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Coordination and Oligomerization of Alkynes at Mononuclear Tungsten Aryloxide Metal Centers

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Reduction of either $[W(OC_6H_3Ph_2\text{-}2,6)_2Cl_4]$ ($OC_6H_3Ph_2$-2,6 = 2,6-diphenylphenoxide) or $[W(OC_6H_3Pr^i{}_2\text{-}2,6)_2Cl_4]$ ($OC_6H_3Pr^i{}_2$-2,6 = 2,6-diisopropylphenoxide) in toluene with sodium amalgam in the presence of alkynes ($EtC{\equiv}CEt$; $PhC{\equiv}CPh$; $4Me\text{-}PhC{\equiv}CPh\text{-}4Me$) leads to a series of alkyne (ac) adducts of general formulae $[(ArO)_2WCl_2(ac)]$ (**1**) and $[(ArO)_2W(ac)_2]$ (**2**). The ^{13}C NMR spectra of **1** and **2** show downfield shifts for the coordinated alkyne carbon atoms. A single crystal X-ray diffraction analysis shows five coordinate $[W(OC_6H_3Ph_2\text{-}2,6)_2Cl_2(C_2Et_2)]$ (**1a**) to adopt a square pyramidal geometry about tungsten with *trans* aryloxide ligands and an axial 3-hexyne. The solid state structure of $[W(OC_6H_3Ph\text{-}2,6)_2(C_2Et_2)_2]$ (**2a**) shows a pseudotetrahedral environment about tungsten with the two 3-hexyne ligands arranged parallel with each other. Reaction of the η^6-arene complex $[W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(OC_6H_3Ph_2\text{-}2,6)(dppm)]$ with 3-hexyne generates the compound $[W(OC_6H_3Ph_2\text{-}2,6)_2(C_4Et_4)]$ (**3**) which contains a tungstacyclopentatriene ring. This ring is nonplanar both in the solid state and solution (NMR). The bis-cyclometalated compounds $[W(OC_6H_3Ph\text{-}C_6H_4)_2(L)_2]$ (L = PMe_2Ph, $PMePh_2$, and py) react with alkynes to form a number of products. From the reaction with 3-hexyne, two new compounds of formula $[W(OC_6H_3PhC_6H_4)_2(C_4Et_4)]$ (**4**) and $[W(OC_6H_3PhC_6H_4)_2(C_6Et_6)]$ (**5**) were isolated. Structural studies on **4** and **5** show them to contain multiple metallacyclic rings formed by transfer of one of the metalated aryloxide carbon atoms to an α-carbon of an intermediate tungstacyclopenta-2,4-diene complex. Crystal data at −100 °C for $WCl_2O_2C_{42}H_{36}$ (**1a**): $a = 9.331(2)$, $b = 12.271(2)$, $c = 16.334(3)$ Å; $\alpha = 107.48(1)$, $\beta = 101.78(2)$, $\gamma = 95.13(2)°$; $Z = 2$, $d_{calcd} = 1.595$ g cm^{-3} in space group $P\bar{1}$; for $WO_2C_{48}H_{46}$ (**2a**) at 20 °C: $a = 11.458(1)$, $b = 17.961(4)$, $c = 10.915(2)$ Å; $\alpha = 104.65(1)$, $\beta = 115.23(1)$, $\gamma = 92.08(1)°$; $Z = 2$, $d_{calcd} = 1.437$ g cm^{-3} in space group $P\bar{1}$; for $WO_2C_{48}H_{46}$ (**3**) at −114 °C: $a = 11.086(2)$, $b = 18.400(7)$, $c = 19.453(5)$ Å; $\alpha = 98.96(2)$, $\beta = 97.14(2)$, $\gamma = 98.67(2)°$; $Z = 4$, $d_{calcd} = 1.454$ g cm^{-3} in space group $P\bar{1}$; for $WO_2C_{48}H_{44}$ (**4**) at 20 °C: $a = 10.805(7)$, $b = 11.662(1)$, $c = 17.008(3)$ Å; $\alpha = 80.12(1)$, $\beta = 84.71(3)$, $\gamma = 63.07(3)°$; $Z = 2$, $d_{calcd} = 1.476$ g cm^{-3} in space group $P\bar{1}$; for $WO_2C_{54}H_{54}$ (**5**) at 20 °C: $a = 9.835(2)$, $b = 11.8298(7)$, $c = 19.620(2)$ Å; $\alpha = 104.748(6)$, $\beta = 98.717(9)$, $\gamma = 104.478(8)°$; $Z = 2$, $d_{calcd} = 1.467$ g cm^{-3} in space group $P\bar{1}$.

Introduction

The coordination chemistry of alkynes at molybdenum and tungsten metal centers has received extensive study.[1] Early work on simple adduct formation[2] was followed by the recognition that alkyne ligands can act as variable-electron donors even in mononuclear molybdenum and tungsten complexes.[3] More recent work on the reactivity of alkyne substrates at mono- and dimolybdenum (tungsten) metal centers has been carried out in the knowledge of the metathesis capabilities of these Group 6 metals.[4–7] In this context the last 10 years have seen the ubiquitous carbonyl and cyclopentadienyl ligands usurped by oxo, alkoxide, siloxide, aryloxide, and related oxygen donor

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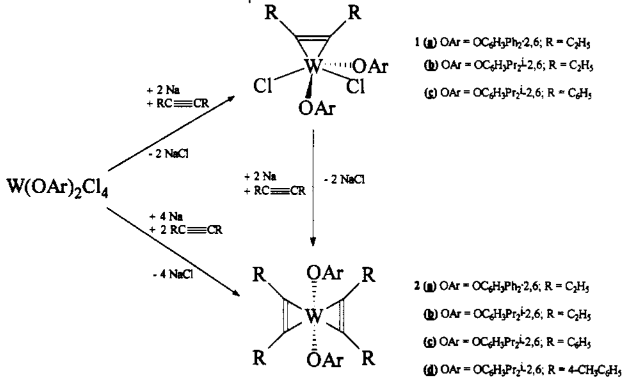
ligands as well as imido and amido functions as supporting groups for this chemistry.[8–10]

During our studies of the early d-block metal organometallic chemistry that can be supported by bulky aryloxide ligation,[11] we have investigated the reduction of mixed chloro aryloxides of tungsten in the presence of alkyne substrates. This paper reports on the coordination characteristics of the resulting alkyne ligands as well as novel metallacyclic compounds formed by coupling of alkynes at these mononuclear tungsten aryloxide metal centers. Some of these results have been previously communicated.[12]

Results and Discussion

Synthesis of Alkyne Complexes. Simple homoleptic aryloxide and mixed chloro, aryloxide derivatives of tungsten(IV) have been known since the work of Funk and Bauman in 1937.[13] More recent work in this area has focused on the synthesis and characterization of an extensive series of aryloxide derivatives of general formula $[W(OAr)_n(Cl)_{6-n}]$ (n = 1–6; OAr = variously substituted phenoxides). The focus of much of this work has been to correlate the stoichiometry and electronic nature of the aryloxide compounds with their activity as olefin metathesis catalyst precursors, a concept pioneered by the Schrock group[5] for well-defined metathesis catalysts, and later applied to the as yet ill-defined tungsten aryl oxide/activator catalyst systems by the Bassett[14] and Bell[15] groups. Our interest in the chemistry of mixed chloro aryloxides of tungsten has been in their potential for the generation of lower valent aryloxide derivatives of tungsten which may prove useful for carrying out organometallic transformations.[16] Previous work by Schrock et al. has shown that mononuclear compounds such as $[W(OC_6H_3Me_2\text{-}2,6)_3Cl_3]$ are useful starting materials for the synthesis of ditungsten aryloxide compounds.[17] Our group has shown that the use of the ligand 2,6-diphenylphenoxide allows the isolation of various low valent, mononuclear derivatives of tungsten. The formation of intramolecular η^6-arene interactions as well as arene CH bond activation was identified.[16]

Scheme I



The tungsten bis(aryloxide) compounds $[W(OC_6H_3Ph_2\text{-}2,6)_2Cl_4]$ and $[W(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_4]$[18] can both be obtained in high yield by reacting WCl_6 with 2 equiv of the parent phenol in hydrocarbon solvents. The 2,6-diphenylphenoxide compound has been shown to be *cis* in the solid state,[16] but *cis*/*trans* isomerization has been shown to occur for both compounds either thermally or by one-electron reduction either chemically or electrochemically.[15] The sodium amalgam (2 Na per W) reduction of deep-red solutions of either tetrachloride in the presence of excess 3-hexyne or PhC≡CPh produces orange solutions from which can be isolated the monoalkyne compounds **1** (Scheme I). Further reduction of toluene solutions of **1** in the presence of excess alkyne leads to the formation of the bis(alkyne) derivatives **2** (Scheme I). A much more efficient synthesis of the bis(alkyne) compounds **2** involves direct reaction of the tetrachloride substrates with sodium amalgam (4 Na per W) and excess alkyne reagent. The molecular geometry shown for the alkyne compounds is based upon the crystallographic results discussed below (Scheme I). Analysis of the crude reaction mixtures generated in the formation of the bis(3-hexyne) compounds **2a** and **2b** showed (^{1}H NMR) the presence of minor amounts of metallacyclic products (*vide infra*).

Spectroscopic Properties of Alkyne Compounds. The ^{1}H and ^{13}C NMR spectra of the mono- and bis(alkyne) complexes **1** and **2** show the expected resonances for the aryloxide ligands. The lack of diastereotopic methyl

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Table I. ^{13}C NMR Chemical Shifts for Selected Molybdenum and Tungsten Alkyne Complexes

complex	$\delta(R^{13}C{\equiv}CR)$ av	ref
$[W(OC_6H_3Ph_2\text{-}2,6)_2Cl_2(C_2Et_2)]$	191.7	this work
$[W(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(C_2Et_2)]$	182.8	this work
$[W(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(C_2Ph_2)]$	183.4	this work
$[WCl_4(C_2Ph_2)]$	270	19
$[W(CO)(detc)_2(C_2H_2)]$	206.6	3b
$[W(CO)(detc)_2(PhC_2H)]$	205.7	3b
$[Mo(CO)(dmtc)_2(C_2H_2)]$	203.7	3b
$[Mo(CO)(dmtc)_2(PhC_2H)]$	205.3	3b
$[Mo(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(C_2Et_2)]$	178.8	20
$[Mo(OC_6H_3Pr^i_2\text{-}2,6)_3Cl(C_2Et_2)]$	188.8	20
$[Mo(OC_6H_3Pr^i_2\text{-}2,6)_4(C_2Et_2)]$	197.7	20
$[Mo(OC_6H_3Me_2\text{-}2,6)_4(C_2Et_2)]$	197.9	20
$[Mo(OC_6H_3Pr^i_2\text{-}2,6)_4(C_2Ph_2)]$	191.6	20
$[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)(C_2Et_2)]$	217.4	20
$[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)(C_2Me_2)]$	219.2	20
$[W(OC_6H_3Ph_2\text{-}2,6)_2(C_2Et_2)_2]$	215.6	this work
$[W(OC_6H_3Pr^i_2\text{-}2,6)_2(C_2Et_2)_2]$	214.9	this work
$[W(OC_6H_3Pr^i_2\text{-}2,6)_2(C_2Ph_2)_2]$	214.2	this work
$[W(OC_6H_3Pr^i_2\text{-}2,6)_2(4Me\text{-}PhC_2Ph\text{-}4Me)_2]$	215.3	this work
$[Mo(detc)_2(PhC_2H)_2]$	180.2	3b
$[Cp^*W(Cl)(C_2Me_2)_2]$	183.7	21
$[Cp^*W(OPh)(C_2Me_2)_2]$	192.9	21

groups observed in the ^1H and ^{13}C NMR spectra of the 2,6-diisopropylphenoxide compounds **1b**,**c** and **2b**–**d** are consistent with the structures represented in Scheme I. The ^1H NMR spectra of these compounds also show the expected resonances for the coordinated alkyne ligands. In all of the 3-hexyne complexes **1a**, **1b**, **2a**, and **2b** the ethyl protons appear as a simple quartet and triplet. Although this is as expected for the monoalkyne compounds, the molecular structure of the bis(3-hexyne) complexes **2a** and **2b** (Scheme I) should result in diastereotopic methylene protons, CH_2CH_3. Variable temperature ^1H NMR spectra of **2a** showed that the methylene proton signal begins to broaden at −50 °C. However, at the lowest temperature of −70 °C limiting, "frozen out" spectra were not observed. Hence, this result implies that the two alkyne units in **2** maintain a head to tail arrangement in solution but undergo rapid rotation on the NMR time scale at ambient temperatures.

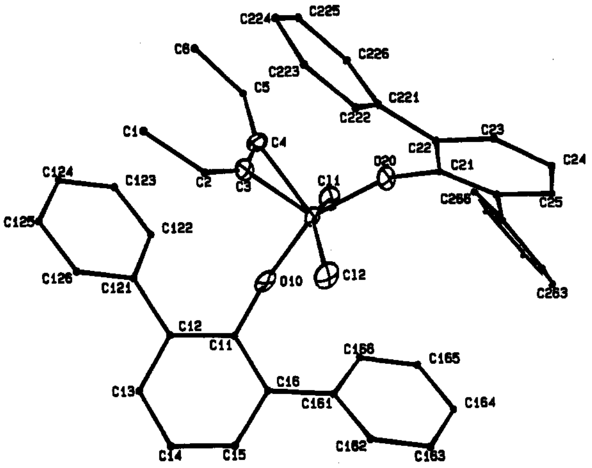

Figure 1. ORTEP view of **1a** emphasizing the central coordination sphere.

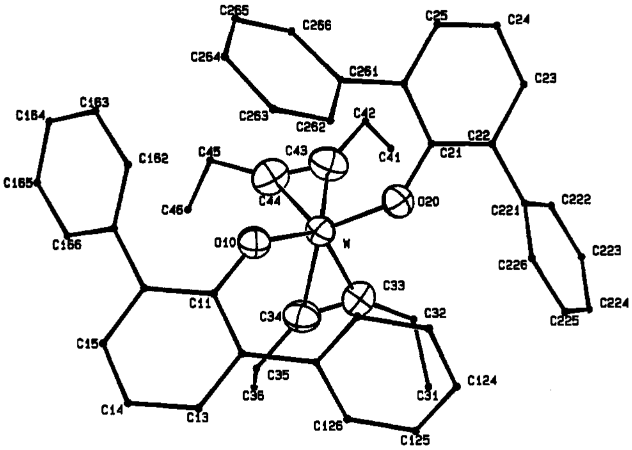

Figure 2. ORTEP view of **2a**.

Table II. Selected Bond Distances (Å) and Angles (deg) for $[W(OC_6H_3Ph_2\text{-}2,6)_2Cl_2(C_2Et_2)]$ (1a)

W–O(10)	1.838(4)	W–O(20)	1.853(4)
W–C(3)	2.021(8)	W–C(4)	2.027(8)
W–Cl(1)	2.373(2)	W–Cl(2)	2.389(2)
C(3)–C(4)	1.30(1)		
O(10)–W–O(20)	154.4(2)	O(10)–W–C(3)	96.8(2)
O(10)–W–C(4)	105.6(2)	O(20)–W–C(3)	105.7(2)
O(20)–W–C(4)	99.7(2)	C(3)–W–C(4)	37.6(3)
Cl(1)–W–Cl(2)	153.40(7)	Cl(1)–W–O(10)	87.2(2)
Cl(1)–W–O(20)	91.3(2)	Cl(1)–W–C(3)	121.0(2)
Cl(1)–W–C(4)	84.6(2)	Cl(2)–W–O(10)	85.5(2)
Cl(2)–W–O(20)	84.6(2)	Cl(2)–W–C(3)	85.3(2)
Cl(2)–W–C(4)	122.0(2)		

The ^{13}C NMR chemical shifts of the alkyne carbon atoms are worthy of some discussion. In Table I are listed the ^{13}C NMR chemical shifts of the alkyne carbon atoms for a range of mononuclear alkyne derivatives of molybdenum and tungsten. The work of Templeton has shown that the carbon-13 chemical shifts of alkyne ligands bound to molybdenum and tungsten metal centers is a sensitive probe of the amount of electron density being donated to the metal center.[1a,3b] It can be seen (Table I) that the monoalkyne complexes **1** have ^{13}C NMR shifts in the region δ 180–195 ppm. These values are comparable to those reported for related monoalkyne complexes containing aryloxide ligands, although not as dramatically downfield as the values of 270 ppm reported for $[W(C_2Ph_2)Cl_4]$.[19] All of the bis(alkyne) compounds **2** have chemical shifts very close to δ 215 ppm for this carbon atom. These values are slightly downfield of the chemical shifts reported for the pentamethylcyclopentadienyl compounds $[Cp^*W(X)(\eta^2\text{-}MeC{\equiv}CMe)_2]$ (X = Cl, 183.7 ppm, X = OPh, 192.9 ppm).[21] The downfield chemical shifts of the alkyne carbon atoms in **1** and **2** indicates considerable electron density being donated to the tungsten metal center, consistent with the solid state structures of **1a** and **2a**.

Solid State Structures of Mono- and Bis(alkyne) Compounds. ORTEP views of **1a** and **2a** are shown in Figures 1 and 2, respectively. The coordination environment about the metal atom in **1a** is best described as slightly distorted square-pyramidal with the alkyne ligand occupying the apical position. The two chloride atoms and aryloxide oxygen atoms are mutually trans with Cl–W–Cl and O–W–O angles of 153.40(7)° and 154.4(2)° (Table II). The alkyne ligand is oriented along the Cl–W–Cl axis. An analysis of the bonding in this compound can be attempted by considering the interactions of the alkyne ligand with the d^2-fragment [*trans*-$WCl_2(OAr)_2$].

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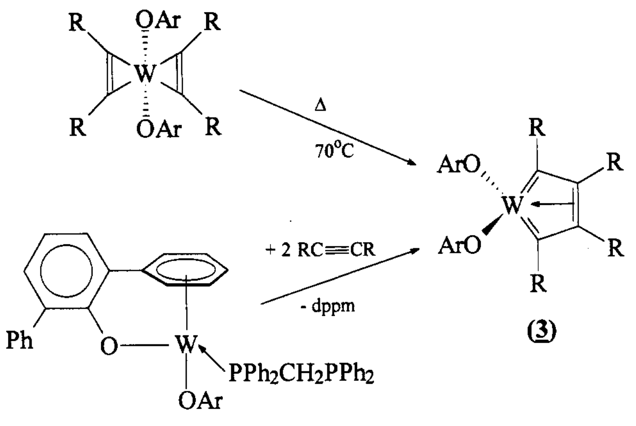
Table III. Selected Bond Distances (Å) and Angles (deg) for $[W(OC_6H_3Ph_2\text{-}2,6)_2(C_2Et_2)_2]$ (2a)

W–O(10)	1.960(3)	W–O(20)	1.959(3)
W–C(33)	2.008(4)	W–C(34)	2.032(4)
W–C(43)	2.017(5)	W–C(44)	2.016(5)
C(33)–C(34)	1.299(7)	C(43)–C(44)	1.291(7)
O(10)–W–O(20)	102.7(1)	O(10)–W–C(33)	126.5(2)
O(10)–W–C(34)	93.3(2)	O(10)–W–C(43)	130.0(2)
O(10)–W–C(44)	98.8(2)	O(20)–W–C(33)	100.2(2)
O(20)–W–C(34)	129.7(2)	O(20)–W–C(43)	93.3(2)
O(20)–W–C(44)	124.4(2)	C(33)–W–C(34)	37.5(2)
C(33)–W–C(43)	95.7(2)	C(33)–W–C(44)	106.8(2)
C(34)–W–C(43)	112.0(2)	C(34)–W–C(44)	99.1(2)
C(43)–W–C(44)	37.3(2)	W–O(10)–C(11)	136.0(2)
W–O(20)–C(21)	131.3(2)		

The σ-donation of two electrons from the alkyne into the d_{z^2} orbital of the metal atom will be accompanied by π-back bonding from the metal into the π^* orbital of the alkyne. If one adopts a coordinate system with the x-axis lying along the O–W–O vector then the two electrons on the metal used in back bonding will occupy the d_{yz} orbital. The d_{xy} and d_{xz} orbitals will be raised in energy due to interaction with the stronger π-donor aryloxide oxygen atoms. Hence, a conformation for the alkyne lying along the y-axis (Cl–W–Cl vector) is electronically favored. A similar structure is observed for the titanium complexes $[Ti(OAr)_2(py)_2(EtC{\equiv}CEt)]$[22] and $[Ti(OAr)_2(py)_2(PhN{=}NPh)]$[23] where the η^2-alkyne and η^2-azobenzene ligands lie along the py–Ti–py axis. Although the solid state structure of 1a can be rationalized using electronic arguments, it should be recognized that the same geometry also minimizes steric interactions between the alkyne and aryloxide ligands (Figure 1).

The solid state structure of 2a (Figure 2, Table III) involves a distorted tetrahedral environment about the metal center with the alkyne units oriented parallel with each other. This is a situation adopted by a large number of bis(alkyne) complexes of Group 6 metals, and an analysis of the bonding in such related systems has been carried out.[1a] A related coordination geometry is observed for the isoelectronic, bis(η^2-iminoacyl) compounds of general formulas $[(ArO)_2M(\eta^2\text{-}R'NCR)_2]$ (M = Ti, Zr, Hf).[24]

Scheme II



OAr = $OC_6H_3Ph_2$-2,6
R = C_2H_5
dppm = $Ph_2PCH_2PPh_2$

The structural parameters for the alkyne units in 1a and 2a are worthy of some comment. A survey of the Cambridge Crystallographic Database up to 1985 has been published reporting tables of bond lengths for organometallic compounds.[25] In the case of terminal alkyne ligands, a total of 40 molybdenum and 36 tungsten derivatives were analyzed. Since 1985 a significant number of compounds of Mo- and W-containing alkyne ligands have also been reported and a 1989 review covers derivatives of Mo(II) and W(II).[1a] Analysis of the data for the compounds published up to 1985 involved calculating average C–C and M–C distances for alkyne units which could be considered as donating two, three, or four electrons to the metal. As expected, the C–C bond lengthened and the M–C bond shortened as the number of electrons donated by the alkyne increased. In compounds 1a and 2a (Tables II and III) the C–C distances are 1.30(1), 1.299(7), and 1.291(7) Å. These distances are consistent with the alkyne unit in 1a and 2a donating greater than two electrons. However, the problems with correlating the C–C distance directly with the number of donated electrons has been pointed out.[1a] The W–C distances in 1a and 2a cover the narrow range of 2.008(4)–2.032(4) Å. Again these values are consistent with alkyne groups which are greater than two-electron donor ligands.[1a,25] If the alkyne units in 1a and 2a did donate 4 electrons each it would lead to a formal 14- and 16-electron configuration, respectively. The C–C and W–C distances in 1a and 2a are significantly different than the values of 1.26(1), 1.27(1), and 2.03–2.04(1) Å in the compound $[Cp^*W(OPh)(MeCCMe)_2]$[21] indicating a definite increase in electron donation of the alkyne ligands in the non-Cp*-containing compounds.

Alkyne Coupling Reactions. During the synthesis of 2a it was noted that the crude reaction mixture contained (NMR) a minor product 3. Furthermore, thermolysis of purified 2a in C_6D_6 solution at 70 °C was found to produce (^1H NMR) significant quantities of 3 along with other unidentified products. The moderate-yield synthesis, purification, and subsequent identification of 3 as a metallacyclic compound formed by coupling of two 3-hexyne units was achieved using a different synthetic strategy (Scheme II). This involved the simple addition of 3-hexyne to solutions of the 16-electron compound $[W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(OC_6H_3Ph_2\text{-}2,6)(\eta^1\text{-dppm})]$.[16b] This compound is formed by sodium amalgam reduction of $[W(OC_6H_3Ph_2\text{-}2,6)_2Cl_4]$ in the presence of dppm.[16b] The low-valent, W(II), metal center is stabilized by a π-interaction with one of the substituent arene rings of a 2,6-diphenylphenoxide ligand. The dppm ligand is bound to the tungsten metal center through only one of the phosphorus atoms both in the solid state and solution.[16b] Addition of 3-hexyne to deep-green solutions of this η^6-arene complex leads to rapid formation of deep-orange solutions that contain 3, small amounts of 2a, and free dppm. The solid state structure of 3 (Figure 3, Table IV) shows the presence of a five-membered metallacyclic ring formed by the coupling of 2 equiv of 3-hexyne. The coupling of two alkyne molecules at transition metal centers is a ubiquitous reaction in organometallic chemistry.[5d,26,29] Typically

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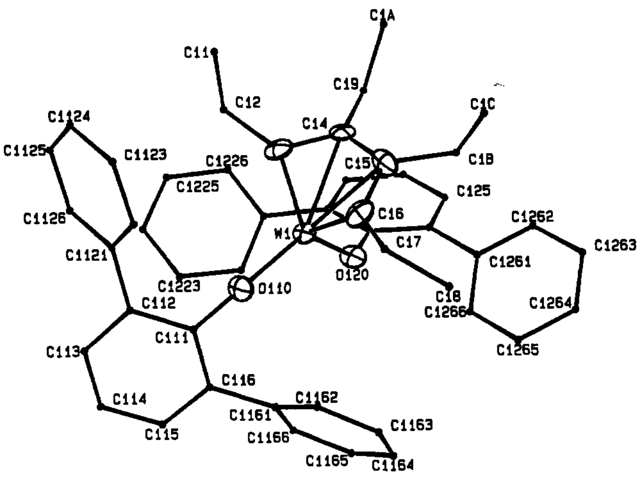


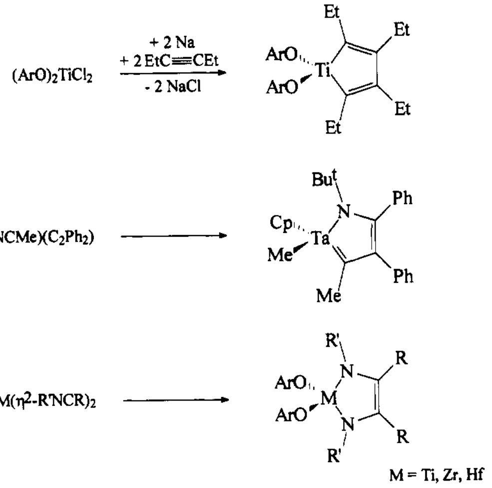
Figure 3. ORTEP view of 3.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[W(OC_6H_3Ph_2\text{-}2,6)_2(C_4Et_4)]$ (3)

Molecule 1			
W(1)–O(110)	1.854(6)	W(1)–O(120)	1.927(5)
W(1)–C(13)	1.891(9)	W(1)–C(14)	2.341(8)
W(1)–C(15)	2.389(8)	W(1)–C(16)	1.912(9)
C(13)–C(14)	1.42(1)	C(14)–C(15)	1.40(1)
C(15)–C(16)	1.42(1)		
O(110)–W(1)–O(120)	116.1(2)	O(110)–W(1)–C(13)	113.9(3)
O(110)–W(1)–C(16)	111.8(3)	O(120)–W(1)–C(13)	113.3(3)
O(120)–W(1)–C(16)	108.9(3)	C(13)–W(1)–C(16)	89.9(4)
W(1)–C(13)–C(14)	88.9(6)	W(1)–C(16)–C(15)	90.4(6)
C(13)–C(14)–C(15)	117.2(8)	C(14)–C(15)–C(16)	116.4(8)
W(1)–O(110)–C(111)	154.5(5)	W(1)–O(120)–C(121)	136.3(5)
Molecule 2			
W(2)–O(210)	1.873(6)	W(2)–O(220)	1.955(5)
W(2)–C(23)	1.915(9)	W(2)–C(24)	2.328(9)
W(2)–C(25)	2.347(9)	W(2)–C(26)	1.929(9)
C(23)–C(24)	1.42(1)	C(24)–C(25)	1.41(1)
C(25)–C(26)	1.43(1)		
O(210)–W(2)–O(220)	121.1(2)	O(210)–W(2)–C(23)	113.7(3)
O(210)–W(2)–C(26)	104.5(3)	O(220)–W(2)–C(23)	112.8(3)
O(220)–W(2)–C(26)	109.7(3)	C(23)–W(2)–C(26)	89.9(3)
W(2)–C(23)–C(24)	87.3(6)	W(2)–C(26)–C(25)	87.4(6)
C(23)–C(24)–C(25)	118.2(8)	C(24)–C(25)–C(26)	116.7(8)
W(2)–O(210)–C(211)	135.1(5)	W(2)–O(220)–C(221)	131.0(5)

either a cyclobutadiene metal complex or metallacyclopenta-2,4-diene results.[5d,f,g,29] Both of these types of products have been widely discussed as intermediates in the catalytic oligomerization of alkynes. The structural and spectroscopic data on compound **3** argue strongly against its formulation as containing a tungstacyclopenta-2,4-diene ring. Instead compound **3** can be considered an example of a steadily growing number of metallacyclopentatriene complexes formed in a six-electron electrocyclic process. In particular the C–C distances alternate as long, short, and long around the ring, while the W–C(α) distances of 1.891(9) and 1.912(9) Å are comparable to those found for tunsten alkylidene groups.[5] The nonplanarity of the ring is highlighted by a fold angle of 60.2(4)° between the planes defined by W, C(13), C(16) and C(13), C(14), C(15), and C(16). The original demonstration of a planar metallacyclopentatriene ring in $[(\eta^5\text{-}C_5H_5)Ru(C_4Ph_2H_2)Br]$ by Singleton et al.[27] has been followed by both planar[28] and folded examples of this functionality.[29] The generation of the metallacyclopentatriene ring in **3** can be formalized as the reductive coupling of two alkyne units by the d^4 W(II) metal fragment $[W(OAr)_2]$. This can be contrasted with the analogous coupling by the d^2 Ti(II) fragment $[Ti(OAr)_2]$ which leads to a planar titanacyclopenta-2,4-diene ring (Scheme III).[30] Compound **3** can also be related to the two isoelectronic, azametallacyclic compounds (Scheme III) formed by intramolecular coupling of either two η^2-iminoacyl or an η^2-iminoacyl and an alkyne ligand, respectively.[31,32] These intramolecular coupling reactions and the structure of the resulting metallacycles have received some theoretical analysis.[32,33]

Scheme III



The spectroscopic properties of compound **3** are consistent with it maintaining a nonplanar structure in solution. In the ^1H NMR spectrum, two nonequivalent ethyl groups are present with both methylene groups appearing as ABX_3 patterns. Exchange of protons within each methylene group does not occur even at 60 °C on the NMR time scale. Hence, a significant barrier to inversion is present for the folded metallacycle.

In an attempt to generate a tungstacyclopenta-2,4-diene complex for comparison with **3**, the reactivity of the d^2 W(IV) derivatives $[W(OC_6H_3Ph\text{-}C_6H_4)_2(L)_2]$ (L = PMe_2Ph, py; $OC_6H_3PhC_6H_4$ = cyclometallated 2,6-diphenylphenoxide)[16b,34] with 3-hexyne was examined. Addition of 3-hexyne to solutions of either the phosphine or pyridine complex led to a similar, complex mixture of products as determined by ^1H NMR. Careful analysis of these spectra indicated the presence of two major components which were identified by X-ray diffraction analysis. Both of these components **4** and **5** crystallize together from the reaction mixtures so that purification of each component was not possible.

The solid state structure of **4** (Figure 4, Table V) shows it to contain 2 equiv of 3-hexyne which have been coupled into a metallacycle about the tungsten metal center. However, it can be seen that one of the cyclometalated

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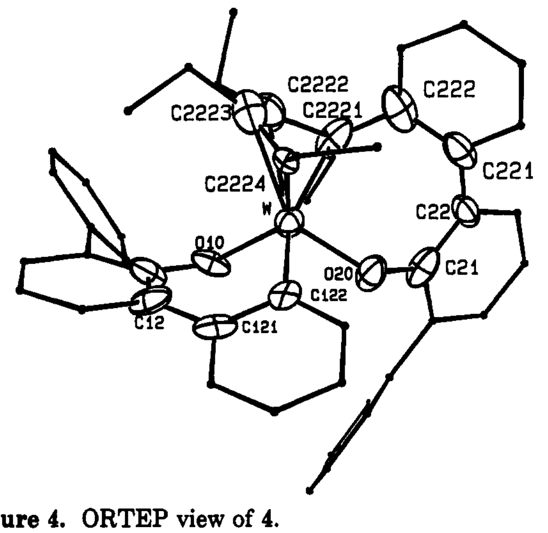
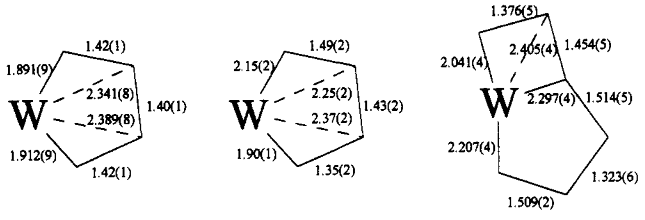


Figure 4. ORTEP view of 4.



(3) (4) (5)

Figure 5. Selected bond distances for the central coordination sphere of 3, 4, and 5.

Table V. Selected Bond Distances (Å) and Angles (deg) for $[W(OC_6H_3PhC_6H_4)_2(C_4Et_4)]$ (4)

W–O(10)	1.861(9)	W–O(20)	1.932(9)
W–C(122)	2.10(1)	W–C(2221)	2.15(2)
W–C(2222)	2.25(2)	W–C(2223)	2.37(2)
W–C(2224)	1.90(1)	C(222)–C(2221)	1.61(2)
C(2221)–C(2222)	1.49(2)	C(2222)–C(2223)	1.43(2)
C(2223)–C(2224)	1.35(2)		
O(10)–W–O(20)	113.1(4)	O(10)–W–C(122)	87.6(4)
O(10)–W–C(2221)	120.2(5)	O(10)–W–C(2224)	121.6(5)
O(20)–W–C(122)	80.8(4)	O(20)–W–C(2221)	87.6(4)
O(20)–W–C(2224)	119.5(5)	C(122)–W–C(2221)	152.2(5)
C(122)–W–C(2224)	77.8(5)	C(2221)–W–C(2224)	86.3(5)
W–C(2221)–C(2222)	73.9(9)	W–C(2224)–C(2223)	92(1)
C(2221)–C(2222)–C(2223)	121(1)	C(2222)–C(2223)–C(2224)	113(1)
W–O(10)–C(11)	124.3(8)	W–O(20)–C(21)	137.3(8)

diphenylphenoxide ligands has been transferred to one of the α-carbon atoms of the five-membered metallacycle. The structural parameters for the metallacycle in 4 are consistent with its formulation as a metallacyclopenta-1,3-diene (Figure 5). The solid state structure of 5 (Figure 6, Table VI) shows that 3 equiv of 3-hexyne have undergone coupling at the tungsten metal center, resulting in an organometallic product that contains 4, 5, 6, and 7 membered metallacyclic rings. Again the cyclometallated 2,6-diphenylphenoxide ligand has been involved in the coupling reaction. The bond distances in 5 indicate the presence of both metallacyclopent-3-ene and metallacyclobutene rings fused together (Figure 5).

Compounds 4 and 5 contain four and six nonequivalent CH_2CH_3 groups, respectively. All of these are diastereotopic so that the ^1H NMR spectra of mixtures show overlapping ABX_3 patterns in the aliphatic region. The two types of diphenylphenoxide ligands also result in the aromatic regions of the spectrum being difficult to interpret. The ^{13}C NMR spectra of 4 and 5 do clearly show the correct number of nonequivalent CH_2CH_3 groups.

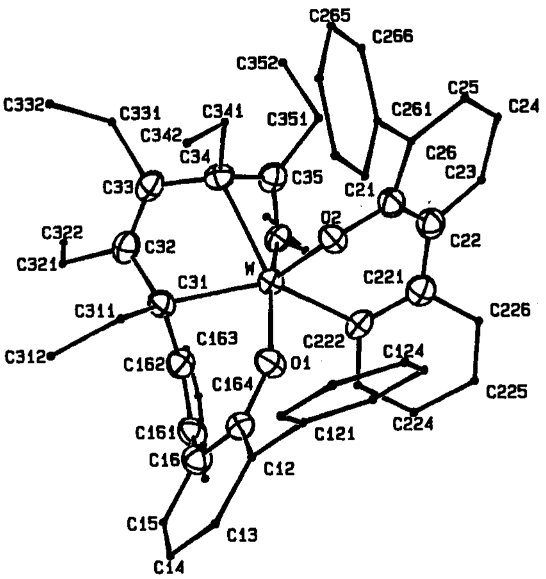


Figure 6. ORTEP view of 5.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $[W(OC_6H_3PhC_6H_4)_2(C_6Et_6)]$ (5)

W–O(1)	1.941(2)	W–O(2)	1.931(2)
W–C(31)	2.207(4)	W–C(34)	2.297(4)
W–C(36)	2.041(4)	W–C(222)	2.140(4)
C(31)–C(32)	1.509(5)	C(32)–C(33)	1.323(6)
C(33)–C(34)	1.514(5)	C(34)–C(35)	1.454(5)
C(35)–C(36)	1.376(5)		
O(1)–W–O(2)	85.7(1)	O(1)–W–C(31)	84.7(1)
O(1)–W–C(34)	139.0(1)	O(1)–W–C(36)	152.7(1)
O(1)–W–C(222)	87.8(1)	O(2)–W–C(31)	138.7(1)
O(2)–W–C(34)	86.7(1)	O(2)–W–C(36)	113.1(1)
O(2)–W–C(222)	88.3(1)	C(31)–W–C(34)	75.0(1)
C(31)–W–C(36)	92.4(1)	C(31)–W–C(222)	131.2(1)
C(34)–W–C(36)	64.9(1)	C(34)–W–C(222)	132.2(1)
C(36)–W–C(222)	73.8(1)	W–C(31)–C(32)	112.6(2)
W–C(34)–C(33)	109.7(2)	C(31)–C(32)–C(33)	115.1(3)
C(32)–C(33)–C(34)	119.7(3)	W–C(34)–C(35)	76.1(2)
W–C(36)–C(35)	87.2(2)	C(34)–C(35)–C(36)	111.3(3)
W–O(1)–C(11)	148.8(2)	W–O(2)–C(21)	124.6(2)

A possible reaction pathway for the formation of 4 and 5 is shown in Scheme IV. This pathway involves initial coupling of two 3-hexyne units to form a tungstacyclopenta-2,4-diene intermediate. Intramolecular transfer of one of the aryl groups of a cyclometalated aryloxide to the α-carbon of the five-membered metallacycle would then yield 4. As formulated, 4 contains a tungsten–carbon double bond. The addition of alkynes to metal alkylidene functions to yield metallacyclobutene rings is well established.[35] The addition of an extra equivalent of 3-hexyne to 4 at this position leads to 5. However, although this last step appears reasonable, addition of 3-hexyne to solutions containing predominantly 4 did not lead to rapid formation of 5 as judged by ^1H NMR. Heating this mixture of 4 and 3-hexyne at 80 °C did lead to formation of 5 along with significant quantities of other products including hexaethylbenzene. The lack of facile conversion of 4 into 5 upon addition of 3-hexyne calls into question the pathway outlined in Scheme IV. This result combined with the generation of both 4 and 5 upon addition of only 2 equiv of 3-hexyne implies the possibility of two distinct pathways

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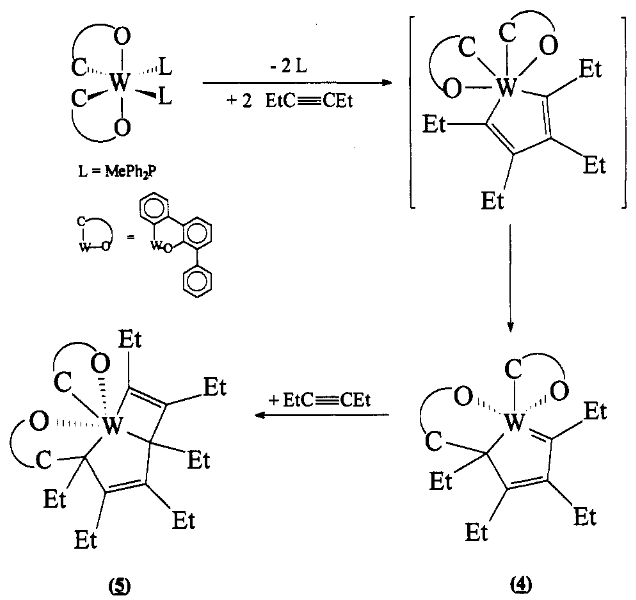
Scheme IV



for their formation. The metallacyclic compounds 4 and 5 resemble intermediates proposed by Schrock et al. in the trimerization of *tert*-butylacetylene by molybdenum alkylidene complexes.[36]

Experimental Section

All operations were carried out under a dry nitrogen atmosphere or in a vacuo either in a Vacuum Atmosphere Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone. [$\mathrm{W(OC_6H_3Ph_2\text{-}2,6)_2Cl_4}$] and [$\mathrm{W(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_4}$] were obtained by previously reported procedures.[18] ^{1}H and ^{13}C NMR spectra were recorded on Varian 500 and Gemini 200 spectrometers and are referenced to $\mathrm{Me_4Si}$ by using protio impurities of commercial benzene-d_6 or toluene-d_8 as internal standards. Microanalyses were obtained from the Purdue Microanalytical Laboratory.

Preparation of [$\mathbf{W(OC_6H_3Ph_2\text{-}2,6)_2Cl_2(C_2Et_2)}$] (1a). To a sodium amalgam (0.12 g, 5.2 mmol Na metal) below toluene (100 mL) was added [$\mathrm{W(OC_6H_3Ph_2\text{-}2,6)_2Cl_4}$] (2.00 g, 2.5 mmol) and 3-hexyne (0.42 g, 5.1 mmol). The mixture was then stirred at room temperature in a dry box for 24 h. The resulting orange suspension was allowed to settle before the solution was decanted off the mercury pool and filtered. Removal of solvent yielded the crude product. Orange crystalline needles were obtained from a concentrated hexane solution. Yield = 1.60 g, 80%. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 0.89 (t, $\mathrm{CH_2C}H_3$), 2.78 (q, $\mathrm{C}H_2\mathrm{CH_3}$), 6.70–7.52 (aromatic H's). Selected ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 12.1 ($\mathrm{CH_2}C\mathrm{H_3}$), 24.1 ($C\mathrm{H_2CH_3}$), 191.7 ($C_2\mathrm{Et_2}$), 156.9 ($\mathrm{WO}C$). Anal. Calcd for $\mathrm{WC_{42}H_{36}O_2Cl_2}$: C, 60.97; H, 4.56; Cl, 8.57. Found: C, 60.69; H, 4.92; Cl, 9.02.

Preparation of [$\mathbf{W(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(C_2Et_2)}$] (1b). An identical procedure to that used for **1a** above, only using Na (0.17 g, 7.4 mmol), [$\mathrm{W(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_4}$] (2.00 g, 2.9 mmol) and 3-hexyne (0.42 g, 5.1 mmol) yielded **1b** as orange blocks from concentrated toluene/hexane (1:1) solution. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 1.12 (d, $\mathrm{CH}Me_2$), 1.27 (t, $\mathrm{CH_2C}H_3$), 3.23 (sept, $\mathrm{C}H\mathrm{Me_2}$), 3.77 (q, $\mathrm{C}H_2\mathrm{CH_3}$), 6.8–7.2 (aromatic H's). Selected ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 23.1 ($C\mathrm{HMe_2}$), 24.0 ($\mathrm{CH}Me_2$), 27.1 ($C\mathrm{H_2CH_3}$), 28.3 ($\mathrm{CH_2}C\mathrm{H_3}$), 160.2 ($\mathrm{WO}C$), 183.41 ($C_2\mathrm{Et_2}$), $^1J(^{183}\mathrm{W}-^{13}\mathrm{C}) = 20.0$ Hz ($C_2\mathrm{Et_2}$). Anal. Calcd for $\mathrm{WC_{30}H_{27}O_2Cl_2}$: C, 52.11; H, 6.41; Cl, 10.25. Found: C, 52.24; H, 6.77; Cl, 10.28.

Preparation of [$\mathbf{W(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(C_2Ph_2)}$] (1c). An identical procedure to that used for **1a** above, only using Na (0.17 g, 7.4 mmol), [$\mathrm{W(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_4}$] (2.00 g, 2.9 mmol), and diphenylacetylene (0.91 g, 5.1 mmol) yielded **1c** as an orange crystalline solid from concentrated toluene/hexane (1:1) solution. ^{1}H NMR indicates that the product crystallizes out with 2 equiv of toluene per W metal center. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 1.15 (d, $\mathrm{CH}Me_2$), 3.46 (sept, $\mathrm{C}H\mathrm{Me_2}$), 6.7–7.6 (aromatic H's), 8.30 (d, ortho protons of acetylene rings). Selected ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 24.0 ($\mathrm{CH}Me_2$), 28.4 ($C\mathrm{HMe_2}$), 160.9 ($\mathrm{WO}C$), 182.8 ($C_2\mathrm{Ph_2}$). Anal. Calcd for $\mathrm{WC_{52}H_{60}O_2Cl_2{\cdot}2C_7H_8}$: C, 64.67; H, 5.64; Cl, 7.34. Found: C, 64.78; H, 5.95; Cl, 7.60.

Preparation of [$\mathbf{W(OC_6H_3Ph_2\text{-}2,6)_2(C_2Et_2)_2}$] (2a). To a sodium amalgam (0.23 g, 10 mmol of Na) below toluene (100 mL) was added [$\mathrm{W(OC_6H_3Ph_2\text{-}2,6)_2Cl_4}$] (2.00 g, 2.5 mmol) and 3-hexyne (0.62 g, 7.6 mmol). The mixture was vigorously stirred at room temperature in a drybox for 24 h. The resulting brown suspension was allowed to settle before the solution was decanted off the mercury pool and filtered. Removal of solvent under vacuum yielded crude **2a**. Yellow crystals were grown from a concentrated benzene/hexane (1:1) solution. Yield = 0.14 g, 60%. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 0.54 (t, $\mathrm{CH_2C}H_3$), 19.4 (q, $\mathrm{C}H_2\mathrm{CH_3}$), 6.50–7.61 (aromatic H's). Selected ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 13.7 ($\mathrm{CH_2}C\mathrm{H_3}$), 27.6 ($C\mathrm{H_2CH_3}$), 161.3 ($\mathrm{WO}C$), 215.6 ($C_2\mathrm{Et_2}$). Anal. Calcd for $\mathrm{WC_{48}H_{46}O_2}$: C, 68.74; H, 5.53. Found: C, 68.63; H, 5.92.

Preparation of [$\mathbf{W(OC_6H_3Pr^i_2\text{-}2,6)_2(C_2Et_2)_2}$] (2b). An identical procedure to that used for **2a** above, only using Na (0.097 g, 4.22 mmol), [$\mathrm{W(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_4}$] (1.00 g, 1.03 mmol), and 3-hexyne (0.25 g, 3.04 mmol) yielded **2b** as yellow crystal from concentrated benzene/hexane (1:1) solution. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 0.98 (t, $\mathrm{CH_2C}H_3$), 3.05 (q, $\mathrm{C}H_2\mathrm{CH_3}$), 1.28 (d, $\mathrm{CH}Me_2$), 3.69 (sept, $\mathrm{C}H\mathrm{Me_2}$). Selected ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 13.9 ($\mathrm{CH_2}C\mathrm{H_3}$), 29.1 ($C\mathrm{H_2CH_3}$), 23.7 ($\mathrm{CH}Me_2$), 27.4 ($C\mathrm{HMe_2}$), 161.6 ($\mathrm{WO}C$), 215.3 ($C_2\mathrm{Et_2}$).

Preparation of [$\mathbf{W(OC_6H_3Pr^i_2\text{-}2,6)_2(C_2Ph_2)_2}$] (2c). An identical procedure to that used for **2a** above, only using Na (0.23 g, 10.0 mmol), [$\mathrm{W(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_4}$] (2.00 g, 2.9 mmol), and diphenylacetylene (1.78 g, 10.0 mmol) yielded **2c** as yellow solid from washing the crude solid with ample amounts of hexane. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 1.10 (d, $\mathrm{CH}Me_2$), 3.66 (sept, $\mathrm{C}H\mathrm{Me_2}$), 6.8–7.2 (aromatic H's), 7.46 (d, ortho protons on acetylene rings). Selected ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 23.7 ($\mathrm{CH}Me_2$), 28.0 ($C\mathrm{HMe_2}$), 161.0 ($\mathrm{WO}C$), 214.9 ($C_2\mathrm{Ph_2}$).

Preparation of [$\mathbf{W(OC_6H_3Pr^i_2\text{-}2,6)_2(4Me\text{-}PhC_2Ph\text{-}4Me)_2}$] (2d). An identical procedure to that used for **2a** above, only using Na (0.12 g, 5.2 mmol), [$\mathrm{W(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_4}$] (0.83 g, 1.2 mmol), and di-*p*-tolylacetylene (0.46 g, 2.2 mmol) yielded **2d** as yellow crystals from washing the crude solid with about 20 mL of hexane. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 1.15 (d, $\mathrm{CH}Me_2$), 2.00 (s, $\mathrm{C_6H_4C}H_3$), 3.73 (sept, $\mathrm{C}H\mathrm{Me_2}$), 6.93, 7.46 (d's, due to aromatic H's from acetylene ligands). Selected ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 21.4 ($\mathrm{C_6H_4}C\mathrm{H_3}$), 23.8 ($\mathrm{CH}Me_2$), 28.0 ($C\mathrm{HMe_2}$), 161.2 ($\mathrm{WO}C$), 214.2 ($\mathrm{W}-C$).

Preparation of [$\mathbf{W(OC_6H_3Ph_2\text{-}2,6)_2(C_4Et_4)}$] (3). To a stirred solution of [$\mathrm{W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(OC_6H_3Ph_2\text{-}2,6)(dppm)}$] (0.25 g, 0.24 mmol) in toluene (25 mL) was added 3-hexyne (0.06 g, 0.73 mmol). An immediate color change from green or orange occurred, and the mixture was left to stir for 2 h. The toluene was removed in vacuo, and the remaining residue was dissolved in hexane and filtered to remove dppm, a white powder. Red crystalline blocks of **3** were obtained by slow evaporation of the resulting hexane solution. Yield = 0.15 g, 60%. Selected ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): The two $\mathrm{ABX_3}$ patterns due to the diastereotopic $\mathrm{CH_3C}H_2$ groups are present at δ 3.31, 3.22 and 1.48, 1.10. The latter signal overlaps the corresponding methyl resonance pattern. The second $\mathrm{CH_2C}H_3$ triplet is well resolved at δ 0.81. Selected ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 249.6 ($\mathrm{W{=}C_\alpha}$); 91.5 ($\mathrm{C_\beta}$); 20.1, 32.7 ($C\mathrm{H_2CH_3}$); 15.9, 16.2 ($\mathrm{CH_2}C\mathrm{H_3}$); 157.0, 158.9 ($\mathrm{WO}C$).

Preparation of [$\mathbf{W(OC_6H_3PhC_6H_4)_2(C_4Et_4)}$] (4). To a solution of [$\mathrm{W(OC_6H_3PhC_6H_4)_2(C_5H_5N)_2}$] (0.31 g, 0.37 mmol) in benzene (20 mL) was added 3-hexyne (0.034 g, 0.41 mmol). An immediate color change from purple to brown occurred, and the

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(36) Strutz, H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* 1985, *107*, 5999.

Table VII. Crystal Data and Data Collection Parameters

	1a	2a	3	4	5
formula	$WCl_2O_2C_{42}H_{36}$	$WO_2C_{48}H_{46}$	$WO_2C_{48}H_{46}$	$WO_2C_{48}H_{44}$	$WO_2C_{54}H_{54}$
formula weight	827.51	838.75	838.75	836.73	918.88
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	9.331(2)	11.458(1)	11.086(2)	10.805(7)	9.835(2)
b, Å	12.271(2)	17.961(4)	18.400(7)	11.662(1)	11.8298(7)
c, Å	16.334(3)	10.915(2)	19.453(5)	17.008(3)	19.620(2)
α, deg	107.48(1)	104.65(1)	98.96(2)	80.12(1)	104.748(6)
β, deg	101.78(2)	115.23(1)	97.14(2)	84.71(3)	98.717(9)
γ, deg	95.13(2)	92.08(1)	98.67(2)	63.07(3)	104.478(8)
V, Å^3	1723(1)	1939(1)	3830(4)	1882(1)	2080(1)
Z	2	2	4	2	2
d_{calc}, g cm^{-3}	1.595	1.437	1.454	1.476	1.467
crystal dimensions, mm	0.64 × 0.14 × 0.06	0.52 × 0.29 × 0.28	0.28 × 0.19 × 0.11	0.43 × 0.43 × 0.20	0.38 × 0.25 × 0.15
temperature, °C	−100	20	−114	20	20
radiation (wavelength)	Mo K_α (0.709 30 Å)	Mo K_α (0.710 73 Å)	Mo K_α (0.710 73 Å)	Mo K_α (0.710 73 Å)	Mo K_α (0.710 73 Å)
monochromator	graphite	graphite	graphite	graphite	graphite
linear abs coef, cm^{-1}	36.14	30.78	31.16	31.71	28.76
absorption correction applied	empirical[a]	empirical[a]	empirical[a]	empirical[a]	empirical[a]
transmission factors: min, max	0.83, 1.00	0.58, 1.00	0.73, 1.00	0.37, 1.00	0.82, 1.00
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
h, k, l limits	0 to 10, −13 to +13, −17 to +16	0 to 12, −19 to +19, −11 to +10	0 to 11, −19 to +19, −20 to +20	−12 to +12, 0 to 18	−10 to 10, −12 to +12, 0 to 21
2θ range, deg	4.00–45.00	4.00–45.00	4.00–45.00	4.00–45.00	4.00–45.00
scan width, deg	1.00 + 0.35 tan(θ)	0.39 + 0.35 tan(θ)	0.82 + 0.35 tan(θ)	0.90 + 0.35 tan(θ)	0.45 − 0.35 tan(θ)
take-off angle, deg	1.90	1.90	1.90	2.95	2.95
programs used	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius Molen	Enraf-Nonius SDP
F_{000}	824.0	848.0	1696.0	844.0	936.0
p-factor used in weighting	0.040	0.040	0.040	0.040	0.040
data collected	4475	5049	9981	4953	5434
unique data	4475	5049	9981	4953	5434
data with $I > 3.0\sigma(I)$	3820	4449	7124	4953	4919
number of variables	424	460	559	460	514
largest shift/esd in final cycle	0.19	0.56	0.08	0.01	0.03
R	0.034	0.023	0.046	0.056	0.019
R_W	0.042	0.030	0.055	0.063	0.026
goodness of fit	1.231	1.042	1.431	1.436	0.878

[a] Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A*: *Found. Crystallogr.* **1983**, *A39*, 158.

resulting mixture was stirred for 12 h. The benzene was removed in vacuo, and the residue was dissolved in 15 mL of hexane. A mixture of dark red crystalline plates of both **4** and **5** were obtained from the slow evaporation of the resulting hexane solution. Selected ^{1}H NMR (C_6D_6, 30 °C): ABX_3 patterns due to the diastereotopic CH_2CH_3 groups are present at δ 3.76, 2.82, and 1.92; other relevant ABX_3 patterns can be found in the region of δ 1.0–2.4. A series of four triplets due to CH_2CH_3 can be seen at δ 1.04, 0.51, 0.20, and −0.09; 6.4–8.2 (aromatic H's).

Preparation of [W($OC_6H_3PhC_6H_4$)$_2$(C_6Et_6)] (5). To a solution of [W($OC_6H_3PhC_6H_4$)$_2$($PMePh_2$)$_2$] (0.14 g, 0.13 mmol) in benzene (20 mL) was added 3-hexyne (0.04 g, 0.49 mmol). An immediate color change from orange to brown occurred, and the mixture was stirred for several hours. The benzene was removed in vacuo. Red brick like crystals of **4** and **5** were obtained from a concentrated toluene/hexane (1:1) solution. Selected ^{1}H NMR (C_6D_6, 30 °C): ABX_3 patterns due to diastereotopic CH_2CH_3 groups are present at δ 3.17, 3.05, 2.82, and 1.74. Other relevant ABX_3 patterns can be found in the region of δ 1.0–2.4. A series of triplets due to CH_2CH_3 can be seen at δ 0.90, 0.77, 0.56, and 0.39, and near δ 1.00; 5.59 (d, aromatic H); 6.40–8.00 (aromatic H's). Selected ^{13}C NMR (C_6D_6, 30 °C): a series of six singlets due to CH_2CH_3 can be seen at δ 20.4, 25.3, 25.9, 28.7, 29.4, and 37.4. Another series of six singlets due to CH_2CH_3 can be seen at δ 12.8, 13.0, 13.5, 14.7, 15.1, and 16.6.

Crystallographic Studies. Crystal data and data collection parameters are contained in Table VII. Further data and details of the crystallographic studies are contained in supplementary material.

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Supplementary Material Available: Full listings of fractional coordinates, anisotropic thermal parameters, and bond lengths and angles (96 pages). Ordering information is given on any current masthead page.

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