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Bis(acetylacetonate) Tungsten(IV) Complexes Containing a π-Basic Diazoalkane or Oxo Ligand

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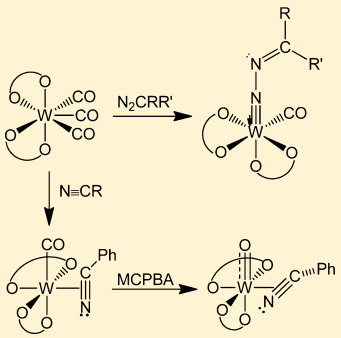
Supporting Information

ABSTRACT: Tungsten(IV) bis(acetylacetonate) (acetylacetonate = acac) complexes were synthesized by incorporating either a diazoalkane or an oxo ligand into the coordination sphere of a tungsten(II) reagent. The reaction of free diazoalkane (N_2CRR') with $W(CO)_3(acac)_2$ leads to loss of two carbon monoxide ligands and coordination of the diazoalkane reagent through the terminal nitrogen to produce $W(CO)(acac)_2(N_2CRR')$. This monomer is best formulated as a tungsten(IV) complex. A second example of converting a d^4 tungsten carbonyl complex to a d^2 product involves oxidation of $W(CO)(acac)_2(PhC{\equiv}N)$ with *m*-chloroperoxybenzoic acid (MCPBA) to replace the CO ligand with an oxygen atom. This increase in metal oxidation state causes rotation of the nitrile ligand by 90° relative to the two bidentate acac ligands. Electrophilic addition at the nitrogen of the π-bound nitrile ligand using methyl triflate (MeOTf) and subsequent nucleophilic addition at carbon with sodium trimethoxyborohydride, $Na[HB(OMe)_3]$, reduces the C≡N bond stereoselectively and produces the neutral imine complex $W(O)(acac)_2(PhHC{=}NMe)$ with a diastereomeric ratio of 11:1.



INTRODUCTION

The reduction of carbon−nitrogen multiple bonds is an important topic spanning several branches of chemistry. In organometallic chemistry, one example of such a reduction is seen in the homogeneous hydrogenation of nitriles.[1−6] Stepwise reduction of σ-bound nitriles to amines has been achieved at a single metal site.[7−9] Sequential addition of nucleophiles and electrophiles to the carbon−nitrogen triple bond produces stepwise reduction of the acetonitrile ligand in $[Tp'W(CO)(RC{\equiv}CR')(N{\equiv}CMe)][BF_4]$.[8,9] Reduction of the carbon−nitrogen bond in diazoalkane ligands ($M{=}N{-}N{=}CR_2$) is another example of metal activation of ligand −C═N− moieties toward the addition of electrophiles and/or nucleophiles.[10−13]

Reduction of a π-bound nitrile ligand to a π-bound iminium ligand has been accomplished in a tungsten(II) bis(acetylacetonate) system by introducing a variable-electron-donating alkyne ligand into the coordination sphere.[14,15] Replacement of the carbon monoxide ligand in the W(II) complex $[W(CO)(\eta^2\text{-}RN{=}CR)(acac)_2]^+$ with a variable electron donor alkyne ligand relieved the iminoacyl ligand of its responsibility to function as a four-electron donor to tungsten. Following addition of a nucleophile to the carbon of the reduced nitrile the nitrogen lone pair of the η^2-imine ligand is available to electrophilic reagents to yield a π-iminium ligand.

We have described a number of tungsten(II) bis(acetylacetonate) complexes with two π-acids in the coordination sphere.[14−17] We now report oxidation of the metal to generate tungsten(IV) bis(acetylacetonate) d^2 complexes with π-basic diazoalkane or oxo ligands in the coordination sphere. We have previously reported the formation of tungsten(IV) oxo complexes in our attempts to produce tungsten imido species.[18] Additionally, sequential diastereoselective reduction of a π-bound nitrile to an imine ligand in a tungsten(IV) oxo coordination sphere is reported.

RESULTS AND DISCUSSION

W(IV) Diazoalkane Synthesis. Three coordination modes are possible for diazoalkane ligands in monomeric metal complexes: side-on coordination through the N−N π-bond or, more commonly, σ-coordination through either nitrogen or the carbon.[10−13] Many stable σ-coordinated diazoalkane complexes have been isolated without extrusion of the N_2 fragment, although thermolysis often leads to N_2 elimination to form metallacarbene complexes or decomposition products.[10−13,19,20] Previous success promoting η^2-coordination of ligands such as nitriles, ketones, and aldehydes to the $W(CO)(acac)_2$ moiety led us to ask whether η^2-coordination of diazoalkane ligands might be possible with this d^4 fragment.

Addition of 1 equiv of (trimethylsilyl)diazomethane to a CH_2Cl_2 solution of $W(CO)_3(acac)_2$ leads to a color change from light brown to green-brown (eq 1). Monitoring the reaction progress via *in situ* IR spectroscopy reveals a single CO absorbance at 1915 cm^{-1} after 30 min, indicative of loss of 2 equiv of carbon monoxide. ^1H NMR spectroscopy indicates formation of a bis(acac) tungsten species with the presence of a trimethylsilyl signal as well as a signal for one proton at 8.00 ppm, compatible with formation of $W(CO)(acac)_2(N_2CHSiMe_3)$ (**1-N_2CHSiMe$_3$**). This result follows

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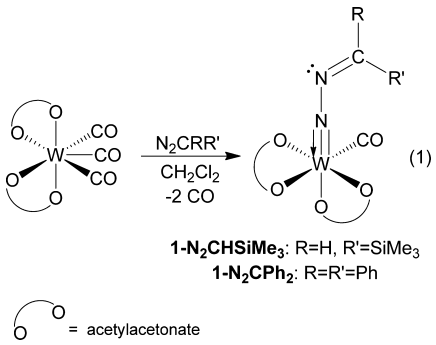

the pattern of reactivity reported by Hillhouse and Haymore in which addition of diazoalkane to $W(CO)_3(S_2CNR_2)_2$ forms a monocarbonyl complex with terminally bound diazoalkane.[21] A ^{13}C NMR signal at 168 ppm for the diazomethane carbon of **1-N_2CHSiMe$_3$** is in the range for end-on coordination of the terminal nitrogen. The ^{13}C NMR signal is broad due to the influence of the adjacent quadrupolar nitrogen. ^{13}C NMR spectroscopy also reveals a lone metal carbonyl signal downfield at 267 ppm.

Reacting diphenyldiazomethane with $W(CO)_3(acac)_2$ produces $W(CO)(acac)_2(N_2CPh_2)$ (**1-N_2CPh$_2$**), a diphenyl analogue of **1-N_2CHSiMe$_3$** (eq 1), with an infrared absorbance at 1910 cm^{-1} for the lone CO ligand. A ^{13}C NMR spectrum of $W(CO)(acac)_2(N_2CPh_2)$ exhibits a carbon monoxide signal at 269 ppm with tungsten satellites ($^1J_{C-W}$ = 209 Hz). The diazomethane N=*C* carbon signal at 161 ppm also presents with tungsten satellites ($^3J_{C-W}$ = 7 Hz).

1-N_2CPh$_2$ was concentrated in a solution of methylene chloride and stored under N_2 at −35 °C. Green-brown X-ray quality crystals formed after four weeks. As anticipated from ^{13}C NMR data, the solid-state structure shows end-on coordination of the diphenyldiazomethane ligand (Figure 1).

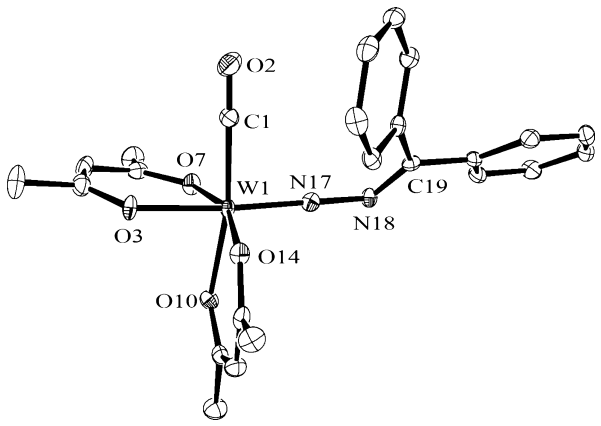

Figure 1. ORTEP diagram (50% ellipsoids) of $W(CO)(Ph_2CN_2)(acac)_2$, **1-N_2CPh$_2$**. Hydrogen atoms and one molecule of CH_2Cl_2 solvent are omitted. Selected interatomic distances (Å) and bond angles (deg): W1−N17 = 1.796(3), N17−N18 = 1.310(4), N18−C19 = 1.302(4), W1−C1 = 2.003(3), W1−O3 = 2.087(2), W1−O7 = 2.065(2), W1−O10 = 2.122(2), W1−O14 = 2.090(2), W1−N17−N18 = 177.2(2), N17−N18−C19 = 120.8(3), O3−W1−O7 = 84.10(9), O10−W1−O14 = 85.94(9).

The W1−N17−N18 linkage is nearly linear (177°), and the N17−N18−C19 linkage is bent; the angle of 121° is in accord with an sp^2-hybridized nitrogen. The W1−N17 bond length is 1.80 Å, while the N17−N18 bond length is 1.31 Å and the N18−C19 bond length is 1.30 Å. The bond lengths are consistent with six-electron donation from the terminal nitrogen to the metal center via a multiple bond.[10,11,13]

Two different formalisms, both valid, exist for evaluating the electron donation of the diazoalkane ligand.[13] In the neutral formalism the ligand bears no charge and donates four electrons to the metal through two covalent bonds and one dative bond. In the ionic formalism, the ligand is considered to be reduced by two electrons to form a hydrazonido moiety with a −2 charge. The hydrazonido ligand donates six electrons to the d^2 W(IV) metal center through one σ- and two π-interactions. The diazoalkane complexes reported here are described using the ionic formalism.

Oxidation of W(II) Alkyne Carbonyl Complexes to W(IV) Alkyne Oxo Complexes. Preparation of W(IV) bis(acetylacetonate) complexes with diazoalkane reagents led us to search for other oxidants that could produce multiply bound ligands in our tungsten bis(acac) system. For octahedral group VI complexes, π-conflicts invariably exist between carbonyl ligands and multiply bound, cylindrically symmetric carbyne or oxo ligands.[22−26] In the case of carbonyl−oxo complexes, the carbonyl and oxo ligands prefer a *cis* geometry to minimize sharing dπ orbitals in this mixed π-acid/π-base system. In contrast, the use of a single-faced π-acid such as an olefin or an alkyne allows selective stabilization of a single dπ orbital to accommodate a π-base and a π-acid in the same coordination sphere. Therefore, mixing oxo ligands with single-faced π-acid ligands should be possible in the coordination sphere of W(IV) d^2 bis(acetylacetonate) complexes.

Oxidation of metal carbonyl species by a metal oxo transfer oxidant, O_2, or other oxidants is well-known.[25−43] Of the group VI metals, molybdenum−oxo linkages have received considerable attention due to their presence in biological enzymes.[37−40] Tungsten−oxo complexes have been implicated as both precursors and active species in olefin metathesis.[43,44] Additionally, a number of tungstoenzymes have received attention in recent years.[39,40]

The oxo ligand, O^{2-}, can be described as a closed-shell anion with a −2 oxidation state.[26] Metal−oxo π-bonding can occur when a metal possesses empty dπ orbitals, hence the prevalence of oxo complexes with high-valent metal centers. When the oxo ligand functions as a dianionic ligand and as a six-electron donor, it can be drawn as a triple bond, as is usually seen for mono-oxo metal complexes. In this work, our focus will be on examples illustrating oxygen atom replacement of CO to produce monomers reflecting simple replacement of CO with O, a formal two-electron oxidation of the metal.

Previous work has explored similar oxidations in the tungsten bisdithiocarbmate system in which an oxygen atom transfer reagent reacts with $W(CO)(S_2CNR_2)_2(\eta^2$-RC≡CR) to form $W(O)(S_2CNR_2)_2(\eta^2$-RC≡CR).[31] Although pyridine N-oxide has proven to be a convenient reagent in numerous group 6 oxidation reactions,[25,41,42] our efforts to oxidize $W(CO)(acac)_2(\eta^2$-PhC≡CH) with pyridine N-oxide were unsuccessful. However, treatment of $W(CO)(acac)_2(\eta^2$-PhC≡CH) (**1-PhC≡CH**) with *m*-chloroperoxybenzoic acid (MCPBA)[45,46] in methylene chloride at 0 °C leads to clean formation of the neutral oxo complex $W(O)(acac)_2(\eta^2$-PhC≡CH) (**2-PhC≡CH**) (eq 2). IR spectroscopy shows the disappearance of a CO absorbance at 1900 cm^{-1} and the appearance of a W=O absorbance at 950 cm^{-1}.

At room temperature, the ^1H NMR spectrum of **2-PhC≡CH** shows a mixture of two isomers in a 1.2:1 ratio.

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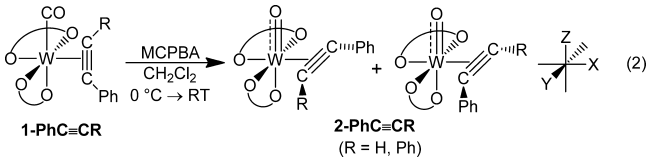

The isomers stem from the 90° rotation of the terminal alkyne ligand from the *xz* plane of the starting materials into the *xy* plane upon coordination of the π-basic oxo ligand (the carbonyl and oxo ligands are sited on the *z*-axis) to produce two rotamers. The parent carbonyl complex **1-PhC≡CH** displays a broad singlet at ~13.0 ppm at room temperature, indicative of alkyne rotation on the NMR time scale. In contrast, the phenylacetylene ligand in the oxo analogue **2-PhC≡CH** does not freely rotate on the NMR time scale. At room temperature two sharp singlets are observed for the terminal alkyne proton at 11.38 and 11.11 ppm, each accompanied by tungsten satellites ($^2J_{W-H}$ = 14 Hz), corresponding to the two distinct spatial arrangements (along either the +*y* or the −*y* axis) of the terminal acetylenic hydrogen.

The symmetric diphenylacetylene derivative W(O)(acac)$_2$(η^2-PhC≡CPh) (**2-PhC≡CPh**) was synthesized to avoid the complications arising from two isomers (eq 2). This complex is more stable than its phenylacetylene counterpart with no decomposition observed after exposure to air for 1 h. In the ^{13}C NMR spectrum of **2-PhC≡CPh**, the two alkyne carbon signals resonate at 172 and 167 ppm, in the range for a three-electron donor alkyne.[47] As is often the case, the oxo ligand can be drawn as either doubly or triply bonded to indicate oxo-to-metal π-bonding. Complexes boasting an alkyne *cis* to an oxo ligand have been investigated, and for metal centers with d^2 configurations it is clear that the alkyne $\pi_\perp$ orbital and a p orbital on the oxo ligand compete for electron donation into a vacant dπ metal orbital to generate a three-center four-electron bond.[27−34]

The solid-state structure of **2-PhC≡CPh** shows the alkyne ligand arranged *cis* to the newly minted oxo ligand, as in the analogous CO complex **1-PhC≡CH** (Figure 2).[17] Note that the C−C bond of the alkyne is perpendicular to the W−O bond of the oxo linkage. This contrasts with the similar precursor alkyne−CO complex, W(CO)(acac)$_2$(η^2-PhC≡CH), in which the C−C alkyne bond is oriented parallel to the W−CO axis of the carbonyl ligand.[17] Oxidation from a d^4 to a d^2 metal center causes rotation of the single-faced π-donor alkyne ligand by 90°, as has been noted in similar carbonyl-to-oxo transformations.[27−34] The W1−C2 and W1−C3 metal−alkyne bonds have lengthened to 2.10 and 2.09 Å from 2.04 Å for the analogous bonds in the precursor complex, indicating decreased bonding to the alkyne ligand. The C2−C3 bond lengthens only slightly to 1.308 Å from 1.302 Å, showing virtually no loss of triple-bond character. Given that the alkyne provides both σ and π forward donation to the metal and accepts metal dπ electron donation into $\pi_\parallel$*, a decrease in $\pi_\perp$ donation from the alkyne seems most likely to cause the lengthening of the M−C bonds. The metal oxygen bond distance is 1.71 Å, typical for mono-oxo tungsten complexes.[26,48]

Orbital Interactions in W(II) and W(IV) Octahedral Complexes. Oxidation of the W(CO)(acac)$_2$(η^2-RC≡CR) system to replace carbon monoxide with an oxo ligand illustrates the interplay of d electron configuration with ligand orientation.[26−35] The W(O)(acac)$_2$ fragment is unambiguously a W(IV) d^2 fragment. The extent of π-donation from O^{2-} is variable and complicates simple electron counting, as shown by our depiction of the tungsten−oxo bond with a dashed bond. Adding an alkyne ligand provides additional electrons, also variable, but surely in accord with a full valence shell. Sitting on the *z* axis, the π-basic oxo ligand, counted as O^{2-}, donates into the vacant d$_{xz}$ and d$_{yz}$ orbitals, raising the energies of those orbitals as they dominate the antibonding molecular orbitals (Figure 3). Coordination of the alkyne ligand along the *x* axis stabilizes the two electrons in the d$_{xy}$ orbital via back-bonding to the alkyne $\pi^*_\parallel$. Donation from $\pi_\perp$ on the alkyne ligand further raises the energy of the d$_{xz}$ orbital as it becomes the most antibonding of a three-center−four-electron π-bonding scheme.[33] In contrast, if the alkyne ligand is aligned parallel to the metal−oxo axis, it will act as a π-acceptor for the d$_{xz}$ orbital and a π-donor for the d$_{xy}$ orbital, resulting in π-conflicts for both of these dπ orbitals.

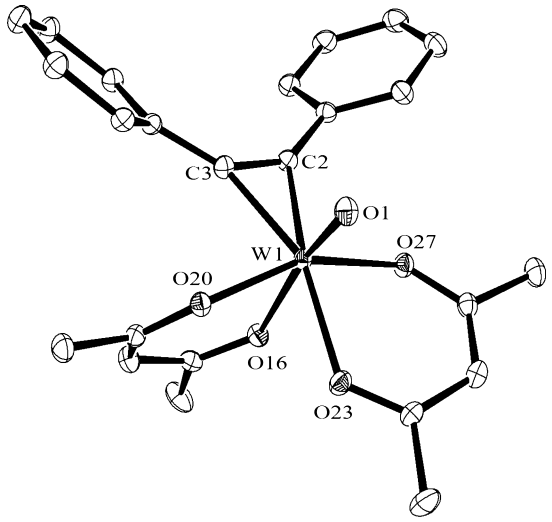

Figure 2. ORTEP diagram (50% ellipsoids) of W(O)(acac)$_2$(η^2-PhC≡CPh), **2-PhC≡CPh**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and bond angles (deg): W1−O1 = 1.7145(12), W1−C2 = 2.0973(14), W1−C3 = 2.0939(14), W1−O16 = 2.1636(12), W1−O20 = 2.0712(11), W1−O23 = 2.1519(11), W1−O27 = 2.0671(11), C2−C3 = 1.3075(19), O16−W1−O20 = 81.30(4), O23−W1−O27 = 82.63(4), C2−W1−C3 = 36.35(5).

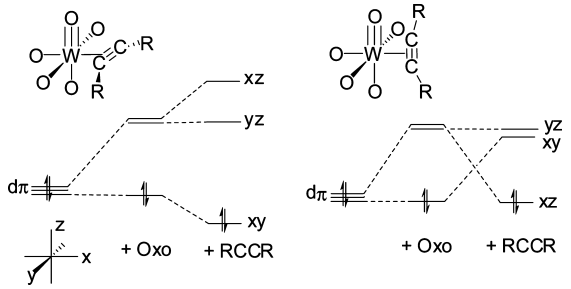

Figure 3. Molecular orbital diagrams for alkyne orientation.[33].

η^2-Binding of Nitrile Ligand in W(O)(acac)$_2$(η^2-PhC≡N). Successful oxidation of tungsten carbonyl alkyne complexes with the W(acac)$_2$(η^2-PhC≡CR) moiety intact led us to explore oxidation reactions of other W(CO)(acac)$_2$ derivatives. Treatment of the neutral nitrile−carbonyl complex W(CO)(acac)$_2$(η^2-PhC≡N) with MCPBA results in the formation of W(O)(acac)$_2$(η^2-PhC≡N) (**2-PhC≡N**), providing another example of a η^2-nitrile complex (eq 3).[49,50] This oxygen atom

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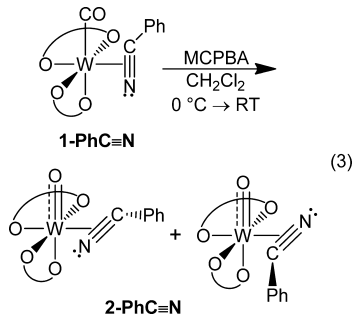

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transfer contrasts with an earlier case in which a W(II) η^2-nitrile complex, Tp′WI(η^2-NCMe)(CO), reacts with the oxygen atom transfer reagent pyridine *N*-oxide to form the acetylimido complex Tp′WI(NC(O)Me)(CO).[51] The ^{1}H NMR spectrum of **2-PhC≡N** shows two isomers in a 1.7:1 ratio. The ^{13}C NMR spectrum shows an upfield shift of the nitrile carbon resonance from 211 ppm to 201 ppm in comparing the W(II) reagent and the W(IV) product. Only small differences were noted relative to the starting material and the product in both the ^{1}H and the ^{13}C NMR spectra.

A sample of **2-PhC≡N** was dissolved in CH_2Cl_2 and layered with hexanes to produce yellow crystals suitable for X-ray analysis. The solid-state structure shows the triple bond of the nitrile ligand in **2-PhC≡N** is arranged *cis* to the newly formed oxo ligand as the C−N bond is perpendicular to the W−oxo linkage (Figure 4). The W1−C3 and W1−N2 bonds have

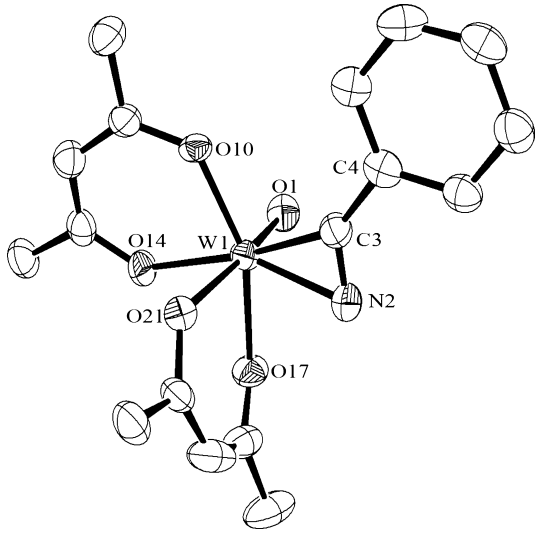
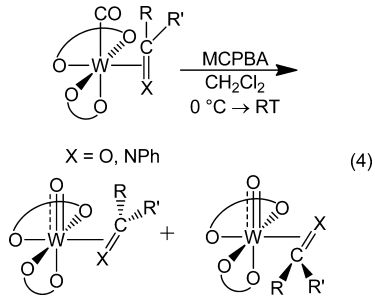


Figure 4. ORTEP diagram (50% ellipsoids) of W(O)(acac)$_2$(η^2-PhC≡N), **2-PhC≡N**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and bond angles (deg): W1−C3 = 2.067(8), W1−N2 = 2.103(6), W1−O1 = 1.719(5), W1−O10 = 2.070(5), W1−O14 = 2.074(5), W1−O17 = 2.046(5), W1−O21 = 2.142(5), N2−C3 = 1.217(10), O10−W1−O14 = 83.1(2), O17−W1−O21 = 83.2(2), N2−W1−C3 = 33.9(3), N2−C3−C4 = 134.2(7).

lengthened to 2.07 and 2.10 Å, respectively, from 2.04 and 2.02 Å in the analogous precursor complex W(CO)(acac)$_2$(η^2-2,6-$Cl_2H_3C_6$C≡N), mirroring the decrease in $\pi_\perp$ donation from the alkyne demonstrated in **2-PhC≡CPh**. The C3−N2 bond shortens slightly to 1.22 Å from 1.27 Å, showing a small increase in triple-bond character.

Synthesis of W(IV) Oxo Imine, Aldehyde, and Ketone Complexes. Oxidation of W(CO)(acac)$_2$(η^2-PhHC═NPh) to W(O)(acac)$_2$(η^2-PhHC═NPh), **2-PhHC═NPh**, with MCPBA produces four isomers in a 13:4:2:1 distribution, as reflected in the ^{1}H NMR spectrum (eq 4). The two



(4)

diastereomers present in the imine-carbonyl precursor can rotate clockwise or counterclockwise 90° into the *xy* plane of the resultant oxo complex, producing four possible products (Figure 5). In the ^{1}H NMR spectrum, the imine proton resonates at 4.49 (major), 4.31, 4.14, and 3.82 ppm in these four isomers. These values are shifted well upfield from chemical ^{1}H NMR signals of 6.15 and 5.71 ppm in the parent CO complex. In the ^{13}C NMR spectrum, the imine carbon resonances are located at 80.9, 80.5, 77.7 (major), and 76.6 ppm. These values are shifted downfield from the two peaks observed at 57.3 (major) and 54.3 ppm in the carbonyl precursor.

Slow evaporation of a solution of **2-PhHC═NPh** in CH_2Cl_2/hexanes produced orange needles suitable for X-ray diffraction. A solid-state structure of **2-PhHC═NPh** reveals the W1−N2 distance is 1.98 Å, elongated from 1.93 Å in the imine-carbonyl precursor and consistent with loss of double-bond character of the W−N bond (Figure 6). The W1−C3 bond tightens significantly to 2.17 Å from 2.24 Å in the precursor. The carbon−nitrogen bond distance is only slightly shortened to 1.387(5) Å from 1.395(8) Å in the imine-carbonyl complex. The shorter W−C bond indicates increased sp^2 character of the carbon atom, as noted in the ^{13}C NMR spectrum.

Addition of MCPBA to W(CO)(acac)$_2$(η^2-PhHC═O) produces W(O)(acac)$_2$(η^2-PhHC═O) (**2-PhHC═O**) with four isomers detected in a 9:6:4:1 ratio by ^{1}H NMR spectroscopy (eq 4). The aldehyde protons are located in the 4.7−5.7 ppm range, well upfield of the range of 6.9−8.2 ppm found for the W(II) precursor complex. The aldehyde carbon is found at 104−108 ppm in the ^{13}C NMR spectrum, compared to 86 and 89 ppm in the precursor. These spectral results mirror those seen for the **2-PhHC═NPh** and suggest increased sp^2 character of the carbon atom of the aldehyde ligand in the oxidized complex.

Oxidation of the carbonyl-acetone complex W(CO)-(acac)$_2$(η^2-Me$_2$C═O) produces W(O)(acac)$_2$(η^2-Me$_2$C═O) in only two isomers in a 1.1:1 ratio due to the symmetry of the ketone (eq 4). The acetone ketone carbon resonates at 115 and 116 ppm compared to 97 ppm in the precursor in the ^{13}C NMR spectrum.

Synthesis of [W(O)(acac)$_2$(η^2-PhC≡NMe)]$^+$. Oxidation was also attempted with cationic W(II) complexes. Addition of MCPBA to the iminoacyl complex [W(CO)(acac)$_2$(η^2-PhC≡NMe)][BAr′$_4$] leads to formation of two W(IV) isomers of [W(O)-(acac)$_2$(η^2-PhC≡NMe)][BAr′$_4$] ([**2-PhC≡NMe**][**BAr′$_4$**]) in

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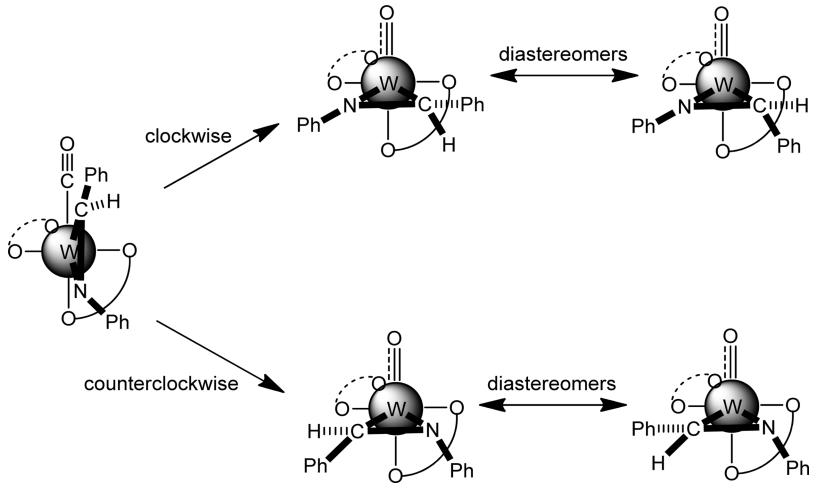


Figure 5. Four possible isomers of **2-PhHC═NPh**.

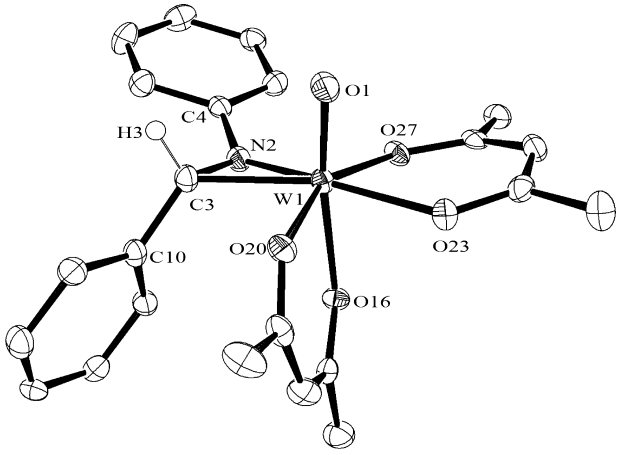
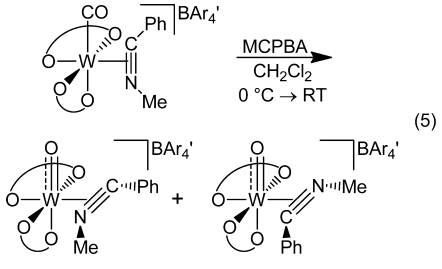


Figure 6. ORTEP diagram (50% ellipsoids) of W(O)(acac)$_2$(η^2-PhHC═NPh), **2-PhHC═NPh**. Nonessential hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and bond angles (deg): W1−N2 = 1.980(3), W1═C3 = 2.166(4), W1−O1 = 1.711(3), W1−O16 = 2.130(2), W1−O20 = 2.068(2), W1−O23 = 2.133(2), W1−O27 = 2.047(2), N2−C3 = 1.387(5), O16−W1−O20 = 80.96(10), O23−W1−O27 = 82.33(10), C3−W1−N2 = 38.76(12).

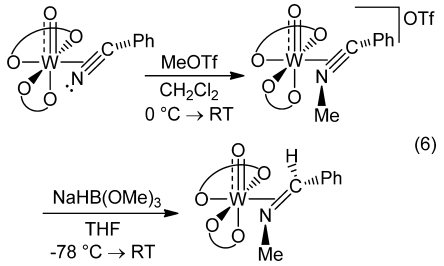
a 1.3:1 ratio (eq 5). The ^{1}H NMR spectrum for [**2-PhC≡NMe**][**BAr′$_4$**] indicates similar chemical shifts to those seen in



the precursor W(II) molecule. In the ^{13}C NMR spectrum, the coordinated iminoacyl carbon has shifted upfield as a result of oxidation, from 221 ppm to 202 and 207 ppm.

Reduction of [W(O)(acac)$_2$(η^2-PhC≡NMe)]$^+$. Successful isolation of a cationic iminoacyl−oxo complex prompted us to further investigate addition reactions to nitrile-derived ligands. Reduction of a π-bound nitrile ligand in **1-PhC≡N** to a π-bound iminium ligand, a stepwise process, passes through an iminoacyl ligand and then an imine.[14,15] This sequential reduction shows little diastereoselectivity in the formation of either the imine or the iminium ligand. Reduction of an iminoacyl to an imine was accomplished with carbon monoxide, isonitrile, or alkyne as a *cis* ligand in the coordination sphere.

Addition of methyl triflate (MeOTf) to a solution of **2-PhC≡N** produces [W(O)(acac)$_2$(η^2-PhC≡NMe)][OTf] (eq 6).



This result is similar to the methylation of W(CO)(acac)$_2$(η^2-PhC≡N).[14] Clean products are formed in a 1:1.1 ratio, with respect to the isomers seen for [**2-PhC≡NMe**][**BAr′$_4$**]. In contrast to the complex with the BAr′$_4$ counterion, [**2-PhC≡NMe**][**OTf**] is not sufficiently robust to withstand chromatography on silica.

Addition of Na[HB(OMe)$_3$] to [**2-PhC≡NMe**][**OTf**] produced *in situ* from methylation of **2-PhC≡N** leads to formation of W(O)(acac)$_2$(η^2-PhHC═NMe) (**2-PhHC═NMe**) (eq 6). The synthesis provides *diastereoselective formation of the imine complex in an 11:1 ratio of the two major isomers* as determined by ^{1}H NMR spectroscopy. Previous syntheses of the carbonyl analogue, W(CO)(acac)$_2$(η^2-PhHC═NMe) (**1-PhHC═NMe**), produced two diastereomers in a 2:1 ratio.[14] The diastereomeric selectivity leading to **2-PhHC═NMe** is surprising given the presence of two isomers of the cationic iminoacyl reagent coupled with the low level of diastereoselectivity seen for formation of **1-PhHC═NMe**.

Oxidation of **1-PhHC═NMe** with MCPBA also produces **2-PhHC═NMe**. Again, significant diastereoselectivity is observed with a ratio of 10:1 for the two major isomers. The imine proton of **2-PhHC═NMe** resonates at 3.83 ppm, well upfield of the precursor signal in the ^{1}H NMR spectrum at 5.56 ppm. Additionally, one of the acac methine protons is found shifted upfield to 4.76 ppm, compared to 5.72 and 5.48 ppm in

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1-PhHC═NMe. The methyl bound to nitrogen is shifted downfield to 4.30 ppm upon metal oxidation from 3.71 ppm in the W(II) reagent. The imine carbon resonates at 85.1 ppm in the ^{13}C NMR spectrum, compared to 60.8 ppm in the parent W(II) complex.

Crystals suitable for X-ray analysis were grown by evaporation of a hexanes solution under an inert atmosphere to provide the solid-state structure of neutral **2-PhHC═NMe** (Figure 7). The geometric results of oxidation from **1-PhHC═NMe** are similar to those observed for oxidation of **1-PhHC═NPh**. The W1−N3 bond length is 2.00 Å, an increase from 1.91 Å in the analogous **1-PhMeC═NMe** complex and close to the value of 1.98 Å for **2-PhHC═NPh**. The W1−C4 bond distance is 2.18 Å, decreased from 2.27 Å in **1-PhMeC═NMe** and again similar to **2-PhHC═NPh** with a value of 2.17 Å. The C4−N3 bond length exhibits virtually no change at 1.384 Å from 1.383 Å in the similar precursor. These changes in bond lengths are consistent with the previous examples of metal oxidation with a heteroatomic single-face π-acid in the coordination sphere.

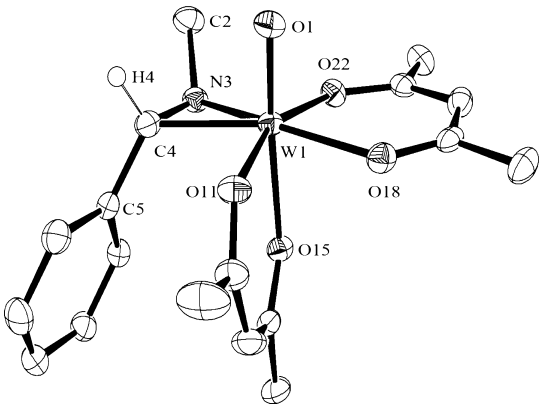

Figure 7. ORTEP diagram of W(O)(acac)$_2$(η^2-PhHC═NMe) (**2-PhHC═NMe**), shown with 50% probability thermal ellipsoids. Nonessential hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and bond angles (deg): W1−C4 = 2.1771(19), W1−N3 = 2.0008(16), W1−O1 = 1.7099(13), W1−O11 = 2.0809(13), W1−O15 = 2.1205(12), W1−O18 = 2.1118, W1−O22 = 2.0584(13), C4−N3 = 1.384(2), O11−W1−O15 = 81.15(5), O18−W1−O22 = 83.35(5), C4−W1−N3 = 38.04(7).

The solid-state structure of **2-PhHC═NMe** provides some insight into the high diastereomeric ratio observed by NMR spectroscopy. Surprisingly, the methyl group on the three-coordinate nitrogen atom is rotated approximately 40° out of the W−N−C plane (Figure 7). In the analogous precursor W(II) complex, **1-PhMeC═NMe**, the *N*-methyl carbon is almost coplanar with the W−N−C triangle. This comparison invites steric or electronic arguments for the deviation from planarity observed for **2-PhHC═NMe**. With the imine group now perpendicular to the W−O axis, the *N*-methyl group would sterically conflict with the adjacent acac group if it were in the W−N−C plane. Additionally, in **1-PhMeC═NMe**, the sp^2-hybridized nitrogen provides effective lone pair donation from a nitrogen p orbital to the metal center, totaling donation of four electrons from the neutral imine ligand. However, the imine ligand in **2-PhHC═NMe** is liberated from this stringent electronic requirement by the addition of the oxo ligand, which is also capable of lone pair donation to complete the valence shell of tungsten. Thus it seems logical that the methyl group on nitrogen is rotated out of the W−N−C plane and oriented *trans* to the imine-phenyl group to minimize unfavorable steric interactions. The H$^-$ nucleophile would presumably prefer to approach the less sterically hindered face of the iminoacyl ligand, thus adding from the oxo face in order to avoid the bulkier acetylacetonate ligand. Finally, there appears to be a π-interaction between the imine phenyl ring and the adjacent acac ligand, most likely providing stabilization for the diastereomer observed in the solid-state structure. This π-interaction places the arene π-cloud near the acac central carbon and is likely the cause of the upfield shift to 4.76 ppm of one acac methine signal in the ^1H NMR spectrum.

Similar arguments presumably apply to the orientation of the imine ligand in **2-PhHC═NPh**. However, this complex shows a lower diastereomeric preference. The two rotamers with the phenyl groups on the imine oriented *trans* to each other would presumably be sterically favored. The most abundant isomer is likely the one observed in the solid-state structure with the phenyl groups *trans* to each other and the phenyl group on carbon participating in a π-interaction with the adjacent acetylacetonate ligand. The two other isomers are populated in much lower ratios.

SUMMARY

Addition of N_2CR_2 to W(CO)$_3$(acac)$_2$ produces W(CO)(acac)$_2$(N_2CR_2) with the diazoalkane ligand acting as a six-electron donor bound through the terminal nitrogen to the tungsten(IV) metal center. Addition of MCPBA to W(CO)(acac)$_2$(η^2-PhC≡N) produces the oxygen-atom-transfer tungsten(IV) product W(O)(acac)$_2$(η^2-PhC≡N). W(O)(acac)$_2$(η^2-PhC≡N) reacts with MeOTf to produce the iminoacyl complex [W(O)(acac)$_2$(η^2-PhC≡NMe)][OTf], a rare example of methylation of a π-bound nitrile ligand.[14,35,52,53] Addition of a nucleophilic hydride reagent results in addition to the iminoacyl carbon to produce W(O)(acac)$_2$(η^2-PhHC≡NMe) with a diastereomeric ratio of 11:1, demonstrating stepwise reduction of a η^2-nitrile ligand to an η^2-imine in a stereoselective manner.

EXPERIMENTAL SECTION

General Information. All air- and moisture-sensitive materials were handled using Schlenk or glovebox techniques under a dry nitrogen or argon atmosphere, respectively. All glassware was oven-dried before use. Methylene chloride, diethyl ether, and hexanes were purified by passage through an activated alumina column under a dry argon atmosphere.[54] THF was distilled from a sodium ketal suspension. Methylene chloride-d_2 was dried over CaH_2 and degassed. W(CO)$_3$(acac)$_2$,[17] W(CO)(L)(acac)$_2$,[16,17] [W(CO)(PhC≡NMe)(acac)$_2$][BAr′$_4$],[14] NaBAr′$_4$,[55] and diphenyldiazomethane[56] were made in accordance with literature procedures. All other reagents were purchased from commercial sources and used without further purification.

NMR spectra were recorded on Bruker DRX 500, DRX400, AMX400, or AMX300 spectrometers. Infrared spectra were recorded on an ASI Applied Systems React IR 1000 FT-IR spectrometer. Elemental analysis was performed by Robertson Microlit, Madison, NJ.

W(CO)(acac)$_2$(N_2CHSiMe$_3$) (1-N_2CHSiMe$_3$). In a representative synthesis, W(CO)$_3$(acac)$_2$ (0.808 g, 1.73 mmol) was dissolved in CH_2Cl_2. A solution of (trimethylsilyl)diazomethane (2.0 M in hexanes, 0.87 mL, 1.74 mmol) was added, and the solution was stirred for 1.5 h. As the reaction progressed, a color change from light brown to green was noted, as well as a shift to a single IR absorbance at 1915 cm^{-1}. Trituration with hexanes led to isolation of a green powder. Yield: 0.730 g, 1.39 mmol, 80%. Chromatography on silica with CH_2Cl_2 produced pure material for analysis. IR (CH_2Cl_2): ν_{CO} = 1915 cm^{-1}.

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^{1}H NMR (CD_2Cl_2, 298 K, δ): 8.00 (s, 1H, N_2CHTMS), 5.81, 5.63 (s, 1H, acac C*H*), 2.62, 2.21, 2.18, 2.00 (s, 3H, acac CH_3), 0.21 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ): 267.45 (*C*O), 192.2, 190.5, 190.3, 187.9 (acac *C*O), 168.1 (N_2CHTMS), 102.3, 101.0 (acac *C*H), 27.5, 27.3, 26.9, 25.9 (acac CH_3), −2.8 ($Si(CH_3)_3$). Anal. Calcd for $C_{15}H_{24}N_2O_5SiW$ (524.29): C, 34.36; H, 4.61; N, 5.34. Found: C, 34.26; H, 4.39; N, 5.19.

W(CO)(acac)$_2$(N_2CPh_2) (1-N_2CPh_2). **1-N_2CPh_2** was prepared in the same manner as **1-$N_2CHSiMe_3$**. Yield: 0.148 g, 0.245 mmol, 76%. Chromatography on silica with CH_2Cl_2 produced pure material for analysis. The product was dissolved in a small amount of methylene chloride and stored at −35 °C to produce green-brown crystals after four weeks. IR (CH_2Cl_2): ν_{CO} = 1910 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 7.27−7.68 (m, 10H, C_6H_5), 5.80, 5.53 (s, 1H, acac C*H*), 2.66, 2.22, 2.17, 1.90 (s, 3H, acac CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ): 268.7 (*C*O, $^1J_{C-W}$ = 209 Hz), 191.7, 190.3, 190.1, 187.7 (acac *C*O), 161.4 (N_2CPh_2, $^3J_{C-W}$ = 7.3 Hz), 128.0−141.5 (C_6H_5) 102.2, 100.8 (acac *C*H), 27.5, 27.4, 27.0, 25.9 (acac CH_3). Anal. Calcd for $C_{24}H_{24}N_2O_5W{\cdot}CH_2Cl_2$ (689.23): C, 43.57; H, 3.80; N, 4.06. Found: C, 43.62; H, 4.01; N, 3.84.

W(O)(acac)$_2$(η^2-PhC≡CH) (2-PhC≡CH). In a representative synthesis, a Schlenk flask was charged with W(CO)(acac)$_2$(η^2-PhC≡CH) (**1-PhC≡CH**) (0.150 g, 0.293 mmol) and 20 mL of CH_2Cl_2. The amber-colored solution was cooled to 0 °C, and 1 equiv of MCPBA (0.066 g, 0.294 mmol) was added under a backflow of N_2. The solution color changed to yellow, and *in situ* IR spectroscopy indicated loss of the lone carbonyl absorbance. The product was chromatographed on NEt_3-treated silica with CH_2Cl_2 to elute an orange-yellow band. Yield: 0.093 g, 0.186 mmol, 63%. Ratio of isomers: 1.1:1. IR (KBr): $\nu_{W=O}$ = 950 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 298 K, δ, major isomer): 11.10 (s, 1H, PhC≡C*H*, $^2J_{W-H}$ = 14 Hz), 7.65 (d, 2H, *o*-C_6H_5), 7.46 (t, 2H, *m*-C_6H_5), 7.36 (t, 1H, *p*-C_6H_5), 5.85, 5.32 (s, 1H, acac C*H*), 2.35, 2.19, 2.14, 1.70 (s, 3H, acac CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ, major isomer): 192.0, 190.2, 189.4, 188.3 (acac *C*O), 175.1 (PhC≡CH, $^1J_{W-C}$ = 29 Hz), 160.4 (PhC≡*C*H, $^1J_{W-C}$ = 38 Hz), 137.4 (*ipso*-C_6H_5, $^2J_{W-C}$ = 7.2 Hz) 131.7 (*o*-C_6H_5), 129.0 (*p*-C_6H_5), 128.6 (*m*-C_6H_5), 103.9, 102.5 (acac *C*H), 27.6, 27.4, 26.5 (acac CH_3, 2:1:1). Anal. Calcd for $C_{18}H_{20}O_5W$ (500.19): C, 43.22; H, 4.03. Found: C, 42.97; H, 3.78.

W(O)(acac)$_2$(η^2-PhC≡CPh) (2-PhC≡CPh). **2-PhC≡CPh** was prepared in the same manner as **2-PhC≡CH**. Yield: 0.076 g, 0.132 mmol, 61%. The product was dissolved in CH_2Cl_2 and layered with hexanes to produce yellow crystals suitable for X-ray analysis. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 7.28−8.10 (m, 10H, C_6H_5), 5.85, 5.34 (s, 1H, acac C*H*), 2.25, 2.16, 2.14, 1.74 (s, 3H, acac CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ): 192.2, 190.1, 189.3, 187.9 (acac *C*O), 172.4, 166.9 (PhC≡*C*Ph), 138.5, 138.0 (*ipso*-C_6H_5), 131.1, 130.9 (*p*-C_6H_5), 128.5, 128.5, 128.4 (*o*, *m*-C_6H_5), 103.9, 102.9 (acac *C*H), 27.6, 27.5, 27.1, 26.6 (acac CH_3). Anal. Calcd for $C_{24}H_{24}O_5W$ (576.28): C, 50.02; H, 4.20. Found: C, 49.79; H, 4.11.

W(O)(acac)$_2$(η^2-PhC≡N) (2-PhC≡N). **2-PhC≡N** was prepared in the same manner as above. Yield: 0.104 g, 0.208 mmol, 71%. Ratio of isomers: 1.7:1. ^{1}H NMR (CD_2Cl_2, 298 K, δ, major isomer): 7.46−8.25 (5H, C_6H_5), 5.92, 5.73 (s, 1H, acac C*H*), 2.47, 2.38, 2.19, 1.70 (s, 3H, acac CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ, major isomer): 200.5 (*C*≡N), 191.7, 190.6, 190.2, 189.4 (acac *C*O), 129.3−137.2 (C_6H_5), 104.5, 104.1 (acac *C*H), 27.6, 27.4, 26.9, 26.5 (acac CH_3). Anal. Calcd for $C_{17}H_{19}NO_5W$ (501.18): C, 40.74; H, 3.82; N, 2.79. Found: C, 40.36; H, 3.76; N, 2.71.

W(O)(acac)$_2$(η^2-PhHC═NPh) (2-PhHC═NPh). **2-PhHC═NPh** was prepared in the same manner as above. Yield: 0.072 g, 0.124 mmol, 76%. Ratio of isomers: 13:4:2:1. Slow evaporation of a solution of **2-PhHC═NPh** in CH_2Cl_2/hexanes produced orange needles suitable for X-ray diffraction. ^{1}H NMR (CD_2Cl_2, 298 K, δ, major isomer): 6.8−8.1 (C_6H_5) 5.85, 4.87 (s, 1H, acac C*H*), 4.49 (s, 1H, N═C*H*Ph), 2.40, 2.16, 2.13, 1.49 (s, 3H, acac CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ, major isomer): 193.8, 190.1, 189.3, 187.7 (acac *C*O), 121.4−156.7 (C_6H_5), 104.5, 101.1 (acac *C*H), 77.7 (*C*═N), 30.0, 28.3, 27.4, 26.8 (acac CH_3). Anal. Calcd for $C_{23}H_{25}O_5NW$ (579.29): C, 47.69; H, 4.35; N, 2.41. Found: C, 47.84; H, 4.54; N, 2.30.

W(O)(acac)$_2$(η^2-PhHC═O) (2-PhHC═O). **2-PhHC═O** was prepared in the same manner as above. Yield: 0.098 g, 0.194 mmol, 84%. Ratio of isomers: 9:6:4:1. ^{1}H NMR (CD_2Cl_2, 298 K, δ, major isomer): 6.8−8.1 (C_6H_5), 5.87, 4.92 (s, 1H, acac C*H*), 5.72 (s, 1H, O═C*H*, $^2J_{W-H}$ = 7 Hz), 2.39, 2.20, 2.12, 1.44 (s, 3H, acac CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ, major isomer): 193.2, 190.0, 189.8, 189.3 (acac *C*O), 125.0−143.3 (C_6H_5), 104.6, 101.6 (acac *C*H), 104.1 (*C*═O, $^1J_{W-C}$ = 22 Hz), 28.1, 27.4, 27.3, 25.8 (acac CH_3). Anal. Calcd for $C_{17}H_{20}O_6W$ (504.18): C, 40.50; H, 4.00. Found: C, 40.78; H, 3.94.

W(O)(acac)$_2$(η^2-Me$_2$C═O) (2-Me$_2$C═O). **2-Me$_2$C═O** was prepared in the same manner as above. Yield: 0.054 g, 0.118 mmol, 74%. Ratio of isomers: 1:1. ^{1}H NMR (CD_2Cl_2, 298 K, δ, both isomers): 5.87, 5.78, 5.68, 5.62 (s, 1H, acac C*H*), 2.99, 2.98, 2.30, 2.03 (s, 3H, $(CH_3)_2$C═O) 2.41, 2.36, 2.33, 2.32, 2.13, 2.11, 1.79, 1.78 (s, 3H, acac CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ, both isomers): 192.9, 191.8, 191.3, 191.1, 190.9, 189.7, 189.6, 188.9 (acac *C*O), 115.6, 115.2 (*C*═O), 104.1, 103.9, 103.4, 102.6 (acac *C*H), 32.1, 31.1, 26.6 (O═C$(CH_3)_2$), 28.0, 27.6, 27.5, 27.4, 27.4, 27.1, 26.8, 26.6, 26.0 (acac CH_3 and O═C$(CH_3)_2$). Anal. Calcd for $C_{13}H_{20}O_6W$ (456.13): C, 34.23; H, 4.42. Found: C, 34.50; H, 4.50.

[W(O)(acac)$_2$(η^2-PhC≡NMe)][OTf] ([2-PhC≡NMe][OTf]). In an NMR tube **2-PhC≡N**, CD_2Cl_2, and MeOTf were combined. The solution turned green in color. ^{1}H NMR spectroscopy shows complete conversion to product. Ratio of isomers: 1.1:1. ^{1}H NMR (CD_2Cl_2, 298 K, δ, major isomer): 7.83−8.40 (C_6H_5), 6.20, 5.99 (s, 1H, acac C*H*), 4.27 (s, 3H, N−CH_3), 2.55, 2.52, 2.30, 1.90 (s, 3H, acac CH_3).

[W(O)(acac)$_2$(η^2-PhC≡NMe)][BAr′$_4$] ([2-PhC≡NMe][BAr′$_4$]). To a solution of **1-PhC≡N** (0.100 g, 0.195 mmol) in CH_2Cl_2 was added methyl triflate (0.033 mL, 0.292 mmol). The solution was stirred for 2 h until a single IR absorbance was noted at 1985 cm^{-1}. NaBAr′$_4$ was added under a backflow of nitrogen to generate **1-PhC≡NMe[BAr′$_4$]** *in situ* after 2 h of stirring. The solution was cannula-filtered to another Schlenk flask and cooled to 0 °C. MCPBA (0.045 g, 0.200 mmol) was added under a backflow of N_2. The brown product was chromatographed on NEt_3-treated silica to elute a red-brown fraction with CH_2Cl_2. Yield: 0.188 g, 0.136 mmol, 70%. Ratio of isomers: 1.3:1. ^{1}H NMR (CD_2Cl_2, 298 K, δ, major isomer): 8.14 (d, 2H, *o*-C_6H_5), 7.87 (t, 2H, *m*-C_6H_5), 7.82 (obscured by BAr′$_4$, 1H, *p*-C_6H_5), 6.22, 5.65 (s, 1H, acac C*H*), 4.33 (s, 3H, N−CH_3), 2.51, 2.44, 2.39, 1.73 (s, 3H, acac CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ, major isomer): 206.6 (*C*≡N), 195.8, 194.1, 191.6, 191.3 (acac *C*O), 138.1 (*ipso*-C_6H_5), 134.0, 130.9 (*o*/*m*-C_6H_5), 125.6 (*p*-C_6H_5), 107.6, 105.8 (acac *C*H), 35.5 (N-CH_3), 27.4, 27.1, 26.8, 26.3 (acac CH_3).

W(O)(acac)$_2$(η^2-PhHC≡NMe) (2-PhHC═NMe). *Method A.* To a yellow solution of **2-PhC≡N** (0.075 g, 0.150 mmol) in CH_2Cl_2 was added MeOTf (0.020 mL, 0.177 mmol). The solution turned pale green after 5 min and was allowed to stir for 1 h. Solvent was removed and THF was added. The solution was cooled to −78 °C, and a cooled solution of Na[HB(OMe)$_3$] was cannula-transferred to the flask. The solution turned yellow in color and was warmed to room temperature and stirred for 10 min. The product was chromatographed on silica with CH_2Cl_2 to elute a yellow band. Yield: 0.034 g, 0.066 mmol, 44%. Ratio of isomers: 11:1. Slow evaporation of a solution of **2-PhHC═NMe** in hexanes under an inert atmosphere produces yellow crystals for X-ray analysis. *Method B.* A red solution of **1-PhHC═NMe** in CH_2Cl_2 was cooled to 0 °C. MCPBA was added under a backflow of N_2 to produce a yellow solution. The solution was warmed to room temperature, and solvent was removed. The product was chromatographed on NEt_3-treated silica with CH_2Cl_2 to elute a pale yellow band. Ratio of isomers: 10:1. ^{1}H NMR (CD_2Cl_2, 298 K, δ, major isomer): 7.16 (t, 2H, *m*-C_6H_5), 6.88 (d, 2H, *o*-C_6H_5), 6.82 (t, 1H, *p*-C_6H_5), 5.81, 4.76 (s, 1H, acac C*H*), 4.30 (s, 3H, N−CH_3), 3.83 (s, 1H, PhC*H*═N), 2.36, 2.09, 1.45 (s, 3:6:3H, acac CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ, major isomer): 193.4, 190.0, 189.3, 188.5 (acac *C*O), 144.1, 126.8, 126.3, 126.2 (C_6H_5), 103.9, 100.4 (acac *C*H), 85.1 (*C*═N, $^1J_{W-C}$ = 17 Hz), 49.2 (N-CH_3), 28.2, 27.4, 27.3, 25.3 (acac CH_3). Anal. Calcd for $C_{18}H_{23}NO_5W$ (517.22): C, 41.80; H, 4.48, N, 2.71. Found: C, 42.76; H, 4.61; N, 2.48.

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■ ASSOCIATED CONTENT

Supporting Information

Full details of the crystal structure analyses for **1-N_2CPh_2**, **2-PhC≡CPh**, **2-PhC≡N**, **2-PhHC═NPh**, and **2-PhHC═NMe**. NMR spectra for **[2-PhC≡NMe][BAr′$_4$]** and **2-PhHCNMe**. This material is available free of charge via the Internet at http://pubs.acs.org.

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