Formal Coupling of Two Alkylidyne Ligands on a Metal Center☆

Andreas Mayr*[a], Cecilia M. Bastos[a], Nancy Daubenspeck[a][1], and Gregory A. McDermott[b][2]

Department of Chemistry, State University of New York at Stony Brook[a],
Stony Brook, New York 11794-3400, U.S.A.

Department of Chemistry, Princeton University[b],
Princeton, New Jersey 08544, U.S.A.

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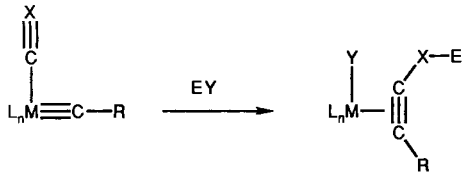
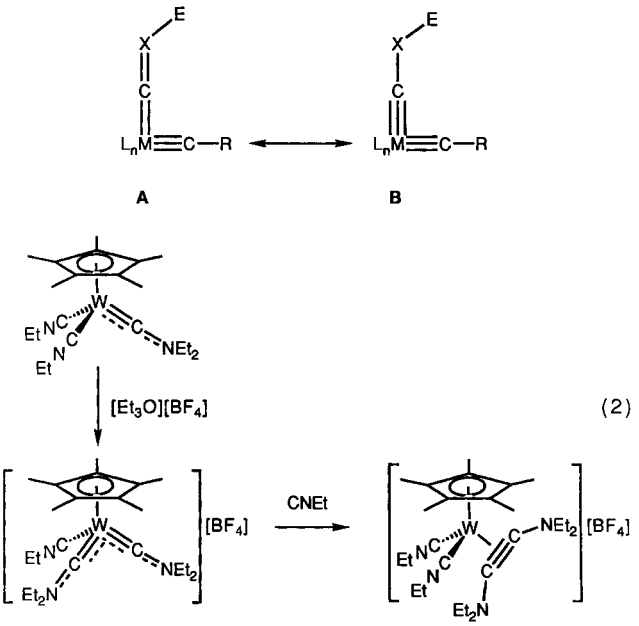
Reaction of the alkylidyne complexes [W(CR)Br(CO)$_3$L] [**2b** (L = CO; R = C_6H_4-OMe-4), **2c** (L = CO, R = C_6H_4-NMe_2-4), **3a** (L = PPh_3; R = Ph), and **3c** (L = PPh_3; R = C_6H_4-NMe_2-4)] with methyllithium in THF at −78°C affords the alkylidyne acyl tungsten complexes Li[W(CR)(COMe)Br(CO)$_3$L] [**4b** (L = CO; R = C_6H_4-OMe-4), **4c** (L = CO, R = C_6H_4-NMe_2-4), **5a** (L = PPh_3; R = Ph), and **5c** (L = PPh_3; R = C_6H_4-NMe_2-4)]. Reaction of complexes **4** and **5** with $C_2O_2Br_2$ at −78°C–0°C in CH_2Cl_2 followed by addition of PPh_3 gives the alkyne complexes [WBr_2(CO)($CH_3C{\equiv}CR$)(PPh_3)$_2$] (**6**). The formation of the alkyne ligands in complexes **6** may be considered as the result of formal coupling of two alkylidyne ligands.

Alkylidyne ligands undergo coupling reactions with other terminal π-bonded ligands under a variety of conditions[3]. It is well-established that alkylidyne-carbonyl coupling may be induced by nucleophiles[4] or photochemically[5]. There is some evidence that alkylidyne-carbonyl coupling may also be induced by electrophiles [Eq. (1); X = O][6,7]. Alkylidyne-isocyanide coupling has so far exclusively been observed as an electrophile-induced process [Eq. (1); X = NR'][8,9]. The electrophile most likely interacts with the carbonyl or isocyanide ligands as shown in **A** and **B**. For example, Schrock and co-workes reported the formation of W(η^2-HCCOAlCl$_3$)Cl(CO)(PMe_3)$_3$ from W(≡CH)Cl(PMe_3)$_4$ and CO in the presence of aluminum reagents such as Al_2Cl_6[6]. The reductive coupling of two carbonyl ligands was successfully demonstrated by Lippard and co-workers[10]. It was soon recognized that the actual coupling step involves the reaction of carbonyl(siloxymethylidyne)metal intermediates with silylating agents[11]. Filippou and co-workers demonstrated the proton-induced coupling of benzylidyne and aminomethylidyne ligands with isocyanide ligands[8]. Proton-induced alkylidyne-isocyanide coupling reactions were also studied in our laboratory, and evidence for the presence of discrete alkylidyne(aminomethylidyne)metal intermediates before the coupling step was found[9]. Earlier, Lippard and co-workers had discovered the reductive coupling of two isocyanide ligands[12]. Further investigations in Lippard's group[13] as well as in Filippou's group[14] revealed that bond formation in the reductive coupling of two isocyanide ligands involves a proton-induced aminomethylidyne-isocyanide coupling step. Recently, Filippou and co-workers were able to isolate a bis(aminomethylidyne)tungsten complex and to demonstrate coupling of the two aminomethylidyne ligands [Eq. (2)][15]. The available experimental information suggests that in the electrophile-promoted coupling



X = O, NR'

(1)



(2)

reactions the carbon–carbon bond-forming step occurs more easily with increasing bis(alkylidyne)character **B** of the immediate coupling precursors[3]. The coupling of two alkylidyne ligands without heteroatom substituents on the alkylidyne carbon atom, i.e. alkyl- or aryl-substituted methylidyne ligands without the possibility for significant stabilization of the immediate coupling precursor by resonance from **A**, is therefore of special interest. This work reports about the realization of this situation. A preliminary report about this work was previously published[16].

Description of the Experiments

Synthesis of the Alkylidynetungsten Complexes

The alkylidyne complexes **2** were prepared by reaction of the acylpentacarbonyltungsten complexes **1**[17] with oxalyl bromide [Eq. (3)][18]. Complexes **2b** and **2c**[19] were isolated

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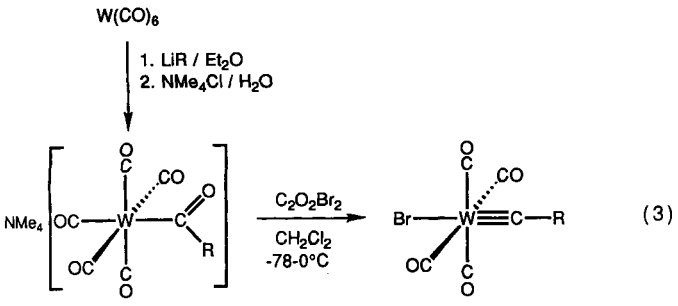
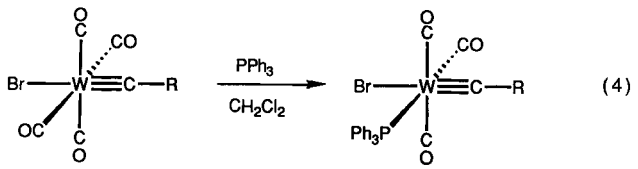
for the present study. The substitution of a single carbonyl ligand in **2a** by triphenylphosphane to give **3a** [Eq. (4)] was previously demonstrated by Fischer and co-workers[20]. Complex **3a** can also be prepared directly from **1a** by reaction with oxalyl bromide, followed by addition of triphenylphosphane, without isolation of the alkylidynetetracarbonyltungsten complex **2a**[19]. This direct method does not work reliably for **3b** and **3c**, leading often to mixtures of the mono- and disubstituted derivatives. However, reaction of purified **2c** with an equivalent amount or a slight deficiency of triphenylphosphane gives the monosubstituted complex **3c** in high yield [Eq. (4)].



(3)

1a-c **2a-c**

a: R = Ph
b: R = C_6H_4-OMe-4
c: R = C_6H_4-NMe_2-4

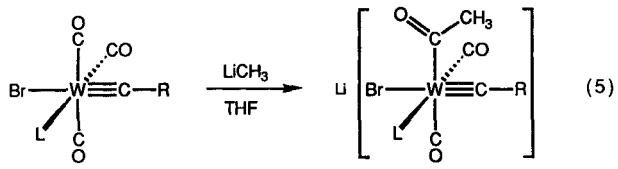


(4)

2a,c **3a,c**

Formation of Acyl(alkylidyne)tungsten Complexes

Reaction of the alkylidyne complexes **2b–c**, **3a**, and **3c** with methyllithium affords the acyl(alkylidyne)tungsten complexes **4b–c**, **5a**, and **5c**, respectively [Eq. (5)]. The tricarbonyl complexes **4** are significantly more stable than the dicarbonyl complexes **5**. At 0°C in THF complexes **4b–c** may be kept for several hours without visible signs of decomposition. Complexes **5a** and **5c** decompose slowly at 0°C.



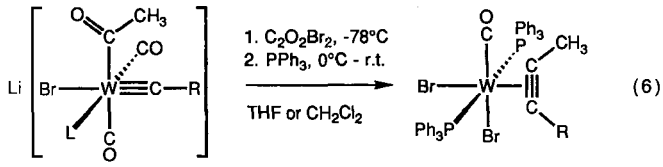
(5)

2b-c; 3a,c **4b-c; 5a,c**

The acyl(alkylidyne)tungsten complexes **4b–c**, **5a**, and **5c** were identified by spectroscopic means. A weak absorption at $\tilde{\nu}$ = 1522 cm^{-1} for complex **5a** is assigned to the C=O stretch of the newly formed acetyl ligand. The ^{13}C-NMR signals for the alkylidyne carbon atom of complexes **4** and **5** are found between δ = 267 and 280, the signals for the acyl carbon atom at δ = 315–320, and the resonance lines for the carbonyl ligands in the range of δ = 204–217. For complex **5a** the available ^{31}P-^{13}C coupling constants provide additional information about the relative arrangement of the ligands. The small coupling constants $^2J_{P,C}$ of ca. 10 Hz between the phosporus atom and the alkylidyne, the acyl, and one of the two carbonyl carbon atoms indicate that these three ligands are in *cis* positions relative to the phosphane ligand. The larger coupling constant $^2J_{P,C}$ between the phosphorus atom and the other carbonyl carbon atom of 47 Hz shows that this carbonyl ligand is oriented *trans* to the phosphane ligand. With the additional assumption that the bromide ligand is coordinated *trans* to the alkylidyne ligand this spectroscopic information establishes the relative arrangement of the ligands in complex **5a** as shown in Eq. (5).

Reaction of the Acyl(alkylidyne)tungsten Complexes with Oxalyl Bromide

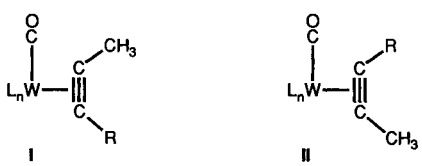
Upon addition of oxalyl bromide to the acyl(alkylidyne) complexes **4** and **5** at −78°C in THF or CH_2Cl_2 the reaction mixture changes color from orange to a dark color, ranging from brown to purple. After warming to 0°C, a slight excess of triphenylphoshane is added, and the solution is allowed to warm further to room temperature. During the final phase of the reaction, which may take a few hours, the reaction solution turns gradually green, indicating the formation of the alkyne complexes **6** [Eq. (6)]. The products are isolated in 30–50% yield. Complex **6a** had previously been repared by reaction of $[\{WBr_2(CO)(MeC{\equiv}CPh)\}_2]$ with PPh_3[21].



(6)

4b-c (L = CO)
5a,c (L = PPh_3) **6a-c**

Compounds **6** belong to a well-established class of four-electron donor alkyne complexes[22] and are therefore easily identified by spectroscopic methods. Most characteristically, the alkyne as well as the carbonyl carbon atoms give rise to ^{13}C-NMR signals in the range of δ = 190–230. At room temperature, two broad resonance lines, if any, are observed for the alkyne carbon atoms. At low temperatures, four distinct signals are observed. For electronic as well as steric reasons the preferred orientation of the alkyne ligand is parallel to the metal–carbonyl axis[22]. Since the alkyne ligands in complexes **6** are unsymmetrically substituted, the appearance of four resonance lines for the alkyne carbon atoms

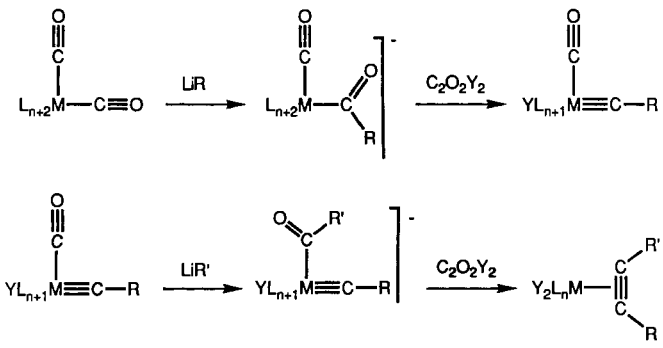


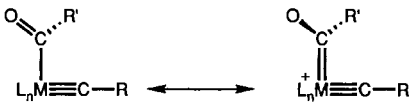
at low temperatures is presumably due to the presence of two isomers with the orientations **I** and **II** of the alkynes.

Discussion

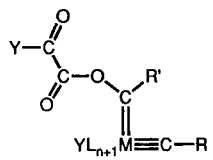
The formal coupling of two alkylidyne ligands involves the repeated application of a carbonyl-to-alkylidyne ligand transformation sequence in the same system [Eq. (3), (5), (6)]. The sequence of steps is shown in abstract form in Scheme 1. The successful execution of this reaction sequence hinged on several critical steps. In the second round of nucleophile and electrophile addition to a carbonyl ligand, i.e. in the reactions shown in Eq. (5) and (6), there was considerable potential for side reactions. Attack of nucleophiles at carbonyl ligands in alkylidyne complexes is not well-documented[23]. However, this type of reactivity is implied by formation of organic carbonyl derivatives of the type $RCH_2C(O)Nu$ in the reaction of $W(CR)Br(CO)_4$ with nucleophiles Nu^- (Nu = OH, OEt, Ph) and HCl[24]. We found that the formation of acyl(alkylidyne)tungsten complexes according to Eq. (5) works best with methyllithium. Other nucleophiles, such as PhLi or $4\text{-}MeOC_6H_4Li$, are less effective[25]. The formation of acyl ligands in Eq. (5) was only one of several possible outcomes. In general, reaction of alkylidyne complexes of the type $W(CR)X(CO)_{4-n}L_n$ with nucleophiles gives one of the following results: addition to the alkylidyne carbon atom, substitution of a carbonyl ligand, or substitution of the halide ligand X[23]. In the reaction of the acyl(alkylidyne) complexes **4** and **5** with oxalyl bromide [Eq. (8)], it was not a priori certain that electrophilic attack would occur at the acyl ligand. The alkylidyne ligand and the halide ligand are established sites for attack by electrophiles[23]. However, the low C=O stretching frequency of the acetyl ligand in complex **4a** reflects significant carbenoid character **C**, and therefore nucleophilicity at the acyl oxygen atom. The reaction of oxalyl bromide with complexes **4** and **5** is believed to give initially alkylidene(alkylidyne) complex intermediates of type **III**. Attempts to observe such an intermediate directly by spectroscopic methods were unsuccessful. However, the (bromooxalyl)carbene complex **IV**, resulting from the reaction of acyl complex **1b** with oxalyl bromide, had previously been characterized by low-temperature ^{13}C-NMR spectroscopy[18]. We therefore believe it is justified to postulate complexes of type **III** as intermediates before the coupling step.

Scheme 1

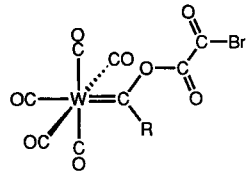




C



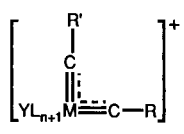
III



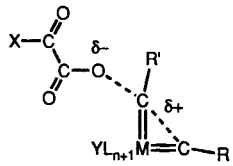
IV

After the formal coupling of the two alkylidyne ligands, which probably takes place at low temperatures, the formation of the alkyne complexes **6** is completed by incorporation of triphenylphosphane. This process may require the replacement of carbonyl ligands by triphenylphosphane, which would explain the slow final phase of the reaction shown in Eq. (6). Overall, the transformations leading to the alkyne complexes **6** occur under very mild conditions.

A question of obvious interest is how the alkyne ligands form. Unfortunately, our experimental results do not provide any direct information concerning the coupling step. The fragmentation of (bromooxalyl)carbene ligands into alkylidyne ligands was proposed to occur by dissociation of bromooxalate from the carbene carbon atom[18]. In the case of intermediate **III** this step would lead to a bis(alkylidyne)metal species **V**. However, the metal center in **V** is not able to from two independent metal–carbon triple bonds. Whether the second alkylidyne ligand in **V** forms fully before the coupling step, cannot be inferred from the currently available experimental results. Since little electronic stabilization of intermediate **V** is possible in the sense of resonance form **A**, it appears more likely that the bond between the two carbon atoms begins to form during the dissociation of the bromooxalate group from intermediate **III** as indicated in **VI**.



V

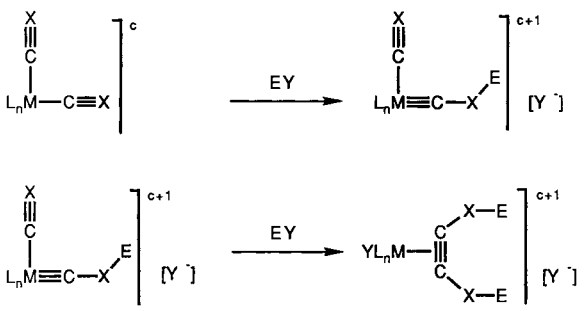


VI

The electronic aspects of methylidyne–methylidyne coupling were studied by Hoffmann and co-workers[26]. It was found that the coupling of two methylidyne ligands is an allowed and energetically favorable process for the electronic situation realized in the present work. Hoffmann and co-workers also investigated the electronic aspects of coupling of two carbonyl and two isocyanide ligands[27]. It was found that coupling of two carbonyl or isocyanide ligands (i.e. in the absence of electrophiles) is allowed, but energetically unfavorable.

The steps involved in the successful coupling of two carbonyl or isocyanide ligands are shown in abstract form in Scheme 2. A comparison of Scheme 1 and Scheme 2 clearly shows the close relationship among these reactions. In all cases two carbonyl (or isocyanide) ligands are sequentially subjected to reactions leading to the formation of alkylidyne ligands. The major difference consists in the methods of carbonyl (or isocyanide)-to-alkylidyne transformation. In Scheme 2 alkylidyne ligands are generated by β-addition of electrophiles to carbonyl or isocyanide ligands. In Scheme 1 formation of alkylidyne ligands is achieved by nucleophile addition followed by oxide abstraction. The coupling reactions depicted in Eq. (1) follow the same pattern, considering that the alkylidyne ligands are generally derived from carbonyl ligands. It is obvious that the formation of alkyne ligands by sequential transformation of carbonyl or isocyanide ligands into alkylidyne ligands can be achieved in a variety of combinations of the basic step. The common feature is that the bond-forming step may be understood as the coupling of two alkylidyne ligands. The relationships between these and other coupling reactions were discussed in more detail in a recent review article[3].

Scheme 2



Coupling of two alkylidyne units has also been achieved in other types of systems. Murahashi and co-workers described the formation of alkynes in the decomposition of bis(α-diazoalkyl)palladium complexes[28]. Fischer and co-workers reported the formation of alkynes or alkyne ligands from alkylidyne complexes under a variety of conditions: pyrolysis[29], oxidation[30], reduction[31], or ligand addition[32]. Studies in Chisholm's[33] group established the interconversion of high-valent alkylidyne complexes and dinuclear alkyne complexes. Coupling of two alkylidyne ligands has been observed in a variety of trinuclear systems[34].

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Experimental

All operations were performed under prepurified nitrogen by using standard Schlenk techniques. The solvents $CH_2Cl_2(CaH_2)$, hexane (CaH_2), diethyl ether (Na/benzophenone), and tetrahydrofuran (Na/benzophenone) were dried and distilled prior to use. The reagents were obtained from commercial sources and used as received without further purification. – NMR: Nicolet 300 and Bruker AC 250; $CDCl_3$ at room temperature (unless noted otherwise), resonances are referenced to residual solvent peaks and reported in δ values relative to TMS. – IR: Perkin-Elmer FT-1600. – Elemental analyses: Schwarzkopf Microanalytical Laboratory. – The acyltungsten complexes **1** were prepared by modified literature methods[17,19].

[W(CC$_6$H$_4$-OMe-4)Br(CO)$_4$] (**2b**)[19]: A solution of complex **1b** (0.57 g, 0.97 mmol) in CH_2Cl_2 (50 ml) is cooled to −78°C. A precooled (−78°C) solution of oxalyl bromide (75 µl, 0.82 mmol, 0.8 equiv.) in CH_2Cl_2 (20 ml) is added. The color of the solution changes from light orange to red-purple. The mixture is stirred at −78°C for 5 min. The solution is allowed to warm briefly to room temperature. The mixture is again cooled to −78°C and filtered through celite. The solvent is removed in vacuo and the product washed with 4 × 10 ml of cold (−78°C) methanol. The product is obtained as a light yellow solid (1.15 g, 55%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2120 cm^{-1} w (CO), 2030 s (CO).

[W(CC$_6$H$_4$-NMe$_2$-4)Br(CO)$_4$] (**2c**)[19]: A solution of complex **1c** (1.98 g, 3.62 mmol) in CH_2Cl_2 (50 ml) is cooled to −78°C. A precooled (−78°C) solution of oxalyl bromide (0.29 ml, 3.08 mmol, 0.85 equiv.) in CH_2Cl_2 (20 ml) is added. The color of the solution changes from light orange to purple. The mixture is stirred at −78°C for 5 min. The solution is allowed to warm briefly to room temperature. The mixture is again cooled to −78°C and filtered through celite. The solvent is removed in vacuo, and the product washed with 4 × 10 ml of cold (0°C) methanol. The product is obtained as a light yellow solid (0.96, 61%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2114 cm^{-1} w (CO), 2024 s (CO).

[W(CC$_6$H$_4$-NMe$_2$-4)Br(CO)$_3$(PPh$_3$)] (**3c**): Complex **2c** (1.15 g, 2.25 mmol) is dissolved in CH_2Cl_2 (30 ml), and triphenylphosphane (0.55 g, 2.07 mmol, 0.9 equiv.) is added. The mixture is stirred at room temperature until the reaction is complete (2 h). The solvent is removed in vacuo and the product washed with hexane. The product is used for further reactions as obtained. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2068 cm^{-1} m (CO), 1988 s (CO). – ^{1}H NMR: δ = 2.98 (s, 6H, Me_2N); 6.37, 6.88 (2 d, 4H, C_6H_4); 7.37–7.42, 7.62–7.70 (2 m, 15H, PPh_3). – ^{13}C NMR: δ = 39.9 (Me_2N); 128.3, 128.4, 130.2, 132.1, 134.0, 134.1, 134.2, 150.6 (C_6H_4 and PPh_3); 200.0 (d, $^2J_{P,C}$ = 7.5 Hz, CO *cis* to PPh_3); 200.8 (d, $^2J_{P,C}$ = 40.8 Hz, CO *trans* to PPh_3); 275.1 (d, $^2J_{P,C}$ = 10 Hz, W≡C). – ^{31}P NMR: δ = −18.92 ($J_{W,P}$ = 248 Hz).

Li[W(CC$_6$H$_4$-OMe-4)(COMe)Br(CO)$_3$] (**4b**): A solution of **2b** (0.63 g, 1.26 mmol) in THF (30 ml) is cooled to −78°C. A 1.4 M solution of CH_3Li (0.90 ml, 1.26 mmol) is added. The color of the solution changes from light yellow to orange. The mixture is warmed to 0°C, and the solvent is removed in vacuo. The product is obtained as a dark orange solid in nearly quantitative yield according to IR and NMR. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2053 cm^{-1} m (CO), 1966 s (CO). – ^{13}C NMR ([D$_8$]THF, −20°C): δ = 55.4 (MeO); 57.8 (CO*Me*); 113.1, 131.9, 142.1, 159.7 (C_6H_4); 204.2, 204.6 (CO); 277.3 (W≡C); 321 (*C*OMe).

Li[W(CC$_6$H$_4$-NMe$_2$-4)(COMe)Br(CO)$_3$] (**4c**): A solution of **2c** (0.82 g, 1.62 mmol) in THF (30 ml) is cooled to −78°C. A 1.4 M solution of CH_3Li (1.15 ml, 1.61 mmol) in ether is added. The color of the solution changes from light yellow to orange. The mixture is warmed to 0°C and the solvent removed in vacuo. The product is obtained in nearly quantitative yield according to IR and NMR. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2046 cm^{-1} m, 1958 s. – ^{1}H NMR ([D$_8$]THF, −20°C): δ = 2.88 (s, 3H, MeCO); 3.02 (s, 6H, Me_2N); 6.52, 7.42 (2 d, 4H, C_6H_4). – ^{13}C NMR ([D$_8$]THF, −20°C): δ = 40.2 (Me_2N); 57.9 (*Me*CO); 110.2, 132.1, 137.4, 150.0 (C_6H_4); 204.7, 205.6 (CO); 280.8 (W≡C); 320 (*C*OMe).

Spectroscopic Characterization of Li[W(CPh)(COMe)-Br(CO)$_2$(PPh$_3$)] (**5a**): In a 10-mm NMR tube **2a** (0.30 g, 0.30 mmol) is dissolved in [D$_8$]THF (5 ml). This solution is cooled to −78°C and placed in the pre-cooled (−80°C) probe of an NMR spectrometer. The ^{13}C-NMR spectrum of the alkylidyne complex **2a** is recorded. The sample is removed from the instrument, and CH_3Li (0.19 ml of a 1.6 M solution in Et_2O, 0.30 mmol) is added with vigorous shaking while the temperature is kept at −78°C. The color of the solution turns bright orange. The sample is returned to the spectrometer, and the ^{13}C-NMR spectrum is recorded. − ^{13}C NMR: δ = 57.6 (CO*Me*); 151.9, 138.6−127.9 (Ph and PPh$_3$); 216.8 ($^2J_{P,C}$ = 7 Hz, CO *cis* to PPh$_3$); 217.4 ($^2J_{P,C}$ = 47 Hz, CO *trans* to PPh$_3$); 267.2 ($^2J_{P,C}$ = 11 Hz, W≡C), 315.1 ($^2J_{P,C}$ = 11 Hz, COMe). − The sample is again removed from the spectrometer, and oxalyl bromide (0.03 ml, 0.3 mmol) is added with vigorous shaking while the temperature is kept at −78°C. The color turns orange-brown. The sample is returned to the NMR spectrometer, and the ^{13}C-NMR spectrum is recorded. However, the spectrum obtained only shows broad featureless humps. No specific information could be obtained from it. − To determine the position of the IR carbonyl absorptions of **5a** a small-scale reaction of complex **2a** with one equivalent of CH_3Li in THF at −78°C was carried out. The IR spectrum was measured at room temperature within less than 1 min. − IR: $\tilde{\nu}$ = 1986 cm^{-1} s (CO), 1916 s (CO), 1522 w (C=O).

Spectroscopic Characterization of Li[W(CC$_6$H$_4$-NMe$_2$-4)(CO-Me)Br(CO)$_2$(PPh$_3$)] (**5c**): To determine the position of the IR carbonyl absorptions of **5c** a small-scale reaction of complex **2c** with one equivalent of CH_3Li in THF at −78°C was carried out. The IR spectrum was measured at room temperature within less than 1 min. − IR: $\tilde{\nu}$ = 1977 cm^{-1} s (CO), 1907 s (CO).

[WBr$_2$(MeC≡CPh)(CO)(PPh$_3$)] (**6a**)[21]: Complex **3a** (2.80 g, 4.00 mmol) is dissolved in cold (0°C) THF (40 ml). The solution is further cooled to −78°C, and CH_3Li (1.3 M solution in Et_2O, 3.08 ml, 4.00 mmol) is added with stirring. The color changes from pale yellow to bright orange. After 10 min, oxalyl bromide (0.37 ml, 4.00 mmol) is added. The color turns purple-brown. The solution is warmed to 0°C and stirred for 5 min. Then triphenylphosphane (1.31 g, 5.00 mmol) is added, and the solution is allowed to warm to room temperature. After ca. 10 min, the color is visibly green. The solution is stirred for 2 h during which time a deep forest-green color develops. The solvent is removed in vacuo to give a deep green foamy solid. The solid is extracted with dry acetone. The product precipitates from the acetone solution upon standing and cooling as a blue-green crystalline solid. The solid is further washed with acetone (2 × 20 ml) and recrystallized from CH_2Cl_2/pentane to give blue-green needles (2.01 g, 50%). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1945 cm^{-1} (CO). − ^{1}H NMR: δ = 2.47 (s, 3H, Me), 7.20−7.65 (m, 35H, Ph, PPh$_3$). − ^{13}C NMR (CD_2Cl_2, −80°C; two rotamers): δ = 22.3, 23.8 (Me); 127.5−138.2 (Ph, PPh$_3$); 217.1, 223.5, 224.3, 229.2 (CO and C≡C).

$C_{46}H_{38}Br_2OP_2W$ (1012.4) Calcd. C 54.57 H 3.78
Found C 54.48 H 3.91

[W(MeC≡CC$_6$H$_4$-OMe-4)Br$_2$(CO)(PPh$_3$)$_2$] (**6b**): A solution of **2b** (0.48 g, 0.97 mmol) in THF (30 ml, precooled to 0°C) is cooled to −78°C. Then CH_3Li (0.65 ml, 1.4 M in ether, 0.97 mmol, 1.0 equiv.) is added. The color of the solution changes from yellow to brown. The mixture is warmed to 0°C and the solvent removed in vacuo. The product is redissolved in CH_2Cl_2 (30 ml), and the mixture is cooled to −78°C. A precooled (−78°C) solution of oxalyl bromide (75 µl, 0.77 mmol, 0.8 equiv.) in CH_2Cl_2 (15 ml) is added. The color of the solution changes from orange to dark brown. The solution is warmed slowly to 0°C, and triphenylphosphane (0.80 g, 3.00 mmol, 3.0 equiv.) is added. The mixture is stirred at room temperature until the reaction is complete (1.5 h). The solvent is removed in vacuo and the product washed with hexane. The raw product contains a significant amount of impurity. Column chromatography at −30°C [SiO_2; CH_2Cl_2/hexane (1:1)] (0.53 g, 65%) affords a blue-green solid, which contains some impurity. Attempts to remove the residual impurity by recrystallization were not successful. − IR (CH_2Cl_2): $\tilde{\nu}$ = 1941 cm^{-1} (CO). − ^{13}C NMR ([D$_8$]THF, −40°C; two rotamers): δ = 214.3, 222.3, 224.4, 225.9, 228.7 (CO, C≡C).

[W(MeC≡CC$_6$H$_4$-NMe$_2$-4)Br$_2$(CO)(PPh$_3$)$_2$] (**6c**) *from* **2c**: **2c** (0.70 g, 1.37 mmol) is dissolved in THF (30 ml, precooled to 0°C) and cooled to −78°C. Then CH_3Li (1.00 ml, 1.4 M in ether, 1.40 mmol, 1.0 equiv.) is added. The color of the solution changes from yellow to brown. The mixture is warmed to 0°C and the solvent removed in vacuo. The product is redissolved in CH_2Cl_2 (30 ml) and cooled to −78°C. A solution of oxalyl bromide (116 µl, 1.26 mmol, 0.9 equiv.) in precooled (−78°C) CH_2Cl_2 (15 ml) is added. The color of the solution changes from orange to dark brown. The solution is warmed slowly to 0°C, and triphenylphosphane (0.73 g, 2.80 mmol, 2.0 equiv.) is added. The mixture is stirred at room temperature until the reaction is complete (3 h). The solvent is removed in vacuo and the product washed with hexane. The product is obtained as a forest-green solid after purification by column chromatography at −30°C [SiO_2; CH_2Cl_2/hexane (1:1)] (0.43 g, 30%). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1939 cm^{-1} s (CO). − ^{1}H NMR: δ = 2.20 (br., 3H, MeCC), 3.09 (s, 6H, Me_2N), 6.56 (br.), 7.1−7.5 (m, 19H, C_6H_4, PPh$_3$). − ^{13}C NMR (CD_2Cl_2, −40°C, two rotamers): δ = 25.9, 27.0 (Me); 42.5, 42.6 (NMe_2); 113.2, 130−136, 154.3 (C_6H_4, PPh$_3$); 213.5, 221.9, 228.2, 229.1, 223.2 (CO, C≡C).

$C_{48}H_{43}Br_2NOP_2W$ (1055.48) Calcd. C 54.62 H 4.11
Found C 54.54 H 4.48

[W(MeC≡CC$_6$H$_4$-NMe$_2$-4]Br$_2$(CO)(PPh$_3$)$_3$] (**6c**) *from* **3c**: A solution of **3c** (0.32 g, 0.63 mmol) in THF (20 ml, precooled to 0°C) is cooled to −78°C. Then CH_3Li (0.45 ml, 1.4 M in ether, 0.63 mmol, 1.0 equiv.) is added. The color of the solution changes from yellow to brown. The mixture is warmed to 0°C and the solvent removed in vacuo. The product is redissolved in CH_2Cl_2 (30 ml), and the mixture is cooled to −78°C. A precooled (−78°C) solution of oxalyl bromide (41 µl, 0.44 mmol, 0.7 equiv.) in CH_2Cl_2 (15 ml) is added. The color of the solution changes from orange to dark brown. The solution is warmed slowly to 0°C, and triphenylphosphane (0.32 g, 1.26 mmol, 2.0 equiv.) is added. The mixture is stirred at room temperature until the reaction is complete (3 h). The mixture is filtered through celite, the solvent removed in vacuo, and the product washed with hexane (0.55 mg; 82%).

☆ Dedicated to Professor *Wolfgang Beck* on the occasion of his 60th birthday.

[1] NSF-REU student, from New York City Technical College, Summer **1990**.
[2] Current Address: SRI International, 333 Ravenswood Ave., Menlo Park, CA 94025, U.S.A.
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