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The chiral bis-tropolonate tungsten(II) tricarbonyl compound, \((\text{trop})_2\text{W(CO)}_3\) (1), has been synthesized and structurally characterized. This seven-coordinate compound readily loses two carbonyl ligands to preferentially bind a series of \(\pi\)-bonding substrates to form six-coordinate complexes of the type \((\text{trop})_2\text{W(CO)}(\eta^2-RCCR)\) (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 \(^{13}\text{C}\) NMR confirms the nitriles are coordinated in an \(\eta^5\) 4-electron donating capacity. Aldehydes, ketones, and imines also react with 1 to form 4-electron donor \(\eta^2\) adducts. The imine adduct \((\text{trop})_2\text{W(CO)}(\eta^2-\text{MeN=C(H)(tol)})\) (5) was characterized crystallographically and the short 1.91 \(\text{A}\) W-N bond distance supports the postulation of 4-electron donation from the imine through \(\text{C=N}\) \(\pi\)-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 \(\text{W}^{\text{IV}}\) oxo alkyne species, \((\text{trop})_2\text{W(O)(\eta^2-RCCR)}\) (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 \(\pi\)-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 \(\pi\)-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, \(^7\) oxidation at the nitrile C-atom, \(^8\) and electrophilic addition to the lone pair on the N-atom. \(^9\) Heteroatom-containing unsaturated substrates, such as ketones and imines can also bond in a \(\eta^2\)-fashion, but again this is an uncommon coordination mode. \(^6\) 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) \(\pi\) 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 of double bond character between the metal atom and the heteroatom of these substrates when \(\eta^2\)-bound.\(^10\) The fourteen-electron (acac)\(_2\text{W}^{\text{IV}}\text{(CO)}\) (acac = acetylacetonate) scaffold has been proven to be effective for coordinating a variety of nitriles, imines, and ketones in an \(\eta^2\)-fashion.\(^4\)\(^\text{d-f}11\)

![Figure 1. Coordination of ketones and imines as 2 and 4 electron donors.](image.png)

One of the drawbacks to the acac ligands that have been used previously to stabilize \(\text{W}^{\text{IV}}\) 4-electron donor complexes is the reactivity of the methyl groups, which are prone to deprotonation by strong bases. Additionally, the acac ligands are nucleophileic at the \(\beta\)-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 nitride ligands in an η² fashion. The tropolonate ligand fills the gap between the 4 and 6 membered rings and can perhaps combine advantages of both. The acac-based nitride/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 d⁴ (trop)₂W⁶(CO) (trop = tropolonate) fragment and alkynes, nitriles, imines, and ketones in an η²-fashion. The parent complex, (trop)₂W⁶(CO)₄, releases 2 equivalents of CO upon reaction with an alkyne, nitrile, imine, or ketone (L) and binds the unsaturated substrate in an η² fashion to form complexes of the type (trop)₂W⁶(CO)(η²-L). The complexes presented here are sensitive to air oxidation, and the alkyne complexes readily form WIV oxides. We also report mechanistic investigations on the exchange of η²-ketones and η²-nitriles and discuss the implications of these studies on the nature of the η² 4-electron interaction.

Results and Discussion

Formation of (trop)₂W⁶(CO)₃

The parent tricarbonyl complex (trop)₂W⁶(CO)₃, I, forms by reacting two equivalents of [HNEt₃][trop] and [NEt₃][W(CO)₆(I)]³⁻; the complex is dark red with a high absorption coefficient. I 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 1391 cm⁻¹ which are about 7–8 cm⁻¹ lower than those for (acac)₂W⁶(CO)₃ indicating that the tropolonate ligands are slightly more donating than the acac ligands. 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 alkene and is similar to the value of 12.95 observed for (acac)₂W⁶(CO)₃(PhCHCH). The room temperature ¹³C NMR spectrum of 2a shows that the carbonyl carbon resonates at 240.9 ppm, in accord with the resonances of known analogous W monocarbonyl species. The carbons of the η²-alkyne were identified at 186.5 and 207.6 ppm.

Figure 2. X-ray structure of (trop)₂W⁶(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(15)-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).

50 The two isomers arising from PhCHCH 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 I with 1-phenyl-1-propyne forms...
Carbons resonate at 195.4 and 201.1 ppm and the peak for the methyl protons resonate as a singlet at 3.44 ppm. The alkyne stretching frequency of 1881 cm⁻¹.

The WRC bond distance of the alkyne is 1.316 Å, indicative of a CRC double bond in a metallocyclopropene. The WRO bond distances of the alkyne are 2.02 Å and 2.06 Å, comparable to those of (acac)₂W(CO)(PhCCMe) (2b), the formation of a monocarboxyl species was indicated by in situ IR spectroscopy with a CO stretch at 1895 cm⁻¹.

Crystals of 2b were obtained from a mixture of CH₂Cl₂/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 2.10 Å, slightly shortened from the W-O bond distances in 1. In accordance with similar acac complexes, 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 1.316 Å, 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 metalloccylopropene. The W-C bond distances of the alkyne are 2.02 Å and 2.06 Å, comparable to those of (acac)₂W(CO)(PhCCCH) (3b).

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 alkyne methyl protons appear at 1.5 ppm downfield shift from free acetonitrile. Furthermore, addition of benzyl nitrile to 1 forms (trop)₂W(CO)(η²-NCCPh₂) (3c), as evidenced by the diastereotopic methylene group resonating 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 CH₂Cl₂/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 2.10 Å, slightly shortened from the W-O bond distances in 1. In accordance with similar acac complexes, 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 1.316 Å, 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 metalloccylopropene. The W-C bond distances of the alkyne are 2.02 Å and 2.06 Å, comparable to those of (acac)₂W(CO)(PhCCCH) (3b).

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).
Relectron configuration, resulting in weaker binding and side Ron coordination of nitriles may be less necessary to reach an from the trop oxygens versus acac oxygens; if this is the case the CO stretches in the trop complexes may be increased  πRdonation.

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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 η₂-4e-donor fashion like the aldehydes. Addition of CH₂N=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 \((\text{trop})_2 \text{W(CO)}(\eta^2-\text{CH}_2\text{N}=\text{C(H)(p-tolyl)})\) (5). The formation of a monocarbonyl species was confirmed by the single broad CO stretch at 1846 cm\(^{-1}\) in the \(\text{CH}_2\text{Cl}_2\) solution IR spectrum. The imine C-H appears shifted upfield to 6.02 ppm in the \(^1\text{H}\) NMR and the imine carbon appears at 59.8 ppm in the \(^{13}\text{C}\) 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 high 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 η²-nitriles and η²-ketone compounds, are stabilized by the presence of excess ligand in solution. For example, \((\text{trop})_2 \text{W(CO)}(\eta^2-\text{acetone})\) (4a) is indefinitely stable when stored under N\(_2\) in acetonitrile, but will decompose in a day if stored in CH\(_2\)Cl\(_2\). It is reasonable that the decomposition pathway of the complex first involves the dissociation of the η²-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 η²-acetone by acetone-d\(_6\) via \(^1\text{H}\) 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 \(^1\text{H}\) 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...
donor complexes and particularly the alkynes are resistant towards exchange. The bulkier substrates, such as MeN=C(H)(tol) and Ph$_2$HCCN 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)$_2$W(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)$_2$W$^{II}$ complexes are highly sensitive to oxidation by O$_2$ in air. Formation of I 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$_2$Cl$_2$ solution of 2 will oxidize in ~4 hr when stirred with Na$_2$SO$_4$, presumably with formation of Na$_2$SO$_3$. A stronger oxidant, such as H$_2$O$_2$, will complete the reaction in less than 5 min. The alkyne derivatives undergo loss of CO and 2-electron oxidation to (trop)$_2$W$^{IV}$(O)(η$^2$-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)$_2$W$^{II}$(CO) complexes have been oxidized by MCPBA, diazoalkanes, or azides, but the compounds do not oxidize in air even on long timescales.

Oxidation of 2b results in the formation of (trop)$_2$W(O)(η$^2$-PhC≡CMe) (6b). As consistent with the known tungsten-oxo alkyn 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)$_2$W(O)(η$^2$-PhC≡CH) (6a). The room temperature $^1$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. This supports the notion that the π-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 π-donate into the empty d$_{xz}$ and d$_{yz}$ orbitals, allowing it to provide up to 6 electrons to the metal between the σ and two π bonds. The alkyne can donate between 2 and 4 electrons depending on the amount of π-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 alkyl and oxo are competing for donation into the d_{xy} orbital and the spectroscopic data suggests roughly equal contribution from both ligands, so this could be considered a 3-electron donor alkyl and 5 electron donor oxo for an 18 electron complex. To accomplish this bonding scheme, the alkyl 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_{xy} orbitals leaving the alkyne ligand in the xy plane for backbonding from d_{xy} into the alkyl π* orbital (Figure 7). There is a with a high barrier to alkyne rotation so two diasteroemers are seen at room temperature.

Conclusions

We have synthesized a series of bis-tropolonate W compounds that coordinate a variety of unsaturated ligands in an η^2 fashion as 4-electron donors. These compounds bind preferentially nitriles, imines, ketones and aldehyde compounds in an η^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 tropolone 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 alkyl complexes can be cleanly oxidized in air to form W(oxo) oxo alkyl species. It may be possible to take advantage of this behavior to use similar complexes as oxidation catalysts with O2 as the terminal oxidant in the future. Attempts to functionalize η^2 nitriles with either electrophilic or nucleophilic reagents have not resulted in stable products. Despite the significantly lower pKa of tropolone versus acetone, the tropolone complexes have lower CO stretches than their acetylacetonate analogs; this seems to indicate that the bite angle of the tropolone ligands allows for more π donation from the oxgens to the tungsten and this overcomes the reduced sigma donation. Future use of 3,7 substituted tropolones 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. NMR solvents CDCl3, CDC13, CD2D, and acetone-d6 were dried by passage through a pipet containing activated alumina in the glove box. [NEt4][W(CO)3] was synthesized according to published procedures. 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 (MAI) method with 3-nitrobenzonitrile as the matrix and an inlet temperature of 75 °C. W(CO)3(trop)_2 (1). In a 500 mL Schlenk flask, [NEt4][W(CO)3] (1 g, 1.72 mmol) was dissolved in CH2Cl2 (150 mL). Stoichiometric addition of elemental iodine (435 mg, 1.72 mmol) resulted in the immediate formation of the orange [NEt4][W(CO)3I] 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 CH2Cl2 (10 mL) was prepared. This mixture was combined with the solution containing [NEt4][W(CO)3I] and then stirred for 12 h at 10 °C 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: (CH2Cl2) νCO = 2020, 1917 cm⁻¹. 1H NMR ([CD2]Cl2, 298 K): δ 7.54 - 7.02 (10H, C-H(O2)). 13C NMR (CD2Cl2, 200 K): δ 118.1, 127.6, 129.8, 138.0, 139.6, 149.4, 161.1, 174.0, 181.9. Anal. Calc'd for C17H16O4: W: C, 53.8; H, 7.6; N, 0.0. Found: C, 41.29; H, 3.94; N, <0.02. Multiple attempts to achieve satisfactory elemental analysis were unsuccessful.

W(CO)3(trop)_3(q°-PhC≡CH) (2a). In a 500 mL Schlenk flask, [NEt4][W(CO)3I] (600 mg, 1.03 mmol) was dissolved in CH2Cl2 (100 mL). Stoichiometric addition of elemental iodine (261 mg, 1.03 mmol) resulted in the immediate formation of the orange [NEt4][W(CO)3I] 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 CH2Cl2 (10 mL) was prepared. This mixture was combined with the solution containing [NEt4][W(CO)3I] 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 mL, 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 CH2Cl2/THF to elute a dark purple band (257 mg, 0.462 mmol, 45%). IR: (CH2Cl2, νCO) 1889 cm⁻¹. 1H NMR ([CD2]Cl2, 298 K): δ 13.04 (s, 1H, PhC≡C≡CH), 7.83-6.93 (m, 15H, C-H(O2), C-H(C≡CH)). 13C NMR ([CD2]Cl2, 298 K): δ 126.4, 127.1, 127.4, 128.5, 129.6, 130.1, 132.0, 137.3, 137.7, 139.0, 139.2, 140.3, 140.4 (trop C-H, C-H(C≡CH)), 171.9, 179.4, 180.4, 184.5 (trop C=O), 186.5 (Ph=CH), 207.6 (Ph=CH), 240.9 (C=O). Elemental Analysis C23H16O4W Theoretical: C, 49.67, H, 2.90, N 0.00; Found: C, 49.81, H, 3.09, N <0.02.

W(CO)3(tro)(η°-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 CH₂Cl₂ with hexanes. IR: (CH₂Cl₂), ν CO = 1895 cm⁻¹. 

ΔH NMR (CD₂Cl₂, 298 K): δ: 8.05 (d, 2H, C₆H₅O₂), 7.30 (m, 3H, m-C₆H₅C=CMc, p-C₆H₅C=CMc), 7.04 (m, 2H, o-C₆H₅C=CMc), 6.92 (d, 1H, C₆H₅O₂), 6.78 (d, 1H, C₆H₅O₂), 6.52 (t, 1H, C₆H₅O₂), 6.43 (t, 2H, C₆H₅O₂), 6.25 (t, 1H, C₆H₅O₂), 6.15 (t, 1H, C₆H₅O₂), 6.04 (t, 1H, C₆H₅O₂), 3.44 (s, 3H, PhC=CH₂). ¹³C NMR (CD₂Cl₂, 298 K): δ: 214.1 (PhC≡CH₂), 125.4, 125.7, 128.0, 128.3, 128.4, 130.1, 130.9, 136.3, 138.0, 133.8, 138.9 (C₆H₅C=CH₃, trop C-H), 180.2, 180.9, 181.0, 185.0 (trop C-O), 195.4 (PhC≡CH₂), 201.1 (PhC≡CH₂), 240.7 (C=O). Elemental Analysis C₆H₅CH₂O₡W Theoretical: C 50.55, H 3.18, N 0.00; Found: C 50.08, H 2.94, N <0.2.

W(CO)(trop)₂(η²-CH₂CN) (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 η²-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: (CH₂Cl₂), ν CO = 1878 cm⁻¹. ¹H NMR (CD₂Cl₂, 298 K): δ 7.95 (d, 2H, C₆H₅O₂), 7.79 - 7.65 (m, 2H, C₆H₅O₂), 7.45 - 7.39 (m, 2H, C₆H₅O₂), 7.33 - 7.25 (m, 2H, C₆H₅O₂), 7.03 (d, 1H, C₆H₅O₂), 6.89 (t, 1H, C₆H₅O₂), 2.61, 2.21 (each a s, 3H, CH₃). ¹³C NMR (CD₂Cl₂, 298 K): δ 32.2, 32.6 (acetone CH₃), 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(η²-Ar(C≡C)O)(Ar = 2,6-dichlorobenzene) (4b). A scintillation vial was charged with 20 mg (0.039 mmol) of I and 10 mL of CH₂Cl₂. Excess 2,6-dichlorobenzaldehyde (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 η²-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: (CH₂Cl₂), ν CO = 1878 cm⁻¹. ¹H NMR (CD₂Cl₂, 298 K): δ 8.12 (s, 1H, O=C=O), 7.96 - 6.87 (13H, C₆H₅O₂, C₆H₅COH). ¹¹C NMR (CD₂Cl₂, 298 K): δ 82.0 (O=CH), 127.8, 128.5, 128.9, 129.0, 129.6, 130.3, 134.2, 134.3, 134.4, 138.9, 139.2, 139.3, 139.9, 140.1, 141.6 (trop C-H, C₆H₅CH₂COH), 177.3, 177.5, 179.7, 184.9 (trop C-O), 232.1 (C=O).

W(CO)(trop)₂(η²-Ar(C≡C)O)(Ar = p-tolyl) (4c). Same as 4b. but using p-tolualdehyde. The ratio of diastereomers is 2.3:1. IR: (CH₂Cl₂), ν CO = 1858 cm⁻¹ (only 1 broad stretch observed for both isomers). ¹H NMR (CD₂Cl₂, 298 K): Major diastereomer: δ 7.99 (s, 1H, O=CH), 7.69 - 5.82 (14H, C₆H₅O₂, CH₃CH₂COH). Minor diastereomer: δ 7.93 (s, 1H, O=CH), 7.69 - 5.82 (14H, C₆H₅O₂, CH₃CH₂COH). ¹¹C NMR (CD₂Cl₂, 298 K): Major diastereomer: δ 21.2 (Ar-CH₃), 84.8 (C-O), 176.2, 176.6, 179.5, 185.5 (trop C-O), 229.9 (C=O). Minor diastereomer: δ 22.1 (Ar-CH₃), 86.2 (C-O), 175.5, 177.2, 185.0 (trop C-O), 229.2 (C=O). Both diastereomers: δ 124.9, 125.9, 127.3, 137.5, 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, 139.0, 139.4, 140.7, 143.2, 145.8 (trop C-H, CH₃CH₂CH₂O₡).

W(CO)(trop)₂(η²-C₆H₅N=CH(C(H)(p-tolyl)) (5). 50 mg of I (0.098 mmol) was added to a Schlenk flask and dissolved in 50 mL of THF. 1.25 equivalents of CH₃N=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 I 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 Et₂O and filtered. Dark, needle-like crystals precipitated from the Et₂O solution after storage at -33°C for several weeks (46 mg, 82 %). The ratio of diastereomers is 5:1. IR: (CH₂Cl₂), ν CO = 1846 cm⁻¹ (only 1 broad stretch observed for both isomers). ¹H NMR (CDCl₃, 298 K): Major diastereomer: δ 5.61 (s, 1H, CH≡N), 3.95 (s, 3H, C≡CH₂). Minor diastereomer: δ 5.75 (s, 3H, C≡CH₂).
Table 2 Crystal data, data collection and structural refinement parameters for complexes, 1, 2b, and 5.

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Acknowledgments

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Notes and references


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The bis-tropolonate tungsten(II)tricarbonyl compound, \((\text{trop})_2\text{W(CO)}_3\), will preferentially bind nitriles, imines, and aldehydes in a side-on fashion. Crystallographic analysis of the imine adduct supports the postulation of 4-electron donation from the imine.