5.7% of all the linear pentene in the solution or roughly twice the amount present at the thermodynamic equilibrium. This clearly illustrates that the kinetically controlled product distribution from the photogenerated catalyst is enriched in the least stable isomer, but, as indicated above, the linear pentenes are ultimately equilibrated to the ratio that would be obtained from any other catalyst.

Quantum yields for isomerization generally exceed unity, indicating that a thermal catalyst is in fact generated. Moreover, the turnover rate of the catalyst must exceed the photoexcitation rate, $\sim 1.6 \times 10^{-6}$ einstein/min, otherwise the initial quantum yields would be less than one. But generally, we have used continuous irradiation to effect photocatalysis, since back reaction of coordinatively unsaturated species with photoejected CO precludes sustained catalysis at 25 °C after irradiation is terminated. The use of continuous irradiation raises the possibility that one could, in fact, drive the linear pentenes to a photostationary state that is enriched in 1-pentene, the least thermodynamically stable isomer. Empirically, this is not found; the ultimate distribution of the linear pentenes is just that found from conventional thermal catalysis.

To summarize our main finding then, we conclude that steric effects of ligands L in $[Fe(CO)_4L]$ or $[Ru_3(CO)_9L_3]$ promote the formation of the least thermodynamically stable pentene at initial stages of the photocatalyzed isomerization of pentene. Examples of other catalytic reactions in which the steric bulk of the phosphorus ligands affects the product distribution are the rhodium catalyzed hydroformylation reactions[4a,d,g,7] and some nickel-catalyzed olefin reaction.[4b,c] In the former system, Pruett and Smith[4a] showed that both the steric and electronic effects are important since increased electron donation from the ligand decreases the percentage of the normal isomer obtained but increased ligand bulk decreases the percentage of the normal isomer even more. In the nickel-catalyzed reaction of butadiene with morpholine Baker and coworkers[4b] showed that the percentage of products resulting from butadiene dimerization could be greatly enhanced by using bulky phosphorus ligands. The electronic effects of the phosphorus ligands on the product distribution were believed to be negligible in comparison. In both of these systems by knowing the nature of the effect of the phosphorus ligands on the product distribution, the reactions can be "tuned" to give the desired results simply by changing the phosphorus ligand. The results of our photocatalyzed 1-pentene isomerization reactions clearly demonstrate that the product distribution of photocatalyzed reactions can also be "tuned" in a similar manner, in this case by changing the steric bulk of the bonded phosphorus ligand. Inasmuch as the alkene isomerization that we have studied depends on the excitation rate (light intensity) it is clear that the activation energy for the catalysis is low. Future studies in this laboratory will include the use of photoexcitation to promote reaction where the temperature is sufficiently low to attempt to reach a situation where some step in the actual catalytic reaction is rate limiting.

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Registry No. 1-pentene, 109-67-1; $Fe(CO)_5$, 13463-40-6; $Fe(CO)_4P(OMe)_3$, 14878-71-8; $Fe(CO)_4P(O\text{-}o\text{-}tolyl)_3$, 18475-05-3; $Fe(CO)_4PPh_3$, 14649-69-5; $Ru_3(CO)_{12}$, 15243-33-1; $Ru_3(CO)_9(P(OMe)_3)_3$, 38686-18-9; $Ru_3(CO)_9(P(O\text{-}o\text{-}tolyl)_3)_3$, 81522-95-4; $Ru_3(CO)_9(PPh_3)_3$, 15663-31-7; $Fe(CO)_4$(1-pentene), 58614-17-8; $Fe(CO)_4$(*cis*-2-pentene), 58476-94-1; $Fe(CO)_4$(*trans*-2-pentene), 58525-49-8; $Fe(CO)_3(PPh_3)_2$, 14741-34-5; $Fe(CO)_3(P(OMe)_3)_2$, 14949-85-0; $Fe(CO)_3(PPh_3)(P(OMe)_3)$, 81522-96-5; $Fe(CO)_3(PPh_3)(P(O\text{-}o\text{-}tolyl)_3)$, 81522-97-6; $Fe(CO)_3(PPh_3)$(1-pentene), 81522-98-7; $Fe(CO)_3(P(OMe)_3)$(1-pentene), 81522-99-8; $Fe(CO)_3(P(O\text{-}o\text{-}tolyl)_3)$(1-pentene), 81523-00-4; $Ru(CO)_3(PPh_3)$(1-pentene), 81523-01-5; $Ru(CO)_3(P(OMe)_3)_2$, 31541-94-3; $Ru(CO)_3(P(O\text{-}o\text{-}tolyl)_3)_2$, 81523-02-6; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; $Ru(CO)_4PPh_3$, 21192-23-4.

Syntheses, Spectral Properties, and Dynamic Solution Behavior of Bis(alkyne)bis(dithiocarbamato)molybdenum(II) Complexes

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Syntheses of a series of bis(alkyne)bis(dithiocarbamato)molybdenum(II) complexes with terminal, alkyl- and aryl-substituted alkynes are reported. Mixed bis(alkyne) complexes of the type $Mo(R^1C{\equiv}CR^2)(R^3C{\equiv}CR^4)(S_2CNR_2)_2$ have been prepared with $R^1 = R^2 = Ph$, $R^3 = Ph$, and $R^4 = H$, $R^1 = R^2 = Ph$, and $R^3 = R^4 = CO_2Me$, and $R^1 = R^2 = Et$, $R^3 = Ph$, and $R^4 = H$. Infrared spectroscopy has been used to probe the stretching frequency of the bound alkyne carbon–carbon multiple bond. The observed ^1H and ^{13}C chemical shift values of the acetylenic protons and carbons are compatible with previous empirical correlations relating alkyne donation from both filled π orbitals to these NMR observables. Dynamic NMR studies suggest that rotation of the bound alkyne ligands is common for these complexes with a barrier to rotation of 15.3 kcal mol^{-1} calculated for $Mo(EtC{\equiv}CEt)_2(S_2CNMe_2)_2$. Molecular orbital calculations based on the extended Hückel method provide insight into the destabilization of the vacant $d\pi$ LUMO of these complexes which results from alkyne $\pi_\perp$ donation and rationalizes the relative inertness of these formal 16-electron molybdenum(II) compounds.

Introduction

Studies of early transition metal alkyne complexes during the past few years have contributed to an emerging appreciation of the unique ability of alkyne ligands to utilize orthogonal metal $d\pi$ orbitals in order to serve simultaneously as both good single-faced π acceptors and good single-faced π donors.[1] The ligand-to-metal π-donor potential of the filled alkyne $\pi_\perp$ bonding component allows variable electron donor interactions which can formally

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[1] Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713.

range from two to four electrons in response to the metal electron configuration and the bonding properties of the ancillary ligands in the coordination sphere.[2]

A number of six-coordinate d^4 monoalkyne carbonyl derivatives have been reported for both groups 5 and 6: $(\pi\text{-}C_5H_5)M(CO)_2(PhC{\equiv}CPh)$ (M = V, Nb, Ta);[3] $(\pi\text{-}C_5H_5)W(CO)Me(RC{\equiv}CR)$,[4] $(\pi\text{-}C_5H_5)M(CO)X(PhC{\equiv}CPh)$;[5] $(\pi\text{-}C_5H_5)M(CO)(SR^1)(CF_3C{\equiv}CCF_3)$ (M = Mo, W).[6] The alkyne carbonyl bis(dithiocarbamate) complexes of molybdenum[7] and tungsten[8] have been extensively studied by McDonald and co-workers at Kettering Laboratory. Oxo analogues of these alkyne carbonyl bis(dithiocarbamate) complexes, $M(O)(RC{\equiv}CR)(S_2CNR^1{}_2)_2$, have been reported for both M = Mo[9] and W.[10] These compounds are formally electron deficient if one considers the alkyne ligand a two-electron donor in analogy to the usual Dewar–Chatt–Duncanson metal–olefin bonding description;[11] note that no olefin analogues of these compounds have been prepared. The lack of electrophilic reactivity associated with these complexes has been attributed to the role of alkyne $\pi_\perp$ donation to the metal in destabilizing the lowest unoccupied orbital (LUMO) which effectively reduces the electrophilic character of the unsaturated metal center.[1]

Less common are monomeric d^4 complexes containing two uncoupled alkynes in the coordination sphere. Reaction of a complexed alkyne with additional alkyne often involves insertion or coupling to form organic products ranging from polyacetylenes or oligomers[12] to alkyne tetramers,[13] cyclotrimerized arenes,[14] metallocyclopentadienes,[15] or π-bound cyclobutadienes.[16] Previously reported early transition metal bis(alkyne) complexes include $(\pi\text{-}C_5H_5)M(CO)(PhC{\equiv}CPh)_2$ (M = V, Nb, Ta)[17] and $(\pi\text{-}C_5H_5)M(RC{\equiv}CR)_2X$ (M = Mo, X = Cl, R = CH_2OH;[18] M = Mo, W, X = Cl, Br, I, R = CF_3;[19] M = Mo, W, X = CO^+, R = CH_3[20]). The synthesis and characterization of $Mo(RC{\equiv}CR)_2(S_2CNR^1)_2$ compounds are addressed in this work.

The rationale for expanding the chemistry of bis(alkyne)bis(dithiocarbamato)molybdenum complexes as first reported by McDonald and co-workers for selected aryl and electron-withdrawing acetylene substituents[7] encompassed the following features: (1) improve and generalize preparative routes for this class of compounds; (2) synthesize mixed bis(alkyne) complexes of the type $Mo(RC{\equiv}CR)(R^1C{\equiv}CR^1)(dtc)_2$ (dtc = $^-S_2CNR_2$) as a basis for future synthetic manipulations; (3) examine vibrational and nuclear magnetic resonance properties of these complexes in light of previously reported data for $MY(RC{\equiv}CR)(dtc)_2$ (M = Mo, W) with Y = CO and O; (4) explore the dynamic solution behavior of *cis*-bis(alkyne) octahedral complexes; (5) extend the chemistry of isolable 16-electron Mo(II) monomers; (6) generate a qualitative molecular orbital basis for understanding the chemical reactivity of this series of complexes.

Experimental Section

Materials and Methods. All manipulations were performed under a dry oxygen-free nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over molecular sieves and degassed prior to use. Molybdenum hexacarbonyl, calcium carbide, sodium dialkyldithiocarbamates, chlorine gas, and alkynes other than the parent acetylene were obtained from commercial sources and used without further purification. Acetylene gas was either generated from calcium carbide and water or obtained from a commercial acetylene cylinder. Acetone, used as a stabilizing agent for liquid acetylene, was removed by use of a dry ice–2-propanol trap. $Mo(CO)_4Cl_2$,[21] $Mo(S_2CNR_2)_2(CO)_2$[22] (1), and $Mo(S_2CNR_2)_2(HC_2R^1)(CO)$[7] were prepared as described previously. Infrared spectra were recorded on a Beckman IR 4250 and calibrated with a polystyrene standard. ^1H NMR (100 MHz) were recorded on a Varian XL-100 spectrometer. ^{13}C NMR (62.89 MHz) were recorded on a WM Bruker 250 spectrometer. Chemical shifts are reported as parts per million downfield of Me_4Si. NMR sample temperatures were measured with a low-temperature thermometer located directly in the probe or by a thermocouple located near the probe. Elemental analyses were performed by Galbraith Laboratories of Knoxville, TN.

Syntheses. $Mo(R^1C{\equiv}CR^2)_2(S_2CNR_2)_2$ (R = Me (a), Et (b); $R^1 = R^2$ = Ph (2); R^1 = H, R^2 = Ph (3); R^1 = Me, R^2 = Ph (4)). The following preparative procedure is general for the synthesis of the alkyne complexes listed above. A solution of $Mo(CO)_2(S_2CNR_2)_2$ (2.0 g) in benzene (30 mL) was prepared. A slight excess of the appropriate alkyne (5–10% in excess of the 2 equiv required) was added to the solution which was brought to reflux. The solution turned green immediately after addition of alkyne. After 1 h the reaction was complete. Solvent was removed in vacuo from the brownish red solution. Chromatography on an alumina column using toluene as an eluent brought off an orange band. The solvent volume was reduced in vacuo followed by addition of an alkane solvent. The solid was filtered, washed with cold alkane solvent, and dried in vacuo to yield bright orange crystals in 80% yield. The products are air stable as solids and moderately air sensitive in solution.

$Mo(PhC_2Ph)_2(S_2CNMe_2)_2$: ^1H NMR ($CDCl_3$) δ 7.40 (m, 20 H, C_6H_5), 3.29 and 3.17 (s, 12 H, CH_3); IR (KBr) ν (C≡C) 1730

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(w) cm^{-1}. Anal. Calcd for $MoS_4N_2C_{34}H_{32}$: C, 58.93; H, 4.66. Found: C, 60.20; H, 4.70.

$Mo(PhC_2Ph)_2(S_2CNEt_2)_2$: ^1H NMR ($CDCl_3$) δ 7.27–7.60 (m, 20 H, C_6H_5), 3.61 (q, 8 H, CH_2), 1.12 (t, 12 H, CH_3); IR (KBr) $\nu(C{\equiv}C)$ 1737 (w) cm^{-1}. Anal. Calcd for $MoS_4N_2C_{38}H_{40}$: C, 60.93; H, 5.39. Found: C, 62.02; H, 5.65.

$Mo(HC_2Ph)_2(S_2CNMe_2)_2$: ^1H NMR ($CDCl_3$) δ 10.43 (s, 2 H, $\equiv CH$), 7.32–7.87 (m, 10 H, C_6H_5), 3.36 and 3.12 (s, 12 H, CH_3); ^{13}C NMR ($CDCl_3$, −40 °C) δ 183.8 (major isomer), 183.6, 181.6 and 181.0 (s, $\equiv \mathit{C}C_6H_5$), 178.1, 178.0, 176.0 (major isomer) and 174.0 (d, $^1J(\equiv CH(av))$ = 212 Hz, $\equiv CH$); IR (KBr) $\nu(C{\equiv}C)$ 1676 (w) cm^{-1}. Anal. Calcd for $MoS_4N_2C_{22}H_{24}$: C, 48.87; H, 4.48. Found: C, 49.17; H, 4.52.

$Mo(HC_2Ph)_2(S_2CNEt_2)_2$: ^1H NMR ($CDCl_3$) δ 10.39 (s, 2 H, $\equiv CH$), 7.29–7.66 (m, 10 H, C_6H_5), 3.73 (q, 8 H, CH_2), 1.06 (t, 12 H, CH_3); IR (KBr) $\nu(C{\equiv}C)$ 1704 (w) cm^{-1}. Anal. Calcd for $MoS_4N_2C_{26}H_{32}$: C, 52.33; H, 5.42. Found: C, 52.14; H, 5.69.

$Mo(MeC_2Ph)_2(S_2CNEt_2)_2$: NMR ($CDCl_3$) δ 7.32–7.47 (m, 10 H, C_6H_5), 3.60 (q, 8 H, CH_2), 1.10 (m, 18 H, CH_2CH_3 and $\equiv CCH_3$); IR (KBr) $\nu(C{\equiv}C)$ 1768 (w) cm^{-1}. Anal. Calcd for $MoS_4N_2C_{28}H_{36}$: C, 53.82; H, 5.82. Found: C, 53.96; H, 5.94.

$Mo(R^1C{\equiv}CR^2)_2(S_2CNR_2)_2$ (R = Me (a), Et (b); $R^1 = R^2$ = Et (5); R^1 = H, R^2 = *n*-Bu (6)). The following preparative procedure is general for the synthesis of the alkyne complexes listed above. A solution of $Mo(CO)_2(S_2CNR_2)_2$ (2.0 g) in toluene (30 mL) was prepared. A slight excess of the appropriate alkyne (5–10% in excess of the 2 equiv required) was added to the solution which was then brought to reflux. The solution color turned green immediately after addition of the alkyne. After 1 h the reaction was complete. Workup was accomplished in the manner described above with the exception that $Mo(EtC_2Et)_2(S_2CNEt_2)_2$ and $Mo(HC_2\text{-}n\text{-}Bu)_2(S_2CNEt_2)_2$, being moderately soluble in alkanes, were dissolved in pentane at room temperature and crystallized when cooled to −20 °C. The solid was filtered, washed with cold pentane, and dried in vacuo to yield bright orange crystals in 80% yield. They are air stable solids and moderately air sensitive in solution.

$Mo(EtC_2Et)_2(S_2CNMe_2)_2$: ^1H NMR ($CDCl_3$) δ 3.46 and 3.22 (s, 12 H, N-CH_3), 3.04 (m, 8 H, CH_2), 1.13 (t, 12 H, $\equiv CCH_2\mathit{CH}_3$); ^{13}C NMR ($CDCl_3$) δ 183.8 and 181.3 (s, $\equiv \mathit{C}CH_2$); IR (KBr) $\nu(C{\equiv}C)$ 1795 (w) cm^{-1}. Anal. Calcd for $MoS_4N_2C_{18}H_{32}$: C, 43.18; H, 6.46. Found: C, 43.19; H, 6.20.

$Mo(EtC_2Et)_2(S_2CNEt_2)_2$: ^1H NMR ($CDCl_3$) δ 3.64 (q, 8 H, $N\mathit{CH}_2CH_3$), 3.07 (m, 8 H, $\equiv C\mathit{CH}_2$), 1.12 (m, 24 H, $NCH_2\mathit{CH}_3$ and $\equiv CCH_2\mathit{CH}_3$); IR (KBr) $\nu(C{\equiv}C)$ 1786 (w) cm^{-1}. Anal. Calcd for $MoS_4N_2C_{22}H_{40}$: C, 47.46; H, 7.26. Found: C, 47.45; H, 7.29.

$Mo(HC_2\text{-}n\text{-}Bu)_2(S_2CNMe_2)_2$: ^1H NMR_3 ($CDCl_3$) δ 9.72 (s, 2, $\equiv CH$), 3.48 and 3.21 (s, 12 H, N-CH_3), 3.12 (m, 4 H, $\equiv C\mathit{CH}_2$), 1.62 (m, 4 H, $\equiv CCH_2\mathit{CH}_2$), 1.26 (m, 4 H, $\equiv CCH_2CH_2\mathit{CH}_2$), 0.87 (t, 6 H, $\equiv CCH_2CH_2CH_2\mathit{CH}_3$); ^{13}C NMR ($CDCl_3$, −40 °C) δ 189.3, 188.3 (major isomer) and 187.7 (s, $\equiv \mathit{C}C_4H_9$), 170.4, 169.2 (major isomer), 167.8 and 167.0 (d, $J(\equiv CH(av))$ = 210 Hz, $\equiv CH$); IR (KBr) $\nu(C{\equiv}C)$ 1717 (w), 1699 (w) cm^{-1}. Anal. Calcd for $MoS_4N_2C_{18}H_{32}$: C, 43.18; H, 6.46. Found: C, 43.42; H, 6.50.

$Mo(HC_2\text{-}n\text{-}Bu)_2(S_2CNEt_2)_2$: ^1H NMR ($CDCl_3$) δ 9.66 (s, 2 H, $\equiv CH$), 3.92 (m, 4 H, $\equiv CCH_2$), 3.63 (q, 8 H, NCH_2), 2.79 (m, 4 H, $\equiv(CH_2\mathit{CH}_2)$, 1.55 (m, 4 H, $\equiv CCH_2CH_2\mathit{CH}_2$), 1.13 and 1.35 (t, 12 H, $\equiv NCH_2CH_3$), 0.83 (t, 6 H, $\equiv CCH_2CH_2CH_2\mathit{CH}_3$); IR (KBr) $\nu(C{\equiv}C)$ 1713 (w) 1696 (w) cm^{-1}. Anal. Calcd for $MoS_4N_2C_{22}H_{40}$: C, 47.46; H, 7.26. Found: C, 46.97, H, 7.28.

$Mo(R^1C{\equiv}CR^1)_2(S_2CNR_2)_2$ (8) (R = Me, Et; $R^1 = CO_2Me$). In a representative reaction dimethylacetylenedicarboxylate (DMAC) (1.05 mL, 1.22 g, 8.56 mmol) was added to a solution of $Mo(CO)(HC{\equiv}CH)(S_2CNMe_2)_2$ (**7a**) (1.54 g, 3.94 mmol) and CH_2Cl_2 (30 mL) in a Schlenk flask. The reaction was stirred 2 h with occasional venting of the flask to allow evolved acetylene gas to escape. The solution was reduced in vacuo to 3 mL. Hexane (10 mL) was added and the solution slowly cooled to −20 °C. $Mo(DMAC)_2(S_2CNMe_2)_2$ (**8a**) (2.3 g, 3.71 mmol), 95% yield, was isolated as air stable garnet crystals.

$Mo(DMAC)_2(S_2CNMe_2)_2$: ^1H NMR ($CDCl_3$) δ 3.85 (s, 12 H, $\mathit{CH}_3O_2CC{\equiv}$), 3.44 and 3.16, (s, 12 H, NCH_3); IR (KBr) $\nu(C{\equiv}C)$ 1819 (w) cm^{-1}. Anal. Calcd for $MoS_4N_2C_{18}H_{24}O_8$: C, 34.83; H, 3.81. Found: C, 34.18; H, 3.81.

$Mo(DMAC)_2(S_2CNEt_2)_2$: ^1H NMR ($CDCl_3$) δ 3.82 (s, 12 H, $CH_3O_2CC{\equiv}$), 3.58 (q, 8 H, CH_2), 1.14 (t, 12 H, NCH_2CH_3). Anal. Calcd for $MoS_4N_2C_{22}H_{32}O_8$: C, 39.04; H, 4.76. Found: C, 39.72; H, 4.95.

$Mo(HC{\equiv}CH)_2(S_2CNR_2)_2$ (9). Three distinct routes were used in attempts to produce the parent bis(acetylene) species. (i) $Mo(S_2CNMe_2)_2(CO)(HC_2H)$ (**7a**) (0.36 g, 0.92 mmol) and 5 mL of toluene were added to a 20-mL Carius tube. The Carius tube was placed in liquid nitrogen and connected in series by vacuum hose with a drying tube and a 100-mL flask and addition funnel. The system was partially evacuated. Acetylene gas was generated from the reaction of H_2O and calcium carbide (0.32 g). After 0.5 h of static vacuum it was assumed acetylene transfer to the Carius tube was complete. The tube was sealed under vacuum and placed in a steel cylinder in an oil bath. The tube was heated 10 h at 90 °C. At the end of that time the solution color had changed from green to orange-brown. The tube was cracked, and the contents were extracted (CH_2Cl_2, 3 × 5 mL) in a Schlenk flask. The solution was reduced in vacuo and chromatographed on a short alumina column with toluene. A very pale orange band (probably $Mo(HC_2H)_2(S_2CNMe_2)_2$) eluted first followed by a small green band composed of starting material. The remaining product stayed at the top of the column as orange-brown decomposition products. Not enough of the pale orange band was collected to identify it as the bis(ethyne) complex. (ii) A solution of $Mo(CO)_2(S_2CNMe_2)_2$ (0.78 g, 1.99 mmol) and 100 mL of xylene in a 300-mL 2-neck Schlenk flask was converted to $Mo(CO)(HC_2H)(S_2CNMe_2)_2$ utilizing commercial acetylene. A 500-mL Schlenk flask containing lumps of calcium carbide (30 g, 470 mmol) was connected by Tygon tubing to a large drying tube containing anhydrous calcium chloride and Drierite indicator. A syringe needle, connected by a syringe needle adapter and Tygon tubing to the exit tube part of the drying tube, was placed through a septum directly into the solution of $Mo(CO)(HC_2H)(S_2CNMe_2)_2$. The solution was heated to reflux. Distilled water was slowly dripped from a dropping funnel onto the calcium carbide generating acetylene gas which bubbled into the xylene solution. A mineral oil bubbler attached to the top of the reflux condenser acted as the outlet for excess pressure buildup in the reaction flask. As the temperature approached reflux, the solution changed from the characteristic green of $Mo(CO)(HC_2H)(S_2CNMe_2)_2$ to a muddy brown. The solution was heated 1.5 h while a steady stream of acetylene was bubbled through the solution. The reflux was terminated when the supply of acetylene was exhausted. After the solution was cooled, the solvent was removed in vacuo and the solid chromatographed as described above. A large amount of unidentified brown decomposition product and very small amounts of $Mo(HC_2H)_2(S_2CNMe_2)_2$ and $Mo(CO)(HC_2H)(S_2CNMe_2)_2$ were separated. The orange band containing $Mo(HC_2H)_2(S_2CNMe_2)_2$ and residual amounts of $Mo(CO)(HC_2H)(S_2CNMe_2)_2$ were rechromatographed on a smaller column to isolate pure $Mo(HC_2H)_2(S_2CNMe_2)_2$. (iii) $Mo(CO)_2(S_2CNEt_2)_2$ (1.0 g, 2.23 mmol) was weighed into a 150-mL stainless-steel bomb in a drybox. The bomb was removed from the drybox and connected to stainless-steel tubing used to admit gas to the bomb chamber. Toluene (25 mL) was added via syringe. Oxygen was removed from the system by a water aspirator. The bomb was pressurized with C_2H_2 to 96 psi and the solution warmed to 90 °C. The bomb was vented twice to monitor the progress of the reaction by soluton IR and remove CO evolved from the reaction. After 5 h the reaction was judged to be complete. The solution was transferred by syringe to a round-bottom Schlenk flask. The residue was extracted with CH_2Cl_2 (3 × 20 mL). The solvent was reduced in vacuo and chroamtographed as described above. A small orange band containing $Mo(HC_2H)_2(S_2CNEt_2)_2$ was eluted followed by a small green band containing $Mo(CO)(HC_2H)(S_2CNEt_2)_2$. A very large amount of decomposition product remained at the top of the column. Solvent from the orange solution was removed in vacuo to yield a gummy orange solid: ^1H NMR ($CDCl_3$) δ 10.46 and 10.12 (s, 4 H, $\equiv CH$), 2.96–3.23 (m, 8 H, CH_2), 0.71–0.91 (m, 12 H, CH_3).

$Mo(HC_2Ph)(PhC_2Ph)(S_2CNEt_2)_2$ (10b). Diphenylacetylene (0.08 g, 0.45 mmol) was added to a solution of $Mo(S_2CNEt_2)_2(HC_2Ph)(CO)$ (0.22 g, 0.42 mmol) in benzene (25 mL). The green solution was brought to reflux. After 1 h there were no bands in the solution IR attributable to ν(CO), and the solution color was orange. The solution was reduced in vacuo. Heptane was added to induce the precipitation of the orange solid identified by the ^{1}H NMR of the downfield acetylenic proton region as containing $\mathrm{Mo(HC_2Ph)(PhC_2Ph)(S_2CNEt_2)_2}$ and $\mathrm{Mo(HC_2Ph)_2(S_2CNEt_2)_2}$ in the ratio 3:1. $\mathrm{Mo(PhC_2Ph)_2(S_2CNEt_2)_2}$ may also have been present in this mixture but could not be positively identified: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 10.63 (br s, 3 integration units, $\equiv$CH of $\mathrm{Mo(HC_2Ph)(PhC_2Ph)(S_2CNEt_2)_2}$ 10.44 (s, 1 integration unit, $\equiv$CH of $\mathrm{Mo(HC_2Ph)_2(S_2CNEt_2)_2}$.

Mo(RC≡CR)(PhC≡CPh)($\mathbf{S_2CNMe_2}$)$_2$ (R = $\mathbf{CO_2Me}$, DMAC). Dimethylacetylenedicarboxylate (0.074 g, 0.52 mmol, 0.064 mL) was added to an orange solution of $\mathrm{Mo(PhC_2Ph)_2(S_2CNMe_2)_2}$ (0.87 g, 1.26 mmol) in toluene (25 mL). The solution was heated to reflux. The reaction, followed by monitoring the ν(C=O) band of the diester alkyne, was judged complete after 3 h. The dark orange-brown solution was reduced in vacuo and chromatographed on an alumina column. An orange band containing $\mathrm{Mo(PhC_2Ph)_2(S_2CNMe_2)_2}$ was eluted with toluene. A second orange band containing $\mathrm{Mo(PhC_2Ph)(DMAC)(S_2CNMe_2)_2}$ was eluted by using a 50:50 mixture of toluene and $\mathrm{CH_2Cl_2}$. Solvent was removed from both solutions to yield <50 mg of each product. The remaining reaction mixture could not be eluted from the column: ^{1}H NMR of $\mathrm{Mo(PhC_2Ph)(DMAC)(S_2CNMe_2)_2}$ ($\mathrm{CDCl_3}$) δ 7.27–7.78 (m, 10 H, $\mathrm{C_6H_5}$), 3.93 (s, 6 H, $\mathrm{CH_3O_4CC}\equiv$), 3.40, 3.24 and 3.04 (s, 12 H, ratio 1:2:1, N-$\mathrm{CH_3}$).

Mo(PhC$_2$H)(EtC$_2$Et)($\mathbf{S_2CNMe_2}$)$_2$ (12a). 3-Hexyne (0.127 g, 1.54 mmol, 0.175 mL) was added to a solution of $\mathrm{Mo(S_2CNMe_2)_2(HC_2Ph)(CO)}$ (0.718 g, 1.79 mmol) in benzene (25 mL). The solution was brought to reflux. After 1 h the solution color was dark orange-brown. The solvent was removed in vacuo. The solid was chromatographed on an alumina column with toluene as eluent. An orange oil was isolated. ^{1}H NMR showed a mixture of $\mathrm{Mo(HC_2Ph)(EtC_2Et)(S_2CNMe_2)_2}$ and $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$ in the ratio of 4:1. Medium-pressure chromatography with an almina column 1 cm × 100 cm, using toluene as the eluent, under 20 psi of pressure yielded partial separation of the two bis(alkynes). A light orange band was eluted slightly before a dark orange band. The light orange band contained $\mathrm{Mo(HC_2Ph)(EtC_2Et)(S_2CNMe_2)_2}$ and $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$ in the ratio 30:1. The dark orange band showed the presence of both these same two compounds in significant amounts: ^{1}H NMR of $\mathrm{Mo(HC_2Ph)(EtC_2Et)(S_2CNMe_2)_2}$ ($\mathrm{CDCl_3}$) δ 10.08 and 9.96 (s, 1 H, $\equiv$CH, two rotational isomers), 7.16–7.62 (m, 5 H, $\mathrm{C_6H_5}$), 3.06–3.47 (m, 16 H, $\mathrm{NCH_3}$ and $\equiv\mathrm{CCH_2}$), 1.14 (m, 6 H, $\equiv\mathrm{CH_2C}H_3$).

Mo(PhC$_2$Ph)(HC$_2$-*n*-Bu)($\mathbf{S_2CNMe_2}$)$_2$ (13a). A fivefold excess of 1-hexyne (0.032 g, 0.385 mmol, 0.043 mL) was added to a solution of $\mathrm{Mo(S_2CNMe_2)_2(CO)(PhC_2Ph)}$ (0.042 g, 0.077 mmol) in $\mathrm{CH_2Cl_2}$ (mL). The solution was stirred 18 h. The solvent was removed in vacuo, leaving an oily orange solid. ^{1}H NMR indicates the presence of both $\mathrm{Mo(PhC_2Ph)_2(S_2CNMe_2)_2}$ and Mo(HC$_2$-*n*-Bu)($\mathrm{PhC_2Ph)(S_2CNMe_2)_2}$ in an approximate ratio of 3:1: ^{1}H NMR of Mo(HC$_2$-*n*-Bu)($\mathrm{PhC_2Ph)(S_2CNMe_2)_2}$ δ 10.02 (s, 1 H, $\equiv$CH), 7.27 (m, 10 H, $\mathrm{CC_6H_5}$), 3.30 (m, 2 H, $\equiv\mathrm{CCH_2}$), 3.15 and 3.02 (s, 12 H, $\mathrm{NCH_3}$), 1.20–1.50 (m, 4 H, $\equiv\mathrm{CCH_2C}H_2\mathrm{C}H_2$), 0.075 (t, 3 H, $\equiv\mathrm{CCH_2CH_2CH_2C}H_3$).

Theoretical Calculations. The extended Hückel method was employed in this study. Program number QCPE 358 from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, was used for these calculations. Values for the parameters used in these calculations were obtained from published sources.[23] The crystallographic coordinates of $\mathrm{W(S_2CNMe_2)_2(CO)(HC_2H)}$[8a] were used to establish the dithiocarbamate geometry. The N–H distance was set at 1.02 Å. The C≡C bond distance was fixed at 1.29 Å. A bent acetylene geometry with C–C–H angles of 135° and C–H distances of 1.07 Å was adopted. A Mo–C(alkyne) distance of 2.17 Å (average) was used based on the comparison of analogous distances in (η^5-$\mathrm{C_5H_5)W(CF_3C_2CF_3)_2Cl}$[19] and ($\eta^5$-$\mathrm{C_5H_5)Nb(PhC_2Ph)_2(CO)}$.[17] The overall geometry was pseudooctahedral with the cis alkynes aligned parallel with respect to one another.

Results

Syntheses. The preparation of bis(alkyne) complexes of the type $\mathrm{Mo(RC{\equiv}CR)_2(dtc)_2}$ (dtc = $^-\mathrm{S_2CNR_2}$) has been briefly described based on the reaction of $\mathrm{Mo(CO)_2(S_2CNEt_2)_2}$ with excess PhC≡CH, $\mathrm{(MeO_2C)_2C_2}$, or related alkynes in methylene chloride at reflux for 18 hours.[7] We wish to report syntheses of new bis(alkyne) complexes of both internal and terminal alkyl alkynes as well as improved routes to the previously available bis(alkyne)bis(dithiocarbamato)molybdenum complexes as depicted in Scheme I. The temperatures accessible in refluxing aromatic solvents substantially decreased the reaction time and consistently produce yields of 70–80% based on the limiting metal carbonyl reagent. Syntheses of compounds with 3-hexyne (**5**) and 1-hexyne (**6**) ligands were not feasible in low boiling chlorinated solvents.

Scheme I

$$\text{(i)}\ \mathrm{Mo(CO)_2(S_2CNR_2)_2 + 2R^1C{\equiv}CR^2} \xrightarrow[80\ °\mathrm{C,\ 1\ h}]{\text{benzene}}$$

1a, R = Me, dmtc
1b, R = Et, detc

$$\mathrm{Mo(R^1C{\equiv}CR^2)_2(S_2CNR_2)_2 + 2CO(g)}$$

2, $R^1 = R^2 = Ph$
3, $R^1 = H, R^2 = Ph$
4, $R^1 = Me, R^2 = Ph$

$$\text{(ii)}\ \mathrm{Mo(CO)_2(S_2CNR_2)_2 + 2R^1C{\equiv}CR^2} \xrightarrow[110\ °\mathrm{C,\ 4\ h}]{\text{toluene}}$$

1a, R = Me,dmtc
1b, R = Et, detc

$$\mathrm{Mo(R^1C{\equiv}CR^2)_2(S_2CNR_2)_2 + 2CO(g)}$$

5, $R^1 = R^2 = Et$
6, $R^1 = H, R^2 = n\text{-}Bu$

The formation of $\mathrm{Mo(DMAC)_2(dtc)_2}$ (**8**) (DMAC = dimethylacetylenedicarboxylate) from $\mathrm{Mo(CO)_2(S_2CNR_2)_2}$ and free dimethylacetylenedicarboxylate occurs at room temperature in 1 h. Column chromatography on alumina, which was utilized to purify products **2**–**6**, was unsuccessful in purifying $\mathrm{Mo(DMAC)_2(dtc)_2}$. Although multiple recrystallizations of the crude reaction product produced pure samples of the desired bis(alkyne) complex, a preferable preparation was realized by employing $\mathrm{Mo(CO)(HC{\equiv}CH)(dtc)_2}$ (**7**) as the reagent of choice for generating $\mathrm{Mo(DMAC)_2(dtc)_2}$ by ligand substitution as shown in Scheme II. This method provided analytically pure product without additional recrystallizations.

Scheme II

$$\text{(i)}\ \mathrm{Mo(CO)_2(S_2CNR_2)_2 + HC{\equiv}CH(g)} \rightarrow$$

1a, R = Me, dmtc
1b, R = Et, detc

$$\underset{\mathbf{7}}{\mathrm{Mo(CO)(HC{\equiv}CH)(S_2CNR_2)_2}} + \mathrm{CO(g)}$$

(ii)

$$\underset{\mathbf{7}}{\mathrm{Mo(CO)(HC{\equiv}CH)(S_2CNR_2)_2}} + \mathrm{(MeO_2C)_2C_2} \xrightarrow{\mathrm{CH_2Cl_2}}$$

$$\underset{\mathbf{8}}{\mathrm{Mo(MeO_2CC{\equiv}CCO_2Me)_2(S_2CNR_2)_2}} + \mathrm{CO(g)} + \mathrm{CH_2H_2(g)}$$

Efforts to effect the synthesis of $\mathrm{Mo(HC{\equiv}CH)_2(dtc)_2}$ in reasonable yields were unsuccessful. Only trace amounts of the desired parent bis(acetylene) complex were isolated from reactions employing excess acetylene with pressures up to 95 psi.

The formation of mixed bis(alkyne) complexes was shown to be technically feasible by synthesis of the representative mixed complexes listed in Scheme III. These

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[23] (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Stockis, A.; Hoffmann, R. *Ibid.* **1980**, *102*, 2952. (c) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

Scheme III

$$\text{(i)}\ \mathrm{Mo(CO)(PhC{\equiv}CH)(dtc)_2 + RC{\equiv}CR} \xrightarrow[80\ ^\circ\mathrm{C},\ 1\ \mathrm{h}]{\text{benzene}} \underset{\substack{\mathbf{10},\ \mathrm{R = Ph}\\ \mathbf{12},\ \mathrm{R = Et}}}{\mathrm{Mo(PhC{\equiv}CH)(RC{\equiv}CR)(dtc)_2}} + \mathrm{Mo(PhC{\equiv}CH)_2dtc_2 + CO(g)}$$

$$\text{(ii)}\ \mathrm{Mo(PhC{\equiv}CPh)_2(dmtc)_2 + RC{\equiv}CR} \xrightarrow[110\ ^\circ\mathrm{C},\ 3\ \mathrm{h}]{\text{toluene}} \underset{\mathbf{11a},\ \mathrm{R = CO_2Me}}{\mathrm{Mo(PhC{\equiv}CPh)(RC{\equiv}CR)(dmtc)_2}} + \mathrm{Mo(RC{\equiv}CR)_2(dmtc)_2}$$

$$\text{(iii)}\ \mathrm{Mo(CO)(PhC{\equiv}CPh)(dmtc)_2 + HC{\equiv}C\text{-}\mathit{n}\text{-}Bu} \xrightarrow[18\ \mathrm{h}]{\mathrm{CH_2Cl_2}} \underset{\mathbf{13a}}{\mathrm{Mo(PhC{\equiv}CPh)(HC{\equiv}C\text{-}\mathit{n}\text{-}Bu)(dmtc)_2}} + \mathrm{Mo(PhC{\equiv}CPh)_2(dmtc)_2 + CO(g)}$$

complexes are formed along with at least one and sometimes both other possible bis(alkyne) products. In the case of $\mathrm{Mo(CO)(PhC{\equiv}CPh)(dtc)_2}$ room temperature reaction with the relatively unreactive 1-hexyne in excess produced substantial amounts of $\mathrm{Mo(PhC{\equiv}CPh)_2(dtc)_2}$ with the desired mixed complex, $\mathrm{Mo(PhC{\equiv}CPh)(HC{\equiv}C\text{-}\mathit{n}\text{-}Bu)(dtc)_2}$, constituting only 25% of the isolated bis(alkyne) material. The mixed product $\mathrm{Mo(PhC{\equiv}CPh)(DMAC)(dtc)_2}$ was successfully purified by column chromatography. Preparation of $\mathrm{Mo(PhC{\equiv}CH)(EtC{\equiv}CEt)(S_2CNMe_2)_2}$ from $\mathrm{Mo(CO)(PhC{\equiv}CH)(S_2CNMe_2)_2}$ and 3-hexyne followed by chromatography on alumina produced the desired mixed alkyne and the bis(phenylacetylene) complex in a 4:1 ratio. Further chromatographic separation with a medium pressure apparatus produced a ratio of $\mathrm{Mo(HC_2Ph)(EtC_2Et)(S_2CNMe_2)_2}$ to $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$ of 30:1. No attempt was made to separate $\mathrm{Mo(HC_2Ph)(PhC_2Ph)(S_2CNMe_2)_2}$ or $\mathrm{Mo(HC_2\text{-}\mathit{n}\text{-}Bu)(PhC_2Ph)(S_2CNMe_2)_2}$ from the bis(alkyne) byproducts generated during their preparation.

Infrared Vibrational Data. The $\nu(\mathrm{C{\equiv}C})$ stretching mode for these compounds can be observed as a very weak band in concentrated KBr disks for each of the bis(alkyne) complexes listed in Table I. Resolution of the two weakly coupled $\nu(\mathrm{C{\equiv}C})$ vibrational frequencies of the two *cis*-alkynes was observed in several cases (Figure 1). The absorption frequencies for the $\mathrm{Mo(RC{\equiv}CR)_2(dtc)_2}$ complexes under investigation ranged from 1676 to 1819 $\mathrm{cm^{-1}}$.

NMR Properties. Proton NMR spectra of $\mathrm{Mo(HC{\equiv}CR)_2(dtc)_2}$ complexes display resonances assigned to terminal acetylenic protons between δ 9.6 and 10.5. At low temperatures (below −50 °C) both $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$ and $\mathrm{Mo(HC_2\text{-}\mathit{n}\text{-}Bu)_2(S_2CNMe_2)_2}$ exhibit four distinct singlets in this low-field region with two of the four mated to one another by equal intensities; all four signals coalesce as the sample is warmed to ambient temperature. Seven resolved ^{1}H methyl signals are observed for the *N*,*N*-dimethyldithiocarbamate ligands in these two complexes in the low-temperature limit; these average to produce two equal intensity signals at room temperature (Figure 2).

Carbon-13 NMR spectra of $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$, $\mathrm{Mo(EtC_2Et)_2(S_2CNMe_2)_2}$, and $\mathrm{Mo(HC_2\text{-}\mathit{n}\text{-}Bu)_2(S_2CNMe_2)_2}$ display acetylenic carbon-13 resonances in the range of 167–190 ppm with internal alkyne carbons downfield of terminal carbon resonances. Gated decoupled carbon-13 spectra of $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$ and $\mathrm{Mo(HC_2\text{-}\mathit{n}\text{-}Bu)_2(S_2CNMe_2)_2}$ served to positively identify terminal alkyne carbons while furnishing ^1J(C–H) coupling constants of 212 and 210 Hz, respectively.

Table I. $\mathrm{Mo(R^1C{\equiv}CR^2)_2(dtc)_2}$ $\nu(\mathrm{C{\equiv}C})$ Infrared Stretching Frequencies

complex	$\nu(\mathrm{C{\equiv}C})$, $\mathrm{cm^{-1}}$
$\mathrm{Mo(PhC_2Ph)_2(S_2CNMe_2)_2}$	1730
$\mathrm{Mo(PhC_2Ph)_2(S_2CNEt_2)_2}$	1737
$\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$	1676
$\mathrm{Mo(HC_2Ph)_2(S_2CNEt_2)_2}$	1704
$\mathrm{Mo(MeC_2Ph)_2(S_2CNEt_2)_2}$	1768
$\mathrm{Mo(EtC_2Et)_2(S_2CNMe_2)_2}$	1795
$\mathrm{Mo(EtC_2Et)_2(S_2CNEt_2)_2}$	1786
$\mathrm{Mo(HC_2\text{-}\mathit{n}\text{-}Bu)_2(S_2CNMe_2)_2}$	1717
$\mathrm{Mo(HC_2\text{-}\mathit{n}\text{-}Bu)_2(S_2CNEt_2)_2}$	1713, 1696
$\mathrm{Mo(DMAC)_2(S_2CNMe_2)_2}$	1819, 1797
$\mathrm{Mo(DMAC)_2(S_2CNEt_2)_2}$	1787

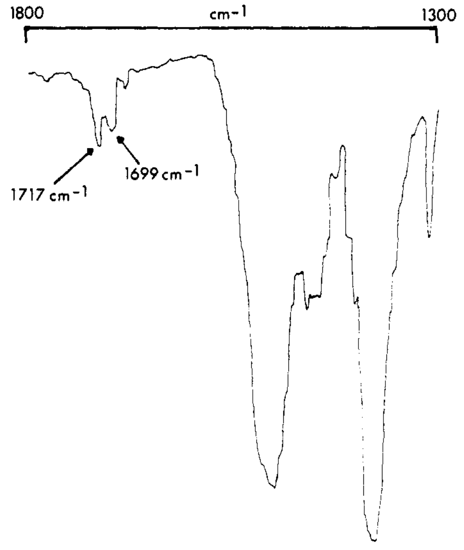

Figure 1. Infrared absorptions assigned to $\nu(\mathrm{C{\equiv}C})$ of $\mathrm{Mo(MeO_2CC{\equiv}CCO_2Me)_2(dmtc)_2}$ (concentrated KBr pellet sample).

The results of a variable-temperature carbon-13 NMR study of the symmetrical bis(3-hexyne) complex, $\mathrm{Mo(EtC_2Et)_2(S_2CNMe_2)_2}$, are shown in Figure 3 where coalescence of the methylene carbons of the alkyne ethyl groups is evident near 313 K. The two signals due to dithiocarbamate methyl groups at low temperatures coalesce near 333 K.

Discussion

Chemical Reactivity Patterns. The chemistry of $\mathrm{M(CO)_3(dtc)_2}$ (M = Mo, W) is characterized by facile carbon monoxide substitution reactions. These reagents have proven to be a fertile source of dithiocarbamate carbonyl derivatives of both molybdenum(II) and tungsten(II) as a result of reaction 1 where L can be ^{13}CO,[24]

$$\mathrm{M(CO)_3(dtc)_2 + L \rightarrow M(CO)_2L(dtc)_2 + CO(g)} \quad (1)$$

$\mathrm{PPh_3}$, $\mathrm{PR_3}$, $\mathrm{P(OR)_3}$,[25] pyridine, or tetrahydrothiophene[26] while with L = hydrazine a bridged dimer has been isolated ($\mathrm{[Mo(CO)_2(dtc)_2]_2N_2H_4}$).[27] Substitution of the dicarbonyl derivatives to form seven-coordinate $\mathrm{M(CO)L_2(dtc)_2}$ complexes is substantially more difficult, but such products have recently been reported with phosphine ligands.[25,28]

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[24] Templeton, J. L. *Adv. Chem. Ser.* **1979**, *No. 173*, 263.

[25] Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 3743.

[26] Nieter, S. J.; Templeton, J. L., unpublished results.

[27] Broomhead, J. A.; Budge, J.; Enemark, J. H.; Feltham, R. D.; Gelder, J. I.; Johnson, P. L. *Adv. Chem. Ser.* **1977**, *No. 162*, 421.

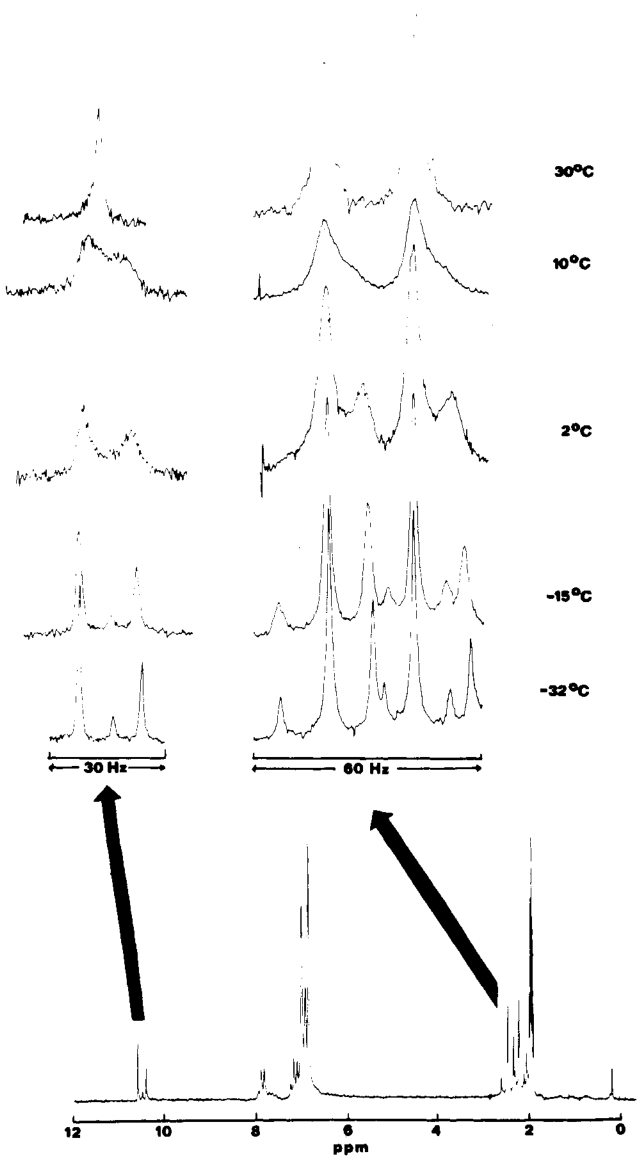

Figure 2. Dynamic ^{1}H NMR spectra of Mo(HC$_2$Ph)$_2$(S$_2$CNMe$_2$)$_2$. Averaging of the four low-temperature acetylenic proton signals and collapse to only two dithiocarbamate methyl signals occurs with increasing temperature.

The rapid formation of M(CO)(RC≡CR)(dtc)$_2$ products from reaction of acetylenes with the tricarbonyl parent compounds at room temperature is accompanied by loss of two carbon monoxide ligands and must be considered surprising in view of the difficulty encountered in preparing other monocarbonyl derivatives of these complexes. Furthermore incorporation of a second alkyne with loss of the lone remaining carbonyl ligand occurs in a facile room temperature reaction for M = Mo with R = CH$_3$O$_2$C. A similar substitution takes place in refluxing benzene or toluene for aryl- and alkylacetylenes, respectively.

The relative rate of conversion of the monocarbonyl(alkyne)molybdenum complexes, Mo(CO)(RC≡CR)(dtc)$_2$, to the bis(alkyne) species, Mo(RC≡CR)$_2$(dtc)$_2$, varies with the nature of the alkyne substituents. Qualitatively the more electron-withdrawing groups promote more rapid formation of the bis(alkyne) product as evident in the observed order (MeO$_2$C)$_2$C$_2$ > Ph$_2$C$_2$, PhC$_2$Me, PhC$_2$H > Et$_2$C$_2$, *n*-BuC$_2$H. Note that formation of the monoalkyne carbonyl reagent is rapid for all of the alkynes studied, and the observed rate variation for formation of the bis(alkyne) complexes from Mo(CO)$_3$(dtc)$_2$ arises solely from the step which involves replacement of the last carbonyl ligand by the second alkyne ligand. Preliminary kinetic data for reaction 2 are in accord with a first-order rate expression

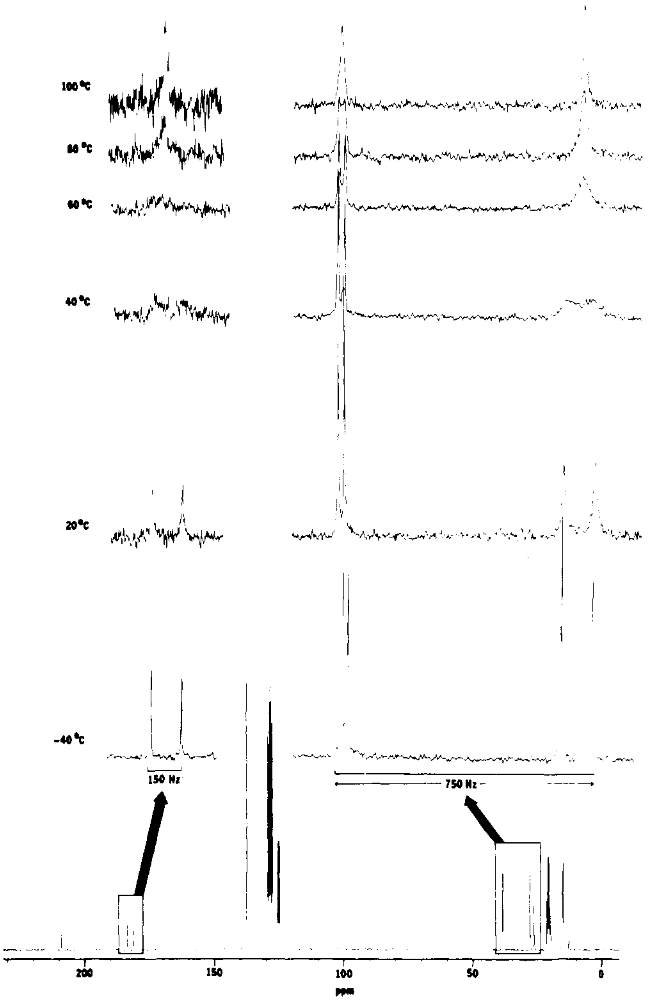

Figure 3. Dynamic ^{13}C NMR of Mo(EtC$_2$Et)$_2$(S$_2$CNMe$_2$)$_2$. Two-site exchange between the inequivalent ends of the alkyne ligands occurs first followed by averaging of the two dithiocarbamate methyl signals at higher temperatures.

$$\mathrm{Mo(CO)(RC{\equiv}CR)(dtc)_2 + RC{\equiv}CR \rightarrow Mo(RC{\equiv}CR)_2(dtc)_2 + CO(g)} \quad (2)$$

which is zero order in added alkyne. Watson and Bergman have obtained similar kinetic results for the exchange reaction of [(π-C$_5$H$_5$)Mo(CH$_3$C≡CCH$_3$)$_2$(CO)]$^+$ with CD$_3$-C≡CCD$_3$.[20] This suggests that the rates observed for transformation of Mo(CO)(RC≡CR)(dtc)$_2$ to Mo(RC≡CR)$_2$(dtc)$_2$ depend on the alkyne in the coordination sphere rather than on reactivity of the free alkyne. More extensive kinetic studies are now in progress to probe the mechanism of this reaction.

The potential utility of selective dimerization and trimerization of unsymmetrical and distinct alkynes in a stepwise manner has not yet been exploited.[29] The preparation of mixed bis(alkyne) complexes is an important step toward mediating alkyne condensations. Previous mixed bis(alkyne) complexes of early transition metals have been limited to complexes such as (π-C$_5$H$_5$)Mo(CF$_3$C≡CCF$_3$)(PhC≡CPh)Cl[19] and [(π-C$_5$H$_5$)Mo(RC≡CR)(R^{1}C≡CR^1)Co]$^+$.[20] A recent study concerning

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

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the isomerization of η^4-cyclobutadiene cobalt complexes has implicated reversible formation of a mixed bis(alkyne) species as the key step in this high-temperature rearrangement process.[30]

Formation of mixed bis(alkyne) dithiocarbamate complexes of molybdenum was accompanied by generation of other bis(alkyne) products as a result of alkyne exchange reactions involving the $\mathrm{Mo(CO)(RC{\equiv}CR)(dtc)_2}$ reagent prior to conversion to bis(alkyne) products. The facile exchange of $\mathrm{Mo(CO)(HC{\equiv}CH)(dtc)_2}$ with added alkyne provides a convenient preparative route to a variety of pure $\mathrm{Mo(CO)(R^1C{\equiv}CR^2)(dtc)_2}$ complexes. That exchange is also important in other cases is supported by the isolation of $\mathrm{Mo(PhC_2Ph)_2(S_2CNMe_2)_2}$ as the major bis(alkyne) product formed when $\mathrm{Mo(CO)(PhC{\equiv}CPh)(S_2CNMe_2)_2}$ is reacted with excess 1-hexyne at room temperature. In separate experiments we have demonstrated that (i) $\mathrm{Mo(CO)(EtC{\equiv}CEt)(dtc)_2}$ is completely converted to $\mathrm{Mo(CO)(PhC{\equiv}CH)(dtc)_2}$ at room temperature within 5 h when phenylacetylene is present in excess and (ii) $\mathrm{Mo(EtC{\equiv}CEt)_2(dtc)_2}$ undergoes no exchange with excess free phenylacetylene at room temperature over a 20-h period. These observations are consistent with rapid alkyne exchange at the monocarbonyl stage relative to substitution of the carbonyl ligand to form bis(alkyne) products which are then reluctant to undergo alkyne exchange.

Spectroscopic Properties. The $\nu(\mathrm{C{\equiv}C})$ stretching mode of many mono- and bis(alkyne)metal complexes is difficult to observe in infrared spectra. We have found that concentrated solid samples of $\mathrm{M(CO)(RC{\equiv}CR)(dtc)_2}$ and $\mathrm{Mo(RC{\equiv}CR)_2(dtc)_2}$ derivatives exhibit a weak but reproducible absorption appropriate for the carbon–carbon stretch of the bound alkyne. The frequency of this absorption is an important experimental observable since it provides information about the strength of the coordinated carbon–carbon triple bond. Donation to the metal from both $\pi_\parallel$ in a σ fashion and from $\pi_\perp$ in a π manner will weaken the multiple bond character of the C≡C linkage as will π acceptance by the vacant $\pi_\parallel{}^*$ orbital of the acetylene ligand. In a qualitative sense the decrease observed in $\nu(\mathrm{C{\equiv}C})$ between free and bound alkyne serves as a measure of the total metal–alkyne bonding interaction. In other words an increase in either donor or acceptor behavior should be reflected by a decrease in the energy of the carbon–carbon vibrational mode.

Large variations in the multiple bond character of bound alkynes are evident in the wide range of frequency shifts, roughly 100–500 cm^{-1}, observed in comparing $\nu(\mathrm{C{\equiv}C})$ of free alkynes with coordination complexes of the same alkyne.[31] In the bis(alkyne)bis(dithiocarbamato)molybdenum(II) complexes reported in this work $\nu(\mathrm{C{\equiv}C})$ decreases ranging from 300 to 500 cm^{-1} are observed upon coordination of the free alkynes. The relative impact of metal–alkyne bonding in a closely related series of compounds can be assessed by employing the observed $\nu(\mathrm{C{\equiv}C})$ frequency as a diagnostic tool. Data for several dimethylacetylenedicarboxylate complexes of molybdenum are compiled in Table II, and the vibrational frequencies are lowered most for the complex formally requiring four-electron donation to attain the inert-gas configuration. The highest frequencies are observed in those cases where alkyne π donation is inhibited by competition with the oxo lone pair for the same vacant metal dπ orbital. The formal three and three and one-third electron donation cases also fit into this sequence.

Table II. Dimethylacetylenedicarboxylate (DMAC) $\nu(\mathrm{C{\equiv}C})$ Frequencies for Molybdenum Complexes

complex	$\nu(\mathrm{C{\equiv}C})$, cm^{-1}	ref
$\mathrm{OMo(DMAC)(dmtc)_2}$	1870	*a*
$\mathrm{OMo(DMAC)(detc)_2}$	1850	*a*
$\mathrm{Mo(DMAC)_2(dmtc)_2}$	1819, 1797	this work
$\mathrm{Mo(DMAC)_2(detc)_2}$	1790	this work
$\mathrm{[Et_4N][Mo(DMAC)_3Cl]}$	1760	*b*
$\mathrm{Mo(DMAC)(CO)(detc)_2}$	1730	*c*

[a] Newton, W. E.; McDonald, J. W.; Corbin, J. L.; Ricard, L.; Weiss, R. *Inorg. Chem.* **1980**, *19*, 1997. [b] Birdwhistell, K. R., unpublished results. [c] Morrow, J. R., unpublished results.

Chemical shift values of acetylenic protons[10] and carbons[2] have previously been empirically correlated with electron donation from the bound alkyne. For the bis(alkyne) complexes reported herein terminal alkyne ligands exhibit proton chemical shifts which are below values reported for complexes where the alkyne ligand donates only two electrons (δ 7–8) and upfield from the 12–13 ppm range associated with the $\mathrm{Mo(CO)(RC{\equiv}CH)(dtc)_2}$ complexes. The molecular orbital description which applies in cases where more than one ligand has π-electron density available for donation to a single metal dπ orbital has been presented.[1] In this context the bis(alkyne) complexes can be considered to contain two formal three-electron donor alkyne ligands. The oxo analogues of the monocarbonyl monoalkyne complex, $\mathrm{M(O)(RC{\equiv}CR)(dtc)_2}$, are not susceptible to such simplistic formalisms, however, since any combination of oxo and alkyne π donation which totals four electrons would satisfy the 18-electron rule guidelines. The ^{1}H NMR data, the infrared $\nu(\mathrm{C{\equiv}C})$ results, and the ^{13}C chemical shift values (167 to 190 ppm for $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$, $\mathrm{Mo(HC_2\text{-}\mathit{n}\text{-}Bu)_2(S_2CNMe_2)_2}$, and $\mathrm{Mo(EtC_2Et)(S_2CNMe_2)_2}$) are consistent with the hypothesis that the alkyne ligand in oxo complexes donates less electron density to the metal than the same alkyne donates in the analogous bis(alkyne) complex. An excellent qualitative discussion of the bonding in $\mathrm{Mo(O)(RC{\equiv}CR)(dtc)_2}$ complexes has been presented previously.[9a]

The one bond coupling constants, $^1J(\mathrm{{\equiv}CH})$, for $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$ and $\mathrm{Mo(HC_2\text{-}\mathit{n}\text{-}Bu)_2(S_2CNMe_2)_2}$ were 212 and 210 Hz, respectively. The $\mathrm{Mo(CO)(PhC{\equiv}CH)(S_2CNMe_2)_2}$ complex exhibited a $^1J(\mathrm{{\equiv}CH})$ value of 215 Hz while earlier studies of $\mathrm{W(CO)(RC{\equiv}CH)(dtc)_2}$[32] and $\mathrm{W(O)(RC{\equiv}CH)(dtc)_2}$[10] revealed coupling constants of 210 and 215 Hz for $^1J(\mathrm{{\equiv}CH})$ in these related tungsten systems. The hybridization of the carbon center can be related to the observed coupling constant when the Fermi contact term dominates this one bond coupling constant.[33] On the basis of the above results, it is clear that the C–H coupling constant is insensitive to changes in the identity of the metal, the oxidation state of the metal, and the donor–acceptor role of the alkyne ligand in this series of group 6 dithiocarbamate alkyne complexes.

Dynamic Solution Behavior. When two identical unsymmetrical alkyne ligands are bound to a *cis*-$\mathrm{M(dtc)_2}$ fragment to form an octahedral complex, there are three potential rotational isomers as depicted in Figure 4 for $\mathrm{Mo(RC{\equiv}CH)_2(dtc)_2}$ complexes. The C_2 symmetry of the bis(dithiocarbamato)molybdenum(II) moiety is retained

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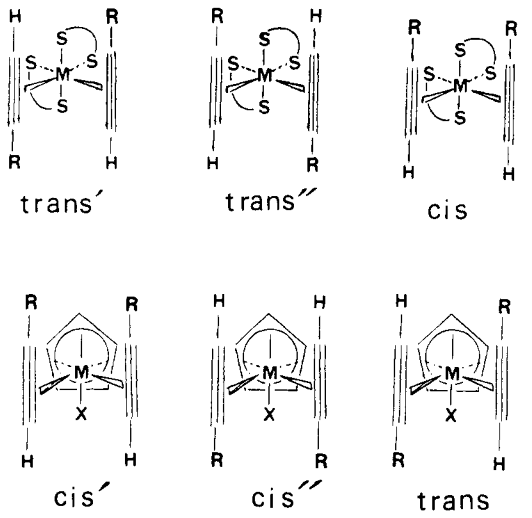

Figure 4. Rotational isomers accessible for bis(alkyne) complexes containing $\mathrm{Mo(dtc)_2}$ and $(\pi\text{-}\mathrm{C_5H_5})\mathrm{MoX}$ fragments.

in the two isomers which can be identified as "trans" based on the relative locations of the two terminal alkyne protons, while the "cis" isomer has no molecular symmetry. This system is complementary to the $(\pi\text{-}\mathrm{C_5H_5})\mathrm{MoCl(RC{\equiv}CH)_2}$ complexes examined by Murray and Faller where the C_s symmetry of the $(\pi\text{-}\mathrm{C_5H_5})\mathrm{MoCl}$ fragment is retained in two cis isomers while the *trans* arrangement produces a C_1 molecule.[18]

The observation of a single resonance for the acetylenic protons of both $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$ and Mo(HC-*n*-Bu)$_2$(S$_2$CNMe$_2$)$_2$ suggested that a dynamic process was exchanging the alkyne environments rapidly on the NMR time scale at room temperature. That both these bis(alkyne) complexes are stereochemically nonrigid in solution was confirmed by variable-temperature ^{1}H studies while $\mathrm{Mo(EtC_2Et)_2(S_2CNMe_2)_2}$ was examined by ^{13}C studies (see Figures 2 and 3). Low-temperature spectra of $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$ are compatible with substantial population of each of the three isomers. The cis isomer can be assigned unambiguously on the basis of intensity relationships. The experimental data provide no distinction between the two trans forms; the most intense of the two trans terminal alkyne resonances will be associated with the trans′ label to facilitate discussion. For $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$ the mole ratio of trans′:cis:trans″ isomers was 2.9:2.3:1.0 as determined by integration of the acetylenic proton resonances at −54 °C. Averaging of these signals occurred with increasing temperature, and a merging of all the acetylenic proton signals, approximating a coalescence, was evident for both $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$ and Mo(HC$_2$-*n*-Bu)$_2$(S$_2$CNMe$_2$)$_2$ at +12 and −1 °C, respectively. For Mo(HC$_2$-*n*-Bu)$_2$(S$_2$CNMe$_2$)$_2$ the isomer ratio was independent of temperature from −58 to −15 °C, but overlap of one of the cis resonances with one trans resonance precluded definitive isomer population analysis. The broad resonance near 10.0 ppm contains one cis proton and both protons of a single trans form, say trans′. The signal intensity ratios are 1.0:2.6:1.4 so the mole ratios of trans′:cis:trans″ are either 0.8:1.0:0.7 or 0.6:1.4:0.5. In either case it is clear than the maximum free energy difference among the three isomers is less than 0.5 kcal for both $\mathrm{Mo(HC_2Ph)_2(S_2CNMe_2)_2}$ and Mo(HC$_2$-*n*-Bu)$_2$(S$_2$CNMe$_2$)$_2$. Spectra of **3a** as a function of temperature (Figure 2) reveal that averaging of the dithiocarbamate methyl groups to produce a simple two-line pattern accompanies the alkyne-exchange process. This is to be expected if alkyne rotation is interconverting the three isomeric forms since the eight independent methyl groups of the three isomers (trans′, 2; trans″, 2; cis, 4) retain only their relationship to the bis(dithiocarbamato)molybdenum fragment once alkyne rotation is rapid on the NMR time scale. Since the alkyl groups reflect the environments of the bound sulfur atoms as long as the $\mathrm{S_2CNR_2}$ fragment remains planar, one can consider the $\mathrm{Mo(dtc)_2}$ moiety to have "cis" and "trans" alkyl groups just as two of the sulfur atoms are cis and two are trans. This is reflected in the two equal intensity methyl signals evident in the high-temperature limit.

Scheme IV

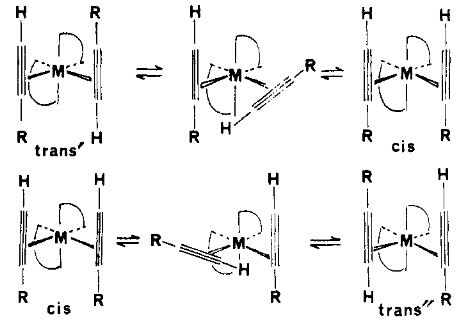

Table III. Activation Barriers Calculated for $\mathrm{Mo(EtC{\equiv}CEt)_2(S_2CNMe_2)_2}$ (5a)

^{13}C site probed	T, °C	k_{obsd}, s^{-1}	$\Delta G^{\ddagger}$, kcal
$\equiv \mathit{C}\mathrm{Et}$	20	20	15.4
	55^a	340	15.5
	100	7200	15.4
$\equiv \mathrm{C}\mathit{C}\mathrm{H_2CH_3}$	20	31	15.2
	42^a	210	15.1
	60	380	15.6
$\equiv \mathrm{CCH_2}\mathit{C}\mathrm{H_3}$	20	35	15.1
		av $\Delta G^{\ddagger}$	15.3
$\mathrm{S_2CN(}\mathit{C}\mathrm{H_3)_2}$	83^a	36	18.5

^{a} Estimated coalescence temperature.

Note that interconversion of the two trans isomers must necessarily involve passage through the cis isomer and vice versa since simultaneous rotation, either conrotatory or disrotatory, leads to a transition state with both *cis*-alkynes in a single meridional plane along with two sulfurs. Such a species would clearly be sterically hindered and too high in energy to provide a facile rearrangement pathway. A series of independent alkyne rotations can account for all of the intramolecular isomerizations observed in this study (see Scheme IV).

A variable-temperature ^{13}C study of $\mathrm{Mo(EtC_2Et)_2(S_2CNMe_2)_2}$ probed the barrier to alkyne rotation based on line-width measurements to monitor the rate of exchange in this equal population, two-site exchange process.[24,34] The data presented in Table III for exchange of each of the carbons in the bound 3-hexyne yield an average ΔG^* value of 15.3 ± 0.2 kcal/mol^{-1}. The data was not considered sufficiently accurate to extract separate enthalpic and entropic contributions to the free energy of activation,[35] but the absence of any discernible trend in ΔG^* between 20 and 100 °C suggests that ΔS^* is small in accord with intramolecular rearrangement.

The two dithiocarbamate methyl signals of $\mathrm{Mo(EtC_2Et)_2(S_2CNMe_2)_2}$ also undergo exchange, but the coalescence temperature of 83 °C coupled with the chem-

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ical shift difference in the low-temperature spectra implies an activation energy of 18.5 kcal mol^{-1}. This barrier is substantially greater than that calculated for alkyne rotation and must be due to an independent dynamic process in any case since even with rapid alkyne rotation the two types of dithiocarbamate alkyl groups retain their environmental integrity. The most likely mechanism for exchange of the alkyl groups on the chelating ligands is rotation around the C–N bond. Alternatively one could envision dechelation of one of the bidentate sulfur ligands to form a five-coordinate intermediate which could rearrange prior to recoordination. Such a process would equilibrate both ends of the alkyne ligands as well as the methyls of the chelating ligands as was observed for $WO(RC\equiv CR)(dtc)_2$ where the dtc alkyl groups and the alkyne terminals underwent exchange with the same activation energy.[10] For the bis(alkyne) complexes the onset of a lower energy process involving rotation of the alkyne ligands prior to exchange of the chelate methyl groups is clear evidence for static dithiocarbamates. The observed $\Delta G^{\ddagger}$ for exchange of the methyl groups of $Mo(EtC_2Et_2)(S_2CNEt_2)_2$ is comparable to activation barriers reported for rotation around the C–N bond in other metal dithiocarbamate complexes.[36]

Molecular Orbital Description. Factors influencing the reactivity of group 6 16-electron d^4 complexes have been probed experimentally and theoretically[37] during the past several years as this class of unsaturated complexes has become more populous. The 16-electron species $[(\pi\text{-}C_5H_5)M(CO)_3]^+$ [38] and $(\pi\text{-}C_5H_5)M(CO)_2R$[39] have been generated and display the extreme electrophilicity normally anticipated for species that are formally electron deficient. Concurrently compounds such as $M(CO)L(S_2CNR_2)_2$ with L = CO[40] and RC≡CR,[7] $Mo(CO)_2(OR)_2(py)_2$,[41] $Mo(CO)_2L_2X_2$,[42] and $Mo(SR)_2(CNR)_4$[43] have been isolated that show varying, but generally surprisingly modest, degrees of electrophilic reactivity. The properties and reactivity patterns of these complexes have been rationalized as reflecting the capability of the ligand complement to destabilize the dπ LUMO by π donation from ligand-to-metal.[1,37,40]

Qualitative molecular orbital considerations suggest a pseudooctahedral d^4 *cis*-$ML_4(RC\equiv CR)_2$ complex would prefer a coparallel alkyne arrangement and extended Hückel calculations support this hypothesis. The structures of $Mo(PhC\equiv CPh)_2(S_2CNEt_2)_2$[8] and related d^4 complexes including $(\pi\text{-}C_5H_5)Nb(PhC\equiv CPh)_2(CO)$[17] and $(\pi\text{-}C_5H_5)\ WCl(CF_3C\equiv CCF_3)_2$[19] confirm this geometrical prediction.

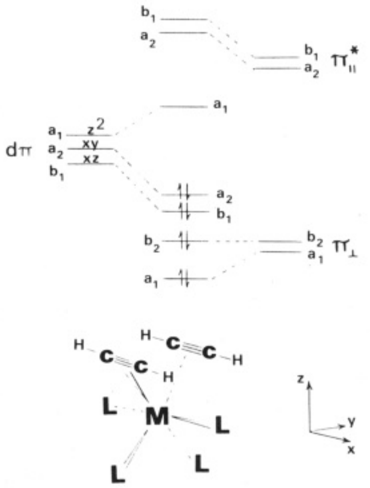

Figure 5. A qualitative interaction diagram for pseudooctahedral d^4 bis(alkyne) complexes of the type *cis*-$M(HC\equiv CH)_2L_4$.

The local C_{2v} symmetry of the $M(RC\equiv CR)_2$ moiety is reduced to C_2 or C_s upon incorporation into $M(RC\equiv CR)_2(dtc)_2$ or $(\pi\text{-}C_5H_5)M(RC\equiv CR)_2X$ complexes, respectively. The salient symmetry separation between the two combinations of alkyne $\pi_\perp$ donor orbitals present in the C_{2v} case is in essence retained in both of the lower symmetry groups. Briefly the octahedral parentage of the complex produces three metal dπ orbitals of symmetry a_1, a_2, and b_1 in the coordinate system shown for C_{2v} symmetry.[44]

The alkyne-filled $\pi_\perp$ orbitals and vacant $\pi_\parallel{}^*$ orbitals are capable of π interactions with the dπ orbitals, and appropriate combinations reveal that the two vacant $\pi_\parallel{}^*$ orbitals generate a_2 and b_1 combinations which find and stabilize bonding mates among the three dπ orbitals (see Figure 5). The two $\pi_\perp$ alkyne orbitals produce a_1 and b_2 combinations. Since only the a_1 combination finds a match among the three dπ levels, the b_2 combination is nonbonding relative to the metal–ligand framework and a three-center, four-electron description is appropriate to describe the $2\pi_\perp$ plus $1d_\pi$ portion of the orbital diagram which results. The orbital energy ordering which results from EHMO calculations corresponds to this picture with the d^4 metal configuration populating the d_{xz} and d_{xy} metal dominated orbitals which are bonding as a result of alkyne $\pi_\parallel{}^*$ mixing. The LUMO then lies 1.62 eV above the HOMO and consists of the antibonding metal d_{z^2} + alkyne $\pi_\perp$ molecular orbital while the $a_1\ \pi_\perp$ bonding combination lies below the b_2 nonbonding $\pi_\perp$ MO. Since the two alkyne ligands donate four electrons from filled $\pi_\parallel$ orbitals and two from the $\pi_\perp\ a_1$ orbital, this can be loosely described as three-electron donation from each acetylene. The difficulties inherent in such a scheme outweigh the chemical insight which such terminology provides in most instances. The simple electron counting procedure leading to a total of 16 metal valence electrons with recognition of the important role ligand π donation can play in influ-

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(44) Note that the nest of three dπ orbitals consists of d_{z^2}, d_{xz}, and d_{xy} for this coordinate system where z is aligned with the C_{2v} symmetry axis. The principal σ interactions with d orbitals involve d_{yz} an $d_{x^2-y^2}$.

encing chemistry of these complexes seems to be the most informative and internally consistent method of categorizing these and related compounds.

The previous EHMO description of $M(HC\equiv CH)_2(dtc)_2$[1] utilized a M—C(alkyne) distance of 2.03 Å and resulted in a calculated barrier to rotation of 40.3 kcal mol^{-1}. The discrepancy between experimental ($\Delta G^{\ddagger}$ of 15.3 kcal mol^{-1}) and calculated energy barriers for $Mo(EtC_2Et)_2(S_2CNMe_2)_2$ was much larger than we had found in $M(CO)(HC\equiv CH)(dtc)_2$ and $M(O)(HC\equiv CH)(dtc)_2$ studies. Although 2.03 Å was the M–C distance reported for $W(CO)(HC\equiv CH)(detc)_2$,[8] structural data for $(\pi\text{-}C_5H_5)Nb(CO)(PhC\equiv CPh)_2$[17] and $(\pi\text{-}C_5H_5)WCl(CF_3C\equiv CCF_3)_2$[19] suggested that a distance of 2.17 Å would be more likely to characterize the bis(alkyne) derivative. The results of such a calculation produced a barrier of 13.2 kcal mol^{-1} for rotation of one alkyne, much nearer the observed value. The variation in calculated barrier as a function of the M–C distance (~2.0 kcal mol^{-1}/0.01 Å) is consistent with a strong dependence of the metal–alkyne π-acceptor and π-donor orbital contributions on nuclear separation.

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Registry No. 1a, 80664-77-3; **1b**, 18947-43-8; **2a**, 81476-35-9; **2b**, 81476-36-0; **3a**, 81476-37-1; **3b**, 74456-80-7; **4b**, 81476-38-2; **5a**, 81476-39-3; **5b**, 81476-40-6; **6a**, 81496-89-1; **6b**, 81476-41-7; **7a**, 74469-87-7; **7b**, 56954-15-5; **8a**, 81476-42-8; **8b**, 81476-43-9; **9a**, 81476-44-0; **9b**, 81476-45-1; **10b**, 81476-46-2; **11a**, 81476-47-3; **12a**, 81476-48-4; **13a**, 81476-49-5; $Mo(S_2CNEt_2)_2(HC_2Ph)(CO)$, 56954-17-7; $Mo(S_2CNMe_2)_2(HC_2Ph)(CO)$, 74456-79-4; $Mo(S_2CNMe_2)_2(PhC_2Ph)(CO)$, 81476-50-8.

Tricarbonylchromium Complexes of $(CH_3)_2EAr_2$ Ligands (E = C, Si, Ge, Sn, and Pb; Ar = C_6H_5, $CH_2C_6H_5$, and *p*-$C_6H_4CH_3$)

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Mono- and bis(arene)tricarbonylchromium complexes of $(CH_3)_2E(C_6H_5)_2[Cr(CO)_3]_x$, where E = C, Si, Ge, Sn, and Pb, and $(CH_3)_2Sn(CH_2C_6H_5)_2[Cr(CO)_3]_x$ and $(CH_3)_2Sn(C_6H_5CH_3\text{-}p)_2[Cr(CO)_3]_x$, where $x = 1$ (mono) and 2 (bis), are prepared from $Cr(CO)_6$ in diglyme–tetrahydrofuran (THF) solutions or from $Cr(CO)_3(NH_3)_3$ in refluxing dioxane. Extraction of the mixture of mono and bis complexes with hot hexane or petroleum ether gives the mono complexes, and subsequent recrystallization of the residue from hot benzene gives the bis. Alternatively, the bis complex can be obtained directly from column chromatography on silica gel after sublimation to remove the mono complex. Proton NMR data are recorded for all 15 fourth group homologues, including the tin-119 and lead-207 coupling constants $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ and $|^2J(^{207}Pb\text{–}C\text{–}^1H)|$, respectively, which for the tin derivatives are consistent with monomeric species in solution containing four-coordinated tin atoms. Tin-119m Mössbauer isomer shift (IS) and quadrupole splitting (QS) values also reflect tin(IV) atoms in a four-coordinated environment. Infrared and Raman data are used to assign $\nu[E(CH_3)_2]$ modes in the E = C, Si, Ge, Sn, and Pb ligands and the mono and bis complexes. Intramolecular contact between the oxygen atoms of the tricarbonylchromium moiety and the element–methyl groups is offered as an explanation for the decrease in the intensity of the infrared $\nu_{sym}(E\text{–}CH_3)$ absorption and the increase in the intensity of the corresponding Raman absorption on successive tricarbonylchromium substitution.

A decade ago we synthesized a series of tricarbonylmetal complexes of tin-substituted arene ligands of the general formulas $(CH_3)_nSn(C_6H_5)_{4-n}[M(CO)_3]_x$, where $n = 2$ or 3 and M = Cr or Mo, $[(CH_3)_3Sn]_2C_6H_4[Cr(CO)_3]_x$, and $(CH_3)_3SnCH_2C_6H_5[Cr(CO)_3]_x$, where $x = 2$ (bis) or 1 (mono), and studied the products by NMR, infrared, laser-Raman, tin-119m Mössbauer, and mass spectroscopies. Mössbauer spectra showed no quadrupole splitting (QS) in any of the free ligands, but small splittings in the complexes which we attributed to enhanced electric field gradients in the tin–phenyl bonds. NMR spectra showed a displacement of chemical shifts of ca. 2 ppm of the aromatic protons in the expected direction on complex formation and only very small differences (1.3–3.7 Hz) in the $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ from the free ligands, consistent with four-coordination at tin in solution where all the complexes are monomeric. Mass spectra indicated that the complexes are monomeric in the gas phase as well. No drastic frequency shifts occurred in the ν(Sn–C) modes on complex formation.[2]

The spectral properties of the bis(tricarbonylchromium) complex $(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$ were remarkable, however. This material exhibited the most intense m/e 171 ($SnCr^+$) peak in the mass spectrum, the largest increase in $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ on complexation and the largest value in absolute magnitude as well, and the largest Mössbauer QS value. Most striking, however, were the vibrational spectra in the ν(Sn–C) region. In the infrared spectrum a discrete ν_{sym}(Sn–C) could not be distinguished from the ν_{asym}(Sn–C) band, and in the Raman only a strong, po-

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