trans-(carbene)$_2$M(CO)$_4$ complexes (M = Cr, Mo, W) which upon oxidation rapidly isomerized to the corresponding cis cations which have a higher oxidation potential of approximately 200 mV. The approximate rates of isomerization and activation energies were determined and are consistent with a nondisassociative twist mechanism. Utilizing the facts that the trans cations isomerize to cis cations with a higher redox couple and that the neutral cis complexes can be photochemically converted into the neutral trans cations, a simple AC photoelectric cell was designed. It was demonstrated that the carbene ligands do not need to contain an aromatic six-electron π-system to undergo this type of oxidatively induced isomerization.

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Registry No. *trans*-(benzothiazolin)$_2$Mo(CO)$_4$, 112021-83-7; *trans*-(benzothiazolin)$_2$W(CO)$_4$, 112021-84-8; *cis*-(Triaz)$_2$Cr(CO)$_4$, 61825-97-6; *cis*-(Triaz)$_2$Mo(CO)$_4$, 60971-03-1; *cis*-(Benazmid)$_2$Mo(CO)$_4$, 61046-06-8; *cis*-(Imid)$_2$Mo(CO)$_4$, 52082-57-2; *cis*-(Imid)$_2$W(CO)$_4$, 52194-73-7; *cis*-(Imidin)$_2$Cr(CO)$_4$, 41654-74-4; *cis*-(Imidin)$_2$Mo(CO)$_4$, 64161-93-9; *cis*-(Imidin)$_2$W(CO)$_4$, 64514-96-1; *trans*-(Triaz)$_2$Cr(CO)$_4$, 61729-86-0; *trans*-(Triaz)$_2$Mo(CO)$_4$, 61009-21-0; *trans*-(Benzimid)$_2$Mo(CO)$_4$, 60971-04-2; *trans*-(Imid)$_2$Mo(CO)$_4$, 52194-74-8; *trans*-(Imid)$_2$W(CO)$_4$, 52082-58-3; *trans*-(Imidin)$_2$Mo(CO)$_4$, 64161-94-0; Mo(CO)$_6$, 13939-06-5; W(CO)$_6$, 14040-11-0; bis(*N*-methylbenzothiazolinylidene), 2786-70-1.

Catalyst Design. The Activation of a Trinuclear Metal Cluster Complex by Metal Atom Substitution

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The trinuclear cluster complex Mo$_2$Ru(CO)$_7$(C$_5$H$_5$)$_2$(μ_3-S) (1) has been shown to produce the oligomerization of HC$_2$Ph. The reaction of 1 with HC$_2$Ph at 98 °C has yielded the products Mo$_2$Ru(CO)$_2$(C$_5$H$_5$)$_2$[μ_3-η^6-HCC(Ph)C(H)C(Ph)C(H)C(Ph)](μ_3-S) (2) in 15% yield and Mo$_2$Ru(CO)$_2$(C$_5$H$_5$)$_2$[μ-η^3-PhCC(H)-CPh][μ_3-η^3-HCC(Ph)CH](μ_3-S) (3) in 11% yield. 2 and 3 were characterized by crystallographic methods. For 2: space group $P2_1/c$, a = 10.899 (2) Å, b = 23.563 (5) Å, c = 14.562 (3) Å, β = 91.97 (2)°, Z = 4. The structure was solved by direct methods and was refined (3060 reflections) to the final value of the residuals R = 0.045 and R_w = 0.045. Compound 2 consists of a sulfur-bridged Mo$_2$Ru cluster that contains 1,3,5-triphenyldimetallahexatrienyl ligand bridging one face of the cluster. The hexatrienyl ligand was formed by the head-to-tail coupling of three HC$_2$Ph molecules. For 3: space group $C2/c$, a = 35.86 (1) Å, b = 12.454 (6) Å, c = 14.622 (3) Å, β = 98.60 (2)°, Z = 8. The structure was solved by direct methods and was refined (1867 reflections) to the final values of the residuals R = 0.054 and R_w = 0.051. Compound 3 consists of a sulfur-bridged Mo$_2$Ru cluster that contains a triply bridging 2-phenyldimetallaallyl ligand and an edge-bridging 1,3-diphenyldimetallaallyl ligand. 3 was formed from 2 by the splitting of the hexatrienyl ligand into two three carbon groupings. Compound 3 was obtained from 2 in 57% yield by heating to 125 °C, but this also yielded Mo$_2$Ru(CO)$_2$(C$_5$H$_5$)$_2$[μ-η^3-HCCPhCPh][μ_3-η^3-HCCPhCH](μ_3-S) (4), an isomer of 3 in 38% yield. 4 was characterized by crystallographic methods: space group $P\bar{1}$, a = 13.545 (2) Å, b = 15.869 (3) Å, c = 9.746 (2) Å, α = 90.37 (2)°, β = 104.11 (1)°, γ = 82.22 (1)°, Z = 2. The structure was solved by the heavy-atom method and refined (2717 reflections) to the final values of the residuals R = 0.044 and R_w = 0.042. 4 differs from 3 only in the structure of the edge-bridging dimetallaallyl group that has phenyl substituents in the 1- and 2-positions whereas 3 has the phenyl substituents in the 1- and 3-positions. 4 was obtained directly from 3, 24% yield, by heating to 125 °C for 3 h. The compound Mo$_2$Ru(CO)$_5$(C$_5$H$_5$)$_2$[μ-η^4-PhCC(H)CC(H)Ph](μ_3-S) (5) was obtained (11% yield) from the reaction of 1 with HC$_2$Ph in the presence of Me$_3$NO. The structure of 5 was determined crystallographically: space group $P\bar{1}$, a = 12.906 (3) Å, b = 13.916 (4) Å, c = 9.708 (4) Å, α = 91.54 (3)°, β = 100.82 (2)°, γ = 95.48 (2)°, Z = 2. The structure was solved by the heavy-atom method and was refined (2522 reflections) to the final values of the residuals R = 0.050 and R_w = 0.054. 5 consists of an open Mo$_2$Ru cluster bridged by a sulfido ligand and a Ph(H)CCC(H)CPh group that is π-bonded to one metal atom and σ-bonded a second metal atom. This ligand appears to have been formed by a head-to-head coupling of two HC$_2$Ph molecules and was accompanied by a hydrogen atom shift. 5 does not appear to be an intermediate in the formation of 2, 3, or 4. The reactivity of 1 is compared with that of Ru$_3$(CO)$_9$(μ_3-HC$_2$Ph)(μ_3-S) and Mo$_2$(CO)$_4$(C$_5$H$_5$)$_2$.

Introduction

The ability to vary the ligands has been one of the most important methods of modifying and controlling the reactivity and catalytic properties of metal complexes.[1-3] However, in polynuclear metal complexes, one has an additional variable: variation of the relative identities of the metal atoms, themselves. It is known that certain multimetallic heterogeneous catalysts exhibit catalytic behavior that exceeds that of their homonuclear components.[4]

Recently, there has been considerable interest in the synthesis and study of heteronuclear metal cluster com-

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plexes.[6] It is believed that these compounds may possess novel reactivity as a result of combining the different reactivity properties of the constituent elements.[6a]

Investigations of the compound $Mo_2(CO)_4(C_5H_5)_2$ have shown that it will react with alkynes to give products formed by the addition and coupling of two, three, and four alkyne molecules at the dimolybdenum center.[7-11] We have investigated the reaction of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ with HC_2Ph under similar conditions and have found that the reaction terminates with the introduction of one HC_2Ph unit.[12] We have now investigated the reactivity of the heteronuclear cluster $Mo_2Ru(CO)_7(C_5H_5)_2(\mu_3\text{-}S)$ (1)[13] formed by the substitution of two ruthenium carbonyl units in $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ by two cyclopentadienyl molybdenum carbonyl units,[14] with HC_2Ph, and have found that the trinuclear center in 2 is active toward HC_2Ph oligomerization.[15] Details of this study are described in this report.

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. CP grade carbon monoxide was purchased from Linde Co. and was used without further purification. Phenylacetylene was purchased from Aldrich Chemical Co. and was distilled and stored under N_2 prior to use. Trimethylamine *N*-oxide dihydrate was purchased from Aldrich Chemical Co. and was converted to its anhydrous form by sublimation. $RuMo_2(CO)_7(C_5H_5)_2(\mu_3\text{-}S)$ was prepared by the published method.[14] High-pressure reactions were performed in a 45-mL Parr Model 4713 high-pressure reaction vessel. Chromatographic separations were performed by TLC in air on Kieselgel 0.25 mm, 60 F_{254}, E. Merck, West Germany. IR spectra were recorded on a Nicolet 5 DXB FT IR spectrophotometer. NMR spectra were run on an IBM NR-80 or a Brüker AM-300 spectrometer operating at 80 and 300 MHz, respectively. Mass spectra were run on a Finnigan Model 4521 mass spectrometer by using electron-impact ionization. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reaction of $Mo_2Ru(CO)_7(C_5H_5)_2(\mu_3\text{-}S)$ (1) with HC_2Ph. Compound 1 (30 mg, 0.046 mmol) in 35 mL of heptane was allowed to react with 50 μL (0.460 mmol) of PhC_2H by heating to reflux for 80 min. The solvent was removed in vacuo. The residue was dissolved in a minimum of CH_2Cl_2 and was chromatographed by TLC with a hexane/CH_2Cl_2 (7/3) solvent mixture. This yielded the following bands in order of elution: 1.2 mg of an orange compound (IR (hexane) ν(CO) 1992 (vs), 1984 (m), 1934 (m) cm^{-1}), which has not been characterized, 4.0 mg of orange $Mo_2Ru(CO)_2(C_5H_5)_2[\mu_3\text{-}\eta^6\text{-}HCC(Ph)CHC(Ph)CHC(Ph)](\mu_3\text{-}S)$ (3) (11%), and 5.6 mg of green $Mo_2Ru(CO)_2(C_5H_5)_2[\mu\text{-}\eta^3\text{-}PhCC(H)CPh][\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH](\mu_3\text{-}S)$ (2) (15%). For 2: IR (hexane) ν(CO) 1982 (vs), 1923 (s) cm^{-1}; ^1H NMR (δ in $CDCl_3$) 7.70–7.01 (m, 17 H), 4.91 (s, 5 H), 4.80 (s, 1 H), 4.47 (s, 5 H). Anal. Calcd for $RuMo_2SO_2C_{36}H_{28}\cdot1.5C_6H_6$: C, 57.82; H, 3.85. Found: C, 57.30; H, 3.98. For 3: IR (hexane) ν(CO) 1994 (vs), 1940 (s) cm^{-1}; ^1H NMR (δ in $CDCl_3$) 9.58 (s, 2 H), 8.11–6.58 (m, 15 H), 6.46 (s, 1 H), 5.25 (s, 10 H). Anal. Calcd for $RuMo_2SO_2C_{36}H_{28}\cdot0.5C_6H_6$: C, 54.67; H, 3.62. Found: C, 54.99; H, 3.64.

Thermolysis of Compound 2. 2 (13 mg, 0.0159 mmol) was refluxed in 30 mL of *n*-octane under CO for 3 h. The solvent was removed in vacuo. The residue was dissolved in minimum of CH_2Cl_2 and was chromatographed by TLC as described above. This resulted in 3.4 mg of orange $Mo_2Ru(CO)_2(C_5H_5)_2[\mu\text{-}\eta^3\text{-}HCC(Ph)C(Ph)][\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH](\mu_3\text{-}S)$ (4) (38%), 5 mg of orange 3 (57%), 4.2 mg of starting material, and 0.8 mg of red 1. (Yields are based on the amount of starting material consumed.) For 4: IR (hexane) ν(CO) 1993 (vs), 1938 (s) cm^{-1}; ^1H NMR (δ in $CDCl_3$) 9.90 (s, 2 H), 7.65–7.01 (m, 15 H), 5.56 (s, 1 H), 5.01 (s, 10 H). Anal. Calcd for $RuMo_2SO_2C_{36}H_{28}\cdot2.0C_6H_6$: C, 59.20; H, 4.11. Found: C, 59.04; H, 4.23.

Reaction of 2 with Carbon Monoxide. 2 (6.1 mg, 0.0075 mmol) dissolved in 8 mL of heptane was placed into a 45-mL Parr high-pressure reaction vessel, pressurized with 25 atm of CO, and then heated to 98 °C for 3 h. After cooling, the solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 was chromatographed by TLC (see above). The separation yielded the following bands: 3.4 mg of compound 1 (78%), 0.6 mg of starting material, 0.5 mg of compound 3 (9%), 0.5 mg of 4 (9%), and a colorless band (1.7 mg) shown to be 1,3,5-triphenylbenzene (74%). The latter was identified by its characteristic mass spectrum (parent ion m/e 306) and by comparison of its ^1H NMR spectrum to that of the reported spectrum (Aldrich Library of NMR Spectra, Aldrich Chemical Co., 1974).

Thermolysis of 3. 3 (6.0 mg, 0.007 mmol) dissolved in 10 mL of octane was heated to reflux for 3 h while being purged with CO. The solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and was chromatographed on silica gel by TLC (hexane/CH_2Cl_2, 7/3). The separation yielded 0.7 mg of 4 (24%) and 3.1 mg of starting material. (Yield is based on the amount of starting material consumed.)

Reaction of 1 with HC_2Ph in the Presence of Me_3NO. HC_2Ph (23 μL, 0.205 mmol) was added to a solution of 1 (27 mg, 0.041 mmol) in 10 mL of CH_2Cl_2 under an N_2 atmosphere. At 25 °C 16 mg (0.205 mmol) of Me_3NO dissolved in 10 mL of CH_2Cl_2 was added dropwise to the vigorously stirred reaction solution over a period of 30 min. During this time, the red solution turned brownish red. The reaction solution was concentrated. The products were separated by TLC using a hexane/CH_2Cl_2 (75/35) solvent mixture as eluent. This yielded 4.5 mg of starting material, 3.0 mg of the dark orange compound $Mo_2Ru(CO)_5(C_5H_5)_2[\mu\text{-}\eta^4\text{-}PhCC(H)CC(H)Ph](\mu_3\text{-}S)$ (5) (11%), and other air-sensitive compounds that decomposed during the separation procedure. For 5: IR (hexane) ν(CO) 2067 (vs), 2004 (s), 1996 (s), 1843 (m), 1797 (w) cm^{-1}; ^1H NMR (δ in $CDCl_3$) 7.23–6.54 (m, 10 H), 6.42 (s, 1 H), 5.93 (s, 1 H), 5.16 (s, 5 H), 5.11 (s, 5 H). Anal. Calcd for $RuMo_2SO_5C_{31}H_{22}\cdot1.0C_6H_{12}$: C, 50.28; H, 3.85. Found: C, 49.99; H, 3.05. Compound 5 is air sensitive in solution.

Reaction of 5 with HC_2Ph. 5 (10 mg, 0.0125 mmol) and 7 μL (0.0625 mmol) of HC_2Ph were dissolved in 40 mL of heptane. This solution was heated to reflux for 25 min. The solvent was then removed in vacuo. The residue was dissolved in a minimum amount of CH_2Cl_2 and was chromatographed by TLC on silica gel using a hexane/CH_2Cl_2 (7/3) solvent mixture as eluent. Several small bands were eluted in insufficient amounts to permit complete characterization. IR spectra of these bands indicated that compounds 2–4 were not among these and no 5 was remaining.

Crystallographic Analyses. Dark green crystals of 2 were obtained by slow evaporation of solvent from solutions in benzene at 25 °C. Orange plates of 3 were obtained by slow evaporation of solvent from a solution in a hexane/benzene (7/3) solvent mixture at 10 °C. Orange plates of 4 were obtained by a similar procedure. Red plates of 5 were obtained by slow evaporation of solvent from solutions in a cyclohexane/methylene chloride (7/3) solvent mixture at 25 °C. Data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 fully automated four-circle diffractometer using grahite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure solving program

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Table I. Crystallographic Data for X-ray Diffraction Studies

	2	3	4	5
(A) Crystal Data				
formula	$RuMo_2SO_2C_{36}H_{28}\cdot 1.5C_6H_6$	$RuMo_2SO_2C_{36}H_{28}\cdot 0.5C_6H_6$	$RuMo_2SO_2C_{36}H_{28}\cdot 2C_6H_6$	$RuMo_2SO_5C_{31}H_{22}\cdot 1.0C_6H_{12}$
temp (±3 °C)	23	23	23	23
space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.899 (2)	35.86 (1)	13.545 (2)	12.906 (3)
b (Å)	23.563 (5)	12.454 (6)	15.869 (3)	13.916 (4)
c (Å)	14.562 (3)	14.622 (3)	9.746 (2)	9.708 (4)
α (deg)	90.0	90.0	90.37 (2)	91.54 (3)
β (deg)	91.97 (2)	98.60 (2)	104.11 (1)	100.82 (2)
γ (deg)	90.00	90.0	82.22 (1)	95.48 (2)
V (Å^3)	3737 (1)	6457 (4)	2012.3 (7)	1703 (2)
M_r	934.8	956.7	976.9	883.6
Z	4	8	2	2
ρ_{calcd} (g cm^{-3})	1.66	1.76	1.61	1.72
(B) Measurement of Intensity Data				
radiation	Mo Kα (0.71073 Å)			
monochromator	graphite			
detector aperture (mm)				
horizontal	4.0			
vertical	4.0			
cryst faces	010, $0\bar{1}0$, 100 $\bar{1}00$, 102, $\bar{1}0\bar{2}$	100, $\bar{1}00$, $\bar{2}01$ $21\bar{1}$, $2\bar{1}0$	$1\bar{1}0$, $\bar{1}10$, 120 $\bar{1}\bar{2}0$, 001, $00\bar{1}$	110, $\bar{1}\bar{1}0$, $2\bar{1}0$ $\bar{2}10$, $10\bar{1}$, 001
cryst size (mm)	0.06 × 0.07 × 0.14	0.04 × 0.25 × 0.20 (triangular)	0.06 × 0.20 × 0.22	0.09 × 0.13 × 0.30
cryst orientatn directn; deg from θ axis	c^*; 3.0	b; 6.6	c^*; 9.4	c^*; 3.3
reflctns measd	$h,k,\pm l$	$h,k,\pm l$	$h,\pm k,\pm l$	$h,\pm k,\pm l$
max 2θ (deg)	45	42	42	42
scan type	moving crystal–stationary counter			
ω-scan width (A + 0.347 tan θ)°, A =	1.10	1.00	1.10	0.80
background at each end of scan	$^1/_4$ scan time			
ω-scan rate[a] (deg/min)	4.0	4.0	4.0	4.0
data used ($F^2 \geq 3.0\sigma(F^2)$)	3060	1867	2717	2522
(C) Treatment of Data				
absorption correctn	empirical	empirical	empirical	empirical
coeff (cm^{-1})	11.3	13.0	10.5	12.4
transmissn coeff				
max	1.00	1.00	1.00	1.00
min	0.79	0.83	0.86	0.78
decay correctn	none	none	none	none
no. of variables	415	217	427	385
P factor	0.02	0.02	0.02	0.02
final residuals				
R_F	0.045	0.054	0.044	0.050
R_w	0.045	0.051	0.042	0.054
goodness of fit indicator	1.47	1.56	1.43	2.05
largest peak in final diff Fourier (e/Å^3)	0.69	1.23	0.74	0.67
max shift on final cycle	0.02	0.47	0.53	0.52

[a] Rigaku software uses a multiple-scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made and the results added to first scan etc. A maximum of three scans was permitted per reflection.

library obtained from the Molecular Structure Corp., College Station, TX. Neutral atom scattering factors were calculated by the standard procedures.[16a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[16b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o^2$ and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Compound 2 crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified on the basis of the systematic absences observed during the collection of data. The coordinates of the heavy atoms were obtained by direct methods (MITHRIL). All remaining non-hydrogen atoms were subsequently obtained from difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the phenyl and cyclopentadienyl rings were calculated by assuming idealized six- and fivefold geometries, respectively. The three hydrogen atoms on the C_6 chain were located in difference Fourier syntheses. The contributions of all hydrogen atoms were added to the structure factor (SF) calculations, but their positions were not refined. Compound 2 crystallized with one and one-half molecules of benzene in the asymmetric crystal unit. Both benzene molecules were satisfactorily refined.

Compound 3 crystallized in the monoclinic crystal system. Absences observed in the data were consistent with those of the space groups Cc and $C2/c$. The latter was chosen and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods and difference Fourier syntheses. Due to the limited amount of data only the atoms heavier than oxygen were refined with anisotropic thermal parameters. The phenyl ring C(21)–C(26) was found to possess a twofold rotational disorder. This was satisfactorily

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(16) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1975; vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1; pp 149–150.

refined by using a 50/50 occupancy of the two sites. The positions of the hydrogen atoms on the phenyl and cyclopentadienyl rings were calculated by assuming idealized geometries. The three remaining hydrogen atoms were located in difference Fourier syntheses. The contributions of all hydrogen atoms were added to the SF calculations, but their positions were not refined. Compound 3 crystallized with one-half molecule of C_6H_6 in the asymmetric crystal unit. This was located and satisfactorily refined.

Compounds 4 and 5 both crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure in each case. Both structures were solved by a combination of Patterson and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the phenyl and cyclopentadienyl rings were calculated. The remaining hydrogen atoms were located in difference Fourier syntheses. The contributions of the hydrogen atoms were added to the SF calculations, but their positions were not refined. Compound 4 crystallized with two molecules of benzene in the asymmetric crystal unit. Both were located and satisfactorily refined. Compound 5 crystallized with one molecule of cyclohexane in the asymmetric crystal unit. The carbon atoms were located but refined poorly with large thermal parameters, indicative of disorder phenomenon.

Tables of positional parameters of the hydrogen atoms and anisotropic thermal parameters for all four analyses are available; see supplementary material. Tables of observed and calculated structure factor amplitudes are available for compounds 4 and 5; see supplementary material. Structure factor amplitudes for compounds 2 and 3 were published previously.[15]

Results

Three products were isolated from the reaction of 1 with HC_2Ph in refluxing heptane solvent. The two principle products were $Mo_2Ru(CO)_2(C_5H_5)_2[\mu_3\text{-}\eta^6\text{-}HCC(Ph)C(H)C(Ph)C(H)CPh](\mu_3\text{-}S)$ (2), 15% yield, and $Mo_2Ru(CO)_2(C_5H_5)_2[\mu\text{-}\eta^3\text{-}PhCC(H)CPh][\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH](\mu_3\text{-}S)$ (3), 11% yield. A minor orange product was also isolated, but thus far, this compound has resisted all attempts of crystallization and is presently structurally uncharacterized.

Efforts were made to induce the elimination of the dimetalla-1,3,5-triphenylhexatrienyl ligand in 2 by treatment with CO, and under 25 atm of CO at 100 °C, these were successful. The product 1,3,5-triphenylbenzene was obtained in 74% yield by a reductive-elimination and cyclotrimerization reaction. The cluster was converted back into 1 in 78% yield.

When heated to 125 °C in octane solvent, compound 2 was converted into 3 in 57% yield, but a new orange compound identified as $Mo_2Ru(CO)_2(C_5H_5)_2[\mu\text{-}\eta^3\text{-}PhCC(Ph)CH][\mu_3\text{-}\eta^3\text{-}HC(Ph)CH](\mu_3\text{-}S)$ (4), an isomer of 3 was obtained in 38% yield. Compound 4 was also obtained directly from 3 in 24% yield in a separate experiment by heating it to 125 °C for 3 h.

In an effort to obtain HC_2Ph addition products to 1 under milder conditions, Me_3NO was added to a solution of 1 and HC_2Ph at 25 °C. From this reaction the new compound $Mo_2Ru(CO)_5(C_5H_5)_2[\mu\text{-}\eta^4\text{-}PhCC(H)CC(H)Ph](\mu_3\text{-}S)$ (5) was isolated in 11% yield. Although the structure of 5 (vide infra) suggests that it is probably not a precursor to 2, 3, or 4, a reaction of 5 with HC_2Ph, under the conditions used for the formation of 2, 3, and 4 from 1 and HC_2Ph, was performed. No detectable amounts of 2, 3, or 4 were obtained from this reaction.

Compounds 2–5 have been characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. The molecular structures of these compounds are described below.

Table II. Positional Parameters and *B*(eq) for $Mo_2Ru(CO)_2[\mu_3\text{-}\eta^6\text{-}HCC(Ph)CHC(Ph)CHC(Ph)](\mu_3\text{-}S)$ (2)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru1	0.87782 (9)	0.16099 (4)	0.44606 (6)	2.56 (4)
Mo1	1.03060 (9)	0.26839 (4)	0.45821 (6)	2.25 (4)
Mo2	1.11448 (9)	0.17320 (4)	0.38443 (6)	2.41 (5)
S1	1.0513 (3)	0.1806 (1)	0.5344 (2)	3.1 (1)
O11	0.865 (1)	0.0359 (4)	0.4768 (7)	6.4 (6)
O12	0.635 (1)	0.1814 (4)	0.5357 (7)	6.7 (6)
C1	0.954 (1)	0.1547 (4)	0.3079 (6)	2.2 (5)
C2	0.845 (1)	0.1875 (4)	0.3041 (6)	2.0 (5)
C3	0.8426 (9)	0.2422 (4)	0.3508 (7)	2.3 (5)
C4	0.914 (1)	0.2921 (4)	0.3327 (7)	2.2 (5)
C5	1.041 (1)	0.2948 (4)	0.3087 (6)	2.4 (5)
C6	1.1346 (9)	0.2547 (4)	0.3316 (6)	2.1 (5)
C11	0.867 (1)	0.0842 (6)	0.4653 (8)	4.0 (7)
C12	0.728 (1)	0.1737 (5)	0.5033 (7)	3.5 (6)
C21	0.7343 (9)	0.1692 (5)	0.2454 (6)	2.6 (5)
C22	0.693 (1)	0.1148 (5)	0.2430 (8)	4.0 (6)
C23	0.597 (1)	0.0997 (5)	0.1834 (9)	4.5 (7)
C24	0.543 (1)	0.1396 (6)	0.1257 (9)	4.4 (7)
C25	0.584 (1)	0.1943 (6)	0.1293 (8)	4.4 (7)
C26	0.680 (1)	0.2099 (5)	0.1877 (8)	3.4 (6)
C31	0.960 (1)	0.3366 (5)	0.5627 (7)	3.5 (6)
C32	1.021 (1)	0.3361 (4)	0.4954 (7)	3.0 (6)
C33	1.143 (1)	0.3482 (5)	0.4985 (7)	3.3 (6)
C34	1.159 (1)	0.3077 (5)	0.5670 (8)	3.7 (6)
C35	1.045 (1)	0.3005 (5)	0.6076 (7)	3.8 (6)
C41	0.8411 (9)	0.3464 (4)	0.3212 (7)	2.3 (5)
C42	0.851 (1)	0.3773 (5)	0.2404 (8)	3.4 (6)
C43	0.784 (1)	0.4262 (6)	0.227 (1)	5.1 (8)
C44	0.707 (1)	0.4443 (5)	0.294 (1)	5.6 (8)
C45	0.695 (1)	0.4127 (6)	0.373 (1)	4.3 (7)
C46	0.759 (1)	0.3636 (5)	0.3867 (8)	3.0 (6)
C51	1.193 (1)	0.1049 (5)	0.2794 (9)	4.1 (7)
C52	1.161 (1)	0.0749 (5)	0.359 (1)	4.5 (7)
C53	1.234 (1)	0.0933 (6)	0.433 (1)	4.9 (8)
C54	1.313 (1)	0.1345 (6)	0.399 (1)	4.8 (7)
C55	1.287 (1)	0.1424 (5)	0.3043 (9)	4.0 (7)
C61	1.2602 (9)	0.2774 (4)	0.3092 (7)	2.2 (5)
C62	1.359 (1)	0.2757 (5)	0.3734 (7)	2.9 (5)
C63	1.473 (1)	0.2962 (5)	0.3491 (8)	3.9 (6)
C64	1.493 (1)	0.3159 (6)	0.264 (1)	4.7 (7)
C65	1.397 (1)	0.3176 (5)	0.2006 (8)	3.9 (6)
C66	1.282 (1)	0.2981 (5)	0.2225 (7)	3.3 (6)
C71	0.699 (2)	−0.0524 (7)	0.167 (1)	8.1 (5)
C72	0.718 (2)	−0.0265 (8)	0.081 (1)	9.0 (5)
C73	0.829 (2)	0.0002 (8)	0.073 (1)	8.3 (5)
C74	0.908 (2)	0.0012 (8)	0.140 (1)	8.9 (5)
C75	0.892 (2)	−0.0228 (8)	0.223 (1)	9.2 (5)
C76	0.779 (2)	−0.0504 (8)	0.235 (1)	9.3 (5)
C81	0.520 (1)	0.0000 (7)	0.407 (1)	6.1 (4)
C82	0.550 (1)	0.0453 (6)	0.460 (1)	5.4 (3)
C83	0.533 (1)	0.0463 (6)	0.552 (1)	5.7 (3)

Structure of 2. An ORTEP diagram of the molecular structure of 2 is shown in Figure 1. Final atomic coordinates are listed in Table II. Intramolecular bond distances and selected intramolecular bond angles are listed in Tables III and IV, respectively. The molecule consists of a triangular cluster of one ruthenium and two molybdenum atoms and a triply bridging sulfido ligand. The two molybdenum–ruthenium bond distances are significantly different, Mo(1)–Ru(1) = 3.031 (1) Å and Mo(2)–Ru(1) = 2.775 (1) Å. Both values depart significantly and in opposite directions from the Mo–Ru distances, 2.8989 (9) and 2.9129 (8) Å, found in 1.[17] The Mo(1)–Mo(2) distance of 2.663 (1) Å is much shorter than that found in 1, 3.0282 (8) Å, and is similar to that of a Mo–Mo double bond (e.g. 2.618 (1) Å as found in $Mo_2(C_5H_5)_2[(MeO_2C)C_2(CO_2Me)(HC_2H)(MeO_2C)C_2(CO_2Me)]$.[10] The metal–sulfur distances in 2 are also slightly shorter than the corresponding distances in 1.

Each molybdenum atom contains an $\eta^5\text{-}C_5H_5$ ring while the ruthenium atom contains two linear terminal carbonyl

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(17) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics*, in press.

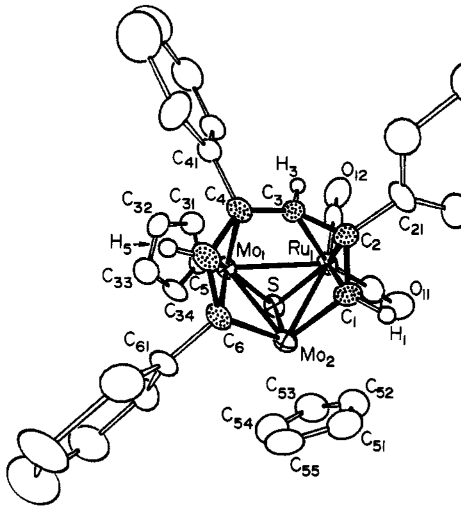


Figure 1. An ORTEP diagram of $Mo_2Ru(CO)_2(C_5H_5)_2[\mu_3-\eta^6-HCC(Ph)CHC(Ph)CHC(Ph)](\mu_3-S)$ (2) showing 50% probability thermal ellipsoids.

Table III. Intramolecular Distances (Å) for $RuMo_2(CO)_2(C_5H_5)_2[\mu_3-\eta^6-HCC(Ph)CHC(Ph)CHC(Ph)](\mu_3-S)$ (2)[a]

atom	atom	dist	atom	atom	dist
Ru1	C11	1.84 (1)	Mo2	C6	2.08 (1)
Ru1	C12	1.89 (1)	Mo2	C1	2.09 (1)
Ru1	C2	2.18 (1)	Mo2	S1	2.318 (3)
Ru1	C1	2.206 (9)	Mo2	C54	2.35 (1)
Ru1	S1	2.297 (3)	Mo2	C55	2.36 (1)
Ru1	C3	2.39 (1)	Mo2	C53	2.39 (1)
Ru1	Mo2	2.775 (1)	Mo2	C51	2.40 (1)
Ru1	Mo1	3.031 (1)	Mo2	C52	2.40 (1)
Mo1	C6	2.22 (1)	O11	C11	1.15 (1)
Mo1	C4	2.26 (1)	O12	C12	1.14 (1)
Mo1	C5	2.27 (1)	C1	C2	1.42 (1)
Mo1	C34	2.27 (1)	C2	C3	1.46 (1)
Mo1	C35	2.30 (1)	C2	C21	1.51 (1)
Mo1	C33	2.31 (1)	C3	C4	1.44 (1)
Mo1	S1	2.355 (3)	C4	C5	1.44 (1)
Mo1	C31	2.36 (1)	C4	C41	1.51 (1)
Mo1	C32	2.37 (1)	C5	C6	1.42 (1)
Mo1	Mo2	2.663 (1)	C6	C61	1.52 (1)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

ligands. However, the most interesting ligand is a 1,3,5-triphenylhexatrienyl group, C(1)–C(6), that bridges the Mo_2Ru face of the cluster opposite that of the sulfido ligand. The two ends of the C_6 chain are σ-bonded to Mo(2), Mo(2)–C(1) = 2.09 (1) Å and Mo(2)–C(6) = 2.08 (1) Å, while all six carbon atoms are π-bonded in two groups to Mo(1) and Ru(1). The group C(1)–C(2)–C(3) is π-bonded to Ru(1) and the group C(4)–C(5)–C(6) is π-bonded to Mo(1). The Mo–C distances are very similar, 2.22 (1)–2.27 (1) Å. The Ru–C distances span a significant range, 2.18 (1)–2.39 (1) Å. The C–C distances show no significant variation and all lie in the narrow range 1.42 (1)–1.46 (1) Å. This implies a fairly uniform bonding and π-electron delocalization from C(1) to C(6).

The ^1H NMR spectrum of 2 shows singlets for the inequivalent C_5H_5 rings, δ 4.91 and 4.47. However, only one resonance, a singlet at 4.80 ppm, was observed that could be attributed to one of the hydrogen atoms bonded directly to the C_6 chain. The two other resonances are believed to be superimposed on the multiplet of signals of the C_6H_5 protons, 7.70–7.01 ppm (17 H).

Structure of 3. An ORTEP drawing of the molecular structure of 3 is shown in Figure 2. Crystallographic positional parameters are listed in Table V. Selected intramolecular bond distances and angles are listed in Tables VI and VII, respectively. The molecule consists of a triangular cluster of one ruthenium and two molyb-

Table IV. Intramolecular Bond Angles (deg) for Compound 2[a]

atom	atom	atom	angle	atom	atom	atom	angle
C11	Ru1	C12	91.6 (5)	C6	Mo2	C1	95.3 (4)
C11	Ru1	C2	114.7 (5)	C6	Mo2	S1	108.5 (3)
C11	Ru1	C1	95.8 (4)	C6	Mo2	Mo1	54.2 (3)
C11	Ru1	S1	99.7 (4)	C6	Mo2	Ru1	109.0 (3)
C11	Ru1	C3	150.3 (5)	C1	Mo2	S1	104.3 (3)
C11	Ru1	Mo2	102.6 (4)	C1	Mo2	Mo1	95.6 (3)
C11	Ru1	Mo1	148.5 (4)	C1	Mo2	Ru1	51.6 (2)
C12	Ru1	C2	104.8 (4)	S1	Mo2	Mo1	55.93 (8)
C12	Ru1	C1	140.5 (4)	S1	Mo2	Ru1	52.68 (8)
C12	Ru1	S1	115.5 (3)	Mo1	Mo2	Ru1	67.73 (3)
C12	Ru1	C3	90.3 (4)	Ru1	S1	Mo2	73.93 (9)
C12	Ru1	Mo2	163.1 (3)	Ru1	S1	Mo1	81.3 (1)
C12	Ru1	Mo1	109.0 (3)	Mo2	S1	Mo1	69.45 (8)
C2	Ru1	C1	37.7 (3)	C2	C1	Mo2	126.5 (7)
C2	Ru1	S1	125.5 (3)	C2	C1	Ru1	70.1 (5)
C2	Ru1	C3	36.9 (3)	Mo2	C1	Ru1	80.4 (3)
C2	Ru1	Mo2	77.9 (3)	C1	C2	C3	119 (1)
C2	Ru1	Mo1	83.7 (3)	C1	C2	C21	121.0 (9)
C1	Ru1	S1	101.4 (3)	C1	C2	Ru1	72.2 (5)
C1	Ru1	C3	65.3 (3)	C3	C2	C21	119.5 (9)
C1	Ru1	Mo2	48.0 (3)	C3	C2	Ru1	79.4 (6)
C1	Ru1	Mo1	83.5 (3)	C21	C2	Ru1	123.9 (7)
S1	Ru1	C3	106.1 (2)	C4	C3	C2	128.4 (9)
C1	Ru1	Mo2	53.40 (8)	C4	C3	Ru1	133.1 (7)
S1	Ru1	Mo1	50.19 (8)	C2	C3	Ru1	63.7 (5)
C3	Ru1	Mo2	82.0 (2)	C3	C4	C5	128 (1)
C3	Ru1	Mo1	56.1 (2)	C3	C4	C41	115.2 (9)
Mo2	Ru1	Mo1	54.37 (3)	C3	C4	Mo1	86.8 (6)
C6	Mo1	C4	69.7 (4)	C5	C4	C41	116.1 (9)
C6	Mo1	C5	36.8 (3)	C5	C4	Mo1	71.9 (6)
C6	Mo1	S1	102.7 (3)	C41	C4	Mo1	125.2 (7)
C6	Mo1	Mo2	49.5 (3)	C6	C5	C4	127 (1)
C6	Mo1	Ru1	97.2 (3)	C6	C5	Mo1	69.7 (5)
C4	Mo1	C5	37.1 (3)	C4	C5	Mo1	71.0 (5)
C4	Mo1	S1	129.8 (3)	C5	C6	C61	111.1 (9)
C4	Mo1	Mo2	94.2 (3)	C5	C6	Mo2	128.1 (7)
C4	Mo1	Ru1	82.3 (3)	C5	C6	Mo1	73.5 (6)
C5	Mo1	S1	133.2 (3)	C61	C6	Mo2	120.8 (7)
C5	Mo1	Mo2	79.3 (3)	C61	C6	Mo1	128.2 (7)
C5	Mo1	Ru1	102.7 (3)	Mo2	C6	Mo1	76.4 (3)
S12	Mo1	Mo2	54.62 (8)	O11	C11	Ru1	177 (1)
S1	Mo1	Ru1	48.50 (7)	O12	C12	Ru1	178 (1)
Mo2	Mo1	Ru1	57.90 (3)				

[a] Estimated standard deviations in the least significant figure are given in parentheses.

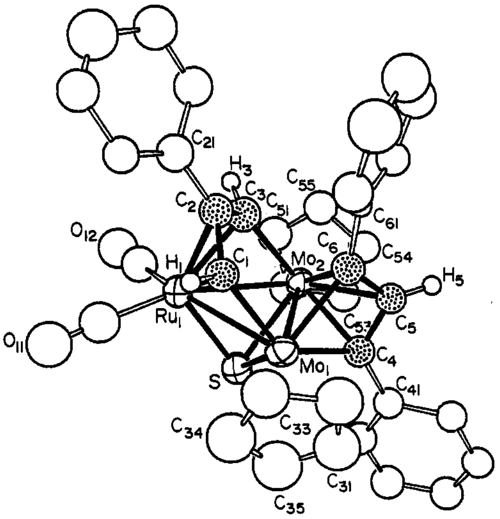


Figure 2. An ORTEP diagram of $Mo_2Ru(CO)_2(C_5H_5)_2[\mu-\eta^3-PhCC(H)C(Ph)[\mu_3-\eta^3-HCC(Ph)CH](\mu_3-S)$ (3) showing 50% probability thermal ellipsoids.

Table V. Positional Parameters and B(eq) for $Mo_2Ru(CO)_2(C_5H_5)_2[\mu\text{-}\eta^3\text{-}PhCC(H)C(Ph)]$-$[\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH](\mu_3\text{-}S)$ (3)

atom	x	y	z	B(eq), Å^2
Ru1	0.125948 (44)	0.17567 (13)	0.05914 (11)	3.51 (8)
Mo1	0.160127 (47)	0.22648 (13)	0.24113 (11)	3.19 (8)
Mo2	0.170685 (44)	0.36019 (13)	0.10382 (10)	2.96 (8)
S	0.18931 (13)	0.17681 (40)	0.11190 (32)	3.6 (2)
O11	0.09649 (38)	−0.0504 (12)	0.05812 (95)	6.4 (4)
O12	0.12055 (36)	0.1694 (11)	−0.14772 (95)	6.4 (4)
C1	0.10361 (48)	0.2240 (14)	0.1838 (11)	3.3 (4)
C2	0.08458 (49)	0.2916 (14)	0.1105 (12)	3.6 (4)
C3	0.11084 (51)	0.3451 (15)	0.0634 (12)	4.2 (4)
C4	0.20364 (46)	0.3455 (14)	0.2388 (11)	3.3 (4)
C5	0.18158 (46)	0.4348 (14)	0.2532 (11)	3.1 (4)
C6	0.14527 (50)	0.3965 (14)	0.2377 (11)	3.5 (4)
C11	0.10710 (56)	0.0365 (18)	0.0578 (14)	5.3 (5)
C12	0.12287 (52)	0.1711 (16)	−0.0697 (13)	4.9 (5)
C21	0.04343 (54)	0.2915 (15)	0.0774 (13)	4.1 (4)
C22A	0.0195 (13)	0.2633 (37)	0.1461 (30)	6 (1)
C22	0.0189 (10)	0.2103 (29)	0.0988 (25)	3.5 (8)
C23A	−0.0194 (13)	0.2582 (39)	0.1164 (33)	6 (1)
C23	−0.0215 (12)	0.2151 (35)	0.0649 (30)	5 (1)
C24	−0.03594 (67)	0.2899 (20)	0.0224 (17)	7.0 (6)
C25A	−0.0141 (14)	0.2976 (39)	−0.0309 (32)	7 (1)
C25	−0.0146 (12)	0.3886 (35)	0.0048 (28)	6 (1)
C26A	0.0276 (14)	0.3023 (39)	−0.0095 (33)	7 (1)
C26	0.0254 (11)	0.3883 (32)	0.0312 (26)	5 (1)
C31	0.19638 (64)	0.1820 (20)	0.3815 (15)	6.6 (6)
C32	0.16144 (66)	0.2163 (18)	0.4011 (14)	6.3 (6)
C33	0.13560 (60)	0.1375 (18)	0.3592 (14)	6.1 (5)
C34	0.15827 (70)	0.0642 (19)	0.3189 (15)	6.9 (6)
C35	0.19334 (71)	0.0954 (21)	0.3357 (16)	7.5 (6)
C41	0.24543 (46)	0.3372 (14)	0.2684 (11)	3.3 (4)
C42	0.26177 (48)	0.3981 (13)	0.3459 (11)	3.2 (4)
C43	0.29962 (49)	0.3897 (14)	0.3774 (11)	3.5 (4)
C44	0.32248 (50)	0.3257 (15)	0.3368 (12)	4.1 (4)
C45	0.30717 (53)	0.2628 (15)	0.2626 (12)	4.5 (4)
C46	0.26898 (51)	0.2718 (15)	0.2306 (12)	4.0 (4)
C51	0.16938 (56)	0.4188 (16)	−0.0491 (13)	5.0 (5)
C52	0.20519 (56)	0.3776 (16)	−0.0213 (13)	5.1 (5)
C53	0.22175 (52)	0.4445 (15)	0.0521 (13)	4.5 (4)
C54	0.19644 (51)	0.5220 (15)	0.0627 (12)	4.0 (4)
C55	0.16308 (54)	0.5055 (16)	0.0014 (13)	4.6 (4)
C61	0.11277 (40)	0.4625 (12)	0.24007 (95)	1.7 (3)
C62	0.11140 (49)	0.5670 (14)	0.2081 (11)	3.5 (4)
C63	0.08266 (55)	0.6365 (16)	0.2247 (13)	5.1 (5)
C64	0.05517 (61)	0.6017 (18)	0.2743 (14)	6.2 (6)
C65	0.05709 (66)	0.5012 (20)	0.3119 (15)	7.5 (6)
C66	0.08675 (53)	0.4345 (15)	0.2943 (12)	4.4 (4)
C71	0.03602 (92)	0.9375 (27)	0.2444 (35)	12 (1)
C72	0.0119 (17)	0.9341 (33)	0.1685 (32)	16 (1)
C73	−0.0252 (13)	0.9378 (30)	0.1717 (31)	15 (1)

denum atoms with a triply bridging sulfido ligand. The ruthenium–molybdenum bond distances, 2.830 (2) and 2.823 (3) Å, are equal, although slightly shorter than those in 1, see above.[17] The molybdenum–molybdenum distance is quite short, 2.679 (2) Å and approximately the same as that in 2. The ruthenium–sulfur distance is similar to that in 2, but the molybdenum-sulfur distances are longer than those in 2 and are more similar to those in 1.

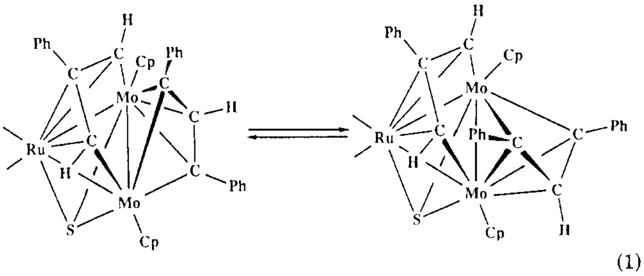
Compound 3 contains two dimetallaallyl ligands. The 2-phenyl-substituted group serves as a triple bridge on the face of the cluster with each end σ-bonded to a molybdenum atom. The entire C_3 unit is π-bonded to the ruthenium atom. A similarly coordinated dimetallaallyl ligand was found in the triruthenium cluster, $Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}MeCC(H)CEt)(\mu\text{-}H)$.[18] The 1,3-diphenyl-substituted group bridges the Mo–Mo edge of the cluster with the ends bonded to Mo(1) and the entire C_3 unit π-bonded to Mo(2). A similarly coordinated dimetallaallyl group was found in the complex $W_2(CH_2SiMe_3)_4(\mu\text{-}CSiMe_3)(\mu\text{-}CPhCPhCSiMe_3)$.[19] The C–C bonding in the two dimetallaallyl groups in 3 is similar, but the C–C–C angle in the edge-bridging group is slightly more acute, 104 (2)°, than that of the triply bridging group, 111 (2)°. Each molybdenum atom in 3 contains a regular η^5-C_5H_5 ring. The ruthenium atom contains two linear terminal carbonyl ligands.

Table VI. Intramolecular Distances (Å) for $RuMo_2(CO)_2(C_5H_5)_2[\mu\text{-}\eta^3\text{-}PhCC(H)C(Ph)]$-$[\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH](\mu_3\text{-}S)$ (3)[a]

atom	atom	dist	atom	atom	dist
Ru1	C11	1.86 (2)	Mo2	C4	2.15 (2)
Ru1	C12	1.87 (2)	Mo2	C6	2.32 (2)
Ru1	C1	2.18 (2)	Mo2	C54	2.33 (2)
Ru1	C3	2.18 (2)	Mo2	C53	2.33 (2)
Ru1	C2	2.28 (2)	Mo2	C55	2.34 (2)
Ru1	S	2.288 (5)	Mo2	C51	2.35 (2)
Ru1	Mo2	2.823 (3)	Mo2	C5	2.35 (2)
Ru1	Mo1	2.830 (2)	Mo2	C52	2.37 (2)
Mo1	C1	2.07 (2)	Mo2	S	2.377 (5)
Mo1	C4	2.16 (2)	O11	C11	1.15 (2)
Mo1	C6	2.18 (2)	O12	C12	1.13 (2)
Mo1	C34	2.32 (2)	C1	C2	1.45 (2)
Mo1	C31	2.33 (2)	C2	C3	1.41 (2)
Mo1	C33	2.33 (2)	C2	C21	1.48 (2)
Mo1	C32	2.34 (2)	C4	C5	1.40 (2)
Mo1	C35	2.35 (2)	C4	C41	1.50 (2)
Mo1	S	2.375 (5)	C5	C6	1.37 (2)
Mo1	Mo2	2.679 (2)	C6	C61	1.43 (2)
Mo2	C3	2.15 (2)			

[a] Estimated standard deviations in the least significant figure are given in parentheses.

Although the cyclopentadienyl rings in 3 are inequivalent in the solid-state structure of the compound, only a single resonance, δ 5.25, of intensity 10 was observed for the protons of these rings in the ^1H NMR spectrum in solution. Similarly, only a single resonance, δ 9.58, of intensity 2 was observed for the inequivalent protons H(1) and H(3) of the triply bridging dimetallaallyl ligand. While it is possible that 3 could adopt a more symmetrical structure in solution, a more likely explanation would involve a dynamical exchange process such as that shown in eq 1 in which the σ- and π-bonding roles of the edge-bridging metallaallyl group are interchanged between the two molybdenum atoms. Unfortunately, attempts to confirm this by dynamical ^1H NMR spectroscopy were unsuccessful. At −80 °C the spectrum was unchanged.



(1)

Structure of 4. An ORTEP drawing of 4 is shown in Figure 3. Crystallographic positional parameters are listed in Table VIII. Selected intramolecular distances and angles are listed in Tables IX and X, respectively. Com-

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[18] Evans, M.; Hursthouse, M. N.; Randall, E. W.; Rosenberg, E.; Milone, L.; Valle, M. *J. Chem. Soc., Chem. Commun.* **1972**, 545.

[19] (a) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182. (b) Clauss, A. D.; Shapley, J. R.; Wilker, C. N.; Hoffmann, R. *Organometallics* **1984**, *3*, 619. (c) Fernandez, J. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3086. (d) Fritch, J. K.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 559.

Table VII. Intramolecular Bond Angles (deg) for Compound 3[a]

atom	atom	atom	angle	atom	atom	atom	angle
C11	Ru1	C12	89.7 (9)	C4	Mo2	C6	58.3 (6)
C11	Ru1	C1	95.0 (8)	C4	Mo2	C5	35.8 (5)
C11	Ru1	C3	144.1 (8)	C4	Mo2	S	76.2 (5)
C11	Ru1	C2	109.9 (8)	C4	Mo2	Mo1	51.6 (4)
C11	Ru1	S	110.5 (6)	C4	Mo2	Ru1	111.0 (5)
C11	Ru1	Mo2	162.6 (6)	C6	Mo2	C5	34.1 (5)
C11	Ru1	Mo1	108.9 (6)	C6	Mo2	S	106.7 (4)
C12	Ru1	C1	151.1 (7)	C6	Mo2	Mo1	51.1 (4)
C12	Ru1	C3	94.6 (8)	C6	Mo2	Ru1	94.2 (4)
C12	Ru1	C2	114.1 (7)	C5	Mo2	C52	130.4 (6)
C12	Ru1	S	104.2 (6)	C5	Mo2	S	109.1 (4)
C12	Ru1	Mo2	101.7 (6)	C5	Mo2	Mo1	64.6 (4)
C12	Ru1	Mo1	154.9 (6)	C5	Mo2	Ru1	123.1 (4)
C1	Ru1	C3	65.5 (7)	S	Mo2	Mo1	55.6 (1)
C1	Ru1	C2	37.9 (6)	S	Mo2	Ru1	51.3 (1)
C1	Ru1	S	100.7 (5)	Mo1	Mo2	Ru1	61.85 (6)
C1	Ru1	Mo2	81.3 (4)	Ru1	S	Mo1	74.7 (2)
C1	Ru1	Mo1	46.7 (4)	Ru1	S	Mo2	74.4 (2)
C3	Ru1	C2	36.9 (6)	Mo1	S	Mo2	68.6 (1)
C3	Ru1	S	102.9 (5)	C2	C1	Mo1	128 (1)
C3	Ru1	Mo2	48.8 (5)	C2	C1	Ru1	75 (1)
C3	Ru1	Mo1	80.3 (5)	Mo1	C1	Ru1	83.3 (6)
C2	Ru1	S	123.2 (5)	C3	C2	C1	111 (2)
C2	Ru1	Mo2	77.5 (4)	C3	C2	C21	123 (2)
C2	Ru1	Mo1	76.1 (4)	C3	C2	Ru1	68 (1)
S	Ru1	Mo2	54.2 (1)	C1	C2	C21	125 (2)
S	Ru1	Mo1	54.0 (1)	C1	C2	Ru1	68 (1)
Mo2	Ru1	Mo1	56.57 (5)	C21	C2	Ru1	124 (1)
C1	Mo1	C4	132.0 (7)	C2	C3	Mo2	128 (1)
C1	Mo1	C6	77.6 (7)	C2	C3	Ru1	75 (1)
C1	Mo1	S	101.2 (5)	Mo2	C3	Ru1	81.3 (6)
C1	Mo1	Mo2	86.9 (5)	C5	C4	C41	125 (2)
C1	Mo1	Ru1	50.0 (5)	C5	C4	Mo2	80 (1)
C4	Mo1	C6	60.5 (6)	C5	C4	Mo1	97 (1)
C4	Mo1	S	76.1 (4)	C41	C4	Mo2	131 (1)
C4	Mo1	Mo2	51.5 (4)	C41	C4	Mo1	130 (1)
C4	Mo1	Ru1	110.6 (4)	Mo2	C4	Mo1	76.9 (5)
C6	Mo1	S	111.7 (5)	C6	C5	C4	104 (2)
C6	Mo1	Mo2	56.0 (4)	C6	C5	Mo2	72 (1)
C6	Mo1	Ru1	97.2 (4)	C4	C5	Mo2	64 (1)
S	Mo1	Mo2	55.7 (1)	C5	C6	C61	123 (2)
S	Mo1	Ru1	51.2 (1)	C5	C6	Mo1	96 (1)
Mo2	Mo1	Ru1	61.58 (6)	C5	C6	Mo2	74 (1)
C3	Mo2	C4	129.4 (6)	C61	C6	Mo1	139 (1)
C3	Mo2	C6	75.3 (6)	C61	C6	Mo2	124 (1)
C3	Mo2	C5	108.1 (6)	Mo1	C6	Mo2	72.9 (5)
C3	Mo2	S	101.1 (5)	O11	C11	Ru1	178 (2)
C3	Mo2	Mo1	84.5 (5)	O12	C12	Ru1	179 (2)
C3	Mo2	Ru1	49.9 (5)				

[a] Estimated standard deviations in the least significant figure are given in parentheses.

pound 4 is simply an isomer of 3 and differs from 3 only in the positions of the substituents on the *edge-bridging* dimetallaallyl group. In 4, the phenyl substituents are located on adjacent carbon atoms, while in 3 the phenyl-substituted carbon atoms were separated by a CH group. In all other respects, the molecular dimensions of 4 are extremely similar to those of 3.

The ^1H NMR spectrum of 4 shows only one resonance, δ 5.01 (10 H), for the cyclopentadienyl rings and only one resonance, δ 9.90 (2 H), for the CH protons of the triply bridging 2-phenyldimetallaallyl group. Evidently, compound 4 is undergoing a dynamical averaging process similar to that of 3; see above.

Structure of 5. An ORTEP drawing of the molecular structure of 5 is shown in Figure 4. Crystallographic positional parameters are listed in Table XI. Selected intramolecular bond distances and angles are listed in Tables XII and XIII, respectively. Compound 5 consists of an open triangular cluster with two metal–metal bonds. The Mo(1)–Mo(2) distance of 3.024 (2) Å is very similar to that in 1.[17] The Ru(1)–Mo(2) distance of 3.015 (2) Å is slightly longer than the Ru–Mo distances in 1, 2, and 3. The Ru(1)···Mo(1) distance (3.558 (2) Å) indicates very little direct bonding.

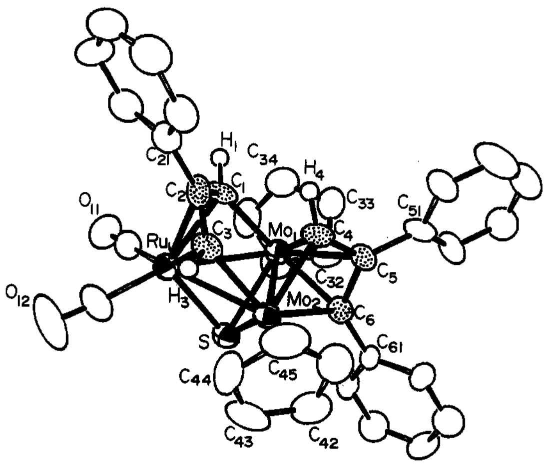

Figure 3. An ORTEP diagram of $Mo_2Ru(CO)_2(C_5H_5)_2[\mu\text{-}\eta^3\text{-}HCC(Ph)CPh][\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH](\mu_3\text{-}S)$ (4) showing 50% probability thermal ellipsoids.

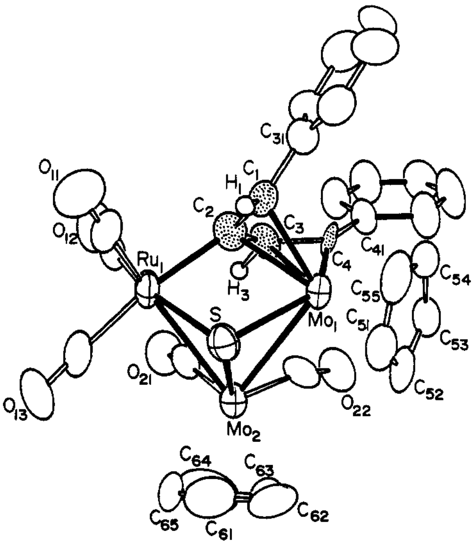

Figure 4. An ORTEP diagram of $Mo_2Ru(CO)_5[\mu\text{-}\eta^4\text{-}PhCC(H)CC(H)Ph](\mu_3\text{-}S)$ (5) showing 50% probability thermal ellipsoids.

The most interesting ligand is the group C(1)–C(4) that contains one hydrogen atom and one phenyl group bonded to C(1), one hydrogen atom bonded to C(3), and a phenyl group bonded to C(4). The four-carbon chain C(1)–C(4) is π-bonded to Mo(1). Atom C(2) is also bonded to Ru(2). Carbon C(4) is believed to possess carbene-like character, since it contains only two substituents, C(3) and C(41), and has an unusually short, metal–carbon bond, Mo(1)–C(4) = 1.97 (1) Å. There appears to be partial multiple bonding throughout the C(1)–C(4) chain, C(1)–C(2) = 1.45 (2) Å, C(2)–C(3) = 1.39 (2) Å, and C(3)–C(4) = 1.42 (2) Å. Each molybdenum atom contains an η^5-C_5H_5 ring. Atom Ru(1) contains three linear terminal carbonyl ligands. The carbonyl ligands on Mo(2) form semibridging interactions with the neighboring metal atoms. Resonances observed at δ 6.42 (1 H) and 5.93 (1 H) in the ^1H NMR spectrum can be attributed to the hydrogen atoms H(1) and H(2).

Discussion

The compound $Ru_3(CO)_9(\mu_3\text{-}HC_2Ph)(\mu_3\text{-}S)$ (6) was formed by the reaction of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (7) with

Table VIII. Positional Parameters and *B*(eq) for $RuMo_2S(CO)_2Cp_2(C_3HPh_2)(C_3H_2Ph)$ (4)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru1	−0.016424 (79)	0.293872 (63)	−0.17036 (11)	2.82 (5)
Mo1	−0.185738 (81)	0.203206 (64)	−0.20135 (11)	2.47 (5)
Mo2	−0.133071 (82)	0.291335 (66)	0.03489 (11)	2.57 (5)
S	−0.02440 (24)	0.17833 (19)	−0.03257 (32)	2.9 (2)
O11	0.08246 (74)	0.22080 (60)	−0.3985 (10)	5.2 (6)
O12	0.17594 (80)	0.37364 (73)	−0.0423 (12)	7.9 (7)
C1	−0.16808 (87)	0.31522 (74)	−0.3093 (12)	3.0 (6)
C2	−0.15104 (87)	0.39474 (69)	−0.2472 (13)	3.1 (6)
C3	−0.12041 (87)	0.39126 (74)	−0.0975 (12)	3.0 (6)
C4	−0.27829 (90)	0.31023 (71)	−0.1170 (11)	2.9 (6)
C5	−0.31872 (86)	0.23999 (70)	−0.0840 (12)	2.7 (6)
C6	−0.23021 (85)	0.18796 (66)	−0.0042 (12)	2.6 (6)
C11	0.0447 (10)	0.24869 (83)	−0.3092 (15)	3.9 (7)
C12	0.1045 (10)	0.34239 (86)	−0.0849 (14)	4.4 (8)
C21	−0.16424 (90)	0.47544 (72)	−0.3318 (13)	2.9 (6)
C22	−0.12870 (96)	0.47908 (81)	−0.4510 (14)	3.9 (7)
C23	−0.1425 (11)	0.55333 (91)	−0.5296 (13)	4.4 (8)
C24	−0.1970 (12)	0.62506 (96)	−0.4868 (17)	5.3 (9)
C25	0.2343 (11)	0.6225 (84)	−0.3724 (17)	5.0 (8)
C26	−0.21760 (96)	0.54652 (84)	−0.2946 (14)	4.0 (7)
C31	−0.1480 (11)	0.06611 (75)	0.2911 (13)	3.7 (7)
C32	−0.2474 (11)	0.07326 (78)	−0.2648 (12)	3.8 (7)
C33	−0.3100 (10)	0.13764 (84)	−0.3587 (14)	3.8 (7)
C34	−0.2526 (12)	0.16958 (81)	−0.4375 (12)	3.9 (8)
C35	−0.1522 (12)	0.12846 (91)	−0.4014 (15)	4.5 (8)
C41	−0.2012 (12)	0.3288 (12)	0.2277 (15)	5 (1)
C42	−0.1200 (14)	0.26510 (87)	0.2745 (14)	4.6 (8)
C43	−0.0306 (11)	0.2966 (12)	0.2712 (14)	5.2 (9)
C44	−0.0574 (13)	0.3811 (11)	0.2161 (14)	5 (1)
C45	−0.1634 (14)	0.39952 (85)	0.1928 (13)	4.7 (8)
C51	−0.42926 (90)	0.22299 (76)	−0.1258 (12)	3.0 (6)
C52	−0.45863 (93)	0.14246 (80)	−0.1192 (13)	3.7 (7)
C53	−0.5611 (12)	0.13294 (93)	−0.1534 (15)	4.8 (8)
C54	−0.6347 (11)	0.2005 (12)	−0.1948 (16)	6 (1)
C55	−0.6059 (12)	0.2824 (10)	−0.1986 (17)	7 (1)
C56	−0.5035 (10)	0.29068 (84)	−0.1676 (14)	4.1 (7)
C61	−0.22369 (3)	0.11510 (69)	0.0936 (11)	2.3 (6)
C62	−0.28835 (88)	0.11755 (70)	0.1823 (12)	2.9 (6)
C63	−0.2810 (10)	0.05316 (86)	0.2791 (13)	3.8 (7)
C64	−0.2099 (1)	−0.01934 (75)	0.2850 (12)	3.5 (7)
C65	−0.14512 (99)	−0.02494 (73)	0.1948 (14)	3.9 (7)
C66	−0.15208 (99)	0.04032 (73)	0.0978 (13)	3.2 (6)
C71	0.2363 (11)	0.15241 (91)	0.2263 (16)	5.7 (4)
C72	0.2669 (12)	0.14162 (94)	0.3720 (17)	6.1 (4)
C73	0.3646 (12)	0.10988 (92)	0.4349 (15)	5.6 (4)
C74	0.4340 (14)	0.0902 (11)	0.3564 (20)	7.8 (5)
C75	0.4051 (13)	0.1011 (10)	0.2125 (18)	6.9 (4)
C76	0.3072 (13)	0.1363 (10)	0.1506 (17)	6.6 (4)
C81	0.5117 (17)	0.3224 (14)	0.3682 (25)	10.4 (6)
C82	0.5650 (15)	0.3793 (13)	0.4505 (21)	9.3 (5)
C83	0.5906 (14)	0.4470 (12)	0.3846 (22)	8.6 (5)
C84	0.5573 (17)	0.4587 (13)	0.2481 (26)	10.5 (6)
C85	0.4998 (17)	0.4045 (16)	0.1699 (24)	10.6 (6)
C86	0.4841 (16)	0.3363 (14)	0.2334 (25)	10.0 (6)

Table IX. Intramolecular Distances (Å) Involving the Non-Hydrogen Atoms for Compound 4[a]

atom	atom	dist	atom	atom	dist
Ru1	C11	1.84 (2)	Mo2	C3	2.10 (1)
Ru1	C12	1.91 (1)	Mo2	C4	2.14 (1)
Ru1	C1	2.15 (1)	Mo2	C6	2.21 (1)
Ru1	C3	2.18 (1)	Mo2	C41	2.33 (1)
Ru1	C2	2.24 (1)	Mo2	C42	2.33 (1)
Ru1	S	2.309 (3)	Mo2	S	2.357 (3)
Ru1	Mo1	2.823 (2)	Mo2	C45	2.36 (1)
Ru1	Mo2	2.839 (2)	Mo2	C44	2.38 (1)
Mo1	C1	2.14 (1)	Mo2	C43	2.39 (1)
Mo1	C6	2.17 (1)	O11	C11	1.17 (1)
Mo1	C4	2.24 (1)	O12	C12	1.13 (1)
Mo1	C33	2.34 (1)	C1	C2	1.42 (1)
Mo1	C34	2.35 (1)	C2	C3	1.42 (2)
Mo1	C32	2.35 (1)	C2	C21	1.49 (1)
Mo1	C5	2.37 (1)	C4	C5	1.38 (1)
Mo1	C31	2.38 (1)	C5	C6	1.42 (1)
Mo1	S	2.379 (3)	C5	C51	1.51 (2)
Mo1	C35	2.38 (1)	C6	C61	1.48 (1)
Mo1	Mo2	2.682 (2)			

[a] Estimated standard deviations in the least significant figure are given in parentheses.

HC_2Ph in a 1/5 ratio at 98 °C. Under these conditions, further alkyne addition does not occur.[12] In contrast at 100 °C $Mo_2(CO)_4(C_5H_5)_2$ readily produces the oligomerization of alkynes.[7-11] In this report, it has been shown that compound 1, formed by replacement of two the ruthenium carbonyl units with two cyclopentadienylmolybdenum dicarbonyl units, is active toward alkyne oligomerization under conditions similar to those of $Mo_2(CO)_4(C_5H_5)_2$ alone.

Compound 2 was obtained from the reaction of 1 with HC_2Ph by the addition and head-to-tail coupling of three HC_2Ph molecules; see Scheme I. The dimetallahexatrienyl ligand is coordinated to all three metal atoms of the cluster. This demonstrates a direct involvement of the ruthenium atom in the oligomerization process, even though the dimolybdenum center may be the site of the initiation of the oligomerization. It was possible to induce the elimination of 1,3,5-triphenylbenzene from 2 by treatment with CO. The metal-containing product was the starting material 1. Thus, it seemed plausible to think that one might be able to perform this cyclotrimerization catalytically. However, these efforts were not successful, evidently because the oligomerization process does not proceed well under the conditions required for arene elimination.

When heated in the absence of CO, 2 underwent a novel transformation that involved the splitting of the dimetallahexatrienyl ligand into two dimetallaallyl ligands as found in 3. This occurs through a rupture of the C(3)–C(4) bond in 2 (see Figure 1) which was originally a C–C triple bonded site in one of the alkyne molecules. The transformation of 2 into 3 is a remarkably simple one. It involves only the cleavage of the C(3)–C(4) bond and the formation of the metal–carbon bonds Mo(2)–C(4) and Mo(1)–C(3), labeling as shown in Figure 1. Compound 3 is an isomer of 2, but the electron count on the metal atoms in this cluster was increased by two as a result of the C–C cleavage. This is possible because 2 is actually electron deficient by the amount of two electrons. Assuming that the hexatrienyl ligand in 2 serves as an eight-electron donor, compound 2 is found to contain only 46 cluster valence electrons, two less than that required by the effective atomic number rule. The dimetallaallyl ligands in 3 each serve as five electron donors; thus 3 is saturated with 48 electrons. Indeed, it may be the electronic unsaturation in the cluster of 2 that provides the driving force for the carbon–carbon bond cleavage step. $Mo_2(CO)_4(C_5H_5)_2$ does not produce C–C bond cleavages in the course of alkyne oligomerizations. It is believed that this difference between $Mo_2(CO)_4(C_5H_5)_2$ and 2 can be attributed to the presence of the ruthenium atom and the role that it plays in creating the state of unsaturation that precedes the carbon–carbon bond cleavage step. Thus, although the introduction of the dimolybdenum unit into 1 may serve to provide an alkyne oligomerization activation site, the chemistry overall is dependent on the entire cluster functioning as a unit. There have been several reports that describe the cleavage of alkyne triple bonds by cluster complexes,[19] but the cleavage of C–C bonds in extended chains is very rare.[20]

The isomerization of 3 into 4 is also quite remarkable, but there is precedence for transformations such as these. Chisholm has shown that the compound W_2-

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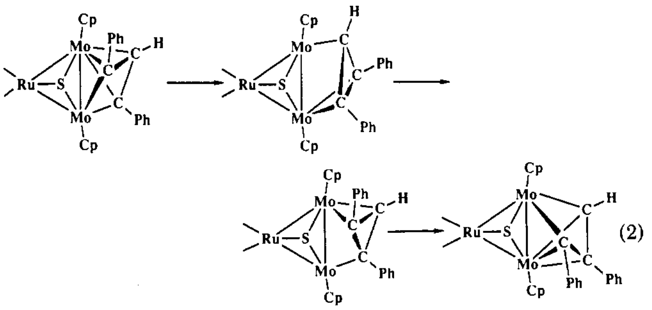
(20) (a) Breil, H.; Wilke, G. *Angew Chem., Int. Ed. Engl.* **1966**, *5*, 898. (b) Dietrich, H.; Dierks, H. *Angew Chem., Int. Ed. Engl.* **1966**, *5*, 899.

Table X. Intramolecular Bond Angles (deg) for Compound 4[a]

atom	atom	atom	angle	atom	atom	atom	angle
C11	Ru1	C12	90.2 (6)	Mo2	Mo1	Ru1	62.02 (4)
C11	Ru1	C1	94.1 (5)	C3	Mo2	C4	75.9 (4)
C11	Ru1	C3	150.9 (5)	C3	Mo2	C6	131.2 (4)
C11	Ru1	C2	114.7 (5)	C3	Mo2	S	101.5 (3)
C11	Ru1	S	105.0 (4)	C3	Mo2	Mo1	86.6 (3)
C11	Ru1	Mo1	102.3 (4)	C3	Mo2	Ru1	49.7 (3)
C11	Ru1	Mo2	155.2 (4)	C4	Mo2	C6	59.9 (4)
C12	Ru1	C1	146.2 (5)	C4	Mo2	S	110.0 (3)
C12	Ru1	C3	94.7 (5)	C4	Mo2	Mo1	54.1 (3)
C12	Ru1	C2	111.3 (5)	C4	Mo2	Ru1	94.4 (3)
C12	Ru1	S	108.5 (4)	C6	Mo2	S	77.1 (3)
C12	Ru1	Mo1	160.6 (4)	C6	Mo2	Mo1	51.6 (3)
C12	Ru1	Mo2	107.4 (4)	C6	Mo2	Ru1	111.0 (3)
C1	Ru1	C3	66.6 (4)	S	Mo2	Mo1	55.89 (8)
C1	Ru1	C2	37.7 (4)	S	Mo2	Ru1	51.77 (8)
C1	Ru1	S	102.7 (3)	Mo1	Mo2	Ru1	61.43 (4)
C1	Ru1	Mo1	48.7 (3)	Ru1	S	Mo2	74.9 (1)
C1	Ru1	Mo2	81.2 (3)	Ru1	S	Mo1	74.0 (1)
C3	Ru1	C2	37.3 (4)	Mo2	S	Mo1	69.0 (1)
C3	Ru1	S	100.6 (3)	C2	C1	Mo1	125.9 (8)
C3	Ru1	Mo1	81.7 (3)	C2	C1	Ru1	74.5 (7)
C3	Ru1	Mo2	47.3 (3)	Mo1	C1	Ru1	82.2 (4)
C2	Ru1	S	122.3 (3)	C3	C2	C1	114 (1)
C2	Ru1	Mo1	77.1 (3)	C3	C2	C21	123 (1)
C2	Ru1	Mo2	75.7 (3)	C3	C2	Ru1	69.2 (7)
S	Ru1	Mo1	54.11 (8)	C1	C2	C21	123 (1)
S	Ru1	Mo2	53.30 (8)	C1	C2	Ru1	67.9 (6)
Mo1	Ru1	Mo2	56.55 (4)	C21	C2	Ru1	132.4 (8)
C1	Mo1	C6	130.8 (4)	C2	C3	Mo2	126.2 (8)
C1	Mo1	C4	75.1 (4)	C2	C3	Ru1	73.5 (7)
C1	Mo1	C5	107.8 (4)	Mo2	C3	Ru1	83.0 (4)
C1	Mo1	S	100.8 (3)	C5	C4	Mo2	99.5 (8)
C1	Mo1	Mo2	85.2 (3)	C5	C4	Mo1	77.5 (7)
C1	Mo1	Ru1	49.0 (3)	Mo2	C4	Mo1	75.4 (4)
C6	Mo1	C4	59.0 (4)	C4	C5	C6	102 (1)
C6	Mo1	C5	36.1 (4)	C4	C5	C51	128 (1)
C6	Mo1	S	77.4 (3)	C4	C5	Mo1	67.8 (7)
C6	Mo1	Mo2	53.0 (3)	C6	C5	C51	129 (1)
C6	Mo1	Ru1	112.9 (3)	C6	C5	Mo1	64.5 (6)
C4	Mo1	C5	34.7 (4)	C51	C5	Mo1	129.1 (8)
C4	Mo1	S	105.6 (3)	C5	C6	C61	129 (1)
C4	Mo1	Mo2	50.5 (3)	C5	C6	Mo1	79.5 (7)
C4	Mo1	Ru1	92.5 (3)	C5	C6	Mo2	95.0 (7)
C5	Mo1	S	109.8 (3)	C61	C6	Mo1	134.6 (8)
C5	Mo1	Mo2	65.1 (3)	C61	C6	Mo2	125.9 (8)
C5	Mo1	Ru1	122.9 (3)	Mo1	C6	Mo2	75.4 (3)
S	Mo1	Mo2	55.12 (8)	O11	C11	Ru1	179 (1)
S	Mo1	Ru1	51.85 (8)	O12	C12	Ru1	176 (1)

[a] Estimated standard deviations in least significant figure are given in parentheses.

(CH$_2$SiMe$_3$)$_4$(μ-CSiMe$_3$)(μ-η^3-C$_3$(Me)$_2$SiMe$_3$] (6) undergoes a similar isomerization that is even rapid on the NMR time scale.[21] The isomerization is proposed to take place via an intermediate containing a μ-metallacyclopropenyl ligand. A similar transformation applied to the edge-bridging C$_3$HPh$_2$ ligand in 3 is shown in eq 2.



(2)

Table XI. Positional Parameters and B(eq) for RuMo$_2$S(CO)$_5$Cp$_2$(C$_4$H$_2$Ph$_2$) (5)

atom	x	y	z	B(eq), Å^2
Ru1	−0.230731 (95)	0.046868 (79)	−0.13968 (13)	3.47 (5)
Mo1	−0.372056 (95)	0.242988 (84)	−0.06415 (13)	2.99 (5)
Mo2	−0.252780 (99)	0.118313 (86)	0.14835 (14)	3.27 (6)
S	−0.38371 (28)	0.06603 (25)	−0.04666 (39)	3.4 (2)
O11	−0.3434 (12)	−0.05566 (90)	−0.4107 (14)	8.6 (8)
O12	−0.01910 (96	0.08354 (88)	−0.2337 (15)	7.7 (7)
O13	−0.19635 (84)	−0.147808 (76)	−0.0012 (13)	5.9 (6)
O21	−0.20035 (87)	0.33771 (74)	0.2141 (11)	5.7 (5)
C1	−0.3751 (11)	0.19478 (92)	−0.2917 (15)	3.5 (6)
C2	−0.2706 (11)	0.1843 (10)	−0.2108 (16)	3.9 (7)
C3	−0.2155 (11)	0.2671 (10)	−0.1399 (15)	3.9 (7)
C4	−0.2726 (10)	0.34597 (93)	−0.1163 (13)	3.1 (6)
C11	−0.2990 (15)	−0.0158 (11)	−0.3093 (19)	5.4 (9)
C12	−0.0968 (15)	0.0678 (10)	−0.1932 (17)	4.9 (8)
C13	−0.2055 (11)	−0.0752 (11)	−0.0532 (17)	3.9 (7)
C21	−0.1129 (14)	0.12457 (94)	0.0998 (16)	4.0 (7)
C22	−0.2279 (12)	0.2582 (11)	0.1672 (15)	4.2 (7)
C31	−0.4010 (14)	0.2705 (10)	−0.3959 (16)	4.0 (7)
C32	−0.3277 (15)	0.3374 (11)	−0.4301 (16)	5.3 (8)
C33	−0.3564 (22)	0.4072 (14)	−0.5295 (22)	8 (1)
C34	−0.4645 (30)	0.4036 (17)	−0.5909 (22)	9 (2)
C35	−0.5338 (21)	0.3378 (20)	−0.5586 (22)	8 (1)
C36	−0.5050 (15)	0.2712 (13)	−0.4641 (18)	6 (1)
C41	−0.2298 (11)	0.44760 (92)	−0.1179 (15)	3.6 (7)
C42	−0.1297 (12)	0.4686 (10)	−0.1425 (18)	4.9 (8)
C43	−0.0867 (13)	0.5651 (12)	−0.1378 (20)	6 (1)
C44	−0.1433 (14)	−0.6393 (11)	−0.1144 (19)	5.4 (8)
C45	−0.2437 (14)	0.6184 (11)	−0.1001 (20)	6 (1)
C46	−0.2866 (12)	0.5249 (10)	−0.0932 (18)	5.1 (8)
C51	−0.5366 (12)	0.2155 (11)	0.0052 (20)	4.3 (8)
C52	−0.4730 (13)	0.2803 (13)	0.1053 (17)	5.0 (8)
C53	−0.4447 (12)	0.3636 (11)	0.0412 (18)	4.3 (8)
C54	−0.4943 (12)	0.3530 (12)	−0.1012 (17)	4.5 (8)
C55	−0.5516 (10)	0.2588 (1)	−0.1204 (19)	4.2 (7)
C61	−0.3357 (20)	−0.0005 (16)	0.2684 (18)	6 (1)
C62	−0.3431 (16)	0.0891 (21)	0.3319 (23)	7 (1)
C63	−0.2446 (27)	0.1280 (13)	0.3879 (22)	8 (1)
C64	−0.1777 (17)	0.0679 (22)	0.3619 (24)	8 (1)
C65	−0.2300 (24)	−0.0111 (16)	0.2919 (21)	7 (1)
C91	0.1997 (31)	0.3401 (30)	0.6814 (42)	17 (1)
C92	0.1943 (38)	0.2839 (35)	0.5669 (56)	20 (2)
C93	0.1005 (39)	0.2491 (28)	0.4881 (40)	17 (1)
C94	0.0170 (33)	0.3085 (35)	0.5047 (44)	18 (1)
C95	0.0238 (33)	0.3760 (30)	0.5957 (48)	18 (1)
C96	0.1197 (34)	0.3984 (24)	0.6897 (36)	15 (1)

Table XII. Intramolecular Distances (Å) for Mo$_2$Ru(CO)$_5$(C$_5$H$_5$)$_2$[μ-η^4-PhCC(H)CC(H)Ph](μ_3-S) (5)[a]

atom	atom	dist	atom	atom	dist
Ru1	C11	1.87 (2)	Mo2	C21	1.94 (2)
Ru1	C12	1.90 (2)	Mo2	C64	2.28 (2)
Ru1	C13	1.94 (2)	Mo2	C63	2.31 (2)
Ru1	C2	2.13 (1)	Mo2	C65	2.31 (2)
Ru1	S	2.354 (4)	Mo2	C62	2.33 (2)
Ru1	Mo2	3.015 (2)	Mo2	S	2.336 (4)
Mo1	C4	1.97 (1)	Mo2	C61	2.34 (2)
Mo1	C3	2.28 (1)	O11	C11	1.14 (2)
Mo1	C1	2.28 (1)	O12	C12	1.15 (2)
Mo1	C54	2.29 (1)	O13	C13	1.14 (2)
Mo1	C2	2.29 (1)	O21	C21	1.17 (2)
Mo1	C53	2.31 (1)	O22	C22	1.18 (2)
Mo1	C55	2.31 (1)	C1	C2	1.45 (2)
Mo1	C51	2.35 (1)	C1	C31	1.50 (2)
Mo1	C52	2.36 (1)	C2	C3	1.39 (2)
Mo1	S	2.465 (4)	C3	C4	1.42 (2)
Mo1	Mo2	3.024 (2)	C4	C41	1.47 (2)
Mo2	C22	1.94 (2)	Mo1	Ru1	3.558 (2)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

An alternative mechanism that involves splitting the dimetallaallyl ligand into alkyne and alkylidyne ligands, rotating the alkyne 180°, and then recombining the two

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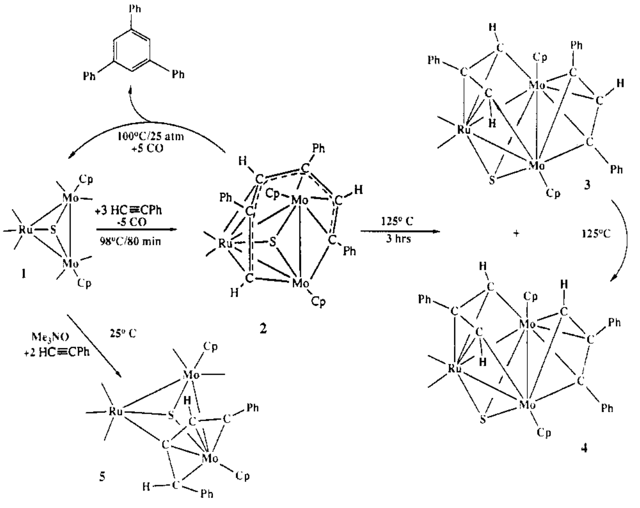
[21] Chisholm, M. H.; Heppert, J. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 1151.

Table XIII. Intramolecular Bond Angles (deg) for Compound 5[a]

atom	atom	atom	angle	atom	atom	atom	angle
C11	Ru1	C12	94.9 (7)	C22	Mo2	Ru1	110.7 (4)
C11	Ru1	C13	91.9 (7)	C22	Mo2	Mo1	59.1 (4)
C11	Ru1	C2	92.4 (6)	C21	Mo2	S	110.5 (5)
C11	Ru1	S	97.2 (5)	C21	Mo2	Ru1	60.6 (4)
C11	Ru1	Mo2	146.2 (5)	C21	Mo2	Mo1	103.3 (4)
C12	Ru1	C13	95.7 (6)	S	Mo2	C61	85.9 (5)
C12	Ru1	C2	91.0 (6)	S	Mo2	Ru1	50.3 (1)
C12	Ru1	S	163.7 (5)	S	Mo2	Mo1	52.9 (1)
C12	Ru1	Mo2	118.8 (5)	Ru1	Mo2	Mo1	72.19 (5)
C13	Ru1	C2	171.7 (6)	Mo2	S	Ru1	80.0 (1)
C13	Ru1	S	94.7 (4)	Mo2	S	Mo1	78.0 (1)
C13	Ru1	Mo2	85.4 (4)	Ru1	S	Mo1	95.1 (1)
C2	Ru1	S	77.7 (4)	C2	C1	C31	125 (1)
C2	Ru1	Mo2	87.1 (4)	C2	C1	Mo1	71.8 (8)
S	Ru1	Mo2	49.7 (1)	C31	C1	Mo1	114.5 (9)
C4	Mo1	C3	38.1 (5)	C3	C2	C1	116 (1)
C4	Mo1	C1	79.8 (5)	C3	C2	Ru1	119 (1)
C4	Mo1	C2	68.4 (5)	C3	C2	Mo1	71.7 (9)
C4	Mo1	S	137.4 (3)	C1	C2	Ru1	120 (1)
C4	Mo1	Mo2	109.7 (4)	C1	C2	Mo1	71.2 (8)
C3	Mo1	C1	63.8 (5)	Ru1	C2	Mo1	107.2 (6)
C3	Mo1	C2	35.4 (5)	C2	C3	C4	119 (1)
C3	Mo1	S	99.3 (4)	C2	C3	Mo1	72.9 (8)
C3	Mo1	Mo2	84.4 (3)	C4	C3	Mo1	59.2 (8)
C1	Mo1	C2	37.0 (5)	C3	C4	C41	124 (1)
C1	Mo1	S	79.2 (3)	C3	C4	Mo1	82.6 (9)
C1	Mo1	Mo2	113.7 (4)	C41	C4	Mo1	152 (1)
C2	Mo1	S	72.5 (3)	O11	C11	Ru1	178 (2)
C2	Mo1	Mo2	84.1 (4)	O12	C12	Ru1	175 (2)
S	Mo1	Mo2	49.1 (1)	O13	C13	Ru1	176 (1)
C22	Mo2	C21	85.2 (6)	O21	C21	Mo2	162 (1)
C22	Mo2	S	111.9 (4)	O22	C22	Mo2	162 (1)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

Scheme I



ligands cannot be ruled out for the **3** → **4** transformation, although it was ruled out in the transformation of **6**.[19] Compound **5** was obtained by Me_3NO-induced decarbonylation of **1** in the presence of HC_2Ph. Two formula equivalents of HC_2Ph were incorporated into **5** and coupled via a carbon–carbon bond formation. However, the resultant C_4 chain contains phenyl groups at the 1- and 4-positions. In addition, a hydrogen atom shift has resulted in a repositioning of one of the acetylenic hydrogen atoms to one of the phenyl-substituted carbon atoms. It is possible that the hydrogen shift may have preceded the C–C coupling step. Vahrenkamp has demonstrated the transformation of terminal alkynes into substituted vinylidene ligands in the cluster complexes.[22,23] A similar transformation in a monoacetylene complex of **1** followed by a C–C bond formation between a HC_2Ph molecule and the vinylidene carbon atom would lead to the ligand found in **5**. It is believed that **5** does not lie on the reaction pathway that leads to **2**.

In this report, it was shown that an active alkyne oligomerization cluster complex could be prepared from an inactive one by the substitution of two of the metal atoms with a dinuclear metal containing grouping that is known to produce alkyne oligomerization. The new cluster, however, has certain chemical properties that distinguish it from the original dimolybdenum oligomerization agent. It is believed that it may be possible, in general, to tune the reactivity of polynuclear metal complexes by the process of selective metal atom substitution. The concept may have value for the systematic synthesis of new multimetallic catalysts.

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Registry No. **1**, 92067-61-3; **2**, 110096-38-3; **3**, 110096-39-4; **4**, 112219-90-6; **5**, 112246-98-7; PhC_2H, 536-74-3; Me_3NO, 1184-78-7; 1,3,5-triphenylbenzene, 612-71-5.

Supplementary Material Available: Tables of C–C ring distances, hydrogen atom positional parameters, and anisotropic thermal parameters for all four structural analyses (18 pages); listings of observed and calculated structure factor amplitudes for the structures of **4** and **5** (36 pages). Structure factor amplitudes for **2** and **3** were published previously.[15] Ordering information is given on any current masthead page.

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(23) Bernhardt, W.; von Schnering, C.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 279.