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ARTICLE TYPE

# Bis-Tropolonate Complexes of Tungsten: Scaffolds for Selective Side-on Binding of Nitriles, Imines and Ketones

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The chiral bis-tropolonate tungsten(II) tricarbonyl compound, $(trop)_2W(CO)_3$ (**1**), has been synthesized and structurally characterized. This seven-coordinate compound readily loses two carbonyl ligands to preferentially bind a series of π-bonding substrates to form six-coordinate complexes of the type $(trop)_2W(CO)(L)$. Alkynes coordinate strongly to form $(trop)_2W(CO)(\eta^2$-RCCR) (**2**) in which spectroscopic data is consistent with the alkyne serving as a 4-electron donor. Compound **1** will also preferentially coordinate organic nitriles in a side-on fashion through the CN triple bond. A dramatic shift in the nitrile carbon signals to greater than 210 ppm in the $^{13}C$ NMR confirms the nitriles are coordinated in an $\eta^2$ 4-electron donating capacity. Aldehydes, ketones, and imines also react with **1** to form 4-electron donor $\eta^2$ adducts. The imine adduct $(trop)_2W(CO)(\eta^2$-MeN=C(H)(tol)) (**5**) was characterized crystallographically and the short 1.91 A W-N bond distance supports the postulation of 4-electron donation from the imine through C=N π-bonding and N lone pair donation. Side-on coordination of ligands of this type is rare and may provide a means towards asymmetric functionalization of these substrates. All of the tropolonate compounds are prone to oxidation in air and the alkyne compounds will oxidize to stable $W^{IV}$ oxo alkyne species, $(trop)_2W(O)(\eta^2$-RCCR) (**6**). This causes a 90° rotation of the alkyne ligand and a reduction in alkyne donation to approximately 3 electrons, to maintain an optimal 18 electron configuration.

## Introduction

Coordination compounds containing four-electron donating alkynes are well known,[1] however compounds featuring a four-electron donor with a heteroatom are uncommon. The HOMO of an organic nitrile is the nitrogen lone pair, and the vast majority of nitriles coordinate to a metal atom through this lone pair. However, there are limited examples of side-on coordination to transition metals,[2] including some that have been structurally characterized.[3] Not all of these side-on nitriles are 4-electron donors as that is not a requirement for this coordination mode, rather they serve as π-acid ligands stabilizing electron-rich metal centers. The binding mode of $\eta^2$-nitriles has been compared to $\eta^2$-alkynes,[4] and the electronic differences of these ligands have also been highlighted, noting the greater π-acceptor capability of the nitrile due to the electronegative N-atom.[5] A variety of reactions at the $\eta^2$-nitrile moiety have been reported,[6] including cleavage of the C-CN bond,[5,7] oxidation at the nitrile C-atom,[4,8] and electrophilic addition to the lone pair on the N-atom.[2d,3a,3b,9]

Heteroatom-containing unsaturated substrates, such as ketones and imines can also bond in an $\eta^2$-fashion, but again this is an uncommon coordination mode.[9c,10] Ketones and imines can also donate 4-electrons to electron deficient metal centers, yet in a different fashion than that of the $\eta^2$-nitrile and $\eta^2$-alkyne. The filled C=X (X = O, NR) π orbital coordinates to the metal as would a traditional alkene. A lone pair on the heteroatom is capable of donating two electrons into an empty $d_\pi$ orbital of the metal atom. For this interaction to occur, it is predicted that the C=X double bond is completely reduced to a single bond to allow the rotation of the heteroatom lone pair to be pointed towards the metal center (Figure 1). Studies by Jackson suggest a high degree

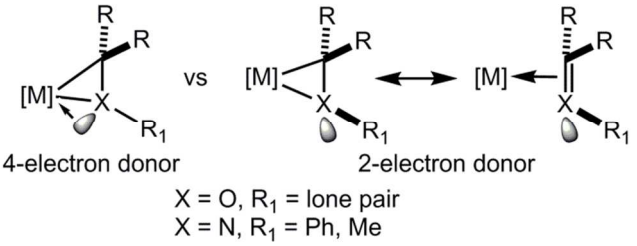
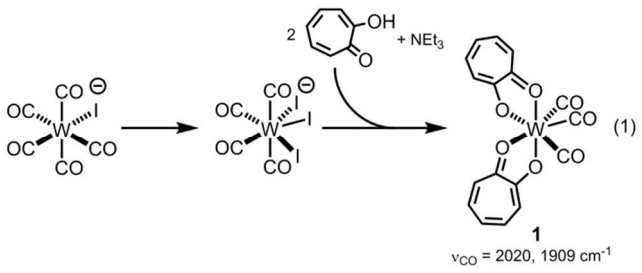



**Figure 1.** Coordination of ketones and imines as 2 and 4 electron donors.

of double bond character between the metal atom and the heteroatom of these substrates when $\eta^2$-bound.[3c] The fourteen-electron $(acac)_2W^{II}(CO)$ (acac = acetylacetonate) scaffold has been proven to be effective for coordinating a variety of nitriles, imines, and ketones in an $\eta^2$-fashion.[3a-d,11]

One of the drawbacks to the acac ligands that have been used previously to stabilize $W^{II}$ 4-electron donor complexes is the reactivity of the methyl groups, which are prone to deprotonation by strong bases. Additionally, the acac ligands are nucleophilic at the β-carbon on the ligand backbone and can undergo undesired reactions with electrophiles at this position. These properties limit the types of reagents that can be used to facilitate organometallic transformations. For example, these chiral compounds could be used to reduce nitriles in an enantiospecific fashion, but many of the reagents of choice for forming new C-C bonds (alkyl lithiums and alkyl magnesiums) will react with the acac ligand and lead to decomposition.

By using the tropolonate ligand this problem is alleviated as the ligand backbone consists entirely of planar conjugated $sp^2$ carbons and is less reactive towards nucleophiles or electrophiles. This allows us to use a much larger toolbox of reagents without




side-reactions on the ligand backbone. The tropolonate ligand features a 5-membered ring when bound to W, whereas acetylacetonate forms a 6-membered ring. The change in geometry of the complex may have significant impact on the reactivity of the $(LX)_2W$ fragment; much work has been done with group 6 carbamate, thiocarbamate, and dithiocarbamate ligands (which form 4-membered rings) and yet none of those species coordinate nitrile ligands in an $\eta^2$ fashion. The tropolonate ligand fills the gap between the 4 and 6 membered rings and can perhaps combine advantages of both. The acac based nitrile/ketone complexes are quite stable and therefore not conducive to catalytic reactions of these ligands, but the smaller chelate ring may result in more lability and thus have more catalytic potential.

This report details the formation of 4-electron interactions between the monomeric $d^4$ $(trop)_2W^{II}(CO)$ (trop = tropolonate) fragment and alkynes, nitriles, imines, and ketones in an $\eta^2$-fashion. The parent complex, $(trop)_2W^{II}(CO)_3$, releases 2 equivalents of CO upon reaction with an alkyne, nitrile, imine, or ketone (L) and binds the unsaturated substrate in an $\eta^2$ fashion to form complexes of the type $(trop)_2W(CO)(\eta^2\text{-L})$. The complexes presented here are sensitive to air oxidation, and the alkyne complexes readily form $W^{IV}$ oxides. We also report mechanistic investigations on the exchange of $\eta^2$-ketones and $\eta^2$-nitriles and discuss the implications of these studies on the nature of the $\eta^2$ 4-electron interaction.

## Results and Discussion

### Formation of $(trop)_2W(CO)_3$

The parent tricarbonyl complex $(trop)_2W(CO)_3$, **1**, forms by reacting two equivalents of $[HNEt_3][trop]$ and $[NEt_4][W(CO)_4(I)_3]$[11]; the complex is dark red with a high absorption coefficient. **1** can be isolated cleanly as a nearly black powder by evaporation of the reaction solvent and extracting the residue with diethyl ether. The compound is significantly less stable than the acac analog and is extremely air- and temperature sensitive. The solution IR spectrum has CO stretches at 2020 and 1917 $cm^{-1}$ which are about 7-8 $cm^{-1}$ lower than those for $(acac)_2W(CO)_3$ indicating that the tropolonate ligands are slightly more donating than the acac ligands. The room temperature $^1H$ NMR spectrum is consistent with a $C_1$ symmetric *cis*-bis-tropolonate complex. Each proton on the tropolonate ligands is chemically inequivalent and has a complex splitting pattern, making peak assignment challenging. At room temperature, the $^{13}C$ NMR spectrum is also consistent with a *cis*-bis-tropolonate species, however, the three carbon monoxide carbons are not observed and presumed to be fluxional at this temperature.

Dark red crystals were obtained from a benzene:hexane mixture and the structure was determined by X-ray diffraction. The X-ray structure confirms the compound to be $(trop)_2W(CO)_3$ as a distorted capped octahedron, similar to $(acac)_2W(CO)_3$ (Figure 2). Compared to the acac complex the metal is more exposed as the smaller tropolonate ligands do not provide as much steric protection for the metal center. Each backbone of the tropolonate ligands is planar and both bite angles are 74°; the acac ligands have bite angles of 86° and 82° showing that they are not only larger, but more flexible than the tropolonate ligands.

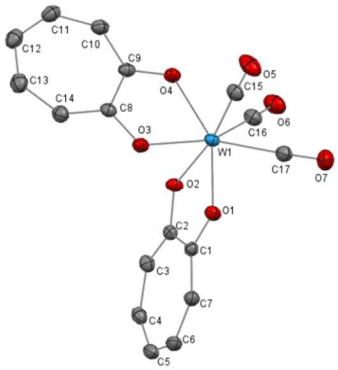


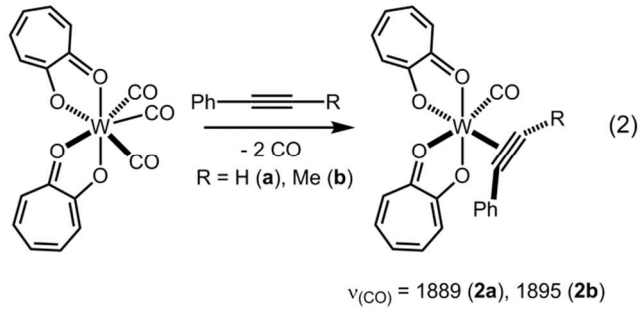

**Figure 2.** X-ray structure of $(trop)_2W(CO)_3$. Thermal ellipsoids are shown at 50% probability and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): W(1)-C(15) 1.9927(19), W(1)-C(16) 2.000(2), W(1)-C(17) 1.998(2), W(1)-O(1) 2.0925(13), W(1)-O(2) 2.1313(13), W(1)-O(3) 2.1177(14), W(1)-O(4) 2.1188(13), C(15)-W(1)-C(17) 71.85(8), C(15)-W(1)-C(16) 101.61(8), C(17)-W(1)-C(16) 69.58(8), O(3)-W(1)-O(4) 74.22(5), O(1)-W(1)-O(2) 74.49(5).

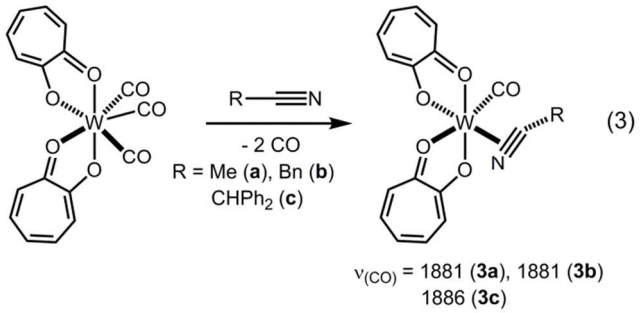
Reaction between **1** and phenylacetylene yields $(trop)_2W(CO)(PhCCH)$ (**2a**) in high yield. Compound **2a** is dark purple, thermally stable at room temperature, and can be purified via silica gel under an inert atmosphere. The solution IR CO stretch for **2a** appears at 1889 $cm^{-1}$, 6 $cm^{-1}$ lower than the corresponding acac complex, again showing that the tropolonate ligands are slightly more donating than acac. The increased donor ability of the tropolonate ligands is counterintuitive based on its pKa of 6.9 versus 9.0 for acetylacetone; based on this data the σ-donor ability of tropolonate should be less than that of acetylacetonate. The observed donor ability of tropolonate could be due to increased $\pi$-donation from the tropolonate oxygens.

The room temperature $^1H$ NMR spectrum of **2a** shows the distinctive signal for the acetylene proton as a broad singlet at 13.08 ppm indicating that the phenylacetylene ligand rotates rapidly on the NMR timescale. The chemical shift of 13.08 ppm falls in the range of what is expected for a 4-electron donor alkyne and is similar to the value of 12.95 observed for $(acac)_2W(CO)(PhCCH)$. The room temperature $^{13}C$ NMR spectrum of **2a** shows that the carbonyl carbon resonates at 240.9 ppm, in accordance with the resonances of known analogous W monocarbonyl species. The carbons of the $\eta^2$-alkyne were identified at 186.5 and 207.6 ppm.

The two isomers arising from PhCCH rotation were frozen by cooling the NMR probe to 263 K. The ratio of isomers was approximately 98:2. At this temperature the two singlets are sharp and appear at 13.19 (major) and 12.49 (minor) ppm; tungsten satellites are visible with coupling constants of 3 and 5 Hz, respectively.

Similarly, reacting **1** with 1-phenyl-1-propyne forms



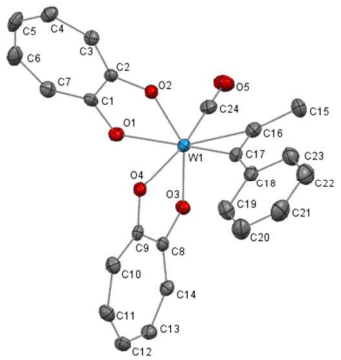




**Figure 3.** X-ray structure of $(trop)_2W(CO)(PhCCMe)$ (**2b**). Thermal ellipsoids are shown at 50% probability and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): W(1)-C(24) 1.929(3), W(1)-C(17) 2.015(3), W(1)-C(16) 2.056(3), W(1)-O(4) 2.1538(18), W(1)-O(1) 2.1613(18), W(1)-O(2) 2.0640(18), W(1)-O(3) 2.0408(18), C(16)-C(17) 1.316(4), C(24)-W(1)-C(17) 107.58(12), C(24)-W(1)-C(16) 69.89(12), C(17)-W(1)-C(16) 37.71(11), O(3)-W(1)-O(4) 75.17(7), O(2)-W(1)-O(1) 73.15(7), C(24)-W(1)-O(4) 163.81(10), O(3)-W(1)-O(2) 152.16(7).

$(trop)_2W(CO)(\eta^2\text{-PhCCMe})$ (**2b**); the formation of a monocarbonyl species was indicated by *in situ* solution IR spectroscopy with a CO stretch at 1895 $cm^{-1}$. The slightly higher stretching frequency of **2b** ($\Delta\nu \approx 6$ $cm^{-1}$) may suggest that the added steric bulk from the methyl group leads to a small reduction in $\pi$-donation to the metal center. The room temperature $^1H$ NMR spectrum of **2b** shows that the alkyne methyl protons resonate as a singlet at 3.44 ppm. The alkyne carbons resonate at 195.4 and 201.1 ppm and the peak for the carbon monoxide carbon was identified at 240.7 ppm.

Crystals of **2b** were obtained from a mixture of $CH_2Cl_2$:hexanes and its structure was determined by X-ray diffraction (Figure 3). The bite angles of the two chelates are 73.2° and 75.2°, slightly deviated from the bite angles of the parent complex **1**, in which both bite angles were 74°. The average W-O bond distance is 2.10Å, slightly shortened from the W-O bond distances in **1**. In accordance with similar acac complexes,[11] the carbonyl and acetylene ligands are shown to be *cis* and parallel. In the solid-state structure of **2b**, the phenyl group of the alkyne ligand orients *distal* to the carbonyl ligand and the methyl group *proximal*. The small bite angle of the tropolonate chelate results in a distorted octahedral geometry. The C-C bond distance of the alkyne is 1.316Å, indicative of a significant loss of triple bond character, yet still shorter than what would be expected for a C-C double bond in a metallocyclopropene. The W-C bond distances of the alkyne are 2.02Å and 2.06Å, comparable to those of $(acac)_2W(CO)(PhCCH)$ (~2.04Å).[11]

Reaction of **1** with acetonitrile results in rapid conversion to a dark red product containing one metal carbonyl stretch at 1881 $cm^{-1}$ and a C-N stretch at 1664 $cm^{-1}$. The acetonitrile methyl protons appear at 3.8 ppm in the $^1H$ NMR spectrum, a dramatic shift from free acetonitrile at 2.0 ppm. This shift is consistent with what is expected for an $\eta^2$ bound acetonitrile.[3c] The $^{13}C$ NMR spectrum further confirms this assignment as the C-N carbon resonates at 212.6 ppm as indicated by correlation to the acetonitrile methyl group by HMBC analysis. This data strongly supports formation of $(trop)_2W(CO)(\eta^2\text{-NCCH}_3)$ (**3a**). Furthermore, addition of benzylnitrile to **1** forms $(trop)_2W(CO)(\eta^2\text{-NCCH}_2Ph)$ (**3b**) as evidenced by the diastereotopic methylene group resonating as a pair of roofed doublets with 16 Hz coupling at 5.25 and 5.33 ppm in the $^1H$ NMR. In addition to the ~1.5 ppm downfield shift from free benzylnitrile (Figure 4), the splitting of the methylene protons is particularly indicative of side-on binding mode as less differentiation between the protons would be expected if the ligand were coordinated through the nitrogen lone pair, rendering the methylene group farther from the chiral metal center. The complex with diphenylacetonitrile, $(trop)_2W(CO)(\eta^2\text{-NCHPh}_2)$ (**3c**), was formed as well. This nitrile again exhibits a dramatic shift of the methane proton upon coordination from 5.12 to 6.64 ppm in the $^1H$ NMR and the nitrile carbon resonates at 217.1 in the $^{13}C$ NMR consistent with an $\eta^2$ binding mode. Unfortunately, X-ray quality single crystals could not be obtained; however, the spectroscopic data strongly indicate side-on binding of the nitrile ligands in these complexes.

Unlike the alkyne analogs, the nitrile complexes are rather unstable and decompose in solution at room temperature in hours; though they are somewhat more stable in the presence of excess nitrile. These complexes also decompose rapidly if they are loaded onto a silica gel column or exposed to air. This instability stands in stark contrast to the acac-based nitrile complexes, which can be purified by column chromatography in air. Attempts to further functionalize the coordinated nitriles were unsuccessful: addition of electrophiles (MeI, MeOTf) and strong nucleophiles ($LiHBEt_3$, MeLi, $ZnMe_2$) all resulted in decomposition. Side-on nitriles in the acac analogs readily react with MeOTf to form isolable cationic iminoacyl complexes.[1a,3a] The CO stretching frequencies of the tropolonate-based compounds are consistently lower energy than their acac analogues so a lack of electron density at the metal to support a cationic species is not the source of the instability. The small bite angle of the tropolonate ligands leaves the metal and tropolonate oxygens relatively exposed and could contribute to the inherent instability. The reason for lower

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# ARTICLE TYPE

**Table 1.** NMR and IR data for selected W acac and trop complexes.

| Complex | IR: ν ($cm^{-1}$) | $^1$H NMR: δ (ppm) | $^{13}$C NMR: δ (ppm) |
|---|---|---|---|
| $(acac)_2W(CO)_3$ | 2028, 1924 (C≡O) | | 231.0, 235.6, 257.8 (C≡O). |
| $(trop)_2W(CO)_3$ **1** | 2020, 1917 (C≡O) | | Not Observed |
| $(acac)_2W(CO)(PhC{\equiv}CH)$ | 1903 (C≡O) | 12.96 (s, 1H, PhC≡C*H*) | 185.6 (PhC≡CH), 211.7 (PhC≡CH) |
| $(trop)_2W(CO)(PhC{\equiv}CH)$ **2a** | 1889 (C≡O) | 13.04 (s, 1H, PhC≡C*H*) | 186.5 (PhC≡CH), 207.6 (PhC≡CH) |
| $(acac)_2W(CO)(CH_3C{\equiv}N)$ | 1895 (C≡O), 1675 (C≡N) | 3.71 (s, 3H, N≡CC*H*$_3$) | 208.8 (N≡C$CH_3$), |
| $(trop)_2W(CO)(CH_3C{\equiv}N)$ **3a** | 1881 (C≡O), 1664 (C≡N) | 3.82 (s, 3H, N≡CC*H*$_3$) | 212.6 (N≡C$CH_3$) |
| $(acac)_2W(CO)((CH_3)C{=}O)$ | 1883 (C≡O) | 2.53, 2.31 (s, 3H, (C*H*$_3$)$_2$C=O) | 97.2 (O=C) |
| $(trop)_2W(CO)((CH_3)_2C{=}O)$ **4a** | 1851 (C≡O) | 2.61, 2.21 (s, 3H, (C*H*$_3$)$_2$C=O) | 92.7 (O=C) |
| $(acac)_2W(CO)(ArCOH)$ | 1866 (major), 1878 (minor) (C≡O) | 8.03 (major), 8.26 (minor) (s, 1H, ArC(=O)*H*) | 89.0 (major), 84.9 (minor) (O=CH) |
| $(trop)_2W(CO)(ArCOH)$ **4b** | 1878 (C≡O) | 8.12 (s, 1H, ArC(=O)*H*) | 82.0 (O=CH) |
| (acac)2W(CO)(MeN=C(H)(Ph) | 1904 (major), 1889 (minor) (C≡O) | 5.56 (major), 5.80 (minor) (s, 1H, N=C(*H*)(Ph) | 60.8 (major), 57.2 (minor) (N=CH) |
| (trop)2W(CO)(MeN=C(H)(tol) **5** | 1846 (C≡O) | 6.02 (s, 1H, N=C(*H*)(Ph) | 59.8 (N=CH) |

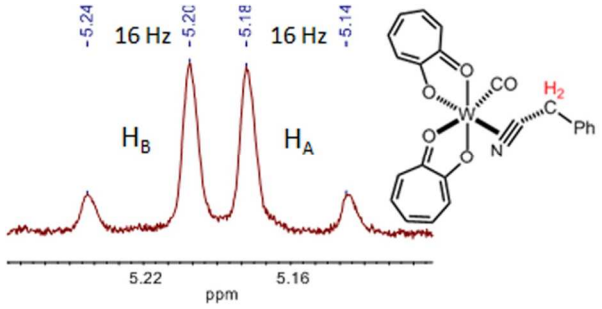
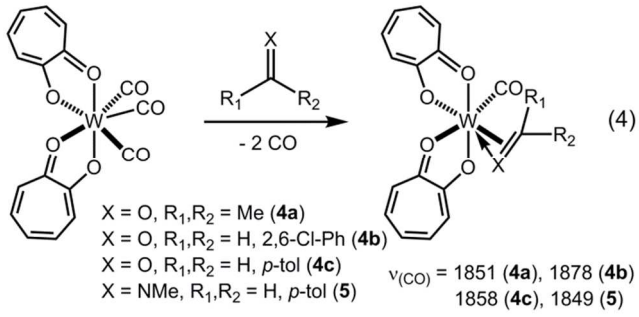



**Figure 4.** Diastereotopic methylene protons of $(trop)_2W(CO)(\eta^2$-$NCCH_2Ph)$.




(4)

CO stretches in the trop complexes may be increased pi-donation from the trop oxygens versus acac oxygens; if this is the case the side-on coordination of nitriles may be less necessary to reach an 18-electron configuration, resulting in weaker binding and activation of the 4-electron donor species.

Compound **1** will also readily react with compounds such as acetone and aryl aldehydes to form complexes in which the carbonyl serves as a 4-electron donor; these complexes tend to be dark purple in color. For example, reaction of **1** with acetone results in the formation of $(trop)_2W(CO)(\eta^2$-acetone) (**4a**). The metal carbonyl appears at 1851 $cm^{-1}$ in $CH_2Cl_2$, and the $^1$H NMR spectrum shows the two diastereotopic methyl groups at 2.58 and 2.18 ppm. The $^{13}$C NMR data is consistent with an $\eta^2$-bound

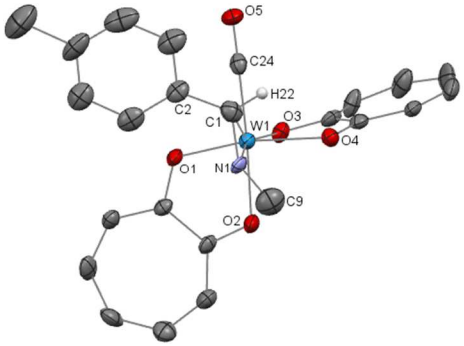



**Figure 5.** X-ray structure of $(trop)_2W(CO)(\eta^2$-$CH_3N=C(H)(p\text{-tolyl}))$ (**5**). Thermal ellipsoids are shown at 50% probability. One of two unique molecules of **5** is displayed; an included $Et_2O$ molecule and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): W-$N_{avg}$ 1.91; W-$C_{avg}$ 2.25; N-$C_{avg}$ 1.39; W1-O1 2.03; W1-O2 2.15; W1-O3 2.08; W1-O4 2.10; W1-C24 1.93; C24-O5 1.18; N1-W1-O4 158.3; C1-W1-O4 150.9. Torsion Angles (°): C24-W1-N1-C1 5.4.

acetone ligand;[3c,12] the acetone carbonyl carbon resonates at 92.7 ppm; some 2-electron donor $\eta^2$-acetone complexes appear upfield of 90 ppm.[13] Aryl aldehyde analogs of **4a** were synthesized via a similar method and in these cases the aldehyde proton provides a nice NMR handle for the compounds. Reaction of **1** with 2,6-dichlorobenzaldehyde or *p*-tolualdehyde results in the formation of $\eta^2$-aldehyde **4b** or **4c**. The formation of a monocarbonyl product is evident by a CO stretches at 1878 and 1858 $cm^{-1}$ in the solution IR, respectively. The 20 $cm^{-1}$ difference in the CO stretching frequencies of **4b** and **4c** seems disproportionally large to be caused by electronic differences in the two aldehydes and probably indicates weaker binding to W because of steric inhibition. The room temperature $^1$H NMR spectrum of **4b** shows the aldehyde proton resonance at 8.12 ppm, while **4c** displays two isomers at in a 2.3:1 ratio 7.99 (major) and 7.93 ppm (minor). The observation of only one major isomer in **4b** suggests that because of the steric bulk of the 2,6-dichlorophenyl ring imparts a high diastereoselectivity to the complex. This contrasts with the corresponding acac complex in which two isomers were observed for this ligand, and in fact the spectroscopic properties of **4b**, are

quite

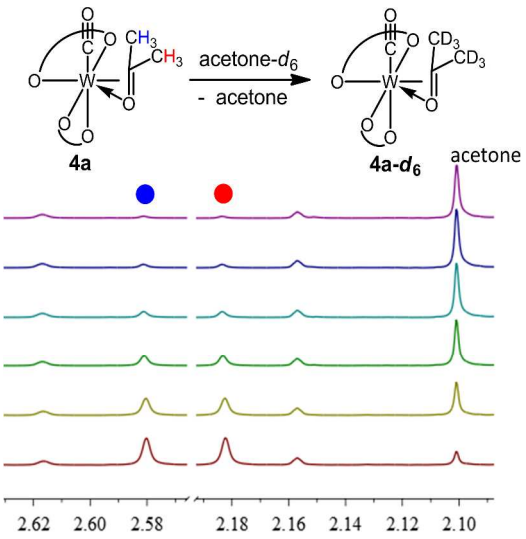
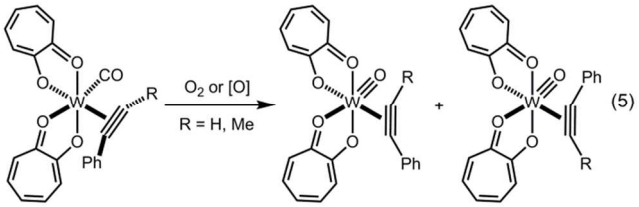



**Figure 6.** Proton NMR spectra of **4a** in acetone-$d_6$ over a 12 hour period.

similar to the properties of the minor acac diastereomer suggesting that the diastereoselectivity has switched by replacement of acac with trop (Table 1). Imines will also bind to the W center in an $\eta^2$ 4e- donor fashion like the aldehydes. Addition of $CH_3N{=}C(H)$(p-tolyl) to **1** and stirring for 2 hours resulted in the loss of 2 equivalents of CO and the formation of a dark blue solution of $(trop)_2W(CO)(\eta^2$-$CH_3N{=}C(H)$(p-tolyl)) (**5**). The formation of a monocarbonyl species was confirmed by the single broad CO stretch at 1846 $cm^{-1}$ in the $CH_2Cl_2$ solution IR spectrum. The imine C-H appears shifted upfield to 6.02 ppm in the $^1$H NMR and the imine carbon appears at 59.8 ppm in the $^{13}$C NMR, both indicating significant reduction of the C=N double bond. Two diastereomers are observed for the imine complex, and the major isomer is favored by a 5:1 ratio. Dark blue/purple crystals were obtained by slow diffusion of pentane into diethyl ether. X-ray crystallography confirmed the structure of **5** as an $\eta^2$-imine serving as a 4-electron donor (Figure 5).

The imine is nearly aligned with the W-CO bond with a torsion angle of only 5°. The tolyl group is located up and back towards O1 on the tropolonate trans to CO and the N-Me is located approximately trans to the tolyl group. The W-N bond distance of 1.91 Å is consistent with partial multiple bond character and the N-C bond distance has lengthened to 1.39 Å indicating significant backbonding from W. The imine is bound asymmetrically to the W with the N nearly in the square plane of O4, O3, and O1; while the C1 carbon is well above the square plane and has a long W-C1 distance of 2.25 Å showing the asymmetric binding of the imine to the tungsten. The nitrogen is not totally planar, but the PhC-NMe torsion angle of 95° is drastically reduced from the planar free imine (180° torsion) and is again consistent with partial W-N multiple bond character.

Spectroscopic data for related $(acac)_2W$ and $(trop)_2W$ tungsten complexes are compiled in Table 1. In general, the CO stretches for the tropolonate complexes are lower in energy than their acac counterparts. Based on the carbonyl stretches we would expect the 4-electron donors in the tropolonate complexes to participate in a higher degree of backbonding than the acac complexes, as




the NMR data suggests. The acetylene proton and the acetonitrile methyl groups both appear shifted downfield in the trop complexes versus acac complexes. The imine (**5**), acetonitrile (**4a**), and tolualdehyde (**4c**) complexes all have CO stretching frequencies that are especially low, ~40 $cm^{-1}$ below the corresponding acetylene and nitrile complexes and similarly below the analogous acac imine and aldehyde complexes. The crystal structure of **5** does not show any dramatic structural differences versus $(acac)_2W(CO)(MeN{=}CHPh)$, so the reason for the dramatic reduction in CO stretching frequency must be due to the smaller bite angle of the tropolonate ligands allowing more optimal π-donation from the oxygen atoms.

## Exchange of 4-Electron Donor Ligands

It has been observed that the more unstable complexes reported here, such as $\eta^2$-nitriles and $\eta^2$-ketone compounds, are stabilized by the presence of excess ligand in solution. For example, $(trop)_2W(CO)(\eta^2$-acetone) (**4a**) is indefinitely stable when stored under $N_2$ in acetone, but will decompose in a day if stored in $CH_2Cl_2$. It is reasonable that the decomposition pathway of the complex first involves the dissociation of the $\eta^2$-ligand. If the local availability of additional ligand is sufficient, the complex can be regenerated. We have explored the ligand exchange in complex **4a** by monitoring the displacement of $\eta^2$-acetone by acetone-$d_6$ via $^1$H NMR spectroscopy. Heteroatom containing 4-electron donor ligands are rare and thus their exchange processes have not been thoroughly explored. Generally, an 18-electron octahedral complex would be expected to undergo dissociative ligand exchange, in this case dissociation of the 4-electron donor ligand would result in a 14-electron intermediate which would likely be unstable and lead to a high reaction barrier. One possibility here is that the 4-electron donor can reorient such that it becomes a 2-electron donor before an incoming ligand coordinates and thus undergo associative ligand exchange without formally exceeding 18-electrons; this would be similar to ring slippage in a cyclopentadienyl complex which is known to accommodate ligand exchange in some systems.[14]

The $^1$H NMR spectra of **4a** in acetone-$d_6$ over a 12 hour period are shown in Figure 6, the only signals that change over time are the signals assigned to the acetone methyl groups, indicating that there is clean conversion of **4a** to **4a-$d_6$** with no side-products being formed. If acetonitrile is added to **4a**, even in neat acetone, rapid conversion to **3a** is observed, indicating that coordination of the side-on nitrile is much more favorable than coordination of the side-on acetone. Likewise, addition of phenylacetylene to **4a** rapidly yields **2a**. These results support an associative mechanism of ligand exchange as the rate of exchange is highly dependent on the incoming ligand. The acetonitrile ligand in **3a** can be displaced by phenylacetylene as well, but we have not observed any exchange of alkyne ligands at room temperature. The triply bonded ligands thusly appear to form more stable 4-electron

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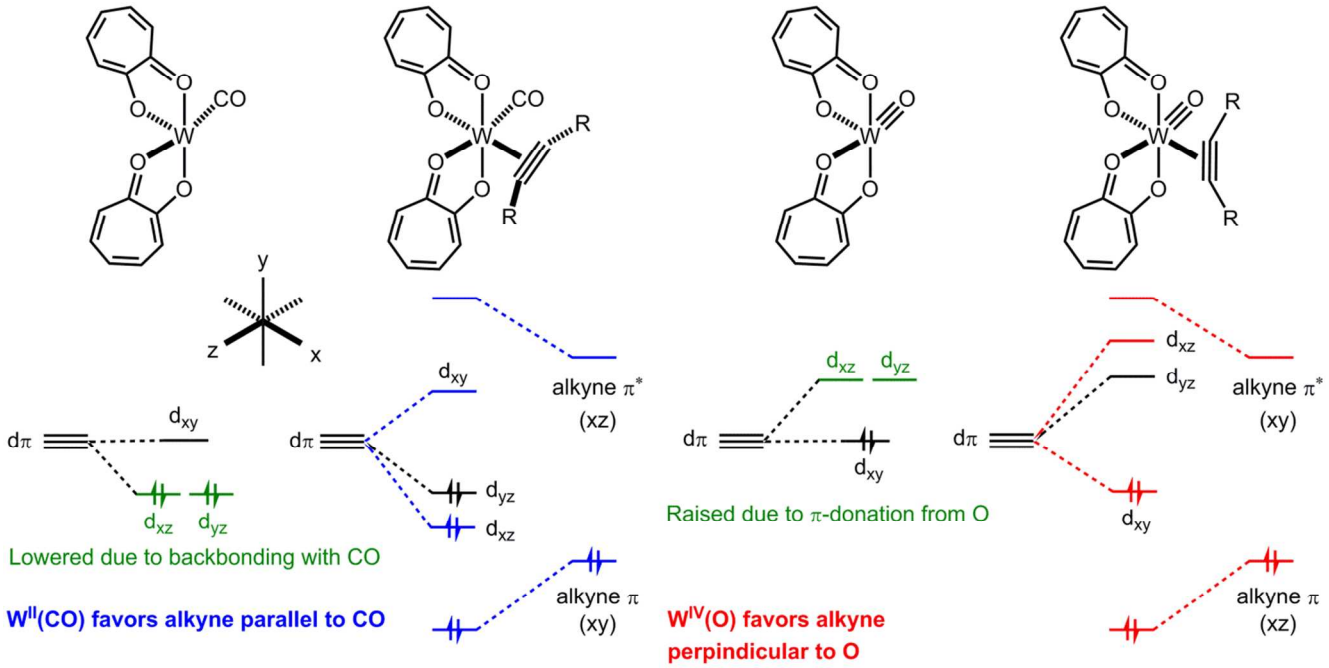


**Figure 7.** d-orbital splitting diagrams for $W^{IV}$ oxo alkyne species.

donor complexes and particularly the alkynes are resistant towards exchange. The bulkier substrates, such as MeN=C(H)(tol) and $Ph_2HCCN$ are more stable than the smaller analogs, most likely due to their additional steric protection of the metal center from associative attack. The ability to readily exchange ligands on the $(trop)_2W(CO)$ framework is important to developing a catalytic cycle for asymmetric reduction of nitriles to imines or similar transformations, because the product must be readily displaced by the starting material in order to turn over the cycle. The related acac complexes can support reduction of nitriles; however displacement of the resulting imines with nitriles to complete a stoichiometric cycle has not been reported, even under forcing conditions.

**Oxidation with $O_2$.**

The $(trop)_2W^{II}$ complexes are highly sensitive to oxidation by $O_2$ in air. Formation of **1** does not occur without rigorous exclusion of oxygen. Upon exposure to air, **1** and its nitrile, ketone, and imine derivatives, **3, 4**, and **5** oxidatively decompose rapidly. Complex **2** is somewhat air stable and only completely oxidizes over several days in solution; however a $CH_2Cl_2$ solution of **2** will oxidize in ~4 hr when stirred with $Na_2SO_4$, presumably with formation of $Na_2SO_3$. A stronger oxidant, such as $H_2O_2$, will complete the reaction in less than 5 min. The alkyne derivatives undergo loss of CO and 2-electron oxidation to $(trop)_2W^{IV}(O)(\eta^2$-alkyne) (**6**) (equation 5). The formation of $W^{IV}$ oxides can be observed by the color change of the strongly absorbing dark red or purple precursors to the pale yellow of the oxides. IR spectroscopy confirms the dissociation of the carbonyl ligand. The $(acac)_2W^{II}(CO)$ complexes have been oxidized by MCPBA, diazoalkanes, or azides, but the compounds do not oxidize in air even on long timescales.[3d,15]

Oxidation of **2b** results in the formation of $(trop)_2W(O)(\eta^2$-PhC≡CMe) (**6b**). As consistent with the known tungsten-oxo alkyne complexes, there are two isomers present. At room temperature, the $^1$H-NMR spectrum shows singlets at 3.28 and 2.89 ppm representing the isomers of the alkyne methyl, present in a 1.4:1 ratio, shifted upfield slightly from the rapidly rotating propyne ligand of the parent carbonyl complex; the methyl protons of which resonate as a sharp singlet at 3.44 ppm. Oxidation of **2a** in the same fashion results in the formation of $(trop)_2W(O)(\eta^2$-PhC≡CH) (**6a**). The room temperature the $^1$H-NMR spectrum shows singlets at 11.25 and 11.16 ppm, also in a 1.4:1 ratio, the peaks have tungsten satellites of 6.9 and 6.5 Hz. These signals represent the acetylene proton on the two rotomers of **6a** and are shifted upfield from the acetylene proton of the parent carbonyl complex, which appears at 13.04 ppm. The chemical shifts of the acetylene protons in the oxidized species are consistent with other 3-electron donor W acetylene species.[1d,9c,16] This supports the notion that the $\pi$-donating oxo ligand reduces the electron donation required from the alkyne ligands to reach an 18-electron configuration.

In this $d^2$ system, the oxo ligand can $\pi$-donate into the empty $d_{xz}$ and $d_{yz}$ orbitals, allowing it to provide up to 6 electrons to the metal between the $\sigma$ and two $\pi$ bonds. The alkyne can donate between 2 and 4 electrons depending on the amount of $\pi$-donation

into the empty $d_{xz}$ orbital. Any combination of 8 total electrons from the oxo and alkyne ligands will give a stable 18 electron count. Both alkyne and oxo are competing for donation into the $d_{xz}$ orbital and the spectroscopic data suggests roughly equal contribution from both ligands, so this could be considered a 3-electron donor alkyne and 5 electron donor oxo for an 18 electron complex.[1d,9c,16] To accomplish this bonding scheme, the alkyne must rotate 90°, now perpendicular to the W-O bond. Because the 2 d-electrons are localized in the $d_{xy}$ orbital due to oxo donation into the $d_{xz}$ and $d_{yz}$ orbitals leaving the alkyne ligand in the xy plane for backbonding from $d_{xy}$ into to the alkyne $\pi^*$ orbital (Figure 7). There is a with a high barrier to alkyne rotation so two diastereomers are seen at room temperature.[3d]

## Conclusions

We have synthesized a series of bis-tropolonate W compounds that coordinate a variety of unsaturated ligands in an $\eta^2$ fashion as 4-electron donors. These compounds bind preferentially nitriles, imines, ketones and aldehyde compounds in an $\eta^2$ fashion as 4-electron donors. In the imine, ketone, and aldehyde complexes there is significant metal heteroatom multiple bond character due to strong π donation from the lone pair. No reaction occurs between compound **1** and ethylene, further indicating the requirement of a heteroatom for binding. The small bite angle of the tropolonate ligands allows the 4-electron donor ligands to readily undergo ligand exchange, but it also leaves the metal exposed and makes the compounds prone to air oxidation. The coordinated alkyne complexes can be cleanly oxidized in air to form $W^{IV}$ oxo alkyne species. It may be possible to take advantage of this behavior to use similar complexes as oxidation catalysts with $O_2$ as the terminal oxidant in the future. Attempts to functionalize $\eta^2$ nitriles with either electrophilic or nucleophilic reagents have not resulted in stable products. Despite the significantly lower pKa of tropolone versus acetylacetone, the tropolonate complexes have lower CO stretches than their acetylacetonate analogs; this seems to indicate that the bite angle of the tropolonate ligands allows for more π donation from the oxygens to the tungsten and this overcomes the reduced sigma donation. Future use of 3,7 substituted tropolonates may provide the advantages of the small bite angle while providing the metal with more kinetic stability by steric protection.

### Experimental

**General procedures.** Reactions were performed under an atmosphere of dry nitrogen or argon using standard glove box and Schlenk techniques. All glassware was oven dried or flame dried under vacuum and cooled under a nitrogen atmosphere before use. Methylene chloride, hexanes, tetrahydrofuran, and diethyl ether were dried by passage through a column of activated alumina under an argon atmosphere.[17] NMR solvents $CD_2Cl_2$, $CDCl_3$, $C_6D_6$, and acetone-$d_6$ were dried by passage through a pipet containing activated alumina in the glove box. $[NEt_4][W(CO)_5I]$ was synthesized according to published procedures.[11,18] All other reagents were used as received.

NMR spectra were recorded on 400 MHz Bruker Avance II and Avance III spectrometers. IR spectra were recorded on a Thermo Scientific Nicolet iS10 spectrometer. X-Ray structural determinations were conducted using a Bruker D8 diffractometer using a Mo source at 100 K for **1** and **2b** and a Bruker APEX II using a Mo source at 153 K for **5**. Elemental analysis was conducted by Robertson Microlit (Ledgewood, NJ). High Resolution Mass Spectrometry was done using a Thermo Scientific Orbitrap Exactive mass spectrometer using the Matrix Assisted Inlet Ionization (MAII) method with 3-nitrobenzonitrile as the matrix and an inlet temperature of 75 °C.[19]

**$W(CO)_3(trop)_2$ (1).** In a 500 mL Schlenk flask, $[NEt_4][W(CO)_5I]$ (1 g, 1.72 mmol) was dissolved in $CH_2Cl_2$ (150 mL). Stoichiometric addition of elemental iodine (435 mg, 1.72 mmol) resulted in the immediate formation of the orange $[NEt_4][W(CO)_4I_3]$ anion. In a separate flask, a solution of tropolone (H-trop) (2 eq, 419 mg, 3.44 mmol) and triethylamine (351 mg, 3.44 mmol) in $CH_2Cl_2$ (10 mL) was prepared. This mixture was combined with the solution containing $[NEt_4][W(CO)_4I_3]$ and then stirred for 12 h at 10 ºC to yield $W(CO)_3(trop)_2$, whose formation was monitored by in situ IR spectroscopy. The solvent volume was reduced *in vacuo*, and then hexanes were added to precipitate most of the ammonium salts. The solution was filtered and the remaining solvent was then evaporated to yield a dark red residue. The product was extracted with diethyl ether and evaporated to yield a dark red powder (97 mg, 0.1892 mmol, 11%). IR: ($CH_2Cl_2$) $\nu_{CO}$ = 2020, 1917 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 7.55 – 7.02 (10H, $C_7H_5O_2$). $^{13}C$ NMR ($CD_2Cl_2$, 200 K): $\delta$ 118.1, 127.6, 129.8, 138.0, 139.6, 149.4, 161.1, 174.0, 181.9. Anal. Calcd for $C_{17}H_{10}O_7W$: C, 40.03; H, 1.98; N, 0.0. Found: C, 41.29; H, 3.94; N, <0.02. Multiple attempts to achieve satisfactory elemental analysis were unsuccessful.

**$W(CO)(trop)_2(\eta^2$-PhC≡CH) (2a).** In a 500 mL Schlenk flask, $[NEt_4][W(CO)_5I]$ (600 mg, 1.03 mmol) was dissolved in $CH_2Cl_2$ (100 mL). Stoichiometric addition of elemental iodine (261 mg, 1.03 mmol) resulted in the immediate formation of the orange $[NEt_4][W(CO)_4I_3]$ anion. In a separate flask, a solution of tropolone (H-trop) (2 eq, 251 mg, 2.06 mmol) and triethylamine (211 mg, 2.06 mmol) in $CH_2Cl_2$ (10 mL) was prepared. This mixture was combined with the solution containing $[NEt_4][W(CO)_4I_3]$ and then stirred for 2 h to yield $W(CO)_3(trop)_2$, whose formation was monitored by in situ IR spectroscopy. Excess phenylacetylene (2 equiv, 226 µL, 2.06 mmol) was added, and the solution slowly changed color from dark red to purple. The reaction was stirred until IR spectroscopy showed a single CO stretch. The solvent volume was reduced *in vacuo*, and then hexanes were added to precipitate most of the ammonium salts. The solution was filtered and the remaining solvent was then evaporated to yield a dark purple residue. Purification occurred on a silica column using 19:1 $CH_2Cl_2$:THF to elute a dark purple band (257 mg, 0.462 mmol, 45%). IR: ($CH_2Cl_2$), $\nu_{CO}$ 1889 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 13.04 (s, 1H, PhC≡C*H*), 7.83-6.93 (m, 15H, $C_7H_5O_2$, $C_6H_5C{\equiv}CH$). $^{13}C$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 126.4, 127.1, 127.4, 128.5, 129.6, 131.0, 132.0, 137.3, 137.7, 139.0, 139.2, 140.3, 140.4 (trop *C*-H, $C_6H_5C{\equiv}CH$), 171.9, 179.4 180.5, 184.5 (trop *C*-O), 186.5 (PhC≡CH), 207.6 (PhC≡*C*H), 240.9 (*C*≡O). Elemental Analysis $C_{23}H_{16}O_5W$ Theoretical: C 49.67, H 2.90, N 0.00; Found: C 49.81, H 3.09, N <0.02.

**$W(CO)(trop)_2(\eta^2$-PhC≡CMe) (2b)** Same procedure as **2a**, but using PhCCMe (2 equiv, 258 µL, 2.06 mmol) rather than PhCCH. A dark red/orange band was eluted from a silica gel column to purify the complex (323 mg, 55%). Black crystals were obtained

by layering $CH_2Cl_2$ with hexanes. IR: ($CH_2Cl_2$), $\nu_{CO}$ 1895 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 8.05 (d, 2H, $C_7H_5O_2$), 7.30 (m, 3H, m-$C_6H_5$C≡CMe, p-$C_6H_5$C≡CMe,), 7.04 (m, 2H, o-$C_6H_5$C≡CMe,), 6.92 (d, 1H, $C_7H_5O_2$), 6.78 (d, 1H, $C_7H_5O_2$), 6.52 (t, 1H, $C_7H_5O_2$), 6.43 (t, 2H, $C_7H_5O_2$), 6.25 (t, 1H, $C_7H_5O_2$), 6.15 (t, 1H, $C_7H_5O_2$), 6.04 (t, 1H, $C_7H_5O_2$), 3.44 (s, 3H, PhC≡CC$H_3$). $^{13}C$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 21.4 (PhC≡C*C*H$_3$), 125.4, 125.7, 128.0, 127.3, 128.3, 128.4, 130.1, 130.9, 136.3, 138.0, 138.3, 138.9 ($C_6H_5$C≡CCH$_3$, trop *C*-H), 180.2, 180.9, 181.0, 185.0 (trop *C*-O), 195.4 (Ph*C*≡CCH$_3$), 201.1 (PhC≡*C*CH$_3$), 240.7 (*C*≡O). Elemental Analysis $C_{24}H_{18}O_5W$ Theoretical: C 50.55, H 3.18, N 0.00; Found: C 50.08, H 2.94, N <0.02.

**W(CO)(trop)$_2$($\eta^2$-CH$_3$C≡N) (3a).** A scintillation vial was charged with 20 mg (0.039 mmol) of **1**, and 10 mL of neat acetonitrile. The resulting solution was stirred for 15 minutes until the solution turned dark red, indicating the formation of the $\eta^2$-acetonitrile complex. The solvent volume was then removed *in vacuo* to yield a dark red residue. The residue was taken up into solution and used immediately as it begins decomposing quickly; reaction proceeded to 100% conversion by NMR. IR: ($CH_2Cl_2$), $\nu_{C\equiv O}$ 1881 $cm^{-1}$, $\nu_{C\equiv N}$ 1664 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 7.89 (d, 1H, $C_7H_5O_2$), 7.75 (m, 1H, $C_7H_5O_2$), 7.60 (m, 2H, $C_7H_5O_2$), 7.37 (m, 2H, $C_7H_5O_2$), 7.23 (d, 1H, $C_7H_5O_2$), 7.21 (d, 1H, $C_7H_5O_2$), 7.14 (d, 1H, $C_7H_5O_2$), 6.93 (t, 1H, $C_7H_5O_2$), 3.82 (s, 3H, N≡CC$H_3$). $^{13}C$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 21.7 (N≡*C*CH$_3$), 124.9, 127.3, 128.4, 129.5, 131.0, 133.6, 139.2, 140.8, 142.0 (trop *C*-H), 173.0, 178.9 (trop *C*-O), 212.6 ($CH_3CN$), 241.8 (*C*≡O).

**W(CO)(trop)$_2$($\eta^2$-PhCH$_2$C≡N) (3b).** A scintillation vial was charged with 20 mg (0.039 mmol) of **1** and 10 mL of $CH_2Cl_2$. Excess (1.25 eq, 5.71 mg, 0.049 mmol) benzylnitrile was then added to the solution. The solution was stirred for 15 minutes until the color changed to dark red and IR spectroscopy revealed a single carbonyl stretch. The solvent volume was then removed *in vacuo* to yield a dark red residue. Attempts to purify the complex from excess benzyl nitrile led to decomposition, reaction proceeded to 100% conversion by NMR. IR: ($CH_2Cl_2$), $\nu_{C\equiv O}$ 1881 $cm^{-1}$, $\nu_{C\equiv N}$ 1682 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 5.25 (d, 1H, PhC*H*HC≡N, $^1J_{H\text{-}H}$ = 16 Hz), 5.33 (d, 1H, PhCH*H*C≡N, $^1J_{H\text{-}H}$ = 16 Hz), 7.96 - 6.91 (16H, aromatic $C_7H_5O_2$, $C_6H_5CH_2C\equiv N$). $^{13}C$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 43.4 (Ph*C*H$_2$C≡N), 126.8, 127.0, 127.9, 129.3, 129.4, 130.4, 130.5, 132.9, 137.8, 137.9, 138.2, 138.7, 139.3, 140.4 (trop *C*-H, $C_6H_5CH_2C\equiv N$), 172.7, 179.5, 181.0, 186.1 (trop *C*-O), 215.5 (PhCH$_2$*C*≡N), 239.8 (*C*≡O).

**W(CO)(trop)$_2$($\eta^2$-Ph$_2$HCC≡N) (3c).** Same as **3b**, but using diphenylacetonitrile (1.25 eq, 9.46 mg, 0.049 mmol), reaction proceeded to 100% conversion by NMR. IR: ($CH_2Cl_2$), $\nu_{C\equiv O}$ 1886 $cm^{-1}$, $\nu_{C\equiv N}$ 1650 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 7.84 - 6.93 (22H, aromatic $C_7H_5O_2$, ($C_6H_5$)$_2$CHC≡N), 6.64 (s, 1H, Ph$_2$C*H*C≡N). $^{13}C$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 58.2 (Ph$_2$*C*HC≡N), 126.4, 126.9, 127.1, 127.5, 127.8, 127.9, 128.3, 128.6, 128.7, 131.5, 132.7, 137.9, 138.7, 139.2, 140.6, 140.8, 141.5, (trop *C*-H, ($C_6H_5$)$_2$CHC≡N), 178.0, 179.1, 179.7, 184.6 (trop *C*-O), 217.1 (Ph$_2$CH*C*≡N), 238.3 (*C*≡O).

**W(CO)(trop)$_2$($\eta^2$-(CH$_3$)$_2$C=O) (4a).** A scintillation vial was charged with 20 mg (0.039 mmol) of **1** and 10 mL of neat acetone. The resulting solution was stirred for 15 minutes until the solution turned purple, indicating the formation of the $\eta^2$-acetone complex. The solvent volume was then removed *in vacuo* to yield a dark purple residue. The residue was taken up into solution and used immediately as it begins decomposing quickly; reaction proceeded to 100% conversion by NMR. IR: ($CH_2Cl_2$), $\nu_{C\equiv O}$ 1851 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 7.95 (d, 2H, $C_7H_5O_2$), 7.79 - 7.65 (m, 2H, $C_7H_5O_2$), 7.45 - 7.39 (m, 2H, $C_7H_5O_2$), 7.33 - 7.25 (m, 2H, $C_7H_5O_2$), 7.03 (d, 1H, $C_7H_5O_2$), 6.89 (t, 1H, $C_7H_5O_2$), 2.61, 2.21 (each a s, 3H, C*H*$_3$). $^{13}C$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 32.2, 32.6 (acetone *C*H$_3$), 92.7 (acetone *C*=O), 127.1, 127.9, 128.0, 129.1, 132.0, 133.8, 137.7, 139.0, 139.2, 140.8 (trop *C*-H), 175.6, 176.3, 179.4, 184.8 (trop *C*-O), 229.8 (*C*≡O).

**W(CO)(trop)$_2$($\eta^2$-ArC(=O)H) (Ar = 2,6-dichlorobenzene) (4b).** A scintillation vial was charged with 20 mg (0.039 mmol) of **1** and 10 mL of $CH_2Cl_2$. Excess 2,6-dichlorobenzaldyde (1.25 eq, 8.72 mg, 0.049 mmol) was added, and the resulting solution was stirred for 15 minutes until the solution turned purple, indicating the formation of the $\eta^2$-aldehyde complex. The solvent volume was then removed *in vacuo* to yield a dark purple residue. The residue was taken up into solution and used immediately as it begins decomposing quickly; reaction proceeded to 100% conversion by NMR. Only 1 diastereomer observed. IR: ($CH_2Cl_2$), $\nu_{C\equiv O}$ 1878 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 8.12 (s, 1H, O=C*H*), 7.96 – 6.87 (13H, $C_7H_5O_2$, $C_6H_3Cl_2COH$). $^{13}C$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 82.0 (O=*C*H), 127.8, 128.5, 128.9, 129.0, 129.6, 130.3, 130.4, 134.2, 134.3, 134.4, 138.9, 139.2, 139.3, 139.9, 140.1, 141.6 (trop *C*-H, $C_6H_3Cl_2COH$), 177.3, 177.5, 179.7, 184.9 (trop *C*-O), 232.1 (*C*≡O).

**W(CO)(trop)$_2$($\eta^2$-ArC(=O)H) (Ar = p-tolyl) (4c).** Same as **4b**. but using *p*-tolualdehyde. The ratio of diastereomers is 2.3:1. IR: ($CH_2Cl_2$), $\nu_{C\equiv O}$ 1858 $cm^{-1}$ (only 1 broad stretch observed for both isomers). $^1H$ NMR ($CD_6H_6$, 298 K): Major diastereomer: $\delta$ 7.99 (s, 1H, O=C*H*), 7.69 – 5.82 (14H, $C_7H_5O_2$, $CH_3C_6H_4$COH), 2.21 (s, 3H, $CH_3C_6H_4COH$). Minor diastereomer: $\delta$ 7.93 (s, 1H, O=C*H*), 7.69 – 5.82 (14H, $C_7H_5O_2$, $CH_3C_6H_4$COH), 2.28 (s, 3H, $CH_3C_6H_4COH$). $^{13}C$ NMR ($CDCl_3$, 298 K): Major diastereomer: $\delta$ 21.2 (Ar-*C*H$_3$), 84.8 (*C*=O), 176.2, 176.6, 179.5, 185.5 (trop *C*-O), 229.9 (*C*≡O). Minor diastereomer: $\delta$ 22.1 (Ar-*C*H$_3$), 86.2 (*C*=O), 175.5, 177.2, 185.0 (trop *C*-O), 229.2 (*C*≡O). Both diastereomers: $\delta$ 124.9, 125.9, 127.3, 137.5, 128.2, 128.2, 128.5, 128.9, 129.9, 130.1, 132.1, 132.3, 134.3, 134.4, 137.5, 137.8, 137.9, 138.0, 138.8, 139.0, 139.4, 140.7, 132.5, 143.2, 145.8 (trop *C*-H, $CH_3C_6H_4CH$=O).

**W(CO)(trop)$_2$($\eta^2$-CH$_3$N=C(H)(p-tolyl)) (5).** 50 mg of **1** (0.098 mmol) was added to a Schlenk flask and dissolved in 50 mL of THF. 1.25 equivalents of CH$_3$N=C(H)(p-tolyl)*HCl (0.123 mmol, 20.7 mg) was added to a separate vial and 10 mL of THF was added. The iminium was deprotonated with potassium *tert*-butoxide (0.123 mmol, 13.8 mg). The solution containing the deprotonated imine was filtered into the solution containing **1** and the reaction mixture was stirred for 2 hrs until the solution turned dark blue. The solvent volume was removed *in vacuo*, and the resulting dark solid was dissolved in $Et_2O$ and filtered. Dark, needle-like crystals precipitated from the $Et_2O$ solution after storage at -33°C for several weeks (46 mg, 82 %). The ratio of diastereomers is 5:1. IR: ($CH_2Cl_2$), $\nu_{C\equiv O}$ 1846 $cm^{-1}$ (only 1 broad stretch observed for both isomers). $^1H$ NMR ($CDCl_3$, 298 K): Major diastereomer: $\delta$ 5.61 (s, 1H, *H*C=N), 3.95 (s, 3H, C=NC*H*$_3$), 2.40 (s, 3H, Ar-C*H*$_3$). Minor diastereomer: $\delta$ 5.75 (s,

**Table 2** Crystal data, data collection and structural refinement parameters for complexes, **1**, **2b**, and **5**.

| Complex | 1 | 2b | 5 |
|---|---|---|---|
| Formula | $C_{17}H_{10}O_7W$ | $C_{48.5}H_{37}ClO_{10}W$ | $C_{100}H_{94}N_4O_{21}W_4$ |
| Molecular Weight | 510.09 | 1182.93 | 2423.19 |
| Crystal System | Triclinic | Monoclinic | Monoclinic |
| Space Group | P-1 | P2(1)/n | C2/c |
| *a*/Å | 7.0951(8) | 10.6825(6) | 36.265(7) |
| *b*/Å | 7.2149(8) | 24.7828(12) | 14.093(3) |
| *c*/Å | 15.5637(18) | 15.8496(9) | 19.302(4) |
| *α*/° | 83.208(2) | 90.00 | 90 |
| *β*/° | 79.978(2) | 99.116(2) | 110.04(3) |
| *γ*/° | 87.293(2) | 90.00 | 90 |
| *V*/Å$^3$ | 778.76(15) | 4143.1 | 9268(4) |
| Color and habit | Red Blade | Purple Blade | Blue Plate |
| Crystal size/ mm | 0.26x0.10x0.08 | 0.16x0.10x0.03 | 0.17x0.17x0.08 |
| *Z* | 2 | 4 | 4 |
| Temperature/ K | 100(2) | 100(2) | 153(2) |
| Radiation type | MoK*α* | MoK*α* | MoK*α* |
| *D*(*calc*), g cm$^{-3}$ | 2.175 | 1.896 | 1.737 |
| *μ*/mm$^{-1}$ | 7.455 | 5.675 | 5.023 |
| Total reflections | 16242 | 77304 | 49279 |
| Unique reflections | 5860 | 15805 | 9492 |
| $R_{int}$ | 0.0181 | 0.0403 | 0.0970 |
| Final *R* indices [*I*>2σ(*I*)] | $R_1$ = 0.0165 $wR_2$ = 0.0387 | $R_1$ = 0.0307 $wR_2$ = 0.0526 | $R_1$ = 0.0371 $wR_2$ = 0.0551 |
| *R* indices (all data) | $R_1$ = 0.0182 $wR_2$ = 0.0394 | $R_1$ = 0.0536 $wR_2$ = 0.0579 | $R_1$ = 0.0886 $wR_2$ = 0.0679 |
| *GOF* | 1.050 | 1.007 | 0.995 |

1H, *H*C=N), 3.88 (s, 3H, C=NC$H_3$), 2.42 (s, 3H, Ar-C$H_3$). Bothdiastereomers: *δ* 7.82 – 6.73 (m, 14H, $C_7H_5O_2$, $CH_3C_6H_4C$=N). $^{13}$C NMR ($CDCl_3$, 298 K): Major diastereomer: *δ* 21.2 (Ar-*C*H$_3$), 44.1 (C=N*C*H$_3$), 58.6 (*C*=N), 126.4, 126.7, 126.8, 127.3, 127.8, 128.5, 129.3, 129.6, 130.3, 131.5, 139.4, 137.6, 139.2, 139.3, 139.9, 144.6 (trop *C*-H, $CH_3C_6H_4C$=N), 179.3, 179.5, 180.3, 185.2 (trop *C*-O), 236.4 (*C*≡O). Minor diastereomer: not observed. Isomers present in a 5:1 ratio. Satisfactory elemental analysis was not obtained despite multiple attempts.

**W(O)(trop)$_2$($\eta^2$-PhC≡CH) (6a).** Methylene chloride (10 mL) was added to a vial containing 20 mg (0.0360 mmol) of **2a**. 3-5 drops of a 30% by weight solution of $H_2O_2$ in $H_2O$ was added to the vial, and the resulting solution turned yellow after stirring for 5 minutes indicating the oxidation of **2a**. $MgSO_4$ was added and the solution was filtered to yield **6a** (17 mg, 0.0313 mmol, 83 %). IR spectroscopy confirmed the disappearance of the monocarbonyl stretch. **6a** can be purified on a silica column using $CH_2Cl_2$ to elute a yellow band. The ratio of diastereomers is 1.4:1. $^1$H NMR ($CD_2Cl_2$, 298 K): Major isomer: *δ* 11.16 (s, 1H, PhC≡C*H*, $^2J_{W-H}$ = 6.5 Hz), 8.04 – 6.77 (m, 15H, $C_7H_5O_2$, $C_6H_5C$≡CH). Minor isomer: *δ* 11.28 (s, 1H, PhC≡C*H*, $^2J_{W-H}$ = 6.9 Hz), 8.04 – 6.77 (m, 15H, $C_7H_5O_2$, $C_6H_5C$≡CH). Isomers present in 1.48:1 ratio. $^{13}$C NMR ($CDCl_3$, 298 K): Major isomer: *δ* 157.3 (PhC≡*C*H), 175.5 (Ph*C*≡CH), 180.1, 180.5, 181.4, 181.9 (trop *C*-O). Minor isomer: *δ* 164.4 (PhC≡*C*H), 169.5 (Ph*C*≡CH), 180.2, 181.0, 181.2, 181.5 (trop *C*-O). Both isomers: *δ* 126.8, 127.1, 127.56, 127.60, 127.7, 128.2, 128.4, 128.5, 128.6, 128.75, 128.80, 130.8, 131.0, 131.4, 132.1, 132.3, 132.6, 132.9, 136.4, 136.7, 138.9, 139.1, 139.57, 139.64, 139.7, 140.8, 140.9. (trop *C*-H, $C_6H_5C$≡CH). HRMS M+H Calcd: 545.06. Found 545.0541.

**W(O)(trop)$_2$($\eta^2$-PhC≡CMe) (6b).** Same as **6a** but using 20 mg of **2b** (0.0351 mmol) and yielding 18 mg of **6b** (0.0323 mmol, 88 %). The ratio of diastereomers is 1.4:1. $^1$H NMR ($CD_2Cl_2$, 298 K): Major isomer: *δ* 7.94 - 6.81 (15H, $C_7H_5O_2$, $C_6H_5C$≡$CH_3$), 3.28 (3H, s, PhC≡CC$H_3$). Minor isomer: *δ* 7.94 - 6.81 (15H, $C_7H_5O_2$, $C_6H_5C$≡$CH_3$), 2.87 (3H, s, PhC≡CC$H_3$). Isomers present in 1.42:1 ratio. $^{13}$C NMR ($CDCl_3$, 298 K): Major isomer: *δ* 15.5 (PhC≡C*C*H$_3$), 167.2 (PhC≡*C*CH$_3$), 167.3 (Ph*C*≡CCH$_3$). Minor isomer: *δ* 16.8 (PhC≡C*C*H$_3$), 160.3 (PhC≡*C*CH$_3$), 174.9 (Ph*C*≡CCH$_3$). Both isomers: 124.0, 125.5, 126.6, 126.7, 127.3, 127.35, 127.42, 127.7, 127.9, 128.12, 128.14, 128.19, 128.20, 128.4, 130.76, 130.79, 131.1, 131.3, 131.4, 132.1, 137.6, 138.3, 138.9, 139.2, 139.5, 139.6, 139.7, 140.1, 140.8, 140.9 (trop *C*-H, $C_6H_5C$≡$CCH_3$), 180.1, 180.2, 180.6, 181.1, 181.1, 181.3, 181.4, 182.0 (trop *C*-O). Anal. Calcd for $C_{23}H_{18}O_5W$*1/3$CH_2Cl_2$: C, 47.78; H, 3.21; N, 0.00. Found: C, 47.89; H, 3.30; N, <0.02. HRMS M+H Calcd: 559.07. Found 559.0696.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic information files (cif) for complexes **1**, **2b**, and **5**,; CCDC reference numbers c. See DOI: 10.1039/b000000x/

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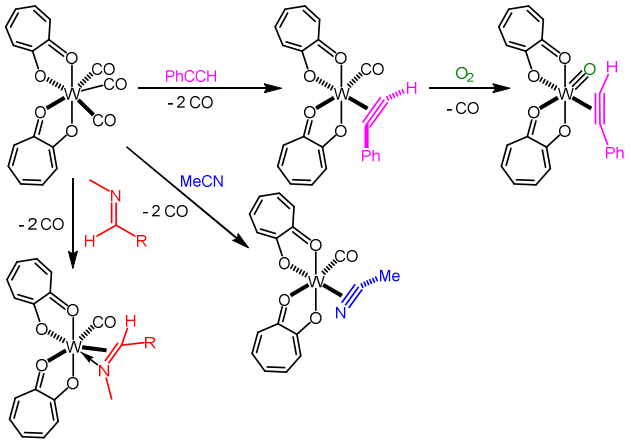


The bis-tropolonate tungsten(II)tricarbonyl compound, $(trop)_2W(CO)_3$ will preferentially bind nitriles, imines, and aldehydes in a side-on fashion. Cyrstallographic analysis of the imine adduct supports the postulation of 4-electron donation from the imine.