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Reactivity of Alkyne Tungsten and Molybdenum Complexes. Heterolytic C–H Bond Activation in Coordinated Alkynes

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Abstract: A general preparative method for $[M(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ complexes (**6**, M = Mo, W) is described. The alkyne ligands were shown to be very labile at temperatures above 100 °C. The reactions of **6** with phosphine and methoxide were investigated. Using triethylamine as cocatalyst, **6** was shown to promote hydrogen exchange between 2-butyne and acetonitrile or acetone.

Introduction

Alkyne complexes of transition metals are intermediates in a number of catalytic and stoichiometric processes.[1] We have investigated the mechanisms of a number of these, e.g., oligomerization reactions,[2] insertion reactions yielding vinyl metal complexes and cyclic ketones,[3] and 1,2 addition of alkyl groups across alkynes.[4] Basic features of the metal–alkyne interaction (such as lability, metal–alkyne bond rotation, and propargyl hydrogen acidity) are therefore of interest. The potential for alkynes to act as four-electron rather than two-electron donors raises the possibility that the chemistry of their complexes may differ substantially from that of the corresponding alkenes due to stabilization of intermediates with unusually low formal valence electron counts.

Indeed, recent papers report[5,6] a number of formally 16-electron molybdenum complexes containing alkyne ligands (e.g., **1** and **2**) for which the closest alkene analogues are[5] 18-electron species (e.g., **3** and **4**). Similarly it might be ex-

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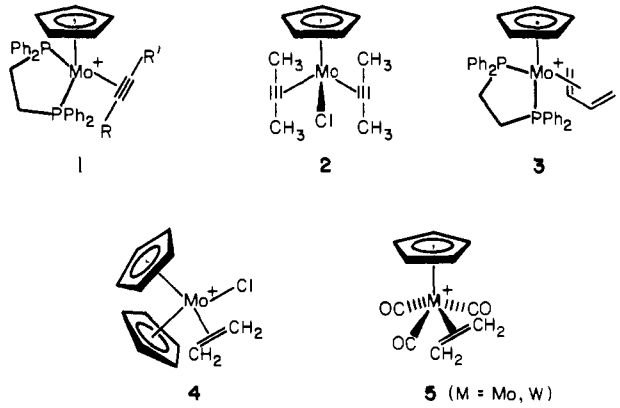


1 2 3 4 5 (M = Mo, W)

pected[7] that the synthetic routes described below for the title compounds would lead to an alkyne analogue of **5**, but such a complex was never observed.

In this paper the chemistry of the coordinately unsaturated complexes $[M(\eta^5\text{-}C_5H_5)(CO)(\eta^2\text{-}2\text{-butyne})_2]^+$ (M = Mo, W) has been examined with respect to ligand lability and nucleophilic substitution. Remarkable thermal and oxidative stability of these complexes was apparent but was in no way due to substitutional inertness.

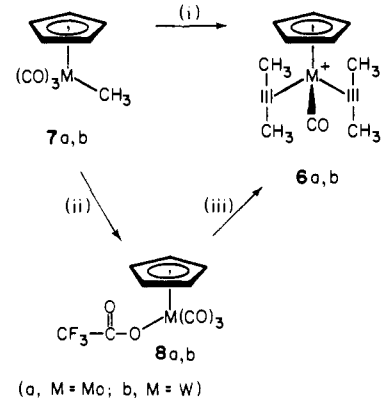
Results

Syntheses of $[M(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ Complexes (M = Mo, W). The bis(2-butyne) complexes **6a** (M = Mo) and **6b** (M = W) were obtained in good yield when the weakly basic methyl complexes **7a** and **7b** were protonated with trifluoroacetic acid in the presence of excess 2-butyne. These cations were most conveniently isolated as the PF_6^- salts. The molybdenum complex **6a** was previously prepared (Bottrill and Green[8]) by direct oxidation of $[Mo(C_5H_5(CO)_3]_2$ with $Ag[BF_4]$ in the presence of alkyne but the tungsten complex was not reported.

As shown in Scheme **I**, an alternative two-step procedure was also effective for preparation of **6.** The trifluoroacetate complexes[3c] **8a** and **8b** reacted with alkyne at 65 °C, losing 1 equiv of CF_3COO^- and 2 equiv of carbon monoxide. The fact that this reaction (labeled iii in Scheme I) required more forcing conditions than the direct route (labeled i in Scheme I) implied that the complexes **8** were not intermediates in the latter process, although initial dissociation of CF_3COO^- from **8** would yield an intermediate, $[M(C_5H_5)(CO)_3]^+$, possibly common to both reactions. Syntheses of **6a** and **6b** via the reactions ii and iii gave cleaner, higher yield reaction mixtures even without purification of **8a** and **8b.**

As solids, **6a** and **6b** showed high thermal stability; no decomposition occurred below 200 and 250 °C, respectively (under nitrogen). In acetonitrile solution, dissociation of the carbonyl ligand was evident above 110 (**6a**) or 150 °C (**6b**) (discussed below). Oxidative stability of the solids **6a** and **6b** was high, with no apparent decomposition in air after 2 weeks. **6b** showed no decomposition in acetonitrile solution when exposed to air for several weeks, whereas **6a** under the same conditions showed ~30% decomposition after 1 week. This oxidative stability seemed remarkable for complexes that are at least formally 16-electron species.

Scheme I



(a, M = Mo; b, M = W)

(i) CF_3COOH/excess butyne/CH_3CN/20° then CH_3OH/$NaPF_6$; (ii) CF_3COOH/benzene/20°; (iii) Excess 2-butyne/CH_3CN/65°C, then $CH_3OH/NaPF_6$

The ^1H NMR spectrum of **6a** was simple, showing a singlet C_5H_5 resonance, and two singlets due to two sets of nonequivalent methyl groups. The spectrum of **6b** had the same features. Structurally, **6a** and **6b** are probably similar to the neutral complex $W(C_5H_5)(CF_3C{\equiv}CCF_3)_2Cl$,[6,9] which approximates an octahedron with three facial sites taken by the cyclopentadienyl ligand, one site by Cl, and with an alkyne unit situated approximately parallel to the W–Cl direction at each of the two remaining sites. Symmetric bonding of the alkyne units was interpreted as evidence that both alkynes were two-electron donors. This general structure is illustrated for **6** in Scheme I. The infrared spectra of both **6a** and **6b** showed a single strong carbonyl stretching band at 2040 cm^{-1}, and also medium-weak absorptions at 1810 (**6a**) and 1800 (**6b**) cm^{-1} which were assigned to the C≡C stretch lowered in energy by complexation.[10]

Carbonyl Lability of $[M(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ (M = Mo, W). When acetonitrile solutions of **6a** were heated, loss of the carbonyl ligand occurred slowly at 110 °C and rapidly at 140 °C, yielding the monoacetonitrile complex **9a** (eq 1, forward). Clean first-order kinetics for conversion of **6a** to

$$\underset{\textbf{6a}}{Mo(C_5H_5)(CO)(2\text{-butyne})_2^+} \underset{\text{>70 °C, THF, CO, } -CH_3CN}{\overset{\text{>110 °C, } CH_3CN,\ -CO}{\rightleftharpoons}} \underset{\textbf{9a}}{Mo(C_5H_5)(CH_3CN)(2\text{-butyne})_2^+} \quad (1)$$

9a were not observed over several half-lives when the reaction was followed by NMR (in NMR tubes sealed with 1 atm nitrogen) at temperatures between 90 and 140 °C, possibly because of the back reaction of **9a** with carbon monoxide as the concentration of free carbon monoxide increased. A first-order (or pseudo-first-order) rate constant for conversion of **6a** to **9a**, obtained from plots of $\ln\{([\mathbf{6a}] + [\mathbf{9a}]) - [\mathbf{6a}]\}$ vs. time over only the first 50% of the reaction at 115 °C, was $\sim 10^{-3}\ s^{-1}$. The rate of this reaction was slower by a factor of ~5 for samples of **6a** sealed under 1 atm carbon monoxide compared to samples sealed under nitrogen.

The back reaction of eq 1 was also demonstrated. Reaction of isolated **9a** with carbon monoxide (~1 equiv, in a sealed NMR tube) in tetrahydrofuran-d_8 was ~50% complete in 35 min at 70 °C and proceeded to completion at 90 °C within 30 min. Exchange of the coordinated acetonitrile in **9a** with free ligand acetonitrile was also rapid at these temperatures (although it was not determined whether this process was associative or dissociative). In a solution of CD_3CN, **9a** underwent ligand exchange (eq 2) rapidly at 70 °C. The reaction was 50% complete at 50 °C after 30 min.

$$\underset{\textbf{9a}}{Mo(C_5H_5)(CH_3CN)(2\text{-butyne})_2^+} \xrightarrow[-CH_3CN]{+CD_3CN} \underset{\textbf{9a-}d_3}{Mo(C_5H_5)(CD_3CN)(2\text{-butyne})_2^+} \quad (2)$$

The tungsten complex **6b** was also observed to lose carbon monoxide on extended heating at 130 °C in acetonitrile solution, yielding the analogue of **9a.**

Reaction of $[M(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ with Bis(diphenyl)phosphinoethane (dppe). Stoichiometry of the tungsten complex **6b** was confirmed by reaction with dppe. At 25 °C, dppe reacted with **6b** over several hours in acetonitrile (eq 3), quantitatively yielding the cation **10b** as violet crystals, plus 1 equiv of 2-butyne (observed by NMR) and 1 equiv of carbon monoxide (quantitatively measured using a Toepler pump). The known molybdenum cation **10a** (a green, crystalline complex previously characterized by Green[5] as the BF_4^- salt) was similarly obtained from the rapid reaction of dppe with **6a.**

$$M(C_5H_5)(CO)(2\text{-butyne})_2^+ + \text{dppe} \rightarrow M(C_5H_5)(2\text{-butyne})(\text{dppe})^+ + 2\text{-butyne} + CO \quad (3)$$

Lability of Coordinated Butyne in $[M(C_5H_5)(CO)(2\text{-butyne})]PF_6$ (M = Mo, W). Addition of 2-pentyne to solutions of **6a** resulted in an equilibrium mixture of complexes containing both coordinated 2-butyne and coordinated 2-pentyne (eq 4).

$$\underset{\textbf{6a}}{Mo(C_5H_5)(CO)(2\text{-butyne})_2^+} \underset{}{\overset{K_1}{\rightleftharpoons}} \underset{\textbf{11a}}{Mo(C_5H_5)(CO)(2\text{-butyne})(2\text{-pentyne})^+} \overset{K_2}{\updownarrow} \underset{\textbf{12a}}{Mo(C_5H_5)(CO)(2\text{-pentyne})_2^+} \quad (4)$$

When observed by NMR the reaction was complete in less than 10–15 min at 20 °C. Differentiation between **11a** and a mixture of **12a** and **6a** was not possible by ^1H NMR (90 MHz). However, the relative amounts of total coordinated butyne and pentyne present in mixtures of **6a** and various amounts of pentyne were obtained from the NMR spectra and it was established that the equilibrium constant K_1K_2 was not significantly less than one.

Mechanistic possibilities for the ligand exchange of 2-butyne in **6a** were probed kinetically using $[Mo(C_5H_5)(CO)(2\text{-butyne-}d_6)_2]PF_6$ (the catalytic synthesis of which is described below) as substrate (eq 5). The reaction was followed by ^1H NMR. At −5 °C the initial rate of exchange (in acetonitrile) was independent of free 2-butyne concentration when the ratios of **6a**-d_6 to 2-butyne were 1:1, 1:10, and 1:16. A first-order rate constant, k_5, obtained by plotting ln {[total **6a**]/[coordinated 2-butyne]} vs. time at 5 °C was 5×10^{-4} s^{-1} (at **6a**-d_{12} to 2-butyne ratio 1:10) and at −5 °C was 3.6×10^{-4} s^{-1}.

$$\underset{\textbf{6a-}d_{12}}{Mo(C_5H_5)(CO)(2\text{-butyne-}d_6)_2^+} \xrightarrow[-\,(\text{butyne-}d_6)]{\overset{k_5}{+\,(\text{butyne})}} \underset{\textbf{6a-}d_6}{Mo(C_5H_5)(CO)(2\text{-butyne})(2\text{-butyne-}d_6)^+} \quad (5)$$

Exchange of the 2-butyne ligands of the tungsten complex **6b**-d_{12} did not occur rapidly below 60–70 °C. The complex $[W(C_5H_5)(CO)(2\text{-heptyne})_2]PF_6$, previously prepared by the general reactions outlined in Scheme I for the butyne analogue, was also formed cleanly and in high yield from **6b** when a solution of **6b** in acetonitrile was heated at 110 °C with excess 2-heptyne.

High-Temperature Site Exchange Processes. Site exchange of the chemically nonequivalent methyl groups of coordinated 2-butyne in **6a** was observable by NMR above 90 °C (acetonitrile solution). Coalescence of the two resonances occurred at 104 °C and the fast exchange limit was reached at 140 °C. Acetonitrile solutions of **6b** behaved similarly, but with coalescence at 135 °C and fast exchange at 155 °C (superimposed on the spectra of **6a** was the gradual appearance of resonances due to **9a**; conversion of **6a** to **9a** (eq 1) was slow on the NMR time scale, as mentioned previously, and slower than the site exchange by an approximate factor of 10^5). The coalescence temperatures of **6a** and **6b** were unaffected whether the samples were sealed under an atmosphere of nitrogen or carbon monoxide (although carbon monoxide retarded conversion of **6a** to **9a**).

Values of $\Delta G^{\ddagger}$ calculated for the methyl group site exchanges were 19.4 (**6a,** 104 °C) and 21.0 kcal/mol (**6b,** 135 °C). In the recorded spectra the peak of added 2-butyne (in 3–20-fold excess over **6a** or **6b**) was not significantly broadened at or around the coalescence temperatures of the coordinated butyne peaks. Computer simulated spectra (obtained using a three-site model with intermolecular exchange rates of 0–40 s^{-1} and intramolecular exchange rates of 0–300 s^{-1}) only compared well with the recorded spectra when the intramolecular exchange was at least 20–30 times faster than intermolecular exchange. Therefore, while it is possible that some contribution to the methyl group site exchange in **6a** observed by NMR is in fact *inter*molecular exchange of 2-butyne, it would appear that the dominant exchange process at 104 °C involves *intra*molecular rotation about the alkyne–metal axis.

An energy barrier for methyl group exchange in **10a** was estimated[5] to be $\Delta G^{\ddagger} = 14.3$ kcal/mol, attributed to intramolecular rotation about the metal–alkyne axis. Recently Faller and Murray calculated[12] the barrier for alkyne rotation in the neutral complex $[Mo(C_5H_5)(ClCH_2C{\equiv}CCH_2Cl)_2Cl]$ ($\Delta G^{\ddagger}_{-68°} = 10.3$ kcal/mol) and estimated a barrier at least 5 kcal/mol higher for the cationic complex $[Mo(C_5H_5)(HOH_2CC{\equiv}CCH_2OH)_2CO]^+$ (for which no exchange broadening was observed up to 85 °C). For the neutral complexes, $[W(C_5H_5)(CO)(R'C{\equiv}CR'')R''']$, free energies of activation for the alkyne rotation were reported[13] to be in the range 16.8–18.2 kcal/mol, and for the corresponding neutral indenyl complexes to be ~18.5 kcal/mol.[14]

The acetonitrile complex **9a** also demonstrated site exchange of methyl groups. $\Delta G^{\ddagger}$ estimated from the rate of exchange (100 s^{-1}) at the coalescence temperature (48 °C) was 15.9 kcal/mol.

Catalytic Deuteration of 2-Butyne. In the presence of triethylamine as cocatalyst, **6a** was a catalyst for deuterium/hydrogen exchange between the deuterated solvents acetonitrile-d_3 or acetone-d_6 and 2-butyne. In the absence of excess 2-butyne, stoichiometric deuteration of the methyl groups of **6a** occurred (eq 6) in less than 1.5 days at 20 °C using 0.1 M solutions of **6a** in acetone-d_6 (or acetonitrile-d_3) with 1 equiv of triethylamine (based on **6a**). Qualitatively the rate of the exchange process was proportional to the concentration of triethylamine, and the reaction could therefore be made to proceed much more rapidly by addition of an excess of this cocatalyst. Although the reactants were insensitive to the presence of trace amounts of water, the amine was of necessity rigorously purified to remove primary and secondary amines since the complex **6a** reacted instantly with compounds containing N–H bonds (including ammonia). The spectral properties of **6a**-d_{12} were identical with those of **6a** except for the absence of singlets in the NMR spectrum due to the butyne methyl groups and the appearance of ν_{CD} at 2200 cm^{-1} with concomitant loss of ν_{CH} at 2950 cm^{-1}.

$$\underset{\textbf{6a}}{Mo(C_5H_5)(CO)(2\text{-butyne})_2^+} \xrightarrow[\text{acetone-}d_6]{N(CH_2CH_3)_3} \underset{\textbf{6a-}d_{12}}{Mo(C_5H_5)(CO)(2\text{-butyne-}d_6)_2^+} \quad (6)$$

Catalytic deuteration of 2-butyne (eq 7) was typically run

$$CH_3C{\equiv}CCH_3 \xrightarrow[\substack{\text{acetone-}d_6 \text{ or}\\ \text{acetonitrile-}d_3}]{\textbf{6a},\ N(CH_2CH_3)_3} CD_3C{\equiv}CCD_3 \quad (7)$$

using [**6a**:$N(CH_2CH_3)_3$:acetone-d_6:2-butyne] concentration ratios (determined by NMR) of [1:5-25:130-200:30-45] at 20 °C, in which cases equilibrium was attained in 12 h or less (~80% deuterium incorporation into the butyne as monitored by signal in the ^1H NMR spectrum). No products other than 2-butyne (d_0-d_6) were observed—for example, no d_0-d_6-methylallenes were formed.

Attempts to utilize the conjugate base-deuterium donor pair $^-OCH_3/DOCH_3$ to effect the proton-exchange reaction were not successful owing to a stoichiometric reaction between **6a** and $^-OCH_3$ (or $^-OCD_3$). In methanol solution, this reaction (eq 8) was extremely rapid at 20 °C, yielding the purple

$$\underset{\textbf{6a}}{Mo(C_5H_5)(CO)(2\text{-butyne})_2^+} + NaOCH_3 \xrightarrow{CH_3OH} \underset{\textbf{13a}}{Mo(C_5H_5)(CO)(2\text{-butyne})(OCH_3)} + NaPF_6 + 2\text{-butyne} \quad (8)$$

complex **13a,** plus 1 equiv of 2-butyne, and $NaPF_6$. Good analytical data were not obtained for **13a** owing to a combination of difficulty of crystallization of the highly nonpolar complex and its extreme air sensitivity. Similar problems were encountered in handling the orange-red tungsten complex $W(C_5H_5)(CO)(2\text{-butyne})(OCH_3)$ (**13b**) which was formed from **6b** and $NaOCH_3$ in methanol over a period of several hours. The ^1H and ^{13}C NMR spectra fully support the formulation of **13** as shown. IR spectra consisted of single carbonyl bands at 1880 (**13a**) and 1890 cm^{-1} (**13b**).

Coordinated methoxide in **13a** exchanged with methanol solvent in minutes at 20 °C (eq 9) as evidenced by disappear-

$$\underset{\textbf{13a}}{Mo(C_5H_5)(CO)(2\text{-butyne})(OCH_3)} \underset{CH_3OH}{\overset{CD_3OH}{\rightleftharpoons}} \underset{\textbf{13a-}d_3}{Mo(C_5H_5)(CO)(2\text{-butyne})(OCD_3)} \quad (9)$$

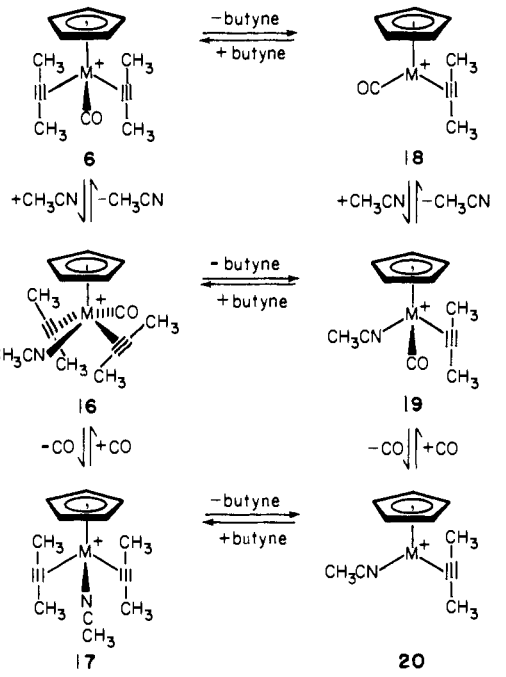
ance of the methoxide resonance of **13a** in the ^1H NMR when CD_3OH was added to a benzene-d_6 solution of **13a.** The reverse reaction also of course occurred readily. These processes could be anticipated to be associative in nature. Thiolate complexes analogous to **13** have been reported.[15]

Discussion

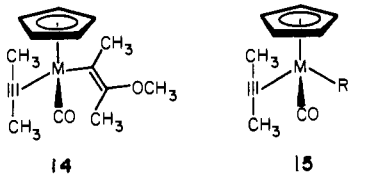
The bisalkyne complexes **6** and **9** were thermodynamically stable, kinetically labile species. Chemistry of the molybdenum and tungsten complexes was in general analogous, although reaction rates were always slower for the tungsten systems. The rapid intramolecular alkyne exchange was a dominant feature of the chemistry and would provide a simple route to substituted alkyne derivatives, as demonstrated for **6b.** This alkyne exchange process was shown qualitatively to be first order in molybdenum complex for **6a,** and independent of free 2-butyne concentration. In acetonitrile (polar coordinating solvents were necessary to dissolve the PF_6^- salts) it may be reasonable to suppose a preequilibrium leading to **16** (Scheme II), but lying heavily on the side of **6a** (no such complex was observed by NMR). This would avoid postulating formation of a $14e^-$ species (e.g., **18** and **20**) during the dissociative process. Alternatively, such species could be justified as having 16 valence electrons if the coordinated butyne were a four-electron donor.

Although formally electron deficient, the complexes **6** showed no tendency to form stable 18-electron complexes such as $[M(C_5H_5)(CO)_2(2\text{-butyne})_2]^+$. However, strong σ-donor

Scheme II



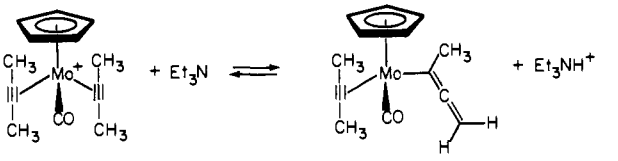
ligands reacted very rapidly with **6** at 20 °C, always with loss of one butyne ligand. In the case of methoxide ion, it was notable that the site of attack was the metal center rather than at an alkyne carbon to give **14.** Nucleophilic attack occurred[7]



at the ethylenic carbon in **5** (see Introduction) but the difference between these reaction courses could be a function of the coordinative unsaturation of **6** rather than the relative affinity of nucleophiles for coordinated alkene vs. alkyne. No molybdenum complexes of generalized structure **15** have been reported, except for ligands R that can function as four-electron donors.[15] The *tungsten* complexes reported by Alt[13,14] do contain R as a simple alkyl ligand.

The implication that complexes **15,** M = Mo, are viable, at least as reaction intermediates for molybdenum, is obvious in considering the proton exchange reaction of **6;** Scheme III

Scheme III



shows the reaction most probably responsible for this exchange. Since the pK_a of $HN^+(CH_2CH_3)_3$ is ~10 and that of free butyne ~35, it is obvious that the hydrogen acidity of 2-butyne has been increased substantially by complexation.

Experimental Section

All manipulations were performed under a dry, oxygen-free atmosphere of nitrogen in a Vacuum Atmospheres 553-2 Dry-Lab, or on a conventional vacuum line, or using double-manifold Schlenk techniques unless otherwise noted. Diethyl ether, tetrahydrofuran, and benzene were stirred over Na/benzophenone under nitrogen with a small amount of tetraglyme until purple, and were vacuum transferred prior to use. Petroleum ether was stirred over (1) a saturated solution of $KMnO_4$, (2) concentrated H_2SO_4, (3) H_2O, (4) CaH_2,

and (5) Na/benzophenone with tetraglyme and was vacuum transferred prior to use. Acetonitrile was dried over P_2O_5, and methanol was dried over CaH_2.

$[Mo(C_5H_5)(CO)_3]_2$ and $W(CO)_6$ were obtained from Alfa. CF_3COOH (Matheson Coleman and Bell) was stored over and vacuum transferred from a small amount of P_2O_5. 2-Butyne (Chemical Samples Co.) was dried over sodium, then distilled. $NaPF_6$ (Alfa) was used as obtained. Deuterated solvents were purchased from Aldrich; acetonitrile-d_3 was dried by storage over alumina, tetrahydrofuran-d_8 and benzene-d_6 were dried over Na/benzophenone, and acetone-d_6 was used as obtained (99.9% d). These solvents were opened and stored under nitrogen.

Infrared (IR) spectra were recorded on a Perkin-Elmer 257 grating spectrophotomer, or on a Beckman 42-10 spectrophotometer, either in solution using 0.10- or 0.05-mm sodium chloride cells or as KBr disks as indicated.

Proton nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-390 spectrometer using the solvent peak as internal reference. Resonances are expressed in units of δ (parts per million downfield from tetramethylsilane). ^{13}C NMR spectra were measured using a Varian XL-100 spectrometer in the Fourier transform mode. Some samples for ^{13}C NMR were recorded in solution with Cr(acetonylacetonate)$_3$ (10-20 mol % based on sample compound) to reduce relaxation times and the chemical shifts were shown to be the same with and without the Cr complex present. Resonances are expressed in units of parts per million downfield from tetramethylsilane. All ^{13}C spectra were totally proton decoupled.

Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., or by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

$[Mo(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ (6a). A. A solution of $CH_3Mo(C_5H_5)(CO)_3$ (0.4 g, 0.001 54 mol), CF_3COOH (0.25 mL, 0.0033 mol), and 2-butyne (0.65 mL, 0.0089 mol) in CH_2Cl_2 (1 mL) was stirred at 20 °C for 24 h. Volatiles were removed under vacuum and the red-brown, oily residue was redissolved in CH_3OH (3 mL). On addition of $NH_4^+PF_6^-$ (0.25 g, 0.001 54 mol) to the CH_3OH solution, yellow solids precipitated. The solids were collected by filtration and recrystallized from CH_3OH/CH_2Cl_2 (2:1) by partial evaporation of solvent. The yellow, microcrystalline solids were again collected by filtration and dried under vacuum, yield 0.42 g (60%).

B. A solution of $Mo(C_5H_5)(CO)_3OC(O)CF_3$ (1.0 g, 0.0028 mol) and 2-butyne (2 mL, 0.027 mol) in acetonitrile (5 mL) was stirred at ~50 °C under vacuum in a tube sealed with a Teflon vacuum stopcock for 8 h. Solvent and evolved carbon monoxide were vacuum transferred from the reaction vessel, leaving a yellow-brown oil. The oil was dissolved in methanol (5 mL) and then added to a solution of NH_4PF_6 (0.46 g, 0.0028 mol) in methanol (5 mL). The product immediately precipitated as a yellow powder, which was collected by filtration and recrystallized from a minimum of acetonitrile by addition of diethyl ether, yield of yellow crystals 1.04 g (79%), mp 258–260 °C dec (the compound progressively darkened above 210 °C). IR (CH_2Cl_2): ν_{CO} 2040 (s), $\nu_{C\equiv C}$ 1810 (w), ν_{P-F} 840 (s) cm^{-1}. ^1H NMR (CD_3CN): δ 5.86 (s, 5 H, C_5H_5), 2.99 (s, 6 H, CH_3), 2.72 (s, 6 H, CH_3) ppm. ^{13}C NMR (CD_3CN): 15.2 and 19.3 (CH_3's), 101.2 (C_5H_5), 144.7 and 163.8 (C≡C) and 221.4 (CO) ppm downfield from Me_4Si. Anal. Calcd for $C_{15}H_{17}F_6MoPO_2$: C, 38.00; H, 3.87; Mo, 21.70. Found: C, 38.14; H, 3.91; Mo, 21.0 (AAS) and 22.4 (as $PbMoO_4$).

$[W(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ (6b). A solution of $W(C_5H_5)(CO)_3OC(O)CF_3$ (0.58 g, 0.0013 mol) and 2-butyne (1 mL, ~0.0 3 mol) in acetonitrile (3 mL) was heated at 65 °C, with stirring, under vacuum in a tube sealed with a Teflon vacuum stopcock. After 1 day the solution was cooled to −196 °C and the evolved carbon monoxide was pumped off. The tube was resealed and further heated at 65 °C for 2 days. The color of the reaction mixture changed over the 3 days from deep red to pale yellow-brown. Solvent and carbon monoxide were vacuum transferred from the reaction mixture. The residues were dissolved in methanol (10 mL) and then filtered. To the filtrate was added NH_4PF_6 (0.22 g, 0.0013 mol). The product immediately precipitated as a white powder which was collected by filtration and recrystallized from a minimum of acetonitrile by slow addition of diethyl ether, yield of white crystals 0.45 g (62%), mp 291–293 °C dec (darkened progressively above 260 °C). IR (CH_2Cl_2): ν_{CO} 2040 (s), $\nu_{C\equiv C}$ 180 (s), ν_{P-F} 840 (s) cm^{-1}. ^1H NMR (CD_3CN): δ 5.96 (s, 5 H, C_5H_5), 3.06 (s, 6 H, CH_3), 2.83 (s, 6 H, CH_3) ppm. ^{13}C NMR (CD_3CN): 14.9 and 19.3 (CH_3's), 99.8 (C_5H_5), 142.2 and 160.4 (C≡C) and 209.12 (CO) ppm downfield from Me_4Si. Anal. Calcd for $C_{15}H_{17}F_6PO_2W$: C, 31.68; H, 3.23; W, 34.63. Found: C, 31.44; H, 3.06; W, 34.4 (AAS).

Reaction of $[Mo(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ with 1,2-Bis(diphenylphosphino)ethane (dppe). Acetonitrile (5 mL) was condensed (−196 °C) onto the solid reactants, $[Mo(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ (0.13 g, 0.002 76 mol) and 1,2-bis(diphenylphosphino)ethane (0.25 g, 0.006 28 mol, i.e., excess), in a 50-mL round-bottom flask attached to the vacuum line. On warming the flask to 25 °C immediate reaction occurred in solution, evidenced by a color change from yellow to deep blue-green and evolution of gas. After 30 min the system was cooled to −196 °C and the evolved gas (carbon monoxide) was measured using a Toepler pump: 0.000 287 mol (1.04 equiv). Solvent was removed from the reaction mixture under vacuum and the green residues were washed with benzene (to remove excess 1,2-bis(diphenylphosphino)ethane), 2 × 5 mL. The green powder was collected by filtration and dried under vacuum. The compound was shown to be the PF_6^- salt of the known cation[5] $Mo(C_5H_5)(dppe)(2\ butyne)^+$ (described in the literature as the BF_4^- salt) by comparison of the low-temperature ^1H NMR spectrum, yield 0.21 g (94%). IR (CH_2Cl_2): 8.40 (s, ν_{P-F}) cm^{-1}. ^1H NMR (−55 °C, CD_3CN): δ 7.48 (m, 20 H, phenyl), 5.09 (s, 5 H, C_5H_5), 3.23 (m, 2 H, PCH_2), 2.86 (s, 3 H, CH_3), and 1.8 (s, 3 H, CH_3). ^1H NMR (30 °C, acetone-d_6): δ 7.33 (m, 20 H, phenyl), 5.30 (t, 5 H, C_5H_5), 3.54 (m, 4 H, PCH_2), and a broad resonance between δ 1.0 and 3.0 (6 H) [lit.[5] ^1H NMR (−50 °C, acetone-d_6, BF_4^- salt): δ 7.4 (20 H, phenyl), 5.35 (t, J_{PH} = 2.4 Hz, 5 H, C_5H_5), 3.5 (m, 4 H, PCH_2), 3.07 (s, CH_3), and 1.25 (s, CH_3)].

Reaction of $[W(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ with dppe. Onto $[W(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ (0.1 g, 0.000 18 mol) and dppe (0.2 g, 0.0005 mol) was condensed a mixtured of acetonitrile (3 mL) and THF (3 mL) under vacuum at −196 °C. The reaction mixture was warmed to 20 °C and stirred for 6 h. After the solution was cooled to −196 °C, evolved carbon monoxide was collected using a Toepler pump: 0.000 168 mol, i.e., 0.94 equiv based on W. Solvent was removed from the reaction mixture under vacuum and the purple residues were washed with benzene (4 × 15 mL), then dried, yield of $[W(C_5H_5)(dppe)(2\text{-butyne})]PF_6$ 0.15 g (98%), mp 229–230 °C dec. IR (CH_3CN): no carbonyl bands. ^1H NMR (CD_3CN, −50 °C): δ 7.53 (m, 20 H, phenyl), 5.14 (t, 5 H, C_5H_5), 3.16 (m, 4 H, CH_2), 2.79 (s, 3 H, CH_3), and 1.08 (s, 3 H, CH_3). Anal. Calcd for $C_{35}H_{35}F_6P_3W$: C, 49.66; H, 4.17. Found: C, 49.82; H, 4.08.

Oxidative Stability of 6a and 6b. A. The color of solid samples of **6a** (yellow) and **6b** (white) remained unchanged after standing in air for several weeks, and could be dissolved to give essentially clean IR and NMR spectra.

B. Solutions of **6a** and **6b** in CD_3CN were left open to air and were periodically monitored by NMR. After 3 days the spectrum of **6b** was unchanged and the spectrum of **6a** showed a small amount (<10%) of decomposition. After 1 week **6b** was unchanged and **6a** showed ~30% decomposition.

Oxidative Stability of 9a. A solution of **9a** in CD_3CN exposed to air showed ~30% decomposition after 1 week.

$[Mo(C_5H_5)(CH_3CN)(2\text{-butyne})_2]PF_6$ (9a). A solution of $[Mo(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ (0.9 g, 0.002 mol) in acetonitrile (30 mL), in a 300-mL vessel under vacuum, was heated using an oil bath at 110 °C. After 8 h solvent was removed under vacuum at 25 °C and the residues were chromatographed (silica gel, 5 × 2 cm, eluting with three bed-volumes of THF). Diethyl ether was added to the yellow-brown eluate until crystals appeared. The crystalline material was collected by filtration after 6 h, and was recrystallized from a minimum of THF by addition of diethyl ether, yield of pale yellow crystals 0.75 g (83%), mp 150–152 °C dec. IR (KBr disk): 3110 (s, ν_{CH} of C_5H_5), 1790 (w, $\nu_{C\equiv C}$) cm^{-1}. ^1H NMR (CD_3CN, 10 °C): δ 5.66 (s, 5 H, C_5H_5), 2.94 (s, 6 H, $CH_3C{\equiv}CCH_3'$), 2.81 (s, 3 H, CH_3CN), 2.46 (s, 6 H, $CH_3C{\equiv}CCH_3'$). At 80 °C the butyne methyl groups appeared as a sharp singlet, δ 2.69. Coalescence occurred at 48 °C. ^{13}C NMR (CD_3CN): 4.3 (CH_3CN), 12.8 and 20.0 ($CH_3C{\equiv}CCH_3$), 101.1 (C_5H_5), 139.1 (CH_3CN), 160.4 and 180.3 ($CH_3C{\equiv}CCH_3$).

Observation of $[W(C_5H_5)(CH_3CN)(2\text{-butyne})_2]PF_6$ (9b). A solution of $[W(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ (0.05 g, 0.000 09 mol) in CH_3CN (0.3 mL) was sealed in an NMR tube under N_2 (1 atm). The sample was heated at 130 °C for 2 days, after which time the complex was 77% converted to a new compound which was assigned the structure $[W(C_5H_5)(CH_3CN)(2\text{-butyne})_2]PF_6$. ^1H NMR (CH_3CN): δ 5.73 (s, 5 H, C_5H_5), 2.96 (s, 6 H, $CH_3C{\equiv}CCH_3$), 2.84 (s, 3 H, CH_3CN), and 2.51 (s, 6 H, $CH_3C{\equiv}CCH_3$). IR (CH_3CN): no carbonyl bands.

After the sealed sample was heated for 4 days at 130 °C, the starting material had converted 100% to the acetonitrile complex.

Exchange of Acetylene on $[Mo(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$. To $[Mo(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ (0.05 g, 0.000 11 mol) in CD_3CN (0.3 mL), at 20 °C under N_2, was added 2-pentyne [(a) ~30, (b) ~60, and (c) ~110 μL, i.e., Mo:pentyne ratios of (a) 1:2.9, (b) 1:5.8, and (c) 1:10.6 by NMR integration]. Although the C_5H_5 resonances of the different possible bisacetylene complexes were not distinguishable by NMR, both methyl groups of complexed pentyne ($CH_3C{\equiv}CCH_2CH_3$) were, and could be integrated relative to free pentyne. Integration showed that [complexed pentyne]:[complexed butyne] was approximately the same as [total pentyne]:[total butyne] in the solution. Spectra taken within 15-20 min of sample preparation did not change further with time.

$[Mo(C_5H_5)(CO)(2\text{-butyne-}d_6)_2]PF_6$ (6a-d_6). A solution of $[Mo(C_5H_5(CO)(2\text{-butyne})_2]PF_6$ (0.7 g, 0.001 58 mol), $N(CH_2CH_3)_3$ (0.3 mL, 0.0022 mol), and acetone-d_6 (6 mL, 0.072 mol) was stirred at 25 °C for 1 day. Volatiles were removed under vacuum and the residues were washed with methanol (2 × 3 mL), then dried under vacuum, yield of yellow crystals 0.7 g. IR (KBr): no peaks between 2800 and 3000 cm^{-1}, ν_{CD} 2210, ν_{CO} 2040 cm^{-1}. ^1H NMR (CD_3CN): δ 5.39 (C_5H_5) ppm.

Catalytic Deuteration of 2-Butyne. A solution of 2-butyne (0.18 mL, 0.0022 mol), $N(CH_2CH_3)_3$ (0.09 g, 0.0009 mol), $[Mo(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ (0.025 g, 0.000 05 mol), and acetone-d_6 (0.4 mL, 0.005 mol) was monitored by NMR. Over time the peak due to 2-butyne decreased, with a corresponding increase in the peak due to acetone. Within 4 h at 30 °C, 2-butyne in solution was 50% deuterated (i.e., approximate equilibrium). Free 2-butyne in solution was taken to >90% deuteration by addition of further acetone-d_6 (1.6 mL, 0.02 mol) and warming the solution at 45 °C for 1 day.

$Mo(C_5H_5)(CO)(2\text{-butyne})(OCH_3)$ (13a). To $[Mo(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ (0.5 g, 0.0011 mol) was added a solution of sodium methoxide, prepared by reacting Na (0.025 g, 0.0011 mol) with methanol (15 mL) at 25 °C. An immediate color change to deep purple was observed. After the solution had stirred for 30 min, diethyl ether (15 mL) was added and the solution was filtered. The filtrate was stripped to dryness and the residues were redissolved in diethyl ether. Removal of ether at −78 °C gave very air-sensitive purple residues which were solid but became oily on warming to room temperature. IR (benzene): ν_{CO} 1870 cm^{-1}. ^1H NMR (benzene-d_6): δ 5.21 (s, 5 H, C_5H_5), 4.35 (s, 3 H, OCH_3), 2.82 and 2.77 (both s, both 3 H, $CH_3C{\equiv}CCH_3$). ^{13}C NMR (CD_3CN): 15.8, 19.5 (CH_3) 72.8 (OCH_3), 97.7 (C_5H_5), 175.5 and 168.7 ($CH_3C{\equiv}CCH_3$), 234.1 (CO) ppm. [When the reaction was followed by NMR, 1 equiv of free 2-butyne (δ 1.71) was observed as product also. Addition of CD_3OD to solutions (e.g., benzene as solvent of $Mo(C_5H_5)(CO)(OCH_3)$(2-butyne) resulted in immediate exchange of methoxide at 25 °C evidenced by loss of the peak due to coordinated methoxide in the NMR; similarly addition of CH_3OH to solutions of $Mo(C_5H_5)(CO)(OCD_3)$(2-butyne) resulted in immediate appearance of a coordinated methoxide peak in the NMR at 25 °C.]

$W(C_5H_5)(CO)(2\text{-butyne})(OCH_3)$ (13b). The procedure described for the molybdenum analogue was followed, using $[W(C_5H_5)(CO)(2\text{-butyne})_2]PF_6$ (0.58 g, 0.0011 mol). The reaction mixture was stirred overnight at 25 °C, giving a deep red solution, and the product (a reddish oil) was isolated as for the molybdenum complex. IR (CH_3OH): ν_{CO} 1890 cm^{-1}. ^1H NMR (benzene-d_6): δ 5.22 (s, 5 H, C_5H_5), 4.27 (s, 3 H, OCH_3) 3.01 and 2.91 (both s, both 3 H, $CH_3C{\equiv}CCH_3$).

Reaction of $[Mo(C_5H_5)(CH_3CN)(2\text{-butyne})_2]PF_6$ with CO. A solution of $[Mo(C_5H_5)(CH_3CN)(2\text{-butyne})_2]PF_6$ (**9a**, 0.045 g, 0.0001 mol) in THF-d_8 (0.3 mL) was sealed in an NMR tube under CO (1-1.5 atm). The sample was heated at 70 °C and monitored by NMR. After 35 min at 70 °C, ~50% of **9a** had been converted to **6a**. The sample was heated at 90 °C for a further 30 min and the reaction went to completion. On cooling to 25 °C, **6a** crystallized from the solution.

Acetonitrile Exchange on $[Mo(C_5H_5)(CH_3CN)(2\text{-butyne})_2]PF_6$. A solution of $[Mo(C_5H_5)(CH_3CN)(2\text{-butyne})_2]PF_6$ (0.045 g, 0.0001 mol) in CD_3CN (0.3 mL) was sealed in an NMR tube under nitrogen, and was observed by NMR at 50-60 °C. The resonance at δ 2.81 (coordinated acetonitrile) decreased by 50% over 30 min at 50 °C. After a further 15 min at 60 °C the peak was completely gone. Correspondingly the signal due to solvent increased. (Exchange of coordinated acetonitrile was not observed over 1 day at 25 °C.) Solvent was removed and residues were rigorously dried on the vacuum line. The IR spectrum (KBr disk) of these residues showed a peak at 220 cm^{-1} due to coordinated CD_3CN.

Variable-Temperature NMR Experiments. All temperatures were measured using a calibrated ethylene glycol standard, inserted in the probe before and after each sample measurement. Samples were equilibrated in the probe for 15 min before recording spectra. Line-shape calculations[11] were made with a Fortran program on the Data General Corp. Nova computer. Free energies of activation were calculated from rate constants by the absolute rate theory.[16]

(1) Aliquots (3 × 0.3 mL) of a solution of **6a** (0.80 g, 0.000 18 mol) in CD_3CN (1 mL) were sealed in NMR tubes: (a) under 1 atm N_2, (b) under 1 atm CO, (c) with 2-butyne (3.6 equiv based on Mo) under N_2. NMR spectra were recorded at 111 °C. The methyl groups at δ 2.99 and 2.72 (at 25 °C) had coalesced; the rates of exchange (based on line-shape analysis assuming a simple two-site exchange, $\Delta\nu$ = 25 Hz and natural line width of 2 Hz) were (a) 80, (b) 80, and (c) 25 s^{-1}.

(2) Aliquots (4 × 0.3 mL) of a solution of **1b** (0.177 g, 0.0002 mol) in CD_3CN (1.2 mL) were sealed in NMR tubes: (a) under 1 atm N_2, (b) under 1 atm CO, (c) with 2-butyne (6.5 equiv based on W) under N_2, and (d) with 2-butyne (12.8 equiv based on W) under N_2. Coalescence of the methyl groups in (a) was reached at 135 °C. At 140 °C, the rates of exchange of the methyl groups were (a) 65, (b) 65, (c) ~25, (d) 1-10 s^{-1}. A natural line width of 2 Hz and $\Delta\nu$ = 21 Hz were used; simple two-site exchange was assumed.

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