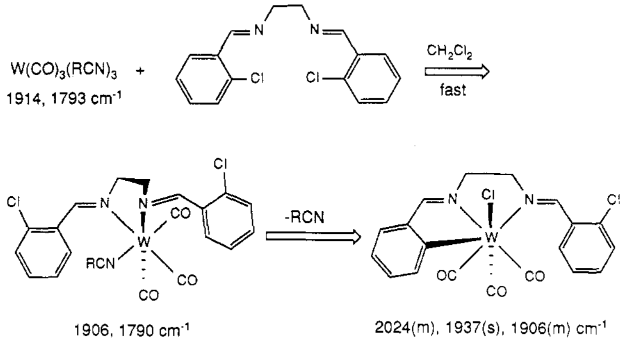


Figure 1. ORTEP representation of W(CO)$_3$(**1b**) including important bond distances (±0.02 Å) involving the metallacycle. Other distances (Å) follow: W1–Br2, 2.651 (2); W1–Cl, 2.02 (2); W1–C2, 2.03 (2); W1–C3, 1.96 (2). Selected bond angles (deg): C3–W1–Br2, 159.5 (5); N2–W1–C2, 174.9 (6); N1–W1–C1, 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_2Cl_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_2O. 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_2Cl_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 $^{13}C\{^1H\}$ 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_2Cl_2/hexane.[7]

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(4) W(CO)$_3$(**1b**). Anal. Calcd for $C_{19}H_{14}N_2Br_2O_3W$: 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 $C_{19}H_{14}N_2Cl_2O_3W$: 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 $C_{19}H_{14}N_2I_2O_3W$: 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.

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