

the B transition state and therefore expected to have a somewhat higher TB-B pseudorotation barrier.⁴⁰

There are many possible mechanisms for interconversion of the TC and TB conformations (TC-TB) of **1**. The pathway which maintains a C_2 axis of symmetry, going through a TT, is the one energetically favored among those considered for cycloheptane.²⁹ We obtain a barrier height of 2.9 kcal/mol for TC-TB interconversion via a TT in **1**. This value, which is significantly lower than the 8.1,³⁹ 8.55,^{29a} and 9.6 kcal/mol⁴¹ barriers calculated for cycloheptane, further reflects the differences between **1** and its hydrocarbon analogue. This difference also extends to the structure of the TT. While for cycloheptane the TT is calculated to have a sequence of torsion angles, ω_3 - ω_5 , which are all of the same sign, the corresponding angles in **1** contain one, ω_4 , which is eclipsed ($\omega_4 = 0.0$). Thus our TT closely resembles a second intermediate TC/TB(a) encountered by Hendrickson³⁹ in the

TC-TB interconversion of cycloheptane. Releasing the symmetry constraint on the TT calculated for **1** followed by geometry optimization yields the TC structure. The TB conformation was obtained by increasing the magnitude of ω_4 in the TT in a driving experiment.³⁷ No intermediates were encountered between the TT and the TC or TB and we observed a uniform decrease in energy along both pathways. Thus, the calculations indicate that the magnitude of the TC-TB interconversion barrier and the ring structure of the TT calculated for **1** differ from that obtained for cycloheptane. In addition, unlike the interconversion process in cycloheptane, we find no intermediates along the TC-TB itinerary for **1**.

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Registry No. 1, 13452-94-3; cycloheptane, 291-64-5.

Supplementary Material Available: Tables of anisotropic thermal parameters and values of $10F_o$ and $10F_c$ (22 pages). Ordering information is given on any current masthead page.

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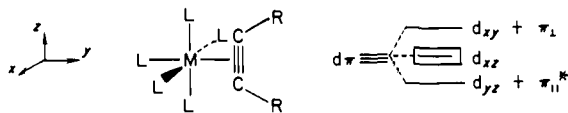
Mixed Olefin-Alkyne Complexes of Molybdenum(II) and Tungsten(II) Dithiocarbamates[†]

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Abstract: Mixed olefin-alkyne complexes of the type $M(\eta^2\text{-olefin})(\eta^2\text{-alkyne})(S_2CNR_2)_2$ ($M = Mo$ and W) have been prepared from $M(CO)(\eta^2\text{-alkyne})(S_2CNR_2)_2$ and electron poor olefins (maleic anhydride, tetracyanoethylene, and *trans*-dicyanoethylene). The range of acceptable alkyne ligands spans alkyl, aryl, and terminal alkynes. The motivation for this work was to incorporate a single-faced π -acid ligand into the octahedral position cis to the alkyne ligand of the $M(\eta^2\text{-alkyne})(S_2CNR_2)_2$ fragment. The resulting family of mixed olefin-alkyne complexes has been characterized by ¹H NMR, ¹³C NMR, infrared, and electronic spectroscopies; cyclic voltammograms have been recorded for a number of the compounds reported here. The structure of $W(\eta^2\text{-maleic anhydride})(\eta^2\text{-PhC}_2\text{H})(S_2CNMe_2)_2$ has been determined: $a = 22.744$ (5) Å, $b = 12.589$ (3) Å, $c = 21.440$ (8) Å, $\beta = 121.52$ (2)°, $Z = 8$, $d_{\text{calcd}} = 1.69$ g cm⁻³, and space group $C2/c$. Several of these olefin-alkyne complexes undergo nucleophilic attack by the phosphorus lone pair of phosphites and phosphines at the terminal carbon of the coordinated alkyne to form η^2 -vinyl products. The η^2 -vinyl ligand present in the $M(\eta^2\text{-PhCCHPR}_2)$ moiety which results can also be described as a cyclic alkylidene or as a metallacyclopentene. These names are in accord with the considerable carbenoid character of the more tightly bound α -carbon as reflected in a low-field ¹³C chemical shift of 220-230 ppm.

Alkyne ligands in monomeric early transition-metal complexes are particularly sensitive to metal $d\pi$ orbital occupancies. A neutral alkyne ligand serves simultaneously as an excellent single-faced π -acid through $\pi_{||}^*$ and as an excellent single-faced π -base through π_{\perp} .¹ For octahedral $L_5M(RC_2R)$ complexes, these divergent metal-alkyne π interactions dictate the location of two $d\pi$ energy levels and leave one $d\pi$ -orbital energy undetermined. In the coordinate system shown below, with the alkyne approaching the metal along the y axis, d_{xz} is the flexible $d\pi$ orbital. The occupancy of this flexible metal-based orbital depends on whether it sees predominately π -donor or π -acceptor ancillary ligands in the xz plane, and it follows that either d^2 or d^4 electron configurations will be preferred for $L_5M(\text{alkyne})$ monomers.



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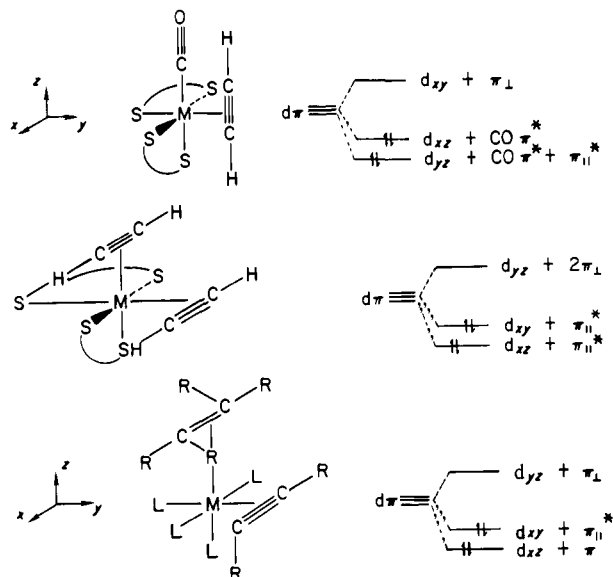
The *cis*-(CO)(RC₂R) fragment found in numerous six-coordinate d^4 $L_4M(CO)(RC_2R)$ complexes² contains a $3c-2e$ bond involving d_{yz} , CO π^* , and alkyne $\pi_{||}^*$ (see below).³ This orbital redundancy suggests that a single-faced π acceptor, such as a carbene or an electron-withdrawing olefin, should suffice in place of the cylindrically symmetrical π -acid carbonyl ligand. The bis(alkyne) complexes, $Mo(RC_2R)_2(S_2CNR_2)_2$, contain a $3c-4e$ bond involving d_{yz} and both filled alkyne π_{\perp} orbitals.^{4,5} Since

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

the two single-faced π -acid alkyne ligands are adequate to stabilize the two filled $d\pi$ orbitals in $M(RC_2R)_2(S_2CNR_2)_2$, and a single alkyne is adequate to drive up the d_{xy} LUMO (lowest unoccupied molecular orbital) in $M(CO)(RC_2R)(S_2CNR_2)_2$ compounds, we anticipated that formation of $M(R_2C=CR_2)(R'C\equiv CR')(S_2CNR_2)_2$ complexes would fulfill the minimal 2c-2e criteria for the three metal $d\pi$ orbitals in these d^4 derivatives. Note that



$M(CO)(R_2C=CR_2)(S_2CNR_2)_2$ complexes have so far proved inaccessible, supposedly reflecting the necessity for alkyne π_{\perp} donation to drive up the $d\pi$ LUMO.⁶ We report here the preparation and properties of a series of $M(\text{olefin})(\text{alkyne})(S_2CNR_2)_2$ complexes ($M = Mo$ and W ; olefin = maleic anhydride, tetracyanoethylene, and *trans*-dicyanoethylene).

Experimental Section

Materials and Methods. All manipulations were performed under a dry oxygen-free nitrogen atmosphere by using standard Schlenk techniques. Solvents were degassed prior to use. Molybdenum hexacarbonyl, sodium dialkyldithiocarbamates, alkynes, and olefins were obtained from commercial sources and used without further purification. Acetylene gas was passed through a dry ice/2-propanol trap to remove acetone which is present as a stabilizing agent. $Mo(CO)_3(S_2CNR_2)_2$ and $W(CO)_3(S_2CNR_2)_2$ were prepared from $[R_4N][Mo(CO)_4I_3]$ and $[R_4N][W(CO)_4I_3]$ as reported previously.⁷ $W(CO)(RC\equiv CR)(S_2CNR_2)_2$ complexes were prepared from $W(CO)_3(S_2CNR_2)_2$ according to literature methods,⁶ and $M(CO)(RC_2R)(S_2CNR_2)_2$ complexes were synthesized as previously reported^{4,5} and purified by column chromatography on alumina with a toluene eluant.

Infrared spectra were recorded on a Beckman IR 4250 and calibrated with a polystyrene standard. ¹H NMR spectra were recorded on a WM Brüker 250 spectrometer (250 MHz) or where indicated on a Varian XL-100 spectrometer (100 MHz). ¹³C NMR were recorded on a WM Brüker 250 spectrometer (62.89 MHz). Chemical shifts are reported as parts per million downfield of SiMe₄. NMR sample temperatures were measured by a thermocouple located near the probe. Visible spectra were recorded on a Hewlett-Packard 84-50A with methylene chloride as solvent.

Electrochemical measurements were made at room temperature with a Bioanalytical Systems CV-27 instrument and recorded with a Houston Instruments 100 x-y recorder. Cyclic voltammograms were recorded by using nitrogen-purged solutions in an auxiliary cell with a side arm and Teflon cap to ensure an oxygen-free nitrogen atmosphere. Tetra-butylammonium perchlorate (recrystallized 4 times from ethanol/hexanes) was used as a supporting electrolyte (0.1 M). Acetonitrile was purchased from Burdick & Jackson and dried with activity I alumina. A platinum bead electrode was used for both working and auxiliary electrodes, and a silver wire was used as a reference electrode. Ferrocene was added to solutions after the electrochemical experiment as a reference. Potentials

were calculated and reported vs. the saturated sodium calomel electrode (SSCE). Any IR drop was uncompensated, and the ferrocene/ferrocenium couple exhibited an 80-mV peak separation under these experimental conditions.

Calculations. The extended Hückel method was employed in this study. Program QCPE358 from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, was used for calculations on $W(H_2C=CH_2)(HC_2H)(S_2CNH_2)_2$ with atomic parameters obtained from published sources.⁸ The crystallographic coordinates of $W(PhC_2H)(MA)(S_2CNEt_2)_2$ were used to establish the dithiocarbamate geometry. The N-H distance for S_2CNH_2 was fixed at 1.05 Å, and the C-H bond distances of the olefin and alkyne were fixed at 1.09 Å. The alkyne and olefin ligands were placed in a idealized parallel geometry with W-C bond lengths of 2.008 and 2.247 Å for alkyne and olefin, respectively, and a dihedral angle of 95° between the tungsten-olefin plane and the tungsten-alkyne plane. The coordinates of the ethylene ligand in $KPt(C_2H_4)Cl_3$ were used to establish the C-H bond angles of the olefin.⁹

Syntheses. $W(MA)(R^1C_2R^2)(S_2CNR_2)_2$ ($MA = \text{maleic anhydride}$. ($R = Et$: $R^1 = H$, $R^2 = Ph$; $R^1 = R^2 = H$; $R^1 = H$, $R^2 = CH_3$; $R^1 = R^2 = Ph$. $R = Me$: $R^1 = H$, $R^2 = Ph$)). The following procedure is general for the synthesis of the olefin-alkyne complexes listed above. A toluene solution of $W(CO)(RC_2R)(S_2CNR_2)_2$ (1.5 mmol in 200 mL) containing a 5-fold excess of maleic anhydride (MA) was refluxed for 20 min. Reaction progress was monitored by following the disappearance of the ν_{CO} infrared absorption of the starting material. Toluene was evaporated from the dark orange-brown solution in vacuo; the residue was then dissolved in methylene chloride and chromatographed on a large Florisil column. The product was washed on the column with 500 mL of methylene chloride. A bright-yellow band containing a metal-olefin complex with no alkyne was eluted with a 1:5 diethyl ether/methylene chloride mixture. A red-orange band was eluted next with 2% methanol in methylene chloride. Red crystals were formed in 30% yield from this fraction after solvent removal, dissolution in methylene chloride/hexane solution, and cooling to -20 °C. These mixed olefin-alkyne complexes of tungsten are relatively air-stable both in solution and as solids.

$W(HC_2Ph)(MA)(S_2CNEt_2)_2$: ¹H NMR ($CDCl_3$) δ 13.30 (s, 1 H, PhC_2H , $J_{W-H} = 6$ Hz), 7.52-7.90 (m, 5 H, C_6H_5), 4.00 and 2.93 (each a d, 1 H, $J = 5$ Hz, =CH), 3.51-4.12 (m, 8 H, NCH_2), 1.13-1.52 (m, 12 H, NCH_2CH_3); ¹³C NMR(¹H) ($CDCl_3$) δ 223.7, 222.9 (s, PhC_2H), 206.8, 206.4 (s, S_2CNEt_2), 172.9, 172.6 (s, (O)CCH=CH-C(O)O), 60.8, 59.8 (s, =CH), 45.2, 45.0, 44.4 (s, NCH_2CH_3), 13.0, 12.8 (s, NCH_2CH_3); IR (CH_2Cl_2) ν_{CO} 1802, 1738 cm^{-1} .

$W(HC_2H)(MA)(S_2CNEt_2)_2$: ¹H NMR (100 MHz) (CD_2Cl_2) δ 13.21 (s, 2 H, $J_{W-H} = 4$ Hz, HC_2H) 3.31-3.92 (m, 9 H, NCH_2 and one =CH), 2.67 (d, 1 H, $J = 4$ Hz, =CH) 0.90-1.39 (m, 12 H, NCH_2CH_3); IR (CH_2Cl_2) ν_{CO} 1802, 1730 cm^{-1} .

$W(CH_3C_2H)(MA)(S_2CNEt_2)_2$: ¹H NMR ($CDCl_3$) δ 13.23 (s, 1 H, CH_3C_2H), 3.53-4.05 (m, 8 H, NCH_2), 3.18 (d, 3 H, $J = 1$ Hz, CH_3C_2H), 2.75, 3.70 (each a d, 1 H, $J = 5.5$ Hz, =CH) 1.02-1.14 (m, 12 H, NCH_2CH_3); IR (CH_2Cl_2) ν_{CO} 1804, 1737 cm^{-1} .

$W(PhC_2Ph)(MA)(S_2CNMe_2)_2$: ¹H NMR ($CDCl_3$) δ 7.36-7.75 (m, 10 H, C_6H_5), 3.82, 2.28 (each a d, 1 H, $J = 5.4$ Hz, =CH), 3.36, 3.27, 3.15, 3.05 (each a s, 3 H, NCH_3); IR (CH_2Cl_2) ν_{CO} 1807, 1737 cm^{-1} .

$W(PhC_2H)(MA)(S_2CNMe_2)_2$: ¹H NMR ($CDCl_3$) δ 13.33 (s, 1 H, $J_{W-H} = 6$ Hz, PhC_2H) 7.55-7.98 (m, 5 H, C_6H_5), 4.10, 2.88 (each a d, 1 H, $J = 5$ Hz, =CH), 3.08, 3.20, 3.35, 3.43 (each a s, 3 H, NCH_3); IR (CH_2Cl_2) ν_{CO} 1807, 1739 cm^{-1} .

$Mo(R^1C_2R^2)(MA)(S_2CNR_2)_2$ ($R = Et$: $R^1 = R^2 = Et$. $R = Me$: $R^1 = R^2 = Me$; $R^1 = H$, $R^2 = Ph$). The following procedure is general for the synthesis of the molybdenum-olefin-alkynes listed above. A benzene solution of $Mo(CO)(C_2R_2)(S_2CNR_2)_2$ (2 mmol in 200 mL) was combined with a 3-fold excess of maleic anhydride and then brought to a gentle reflux for 1 min. Reaction was complete as judged by IR. Solvent was removed from the dark-brown solution, and the residue was dissolved in methylene chloride and chromatographed on a large Florisil column. A green band containing no coordinated maleic anhydride was eluted first with methylene chloride from the 2-butyne-maleic anhydride crude product mixture. The 2-butyne-olefin complex was then eluted as an orange band with a diethyl ether/methylene chloride solvent mixture. This was followed by a second green band containing bound maleic anhydride (by IR) and displaying a complex ¹H NMR spectrum of multiple singlets. The 3-hexyne-maleic anhydride product mixture yielded a green band eluted with methylene chloride and containing no

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bound olefin by IR followed by the 3-hexyne-olefin complex which eluted as an orange band with a 1:1 diethyl ether-methylene chloride mixture. Orange crystals of both olefin-alkyne complexes (2-butyne and 3-hexyne) were obtained in 20% yield from methylene chloride-hexane solutions cooled to -20°C . The phenylacetylene-maleic anhydride complex was eluted with a 1:3 diethyl ether-methylene chloride mixture as a greenish-gold band. Dark-gold crystals were obtained in 20% yield upon cooling a methylene chloride-hexane solution to -20°C . All complexes were moderately air-stable in solution and as solids.

Mo(CH₃CH₂C₂CH₂CH₃)(MA)(S₂CNEt₂)₂: IR (CH₂Cl₂) ν_{CO} 1805, 1743 cm⁻¹.

Mo(CH₃C₂CH₃)(MA)(S₂CNMe₂)₂: ¹H NMR (100 MHz) (CDCl₃) δ 3.98, 3.30 (each a d, 1 H, $J = 5$ Hz, =CH), 3.50, 3.44, 3.26, 3.12 (each a s, 3 H, NCH₃), 3.00 (s, 6 H, CH₃C₂CH₃); IR (CH₂Cl₂) ν_{CO} 1804, 1748 cm⁻¹.

Mo(PhC₂H)(MA)(S₂CNMe₂)₂: ¹H NMR (CDCl₃) δ 12.31 (s, 1 H, PhC₂H), 7.44-7.88 (m, 5 H, Ph), 4.40, 3.12 (each a d, 1 H, $J = 5.3$ Hz, =CH), 3.47, 3.38, 3.22, 3.09 (each a s, 3 H, NCH₃); IR (THF) ν_{CO} 1800, 1745 cm⁻¹.

W(TCNE)(R¹C₂R²)(S₂CNEt₂)₂ (TCNE = (NC)₂C₂(CN)₂, R¹ = R² = CH₃, R¹ = R² = Ph, R¹ = Ph, R² = H). The following procedure is general for the synthesis of the above olefin-alkyne complexes. Two equivalents of tetracyanoethylene were added to a hexane solution of W(CO)(C₂R₂)(S₂CNEt₂)₂ (1 mmol in 200 mL) at room temperature, and the solution was stirred overnight. The hexane solvent was filtered off, and the light-brown solid which remained was dissolved in methylene chloride and chromatographed on Florisil. The column was eluted with methylene chloride to remove traces of the metal carbonylalkyne reagent as well as an unidentified blue-purple material. A yellow-orange band was eluted with a 1:3 diethyl ether-methylene chloride mixture. Air-stable orange crystals (15% yield) were isolated upon cooling a methylene chloride-hexane solution to -20°C .

W(CH₃C₂CH₃)(TCNE)(S₂CNEt₂)₂: ¹H NMR (CDCl₃) δ 3.43-4.11 (m, 8 H, NCH₂), 3.26 (s, 6 H, CH₃C₂CH₃), 1.46, 1.36, 1.28, 1.16 (each a t, 3 H, NCH₂CH₃).

W(PhC₂Ph)(TCNE)(S₂CNEt₂)₂: ¹H NMR (CDCl₃) δ 7.25-7.90 (m, 10 H, C₆H₅), 3.40-3.95 (m, 8 H, NCH₂), 1.45 (t, 3 H, NCH₂CH₃), 1.20-1.38 (m, 9 H, NCH₂CH₃); IR (KBr) ν_{CN} (olefin) 2194 cm⁻¹ (w).

W(PhC₂H)(TCNE)(S₂CNEt₂)₂: ¹H NMR (CDCl₃) δ 13.34 (s, 1 H, $J_{\text{W-H}} = 13$ Hz, C-H), 7.75-8.20 (m, 5 H, C₆H₅), 3.52-4.13 (m, 8 H, NCH₂), 1.23-1.68 (m, 12 H, NCH₂CH₃); IR (KBr) ν_{CN} (olefin) 2214 cm⁻¹ (w).

W(DCNE)(R¹C₂R²)(S₂CNR₂)₂ (DCNE = *trans*-NCCH=CHCN, R¹ = Me, R¹ = R² = Ph, R¹ = Et, R¹ = H, R² = Ph). The following procedure is general for the synthesis of the olefin-alkynes listed above. A benzene solution of W(CO)(RC₂R)(S₂CNR₂)₂ (1 mmol in 200 mL) was refluxed with a 3-fold excess of olefin for 12 h at which time the reaction was complete as judged by IR. Solvent was removed in vacuo, and the remaining dark oil was dissolved in methylene chloride and chromatographed on a Florisil column. A bright-orange band was eluted with a 1:2 diethyl ether/methylene chloride mixture. Bright-orange air-stable crystals were obtained in 60% yield from a methylene chloride-hexane solution cooled to -20°C .

W(PhC₂Ph)(DCNE)(S₂CNMe₂)₂: ¹H NMR (CDCl₃) δ 7.52-8.09 (m, 10 H, C₆H₅), 3.44, 3.31, 3.23, 3.13 (each a s, 3 H, NCH₃), 2.95, 1.67 (each a d, 1 H, $J = 9$ Hz, =CH).

W(PhC₂H)(DCNE)(S₂CNEt₂)₂: ¹H NMR (CDCl₃) δ 13.35 (major isomer, s, PhC₂H), 12.85 (minor isomer, s, PhC₂H), 7.50-8.05 (m, 5 H, C₆H₅), 3.45-4.10 (m, 8 H, NCH₂), 2.95 and 0.70 (major isomer, each d, $J = 9.5$ Hz, =CH), 2.83 (minor isomer, d, $J = 11$ Hz, =CH), 1.13-1.45 (m, 12 H, NCH₂CH₃); IR (KBr) ν_{CN} (olefin) 2196 cm⁻¹ (ms).

Mo(HC₂H)(DCNE)(S₂CNEt₂)₂. A benzene solution of Mo(CO)(HC₂H)(S₂CNEt₂)₂ (1 mmol in 200 mL) was refluxed for 5 min with a 3-fold excess of olefin. Solvent was removed in vacuo, and the resulting brown oil was dissolved in methylene chloride and chromatographed on a Florisil column. A light-yellow band and a purple band were eluted with methylene chloride. The desired product was eluted as a brown-gold band with a 1:3 diethyl ether-methylene chloride mixture. The olefin-alkyne product was isolated as a moderately air-sensitive dark-brown powder in 20% yield from a methylene chloride-hexane solution after cooling to -20°C : ¹H NMR (CDCl₃) δ 11.55, 11.53 (each a s, two isomers, C₂H₂), 3.85-3.50 (m, 8 H, NCH₂), 3.88, 2.48, 1.75 (each a d, three resonances of two isomers, =CH), 1.18-1.38 (m, 12 H, NCH₂CH₃); IR (KBr) ν_{CN} (olefin) 2191 cm⁻¹ (ms).

M(η^2 -PhCCHPR₃)(MA)(S₂CNR¹)₂ (M = W, R¹ = Et; R = Me, OEt. M = W, R¹ = Me; R = OMe. M = Mo, R¹ = Me, R = Me). The following procedure is general for the synthesis of the complexes listed above. A 10-fold excess of phosphine or phosphite was added to a tetrahydrofuran solution of M(PhC₂H)(MA)(S₂CNR₂)₂ (0.5 mmol in 50 mL), and the solution was stirred for 1 h. A yellow-gold powder

Table I. Crystallographic Data for W(MA)(PhC₂H)(detc)₂

molecular formula	WS ₄ O ₃ N ₂ C ₁₈ H ₂₀ ¹ / ₂ CH ₂ Cl ₂
fw, g/mol	666.94
space group	C2/C
cell parameters	
<i>a</i> , Å	22.744 (5)
<i>b</i> , Å	12.589 (3)
<i>c</i> , Å	21.440 (8)
β , deg	121.52 (2)
vol, Å ³	5231
ρ (calcd), g/cm ³	1.69
<i>Z</i>	8
Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo K α (0.71073)
linear absorpt coeff, cm ⁻¹	49.95
scan type	$\omega/1.67\theta$
scan width, deg	1.1 + 0.35 tan θ
background	25% of full scan width on both sides
θ limits	1° < θ < 25°
quadrant collected	+ <i>h</i> , + <i>k</i> , \pm <i>l</i>
unique data	5124
data with $I \geq 3\sigma(I)$	3069
<i>R</i>	0.056
<i>R</i> _w	0.058
largest parameter shift	0.49
error in an observation of unit wt	2.51
no. of variables	265

precipitated, and further precipitation was induced by addition of diethyl ether and cooling to -20°C . The yellow powder was washed with a diethyl ether/hexanes mixture and then recrystallized from a mixture of methylene chloride, diethyl ether, and hexanes. The W(MA)[η^2 -PhC₂HP(OEt)₃](S₂CNEt₂)₂ complex was chromatographed on Florisil and eluted with a 5% methanol-methylene chloride mixture after washing the product on the column with methylene chloride. The air-stable bright-yellow solids were obtained in greater than 50% yield.

W(η^2 -PhC₂HPMe₃)(MA)(S₂CNEt₂)₂: ¹H NMR (CDCl₃) δ 6.95-7.62 (m, 5 H, C₆H₅), 3.53-3.91 (m, 9 H, NCH₂CH₃ and =CH), 2.97 (d, 1 H, $^2J_{\text{W-H}} = 13.2$ Hz, $^2J_{\text{P-H}} = 29$ Hz, CHPMe₃), 2.68 (d, 1 H, $J = 4.3$ Hz, =CH), 1.65 (d, 9 H, $^2J_{\text{P-H}} = 13.5$ Hz, PMe₃), 1.12-1.35 (m, 12 H, NCH₂CH₃); ¹³C NMR {¹H} (CDCl₃) δ 226.8 (d, $^2J_{\text{P-C}} = 11$ Hz, CPh), 206.8, 206.3 (s, S₂CNEt₂), 173.5, 173.2 (s, COCH=CHC(O)O), 59.0, 56.9 (s, =CH), 44.3, 44.1, 44.0, 43.3 (s, NCH₂), 10-18.4 (PCH₃ and NCH₂CH₃); ³¹P NMR {¹H} (CDCl₃) 34.6 (s, $^2J_{\text{P-W}} = 36$ Hz); IR (THF) ν_{CO} 1796, 1731 cm⁻¹.

W(PhC₂HP(OEt)₃)(MA)(S₂CNEt₂)₂: ¹H NMR (CD₂Cl₂) δ 6.95-7.91 (m, 5 H, C₆H₅), 3.52-4.21 (m, 14 H, PCH₂ and NCH₂), 2.99 (d, 1 H, $^2J_{\text{W-H}} = 12$ Hz, $^2J_{\text{P-H}} = 29$ Hz, CHP(OEt)₃), 2.56 (d, 1 H, $J = 4$ Hz, =CH), 1.12-1.44 (m, 21 H, PCH₂CH₃ and NCH₂CH₃); ³¹P NMR (CD₂Cl₂) δ 61.2 (s, $^2J_{\text{W-P}} = 39$ Hz); IR (THF) ν_{CO} 1800, 1732, cm⁻¹.

W[PhC₂HP(OMe)₃](MA)(S₂CNMe₂)₂: ¹³C NMR (CDCl₃) δ 222.2 (d, $^2J_{\text{P-C}} = 10$ Hz, CPh), 208.5, 208.2 (s, S₂CNMe₂), 173.7, 173.2 (s, C(O)CH=CHC(O)O), 60.2, 57.9 (d, $J_{\text{C-H}} = 171$ Hz, =CH), 55.8, 55.6, 49.0, 48.8 (s, NCH₃), 39.05 (d, $J_{\text{P-C}} = 29$ Hz, POCH₃), 11.6 (dd, $^1J_{\text{C-H}} = 158$ Hz, $^1J_{\text{P-C}} = 164$ Hz, CHP(OMe)₃).

Mo(PhC₂HPMe₃)(MA)(S₂CNMe₂)₂: ¹H NMR (CDCl₃) δ 7.0-7.62 (m, 5 H, C₆H₅), 3.42, 3.48, 3.24, 3.21 (each a s, 3 H, NCH₃), 2.92 (d, 1 H, $J = 4$ Hz, =CH), 2.35 (d, 1 H, $^2J_{\text{P-H}} = 24$ Hz, CHPMe₃), 1.17 (d, $J_{\text{P-H}} = 11.4$ Hz, PMe₃).

Collection of Diffraction Data. Orange crystals of W(MA)(PhC₂H)(S₂CNEt₂)₂ were grown by layering hexanes on top of a methylene chloride solution of the complex. A prism having approximate dimensions 0.5 × 0.5 × 0.8 mm was selected, mounted on a glass wand, and coated with epoxy cement. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.¹⁰ A C-centered monoclinic cell was indicated by 25 centered reflections found in the region 30° < 2 θ < 35°. The unit cell parameters are listed in Table I.

Diffraction data were collected in the quadrant +*h*, +*k*, +*l* under the conditions specified in Table I. Three reflections chosen as intensity standards were monitored every 3 h and showed no significant (<1.5%) decay. The crystal was checked for orientation after every 300 reflections, and recentering was performed if the scattering vectors varied by more than 0.15°. ψ scans with nine reflections having 80° < χ < 90°

(10) Programs utilized during solution and refinement were from the Enraf-Nonius structure determination package.

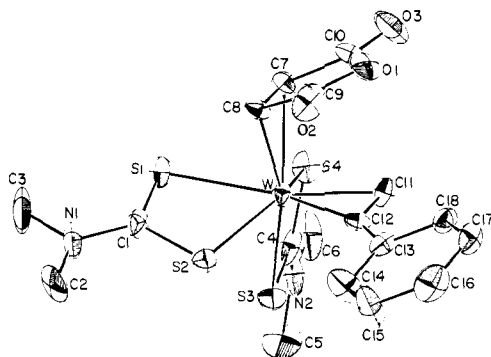


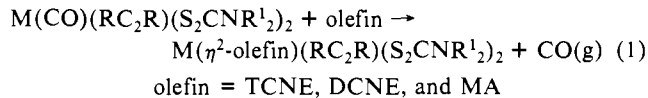
Figure 1. Molecular structure of $W(\text{MA})(\text{PhC}_2\text{H})(\text{S}_2\text{CNMe}_2)_2$ showing the atomic labeling scheme.

were performed to provide an empirical correction for absorption. Only the 3016 reflections having $I > 3\sigma(I)$ ¹¹ were used in the structure solution and refinement. The data were corrected for Lorentz-polarization effects and absorption during the final stages of refinement.

Solution and Refinement of the Structure. The structure was solved by using the heavy-atom method. The space group $C2/c$ was deduced from the presence of systematic absences for $h0l$, $l \neq 2n$, $0k0$, $k \neq 2n$, and hkl , $h + k \neq 2n$. The tungsten atom was located in a three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were obtained from subsequent Fourier and difference Fourier calculations. It was found that methylene chloride was present in the crystal lattice in a general position with an occupancy factor of 0.5. The positions of the hydrogen atoms were calculated by using a C-H distance of 0.95 Å with isotropic thermal parameters set at 5.0×10^{-2} Å for the hydrogen atoms. Full-matrix least-squares refinement¹² using isotropic thermal parameters for the phenyl carbons, the methylene chloride, and the hydrogens and anisotropic thermal parameters for all the other atoms converged with $R = 0.057$ and $R_w = 0.058$.¹³ The final difference Fourier map contained two peaks with intensities near $1.0 \text{ e}/\text{Å}^3$; both of these were residual electron density near tungsten.

Results and Discussion

The formation of bis(alkyne) dithiocarbamate group 6 derivatives upon thermal dissociation of carbon monoxide from $\text{Mo}(\text{CO})(\text{RC}_2\text{R})(\text{S}_2\text{CNR}'_2)_2$ reagents in the presence of excess alkyne^{4,5} prompted us to attempt analogous reactions with added olefins. Isolation of $\text{M}(\eta^2\text{-olefin})(\eta^2\text{-alkyne})(\text{S}_2\text{CNR}'_2)_2$ products has been accomplished for both molybdenum and tungsten with maleic anhydride (MA), *trans*-dicyanoethylene (DCNE), or tetracyanoethylene (TCNE) as the olefin ligand (eq 1). Elec-



tron-withdrawing olefin substituents are crucial to the preparation of these mixed olefin-alkyne complexes.

The MA and DCNE complexes form in refluxing toluene and benzene, respectively, under conditions that are compatible with thermal loss of carbon monoxide as a first step. The $\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})(\text{S}_2\text{CNR}'_2)_2$ reagent readily undergoes reversible dissociation of carbon monoxide, and it decomposes with loss of CO at 90 °C in 30 min in the absence of free ligand.¹⁴ Although similar kinetic studies are not available for the tungsten analogues, substitution of the carbonyl ligand in $\text{W}(\text{CO})(\text{PhC}_2\text{Ph})(\text{S}_2\text{CNR}'_2)_2$ by alkyne¹⁵ and by sulfur¹⁶ takes place at temperatures of 77 and 110 °C, respectively. The facile synthesis of TCNE complexes

(11) $I = S(C + RB)$ and $\sigma(I) = [2s^2(c + R^2B) + (\rho I)^2]^{1/2}$, where S = scan rate, C = total integrated peak count, R = ratio of scan time to background count limit, B = total background count, and $\rho = 0.01$ is a correction factor.

(12) The function minimized was $\sum w(|F_o| - |F_c|)^2$. Scattering factors were taken from: Cromer, D. T.; Weber, J. T. "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.

(13) $R = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

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Table II. Final Atomic Positional Parameters for $W(\text{MA})(\text{PhC}_2\text{H})(\text{S}_2\text{CNEt}_2)_2$

atom	x^a	y	z
W	0.13077 (3)	0.19741 (5)	0.07078 (3)
Cl(1)	0.2599 (4)	0.3159 (8)	0.4191 (5)
Cl(2)	0.1360 (7)	0.3883 (13)	0.3992 (7)
S(1)	0.0636 (2)	0.0613 (3)	-0.0296 (2)
S(2)	0.2022 (2)	0.1311 (3)	0.0210 (2)
S(3)	0.0907 (2)	0.3254 (3)	-0.0322 (2)
S(4)	0.0132 (2)	0.2662 (3)	0.0321 (2)
O(1)	0.1990 (4)	0.1120 (8)	0.2519 (4)
O(2)	0.2829 (4)	0.0312 (8)	0.2418 (5)
O(3)	0.0974 (5)	0.1617 (10)	0.2328 (5)
N(1)	0.1389 (6)	-0.016 (1)	-0.0856 (6)
N(2)	-0.0355 (6)	0.404 (1)	-0.0825 (6)
C(1)	0.1333 (7)	0.050 (1)	-0.0366 (6)
C(2)	0.1970 (7)	-0.025 (1)	-0.0923 (7)
C(3)	0.0777 (10)	-0.076 (2)	-0.1342 (9)
C(4)	0.01566 (8)	0.339 (1)	-0.0328 (8)
C(5)	-0.0336 (9)	0.467 (1)	-0.1345 (8)
C(6)	-0.0962 (9)	0.417 (2)	-0.0812 (9)
C(7)	0.1067 (7)	0.085 (1)	0.1349 (6)
C(8)	0.1660 (5)	0.046 (1)	0.1370 (6)
C(9)	0.2225 (6)	0.058 (1)	0.2132 (6)
C(10)	0.1299 (7)	0.124 (1)	0.2096 (6)
C(11)	0.1628 (6)	0.302 (1)	0.1528 (6)
C(12)	0.2166 (7)	0.269 (1)	0.1500 (6)
C(13)	0.2936 (6)	0.280 (1)	0.1961 (6)
C(14)	0.3349 (6)	0.256 (2)	0.1692 (7)
C(15)	0.4019 (7)	0.269 (2)	0.2114 (7)
C(16)	0.4321 (7)	0.300 (2)	0.2831 (8)
C(17)	0.3909 (6)	0.322 (1)	0.3125 (7)
C(18)	0.3215 (6)	0.313 (1)	0.2677 (6)
C(19)	0.215 (1)	0.336 (2)	0.393 (1)

^aNumbers in parentheses are the estimated standard deviations of the coordinates and refer to the last significant digit of the entry.

Table III. Selected Bond Distances (Å) in $W(\text{MA})(\text{PhC}_2\text{H})(\text{S}_2\text{CNEt}_2)_2$

W-C7	2.233 (9)	C7-C10	1.49 (1)
W-C8	2.261 (8)	C8-C9	1.47 (1)
W-C11	2.006 (8)	C10-O3	1.18 (1)
W-C12	2.01 (1)	C10-O1	1.35 (1)
W-S1	2.543 (2)	C9-O2	1.22 (1)
W-S2	2.508 (2)	C9-O1	1.38 (1)
W-S3	2.490 (2)	C11-C12	1.32 (1)
W-S4	2.504 (2)	C12-C13	1.50 (1)
C7-C8	1.41 (1)		

Table IV. Selected Bond Angles (deg) in $W(\text{MA})(\text{PhC}_2\text{H})(\text{S}_2\text{CNEt}_2)_2$

S1-W-S2	69.6 (1)	S4-W-C8	117.8 (2)
S1-W-S3	84.6 (1)	S4-W-C11	84.1 (2)
S1-W-S4	83.6 (1)	S4-W-C12	121.5 (3)
S1-W-C7	82.0 (2)	C7-W-C8	36.7 (3)
S1-W-C8	79.7 (2)	C7-W-C11	88.4 (3)
S1-W-C11	165.3 (2)	C7-W-C12	101.9 (3)
S1-W-C12	154.9 (3)	C8-W-C11	99.1 (3)
S2-W-S3	81.7 (1)	C8-W-C12	88.8 (3)
S2-W-S4	142.3 (1)	C11-FW-C12	38.5 (3)
S2-W-C7	118.2 (2)	C8-C7-C10	106.6 (8)
S2-W-C8	83.7 (2)	C7-C8-C9	105.3 (7)
S2-W-C11	125.0 (2)	C11-C12-C13	136.6 (8)
S2-W-C12	87.1 (3)	C9-O1-C10	109.4 (8)
S3-W-S4	69.5 (1)	O1-C9-O2	121 (1)
S3-W-C7	149.6 (2)	O1-C9-C8	109.6 (8)
S3-W-C8	161.5 (2)	O2-C9-C8	128 (1)
S3-W-C11	98.6 (2)	O1-C10-O3	121 (1)
S3-W-C12	101.8 (2)	O1-C10-C7	108.6 (9)
S4-W-C7	82.0 (2)	O3-C10-C7	129 (1)

at room temperature is anomalous and suggests that a mechanism other than initial CO loss is operative for this unusually reactive olefin.

No olefin containing products were isolated from reaction of styrene with $W(\text{CO})(\text{PhC}_2\text{Ph})(\text{S}_2\text{CNMe}_2)_2$, $W(\text{CO})-$

(MeC₂Me)(S₂CNMe₂)₂, or Mo(CO)(MeC₂Me)(S₂CNMe₂)₂. Although both styrene and diethyl fumarate react with W(CO)(PhC₂Ph)(S₂CNR₂)₂ in refluxing toluene, the only product characterized was a (sulfido)(alkyne)tungsten(IV) complex, W(S)(PhC₂Ph)(S₂CNR₂)(SCNR₂).¹⁶

Structure of W(MA)(PhC₂H)(S₂CNEt₂)₂. The solid-state molecular structure of (η²-maleic anhydride)(η²-phenylacetylene)bis(*N,N*-diethyldithiocarbamato)tungsten(II) is shown in Figure 1 where the atomic numbering scheme is defined. Final atomic positional parameters are listed in Table II while bond distances and angles are listed in Tables III and IV, respectively. The geometry is best described as a distorted octahedron with the olefin and the alkyne each occupying one site. The four sulfur atoms complete the coordination sphere with one sulfur trans to the alkyne, one sulfur trans to the olefin, and the remaining two sulfur atoms mutually trans to each other. The olefin and alkyne C₂ units are cis and parallel. The alkyne-phenyl substituent is bent away from the metal (C-C-Ph = 137°); the plane of the phenyl ring is canted by 24.1° relative to the tungsten-alkyne [W-C(11)-C(12)] plane. The acid anhydride ring of the bound olefin is directed toward the alkyne and is nearly parallel to the phenyl ring.

The stark contrast between the metal-alkyne and metal-olefin bonding extent in group 6 d⁴ metal complexes is reflected in the disparate metal-carbon distances of this mixed olefin-alkyne-tungsten derivative. The average W-C alkyne bond length of 2.01 Å found here is comparable to M-C distances found in other monomeric d⁴ Mo and W complexes where the alkyne ligand can be considered a "four-electron" donor: (π-C₅H₅)Mo(CO)(CF₃C₂CF₃)(SC₆F₅), 2.03 Å;^{2f} W(CO)(HC₂H)(S₂CNEt₂)₂, 2.03 Å;^{2b} Mo(CO)(PhC₂H)(PEt₃)₂Br₂, 1.99 Å,³ and Mo(PhC₂Ph)-(meso-tetratolylporphyrin), 1.97 Å.¹⁷ The average W-C bond length of 2.25 Å to the maleic anhydride ligand is then 0.24 Å longer than the average metal-alkyne bond distance. A comparable Mo-C olefin distance of 2.29 Å is found in the Mo(IV) complex, Mo(O)(TCNE)(S₂CN-*n*-Pr₂)₂.¹⁸ The contrast between olefin and alkyne bond distances reported here for W(MA)-(PhC₂H)(S₂CNEt₂)₂ is also evident in [(π-C₅H₅)Mo(MeC₂Me)(η²-*o*-Ph₂PC₆H₄CH=CH₂)] [BF₄].¹⁹ The olefin ligand in this cationic complex is part of a chelate ring with phosphorus anchoring the other end to the metal. In both olefin-alkyne complexes, [(π-C₅H₅)Mo(MeC₂Me)(η²-*o*-Ph₂PC₆H₄CH=CH₂)]⁺ and W(MA)(PhC₂H)(S₂CNEt₂)₂, the unsaturated C₂ ligands are in cis positions relative to one another in a parallel configuration. The cation has average W-C distances of 2.00 Å to the 2-butyne ligand and 2.27 Å to the styrene-derived ligand,¹⁹ quite close to values we find for the unchelated C₂ ligands in the tungsten complex.

The W-S dithiocarbamate bond lengths fall in a fairly narrow range: 2.49–2.54 Å. The sulfur atom located trans to the alkyne is slightly elongated (2.54 Å) relative to the remaining three sulfur atoms. This distance probably reflects the trans influence of the phenylacetylene ligand. Similar M-S distances are found in other molybdenum and tungsten dithiocarbamate-alkyne derivatives.^{2b,5b,16} The two mutually trans dithiocarbamate sulfur atoms exhibit W-S distances (2.51 and 2.50 Å) which are typical of tungsten complexes where the dithiocarbamate sulfur p_π orbital confronts a filled metal dπ orbital.^{2b,16} The sulfur atom opposite the maleic anhydride ligand is 2.49 Å from the metal center.

Molecular Orbital Description. Important metal dπ-ligand π interactions are shown in Figure 2 for the model compound W(H₂C=CH₂)(HC₂H)(S₂CNH₂)₂ with a pseudo-octahedral geometry. Note that the cis parallel ethylene-acetylene ground-state geometry produces a one-to-one correspondence between metal dπ orbitals and C₂ ligand π orbitals. As a result, three two-center, two-electron metal-ligand π bonds exist in this molecular configuration.

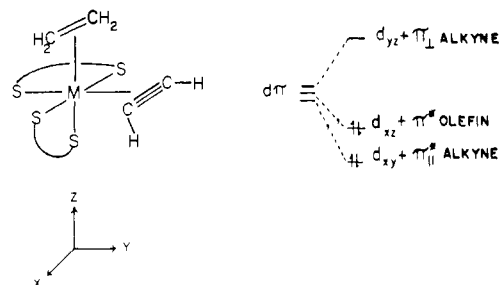


Figure 2. Schematic representation of M(C₂H₂)(C₂H₄)(S₂CNR₂)₂ and a qualitative MO diagram of the dπ-dominated orbitals.

The LUMO, dominated by metal d_{yz} character, is destabilized by donation from the filled alkyne π_⊥ orbital. The bonding mate, dominated by the low-lying alkyne π_⊥ orbital, is not shown in Figure 2. The d⁴ metal configuration places paired electrons in both remaining dπ orbitals, d_{xy} and d_{xz}, which are stabilized by back-bonding to vacant alkyne π_{||}* and olefin π* orbitals, respectively. The vacant antibonding combinations, dominated by C₂ π* orbitals, lie above the orbitals shown in Figure 2. Although the ethylene-stabilized dπ orbital, d_{xz}, is calculated to be the HOMO (highest occupied molecular orbital) in this model compound, the presence of highly electron-withdrawing substituents no doubt enhances back-donation from metal-to-olefin π* in the molecules we have actually isolated. The question of relative olefin and alkyne π acidity is better addressed experimentally, albeit indirectly, by the electrochemical measurements discussed below.

Extended Hückel calculations have been employed to assess the validity of qualitative molecular orbital arguments relevant to C₂ ligand rotational barriers. We have previously found calculated alkyne rotational barriers in M(CO)(η²-alkyne)(S₂CNR₂)₂⁶ and M(O)(η²-alkyne)(S₂CNR₂)₂²⁰ to be helpful in interpreting experimental variable temperature NMR spectra. As mentioned in the introduction, the alkyne π_{||}* and π_⊥ orbitals dominate the molecular orbitals arising from two orthogonal dπ orbitals, in this case d_{yz} and d_{xy} combinations. Note that the olefin has only one orbital of M-L π character, π*, which is aligned for overlap with d_{xz} and is thus independent of the alkyne orientation. Rotation of the alkyne would be expected to continuously alter the orthogonal d_{xy} and d_{yz} combinations which are stabilized and destabilized, respectively, until at 90° relative to the ground-state geometry the original ordering of d_{xy} and d_{yz} would be reversed. No large energy changes would be anticipated for such a rotation, in accord with the calculated barrier (12.5 kcal mol⁻¹).

Rotation of the olefin, while maintaining the original alkyne orientation, destroys the one-to-one match of ligand π-dπ orbitals, however. Olefin stabilization of the filled d_{yz} orbital is lost as the olefin rotates to turn on π* overlap with d_{yz}, and as a result, a high barrier is calculated for rotation of the olefin ligand (75.5 kcal mol⁻¹).

NMR Properties. Proton NMR spectra of M(olefin)-(RC₂H)(S₂CNR₂)₂ complexes display low-field resonances (11.5–13.5 ppm) assigned to terminal alkyne protons. Olefin protons for MA and DCNE appear as an AB pattern with coupling constants of 4–5 Hz for maleic anhydride complexes and 9–11 Hz for DCNE complexes. Four distinct methyl signals are observed for alkyl groups on the chelates of the dimethyldithiocarbamate derivatives, while the diethyldithiocarbamate complexes display four overlapping triplets assigned to the methyl protons and a complex multiplet assigned to the diastereotopic methylene protons of the ethyl groups.

The ¹³C NMR spectrum of W(MA)(HC₂Ph)(S₂CNEt₂)₂ exhibited weak resonances at 206.8 and 206.4 ppm assigned to the central carbons of the two dithiocarbamate chelates, and signals at 223.7 and 222.9 ppm attributed to the two alkyne carbons. Resonances at 172.9 and 172.6 and 60.8 and 59.8 ppm are assigned

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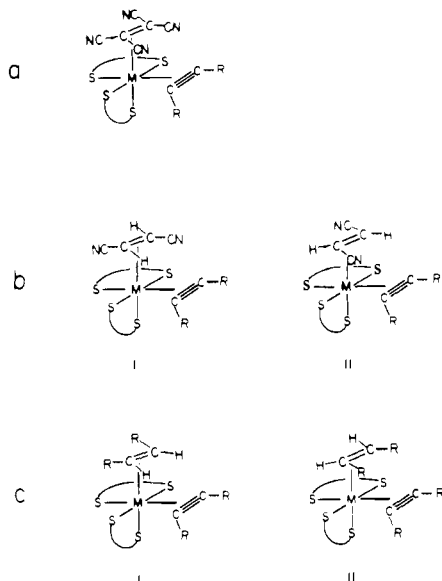


Figure 3. Potential isomers (excluding enantiomers) of $M(\text{olefin})(\text{RC}_2\text{R})(\text{S}_2\text{CNR}_2)_2$ for (a) a symmetrically tetrasubstituted olefin, (b) a symmetrically substituted *trans*-olefin, and (c) a symmetrically substituted *cis*-olefin.

to the two carbonyl carbons and the two olefinic carbons, respectively, of the maleic anhydride ligand. Normal chemical shifts characterized the ethyl and phenyl groups of the dithiocarbamate and alkyne ligands.

Carbon-13 chemical shifts have been empirically correlated with the extent of electron donation from the filled alkyne π_{\perp} orbital to the metal.²¹ The average ¹³C shift of 223 ppm for the metal-bound alkyne carbons in $W(\text{MA})(\text{PhC}_2\text{H})(\text{S}_2\text{CNET}_2)_2$ falls within the range of four-electron donor alkynes. A rough perspective is provided by tungsten complexes²¹ where alkynes need to serve as 4-, 3^{1/3}-, 3-, and 2-electron donors to fulfill the 18-electron rule, respectively: $W(\text{CO})(\text{PhC}_2\text{H})(\text{S}_2\text{CNET}_2)_2$, 206 ppm; $W(\text{CO})(\text{EtC}_2\text{Et})_3$, 181 ppm;⁶ $[(\pi\text{-C}_5\text{H}_5)W(\text{CO})(\text{MeC}_2\text{Bu})_2]^+$, 152 ppm; *fac*- $W(\text{CO})_3(\text{dppe})(\eta^2\text{-PhC}_2\text{H})$, 90 ppm.^{2c} For terminal alkyne ligands, the acetylenic proton is also a useful NMR probe.²⁰ Here again, the olefin-alkyne complexes of both molybdenum and tungsten exhibit low-field chemical shifts indicative of extensive alkyne π_{\perp} to metal $d\pi$ donation ($\equiv\text{CH}$, 11.5–13.5 ppm).

Room-temperature ¹H NMR spectra of $\text{Mo}(\text{HC}_2\text{H})(\text{DCNE})(\text{S}_2\text{CNET}_2)_2$ and $W(\text{HC}_2\text{H})(\text{MA})(\text{S}_2\text{CNET}_2)_2$ exhibit a single alkyne resonance. No broadening of this alkyne resonance was observed for either complex when the samples were cooled to -99 °C. The DCNE complexes $W(\text{PhC}_2\text{H})(\text{DCNE})(\text{S}_2\text{CNET}_2)_2$, $W(\text{PhC}_2\text{Ph})(\text{DCNE})(\text{S}_2\text{CNMe}_2)_2$, and $\text{Mo}(\text{HC}_2\text{H})(\text{DCNE})(\text{S}_2\text{CNET}_2)_2$ display four, two, and four olefin resonances, respectively, as isolated. Prolonged heating of $W(\text{PhC}_2\text{Ph})(\text{DCNE})(\text{S}_2\text{CNMe}_2)_2$ generates an additional pair of olefin signals, presumably reflecting the formation of a second isomer (see discussion below). No evidence for exchange of olefin protons was observed for the tungsten complexes at temperatures up to 100 °C nor for the molybdenum complexes up to 77 °C.

Given the *cis* parallel geometry of the olefin and alkyne ligands in $d^4 M(\eta^2\text{-olefin})(\eta^2\text{-alkyne})(\text{S}_2\text{CNR}_2)_2$ complexes, the number of NMR distinguishable isomers depends on the substitution pattern of the olefin and the alkyne. For a tetrasubstituted olefin (e.g., TCNE) and a symmetric alkyne ligand, only one isomer should exist (two enantiomers will exist due to the presence of the chelate rings; see Figure 3a). For $W(\text{TCNE})(\text{MeC}_2\text{Me})(\text{S}_2\text{CNET}_2)_2$, a single set of four alkyl signals is observed for the dithiocarbamate ethyl groups as predicted for only one isomer. However, the single singlet due to the two inequivalent alkyne methyl groups suggests that rotation of the 2-butyne ligand is rapid on the NMR time scale. A low barrier-to-alkyne rotation

is compatible with NMR data collected for other olefin-alkyne complexes (*vide infra*), but we cannot definitively rule out coincidental chemical shift values.

Binding a symmetrically substituted *trans*-olefin (e.g., DCNE) to an $M(\text{RC}_2\text{R})(\text{S}_2\text{CNR}_2)_2$ fragment produces two pairs of enantiomers (see Figure 3b). Again we neglect enantiomers in the discussion since they are indistinguishable by normal NMR techniques. In each of the two diastereomers, one of the two distinct olefin substituents will lie over an alkyne substituent. The two diastereomers differ in the location of the two olefin substituents away from the alkyne ligand relative to the chelate ring in the plane of the alkyne. One substituent will sit roughly above the bite of the dithiocarbamate which has both sulfur atoms *cis* to the olefin while the other olefin substituent will be above the quadrant defined by the two *cis* sulfur atoms which are not connected to one another. Each isomer should give rise to distinct NMR environments for the olefin substituents, with the two isomers probably of similar energy.

The ¹H NMR of $\text{Mo}(\text{DCNE})(\text{HC}_2\text{H})(\text{S}_2\text{CNET}_2)_2$ exhibits four doublets of roughly equal intensity which can be assigned to the *trans* protons of a static olefin in two isomers. No exchange of these olefin signals was observed at temperatures up to 77 °C, consistent with a relatively large barrier to olefin rotation as rationalized by molecular orbital considerations (*vide supra*). Only two signals due to the acetylene protons of $\text{Mo}(\text{DCNE})(\text{HC}_2\text{H})(\text{S}_2\text{CNET}_2)_2$ are observed down to -100 °C. In conjunction with the olefin signals which imply two isomers, this indicates that averaging of the two ends of the acetylene ligand is occurring to produce only one terminal alkyne proton signal per isomer.

No exchange of olefin ¹H signals was observed in spectra of tungsten complexes containing *trans*-dicyanoethylene up to temperatures of 130 °C [$W(\text{DCNE})(\text{PhC}_2\text{Ph})(\text{S}_2\text{CNMe}_2)_2$ and $W(\text{DCNE})(\text{PhC}_2\text{H})(\text{S}_2\text{CNET}_2)_2$]. Only one set of olefinic doublets was present in the sample of $W(\text{DCNE})(\text{PhC}_2\text{Ph})(\text{S}_2\text{CNMe}_2)_2$ as isolated, but heating to 100 °C generated a second NMR detectable isomer. Recall that data obtained for $\text{Mo}(\text{DCNE})(\text{HC}_2\text{H})(\text{S}_2\text{CNET}_2)_2$ indicated that both diastereomers were of comparable energy.

Two diastereomers (plus their enantiomers) also arise from binding of the two faces of a symmetrically substituted *cis*-olefin (e.g., MA) to an $M(\text{RC}_2\text{R})(\text{S}_2\text{CNR}_2)_2$ fragment. These isomers have both like olefin substituents either over or away from the alkyne, and a significant energy difference between the two seems probable. We have detected only a single isomer for the maleic anhydride complexes by ¹H and ¹³C NMR; the two ends of the olefin and the two halves of the alkyne are necessarily in different environments. Since olefin rotation does not interconvert the olefin protons for the *cis*-olefin case, no fluxional information is contained in the olefin ¹H doublets which are 0.7 ppm apart for $W(\text{MA})(\text{HC}_2\text{H})(\text{S}_2\text{CNET}_2)_2$. Only one acetylenic proton signal is observed for $W(\text{MA})(\text{HC}_2\text{H})(\text{S}_2\text{CNET}_2)_2$ down to -99 °C, again suggesting facile alkyne rotation. Coincidental chemical shifts are unlikely since similar terminal alkyne environments in $W(\text{O})(\text{HC}_2\text{H})(\text{S}_2\text{CNR}_2)_2$ complexes easily differentiate the two ends of the alkyne in ¹H NMR spectra.²⁰ Dynamic processes that average the two halves of alkynes which differ only with respect to the position of chelates have been frozen out for $\text{Mo}(\text{CH}_3\text{C}_2\text{CH}_3)_2(\text{S}_2\text{CNMe}_2)_2$,^{5a} $W(\text{O})(\text{C}_2\text{H}_2)(\text{S}_2\text{CNMe}_2)_2$,²⁰ $W(\text{S})(\text{C}_2\text{Ph}_2)(\text{S}_2\text{CNET}_2)_2$,¹⁶ and $\text{Mo}(\text{CH}_3\text{C}_2\text{CH}_3)_2(\text{S}_2\text{CNC}_4\text{H}_7)_2$.^{5b}

Alkyne rotation has been observed in other complexes requiring involvement of the alkyne π_{\perp} electrons to fulfill the 18-electron rule: $W(\text{CO})(\text{C}_2\text{H}_2)(\text{S}_2\text{CNET}_2)_2$,⁶ $[\text{Mo}(\text{CO})(\text{MeC}_2\text{Me})(\text{PEt}_3)(\eta^5\text{-C}_9\text{H}_7)][\text{BF}_4]$,^{2h} and $\text{Mo}(\text{CO})(\text{MeC}_2\text{Me})(\text{PEt}_3)_2\text{Br}_2$.³ In these complexes, the carbonyl ligand creates a three-center, two-electron bond with a metal $d\pi$ orbital and the alkyne π_{\perp}^* in the ground-state geometry. Loss of this favorable interaction upon alkyne rotation increases the barrier substantially relative to the single-faced π -acid olefin case reported here.

Infrared Spectra. The olefin-alkyne complexes display prominent infrared absorptions associated with the functional groups of the olefin ligand. The DCNE complexes exhibit an absorption

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Table V. Visible Transition Energies and Electrochemical Reduction and Oxidation Potentials for M(L)(alkyne)(S₂CNR₂)₂

	λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹) ^a	cm ⁻¹	E_R (V) ^b	$E_{p/2OX}$ (V) ^c
W(PhC ₂ H)- (MA)(S ₂ CNEt ₂) ₂	465 (390)	21 500	-1.13	0.78
W(PhC ₂ H)(DCNE)- (S ₂ CNEt ₂) ₂	455 (560)	21 980	-1.42	0.89
W(PhC ₂ H)(TCNE)- (S ₂ CNEt ₂) ₂			-0.88	1.62
W(PhC ₂ H) ₂ - (S ₂ CNEt ₂) ₂			-2.24	0.82
W(PhC ₂ H)- (CO)(S ₂ CNEt ₂) ₂	610 (180)	16 390	-1.65	0.36
W(MeC ₂ H)- (MA)(S ₂ CNEt ₂) ₂	455 (330)	21 980	-2.02	0.87
Mo(PhC ₂ H)- (MA)(S ₂ CNEt ₂) ₂	600 (360), 810 (240)	16 670, 12 340	-1.07	0.61
Mo(HC ₂ H)(DCNE)- (S ₂ CNEt ₂) ₂	550 (300)	18 180	-1.05	0.56
Mo(CH ₃ C ₂ CH ₃)- (MA)(S ₂ CNEt ₂) ₂			-1.27	0.72

^a Electronic spectra were recorded in CH₂Cl₂. ^b All reduction waves exhibit an anodic current to cathodic current ratio of unity and a peak-to-peak separation of 80 mV equal to the peak-to-peak separation of the ferrocene/ferricinium couple under identical conditions. ^c All oxidative processes are irreversible.

at 2080–2100 cm⁻¹ which is displaced from that of the free olefin (2200 cm⁻¹), and the maleic anhydride complexes display two absorptions of unequal intensity at ca. 1804 and 1741 cm⁻¹ displaced from the free olefin absorptions at 1850 and 1781 cm⁻¹. The TCNE complexes display a weak absorption at ca. 2200 cm⁻¹ which compares to absorptions at 2228 and 2260 cm⁻¹ in the free olefin.

Cyclic Voltammetry and Electronic Spectroscopy. All olefin-alkyne complexes examined by cyclic voltammetry exhibited a reversible reduction as judged by the cathodic and anodic peak separation compared to the ferrocene/ferrocenium couple under identical conditions; the ratio of the anodic-to-cathodic current was unity. Formal reduction potentials ranged from -0.88 to -2.02 V vs. SSCE. All complexes exhibited an irreversible oxidation, and half-peak potentials measured at 200 mV s⁻¹ ranged from +0.56 to +1.62 V vs. SSCE. Electrochemical and electronic absorption data are presented in Table V.

Oxidation potentials have been correlated to HOMO energies in organic π systems²² and to the π acidity of the ligands in inorganic complexes.²³ Oxidation potentials for a series of W(X)(PhC₂H)(S₂CNEt₂)₂²⁴ complexes with X = CO, alkyne, and olefin, as listed in Table V, indicate that TCNE is the strongest π -acid by this criterion. This is consistent with the extremely electrophilic character of TCNE.²⁵ Maleic anhydride, *trans*-dicyanoethylene, and phenylacetylene appear to be comparable in π -acid strength, while carbon monoxide produces the lowest oxidation potential; i.e., it seems to be the poorest π -acid in this series. The highly electron-withdrawing substituents on the olefins we have used as ligands are no doubt important in this π -acidity ranking.

Infrared ν_{CO} frequencies provide additional evidence for the superior π -acid strength of alkyne ligands relative to CO in d⁴ complexes. In the following two W(II) complexes, CO competes against alkyne and CO, respectively, for metal d π electron density: W(CO)(PhC₂H)(S₂CNEt₂)₂, 1927 cm⁻¹;⁶ W(CO)₂(S₂CNEt₂)₂,

1910, 1820 (1865 cm⁻¹ average).²⁶ The π -acidity ordering found here is not general for other complexes or other electron configurations, e.g., for the cationic *cis*-[Os(bpy)₂ClX]⁺ complex, the π -acid strength of carbon monoxide exceeds that of alkyne ligands: CO > (CH₃O(=O)C)₂C₂ > CH₂=CH₂ > 3-hexyne.^{23a}

Reduction potentials have been correlated with LUMO energies in organic π systems.²⁷ An examination of the molecular orbital structure of the complexes M(X)(alkyne)(S₂CNR₂)₂ (X = CO, alkyne, and olefin) suggests a correspondence between the d π LUMO energy and the π donor strength of the alkyne. This correlation was verified for cases with X = alkyne or CO by a combination of electrochemical and visible spectroscopic measurements on a series of M(CO)(alkyne)(S₂CNR₂)₂ (M = Mo and W) and Mo(alkyne)₂(S₂CNR₂)₂ complexes with a wide variety of alkynes.²⁴ A similar trend is seen for X = MA in Table V. Substitution of propyne or butyne for phenylacetylene on W or Mo-maleic anhydride complexes, respectively, yields more negative reduction potentials for the more electron-rich and stronger π -donor alkyl-substituted alkyne derivatives.

Visible electronic transitions with extinction coefficients of 10²–10³ are characteristic of many formal 16-electron Mo(II) and W(II) complexes containing both π -acceptor and π -donor ligands.³ These absorptions have been assigned as transitions between a metal d π -based HOMO and a low-lying d π LUMO.²⁴ Visible spectra of selected DCNE and MA complexes of tungsten exhibit absorption maxima between 450 and 465 nm with extinction coefficients on the order of 10² M⁻¹ cm⁻¹ (Table V). In TCNE complexes, this region of the visible spectrum is masked by an intense absorption (λ_{\max} = 400 nm, ϵ ~ 10⁴ M⁻¹ cm⁻¹). Molybdenum complexes which we examined exhibited an analogous transition which was shifted to lower energies relative to the tungsten complexes, a pattern observed previously.²⁴ Mo-(PhC₂H)(MA)(S₂CNEt₂)₂ displays a second transition in the near infrared. Two singlet transitions within the manifold of d π orbitals are possible for diamagnetic d⁴ octahedral complexes: from d_{xy}²d_{xz}²d_{yz}⁰ to d_{xy}²d_{xz}¹d_{yz}¹ or d_{xy}¹d_{xz}²d_{yz}¹. It may be that both transitions are observable only for Mo(MA)(PhC₂H)(S₂CNEt₂)₂ with the higher energy transition in other MA complexes masked by more intense charge-transfer transitions in the ultraviolet and near-visible region of the spectrum as is typical of molybdenum(II) and tungsten(II) bis(dithiocarbamate) complexes.²⁸

Nucleophilic Addition to Terminal Alkyne Ligands. Formation of metalocyclopropene products from attack of phosphite or phosphine nucleophiles at the terminal carbon of phenylacetylene in M(MA)(PhC₂H)(S₂CNR₂)₂ (M = Mo and W) has been documented by ¹H, ¹³C, and ³¹P NMR. Addition of excess phosphine or phosphite to tetrahydrofuran solutions of phenylacetylene complexes, M(PhC₂H)(MA)(S₂CNR₂)₂ (M = Mo and W), yielded adducts of the type M(PhC₂HPR₃)(MA)(S₂CNR₂)₂ quantitatively. The trimethylphosphine adduct of W(MA)-(PhC₂H)(S₂CNEt₂)₂ has no low-field ¹H signal characteristic of four-electron donor alkyne ligands, but rather resonances at 2.91 and 3.03 ppm integrate for one proton. Two-dimensional NMR heteronuclear correlation experiments established that the splitting of this proton into two signals is due to coupling to phosphorus (²J_{PH} = 29 Hz). Small side bands on each of these two signals reflect coupling to ¹⁸³W which is 14% naturally abundant (²J_{WH} = 12 Hz). A similar loss of the low-field proton resonance of the bound alkyne with appearance of a doublet centered at 2.35 ppm (²J_{PH} = 24 Hz) occurs upon addition of PMe₃ to Mo(MA)-(PhC₂H)(S₂CNMe₂)₂. The formula M(MA)-(PhC₂H)(S₂CNMe₂)₂ will be used to represent the η^2 -vinyl (or metalocyclopropene) product shown schematically below.

The carbon-13 NMR spectrum of W(MA)[PhC₂HP(OMe)₃](S₂CNMe₂)₂ exhibits normal maleic anhydride and dithiocarbamate ligand resonances. The four-coordinate carbon which results from binding of phosphorus resonates at high field

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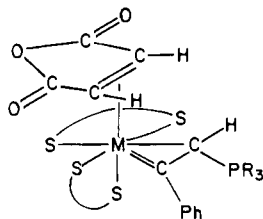
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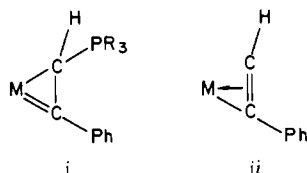
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(11.6 ppm) and is strongly coupled to both hydrogen and phosphorus ($^1J_{\text{CH}} = 158$ Hz, $^1J_{\text{CP}} = 164$ Hz). The alkyldene character of the acetylenic carbon adjacent to the site of attack is reflected in its low-field ^{13}C chemical shift of 222.2 ppm. Hence, NMR data suggest that representation i, the metallocyclopropene, is preferred.



Phosphorus-tungsten coupling constants of 39 and 36 Hz observed in ^{31}P NMR spectra of $\text{W}(\text{MA})[\text{PhC}_2\text{HP}(\text{OEt})_3](\text{S}_2\text{CNMe}_2)_2$ and $\text{W}(\text{MA})[\text{PhC}_2\text{HPMe}_3](\text{S}_2\text{CNEt}_2)_2$ are nearly an order of magnitude smaller than normal one-bond W-P coupling constants.²⁹ They are quite reasonable in magnitude for $^2J_{\text{WP}}$ through the intermediate carbon atom.

Nucleophilic attack to form η^2 -vinyl ligands from alkynes has been reported in other complexes where the alkyne donates more than two electrons to the metal. Metallocyclopropene products are formed upon addition of heteroatom nucleophiles or isonitriles to the metal-bound hexafluorobutene or dimethylacetylene dicarboxylate in $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{alkyne})_2\text{X}$ ($\text{M} = \text{Mo}$ and W) complexes.³⁰ Addition of lithium diphenylcuprate to a cationic molybdenum-1-hexyne complex yields an η^2 -vinyl ligand,^{31a} while hydride addition to the molybdenum-alkyne complex in the presence of phosphine produces an η^1 -vinyl ligand.^{31b} Even though the metallocyclopropene complexes reported herein are synthesized in the presence of excess phosphine or phosphite, we see no evidence of metal-bound phosphorus with concomitant η^1 -vinyl

formation. Dissociation of triethylphosphite from $\text{W}(\text{MA})[\text{PhC}_2\text{HP}(\text{OEt})_3](\text{S}_2\text{CNMe}_2)_2$ to regenerate the olefin-alkyne complex is facile at room temperature.

The PhC_2HPR_3 ligand generated by phosphine or phosphite addition to the phenylacetylene ligand can be considered to donate four electrons to the metal. A simple electron-counting analogue would be the HC_2H_2^- ligand, conceptually generated by either hydride addition to HC_2H or by proton removal from $\text{H}_2\text{C}_2\text{H}_2$. An orbital analogy between η^2 -vinyl ligands and four-electron-donor alkynes exists.^{31a,32} This orbital link is compatible with formation of η^2 -vinyl ligands from four-electron-donor alkyne ligands, while η^1 -vinyl ligands form from two-electron-donor alkyne ligands. Reger and co-workers have systematically investigated the formation of (η^1 -vinyl)iron derivatives resulting from nucleophilic attack on alkyne ligands serving as two-electron donors in $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{L}(\text{alkyne})]^+$ complexes.³³

Complexes $\text{M}(\text{MA})(\text{RC}_2\text{R})(\text{S}_2\text{CNR}^1_2)_2$ ($\text{M} = \text{Mo}$, $\text{R} = \text{CH}_3$; $\text{M} = \text{W}$, $\text{R} = \text{Ph}$), with no terminal alkyne proton, are resistant to phosphorus nucleophiles in refluxing tetrahydrofuran for several hours. Excess phenylacetylene reacts slowly with $\text{W}(\text{MA})-(\text{PhC}_2\text{Ph})(\text{S}_2\text{CNR}_2)_2$ in refluxing toluene over a period of days while $\text{W}(\text{MA})(\text{PhC}_2\text{H})(\text{S}_2\text{CNR}_2)_2$ reacts in hours under the same conditions with loss of alkene to form bis(alkyne) products. The reluctance of these internal alkyne complexes to react with nucleophiles was unexpected. The olefin-alkyne complex $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{MeC}_2\text{Me})(\eta^2\text{-}o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{CH}_2)][\text{BF}_4]$ reacts with acetonitrile at reflux to yield an olefin-alkyne coupling product: $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CH}_3\text{CN})(\eta^4\text{-}o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{CH}-\text{CMe}=\text{CHMe})[\text{BF}_4]$.¹⁹ Formation of cyclohexadiene complexes occurs under mild conditions when $\text{Rh}(\text{HC}_2\text{H})(\text{CF}_3\text{C}_2\text{CF}_3)(\text{acac})$ reacts with excess hexafluorobutene.³⁴ Although the $\text{M}(\eta^2\text{-olefin})(\eta^2\text{-alkyne})(\text{S}_2\text{CNR}_2)_2$ complexes might have been expected to resemble $\text{Mo}(\text{CO})(\eta^2\text{-alkyne})(\text{S}_2\text{CNR}_2)_2$ in their behavior toward nucleophiles and undergo substitution of the alkyne ligand by 2 equiv of PR_3 or CO , the lack of reactivity displayed by the internal alkyne complexes we have prepared is more reminiscent of $\text{M}(\eta^2\text{-alkyne})_2(\text{S}_2\text{CNR}_2)_2$ complexes.³⁵

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Supplementary Material Available: Tables of thermal parameters, complete bond distances, calculated hydrogen positions, and calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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