I of peroxidases and catalases. Studies of detailed electronic structure and reactivity of the compound are currently underway in our laboratories.

Acknowledgment. H.F. thanks Prof. N. Ono for many valuable comments about the porphyrin synthesis. This research was supported in part by a grant from the Nissan Science Foundation.

Contribution from the Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Preparation of Complexes of the Forms $WCp^*(OR)_3Cl$, $WCp^*(OR)_4$, and $WCp^*(X)(\eta^2\text{-alkyne})_2$ (X = OR, Cl)

Marie B. O'Regan, Michael G. Vale, Joseph F. Payack, and Richard R. Schrock*

Received March 21, 1991

Introduction

Mono-Cp* (Cp* = η^5-C_5Me_5) tetrachloride complexes of the type MCp^*Cl_4 (M = Mo, W) can be prepared readily by the "PCl_5 method".[1,2] The PCl_5 method has also now been used successfully to prepare a variety of other Mo and W cyclopentadienyl tetrachloride starting materials[3] and cyclopentadienyl dichloro nitrosyl complexes of molybdenum and tungsten.[4] The ready availability of tetrahalide complexes has provided an entry into a variety of mono-Cp* complexes of Mo and W in which the metal is in a relatively high oxidation state,[5-12] as well as permethyltungstenocene derivatives.[13,14] On the basis of an X-ray study of square pyramidal W(η^5-C_5H_4-*i*-Pr)Cl_4,[3] it now seems likely that all tetrahalide species are actually monomers, even though differential vapor pressure measurements in dichloromethane suggested that W(η^5-C_5Et_4-*t*-Bu)Cl_4 was a dimer.[15] $ReCp^*Cl_4$ and a large variety and number of related compounds have now also been prepared,[16] although the PCl_5 method so far has not figured as prominently in Re chemistry as it has in Mo and W chemistry.

We have been interested in particular in the synthesis and use of MCp^*Me_4 complexes (M = Mo,[8] W[7]) as a route to a variety of dinitrogen and hydrazido or hydrazine complexes containing the MCp^*Me_3 core. WCp^*Me_4 can be oxidized readily to yield $[WCp^*Me_4]^+$, but the oxidation of $MoCp^*Me_4$ is not reversible, and $[MoCp^*Me_4]^+$ cannot be isolated or synthesized in situ.[8] Neither WCp^*Me_4 nor $MoCp^*Me_4$ can be reduced readily. Reduction of $WCp^*Me_3(OTf)$ (OTf = OSO_2CF_3) under dinitrogen yields $[WCp^*Me_3]_2(\mu\text{-}N_2)$ in >90% yield.[9] Reduction of $MoCp^*Me_3(OTf)$ fails to yield $[MoCp^*Me_3]_2(\mu\text{-}N_2)$, even though that species can be prepared by another route.[8] Recently, related chemistry of complexes that contain the $ReCp^*Me_3$ core has been published in preliminary form.[17]

In order to further broaden the chemistry of M(V) and M(VI) mono-Cp* complexes of Mo and W, access to M(V) mono-Cp* starting materials that are less easily reduced than the MCp^*Cl_4 species[3,15,18] is required. Dinitrogen activation by a complex containing ligands other than alkyl groups is also desirable, since alkyl groups are not likely to be stable toward protons over the long term in a catalytic dinitrogen reduction system. We report here the synthesis and characterization of a series of W(V) complexes of the types $WCp^*(OR)_3Cl$ and $WCp^*(OR)_4$ and initial studies of the reactivity of these complexes that include the synthesis of complexes of the type $WCp^*(X)(\eta^2\text{-alkyne})_2$ (X = OR, Cl).

Results

The paramagnetic complexes $WCp^*(OR)_3Cl$ [R = C_6H_5 (**1a**), Me (**1b**)] and $WCp^*(OR)_4$ [R = C_6H_5 (**2a**), 3,5-$C_6H_3Me_2$ (**2b**), 4-C_6H_4OMe (**2c**), 4-C_6H_4-*t*-Bu (**2d**), 4-C_6H_4Me (**2e**)] can be prepared at room temperature in ether or toluene in less than 1 h by adding a stoichiometric amount of alcohol and NEt_3 to a slurry of WCp^*Cl_4. Adding less than 3 equiv of alcohol typically leads to mixtures of $WCp^*(OR)_xCl_{4-x}$ species (x = 1-3). However, a chelating bis(alkoxide) complex, $WCp^*(OCMe_2CMe_2O)Cl_2$ (**3**), can be prepared by adding 1 equiv of pinacol to WCp^*Cl_4 in an analogous fashion. **1b** and **3** do not react further with excess alcohol in the presence of NEt_3 at room temperature, unlike analogous intermediates in reactions involving phenols. All monomeric species are presumed to possess square pyramidal structures on the basis of the structures of W(η^5-C_5H_4-*i*-Pr)Cl_4[3] and W(η^5-$C_5Et_3Me_2$)Me_4.[15] However, $[WCp^*Me_4]^+$ has been shown to be a trigonal bipyramid in the solid state at −65 °C,[2] perhaps the only known example of a M(cyclopentadienyl)X_4 species with this geometry. For this reason, the possibility that the W(V) alkoxide species possesses a trigonal bipyramidal structure cannot be excluded.

Table I. Preliminary Electrochemical Data[a]

complex	$E_{1/2}$(red), V	$E_{pa} - E_{pc}$, mV	E_p(ox),[b] V
$WCp^*(OC_6H_5)_3Cl$ (**1a**)	−1.44	620	+0.32
$WCp^*(OC_6H_5)_4$ (**2a**)	−1.85	1350	
$WCp^*(O\text{-}3,5\text{-}C_6H_3Me_2)_4$ (**2b**)	−1.55	620	+0.39

[a] In THF vs Ag/Ag^+ in acetonitrile at a 200 mV s^{-1} sweep rate. [b] Irreversible.

The results of preliminary cyclic voltammetry studies on three compounds are shown in Table I. The alkoxide complexes cannot be oxidized with ferrocene to give W(VI) cations, because the oxidation potentials are too positive and the oxidations are irreversible. In contrast, square pyramidal WCp^*Me_4 is oxidized relatively easily in dichloromethane (E_{pa} = −0.305 V vs $E_{1/2}$ for ferrocene/ferrocenium), while trigonal bipyramidal $[WCp^*Me_4]^+$ is reduced at E_{pc} = −0.865 V vs $E_{1/2}$ for ferrocene/ferrocenium.[2] A reversible reduction wave is observed for all complexes in Table I between −1.2 and −1.9 V, in contrast to WCp^*Me_4, for which no reduction wave was observed in dichloromethane. We have used phenoxide ligands to stabilize Mo(VI) centers via π donation in complexes of the type $[MoCp^*Me_3(OAr)][PF_6]$.[8] But since there are only two orbitals capable of accepting π-electron density in square pyramidal MCp^*L_4 complexes[19] (d_{xy} and d_{z^2}), π donation from two otherwise relatively electronegative phenoxide ligands

(1) Murray, R. C.; Blum, L.; Liu, A. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 954.
(2) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.
(3) Green, M. L. H.; Hubert, J. D.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1990**, 3793.
(4) Dryden, N. H.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1991**, *10*, 2077.
(5) Murray, R. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 4557.
(6) Okuda, J.; Murray, R. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 1681.
(7) Liu, A. H.; O'Regan, M. B.; Finch, W. C.; Payack, J. F.; Schrock, R. R. *Inorg. Chem.* **1988**, *27*, 3574.
(8) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338.
(9) O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331.
(10) Glassman, T. E.; Vale, M. G.; Schrock, R. R. *Organometallics* **1991**, *10*, 4046.
(11) Schrock, R. R.; Glassman, T. E.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 725.
(12) Rau, M. S.; Kretz, C. M.; Mercando, L. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1991**, *113*, 7420.
(13) Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391.
(14) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172.
(15) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574.
(16) Hermann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297.
(17) Vale, M. G.; Schrock, R. R. *Organometallics* **1991**, *10*, 1661.
(18) Harlan, C. J.; Jones, R. A.; Koschmieder, S. U.; Nunn, C. M. *Polyhedron* **1990**, *9*, 669.
(19) Kubáček, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

0020-1669/92/1331-1112$03.00/0

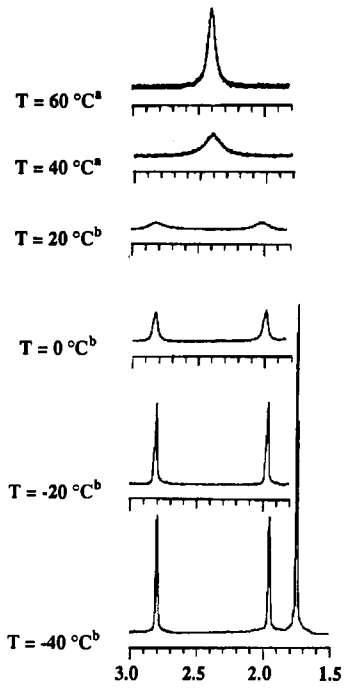

Figure 1. Variable-temperature proton NMR spectrum of $WCp^*(OC_6H_5)(MeC{\equiv}CMe)_2$: (a) solvent = C_6D_6; (b) solvent = CD_2Cl_2.

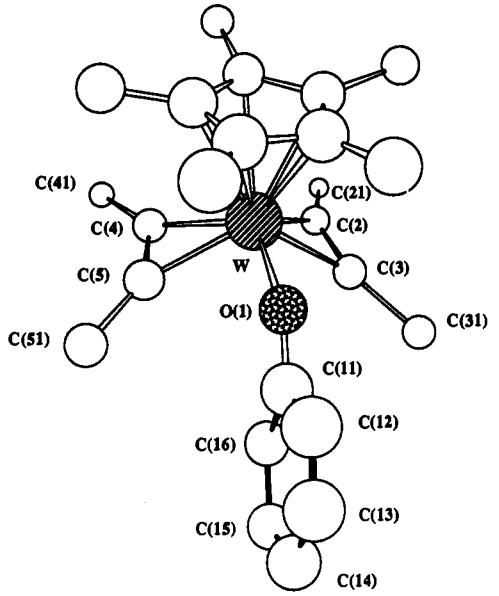

Figure 2. View of the structure of $WCp^*(OC_6H_5)(MeC{\equiv}CMe)_2$.

apparently cannot compensate for the loss of the four strongly σ-donating Me groups, and the oxidation potential at the W center therefore increases.

Reduction of $WCp^*(OC_6H_5)_4$ (**2a**) with 0.5% sodium amalgam under an atmosphere of dinitrogen did not yield any product we could identify. However, when the reduction was carried out in the presence of 2 equiv of several alkynes, a single diamagnetic product of the same type was obtained in high yield in each case (eq 1). Proton and carbon NMR studies are fully consistent with

$$WCp^*(OPh)_4 + 2RC{\equiv}CR' \xrightarrow[Et_2O]{3Na/Hg} WCp^*(OPh)(\eta^2\text{-}RC{\equiv}CR')_2 + 3NaOPh \quad (1)$$

R = R′ = H (**4a**)
R = H, R′ = TMS (**4b**)
R = H, R′ = C_6H_5 (**4c**)
R = R′ = Me (**4d**)

the proposed formulation of these products as pseudotetrahedral bis(alkyne) complexes. The alkyne ligands are equivalent on the ^1H and ^{13}C NMR time scales at room temperature in **4a**. When the sample is cooled to −60 °C the proton resonance for the alkyne protons in **4a** broadens, but it does not disappear into the baseline. Low-temperature ^1H NMR studies of **4b** and **4c** also were consistent with a fluxional process; e.g., the acetylenic proton resonance is broadened into the baseline at −50 °C in the case of **4c**. In the case of **4d**, however, the fluxional process could be observed in its entirety (Figure 1), presumably because of increased steric hindrance to rotation around the metal–alkyne (centroid) axis. Coalescence of the inequivalent acetylenic Me resonances in **4d** occurs at approximately 35 °C to give a ΔG^*(308K) of 14.2 kcal/mol. Synthesis of an analogous complex containing $Me_3SiC{\equiv}CSiMe_3$ was not successful, probably because steric factors are prohibitive in this case.

An X-ray crystallographic study of **4d** confirms the proposed pseudotetrahedral structure (Figure 2). Bond distances and angles are listed in Table II, and final positional parameters in Table III. The alkyne carbon–carbon bond lengths are 1.26 and 1.27 Å, and the methyl groups are bent back from the C≡C axis by approximately 40°, consistent with a significant degree of reduction

Table II. Bond Distances (Å) and Bond Angles (deg) for $WCp^*(OC_6H_5)(MeC{\equiv}CMe)_2$ (**4d**)

Bond Distances			
W–Cp*(cent)	2.070 (1)	C(3)–C(31)	1.50 (2)
W–O(1)	2.072 (7)	C(4)–C(41)	1.50 (2)
W–C(2)	2.03 (1)	C(5)–C(51)	1.51 (2)
W–C(3)	2.04 (1)	O(1)–C(11)	1.30 (1)
W–C(4)	2.03 (1)	C(11)–C(12)	1.39 (1)
W–C(5)	2.04 (1)	C(12)–C(13)	1.36 (1)
C(2)–C(3)	1.26 (1)	C(13)–C(14)	1.37 (2)
C(4)–C(5)	1.27 (1)	C(14)–C(15)	1.38 (2)
C(2)–C(21)	1.49 (2)	C(15)–C(16)	1.37 (1)
Bond Angles			
O(1)–W–Cp*(cent)	105.5 (3)	W–C(2)–C(3)	72.4 (8)
C(2)–W–Cp*(cent)	112.5 (4)	W–C(2)–C(21)	146.6 (9)
C(3)–W–Cp*(cent)	122.2 (5)	C(3)–C(2)–C(21)	141 (1)
C(4)–W–Cp*(cent)	110.9 (4)	W–C(3)–C(2)	71.6 (7)
C(5)–W–Cp*(cent)	121.7 (4)	W–C(3)–C(31)	147 (1)
O(1)–W–C(2)	119.6 (4)	C(2)–C(3)–C(31)	141 (1)
O(1)–W–C(3)	83.8 (4)	W–C(4)–C(5)	72.4 (7)
O(1)–W–C(3)	122.7 (4)	W–C(4)–C(41)	148 (1)
O(1)–W–C(4)	86.7 (4)	C(5)–C(4)–C(41)	139 (1)
W–O(1)–C(11)	137.1 (7)	W–C(5)–C(4)	71.3 (7)
C(2)–W–C(3)	36.0 (4)	W–C(5)–C(51)	147 (1)
C(4)–W–C(5)	36.3 (4)	C(4)–C(5)–C(51)	142 (1)

Table III. Positional Parameters and B(eq) for $WCp^*(OC_6H_5)(MeC{\equiv}CMe)_2$ (**4d**)

atom	x	y	z	B(eq), Å^2
W	0.27145 (4)	0.24633 (4)	0.05022 (2)	2.69 (2)
O(1)	0.3121 (8)	0.1772 (6)	−0.0564 (4)	3.9 (4)
C(2)	0.077 (1)	0.3003 (8)	0.0662 (6)	3.3 (5)
C(3)	0.081 (1)	0.2729 (9)	−0.0060 (7)	4.5 (6)
C(4)	0.252 (1)	0.1755 (8)	0.1555 (7)	3.8 (6)
C(5)	0.296 (1)	0.1165 (8)	0.1049 (7)	3.4 (5)
C(6)	0.383 (1)	0.3743 (8)	0.1253 (7)	3.5 (5)
C(7)	0.488 (1)	0.3067 (8)	0.1144 (7)	3.4 (5)
C(8)	0.507 (1)	0.2977 (9)	0.0355 (7)	4.1 (6)
C(9)	0.416 (1)	0.3647 (9)	−0.0072 (7)	4.2 (6)
C(10)	0.343 (1)	0.4098 (9)	0.0494 (8)	4.5 (6)
C(11)	0.260 (1)	0.1059 (8)	−0.0980 (6)	3.8 (6)
C(12)	0.318 (1)	0.0820 (8)	−0.1708 (6)	3.7 (5)
C(13)	0.269 (1)	0.006 (1)	−0.2153 (7)	4.5 (6)
C(14)	0.160 (1)	−0.050 (1)	−0.1920 (7)	4.7 (7)
C(15)	0.101 (1)	−0.027 (1)	−0.1207 (7)	4.7 (6)
C(16)	0.148 (1)	0.048 (1)	−0.0750 (7)	4.5 (6)
C(21)	−0.022 (1)	0.341 (1)	0.1241 (8)	6.1 (8)
C(31)	−0.010 (1)	0.266 (1)	−0.0819 (9)	9 (1)
C(41)	0.207 (1)	0.178 (1)	0.2408 (7)	5.2 (7)
C(51)	0.338 (2)	0.013 (1)	0.097 (1)	6.7 (9)
C(61)	0.341 (2)	0.411 (1)	0.205 (1)	7 (1)
C(71)	0.567 (1)	0.256 (1)	0.1826 (8)	6.6 (7)
C(81)	0.610 (1)	0.234 (1)	−0.005 (1)	8 (1)
C(91)	0.409 (2)	0.382 (1)	−0.0961 (8)	8 (1)
C(101)	0.241 (2)	0.495 (1)	0.034 (1)	9 (1)

of the alkyne ligand by the metal[20,21] or, alternatively, their behavior as $2\pi,1\sigma$ ligands.[22] The ^{13}C resonances (typically >170 ppm) and J_{CH} coupling (≈196 Hz) in the alkyne ligands in **4a–d** support this conclusion.[23] Therefore the oxidation state of the metal could be viewed as being anything between W(II) and W(VI).

Reduction of WCp^*Cl_4 with 0.5% sodium amalgam in the presence of terminal and internal alkynes yields monochloro complexes analogous to the phenoxide complexes **4** (eq 2).

$$WCp^*Cl_4 + 2RC{\equiv}CR' \xrightarrow[Et_2O]{3Na/Hg} WCp^*Cl(\eta^2\text{-}RC{\equiv}CR')_2 + 3NaCl \quad (2)$$

R = H, R′ = TMS (**5a**)
R = R′ = Me (**5b**)

However, the yields of **5a** and **5b** (typically (<60%) are lower than those of the phenoxide complexes (typically >90%). Most likely, formation of dimeric species which do not react with alkynes to give complexes of the type $WCp^*Cl(alkyne)_2$[3,24] competes with formation of an initial alkyne adduct which is then reduced further in the presence of alkyne to give the observed product. No analogous product could be isolated upon reduction of WCp^*Cl_4 in the presence of acetylene itself. Interestingly, the alkyne Me groups in **5b** are inequivalent at room temperature, and there is no sign of broadening of the methyl resonances in the proton NMR spectrum at 60 °C. Therefore the barrier to alkyne rotation apparently is significantly higher in the chloride complexes than in the phenoxide complexes.

Discussion

In view of the lack of success at binding dinitrogen to W(IV) and Mo(IV) complexes that contain good π-electron-donating phenoxide or thiophenoxide ligands[25,26] and the fact that dinitrogen is proposed to bind to a WCp^*Me_3 fragment fleetingly to give a highly reactive polarized intermediate,[9] dinitrogen may be activated most efficiently in d^2 systems in which only a single π bond (i.e., to the incoming dinitrogen ligand) can form. Therefore, it now does not seem surprising that reduction of $WCp^*(phenoxide)_4$ complexes under dinitrogen did not yield isolable dinitrogen-containing products such as $[WCp^*(phenoxide)_3]_2(\mu\text{-}N_2)$. Although $\mu\text{-}N_2$ complexes that contain one π-bonding ligand are known, e.g. *trans*-$[WCp^*XMe_2]_2(\mu\text{-}N_2)$, there is some structural evidence that donation of π-electron density by X will populate a W–N antibonding orbital and lead to loss of the N–N ligand as dinitrogen.[9]

One of the most interesting features of complexes of the type $WCp^*X(alkyne)_2$ is that they are members of a class that include (for example) complexes as diverse as $W(CO)(alkyne)_3$,[27] $[ReCp^*Cl(alkyne)_2]^+$,[28] $ReMeO_3$,[16] $W(NR)_3L$,[29] $[Re(2\text{-}butyne)_2(O)L]^+$ and related compounds,[30] and $Re(N\text{-}t\text{-}Bu)_3(OSiMe_3)$.[31] All such complexes contain three ligands (cyclopentadienyl, alkyne, imido, or oxo) that actually, or in the extreme, can be said to bind to a metal through two π bonds and one σ bond ($2\pi,1\sigma$ ligands). If that is assumed to be the case, then a ligand-based essentially nonbonding MO must contain a pair of electrons in order to avoid a 20-electron count in metal-based orbitals.[27,32,33] Within this group, alkyne ligands especially have received a good deal of attention, in particular with respect to what extent they behave as $2\pi,1\sigma$ ligands in various circumstances. Rotation of alkyne ligands around the metal–alkyne (centroid) bond has been observed in a variety of circumstances,[22] but how the barrier to rotation correlates with the precise nature of metal–alkyne bonding is not yet clear. A recent example is rotation of the 2-butyne ligands in $[ReCp^*Cl(MeC{\equiv}CMe)_2][SbF_6]$, a species whose structure is very similar to the structure of **5**; the activation barrier is approximately 15 kcal/mol.[16] In view of the diverse results concerning alkyne ligand rotation, it is not surprising to find that the barriers to alkyne rotation in **4** and **5** differ significantly.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres HE43-2 drybox or by using standard Schlenk techniques. Solvents were purified by standard techniques. Deuterated NMR solvents were passed through a column of activated alumina and stored over 4-Å molecular sieves. NMR data are listed in parts per million relative to Me_4Si for ^1H and ^{13}C. Coupling constants are quoted in hertz. Acetylene was passed through a column of alumina (24 in. × 1 in.) prior to use.

Electrochemical data were obtained using a Princeton Applied Research Model 173 potentiostat/galvanostat and Model 175 universal programmer, in conjunction with a Houston Instruments RE-0089 X-Y recorder. Cyclic voltammograms were obtained in the drybox at approximately 25 °C in tetrahydrofuran using tetraethylammonium tetrafluoroborate (~0.1 M) as the electrolyte. $E_{1/2}$ values are referenced to Ag/Ag^+ in acetonitrile and are uncorrected for junction potentials.

Preparation of Complexes. $WCp^*(OC_6H_5)_3Cl$ (1a). WCp^*Cl_4 (0.700 g, 1.500 mmol) was suspended in 50 mL of ether, and a solution of phenol (0.429 g, 4.50 mmol) and triethylamine (635 μL, 4.50 mmol) in 10 mL of ether was added dropwise over a period of 3–5 min. After 30 min, $[Et_3NH]Cl$ was filtered off and the solvent was removed from the filtrate in vacuo to leave red crystalline $WCp^*(OC_6H_5)_3Cl$ (0.944 g, 1.47 mmol, 98%). The crude product was recrystallized from ether. EPR (ether): $\langle g\rangle$ = 1.856 ($\Delta\nu_{1/2}$ = 101 G). Anal. Calcd for $WC_{28}H_{30}O_3Cl$: C, 53.01; H, 4.73; Cl, 5.59. Found: C, 52.68; H, 4.78; Cl, 5.88.

$WCp^*(OMe)_3Cl$ (1b). The procedure was the same as that used to prepare **1a**, employing WCp^*Cl_4 (1.00 g, 2.17 mmol) in 70 mL of ether and a solution of methanol (264 μL, 6.51 mmol) and triethylamine (908 μL, 6.51 mmol) in 10 mL of ether; yield 0.920 g (95%) of red crystalline $WCp^*(OMe)_3Cl$. EPR (ether): $\langle g\rangle$ = 1.890 ($\Delta\nu_{1/2}$ = 86 G). Anal. Calcd for $WC_{13}H_{24}O_3Cl$: C, 34.88; H, 5.37; Cl, 7.93. Found: C, 34.75; H, 5.08; Cl, 8.22.

$WCp^*(OC_6H_5)_4$ (2a). WCp^*Cl_4 (0.300 g, 0.651 mmol) was suspended in 20 mL of ether, and a solution of phenol (0.245 g, 2.60 mmol) and triethylamine (363 μL, 2.60 mmol) in 8 mL of ether was added dropwise over a period of 2–3 min. The reaction mixture was filtered after 30 min, and the solvent was removed from the filtrate in vacuo to yield orange crystalline $WCp^*(OC_6H_5)_4$ (0.372 g, 0.540 mmol, 83%). The product was recrystallized from ether. EPR (ether): $\langle g\rangle$ = 1.853 ($\Delta\nu_{1/2}$ = 69 G). Anal. Calcd for $WC_{34}H_{35}O_4$: C, 59.06; H, 5.10. Found: C, 58.89; H, 4.93.

$WCp^*(O\text{-}3,5\text{-}C_6H_3Me_2)_4$ (2b). The procedure was the same as that for **2a**, employing WCp^*Cl_4 (0.336 g, 0.729 mmol) in 10 mL of ether and a solution of 3,5-dimethylphenol (0.267 g, 2.92 mmol) and triethylamine (305 μL, 2.92 mmol) in 8 mL of ether. The crude product, a red oil, was dissolved in a 1:1 mixture of pentane, and the solution was cooled to −40 °C to yield $WCp^*(O\text{-}3,5\text{-}C_6H_3Me_2)_4$ (0.492 g, 0.612 mmol, 84%) as a red powder. EPR (ether): $\langle g\rangle$ = 1.850 ($\Delta\nu_{1/2}$ = 79 G). Anal. Calcd for $WC_{42}H_{51}O_4$: C, 62.77; H, 6.40. Found: C, 62.86; H, 6.49.

$WCp^*(O\text{-}4\text{-}C_6H_4OMe)_4$ (2c). The procedure was the same as that for **2a**, employing WCp^*Cl_4 (0.100 g, 0.217 mmol) in 10 mL of toluene and a solution of *p*-hydroxyanisole (0.108 g, 0.868 mmol) and triethylamine (121 μL, 0.868 mmol) in 6 mL of toluene. The crude product, a red oil, was isolated as a red powder from ether; yield 0.126 g (0.176 mmol, 81%). The solid was recrystallized from ether layered with THF. EPR (ether): $\langle g\rangle$ = 1.855 ($\Delta\nu_{1/2}$ = 59 G). Anal. Calcd for $WC_{38}H_{43}O_8$: C, 56.24; H, 5.34. Found: C, 56.33; H, 5.01.

$WCp^*(O\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu)_4$ (2d). The procedure was the same as that for **2a**, employing WCp^*Cl_4 (0.100 g, 0.217 mmol) in 10 mL of ether

(20) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.
(21) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.
(22) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466 and references therein.
(23) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532.
(24) Green, J. C.; Green, M. L. H.; Mountford, P.; Parkington, M. J. *J. Chem. Soc., Dalton Trans.* **1990**, 3407.
(25) Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264.
(26) Roland, E.; Walborsky, E. C.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5795.
(27) Tate, D. P.; Augl, J. M.; Ritchey, W. M.; Ross, B. L.; Grasselli, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 3261.
(28) Herrmann, W. A.; Fischer, R. A.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1263.
(29) Chao, Y.; Rodgers, P. M.; Wigley, D. E.; Alexander, S. J.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 6326.
(30) Mayer, J. M.; Tulip, T. H.; Calabrese, J. C.; Valencia, E. *J. Am. Chem. Soc.* **1987**, *109*, 157.
(31) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965.
(32) Chu, S.-Y.; Hoffmann, R. *J. Phys. Chem.* **1982**, *86*, 1289.
(33) King, R. B. *Inorg. Chem.* **1968**, *7*, 1044.

Table IV. Crystallographic Data for $WCp^*(OC_6H_5)(MeC{\equiv}CMe)_2$ (**4d**)

empirical formula	$WC_{24}H_{32}O$
fw	520.37
a	9.5498 (6) Å
b	13.9860 (9) Å
c	16.627 (1) Å
β	92.679 (6)°
V	2218.4 (4) Å^3
space group	$P2_1/n$
Z	4
ρ(calcd)	1.558 g cm^{-3}
μ	53.3 cm^{-1}
final R, R_w[a]	0.044, 0.044
max peak on final diff map	1.03 e/Å^3
min peak on final diff map	−1.57 e/Å^3

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

and a solution of 4-*tert*-butylphenol (0.130 g, 0.868 mmol) and triethylamine (121 μL, 0.868 mmol) in 4 mL of ether; yield 0.189 g (0.209 mmol, 97%). $WCp^*(O\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu)_4$ could be isolated as orange needles from pentane. EPR (THF): $\langle g\rangle = 1.853$ ($\Delta\nu_{1/2} = 59$ G). Anal. Calcd for $WC_{50}H_{67}O_4$: C, 65.57; H, 7.37. Found: C, 65.36; H, 7.35.

$WCp^*(O\text{-}4\text{-}C_6H_4Me)_4$ (2e). The procedure was the same as that for **2a**, employing WCp^*Cl_4 (0.100 g, 0.217 mmol) in 10 mL of ether and a solution of 4-methylphenol (0.094 g, 0.868 mmol) and triethylamine (121 μL, 0.868 mmol) in 4 mL of ether; yield 0.132 g (0.179 mmol, 83%). $WCp^*(O\text{-}4\text{-}C_6H_4Me)_4$ was recrystallized from a mixture of ether and pentane at −40 °C. EPR (ether): $\langle g\rangle = 1.854$ ($\Delta\nu_{1/2} = 60$ G). Anal. Calcd for $WC_{38}H_{43}O_4$: C, 61.05; H, 5.80. Found: C, 61.21; H, 5.79.

$WCp^*(OCMe_2CMe_2O)Cl_2$ (3). WCp^*Cl_4 (1.50 g, 3.26 mmol) was suspended in 50 mL of ether, and a solution of pinacol (0.385 g, 3.26 mmol) and triethylamine (909 μL, 6.52 mmol) in 10 mL of ether was added dropwise over 3–5 min. After 30 min, the dark red mixture was filtered. The solvent was removed in vacuo from the filtrate to yield red/purple crystals of $WCp^*(OCMe_2CMe_2O)Cl_2$ (0.920 g, 2.06 mmol, 95%). EPR (ether): $\langle g\rangle = 1.856$ ($\Delta\nu_{1/2} = 72$ G). Anal. Calcd for $WC_{16}H_{27}O_2Cl_2$: C, 38.01; H, 5.38; Cl, 14.02. Found: C, 38.13; H, 4.79; Cl, 14.27.

$WCp^*(OC_6H_5)(\eta^2\text{-}HC{\equiv}CH)_2$ (4a). $WCp^*(OC_6H_5)_4$ (0.050 g, 0.072 mmol) was dissolved in 10 mL of ether, and excess alkyne was bubbled into the solution via a gastight syringe. Sodium amalgam (0.5%; 1.0 g, 0.22 mmol) was added directly to the stirring solution. The reaction mixture was stirred for 1 h at room temperature; it slowly became light yellow. The mixture was filtered, and the solvent was removed from the dark yellow filtrate in vacuo. The resulting residue was extracted with pentane, and the mixture was filtered. The solvent was removed from the filtrate in vacuo to yield yellow $WCp^*(OC_6H_5)(\eta^2\text{-}HC{\equiv}CH)_2$ (0.030 g, 0.065 mmol, 90%): ^{1}H NMR (C_6D_6) δ 10.63 (s, 4 H, HC≡CH), 7.40 (t, 2 H, H_o), 7.08 (t, 1 H, H_p), 6.85 (d, 2 H, H_m), 1.49 (s, 15 H, Cp*); ^{13}C NMR (CD_2Cl_2) δ 184.2 (d, $J_{CH} = 198$, $J_{CW} = 21$, HC≡*C*H), 170.0 (s, C_{ipso}), 129.1 (d, C_{aryl}), 121.4 (d, C_{aryl}), 114.89 (d, C_{aryl}), 111.3 (s, C_5Me_5), 10.76 (q, C_5Me_5). Anal. Calcd for $WC_{20}H_{24}O$: C, 51.74; H, 5.21. Found: C, 51.98; H, 5.50.

$WCp^*(OC_6H_5)(\eta^2\text{-}HC{\equiv}CSiMe_3)_2$ (4b). $WCp^*(OC_6H_5)_4$ (0.190 g, 0.275 mmol) was dissolved in 20 mL of ether, and (trimethylsilyl)-acetylene (77.6 μL, 0.550 mmol) was added to the stirred solution, followed by 0.5% sodium amalgam (3.79 g, 0.825 mmol). The reaction was stirred for 1 h at room temperature and filtered. The solvents were removed from the filtrate in vacuo, the residue was extracted with pentane, and the extract was filtered to remove the white, insoluble $NaOC_6H_5$ (0.096 g, 73%). The filtrate was concentrated and cooled to −40 °C to yield orange needles of $WCp^*(OC_6H_5)(\eta^2\text{-}HC{\equiv}CSiMe_3)_2$ (0.150 g, 0.247 mmol, 90%): ^{1}H NMR (C_6D_6) δ 12.29 (s, 2 H, 2*H*C≡CSiMe$_3$), 7.31 (t, 2 H, H_o), 6.81 (t, 1 H, H_p), 6.62 (d, 2 H, H_m), 1.52 (s, 15 H, Cp*), 0.12 (s, 18 H, 2HC≡C*SiMe*$_3$); ^{13}C NMR (CD_2Cl_2) δ 207.5 (d, $J_{CH} = 196$, $J_{CW} = 19$, HC≡SiMe$_3$), 186.6 (s, HC≡*C*SiMe$_3$), 171.0 (s, C_{ipso}), 128.9 (d, C_{aryl}), 121.7 (d, C_{aryl}), 113.6 (d, C_{aryl}), 109.8 (s,C_5Me_5), 11.2 (q, C_5Me_5), 0.65 (q, HC≡C*SiMe*$_3$). Anal. Calcd for $WC_{26}H_{40}OSi_2$: C, 51.31; H, 6.62. Found: C, 51.53; H, 6.81.

$WCp^*(OC_6H_5)(\eta^2\text{-}PhC{\equiv}CH)_2$ (4c). $WCp^*(OC_6H_5)_4$ (0.100 g, 0.145 mmol) was dissolved in 16 mL of ether, and phenylacetylene (31.8 μL, 0.290 mmol) was added to the stirred solution, followed by 0.5% sodium amalgam (2.00 g, 0.435 mmol). After 1 h, the light orange mixture was filtered and the solvents were removed from the filtrate in vacuo. The resulting residue was extracted with pentane, and the extract was filtered. The filtrate was concentrated and cooled to −40 °C to yield orange crystals of $WCp^*(OC_6H_5)(\eta^2\text{-}PhC{\equiv}CH)_2$ (0.078 g, 0.131 mmol, 90%) after 24 h: ^{1}H NMR (CD_2Cl_2) δ 11.0 (br s, 2 H, η^2-PhC≡C*H*), 7.8 (d, 4 H, η^2-*Ph*C≡CH), 7.4 (t, 2 H, H_o), 7.3 (t, 1 H, H_p), 6.9 (t, 2 H, η^2-*Ph*C≡CH), 6.45 (d, 2 H, H_m), 6.35 (d, 4 H, η^2-*Ph*C≡CH), 1.87 (s, 15 H, Cp*); ^{13}C NMR (CD_2Cl_2) δ 180.4 (d, $J_{CH} = 194$, η^2-PhC≡*C*H), 169.2 (s, η^2-PhC≡CH), 137.2 (s, C_{ipso}), 132.3 (s, C_{ipso}), 131.3 (d, C_{aryl}), 128.9 (d, C_{aryl}), 128.5 (d, C_{aryl}), 121.8 (ddd, C_{aryl}), 114.5 (ddd, C_{aryl}), 111.1 (s, C_5Me_5), 11.3 (q, C_5Me_5). Anal. Calcd for $WC_{32}H_{32}O$: C, 62.35; H, 5.23. Found: C, 62.39; H, 5.34.

$WCp^*(OC_6H_5)(\eta^2\text{-}MeC{\equiv}CMe)_2$ (4d). $WCp^*(OC_6H_5)_4$ (0.300 g, 0.434 mmol) was dissolved in 20 mL of cold ether, and 2-butyne (0.070 μL, 0.868 mmol) was added to the solution, followed by 0.5% sodium amalgam (6.00 g, 1.30 mmol). The dark orange reaction mixture was stirred for 1 h at room temperature and filtered. The solvent was removed in vacuo from the yellow filtrate, and the residue was recrystallized from pentane at −40 °C to yield yellow crystals of $WCp^*(OC_6H_5)(\eta^2\text{-}MeC{\equiv}CMe)_2$ (0.204 g, 0.395 mmol, 91%): ^{1}H NMR (CD_2Cl_2, 25 °C) δ 6.90 (t, 2 H, H_o), 6.37 (t, 1 H, H_p), 6.15 (d, 2 H, H_m), 2.84 (br s, 6 H, MeC≡CMe), 2.13 (br s, 6 H, MeC≡CMe), 1.80 (s, 15 H, Cp*); ^{13}C NMR (CD_2Cl_2, −40 °C) δ 192.9 (s, Me*C*≡*C*Me), 176.9 (s, Me*C*≡*C*Me), 168.5 (s, C_{ipso}), 128.2 (d, C_{aryl}), 120.4 (d, C_{aryl}), 112.1 (d, C_{aryl}), 109.3 (s, C_5Me_5), 18.8 (q, *Me*C≡C*Me*), 14.9 (q, *Me*C≡C*Me*), 9.90 (q, C_5Me_5). Anal. Calcd for $WC_{24}H_{32}O$: C, 55.40; H, 6.20. Found: C, 55.41; H, 6.27.

$WCp^*Cl(\eta^2\text{-}Me_3SiC{\equiv}CH)_2$ (5a). WCp^*Cl_4 (0.300 g, 0.434 mmol) was dissolved in 20 mL of cold THF, and $Me_3SiC{\equiv}CH$ (122.5 μL, 0.868 mmol) was added to the solution, followed by 0.5% sodium amalgam (6.00 g, 1.30 mmol). After 1 h, the reaction mixture was filtered and the solvent was removed from the dark green filtrate in vacuo. The light green $WCp^*Cl(\eta^2\text{-}Me_3SiC{\equiv}CH)_2$ (0.100 g, 0.195 mmol, 45%) was recrystallized from pentane at −40 °C: ^{1}H NMR (C_6D_6) δ 11.98 (s, 2 H, 2 $Me_3SiC{\equiv}C\mathit{H}$), 1.51 (s, 15 H, Cp*), 0.41 (s, 18 H, 2 *Me*$_3$SiC≡CH); ^{13}C NMR (C_6D_6) δ 201.4 (d, $Me_3SiC{\equiv}\mathit{C}H$, $J_{CH} = 198$ Hz), 179.4 (s, $Me_3SiC{\equiv}CH$), 108.1 (s, C_5Me_5), 10.9 (q, C_5Me_5), 1.1 (q, *Me*$_3$SiC≡CH). Anal. Calcd for $WC_{20}H_{35}ClSi_2$: C, 43.60; H, 6.40. Found: C, 43.39; H, 6.21.

$WCp^*Cl(\eta^2\text{-}MeC{\equiv}CMe)_2$ (5b). WCp^*Cl_4 (0.300 g, 0.434 mmol) was dissolved in 20 mL of cold THF, and 2-butyne (0.070 μL, 0.0868 mmol) was added to the solution, followed by 0.5% sodium amalgam (6.00 g, 1.30 mmol). After 1 h, the reaction mixture was filtered and the solvent was removed in vacuo from the dark yellow filtrate. The residue was recrystallized from pentane at −40 °C to yield yellow $WCp^*Cl(\eta^2\text{-}MeC{\equiv}CMe)_2$ (0.139 g, 0.282 mmol, 65%): ^{1}H NMR (C_6D_6) δ 2.84 (s, 6 H, MeC≡CMe), 2.13 (s, 6 H, MeC≡CMe), 1.80 (s, 15 H, Cp*); ^{13}C NMR (C_6D_6) δ 183.7 (s, Me*C*≡*C*Me, $J_{CW} = 17$), 175.1 (s, Me*C*≡*C*Me), 108.3 (s, C_5Me_5), 17.9 (q, *Me*C≡C*Me*), 12.3 (q, *Me*C≡C*Me*), 10.5 (q, C_5Me_5). Anal. Calcd for $WC_{18}H_{27}Cl$: C, 46.72; H, 5.88. Found: C, 46.77; H, 6.28.

X-ray Structure of $WCp^*(OC_6H_5)(MeC{\equiv}CMe)_2$ (4d). A yellow prismatic crystal of $WCp^*(OC_6H_5)(MeC{\equiv}CMe)_2$ having approximate dimensions of 0.280 × 0.280 × 0.180 mm was mounted on a glass fiber. Data were collected at 25 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. A total of 5612 reflections were collected in the range $3.0° < 2\theta < 55.00°$, with 5303 being unique. No crystal decay was evident during data collection. An empirical absorption correction was applied, using the program DIFABS, which resulted in transmission factors ranging from 0.86 to 1.25. The structure was solved by the Patterson methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions and refined isotropically. The final cycle of full-matrix least-squares refinement was based on 2622 reflections ($I > 3.00\sigma(I)$) and 235 variables and used the TEXSAN crystallographic software package from the Molecular Structure Corp.

Acknowledgment. R.R.S. thanks the National Institutes of Health for partial support of this work (Grant GM 31978), and M.G.V. thanks the National Science Foundation for a predoctoral fellowship. We also thank Dr. William M. Davis for collecting the X-ray data for **4d**.

Registry No. **1a**, 139042-28-7; **1b**, 139042-29-8; **2d**, 139042-30-1; **2b**, 139042-31-2; **2c**, 139042-32-3; **2d**, 139042-33-4; **2e**, 139042-34-5; **3**, 139042-35-6; **4a**, 139042-36-7; **4b**, 139042-37-8; **4c**, 139042-38-9; **4d**, 139042-39-0; **5a**, 139042-40-3; **5b**, 139042-41-4; WCp^*Cl_4, 96055-85-5; $Me_3SiC{\equiv}CH$, 1066-54-2; 3,5-dimethylphenol, 108-68-9; *p*-hydroxyanisole, 150-76-5; 4-*tert*-butyphenol, 98-54-4; 4-methylphenol, 106-44-5; pinacol, 76-09-5; acetylene, 74-86-2; phenylacetylene, 536-74-3; 2-butyne, 503-17-3.

Supplementary Material Available: A labeled ORTEP drawing and tables of final thermal parameters and bond distances and angles (9 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.