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Reactions of a Cobalt–Molybdenum and Related Cobalt–Tungsten Tetrahedral Clusters with Phenylacetylene: Formation of Tetrametallic Alkyne Clusters or Cluster Fragmentation?

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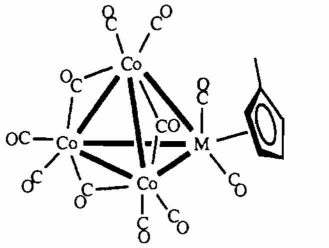
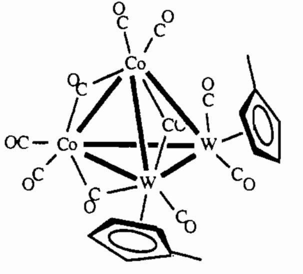
The reactions of the tetrahedral mixed-metal clusters $Co_3M(CO)_{11}(\eta^5\text{-}C_5H_4Me)$ (M = Mo, **1a**; M = W, **1b**), $Co_2W_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (**2**), and $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (**3**) with PhC_2H have been investigated. **1a** affords the cluster $Co_3Mo(CO)_9(\mu_4\text{-}\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_4Me)$ (**5**) when treated with this alkyne. The structure of **5** was established by an X-ray diffraction study. It consists of a Co_3Mo butterfly core with the molybdenum atom in a wing-tip position. A $\mu_4\text{-}PhC_2H$ ligand interacts with all the metals. **5**, $C_{23}H_{13}O_9Co_3Mo$, crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 9.272$ (2) Å, $b = 14.608$ (2) Å, $c = 17.752(3)$ Å, $\beta = 95.132(9)°$, $V = 2394$ (1) Å^3, and $Z = 4$. The structure was refined to $R = 0.030$ and $R_w = 0.040$ using the 2235 unique data with $I > 3\sigma(I)$. The cluster $Co_2W_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (**2**) affords $Co_2W_2(\mu_4\text{-}\eta^2\text{-}PhC_2H)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**7**), which has a $Co_2W_2C_2$ butterfly core geometry, when treated with PhC_2H. In contrast, its tricobalt-tungsten analogue $Co_3W(CO)_{11}(\eta^5\text{-}C_5H_4Me)$ (**1b**) and the sterically congested tritungsten cluster $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (**3**) rupture when treated with PhC_2H. The products included PhC_2H oligomers, the cobalt tungstenacycle $(\eta^5\text{-}C_5H_4Me)(OC)_2W\{\mu\text{-}\eta^2,\eta^4\text{-}C(Ph)C(H)C(H)C(Ph)\}Co(CO)_2$ (Co–W) (**6**), and the species $(OC)_2Co\{\mu\text{-}\eta^3,\eta^3\text{-}C(H)C(Ph)C(H)C(Ph)C(H)C(Ph)\}W(CO)(\eta^5\text{-}C_5H_4Me)$ (Co–W) (**8**). The reaction of $CoW(CO)_7(\eta^5\text{-}C_5H_4Me)$ (Co–W) (**4**) with PhC_2H affords $CoW(CO)_5(\mu\text{-}\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_4Me)$ (Co–W) (**9**), **6**, and **8**. Reaction of **9** with PhC_2H yields the tungstenacyclopentadiene species **6**. The flyover species **8** is not formed from addition of PhC_2H to **6**.

Introduction

We recently reported the synthesis of the clusters $Co_3M(CO)_{11}(\eta^5\text{-}C_5H_4Me)$ (M = Mo, **1a**; M = W, **1b**), $Co_2W_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (**2**), and $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (**3**).[1] The CoW_3 cluster completed the set of 60-electron clusters with Co_xW_{4-x} (x = 1–4) tetrahedral metallic cores. The reactivity of $Co_4(\mu\text{-}CO)_3(CO)_9$ with alkynes has long been known,[2] but reactions of **1–3** with these ligands had not yet been investigated in a comparative fashion. These clusters provide an interesting template on which to investigate how the reactivity of these molecules varies as a function of the Co:W ratio. Herein, we describe how these cobalt–tungsten clusters and a cobalt–molybdenum analogue behave toward PhC_2H. The products obtained from these cluster reactions led us to investigate how the heterobimetallic species $CoW(CO)_7(\eta^5\text{-}C_5H_4Me)$ (Co–W) (**4**) behaved toward phenylacetylene.



1a, M = Mo
1b, M = W



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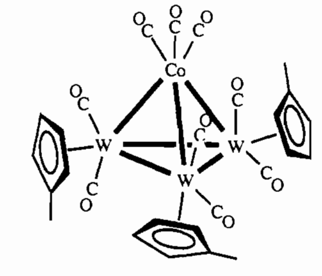

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Results and Discussion

(1) (a) Reaction of $Co_3Mo(CO)_{11}(\eta^5\text{-}C_5H_4Me)$ (1a) with PhC_2H. The titled cluster was prepared by reacting the heterobimetallic species $CoMo(CO)_7(\eta^5\text{-}C_5H_4Me)$ (**4**) with dicobalt octacarbonyl.[1] The reaction of **1a** with PhC_2H did not proceed at ambient temperatures, but when the reactants were maintained at elevated temperatures in toluene, a color change (purple brown to black) was observed. The resultant solution consisted of various components that were partially separated by silica gel chromatography. A slower moving purple-black band incorporated a single species (**5**); a faint yellow band contained various uncharacterized compounds.

(b) Spectroscopic and Structural Data for 5. The color and chromatographic mobility of **5** suggested that this species was a metal cluster. ^1H NMR data (Table I) were of limited utility but did indicate the presence of PhC_2H and methylcyclopentadienyl ligands in a 1:1 ratio. The absence of a mirror plane that bisected the dienyl ligand was inferred from the ABCD pattern observed for the aromatic C_5H_4Me protons. The IR spectrum of **5** (Table II) disclosed terminal, semibridging, and doubly bridging carbonyl ligands. A parent ion with a m/e ratio of 708 was exhibited in the MS data for **5**, with an isotopic envelope consistent with a single molybdenum atom being present. Ions corresponding to the loss of 1–9 CO ligands from the molecular ion were also noted. Data are in agreement with **5** having the formula $Co_3Mo(CO)_9(\mu_4\text{-}\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_4Me)$. The reaction is described by eq 1.

$$\underset{\textbf{1a}}{Co_3Mo(CO)_{11}(\eta^5\text{-}C_5H_4Me)} + PhC_2H \rightarrow \underset{\textbf{5}}{Co_3Mo(CO)_9(\mu_4\text{-}PhC_2H)(\eta^5\text{-}C_5H_4Me)} + \ldots \quad (1)$$

As the molecular geometry of **5** could not be ascertained, an X-ray diffraction study was undertaken. Tables of selected crystal data, atomic positional parameters, and important bond lengths and bond angles are collected in Tables III–VI, respectively. Figure 1 shows a molecular plot.

(c) Description of the Structure. **5** is a 60-electron Co_3Mo cluster in which the metals adopt a butterfly geometry: the molybdenum atom resides in one of the wing-tip positions. A PhC_2H ligand bridges all four metals in a $\mu_4\text{-}\eta^2$-fashion, and the cluster has a pseudooctahedral asymmetric Co_3MoC_2 core. The asymmetry stems partly from the different constituent atoms of

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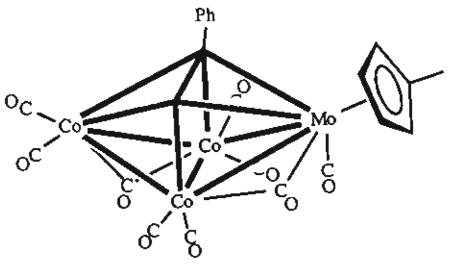

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this core. The two cobalt atoms in the hinge position and the core carbon atoms C(41) and C(42) are almost coplanar, but the octahedron is slightly opened up around C(41), presumably because of the steric congestion resulting from the phenyl group riding on this carbon atom. This is reflected in the differing bond lengths involving comparable atoms for C(41) and C(42) [Mo–C(41) = 2.285 (7) Å, Mo–C(42) = 2.219 (6) Å; Co(1)–C(41) = 2.100 (7) Å, Co(1)–C(42) = 2.063 (6) Å]. There is also asymmetry in the metal–metal bond lengths. The two Mo–Co bonds are distinctly different [2.657 (1) and 2.716 (1) Å for Mo–Co(2)[3] and Mo–Co(3), respectively], but both are within normal ranges observed for cobalt–molybdenum single bonds.[4-7] In the trigonal-bipyramidal cluster $Co_3Mo_2(CO)_7(\mu_3\text{-}S)_2(\eta^5\text{-}C_5H_5)_2$, Co–Mo distances span the 2.652 (1)–2.750 (1) Å range.[8]

The hinge Co(2)–Co(3) bond of 2.549 (1) Å is similar to the (hinge) Co–Co bond distance of 2.554 (1) Å found in the related butterfly cluster $Co_2Mo_2(\mu\text{-}\eta^4\text{-}MeC_2Me)(\eta^5\text{-}C_5H_5)_2$.[5] These bonds are longer than the other two (wing tip–hinge) Co–Co bonds [Co(1)–Co(2) = 2.442 (1) Å; Co(1)–Co(3) = 2.458 (1) Å].[9] Some of the CO ligands exhibit significant bridging character so as to even out electron density in the cluster. The Mo–Co(2) and the Co(1)–Co(3) bonds are bridged by C(B1)–O(B1) and C(13)–O(13), respectively, while C(7)–O(7) (on Mo) semibridges to Co(3).

While tetrametallic alkyne clusters usually adopt the butterfly-type structure seen here, examples that embody a planar tetrametallic framework are known.[10] It is significant that a regiospecific cluster product is obtained in which the molybdenum atom in **5** lies in a wing-tip position. Though more examples exist in which the unique metal resides in the hinge position, such atoms are found in wing-tip positions in butterfly-type alkyne clusters with M'_3M metallic cores.[11] Site selective attack in mixed-metal clusters has been noted: the Co–Co bond is ruptured in each case when the tetrahedral clusters $Co_2Ru_2(CO)_{13}$[12] and $Co_2Rh_2(CO)_{12}$,[13] respectively, are reacted with alkynes, to yield to $\mu_4\text{-}\eta^2\text{-}RC_2R$ clusters. Metal-specific alkyne attack was also reported for $Ir_2W_2(CO)_{10}(\eta^5\text{-}C_5H_5)_2$.[14] Energy differences between metal isomers may be small: framework isomerism is observed[15] for both sets of butterfly clusters with Co_2FeRuC_2 and $CoMoRhRuC_2$ cores.

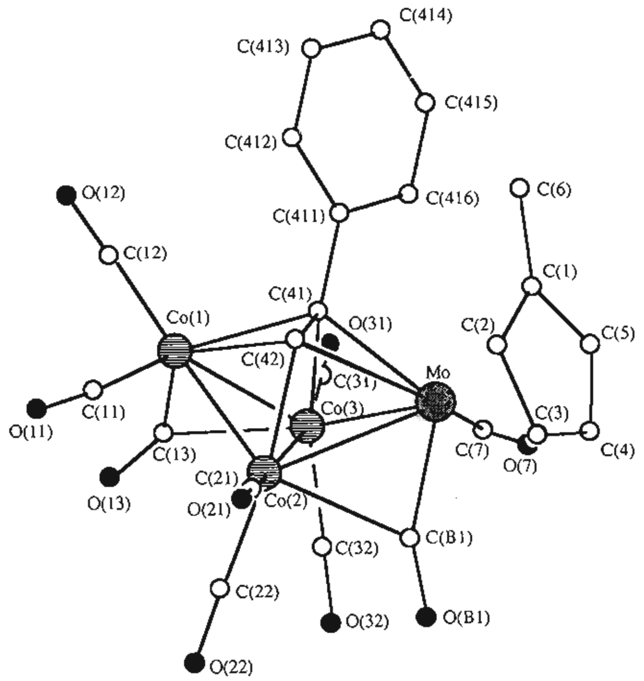

Figure 1. Molecular Editor plot of the structure of $Co_3Mo(CO)_9(\mu_4\text{-}\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_4Me)$ (**5**). Hydrogen atoms are not shown.

(2) Reaction of $Co_3W(CO)_{11}(\eta^5\text{-}C_5H_4Me)$ (1b) with PhC_2H. The cluster $Co_3W(CO)_{11}(\eta^5\text{-}C_5H_4Me)$ (**1b**), the tricobalt–tungsten analogue of **1a**, was also treated with PhC_2H. The reaction surprisingly did not proceed in an analogous fashion, as shown in eq 2. Two yellow bands eluted when the reaction mixture was

$$\underset{\mathbf{1b}}{Co_3W(CO)_{11}(\eta^5\text{-}C_5H_4Me)} + PhC_2H \rightarrow \mathbf{6} + 1,2,4\text{-}C_3H_3Ph_3 + 1,3,5\text{-}C_3H_3Ph_3 + \ldots \quad (2)$$

subjected to chromatography. The first incorporated purely organic products, and subsequent analysis by ^1H NMR and MS showed that it consisted of a mixture of 1,2,4- and 1,3,5-triphenylbenzenes. The second band also was a combination of products, but it contained one predominant component (**6**). Spectroscopic data suggested the presence of both tungsten and cobalt in this mixture. **6** was isolated pure in other reactions, and a discussion of its structure and characterization will be postponed (vide infra).

(3) Reaction of $Co_2W_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (2) with PhC_2H. The titled cluster was heated with PhC_2H in toluene. The dark green color of **2** gave way to a nondescript dark brown color as the reaction proceeded. Chromatography led to the recovery of **2** as the major reaction product. Two other species (colored pale yellow and purple, respectively) also formed in low yields. The yellow band was identified as 1,2,4- and 1,3,5-triphenylbenzenes.

Analysis of the purple species (**7**) indicated cobalt and tungsten were present. Multiplets in the phenyl region of the ^1H NMR spectrum were observed, and resonances for aliphatic and aromatic methylcyclopentadienyl protons (ABCD type pattern) were also noted. Signal integration revealed that the phenyl and methylcyclopentadienyl groups were in a 1:2 ratio. A singlet at δ 7.40 ppm, with $^{183}W\text{-}^1H$ coupling (J_{WH} = 3.8 Hz), was assigned to a PhC_2H proton. The satellites had an intensity of ≈12% of the main peak, suggesting coupling to two equivalent tungsten atoms. IR $\nu(CO)$ bands were observed in the IR spectrum of **7** in regions of the IR spectrum characteristic of both terminal and bridging carbonyl ligands. The observation of some high-energy $\nu(CO)$ stretches implied that cobalt was present.

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(3) This bond is bridged by a carbonyl ligand.

(4) The Co–Mo single bond in the alkyne-bridged species $CoMo(\mu\text{-}CF_3C_2CF_3)(CO)_5(\eta\text{-}C_5H_5)$ is 2.692 (1) Å: Jensen, S. D.; Robinson, B. H.; Simpson, J. *Organometallics* **1986**, *5*, 1690. Values observed in CoMo clusters range from 2.682 (1) to 2.752 (4) Å.[5-7]

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Table I. NMR Data[a] for the Reported Complexes

complex	$C_5\mathit{H}_4Me$[b]	$C_5H_4\mathit{Me}$	$\mathit{Ph}C_2H$	$PhC_2\mathit{H}$
$Co_3Mo(CO)_9(PhC_2H)Cp'$ (**5**)	5.14, 5.23 (3 H)	1.87	7.13–7.27 (5 H)	8.99
$CoW(CO)_4(PhC_2H)_2Cp'$ (**6**)[c]	4.79 (2 H), 4.84 (2 H)	1.68	7.14–7.36 (10 H)	6.7 (2 H), J_{WH} = 6.2
$Co_2W_2(CO)_8(PhC_2H)Cp'_2$ (**7**)	4.51, 4.85, 5.00 (2 H)	2.13	6.45, 6.93, 7.06, 7.21 (2 H)	7.41 (J_{WH} = 3.8)
$CoW(CO)_4(PhC_2H)_3Cp'$ (**8**)	4.06 (2 H), 4.16, 4.34	1.75	6.95–7.85 (15 H)	4.60 (d, J_{HH} = 3.2), 6.79 (d, J_{HH} = 1.0), 6.8 (d of d, J_{HH} = 1.0, 3.2)
$CoW(CO)_5(PhC_2H)Cp'$ (**9**)	5.26, 5.32 (2 H), 5.39	2.19	7.08–7.30 (5 H)	5.61 (J_{WH} = 2.6)

[a] Spectra were recorded on a GE GN 300-MHz instrument in chloroform-d_1. Unless otherwise stated, all signals (in ppm, *J* in Hz) except those of the *Me* (3 H) and $PhC_2\mathit{H}$ protons are multiplets; Cp′ = C_5H_4Me. [b] ABCD type multiplets except for **6**, which exhibits an AA′BB′ pattern. [c] ^{13}C NMR (acetone-d_6, −20 °C): δ 226.5 (W–*C*O's, J_{WC} = 133 Hz), 205.0 (Co–*C*O's), 157.3 (Ph*C*CH, J_{WC} = 73), 154.1 [C(1), Ph], 128.7, 128.5, and 126.9 [C(2), C(3), and C(4), Ph], 120.4 (PhC*C*H, J_{WC} = 8), 106.0 [*C*(Me), Cp′], 91.8 and 88.7 [C(2) and C(3), Cp′], 12.4 (*Me*).

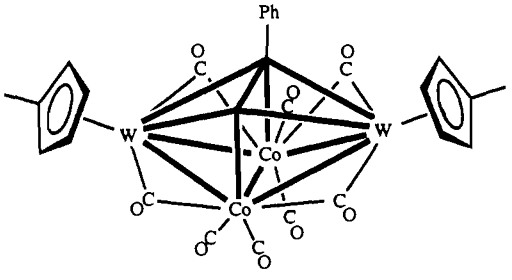
Table II. IR Data for the New Complexes

complex	ν(CO), cm^{-1} (in CH_2Cl_2)
$Co_3Mo(CO)_9(PhC_2H)Cp'$ (**5**)	2074 (s), 2039 (vs), 1864 (w), 1811 (vw)
$CoW(CO)_4(PhC_2H)_2Cp'$ (**6**)	2024 (vs), 1969 (s), 1904 (w)
$Co_2W_2(CO)_8(PhC_2H)Cp'_2$ (**7**)	2048 (vs), 2013 (vs), 1980 (m), 1841 (m), 1794 (m)
$CoW(CO)_4(PhC_2H)_3Cp'$ (**8**)	2013 (vs), 1967 (s), 1941 (w)
$CoW(CO)_5(PhC_2H)Cp'$ (**9**)	2066 (m), 2052 (s), 2005 (s), 1987 (s), 1976 (s), 1961 (m), 1942 (s), 1917 (vw), 1885 (w)

Table III. Crystallographic Data

$MoCo_3O_9C_{24}H_{13}$	fw 706.09
a = 9.272 (2) Å	space group $P2_1/n$ (No. 14)
b = 14.608 (2) Å	λ = 0.71073 Å
c = 17.752 (3) Å	ρ_{calc} = 1.958 g cm^{-3}
β = 95.132 (9)°	μ = 25.90 cm^{-1}
V = 2394 (1) $Å^3$	transm coeff = 1.000–0.851
Z = 4	$R(F_o)$ = 0.030
T = 20 °C	$R_w(F_o)$ = 0.040

Owing to the small sample quantity, spectroscopic data for **7** were limited. However, it can be formulated as $Co_2W_2(\mu_4\text{-}\eta^2\text{-}PhC_2H)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$. Related clusters have been reported. The cyclopentadienyliridium analogue of **2** also undergoes W–W bond cleavage with alkynes to afford isostructural $Ir_2W_2(\eta_4\text{-}\eta^2\text{-}RC_2R)(CO)_8$ species as the major reaction products.[14] The species $Co_2M_2(\mu_4\text{-}\eta^2\text{-}MeC_2Me)(CO)_8(\eta^5\text{-}C_5H_5)_2$ (M = Mo, W)[5] have been synthesized from $Co_2M(\mu_3\text{-}CMe)$ clusters in fragmentation and skeletal reorganization reactions. The molybdenum species was structurally characterized. IR data for these clusters and **7** are similar when one takes into account the different ancillary ligands present (PhC_2H or MeC_2Me and $\eta^5\text{-}C_5H_4Me$ or $\eta^5\text{-}C_5H_5$ groups, respectively, in **7** and in these clusters). The parent ion of **7** was not observed in the mass spectrum, but a peak corresponding to the $(M - 3CO)^+$ ion was noted, with the correct isotopic envelope for a $(Co_x)W_2$ species.[16] The reaction is described by eq 3.



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$$\underset{\mathbf{2}}{Co_2W_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2} + PhC_2H \rightarrow \underset{\mathbf{7}}{Co_2W_2(\mu_4\text{-}PhC_2H)(CO)_8(\eta^5\text{-}C_5H_4Me)_2} + 1,2,4\text{-}C_3H_3Ph_3 + 1,3,5\text{-}C_3H_3Ph_3 \quad (3)$$

Table IV. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*[a] Å
Mo	0.17015 (6)	0.17179 (4)	0.63703 (3)	2.83 (1)
Co(1)	0.0408 (1)	0.28081 (6)	0.81437 (5)	2.85 (2)
Co(2)	0.2489 (1)	0.18997 (7)	0.78390 (5)	3.20 (2)
Co(3)	−0.00903 (9)	0.13604 (6)	0.74639 (5)	2.63 (2)
O(7)	−0.0518 (6)	0.0181 (4)	0.5954 (3)	6.4 (1)
O(11)	0.2576 (7)	0.3486 (4)	0.9275 (3)	7.2 (2)
O(12)	−0.1889 (7)	0.4072 (5)	0.8476 (4)	8.2 (2)
O(13)	−0.0665 (6)	0.1415 (4)	0.9092 (3)	5.1 (1)
O(21)	0.5363 (6)	0.2704 (5)	0.7990 (4)	8.4 (2)
O(22)	0.3180 (7)	0.0484 (4)	0.8982 (3)	7.2 (2)
O(31)	−0.3212 (5)	0.1092 (4)	0.7144 (4)	6.1 (2)
O(32)	0.0540 (7)	−0.0525 (4)	0.7948 (4)	6.5 (2)
O(B1)	0.3670 (6)	0.0201 (4)	0.7117 (3)	5.2 (1)
C(1)	0.1842 (9)	0.2584 (6)	0.5274 (4)	5.5 (2)
C(2)	0.3234 (9)	0.2585 (6)	0.5683 (4)	5.2 (2)
C(3)	0.371 (1)	0.1677 (8)	0.5681 (6)	7.7 (3)
C(4)	0.270 (1)	0.1148 (8)	0.5337 (5)	7.7 (3)
C(5)	0.1573 (9)	0.1676 (6)	0.5070 (4)	5.1 (2)
C(6)	0.103 (2)	0.3376 (9)	0.5047 (8)	11.4 (4)
C(7)	0.0224 (8)	0.0758 (5)	0.6193 (4)	4.1 (2)
C(11)	0.1780 (9)	0.3178 (6)	0.8831 (5)	5.0 (2)
C(12)	−0.099 (1)	0.3583 (5)	0.8338 (4)	4.9 (2)
C(13)	−0.0312 (8)	0.1777 (5)	0.8554 (4)	3.4 (2)
C(21)	0.4252 (9)	0.2401 (6)	0.7926 (5)	4.9 (2)
C(22)	0.2897 (8)	0.1033 (6)	0.8549 (4)	4.3 (2)
C(31)	−0.2005 (8)	0.1204 (5)	0.7252 (4)	3.5 (2)
C(32)	0.0291 (8)	0.0207 (5)	0.7757 (4)	3.8 (2)
C(41)	0.0087 (7)	0.2568 (4)	0.6974 (4)	2.8 (1)
C(42)	0.1542 (7)	0.2846 (4)	0.7196 (3)	2.6 (1)
C(B1)	0.2925 (8)	0.0839 (5)	0.6993 (4)	3.6 (2)
C(411)	−0.1034 (7)	0.3118 (4)	0.6524 (4)	2.8 (1)
C(412)	−0.1060 (8)	0.4071 (5)	0.6604 (4)	3.5 (2)
C(413)	−0.2070 (9)	0.4588 (5)	0.6180 (4)	4.5 (2)
C(414)	−0.3059 (8)	0.4186 (6)	0.5665 (4)	4.7 (2)
C(415)	−0.3046 (8)	0.3259 (6)	0.5575 (4)	4.1 (2)
C(416)	−0.2037 (7)	0.2724 (5)	0.5990 (4)	3.5 (2)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

(4) Reaction of $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (3) with PhC_2H. (a) Description of the Reaction and Spectroscopic Data. This reaction led to the isolation of three new species, in addition to recovery of **3**. One of these compounds was characterized spectroscopically as the ditungsten alkyne-bridged complex $W_2(\mu\text{-}\eta^2\text{-}PhC_2H)(CO)_4(\eta^5\text{-}C_5H_4Me)_2$ (W–W). The second (yellow) and third (purple) components of the reaction mixture both contained cobalt and tungsten. Their spectroscopic signatures and structural characterization are discussed here.

The yellow product separated chromatographically from the reaction mixture, and this proved to be complex **6**. (This species was also the major product of a yellow band isolated in the reaction of **2** with PhC_2H.) ^1H NMR data showed the existence of a $\eta^5\text{-}C_5H_4Me$ group. The appearance of the aromatic protons (which formed an AA′BB multiplet) indicated that an effective mirror plane of symmetry bisected this ligand. Multiplets in the phenyl

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(16) Cobalt has only one naturally occurring isotope—^{59}Co.

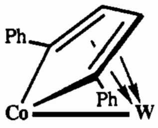
region of the spectrum disclosed that there were two phenyl groups per methylcyclopentadienyl ligand in **6**. A singlet in the olefinic region of the spectrum was flanked by ^{183}W satellites (J_{WH} = 6.2 Hz).

The IR spectrum of **6** showed ν(CO) bands at frequencies characteristic of terminal CO ligands. MS data showed a parent peak with an m/e ratio of 638 amu and an isotopic envelope typical of a $(Co_x)W$ species. Peaks corresponding to loss of one and two CO ligands were observed. These data are consistent with $CoW(CO)_4(PhC_2H)(\eta^5\text{-}C_5H_4Me)$ representing the formula of **6**.

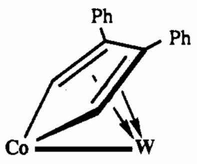
The purple complex (**8**) was isolated in low yields, and this complicated the structural elucidation of this species. ^1H NMR data revealed the existence of a $\eta^5\text{-}C_5H_4Me$ group and suggested the presence of tungsten in this molecule. Aromatic protons of this group resonated as an ABCD type multiplet, indicating the absence of a formal mirror plane. Phenyl resonances were also observed; integration of these signals showed a phenyl to methylcyclopentadienyl ligand ratio of 3:1. Three multiplets, each integrating to a single proton, were seen in the olefinic region of the spectrum. The IR spectrum of **8** resembled that of **6** in that it exhibited terminal ν(CO) stretches only. MS data are in accord with **8** having the empirical formula $CoW(CO)_3(PhC_2H)_3(\eta^5\text{-}C_5H_4Me)$.

$$\underset{\mathbf{3}}{CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3} + PhC_2H \rightarrow \underset{\mathbf{6}}{CoW(CO)_4(PhC_2H)_2(\eta^5\text{-}C_5H_4Me)} + \underset{\mathbf{8}}{CoW(CO)_3(PhC_2H)_3(\eta^5\text{-}C_5H_4Me)} + W_2(\mu\text{-}\eta^2\text{-}PhC_2H)(CO)_4(\eta^5\text{-}C_5H_4Me)_2 \quad (4)$$

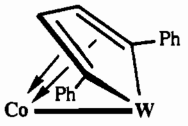
(b) Elucidation of the Structures of Complexes 6 and 8. The observation that only one isomer, out of many possible ones, is obtained for both **6** and **8** is noteworthy. For **6**, the ^1H NMR data, especially the olefinic resonances noted for the $PhC_2\mathit{H}$ protons, suggested that the two alkynes had linked with a metal to form a metallacyclopentadiene complex. Two PhC_2H ligands can be tethered in three possible ways: head-to-head, head-to-tail, or tail-to-tail. In each case the metallacycle can incorporate either cobalt- or tungsten-carbon σ bonds, so six possible isomers may be envisioned. To preserve the mirror plane of symmetry observed in NMR spectra, only head-to-head or tail-to-tail alkyne linkages are viable, narrowing down the remaining feasible options to those depicted schematically (I–IV).



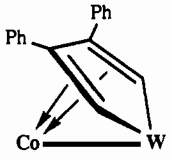
I



II



III



IV

I, II: Co = $Co(CO)_3$; W = $W(CO)(\eta^5\text{-}C_5H_4Me)$

III, IV: Co = $Co(CO)_2$; W = $W(CO)_2(\eta^5\text{-}C_5H_4Me)$

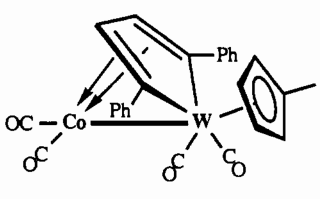
More detailed ^1H and ^{13}C NMR analyses help to deduce the structure of **6**. α-Protons on formally sp^2-hybridized carbon atoms typically resonate at low field in ^1H NMR spectra.[17] This would reject isomers II and IV. Furthermore, if I correctly portrayed the structure of **6**, the ^{183}W–^{13}C coupling constants for the *C*(Ph) and *C*(H) carbon atoms would be approximately equal. This is not the case: J_{WC} values are 73 and 8 Hz, respectively. This eliminates I and indicates that III, $(\eta^5\text{-}C_5H_4Me)(OC)_2\overline{W\{\mu\text{-}\eta^2,\eta^4\text{-}C(Ph)C(H)C(H)C}(Ph)\}Co(CO)_2$ (Co–W), best represents **6**.

Table V. Bond Distances (Å) for **5**, with Esd's in Parentheses

Mo–Co(2)	2.657 (1)	Co(1)–C(42)	2.063 (6)
Mo–Co(3)	2.716 (1)	Co(2)–Co(3)	2.549 (1)
Mo–C(1)	2.336 (8)	Co(2)–C(21)	1.79 (1)
Mo–C(2)	2.329 (8)	Co(2)–C(22)	1.803 (9)
Mo–C(3)	2.32 (1)	Co(2)–C(42)	1.951 (7)
Mo–C(4)	2.283 (9)	Co(2)–C(B1)	2.219 (7)
Mo–C(5)	2.302 (8)	Co(3)–C(7)	2.464 (8)
Mo–C(7)	1.966 (8)	Co(3)–C(13)	2.057 (7)
Mo–C(41)	2.285 (7)	Co(3)–C(31)	1.796 (8)
Mo–C(42)	2.219 (6)	Co(3)–C(32)	1.790 (8)
Mo–C(B1)	1.983 (8)	Co(3)–C(41)	1.980 (7)
Co(1)–Co(2)	2.442 (1)	O(7)–C(7)	1.145 (9)
Co(1)–Co(3)	2.458 (1)	O(11)–C(11)	1.125 (9)
Co(1)–C(11)	1.767 (9)	O(12)–C(12)	1.140 (9)
Co(1)–C(12)	1.778 (9)	O(13)–C(13)	1.163 (8)
Co(1)–C(13)	1.826 (8)	O(21)–C(21)	1.118 (9)
Co(1)–C(41)	2.100 (7)	O(22)–C(22)	1.125 (9)
O(31)–C(31)	1.130 (8)	C(41)–C(42)	1.430 (9)
O(32)–C(32)	1.138 (9)	C(41)–C(411)	1.489 (9)
O(B1)–C(B1)	1.170 (8)		

Table VI. Key Bond Angles (deg) for **5**, with Esd's in Parentheses

Co(2)–Mo–Co(3)	56.63 (3)	Co(2)–Mo–C(41)	67.6 (2)
Co(2)–Mo–C(42)	46.1 (2)	Co(3)–Mo–C(41)	45.6 (2)
Co(3)–Mo–C(42)	65.8 (2)	C(41)–Mo–C(42)	100.6 (3)
Co(2)–Co(1)–C(3)	62.69 (4)	Co(2)–Co(1)–C(41)	74.7 (2)
Co(2)–Co(1)–C(42)	50.5 (2)	Co(3)–Co(1)–C(41)	50.7 (2)
Co(3)–Co(1)–C(42)	73.1 (2)	C(41)–Co(1)–C(42)	40.2 (2)
Mo–Co(2)–Co(1)	96.80 (4)	Mo–Co(2)–Co(3)	62.86 (3)
Mo–Co(2)–C(42)	55.0 (2)	Co(1)–Co(2)–Co(3)	58.96 (4)
Co(1)–Co(2)–C(42)	54.6 (2)	Co(3)–Co(2)–C(42)	72.8 (2)
Mo–Co(3)–Co(1)	94.90 (4)	Mo–Co(3)–Co(2)	60.51 (3)
Mo–Co(3)–C(41)	55.6 (2)	Co(1)–Co(3)–Co(2)	58.34 (4)
Co(1)–Co(3)–C(41)	55.2 (2)	Co(2)–Co(3)–C(41)	74.1 (2)
Mo–C(41)–Co(1)	120.9 (3)	Mo–C(41)–Co(3)	78.8 (2)
Mo–C(41)–C(42)	69.0 (4)	Co(1)–C(41)–Co(3)	74.0 (2)
Co(1)–C(41)–C(42)	68.5 (4)	Co(3)–C(41)–C(42)	104.2 (5)
Mo–C(42)–Co(1)	126.0 (3)	Mo–C(42)–Co(2)	78.9 (2)
Mo–C(42)–C(41)	74.0 (4)	Co(1)–C(42)–Co(2)	74.9 (2)
Co(1)–C(42)–C(41)	71.3 (4)	Co(2)–C(42)–C(41)	108.9 (5)
Mo–C(7)–O(7)	166.3 (7)	Mo–C(B1)–O(B1)	156.9 (6)
Co(2)–C(B1)–O(B1)	124.7 (6)	Co(1)–C(11)–O(11)	173.4 (9)
Co(1)–C(12)–O(12)	178.6 (8)	Co(1)–C(13)–O(13)	147.3 (6)
Co(3)–C(13)–O(13)	134.2 (6)	Co(2)–C(21)–O(21)	178.8 (8)
Co(2)–C(22)–O(22)	178.2 (8)	Co(3)–C(31)–O(31)	177.6 (7)
Co(3)–C(32)–O(32)	179.5 (6)		



6

The head-to-head linkage observed here for the two PhC_2H ligands has precedence. A species with a similar PhC_2H connectivity has been isolated previously by our group. The $MoNi_2$

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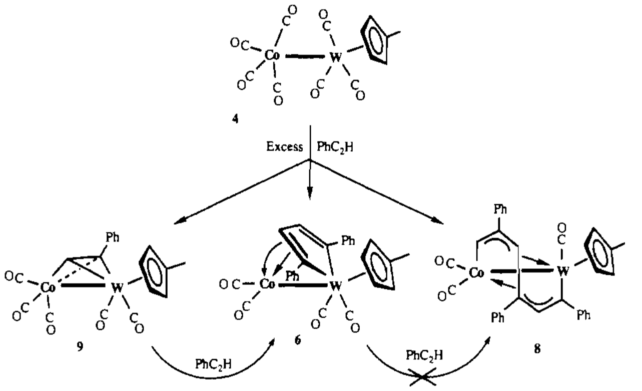
[17] α-Protons in alkenyl species resonate in the δ 7.5–9.5 ppm chemical shift range in ^1H NMR spectra, though there is some metal dependance: Chetcuti, M. J.; Fanwick, P. E.; Gordon, J. C.; Green, K. A.; Morgenstern, D. *Organometallics* **1989**, *8*, 1790 and cited references.

$$\underset{\mathbf{4}}{\text{CoW(CO)}_7(\eta^5\text{-C}_5\text{H}_4\text{Me})} + \text{PhC}_2\text{H} \rightarrow \underset{\mathbf{9}}{\text{CoW(CO)}_5(\mu\text{-}\eta^2\text{-PhC}_2\text{H})(\eta^5\text{-C}_5\text{H}_4\text{Me})\ (\text{Co–W})} +$$
$$\underset{\mathbf{6}}{(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{OC})_2\overline{\text{W}\{\mu\text{-}\eta^2,\eta^4\text{-C(Ph)C(H)C(H)C}}\text{(Ph)}\}\text{Co(CO)}_2\ (\text{Co–W})} \quad (5)$$

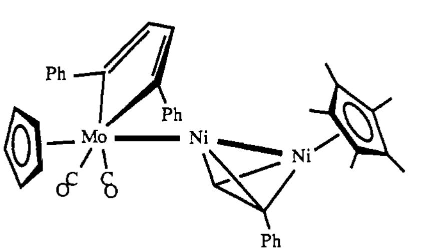
$$\underset{\mathbf{4}}{\text{CoW(CO)}_7(\eta^5\text{-C}_5\text{H}_4\text{Me})\ (\text{Co–W})} + \text{excess PhC}_2\text{H} \rightarrow \underset{\mathbf{6}}{(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{OC})_2\overline{\text{W}\{\mu\text{-}\eta^2,\eta^4\text{-C(Ph)C(H)C(H)C}}\text{(Ph)}\}\text{Co(CO)}_2\ (\text{Co–W})} +$$
$$\underset{\mathbf{8}}{(\text{OC})_2\text{Co}\{\mu\text{-}\eta^3,\eta^3\text{-C(H)C(Ph)C(H)C(Ph)C(H)C(Ph)}\}\text{W(CO)}(\eta^5\text{-C}_5\text{H}_4\text{Me})\ (\text{Co–W})} +$$
$$\underset{\mathbf{9}}{\text{CoW(CO)}_5(\mu\text{-}\eta^2\text{-PhC}_2\text{H})(\eta^5\text{-C}_5\text{H}_4\text{Me})\ (\text{Co–W})} + \text{Co}_2\text{(CO)}_6(\mu\text{-}\eta^2\text{-PhC}_2\text{H})\ (\text{Co–Co}) \quad (6)$$

Scheme I. Reaction of CoW(CO)$_7$(η^5-C$_5$H$_4$Me) (Co–W) (**4**) with PhC$_2$H[a]



[a] The μ-PhC$_2$H complex CoW(CO)$_5$(μ-η^2-PhC$_2$H)(η^5-C$_5$H$_4$Me) (Co–W) (**9**) and the tungstenacycle (η^5-C$_5$H$_4$Me)(OC)$_2$W{μ-η^2,η^4-C(Ph)C(H)C(H)C(Ph)}Co(CO)$_2$ (Co–W) (**6**) form sequentially. However, the flyover species (OC)$_2$Co{μ-η^3,η^3-C(H)C(Ph)C(H)C(Ph)C(H)C(Ph)}W(CO)(η^5-C$_5$H$_4$Me) (Co–W) (**8**) is not produced from **6**.

complex (η^5-C$_5$H$_4$Me)(CO)$_2$Mo{μ-η^2,η^4-C(Ph)C(H)C(H)C(Ph)}Ni(μ-η^2-PhC$_2$H)}Ni(η^5-C$_5$Me$_5$)

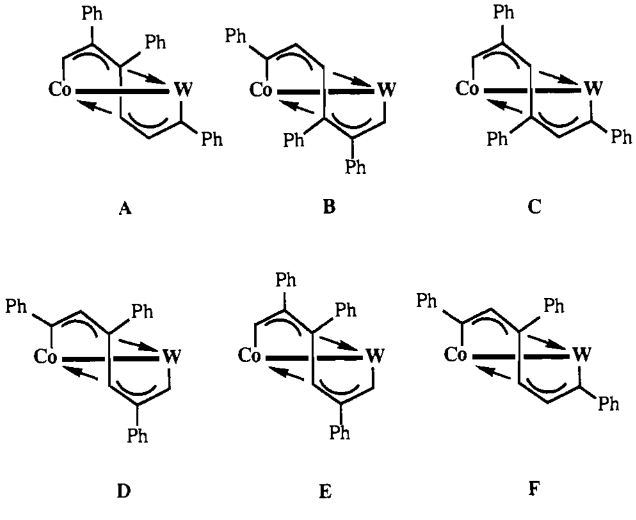


which contains a molybdenacyclopentadiene ring, was isolated from the reaction of (η^5-C$_5$Me$_5$)Ni–Mo(CO)$_3$(η^5-C$_5$H$_4$Me) with PhC$_2$H.[18] This species has a similar alkyne linkage.

Data for **8** imply that it is a heterobimetallic complex with three alkyne groups incorporated in the molecule. Two pointers lead us to believe that the alkynes are linked. A strong CIMS peak with a *m/e* ratio of 312 amu may be attributed to a (C$_6$H$_3$Me$_3$ + H)$^+$ cation. This cation results from the coupling of three PhC$_2$H groups that are presumably already linked in **8**. Fragmentation of **8** during the chemical ionization process dislodges this fragment (and transfers a proton to it).

Second, all PhC$_2$*H* protons are coupled in the ^{1}H NMR spectra of **8**. To a first approximation one signal appears as a doublet of doublets, while the other two resonances are doublets. This indicates that the PhC$_2$H ligands likely form part of the same chain: the central C(*H*) group couples with both flanking C(*H*) protons; other protons only interact with the central C(*H*) moiety.

We infer from these data that **8** contains three linked PhC$_2$H groups that are arrayed in a "flyover-bridge" geometry. The number of plausible isomeric "flyover-bridge" isomers was reduced by careful spectral data analyses. The small values of the ^{1}H–^{1}H coupling constants indicate that there are no vicinal *H*C–C*H* protons.[19] This eliminates A, B, and F as viable options. Furthermore, the absence of ^{183}W–^{1}H coupling for any of these resonances excludes D and E (as well as B). Structure C, (OC)$_2$Co{μ-η^3,η^3-C(H)C(Ph)C(H)C(Ph)C(H)C(Ph)}W(CO)(η^5-C$_5$H$_4$Me) (Co–W), is the prime candidate for the structure of **8** on the basis of these arguments.



Co = Co(CO)$_2$; W = W(CO)(η^5-C$_5$H$_4$Me)

Reaction of the Heterobimetallic Species CoW(CO)$_7$(η^5-C$_5$H$_4$Me) (4) with PhC$_2$H. While the reactions of some of the Co$_x$W$_{4-x}$ clusters with alkynes afforded metal–alkyne cluster species, in many cases, cluster fragmentation to dimetallic molecules was also observed. In order to gain insight into the formation of these species, we initiated a study of the reaction of the mixed-metal heterobimetallic species CoW(CO)$_7$(η^5-C$_5$H$_4$Me) (**4**) with PhC$_2$H. The cobalt–tungsten species reacts with a slight excess of PhC$_2$H (1:1.2) to afford **9** as the main product (eq 5). In addition a yellow species was formed in low yields that was identified by IR spectroscopy as the previously characterized species (η^5-C$_5$H$_4$Me)(OC)$_2$W{μ-η^2,η^4-C(Ph)C(H)C(H)C(Ph)}Co(CO)$_2$ (Co–W) (**6**).

Complex **9** was characterized spectroscopically. NMR, IR, and MS and data indicate that this complex is the μ-alkyne species CoW(CO)$_5$(μ-η^2-PhC$_2$H)(η^5-C$_5$H$_4$Me). The alkyne methine proton exhibits a small coupling to the tungsten (J_{WH} = 2.6 Hz). Bridging alkyne complexes analogous to **9** have been prepared indirectly using alternative synthetic pathways,[4,20] and during the

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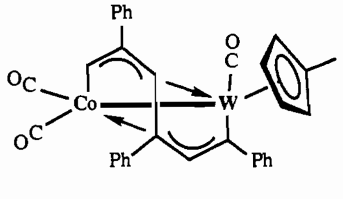
[18] Chetcuti, M. J.; DeLiberato, L.; Fanwich, P. E.; Grant, B. E. *Inorg. Chem.* **1990**, *29*, 1295.

[19] Values for J_{HH} in *cis*-*H*C=C*H* olefinic species range from 6 to 12 Hz: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. In *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley and Sons: New York, 1981.

course of this work, complexes similar to **9** were reported by Mathieu and co-workers.[21]

Excess PhC_2H (1:2.4 molar ratio) reacted with **4** was to yield a mixture of four species (eq 6), which was separated using chromatographic techniques. The bridging alkyne complex **9** and the metallacyclopentadiene species **6** were formed in approximately equal yields, and these formed the bulk of the products (≈80%). The Co_2 μ-alkyne compound $Co_2(CO)_6(\mu\text{-}\eta^2\text{-}PhC_2H)$ (Co–Co) was also isolated, along with small quantities of the tris(alkyne) flyover species $(OC)_2Co\{\mu\text{-}\eta^3,\eta^3\text{-}C(H)C(Ph)C(H)C(Ph)C(H)C(Ph)\}W(CO)(\eta^5\text{-}C_5H_4Me)$ (Co–W) (**8**).



8

In order to probe the formation of these species, further experiments were performed. **9** was isolated and reacted with excess PhC_2H. Complex **6** was formed quantitatively from **9**, and no other organometallic compounds were observed. The formation of **6** from **9** is corroborated by the parallel formation of $(OC)_2Co\{\mu\text{-}\eta^2,\eta^4\text{-}\overline{C(Ph)C(Ph)C(Ph)C(Ph)\}W}(CO)_2(\eta^5\text{-}C_5H_5)$ (Co–W) from the reaction of $CoW(CO)_5(\mu\text{-}\eta^2\text{-}PhC_2Ph)(\eta^5\text{-}C_5H_5)$ (Co–W) with PhC_2Ph.[21,22]

We attempted to react **6** with PhC_2H. After the mixture was refluxed refluxing for 1 day with 1 equiv of phenylacetylene, no reaction had taken place (by IR). The mixture was refluxed further, and after 1 week, noticeable decomposition had set in. Only IR bands attributed to **6** were noted, and **8** was never isolated or observed as a product from this reaction. These experiments establish that **6** forms from **9** and clearly indicate that the fly-over species **8** is *not* formed by alkyne insertion into **6**. These results also bolster the arguement that the incorporation of a C(Ph)C(H)C(H)C(Ph)*C(H)C(Ph) or* a C(Ph)C(H)C(H)C(Ph)*C(Ph)C(H)* linkage in **8** is unlikely, in agreement with the presumed structure of this complex. Scheme I summarizes these results.

Conclusions. A number of points emerge from these reactions. Steric congestion in $Co_3W(CO)_{11}(\eta^5\text{-}C_5H_4Me)$ (**1b**), $Co_2W_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (**2**), and $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (**3**) increases steadily as the number of tungsten atoms in the cluster increases.[1] **3** is a highly sterically congested species, and it is not surprising that cluster-containing products are not obtained when this CoW_3 cluster was treated with PhC_2H. Steric strain resulting from carbonyl/alkyne substitution probably leads to the cluster opening up and to subsequent fragmentation. Dimetallic species including $W_2(CO)_4(\mu\text{-}\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_4Me)_2$, and cobalt-tungsten bis- and tris(alkyne) species **6** and **8** are obtained.

For **1a** and **2**, the reactions with PhC_2H lead to products that retain a tetrametallic core. However, the clusters relieve steric strain by affording species with butterfly core geometries in both cases: for **1a**, the Co–Mo bond is ruptured, while, in **2**, the W–W bond is cleaved. We do not understand why the reaction of **1b** with PhC_2H does not culminate in a $Co_3W(PhC_2H)$ cluster analogous to **4**. However, the reaction of the tetracobalt cluster $Co_4(CO)_{12}$ with alkynes has been noted to yield either $Co_4(CO)_{10}(\mu\text{-}\eta^2\text{-}RC_2R')$ butterfly clusters *or* $Co_2(CO)_6(\mu\text{-}\eta^2\text{-}RC_2R')$ dimetallatetrahedrane complexes depending on reaction conditions.[2c] In addition, we have noted[1] that reactions of tungsten species with dicobalt octacarbonyl proceed to give products that are quite different from corresponding those of reactions of analogous molybdenum species with $Co_2(CO)_8$.[23,24]

Metallacyclopentadienyl species result from these cluster fragmentation reactions. Cobalt and tungsten are both known to form metallacyclopentadienyl complexes.[15,25–27] Indeed cobalt–tungsten[20,26,28] and some related cobalt–molybdenum[22] heterobimetallic metallacyclopentadienyl species are recognized. Even within this limited set of examples, both cobalta- and tungstenacycles are known. It is not clear what parameters govern the stability of a particular metallacycle isomer, but we have only isolated tungstenacyclopentadienyl species from these cluster degradation reactions. The reaction of PhC_2H with $Co_2Mo_2(\mu_3\text{-}\eta^2\text{-}PhC_2H)(\mu_3\text{-}S)_3(CO)_2(\eta^5\text{-}C_5H_4Me)_2$ has been shown to afford the molybdenacyclopentadienyl cluster species $Co_2Mo_2\{\mu_3\text{-}\eta^2,\eta^4\text{-}C(Ph)C(H)C(H)C(Ph)\}(\mu_3\text{-}S)_3(CO)_2(\eta^5\text{-}C_5H_4Me)_2$.[29] Nevertheless, we have not observed *cluster-bound* metallacyclopentadienyl species, even when stable alkyne clusters (**5** and **7**) were isolated.

The same linked-alkyne heterobimetallic products are obtained from both the cluster fragmentation reactions and from the reaction of $CoW(CO)_7(\eta^5\text{-}C_5H_4Me)$ (**4**) with PhC_2H. The alkyne coupling presumably takes place at a dimetal center that either is preformed or else is an intermediate in the cluster breakup. It appears that PhC_2H insertion into M–C(Ph) bonds does not take place readily. Alkyne insertion into the M–C(H) bond of $CoW(CO)_5(\mu\text{-}\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_4Me)$ (Co–W) (**9**) leads to the bis(alkyne) species **6**. However, as **6** has no W–C(H) bonds, further alkyne addition is inhibited (probably on steric grounds) and no flyover complex resulting from additional alkyne insertion was noted. The steric congestion of **6** probably contributes to its inherent stability as other metallacyclopentadiene isomers with M–C(H) σ bonds are not seen.

Complex **8** is formed in low yield and only one isomer was isolated. One may speculate that **8** assembles from alkyne insertion into a metallacyclopentadiene species other than **6**. PhC_2H insertion into a W–C(H) σ bond of $(\eta^5\text{-}C_5H_4Me)(OC)_2\overline{W\{\mu\text{-}\eta^2,\eta^4\text{-}C(H)C(Ph)C(H)C}(Ph)\}Co(CO)_2$ could lead to **8**. Other (unobserved) isomeric species may undergo reductive elimination and cyclization of the tris(alkyne) ligand accounting for the triphenylbenzenes noted.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using Schlenk or vacuum-line techniques. Solvents were predried over 4-Å molecular sieves. Diethyl ether, toluene, and hexanes were distilled over sodium or sodium benzophenone ketyl. Dichloromethane was distilled over CaH_2. PhC_2H was obtained from Aldrich and was used as received. The syntheses of **1a**, **1b**, **2**, and **3** has been reported.[1] NMR spectra were recorded on a GE NT- or GN-300 spectrometer at 20 °C, in chloroform-d_1 unless otherwise stated. $Cr(acac)_3$ was used for ^{13}C NMR spectra as a shiftless relaxation reagent. IR spectra were obtained on an IBM IR-32 FT instrument. NMR and IR data are collected in Tables I and II. Mass spectra were obtained on a Finnegan-Matt instrument. All parent ions show the appropriate isotopomer pattern.

Reaction of $Co_3Mo(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_4Me)$ (1a) with PhC_2H. **1a** (60 mg, 0.091 mmol) was dissolved in toluene (20 mL) in a Schlenk tube

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(23) We reported that the reaction of $Co_2(CO)_8$ with $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ (W≡W) afforded the Co_2W_2 cluster 2.[1] However, Curtis and his group[24] noted that the reaction between $Co_2(CO)_8$ and $[Mo(CO)_2(\eta^5\text{-}C_5H_5)]_2$ (Mo≡Mo) did not afford analogous Co_2Mo_2 clusters.

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equipped with a stirrer bar. PhC_2H (0.01 mL, 0.09 mmol) was syringed in under a nitrogen flow and the reaction allowed to stir at ≈65 °C under a vigorous N_2 purge for ≈2 h. The dark solution was pumped to dryness, redissolved in an ether/toluene/hexanes mixture (2:1:1), and subjected to chromatography on silica gel using hexanes as the initial eluent. Three major bands (yellow, gray-black, and red-brown in order of elution) were removed from the column by the addition of a few percent of diethyl ether to the eluent. The yellow band was pumped to dryness. A ^1H NMR spectrum showed that this band contained a complex mixture of products. This proved to be inseparable in our hands. The other two bands were pumped to dryness and redissolved in an ether/hexanes mixture (1:1). Concentration of these bands and cooling of the solutions at −20 °C led to black crystals of $Co_3Mo(CO)_{11}(\eta^4\text{-}\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_4Me)$ (**5**) (11 mg, 0.014 mmol, 17%) and purple-brown $Co_3Mo(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_4Me)$ (**1a**) (10 mg, 0.015 mmol).

Reaction between the Tricobalt-Tungsten Cluster $Co_3W(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_4Me)$ (1b) and PhC_2H. **1b** (70 mg, 0.094 mmol) was dissolved in toluene (20 mL) in a Schlenk tube equipped with a stirrer bar. PhC_2H (0.01 mL, 0.09 mmol) was added via a microsyringe under a nitrogen flow, and the reaction mixture stirred overnight at 55–60°C. The resulting yellow-brown solution was then pumped to dryness and redissolved in a hexanes/ether mixture (≈3:1) and subjected to silica gel chromatography, using hexanes as the initial eluent. Several minor bands were seen, but only the two major bands were collected; these were purple-brown and yellow in order of elution. Both bands were removed by the addition of about 5% ether to the eluent. A fibrous solid deposited when the first band was concentrated. This was harvested by removal of the mother liquor and pumped to dryness to yield a mixture of the (spectroscopically identified) 1,2,4- and 1,3,5-isomers of triphenylbenzene (≈15 mg, 0.049 mmol). An ^1H NMR spectrum of the species contained in the second band revealed that a mixture of products were present, that included **6** as a major component. Total yield of the yellow band was ≈25 mg. Attempts to separate this mixture into its components were unsuccessful.

Reaction of the Dicobalt-Ditungsten Cluster $Co_2W_2(\mu\text{-}CO)_3(CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (2) with PhC_2H. Complex **2** (130 mg, 0.141 mmol), was placed in a degassed Schlenk tube that was equipped with stirrer bar. Toluene (15 mL) was added to this material followed by PhC_2H (15 μL, 0.14 mmol). The reaction mixture was allowed to stir at 55–60 °C for 1 day under a vigorous N_2 purge. The solution was then pumped to dryness, and the resulting solid was dissolved in a hexanes/ether/dichloromethane mixture (2:1:1) and subjected to chromatography on silica gel using hexanes as the initial eluent. Three main bands were collected on slow addition of ether to the eluent (≈1:1 hexanes/ether). In order of elution, the bands collected were purple-brown (first), green, and purple. A dark solid (10 mg, 0.033 mmol) resulting from the first band was harvested from hexanes and was spectroscopically identified as an isomeric mixture of 1,2,4- and 1,3,5-triphenylbenzenes. Concentration and cooling of the green band to −20 °C afforded crystals of unreacted **2**. The last band deposited microcrystals (10 mg, 0.010 mmol, 7%) of **7** from a cold hexanes/ether solution (1:1). EIMS for **7**: *m/e* 886 ($(M - 3CO)^+$) and ions corresponding to loss of 1–5 more CO ligands. HRMS for **7**: calcd for $(M - 3CO)^+$, *m/e* 885.9001; found, *m/e* 885.9003.

Reaction of $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (3) with PhC_2H. **3** (90 mg, 0.082 mmol) was placed in a Schlenk tube equipped with a magnetic stirrer bar. A needle was placed through a pierced septum to allow an N_2 purge. A 20-mL volume of toluene was added, and 0.01 mL (0.09 mmol) of PhC_2H was syringed in under N_2 flow. The reaction mixture was stirred at 65–70 °C overnight under a vigorous N_2 purge. The resulting orange-brown solution was pumped to dryness, dissolved in a hexanes/ether mixture (≈2:1), and subjected to silica gel chromatography using hexanes as the initial eluent. Several bands were observed: a red-brown band was collected in hexanes and pumped to dryness. This was identified as $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2(\mu\text{-}PhC_2H)$ by ^1H NMR, IR, and MS. Two yellow bands and a purple band followed by adding ≈5% ether to the eluent. The solutions were concentrated and cooled. The yellow solutions yielded orange crystals of $(\eta^5\text{-}C_5H_4Me)(OC)_2W\{\mu\text{-}\eta^2,\eta^4\text{-}C(Ph)C(H)C(H)C(Ph)\}Co(CO)_2$ (Co–W) (**6**) (15 mg, 0.0235 mmol, 29%) and yellow crystals of $(OC)_2Co\{\mu\text{-}\eta^3,\eta^3\text{-}C(H)C(Ph)C(H)C(Ph)C(H)C(Ph)\}W(CO)(\eta^5\text{-}C_5H_4Me)$ (Co–W) (**8**) (5 mg, 0.0068 mmol, 8%), respectively. CIMS data for **6**: *m/e* 638 (M^+), 610 ($(M - CO)^+$), 582 ($(M - 2CO)^+$). HRMS data for **6**: calcd for M^+ *m/e*, 638.0129; found, *m/e* 638.0117. CIMS data for **8**: *m/e* 712 ($(M + H)^+$) and ions corresponding to loss of 1, 2, and 3 CO ligands. The purple band was identified as $CoW_3(CO_9(\eta^5\text{-}C_5H_4Me)_3$ (**3**) by IR spectroscopy.

Reaction of $CoW(CO)_7(\eta^5\text{-}C_5H_4Me)$ (Co–W) (4) with PhC_2H (1:1.2 Molar Ratio). **4** (125 mg, 0.241 mmol) was dissolved in toluene (20 mL) in a Schlenk tube equipped with a magnetic stirrer bar. PhC_2H (0.033 mL, 0.30 mmol) was added via syringe. The reaction mixture was stirred at room temperature for 45 min under a vigorous N_2 purge. No apparent reaction occurred, so the mixture was then heated to ≈55 °C and stirred for ≈75 min, after which time the solution changed from red to orange. The solution was pumped to dryness, dissolved in hexanes, and subjected to silica gel chromatography. This yielded (in order of elution) yellow (very minor), orange, and yellow bands, all of which were removed by addition of a small amount of ether to the eluent. Each band was collected in turn and pumped to dryness to yield oily solids. Unfortunately, it proved impossible to characterize the first band due to the small amounts of material and to the onset of decomposition. The orange band was spectroscopically identified as $CoW(CO)_5(\mu\text{-}\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_4Me)$ (Co–W) (**9**) (50 mg, 0.089 mmol, 37%). The yellow band was identified by IR spectroscopy as **6** (20 mg, 0.0313 mmol, 13%). EIMS for **9**: *m/e* 564 (M^+) and ions corresponding to loss of 1–5 CO ligands. HRMS data for **9**: calcd for M^+, 563.9608; found, *m/e* 563.9608.

Reaction of $CoW(CO)_7(\eta^5\text{-}C_5H_4Me)$ (Co–W) (4) with PhC_2H (1:2.4). **4** (110 mg, 0.212 mmol) was placed in a Schlenk tube equipped with a magnetic stirrer bar. Toluene (20 mL) was added, and PhC_2H (57 μL, 0.52 mmol) was syringed in under an N_2 flow. The reaction mixture was stirred for 1.5 h at 55 °C under a vigorous N_2 purge, during which time the solution turned from red to yellow-brown. After the solution was pumped to dryness, the resulting oily solid was redissolved in a hexanes/toluene/dichloromethane mixture and subjected to preliminary chromatography on silica gel. On addition of a small amount of ether to the eluent, two main bands (yellow-brown and yellow, respectively) were collected. The impure bands were recombined; further chromatography (using hexanes) led to the recovery of the three main components (two orange bands and a yellow band). The first two bands were pumped to dryness and characterized as $Co_2(CO)_6(\mu\text{-}\eta^2\text{-}PhC_2H)$ and **9**. ^1H NMR spectroscopy revealed that the third band contained **6** and **8** (in a ratio of ≈30:1, respectively). Exact yields were not obtained, but the mixed-metal products (**9** and the mixture of **6** and **8**) accounted for ≥80% of the isolated material.

Reaction of $CoW(CO)_5(\mu\text{-}\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_4Me)$ (Co–W) (9) with PhC_2H (1:1.2). **9** (50 mg, 0.097 mmol) was dissolved in toluene (8 mL) in a Schlenk tube equipped with a magnetic stirrer bar. PhC_2H (12 μL, 0.11 mmol) was syringed in under N_2 flow. The reaction mixture was allowed to stir at ≈70 °C under an N_2 purge for ≈1 h, during which time the solution changed color from red to brown. The reaction mixture was then pumped to dryness, and an IR spectrum run in dichloromethane confirmed that clean quantitative conversion of **9** to **6** had taken place.

Attempted Reaction between $(\eta^5\text{-}C_5H_4Me)(OC)_2W\{\mu\text{-}\eta^2,\eta^4\text{-}C(Ph)C(H)C(H)C(Ph)\}Co(CO)_2$ (Co–W) (6) and PhC_2H To Form 8. **6** (15 mg, 0.024 mmol) was placed in a Schlenk tube equipped with a magnetic stirrer bar and a reflux condenser. Toluene (10 mL) was added followed by PhC_2H (2.6 μL, 0.024 mmol). The reaction mixture was refluxed for ≈1 day, after which time an aliquot was removed and pumped to dryness. The sample was dissolved in dichloromethane and the IR spectrum obtained. No spectral change from that of **6** was noted. The reaction mixture was then allowed to stir under reflux for a further 1 week, at which time the solution was pumped to dryness. Notable decomposition had occurred, but **8** could not be detected in the IR spectrum of the residue.

X-ray Diffraction Study of $Co_3Mo(\eta^5\text{-}C_5H_4Me)(CO)_{11}(\mu_4\text{-}PhC_2H)$ (5). A dark red crystal of **5**, grown from an ether/hexanes solution at −20 °C, was mounted on a glass capillary tube and placed on an Enraf-Nonius CAD 4 diffractometer at 20 ± 1 °C. Cell constants and an orientation matrix were obtained from least-squares refinement of 25 reflections in the range $16 \le \theta \le 19°$. Due to systematic absence of $h0l$, $h + l = 2n$, and $0k0$, $k = 2n$, and from subsequent least-squares refinement, the space group was determined to be $P2_1/n$.

Data were corrected for Lorentz and polarization effects; an empirical absorption correction was applied.[30] Of the 3268 unique reflections, the 2235 with $I < 3\sigma(I)$ were used in refinement. The structure was solved on a VAX computer using SDP/VAX software and the SHELX-86[31] solution package. Remaining atoms were located from succeeding Fourier maps; hydrogen atoms, located and added to the structure factor calculations, were not refined. Scattering factors were from Cromer and Waber.[32] Anomalous dispersion effects were included in F_c. The highest peak in

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the difference Fourier had a height of 0.70 e/Å^3 (estimated error based on ΔF = 0.20).

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Supplementary Material Available: An ORTEP plot and full tables of data collection parameters, bond lengths, bond angles, positional parameters for hydrogen atoms, and thermal parameters for all atoms of complex **5** (14 pages); a listing of calculated and experimental structure factors (10 pages). Ordering information is given on any current masthead page.

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(34) Reference 32, Table 2.3.1.

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Cluster Synthesis. 36. New Platinum–Ruthenium and Platinum–Osmium Carbonyl Cluster Complexes from the Reactions of the Complexes $Pt_2M_4(CO)_{18}$ (M = Ru, Os) with Cycloocta-1,5-diene in the Presence of UV Irradiation

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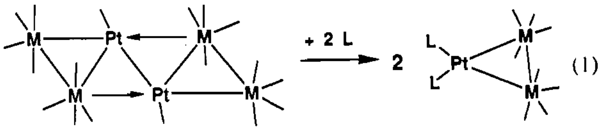
The reactions of $Pt_2M_4(CO)_{18}$ (**1a**, M = Ru; **1b**, M = Os) with cycloocta-1,5-diene (COD) in the presence of UV irradiation were studied. The reaction of **1a** yielded the new mixed-metal cluster compounds $PtRu_4(CO)_{12}(\mu_4\text{-}CO)(COD)$ (**2**) (11%) and $Pt_4Ru_5(CO)_{20}(COD)$ (**3**) (16%). Compounds **2** and **3** were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. The cluster of **2** consists of a butterfly tetrahedron of four ruthenium atoms that is capped on one of the triangular faces by a Pt(COD) group. A $\mu_4\text{-}\eta^2$-CO ligand lies in the fold of the butterfly. The cluster of compound **3** consists of nine metal atoms and can be described as combination of a Pt_3Ru_3 octahedron fused to a Pt_3Ru_2 square pyramid with a common Pt_3 face and a Pt(COD) capping group on the Ru_3 face of the octahedron. The reaction of **1b** yielded the hexanuclear products $Pt_2Os_4(CO)_{17}$ (**5**) (29%) and $Pt_2Os_4(CO)_{15}(COD)$ (**6**) (25%) and small amounts of the known hexanuclear compounds $Pt_2Os_4(CO)_{12}(COD)_2$ (**8**) (6%) and $PtOs_2(CO)_8(COD)$ (**4**) (7%). Compound **6** was characterized crystallographically. The cluster of **6** exhibits the well-known triangle of triangles "raft" structure with a Pt(COD) grouping on one of the outer triangles and one Pt(CO) group in the inner triangle. Compound **5** is believed to possess a structure similar to **6** but with two CO ligands in the place of the COD ligand. Cyclic voltammetric measurements on compound **5** showed the presence of two reversible one-electron reductions at $E_{1/2}$ = −0.57 and −0.84 V. Compound **6** shows two quasireversible one-electron reductions at $E_{1/2}$ = −0.67 and −0.93 V. Crystal data: for **2**, space group = $P\bar{1}$, a = 10.544 (1) Å, b = 17.064 (4) Å, c = 8.847 (2) Å, α = 104.31 (2)°, β = 98.36 (2)°, γ = 74.27 (2)°, Z = 2, 2355 reflections, R = 0.028; for **3**, space group = $C2/c$, a = 26.361 (4) Å, b = 9.474 (4) Å, c = 31.211 (4) Å, β = 94.85 (1)°, Z = 8, 3769 reflections, R = 0.026; for **6**, space group = $Pbca$, a = 14.781 (3) Å, b = 35.83 (2) Å, c = 11.548 (2) Å, Z = 8, 2047 reflections, R = 0.035.

Introduction

Interest in the chemistry of heteronuclear cluster complexes containing platinum[1] has been stimulated by the importance of heterobimetallic "clusters" containing platinum as catalysts in the petroleum-refining process.[2] We have recently found that the reactions of $Pt(COD)_2$ (COD = cycloocta-1,5-diene) with the pentacarbonyl complexes of iron, ruthenium, and osmium readily yield new mixed-metal carbonyl cluster complexes containing platinum.[3-5] The compounds $Pt_2M_4(CO)_{18}$ (**1a**, M = Ru;[4] **1b**, M = Os[5,6]) have been obtained by this method. These molecules have been shown to have a puckered ladderlike structure consisting of two mutually bonded Pt(CO) groupings between pairs of mutually bonded $M(CO)_4$ groups. The molecules can be split in two by reaction with dppe[4] or CO at 50 atm/25 °C[6] (eq 1). Thermal decarbonylation of **1b** in the presence of COD has yielded the new complexes $Pt_2Os_4(CO)_{12}(COD)_2$ and $Pt_2Os_4(CO)_{11}(COD)_2$.[7] The latter is electronically unsaturated and has been shown to engage in facile addition of selected small molecules.[7] In a continuation of our studies of the compounds **1**, we have now investigated the nature of their reactions with COD in the presence of UV irradiation. Details of this study are described in this report.



(1)

$Pt_2M_4(CO)_{18}$ $PtM_2(CO)_8L_2$

M = Ru, Os L_2 = dppe, 2 CO

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. $Pt_2Ru_4(CO)_{18}$[4] and $Pt_2Os_4(CO)_{18}$[5] were prepared by the previously reported procedures. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Bruker AM-300 FT-NMR spectrometer. Elemental microanalyses were performed by Desert Analytics, Tucson, AZ. TLC separations were performed in air by using silica gel (60 Å, F_{254}) on plates (Whatman, 0.25 mm). UV irradiations were performed on reaction solutions contained in Pyrex glassware by using either an 85-W external high-pressure mercury lamp obtained from George Gates & Co. Franklin Square, NY, or a 1000-W medium-pressure mercury lamp.

Reaction of 1a with COD under UV Irradiation. A 25.0-mg sample of $Pt_2Ru_4(CO)_{18}$ (**1a**) (0.0193 mmol) and 250 μL of COD (2.00 mmol) were dissolved in 450 mL of hexane. The solution was irradiated with the medium-pressure UV lamp (1000 W) at 25 °C in the presence of a slow purge of nitrogen for 21 h. The solvent was removed on a rotary evaporator, and the residue was separated from the mixture by TLC on silica gel with a hexane/CH_2Cl_2 (4/1) solvent mixture. This yielded, in

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