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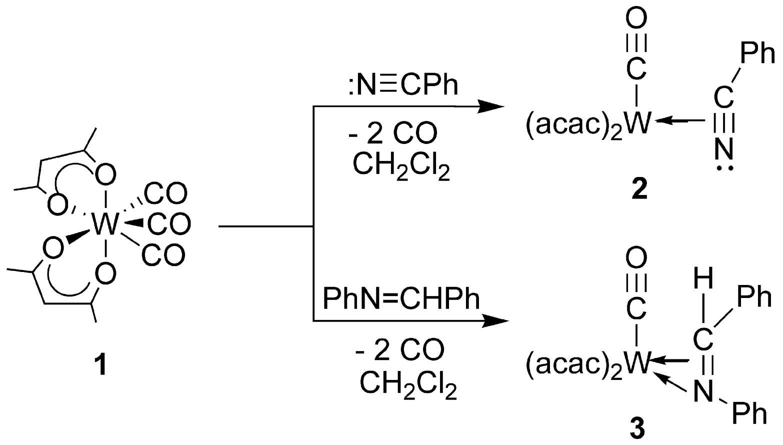

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Tungsten(II) Monocarbonyl Bis(acetylacetonate): A Fourteen-Electron Docking Site for η^2 Four-Electron Donor Ligands

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Organometallic complexes of d^4 tungsten and molybdenum often promote formal four-electron bonding of alkynes,[1−3] and nitriles[4−9] from the triple bond. Molecules containing a carbon−heteroatom double bond such as imines,[10−13] and aldehydes and ketones,[14−18] typically bind to these metals as formal two-electron donors whether bound as η^1 or η^2 ligands.

We recently reported the reactivity of $W(CO)_3(acac)_2$, **1**, (acac = acetylacetonate) with four-electron donor alkynes and two-electron donor phosphines.[19] Coordination of alkynes as formal four-electron donor ligands via the C≡C triple bond π-electrons[19] prompted us to explore isoelectronic nitrile reagents as possible four-electron donor ligands to this tungsten(II) center. Indeed, when $W(CO)_3(acac)_2$ **1** is exposed to nitriles, two equivalents of carbon monoxide are released to accommodate coordination of an η^2-nitrile ligand. Monitoring reaction progress via IR spectroscopy revealed the growth of a single CO stretch consistent with the formation of $W(CO)(acac)_2(\eta^2\text{-N}{\equiv}CR)$ [R = Me (**2a**), Ph (**2b**)] (Scheme 1).

The ^{1}H NMR spectrum of the acetonitrile adduct, $W(CO)(acac)_2(\eta^2\text{-N}{\equiv}CCH_3)$, **2a**, exhibits two singlets for the acac methine protons and four singlets for the acac methyl groups. The methyl group of the bound acetonitrile resonates downfield at 3.71 ppm, suggestive of a π-bound nitrile ligand. More diagnostic than proton NMR data is the ^{13}C NMR chemical shift for the nitrile carbon at 208.7 ppm, consistent with data reported for other four-electron donor nitriles.[4−9]

The X-ray structure of the 2,6-dichlorobenzonitrile derivative **2c** shows two acac chelates and one carbon monoxide ligand bound to tungsten with a π-bound nitrile ligand occupying the sixth site of a primitive octahedron. The η^2-nitrile ligand is located cis to carbon monoxide, and the C≡N triple bond is approximately parallel to the W−C≡O axis (Figure 1). The carbon atom in the nitrile ligand is located *proximal* to carbon monoxide and the nitrogen atom is located *distal* to CO. Bond distances to the nitrile ligand are nearly equal: $W(1)-C(4) = 2.04$ Å and $W(1)-N(3) = 2.02$ Å. The carbon−nitrogen triple bond distance in the coordinated nitrile ligand is 1.27 Å.

Selective coordination of nitrile reagents through the π-system reflects the propensity of the $W(CO)(acac)_2$ fragment to bind a ligand that will provide four electrons to the metal. Could other small molecules containing heteroatom π-bonds serve as formal four-electron donors to the 14-electron $W(CO)(acac)_2$ fragment?

Surprisingly, treatment of **1** with *N*-benzylideneaniline (PhN=CHPh) in CH_2Cl_2 at room temperature generates an η^2-imine complex of the formula $W(CO)(acac)_2(\eta^2\text{-PhN}{=}CHPh)$, **3** (Scheme 1). Coordination of the imine to tungsten creates a new stereocenter at the imine carbon, with tungsten as a second stereocenter. Formation of two diastereomers in a 2:1 ratio is indicated in the ^{1}H NMR spectrum by an upfield shift in the imine proton to 6.15 (major) and 5.71 (minor) ppm. An even more dramatic upfield shift is observed for the imine carbon which resonates at 57.3 (major) and 54.3 (minor) ppm in the ^{13}C NMR spectrum. Although η^2-imine complexes are well-known,[10−13] simple substitution of two carbon monoxide ligands by an imine reagent at room temperature is unprecedented.

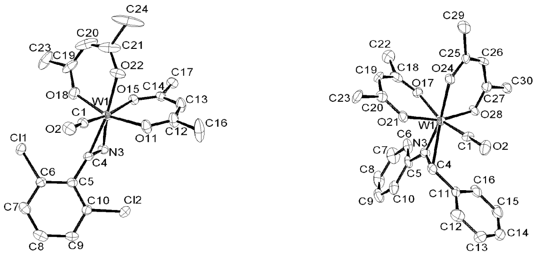
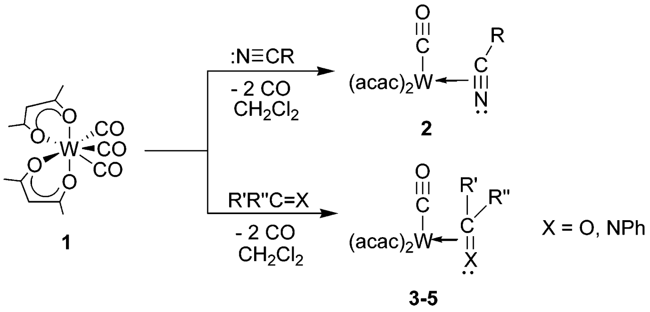


Figure 1. (Left) ORTEP diagram of $W(CO)(acac)_2(\eta^2\text{-2,6-dichlorobenzonitrile})$ **2c**; (right) ORTEP diagram of $W(CO)(acac)_2(\eta^2\text{-PhN}{=}CHPh)$ **3**. Hydrogen atoms are omitted for clarity.

Scheme 1



2a. N≡CMe **3**. PhN=CHPh **4a**. O=CHPh **5**. O=C(CH$_3$)$_2$
2b. N≡CPh **4b**. O=CHAr
2c. N≡CAr Ar = 2,6-dichlorophenyl

Similar results were obtained upon addition of benzaldehyde to tricarbonyl reagent **1**. The ^{1}H NMR spectrum for $W(CO)(acac)_2(\eta^2\text{-O}{=}CHPh)$, **4a**, shows two diastereomers in a 5:4 ratio. Coordination to the tungsten(II) center shifts the aldehyde proton upfield to 7.73 (major) and 7.66 (minor) ppm. ^{13}C NMR data shows the coordinated aldehyde carbon shifted upfield to 88.9 (major) and 86.7 (minor) ppm.

To check ketone reactivity, **1** was stirred in neat acetone. As with the imine and aldehyde substrates, IR spectroscopy suggested a tungsten product retaining one CO ligand. Note that $W(CO)(acac)_2[\eta^2\text{-O}{=}C(CH_3)_2]$, **5**, lacks a second stereocenter, so only one product was observed in the ^{1}H NMR spectrum. The diastereotopic methyl groups of coordinated acetone resonate at 2.53 and 2.31 ppm in the ^{1}H NMR spectrum, while the ketone carbon resonates upfield at 97.2 ppm in the ^{13}C NMR spectrum.

X-ray structures of complexes with imine **3** (Figure 1), aldehyde **4b**, and ketone **5** (Figure 2) ligands show η^2-coordination of the organic substrate with the C=X (X = N, O) unit aligned nearly parallel to the W−C≡O axis. This system exhibits a definitive preference for positioning the carbon atom *proximal* to CO and

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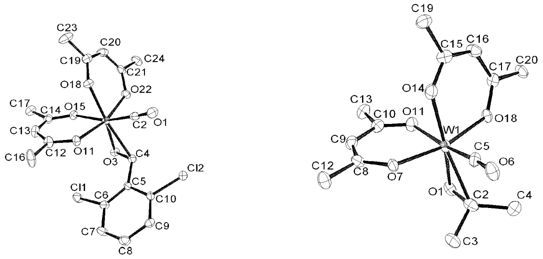

Figure 2. (Left) ORTEP diagram of W(CO)(acac)$_2$(η^2-2,6-dichlorobenzaldehyde) **4b**; (right) ORTEP diagram of W(CO)(acac)$_2$(η^2-acetone) **5**.

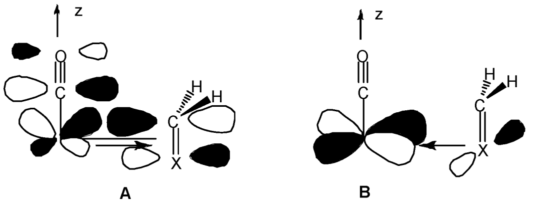

Figure 3. Orbital interactions of tungsten and π-bound substrate.

Table 1. Selected Bond Lengths (in Å) for Complexes **2c**, **3**, **4b**, **5**

	2c	3	4b	5
W−C	2.038(5)	2.237(7)	2.210(3)	2.211(8)
W−X^a	2.018(5)	1.934(6)	1.954(4)	1.934(5)
X^a−C	1.270(7)	1.403(8)	1.377(4)	1.380(10)

^{a} X = N (**2c**, **3**), O (**4b**, **5**).

Table 2. Selected Bond Lengths (in Å) from DFT Studies of W(acac)$_2$(CO)(CH$_2$O) (**6**), W(acac)$_2$(CO)(CH$_2$O)$^{2-}$ (**7**), and Os(acac)$_2$(CO)(CH$_2$O) (**8**)

	6	7	8
M−C	2.167	2.126	2.150
M−O	1.926	2.057	2.092
O−C	1.372	1.376	1.304

the heteroatom *distal* to CO. This geometry allows optimal back-donation to both carbon monoxide and the carbon of the C═X entity (A) (Figure 3) while simultaneously enabling lone pair donation from the heteroatom into the vacant d$_{xy}$ orbital (B).

Structural data for complexes **3**, **4b**, and **5** present a skewed bonding arrangement for each η^2-ligand. Bond lengths from tungsten to the carbon and to the heteroatom differ substantially relative to the analogous W−C and W−N bonds in the nitrile complex, **2c** (Table 1). The average tungsten−carbon bond length for these three structures is 2.22 Å, and the average tungsten−heteroatom bond length is 1.94 Å, reflecting significant W−X double-bond character. Upon coordination to tungsten, the C═X double bond in each substrate lengthens approximately 0.1 Å, a considerable loss of C═X double-bond character. Structural data do not reflect additional π-electron donation from the acetylacetonate chelates.

To gain additional insight into the structural features arising from the four-electron binding mode of heteroatom π-bonds, DFT calculations[20] were carried out on d^4 W(acac)$_2$(CO)(η^2-CH$_2$O) (**6**), together with the hypothetical d^6 model complexes, [W(acac)$_2$(CO)(η^2-CH$_2$O)]$^{2-}$ (**7**) and Os(acac)$_2$(CO)(η^2-CH$_2$O) (**8**), where the aldehyde is restricted to a two-electron donor role. Metric parameters of the optimized DFT structures are summarized in Table 2. As in the structurally characterized aldehyde complex, **4b**, the lowest-energy rotamer of the model formaldehyde complex **6** positions the oxygen atom *distal* to CO, with the *proximal* rotamer lying 11.5 kcal mol^{-1} higher in energy. The difference in the M−C and M−O distances in **4b** (0.26 Å) is reproduced well in the calculated structure for **6** (0.24 Å). Calculated structures for both of the d^6 complexes show a significantly longer M−O bond, which gives rise to a smaller difference between the M−O and M−C distances (0.06 Å). These calculated structural features are consistent with the absence of lone-pair donation from oxygen in these η^2-aldehyde adducts. Additionally, the lowest energy rotamer of the d^6 complexes aligns the C═O unit perpendicular to CO, allowing backbonding to the η^2-aldehyde from d$_{xy}$ without competition from CO.

In summary, we report a tungsten(II) d^4 center that seeks four-electrons from η^2-nitriles, imines, aldehydes, and ketones. Nitrile ligands donate four electrons from the two orthogonal π-orbitals of the triple bond. Imines, aldehydes, and ketones also provide four electrons to the d^4 metal center, but two originate in the C═X π-bond and the other two arise from a lone pair on the heteroatom.

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Supporting Information Available: Experimental procedures and characterization of complexes **2a-5**, X-ray data for **2c**, **3**, **4b**, and **5** (CIF), and DFT computational details of **6**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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