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

P. B. Winston, S. J. N. Burgmayer, T. L. Tonker, and J. L. Templeton*

W. R. Kenan, Jr. Laboratory, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

Received June 20, 1985

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 ¹³C 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)(PhC₂H)(PEt₃)₂Br₂ 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; $\beta = 98.04$ (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 molvbdenum 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 π_{\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 $(\pi$ - C_5H_5)M(CO)₂(PhC₂Ph) (M = V, Nb, Ta),³ Mo(TPP)- (PhC_2Ph) , ${}^{4}[(\pi-C_5H_5)M_0(CO)L(RC_2R)][BF_4]$, ${}^{5}(\pi-C_5H_5)W_{-}$ $(CO)Me(RC_2R)$, ⁶ $(\pi$ -C₅H₅ $)M(CO)X(PhC_2Ph)$, ⁷ $(\pi$ -C₅H₅)M- $(CO)(SR)(CF_3C_2CF_3),^{\$} M(CO)(RC_2R)(S_2CNR_2)_2 (\check{M} =$ Mo,⁹ W¹⁰), and $[Co(PhC_2Ph)(PMe_3)_3][BF_4]$.¹¹ In complexes containing an alkyne ligand and additional π -donor ligands (e.g., RC₂R, O²⁻, RS⁻) the set of π -donor ligands compete with one another for vacant metal $d\pi$ orbitals: $(\pi - C_5 H_5) M(CO) (PhC_2 Ph)_2$ (M = V, Nb, Ta),¹² ($\pi - C_5 H_5$)M-

(2) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. Inorg. Chem. 1982, 21.466.

(3) (a) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Pasynskii, A. A. Dokl. Akad. Nauk SSSR 1968, 182, 112 (Engl. Transl. 789). (b) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Pasynskii, A. A. Izv. Akad. Nauk SSSR, Ser. Khim. 1969, 100 (Engl. Transl. 87). (c) For a review of this chemistry see: Gusev, A. I.; Struchkov, Yu. T. J. Struct. Chem. (Engl. Transl.) 1970, 11, 340

(4) DeCian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. J. Am. Chem. Soc. 1981, 103, 1850.

- (5) Sünkel, K.; Nagel, U.; Beck, W. J. Organomet. Chem. 1981, 222, 251.
- (6) (a) Alt, H. G. J. Organomet. Chem. 1977, 127, 349. (b) Alt, H. G.;
- Eichner, M. E.; Jansen, B. M. Angew. Chem., Int. Ed. Engl. 1982, 21, 861. (7) Davidson, J. L.; Sharp, D. W. A. J. Chem. Soc., Dalton Trans. 1975, 2531.
- (8) Howard, J. A. K.; Stanfield, R. F. D. J. Chem. Soc., Dalton Trans. 1976. 246
- (9) McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. J. Organomet. Chem. 1975, 92, C25.
- (10) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. J. Am. Chem. Soc. 1978, 100, 1318.
- (11) (a) Capelle, B.; Beauchamp, A. L.; Dartiguenave, M.; Dartiquenave, Y. J. Chem. Soc., Chem. Commun. 1982, 566. (b) Capelle, B.; Dartiquenave, M.; Dartiquenave, Y.; Beauchamp, A. L. J. Am. Chem. Soc. 1983, 105, 4662.
- (12) Nesmeyanov, A. N.; Gusen, A. I.; Pasynskii, A. A.; Nisimov, K. N.; Kolobova, N. E.; Struchkov, Yu. T. J. Chem. Soc. D 1969, 277.

 $(RC_2R)_2X$ (M = Mo, X = Cl, R = CH₂OH;¹³ M = Mo, W, $X_{1} = CI_{1}$, Br, I, $R = CF_{3}$;¹⁴ M = Mo, W, X = CO⁺, R = CH₃¹⁵), Mo(RC₂R)₂(S₂CNR'₂)₂,^{9,16} W(CO)(RC₂R)₃,¹⁷ [W-(RC₂R)₃SnPh₃]⁻¹⁸ M(O)(RC₂R)(S₂CNR'₂)₂ (M = Mo,¹⁹ W²⁰), W(S)(PhC₂Ph)(S₂CNR'₂)₂,²¹ and Mo(CN-t-Bu)₂-(RC₂R)(S-t-Bu)₂.²² The degree of π_{\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 = PMe₃, AsMe₃, CN-t-Bu) were reported by Umland and Vahrenkamp in 1982.²⁷ Another recent relevant report is that of Bennett and Boyd, who prepared

- (13) Faller, J. W.; Murray, H. H. J. Organomet. Chem. 1979, 172, 171.
- (14) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. J. Chem. Soc., Dalton Trans. 1976, 738.
 - (15) Watson, P. L.; Bergman, R. G. J. Am. Chem. Soc. 1980, 102, 2698.
 - Herrick, R. S.; Templeton, J. L. Organometallics 1982, 1, 842.
 (17) (a) King, R. B. Inorg. Chem. 1968, 7, 1044. (b) Tate, D. P.; Augl,
- J. M. J. Am. Chem. Soc. 1963, 85, 2174.
- (18) Maher, J. M.; Fox, J. R.; Foxman, B. M.; Cooper, N. J. J. Am. Chem. Soc. 1984, 106, 234'

- (19) (a) Schneider, P. W.; Bravard, D. C.; McDonald, J. W.; Newton,
 W. E. J. Am. Chem. Soc. 1972, 94, 8640. (b) Maatta, E. A.; Wentworth,
 R. A. D. Inorg. Chem. 1979, 18, 524. (c) Maatta, E. A.; Wentworth, R.
 A. D.; Newton, W. E.; McDonald, J. W.; Watt, G. D. J. Am. Chem. Soc.
- 1978, 100, 1320.
- (20) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.;
 Newton, W. E. Inorg. Chem. 1981, 20, 1248.
 (21) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. Organometallics
- 1985, 4, 745.
- (22) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Hoffmann, R. Organometallics 1982, 1, 227.
 (23) Templeton, J. L.; Winston, P. B.; Ward, B. C. J. Am. Chem. Soc.
- 1981, 103, 7713.
- (24) A preliminary communication of some of this work has appeared: Winston, P. B.; Burgmayer, S. J. N.; Templeton, J. L. Organometallics 1983. 2. 167
- (25) Davidson, J. L.; Vasapollo, G. Polyhedron 1983, 2, 305.
 (26) Davidson, J. L.; Vasapollo, G. J. Chem. Soc., Dalton Trans. 1985,
- 2239. (27) Umland, P.; Vahrenkamp, H. Chem. Ber, 1982, 115, 3580.

⁽¹⁾ Mingos, D. M. P. Comprehensive Organometallic Chemistry; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, pp 60-61.

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 $M_2(O)(C_8H_{12})(S_2CNR_2)_2^{28}$ and $M_0(O)(C_8H_{12})(S_2CNR_2)_2$.

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 (¹H, 250 MHz; ¹³C, 62.3 MHz; ³¹P, 101 MHz) or on a Varian XL-100 (1H). 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 ¹H and ¹³C signals while ³¹P 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 $[(n-C_4H_9)_4N]$ - $[ClO_4]$ 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. $Mo(CO)_3(PEt_3)_2 Br_2$ (1). A solution of Mo-(CO)₄(PEt₃)₂ (1.72 g, 3.87 mmol) in CH₂Cl₂ was titrated with a dilute stock solution of bromine in CH₂Cl₂ 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- $(CO)_3(PEt_3)_2$ Br₂ 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 $M_0(\bar{C}O)_3(\bar{PEt}_3)_2Br_2$ (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 Et₂O to precipitate Mo(CO)₂(PEt₃)₂Br₂ as deep blue crystals in very high yield: IR (CH₂Cl₂, 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 Et₂O which solubilized the product. The extractions were continued until the Et₂O 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)(PhC₂H)(PEt₃)₂Br₂ was obtained by cooling a saturated toluene solution to -30 °C: ¹H 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, CH₃CH₂P), 0.78 (m, 18 H, CH₃CH₂P); ¹³C NMR (CD_2Cl_2) δ 230.9 (br s, CO), 224.8 (dt, ¹ J_{CH} = 204 Hz, ${}^{2}J_{CP} = 5 \text{ Hz}, \text{ HC} \Longrightarrow$, 224.7 (q, ${}^{2}J_{CH} = 5 \text{ Hz}, {}^{2}J_{CP} = 5 \text{ Hz}, \text{ PhC} \Longrightarrow$); ${}^{31}\text{P} \text{ NMR} (\text{CDCl}_2) \delta 10.0 \text{ (s, PEt_3); IR (CH_2Cl_2, cm^{-1}) } \nu_{C0} 1950$; 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 CH₂Cl₂ (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%): ¹H NMR (CD_2Cl_2) δ 8.58 (m, 4 H, o-py), 7.68 (m, 2 H, p-py) 7.32 $(4 \text{ H}, m\text{-py}), 3.38 \text{ (s, 6 H, Me)}; \text{ IR } (\text{CH}_2 \text{Cl}_2, \text{ cm}^{-1}) \nu_{CO} 1937; \text{ IR } (\text{KBr},$ cm⁻¹) v_{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 Et₂O 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: ¹H NMR (CD₂Cl₂) & 3.18 (s, 6 H, Me), 1.51 (m, 12 H, CH₃CH₂P), 0.87 (m, 18 H, CH₃CH₂P); ¹³C NMR (CD₂Cl₂ at -50 °C) $\delta 237.4$ (t, ${}^{2}J_{CP} = 6$ Hz, MeC=), 231.3 (t, ${}^{2}J_{CP} = 9$ Hz, CO), 229.3 (t, ${}^{2}J_{CP} = 5$ Hz, CMe), 22.56 and 22.49 (s, CH₃C₂CH₃); ${}^{31}P$ NMR (CD₂Cl₂) δ 9.1 (s, PEt₃); ${}^{31}P$ NMR (CDCl₂, at -90 °C) δ 9.8 (s, PEt₃); IR (CH₂Cl₂, cm⁻¹) ν_{CO} 1939 s, $\nu_{C=C}$ 1645 vw; IR (KBr, cm⁻¹) ν_{CO} 1926. 5: ¹H NMR (CD₂Cl₂) δ 3.20 (t, ⁴J_{HP} = 1.4 Hz, $CH_3C_2CH_3$; IR (CH_2Cl_2 , cm⁻¹) ν_{CO} 1943 s, $\nu_{C=C}$ 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)

 $Mo(CO)(R^{1}C_{2}R^{2})(PEt_{3})_{2}Br_{2}$ ($R^{1} = R^{2} = Ph$ (7); $R^{1} = R^{2} =$ Et (8); $\mathbf{R}^1 = \mathbf{H}$, $\mathbf{\bar{R}}^2 = \mathbf{n} \cdot \mathbf{Bu}$ (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 (CH₂Cl₂, cm⁻¹) ν_{CO} 1951; IR (KBr, cm⁻¹) ν_{CO} 1942. 8: IR (CH₂Cl₂, cm⁻¹) ν_{CO} 1939. 9: ¹H NMR (CDCl₃) δ 13.68 (s, 1 H, HC=); IR (1,2-ClCH₂CH₂Cl, cm⁻¹) ν_{CO} 1944. Anal. Found (Calcd): C, 46.44 (46.43); H, 6.18 (5.78); Br, 22.68 (22.80).

 $M_0(CO)(RC_2R)(PPh_3)_2X_2$ (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(PPh₃)₂Cl₂ (2.0 g, 2.58 mmol) in CH₂Cl₂ (30 mL). The suspension was boiled for 8 h during which time the solid Mo(CO)₃(PPh₃)₂Cl₂ 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)(MeC₂Me)(PPh₃)₂Cl₂ (10) (0.65 g, 0.84 mmol, 33%): ¹H NMR (CD₂Cl₂) δ 7.72–7.32 (m, 30 H, Ph), 2.42 (t, 6 H, ⁴J_{HP} = 1.6 Hz, $CH_3C_2CH_3$; ¹³C NMR ($CD_2Cl_2/CDCl_3$, 3:2) δ 240.0 (s, MeC_2Me) 228.6 (t, ${}^{2}J_{CP}$ = 9 Hz, CO), 22.6 (s, CH₃C₂CH₃); ³¹P NMR (CD₂Cl₂)
$$\begin{split} &\delta 18.5 \text{ (s, PPh_3); IR (CH_2Cl_2, cm^{-1}) } \nu_{C0} 1956 \text{ s, } \nu_{C==C} 1670 \text{ vw; IR} \\ &(\text{KBr, cm}^{-1}) \nu_{C0} 1937. 11: \text{ IR (CH_2Cl_2, cm}^{-1}) \nu_{C0} 1946. 12: \text{ IR} \\ &(\text{CH}_2\text{Cl}_2 \text{ cm}^{-1}) \nu_{C0} 1950. \text{ Anal. Found (Calcd): C, 56.83 (57.09);} \\ &V_{L} = 1000 \text{ cm}^{-1} \text{$$
H, 4.46 (4.22); Br, 18.76 (18.53).

 $\begin{array}{l} Mo(CO)(R^{1}C_{2}R^{2})(dppe)Cl_{2} \ (dppe=Ph_{2}PCH_{2}CH_{2}PPh_{2}; R^{1}\\ =H, \ R^{2}=n-Bu \ (13); \ R^{1}=R^{2}=Me \ (14); \ R^{1}=R^{2}=Et \ (15)). \end{array}$ The preparation of 13 is representative of the route used for the three alkyne complexes above. A yellow-orange dichloroethane

 ⁽²⁸⁾ Bennett, M. A.; Boyd, I. W. J. Organomet. Chem. 1985, 290, 165.
 (29) (a) Colton, R.; Tomkins, I. B. Aust. J. Chem. 1966, 19, 1143. (b)
 Colton, R.; Tomkins, I. B. Ibid. 1966, 19, 1519. (c) Anker, M. W.; Colton, R.; Tomkins, I. B. Ibid. 1967, 20, 9.

 ⁽³⁰⁾ Colton, R.; Rix, C. J. Aust. J. Chem. 1968, 21, 1155.
 (31) Anker, M. W.; Colton, R.; Rix, C. J.; Tomkins, I. B. Aust. J. Chem. 1969, 22, 1341.

^{(32) (}a) Darensbourg, D. J. Inorg. Chem. 1979, 18, 14. (b) Darensbourg, D. J.; Kump, R. L. Inorg. Chem. 1978, 17, 2680.

Molybdenum(II) and Tungsten(II) Alkyne Complexes

(30-mL) slurry of [Mo(CO)₂(dppe)_{1.5}Cl₂]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 Et₂O. The green crystals of $Mo(CO)(HC_2-n-Bu)(dppe)Cl_2$ were washed repeatedly with Et₂O 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 (CH₂Cl₂, cm⁻¹) $\nu_{\rm CO}$ 1981; IR (KBr, cm⁻¹) $\nu_{\rm CO}$ 1971. 14: ¹H NMR (CD₂Cl₂) δ 3.11 (s, 3 H, CH₃C₂CH₃), 1.56 (s, 3 H, CH₃C₂CH₃); IR (CH₂Cl₂, cm⁻¹) $\nu_{\rm CO}$ 1970; IR (KBr, cm⁻¹) $\nu_{\rm CO}$ 1963. 15: ¹H NMR (CD₂Cl₂) δ 1.28 (t, 3 H, $CH_3CH_2C \equiv$), 0.38 (t, 3 H, $\equiv CCH_2CH_3$); ³¹P NMR (C- D_2Cl_2) δ 47.5 (s, P_A), 23.94 (s, P_B); IR (CH₂Cl₂, cm⁻¹) ν_{CO} 1977; IR (KBr, cm⁻¹) ν_{CO} 1946; IR (Nujol, cm⁻¹) $\nu_{C=C}$ 1671 vw. Anal. Found (Calcd): C, 58.22 (58.68); H, 5.14 (5.08); Cl, 10.63 (10.50). $Mo(CO)(R^{1}C_{2}R^{2})(dppe)Br_{2} (R^{1} = H, R^{2} = n - Bu (16); R^{1} =$ $\mathbf{R}^2 = \mathbf{Et}$ (17); $\mathbf{R}^1 = \mathbf{H}$, $\mathbf{R}^2 = \mathbf{Ph}$ (18); $\mathbf{R}^1 = \mathbf{R}^2 = \mathbf{Ph}$ (19)). Compounds 16-19 were prepared as described above for Mo- $(CO)(HC_2-n-Bu)(dppe)Cl_2$ (13) except that $Mo(CO)_3(dppe)Br_2$ was used as the metal reagent. 16: ¹H NMR (CDCl₃) δ 10.76 (dd, 1 H, ${}^{3}J_{HP_{A}} = 20$ Hz, ${}^{3}J_{HP_{B}} = 4$ Hz, major isomer, HC=), 10.68 (dd, minor isomer, HC=), 8.0-6.0 (m, 20 H, Ph), 4.0-3.0 (m, 4 H, minor isomer, $H \subseteq J$, 8.0–0.0 (m, 20 ri, Fm), 4.0–0.0 (m, 4 m, PCH₂CH₂P), 2.72 (m, 2 H, CCH₂), 1.6–1.2 (m, 4 H, C₂CH₂-(CH₂)₂CH₃), 0.84 (t, 3 H, CH₂CH₃); ¹³C NMR (CDCl₃), 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_B} = 7 Hz, CO), 218.7 (s, \equiv C-n-Bu), 199 (m, \equiv CH); minor isomer, δ 48.7 (s, \equiv 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 (CH₂Cl₂, cm⁻¹) ν_{CO} 1985; IR (KBr) ν_{CO} 1979. 17: ¹H NMR (CD₂Cl₂) δ 1.32 (t, 3 H, CH₃CH₂C=), 0.40 (t, 3 H, \equiv CCH₂CH₃); ³¹P NMR (CD₂Cl₂) δ 42.3 (s, P_B), 20.5 (s, P_A); IR $(CH_2Cl_2, cm^{-1}) \nu_{CO}$ 1985; IR (KBr, cm⁻¹) ν_{CO} 1948; IR (Nujol, cm⁻¹) $\nu_{C=C}$ 1625 vw. 18: ¹H NMR (CD₂Cl₂), major isomer, δ 10.84 (dd, 1 H, ²J_{HP_A} = 21 Hz, ²J_{HP_B} = 5 Hz, HC=), minor isomer, δ 10.78 (dd, HC=); ¹³C NMR (CD₂Cl₂/CDCl₃, 6:4), major isomer, δ 222.1 (dd, ${}^{2}J_{CP_{A}} = 59 \text{ Hz}, {}^{2}J_{CP_{B}} = 6 \text{ Hz}, CO), 210.8 (s, CPh), 201.3 (dd, {}^{2}J_{CP_{A}} = 24 \text{ Hz}, {}^{2}J_{CP_{B}} = 6 \text{ Hz}, CO), 210.8 (s, CPh), 201.3 (dd, {}^{2}J_{CP_{A}} = 24 \text{ Hz}, {}^{2}J_{CP_{B}} = 6 \text{ Hz}, CO), 212.0 (s, =CPh), 203.4 (dd, {}^{2}J_{CP_{A}} = 59 \text{ Hz}, {}^{2}J_{CP_{B}} = 6 \text{ Hz}, CO), 212.0 (s, =CPh), 203.4 (dd, {}^{2}J_{CP_{A}} = 24 \text{ Hz}, {}^{2}J_{CP_{B}} = 10 \text{ Hz}, =CH), 3^{12}P \text{ NMR} (CD_2Cl_2), major isomer, <math>\delta$ 42.8 (d, {}^{2}J_{P_{A}P_{B}} = 3 \text{ Hz}, P_{B}), 30.2 (P_{A}), minor isomer, δ 47.9 (d, ${}^{2}J_{P_{A}P_{B}} = 4 \text{ Hz}, P_{B}), 33.1 (P_{A}); \text{ IR} (1,2-CH_2ClCH_2Cl, cm^{-1})$ ν_{CO} 1995; IR (KBr, cm⁻¹) ν_{CO} 1979. 19: IR (KBr, cm⁻¹) ν_{CO} 1997. 19: PA

 $W(CO)(R^{1}C_{2}R^{2})(PEt_{3})_{2}Cl_{2}$ ($R^{1} = R^{2} = Ph$ (20); $R^{1} = H, R^{2}$ = Ph (21)) and $W(CO)(MeC_2Me)(PPh_3)_2Cl_2$ (22). Yellow W(CO)₃(PEt₃)₂Cl₂ (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 Et₂O precipitated additional impurities. Filtration produced a blue-green solution which was evaporated to an oil. Trituration with hexanes yielded the desired $\hat{W}(CO)(PhC_2Ph)(PEt_3)_2Cl_2$ (20) product as a bluepurple solid (1.25 g, 1.59 mmol, 45%): IR (CH₂Cl₂, 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-CH₂ClCH₂Cl, cm⁻¹) ν_{CO} 1932. Formation of 22 required only 2 h of heating: ¹H NMR $(CD_2Cl_2) \delta$ 7.8–7.2 (m, 30 H, PPh₃), 2.44 (t, 6 H, ${}^4J_{HP}$ = 1.5 Hz, $CH_3C_2CH_3$; ³¹P NMR (CD₂Cl₂) δ -10.6 (s, 14% d due to ¹⁸³W (I = 1/2, ${}^{1}J_{PW} = 275 \text{ Hz}$; IR (CH₂Cl₂, cm⁻¹) ν_{CO} 1941; IR (KBr, cm⁻¹)

 $\nu_{\rm CO}$ 1926. ¹³CO Enrichment of 3 and 16. A green CDCl₃ solution of $Mo(CO)(HC_2Ph)(PEt_3)_2Br_2$ (3) was stirred under an atmosphere of 90% ¹³CO at room temperature. An enrichment to approximately 10% ¹³CO was achieved after 24 h as judged by infrared intensities. The same procedure for $Mo(CO)(HC_2-n-Bu)(dppe)Br_2$ (16) led to 20% enrichment after 5 h and 60% ¹³CO incorporation after 24 h. Mo(¹³CO)(HC₂-n-Bu)(dppe)Br₂ (16*): ³¹P NMR $(\text{CDCl}_3) \delta 43.7 \text{ (s, P_B)}, 28.9 \text{ (d, } {}^2J_{\text{PC}} = 58 \text{ Hz}, \text{P}_{\text{A}}); \text{ IR (CDCl}_3, \text{ cm}^{-1})$ ν_{12}_{CO} 1995, ν_{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 $0.30 \times 0.40 \times 0.40$ mm

Table I. Crystallographic Data and Collection Parameters

10r MO(CO)(PRC ₂ R)(PEt ₃) ₂ Dr ₂		
mol formula	$C_{21}H_{36}Br_2M_0OP_2$	
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	
o(calcd) g cm ⁻³	1.614	
Z	4	
radiatn (wavelength)	Mo Kα (0.71073 Å)	
μ , cm ⁻¹	39.5	
scan type	$w/1.33\theta$	
scan width	$1.1^{\circ} + 0.35 \tan \theta$	
bkgd scan	25% of full peak width on each side	
scan range	$1.0^{\circ} \leq \theta \leq 26.0^{\circ}$	
quadrant collected	$\pm h, \pm k, \pm l$	
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	
Rw	0.035	
error in obsvn of unit wt	1.52	

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 $30^{\circ} < 2\theta < 34^{\circ}$ 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.

Diffraction data were collected in the quadrant $(\pm h, +k, +l)$ 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 $80^\circ < \chi < 90^\circ$ were used to calculate an empirical absorption correction. A total of 4526 unique reflections were collected in the region $2^{\circ} < 2\theta < 52^{\circ}$; 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 + 11 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 package³⁴ 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 leastsquares 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 $0.29 \text{ e}/\text{Å}^3$. 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

⁽³³⁾ Programs utilized during data collection and structure solution

⁽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. 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

$$Mo(CO)_6 + Br_2 \rightarrow Mo(CO)_4 Br_2 + 2CO(g)$$
 (1)

$$M_0(CO)_4Br_2 + 2PEt_3 \rightarrow M_0(CO)_3(PEt_3)_2Br_2 + CO(g)$$
(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

$$M_0(CO)_6 + 2 \text{ piperidine} \xrightarrow{\Delta} cis-M_0(CO)_4(pip)_2 + 2CO(g)$$
 (3)

$$M_0(CO)_4(pip)_2 + 2PEt_3 \xrightarrow{\Delta} M_0(CO)_4(PEt_3)_2 + 2pip$$
(4)

$$M_0(CO)_4(PEt_3)_2 + Br_2 \rightarrow M_0(CO)_3(PEt_3)_2Br_2 + CO(g)$$
(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

 $M_0(CO)_3L_2X_2 + R^1C_2R^2 \xrightarrow{CH_2Cl_2} M_0(CO)(R^1C_2R^2)L_2X_2$ (6)

$$\Delta$$

Mo(CO)(R¹C₂R²)L₂X₂ (7)

M = Mo, W; L = PEt₃, $1/_2$ dppe; X = Cl, Br; R¹ = R² = Ph, Et, Me; R¹ = H, R² = Ph or *n*-Bu



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

Table II. Atomic Positions for Mo(CO)(PhC₂H)(PEt₃)₂Br₂

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)
P 2	0.0978 (4)	0.1076(2)	0.3794 (1)
01	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-

Table III. Intramolecular Bond Distances (Å) in Mo(CO)(PhC₂H)(PEt₂)₂Br₂

Mo-Br1	2.673 (1)	C2-C3	1.27 (1)	
Mo-Br2 Mo-P1 Mo-P2 Mo-C1 Mo-C2 Mo-C3	2.700 (1) 2.547 (3) 2.538 (3) 1.939 (10) 1.988 (10) 1.982 (9)	C2-H1 C3-C4 C4-C5 C5-C6 C6-C7 C7-C8	$\begin{array}{c} 1.10 \ (7) \\ 1.54 \ (1) \\ 1.41 \ (1) \\ 1.38 \ (1) \\ 1.38 \ (1) \\ 1.35 \ (1) \end{array}$	
P1-C10 P1-C12 P1-C14 P2-C16 P2-C18 P2-C18	1.79 (1) 1.83 (1) 1.81 (1) 1.80 (1) 1.80 (1)	C8-C9 C9-C4 C10-C11 C12-C13 C14-C15	$\begin{array}{c} 1.30 \ (1) \\ 1.40 \ (1) \\ 1.36 \ (1) \\ 1.52 \ (1) \\ 1.49 \ (2) \\ 1.49 \ (1) \end{array}$	
C1O1 C1C2 C1C2 C1H1	1.16 (1) 2.29 (1) 2.64 (7)	C16-C17 C18-C19 C20-C21	1.50 (1) 1.50 (2) 1.50 (2)	

Table IV. Intramolecular Bond Angles (deg) for Mo(CO)(PhC₂H)(PEt₃)₂Br₂

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)	C12P1C14	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)	MoC3C4	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)	C4C5C6	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 $Mo(CO)(PhC_2H)$ -(PEt₃)₂Br₂ 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 ${}^{4}J_{HP}$ 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)-(MeC₂Me)(PEt₃)₂Br₂ (6), but upon cooling two distinct

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

	•			
complex	<i>T</i> _c , K	Δw , Hz	$\Delta \overline{G^*}$	ref
$\overline{M_0(CO)(M_eC_2M_e)(PEt_3)_2Br_2}$	256	18.4	13.0	this work
$M_0(CO)(MeC_2Me)(PEt_3)_2Cl_2$	215	5.0	11.4	this work
$M_0(CO)(MeC_2Me)(py)_2Cl_2$	189	33.0	9.3	this work
$M_0(CO)(MeC_2Me)(PPh_3)_2Cl_2$	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 ₂ Me)(CNBu ^t) ₂ Br ₂			11.8	26
$W(CO)(MeC_2Me)(S_2CNEt_2)_2$			11.1	55
$[(\pi - C_5 H_5)M_0(MeC_2Me)(CO)]$	285	9	14.9	69
(PEt ₃)][BF ₄]				
$[(\pi - C_5 H_5)M_0(MeC_2Me)(CO)-$	268	81	12.8	69
(PPh ₃)][BF ₄]				
$[(\pi - C_5 H_5)M_0(MeC_2Me)(dppe)]$ -	306	177	14.2	69
[BF ₄]				

signals appear with a coalescence temperature (T_c) of 256 K. Similar averaging processes are observed for the 2butyne 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, ΔG^* , were extracted from the variable-temperature NMR data by using the Eyring equation after calculating $k_{\rm ex}$ at T_c from the Gutowsky-Holm equation.³⁷

Carbon-13 NMR spectra of 3, 6, 10, 14, and 15 revealed acetylenic and carbonyl ¹³C resonances in the range from 190 to 240 ppm. Gated decoupled spectra of Mo(CO)-(PhC₂H)(PEt₃)₂Br₂ and Mo(CO)(HC₂-n-Bu)(dppe)Br₂ 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 PEt₃ or PPh₃ ligands. The single ³¹P resonance of Mo(CO)-(MeC₂Me)(PEt₃)₂Br₂ (6) remained sharp when cooled to -90 °C. A ¹J_{WP} coupling constant of 275 Hz was measured for W(CO)(MeC₂Me)(PPh₃)₂Cl₂ (22).

The dppe derivatives differed distinctly from complexes containing monodentate phosphines as two distinct phosphorus environments were evident in ³¹P spectra of $Mo(CO)(EtC_2Et)(dppe)X_2$ (X = Cl (15); X = Br (17)). Unsymmetrical alkyne derivatives, $Mo(CO)(RC_2H)$ -(dppe)Br₂ (R = n-Bu (16); R = Ph (18)), displayed an intense pair of singlets as well as a weak pair of singlets in the ³¹P 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)(MeC₂Me)(dppe)Cl₂ had a single strong absorption at 285 cm⁻¹ while Mo(CO)(MeC₂Me)L₂Cl₂ complexes exhibited two absorptions attributable to Mo-Cl stretching modes (L = PEt₃, 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 14 000 and 17 000 cm⁻¹ for the vivid green molybdenum compounds ($\epsilon \approx 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$). The four blue-purple tungsten complexes have higher energy absorptions (17 000–18 000 cm⁻¹).

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

^{(37) (}a) Faller, J. W. Adv. Organomet. Chem. 1977, 16, 211. (b) Templeton, J. L. Adv. Chem. Ser. 1979, No. 173, 263.

Table VI. Electronic Absorption and Electrochemical Data for M(CO)(RC=CR)L₂X₂ Complexes

	λ		
complex	$(\epsilon_{\max})^{a,b}$	$E_{\rm P/2}({\rm ox})^{\rm c}$	$E_{\rm P/2}(\rm red)$
Mo(CO) ₂ (PPh ₃) ₂ Cl ₂	17.76 (510) ^a		
$Mo(CO)_2(PEt_3)_2Br_2(2)$	17.61 (600)ª		
Mo(CO)(HC=CPh)-	15.02 (260)	0.87	-1.00
$(PEt_3)_2Br_2$ (3)			
$Mo(CO)(MeC \equiv CMe)(py)_2Cl_2$	14.47 (130)	0.90	-1.18
(4)			
Mo(CO)(MeC=CMe)-	16.61 (40)	0.87	-1.18
$(PEt_3)_2Cl_2$ (5)			
Mo(CO)(MeC=CMe)-	16.26 (50)	0.87	-1.18
$(\operatorname{PEt}_3)_2\operatorname{Cl}_2(6)$			
Mo(CO)(PhC≡CPh)-	$15.24 \ (170)^d$		
$(\mathbf{PEt}_3)_2\mathbf{Br}_2\ (7)$			
$M_0(CO)(MeC \equiv CMe)$ -	15.85 (50)	0.96	-1.19
$(PPh_3)_2Cl_2$ (10)			
Mo(CO)(MeC=CMe)(dppe)-	16.05		
Cl_2 (14)			
$Mo(CO)(EtC = CEt)(dppe)Cl_2$	16.03		
(15)			
Mo(CO)(HC=C-n-Bu)(dppe)-	15.27		
$Br_2(16)$			
$Mo(CO)(EtC = CEt)(dppe)Br_2$	15.75		
(17) $\mathbf{M}_{2}(\mathbf{OO})(\mathbf{MO}_{2}(\mathbf{OO})) (\mathbf{A}_{2}(\mathbf{OO}))$	14 50 (100)		
$Mo(CO)(HC=CPn)(appe)Br_2$	14.70 (100)		
(10) W(CO)(DhC-CDh)(DEt) (O)	17 10 (000)		
$(U)(PnC=CPn)(PEt_3)_2Cl_2$	17.12 (290)		
(20) W(CO)(UC-CDE)(DE4.) Cl	17.00		
$(00)(\Pi \cup = \cup \Gamma \Pi)(\Gamma \subseteq \mathfrak{l}_3)_2 \cup \mathfrak{l}_2$	17.09		
$W(CO)(M_{0}C - CM_{0})$	19.00		
(OO)(MeC=OMe)-	10.02		
(1 1 113/2012 (22)			

^aTransition energies in 10³ cm⁻¹; extinction coefficients in L mol⁻¹ cm⁻¹. ^bCH₂Cl₂ solution unless otherwise noted. ^cVolts vs. SSCE in $CH_3CN/0.10$ M [($n-C_4H_9$)₄N]ClO₄. ^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

 $\begin{array}{c} \textbf{Chemical Reactivity Patterns.} & Many \ Mo(CO)_{3}L_{2}X_{2} \\ complexes reversibly \ lose \ CO.^{29,36} & Ligand \ substitution \end{array}$ reactions of $Mo(CO)_3L_2X_2$ reagents with anionic chelating ligands (quinolinates,³⁸ xanthates,³⁹ dithiophosphinates,³⁹ and dithiocarbamates³⁹) 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 d⁴ products.⁴⁰ Substitution of a CO ligand in Mo(II) d⁴ dicarbonyl compounds is more difficult, but Mo(CO)L₄X₂ 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)(RC₂R)(PEt₃)₂Br₂ products. The facility with which an alkyne replaces two CO ligands is consistent with its ability to act as a fourelectron donor. Donation from the alkyne π_{\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 $(\pi - C_5 H_5) Ta(RC_2 R)X_2$ 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)- $(RC_2\hat{R})L_2X_2$ products from $M(CO)_3L_2X_2$ reagents is presented in Scheme IV. Equation 8 is known for the

Scheme IV

$$M(CO)_{3}L_{2}X_{2} \rightleftharpoons M(CO)_{2}L_{2}X_{2} + CO(g)$$
(8)

$$M(CO)_{2}L_{2}X_{2} + RC_{2}R \rightleftharpoons M(CO)_{2}(RC_{2}R)L_{2}X_{2} \quad (9)$$

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

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

$$Mo(CO)_3(py)_2X_2 \rightarrow Mo(CO)_2(py)_2X_2 + CO(g)$$
 (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)-(PhC₂H)(PEt₃)₂Br₂ and Mo(CO)(HC₂-n-Bu)(dppe)Br₂ retain the coordinated alkyne under 1 atm of carbon monoxide. Addition of ¹³CO 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)(RC₂R) fragment with the alkyne parallel to the M-CO axis is common for octahedral d⁴ monomers. This configuration, which optimizes both the π -donor and π -acceptor roles of the alkyne ligand, is found in $(\pi$ -C₅H₅)M(CO)(RC₂R)X (M = Mo, W),^{7,8} W(CO)-(HC₂OAlCl₃)(PMe₃)₃Cl,⁴⁷ and M(CO)(RC₂R)(S₂CNR'₂)₂¹⁰ compounds. The three-center, two-electron interaction which stabilizes d_{xz} by mixing with both CO π^* and alkyne

^{(38) (}a) Day, R. O.; Batschelet, W. H.; Archer, R. D. Inorg. Chem. 1980, 19, 2113. (b) Batschelet, W. H.; Archer, R. D.; Whitcomb, D. R. Inorg. Chem. 1979, 18, 48. (39) Chen, G. J.-J.; Yelton, R. O.; McDonald, J. W. Inorg. Chim. Acta

^{1977. 22. 249.}

⁽⁴⁰⁾ Templeton, J. L.; Ward, B. C. J. Am. Chem. Soc. 1981, 103, 3743.
(41) (a) Carmona, E.; Doppert, K.; Marin, J. M.; Poveda, M. L.; Sanchez, L.; Sanchez-Delgado, R. Inorg. Chem. 1984, 23, 530. (b) Crichton, B. A. L.; Dilworth, J. R.; Pickett, C. J.; Chatt, J. J. Chem. Soc., Dalton Trans. 1981, 892.

⁽⁴²⁾ Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. Inorg. Chem. 1981, 20, 387.

⁽⁴³⁾ Angelici, R. J.; Basolo, F. J. Am. Chem. Soc. 1962, 84, 2495.
(44) (a) Angelici, R. J. Organomet. Chem. Rev., Sect. A 1968, 3, 173.
(b) Darensbourg, D. J. Adv. Organomet. Chem. 1982, 21, 113.

⁽⁴⁵⁾ Herrick, R. S.; Leazer, D. M.; Templeton, J. L. Organometallics 1983, 2, 834.

⁽⁴⁶⁾ Drew, M. G. B. Prog. Inorg. Chem. 1977, 23, 67.

⁽⁴⁷⁾ Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. Organometallics 1982, 1, 766.

Molybdenum(II) and Tungsten(II) Alkyne Complexes

Table VII. ¹H and ¹⁸C Chemical Shifts^a for Selected Terminal Alkyne Molybdenum and Tunsten Complexes

complex	¹ Η δ (CH)	$\frac{^{13}C(RC = CR')}{CR'}$	ref
Mo(CO)(PhC ₂ H)(PEt ₃) ₂ Br ₂	13.0	225, 225	this work
$M_0(CO)(PhC_2H)(S_2CNEt_2)_2$	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
$\frac{Mo(PhC_2H)(CN-t-Bu_2)(S-t-Bu_2)}{Bu_2}$	10.40	184, 172	22
$(\pi - C_5 \tilde{H}_5)_2 Mo(HC_2 H)$	7.66	118	b, 56

^a Ppm downfield from Si(CH₃)₄. ^b Thomas, J. L. Inorg. Chem. 1978, 17, 1507.

 π_{\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 metallacvclobutenone as a contributing resonance structure. metallacyclobutene ring found in The $(\pi$ -C₅H₅)₂TiCH₂CPh=CPh⁴⁸ 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 π_{\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 $[Co(PhC_{2}Ph)L_{2}]^{+}$ and $[C_0(PhC_2Ph)L_2(CH_2CN)]^+$ (L = PMe₂) 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 π_{\perp} electron donation), and consequently the Mo-C alkyne distances in Mo(PhC₂Ph)(TTP) (1.97 Å, average) reflect enhanced π_{\perp} donation.⁴ A representative 18-electron compound, without invoking π_{\perp} donation, is (π - $C_5H_5)_2Mo(PhC_2Ph)$, where the alkyne carbons are 2.14 Å from the metal.^{4,49} Other d⁴ monocarbonyl alkyne derivatives with 4-electron alkyne donation exhibit M-C distances near 2.00 Å: W(CO)(HC₂H)(S₂CNEt₂)₂, 2.03 Å;¹⁰ $(\pi$ -C₅H₅)Mo(CO)(CF₃C₂CF₃)(SC₆F₅), 2.03 Å,[§] and W-(CO)(HC₂OAlCl₃)(PMe₃)₃Cl, 2.02 Å.⁴⁷ Slightly longer M–C distances are characteristic for formal 3-electron donor alkynes (Mo(MeC₂Me)₂(S₂CNC₄H₄)₂, 2.05 Å;⁵⁰ (π -C₅H₅)W-(CF₃C₂CF₃)₂Cl, 2.06 Å¹⁴), and even longer metal-alkyne bonds are found when the alkyne competes with a cis oxide or sulfide π -donor ligand $[(\pi - C_5 H_5) W(O)(PhC_2 Ph)Ph, 2.11$ Å;⁵¹ $(\pi - C_5H_5)Mo(O)(CF_3C_2CF_3)(SC_6F_5)$, 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 Å²¹]. 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)(RC₂R')(PEt₃)₂X₂ and $M(CO)(RC_2R)(S_2CNEt_2)_2$

complex	λ_{max} , cm ⁻¹	$\nu_{\rm CO}, {\rm cm}^{-1}$
Mo(CO)(MeC ₂ Me)(PEt ₃) ₂ Br ₂	16 300	1937
$M_0(CO)(MeC_2Me)(S_2CNEt_2)_2$	15 200	1914
Mo(CO)(PhC ₂ H)(PEt ₃) ₂ Br ₂	15000	1950
$M_0(CO)(PhC_2H)(S_2CNEt_2)_2$	14 300	1919
$W(CO)(PhC_2H)(PEt_3)_2Cl_2$	17 200	1932
$W(CO)(PhC_2H)(S_2CNEt_2)_2$	16 500	1925

Spectral Properties. The acetylenic ¹H^{20,54} and ¹³C⁵⁵ 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 ¹³C alkyne chemical shifts of the dppe derivatives are typical of 4electron 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 ¹³C alkyne chemical shifts, and the number of electrons the alkvne 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 ${}^{1}J_{CH}$ coupling constant for Mo(CO)(PhC₂H)- $(PEt_3)_2Br_2$ is 204 Hz and leads to an estimated s character of $\rho = 0.41^{58}$ for the C-H bond, consistent with rehybridization toward sp² upon ligation to the metal. These ${}^{1}J_{CH}$ alkyne coupling constants are generally insensitive to the oxidation state of the metal and the identity of the ancillary ligands: Mo(CO)(HC₂-n-Bu)(dppe)Br₂, 215 Hz; $Mo(CO)(HC_2Ph)(S_2CNEt_2)_2$, 215 Hz; $Mo(HC_2Ph)_2$ -(S₂CNMe₂)₂, 212 Hz;¹⁶ W(CO)(HC₂OAlCl₃)(PMe₃)₃Cl, 203 Hz;⁴⁴ W(O)(HC₂Ph)(S₂CNEt₂)₂, 215 Hz;²⁰ and (dppe)-(OC)₃W(HC₂Ph), 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 $M(\bar{C}O)(\bar{R}C_2R)L_2X_2$ complex has a higher $\nu_{\rm CO}$ frequency than its M(CO)(RC₂R)(S₂CNR'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)(PhC₂H)- $(PEt_3)_2Br_2$ 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 $d\pi$ electron density in these d⁴ complexes.

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

⁽⁴⁸⁾ Tebbe, F. N.; Harlow, R. L. J. Am. Chem. Soc. 1980, 102, 6149.
(49) Nakamura, A.; Otsuka, S. J. Am. Chem. Soc. 1972, 94, 1886.
(50) Herrick, R. S.; Burgmayer, S. J. N.; Templeton, J. L. Inorg. Chem.

^{1983, 22, 3275.} (51) Bokiy, N. G.; Gatilov, Yu. V.; Struchkov, Yu. T.; Ustynyuk, N. A.

J. Organomet. Chem. 1973, 54, 213. (52) Newton, W. E.; McDonald, J. W.; Corbin, J. L.; Ricard, L.; Weiss, R. Inorg. Chem. 1980, 19, 1997.

^{(53) (}a) Coucouvanis, D. Prog. Inorg. Chem. 1979, 26, 301. (b) Templeton, J. L.; Ward, B. C. J. Am. Chem. Soc. 1980, 102, 6568

⁽⁵⁴⁾ McDonald, J. W.; Corbin, J. L.; Newton, W. E. J. Am. Chem. Soc. 1975, 97, 1970.

 ⁽⁵⁵⁾ Ward, B. C.; Templeton, J. L. J. Am. Chem. Soc. 1980, 102, 1532.
 (56) Templeton, J. L.; Ward, B. C. J. Am. Chem. Soc. 1980, 102, 3288.
 (57) Theopold, K. H.; Holmes, S. J.; Schrock, R. R. Angew. Chem.

Suppl. 1983, 1409.

⁽⁵⁸⁾ Drago, R. S. Physical Methods in Chemistry; W. B. Saunders: Philadelphia, 1977; pp 218-220. (59) Birdwhistell, K. R., unpublished results.



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

for five of the complexes we prepared, and we tentatively assign this to the C=C stretch of the coordinated alkyne. Donation from both π_{\parallel} and π_{\perp} as well as acceptance of metal $d\pi$ electron density into π_{\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 complexes⁶⁰ 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 $Mo(CO)(\eta^2-alkyne)(PEt_3)_2Br_2$ pair with the MeC₂Me derivative 6 having λ_{max} 1400 cm⁻¹ higher in energy than the less electron-rich PhC₂H analogue 3. Presumably the molecular ortibal scheme used for the $M(CO)(\eta^2$ -alkyne)(S₂CNR₂)₂ complexes⁶⁰ would apply in a general way to $M(CO)(\eta^2-alkyne)L_2X_2$ 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 2butyne 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_{vz} HOMO is roughly independent of alkyne substituent variations. On the other hand changes in L create changes in the oxidation potentials of

 $\begin{array}{l} Mo(CO)(MeC_2Me)L_2Cl_2 \ complexes \ as \ expected \ (PPh_3, 10, 0.96 \ V; \ py, \ 4, \ 0.90 \ V; \ PEt_3, \ 6, \ 0.87 \ V). \\ \hline \ Isomer \ Considerations. \ The geometries \ of \ M(CO)-(RC_2R)L_2X_2 \ and \ M(CO)(RC_2R)(dppe)X_2 \ were \ probed \ by \end{array}$ NMR and IR spectroscopies. If one assumes a cis-M-

 $(CO)(\eta^2$ -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)(PhC₂H)(PEt₃)₂Br₂ (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 ³¹P 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 ${}^{2}J_{PC}$ coupling constants in Mo(II) and W(II) complexes⁶³ 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(PPh₃)₂Cl₂⁶⁴ and W(CHCMe₃)(CO)(PMe₃)₂Cl₂⁶⁵ 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 $Mo(CO)(HC_2-n-Bu)(dppe)Br_2$ derivatives, as evidenced by two signals for the terminal alkyne proton and two pairs of intensity matched singlets in the ³¹P spectra of each complex, we believe only the orientation of the alkyne differentiates these isomers. Accordingly the ³¹P 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 ${}^{2}J_{P_{A}P_{B}}$ coupling constant is common for dppe complexes.⁶⁶ Enrichment of Mo- $(CO)(HC_2-n-Bu)(dppe)Br_2$ with ¹³CO revealed one large ${}^{2}J_{\rm PC}$ 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 $W(CO)(\eta^2-RC=CO)(dppe)(S_2CNEt_2)$ has been reported, and the ³¹P 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 ³¹P signals at 39 and 13 ppm which are reasonably assigned as cis and trans to the RC₂OMe ligand, respectively.⁶⁸ This suggests that the ³¹P 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-

⁽⁶⁰⁾ Templeton, J. L.; Herrick, R. S.; Morrow, J. R. Organometallics 1984, 3, 535.

^{(61) (}a) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. J. Am. Chem. Soc. 1982, 104, 1263. (b) Kazlauskas, R. S.; Wrighton, M. S. J. Am. Chem. Soc. 1982, 104, 6005. (c) Cotton, F. A.; Meadows, J. H. Inorg. Chem. 1984, 23, 4688

^{(62) (}a) Hoijtink, G. J. Recl. Trav. Chim. Pays-Bas 1955, 74, 1525. (b) Vlcek, A. A. Rev. Chim. Miner. 1968, 5, 299.

⁽⁶³⁾ Chisholm, M. H.; Godleski, S. Prog. Inorg. Chem. 1976, 20, 299. (64) Visscher, M. O.; Caulton, K. G. J. Am. Chem. Soc. 1972, 94, 5923.
 (65) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman,

⁽⁶⁶⁾ Garrou, P. E. Chem. Rev. 1981, 81, 229.
(67) (a) Mann, B. E. J. Chem. Soc., Dalton Trans. 1973, 2012. (b) Braterman, P. S.; Milne, D. W.; Randall, E. W.; Rosenberg, E. Ibid. 1973, 1027

⁽⁶⁸⁾ Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L., J. Am. Chem. Soc. 1985, 107, 4474.

Molybdenum(II) and Tungsten(II) Alkyne Complexes

sorption in the ν (Mo-Cl) region of the infrared spectrum of Mo(CO)(MeC₂Me)(dppe)Cl₂ as expected for the *trans*-dichloro arrangement found only in II.

In W(CO)(MeC₂Me)L₂Br₂ complexes with L = CN-t-Bu and P(OMe)₃ Davidson and Vasapollo found NMR data indicated *cis*-L₂ structures. In the W(CO)(MeC₂Me)[P-(OMe)₃]₂Br₂ case it was possible to observe isomerization of the *cis*-L₂ complex to the thermodynamically favored *trans*-L₂ 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 L₂ 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 < PPh₃ < PEt₃) 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 PEt₃ relative to PPh₃ in [(π -C₅H₅)Mo(CO)-(MeC₂Me)L][BF₄] complexes.⁶⁹ The rotational barrier seems nearly independent of the metal in M(CO)-(MeC₂Me)(PPh₃)₂Cl₂; similar behavior was apparent in the M(CO)(HC₂H)(S₂CNR₂)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 π_{\parallel}^* acceptance of metal $d\pi$ electron density and π_{\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)(MeC₂Me)[P(OMe)₃]₂Br₂ 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-L₂ class, exist as two distinct isomers on the NMR time scale due to a high rotational barrier.

Acknowledgment. This work was generously supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 1, 25640-93-1; 2, 25685-65-8; 3, 83801-84-7; 3*, 102829-89-0; 4, 102829-72-1; 5, 102829-73-2; 6, 83801-85-8; 7, 102829-74-3; 8, 102829-75-4; 9, 102829-76-5; 10, 102829-77-6; 11, 102829-78-7; 12, 102829-79-8; 13, 102829-80-1; 14, 102829-81-2; 15, 102829-82-3; 16, 102829-83-4; 16*, 102829-90-3; 17, 102829-84-5; 18, 102829-85-6; 19, 102829-86-7; 20, 102829-87-8; 21, 102851-24-1; 22, 102829-88-9; $Mo(Co)_4(PEt_3)_2$, 19217-81-3; $Mo(CO)_2(Py)_2Cl_2$, 20492-45-9; $Mo(CO)_2(PEt_3)Cl_2$, 40904-19-6; $Mo(CO)_3(PPh_3)_2Cl_2$, 17250-39-4; $Mo(CO)_3(PPh_3)_2Br_2$, 17250-41-8; $[Mo(CO)_2-(dppe)_{1.5}Cl_2]_2$, 25766-36-3; $Mo(CO)_3(dppe)Br_2$, 17192-22-2; W-(CO)_3(PEt_3)_2Cl_2, 79737-89-6; W(CO)_3(PPh_3)_2Cl_2, 18130-04-6; phenylacetylene, 536-74-3; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5; 3-hexyne, 928-49-4; 1-hexyne, 693-02-7.

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.

⁽⁶⁹⁾ Allen, S. R.; Baker, P. K.; Barnes, S. G.; Green, M.; Trollope, L.; Manojlovic-Muir, L.; Muir, K. W. J. Chem. Soc., Dalton Trans. 1981, 873.