2114 *Organometallics* 1991, *10,* 2114-2120

Alkylidyne-Alkyne Coupling Reactions. Reactions of $Mo_2Co(CO)_7Cp_2(\mu_3\text{-}CH)$ with EtC_2Et and PhC_2Ph

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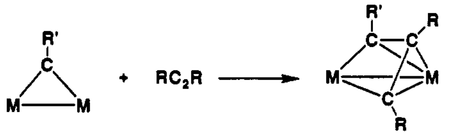
Received November 5, 1990

The reaction of $Mo_2Co(CO)_7Cp_2(\mu_3\text{-}CH)$ with EtC_2Et has yielded two isomeric products $Mo_2Co(CO)_5Cp_2[\mu_3\text{-}OCC(Et)C(Et)CH]$ (**2a**, 3%, **2b**, 18%). Both products were characterized crystallographically and were found to contain triply bridging OCC(Et)C(Et)CH ligands formed by the coupling of the methylidyne ligand to one EtC_2Et molecule and one CO ligand. The CO group bridges the face of a Mo_2Co triangular cluster with the oxygen atom coordinated to one of the molybdenum atoms, Mo–O = 2.142 (5) Å in **2a** and 2.150 (4) Å in **2b**. The isomers were equilibrated as 1.0/1.7 **2a**/**2b** at 52 °C in 7 days. The reaction of 1 with PhC_2Ph yielded two products $Mo_2Co(CO)_2Cp_2[\mu_3\text{-}C(Ph)C(H)C(Ph)C(Ph)](\mu_3\text{-}CPh)$ (**3**, 18%) and $Mo_2Co(CO)_2Cp_2(\mu_3\text{-}CO)(\mu\text{-}PhC_2Ph)[\mu_3\text{-}C(H)C(Ph)C(Ph)]$ (**4**, 30%). Compound **3** contains a dimetallatriphenylbutadiene ligand and a triply bridging benzylidyne ligand. These were formed by the coupling of two PhC_2Ph molecules to the methylidyne ligand and the splitting off of one CPh group. Compound **4** contains a triply bridging dimetalladiphenylallyl ligand formed by the coupling of one PhC_2Ph molecule to the methylidyne ligand. Compounds **3** and **4** are both electron deficient and both contain Mo_2Co clusters with unusually short Mo–Mo bonds. Compound **3** also contains an unusual agostic phenyl interaction. Crystal Data: for **2a**, space group = $P2_1/a$, a = 15.035 (3) Å, b = 9.373 (4) Å, c = 16.494 (3) Å, β = 100.65 (1)°, Z = 4, 1659 reflections, R = 0.029; for **2b**, space group = $Pbca$, a = 16.966 (3) Å, b = 25.777 (5) Å, c = 10.310 (1) Å, Z = 8, 2349 reflections, R = 0.027; for **3**, space group = $C2/c$, a = 34.08 (2) Å, b = 11.436 (4) Å, c = 18.80 (1) Å, β = 118.62 (4)°, Z = 8, 2254 reflections, R = 0.040; for **4**, space group = $C2/c$, a = 35.896 (9) Å, b = 13.243 (5) Å, c = 16.899 (3) Å, β = 96.62 (2)°, Z = 8, 2535 reflections, R = 0.048.

Introduction

The coupling of alkylidyne ligands to alkynes in polynuclear metal complexes has been a source of great interest.[1,2] The most common product is the dimetallaallyl ligand that may bridge two or three metal atoms in the di-σ + π bonding mode (eqs 1[1] and 2[2]).



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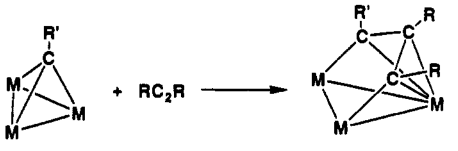

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In recent studies, we have been investigating the ability of heteronuclear cluster complexes containing the $Cp_2Mo_2(CO)_4$ grouping to induce the coupling of alkyne ligands.[3] We have now investigated the reactions of the heteronuclear cluster $Mo_2Co(CO)_7Cp_2(\mu_3\text{-}CH)$ (1) with the disubstituted alkynes EtC_2Et and PhC_2Ph. These reactions proceed by coupling of the alkynes to the alkylidyne ligand but also include coupling to CO in the EtC_2Et reaction and alkyne splitting in the PhC_2Ph reaction. The results of this study are reported here.

Experimental Section

General Procedures. Reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were dried over sodium and deoxygenated by purging with nitrogen prior to use. 3-Hexyne and diphenylacetylene were purchased from Aldrich and were used without further purification. The reagents $Mo_2CoCp_2(CO)_7(\mu_3\text{-}CH)^4$ (1) and $Co_3(CO)_9(\mu_3\text{-}CH)^5$ were prepared by published procedures. IR spectra were recorded on a Nicolet 5 DXB FT-IR spectrophotometer. A Bruker AM-300 FT-NMR spectrometer was used to obtain ^1H NMR spectra. Elemental microanalyses were performed by Desert Analytics, Tucson, AZ. TLC separations were performed by using silica gel (60 Å, F_{254}) on plates (Whatman 0.25 mm).

Reaction of 1 with EtC_2Et. A 10-μL (0.09-mmol) amount of EtC_2Et was added to a solution of 1 (24.4 mg, 0.04 mmol) in 15 mL of hexane. The reaction mixture was heated to reflux for 3 h, after which the hexane was removed in vacuo. The residue was dissolved in a minimal amount of dichloromethane and was chromatographed by TLC on silica gel. Elution with a hexane/dichloromethane (50/50) solvent mixture yielded 0.4 mg of 1, 0.8 mg of $Cp_2Mo_2Co(CO)_5(CHC(Et)C(Et)CO)$ (**2a**, 3%) as a brown band, and 4.7 mg of $Cp_2Mo_2Co(CO)_5(CHC(Et)C(Et)CO)$ (**2b**, 18%) as a brown band. Other products were obtained but could not be characterized due to their very low yields. Analytical data for **2a**: IR (ν(CO), cm^{-1}, in hexane) 2007 (vs), 1963 (vs), 1924 (s), 1907 (vs), 1842 (m); ^1H NMR (δ in $CDCl_3$) 7.79 (s, 1 H), 5.41 (s, 5 H), 5.03 (s, 5 H), 2.60–2.45 (m, 2 H), 1.90–1.65 (m, 2 H), 1.29 (t, 3 H, J_{H-H} = 8.1 Hz), 1.10 (t, 2 H, J_{H-H} = 8.1 Hz). Anal. Calcd for **2a**: C, 42.88; H, 3.29. Found: C, 42.57; H, 3.03. Analytical data for **2b**: IR (ν(CO), cm^{-1}, in hexane) 2025 (vs), 1968 (s), 1954 (m), 1920 (w), 1813 (m); ^1H NMR (δ in $CDCl_3$) 7.69 (s, 1 H), 5.45 (s, 5 H), 4.50 (s, 5 H), 2.73–2.48 (m, 2 H), 1.98–1.70 (m, 2 H), 1.27 (t, 3 H, J_{H-H} = 8.6 Hz), 1.12 (t, 3 H, J_{H-H} = 7.6 Hz). Anal. Calcd for **2b**: C, 42.88; H, 3.29. Found: C, 41.82; H, 3.12.

Isomerization of 2b to 2a. A solution of **2b** in toluene-d_8 was placed in a NMR tube and sealed under vacuum. An equilibrium mixture of 1.0/1.7 **2a**/**2b** was produced by heating to 52 °C for 7 days.

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Table I. Crystal Data for Compounds 2a, 2b, 3, and 4

	compd			
	2a	**2b**	**3**	**4**
empirical formula	$Mo_2CoO_6C_{23}H_{21}$	$Mo_2CoO_6C_{23}H_{21}$	$Mo_2CoO_2C_{41}H_{31}$	$Mo_2CoO_3C_{42}H_3 \cdot C_6H_6$
fw	644.23	644.23	806.51	912.63
cryst system	monoclinic	orthorhombic	monoclinic	monoclinic
lattice params				
a, Å	15.035 (3)	16.966 (3)	34.08 (2)	35.896 (9)
b, Å	9.373 (4)	25.777 (5)	11.436 (4)	13.243 (5)
c, Å	16.494 (3)	10.310 (1)	18.80 (1)	16.899 (3)
β, deg	100.65 (2)		118.62 (4)	96.62 (2)
V, Å^3	2284 (2)	4509 (1)	6433 (7)	7980 (4)
space group	$P2_1/a$ (No. 14)	$Pbca$ (No. 61)	$C2/c$ (No. 15)	$C2/c$ (No. 15)
z value	4	8	8	8
D_{calc}, g/cm^3	1.87	1.90	1.67	1.52
μ(Mo Kα), cm^{-1}	18.1	18.3	12.9	10.5
temp, °C	23	23	23	23
$2\theta_{max}$, deg	40.0	46.0	42.0	40.0
no. of observns ($I > 3\sigma(I)$)	1659	2349	2254	2535
no. of variables	289	289	210	312
residuals: R, R_w	0.029; 0.028	0.027; 0.031	0.040; 0.039	0.048; 0.054
goodness of fit indicator	1.11	1.17	1.32	2.06
max shift in final cycle	0.00	0.03	0.01	0.40
largest peak in final diff map, e/Å^3	0.35	0.54	0.50	0.64
abs corr	empirical	empirical	empirical	empirical

Reaction of 1 with PhC_2Ph. A 34.5-mg (0.20-mmol) amount of PhC_2Ph was added to a solution of **1** (64.3 mg, 0.11 mmol) in 15 mL of hexane. The reaction mixture was heated to reflux for 2 h and 45 min. The solution was chromatographed over a silica column using a hexane/dichloromethane, (10/1) solvent mixture. The first band was green, **1**, 4.6 mg. The second band was eluted with a hexane/dichloromethane (3/1) solvent mixture to yield 15.0 mg of brown $Mo_2Co(CO)_2Cp_2(C(Ph)CHC(Ph)C(Ph)(\mu_3\text{-}CPh)$ (**3**, 18%). Finally, elution with acetone yielded a green band, 24.7 mg of $Mo_2Co(CO)_3Cp_2(\mu\text{-}PhC_2Ph)[\mu_3\text{-}CHC(Ph)C(Ph)]$ (**4**, 30%). Analytical data for **3**: IR (ν(CO), cm^{-1}, in hexane) 1986 (vs), 1938 (s); ^{1}H NMR (δ in $CDCl_3$) 7.24–5.97 (m, 20 H), 5.23 (s, 5 H), 4.87 (s, 5 H). Anal. Calcd for **3**: C, 61.06; H, 3.87. Found: C, 60.02; H, 3.89. Analytical data for **4**: IR (ν(CO), cm^{-1}, in hexane) 2016 (vs), 1974 (s), 1666 (m). ^{1}H NMR (δ in $CDCl_3$) 8.75 (s, 1 H), 7.45–5.98 (m, 21 H), 5.09 (s, 5 H), 4.85 (s, 5 H). Anal. Calcd for **4**: C, 60.45; H, 3.74. Found: C, 60.68; H, 3.84.

Reaction of $Co_3(CO)_9(\mu_3\text{-}CH)$ (5) with EtC_2Et. A 50-mg (0.11-mmol) amount of **5** and 26 μL (0.23 mmol) of EtC_2Et were dissolved in 15 mL of hexane. The reaction mixture was heated to reflux for 1 h and 45 min. The solution was chromatographed over a silica gel column using a hexane/dichloromethane (9/1) solvent mixture. The first band was $Co_2(CO)_6(EtC_2Et)$, 6.5 mg, 19%. The second band yielded was unreacted **5**, 8.8 mg.

Reaction of 5 with PhC_2Ph. A 51.2-mg (0.11-mmol) sample of **5** and 40.3 mg (0.23 mmol) of PhC_2Ph were dissolved in 15 mL of hexane. The reaction mixture was heated to reflux for 45 min. The solution was chromatographed over a silica gel column using a hexane/dichloromethane, (9/1) solvent mixture. The first band was **5**, 14.1 mg. A second band was eluted with a hexane/dichloromethane (3/1) solvent mixture to yield 24.4 mg of $Co_2(CO)_6(PhC_2Ph)$, 63%.

Attempted Reaction of 3 with CO. A 14.4-mg amount of **3** was dissolved in 20 mL of heptane, and the solution was placed under an atmosphere of CO. After 1 h there was no evidence of a reaction as determined by IR spectroscopy. The solution was then heated to reflux for an additional 4 h. After this time there was still no evidence of a reaction.

Attempted Thermolysis of 4. A 35-mg amount of **4** was dissolved in 15 mL of hexane. This solution was heated to reflux for 4 h and 30 min. IR spectroscopy of the solution showed no change from **4**. A similar treatment in a refluxing heptane solution led to the decomposition of **4** with no evidence for formation of **3**.

Crystallographic Analyses. Crystals of compounds **2a** and **2b** suitable for diffraction analyses were grown by slow evaporation of hexane/CH_2Cl_2 solutions at −20 °C. Crystals of compound **3** were grown by slow evaporation of hexane/methanol solutions at −10 °C. Crystals of compound **4** were grown by slow evaporation of hexane/benzene solutions at 0 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 15 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. VAXstation 3520 computer by using the TEXSAN structure solving program library (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. The data were corrected for Lorentz and polarization effects (Lp). Neutral-atom scattering factors were calculated by the standard procedures.[6a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[6b] Full-matrix least-squares refinements minimized the function $\Sigma_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net}^2)^2]^{1/2}Lp$.

Compound **2a** crystallized in the monoclinic crystal system. The space group $P2_1/a$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound **2b** crystallized in the orthorhombic crystal system. The space group $Pbca$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compounds **3** and **4** both crystallized in the monoclinic crystal system. The systematic absences in the data were consistent with either of the space groups $C2/c$ or Cc. The centrosymmetric space group $C2/c$ was selected initially for both structures and was confirmed in each case by the successful solution and refinement of the structure. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. Due to the limited amount of diffraction data for **3**, only the metal atoms and carbonyl oxygen atoms were refined anisotropically. For **4** only the metal atoms, carbonyl ligands, and carbon atoms of the cyclopentadienyl rings were refined anisotropically. In the

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[6] (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

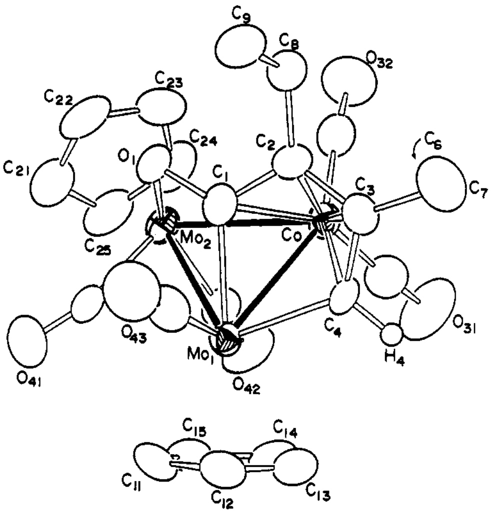

Figure 1. ORTEP diagram of $Mo_2Co(CO)_5Cp_2[\mu_3\text{-}OC(Et)C(Et)CH]$ (**2a**), showing 50% probability thermal ellipsoids.

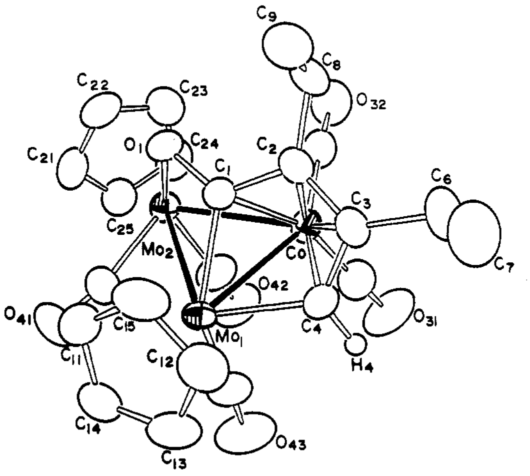

Figure 2. ORTEP diagram of $Mo_2Co(CO)_5Cp_2[\mu_3\text{-}OC(Et)C(Et)CH]$ (**2b**), showing 50% probability thermal ellipsoids.

final cycles of refinement of 4, a molecule of benzene that was cocrystallized from the crystallization solvent was located in the lattice. It was included in the calculations and was satisfactorially refined. All hydrogen atom positions were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined. Tables of the positional parameters of the hydrogen atoms, anisotropic thermal parameters, and structure factor amplitudes are available with the supplementary material for all four structures.

Results

Two isomeric products with the formula $Mo_2Co(CO)_5Cp_2[\mu_3\text{-}OCC(Et)C(Et)CH]$ (**2a**, 3%; **2b**, 18%) were obtained from the reaction of 1 with EtC_2Et at 68 °C. The isomers exhibited similar IR and ^1H NMR spectra and were characterized uniquely only by single-crystal X-ray diffraction analyses. The molecular structures of **2a** and **2b** are shown in Figures 1 and 2. Final atomic positional parameters are listed in Tables II and III. Selected interatomic distances and angles are listed and compared in Tables IV and V. Both compounds contain Mo_2Co clusters with three metal-metal bonds. The Mo–Mo distances, 2.891 (1) Å in **2a** and 2.9292 (8) Å in **2b**, are similar to that found in 1, 2.937 (2) Å.[7] The Mo(1)–Co distance in **2a** at 2.713 (1) Å is shorter than that in **2b**, 2.7714 (9) Å, but similar to that in **1**, 2.712 (2) Å. Conversely, the Mo(2)–Co distance in **2a**, 2.853 (1) Å, is slightly longer than that in **2b**, 2.8285 (9) Å. Both molybdenum atoms contain a cyclopentadienyl ligand. The most interesting ligand is the triply bridging OCC(Et)C(Et)CH group. Its CO grouping is coordinated to the face of the

Table II. Positional Parameters and *B*(eq) Values for 2a

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mo(1)	0.74937 (5)	1.17010 (8)	0.83039 (4)	2.31 (3)
Mo(2)	0.59735 (5)	0.97635 (8)	0.79827 (4)	2.47 (3)
Co	0.69909 (7)	1.0607 (1)	0.67643 (6)	2.53 (5)
O(1)	0.5450 (3)	1.1814 (5)	0.7569 (3)	2.8 (2)
O(31)	0.8457 (5)	0.8658 (8)	0.6655 (5)	7.0 (4)
O(32)	0.5766 (5)	0.8998 (8)	0.5542 (4)	7.0 (4)
O(41)	0.6246 (4)	1.0871 (7)	0.9778 (4)	4.9 (3)
O(42)	0.7657 (4)	0.7703 (7)	0.8321 (4)	5.1 (3)
O(43)	0.6593 (5)	1.4580 (7)	0.8545 (4)	6.1 (4)
C(1)	0.6249 (5)	1.2048 (7)	0.7392 (5)	2.5 (4)
C(2)	0.6326 (5)	1.2563 (8)	0.6575 (5)	2.6 (4)
C(3)	0.7223 (6)	1.2748 (8)	0.6472 (5)	2.8 (4)
C(4)	0.7851 (5)	1.2224 (8)	0.7155 (5)	2.4 (4)
C(6)	0.7503 (6)	1.335 (1)	0.5705 (5)	3.9 (4)
C(7)	0.7504 (6)	1.496 (1)	0.5736 (6)	5.4 (5)
C(8)	0.5484 (6)	1.2901 (9)	0.5977 (5)	3.5 (4)
C(9)	0.5077 (6)	1.434 (1)	0.6140 (6)	5.1 (5)
C(11)	0.8194 (6)	1.188 (1)	0.9667 (5)	4.5 (5)
C(12)	0.8683 (6)	1.273 (1)	0.9210 (6)	3.8 (4)
C(13)	0.9097 (6)	1.190 (1)	0.8711 (6)	4.1 (5)
C(14)	0.8864 (5)	1.046 (1)	0.8847 (6)	3.8 (5)
C(15)	0.8315 (6)	1.047 (1)	0.9446 (6)	4.2 (5)
C(21)	0.4781 (6)	0.871 (1)	0.8510 (6)	4.6 (5)
C(22)	0.4414 (5)	0.935 (1)	0.7771 (7)	4.4 (5)
C(23)	0.4761 (7)	0.867 (1)	0.7130 (6)	4.8 (5)
C(24)	0.5369 (7)	0.763 (1)	0.7500 (8)	5.0 (6)
C(25)	0.5383 (6)	0.766 (1)	0.8342 (7)	4.5 (5)
C(31)	0.7888 (6)	0.942 (1)	0.6721 (5)	3.7 (4)
C(32)	0.6227 (6)	0.965 (1)	0.6049 (6)	4.1 (5)
C(41)	0.6267 (5)	1.059 (1)	0.9084 (6)	3.3 (4)
C(42)	0.7088 (6)	0.853 (1)	0.8184 (5)	3.5 (4)
C(43)	0.6919 (6)	1.350 (1)	0.8447 (5)	3.8 (5)

Table III. Positional Parameters and *B*(eq) Values for 2b

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mo(1)	0.07735 (03)	0.135511 (17)	0.52176 (04)	2.19 (2)
Mo(2)	0.23969 (03)	0.147616 (18)	0.42988 (05)	2.45 (2)
Co	0.19600 (04)	0.07144 (03)	0.61381 (07)	2.67 (3)
O(1)	0.2264 (02)	0.19004 (13)	0.6081 (03)	2.7 (2)
O(31)	0.1647 (03)	-0.03427 (17)	0.5320 (06)	6.6 (3)
O(32)	0.3631 (03)	0.05908 (19)	0.6631 (05)	6.0 (3)
O(41)	0.1164 (03)	0.19101 (19)	0.2414 (04)	5.0 (2)
O(42)	0.2055 (03)	0.04327 (18)	0.2850 (05)	5.7 (3)
O(43)	0.0229 (03)	0.0463 (02)	0.3353 (05)	6.8 (3)
C(1)	0.1765 (03)	0.15366 (19)	0.6416 (05)	2.2 (2)
C(2)	0.1836 (03)	0.1260 (02)	0.7642 (05)	2.6 (2)
C(3)	0.1289 (03)	0.0853 (02)	0.7792 (05)	2.8 (3)
C(4)	0.0815 (03)	0.0775 (02)	0.6681 (05)	2.9 (3)
C(6)	0.1239 (04)	0.0515 (03)	0.8997 (06)	4.5 (3)
C(7)	0.0599 (04)	0.0684 (03)	0.9908 (07)	6.1 (4)
C(8)	0.2423 (04)	0.1445 (02)	0.8642 (05)	3.7 (3)
C(9)	0.2057 (04)	0.1866 (03)	0.9463 (06)	4.6 (3)
C(11)	0.0286 (03)	0.2188 (02)	0.5089 (06)	3.6 (3)
C(12)	-0.0273 (04)	0.1632 (03)	0.6520 (06)	4.1 (3)
C(13)	-0.0562 (03)	0.1515 (03)	0.5279 (07)	4.1 (3)
C(14)	-0.0216 (03)	0.1864 (02)	0.4390 (06)	3.6 (3)
C(15)	0.0246 (03)	0.2050 (02)	0.6408 (06)	4.0 (3)
C(21)	0.3098 (04)	0.2032 (02)	0.2931 (07)	4.1 (3)
C(22)	0.3467 (04)	0.2062 (03)	0.4152 (07)	4.2 (3)
C(23)	0.3773 (04)	0.1570 (03)	0.4449 (07)	4.7 (4)
C(24)	0.3601 (04)	0.1233 (03)	0.3415 (07)	4.6 (3)
C(25)	0.3163 (04)	0.1520 (03)	0.2493 (06)	4.1 (3)
C(31)	0.1776 (04)	0.0074 (03)	0.5614 (07)	4.3 (3)
C(32)	0.2986 (04)	0.0649 (02)	0.6402 (06)	3.6 (3)
C(41)	0.1502 (03)	0.1733 (02)	0.3308 (06)	3.3 (3)
C(42)	0.2137 (04)	0.0799 (03)	0.3476 (06)	4.1 (3)
C(43)	0.0473 (04)	0.0785 (03)	0.4005 (06)	4.0 (3)

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[7] Blumhofer, R.; Fischer, K.; Vahrenkamp, H. *Chem. Ber.* **1986**, *119*, 194.

Table IV. Intramolecular Distances (Å) for 2a and 2b[a]

	distances	
	2a	**2b**
Mo(1)-Mo(2)	2.891 (1)	2.9292 (8)
Mo(1)-Co	2.713 (1)	2.7714 (9)
Mo(1)-C(1)	2.198 (8)	2.139 (5)
Mo(1)-C(4)	2.121 (7)	2.126 (5)
Mo(1)-C(43)	1.93 (1)	1.996 (6)
Mo(2)-Co	2.853 (1)	2.8285 (9)
Mo(2)-O(1)	2.140 (5)	2.150 (3)
Mo(2)-C(1)	2.420 (8)	2.436 (5)
Mo(2)-C(41)	1.95 (1)	1.946 (6)
Mo(2)-C(42)	2.01 (1)	1.990 (6)
Co-C(1)	2.137 (7)	2.164 (5)
Co-C(2)	2.085 (8)	2.104 (5)
Co-C(3)	2.109 (8)	2.081 (5)
Co-C(4)	2.019 (7)	2.027 (5)
Co-C(31)	1.76 (1)	1.765 (6)
Co-C(32)	1.74 (1)	1.771 (6)
O(1)-C(1)	1.307 (8)	1.310 (6)
C(1)-C(2)	1.46 (1)	1.456 (7)
C(2)-C(3)	1.40 (1)	1.411 (7)
C(2)-C(8)	1.49 (1)	1.510 (8)
C(3)-C(4)	1.42 (1)	1.413 (7)
C(3)-C(6)	1.51 (1)	1.519 (8)
C(6)-C(7)	1.52 (1)	1.50 (1)
C(8)-C(9)	1.52 (1)	1.511 (9)
C(Cp)-C(av)	1.155 (9)	1.40 (1)
O-C(av)	1.40 (1)	1.14 (1)

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

cluster, Mo(2)-O(1) = 2.140 (5) Å in **2a** and 2.150 (4) Å in **2b**. C(1) bridges the Mo(1)-Co bond fairly symmetrically in **2b**, Mo(1)-C(1) = 2.139 (5) Å, Co-C(1) = 2.164 (5) Å, but slightly asymmetrically in **2a**, Mo(1)-C(1) = 2.198 (8) Å, Co-C(1) = 2.137 (7) Å. The Mo(2)-C(1) distances are fairly long, 2.420 (8) and 2.436 (5) Å in **2a** and **2b**, and are believed to be nonbonding interactions. The remainder of the carbon chain C(2)-C(3)-C(4) is π-bonded to Co. These distances range from 2.019 to 2.109 Å. C(4) is also a bridging atom and is bonded to Mo(1), Mo(1)-C(4) = 2.121 (7) Å in **2a** and 2.126 (5) Å in **2b**. Atoms C(2) and C(3) each contain an ethyl substituent, while C(4) has only a hydrogen atom substituent. The principal difference between **2a** and **2b** is the ligand conformation on Mo(1). In **2a** the CO ligand lies on the same side of the Mo_2Co plane as the CO group of the OCC(Et)C(Et)CH ligand, while in **2b** the CO ligand lies on the other side of the Mo_2Co plane. Compounds **2a** and **2b** can be separated in a pure form by TLC at 25 °C but isomerize to a 1.0/1.7 **2a**/**2b** equilibrium when heated to 52 °C for 7 days.

Two products $Mo_2Co(CO)_2Cp_2[\mu_3\text{-}C(Ph)C(H)(C(Ph)C(Ph)](\mu_3\text{-}CPh)$ (**3**, 18% yield) and $Mo_2Co(CO)_2Cp_2(\mu_3\text{-}CO)(\mu\text{-}PhC_2Ph)[\mu_3\text{-}C(H)C(Ph)C(Ph)]$ (**4**, 30% yield) were obtained from the reaction of **1** with PhC_2Ph at 68 °C. Both of these products were characterized by X-ray crystallographic analyses also. An ORTEP diagram of **3** is shown in Figure 3. Final atomic positional parameters are listed in Table VI. Selected bond distances and angles are listed in Tables VII and VIII. The molecule contains a Mo_2Co triangular cluster of metal atoms. The Mo-Mo bond is unusually short at 2.579 (2) Å, but the Mo-Co distances are only slightly shorter, 2.650 (2) and 2.663 (2) Å, than those in **1**, **2a**, and **2b**. Each molybdenum atom contains one cyclopentadienyl ligand. The cobalt atom contains two linear terminal carbonyl groups. There is a triply bridging benzylidyne ligand centered at C(10), and a four-carbon group, C(1)-C(2)-C(3)-C(4), that could be described as a dimetallatriphenylbutadiene ligand. These four atoms are π-bonded to Mo(2), while C(1) and C(4) are also σ-bonded to Mo(1). The shortness of the C-C bonds, C(1)-C(2) = 1.43 (1) Å, C(2)-C(3) = 1.42 (1) Å, and C(3)-C(4) = 1.45 (1) Å, is suggestive of the expected unsa-

Table V. Intramolecular Bond Angles (deg) for 2a and 2b[a]

	angles	
	2a	**2b**
Mo(2)-Mo(1)-Co	61.11 (3)	59.42 (2)
Mo(2)-Mo(1)-C(1)	54.8 (2)	54.8 (1)
Mo(2)-Mo(1)-C(4)	107.7 (2)	105.9 (1)
Co-Mo(1)-C(1)	50.2 (2)	50.3 (1)
Co-Mo(1)-C(4)	47.4 (2)	46.6 (1)
C(1)-Mo(1)-C(4)	71.2 (3)	73.6 (2)
C(1)-Mo(1)-C(43)	67.0 (3)	136.4 (2)
C(4)-Mo(1)-C(43)	95.8 (3)	86.3 (2)
Mo(1)-Mo(2)-Co	56.38 (3)	57.51 (2)
Mo(1)-Mo(2)-O(1)	74.1 (1)	71.3 (1)
Mo(1)-Mo(2)-C(1)	47.9 (2)	45.9 (1)
Mo(1)-Mo(2)-C(41)	62.9 (2)	58.1 (2)
Mo(1)-Mo(2)-C(42)	73.9 (2)	80.6 (2)
Co-Mo(2)-O(1)	74.9 (1)	75.7 (1)
Co-Mo(2)-C(1)	46.9 (2)	47.8 (1)
Co-Mo(2)-C(41)	119.2 (2)	112.5 (2)
Co-Mo(2)-C(42)	74.7 (2)	67.6 (2)
O(1)-Mo(2)-C(1)	32.6 (2)	32.4 (1)
O(1)-Mo-(2)-C(41)	87.0 (3)	101.2 (2)
O(1)-Mo(2)-C(42)	144.5 (3)	141.9 (2)
C(1)-Mo(2)-C(41)	89.9 (3)	96.0 (2)
C(1)-Mo(2)-C(42)	112.0 (3)	109.9 (2)
Mo(1)-Co-Mo(2)	62.51 (3)	63.07 (2)
Mo(1)-Co-C(31)	101.2 (3)	108.9 (2)
Mo(1)-Co-C(32)	150.0 (3)	145.4 (2)
C(1)-Co-C(4)	74.4 (3)	75.0 (2)
Mo(2)-O(1)-C(1)	85.6 (4)	85.9 (3)
Mo(1)-C(1)-Mo(2)	77.3 (2)	79.3 (2)
Mo(1)-C(1)-Co	77.5 (2)	80.2 (2)
Mo(1)-C(1)-O(1)	121.6 (5)	120.9 (3)
Mo(1)-C(1)-C(2)	118.7 (5)	117.4 (3)
Mo(2)-C(1)-Co	77.2 (2)	75.6 (1)
Mo(2)-C(1)-O(1)	61.8 (4)	61.7 (2)
Mo(2)-C(1)-C(2)	135.6 (5)	135.2 (3)
Co-C(1)-O(1)	125.9 (5)	124.6 (3)
O(1)-C(1)-C(2)	119.7 (7)	121.7 (4)
C(1)-C(2)-C(3)	113.3 (7)	113.9 (4)
C(1)-C(2)-C(8)	118.8 (7)	119.6 (4)
C(3)-C(2)-C(8)	127.8 (7)	126.4 (5)
C(2)-C(3)-C(4)	112.0 (7)	113.0 (5)
C(2)-C(3)-C(6)	124.7 (8)	123.6 (5)
C(4)-C(3)-C(6)	123.1 (7)	123.4 (5)
Mo(1)-C(4)-Co	81.9 (3)	83.7 (2)
Mo(1)-C(4)-C(3)	123.3 (5)	119.6 (4)
Co-C(4)-C(3)	73.4 (4)	71.9 (3)
Mo(2)-C(41)-O(41)	162.0 (7)	157.3 (5)
M-C-O(av)	175.5 (8)	174.2 (5)

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

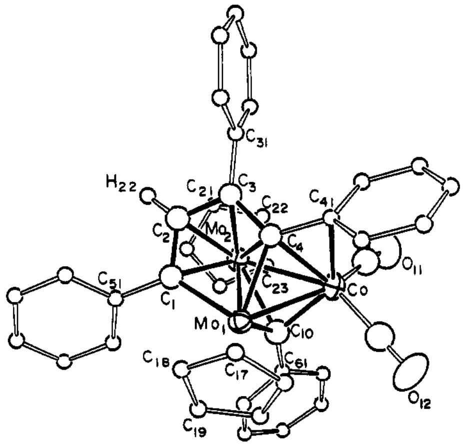

Figure 3. ORTEP diagram of $Mo_2Co(CO)_2Cp_2[\mu_3\text{-}C(Ph)C(H)C(Ph)C(Ph)](\mu_3\text{-}CPh)$ (**3**).

Table VI. Positional Parameters and *B*(eq) for 3

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mo(1)	0.08343 (03)	0.04246 (07)	0.16134 (05)	2.31 (3)
Mo(2)	0.15589 (03)	0.12968 (07)	0.17224 (05)	2.37 (3)
Co	0.10858 (04)	0.25414 (12)	0.22423 (08)	2.77 (5)
O(11)	0.1773 (02)	0.4318 (07)	0.3055 (05)	5.8 (4)
O(12)	0.0577 (02)	0.2616 (07)	0.3113 (04)	5.6 (4)
C(1)	0.1128 (03)	-0.0179 (08)	0.0944 (05)	2.4 (2)
C(2)	0.1175 (03)	0.0660 (08)	0.0424 (05)	2.6 (2)
C(3)	0.1021 (03)	0.1818 (08)	0.0419 (05)	2.3 (2)
C(4)	0.0809 (03)	0.1957 (08)	0.0926 (05)	2.1 (2)
C(10)	0.1363 (03)	0.1031 (08)	0.2622 (05)	2.9 (2)
C(11)	0.1501 (04)	0.3645 (10)	0.2716 (06)	3.6 (2)
C(12)	0.0764 (03)	0.2605 (09)	0.2742 (06)	3.5 (2)
C(15)	0.0506 (03)	-0.0437 (09)	0.2346 (06)	3.9 (2)
C(16)	0.0179 (03)	0.0304 (09)	0.1777 (06)	3.5 (2)
C(17)	0.0061 (03)	-0.0114 (09)	0.0995 (06)	3.4 (2)
C(18)	0.0314 (03)	-0.1135 (09)	0.1087 (06)	3.5 (2)
C(19)	0.0584 (03)	-0.1351 (09)	0.1919 (06)	3.9 (2)
C(21)	0.2171 (03)	0.1714 (09)	0.1503 (06)	3.5 (2)
C(22)	0.2182 (03)	0.2544 (09)	0.2061 (06)	3.5 (2)
C(23)	0.2250 (03)	0.1956 (09)	0.2766 (06)	4.0 (2)
C(24)	0.2283 (03)	0.0741 (09)	0.2645 (06)	3.7 (2)
C(25)	0.2229 (03)	0.0598 (09)	0.1858 (06)	3.6 (2)
C(31)	0.1021 (03)	0.2665 (08)	-0.0183 (05)	2.5 (2)
C(32)	0.1370 (03)	0.3400 (09)	-0.0051 (06)	3.8 (2)
C(33)	0.1369 (04)	0.4083 (09)	-0.0668 (06)	4.3 (2)
C(34)	0.1001 (04)	0.4064 (09)	-0.1426 (06)	4.3 (2)
C(35)	0.0653 (04)	0.3360 (10)	-0.1573 (07)	4.5 (3)
C(36)	0.0661 (03)	0.2660 (09)	-0.0956 (06)	3.5 (2)
C(41)	0.0597 (03)	0.3092 (08)	0.0956 (05)	2.5 (2)
C(42)	0.0168 (03)	0.3121 (09)	0.0915 (06)	3.3 (2)
C(43)	-0.0019 (03)	0.4172 (09	0.0969 (06)	3.9 (2)
C(44)	0.0201 (04)	0.5194 (10)	0.1054 (06)	4.4 (2)
C(45)	0.0605 (03)	0.5216 (09)	0.1079 (06)	4.0 (2)
C(46)	0.0809 (03)	0.4176 (09)	0.1038 (05)	3.1 (2)
C(51)	0.1270 (03)	-0.1404 (08)	0.0901 (05)	2.6 (2)
C(52)	0.1156 (03)	-0.1952 (09)	0.0174 (06)	3.7 (2)
C(53)	0.1307 (04)	-0.3080 (10)	0.0158 (07)	4.5 (3)
C(54)	0.1549 (04)	-0.3685 (10)	0.0865 (06)	4.4 (2)
C(55)	0.1653 (03)	-0.3184 (09)	0.1579 (06)	3.8 (2)
C(56)	0.1515 (03)	-0.2033 (09)	0.1605 (06)	3.6 (2)
C(61)	0.1650 (03)	0.0651 (08)	0.3471 (06)	3.0 (2)
C(62)	0.1860 (04)	0.1425 (10)	0.4116 (07)	4.6 (3)
C(63)	0.2177 (04)	0.1033 (11)	0.4889 (07)	5.3 (3)
C(64)	0.2287 (04)	-0.0107 (11)	0.5012 (07)	5.4 (3)
C(65)	0.2070 (04)	-0.0910 (11)	0.4426 (07)	5.6 (3)
C(66)	0.1743 (04)	-0.0520 (10)	0.3651 (07)	4.8 (3)

Table VII. Intramolecular Distances (Å) for 3[a]

Mo(1)–C(10)	2.01 (1)	Mo(2)–C(4)	2.382 (9)
Mo(1)–C(1)	2.066 (9)	Mo(2)–Co	2.663 (2)
Mo(1)–C(4)	2.155 (9)	Co–C(12)	1.76 (1)
Mo(1)–C(15)	2.37 (1)	Co–C(11)	1.78 (1)
Mo(1)–C(18)	2.37 (1)	Co–C(10)	1.93 (1)
Mo(1)–C(19)	2.38 (1)	Co–C(41)	2.272 (9)
Mo(1)–C(17)	2.40 (1)	Co–C(4)	2.287 (9)
Mo(1)–C(16)	2.40 (1)	O(11)–C(11)	1.14 (1)
Mo(1)–Mo(2)	2.579 (2)	O(12)–C(12)	1.15 (1)
Mo(1)–Co	2.650 (2)	C(1)–C(2)	1.43 (1)
Mo(2)–C(10)	2.116 (9)	C(1)–C(51)	1.50 (1)
Mo(2)–C(1)	2.256 (9)	C(2)–C(3)	1.42 (1)
Mo(2)–C(2)	2.268 (9)	C(3)–C(4)	1.45 (1)
Mo(2)–C(25)	2.31 (1)	C(3)–C(31)	1.49 (1)
Mo(2)–C(24)	2.33 (1)	C(4)–C(41)	1.50 (1)
Mo(2)–C(3)	2.327 (9)	C(10)–C(61)	1.48 (1)
Mo(2)–C(23)	2.35 (1)	C(Cp)–C(av)	1.41 (1)
Mo(2)–C(21)	2.36 (1)	C(Ph)–C(av)	1.38 (1)
Mo(2)–C(22)	2.38 (1)		

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

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

C(4)–Mo(1)–Mo(2)	59.6 (2)	C(41)–Co–Mo(1)	82.1 (2)
C(4)–Mo(1)–Co	55.7 (2)	C(41)–Co–Mo(2)	91.2 (2)
Mo(2)–Mo(1)–Co	61.21 (4)	C(4)–Co–Mo(1)	51.1 (2)
C(10)–Mo(2)–Co	46.0 (2)	C(4)–Co–Mo(2)	56.9 (2)
C(4)–Mo(2)–Mo(1)	51.3 (2)	Mo(1)–Co–Mo(2)	58.08 (5)
C(4)–Mo(2)–Co	53.6 (2)	C(3)–C(2)–C(1)	117.8 (8)
Mo(1)–Mo(2)–Co	60.71 (5)	C(2)–C(3)–C(4)	113.2 (8)
C(12)–Co–Mo(1)	97.2 (3)	Mo(1)–C(4)–Co	73.2 (3)
C(12)–Co–Mo(2)	149.6 (4)	Mo(1)–C(4)–Mo(2)	69.1 (2)
C(11)–Co–Mo(1)	151.5 (3)	Co–C(4)–Mo(2)	69.5 (2)
C(11)–Co–Mo(2)	94.9 (3)	C(61)–C(10)–Co	127.8 (7)
C(10)–Co–C(41)	128.3 (4)	C(61)–C(10)–Mo(1)	138.1 (7)
C(10)–Co–C(4)	90.8 (3)	C(61)–C(10)–Mo(2)	127.3 (6)
C(10)–Co–Mo(1)	49.1 (3)	C(4)–C(41)–Co	71.3 (5)
C(10)–Co–Mo(2)	51.9 (3)	C–O(av)–Co	176 (1)
C(41)–Co–C(4)	38.4 (3)		

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

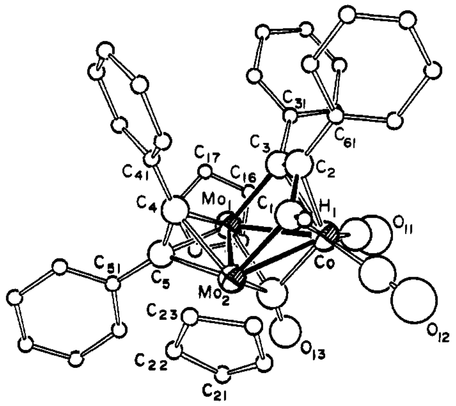

Figure 4. ORTEP diagram of Mo$_2$Co(CO)$_2$Cp$_2$(μ_3-CO)(μ-PhC$_2$Ph)[μ_3-C(H)C(Ph)C(Ph)] (4).

turation in the group, while the near equivalence of the three bonds indicates that the unsaturation is fully delocalized. Interestingly, the phenyl group on C(4) is weakly bonded to the cobalt atom, Co–C(41) = 2.272 (9) Å and Co–C(4) = 2.287 (9) Å. This weak "agostic-like"[8] interaction may be due to the unusual unsaturation present in the molecule; vide infra. This interaction does not appear to affect the C(4)–C(41) distance significantly, since this distance, 1.50 (1) Å, is not significantly different from the distances in the groups C(3)–C(31) and C(1)–C(51), 1.49 (1) and 1.50 (1) Å, for which no agostic-like interactions are present.

An ORTEP diagram of the molecular structure of 4 is shown in Figure 4. Final atomic positional parameters are listed in Table IX. Selected bond distances and angles are listed in Tables X and XI. This molecule also consists of a triangular Mo$_2$Co cluster with an unusually short Mo–Mo distance of 2.567 (2) Å. The Mo–Co distances are similar, 2.673 (2) and 2.697 (2) Å, to those in **1**, **2a**, **2b**, and **3**. Each molybdenum atom has a cyclopentadienyl ligand, while the cobalt atom contains two linear terminal carbonyl groups. There is a triply bridging carbonyl ligand C(13)–O(13) with the usual low-frequency infrared absorption, 1666 cm^{-1}. A dimetallaphenylallyl ligand bridges the Mo$_2$Co triangle and is π-bonded to the cobalt atom and σ-bonded to each of the molybdenum atoms. Finally, there is a bridging PhC$_2$Ph ligand across the Mo–Mo bond in the usual μ-$\perp$ bonding mode.[10]

Previous studies have shown that the alkylidynetricobalt carbonyl cluster complexes **5** react with alkynes by cluster fragmentation to yield the well-known alkyne-bridged

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[8] We have used the term "agostic-like" rather than agostic, since the latter term is normally reserved for three-center, two-electron metal–hydrogen–carbon interactions.[9]

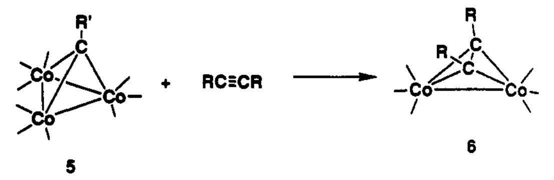
[9] (a) Brookhart, M.; Green, M. H. L.; Wong, L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299 and references therein.

[10] Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Radio Chem.* **1985**, *29*, 169.

Table IX. Positional Parameters and B(eq) Values for 4

atom	x	y	z	B(eq), Å^2
Mo(1)	0.40325 (3)	0.10486 (9)	0.61378 (6)	3.37 (6)
Mo(2)	0.34754 (3)	0.05591 (9)	0.51192 (7)	3.34 (6)
Co	0.33951 (5)	0.2092 (1)	0.6136 (1)	3.9 (1)
O(11)	0.3503 (4)	0.257 (1)	0.7822 (6)	8.4 (7)
O(12)	0.2587 (3)	0.225 (1)	0.5929 (7)	8.4 (8)
O(13)	0.3363 (3)	0.0080 (7)	0.6902 (5)	4.9 (5)
C(1)	0.3374 (3)	0.211 (1)	0.4928 (7)	3.8 (3)
C(2)	0.3629 (3)	0.288 (1)	0.5211 (7)	3.4 (3)
C(3)	0.3910 (3)	0.262 (1)	0.5807 (7)	3.4 (3)
C(4)	0.4029 (3)	0.0840 (9)	0.4800 (7)	3.4 (3)
C(5)	0.4037 (3)	-0.004 (1)	0.5205 (7)	3.2 (3)
C(11)	0.3461 (4)	0.241 (1)	0.715 (1)	5.1 (8)
C(12)	0.2907 (5)	0.220 (1)	0.6004 (9)	5.7 (9)
C(13)	0.3504 (4)	0.057 (1)	0.6413 (8)	4.5 (8)
C(15)	0.4244 (5)	0.075 (3)	0.748 (1)	7 (1)
C(16)	0.4396 (7)	0.166 (1)	0.728 (1)	6 (1)
C(17)	0.4638 (5)	0.147 (2)	0.672 (1)	7 (1)
C(18)	0.4633 (7)	0.046 (2)	0.659 (1)	7 (1)
C(19)	0.4393 (8)	0.004 (2)	0.705 (2)	8 (1)
C(21)	0.308 (1)	-0.077 (3)	0.500 (2)	16 (3)
C(22)	0.3294 (7)	-0.087 (2)	0.439 (2)	9 (1)
C(23)	0.3214 (8)	-0.011 (3)	0.3898 (9)	7 (1)
C(24)	0.2933 (9)	0.042 (1)	0.422 (2)	10 (2)
C(25)	0.2872 (8)	-0.007 (4)	0.482 (2)	17 (3)
C(31)	0.4172 (3)	0.347 (1)	0.6121 (7)	3.9 (3)
C(32)	0.4483 (4)	0.365 (1)	0.5743 (8)	4.8 (3)
C(33)	0.4735 (4)	0.443 (1)	0.5998 (9)	5.9 (4)
C(34)	0.4662 (4)	0.504 (1)	0.662 (1)	6.0 (4)
C(35)	0.4360 (5)	0.489 (1)	0.699 (1)	6.5 (4)
C(36)	0.4103 (4)	0.408 (1)	0.6762 (9)	5.8 (4)
C(41)	0.4212 (3)	0.1368 (9)	0.4192 (7)	3.1 (3)
C(42)	0.4595 (4)	0.144 (1)	0.4240 (8)	4.4 (3)
C(43)	0.4767 (4)	0.198 (1)	0.3648 (9)	5.2 (3)
C(44)	0.4556 (4)	0.243 (1)	0.3042 (8)	5.1 (3)
C(45)	0.4176 (4)	0.236 (1)	0.2989 (8)	5.0 (3)
C(46)	0.4002 (4)	0.182 (1)	0.3559 (8)	4.1 (3)
C(51)	0.4179 (3)	-0.108 (1)	0.5142 (7)	3.4 (3)
C(52)	0.4401 (3)	-0.135 (1)	0.4554 (7)	4.3 (3)
C(53)	0.4513 (4)	-0.236 (1)	0.4466 (8)	5.2 (3)
C(54)	0.4398 (4)	-0.307 (1)	0.4995 (9)	5.7 (4)
C(55)	0.4180 (4)	-0.280 (1)	0.5566 (9)	5.4 (3)
C(56)	0.4069 (4)	-0.181 (1)	0.5643 (8)	4.6 (3)
C(61)	0.3550 (4)	0.395 (1)	0.4914 (7)	4.1 (3)
C(62)	0.3287 (5)	0.450 (1)	0.522 (1)	7.2 (4)
C(63)	0.3213 (5)	0.553 (1)	0.492 (1)	8.5 (5)
C(64)	0.3411 (5)	0.588 (1)	0.437 (1)	7.6 (5)
C(65)	0.3673 (5)	0.536 (1)	0.408 (1)	6.8 (4)
C(66)	0.3755 (4)	0.437 (1)	0.4354 (9)	5.9 (4)
C(71)	0.763 (1)	0.124 (3)	0.729 (2)	9 (1)
C(72)	0.755 (1)	0.214 (4)	0.697 (2)	10 (1)
C(73)	0.775 (1)	0.276 (3)	0.686 (2)	8 (1)
C(74)	0.810 (1)	0.237 (3)	0.703 (2)	7.1 (9)
C(75)	0.816 (1)	0.149 (3)	0.721 (2)	9 (1)
C(76)	0.791 (1)	0.078 (3)	0.743 (2)	9 (1)

dicobalt hexacarbonyl complexes $Co_2(CO)_6(\mu\text{-}RC_2R)$ (**6**, R′ = Me, Ph, CO_2Me; eq 3).[11] We have investigated the



(3)

corresponding reaction of **5**, R = H, and obtained a similar result. There was no evidence for products involving coupling of the methylidyne ligand of **5** to EtC_2Et or PhC_2Ph.

Discussion

It is well-known that $[CpMo(CO)_2]_2$ will react with alkynes to produce alkyne oligomerization.[12] It has been shown that sulfur-bridged metal clusters containing the Cp_2Mo_2 grouping also possess the ability to couple alkynes.[3,13] It was our goal to determine if the alkylidyne-bridged cluster **1** would also exhibit the ability to couple alkynes. This result was not achieved. In the reactions of **1**, both with EtC_2Et and PhC_2Ph, we observed preferred reactions that involved coupling of the alkyne to the methylidyne ligand (eqs 4 and 5).

Table X. Intramolecular Distances (Å) for 4[a]

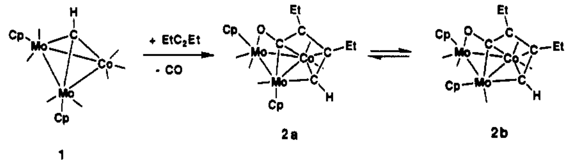
Mo(1)–C(13)	2.10 (1)	Co–C(2)	2.13 (1)
Mo(1)–C(5)	2.13 (1)	O(11)–C(11)	1.14 (1)
Mo(1)–C(3)	2.19 (1)	O(12)–C(12)	1.14 (2)
Mo(1)–C(4)	2.28 (1)	O(13)–C(13)	1.21 (1)
Mo(1)–Mo(2)	2.567 (2)	C(1)–C(2)	1.42 (2)
Mo(1)–Co	2.673 (2)	C(2)–C(3)	1.39 (1)
Mo(2)–C(1)	2.10 (1)	C(2)–C(61)	1.52 (2)
Mo(2)–C(4)	2.15 (1)	C(3)–C(31)	1.52 (2)
Mo(2)–C(5)	2.15 (1)	C(4)–C(5)	1.34 (1)
Mo(2)–C(13)	2.18 (1)	C(4)–C(41)	1.46 (1)
Mo(2)–Co	2.697 (2)	C(5)–C(51)	1.48 (2)
Co–C(12)	1.75 (2)	C(Cp)–Mo(av)	2.32 (2)
Co–C(11)	1.76 (2)	C(Cp)–C(av)	1.33 (3)
Co–C(1)	2.03 (1)	C(Ph)–C(av)	1.38 (2)
Co–C(13)	2.10 (1)	C(ben)–C(av)	1.26 (4)
Co–C(3)	2.11 (1)		

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

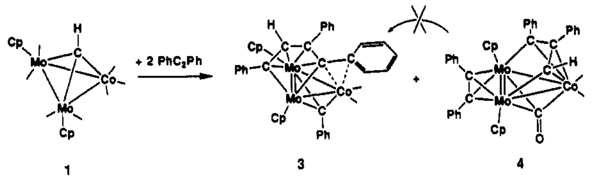
Table XI. Intramolecular Bond Angles (deg) for 4[a]

Mo(2)–Mo(1)–Co	61.91 (6)	C(61)–C(2)–Co	128.6 (9)
C(1)–Mo(2)–C(4)	86.7 (5)	C(2)–C(3)–C(31)	116 (1)
C(1)–Mo(2)–C(5)	120.8 (5)	C(31)–C(3)–Co	132.6 (9)
Mo(1)–Mo(2)–Co	60.98 (5)	C(31)–C(3)–Mo(1)	121.2 (8)
C(12)–Co–C(11)	97.2 (7)	C(5)–C(4)–C(41)	142 (1)
C(12)–Co–C(13)	105.3 (7)	C(41)–C(4)–Mo(2)	139.7 (9)
C(12)–Co–Mo(1)	152.5 (6)	C(41)–C(4)–Mo(1)	133.6 (8)
C(12)–Co–Mo(2)	99.1 (5)	C(4)–C(5)–C(51)	139 (1)
C(11)–Co–C(1)	164.6 (6)	C(51)–C(5)–Mo(1)	135.5 (9)
C(11)–Co–Mo(1)	95.9 (5)	C(51)–C(5)–Mo(2)	131.5 (9)
C(11)–Co–Mo(2)	142.2 (5)	O(13)–C(13)–Co	126 (1)
Mo(1)–Co–Mo(2)	57.11 (5)	O(13)–C(13)–Mo(1)	141 (1)
C(3)–C(2)–C(1)	117 (1)	O(13)–C(13)–Mo(2)	135 (1)
C(3)–C(2)–C(61)	124 (1)	O–C(av)–Co	178 (2)
C(1)–C(2)–C(61)	118 (1)		

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



(4)



(5)

The coupling of the EtC_2Et molecule to the methylidyne ligand in **1** was accompanied by the coupling to a CO ligand. We suspect that the reaction may have proceeded

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through an intermediate containing a dimetallaallyl ligand such as that observed in 4 before the coupling to the CO ligand. Stone has recently reported examples of the coupling of CO to dimetallaallyl ligands in dinuclear metal complexes.[14] Our reaction appears to be unique, since the oxygen atom of the CO grouping has become coordinated to one of the metal atoms. The product exists as a mixture of isomers **2a** and **2b** that slowly interconvert at 52 °C. The isomerization mechanism was not established but could be as simple as a polytopal rearrangement of Cp and CO ligands on Mo(1) involving a 180° rotation of the Cp/CO pair.

The reaction of 1 with PhC_2Ph yielded two products, **3** and **4**. In both products, the methylidyne ligand is bonded to PhC_2Ph groups. In **4**, this resulted in the formation of a triply bridging dimetalladiphenylallyl ligand. A second molecule of PhC_2Ph was added to the cluster, but it did not couple to the dimetallallyl ligand. Compound **4** contains only 46 valence electrons, which is 2 less than that required by the effective atomic number rule. We think that this electronic unsaturation is at least partially responsible for the short Mo–Mo distance in this compound.

The formation of compound **3** must have involved several unobserved rearrangements. The presence of a triply bridging benzylidyne ligand must be due to a splitting of a PhC_2Ph molecule. This was probably achieved intramolecularly, since an odd PhC grouping is incorporated into the dimetallabutadiene ligand that is also present in this molecule. This ligand contains two adjacent CPh groupings coupled to a CH and the odd CPh group. Although it seems that **4** could be an intermediate en route to **3**, we have *not* yet been able to transform **4** to **3**.

If one ignores the agostic-like C–Ph interaction, **3** has only 44 valence electrons. The shortness of the Mo–Mo bond in **3** is probably also a result of this unsaturation. However, a more interesting result is the unusual agostic interaction of the C–Ph group to the cobalt atom. This ligation could increase the electron count on the metal atoms by 2. While there are fair number of reports of agostic hydrogen interactions in organometallic complexes,[9] there are only a few examples of related interactions involving phenyl groups.[15] Such interaction can lead to the cleavage of the phenyl-C carbon–carbon bond,[15] but this was not observed by us in thermal treatments of **3**. We also suspected that the agostic phenyl interaction in **3** could be easily replaced by ligand addition; however, attempts to do this by the addition of CO to **3** produced no reaction.

Although the coupling of alkynes by alkylidynetricobalt carbonyl cluster precursors is known, the reaction is actually due to dicobalt carbonyl fragmentation products.[11] The methylidynedimolybdenumcobalt cluster **1** will add alkynes without fragmentation, but alkyne oligomerization is precluded by facile coupling to the methylidyne ligand.

Acknowledgment. These studies were supported by the National Science Foundation under Grant No. CHE-8919786. We thank Mr. Gong Chen for assistance with the structural analyses.

Supplementary Material Available: For all of the structural analyses, tables of hydrogen atom parameters and anisotropic thermal parameters (16 pages); tables of structure factor amplitudes (62 pages). Ordering information is given on any current masthead page.

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