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Molybdenum(II) and Tungsten(II) $M(CO)(RC_2R')L_2X_2$ Alkyne Complexes

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A series of molybdenum and tungsten alkyne complexes, $M(CO)(RC_2R')L_2X_2$ (various combinations of M = Mo, W; L = PPh_3, PEt_3, py; L_2 = dppe ($Ph_2PCH_2CH_2PPh_2$); X = Cl, Br), has been prepared by treating $M(CO)_nL_2X_2$ (n = 2 or 3) reagents with free alkyne. Nuclear magnetic resonance, infrared, and electronic absorption spectroscopies have been used to probe the metal–alkyne bonding interaction. Both ^1H and ^{13}C NMR chemical shift values for the alkyne ligands are compatible with a "four-electron" donor description for the alkyne ligands in these complexes. Dynamic NMR studies of complexes containing 2-butyne revealed metal–alkyne rotational barriers ranging from 9 to 13 kcal/mol. The structure of $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$ has been determined and refined to R = 0.048 and R_w = 0.035 using 1660 reflections [monoclinic, $P2_1/n$; a = 7.995 (3) Å, b = 14.559 (4) Å, c = 22.209 (10) Å; β = 98.04 (3)°; Z = 4]. The molecule adopts a distorted octahedral geometry with the alkyne cis and parallel to the carbon monoxide ligand. The phosphine ligands are mutually trans with the bromides cis. Strong metal–alkyne bonding is evident in the short M–C distances (1.99-Å average). The molecule possesses effective C_s symmetry with Mo, Br1, Br2, CO, and the entire alkyne, including the phenyl substituent, defining the mirror plane.

Introduction

An important aspect of the abundant alkyne chemistry which is unfolding for molybdenum and tungsten is the dual π-acid and π-base role simultaneously fulfilled by alkyne ligands in early transition-metal monomers.[1] Recognition of variable electron donation to the metal from the filled alkyne $\pi_\perp$ orbital has supplemented the classical Dewar–Chatt–Duncanson model of olefin bonding.[2] It is the additional donation of electron density from the second filled π-orbital of the alkyne that accounts for the stability of formally electron deficient complexes such as $(\pi\text{-}C_5H_5)M(CO)_2(PhC_2Ph)$ (M = V, Nb, Ta),[3] $Mo(TPP)(PhC_2Ph)$,[4] $[(\pi\text{-}C_5H_5)Mo(CO)L(RC_2R)][BF_4]$,[5] $(\pi\text{-}C_5H_5)W(CO)Me(RC_2R)$,[6] $(\pi\text{-}C_5H_5)M(CO)X(PhC_2Ph)$,[7] $(\pi\text{-}C_5H_5)M(CO)(SR)(CF_3C_2CF_3)$,[8] $M(CO)(RC_2R)(S_2CNR_2)_2$ (M = Mo,[9] W[10]), and $[Co(PhC_2Ph)(PMe_3)_3][BF_4]$.[11] In complexes containing an alkyne ligand and additional π-donor ligands (e.g., RC_2R, O^{2-}, RS^-) the set of π-donor ligands compete with one another for vacant metal $d\pi$ orbitals: $(\pi\text{-}C_5H_5)M(CO)(PhC_2Ph)_2$ (M = V, Nb, Ta),[12] $(\pi\text{-}C_5H_5)M(RC_2R)_2X$ (M = Mo, X = Cl, R = CH_2OH;[13] M = Mo, W, X, = Cl, Br, I, R = CF_3;[14] M = Mo, W, X = CO^+, R = CH_3[15]), $Mo(RC_2R)_2(S_2CNR'_2)_2$,[9,16] $W(CO)(RC_2R)_3$,[17] $[W(RC_2R)_3SnPh_3]^-$,[18] $M(O)(RC_2R)(S_2CNR'_2)_2$ (M = Mo,[19] W[20]), $W(S)(PhC_2Ph)(S_2CNR'_2)_2$,[21] and $Mo(CN\text{-}t\text{-}Bu)_2(RC_2R)(S\text{-}t\text{-}Bu)_2$.[22] The degree of $\pi_\perp$ donation as described in molecular orbital terms can be considered to span a continuum from two-electron donor alkyne ligands at one extreme to four-electron donors at the other.[23]

We have synthesized molybdenum and tungsten monocarbonylalkyne derivatives of the type $M(CO)(RC_2R)L_2X_2$ for a variety of alkynes and neutral ligands.[24] Davidson and Vasapollo communicated work with analogous tungsten complexes, $W(CO)(RC_2R)L_2Br_2$, with phosphines, phosphites, and isocyanides as the neutral ligands.[25] A very nice full paper has recently provided additional details of these studies.[26] Related tungsten dicarbonyl alkyne derivatives of the type $W(CO)_2(RC_2R)I_2L$ (L = PMe_3, $AsMe_3$, CN-t-Bu) were reported by Umland and Vahrenkamp in 1982.[27] Another recent relevant report is that of Bennett and Boyd, who prepared

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cyclooctyne (C_8H_{12}) complexes of molybdenum and tungsten including $M(CO)(C_8H_{12})(PEt_3)_2Br_2$ (M = Mo, W) as well as $M(CO)(C_8H_{12})(S_2CNR_2)_2$, $MX_2(C_8H_{12})(S_2CNR_2)_2$, and $Mo(O)(C_8H_{12})(S_2CNR_2)_2$.[28]

Experimental Section

Materials and Procedures. All manipulations were performed under an atmosphere of prepurified nitrogen gas using standard Schlenk techniques. Solvents were purged with a nitrogen stream prior to use. Molybdenum and tungsten hexacarbonyls, phosphines, pyridine, chlorine, bromine, carbon monoxide, and alkynes were obtained from commercial sources and used as received. $M(CO)_3(PPh_3)_2Cl_2$ (M = Mo, W),[29] $Mo(CO)_2(py)_2Cl_2$,[30] $Mo(CO)_3(dppe)X_2$ (X = Cl, Br),[31] and $Mo(CO)_4(PEt_3)_2$[32] were prepared according to literature procedures.

Physical Measurements. NMR spectra were recorded with a Bruker 250 spectrometer (^{1}H, 250 MHz; ^{13}C, 62.3 MHz; ^{31}P, 101 MHz) or on a Varian XL-100 (^{1}H). NMR samples were degassed through several freeze–evacuate–thaw cycles prior to sealing in vacuo. Chemical shifts are reported as parts per million downfield relative to Me_4Si for both ^{1}H and ^{13}C signals while ^{31}P are reported relative to an external H_3PO_4 standard. Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer as either solids in KBr pellets or as solutions in matched 0.10-mm NaCl cells; spectra were calibrated with a polystyrene reference. Electronic absorption spectra were recorded by using 1.0-cm cells and a Perkin-Elmer 552 spectrophotometer. Cyclic voltammograms were obtained with samples in acetonitrile (Burdick and Jackson) or methylene chloride solutions containing 0.10 M $[(n\text{-}C_4H_9)_4N][ClO_4]$ as supporting electrolyte. A platinum bead served as the working electrode with a platinum wire as the auxiliary electrode. Potentials are reported relative to the saturated sodium chloride calomel electrode (SSCE) and are uncorrected for junction potential effects. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Syntheses. $Mo(CO)_3(PEt_3)_2Br_2$ (1). A solution of $Mo(CO)_4(PEt_3)_2$ (1.72 g, 3.87 mmol) in CH_2Cl_2 was titrated with a dilute stock solution of bromine in CH_2Cl_2 at room temperature. Reaction progress was monitored by infrared solution sampling techniques between 1600 and 2200 cm^{-1}. The bromine addition was stopped when only the three strong CO absorptions of $Mo(CO)_3(PEt_3)_2Br_2$ were observed after the solution was flushed with CO gas to convert any dicarbonyl that had formed to the desired tricarbonyl derivative. Solvent removal in vacuo produced an oil which yielded a green powder when triturated with hexanes. Treatment of the green solid, a mixture of **1** (yellow) and $Mo(CO)_2(PEt_3)_2Br_2$ (**2**, blue), with carbon monoxide produced pure $Mo(CO)_3(PEt_3)_2Br_2$ (**1**) (1.85 g, 3.22 mmol, 83%): IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2020 s, 1951 s, 1912 m; IR (KBr, cm^{-1}) ν_{CO} 2015 s, 1941 s, 1904 s.

$Mo(CO)_2(PEt_3)_2Br_2$ (2). A solution of **1** in CH_2Cl_2 was boiled for 4 h to form a blue solution of **2**. The volume of solvent was reduced prior to adding Et_2O to precipitate $Mo(CO)_2(PEt_3)_2Br_2$ as deep blue crystals in very high yield: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1949 m, 1869 s; IR (KBr, cm^{-1}) ν_{CO} 1925 m, 1850 s.

$Mo(CO)(PhC_2H)(PEt_3)_2Br_2$ (3). In a representative reaction **2** (2.12 g, 3.87 mmol) was dissolved in CH_2Cl_2 (50 mL) and a threefold excess of phenylacetylene was added. When the deep blue solution was heated for 28 h, a dark green-brown color was present. The solution was allowed to cool, and solvent was removed under vacuum to leave a dark brown residue. A dark oil was washed away with cold Et_2O (0 °C), and the remaining tan solid was then treated with warm Et_2O which solubilized the product. The extractions were continued until the Et_2O supernatant was colorless; the solutions collected were then combined, and partial solvent removal yielded forest green crystals of **3** (1.20 g, 1.93 mmol, 50%). Analytically pure $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$ was obtained by cooling a saturated toluene solution to −30 °C: ^{1}H NMR (CD_2Cl_2) δ 13.00 (s, 1 H, HC≡), 8.35 (m, 2 H, Ph), 7.48 (m, 3 H, Ph), 1.53 (m, 12 H, CH_3CH_2P), 0.78 (m, 18 H, CH_3CH_2P); ^{13}C NMR (CD_2Cl_2) δ 230.9 (br s, CO), 224.8 (dt, $^1J_{CH}$ = 204 Hz, $^2J_{CP}$ = 5 Hz, HC≡), 224.7 (q, $^2J_{CH}$ = 5 Hz, $^2J_{CP}$ = 5 Hz, PhC≡); ^{31}P NMR ($CDCl_2$) δ 10.0 (s, PEt_3); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1950; IR (KBr, cm^{-1}) ν_{CO} 1946. Anal. Found (Calcd): C, 40.45 (40.53); H, 5.89 (5.84); Br, 25.97 (25.68); Mo, 15.05 (15.42).

$Mo(CO)(MeC_2Me)(py)_2Cl_2$ (4). A solution of $Mo(CO)_2(py)_2Cl_2$ (0.50 g, 1.31 mmol) in CH_2Cl_2 (30 mL) was treated with excess 2-butyne (0.50 mL, 0.35 g, 6.4 mmol). When the solution was heated to reflux for 30 min, the original yellow color was replaced by a deep green. After being heated for an additional 30 min, the solution was cooled to room temperature and filtered to remove a gray flocculent material. Reduction of the solution volume to 10 mL and cooling to −30 °C yielded dark blue-green crystals of $Mo(CO)(MeC_2Me)(py)_2Cl_2$ (**4**) (0.43 g, 1.06 mmol, 80%): ^{1}H NMR (CD_2Cl_2) δ 8.58 (m, 4 H, *o*-py), 7.68 (m, 2 H, *p*-py) 7.32 (4 H, *m*-py), 3.38 (s, 6 H, Me); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1937; IR (KBr, cm^{-1}) ν_{CO} 1916. Anal. Found (Calcd): C, 43.94 (44.24); H, 3.99 (3.97); Cl, 17.41 (17.41).

$Mo(CO)(MeC_2Me)(PEt_3)_2X_2$ (X = Cl (5); X = Br (6)). Both compounds were prepared by analogous procedures. The synthesis of **6** resulted from the addition of 2-butyne (1.0 mL, 0.70 g, 13 mmol) to **2** (0.55 g, 1.0 mmol) in 30 mL of 2:1 Et_2O/CH_2Cl_2. The solution was boiled for 18 h, cooled, filtered, and reduced to a greenish brown residue. Washing with Et_2O removed an orange oil from the desired light green product. Recrystallization from toluene yielded pure $Mo(CO)(MeC_2Me)(PEt_3)_2Br_2$ (**6**) as green prisms: ^{1}H NMR (CD_2Cl_2) δ 3.18 (s, 6 H, Me), 1.51 (m, 12 H, CH_3CH_2P), 0.87 (m, 18 H, CH_3CH_2P); ^{13}C NMR (CD_2Cl_2 at −50 °C) δ 237.4 (t, $^2J_{CP}$ = 6 Hz, MeC≡), 231.3 (t, $^2J_{CP}$ = 9 Hz, CO), 229.3 (t, $^2J_{CP}$ = 5 Hz, CMe), 22.56 and 22.49 (s, $CH_3C_2CH_3$); ^{31}P NMR (CD_2Cl_2) δ 9.1 (s, PEt_3); ^{31}P NMR ($CDCl_2$, at −90 °C) δ 9.8 (s, PEt_3); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1939 s, $\nu_{C\equiv C}$ 1645 vw; IR (KBr, cm^{-1}) ν_{CO} 1926. **5**: ^{1}H NMR (CD_2Cl_2) δ 3.20 (t, $^4J_{HP}$ = 1.4 Hz, $CH_3C_2CH_3$); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1943 s, $\nu_{C\equiv C}$ 1645 vw; IR (KBr, cm^{-1}) ν_{CO} 1922. Anal. Found (Calcd): C, 35.90 (35.56); H, 6.51 (6.33); Br, 27.59 (27.83).

$Mo(CO)(R^1C_2R^2)(PEt_3)_2Br_2$ ($R^1 = R^2$ = Ph (7); $R^1 = R^2$ = Et (8); R^1 = H, R^2 = *n*-Bu (9)). The preparation of **8** and **9** is analogous to that described for 7. Diphenylacetylene (0.64 g, 3.6 mmol) was added to a deep blue solution of **2** (1.65 g, 3.0 mmol) in 1,2-dichloroethane (40 mL). After the solution was heated vigorously for 3 h, the solvent was evaporated under vacuum to leave a viscous residue. An orange oil was removed from the residual material by washing with hexanes; the desired product 7 remained as a yellow-green solid (1.62 g, 2.32 mmol, 77%). 7: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1951; IR (KBr, cm^{-1}) ν_{CO} 1942. 8: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1939. **9**: ^{1}H NMR ($CDCl_3$) δ 13.68 (s, 1 H, HC≡); IR (1,2-$ClCH_2CH_2Cl$, cm^{-1}) ν_{CO} 1944. Anal. Found (Calcd): C, 46.44 (46.43); H, 6.18 (5.78); Br, 22.68 (22.80).

$Mo(CO)(RC_2R)(PPh_3)_2X_2$ (X = Cl, R = Me (10); X = Cl, R = Et (11); X = Br, R = Me (12)). The preparations of **11** and 12 are analogous to that of **10**. An excess of 2-butyne (1.0 mL, 0.70 g, 13 mmol) was added to a suspension of $Mo(CO)_3(PPh_3)_2Cl_2$ (2.0 g, 2.58 mmol) in CH_2Cl_2 (30 mL). The suspension was boiled for 8 h during which time the solid $Mo(CO)_3(PPh_3)_2Cl_2$ reagent slowly dissolved and reacted. After cooling, a small amount of blue-gray precipitate was removed by filtration. The filtrate was evaporated to dryness and then washed with Et_2O (3 × 10 mL) to remove an orange byproduct. Recrystallization of the remaining light green solid from CH_2Cl_2/Et_2O yielded green plates of $Mo(CO)(MeC_2Me)(PPh_3)_2Cl_2$ (**10**) (0.65 g, 0.84 mmol, 33%): ^{1}H NMR (CD_2Cl_2) δ 7.72–7.32 (m, 30 H, Ph), 2.42 (t, 6 H, $^4J_{HP}$ = 1.6 Hz, $CH_3C_2CH_3$); ^{13}C NMR ($CD_2Cl_2/CDCl_3$, 3:2) δ 240.0 (s, MeC_2Me) 228.6 (t, $^2J_{CP}$ = 9 Hz, CO), 22.6 (s, $CH_3C_2CH_3$); ^{31}P NMR (CD_2Cl_2) δ 18.5 (s, PPh_3); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1956 s, $\nu_{C\equiv C}$ 1670 vw; IR (KBr, cm^{-1}) ν_{CO} 1937. 11: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1946. **12**: IR (CH_2Cl_2 cm^{-1}) ν_{CO} 1950. Anal. Found (Calcd): C, 56.83 (57.09); H, 4.46 (4.22); Br, 18.76 (18.53).

$Mo(CO)(R^1C_2R^2)(dppe)Cl_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$; R^1 = H, R^2 = *n*-Bu (13); $R^1 = R^2$ = Me (14); $R^1 = R^2$ = Et (15)). The preparation of **13** is representative of the route used for the three alkyne complexes above. A yellow-orange dichloroethane

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(30-mL) slurry of $[Mo(CO)_2(dppe)_{1.5}Cl_2]_2$ (0.48 g, 0.29 mmol) was treated with excess 1-hexyne (0.50 mL, 0.36 g, 4.4 mmol) and heated to reflux for 45 min. The solution color changed from orange to deep green during this time. Cooling and solvent evaporation left an oil which was dissolved in hot toluene. Precipitation of the product was induced by cooling and adding Et_2O. The green crystals of $Mo(CO)(HC_2\text{-}n\text{-}Bu)(dppe)Cl_2$ were washed repeatedly with Et_2O to remove any free dppe. Products **14** and **15** were less soluble than **13** and precipitated from the 1,2-dichloroethane reaction solution as blue powders. They were isolated and washed extensively with Et_2O. **13**: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1981; IR (KBr, cm^{-1}) ν_{CO} 1971. **14**: ^1H NMR (CD_2Cl_2) δ 3.11 (s, 3 H, $CH_3C_2CH_3$), 1.56 (s, 3 H, $CH_3C_2CH_3$); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1970; IR (KBr, cm^{-1}) ν_{CO} 1963. **15**: ^1H NMR (CD_2Cl_2) δ 1.28 (t, 3 H, $CH_3CH_2C\equiv$), 0.38 (t, 3 H, $\equiv CCH_2CH_3$); ^{31}P NMR (CD_2Cl_2) δ 47.5 (s, P_A), 23.94 (s, P_B); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1977; IR (KBr, cm^{-1}) ν_{CO} 1946; IR (Nujol, cm^{-1}) $\nu_{C\equiv C}$ 1671 vw. Anal. Found (Calcd): C, 58.22 (58.68); H, 5.14 (5.08); Cl, 10.63 (10.50).

$Mo(CO)(R^1C_2R^2)(dppe)Br_2$ (R^1 = H, R^2 = *n*-Bu (16); R^1 = R^2 = Et (17); R^1 = H, R^2 = Ph (18); R^1 = R^2 = Ph (19)). Compounds **16–19** were prepared as described above for $Mo(CO)(HC_2\text{-}n\text{-}Bu)(dppe)Cl_2$ (**13**) except that $Mo(CO)_3(dppe)Br_2$ was used as the metal reagent. **16**: ^1H NMR ($CDCl_3$) δ 10.76 (dd, 1 H, $^3J_{HP_A}$ = 20 Hz, $^3J_{HP_B}$ = 4 Hz, major isomer, $HC\equiv$), 10.68 (dd, minor isomer, $HC\equiv$), 8.0–6.0 (m, 20 H, Ph), 4.0–3.0 (m, 4 H, PCH_2CH_2P), 2.72 (m, 2 H, CCH_2), 1.6–1.2 (m, 4 H, $C_2CH_2(CH_2)_2CH_3$), 0.84 (t, 3 H, CH_2CH_3); ^{13}C NMR ($CDCl_3$), major isomer, δ 220.5 (dd, $^2J_{CP_A}$ = 58 Hz, $^2J_{CP_B}$ = 7 Hz, CO), 218.1 (br s, $\equiv C$-*n*-Bu), 197.0 (ddd, $^1J_{CH}$ = 215 Hz, $^2J_{CP_A}$ = 22 Hz, $^2J_{CP_B}$ = 3 Hz, $\equiv CH$); minor isomer, δ 219.0 (dd, $^2J_{CP_A}$ = 58 Hz, $^2J_{CP}$ = 7 Hz, CO), 218.7 (s, $\equiv C$-*n*-Bu), 199 (m, $\equiv CH$); ^{31}P NMR ($CDCl_3$), major isomer, δ 43.7 (s, P_B), 28.9 (s, P_A); minor isomer, δ 48.7 (s, P_B), 31.3 (s, P_A); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1985; IR (KBr) ν_{CO} 1979. **17**: ^1H NMR (CD_2Cl_2) δ 1.32 (t, 3 H, $CH_3CH_2C\equiv$), 0.40 (t, 3 H, $\equiv CCH_2CH_3$); ^{31}P NMR (CD_2Cl_2) δ 42.3 (s, P_B), 20.5 (s, P_A); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1985; IR (KBr, cm^{-1}) ν_{CO} 1948; IR (Nujol, cm^{-1}) $\nu_{C\equiv C}$ 1625 vw. **18**: ^1H NMR (CD_2Cl_2), major isomer, δ 10.84 (dd, 1 H, $^2J_{HP_A}$ = 21 Hz, $^2J_{HP_B}$ = 5 Hz, $HC\equiv$), minor isomer, δ 10.78 (dd, $HC\equiv$); ^{13}C NMR ($CD_2Cl_2/CDCl_3$, 6:4), major isomer, δ 222.1 (dd, $^2J_{CP_A}$ = 59 Hz, $^2J_{CP_B}$ = 6 Hz, CO), 210.8 (s, *C*Ph), 201.3 (dd, $^2J_{CP_A}$ = 24 Hz, $^2J_{CP_B}$ = 10 Hz, $\equiv CH$), minor isomer, δ 221.7 (dd, $^2J_{CP_A}$ = 59 Hz, $^2J_{CP_B}$ = 6 Hz, CO), 212.0 (s, $\equiv CPh$), 203.4 (dd, $^2J_{CP_A}$ = 24 Hz, $^2J_{CP_B}$ = 10 Hz, $\equiv CH$); ^{31}P NMR (CD_2Cl_2), major isomer, δ 42.8 (d, $^2J_{P_AP_B}$ = 3 Hz, P_B), 30.2 (P_A), minor isomer, δ 47.9 (d, $^2J_{P_AP_B}$ = 4 Hz, P_B), 33.1 (P_A); IR (1,2-CH_2ClCH_2Cl, cm^{-1}) ν_{CO} 1995; IR (KBr, cm^{-1}) ν_{CO} 1979. **19**: IR (KBr, cm^{-1}) ν_{CO} 1990.

$W(CO)(R^1C_2R^2)(PEt_3)_2Cl_2$ (R^1 = R^2 = Ph (20); R^1 = H, R^2 = Ph (21)) and $W(CO)(MeC_2Me)(PPh_3)_2Cl_2$ (22). Yellow $W(CO)_3(PEt_3)_2Cl_2$ (2.37 g, 3.57 mmol) was dissolved in 60 mL of 1,2-dichloroethane, and diphenylacetylene (0.85 g, 4.8 mmol) was added. The solution was heated to reflux for 6 days, cooled, and filtered to remove an insoluble light blue byproduct. The volume of solvent was reduced to 10 mL, and addition of Et_2O precipitated additional impurities. Filtration produced a blue-green solution which was evaporated to an oil. Trituration with hexanes yielded the desired $W(CO)(PhC_2Ph)(PEt_3)_2Cl_2$ (**20**) product as a blue-purple solid (1.25 g, 1.59 mmol, 45%): IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1938; IR (KBr, cm^{-1}) ν_{CO} 1936. Preparation of **21** was similar, but only 1 day of heating was required: IR (1,2-CH_2ClCH_2Cl, cm^{-1}) ν_{CO} 1932. Formation of **22** required only 2 h of heating: ^1H NMR (CD_2Cl_2) δ 7.8–7.2 (m, 30 H, PPh_3), 2.44 (t, 6 H, $^4J_{HP}$ = 1.5 Hz, $CH_3C_2CH_3$); ^{31}P NMR (CD_2Cl_2) δ −10.6 (s, 14% d due to ^{183}W (I = $^1/_2$), $^1J_{PW}$ = 275 Hz); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1941; IR (KBr, cm^{-1}) ν_{CO} 1926.

^{13}CO Enrichment of 3 and 16. A green $CDCl_3$ solution of $Mo(CO)(HC_2Ph)(PEt_3)_2Br_2$ (**3**) was stirred under an atmosphere of 90% ^{13}CO at room temperature. An enrichment to approximately 10% ^{13}CO was achieved after 24 h as judged by infrared intensities. The same procedure for $Mo(CO)(HC_2\text{-}n\text{-}Bu)(dppe)Br_2$ (**16**) led to 20% enrichment after 5 h and 60% ^{13}CO incorporation after 24 h. $Mo(^{13}CO)(HC_2\text{-}n\text{-}Bu)(dppe)Br_2$ (**16***): ^{31}P NMR ($CDCl_3$) δ 43.7 (s, P_B), 28.9 (d, $^2J_{PC}$ = 58 Hz, P_A); IR ($CDCl_3$, cm^{-1}) $\nu_{^{12}CO}$ 1995, $\nu_{^{13}CO}$ 1949.

Collection of X-ray Diffraction Data for $Mo(CO)(HC_2Ph)(PEt_3)_2Br_2$ (3). A well-formed dark emerald green parallelpiped of approximate dimensions 0.30 × 0.40 × 0.40 mm was selected, mounted on a glass fiber, and coated with expoxy cement. Diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer.[33] Twenty-five reflections located in the region 30°<2θ<34° were centered, and angular data were refined by least-squares calculations. A monoclinic lattice system was indicated with cell constants as listed in Table I.

Table I. Crystallographic Data and Collection Parameters for $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$

mol formula	$C_{21}H_{36}Br_2MoOP_2$
fw	622.23
space group	$P2_1/n$
a, Å	7.995 (3)
b, Å	14.559 (3)
c, Å	22.209 (8)
β, deg	98.04 (3)
V, Å^3	2560 (2)
ρ(obsd) (in $CCl_4/CHBr_3$), g cm^{-3}	1.60
ρ(calcd), g cm^{-3}	1.614
Z	4
radiatn (wavelength)	Mo Kα (0.71073 Å)
μ, cm^{-1}	39.5
scan type	w/1.33θ
scan width	1.1° + 0.35 tan θ
bkgd scan	25% of full peak width on each side
scan range	1.0° ≤ θ ≤ 26.0°
quadrant collected	±h,+k,+l
no. of reflctns collected	4526
no. of data $I > 3\sigma(I)$	1660
no. of variables	248
largest parameter shift	0.26
largest residual electron density	0.29 e Å^{-3}
R	0.048
R_w	0.035
error in obsvn of unit wt	1.52

Diffraction data were collected in the quadrant (±h,+k,+l) under the conditions listed in Table I. Three reflections chosen as intensity standards were monitored every 5 h and showed no significant (<1.0%) decay. The crystal was checked every 300 reflections for recentering, which was necessary only when the scattering vectors varied by more than 0.15°. Psi scans of nine reflections having 80° < χ < 90° were used to calculate an empirical absorption correction. A total of 4526 unique reflections were collected in the region 2° < 2θ < 52°; the data were reduced and corrected for Lorentz–polarization effects.

Solution and Refinement of the Structure. Preliminary inspection of the diffraction data indicated systematic absences corresponding to $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ which define the monoclinic space group $P2_1/n$. An initial attempt to solve the structure with the heavy-atom technique from the Patterson map was unsuccessful. The space group assignment was eventually confirmed by successful determination of the structure through application of direct methods using the MULTAN package[34] and difference Fourier techniques. The molybdenum atom position was determined from an E-map and the rest of the non-hydrogen atoms were located in subsequent difference electron maps. The atomic positions were refined by using 1660 reflections with $F_o^2 > 3\sigma(R_o^2)$ and full-matrix least-squares refinement. Isotropic refinement of the 27 non-hydrogen atoms gave R = 0.091 and R_w = 0.098.[35] Allowing anisotropic motion and including the correction for absorption produced R = 0.058 and R_w = 0.048. At this point a difference Fourier map was featureless with a maximum peak of 0.29 e/Å^3. The terminal acetylenic hydrogen, H1, was found in this map. All other hydrogen positions were calculated (d_{C-H} = 0.95 Å) and fixed. The final refinement of 248 variables, which included isotropic

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[33] Programs utilized during data collection and structure solution and refinement were provided by Enraf-Nonius as part of the Structure Determination Package (SDP, 3rd ed., August 1978; revised June 1979).

[34] Germain, G.; Main, P.; Wolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368.

[35] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [2F_o/\sigma(F_o^2)]^2$ and $\sigma(F_o^2) = [\sigma^2(I) + \rho^2 I^2]^{1/2}$ with ρ assigned a value of 0.01. Expressions for the residuals are $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o - F_c|)^2/\sum w(F_o^2)]^{1/2}$.

movement for H1, converged when the largest parameter shift was 0.26 of the associated standard deviation with $R = 0.048$ and $R_w = 0.035$.

Results

Syntheses. The reaction of $Mo(CO)_3(PEt_3)_2Br_2$ (1) with alkynes to form complexes of the type $M(CO)(RC_2R)L_2X_2$ guided use of a number of $M(CO)_nL_2X_2$ reagents ($n = 2$ or 3; M = Mo or W). Synthesis of $Mo(CO)_3(PEt_3)_2Br_2$ has been reported as in Scheme I,[29] but we encountered low

Scheme I

$$Mo(CO)_6 + Br_2 \rightarrow Mo(CO)_4Br_2 + 2CO(g) \quad (1)$$

$$Mo(CO)_4Br_2 + 2PEt_3 \rightarrow Mo(CO)_3(PEt_3)_2Br_2 + CO(g) \quad (2)$$

yields (30%) in the first step, and the desired product 1 was difficult to separate from $Mo(CO)_6$, PEt_3, and oxidized molybdenum contaminants. An improved route to $Mo(CO)_3(PEt_3)_2Br_2$ is presented in Scheme II. The $Mo(CO)_4(PEt_3)_2$ reagent, prepared in large quantities from $Mo(CO)_4(pip)_2$,[32] can be stored in a drybox. Careful ox-

Scheme II

$$Mo(CO)_6 + 2 \text{ piperidine} \xrightarrow{\Delta} cis\text{-}Mo(CO)_4(pip)_2 + 2CO(g) \quad (3)$$

$$Mo(CO)_4(pip)_2 + 2PEt_3 \xrightarrow{\Delta} Mo(CO)_4(PEt_3)_2 + 2pip \quad (4)$$

$$Mo(CO)_4(PEt_3)_2 + Br_2 \rightarrow Mo(CO)_3(PEt_3)_2Br_2 + CO(g) \quad (5)$$

idation of $Mo(CO)_4(PEt_3)_2$ with a dilute solution of bromine in CH_2Cl_2, monitored by solution infrared spectroscopy in the CO region, generates an orange solution of 1.[36] Addition of methanol to the CH_2Cl_2 solution of 1 under a CO atmosphere followed by cooling yields yellow microprisms of 1. The CO atmosphere inhibits loss of CO which leads to a mixture of 1 and 2 and complicates the isolation procedure. The blue dicarbonyl 2 can be generated by boiling a CH_2Cl_2 solution of 1 for 4 h.

The substitution reactions summarized in Scheme III provided a general route to $M(CO)(RC_2R)L_2X_2$ complexes. Internal alkynes consistently produced high yields (>70%) while terminal alkynes led to low yields (<50%). Yields of phenylacetylene and 2-butyne complexes were low when high boiling solvents were refluxed, so hot CH_2Cl_2 solutions and long reaction times were used. With other alkynes molybdenum reagents generally led products in a few hours while tungsten reacted much more slowly. The qualitative rate of alkyne complex formation was (1) Cl > Br; (2) Mo > W; (3) $MeC_2Me > HC_2Ph > PhC_2Ph$, and (4) py > $PEt_3 \approx PPh_3$.

Scheme III

$$Mo(CO)_3L_2X_2 + R^1C_2R^2 \xrightarrow[\Delta]{CH_2Cl_2} Mo(CO)(R^1C_2R^2)L_2X_2 \quad (6)$$

L = PEt_3, PPh_3, py; X = Cl, Br; R^1 = H, R^2 = Ph or n-Bu; $R^1 = R^2 = CH_3$

$$M(CO)_3L_2X_2 + R^1C_2R^2 \xrightarrow[\Delta]{1,2\text{-}CH_2ClCH_2Cl} Mo(CO)(R^1C_2R^2)L_2X_2 \quad (7)$$

M = Mo, W; L = PEt_3, $^1/_2$dppe; X = Cl, Br; $R^1 = R^2$ = Ph, Et, Me; R^1 = H, R^2 = Ph or n-Bu

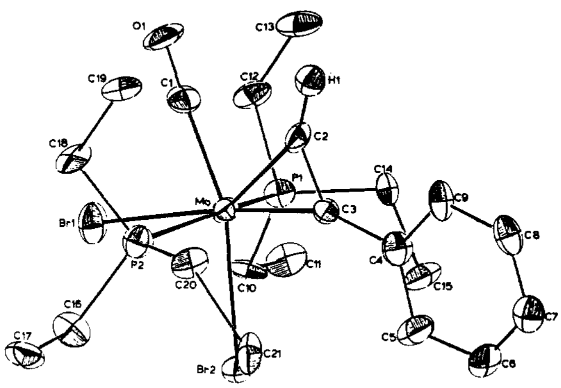

Figure 1. An ORTEP view of $Mo(CO)(PhC{\equiv}CH)(PEt_3)_2Br_2$ showing the atomic labeling scheme.

Table II. Atomic Positions for $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$

atom	x	ν_{CO},	z
Mo	0.0946 (1)	0.28071 (8)	0.36571 (4)
Br1	−0.0567 (2)	0.2733 (1)	0.46560 (5)
Br2	−0.2196 (1)	0.2620 (1)	0.30424 (5)
P1	0.0290 (4)	0.4512 (2)	0.3731 (2)
P2	0.0978 (4)	0.1076 (2)	0.3794 (1)
O1	0.392 (1)	0.2996 (6)	0.4706 (3)
C1	0.279 (1)	0.2921 (8)	0.4321 (5)
C2	0.311 (1)	0.2896 (8)	0.3313 (4)
C3	0.189 (1)	0.2835 (8)	0.2878 (5)
C4	0.178 (1)	0.2791 (8)	0.2182 (4)
C5	0.022 (1)	0.2814 (9)	0.1799 (5)
C6	0.021 (1)	0.2811 (9)	0.1177 (5)
C7	0.171 (1)	0.2744 (8)	0.0935 (5)
C8	0.321 (1)	0.2713 (9)	0.1303 (5)
C9	0.325 (1)	0.2751 (8)	0.1934 (4)
C10	−0.182 (1)	0.4816 (8)	0.3837 (5)
C11	−0.226 (2)	0.5828 (9)	0.3853 (6)
C12	0.159 (2)	0.5099 (9)	0.4358 (6)
C13	0.339 (2)	0.5244 (10)	0.4271 (6)
C14	0.072 (2)	0.5162 (9)	0.3076 (5)
C15	−0.054 (2)	0.5022 (9)	0.2520 (5)
C16	−0.097 (1)	0.0570 (8)	0.3945 (5)
C17	−0.113 (2)	−0.0458 (9)	0.3971 (6)
C18	0.249 (2)	0.0673 (9)	0.4412 (6)
C19	0.430 (2)	0.0749 (10)	0.4305 (6)
C20	0.157 (1)	0.0439 (8)	0.3158 (5)
C21	0.024 (2)	0.0429 (9)	0.2608 (6)
H1	0.45 (1)	0.289 (5)	0.339 (3)

[a] Numbers in parentheses are the estimated standard deviations of the coordinates and refer to the last significant digit(s) of the preceding number.

The relative ease of formation of the chelating dppe derivatives 16–19 was surprising in view of the reluctance of $Mo(CO)_3(dppe)Br_2$ to lose carbon monoxide. Nonetheless this reagent rapidly substitutes two carbonyl ligands with a single alkyne in refluxing dichloroethane to form $Mo(CO)(RC_2R)(dppe)Br_2$ products. All the alkyne complexes reported here are moderately air stable as solids. They are sensitive to oxidation in solution, particularly for 2-butyne or dppe derivatives.

We were unable to prepare the parent acetylene (HC_2H) analogues of any of these compounds. Iodo analogues of the chloride and bromide complexes also proved elusive. Disappearance of $M(CO)_3L_2I_2$ reagents was slow in the presence of free alkynes, and only decomposition products were characterized. Efforts to prepare $M(RC_2R)_2L_2X_2$ compounds by thermal substitution of the lone carbonyl in $M(CO)(RC_2R)L_2X_2$ complexes were uniformly unsuccessful.

Crystal Structure of $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$ (3). The molecular structure of 3 is depicted in Figure 1 where the atomic labeling scheme is presented. Atomic positional parameters are presented in Table II with in-

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[36] Moss, J. R.; Shaw, B. J. *J. Chem. Soc. A* **1970**, 595.

Table III. Intramolecular Bond Distances (Å) in $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$

Mo–Br1	2.673 (1)	C2–C3	1.27 (1)
Mo–Br2	2.700 (1)	C2–H1	1.10 (7)
Mo–P1	2.547 (3)	C3–C4	1.54 (1)
Mo–P2	2.538 (3)	C4–C5	1.41 (1)
Mo–C1	1.939 (10)	C5–C6	1.38 (1)
Mo–C2	1.988 (10)	C6–C7	1.38 (1)
Mo–C3	1.982 (9)	C7–C8	1.35 (1)
P1–C10	1.79 (1)	C8–C9	1.40 (1)
P1–C12	1.83 (1)	C9–C4	1.36 (1)
P1–C14	1.81 (1)	C10–C11	1.52 (1)
P2–C16	1.80 (1)	C12–C13	1.49 (2)
P2–C18	1.80 (1)	C14–C15	1.49 (1)
P2–C20	1.81 (1)	C16–C17	1.50 (1)
C1–O1	1.16 (1)	C18–C19	1.50 (2)
C1···C2	2.29 (1)	C20–C21	1.50 (2)
C1···H1	2.64 (7)		

Table IV. Intramolecular Bond Angles (deg) for $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$

Br1–Mo–Br2	85.4 (1)	Mo–P1–C10	117.1 (4)
Br2–Mo–P1	86.9 (1)	Mo–P1–C12	113.8 (4)
Br2–Mo–P2	87.3 (1)	Mo–P1–C14	113.2 (4)
Br2–Mo–C1	161.2 (3)	C10–P1–C12	103.3 (6)
Br–Mo–C2	127.5 (3)	C10–P1–C14	105.5 (5)
Br2–Mo–C3	90.1 (3)	C12–P1–C14	102.4 (6)
Br1–Mo–P1	82.2 (1)	Mo–P2–C16	115.8 (4)
Br1–Mo–P2	81.9 (1)	Mo–P2–C18	114.2 (4)
Br1–Mo–C1	75.9 (3)	Mo–P2–C20	114.6 (4)
Br1–Mo–C2	147.1 (3)	C16–P2–C18	103.4 (6)
Br1–Mo–C3	174.4 (3)	C18–P2–C20	102.0 (6)
P1–Mo–P2	163.5 (1)	C16–P2–C20	105.3 (5)
P1–Mo–C1	90.5 (4)	Mo–C1–O1	178.2 (9)
P1–Mo–C2	99.2 (3)	Mo–C1–C2	55.4 (4)
P1–Mo–C3	98.3 (3)	Mo–C2–C1	53.4 (3)
P2–Mo–C1	90.0 (4)	Mo–C2–C3	71.0 (6)
P2–Mo–C2	96.6 (4)	Mo–C3–C2	71.6 (6)
P2–Mo–C3	97.2 (4)	Mo–C3–C4	154.4 (7)
C1–Mo–C2	71.2 (4)	C2–C3–C4	134.0 (9)
C1–Mo–C3	108.6 (4)	C3–C4–C5	121.7 (9)
C2–Mo–C3	37.4 (3)	C4–C5–C6	118.7 (9)
P1–C10–C11	118.2 (8)	C5–C6–C7	120.6 (10)
P1–C12–C13	115.0 (9)	C6–C7–C8	120.6 (10)
P1–C14–C15	115.0 (8)	C7–C8–C9	119.9 (10)
P2–C16–C17	119.7 (8)	C8–C9–C4	120.3 (10)
P2–C18–C19	114.5 (9)		
P2–C20–C21	114.2 (8)		

tramolecular bond distances and angles listed in Tables III and IV. Although no crystallographic symmetry is imposed on the molecule, the observed structure has virtual C_s symmetry with the metal, carbon monoxide, both bromides, and the phenylacetylene ligand lying in the mirror plane.

The most salient features of the $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$ structure are as follows: (1) the alkyne parallel to the M–CO axis, (2) one alkyne carbon close to the carbonyl carbon, 2.29 Å, (3) the alkyne C–C distance, 1.27 Å, (4) the cis bent alkyne geometry, and (5) the distal and proximal locations of the phenyl and hydrogen alkyne substituents relative to the carbonyl ligand, respectively.

NMR Properties. Proton signals near 10.8 ppm characterized the acetylenic hydrogens of the dppe complexes $Mo(CO)(HC_2R)(dppe)X_2$. The resonance appeared as a doublet of doublets, indicating two distinct $^3J_{HP}$ coupling constants. Other terminal alkyne complexes, $M(CO)(HC_2R)L_2X_2$, exhibited acetylenic proton signals between 12.5 and 13.5 ppm with no $^3J_{HP}$ coupling.

Most of the 2-butyne complexes with monodentate phosphines exhibited $^4J_{HP}$ coupling constants of 1.5 Hz to the alkyne methyl protons. A single methyl signal at 3.18 ppm is observed at room temperature for $Mo(CO)(MeC_2Me)(PEt_3)_2Br_2$ (**6**), but upon cooling two distinct signals appear with a coalescence temperature (T_c) of 256 K. Similar averaging processes are observed for the 2-butyne derivatives **4**, **5**, **10**, and **22** as listed in Table V. Derivatives containing the chelating dppe ligand showed separate ^1H methyl signals for the two ends of the 2-butyne ligand in **14** and for the 3-hexyne ligand in **15** and **17**. Activation barriers, $\Delta G^{\ddagger}$, were extracted from the variable-temperature NMR data by using the Eyring equation after calculating k_{ex} at T_c from the Gutowsky–Holm equation.[37]

Table V. Rotational Barriers for 2-Butyne Complexes of Mo(II) and W(II)

complex	T_c, K	$\Delta\omega$, Hz	$\Delta G^{\ddagger}$	ref
$Mo(CO)(MeC_2Me)(PEt_3)_2Br_2$	256	18.4	13.0	this work
$Mo(CO)(MeC_2Me)(PEt_3)_2Cl_2$	215	5.0	11.4	this work
$Mo(CO)(MeC_2Me)(py)_2Cl_2$	189	33.0	9.3	this work
$Mo(CO)(MeC_2Me)(PPh_3)_2Cl_2$	208	132	9.6	this work
$W(CO)(MeC_2Me)(PPh_3)_2Cl_2$	191	16.4	9.6	this work
$W(CO)(MeC_2Me)(PPh_3)_2Br_2$			10.1	26
$W(CO)(MeC_2Me)(CNBu^t)_2Br_2$			11.8	26
$W(CO)(MeC_2Me)(S_2CNEt_2)_2$			11.1	55
$[(\pi\text{-}C_5H_5)Mo(MeC_2Me)(CO)(PEt_3)][BF_4]$	285	9	14.9	69
$[(\pi\text{-}C_5H_5)Mo(MeC_2Me)(CO)(PPh_3)][BF_4]$	268	81	12.8	69
$[(\pi\text{-}C_5H_5)Mo(MeC_2Me)(dppe)][BF_4]$	306	177	14.2	69

Carbon-13 NMR spectra of **3**, **6**, **10**, **14**, and **15** revealed acetylenic and carbonyl ^{13}C resonances in the range from 190 to 240 ppm. Gated decoupled spectra of $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$ and $Mo(CO)(HC_2\text{-}n\text{-}Bu)(dppe)Br_2$ allowed measurement of the alkyne $^1J_{CH}$ coupling constants of 204 and 215 Hz, respectively.

Phosphorus-31 NMR of $M(CO)(RC_2R)L_2X_2$ complexes **3**, **6**, **10**, and **22** exhibited a singlet for the two PEt_3 or PPh_3 ligands. The single ^{31}P resonance of $Mo(CO)(MeC_2Me)(PEt_3)_2Br_2$ (**6**) remained sharp when cooled to −90 °C. A $^1J_{WP}$ coupling constant of 275 Hz was measured for $W(CO)(MeC_2Me)(PPh_3)_2Cl_2$ (**22**).

The dppe derivatives differed distinctly from complexes containing monodentate phosphines as two distinct phosphorus environments were evident in ^{31}P spectra of $Mo(CO)(EtC_2Et)(dppe)X_2$ (X = Cl (**15**); X = Br (**17**)). Unsymmetrical alkyne derivatives, $Mo(CO)(RC_2H)(dppe)Br_2$ (R = *n*-Bu (**16**); R = Ph (**18**)), displayed an intense pair of singlets as well as a weak pair of singlets in the ^{31}P spectrum suggesting the presence of two isomers.

Infrared and Electronic Absorption Properties. Each alkyne complex isolated exhibits a strong infrared absorption between 1930 and 1995 cm^{-1} attributed to the lone carbon monoxide ligand. A weak absorption between 1620 and 1675 cm^{-1} was observed for a few complexes; presumably this normal mode has considerable C≡C character. $Mo(CO)(MeC_2Me)(dppe)Cl_2$ had a single strong absorption at 285 cm^{-1} while $Mo(CO)(MeC_2Me)L_2Cl_2$ complexes exhibited two absorptions attributable to Mo–Cl stretching modes (L = PEt_3, 339, 306 cm^{-1}; L = py, 347, 293 cm^{-1}).

A low-energy visible transition characterized all the alkyne complexes examined (Table VI). These transitions are between 14000 and 17000 cm^{-1} for the vivid green molybdenum compounds ($\epsilon \approx 10^2$ L mol^{-1} cm^{-1}). The four blue-purple tungsten complexes have higher energy absorptions (17000–18000 cm^{-1}).

Cyclic Voltammetry. Cyclic voltammograms of five molybdenum derivatives revealed a chemically reversible

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Table VI. Electronic Absorption and Electrochemical Data for $M(CO)(RC{\equiv}CR)L_2X_2$ Complexes

complex	λ_{max} (ϵ_{max})[a,b]	$E_{P/2}$(ox)[c]	$E_{P/2}$(red)[c]
$Mo(CO)_2(PPh_3)_2Cl_2$	17.76 (510)[a]		
$Mo(CO)_2(PEt_3)_2Br_2$(2)	17.61 (600)[a]		
$Mo(CO)(HC{\equiv}CPh)(PEt_3)_2Br_2$ (**3**)	15.02 (260)	0.87	−1.00
$Mo(CO)(MeC{\equiv}CMe)(py)_2Cl_2$ (**4**)	14.47 (130)	0.90	−1.18
$Mo(CO)(MeC{\equiv}CMe)(PEt_3)_2Cl_2$ (**5**)	16.61 (40)	0.87	−1.18
$Mo(CO)(MeC{\equiv}CMe)(PEt_3)_2Cl_2$ (**6**)	16.26 (50)	0.87	−1.18
$Mo(CO)(PhC{\equiv}CPh)(PEt_3)_2Br_2$ (**7**)	15.24 (170)[d]		
$Mo(CO)(MeC{\equiv}CMe)(PPh_3)_2Cl_2$ (**10**)	15.85 (50)	0.96	−1.19
$Mo(CO)(MeC{\equiv}CMe)(dppe)Cl_2$ (**14**)	16.05		
$Mo(CO)(EtC{\equiv}CEt)(dppe)Cl_2$ (**15**)	16.03		
$Mo(CO)(HC{\equiv}C\text{-}n\text{-}Bu)(dppe)Br_2$ (**16**)	15.27		
$Mo(CO)(EtC{\equiv}CEt)(dppe)Br_2$ (**17**)	15.75		
$Mo(CO)(HC{\equiv}CPh)(dppe)Br_2$ (**18**)	14.70 (100)		
$W(CO)(PhC{\equiv}CPh)(PEt_3)_2Cl_2$ (**20**)	17.12 (290)		
$W(CO)(HC{\equiv}CPh)(PEt_3)_2Cl_2$ (21)	17.09		
$W(CO)(MeC{\equiv}CMe)(PPh_3)_2Cl_2$ (**22**)	18.02		

[a] Transition energies in 10^3 cm^{-1}; extinction coefficients in L mol^{-1} cm^{-1}. [b] CH_2Cl_2 solution unless otherwise noted. [c] Volts vs. SSCE in CH_3CN/0.10 M $[(n\text{-}C_4H_9)_4N]ClO_4$. [d] In dichloroethane.

reduction wave between −1.0 and −1.2 V vs. SSCE (Table VI) as well as several irreversible oxidative waves. The half-wave potential for the onset of the first oxidation was typically around +0.9 V.

Discussion

Chemical Reactivity Patterns. Many $Mo(CO)_3L_2X_2$ complexes reversibly lose CO.[29,36] Ligand substitution reactions of $Mo(CO)_3L_2X_2$ reagents with anionic chelating ligands (quinolinates,[38] xanthates,[39] dithiophosphinates,[39] and dithiocarbamates[39]) have been reported. Replacement of one carbonyl ligand is facile for $Mo(CO)_3L_2X_2$ and probably reflects the more favorable CO to metal $d\pi$ electron ratio in the dicarbonyl d^4 products.[40] Substitution of a CO ligand in Mo(II) d^4 dicarbonyl compounds is more difficult, but $Mo(CO)L_4X_2$ complexes are accessible.[41]

In contrast to the above generalizations for two-electron donor ligands, addition of alkynes to $Mo(CO)_3(PEt_3)_2Br_2$ readily forms monocarbonyl $Mo(CO)(RC_2R)(PEt_3)_2Br_2$ products. The facility with which an alkyne replaces two CO ligands is consistent with its ability to act as a four-electron donor. Donation from the alkyne $\pi_\perp$ orbital destabilizes the $d\pi$ LUMO (lowest unoccupied molecular orbital) and accounts for the stability of these compounds.

Trends in the relative rate of product formation ($MeC_2Me > PhC_2H > PhC_2Ph$) are compatible with steric factors, although the 2-butyne is also electron-rich relative to the phenylalkynes. A similar rate dependence on alkynes was observed for formation of $(\pi\text{-}C_5H_5)Ta(RC_2R)X_2$ products.[42] The tungsten complexes $W(CO)(RC_2R)(PEt_3)_2Cl_2$ vary dramatically in this regard with 2 h adequate to form the 2-butyne derivative (**22**), 1 day for the PhC_2H product (**21**), and 6 days for PhC_2Ph to react completely (**20**). The halide trend (Cl > Br) is that usually seen (the lighter halide promotes CO loss),[43] and the lability of molybdenum carbonyls relative to tungsten is common.[44]

A plausible mechanism for formation of $M(CO)(RC_2R)L_2X_2$ products from $M(CO)_3L_2X_2$ reagents is presented in Scheme IV. Equation 8 is known for the phosphine complexes.[29,36] This scheme accounts for the tricarbonyl observed when pure dicarbonyl is reacted with alkyne since the CO released is scavenged by $Mo(CO)_2L_2X_2$. Reactions with alkyne are completely inhibited by 1 atm of carbon monoxide. One explanation for the enhanced rate of reaction when L = py is that loss of CO from $Mo(CO)_3(py)_2X_2$ is irreversible (eq 11).[30]

Scheme IV

$$M(CO)_3L_2X_2 \rightleftharpoons M(CO)_2L_2X_2 + CO(g) \tag{8}$$

$$M(CO)_2L_2X_2 + RC_2R \rightleftharpoons M(CO)_2(RC_2R)L_2X_2 \tag{9}$$

$$M(CO)_2(RC_2R)L_2X_2 \rightarrow M(CO)(RC_2R)L_2X_2 + CO(g) \tag{10}$$

$$Mo(CO)_3(py)_2X_2 \rightarrow Mo(CO)_2(py)_2X_2 + CO(g) \tag{11}$$

In contrast to the chemistry of $Mo(CO)(RC_2R)(S_2CNEt)_2$, where addition of CO gas produces $Mo(CO)_3(S_2CNEt_2)_2$ and free alkyne,[45] both $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$ and $Mo(CO)(HC_2\text{-}n\text{-}Bu)(dppe)Br_2$ retain the coordinated alkyne under 1 atm of carbon monoxide. Addition of ^{13}CO gas to solutions of these reagents leads to carbonyl exchange which is faster for the chelated dppe derivative than for the triethylphosphine complex.

Description of the Molecular Structure of $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$ (3). The inner coordination sphere of **3** can be considered to be octahedral with the alkyne viewed as a single ligand. Alternatively one can describe the structure as a pentagonal bipyramid with each alkyne carbon occupying an equatorial site (along with the two bromides and the carbonyl) while the phosphine ligands reside in the two axial positions. The Mo–Br (2.67, 2.70 Å) and Mo–P (2.54, 2.55 Å) distances are typical of Mo(II) complexes.[46]

The *cis*-$M(CO)(RC_2R)$ fragment with the alkyne parallel to the M–CO axis is common for octahedral d^4 monomers. This configuration, which optimizes both the π-donor and π-acceptor roles of the alkyne ligand, is found in $(\pi\text{-}C_5H_5)M(CO)(RC_2R)X$ (M = Mo, W),[7,8] $W(CO)(HC_2OAlCl_3)(PMe_3)_3Cl$,[47] and $M(CO)(RC_2R)(S_2CNR'_2)_2$[10] compounds. The three-center, two-electron interaction which stabilizes d_{xz} by mixing with both CO π^* and alkyne

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Table VII. ^1H and ^{13}C Chemical Shifts[a] for Selected Terminal Alkyne Molybdenum and Tunsten Complexes

complex	^1H δ (CH)	$^{13}C(RC\equiv CR')$	ref
$Mo(CO)(PhC_2H)(PEt_3)_2Br_2$	13.0	225, 225	this work
$Mo(CO)(PhC_2H)(S_2CNEt_2)_2$	12.6	209, 205	9, 56
$Mo(CO)(PhC_2H)(dppe)Br_2$	10.84	211, 201	this work
$Mo(PhC_2H)_2(S_2CNEt_2)_2$	10.39	183, 177	16, 56
$Mo(PhC_2H)(CN\text{-}t\text{-}Bu_2)(S\text{-}t\text{-}Bu)_2$	10.40	184, 172	22
$(\pi\text{-}C_5H_5)_2Mo(HC_2H)$	7.66	118	b, 56

[a] Ppm downfield from $Si(CH_3)_4$. [b] Thomas, J. L. *Inorg. Chem.* 1978, *17*, 1507.

$\pi_{\parallel}^{*}$[23] is manifest in the slippage of the alkyne toward the carbonyl ligand. The relatively short C1⋯C2 separation of 2.29 Å is consistent with a weak 3-c, 2-e attraction between these nominally noninteracting carbonyl and alkyne carbon atoms. In the limit one could recognize a metallacyclobutenone as a contributing resonance structure. The metallacyclobutene ring found in $(\pi\text{-}C_5H_5)_2TiCH_2CPh{=}CPh$[48] illustrates actual carbon–carbon bond formation between an alkyne and a carbene ligand. In this case one could consider the uncoupled cis carbene–alkyne parent geometry as a potential minor resonance form.

The alkyne C–C distance (1.27 Å) is relatively insensitive to the extent of donation from $\pi_{\perp}$ to the metal,[10,11] but the metal-to-alkyne carbon bond length does vary in response to the donor role of the alkyne. Consider $[Co(PhC_2Ph)L_3]^+$ and $[Co(PhC_2Ph)L_3(CH_3CN)]^+$ ($L = PMe_3$) where Co–C distances of 1.85 Å characterized the former, a "4-electron donor" alkyne, and Co–C distances of 1.98 Å are found for the latter, a "2-electron donor" alkyne ligand.[11] The Mo–C distances of 1.98 and 1.99 Å found in **3** are among the shortest reported to date for molybdenum alkyne complexes. The porphyrin complex characterized by Weiss formally counts to only 14 electrons (neglecting alkyne $\pi_{\perp}$ electron donation), and consequently the Mo–C alkyne distances in $Mo(PhC_2Ph)(TTP)$ (1.97 Å, average) reflect enhanced $\pi_{\perp}$ donation.[4] A representative 18-electron compound, without invoking $\pi_{\perp}$ donation, is $(\pi\text{-}C_5H_5)_2Mo(PhC_2Ph)$, where the alkyne carbons are 2.14 Å from the metal.[4,49] Other d^4 monocarbonyl alkyne derivatives with 4-electron alkyne donation exhibit M–C distances near 2.00 Å: $W(CO)(HC_2H)(S_2CNEt_2)_2$, 2.03 Å;[10] $(\pi\text{-}C_5H_5)Mo(CO)(CF_3C_2CF_3)(SC_6F_5)$, 2.03 Å,[8] and $W(CO)(HC_2OAlCl_3)(PMe_3)_3Cl$, 2.02 Å.[47] Slightly longer M–C distances are characteristic for formal 3-electron donor alkynes ($Mo(MeC_2Me)_2(S_2CNC_4H_4)_2$, 2.05 Å;[50] $(\pi\text{-}C_5H_5)W(CF_3C_2CF_3)_2Cl$, 2.06 Å[14]), and even longer metal–alkyne bonds are found when the alkyne competes with a cis oxide or sulfide π-donor ligand [$(\pi\text{-}C_5H_5)W(O)(PhC_2Ph)Ph$, 2.11 Å;[51] $(\pi\text{-}C_5H_5)Mo(O)(CF_3C_2CF_3)(SC_6F_5)$, 2.10 Å;[14] $Mo(O)(RC_2R)(S_2CNMe_2)_2$, $R = COC_6H_4Me$, 2.12 Å;[52] $W(S)(PhC_2Ph)(S_2CNEt_2)_2$, 2.08 Å[21]]. Comparison of both structural and spectral data (vide infra) for $M(CO)(RC_2R)L_2X_2$ and $M(CO)(RC_2R)(S_2CNEt_2)_2$ suggests that the alkyne contributes more electron density in the ML_2X_2 derivatives, consistent with the known π-donor capabilities of dithiocarbamate ligands.[53]

Table VIII. Comparative Electronic Absorption Data and ν_{CO} Vibrational Data for $M(CO)(RC_2R')(PEt_3)_2X_2$ and $M(CO)(RC_2R)(S_2CNEt_2)_2$

complex	λ_{max}, cm^{-1}	ν_{CO}, cm^{-1}
$Mo(CO)(MeC_2Me)(PEt_3)_2Br_2$	16300	1937
$Mo(CO)(MeC_2Me)(S_2CNEt_2)_2$	15200	1914
$Mo(CO)(PhC_2H)(PEt_3)_2Br_2$	15000	1950
$Mo(CO)(PhC_2H)(S_2CNEt_2)_2$	14300	1919
$W(CO)(PhC_2H)(PEt_3)_2Cl_2$	17200	1932
$W(CO)(PhC_2H)(S_2CNEt_2)_2$	16500	1925

Spectral Properties. The acetylenic ^1H[20,54] and ^{13}C[55] chemical shift values reported here are comparable to literature values for 4-electron donor alkyne ligands (see Table VII). The 10.8 ppm ^1H chemical shift of the acetylenic proton in $Mo(CO)(HC_2R)(dppe)Br_2$ (R = Ph, n-Bu) complexes is significantly higher than the 13.0 ppm region of other 4-electron donor complexes. Since the ^{13}C alkyne chemical shifts of the dppe derivatives are typical of 4-electron donors, it may be that the terminal alkyne hydrogen is located in the shielding cone of one of the phenyl rings of the chelating phosphine ligand.

An empirical correlation has been noted between ^{13}C alkyne chemical shifts, and the number of electrons the alkyne would need to donate to attain an inert-gas configuration at the metal.[56] The low-field chemical shifts of the $M(CO)(RC_2R)L_2X_2$ compounds suggest that the halides are poor π-donor ligands relative to dithiocarbamates, oxides, and sulfides. Data obtained for higher oxidation state complexes such as $[W(EtC_2Et)Cl_5]^-$ (δ 284)[57] support this conclusion.

The $^1J_{CH}$ coupling constant for $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$ is 204 Hz and leads to an estimated s character of $\rho = 0.41$[58] for the C–H bond, consistent with rehybridization toward sp^2 upon ligation to the metal. These $^1J_{CH}$ alkyne coupling constants are generally insensitive to the oxidation state of the metal and the identity of the ancillary ligands: $Mo(CO)(HC_2\text{-}n\text{-}Bu)(dppe)Br_2$, 215 Hz; $Mo(CO)(HC_2Ph)(S_2CNEt_2)_2$, 215 Hz; $Mo(HC_2Ph)_2(S_2CNMe_2)_2$, 212 Hz;[16] $W(CO)(HC_2OAlCl_3)(PMe_3)_3Cl$, 203 Hz;[44] $W(O)(HC_2Ph)(S_2CNEt_2)_2$, 215 Hz;[20] and $(dppe)(OC)_3W(HC_2Ph)$, 231 Hz.[59]

The electron-poor nature of the $M(CO)(RC_2R)L_2X_2$ complexes relative to their bis(dithiocarbamate) cousins suggested by structural and NMR data is also evident in carbonyl stretching frequencies listed in Table VIII. In every case the $M(CO)(RC_2R)L_2X_2$ complex has a higher ν_{CO} frequency than its $M(CO)(RC_2R)(S_2CNR'_2)_2$ counterpart. The single-faced π-acidity of the phenylacetylene ligand can be gauged by comparison of the 1950 cm^{-1} frequency of the lone carbonyl in $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$ with the average of the two carbonyls in the $Mo(CO)_2(PEt_3)_2Br_2$ compound, 1909 cm^{-1}. These data suggest that phenylacetylene is more effective than a second carbon monoxide ligand in removing metal dπ electron density in these d^4 complexes.

The $\nu_{C\equiv C}$ stretching vibration offers a probe of the carbon–carbon multiple-bond order. We were able to observe a weak absorption between 1625 and 1675 cm^{-1}

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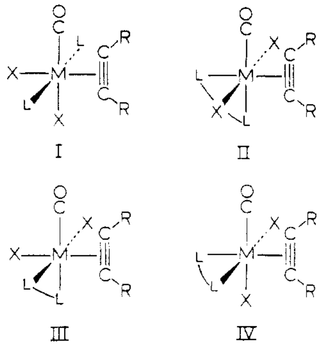

Figure 2. Possible isomers for $M(CO)(RC{\equiv}CR)L_2X_2$ complexes with *cis*-$(CO)(RC{\equiv}CR)$ fragments. Only isomers II, III, and IV are accessible to $M(CO)(RC{\equiv}CR)(dppe)X_2$ complexes.

for five of the complexes we prepared, and we tentatively assign this to the $C{\equiv}C$ stretch of the coordinated alkyne. Donation from both $\pi_{\parallel}$ and $\pi_{\perp}$ as well as acceptance of metal $d\pi$ electron density into $\pi_{\parallel}{}^*$ all contribute to reduction of the acetylenic bond order. Substantial reduction of the carbon–carbon bond strength is indicated by the decrease of 688 cm^{-1} observed upon coordination of 2-butyne to form $Mo(CO)(MeC_2Me)(PEt_3)_3Cl_2$.

The low-energy visible absorption common to these alkyne derivatives is assigned as a d–d transition on the basis of both their energy and their intensity (see Table VI). In a study of 20 $M(CO)(RC_2R)(S_2CNR'_2)_2$ complexes[60] it was found that electron-releasing alkyne substituents blue shift the visible absorption, supposedly reflecting the increased energy of the $d\pi$–$\pi_{\perp}$ antibonding combination which constitutes the LUMO. The same trend is apparent here as illustrated by the $Mo(CO)(\eta^2\text{-alkyne})(PEt_3)_2Br_2$ pair with the MeC_2Me derivative **6** having λ_{max} 1400 cm^{-1} higher in energy than the less electron-rich PhC_2H analogue **3**. Presumably the molecular ortibal scheme used for the $M(CO)(\eta^2\text{-alkyne})(S_2CNR_2)_2$ complexes[60] would apply in a general way to $M(CO)(\eta^2\text{-alkyne})L_2X_2$ species. Other formal 16-electron complexes exhibit low-intensity visible transitions which may be localized in the $d\pi$ manifold.[61]

The reversible reduction characterizing $Mo(CO)(RC_2R)L_2X_2$ compounds may be crudely associated with adding an electron to the LUMO of these compounds.[60,62] The larger dependence of the LUMO on the alkyne substituents relative to the HOMO is reflected in the larger variation of reduction potentials relative to the range of oxidation potentials. The reduction potential of the 2-butyne derivative **6** is 0.18 V more negative than that of the phenylacetylene complex **3**. This energy difference is comparable to the blue shift of 0.17 V in λ_{max} for these two complexes. In contrast the oxidation potentials of **3** and **6** are within experimental error of one another and support the hypothesis that the d_{yz} HOMO is roughly independent of alkyne substituent variations. On the other hand changes in L create changes in the oxidation potentials of $Mo(CO)(MeC_2Me)L_2Cl_2$ complexes as expected (PPh_3, **10**, 0.96 V; py, **4**, 0.90 V; PEt_3, **6**, 0.87 V).

Isomer Considerations. The geometries of $M(CO)(RC_2R)L_2X_2$ and $M(CO)(RC_2R)(dppe)X_2$ were probed by NMR and IR spectroscopies. If one assumes a *cis*-$M(CO)(\eta^2\text{-alkyne})$ fragment will be present in all cases, four isomers are accessible for monodentate L ligands and three for the bidentate dppe derivatives (see Figure 2).

The solid-state structure of $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$ (**3**) corresponds to isomer I of Figure 2, and spectroscopic studies of all the $M(CO)(RC_2R)L_2X_2$ complexes in solution confirm this ligand distribution. A single, sharp ^{31}P NMR signal is observed over a temperature range of −90 to +30 °C for $Mo(CO)(MeC_2Me)(PEt_3)_2Br_2$ and $Mo(CO)(MeC_2Me)(PPh_3)_2Cl_2$, as well as for **3**. For a rigid geometry only isomer I is in accord with this data. The trans phosphine configuration is also indicated by coupling constant considerations. Both alkyne carbon nuclei and the carbonyl carbon of $Mo(CO)(MeC_2Me)(PEt_3)_2Br_2$ are split into triplets by the two phosphorus nuclei (6, 5, and 9 Hz to these three carbons, respectively). The 5–10 Hz range of these values is typical of cis $^2J_{PC}$ coupling constants in Mo(II) and W(II) complexes[63] and suggests axial phosphines as in I with the other five metal-bound atoms lying in the equatorial plane. Related trans phosphine, cis chloro geometries are found in $Mo(NO)_2(PPh_3)_2Cl_2$[64] and $W(CHCMe_3)(CO)(PMe_3)_2Cl_2$[65] as well.

The disposition of the chelating dppe ligand in $M(CO)(RC_2R)(dppe)X_2$ complexes was not unambiguously determined. Although two isomers were clearly present for the unsymmetrical alkyne $Mo(CO)(PhC_2H)(dppe)Br_2$ and $Mo(CO)(HC_2\text{-}n\text{-}Bu)(dppe)Br_2$ derivatives, as evidenced by two signals for the terminal alkyne proton and two pairs of intensity matched singlets in the ^{31}P spectra of each complex, we believe only the orientation of the alkyne differentiates these isomers. Accordingly the ^{31}P NMR spectrum of $Mo(CO)(EtC_2Et)(dppe)Br_2$ shows only one pair of singlets for the inequivalent phosphorus nuclei. The absence of an observable $^2J_{P_AP_B}$ coupling constant is common for dppe complexes.[66] Enrichment of $Mo(CO)(HC_2\text{-}n\text{-}Bu)(dppe)Br_2$ with ^{13}CO revealed one large $^2J_{PC}$ of 58 Hz while the second phosphorus resonance showed no coupling. This suggests that one end of the dppe chelate is approximately trans to CO, and thus isomer IV can be eliminated. Although neither isomer II nor III can be rigorously eliminated with the data available, two arguments favor isomer II. The nearly 20-ppm difference in chemical shifts for P_A and P_B suggests that the ligands trans to the two ends of the dppe differ dramatically in their trans influence. Chemical shifts in the 40–50 ppm range are common for dppe phosphorus trans to carbonyl ligands,[67] while higher chemical shifts are found for trans η^2-ketenyl and η^2-alkyne ligands.[68] The structure of $W(CO)(\eta^2\text{-}RC{=}CO)(dppe)(S_2CNEt_2)$ has been reported, and the ^{31}P NMR has signals at 48 and 23 ppm assigned to nuclei cis and trans to the ketenyl ligand, respectively. Formation of the related alkyne cation by methylation of the ketenyl oxygen generates ^{31}P signals at 39 and 13 ppm which are reasonably assigned as cis and trans to the RC_2OMe ligand, respectively.[68] This suggests that the ^{31}P signals in the 20–30 ppm range are trans to the alkyne while those in the 40–50 ppm range are trans to the carbon monoxide. The conclusion that only isomer II is present is consistent with the observation of a single strong ab-

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sorption in the ν(Mo–Cl) region of the infrared spectrum of $Mo(CO)(MeC_2Me)(dppe)Cl_2$ as expected for the *trans*-dichloro arrangement found only in II.

In $W(CO)(MeC_2Me)L_2Br_2$ complexes with L = CN-*t*-Bu and $P(OMe)_3$ Davidson and Vasapollo found NMR data indicated *cis*-L_2 structures. In the $W(CO)(MeC_2Me)[P(OMe)_3]_2Br_2$ case it was possible to observe isomerization of the *cis*-L_2 complex to the thermodynamically favored *trans*-L_2 geometry.[25] They also favored assigning the cis complex as isomer II on the basis of spectral details for their complexes.[26]

Dynamic Solution Properties. Variable-temperature NMR studies of $M(CO)(MeC_2Me)L_2X_2$ compounds can be interpreted as reflecting rotation of the alkyne ligand around the axis defined by the metal and the midpoint of the C_2 linkage. Retention of $^2J_{CP}$ and $^4J_{HP}$ coupling in the fast-exchange limit confirmed the intramolecular nature of the exchange process. The calculated energy barriers fall between 9 and 13 kcal mol^{-1}, reminiscent of previous values found for Mo(II) and W(II) complexes (see Table V).

The trans L_2 ground-state geometry would seem to minimize steric repulsion, so simple steric arguments would favor increased rotational barriers for larger L ligands. The observed trend ($py < PPh_3 < PEt_3$) does not follow this guideline, so some electronic factor must also be involved. A higher barrier to alkyne rotation was also seen for the smaller PEt_3 relative to PPh_3 in $[(\pi\text{-}C_5H_5)Mo(CO)(MeC_2Me)L][BF_4]$ complexes.[69] The rotational barrier seems nearly independent of the metal in $M(CO)(MeC_2Me)(PPh_3)_2Cl_2$; similar behavior was apparent in the $M(CO)(HC_2H)(S_2CNR_2)_2$ (M = Mo, W) pair.

Given the relatively narrow range of ΔG^{*} values reported here, it is probably not worthwhile to speculate on the origins of these minor energy variations. Since both $\pi_{\parallel}{}^*$ acceptance of metal $d\pi$ electron density and $\pi_{\perp}$ donation into the metal $d\pi$ manifold will influence the rotational barrier, it will be the interplay of these factors as modified by steric interactions that will determine the activation energy.

Davidson and Vasapollo found that the *trans*-$W(CO)(MeC_2Me)[P(OMe)_3]_2Br_2$ complex exhibited only a single 2-butyne methyl resonance down to −85 °C (188 K), probably indicating a lower rotational barrier than any of the five we measured. The *cis*-$[P(OMe)_3]_2$ isomer had a substantially higher barrier for alkyne rotation as reflected in the coalescence temperature of −14 °C (287 K).[25,26] This is compatible with the trend we see in that the dppe derivatives with unsymmetrical alkynes, necessarily in the *cis*-L_2 class, exist as two distinct isomers on the NMR time scale due to a high rotational barrier.

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Supplementary Material Available: Tables of thermal parameters, infrared data, and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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