

# Syntheses and Chemistry of the Diynyl Complexes $M(C\equiv CC\equiv CH)(CO)_3(\eta-C_5H_5)$ ( $M = Mo, W$ ): Crystal Structures of $W(C\equiv CC\equiv CSiMe_3)(CO)_3(\eta-C_5H_5)$ , $W\{C\equiv CC[CH=C(CN)_2]=C(CN)_2\}(CO)_3(\eta-C_5H_5)$ , and *cis*- $W(C\equiv CPh)(CO)_2(PPh_3)(\eta-C_5H_5)$

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Reactions of buta-1,3-diyne with appropriate metal halides, carried out in the presence of CuI in NH<sub>4</sub>Et<sub>2</sub>, have given high yields of  $M(C\equiv CC\equiv CH)(CO)_n Cp$  [ $M = W$  (**1-W**), Mo (**1-Mo**),  $n = 3$ ;  $M = Fe$ ,  $n = 2$  (**2**)]. Complex **1-W** was metalated with LiNPr<sup>1</sup><sub>2</sub>; subsequent reactions with SiClMe<sub>3</sub> or PCIPh<sub>2</sub> gave  $W(C\equiv CC\equiv CR)(CO)_3 Cp$  [ $R = SiMe_3$  (**3**) or P(O)Ph<sub>2</sub> (**4**)] in modest to high yield. Coupling of **1** with iodoarenes, catalyzed by a mixed Cu<sup>I</sup>-Pd<sup>0</sup> catalyst, gave  $M(C\equiv CC\equiv CAr)(CO)_3 Cp$  [ $M = W$ , Ar = Ph (**5-W**), tol (**6**), C<sub>6</sub>H<sub>4</sub>OMe-4 (**7**), C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me-4 (**8**);  $M = Mo$ , Ar = Ph (**5-Mo**)]. Oxidative coupling of **1** (CuCl-tmed-O<sub>2</sub>) gave  $\{M(CO)_3 Cp\}_2(\mu-C_8)$  [ $M = W$  (**9-W**), Mo (**9-Mo**)]. Addition of tetracyanoethene to **1-W** occurred at the C≡C triple bond further from the metal atom, to give  $W\{C\equiv CC[=C(CN)_2]CH=C(CN)_2\}(CO)_3 Cp$  (**10**). Substitution of CO by PPh<sub>3</sub> was difficult, but the Me<sub>3</sub>NO-induced reaction with **5-W** afforded *cis*- $W(C\equiv CC\equiv CPh)(CO)_2(PPh_3)Cp$  (**11**) in low yield. The X-ray crystal structures of **3** and **10**, together with that of *cis*- $W(C\equiv CPh)(CO)_2(PPh_3)Cp$  (**12**), are reported.

## Introduction

The study of metal complexes containing all-carbon ligands is now an area of intense activity.<sup>1–4</sup> In addition to their inherent interest these compounds are considered as precursors to potentially useful new materials and nanoscale devices. For example, poly-yndiyl complexes, in which an unsaturated C<sub>n</sub> chain links two metal centers, have attracted the attention of several groups as possible models of and potential precursors to one-dimensional molecular wires.<sup>5–8</sup> Several groups have revealed the rich electrochemistry of these systems.<sup>5,9,10</sup> Their unsaturation also makes them potentially attractive monomers in as yet unrealized oligomerization and polymerization reactions.<sup>11</sup>

Previous reports from this group have described the use of the bis(tertiary phosphine) ligands 1,2-bis(diphe-

nylphosphino)acetylene (Ph<sub>2</sub>PC≡CPh<sub>2</sub>, dppa)<sup>12</sup> and 1,4-bis(diphenylphosphino)buta-1,3-diyne (Ph<sub>2</sub>PC≡CC≡CPh<sub>2</sub>, bdpp)<sup>13</sup> as precursors to cluster complexes containing the ligands C<sub>2</sub> and C<sub>4</sub>, respectively. The open pentanuclear cluster Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>)(μ-SMe)<sub>2</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>11</sub>, in particular, is a rich source of novel and interesting transformations.<sup>14</sup> The binuclear diyndiyl complex {Cp(Ph<sub>3</sub>P)<sub>2</sub>Ru}C≡CC≡C{Ru(PPh<sub>3</sub>)<sub>2</sub>Cp} has been obtained from Ru(thf)(PPh<sub>3</sub>)<sub>2</sub>Cp and LiC≡CC≡CLi,<sup>15</sup> or from RuCl(PPh<sub>3</sub>)<sub>2</sub>Cp and SiMe<sub>3</sub>CC≡CSiMe<sub>3</sub>,<sup>9</sup> and exhibits an unusually large range of oxidation states.<sup>9</sup> Many other complexes containing C<sub>4</sub> or related diyndyl ligands have been obtained from reactions of SiMe<sub>3</sub>CC≡CC≡CR ( $R = H, SiMe_3$ ).<sup>16</sup>

In seeking to extend these studies, we required access to a range of diyndyl complexes,  $\{L_n M\}C\equiv CC\equiv CR$ , and diyndiyl complexes,  $\{L_n M\}C\equiv CC\equiv C\{ML_n\}$ . Several examples of such complexes have been described. Synthetic routes of general application include (i) reactions of diyndyl anions with metal complexes containing a readily displaced ligand, such as halide or triflate,<sup>15,17–19</sup>

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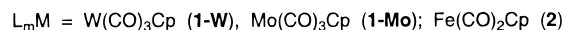
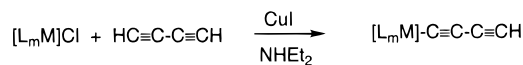
(ii) oxidative addition of 1,3-diyne to electron-rich metal centers, such as  $\text{RhCl}(\text{PPr}^i_3)_2$ ;<sup>20</sup> (iii) reactions between metal halide complexes and trimethyltin diynes  $\text{Me}_3\text{SnC}\equiv\text{CC}\equiv\text{CR}$ ,<sup>20d,21</sup> sometimes in the presence of palladium(0) catalysts;<sup>22</sup> (iv) deprotonation of intermediate vinylidene or metallacumulene complexes;<sup>21,23</sup> and (v) reactions of 1,3-diyne with metal halides in the presence of Cu(I) catalysts.<sup>24</sup> Despite the growing number of complexes of this type which have been made, their reactivity remains relatively unexplored. Given the extensive chemistry associated with the  $\text{C}\equiv\text{C}$  triple bond in both organic and organometallic chemistry, transition metal complexes containing diynyl ligands would be expected to exhibit a wide range of reactions.

One of the drawbacks to the preparation of diynyl complexes  $\{\text{L}_n\text{M}\}\text{C}\equiv\text{CC}\equiv\text{CR}$  ( $\text{R} = \text{H}$ , alkyl, aryl, etc.) by the above methods is the requirement for prior synthesis of the corresponding 1,3-diyne,  $\text{HC}\equiv\text{CC}\equiv\text{CR}$ . Examples include the synthesis of  $\text{Ni}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)\text{Cp}$  from  $\text{BrMgC}\equiv\text{CC}\equiv\text{CH}$ , which was prepared from  $\text{HC}\equiv\text{CC}\equiv\text{CH}$ ,<sup>17</sup>  $\text{RhHCl}(\text{C}\equiv\text{CC}\equiv\text{CPh})(\text{PPr}^i_3)_2$  from  $\{\text{RhCl}(\text{P}^i\text{Pr}_3)_2\}_n$  and  $\text{HC}\equiv\text{CC}\equiv\text{CPh}$ <sup>20b</sup> and  $\text{Re}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{PPh}_3)(\text{NO})\text{Cp}^*$  from  $[\text{Re}(\text{ClC}_6\text{H}_5)(\text{PPh}_3)(\text{NO})\text{Cp}^*]\text{BF}_4$  and  $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$  in the presence of  $\text{KOBu}^t$ .<sup>5</sup> An attractive alternative would be to functionalize buta-1,3-diyne complexes  $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{CH}$  by reactions of the diyne proton. We have found that buta-1,3-diyne,  $\text{HC}\equiv\text{CC}\equiv\text{CH}$ , is a suitable reagent for the preparation of these complexes and have further demonstrated that the 1,3-diyne ligand is indeed readily amenable to substitution, making these complexes convenient materials for the preparation of substituted diynyl complexes. In addition, the metal center and the  $\text{C}\equiv\text{C}$  triple bond are also reaction centers. The present paper describes the development of a simple and reliable synthetic approach to these complexes, as exemplified by the tungsten, molybdenum, and iron derivatives,  $\text{M}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_n\text{Cp}$  ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ,  $n = 3$ ;  $\text{M} = \text{Fe}$ ,  $n = 2$ ). Some of this work has been described in preliminary fashion.<sup>8</sup>

## Results and Discussion

**Synthesis of 1,3-Diynyl Complexes.** The bright yellow, air stable, and mildly light sensitive diynyl complex  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$  (**1-W**, Scheme 1) was obtained in excellent (90%) yield from the CuI-catalyzed reaction between  $\text{WCl}(\text{CO})_3\text{Cp}$  and buta-1,3-diyne (Scheme 1). The reactions were carried out in tetrahydrofuran solution containing diethylamine, which serves both to generate the active diynylcopper intermediate

## Scheme 1



and to remove the HCl as diethylammonium chloride. The complex is readily characterized from its spectral properties and elemental analysis. The IR spectrum of **1-W** contained strong  $\nu(\text{CO})$  absorptions at 2044 and 1958  $\text{cm}^{-1}$ , characteristic of the  $\text{W}(\text{CO})_3\text{Cp}$  fragment. The terminal  $\text{C}\equiv\text{CH}$  group gave rise to weak  $\nu(\equiv\text{CH})$  and  $\nu(\text{C}\equiv\text{C})$  bands at 3260 and 2145  $\text{cm}^{-1}$ , respectively. Sharp singlet resonances in the  $^1\text{H}$  NMR spectrum at  $\delta$  2.03 and 5.66 are assigned to the terminal  $\equiv\text{CH}$  and the Cp protons, respectively.

Besides resonances which could be assigned to the Cp carbons at  $\delta$  91.51 and the three CO groups between  $\delta$  210 and 227, four signals in the  $^{13}\text{C}$  NMR spectrum between  $\delta$  63.3 and 110.5 arise from the carbons of the  $\text{C}_4$  chain (Table 1). In assigning these carbon resonances, we note that those for  $\text{C}_\alpha$ ,  $\text{C}_\beta$ , and  $\text{C}_\gamma$  ( $\text{C}_\alpha$  is bonded to W) show satellite signals arising from coupling to  $^{183}\text{W}$ . Previous assignments of the  $^{13}\text{C}$  resonances in buta-1,3-diyne complexes have been based on trends found in values for  $J_{\text{CP}}$  in phosphine-substituted complexes, so that  $^2J_{\text{CP}} > ^4J_{\text{CP}} > ^3J_{\text{CP}}$ ,<sup>5</sup> or from the H-coupled  $^{13}\text{C}$  NMR spectra obtained for  $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{CH}$ .<sup>7</sup> Arguments that the chemical shift moves downfield as the metal center is approached have also been employed.<sup>7</sup> In the case of **1-W**, the diynyl resonance at lowest field ( $\delta$  110.52) exhibits only unresolved coupling to  $^{183}\text{W}$ , while the resonances at  $\delta$  71.60 and 70.13 show measurable coupling constants of 88 and 94 Hz, respectively. We have tentatively assigned the lowest field resonance to  $\text{C}_\alpha$  in keeping with the established patterns for these systems (Table 1) and have assumed the magnitude of  $J_{\text{CW}}$  for the  $\text{C}_\beta$  and  $\text{C}_\gamma$  carbons follows the trend previously observed for  $J_{\text{CP}}$  in  $\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{dppe})\text{Cp}^*$  ( $\text{R} = \text{H}$ ,  $\text{SiMe}_3$ ),<sup>7</sup> so that  $^4J_{\text{CW}}$  [to  $\text{C}_\gamma$ ; 94 Hz]  $>$   $^3J_{\text{CW}}$  [to  $\text{C}_\beta$ ; 88 Hz].

The electrospray mass spectrum (ES MS) of a solution of **1-W** in aqueous NCMe at low cone voltages showed the ions  $[\text{M} + \text{MeCN} - n\text{CO}]^+$  ( $n = 0-2$ ); similar solvated  $[\text{M} + \text{solvent}]^+$  ions are frequently encountered with this technique. At higher cone voltages only  $[\text{M} + \text{H} - 3\text{CO}]^+$  was observed.

The dark yellow molybdenum analogue  $\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$  (**1-Mo**) was prepared from  $\text{MoI}(\text{CO})_3\text{Cp}$  and buta-1,3-diyne (60%) in an analogous manner. The spectral properties of **1-Mo** were not significantly different from those of **1-W**. The absence of a spin-active metal nucleus resulted in the observation of four sharp singlets in the  $^{13}\text{C}$  NMR spectrum for the four-carbon chain, which are assigned by analogy with those found for **1-W**. The  $\equiv\text{CH}$  proton was found at  $\delta$  2.04 in the  $^1\text{H}$  NMR spectrum. The molybdenum complex is considerably more light sensitive than **1-W**, becoming discolored after only a few minutes exposure to laboratory fluorescent lighting.

The diynyl-iron complex  $\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_2\text{Cp}$  (**2**) was obtained from the diyne and  $\text{FeCl}(\text{CO})_2\text{Cp}$ . The spectral data obtained for **2** were in good agreement with those previously reported for the same complex

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**Table 1.**  $^{13}C$  NMR Data for Diynyl Complexes,  $\{ML_n\}C_\alpha\equiv C_\beta C_\gamma\equiv C_\delta-R$ 

complex $ML_n$	R	number	chemical shift ( $J$ , Hz)				notes	ref
			$C_\alpha$	$C_\beta$	$C_\gamma$	$C_\delta$		
$W(CO)_3Cp$	H	<b>1-W</b>	110.52 (br)	71.60 ( $J_{CW}$ 88)	70.13 ( $J_{CW}$ 94)	63.60		this work
$Mo(CO)_3Cp$	H	<b>1-Mo</b>	110.46	87.25	70.27	62.10		this work
$Re(NO)(PPh_3)Cp^*$	H		102.1	110.8	72.4	65.2		5
$Fe(CO)_2Cp$	H	<b>2</b>	96.80	89.85	70.88	54.35		18, 22; this work
$Fe(CO)(PPh_3)Cp$	H		109.4 ( $J_{CP}$ 39.4)	99.1	72.1	54.3	<i>a</i>	18
$Fe(CO)_2Cp^*$	H		106.4	92.8	71.9	53.5		33
$Fe(dppe)Cp^*$	H		136.6 ( $J_{CP}$ 38)	100.7 ( $J_{CH}$ 5)	75.1 ( $J_{CP}$ 3; $J_{CH}$ 50)	50.5 ( $J_{CH}$ 248)	<i>b</i>	7
$Ru(PPh_3)_2Cp$	H		116.4 ( $J_{CP}$ 24.6)	94.4	73.9	128.4		15
$Ru(CO)_2(PEt_3)_2$	H		101.3	91.7	72.1	54.5		28
$Re(NO)(PPh_3)Cp^*$	Me		96.8	111.6	69.1	71.9		5
$W(CO)_3Cp$	$SiMe_3$	<b>3</b>	111.74 (br)	110.86	90.04	73.59		this work
$Re(NO)(PPh_3)Cp^*$	$SiMe_3$		105.8 ( $J_{CP}$ 15.9)	112.3	93.5 ( $J_{CP}$ 2.7)	80.6	<i>b</i>	5
$Fe(CO)_2Cp^*$	$SiMe_3$		106.3	96.5	94.7	69.5	<i>b</i>	7
$Fe(dppe)Cp^*$	$SiMe_3$		98.14	91.9	91.1	71.0	<i>a</i>	19
$trans-RuCl(dppe)_2$	$SiMe_3$		142.2 ( $J_{CP}$ 38)	102.3 ( $J_{CP}$ 2)	96.2 ( $J_{CP}$ 3)	64.7	<i>b</i>	7
$Rh(CO)(PPr^i_3)_2$	$SiMe_3$		95.95 (br)	96.11 ( $J_{CRh}$ 43.3; $J_{CP}$ 22.1)	67.11 ( $J_{CRh}$ 13.1; $J_{CP}$ 2.5)	77.2	<i>a</i>	e
$IrHCl(PPr^i_3)_2$	$SiMe_3$		121.3 ( $J_{CP}$ 11.2)	103.0	93.2	77.2	<i>c</i>	20d
$IrHCl(py)(PPr^i_3)$	$SiMe_3$		80.0 ( $J_{CP}$ 11.4)	94.4	92.5	75.5	<i>c</i>	f
$W(CO)_3Cp$	$P(O)Ph_2$	<b>4</b>	110.57 ( $J_{CW}$ 16)	91.32	d	d		this work
$W(CO)_3Cp$	Ph	<b>5-W</b>	111.03 ( $J_{CW}$ 22)	d	76.19	73.78		this work
$Mo(CO)_3Cp$	Ph	<b>5-Mo</b>	110.92	d	76.42	72.59		this work
$W(CO)_2(PPh_3)Cp$	Ph	<b>11</b>	113.27 ( $J_{CW}$ 8)	100.14	72.75	72.2		this work
$Rh(CO)(PPr^i_3)_2$	Ph		126.33 ( $J_{CRh}$ 43.4; $J_{CP}$ 21.6)	102.22 ( $J_{CRh}$ 12.7; $J_{CP}$ 3.2)	79.15 (br)	71.95 ( $J_{PC}$ 2.1)	<i>c</i>	20c
$W(CO)_3Cp$	$C\equiv CC\equiv C$	<b>9-W</b>	112.39	91.60	63.70	60.91		this work
$Mo(CO)_3Cp$	$\{W(CO)_3Cp\}$	<b>9-Mo</b>	112.24	92.22	63.47	59.95		this work
$Re(NO)(PPh_3)Cp^*$	$\{Mo(CO)_3Cp\}$		109.7	113.3	66.6	64.5		32
$Fe(CO)_2Cp^*$	$C\equiv CC\equiv C$		110.8 ( $J_{CP}$ 16.9)	94.8	61.61 ( $J_{CP}$ 2.72)	51.4		33
$Fe(dppe)Cp^*$	$\{Fe(CO)_2Cp^*\}$		139.45 ( $J_{CP}$ 42)	101.8	62.7 ( $J_{CP}$ 3)	50.6	<i>c</i>	7
	$C\equiv CC\equiv C$							
	$\{Fe(dppe)Cp^*\}$							

<sup>a</sup> Not individually assigned. <sup>b</sup> Assignment based on  $^2J_{CP} > ^4J_{CP} > ^3J_{CP}$ . <sup>c</sup> Assignment based on  $\delta$  being further downfield as C is closer to Fe, also on values of  $J_{CP}$ . <sup>d</sup> Not observed. <sup>e</sup> Dahlenburg, L.; Weiss, A.; Bock, M.; Zahl, A. *J. Organomet. Chem.* **1997**, *541*, 465. <sup>f</sup> Werner, H.; Lass, R. W.; Gevert, G.; Wolf, J. *Organometallics* **1997**, *16*, 4077.

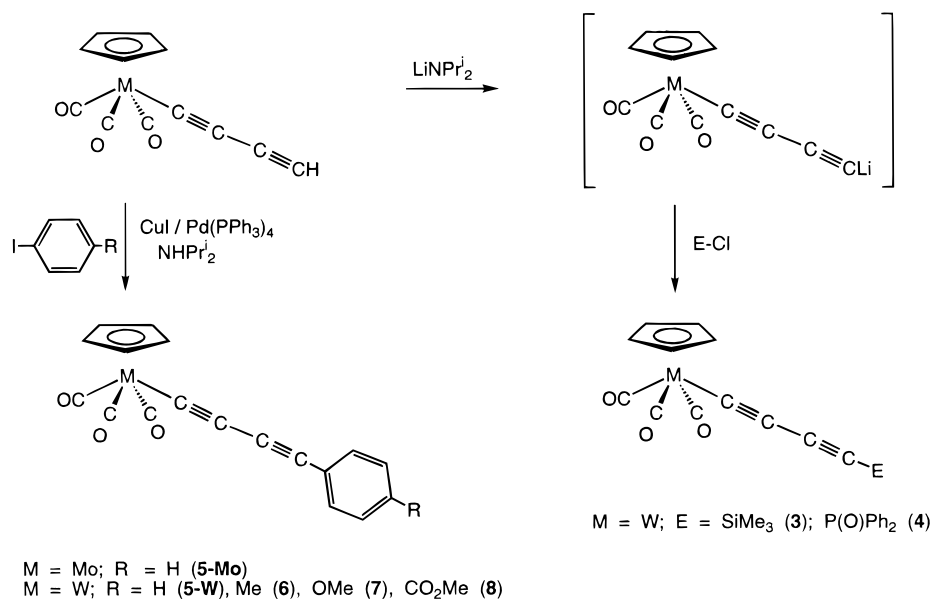
obtained from the Pd(0)-catalyzed reaction between  $Me_3-Sn-C\equiv CC\equiv CH$  and  $FeI(CO)_2Cp^{22}$  or by treating  $Fe(C\equiv CC\equiv C-SiMe_3)(CO)_2Cp$  with fluoride ion.<sup>18</sup>

**Functionalization and Reactivity Studies.** Established methods for the preparation of asymmetrically substituted organic diynes generally involve cross-coupling of smaller acetylenic fragments.<sup>25</sup> In contrast, most diynyl complexes  $\{ML_n\}C\equiv CC\equiv CR$  have been prepared using reactions in which a preformed diyne is the source of the diynyl ligand. We have found that the readily available stable 1,3-diynyl complexes described above can be used to synthesize a range of substituted diynyl complexes,  $\{ML_n\}C\equiv CC\equiv CR$  (Scheme 2). The reaction conditions used to effect the various transformations are described below.

**(a) Metalation with Lithium Diisopropylamide (LDA).** Metalation of 1-alkynes with organolithium reagents provides a convenient route to organolithium compounds which can then be used as reactive intermediates in further syntheses. Reactions of **1-W** with  $LiBu^n$  resulted in extensive decomposition of the diynyl complex. Complex **2** has been reported to react sluggishly with  $LiBu^n$  and cleaner results were obtained using the bulkier reagent  $LiBu^s$ .<sup>18</sup> It seems likely that the reactions of **1-W** and **2** with  $LiBu^n$  are complicated by nucleophilic attack at the carbonyl ligands. In contrast, the carbonyl-free diynyl complex  $Re(C\equiv CC\equiv CH)(NO)(PPh_3)Cp^*$ <sup>5</sup> is readily metalated by  $LiBu^n$ .

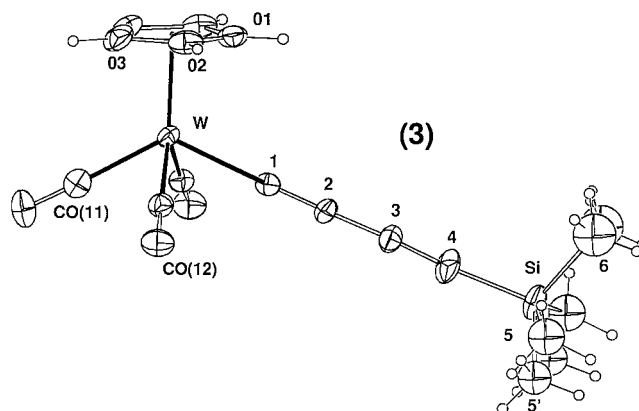
Complex **1-W** was cleanly metalated by treatment with 1 equiv of  $LiNPr^i_2$  (LDA) at  $-78^\circ C$  (Scheme 2), when the initially yellow solution rapidly darkened to orange. Quenching of this solution, which is assumed

Scheme 2



to contain  $W(C\equiv CC\equiv CLi)(CO)_3Cp$ , with  $SiClMe_3$  afforded  $W(C\equiv CC\equiv CSiMe_3)(CO)_3Cp$  (**3**, Scheme 2) in high yield (80%). We have also obtained complex **3**, albeit in only 36% yield, from the reaction between  $WCl(CO)_3Cp$  and  $LiC\equiv CC\equiv CSiMe_3$  in a manner similar to that described by Wong and co-workers for complex **2**.<sup>18</sup> Characterization of **3** followed from elemental analysis and from its spectral properties. The IR spectrum contained two weak  $\nu(C\equiv C)$  bands at 2174 and 2127  $cm^{-1}$ , together with three  $\nu(CO)$  absorptions at 2045, 2026, and 1957  $cm^{-1}$ . The  $^1H$  NMR spectrum contained the expected Cp and  $SiMe_3$  resonances at  $\delta$  5.66 and 0.20, respectively. In the  $^{13}C$  NMR spectrum, four resonances between  $\delta$  73.6 and 111.7 were assigned to the four carbons of the  $C_4$  chain; the Me and Cp signals are at  $\delta$  0.00 and 91.53, respectively. The FAB mass spectrum contained  $M^+$  at  $m/z$  454.

**Molecular Structure of  $W(C\equiv CC\equiv CSiMe_3)(CO)_3Cp$  (**3**).** The molecular structure of **3** has been confirmed by a single-crystal X-ray structural determination. Yellow needles of **3** were obtained from the minimum volume of  $CH_2Cl_2$  and *n*-hexane at  $-20^\circ C$ . A plot of the molecular structure is of **3** is shown in Figure 1, selected bond lengths and angles are given in Table 2, and crystal and refinement data are given in Table 3. The methyl groups attached to Si are disordered over two sites. There is a plane of symmetry passing through C(1)–W–C(11). The molecule is a conventional piano stool structure, the structural features of the  $W(CO)_3Cp$  group being unexceptional and closely similar to those found in  $WPh(CO)_3Cp$ <sup>26</sup> and  $\{W(CO)_3Cp\}_2(\mu-C_2)$ ,<sup>27</sup> for example. The important feature is the coordination of the diynyl ligand. The W–C(1) bond is 2.124(8) Å [cf. 2.172(22) Å in  $\{W(CO)_3Cp\}_2(\mu-C_2)$ ,<sup>27</sup> and successive C–C separations along the C(1)–C(2)–C(3)–C(4) chain are 1.22, 1.36, and 1.22(1) Å, indicating that the  $C\equiv C$  triple bonds are largely localized between C(1) and C(2) and between C(3) and C(4). However, the  $C\equiv C$  triple bonds



**Figure 1.** Plot of a molecule of  $W(C\equiv CC\equiv CSiMe_3)(CO)_3(\eta-C_5H_5)$  (**3**), showing atom numbering scheme. In this and the following figures, non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

are longer than that in  $W(C\equiv CPh)(CO)_2(PPh_3)Cp$  (see below), suggesting some electron delocalization, which is facilitated by the  $SiMe_3$  group.<sup>28</sup> The C(4)–Si separation [1.82(1) Å] is normal. The six-atom W–C(1)–C(2)–C(3)–C(4)–Si chain is essentially linear, with angles at C(1–4) of 179.0(8), 179(1), 177(1), and 177(1)°, again consistent with the diynyl formulation. These dimensions are comparable to those found in *trans*- $Ru(C\equiv CC\equiv CSiMe_3)_2(CO)_2(PEt_3)_2$ .<sup>28</sup>

Sequential treatment of **1-W** with LDA and  $PClPh_2$  resulted in the formation of a large amount of black material, presumably polymeric, possibly carbon, which could not be characterized. However, extensive chromatographic purification of the reaction mixture afforded a yellow solid in low yield (16%). This compound, initially reported as the tertiary alkynylphosphine,<sup>8</sup> proved to be the corresponding phosphine oxide,  $W\{C\equiv CC\equiv CP(O)Ph_2\}(CO)_3Cp$  (**4**). In addition to the usual  $\nu(C\equiv C)$  and  $\nu(CO)$  bands from the tungsten–diynyl fragment, found at 2138 and at 2051, 2031, and 1962

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Table 2. Selected Bond Parameters for Complexes 3, 10, and 12

	3	10	12
Bond Distances (Å)			
W–C(1)	2.124(8)	2.102(6)	2.141(8)
W–C(cp)	2.295(6)–2.347(7)	2.297(8)–2.34(1)	2.278(8)–2.403(9)
(av)	2.32	2.32	2.33
W–C(11)	2.01(1)	2.007(8)	1.975(8)
W–C(12)	2.013(7)	1.965(8)	1.937(9)
W–C(13)		1.99(1)	
W–P			2.491(2)
C(1)–C(2)	1.22(1)	1.207(9)	1.19(1)
C(2)–C(3)	1.36(1)	1.395(9)	1.43(1)
C(3)–C(4)	1.22(1)	1.381(9)	
C(3)–C(5)		1.44(1)	
C(5)–C(6)		1.35(1)	
C(4)–Si	1.82(1)		
Bond Angles (deg)			
W–C(1)–C(2)	179.0(8)	177.5(6)	178.1(7)
C(1)–C(2)–C(3)	179(1)	173.8(7)	177.3(8)
C(2)–C(3)–C(4)	177(1)	120.5(6)	
C(3)–C(4)–Si	177(1)		
C(2)–C(3)–C(5)		121.5(6)	
C(3)–C(5)–C(6)		127.0(6)	
C(1)–W–C(11)	127.1(4)	129.8(3)	129.9(3)
C(1)–W–C(12)	75.3(2)	75.3(3)	76.9(3)
C(1)–W–C(13)		75.4(6)	75.1(2) <sup>a</sup>
C(11)–W–C(12)	76.7(2)	77.6(3)	75.7(3)
C(11)–W–C(13)		77.2(3)	80.2(2) <sup>a</sup>
C(12)–W–C(13)	114.1(3)	112.6(4)	115.8(2) <sup>a</sup>

<sup>a</sup> For C(13), read P(1).

Table 3. Crystal Data and Refinement Details for Complexes 3, 10, and 12

	3	10	12
formula	C <sub>15</sub> H <sub>14</sub> O <sub>3</sub> SiW	C <sub>18</sub> H <sub>6</sub> N <sub>4</sub> O <sub>3</sub> W	C <sub>33</sub> H <sub>25</sub> O <sub>2</sub> PW
mol wt	454.2	510.1	668.4
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> / <i>m</i>	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> , Å	6.532(5)	20.542(7)	20.285(8)
<i>b</i> , Å	9.561(9)	13.653(3)	19.458(8)
<i>c</i> , Å	13.701(10)	12.372(3)	13.709(6)
$\beta$ , deg	101.55(7)		
<i>V</i> , Å <sup>3</sup>	838	3470	5411
<i>Z</i>	2	8	8
<i>D</i> <sub>c</sub> , g cm <sup>-3</sup>	1.80	1.95	1.64
<i>F</i> (000)	432	1920	2624
cryst size, mm	0.56 × 0.50 × 0.02	0.28 × 0.32 × 0.60	0.25 × 0.25 × 0.60
<i>A</i> <sup>+</sup> (min, max)	1.17, 10.7	3.3, 5.1	2.00, 3.0
$\mu$ , cm <sup>-1</sup>	70	67	44
2 $\theta$ <sub>max</sub> , deg	60	60	56
<i>N</i>	3643	4954	5124
<i>N</i> <sub>o</sub>	2518	2889	3333
<i>R</i>	0.045	0.036	0.040
<i>R</i> <sub>w</sub>	0.047	0.037	0.041

cm<sup>-1</sup>, respectively, the IR spectrum of **4** contained a strong  $\nu$ (PO) band near 1200 cm<sup>-1</sup>, while the <sup>31</sup>P spectrum contained a single resonance at  $\delta$  5.6. The latter is in the region associated with P(V) compounds and may be compared with the value for P(O)(C≡CBu<sup>t</sup>)-Ph<sub>2</sub> at  $\delta$  1.1.<sup>29</sup> It is likely that oxidation of the desired phosphine occurred during the extensive purification process, during which air was not rigorously excluded.

**(b) Palladium(0)/Copper(I)-Catalyzed Coupling Reactions with Iodoarenes and -alkynes.** 1-Alkynes undergo facile cross-coupling reactions with aryl and vinyl halides in the presence of basic amines and a mixed Cu(I)–Pd(0) catalyst (Sonogashira reaction).<sup>30</sup> Complexes **1** readily enter into this reaction. The

compounds M(C≡CC≡CPh)(CO)<sub>3</sub>Cp [M = W (**5-W**); Mo (**5-Mo**)] were prepared by treating diisopropylamine solutions of **1** with an excess of iodobenzene in the presence of catalytic amounts of Pd(PPh<sub>3</sub>)<sub>4</sub> and CuI (Scheme 2). Both complexes exhibit very similar spectral properties. Most significantly, the <sup>13</sup>C NMR spectra contained distinct resonances for each of the four carbon nuclei of the C<sub>4</sub> chain between  $\delta$  72.6 and 111.0. The FAB mass spectrum of **8** contained M<sup>+</sup> at *m/z* 458 together with [M – CO]<sup>+</sup>. The electrospray mass spectrum of **9** was obtained in the presence of NaOMe<sup>31</sup> and contained [M + OMe]<sup>-</sup> as highest mass ion at *m/z* 402.

Similar reactions of **1-W** with 4-iodotoluene, 4-iodoanisole, and methyl 4-iodobenzoate in the presence of the mixed catalyst gave the substituted derivatives W(C≡CC≡CC<sub>6</sub>H<sub>4</sub>R)(CO)<sub>3</sub>Cp [R = Me **6** (35%), OMe **7** (51%), CO<sub>2</sub>Me **8** (89%) (Scheme 2)]. All complexes were characterized from their spectral properties which resembled those of **5-W**. In addition, appropriate resonances for the OMe, Me, and CO<sub>2</sub>Me groups were also present in their <sup>1</sup>H NMR spectra. Thus a variety of aryl-substituted derivatives M(C≡CC≡CC<sub>6</sub>H<sub>4</sub>R)(CO)<sub>3</sub>-Cp can be obtained, of which the diynyl ligands are all derived from buta-1,3-diyne as the diynyl precursor, thus avoiding the need to use separate 1-substituted diynes as precursors for each complex.

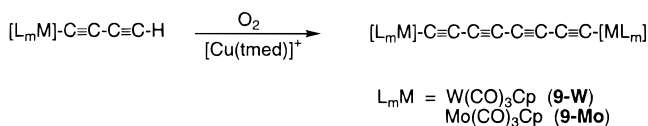
**(c) Oxidative Coupling Reactions.** Symmetrically substituted conjugated poly-ynes are readily obtained by oxidative coupling of alkynylcoppers (Glaser, Eglinton, and Hay reactions). A variety of oxidizing agents has been employed, and the Cu(I) derivative often needs to be present in only trace amounts.<sup>25</sup> Recently the

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## Scheme 3



dimetalated tetraynes  $\{ML_n\}C\equiv CC\equiv CC\equiv C\{ML_n\}$  [ $ML_n = Re(NO)(PPh_3)Cp^*$ ,<sup>32</sup>  $Fe(dppe)Cp^*$ ,<sup>7</sup>] were prepared by Eglinton coupling of the appropriate diyne precursors. This method utilizes a stoichiometric amount of  $Cu(OAc)_2$ , and the reactions are typically performed in pyridine at elevated temperatures.<sup>25</sup> However, similar attempts to couple the diyne ligands in **1** resulted only in extensive decomposition of the diyne reagent.

Homocoupling of the diyne ligand in **1** was achieved through use of the milder Hay conditions [ $CuCl/N,N,N,N$ -tetramethylethylenediamine (tmcd)/ $O_2$ ] and the corresponding tetrayne–diyl complexes  $\{Cp(CO)_3M\}C\equiv CC\equiv CC\equiv C\{M(CO)_3Cp\}$  [ $M = W$  (**9-W**);  $Mo$  (**9-Mo**)] were obtained in good yield (Scheme 3). The very recent report by Akita and co-workers described the use of similar conditions in the preparation of another carbonyl-containing tetrayne–diyl complex  $[Cp^*(OC)_2Fe]C\equiv CC\equiv CC\equiv C\{Fe(CO)_2Cp^*\}$ .<sup>33</sup>

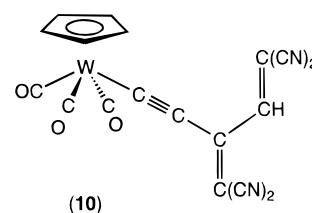
Both of these complexes are rather more light sensitive than their diyne precursors. The spectral properties of both complexes are similar, with each complex having a single, weak  $\nu(C\equiv C)$  band (2190  $cm^{-1}$ , **9-W**; 2140  $cm^{-1}$ , **9-Mo**) together with strong  $\nu(CO)$  bands (2043 and 1959  $cm^{-1}$ , **9-W**; 2049, 1973  $cm^{-1}$ , **9-Mo**). In addition to the expected resonances from the Cp ( $\delta$  91.66) and CO ligands ( $\delta$  210.3 and 227.3), the four magnetically inequivalent carbon nuclei of the tetrayne–diyl bridge were found as well-resolved peaks of low intensity near  $\delta$  112 ( $C_\alpha$ ), 92 ( $C_\beta$ ), 64 ( $C_\gamma$ ), and 61 ( $C_\delta$ ) (Table 1). In the case of **9-W**, the resonance at lowest field is broadened by coupling to  $^{183}W$ ; the remainder of the resonances were assigned by analogy with those in **1**. The relatively low chemical shift found for C(4) follows the trend previously found for other complexes of this type and previously, for organic long-chain poly-yne which approach a limiting value of  $\delta$  60 ppm.<sup>33</sup>

The ES MS spectra were obtained in the presence of a small amount of  $Ag^+$ , which has previously been shown to increase the viability of this technique with organometallics.<sup>34</sup> The spectra of **9-W** contained peaks at high mass numbers corresponding to silver-containing aggregate ions, including  $[Ag_2\{W_2(C_8)(CO)_6Cp_2\}]^+$  and  $[Ag(NCMe)\{W_2(C_8)(CO)_6Cp_2\}]^+$ . At higher cone voltages, fragment ions formed by successive loss of CO groups were formed. For **9-Mo**, the ion  $[Ag(NCMe)\{Mo_2(C_8)(CO)_6Cp_2\}]^+$  was the only high mass ion observed. In light of the formation of complexes containing group 11 cations attached to molecular tweezer

complexes such as  $Ti(C\equiv CPh)_2(\eta-C_5H_4SiMe_3)_2$ ,<sup>19,35</sup> it is interesting to speculate about the possibility of related complexes being formed between **1** and group 11 cations: experiments to test this hypothesis are under way.

**(d) Reactions with Tetracyanoethene.** The reactions of tetracyanoethene (tcne) and related electron-deficient fluoro-olefins with alkynyl complexes of several metals have been studied in detail.<sup>36–40</sup> In general, the reactions proceed via intensely colored short-lived paramagnetic intermediates to give cyclobutenyl complexes. Subsequent ring-opening and chelate-forming reactions have given a series of buta-1,3-dien-2-yl and allylic complexes (Scheme 4).

The reaction between **1-W** and tcne in  $CH_2Cl_2$  proceeded similarly via a short-lived, deep green intermediate to give a deep purple solution from which crystals of  $W\{C\equiv CC[=C(CN)_2]CH=C(CN)_2\}(CO)_3Cp$  (**10**) were obtained. The IR spectrum of **10** contained the expected



$\nu(CN)$  (2221  $cm^{-1}$ ),  $\nu(C\equiv C)$  (2078  $cm^{-1}$ ) and  $\nu(CO)$  bands (2030 and 1970  $cm^{-1}$ ). The  $^{13}C$  NMR spectrum contained singlet resonances at  $\delta$  221.0, 148.7, 94.4, and 91.9 which were assigned to the carbon atoms of the butadienyl part of the ligand by comparison with the spectrum of  $W\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(CO)_3Cp$ .<sup>38</sup> A low-field resonance ( $\delta$  7.63) in the  $^1H$  NMR spectrum was assigned to the butadienyl proton and suggested that reaction had occurred at the outer  $C\equiv C$  triple bond. The organic ligand is probably formed by cycloaddition of the tcne molecule to the outer  $C\equiv C$  triple bond, followed by opening of the resulting cyclobutenyl ring to give a *trans*-butadienyl group. This conclusion was confirmed by a single-crystal X-ray diffraction study, the details of which are reported below. The reaction of tcne with the triple bond removed from the metal center indicates that this external  $C\equiv C$  bond is still rather electron rich.

**Molecular Structure of  $W\{C\equiv CC[=C(CN)_2]CH=C(CN)_2\}(CO)_3Cp$  (**10**).** A molecule of **10** is shown in Figure 2, and selected bond lengths and angles are given in Table 2. The structural features of the  $W(CO)_3Cp$  group are similar to those found for **3**. The  $W-C(1)$  and  $C(1)-C(2)$  bond lengths are 2.102(6) and 1.207(9) Å, with  $W-C(1)-C(2)$  and  $C(1)-C(2)-C(3)$  angles of 177.5(6) and 173.8(7)°, respectively. Within the organic ligand, distances and angles are consistent with  $sp^2$

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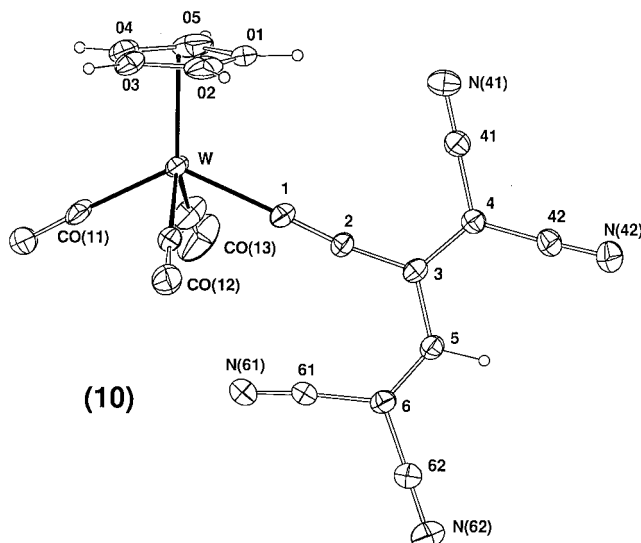
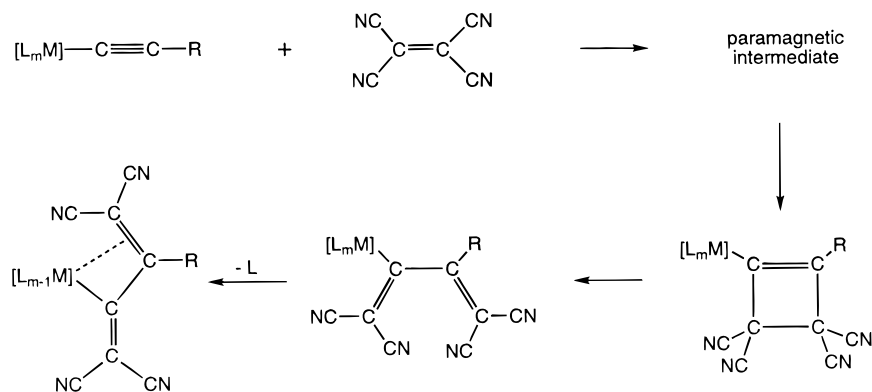
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Scheme 4



**Figure 2.** Plot of a molecule of  $W\{C\equiv CC[CH=C(CN)_2]=C(CN)_2\}(CO)_3(\eta-C_5H_5)$  (**10**), showing atom numbering scheme.

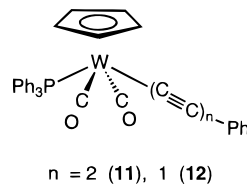
hybridization for C(3–6). This part of the ligand closely resembles that found in  $Ru\{C[=C(CN)_2]CPh=C(CN)_2\}-(dppe)Cp$ , formed by a similar addition of tcne to  $Ru(C\equiv CPh)(dppe)Cp$ .<sup>38</sup> The cyanocarbon ligand is essentially planar, and, given the intense color of this complex, it seems reasonable to suggest that extensive electron delocalization occurs throughout this part of the molecule.

Attempts to add a second equivalent of tcne to **10** were unsuccessful. As tcne adds readily to the triple bonds in more sterically congested acetylide complexes such as  $Ru(C\equiv CPh)(PPh_3)_2Cp$  and  $W(C\equiv CPh)(CO)_3Cp$ , it is unlikely that steric factors are involved. Instead it seems more probable that the electron-withdrawing cyano groups, which are conjugated with the  $C\equiv C$  triple bond in **10**, deactivate this site thereby precluding further [2+2] cycloaddition. We note that tcne also adds to electron-rich  $C=C$  double bonds, such as those found in vinyl ethers, vinyl sulfides, enamines, and *N*-vinyl-sulfonamides, for example.<sup>41</sup>

**(e) Trimethylamine *N*-Oxide Assisted Carbonyl–Phosphine Exchange Reactions of  $W\{C\equiv C\}_nPh-(CO)_3Cp$ .** Substitution reactions of the carbonyl ligands in  $WX(CO)_3Cp'$  complexes ( $X = H$ , halide, alkyl;  $Cp' = Cp$ ,  $Cp^*$ ) have been examined using a variety of

thermal, photochemical, and chemical methods. Oxidative decarbonylation by trimethylamine *N*-oxide (tmno) in the presence of the ligand has become established as a convenient route for the preparation of a wide range of substituted metal carbonyls.<sup>42</sup> We therefore chose to examine the use of this reagent in the synthesis of tertiary phosphine-substituted derivatives of **1-W**.

A mixture of  $W(C\equiv CC\equiv CPh)(CO)_3Cp$  (**5-W**) and  $PPh_3$  in  $CH_2Cl_2$  was treated with tmno to give *cis*- $W(C\equiv CC\equiv CPh)(CO)_2(PPh_3)Cp$  (**11**) in low yield (20%). The



simple acetylide analogue *cis*- $W(C\equiv CPh)(CO)_2(PPh_3)Cp$  (**12**), which has been reported briefly by others,<sup>43</sup> was obtained in a similar manner from  $W(C\equiv CPh)(CO)_3Cp$  and fully characterized by a single-crystal X-ray study, the details of which are reported below. The compositions of **11** and **12** were established from microanalytical data and the usual spectral techniques, including electrospray mass spectra which were obtained from methanolic NaOMe solutions, and contained  $[M + Na]^+$  as highest ions. We have observed many similar  $[M + Na]^+$  ions in the ES mass spectra of diynyl complexes.<sup>8,44</sup> These curious species are the subject of further investigations.

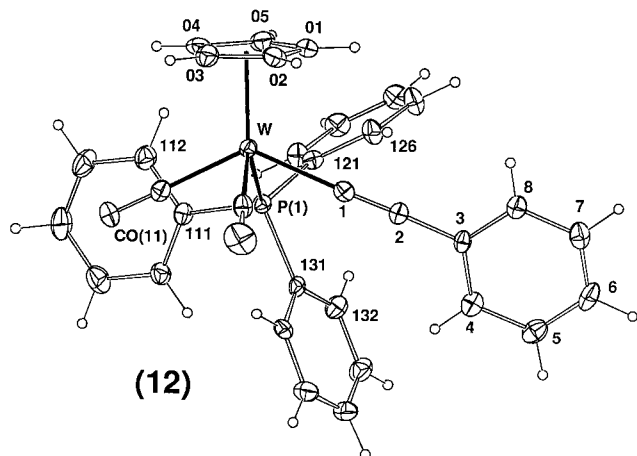
Both *cis* and *trans* isomers of  $WX(CO)_2(L)Cp'$  are known, and in some instances the reactions produce a mixture of isomers, the proportions of which depend on the nature of X, the incoming ligand L, and the preparative method employed. Although the factors controlling the relative stabilities of the isomers are not always clear, it has been suggested that the position of the equilibrium may be a delicate balance between the *trans* influence of the ligands and the steric interactions

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**Figure 3.** Plot of a molecule of  $W(C\equiv CPh)(CO)_2(PPh_3)(\eta-C_5H_5)$  (**12**), showing atom numbering scheme.

between the ligands L and X.<sup>45</sup> Both isomers of  $WX(CO)_2(L)Cp$  give similar two-band  $\nu(CO)$  patterns in the IR region, although the spectra of the *trans* isomers typically show less intense symmetric and more intense antisymmetric  $\nu(CO)$  bands than the *cis* isomers.<sup>46,47</sup> The IR  $\nu(CO)$  spectra of both complexes prepared here have similar two-band patterns. The stronger, symmetric stretch was found at 1953 (**11**) or 1949 (**12**)  $cm^{-1}$ , while the antisymmetric vibration gave rise to a weaker absorption at 1875 or 1863  $cm^{-1}$ , respectively.

However, it is the  $^{13}C$  carbonyl resonances which provide the simplest method of distinguishing between the isomers, as the *trans* form contains only a single  $^{13}CO$  resonance, while the inequivalent carbonyl ligands in the *cis* isomer give rise to two resonances.<sup>48</sup> The  $^{13}C$  NMR spectra of **11** and **12** each contained two distinct resonances arising from the inequivalent carbonyl ligands in a *cis* geometry.

**Molecular Structure of *cis*- $W(C\equiv CPh)(CO)_2(PPh_3)Cp$  (**12**).** A molecule of **12** is shown in Figure 3 and selected bond lengths and angles are given in Table 2. The structure determination confirms the *cis* arrangement of CO groups [angles  $C(11)-W-C(12)$ , 75.7(3);  $P-W-C(1)$ , 75.1(2)°]. The presence of the bulky phosphine ligand results in some distortion of the normal coordination about the metal atom, with  $P-W-C(11, 12)$  angles of 80.2 and 115.8(2)°, respectively compressed and enlarged compared with the usual values of ca. 127 and 75° found in **5-W** and **10** above. The  $W-P$  distance is 2.491(2) Å [cf. 2.457(1) Å in *trans*- $W\{C(O)Me\}(CO)_2(PPh_3)Cp$ ]<sup>49</sup>, and the  $W-C(1)$  separation is 2.141(8) Å, somewhat longer than those found in **5-W** and **10**. Conversely, the  $W-CO$  distances [1.975, 1.937(8) Å] are shorter, due to increased electron back-bonding as a result of the presence of the  $PPh_3$  ligand. The phenylethynyl ligand has  $C(1)-C(2)$  of 1.19(1) Å and  $C(2)-C(3)$  of 1.43(1) Å, which are within the normal ranges; angles at  $C(1)$  and  $C(2)$  are 178.1(7) and 177.3(8)°.

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## Conclusion

We have demonstrated that the Cu(I)-catalyzed coupling of buta-1,3-diyne with several metal halides affords the corresponding buta-1,3-diyne-1-yl complexes in high yield. Application of conventional organic reactions to the tungsten complex has allowed the preparation of related diynyl, diyndiyl, and octayndiyl complexes in high yield. In addition, substitution of CO with a tertiary phosphine ligand at the metal center proceeds with retention of the diynyl ligand. In all these cases, the poly-yne ligands are obtained from easily accessible buta-1,3-diyne as the precursor.

## Experimental Section

**General Reaction Conditions.** All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques. Solvents were dried, distilled, and degassed before use. Light petroleum refers to a fraction of bp 60–80 °C. Elemental analyses were by the Canadian Microanalytical Service (Delta, BC, Canada). Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF<sub>254</sub>, 0.5 mm thick).

**Instrumental Conditions.** Infrared: Perkin-Elmer 1700X FT-IR. NMR: Bruker ACP300 ( $^1H$  at 300.13 MHz,  $^{13}C$  at 75.47 MHz) and Varian Gemini 200 ( $^1H$  at 199.98 MHz,  $^{13}C$  at 50.29 MHz) spectrometers. For the  $^{13}C$  data, all signals are singlets unless otherwise indicated. Listed values of  $J_{CW}$  refer to the doublet signals arising from the presence of  $^{183}W$  (ca. 15% natural abundance), which appear about the singlet. Chemical shifts are referenced to  $SiMe_4$  ( $^1H$  and  $^{13}C$ ) and external  $H_3PO_4$  ( $^{31}P$ ). FAB mass spectra: VG ZAB 2HF spectrometer (3-nitrobenzyl alcohol as matrix; exciting gas, Ar; FAB gun voltage, 7.5 kV; current, 1 mA; accelerating potential, 7 kV). ES mass spectra: The samples were dissolved in acetonitrile/water (1/1), unless otherwise indicated, and injected into a 10  $\mu L$  injection loop attached to a VG Platform II mass spectrometer. Nitrogen was used as the drying and nebulizing gas. Samples were examined over a range of cone voltages (20–90 V) to find the best conditions. Chemical aids to ionization were used when required.<sup>31,34</sup>

**Reagents.** The compounds  $HC\equiv C\equiv CH$ ,<sup>50</sup>  $SiMe_3C\equiv CC\equiv CSiMe_3$ ,<sup>51</sup>  $WCl(CO)_3Cp$ ,<sup>52</sup>  $MoI(CO)_3Cp$ ,<sup>53</sup>  $FeCl(CO)_2Cp$ ,<sup>54</sup>  $LiNPr^i$  (LDA),<sup>55</sup>  $Pd(PPh_3)_4$ ,<sup>56</sup> and 4-MeOC<sub>6</sub>H<sub>4</sub>I<sup>57</sup> were prepared by literature methods. *N,N,N,N*-Tetramethylethylenediamine (Merck),  $C_6H_5I$  and 4-MeC<sub>6</sub>H<sub>4</sub>I (Aldrich), trimethylamine *N*-oxide (Aldrich), and  $PClPh_2$  (Aldrich) were purchased and purified by standard methods prior to use.  $CuCl$  (Ajax),  $CuI$  (Ajax),  $PPh_3$  (Strem), and  $SiClMe_3$  (Aldrich) were purchased and used as received.

**PRECAUTIONARY WARNING!** While no problems have been experienced in the preparation, manipulation and reactions of buta-1,3-diyne in this laboratory, this compound must be handled with the necessary degree of respect at all times, especially in the presence of Cu(I). Neat  $HC\equiv C\equiv CH$  should never be isolated. As a matter of routine precaution, solutions of this reagent (2–3 M) were kept cold (ca. –78 °C) under dry nitrogen and used within 5 days of preparation. All manipula-

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tions of this compound were performed behind an explosion-proof shield.

**Preparation of Buta-1,3-diyn-1-yl Complexes.**  $W(C\equiv CC\equiv CH)(CO)_3Cp$  (**1-W**).  $WCl(CO)_3Cp$  (2.5 g, 6.79 mmol) was dissolved in mixture of thf (20 mL) and  $NH_4Et_2$  (50 mL). To this solution was added  $CuI$  (150 mg, 0.79 mmol), followed immediately by buta-1,3-diyne (7 mL of a 3M solution in thf). The reaction mixture rapidly changed color from red to yellow-orange, and a white precipitate of  $[NH_2Et_2]Cl$  formed. After 5 min, the solution was filtered and the solvent was removed. The residue was extracted ( $CH_2Cl_2$ ) and loaded onto a column of alumina. Elution with light petroleum/acetone (7/3) gave a bright yellow band. Concentration of the eluant (ca. 10 mL) resulted in the precipitation of  $W(C\equiv CC\equiv CH)(CO)_3Cp$  (**1-W**) (2.3 g, 89%) as a bright yellow powder, which was collected, washed with cold hexane, and air-dried. The compound was best stored in the dark at  $-18^\circ C$ . Anal. Found for  $C_{12}H_6O_3W$ : C, 37.38; H, 1.54. Calcd: C, 37.72; H, 1.57. IR ( $CH_2Cl_2$ ):  $\nu(\equiv CH)$  3260 m,  $\nu(C\equiv C)$  2145 m,  $\nu(CO)$  2044 s, 1958 s (br)  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  5.66 (s, 5H, Cp); 2.03 (s, 1H,  $\equiv CH$ ); ( $C_6D_6$ ) 4.42 (s, 5H, Cp), 1.80 (s, 1H,  $\equiv CH$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  227.41 (d,  $J_{CW} = 70$  Hz, CO), 210.87 (d,  $J_{CW} = 70$  Hz, CO), 110.52 (br,  $C_\alpha$ ), 91.51 (s, Cp), 71.60 (d,  $J_{CW} = 88$  Hz,  $C_\beta$ ), 70.13 (d,  $J_{CW} = 94$  Hz,  $C_\gamma$ ), 63.30 (s,  $C_\delta$ ). ES MS (low cone voltage) ( $m/z$ ): 396,  $[M - CO + NMe + H]^+$ ; 368,  $[M - 2CO + NMe + H]^+$ ; 355,  $[M - CO + H]^+$ ; (high cone voltage) 299,  $[M - 3CO + H]^+$ .

**Mo( $C\equiv CC\equiv CH$ )( $CO$ ) $_3$ Cp (**1-Mo**).** In a reaction similar to that described for the tungsten analogue, dark yellow Mo( $C\equiv CC\equiv CH$ )( $CO$ ) $_3$ Cp (**1-Mo**) was isolated in 60% yield (0.95 g) from  $MoI(CO)_3Cp$  (2 g, 5.4 mmol) and buta-1,3-diyne. The compound was eluted with light petroleum/acetone (9/1). Anal. Found for  $C_{12}H_6O_3Mo$ : C, 49.02; H, 2.63. Calcd: C, 48.69; H, 2.03. IR ( $CH_2Cl_2$ ):  $\nu(C\equiv C)$  2145 m,  $\nu(CO)$  2050 s, 1970 br  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  5.58 (s, 5H, Cp), 2.04 (s, 1H,  $C\equiv CH$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  237.39 (s, CO), 221.86 (s, CO), 110.46 (s,  $C_\alpha$ ), 92.94 (s, Cp), 87.25 (s,  $C_\beta$ ), 70.27 (s,  $C_\gamma$ ), 62.10 (s,  $C_\delta$ ). FAB MS ( $m/z$ ): 293,  $M^+$ ; 266–210,  $[M - nCO]^+$  ( $n = 1-3$ ).

**Fe( $C\equiv CC\equiv CH$ )( $CO$ ) $_2$ Cp (**2**).** A solution of  $FeCl(CO)_2Cp$  (200 mg, 0.83 mmol) in  $NH_4Et_2$  (20 mL) was treated with a catalytic amount of  $CuI$ , followed by buta-1,3-diyne (4 mmol as a 3 M thf solution). The deep red solution darkened, was stirred for 5 min, and filtered through Celite. The volatiles were removed, and the residue was purified by preparative TLC (light petroleum/acetone, 7/3). The first band (maroon,  $R_f = 0.8$ ) contained a trace amount of  $\{Fe(CO)_2Cp\}_2$ . The major band (yellow,  $R_f = 0.6$ ) contained  $Fe(C\equiv CC\equiv CH)(CO)_2Cp$  (**2**) (67 mg, 32%). IR ( $CH_2Cl_2$ ):  $\nu(C\equiv C)$ : 2149 m,  $\nu(CO)$  2050 s, 2003 s  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  5.07 (s, 5H, Cp), 1.47 (s, 1H,  $C\equiv CH$ ) [lit.<sup>22</sup> 2149.5, 2049.9, 2002.5  $cm^{-1}$ ;  $\delta$  5.02, 1.41].

**Reactions of  $M(C\equiv CC\equiv CH)(CO)_3Cp$  (**1-M**).** **Preparation of  $W(C\equiv CC\equiv CSiMe_3)(CO)_3Cp$  (**3**).** A solution of **1-W** (200 mg, 0.52 mmol) in thf (15 mL) was cooled to  $-78^\circ C$ , and lithium diisopropylamide (0.5 M solution in thf/hexane, 1.04 mL, 0.52 mmol) was added dropwise to the stirred solution. The solution became orange and was allowed to stir for 5 min before  $SiClMe_3$  (66  $\mu L$ , 57 mg, 0.52 mmol) was added. The solution was allowed to warm to room temperature over 20 min, and solvent was removed. The filtered (Celite) extracts ( $CH_2Cl_2$ ) were concentrated to ca. 10 mL and diluted with a similar volume of *n*-hexane. Further concentration resulted in the precipitation of  $W(C\equiv CC\equiv CSiMe_3)(CO)_3Cp$  (**3**) as a pale yellow powder, which was washed with several portions of cold hexane and air-dried (190 mg, 80%). Anal. Found for  $C_{15}H_{14}O_3SiW$ : C, 39.18; H, 3.11. Calcd: C, 39.68; H, 3.08. IR ( $CH_2Cl_2$ ):  $\nu(C\equiv C)$  2174 w, 2127 w,  $\nu(CO)$  2045 vs, 2026 m, 1957 br  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  5.66 (s, 5H, Cp), 0.20 (s, 9H,  $SiMe_3$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  227.53 (s, CO), 210.56 (d,  $J_{CW} = 77$  Hz, CO), 111.74 (br,  $C_\alpha$ ), 110.86 (s,  $C_\beta$ ), 91.53 (s, Cp), 90.04 (s,  $C_\gamma$ ),

73.59 (s,  $C_\delta$ ); 0.00 (s,  $SiMe_3$ ). FAB MS ( $m/z$ ): 454,  $M^+$ ; 426,  $[M - CO]^+$ ; 370,  $[M - 3CO]^+$ .

Complex **3** was also prepared as follows: a solution of  $WCl(CO)_3Cp$  (200 mg, 0.54 mmol) in thf (10 mL) was cooled to  $-78^\circ C$  and treated dropwise with  $LiC\equiv CC\equiv CSiMe_3$  [0.12 M, 5 mL, 0.6 mmol; solution prepared from 1,4-bis(trimethylsilyl)buta-1,3-diyne (250 mg, 1.23 mmol) in thf (10 mL) at  $-78^\circ C$  treated dropwise with  $MeLi\cdot LiBr$  (1.5 M solution in  $Et_2O$ , 0.860 mL, 1.23 mmol)].<sup>18,58</sup> After warming to room temperature over 1 h preparative TLC (light petroleum/acetone, 7/3) afforded  $W(C\equiv CC\equiv CSiMe_3)(CO)_3Cp$  (**3**) (88 mg, 36%) from the yellow band ( $R_f = 0.7$ ) after crystallization ( $CH_2Cl_2$ /hexane at  $-20^\circ C$ ) and unchanged  $WCl(CO)_3Cp$  (orange band,  $R_f = 0.6$ , 50 mg, 25%).

**Preparation of  $W\{C\equiv CC\equiv CP(O)Ph_2\}(CO)_3Cp$  (**4**).** A cold ( $-78^\circ C$ ) solution of **1-W** (1.0 g, 2.60 mmol) in thf (100 mL) was treated dropwise with lithium diisopropylamide (0.5 M solution in thf/hexane, 5.5 mL, 2.8 mmol) and stirred for 10 min. Freshly distilled  $PClPh_2$  (0.5 mL, 2.8 mmol) was added slowly, and the solution was allowed to warm to room temperature over 2 h. Solvent was removed, and the residue taken up in  $CH_2Cl_2$  and loaded onto a squat  $Al_2O_3$  column. The column was washed initially with  $CH_2Cl_2$  to remove any unchanged  $W(C\equiv CC\equiv CH)(CO)_3Cp$  and then with acetone to give crude  $W\{C\equiv CC\equiv CP(O)Ph_2\}(CO)_3Cp$  (**4**) (250 mg, 16%), which was purified further by preparative TLC (light petroleum/acetone, 6/4) and crystallization ( $CH_2Cl_2$ /hexane). Anal. Found for  $C_{24}H_{15}O_4PW$ : C, 49.11; H, 2.63. Calcd: C, 49.40; H, 2.57. IR ( $CH_2Cl_2$ ):  $\nu(C\equiv C)$  2138 m,  $\nu(CO)$  2051 s, 2031 m, 1962 (br); (Nujol)  $\nu(PO)$  1199  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.89–7.47 (m, 10H,  $PPh_2$ ), 5.69 (s, 5H, Cp).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  225.43 (s, CO); 210.23 (d,  $J_{CW} = 71$  Hz, CO), 134.33–128.45 (Ph), 110.57 (d,  $J_{CW} = 16$  Hz,  $C_\alpha$ ), 91.64 (s, Cp), 91.32 (s,  $C_\beta$ ). FAB MS ( $m/z$ ): 583,  $M^+$ ; 555,  $[M - CO]^+$ ; 498,  $[M - 3CO]^+$ .

**Preparation of  $W(C\equiv CC\equiv CPh)(CO)_3Cp$  (**5-W**).** Dry  $NHPr_2$  (50 mL) was introduced into a flame-dried Schlenk flask and rigorously deoxygenated by three freeze–pump–thaw sequences. Solid **1-W** (1.0 g, 2.62 mmol) was added followed by freshly distilled iodobenzene (801 mg, 3.93 mmol),  $Pd(PPh_3)_4$  (151 mg, 0.13 mmol) and  $CuI$  (50 mg, 0.26 mmol) in that order. The solution was stirred in the dark for 16 h. The yellow precipitate obtained was filtered, washed with several portions of cold hexane, dissolved in the minimum volume of  $CH_2Cl_2$ , and purified on a squat column of  $Al_2O_3$  (30  $\times$  50 mm). Elution with light petroleum/acetone (7/3) gave a bright yellow fraction, which was concentrated to give  $W(C\equiv CC\equiv CPh)(CO)_3Cp$  (**5-W**) as a bright yellow microcrystalline powder (650 mg). Similar treatment of the filtrate from the reaction mixture on a longer  $Al_2O_3$  column gave a further 140 mg of **5-W**. The total yield was 790 mg (66%). The microanalytical sample was recrystallized from acetone/hexane. Anal. Found for  $C_{18}H_{10}O_3W$ : C, 46.80; H, 2.29. Calcd: C, 47.20; H, 2.18. IR ( $CH_2Cl_2$ ):  $\nu(C\equiv C)$  2183 m, 2059 m,  $\nu(CO)$  2038 vs, 1956 br  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.27–7.46 (m, 5H, Ph), 5.68 (s, 5H, Cp).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  227.60 (d,  $J_{CW} = 60$  Hz, CO), 210.64 (d,  $J_{CW} = 71$  Hz, CO), 132.38 (s,  $\sigma$ -C), 128.16 (s, *m*-C), 127.97 (s, *p*-C), 123.05 (s, *i*-C), 111.03 (d,  $J_{CW} = 22$  Hz,  $C_\alpha$ ), 91.62 (s, Cp), 76.19, 73.78 (2  $\times$  s,  $C_\gamma$  and  $C_\delta$ ). FAB MS ( $m/z$ ): 458,  $M^+$ ; 430,  $[M - CO]^+$ .

**Preparation of  $Mo(C\equiv CC\equiv CPh)(CO)_3Cp$  (**5-Mo**).** Using conditions similar to those described above for **5-W**, a solution of  $Mo(C\equiv CC\equiv CH)(CO)_3Cp$  (100 mg, 0.34 mmol) in dry, degassed  $NHPr_2$  was treated with  $PhI$  (100 mg, 0.50 mmol),  $Pd(PPh_3)_4$  (20 mg, 0.017 mmol), and  $CuI$  (7 mg, 0.03 mmol) and stirred for 16 h in the dark. Preparative TLC (light petroleum/acetone, 7/3) separated many bands. A bright yellow band ( $R_f = 0.57$ ) yielded very light-sensitive  $Mo(C\equiv CC\equiv CPh)(CO)_3Cp$

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(**5-Mo**) (50 mg, 40%) after crystallization ( $\text{CH}_2\text{Cl}_2/\text{hexane}$ ). Other bands were not investigated further. Anal. Found for  $\text{C}_{18}\text{H}_{10}\text{O}_3\text{Mo}$ : C, 57.70; H, 2.73. Calcd: C, 58.38; H, 2.70. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{C}\equiv\text{C})$  2183 m,  $\nu(\text{CO})$  2059 m, 2042 vs, 1970 br  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.46–7.27 (m, 5H, Ph), 5.58 (s, 5H, Cp).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  237.50 (s, CO), 221.77 (s, CO), 132.31 (s, *o*-C), 128.15 (s, *m*-C), 127.92 (s, *p*-C), 123.15 (s, *i*-C), 110.92 (s,  $\text{C}_\alpha$ ), 93.02 (s, Cp), 76.42 (s,  $\text{C}_\beta$ ), 72.59 (s,  $\text{C}_\gamma$ ). ES MS (with added NaOMe; low cone voltage) ( $m/z$ ): 402,  $[\text{M} + \text{OMe}]^+$ .

**Preparation of  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_3\text{Cp}$  (**6**).**  $\text{NHPr}_2$  (5 mL) was added to a solid mixture of **1-W** (100 mg, 0.26 mmol), 4-MeC<sub>6</sub>H<sub>4</sub>I (60 mg, 0.28 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (15 mg), and CuI (5 mg). The mixture was degassed and was stirred at 50 °C for 24 h. After removal of solvent, the solid residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> with benzene as eluant. An orange solution was obtained. The product was precipitated from benzene/hexane, washed with hexane, and dried in vacuo at room temperature to give  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_3\text{Cp}$  (**6**) (55 mg, 51%), mp 168–170 °C (dec). Anal. Found for  $\text{C}_{19}\text{H}_{12}\text{O}_3\text{W}$ : C, 48.21; H, 2.55. Calcd: C, 48.33; H, 2.56. IR (Nujol):  $\nu(\text{C}\equiv\text{C})$  2180 m;  $\nu(\text{CO})$  2056 m, 2030 s, 1956 (sh), 1936 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.32 (s, 3H, Me), 5.64 (s, 5H, Cp), 7.04 (d, 2H,  $J_{\text{HH}} = 8$  Hz,  $\text{H}_m$  or  $\text{H}_o$  of C<sub>6</sub>H<sub>4</sub>), 7.31 (d, 2H,  $J_{\text{HH}} = 8$  Hz,  $\text{H}_o$  or  $\text{H}_m$  of C<sub>6</sub>H<sub>4</sub>). FAB MS ( $m/z$ ): 472,  $\text{M}^+$ ; 444,  $[\text{M} - \text{CO}]^+$ ; 388,  $[\text{M} - 3\text{CO}]^+$ .

**Preparation of  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{OMe-4})(\text{CO})_3\text{Cp}$  (**7**).** A similar reaction with **1-W** (100 mg, 0.26 mmol), 4-MeOC<sub>6</sub>H<sub>4</sub>I (90 mg, 0.38 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg, 0.009 mmol), and CuI (7 mg) in  $\text{NHPr}_2$  (5 mL) at 40 °C overnight afforded orange  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{OMe-4})(\text{CO})_3\text{Cp}$  (**7**) (47 mg, 35%), mp 148–151 °C (dec). Anal. Found for  $(\text{C}_{19}\text{H}_{12}\text{O}_4\text{W}\cdot 0.2\text{CH}_2\text{Cl}_2)$ : C, 45.54; H, 2.38. Calcd: C, 45.65; H, 2.47. IR (Nujol):  $\nu(\text{C}\equiv\text{C})$  2174 w,  $\nu(\text{CO})$  2052 m, 2031 s, 1951 s, 1934 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.78 (s, 3H, Me), 5.64 (s, 5H, Cp), 6.79 (d, 2H,  $J_{\text{HH}} = 9$  Hz,  $\text{H}_m$  or  $\text{H}_o$  of C<sub>6</sub>H<sub>4</sub>), 7.36 (d, 2H,  $J_{\text{HH}} = 9$  Hz,  $\text{H}_o$  or  $\text{H}_m$  of C<sub>6</sub>H<sub>4</sub>). FAB MS ( $m/z$ ): 488,  $\text{M}^+$ ; 460,  $[\text{M} - \text{CO}]^+$ .

**Preparation of  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me-4})(\text{CO})_3\text{Cp}$  (**8**).** A similar reaction with **1-W** (100 mg, 0.26 mmol), 4-IC<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>CH<sub>3</sub> (105 mg, 0.40 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg, 0.009 mmol), and CuI (5 mg) in  $\text{NHPr}_2$  (5 mL) at 65 °C for 5 h gave yellow  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me-4})(\text{CO})_3\text{Cp}$  (**8**) (120 mg, 89%), mp 161–164 °C (dec). Anal. Found for  $(\text{C}_{20}\text{H}_{12}\text{O}_5\text{W}\cdot 0.1\text{CH}_2\text{Cl}_2)$ : C, 45.89; H, 2.49. Calcd: C, 46.02; H, 2.34. IR (Nujol):  $\nu(\text{C}\equiv\text{C})$  2179 m,  $\nu(\text{CO})$  2058 m, 2030 s, 1966 s, 1931 s;  $\nu(\text{CO}_2)$  1713 m, 1601 m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.89 (s, 3H, Me), 5.66 (s, 5H, Cp), 7.45 (d, 2H,  $J_{\text{HH}} = 8.5$  Hz,  $\text{H}_m$  or  $\text{H}_o$  of C<sub>6</sub>H<sub>4</sub>), 7.93 (d, 2H,  $J_{\text{HH}} = 8.5$  Hz,  $\text{H}_o$  or  $\text{H}_m$  of C<sub>6</sub>H<sub>4</sub>). ES MS (MeCN/H<sub>2</sub>O with Ag<sup>+</sup>) ( $m/z$ ): 516,  $\text{M}^+$ ; 488,  $[\text{M} - \text{CO}]^+$ ; 450,  $[\text{M} - 2\text{CO}]^+$ ; 432,  $[\text{M} - 3\text{CO}]^+$ ; 373,  $[\text{M} - 3\text{CO} - \text{CO}_2\text{Me}]^+$ ; 136,  $[\text{HC}_6\text{H}_4\text{CO}_2\text{Me}]^+$ .

**Preparation of  $\text{W}[\text{C}\equiv\text{CC}\{\text{CH}=\text{C}(\text{CN})_2\}\text{C}\{\text{C}(\text{CN})_2\}\text{H}](\text{CO})_3\text{Cp}$  (**10**).** A solution of **1-W** (200 mg, 0.52 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was treated with tetracyanoethene (67 mg, 0.52 mmol) and stirred for 5 min. The initially yellow solution acquired an intense purple color during this time. Solvent was removed, and the residue was extracted with the minimum volume of fresh  $\text{CH}_2\text{Cl}_2$  and then filtered dropwise into rapidly stirred hexane. The resulting purple precipitate was collected and crystallized ( $\text{CH}_2\text{Cl}_2/\text{hexane}$ ) to give  $\text{W}\{\text{C}\equiv\text{CC}[\text{C}(\text{CN})_2]\text{C}[\text{C}(\text{CN})_2\text{H}]\}(\text{CO})_3\text{Cp}$  (**10**) as dark purple blocks (225 mg, 84%). Crystals suitable for the X-ray study were obtained from 1,2-dichloroethane/hexane. Anal. Found for  $\text{C}_{18}\text{H}_6\text{O}_3\text{N}_4\text{W}$ : C, 42.21; H, 1.32. Calcd: C, 42.35; H, 1.18. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CN})$  2221 w,  $\nu(\text{C}\equiv\text{C})$  2078 m,  $\nu(\text{CO})$  2030 s, 1970 br  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.62 (s, 1H, CH=), 5.80 (s, 5H, Cp).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  221.05 [s, C(3)], 209.15 (s, CO), 148.70 [s, C(2)], 94.41 [s, C(4)], 92.19 (s, Cp), 91.90 [s, C(1)]. FAB MS ( $m/z$ ): 510,  $\text{M}^+$ .

**Oxidative Coupling of  $\text{M}(\text{C}\equiv\text{CCH})(\text{CO})_3\text{Cp}$ .** **Preparation of the Hay Catalyst (CuCl/tmed).** Cuprous chloride (100 mg, 1.01 mmol) was suspended in dry acetone (5 mL),

treated with tmed (150  $\mu\text{L}$ , 117 mg, 1.01 mmol), and stirred for 15 min. The finely divided suspension of unreacted CuCl was allowed to settle prior to use in the coupling reactions.

**Preparation of  $\{\text{Cp}(\text{CO})_3\text{W}\}(\text{C}\equiv\text{C})_4\{\text{W}(\text{CO})_3\text{Cp}\}$  (**9-W**).** The Hay catalyst was added in small portions to a solution of **1-W** (500 mg, 1.3 mmol) in acetone (40 mL) while a stream of O<sub>2</sub> or air was bubbled through the reaction mixture until the reaction was judged complete (TLC). Solvent was removed, and the residue was purified by column chromatography on Al<sub>2</sub>O<sub>3</sub>. A light petroleum/acetone gradient (6/4 to 4/6) was used to elute a yellow-orange band, which yielded  $\{\text{Cp}(\text{CO})_3\text{W}\}(\text{C}\equiv\text{C})_4\{\text{W}(\text{CO})_3\text{Cp}\}$  (**9-W**) (420 mg, 85%) as an orange, microcrystalline solid. The analytical sample was crystallized as the 0.2 $\text{CH}_2\text{Cl}_2$  solvate (NMR) from  $\text{CH}_2\text{Cl}_2/\text{hexane}$ . Anal. Found for  $\text{C}_{24}\text{H}_{10}\text{O}_6\text{W}_2\cdot 0.2\text{CH}_2\text{Cl}_2$ : C, 37.22; H, 1.57. Calcd: C, 37.31; H, 1.35. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{C}\equiv\text{C})$  2190 w,  $\nu(\text{CO})$  2043 s, 1959 vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.67 (s, Cp).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  227.32 (s, CO), 210.26 (s, CO), 112.39 (br,  $\text{C}_\alpha$ ), 91.66 (s, Cp), 91.60 (s,  $\text{C}_\beta$ ), 63.70 (s,  $\text{C}_\gamma$ ), 60.91 (s,  $\text{C}_\delta$ ). ES MS (with Ag<sup>+</sup>) ( $m/z$ ): 1631,  $[2\text{M} + \text{Ag}]^+$ ; 1575,  $[2\text{M} + \text{Ag} - 2\text{CO}]^+$ ; 911–854,  $[\text{M} + \text{Ag} + \text{NCMe} - n\text{CO}]^+$  ( $n = 0-2$ ); 813,  $[\text{M} + \text{Ag} - 2\text{CO}]^+$ .

**Preparation of  $\{\text{Cp}(\text{CO})_3\text{Mo}\}(\text{C}\equiv\text{C})_4\{\text{Mo}(\text{CO})_3\text{Cp}\}$  (**9-Mo**).** Similarly, **1-Mo** (200 mg, 0.68 mmol) in acetone (25 mL) gave  $\{\text{Cp}(\text{CO})_3\text{Mo}\}(\text{C}\equiv\text{C})_4\{\text{Mo}(\text{CO})_3\text{Cp}\}$  (**9-Mo**) as a highly light-sensitive, burnt orange powder (80–120 mg, 40–60%). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{C}\equiv\text{C})$  2140 w,  $\nu(\text{CO})$  2049 s, 1973 vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.78 (s, 5H, Cp);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  237.22, 221.41 (2 x s, CO), 112.24 (s,  $\text{C}_\alpha$ ), 93.12 (s, Cp), 92.22 (s,  $\text{C}_\beta$ ), 63.47 (s,  $\text{C}_\gamma$ ), 59.95 (s,  $\text{C}_\delta$ ). ES MS (with Ag<sup>+</sup>) ( $m/z$ ): 734,  $[\text{M} + \text{Ag} + \text{NCMe}]^+$ .

**Preparation of *cis*- $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)\text{Cp}$  (**11**).** A solution of  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CPh})(\text{CO})_3\text{Cp}$  (**5-W**) (240 mg, 0.52 mmol) and PPh<sub>3</sub> (145 mg, 0.55 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) was purged with nitrogen and treated with tmno in portions until the reaction was complete (IR). The solution was filtered through a pad of silica gel and then further purified by preparative TLC to give yellow  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)\text{Cp}$  (**11**) (67 mg, 20%) after crystallization ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ ). Anal. Found for  $\text{C}_{35}\text{H}_{25}\text{O}_2\text{PW}$ : C, 61.01; H, 3.89. Calcd: C, 60.71; H, 3.61. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{C}\equiv\text{C})$  2172 m,  $\nu(\text{CO})$  2039 w, 1953 vs, 1875 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.52–7.20 (m, 20H, PPh<sub>3</sub> and Ph), 5.44 (s, 5H, Cp).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  243.15 (d,  $J_{\text{CP}} = 22$  Hz, CO), 222.63 (d,  $J_{\text{CP}} = 20$  Hz, CO), 135.05–124.00 (m, Ph), 113.27 (d,  $J_{\text{CW}} = 8$  Hz,  $\text{C}_\alpha$ ), 100.14 (s,  $\text{C}_\beta$ ), 91.23 (s, Cp), 72.75, 72.2 (2 x s,  $\text{C}_\gamma$  and  $\text{C}_\delta$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}}$  21.00 (t,  $J_{\text{PW}} = 121.5$  Hz, PPh<sub>3</sub>). ES MS (low cone voltage with NaOMe) ( $m/z$ ): 715,  $[\text{M} + \text{Na}]^+$ .

**Preparation of *cis*- $\text{W}(\text{C}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)\text{Cp}$  (**12**):** A solution of  $\text{W}(\text{C}\equiv\text{CPh})(\text{CO})_3\text{Cp}$  (100 mg, 0.23 mmol) and PPh<sub>3</sub> (70 mg, 0.27 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was purged with nitrogen and treated with freshly sublimed tmno in several portions until the reaction was judged complete (IR; the  $\nu(\text{CO})$  2038  $\text{cm}^{-1}$  band of the starting material was monitored). Preparative TLC (light petroleum/acetone, 7/3) gave bright yellow needles of  $\text{W}(\text{C}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)\text{Cp}$  (**12**) (67 mg, 44%) from the major band. Anal. Found for  $\text{C}_{33}\text{H}_{25}\text{O}_2\text{PW}$ : C, 59.51; H, 3.20. Calcd: C, 59.29; H, 3.74. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{C}\equiv\text{C})$  2089 w,  $\nu(\text{CO})$  1949 vs, 1863 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.53–6.53 (m, 20H, Ph), 5.46 (s, 5H, Cp).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  244.54 (br, CO), 228.79 (d,  $J_{\text{CP}} = 5$  Hz, CO), 133.82–124.75 (m, Ph), 91.22 (s, Cp). ES MS ( $m/z$ ): (low cone voltage) 668,  $\text{M}^+$ ; (low cone voltage with NaOMe) 691,  $[\text{M} + \text{Na}]^+$ ; (high cone voltage) 668–612,  $[\text{M} - n\text{CO}]^+$  ( $n = 0-2$ ).

**Crystallography.** Unique room-temperature four-circle diffractometer data sets were recorded (monochromatic Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å;  $T \sim 295$  K) and used in the full-matrix least-squares refinements after analytical absorption correction. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms; ( $x$ ,  $y$ ,  $z$ ,  $U_{\text{iso}}\text{H}$ ) were included constrained at estimated values. Conventional residuals  $R$ ,

$R_w$  on  $|F|$  at convergence are given, statistical weights derivative of  $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$  being employed. Neutral atom complex scattering factors were employed, and computations were made using the XTAL 3.4 program system<sup>59</sup> implemented by S. R. Hall. Pertinent results are given in the figures and tables; material deposited comprises all coordinates and thermal parameters and full molecular non-hydrogen geometries.

**Abnormal Features/Variations in Procedure. For Compound 3.** Methyl groups were modeled over two sets of sites, disordered about the mirror plane and necessarily of equal occupancy in the present space group. Deterioration of the crystal by ca. 12% over the course of data collection was compensated for by scaling.

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(59) Hall, S. R., King, G. S. D., Stewart, J. M., Eds. *The XTAL 3.4 Users Manual*; University of Western Australia: Lamb, Perth, 1994.

**For Compound 12.** Merging of a redundant data set measured over a quadrant of reciprocal space after absorption correction yielded  $R_{\text{int}} = 0.045$ .

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for **3**, **10**, and **12** are available through the Internet only. Access information is given on any current masthead page. Crystallographic data have also been deposited with Cambridge and can be obtained by referencing 102116 for **3**, 102117 for **10**, and 102118 for **12**.

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