

Electronic Spectroscopy and Electrochemistry of Alkyne Dithiocarbamate Complexes of Molybdenum(II) and Tungsten(II)

Joseph L. Templeton,* Richard S. Herrick, and Janet R. Morrow

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

Received June 30, 1983

The divergent influence of ligand π acceptance and π donation on the frontier orbitals of $M(\text{CO})(\text{RC}\equiv\text{CR}')(\text{dtc})_2$ ($\text{dtc} = \text{S}_2\text{CNR}_2$; $M = \text{Mo}$ and W) and $\text{Mo}(\text{RC}\equiv\text{CR}')_2(\text{dtc})_2$ has been probed by electronic spectral and cyclic voltammetric studies. The prevailing molecular orbital model with the $d\pi$ LUMO dependent upon alkyne π_{\perp} donation is compatible with trends in both optical transition energies ($E_{h\nu}$) and reduction potentials (E_R°). These formal 16-electron monomers, stabilized by ligand π donation, tend to display chemically reversible reductions and irreversible oxidations, in accord with naive chemical expectations for unsaturated molecules. The observed relationship between $E_{h\nu}$ and E_R° supports the proposed LUMO parentage while the $\nu(\text{CO})$ correlation with $E_{p/2}$ (oxidation) is consistent with the $d\pi$ HOMO origin. These results illustrate the dual π donor/ π acceptor role of alkyne ligands toward orthogonal $d\pi$ orbitals.

Introduction

The properties of $M(\text{CO})(\text{RC}\equiv\text{CR}')(\text{dtc})_2$ ($M = \text{Mo}$, W ; $\text{dtc} = \text{S}_2\text{CNR}_2$) compounds have been interpreted as reflecting donation from both filled alkyne π -bonding orbitals,¹ commonly referred to as π_{\parallel} (M - L σ donation) and π_{\perp} (M - L π donation).² Other six-coordinate d^4 monomers with alkyne ligands also display unusual properties for compounds that are formally electron-deficient unless the alkyne π_{\perp} electrons are taken into account.³

Large chemical shift ranges characterize both acetylenic ^1H (6-14 ppm)⁴ and ^{13}C (110-230 ppm)⁵ nuclei in monomeric molybdenum and tungsten alkyne compounds. Empirical correlations between δ values and electron-counting formalisms have been presented. The carbon-carbon stretching frequency, $\nu(\text{C}\equiv\text{C})$, for bound alkynes in a series of related compounds has also been cited as a useful observable for recognizing donation from π_{\perp} as well as π_{\parallel} .⁶ Neither of these spectroscopic methods is applicable to compounds with non-alkyne π -donor ligands. Furthermore, the relationship of NMR or IR properties to molecular orbital structures is indirect at best, and, although the empirical correlations that have been reported are of value, they fail to probe the frontier orbitals of the molecule directly.

The extent of ligand π donation in electron-deficient compounds can best be considered on a continuum molecular orbital basis.⁷ We have undertaken spectral and electrochemical studies of $M(\text{CO})(\text{alkyne})(\text{dtc})_2$ ($M = \text{Mo}$, W) compounds to probe alkyne π_{\perp} donation into the $d\pi$ LUMO (lowest unoccupied molecular orbital). We report here electronic absorption and cyclic voltammetry data which suggest that these techniques may be of widespread utility for assessing ligand π donation in formally electron-deficient monomers.

Experimental Section

Physical Measurements. Electronic spectra were recorded with a Cary 14 spectrophotometer. Infrared spectra were recorded with a Beckman IR 4250, and a polystyrene standard was used for calibration. Electrochemical measurements were made at room temperature with a PAR Model 175 universal programmer as sweep generator for cyclic voltammetry experiments with a PAR Model 173 potentiostat for potential control. Cyclic voltammograms were recorded by using argon-purged solutions containing 0.10 M tetraethylammonium or tetrabutylammonium perchlorate (each recrystallized four times from ethanol) as supporting electrolyte. Acetonitrile and N,N -dimethylformamide were purchased from Burdick & Jackson and dried with activity I alumina. A platinum bead electrode was the working electrode for cyclic voltammograms, and the auxiliary electrode was a platinum wire. Data were collected at a scan rate of 200 mV/s unless otherwise indicated. Potentials are reported vs. the saturated sodium chloride calomel electrode (SSCE) and are uncorrected for junction potential effects. For reversible couples the $E_{1/2}$ values were calculated as the average of the E_p values for the anodic and cathodic waves from cyclic voltammetry. E_R° values are used as formal reduction potentials with the assumption that diffusion coefficient differences for oxidized and reduced species are negligible, i.e., that $\ln(D_R/D_O) \approx 0$. For irreversible waves only the value of $E_{p/2}$ is reported.

Materials and Methods. All manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were purged with nitrogen gas prior to use. Molybdenum hexacarbonyl and tungsten hexacarbonyl, sodium dialkyldithiocarbamates, and all alkynes except for 2-butyne-1,4-diol were obtained from commercial sources and used as received. Professor S. A. Evans generously provided $\text{HOCH}_2\text{-C}\equiv\text{CCH}_2\text{OH}$.

(1) (a) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* 1978, 100, 1318. (b) McDonald, J. W.; Corbin, J. L.; Newton, W. E. *J. Am. Chem. Soc.* 1975, 97, 1970.

(2) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* 1982, 21, 466.

(3) (a) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Am. Chem. Soc., Dalton Trans.* 1976, 738. (b) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* 1977, 99, 5795. (c) Faller, J. W.; Murray, H. H. *J. Organomet. Chem.* 1979, 172, 171. (d) Howard, J. A. K.; Stansfield, R. F. D.; Woodward, P. J. *J. Chem. Soc., Dalton Trans.* 1976, 246. (e) Davidson, J. L.; Sharp, D. W. A. *Ibid.* 1975, 2531. (f) Davidson, J. L. *J. Chem. Soc., Chem. Commun.* 1980, 113. (g) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* 1980, 102, 2698. (h) Cotton, F. A.; Hall, W. T. *Ibid.* 1978, 101, 5094. (i) DeCian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *Ibid.* 1981, 103, 1850. (j) Kamata, M.; Koshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Hoffmann, R. *Organometallics* 1982, 1, 227. (k) Capelle, B.; Beauchamp, A. L.; Dartiguenave, M.; Dartiguenave, Y. *J. Chem. Soc., Chem. Commun.* 1982, 566. (l) Alt, H. G. *J. Organomet. Chem.* 1977, 127, 349. (m) Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* 1982, 1, 766.

(4) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* 1981, 20, 1248.

(5) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* 1980, 102, 3288.

(6) Herrick, R. S.; Templeton, J. L. *Organometallics* 1982, 1, 842.

(7) Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* 1981, 103, 7713.

Monocarbonyl monoalkyne complexes, $M(\text{CO})(\text{RC}\equiv\text{CR}')(\text{detc})_2$, were prepared as described by McDonald and co-workers for $M = \text{Mo}$, $R = R' = \text{H}$, and $R = R' = \text{Ph}$.⁸ Analogous tungsten complexes were prepared from $\text{W}(\text{CO})_3(\text{detc})_2$ according to literature methods for $R = R' = \text{H}$, $R = R' = \text{Ph}$, $R = R' = \text{Me}$, $R = R' = \text{Et}$, and $R = \text{Ph}$, $R' = \text{H}$.⁹ Bis(alkyne)bis(dithiocarbamate)molybdenum(II) complexes were prepared by previously reported methods.^{6,8}

(η^2 -Dimethyl acetylenedicarboxylate)carbonylbis(diethylthiocarbamate)molybdenum(II), $\text{Mo}(\text{CO})(\text{DMAC})(\text{detc})_2$. A stoichiometric amount of the alkyne reagent (DMAC, $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$) was added dropwise to a CH_2Cl_2 solution of $\text{Mo}(\text{CO})(\text{HC}\equiv\text{CH})(\text{detc})_2$ at -78°C . When the reaction was judged complete based on disappearance of the reagent $\nu(\text{CO})$ absorption (1932 cm^{-1}), an excess of petroleum ether was added at -78°C . The dark green crystals that formed were moderately air stable. If the reaction flask is allowed to warm to room temperature, formation of $\text{Mo}(\text{DMAC})_2(\text{detc})_2$ and product decomposition occur: IR (CH_2Cl_2) $\nu(\text{CO})$ 1975 cm^{-1} .

(η^2 -Bis(trimethylsilyl)acetylene)carbonylbis(diethylthiocarbamate)molybdenum(II), $\text{Mo}(\text{CO})(\text{Me}_3\text{SiC}_2\text{SiMe}_3)(\text{detc})_2$. A solution of $\text{Mo}(\text{CO})_3(\text{detc})_2$ in CH_2Cl_2 was stirred with a twofold excess of alkyne for 20 min. The solution volume was reduced to 5 mL in vacuo and then extracted with petroleum ether. When cooled to -20°C , the petroleum ether solution yielded moderately air-stable light brown crystals of $\text{Mo}(\text{CO})(\text{Me}_3\text{SiC}_2\text{SiMe}_3)(\text{detc})_2$: IR (CH_2Cl_2) $\nu(\text{CO})$ 1910 cm^{-1} .

(η^2 -Propargyl chloride)carbonylbis(diethylthiocarbamate)molybdenum(II), $\text{Mo}(\text{CO})(\text{CH}_2\text{C}\equiv\text{CH})(\text{detc})_2$. A procedure analogous to the above preparation of the bis(trimethylsilyl)acetylene complex led to low yields of dark green $\text{Mo}(\text{CO})(\text{ClCH}_2\text{C}_2\text{H})(\text{detc})_2$. Brown oily byproducts invariably formed even when less than a stoichiometric amount of propargyl chloride was used. Attempts to purify $\text{Mo}(\text{CO})(\text{ClCH}_2\text{C}_2\text{H})(\text{detc})_2$ by chromatography (alumina, Florisil) resulted in decomposition of the product: IR (CH_2Cl_2) $\nu(\text{CO})$ 1939 cm^{-1} .

(η^2 -Ethoxyacetylene)carbonylbis(diethylthiocarbamate)molybdenum(II), $\text{Mo}(\text{CO})(\text{EtOC}_2\text{H})(\text{detc})_2$. A stoichiometric amount of alkyne was added to a CH_2Cl_2 solution of $\text{Mo}(\text{CO})(\text{HC}_2\text{H})(\text{detc})_2$. After 1 h the solution color had changed from green to brown, and the reaction was judged complete by infrared spectroscopy. No clean product was isolated: IR (CH_2Cl_2) $\nu(\text{CO})$ 1937 cm^{-1} .

(η^2 -1-(Diethylamino)propyne)carbonylbis(dimethylthiocarbamate)molybdenum(II), $\text{Mo}(\text{CO})(\text{Et}_2\text{NC}_2\text{Me})(\text{dmtc})_2$. A stoichiometric amount of (diethylamino)propyne was added to a CH_2Cl_2 solution of $\text{Mo}(\text{C}_2\text{H}_2)(\text{CO})(\text{dmtc})_2$. The solution changed from bright green to dark green within 5 min, and the reaction was judged to be complete by IR at this time. Solvent was removed in vacuo, and the resulting oil was extracted with a 9:1 cyclohexane/toluene mixture. Green crystals were obtained following solvent evaporation and cooling to -20°C .

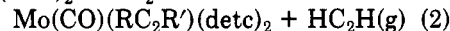
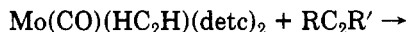
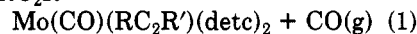
(η^2 -Dimethyl acetylenedicarboxylate)carbonylbis(diethylthiocarbamate)tungsten(II), $\text{W}(\text{CO})(\text{DMAC})(\text{detc})_2$. A toluene solution of $\text{W}(\text{CO})_3(\text{detc})_2$ and a stoichiometric amount of $\text{CH}_3\text{O}_2\text{CC}_2\text{CO}_2\text{CH}_3$ were stirred at room temperature for 3 days. The solution was then reduced to an oil in vacuo and dissolved in a minimum amount of methanol. Crystallization was induced by cooling to -20°C . Low yields reflect formation of some bis(alkyne) product, $\text{W}(\text{DMAC})_2(\text{detc})_2$. The dark green crystals of $\text{W}(\text{CO})(\text{DMAC})(\text{detc})_2$ were air stable: IR (CH_2Cl_2) $\nu(\text{CO})$ 1956 cm^{-1} .

(η^2 -Alkyne)carbonylbis(diethylthiocarbamate)tungsten(II), $\text{W}(\text{CO})(\text{RC}_2\text{R}')(\text{detc})_2$ ($R = \text{EtO}$, $R' = \text{H}$; $R = \text{Et}_2\text{N}$, $R' = \text{CH}_3$; $R = R' = \text{CH}_2\text{OH}$). A stoichiometric amount of alkyne was added to $\text{W}(\text{CO})_3(\text{detc})_2$ in toluene. Reaction was judged to be complete in 10 min for the ethoxy- and (diethylamino)alkynes and within 1 h for the (hydroxymethyl)alkyne. The solvent volume was reduced in vacuo; cyclohexane was added prior to cooling to -20°C to induce crystallization. $\text{W}(\text{CO})(\text{EtOC}_2\text{H})(\text{detc})_2$: dark green crystals; IR (PhMe) $\nu(\text{CO})$ 1930 cm^{-1} . $\text{W}(\text{CO})(\text{HOCH}_2\text{C}_2\text{CH}_2\text{OH})(\text{detc})_2$: bright green crystals; IR

(PhMe) $\nu(\text{CO})$ 1930 cm^{-1} . $\text{W}(\text{CO})(\text{Et}_2\text{NC}_2\text{Me})(\text{detc})_2$: reddish brown crystals; IR (PhMe) $\nu(\text{CO})$ 1904 cm^{-1} .

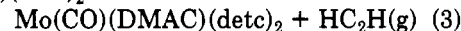
Results

Syntheses. Numerous alkynes react cleanly with $\text{Mo}(\text{CO})_2(\text{detc})_2$ to form $\text{Mo}(\text{CO})(\text{alkyne})(\text{detc})_2$ compounds. For aryl- and alkylalkynes this route (eq 1), followed by $\text{Mo}(\text{CO})_2(\text{detc})_2 + \text{RC}_2\text{R}' \rightarrow$



chromatographic purification, is the synthetic method of choice. The parent acetylene complex $\text{Mo}(\text{CO})(\text{HC}_2\text{H})(\text{detc})_2$ is also a suitable precursor to monocarbonyl monoalkyne derivatives (eq 2). The alkyne exchange route is preferable in cases where the resulting alkyne complex does not chromatograph readily, e.g., with heteroatom alkyne substituents. The $\text{Mo}(\text{CO})(\text{HC}_2\text{H})(\text{detc})_2$ reagent is easily prepared and purified, and, unlike the dicarbonyl reagent, it is not easily oxidized by air.

The ease with which $\text{Mo}(\text{CO})(\text{DMAC})(\text{detc})_2$ (DMAC = $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$, dimethyl acetylenedicarboxylate) reacts with free DMAC to form $\text{Mo}(\text{DMAC})_2(\text{detc})_2$ required that reaction 3 be performed at -78°C in order to $\text{Mo}(\text{CO})(\text{HC}_2\text{H})(\text{detc})_2 + \text{DMAC} \rightarrow$



isolate the monocarbonyl alkyne product $\text{Mo}(\text{CO})(\text{DMAC})(\text{detc})_2$. The tungsten analogue was also prepared by using relatively mild reaction conditions: $\text{W}(\text{CO})_3(\text{detc})_2$ and DMAC were stirred at room temperature for 3 days. The formation of $\text{W}(\text{CO})(\text{DMAC})(\text{detc})_2$ and $\text{W}(\text{DMAC})_2(\text{detc})_2$ in solution was monitored by observing the infrared $\nu(\text{C}=\text{O})$ stretching absorption of the ester groups ($\text{W}(\text{CO})(\text{DMAC})(\text{detc})_2$, 1721 cm^{-1} ; $\text{W}(\text{DMAC})_2(\text{detc})_2$, 1764 cm^{-1} ; free DMAC, 1737 cm^{-1}).

Infrared and Visible Spectroscopy. Stretching frequencies for the carbonyl ligand in $M(\text{CO})(\text{RC}_2\text{R}')(\text{detc})_2$ compounds range between 1900 and 1980 cm^{-1} as listed in Tables I and II for Mo and W, respectively. All of the $M(\text{CO})(\text{RC}\equiv\text{CR}')(\text{detc})_2$ compounds investigated exhibit a low-energy visible transition (λ_{max} ranges from 540 to 720 nm) with an extinction coefficient on the order of $10^2\text{ M}^{-1}\text{ cm}^{-1}$ as indicated in Tables I and II. The bis(alkyne)molybdenum derivatives $\text{Mo}(\text{RC}\equiv\text{CR}')_2(\text{detc})_2$ are yellow to orange in color and display a visible absorption band (350 – 440 nm) with extinction coefficients ranging from 2×10^3 to $5 \times 10^3\text{ M}^{-1}\text{ cm}^{-1}$ (Table III).

Cyclic Voltammetry. The $\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{detc})_2$ compounds examined by cyclic voltammetry exhibit either a chemically reversible or quasi-reversible reduction as judged by the ratio of the anodic current to cathodic current (i_a/i_c) which is electrochemically irreversible based on the separation between cathodic and anodic peak voltages compared to the value for the reversible ferrocene/ferrocenium couple.¹⁰ The formal reduction potentials (E_R°) for these compounds range from -1.39 to -1.70 V vs. SSCE. Three of the tungsten analogues ($\text{W}(\text{CO})(\text{RC}_2\text{R}')(\text{detc})_2$ ($R = R' = \text{PPh}_2$; $R = \text{EtO}$, $R' = \text{H}$; $R = \text{NET}_2$, $R' = \text{Me}$) exhibited only an irreversible reduction wave. For tungsten complexes where E_R° was determined the reduction potentials ranged from -1.43 to -1.83 V vs. SSCE. Four of the $\text{Mo}(\text{RC}_2\text{R}')_2(\text{detc})_2$ complexes exhibited formal reduction potentials between -0.88 and -1.74 V , while the $n\text{-BuC}_2\text{H}$ and EtC_2Et bis(alkyne) derivatives

(8) McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. *J. Organomet. Chem.* **1975**, *92*, C25.

(9) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532.

(10) Gagne, R. R.; Koval, C. A.; Linsensky, G. C. *Inorg. Chem.* **1980**, *19*, 2855.

Table I. Mo(CO)(RC≡CR')(detc)₂ Data

RC ₂ R'	λ _{max} , ^a nm	E _{hν} , cm ⁻¹	ε, M ⁻¹ cm ⁻¹	ν(CO), ^a cm ⁻¹	E _{p/2} (ox), ^b V	E _R ^o , ^c V	ΔE, ^d mV	i _a /i _c ^e
R = R' = CO ₂ Me(DMAC)	720	13 890		1975				
R = R' = SiMe ₃	710	14 080	105	1910	0.44	-1.50	130	1
R = R' = Ph	700	14 290	120	1932	0.38	-1.39	85	1
R = Ph, R' = H	695	14 390	110	1934	0.39	-1.42	110	1
R = R' = H	698	14 330	110	1932	0.38	-1.46	140	<1
R = CH ₂ Cl, R' = H	685	14 600	70	1939	0.42	-1.57	120	1
R = R' = Et	660	15 150	120	1908	0.35	-1.70	240	1
R = R' = Me	660	15 150	110	1920	0.36	-1.64	140	1
R = EtO, R' = H	645	15 500		1937				
R = NEt ₂ , R' = Me ^f	580	17 240	90	1913				

^a Spectra were recorded in CH₂Cl₂. ^b All oxidative processes were irreversible. ^c Electrode potentials were measured in CH₃CN solutions with (Et₄N)(ClO₄) as supporting electrolyte and are reported relative to a saturated sodium calomel reference. ^d This is the peak-to-peak separation for the reductive wave. ^e This is the ratio of the anodic current to the cathodic current for the reductive wave. ^f The dithiocarbamate ligands in this complex are S₂CNMe₂ (dmtc).

Table II. W(CO)(RC≡CR')(detc)₂ Data

RC ₂ R'	λ _{max} , ^a nm	E _{hν} , cm ⁻¹	ε, M ⁻¹ cm ⁻¹	ν(CO), ^b cm ⁻¹	E _{p/2} (ox), ^c V	E _R ^o , ^d V	ΔE, ^e mV	i _a /i _c ^f
R = R' = CO ₂ Me(DMAC)	630	15 870	100	1956	0.60	-1.43	80	<1
R = R' = PPh ₂	630	15 870	150	1927	0.35	-1.59	320	<1
R = R' = Ph	620	16 130	250	1927	0.35	-1.59	65	1
R = R' = H	612	16 340	120	1925				
R = Ph, R' = H	610	16 390	180	1924	0.36	-1.65	110	1
R = R' = CH ₂ OH	600	16 670		1920				
R = R' = Et	583	17 150	100	1910				
R = R' = Me	575	17 390	120	1910	0.31	-1.83	210	<1
R = EtO, R' = H	575	17 390	175	1930	0.38	-1.87 ^g		
R = Et ₂ N, R' = Me	545	18 350	150	1904	0.24	-2.14 ^{g,h}		

^a Electronic spectra were recorded in CH₂Cl₂. ^b Infrared spectra were recorded in toluene. ^c All oxidative processes were irreversible. ^d Electrode potentials were measured in CH₃CN solutions with (Et₄N)(ClO₄) as supporting electrolyte unless otherwise indicated. Potentials are reported relative to a saturated sodium chloride calomel reference. ^e This is the peak-to-peak separation for the reductive wave. ^f This is the ratio of the anodic current to the cathodic current for the reductive wave. ^g This reduction is irreversible. ^h Recorded in DMF with (Et₄N)(ClO₄) as supporting electrolyte.

Table III. Mo(RC≡CR')₂(detc)₂ Data

RC ₂ R'	λ _{max} , ^a nm	E _{hν} , cm ⁻¹	10 ³ ε, M ⁻¹ cm ⁻¹	E _{p/2} (ox), ^b V	E _R ^o , ^c V	ΔE, ^d mV	i _a /i _c ^e
R = R' = CO ₂ Me(DMAC)	435	23 000	2.0	1.07	-0.88	100	1
R = R' = Ph	403	24 810	5.0	0.99	-1.53	230	1
R = Ph, R' = Me	388	25 770	3.6	0.83	-1.74	100	<1
R = Ph, R' = H	381	26 250	2.5	0.85	-1.59	100	1
R = <i>n</i> -Bu, R' = H	357	28 000	4.0	0.90	-1.92 ^f		
R = R' = Et	349	28 650	4.4	0.84	-2.11 ^f		

^a Electronic spectra were recorded in CH₂Cl₂. ^b All oxidative processes are irreversible. ^c Electrode potentials were measured in DMF with (Et₄N)(ClO₄) as supporting electrolyte. ^d This is the peak-to-peak separation for the reductive wave. ^e This is the ratio of the anodic current to the cathodic current for the reductive wave. ^f This reduction is irreversible.

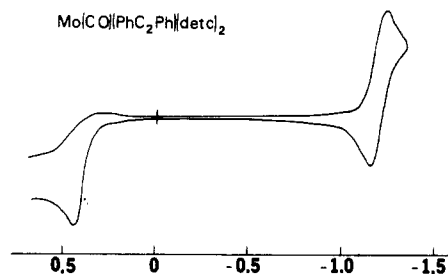


Figure 1. Cyclic voltammogram of Mo(CO)(PhC₂Ph)(detc)₂ in CH₃CN with potentials referenced to SSCE.

were characterized by irreversible reductions with E_{p/2} values of -1.92 and -2.11 V. None of the alkyne complexes studied exhibited a reversible oxidation. Oxidative E_{p/2} values for the monocarbonyl complexes clustered around +0.4 V while the bis(alkyne) derivatives displayed an oxidative process near +0.9 V. Electrochemical data are

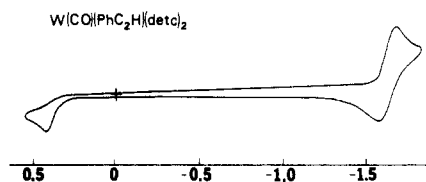


Figure 2. Cyclic voltammogram of W(CO)(PhC₂H)(detc)₂ in CH₃CN with potentials referenced to SSCE.

collected in Tables I, II, and III for Mo(CO)(RC₂R')(detc)₂, W(CO)(RC₂R')(detc)₂, and Mo(RC₂R')₂(detc)₂, respectively. Cyclic voltammograms of Mo(PhC₂Ph)(CO)(detc)₂ and W(PhC₂H)(CO)(detc)₂ are presented in Figures 1 and 2, respectively.

Discussion

M(CO)(alkyne)(detc)₂ Electronic Spectra. The general expectation that formal 16-electron monomers with

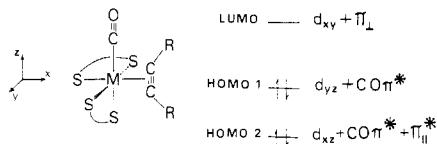


Figure 3. Qualitative molecular orbital scheme for d^4 $M(\text{CO})(\text{RC}_2\text{R})(\text{dtc})_2$.

a $d\pi$ LUMO dominated by metal–ligand π^* character would display lower energy electronic absorptions than related saturated compounds is compatible with the observation of well-defined visible transitions for $M(\text{CO})$ -alkyne)($\text{dtc})_2$ ($M = \text{Mo}, \text{W}$) and $\text{Mo}(\text{alkyne})_2(\text{dtc})_2$ compounds. The vivid greens and blues common to $M(\text{CO})(\text{alkyne})(\text{dtc})_2$ compounds are attributable to the window left by this absorption in the red region of the spectrum.

The molecular orbital scheme which has emerged for these d^4 complexes can be quickly constructed from the pseudooctahedral geometry which assists in recognizing the LUMO, HOMO 1, and HOMO 2 in Figure 3 as descendants of the three $d\pi$ metal orbitals.⁷ The C_1 molecular point group eliminates symmetry guidelines for electronic transition assignments. We believe the observed visible transition corresponds to the HOMO \rightarrow LUMO excitation and leads to singlet excited state which can be represented as $d_{xz}^2 d_{yz}^1 d_{xy}^1$. Other potential assignments include the triplet excited state of this same $d_{yz}^1 d_{xy}^1$ configuration or excitation from the d_{xz} HOMO 2 orbital. The magnitude of the extinction coefficients ($10^2 \text{ M}^{-1} \text{ cm}^{-1}$) is large even for a spin-allowed d – d transition and makes the triplet assignment unattractive. Furthermore, extinction coefficients are typically much larger for third-row transition metals than for second-row metals when spin changes are involved (due to larger spin–orbit coupling constants for the heavier metals). Here Mo and W display similar intensities. Although extended Hückel calculations are not suitable for quantitative transition energy predictions, the calculated energy gap of 0.38 eV (3000 cm^{-1}) between the d_{yz} (HOMO 1) and d_{xz} (HOMO 2) orbitals suggests that these two levels are far from degenerate. No low-energy transition was observed in the near-infrared region (800–2000 nm) for $\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})(\text{detc})_2$ or $\text{W}(\text{HC}_2\text{Ph})(\text{CO})(\text{detc})_2$. This is consistent with the hypothesis that the HOMO 2 \rightarrow LUMO transition lies above the observed visible transition in energy and is obscured by other more intense ultraviolet absorptions.

The visible transition energy for a series of $M(\text{CO})$ -alkyne)($\text{dtc})_2$ compounds should probe the d_{xy} LUMO location as it responds to alkyne π_\perp donation, if indeed λ_{max} reflects the frontier orbital energy gap. The HOMO, d_{yz} plus $\text{CO } \pi^*$ (δ overlap of d_{yz} with alkyne π_\perp is negligible), should only respond to alkyne substituent variations indirectly. The transition energies for $\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{dtc})_2$ compounds increase in the order shown in eq 4 where $\text{CO}_2\text{Me} < \text{SiMe}_3 < \text{Ph} < \text{H} < \text{CH}_2\text{Cl}, \text{H} < \text{Et} < \text{OEt}, \text{H} < \text{NEt}_2, \text{Me}$ (4)

$\text{CO}_2\text{Me} < \text{PPh}_2 < \text{Ph} < \text{Ph}, \text{H} < \text{CH}_2\text{OH} < \text{Et} < \text{Me} < \text{EtO}, \text{H} < \text{NEt}_2, \text{Me}$ (5)

R is listed for RC_2R and R, R' is listed for $\text{RC}_2\text{R}'$ alkynes. Similar trends characterize the tungsten monocarbonyl monoalkyne derivatives (eq 5). Tungsten complexes invariably absorb at higher energies than their molybdenum counterparts, with the five analogous Mo, W pairs exhibiting relatively constant energy differences of 1800–2000 cm^{-1} . Tungsten typically forms stronger metal–ligand π bonds than molybdenum.¹¹

The qualitative trend in electronic transition energies does not correlate with substituent electronegativity values. Consideration of Hammett σ values for the alkyne substituents is suggested by the proposed role of the alkyne π_\perp orbital in influencing the LUMO, and either σ_P or σ_R factors are found to be compatible with the qualitative energy ordering.¹² (Recall that $\sigma_P = \sigma_R + \sigma_I$ breaks σ total (σ_P) into a sum of resonance (σ_R) and inductive (σ_I) components.)

Substituent π effects are reflected in these results. Although silicon is less electronegative than carbon, the visible transition in the (bis(trimethylsilyl)acetylene)molybdenum complex is near the low-energy end of the range, roughly 1200 cm^{-1} below the 3-hexyne analogue. This result indicates that vacant silicon 3d orbitals compete effectively with the metal d_{xy} LUMO for alkyne π_\perp electron density. A similar rationale applies to the alkyne ligand in $\text{W}(\text{CO})(\text{Ph}_2\text{PC}_2\text{PPh}_2)(\text{detc})_2$ in spite of the PPh_2 lone-pair electrons. The bis(diphenylphosphino)acetylene appears as electron poor in the π_\perp sense as the DMAC ligand in $\text{W}(\text{CO})(\text{DMAC})(\text{detc})_2$. Recalling the SiMe_3 results guides one to conclude that rather than providing phosphorus lone-pair electron density, vacant phosphorus 3d orbitals are delocalizing alkyne π_\perp electron density away from the metal.

At the other extreme the high-energy transitions observed for complexes with EtOC_2H and $\text{Et}_2\text{NC}_2\text{Me}$ indicate that these electron-rich heteroatom alkynes are providing increased π_\perp electron density to the metal. In valence bond terms resonance structure **b** is a contributing form.



Note that the structure of $[(\text{RNC})_4\text{Mo}(\text{R}(\text{H})\text{NC}_2\text{N}(\text{H})\text{R})\text{I}]^+$ ($\text{R} = t\text{-Bu}$) exhibits a planar RNCCNR geometry which is consistent with delocalization of the nitrogen lone-pair electrons into the alkyne π_\perp orbitals.¹³ The delocalized metal–alkyne π_\perp system in this series of molecules has been discussed, and a visible transition near 500 nm with $\epsilon \approx 600 \text{ M}^{-1} \text{ cm}^{-1}$ has been assigned to a $d\pi$ localized transition within the C_{2v} framework of these cations.¹⁴

$M(\text{CO})(\text{alkyne})(\text{dtc})_2$ Electrochemistry. The reduction potentials for the seven tungsten compounds studied follow the same qualitative order (eq 6) as the

$\text{CO}_2\text{Me} > \text{PPh}_2 > \text{Ph} > \text{Ph}, \text{H} > \text{Me} > \text{OEt}, \text{H} > \text{NEt}_2, \text{Me}$ (6)

visible transition energies. Of the $\text{Mo}(\text{CO})(\text{alkyne})(\text{dtc})_2$ compounds for which E_R° was determined (eq 7), only the bis(trimethylsilyl)alkyne complex qualitatively differs from its visible transition energy ranking (recall it was comparable to DMAC at the low end of the scale).

$\text{Ph} > \text{H} > \text{SiMe}_3 > \text{CH}_2\text{Cl}, \text{H} > \text{Me} > \text{Et}$ (7)

Correlations of LUMO energies with reduction potentials are common for organic π systems,¹⁵ and likewise

(11) (a) Griffith, W. P. *Coord. Chem. Rev.* 1970, 5, 459. (b) Griffith, W. P. *Ibid.* 1971, 8, 369.

(12) (a) Taft, R. W.; Deno, N. C.; Skell, P. S. *Annu. Rev. Phys. Chem.* 1958, 9, 287. (b) Wells, P. R.; Ehrenson, S.; Taft, R. W. *Prog. Phys. Org. Chem.* 1968, 6, 147.

(13) (a) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* 1977, 99, 617. (b) Corfield, P. W. R.; Baltusis, L. M.; Lippard, S. J. *Inorg. Chem.* 1981, 20, 922.

(14) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* 1982, 104, 1263.

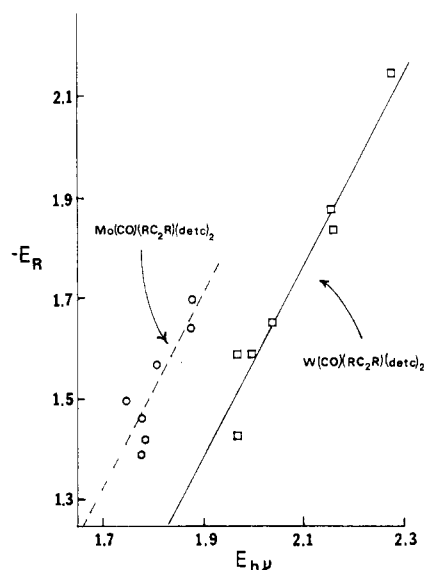


Figure 4. Reduction potential (E_R°) plotted as a function of visible transition energy ($E_{h\nu}$) for $M(\text{CO})(\text{RC}_2\text{R})(\text{detc})_2$ complexes [Mo (O), W (□)].

HOMO energies correlate well with oxidation potentials in a large number of systems.¹⁶ If factors such as solvation energy, entropy changes, low-lying orbital energy changes, and electronic repulsion terms for electron transfer and electronic excitation remain constant within a series of related complexes, a linear relationship may link electrochemical events and electronic transitions.¹⁷ Recall that redox potentials are inherently a thermodynamic measure of the ground-state energy difference between two chemical species differing by addition of an electron and need not relate to simple orbital energy gaps. Absorption spectra, on the other hand, probe an energy difference between ground-state and excited-state configurations. Even for closely related compounds, as in this study, comparison of optical transition energies and electrochemical potentials must be undertaken with caution. In spite of these limitations, applications of these concepts to more complex molecular bonding schemes have been reported.¹⁸ The MO model set forth for $\text{Mo}(\text{CO})(\text{alkyne})(\text{dte})_2$ suggests that alkyne substituent variations will alter the LUMO energy through π_\perp donation while only indirectly influencing the HOMO due to the composition of these orbitals. The major response to differing alkyne ligands is indeed localized in E_R° where reduction potentials span 0.31 V while $E_{p/2}$ oxidation values vary only 0.09 V among these six compounds. The data available for tungsten compounds are not so easily catalogued as E_R° values span 0.71 V and $E_{p/2}$ ranges over 0.36 V. Note that these ranges drop to 0.24 and 0.07 V, respectively, when the extreme values associated with the electron-poor DMAC and electron-rich $\text{Et}_2\text{NC}_2\text{Me}$ ligands are omitted.

The HOMO \rightarrow LUMO electronic transition assignment and the MO prediction that this gap will be subject to LUMO energy variations while the HOMO remains relatively constant merge in Figure 4 where E_R° is plotted vs.

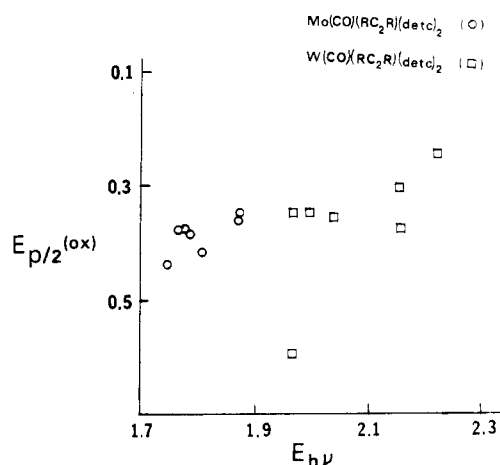


Figure 5. Oxidative half-wave potential ($E_{p/2}$) plotted as a function of visible transition energy ($E_{h\nu}$) for $M(\text{CO})(\text{RC}_2\text{R})(\text{detc})_2$ complexes [Mo (O), W (□)].

$E_{h\nu}$ for $M(\text{CO})(\text{alkyne})(\text{dte})_2$ compounds. Separate linear least-squares fit lines are presented for Mo and W, with slopes of 1.92 and 1.93, respectively, and correlation coefficients of 0.85 and 0.98. The low correlation coefficient for the molybdenum complexes indicates that these limited data do not define a quantitative relationship between E_R° and $E_{h\nu}$, but the trend seen in the tungsten data is evident in the slope for molybdenum, too. The plots in Figure 4 conform to logical qualitative expectations based on the MO model and the alkyne substituent donor-acceptor properties. The hypothetical slope of such a plot would be unity if the assumptions mentioned above applied rigorously and *only* the LUMO responded to substituent changes while the HOMO remained constant. If *both* the HOMO and LUMO were equally influenced by alkyne substituent changes, an infinite slope would result since $E_{h\nu}$ would remain constant and only the reduction potential would change. The observed slopes, approximately 2, are compatible with a molecular orbital scheme where the CO π^* dominated HOMO is only slightly influenced by the alkyne substituents while the $d\pi$ LUMO varies dramatically due to its π_\perp donation component. A plot of $E_{p/2}(\text{oxidation})$ vs. $E_{h\nu}$ is presented in Figure 5 where the relative constancy of $E_{p/2}$ obscures any relationship between these observables. Note the difficulty of oxidation when the extremely electron-withdrawing DMAC is a ligand ($E_{p/2} = 0.60$ V).

$M(\text{CO})(\text{alkyne})(\text{dte})_2 \nu(\text{CO})$ Frequencies. The π -acid character of alkyne ligands is experimentally evident in the $\nu(\text{CO})$ frequencies that fall between 1900 and 2000 cm^{-1} for all the $M(\text{CO})(\text{alkyne})(\text{dte})_2$ compounds prepared. In $\text{Mo}(\text{CO})\text{L}_2(\text{dte})_2$ complexes the lone carbonyl ligand monopolizes the d^4 metal electron density as evident in the low $\nu(\text{CO})$ frequencies of these compounds ($\text{L} = \text{PMePh}_2$, 1755 cm^{-1} ; $\text{L}_2 = \text{dppe}$, 1790 cm^{-1}).¹⁹ A more informative comparison is available since the average $\nu(\text{CO})$ frequency for $M(\text{CO})_2(\text{dte})_2$ compounds directly reflects competition between the two π -acid carbonyl ligands: $\text{Mo}(\text{CO})_2(\text{S}_2\text{CN}-i\text{-Pr}_2)_2$, 1934, 1842 (1888 cm^{-1} average);²⁰ $\text{W}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2$, 1910, 1820 (1865 cm^{-1} average).²¹ The implication is that the alkyne ligands compete more effectively than carbon monoxide for available $d\pi$ electron density. The single-faced π -donor and π -acceptor prop-

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

(16) (a) Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* 1975, 14, 247. (b) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* 1963, 85, 2124. (c) Hoijtink, G. *J. Recl. Trav. Chim. Pays-Bas* 1958, 77, 555.

(17) (a) Vlcek, A. A. *Electrochimica Acta* 1968, 13, 1063. (b) Peover, M. E. *Ibid.* 1968, 13, 1083. (c) Masek, J. *Inorg. Chim. Acta Rev.* 1969, 3, 99.

(18) (a) Fordyce, W. A.; Pool, K. H.; Crosby, G. A. *Inorg. Chem.* 1982, 21, 1027. (b) Matsubara, T.; Ford, P. C. *Inorg. Chem.* 1976, 15, 1107. (c) Templeton, J. L. *J. Am. Chem. Soc.* 1979, 101, 4906.

(19) Crichton, B. A. L.; Dilworth, J. R.; Pickett, C. J.; Chatt, J. J. *Chem. Soc., Dalton Trans.* 1981, 892.

(20) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* 1980, 102, 6568.

(21) Broomhead, J. A.; Young, C. G. *Aust. J. Chem.* 1982, 35, 277.

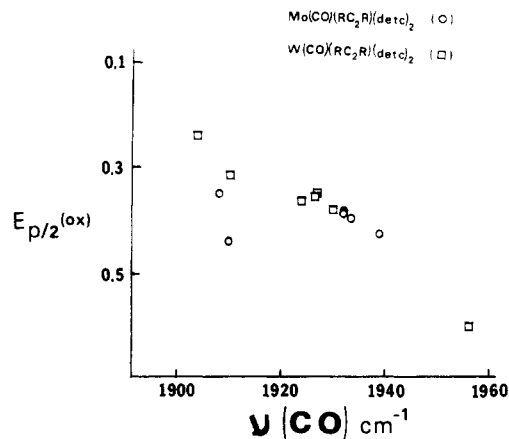


Figure 6. Oxidative half-wave potential ($E_{p/2}$) plotted as a function of carbonyl stretching frequency ($\nu(\text{CO})$) for $\text{M}(\text{CO})(\text{RC}_2\text{R})(\text{detc})_2$ complexes. [Mo (O), W (□)].

erties of alkynes have been noted previously,²² and the ν_{CO} frequencies of $\text{M}(\text{CO})(\text{alkyne})(\text{detc})_2$ complexes attests to the π -acid strength of the vacant alkyne π^* orbital.

Redox properties and carbonyl stretching frequencies have been correlated with one another in several classes of metal carbonyl compounds.²³ The plot of $E_{p/2}$ vs. $\nu(\text{CO})$ shown in Figure 6 is compatible with the postulate that oxidation potentials as a function of alkyne are associated with net changes in metal electron density while $\nu(\text{CO})$ responds similarly to metal $d\pi$ electron density available for back-bonding. In contrast to the specific π effects probed by E_{R° and E_{H° , values of $\nu(\text{CO})$ and $E_{p/2}$ for the tungsten ethoxyacetylene complex reflect the electronegativity of the oxygen bound to the alkyne carbon. The electropositive trimethylsilyl substituents generate one of the lowest $\nu(\text{CO})$ values of any alkyne (1910 cm^{-1} for Mo). The $\nu(\text{CO})$ abscissa correlates with $E_{p/2}$ much better than the E_{H° abscissa of Figure 5 in accord with CO π^* domination of the $d\pi$ HOMO. The conceptual link between $E_{p/2}$ and the HOMO then logically ties $\nu(\text{CO})$ to $E_{p/2}$ as reflected in the graph.

Mo(alkyne)₂(detc)₂ Electronic Spectra and Electrochemistry. The observed electronic transition energies for $\text{Mo}(\text{RC}_2\text{R}')(\text{detc})_2$ compounds lie well above the visible absorption energies reported for $\text{M}(\text{CO})(\text{RC}_2\text{R}')(\text{detc})_2$ complexes. This pattern is reinforced if comparison is limited to the molybdenum monocarbonyl complexes, as is appropriate since only molybdenum bis(alkyne) derivatives have been prepared and studied.

Development of the MO level ordering scheme for $\text{M}(\text{alkyne})_2(\text{detc})_2$ here would be redundant. Suffice it to note that the frontier orbitals can once again be readily derived from their octahedral $d\pi$ ancestors. For symmetrical alkynes a C_2 molecular symmetry is accessible with the central $\text{MoS}_4(\text{C}_2)_2$ core conforming to C_{2v} criteria, and these symmetry labels are designated as a point of departure in Figure 7. The single-faced π system of the chelating dithiocarbamate ligands invalidates the simplification possible by focusing only on the ligating atoms for electronic transition assignments. Regardless of the analysis there is no symmetry requirement that the two filled $d\pi$ levels be degenerate. An alkyne-Mo-alkyne angle of 90° would lead to equal overlap of the two π^* alkyne acceptor

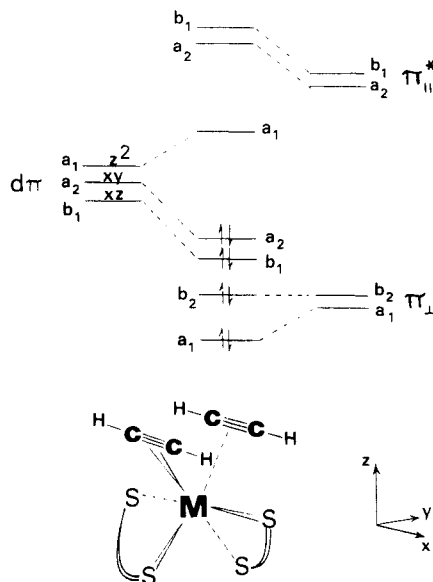


Figure 7. Qualitative molecular orbital scheme for d^4 $\text{M}(\text{RC}_2\text{R})_2(\text{detc})_2$.

orbitals with the two symmetry-adapted $d\pi$ orbitals which house the d^4 electrons. Structures of several bis(alkyne) d^4 derivatives are available in the literature,²⁴ and the bis(2-butyne)bis(1-pyrrolicarbothioato)molybdenum(II) complex exhibits an obtuse alkyne-M-alkyne angle of 99° which would increase π^* overlap with the a_2 $d\pi$ orbital perpendicular to the molecular symmetry axis.^{24a} The only allowed transition within the $d\pi$ manifold for C_2 symmetry is the ${}^1A_1 \rightarrow {}^1B_1$ ($b_1 \rightarrow a_1$) while the ${}^1A_1 \rightarrow {}^1A_2$ ($a_2 \rightarrow a_1$) is forbidden. All transitions are symmetry allowed in the actual C_2 point group. The large extinction coefficients ($\epsilon \geq 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) probably reflect the covalency of the metal-alkyne bonds. Substantial ligand character in these frontier orbitals derived from metal $d\pi$ orbitals, mostly of alkyne π^* and π_\perp origin, is compatible with absorption intensities of this magnitude.²⁵

The electronic transition energies suggest that the HOMO-LUMO gap is greater in the $\text{Mo}(\text{alkyne})_2(\text{detc})_2$ complexes than in the $\text{Mo}(\text{CO})(\text{alkyne})(\text{detc})_2$ series, and the redox properties listed in Table III substantiate this hypothesis. The bis(alkyne) derivatives are in general both harder to reduce and harder to oxidize than their monocarbonyl analogues. As the highest lying orbital in a three-center-four-electron bonding description, the a_1 LUMO is now destabilized by π_\perp donation from two alkynes rather than just one. Furthermore, the HOMO position is now determined by overlap with two alkyne π^* orbitals rather than one CO π^* orbital. The potentials associated with both reduction and oxidation reflect the strength of these alkyne- $d\pi$ interactions, respectively.

The $\text{Mo}(\text{alkyne})_2(\text{detc})_2$ compounds are quite robust and, surprisingly, they are poor electrophiles.²⁶ These chemical properties no doubt stem from their molecular architecture which supplements the octahedral framework with efficient utilization of the $d\pi$ levels as bonding and antibonding complements of vacant and filled alkyne π orbitals, π^* and π_\perp , respectively.

(22) Winston, P. B.; Nieter-Burgmayer, S. J.; Templeton, J. L. *Organometallics* 1983, 2, 167.

(23) (a) Connelly, N. G.; Kitchen, M. D. *J. Chem. Soc., Dalton Trans.* 1977, 931. (b) Connelly, N. G.; Demidowicz, Z.; Kelly, R. L. *Ibid.* 1975, 2335. (c) Chatt, J.; Leigh, G. J.; Neukomm, H.; Pickett, C. J.; Stanley, D. R. *Ibid.* 1980, 121.

(24) (a) Herrick, R. S.; Nieter-Burgmayer, S. J.; Templeton, J. L. *Inorg. Chem.* 1983, 22, 3275. (b) Davidson, J. L.; Green, M.; Sharp, D. W. A.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* 1974, 706. (c) Nesmeyanov, A. N.; Gusev, A. I.; Pasyanski, A. A.; Anisimov, K. N.; Kolobova, N. E.; Struchkov, Yu. T. *Ibid.* 1969, 277.

(25) Wrighton, M. *Chem. Rev.* 1974, 74, 401.

(26) Herrick, R. S.; Nieter-Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* 1983, 105, 2599.

We foresee extension of these spectroscopic probes to other formally electron-deficient monomers to assess the extent of ligand π donation in organometallic compounds. Control of LUMO properties through ligand π donation has important implications for unsaturated intermediates as well as for formal 16-electron complexes which can be isolated.²⁷

Acknowledgment. We wish to thank Professor T. J. Meyer for his constructive scientific suggestions and also for his generosity in providing equipment for the electrochemical measurements. We are grateful to C. R. Leidner for helpful discussions concerning the electrochemical studies. We thank the donors the Petroleum Research Fund, administered by the American Chemical Society,

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

and the NSF (CHE-8310121) for financial support.

Registry No. Mo(CO)(MeO₂CC=CCO₂Me)(detc)₂, 56954-20-2; Mo(CO)(Me₃SiC=CSiMe₃)(detc)₂, 88303-34-8; Mo(CO)(PhC=CPh)(detc)₂, 56954-16-6; Mo(CO)(PhC=CH)(detc)₂, 56954-17-7; Mo(CO)(HC=CH)(detc)₂, 56954-15-5; Mo(CO)(ClCH₂C=CH)(detc)₂, 88303-35-9; Mo(CO)(EtC=CEt)(detc)₂, 88303-36-0; Mo(CO)(MeC=CMe)(detc)₂, 88303-37-1; Mo(CO)(EtOC=CH)(detc)₂, 88303-38-2; Mo(CO)(Et₂NC=CMe)(detc)₂, 88303-39-3; W(CO)(MeO₂CC=CCO₂Me)(detc)₂, 88303-40-6; W(CO)(Ph₂PC=CPh₂)(detc)₂, 73848-25-6; W(CO)(PhC=CPh)(detc)₂, 73848-23-4; W(CO)(HC=CH)(detc)₂, 66060-14-8; W(CO)(PhC=CH)(detc)₂, 73848-24-5; W(CO)(HOCH₂C=CCH₂O)(detc)₂, 88303-41-7; W(CO)(EtC=CEt)(detc)₂, 73848-22-3; W(CO)(MeC=CMe)(detc)₂, 73856-95-8; W(CO)(EtOC=CH)(detc)₂, 88303-42-8; W(CO)(Et₂NC=CMe)(detc)₂, 88303-43-9; Mo(MeO₂CC=CCO₂Me)₂(detc)₂, 81476-43-9; Mo(PhC=CPh)₂(detc)₂, 81476-36-0; Mo(PhC=CMe)₂(detc)₂, 81476-38-2; Mo(PhC=CH)₂(detc)₂, 74456-80-7; Mo(*n*-BuC=CH)₂(detc)₂, 81476-41-7; Mo(EtC=CEt)₂(detc)₂, 81476-40-6; Mo(CO)₃(detc)₂, 18866-21-2; W(CO)₃(detc)₂, 72827-54-4.

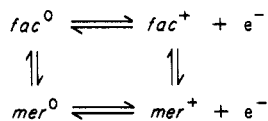
Study of Substituent Effects, Isomerization and Cross Redox Reactions Associated with Electrochemical Oxidation of Mo(CO)₃P₃ Systems

A. M. Bond,^{*1} S. W. Carr,² and R. Colton²

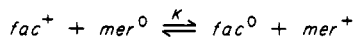
Division of Chemical and Physical Sciences, Deakin University, Waurn Ponds, Victoria, 3217, Australia, and the Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia

Received August 10, 1983

Homogeneous and heterogeneous aspects of the redox couple [Mo(CO)₃P₃]⁺⁰ (P = monodentate phosphorus ligand) have been examined by polarographic, voltammetric, and spectroscopic methods in dichloromethane solution. The tricarbonyl compounds in each oxidation state can exist in both facial (*fac*⁺, *fac*⁰) and meridional (*mer*⁺, *mer*⁰) forms. The cyclic voltammograms at room temperature often showed the form of quasi-reversible couples; however, they did not fit theoretical models for simple electron transfer. With use of low temperatures and a variety of scan rates, it was deduced that the electrode processes could be explained in terms of parts of the square reaction scheme



and the cross redox reaction.



At low temperatures it was possible to calculate $E^\circ(\text{fac}^{+0})$ and $E^\circ(\text{mer}^{+0})$ and hence calculate the equilibrium constant, K , for the cross redox reaction. Both K and the E° values showed a very large dependence on the nature of the phosphorus ligand. For *fac*-Mo(CO)₃P₃, a satisfactory linear correlation between carbon-13 NMR chemical shift ($\delta(^{13}\text{C})$) of the carbonyl ligands and $E^\circ(\text{fac}^{+0})$ was obtained, but similar correlations were not observed between $E^\circ(\text{fac}^{+0})$ and either $\delta(^{31}\text{P})$ of the phosphorus ligands or $\delta(^{95}\text{Mo})$ of the central molybdenum atom.

Introduction

Recently there has been considerable interest in the oxidation of 18-electron carbonyl compounds to the 17-electron configuration. A substantial theoretical effort has been made to attempt to understand the effect of the number of carbonyl groups, the influence of the other

ligands, the geometry of the complexes, and any structural differences between the 18- and 17-electron states.

A number of workers have attempted to provide a quantitative study of the thermodynamic factors that effect the electrochemical oxidation. For example, Pickett and Pletcher³ have developed a three-parameter equation for correlating the one-electron oxidation potential of the

(1) Deakin University.

(2) University of Melbourne.

(3) Pickett, C. J.; Pletcher, D. J. *Organomet. Chem.* 1975, 102, 327.