Synthesis and Reactivity of a W(0) Anion Stabilized by Chelating Tertiary Amines. Oxidative Addition and Reductive Elimination of a Carbon-Tin Bond at Tungsten

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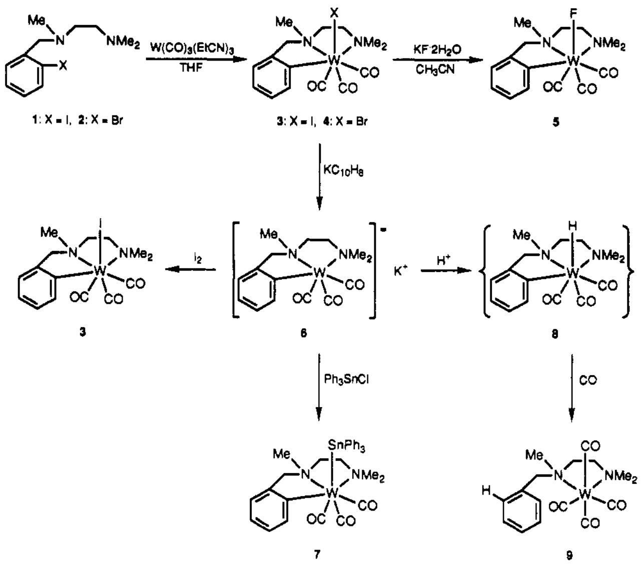
Much of the extensive chemistry developed for group 6 CpM$(CO)_3X$ (M = Cr, Mo, W) compounds[1] derives from reactions of the corresponding zerovalent anions $[CpM(CO)_3]^-$. Recent research in our laboratory[2] has established chelate-assisted oxidative addition as a method of generating new complexes of the formula $LW(CO)_3X$, where L is a tridentate monoanionic [C,N,N′] chelating ligand which can be considered to be pseudoisoelectronic with the cyclopentadienyl anion.[3] In this work we report the synthesis of tungsten(II) complexes of a saturated η^3-[C,N,N′] ligand and the reaction chemistry of a novel $[LW(CO)_3]^-$ anion stabilized by hard aliphatic nitrogen donor ligands. In the course of this investigation, we have discovered a mild and reversible insertion reaction of a tin–phenyl carbon bond which may be relevant to metal-catalyzed cross coupling reactions of organotin reagents.[4]

As shown in Scheme I, addition of the aryl halide ligand **1** or **2** to a THF solution of $W(CO)_3(EtCN)_3$[5] results in the oxidative addition of the carbon–halogen bond to afford the W(II) iodide **3** or bromide **4**, which were isolated as yellow crystalline solids in 77% and 84% yields, respectively, by crystallization from toluene.[6] Unlike the related Schiff base ligand system,[2] the fluoride **5** cannot be prepared by oxidative addition but is readily isolated by metathesis with $KF\cdot 2H_2O$. Full spectroscopic characterization of these complexes has been achieved,[6] and their structures have also been confirmed by elemental analysis and X-ray crystallography.[7] In contrast to similar imine systems,[2] the flexibility of the ligand backbone causes these 7-coordinate complexes to be fluxional on the NMR time scale at room temperature.

Scheme I



Two-electron reduction of the tungsten halides with either Na/Hg amalgam or potassium naphthalide affords the air-sensitive W(0) anion **6** as evidenced by the dramatic lowering of carbonyl stretching frequencies in its solution IR spectrum (ν_{CO} = 1858, 1730, 1706 cm^{-1}). These bands are approximately 45 cm^{-1} lower than for $[CpW(CO)_3]^-$,[8] which is indicative of a very basic metal center for **6**. Crystallization from THF affords **6** as a room temperature stable yellow solid. In contrast to other systems in which hard donor ligands have been utilized as leaving groups upon reduction of a metal center,[9] it appears that the chelating tertiary amine ligand in **6** retains coordination to the tungsten anion.[10] Addition of PPh_3 or pyridine to solutions of **6** does not effect its IR spectrum. In addition, a static $^{13}C\{^1H\}$ NMR spectrum is observed for **6** as expected for an octahedral d^6 complex, and the phenyl *ipso* and carbonyl carbons shift downfield relative to their tungsten(II) precursors.

The nature of this anion was investigated by reactions with several electrophiles. Iodine regenerates **3** in quantitative spectroscopic yield. Reaction of the anion with Ph_3SnCl affords the air-stable triphenyltin adduct $LW(CO)_3SnPh_3$ (**7**). Spectroscopic parameters (ν_{CO} = 1952, 1857, 1838 cm^{-1}) are in accord with the formulation of **7**, and this was confirmed by X-ray crystallography as shown in Figure 1.[11] The geometry about the seven-coordinate tungsten atom is best described as a capped octahedron with the triphenyltin group capping the triangular face comprised of C1, C2, and C4. All bond distances are as

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(1) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Elmsford, NY, 1982; Vol. 3.

(2) (a) Richmond, T. G.; King, M. A.; Kelson, E. P.; Arif, A. M. *Organometallics* **1987**, *6*, 1995. (b) Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 8091. (c) Osterberg, C. E.; King, M. A.; Arif, A. M.; Richmond, T. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 888. (d) Richmond, T. G. *Coord. Chem. Rev.* **1990**, *105*, 221. (e) Lucht, B.; Poss, M. J.; King, M. A.; Richmond, T. G. *J. Chem. Soc., Chem. Commun.* **1991**, 400,

(3) An isomeric [N,C,N′] ligand which favors meridional coordination has been extensively investigated by van Koten and co-workers. For example, see: van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681. Abbenhuis, H. C. L.; Feiken, N.; Grove, D. M.; Jastrzebski, J. T. B. H.; Kooijman, H.; van der Sluis, P.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9773. For Pd complexes of [C,N,N′] ligands see: Alsters, P. L.; Engel, P. F.; Hogerheide, M. P.; Copijn, M.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1831.

(4) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508–524 and references therein. For a 100-fold rate enhancement of a palladium-catalyzed cross-coupling reaction using a pendant (dimethylamino)tin reagent see: Brown, J. M.; Pearson, M.; Jastrzebski, J. T. B. H.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1440.

(5) Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692.

(6) Full experimental details and spectroscopic parameters are supplied in the supplementary material. ν_{CO}(THF): **3**, 2003 (s), 1910 (s), 1900 (m), 1882 (w) cm^{-1}; **4**, 2008 (s), 1919 (s), 1914 (s) sh, 1896 (w), 1878 (m) cm^{-1}; **5**, 2001 (m), 1903 (s), 1866 (m) cm^{-1}.

(7) Buffin, B. P.; Poss, M. J.; Arif, A. M.; Richmond, T. G. Manuscript in preparation.

(8) ν_{CO} = 1896 (s), 1786 (s), 1746 (s) cm^{-1} (THF). Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263.

(9) Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1985**, *4*, 1354 and references therein.

(10) Metal carbonyl anions with saturated amine ligands are rare. See: Rehder, D. *J. Organomet. Chem.* **1972**, *37*, 303. Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1. For examples of group 6 metal carbonyl anions which contain nitrosyl and unsaturated chelating nitrogen ligands such as tris(pyrazolyl)borate see: Kirtley, S. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Elmsford, NY, 1982; Vol. 3. Alonso, F. J. G.; Llamazares, A.; Riera, V.; Vivanco, M.; Granda, S. G.; Diaz, M. R. *Organometallics* **1992**, *11*, 2826.

(11) X-ray data for 7 ($C_{33}H_{34}N_2SnO_3W$): Space group $P2_1$ with a = 10.372(1) Å, b = 17.937(2) Å, c = 11.619(2) Å, β = 92.838(4)°, V = 2158.9 Å^3, and Z = 2 based on 3264 observations at 18 °C (Mo Kα, $2° < 2\theta < 50°$, μ = 33.394 cm^{-1}, empirical absorption correction applied) with $I > 3\sigma(I)$ and 420 variables to yield R = 0.0381, R_w = 0.0431, and GOF = 2.52.

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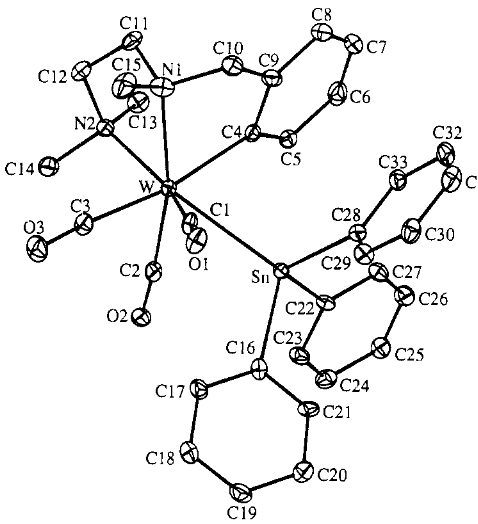
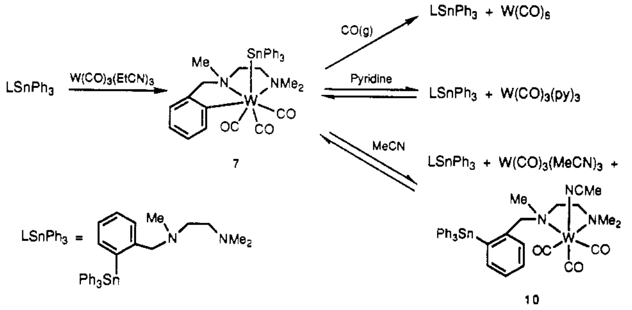


Figure 1. ORTEP representation of 7 illustrating the atom-labeling scheme. Seleced bond distances (Å) and angles (deg) for 7: W–Sn, 2.8273(7); W–N1, 2.23(1); W–N2, 2.371(8); W–C4, 2.20(1); Sn–W–N1, 125.5(3); N1–W–C4, 75.7(4); N2–W–C4, 85.2(3); N1–W–C2, 164.7(4); N2–W–C1, 155.7(3); C3–W–C4, 170.3(4).

Scheme II



expected with a W–Sn distance of 2.8273(7) Å.[12] The flexible ligand is folded along the W–N1 bond axis with a N2–W–C4 angle of 85.2(3)°. This is in marked contrast to the related W(II) fluoride, which exhibits a capped octahedral geometry in which C4 of the phenyl ligand is the capping atom and the ligand folding angle N2–W–C4 is 126.3(2)°.[7] Attempts to observe formation of the hydride **8** by ^{1}H NMR when the anion **6** was treated with various proton sources were unsuccessful, and a rapid reductive elimination to afford **9** occurred even at –80 °C.

The behavior of **7** provides a model for the reactivity of the putative hydride **8**. As illustrated in Scheme II, reductive elimination of a carbon–tin bond and displacement of the chelating ligand occurs when a THF solution of the W(II) stannyl product **7** is placed under 30 psi of CO(g) and heated to 60 °C for approximately 24 h to afford $W(CO)_6$ as the only metal carbonyl product. Removal of solvent under vacuum and sublimation of $W(CO)_6$ affords a white solid which has been identified as the tetraorganotin ligand $LSnPh_3$ by consideration of ^{1}H, ^{13}C, and ^{119}Sn NMR data.[13] Reductive elimination of the C–Sn bond can also be observed with other donor ligands. Placement of **7** in a 0.6 M solution of pyridine in THF and heating to 50 °C results in reductive elimination and formation of $W(CO)_3(py)_3$ (ν_{CO} = 1900, 1780 cm^{-1})[14] as the only carbonyl-containing species as determined by IR spectroscopy. However, lower concentrations of pyridine (ca. 0.2 M or below) results in the establishment of an equilibrium between the W(II) tin product **7** and $W(CO)_3(py)_3$ as depicted in Scheme II. Dissolution of complex **7** in acetonitrile results in another oxidative addition-reductive elimination equilibrium as shown in Scheme II. The formation of both **10** and $W(CO)_3(MeCN)_3$ (ν_{CO} = 1912, 1791 cm^{-1})[5] is consistent with our thermochemical measurements of binding abilities of this class of ligands relative to acetonitrile.[15]

As anticipated from the reversible nature of the equilibria noted above, room-temperature oxidative addition of a carbon–tin bond occurs when the ligand $LSnPh_3$ is added to a THF solution of $W(CO)_3(EtCN)_3$ (Scheme II). An immediate change to the characteristic yellow color of the W(II) triphenyltin complex is noted, and removal of released EtCN under vacuum and dissolution in fresh THF completes conversion to the oxidative addition product **7**.

Chelate-assisted oxidative addition of carbon–halogen bonds provides access to a robust tridentate monoanionic ligand system for organometallic chemistry. In contrast to cyclopentadienyl ligand complexes, the hydride ligand is kinetically labile and thermodynamically unstable, but the fluoride ligand is stabilized in the tungsten(II) tricarbonyl complexes of the [C,N,N′] ligand L.[16] Accordingly our observation of carbon–fluorine activation in the presence of a carbon–hydrogen bond can be rationalized in terms of these observations.[2e] Despite the presence of hard donor ligands, the [C,N,N′] ligand is capable of supporting a zerovalent metal carbonyl anion and its triphenyltin adduct exhibits reversible oxidative addition-reductive elimination behavior. A related reaction has recently been reported in an iron carbonyl complex.[17] The flexible nature of this ligand set suggests a diverse coordination chemistry will continue to unfold in these systems.

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Supplementary Material Available: Text and tables for an experimental section containing the preparation and spectroscopic characterization of compounds and text and tables providing a full description of the crystal structure determination for 7 including a summary of crystal data, atomic coordinates, thermal parameters, and bond distances and angles (17 pages). Ordering information is given on any current masthead page.

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(12) For example: W–Sn = 2.837(1) Å in the tungsten alkylidene [CpW{=C(H)C_6H_4Me-4}$(CO)_2(SnPh_3)$] (Hodgson, D.; Howard, J. A. K.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1331) and 2.812(1) Å in the pentacarbonyl tungsten anion $[W(CO)_5(SnPh_3)]^-$ (Darensbourg, M. Y.; Liaw, W.-F.; Reibenspies, J. *Inorg. Chem.* **1988**, *27*, 2555).

(13) ^{119}Sn{^{1}H} NMR: δ = –147.9 ppm ($CDCl_3$). Exact mass spectroscopy (FAB): Calcd for $LSnPh_3$, *m/z* 541.1665; obsd, *m/z* 541.1662.

(14) Gonzalez, A. A.; Zhang, K.; Nolan, S. P. de la Vega, R. L.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429.

(15) Hoff, C. D.; Richmond, T. G. Unpublished results, 1992.

(16) To our knowledge $CpW(CO)_3F$ has yet to be prepared. For a review of metal carbonyl fluorides see: Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553.

(17) Schubert, U.; Grubert, S.; Schulz, U.; Mock, S. *Organometallics* **1992**, *11*, 3163.