Inorg. Chem. **2006**, *45*, 6205–6213

Inorganic Chemistry
Article

Bis(acetylacetonato)tricarbonyl Tungsten(II): A Convenient Precursor to Chiral Bis(acac) Tungsten(II) Complexes

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Received January 6, 2006

Two equivalents of acetylacetonate (acac) have been successfully introduced into a monomeric tungsten(II) coordination sphere. With the tetracarbonyltriiodotungsten(II) anion as a precursor, the formation of a tungsten(II) bis(acac) tricarbonyl complex, $W(CO)_3(acac)_2$, **1**, has been accomplished. The addition of PMe_3 or PMe_2Ph to tricarbonyl complex **1** formed tungsten(II)bis(acac)dicarbonylphosphine complexes **2a** and **2b**, respectively. Single-crystal X-ray diffraction studies of the parent tricarbonyl complex, **1**, and dicarbonyl trimethylphosphine complex **2a** confirmed seven-coordinate geometries for both complexes. Variable-temperature ^1H and $^{13}C\{^1H\}$ NMR spectroscopy revealed fluxional behavior for these seven-coordinate molecules: rapid exchange of the three carbon monoxide ligands in **1** was observed, and movement of the phosphine ligand through a mirror plane in a C_S intermediate species was observed for both **2a** and **2b**. Tricarbonyl complex **1** reacted readily with alkyne reagents to form bis(acac)monocarbonylmonoalkynetungsten(II) complexes **3a** ($PhC\equiv CH$) and **3b** ($MeC\equiv CMe$). Variable-temperature ^1H NMR spectroscopy was used to probe rotation of the alkyne ligand in **3a** and **3b**. The introduction of two alkyne ligands was accomplished thermally using excess $PhC\equiv CPh$ to form bis(alkyne) complex **4** which was characterized crystallographically, as well as by ^1H and ^{13}C NMR spectroscopy. The availability of $W(CO)_3(acac)_2$ as a source of the $W(acac)_2$ d^4 moiety lies at the heart of the chemistry reported here.

I. Introduction

Widespread use of acetylacetonato (acac) derivatives as ligands over the past four decades[1−5] and the recent renaissance of NacNac chemistry[6−10] provide a wealth of literature knowledge for launching Group VI d^4 $(acac)_2ML_n$ chemistry. Periana's developments in C−H activation[11−13] used an iridium(III) bis(acac) fragment. To date, few complexes of Group VI metals with two acac ligands have been reported. Monomeric Group VI d^4 complexes containing anionic bidentate S-donor dialkyldithiocarbamate (dtc) ligands have been thoroughly investigated, but examples with two anionic bidentate O-donor ligands bound to Group VI metals are scarce. Higher oxidation states of molybdenum, such as IV[14] and VI,[15] readily bind two equivalents of acetylacetonate. The venerable $Mo(O)_2(acac)_2$ complex has been used as a catalyst for the epoxidation of olefins[16] and as a catalyst in dehydrative cyclizations.[17] Dimeric d^4 paddlewheel complexes of tungsten(II) and molybdenum(II) that boast bidentate anionic oxygen chelates, including acac, have multiple bonding between metal centers.[18] Chromium(II) bis(acac)[19]

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10.1021/ic0600329 CCC: $33.50

is one of few Group VI d^4 complexes in the literature with two coordinated acac chelates. No low-valent monomeric Group VI complex has been available as a convenient source of the metal bis(acac) fragment for developing additional chemistry.

One motivation for using oxygen donor ligands to build a chiral bis(L- -X)$_2$M d^{4}moiety comparable to (dtc)$_2$W(CO)$_3$ was to use a more robust fragment as an auxiliary. The rich chemistry of (dtc)$_2$WL$_3$ includes sulfur redox chemistry, evident in unwanted dtc C−S cleavage reactions.[20−27] We chose to investigate acac to better control both electronic and steric factors around the metal center and to avoid the undesirable reactivity of the sulfur donor chelates. Acetylacetonate was an attractive choice because of its ease of preparation and storied history. Previous attempts to coordinate acac to tungsten(II) carbonyl complexes generated a series of mono(acac) complexes;[28−33] only one W(II) bis(acac) complex has been reported.[34] Coordination of two formato ligands to a Group VI d^4 metal has been reported, but attempts to incorporate acetylacetonate into that system yielded only mono(acac) derivatives.[35] We report the coordination of two acetylacetonate ligands to tungsten(II) centers to form d^4 W(II) bis(acac) derivatives.

II. Experimental

General Information. Reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Methylene chloride, diethyl ether, hexanes, toluene, and pentane were purified by passage through an activated alumina column under a dry argon atmosphere. Methylene chloride-d_2 was dried over CaH$_2$ and degassed. All other reagents were purchased from commercial sources and were used without further purification.

NMR spectra were recorded on a Bruker DRX400, AMX400, or AMX300 spectrometer. Infrared spectra were recorded on an ASI Applied Systems ReactIR 1000 FT-IR spectrometer. Elemental analysis was performed by Atlantic Microlab, Norcross, GA.

The [NEt$_4$][W(CO)$_5$I] reagent was made following a literature procedure.[36] It was important to purify this reagent prior to use via chromatography on an alumina column with acetone as the eluent.

W(CO)$_3$(acac)$_2$ (1). In a 200 mL Schlenk flask, [NEt$_4$][W(CO)$_5$I] (590 mg, 1.0 mmol) was dissolved in CH$_2$Cl$_2$ (20 mL). Stoichiometric addition of elemental iodine (265 mg, 1.0 mmol) resulted in the immediate formation of the orange [NEt$_4$][W(CO)$_4$I$_3$] anion. In a separate flask, a solution of 2,4-pentanedione (H-acac) (0.220 mL, 2.05 mmol) in CH$_2$Cl$_2$ (10 mL) was deprotonated by triethylamine (0.285 mL, 2.05 mmol) to yield [acac]$^-$ in situ. This solution was combined with the solution containing the tetracarbonyl triiodide complex and then stirred for 2 h to yield W(CO)$_3$(acac)$_2$, whose formation was monitored by in situ IR spectroscopy. The solvent volume was reduced in vacuo, and then hexanes were added. The remainder of the CH$_2$Cl$_2$ solvent was removed, and the dark red residual liquid was cannula filtered into another flask and stored at −30 °C for crystallization (90 mg, 20%). IR: (hexanes) ν_{CO} 2028, 1924; (KBr) ν 2026, 1908, 1895 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ 5.67 (s, 2H, acac C*H*), 2.08 (s, 12H, acac C*H*$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ 27.4 (acac *C*H$_3$), 102.8 (acac *C*H), 190.1 (acac *C*O), 242.5 ($C\equiv O$). ^{13}C{^{1}H} NMR (CDCl$_2$F, 153 K): δ 231.0 ($C\equiv O$), 235.6 ($C\equiv O$), 257.8 ($C\equiv O$). Anal. Calcd for C$_{13}$H$_{14}$O$_7$W: C, 33.50; H, 3.03. Found: C, 33.10; H, 3.19.

W(CO)$_2$(PMe$_3$)(acac)$_2$ (2a). A flask was charged with 195 mg of W(CO)$_3$(acac)$_2$ **1**, which was dissolved in 10 mL of CH$_2$Cl$_2$. In a separate flask, trimethylphosphine (0.040 mL) was added to hexanes (7 mL). The phosphine solution was cannula filtered into the flask containing **1**, and the reaction mixture was stirred for 1 h. The reaction progress was monitored via IR spectroscopy, and the appearance of two new absorptions suggested formation of a dicarbonyl product. The solvent was removed in vacuo to yield a dark red solid (110 mg, 54%). IR: (hexanes) ν_{CO} 1928, 1831 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ 5.75, 5.37 (each a s, each 1H, acac C*H*), 2.15 (br s, 6H, acac C*H*$_3$), 1.93 (s, 6H, acac C*H*$_3$), 1.52 (d, P−C*H*$_3$, $^2J_{P-H}$ = 10 Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ 14.6 (d, P*Me*$_3$, $^1J_{C-P}$ = 33 Hz), 27.3, 27.4 (acac *C*H$_3$), 101.1, 102.2 (acac *C*H), 188.6, 188.9, 189.7 (acac *C*O). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 193 K): δ 246.7 ($C\equiv O$, $^1J_{W-C}$ = 166 Hz, $^2J_{C-P}$ = 8 Hz), 276.6 ($C\equiv O$, $^1J_{W-C}$ = 144 Hz, $^2J_{P-C}$ = 41 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ 11.21 (s, $^1J_{W-P}$ = 217 Hz). Anal. Calcd for C$_{15}$H$_{23}$O$_6$PW: C, 35.45; H, 4.57. Found: C, 34.76; H, 4.57.

W(CO)$_2$(PMe$_2$Ph)(acac)$_2$ (2b). A flask was charged with 120 mg of W(CO)$_3$(acac)$_2$ **1**, which was dissolved in 10 mL of CH$_2$Cl$_2$. In a separate flask, dimethylphenylphosphine (0.035 mL) was added to hexanes (7 mL). The phosphine solution was cannula transferred into the flask with containing **1**, and the reaction mixture was monitored via IR spectroscopy. Two new CO absorptions appeared within 30 min, at which point the solvent was removed in vacuo to yield a dark red solid (50 mg, 31%). IR: (hexanes) ν_{CO} 1930, 1835 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ 7.50−7.51 (m, 2H, P−C$_6$*H*$_5$), 7.40−7.43 (m, 3H, P−C$_6$*H*$_5$), 5.76, 5.40 (each a s, each 1H, acac C*H*), 2.16, 2.12 (each a s, each 3H, acac C*H*$_3$), 1.94 (s, 6H, acac C*H*$_3$), 1.76 (d, 6H, P*Me*$_2$Ph, $^2J_{P-H}$ = 10 Hz). ^{1}H NMR (CD$_2$Cl$_2$, 193 K): δ 7.43 (s, 5H, P−C$_6$*H*$_5$), 5.85, 5.44 (each a s, each 1H, acac C*H*), 2.19, 2.16, 1.96, 1.91 (each a s, each 3H, acac C*H*$_3$), 1.73, 1.66 (each a d, each 3H, P−C*H*$_3$, $^2J_{P-H}$ = 10 Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ 13.7 (d, P*Me*$_2$Ph, $^1J_{P-C}$ = 33 Hz), 27.3, 27.5 (acac *C*H$_3$), 101.1, 102.3 (acac *C*H), 128.5 (d, *o*-*C*$_6$H$_5$, $^2J_{P-C}$ = 9 Hz), 130.3 (*p*-*C*$_6$H$_5$), 131.2 (d, *m*-*C*$_6$H$_5$, $^3J_{P-C}$ = 8 Hz), 135.6 (d, *ipso*- *C*$_6$H$_5$, $^1J_{P-C}$ = 49 Hz), 188.6, 188.9, 189.9

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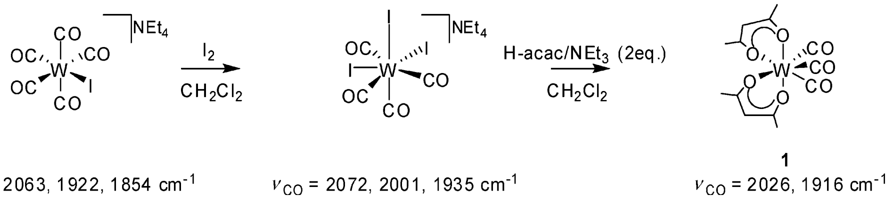
Scheme 1. Synthetic Route to Heptacoordinate $W(CO)_3(acac)_2$ (**1**)



(acac CO). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 193 K): δ 245.9 (d, $C{\equiv}O$, $^2J_{P-C} = 8$ Hz), 277.3 (d, $C{\equiv}O$, $^2J_{P-C} = 43$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.7 (s, $^1J_{P-W} = 225$ Hz).

$W(CO)(\eta^2$-$PhC{\equiv}CH)(acac)_2$ (3a). A flask was charged with 75 mg of $W(CO)_3(acac)_2$ **1**, which was dissolved in 10 mL of CH_2Cl_2. Excess phenylacetylene (2 equiv) was added, and the solution changed color from dark red to brown. The reaction was stirred until IR spectroscopy showed a single CO stretch, and the solvent was removed in vacuo to yield a brown solid. Purification occurred on a silica column using CH_2Cl_2 and hexanes to elute a dark orange/brown band. Black crystals were obtained by layering CH_2Cl_2 with hexanes (56 mg, 68%). IR: (hexanes) ν_{CO} 1920; (KBr) ν_{CO} 1903 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 12.96 (br s, 1H, $PhC{\equiv}CH$), 7.58−7.60 (m, 2H, C_6H_5 *ortho*), 7.44−7.48 (m, 2H, C_6H_5 *meta*), 7.28−7.32 (m, 1H, C_6H_5 *para*), 5.58, 5.51 (each a s, each 1H, acac CH), 2.20, 2.16, 2.14, 1.89 (each a s, each 3H, acac CH_3). ^1H NMR (CD_2Cl_2, 193 K): δ 13.00 (s, $PhC{\equiv}CH$, major rotamer, 98%), 12.49 (s, $PhC{\equiv}CH$, minor rotamer, 2%). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 26.1, 26.6, 26.7, 28.3 (acac CH_3), 100.2, 102.1 (acac CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 193 K): δ 128.3 (C_6H_5-*ortho*), 129.5 (C_6H_5-*para*), 130.7 (C_6H_5-*meta*), 133.9 (C_6H_5-*ipso*) 185.4, 187.8, 188.2, 194.9 (acac CO), 185.6 ($PhC{\equiv}CH$), 211.7 ($PhC{\equiv}CH$), 240.9 ($C{\equiv}O$). Anal. Calcd for $C_{19}H_{20}O_5W$: C, 44.56; H, 3.94; O, 15.62. Found: C, 44.71; H, 3.93; O, 15.51.

$W(CO)(\eta^2$-$MeC{\equiv}CMe)(acac)_2$ (3b). A flask was charged with 140 mg of $W(CO)_3(acac)_2$ **1**, which was dissolved in 10 mL of CH_2Cl_2. Excess 2-butyne (2 equiv) was added, and the reaction mixture was stirred until the IR spectrum displayed a single CO absorption. The solvent was removed in vacuo, and the brown product was triturated with hexanes. Purification occurred on a silica column using CH_2Cl_2 and hexanes to elute a dark orange/brown band (85 mg, 61%). IR: (hexanes) ν_{CO} 1906 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 5.53, 5.49 (each a s, each 1H, acac CH), 3.14 (br s, 6H, $H_3C{-}C{\equiv}C{-}CH_3$), 2.18, 2.16, 2.09, 1.86 (each a s, each 3H, acac CH_3). ^1H NMR (CD_2Cl_2, 250 K): δ 3.18, 3.13 (each a s, each 3H, $H_3C{-}C{\equiv}C{-}CH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 26.2, 26.7, 26.8, 28.4 (acac CH_3), 100.2, 101.7 (acac CH), 186.1, 187.6, 188.1, 194.4 (acac CO). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 193 K): δ 16.2, 20.1 (H_3C-$C{\equiv}C$-CH_3), 188.4 ($H_3C{-}C{\equiv}C{-}CH_3$), 209.2 (H_3C-$C{\equiv}C$-CH_3), 242.4 ($C{\equiv}O$). Anal. Calcd for $C_{15}H_{20}O_5W$: C, 38.81; H, 4.35; O, 17.23. Found: C, 38.51; H, 4.46; O, 16.83.

$W(\eta^2$-$PhC{\equiv}CPh)_2(acac)_2$ (4). Complex **1** was generated in situ from 590 mg of $[NEt_4][W(CO)_5I]$, and then it was extracted into toluene, which was cannula filtered to a separate flask. Excess diphenylacetylene (∼5 equiv) was added, and the solution was refluxed until IR spectroscopy indicated an absence of the metal carbonyl stretches. The solvent was removed in vacuo, and the crude material was chromatographed on alumina using toluene as an eluent, yielding a dark yellow band. The toluene was removed on a rotary evaporator, and the yellow product was washed with pentane to remove excess alkyne. Bright yellow crystals were grown by slow evaporation of a solution of **4** in CH_2Cl_2/hexanes (150 mg, 20%). IR: (KBr) $\nu_{C{\equiv}C}$ 1742 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 7.15−7.85 (m, 20H, C_6H_5), 5.44 (s, 2H, acac CH), 2.17, 1.82 (each a s, each 6H, acac CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 26.6, 28.1 (acac CH_3), 102.0 (acac CH), 127.7, 128.0, 128.2, 128.7, 128.8, 129.7, 130.9, 129.9, 141.1 ($H_5C_6C{\equiv}CC_6H_5$), 185.4, 190.4 (acac CO), 194.3, 201.4 ($PhC{\equiv}CPh$). Anal. Calcd for $C_{38}H_{34}O_4W$: C, 61.79; H, 4.65; O, 8.66. Found: C, 61.93; H, 4.57; O, 8.61.

III. Results and Discussion

Synthesis of $W(CO)_3(acac)_2$ (1). Stoichiometric amounts of $[NEt_4][W(CO)_5I]$ and elemental iodine were stirred in methylene chloride at room temperature. Oxidation to tungsten(II) resulted in formation of the seven-coordinate anionic species, $[NEt_4][W(CO)_4I_3]$,[37] which was subjected to 2 equiv of deprotonated 2,4-pentanedione. Coordination of two chelates results in liberation of one carbon monoxide ligand and three iodide ligands, ultimately forming the bis(acetylacetonato)tricarbonyl tungsten(II) complex, **1** (Scheme 1).

X-ray Structure of $W(CO)_3(acac)_2$ (1). Crystals for X-ray diffraction studies were generated from a concentrated solution of **1** in hexanes at −30 °C. The red needlelike crystals were air and solvent sensitive, decomposing after a few hours. The crystal structure confirmed the formulation as a heptacoordinate tungsten(II) complex containing three metal carbonyl ligands, all cis relative to one another, and two acetylacetonate ligands, both chelated to the metal (Figure 1). Coordination of two bidentate chelates in this fashion generates a chiral metal center; the cis orientation of the carbon monoxide ligands maximizes their ability to accept π-electron density from the d^4 tungsten(II) center.

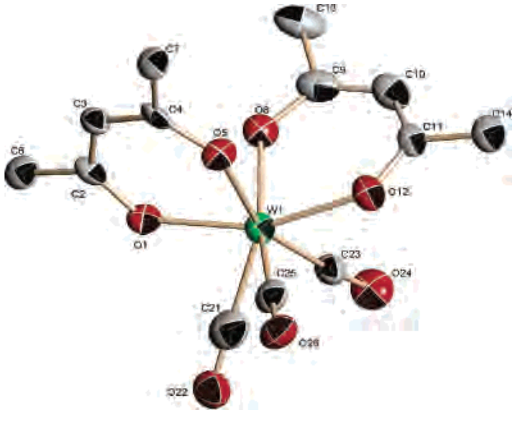


Figure 1. ORTEP diagram of $W(CO)_3(acac)_2$ (**1**).

The bite angles adopted by the two acac chelates in **1** are 86.2 and 82.4°. Note that coordination of the two acac chelates to the smaller chromium metal in planar $Cr(acac)_2$ yielded bite angles of approximately 90°.[19] The related Mo(VI) d^0 complex, $Mo(acac)_2(O)_2$, contained acac chelate bite

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Table 1. Selected Bond Lengths (Å) in $W(CO)_3(acac)_2$ (**1**)

W(1)−C(25)	1.960(12)
W(1)−C(21)	1.994(15)
W(1)−C(23)	1.997(11)
W(1)−O(8)	2.083(7)
W(1)−O(12)	2.092(7)
W(1)−O(1)	2.106(7)
W(1)−O(5)	2.115(7)

Table 2. Selected Bond Angles (deg) in $W(CO)_3(acac)_2$ (**1**)

C(25)−W(1)−C(21)	69.7(5)
C(25)−W(1)−C(23)	104.5(4)
C(21)−W(1)−C(23)	67.9(4)
O(8)−W(1)−O(12)	86.2(3)
O(1)−W(1)−O(5)	82.4(3)

angles of 81 and 84°,[38] respectively, close to the values observed here for the acac ligands.

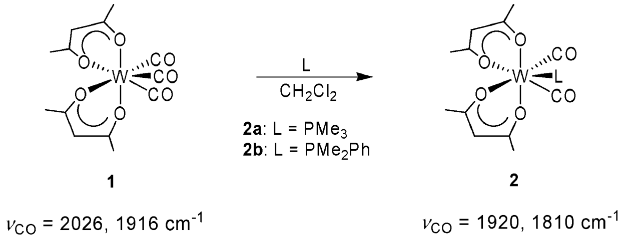
The tungsten−oxygen bond lengths to the four acac oxygen atoms ranged from 2.08 to 2.12 Å for $W(CO)_3(acac)_2$, comparable to the other Group VI bis(acac) distances. The molybdenum(VI) dioxo complex showed a wider range of metal−oxygen bond lengths (1.97−2.21 Å),[38] reflecting the trans effect of the oxo ligands. Both the C−C and C−O bond lengths within each chelate ring reflected delocalization of π-electron density. Each carbon−carbon and carbon−oxygen bond was shorter than a typical single bond, yet longer than a typical double bond. The same geometric description of the chelate ring holds true for other structures determined and discussed herein.

The three carbon monoxide ligands exhibited typical tungsten−carbon bond lengths for tungsten carbonyl complexes: 1.96, 1.99, and 2.00 Å.[39] Ligand−metal−ligand bond angles among the three carbon monoxide ligands with a common tungsten central atom in $W(CO)_3(acac)_2$ (67.9, 69.7, and 104.5°) were slightly smaller than but surprisingly comparable to the OC−W−CO angles in $W(CO)_3(dtc)_2$ (71.7, 74.4, and 107.8°).[40]

NMR Data for $W(CO)_3(acac)_2$ (1). The room temperature ^1H NMR spectrum of $W(CO)_3(acac)_2$ showed two singlets in a 6:1 ratio: one for the twelve acac methyl protons (2.08 ppm) and one for the two acac methine protons (5.67 ppm). As a result of the chiral tungsten(II) center and an absence of any rotation axis, all four acac methyl groups and both acac methine protons are positioned in unique chemical environments in the solid state, so the room temperature ^1H NMR spectrum is clearly incompatible with a static structure in solution. The simplicity of the spectrum, combined with the C_1 symmetry of the solid-state structure, suggested that a fluxional process equilibrates all four methyl environments and both methine environments on the NMR time scale.

At ambient temperature, the ^{13}C NMR spectrum also reflected fluxionality. A single peak was observed for all four acac methyl carbons (27.4 ppm), one for the two acac methine carbons (102.8 ppm), one for the four acac carbonyl carbons (190.1 ppm), and one for the three metal carbonyl carbons (242.5 ppm). Lowering of the acquisition temperature to 153 K resolved these signals into separate resonances. The room-temperature carbon monoxide peak was resolved into three distinct resonances (231, 236, and 258 ppm), compatible with the C_1 symmetry of the solid-state structure. Resolution of these three metal carbonyl carbon peaks at low temperature confirmed the fluxionality of this seven-coordinate molecule.

Scheme 2. Synthetic Route to Heptacoordinate W(II) Dicarbonylphosphine Complexes



Synthesis of $W(CO)_2(L)(acac)_2$ (2) [L = PMe_3 (2a) or PMe_2Ph (2b)]. The addition of one equivalent of the appropriate phosphine to a solution of tricarbonyl complex **1** in methylene chloride led to replacement of one carbonyl ligand by the added phosphine, forming a dicarbonylbis(acac)phosphine tungsten(II) complex (Scheme 2).

X-ray Structure of $W(CO)_2(PMe_3)(acac)_2$ (2a). Dark red crystals were grown from a solution of **2a** in methylene chloride layered with hexanes, which was cooled to −30 °C for 10 days. The X-ray structure of **2a** confirmed the identity of this heptacoordinate tungsten(II) complex containing two acetylacetonate chelates, two carbon monoxide ligands, and one trimethylphosphine ligand in the coordination sphere (Figure 2). The two carbonyl ligands were cis to one another, consistent with maximization of π-back-bonding from the two filled dπ orbitals on the d^4 metal center to CO π^* orbitals. The two tungsten−carbon bond lengths (1.96 and 1.97 Å) were nearly equal, and their values are typical of W−C distances for tungsten−carbonyl complexes.[39]

Bond angles among the two carbon monoxide ligands and the phosphine ligand with tungsten as the vertex can be definitively mapped to comparable angles among the three carbonyl ligands in **1**. Two acute angles and a third obtuse angle, which is ~35° larger, characterize the ML_3 fragment geometries of both **1** and **2a**. The phosphorus atom constitutes one leg of the obtuse angle in the bis(acac) phosphine

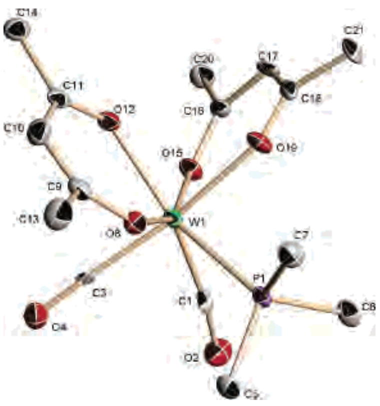


Figure 2. ORTEP diagram of $W(CO)_2(PMe_3)(acac)_2$ (**2a**).

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(38) Krasochka, O. N.; Sokolova, Y. A.; Atovmyan, L. O. *J. Struct. Chem.* **1975**, *16*, 696.
(39) Drew, M. G. B.; Rix, C. J. *J. Organomet. Chem.* **1975**, *102*, 467.
(40) Templeton, J. L.; Ward, B. C. *Inorg. Chem.* **1980**, *19*, 1753.

Table 3. Selected Bond Lengths (Å) in $W(CO)_2(PMe_3)(acac)_2$ (**2a**)

W(1)−C(3)	1.962(7)
W(1)−C(1)	1.971(8)
W(1)−O(12)	2.118(5)
W(1)−O(15)	2.128(5)
W(1)−O(8)	2.141(5)
W(1)−O(19)	2.183(5)
W(1)−P(1)	2.496(2)

Table 4. Selected Bond Angles (deg) in $W(CO)_2(PMe_3)(acac)_2$ (**2a**)

C(3)−W(1)−C(1)	73.2(3)
C(1)−W(1)−P(1)	71.4(2)
C(3)−W(1)−P(1)	107.6(2)
O(15)−W(1)−O(19)	83.5(2)
O(12)−W(1)−O(8)	82.6(2)

complexes. This thermodynamically preferred isomer is no doubt easily accessible on the soft seven-coordinate energy surface.

Tungsten−oxygen bond lengths for the two acetylacetonate ligands range from 2.12 to 2.18 Å and are, on average, slightly longer for the dicarbonyl phosphine complex **2a** than for the parent tricarbonyl complex **1**. Increased σ-donation from the phosphine relative to the displaced carbon monoxide provides more electron density to the tungsten(II) center, perhaps lengthening the tungsten−oxygen bonds. More likely, the replacement of one small carbonyl ligand by a bulky phosphine ligand crowds the coordination sphere and lengthens the tungsten−oxygen bonds.

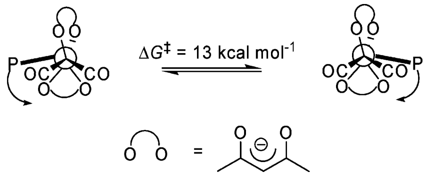
In accordance with the steric hindrance created by trimethylphosphine, the bite angles of the acac chelates in the phosphine complex were, on average, slightly smaller than those in the parent tricarbonyl complex. The loss of carbon monoxide and coordination of a bulkier phosphine ligand perhaps forces the two acac chelates to adopt a smaller bite angle in a crowded seven-coordinate tungsten coordination sphere.

The tungsten−phosphorus bond length in the bis(acac) trimethylphosphine complex, **2a**, was 2.49 Å. This value is slightly shorter than bond lengths reported for other tungsten(II)−carbonyl−phosphine complexes.[41,42] In **2a**, the chelates adopt a slightly different conformation than in precursor complex **1** to accommodate the incoming phosphine ligand.

NMR Data for $W(CO)_2(L)(acac)_2$. The room temperature ^{1}H NMR spectrum of dimethylphenylphosphine complex **2b** showed a distinct peak for each of the two methine protons (5.76 and 5.40 ppm), indicating two inequivalent acac environments. In the room-temperature ^{1}H NMR spectrum, the PMe_2Ph ligand displays a lone doublet (1.77 ppm, $^2J_{P-H} = 10$ Hz) in the upfield methyl region. Note that the solid state structure should lead to two doublets as a result of phosphorus coupling to two distinct diastereotopic methyl groups. Only three acac methyl peaks were observed, with one integrating for 6H and the other two appearing as much broader signals and integrating for 3H.

A rapid rearrangement on the NMR time scale seemed likely, and indeed, the fluxional process was sufficiently slow at 193 K to allow observation of all four unique acac methyl peaks (2.16, 2.12, 1.96, and 1.91 ppm). More informative was the presence of two doublets from the methyl groups of the PMe_2Ph ligand (1.73 and 1.66 ppm, $^2J_{P-H} = 10$ Hz). These two methyl groups are diastereotopic at low temperature, so the phosphine ligand is indeed bound to a chiral tungsten center. Evidence of *intramolecular* fluxionality was provided by the $^{31}P\{^1H\}$ NMR spectrum at room temperature in which the lone singlet displayed tungsten satellites (^{183}W (14.28%), $I = 1/2$). Tungsten satellites would not be present if the phosphine ligand were rapidly dissociating and exchanging with other metal centers. These data indicated that an intramolecular rearrangement process is rapidly exchanging both the acac sites and the two carbonyl ligand sites at room temperature, as well as equilibrating the two phosphine methyl groups.

Scheme 3. Proposed Movement of Phosphine Ligand[a]



[a] Viewed parallel to the averaged mirror plane which is vertical and perpendicular to the paper.

Additional experiments were conducted using variable-temperature NMR to probe activation energies for the fluxional process. The activation barrier, $\Delta G^{\ddagger}$, was calculated from the Eyring equation after the Gutowsky−Holm equation was used to calculate k_{ex} at the coalescence temperature.[43] At 210 K, in the ^{1}H NMR spectrum, the two phosphine methyl signals coalesced into a broad singlet, prior to emerging into the doublet seen at ambient temperature. The coalescence temperature and chemical shift difference led to a calculated activation energy of 13.0 kcal/mol. The acac methyl groups remained as distinguishable singlets until coalescence occurred at 213 K, which, combined with the low-temperature chemical shift difference, yielded an activation energy of 13.2 kcal/mol. Both the phosphine methyl and the acac methyl exchange processes are attributed to a single fluxional process with an activation barrier near 13 kcal mol^{-1}.

The low-temperature ^{1}H NMR data for **2b** was consistent with the static C_1 tungsten(II) bis(acac) phosphine structure observed in the solid state for **2a**. At room temperature, the coalescence of the two diastereotopic phosphine methyl signals and convergence of only one pair of acac methyl signals suggested the presence of an effective mirror plane (as a result of the intramolecular fluxional process) *containing* one acac metallacycle and *bisecting* the other. One can imagine that the phosphine ligand swings through the mirror plane, thus converting the diastereotopic methyl groups to enantiomers of one another as it passes through the C_S intermediate structure.

The room-temperature ^{13}C NMR spectrum provided further insight into the fluxional behavior displayed by the phosphine

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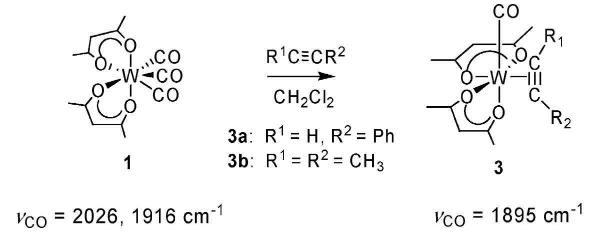
(41) Drew, M. G. B.; Tomkins, I. B.; Colton, R. *Aust. J. Chem.* **1970**, *23*, 2517.
(42) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.
(43) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

Scheme 4. Synthetic Route to W(II) Mono(carbonyl) Mono(alkyne) Complexes



complex, **2b**. One key feature was the presence of two acac α-carbon peaks, indicating inequivalent chelate environments even in the fast-exchange limit. Three resonances appeared for the acac ketone carbons, consistent with the presence of an effective mirror plane at room temperature. Two of these keto carbons are unique and lie in the mirror plane, and the remaining two are equivalent to one another and lie on opposite sides of it. However, rather than three acac methyl carbon peaks, the spectrum showed only two. Given the fact that three acac methyl carbons should be observed on the basis of the analogy to the ^{1}H NMR spectrum, the data suggested that one purely coincidental chemical shift overlap occurred. A methyl doublet was observed upfield at 13.7 ppm ($^1J_{\mathrm{P-C}} = 33$ Hz) for the PMe_2Ph ligand. The presence of only one doublet demonstrated that the mirror plane also relates the two phosphine methyl carbons to one another. The two metal carbonyl peaks appeared as a broad singlet in the ^{13}C NMR spectrum at room temperature; this signal decoalesced at low temperature. At 193 K, the metal carbonyl carbons appeared as widely separated doublets at 245.9 ($^2J_{\mathrm{P-C}} = 8$ Hz) and 277.3 ppm ($^2J_{\mathrm{P-C}} = 43$ Hz). On the basis of an empirical correlation of the $^2J_{\mathrm{P-C}}$ coupling constant with angle, the larger coupling constant suggests that carbon lies at a more obtuse angle to the phosphine ligand than the carbon with the smaller coupling constant.[44,45] (Since these complexes are seven-coordinate, not octahedral, the distinction is not between cis and trans but rather between acute and obtuse.) The crystallographic data showed that a larger angle exists between P1 and C3, so presumably this C3 carbon resonates at low field and displays the larger coupling constant.

Synthesis of W(CO)(η^2-R^{1}C≡CR^2)(acac)$_2$ [R^1 = Ph, R^2 = H (3a), R^1 = R^2 = CH$_3$ (3b)]. The addition of 1 equiv of alkyne to tricarbonyl complex **1** at ambient temperature displaced two carbon monoxide ligands resulting in η^2-coordination of the incoming alkyne ligand and yielding a monocarbonylmonoalkynebis(acac)tungsten(II) complex (Scheme 4).

X-ray Structure of W(CO)(η^2-PhC≡CH)(acac)$_2$ (3a). Black crystals of **3a** were obtained via evaporation from a solution of methylene chloride and hexanes following column chromatography. The X-ray crystal structure of **3a** showed a tungsten atom surrounded by two acetylacetonate ligands, one carbon monoxide ligand, and one phenylacetylene ligand bound in an η^2-manner (Figure 3). The two chelates exhibited bite angles of 82.4 and 85.4°, similar to those present in the parent tricarbonyl complex **1**. The average W−O bond distance was 2.10 Å, also comparable to the W−O distances in **1**.

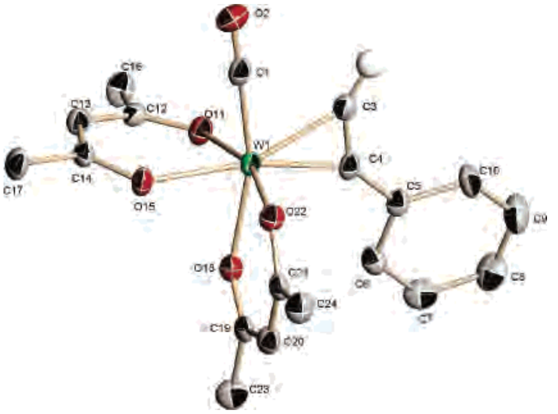


Figure 3. ORTEP diagram of W(CO)(η^2-PhC≡CH)(acac)$_2$ (**3a**).

Table 5. Selected Bond Lengths (Å) in W(CO)(η^2-PhC≡CH)(acac)$_2$ (**3a**)

W(1)−C(1)	1.946(6)
W(1)−C(3)	2.036(5)
W(1)−C(4)	2.037(5)
W(1)−O(11)	2.058(4)
W(1)−O(15)	2.117(3)
W(1)−O(18)	2.145(3)
W(1)−O(22)	2.070(3)
C(3)−C(4)	1.301(8)

Table 6. Selected Bond Angles (deg) in W(CO)(η^2-PhC≡CH)(acac)$_2$ (**3a**)

C(1)−W(1)−C(3)	72.0(2)
C(1)−W(1)−C(4)	109.2(2)
C(3)−W(1)−C(4)	37.3(2)
O(11)−W(1)−O(15)	82.4(1)
O(18)−W(1)−O(22)	85.4(1)

The solid-state structure showed that the alkyne and carbonyl ligands are cis with respect to each other and that they adopt a parallel configuration in terms of the C≡C triple bond axis and the W−C≡O axis. The phenyl ring on the alkyne is oriented anti to the carbonyl ligand.

The triple-bond carbons (C3 and C4) in the alkyne ligand were separated by 1.30 Å, indicating a loss of some triple-bond character upon coordination to the tungsten(II) center. This bond length is actually closer to that of a carbon−carbon double bond, and thus, it is compatible with a metallacyclopropene resonance description. Formally, **3a** can be classified as either a six- or seven-coordinate molecule, and the metal−ligand bond angles reflect this ambiguity. It is easy to map the geometry of **3a** onto a distorted octahedral skeleton with the alkyne ligand occupying a single site. An angle of 161.5° was reported for O11−W1−O22, and one of 163.5° was reported for O18−W1−C1. These values reflect significant deviation from an ideal octahedral geometry, as the atoms constituting these angles have shifted to accommodate the incoming alkyne ligand.

NMR Data for W(CO)(η^2-RC≡CR′)(acac)$_2$. The room temperature ^{1}H NMR spectrum of **3a** displayed four unique methyl signals and two unique methine signals, reflecting the inequivalent environments of the two β-diketonate

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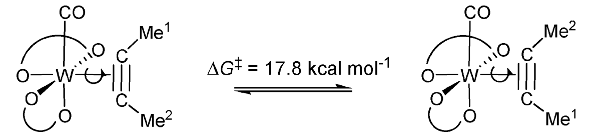
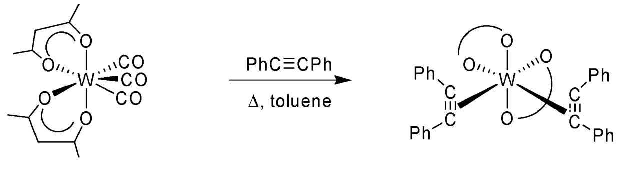
[44] Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 3743.
[45] Day, R. O.; Batschelet, W. H.; Archer, R. D. *Inorg. Chem.* **1980**, *19*, 2113.

Scheme 5. Rotation of the Alkyne Ligand along the Metal−Alkyne Centroid



Scheme 6. Synthetic Route to W(η^2-PhC≡CPh)$_2$(acac)$_2$ (**4**)



1

4

ligands. The terminal alkyne proton, resonating at 12.95 ppm, appeared as a broad singlet at room temperature. On the basis of the empirical correlation between terminal alkyne proton chemical shifts of the coordinated acetylenic proton and electron donation, the alkyne ligand donates four electrons to the tungsten atom.[46−49] The broadness of the acetylenic proton peak can be attributed to the rotation about the formal metal−alkyne centroid interconverting two isomers.[46,47] The observation of both alkyne rotamers was accomplished by low-temperature NMR. At 193 K, the broad acetylenic proton signal separated into two sharp singlets; the major isomer (∼98%) resonated at 12.98 ppm, and the minor isomer (∼2%) resonated at 12.49 ppm. The phenyl ring does not reflect the fluxionality of the alkyne ligand in the ^{1}H NMR spectrum: the ortho, meta, and para protons remained sharp and distinguishable at all temperatures. Presumably the chemical shift variations for the aromatic protons are much less than the roughly one-half ppm of the terminal alkyne proton, so exchange with the minor isomer does not noticeably broaden the aromatic peaks. The acetylacetonate ligands and carbon monoxide ligand remained static as the alkyne ligand rotates, and presumably the chemical shift differences between the isomers are small so that no evidence of fluxionality was observed in the proton signals for these ligands by NMR spectroscopy.

At room temperature, the ^{13}C NMR spectrum of **3a** also reflected the helical coordination mode of the two acac ligands. Four distinct signals were present, both for the acac methyl carbons and for the acac ketone carbons, as well as two signals for the central acac α-carbons, compatible with C_1 symmetry for this complex. The metal carbonyl carbon and the carbon atoms of the alkyne ligand were detected only at low temperature. Rotation of the alkyne ligand at room-temperature broadened the carbon signals to the point that these ^{13}C peaks were not observable. At 193 K it was possible to assign resonances for the triple-bond carbons, as well as for the carbon atoms in the phenyl ring. Chemical shift values for the alkyne carbons in both **3a** (211.7 and 185.6 ppm) and **3b** (209.2 and 188.4 ppm) were shifted downfield nearly 80−100 ppm from the two-electron donor alkyne ligands.[46,50,51] These ^{13}C chemical shifts suggest that the alkyne ligand in these tungsten(II) bis(acac) complexes acts as a four-electron donor to the metal center, resulting in a formal eighteen-electron complex.

Table 7. Selected Bond Lengths (Å) in W(η^2-PhC≡CPh)$_2$(acac)$_2$ (**4**)

W(1)−C(16)	2.062(1)
W(1)−C(30)	2.067(1)
W(1)−C(15)	2.068(1)
W(1)−C(29)	2.073(1)
W(1)−O(1)	2.116(1)
W(1)−O(8)	2.130(1)
W(1)−O(5)	2.137(1)
W(1)−O(12)	2.144(1)
C(15)−C(16)	1.314(2)
C(29)−C(30)	1.311(2)

Table 8. Selected Bond Angles (deg) in W(η^2-PhC≡CPh)$_2$(acac)$_2$ (**4**)

C(16)−W(1)−C(15)	37.11(5)
C(30)−W(1)−C(29)	36.92(5)
O(1)−W(1)−O(5)	82.45(4)
O(8)−W(1)−O(12)	82.81(4)

Trapping of the tricarbonyl complex **1** with a symmetric alkyne, in this case 2-butyne to yield **3b**, allowed extraction of the rotational barrier for the alkyne ligand. The rotational activation barrier, $\Delta G^{\ddagger}$, was calculated from the Eyring equation after the Gutowsky−Holm equation was used to calculate k_{ex} at the coalescence temperature. Variable-temperature NMR indicated a coalescence temperature of 286 K for the rotating 2-butyne ligand, and the barrier to rotation for this symmetric alkyne derivative was found to be 17.8 kcal mol^{-1} (Scheme 5).

The room-temperature ^{13}C NMR spectrum of **3b** also reflected helical coordination of the acac ligands. As for the phenylacetylene derivative **3a**, 10 distinct peaks were observed for the 10 unique carbons that constitute the two anionic chelates in **3b**. Two broad peaks representing the two methyl carbons on the alkyne ligand were resolved into sharp singlets in the low-temperature spectrum. The characterization data for **3b** here differs from the data reported earlier for this same complex, which was synthesized by a different route. The discrepancy lies in the ^{1}H and ^{13}C NMR data: two methine proton peaks and two acac methyl peaks were reported[34] in contrast to the C_1 symmetry reflected in two methine peaks and four acac methyl groups observed in this work. Additionally, the signals reported for the metal carbonyl carbon and the triple-bond carbon are assigned differently here. The NMR data presented here for both alkyne derivatives is compatible with the observed solid state conformation of **3a**.

Synthesis of W(η^2-PhC≡CPh)$_2$(acac)$_2$ (4). Tricarbonyl reagent **1** was refluxed with excess diphenylacetylene which led to replacement of all three carbon monoxide ligands by two alkyne ligands, resulting in tungsten(II) bis(acac) bis(diphenylacetylene), complex **4** (Scheme 6).

X-ray Structure of W(η^2-PhC≡CPh)$_2$(acac)$_2$ (4). Bright yellow crystals of complex **4** were grown by evaporating a solution of **4** in methylene chloride and hexanes. X-ray

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(46) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532.
(47) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.
(48) McDonald, J. W.; Corbin, J. L.; Newton, W. E. *J. Am. Chem. Soc.* **1975**, *97*, 1970.
(49) King, R. B. *Inorg. Chem.* **1968**, *7*, 1044.
(50) Thomas, J. L. *Inorg. Chem.* **1978**, *17*, 1507.
(51) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

Table 9. Crystal and Data Collection Parameters for $W(CO)_3(acac)_2$ (**1**), $W(CO)_2(PMe_3)(acac)_2$ (**2a**), $W(CO)(\eta^2\text{-}PhC{\equiv}CH)(acac)_2$ (**3a**), $W(\eta^2\text{-}PhC{\equiv}CPh)_2(acac)_2$ (**4**)

empirical formula	$C_{13}H_{14}O_7W$	$C_{15}H_{23}O_6PW$	$C_{19}H_{20}O_5W$	$C_{38}H_{34}O_4W$
complex	**1**	**2a**	**3a**	**4**
fw	466.09	514.15	512.24	738.50
color	red	dark red	black	bright yellow
temp	100 K	100 K	100 K	100 K
wavelength	0.71703 Å	0.71703 Å	0.71703 Å	0.71703 Å
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
unit cell dimensions	$a = 15.261$ Å	$a = 12.891$ Å	$a = 8.439$ Å	$a = 9.545$ Å
	$b = 15.416$ Å	$b = 9.4512$ Å	$b = 20.224$ Å	$b = 9.897$ Å
	$c = 12.883$ Å	$c = 15.714$ Å	$c = 11.192$ Å	$c = 16.929$ Å
	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 98.517°$
	$\beta = 94.87°$	$\beta = 105.093°$	$\beta = 106.649°$	$\beta = 91.869°$
	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 91.631°$
vol	3020 Å^3	1848 Å^3	1830 Å^3	1580Å^3
Z	8	4	4	2
density (calcd)	2.050 Mg/m^3	1.848 Mg/m^3	1.866 Mg/m^3	1.552 Mg/m^3
abs coeff	7.68 mm^{-1}	6.36 mm^{-1}	6.35 mm^{-1}	6.70 mm^{-1}
F(000)	1776	1000	998	736
cryst size	$0.30 \times 0.05 \times 0.05$ mm^3	$0.25 \times 0.20 \times 0.10$ mm^3	$0.20 \times 0.20 \times 0.10$ mm^3	$0.35 \times 0.20 \times 0.15$ mm^3
θ range	1.88−24.07°	2.71−25.00°	5.00−56.00°	2.08−30.00°
index ranges	$-17 \le h \le 17$	$-14 \le h \le 15$	$-11 \le h \le 10$	$-13 \le h \le 13$
	$-17 \le k \le 17$	$-11 \le k \le 10$	$0 \le k \le 26$	$-13 \le k \le 13$
	$-14 \le l \le 12$	$-18 \le l \le 18$	$0 \le l \le 14$	$-23 \le l \le 23$
reflns collected	13 400	10 605	17 909	44 704
independent reflns	2347	3237	4433	9174
	$R_{int} = 0.0694$	$R_{int} = 0.0313$	$R_{int} = 0.042$	$R_{int} = 0.0218$
data/restraints/params	2347/0/195	3237/0/216	4433/0/227	9174/0/392
GOF on F^2	1.083	1.177	1.313	1.031
final R indices	R1 = 0.0379	R1 = 0.0338	R1 = 0.032	R1 = 0.0139
[$I > 2\sigma(I)$]	wR2 = 0.0709	wR2 = 0.0742	wR2 = 0.039	wR2 = 0.0341
R indices	R1 = 0.0689	R1 = 0.0420	R1 = 0.044	R1 = 0.0145
(all data)	wR2 = 0.0837	wR2 = 0.0769	wR2 = 0.141	wR2 = 0.0343
largest diff. peak and hole	1.273 and −1.355 e Å^{-3}	1.859 and −1.382 e Å^{-3}	2.000 and −1.430 e Å^{-3}	0.907 and −0.652 e Å^{-3}

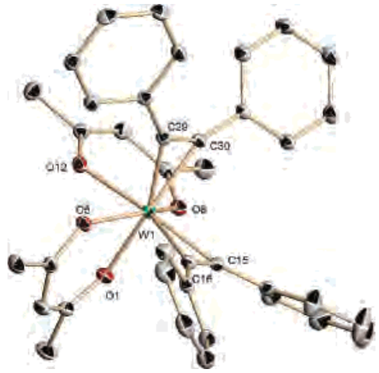

Figure 4. ORTEP diagram of $W(\eta^2\text{-}PhC{\equiv}CPh)_2(acac)_2$ (**4**).

diffraction studies of **4** verify coordination of two acetylacetonate ligands and two diphenylacetylene ligands in a cis fashion to a tungsten center (Figure 4). Both alkyne ligands are parallel to one another; the triple bonds are aligned. This mode of coordination has been observed in other group VI bis(alkyne) complexes with two anionic bidentate chelates.[52,53] The tungsten−oxygen bond lengths (2.12−2.14 Å) are slightly longer, on average, than those seen in complexes **1** and **3a**, but they are comparable to those of the phosphine adduct, complex **2a**. The bite angles of the oxygen donor chelates are nearly equal in **4** (82.5 and 82.8°), reflecting the C_2 symmetry generated by coordination of two symmetric alkynes.

NMR Data for $W(\eta^2\text{-}PhC{\equiv}CPh)_2(acac)_2$ (4). The room-temperature ^{1}H NMR spectrum for **4** showed two acac methyl resonances (2.17 and 1.82 ppm) and one acac methine resonance (5.44 ppm) in addition to indistinguishable multiplets in the aromatic region (7.15−7.85 ppm), consistent with formation of a bis(acac)bis(alkyne) complex. For symmetric alkyne ligands, such as diphenylacetylene, these molecules contain a C_2 axis. The two acac ligands are equivalent to one another because of the C_2 axis, but within each acac ligand, one of the methyl proton reporter groups is cis to an alkyne ligand and one is trans, thus producing two methyl signals in the ^{1}H NMR.

The room-temperature ^{13}C NMR data for **4** confirmed the presence of a 2-fold axis generated by the coordination of two coparallel alkynes to the tungsten(II) bis(acac) fragment. The spectrum mimicked the behavior displayed in the ^{1}H NMR spectrum: two resonances were present for the four acac methyl carbons (26.6 and 28.1 ppm), and one resonance appeared for the two acac α-carbons, (102.0 ppm). Likewise, only two peaks were present for the four acac ketone carbons (185.4 and 190.4 ppm).

Previous studies have shown that the number of electrons donated by η^2-bound alkyne ligands roughly correlates with the chemical shift of the alkyne carbons.[51] The alkyne carbons of **4** were slightly broadened in the room-temperature ^{13}C NMRspectrum, suggesting that the rate of rotation of the alkyne ligands was approaching the NMR time scale. The chemical shifts of these two alkyne carbons appeared at $\delta = 194.3$ and 201.4 ppm (av = 197.9 ppm). This

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(52) Herrick, R. S.; Nieter-Burgmayer, S. J.; Templeton, J. L. *Inorg. Chem.* **1983**, *22*, 3275.

(53) Herrick, R. S.; Templeton, J. L. *Organometallics* **1982**, *1*, 842.

averaged ^{13}C chemical shift is farther downfield than comparable values for other complexes containing two alkyne ligands that formally donate three electrons each to the metal center.[51−53] Perhaps this stems from the electronegativity of the oxygen-donor chelates. Surrounded by four oxygen atoms, the tungsten center is more electron deficient than in the analogous dithiocarbamate complexes, and as a result, the two alkyne ligands provide greater π-electron donation to counteract this effect. Of course, formal electron counting is merely a method of bookkeeping and is not sophisticated enough to track the continuum of bonding options available to alkyne ligands.

IV. Summary

Chiral, neutral, monomeric complexes containing the $W(II)(acac)_2$ (acac = acetylacetonate) moiety have been synthesized from a convenient starting material, the pentacarbonyl iodotungsten(0) anion. Oxidation of the tungsten(0) reagent with elemental iodine and the subsequent addition of two equivalents of the acac anion resulted in the formation of a reactive seven-coordinate 18-electron tricarbonyl complex, $W(CO)_3(acac)_2$ (**1**). The addition of phosphine nucleophiles (L = PMe_3 (**2a**), PMe_2Ph (**2b**)) to **1** generated seven-coordinate complexes of the type $W(CO)_2(L)(acac)_2$. The parent complex, **1**, also reacted readily with alkynes ($PhC\equiv CH$ (**3a**) and $MeC\equiv CMe$ (**3b**)) to form complexes of the type $W(CO)(\eta^2\text{-}R^1C\equiv CR^2)(acac)_2$. Refluxing **1** with excess diphenylacetylene led to coordination of two alkyne ligands and yielded the bis(alkyne) complex, $W(PhC\equiv CPh)_2(acac)_2$ (**4**). X-ray crystallography provided structural assignments for a representative molecule from each class of these complexes, and variable-temperature ^1H and ^{13}C NMR was used to probe the fluxional processes within this series of bis(acetylacetonate) tungsten d^4 complexes.

Acknowledgment. We thank the National Science Foundation (CHE-0414726) for financial support.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0600329