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Structure of $[(\mu_3\text{-CH})\text{CoMo}_2(\text{CO})_7(\eta^5\text{-C}_5\text{H}_5)]$; a Cobaltodimolybdenum Triangular Carbonyl Cluster Capped by an Alkylidyne Unit

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Abstract. Heptacarbonylbis(η^5 -cyclopentadienyl)- μ_3 -methylidyne-cobaltodimolybdenum (1) is one of the products isolated from the reaction of the cyclopentadienyltricarbonylmolybdenum anion, $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$, and nonacarbonyl- μ_3 -chloromethylidyne-tricobalt, $(\mu_3\text{-CCl})\text{Co}_3(\text{CO})_9$. The crystal and molecular structure of (1) has been determined. The compound crystallizes in the monoclinic space group $P2_1/c$ with $M_r = 590.09$, $a = 10.007$ (2), $b = 12.886$ (2), $c = 16.536$ (4) Å, $\beta = 116.74$ (1)°, $V = 1908$ (1) Å³, $Z = 4$, $D_x = 2.05$ g cm⁻³. $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 21.58$ cm⁻¹, $F(000) = 1144$, $T = 295$ K, $R = 0.020$ for 2818 independent reflections with $I > 3\sigma(I)$. The structure consists of a cobaltodimolybdenum triangle capped by an alkylidyne unit and with the two cyclopentadienyl groups in a *transoid* arrangement.

Introduction. $(\mu_3\text{-CH})\text{CoMo}_2(\text{CO})_7(\eta^5\text{-C}_5\text{H}_5)_2$, (1), is one of a number of related alkylidyne clusters that can be obtained by exchange of the cobalt atoms in the metal triangle of $(\mu_3\text{-CR})\text{Co}_3(\text{CO})_9$ ($R = \text{H, Cl, Me, Ph etc.}$) by reaction with transition-metal car-

bonyl anions, or with transition-metal carbonyl dimers (Blumhofer, Fischer & Vahrenkamp, 1986; Duffy, Kassis & Rae, 1990; Duffy, Kassis & Rae, unpublished; Beurich & Vahrenkamp, 1982). This paper reports the structure of (1), which was synthesized *via* the reaction of $(\mu_3\text{-CCl})\text{Co}_3(\text{CO})_9$ with the metal-transfer reagent $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$.

Experimental. $(\mu_3\text{-CH})\text{CoMo}_2(\text{CO})_7(\eta^5\text{-C}_5\text{H}_5)_2$ crystallizes as green/black crystals in the monoclinic space group $P2_1/c$. An irregularly shaped crystal of maximum dimensions $0.16 \times 0.14 \times 0.08$ mm was mounted on a quartz fibre and the lattice parameters ($T = 295$ K, 24 reflections, θ range 20–23°) were determined and refined with the least-squares routine on an Enraf-Nonius CAD-4 four-circle diffractometer equipped with a graphite monochromator.

A total of 3341 unique reflections (of 3728 collected) were collected in the range $1.5 < \theta < 25^\circ$ using an ω - 2θ scan mode ($R_{\text{int}} = 0.014$). The intensity of one standard reflection was measured after every 2000 s of X-ray exposure. No decomposition occurred during data collection. Lorentz, polarization and absorption corrections (Gaussian integration method, maximum and minimum transmission

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factors were 0.845 and 0.692 respectively) were applied to all reflections using locally written programs. 2818 independent reflections with $I > 3\sigma(I)$ were used in the structure refinement calculations using *BLOCKLS* (based on *ORFLS*, Busing, Martin & Levy, 1962). Scattering factors for neutral atoms were obtained from Ibers & Hamilton (1974).

The atomic coordinates of the three heavy atoms were obtained by direct methods, *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). A Fourier analysis based on the three metal positions gave an R value of 0.23. The associated and subsequent difference Fourier revealed all non-hydrogen atoms in chemically reasonable positions. With all non-hydrogen atoms anisotropic and the hydrogen atoms included in positions located from a difference map (refined with temperature factors equal to those of the atoms to which they are attached) the refinement converged, *BLOCKLS* {based on F , 286 parameters refined, reflection weights used were $1/\sigma^2(F_o)$ with $\sigma^2(F_o)$ being derived from $[\sigma^2(I_o) + 0.04I_o^2]^{1/2}$ }, with final agreement indices of $R = 0.020$ and $wR = 0.027$. $\Delta/\sigma_{\max} < 1$ and $\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$. Fig. 1 shows the molecular structure (*ORTEPII*, Johnson, 1976) of (1) and the numbering scheme employed. Table 1 lists the atomic coordinates of the non-hydrogen atoms and U_{eq} values, and Table 2 lists selected bond lengths and bond angles.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54230 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters and standard deviations for the non-hydrogen atoms of (μ_3 -CH)-CoMo₂(CO)₇(η^5 -C₅H₅)₂

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq} (\AA^2)
Mo(1)	0.20417 (2)	0.14794 (2)	0.34490 (2)	0.018 (1)
Mo(2)	0.46063 (3)	0.27893 (2)	0.36058 (2)	0.023 (1)
Co(1)	0.25750 (4)	0.18922 (3)	0.20078 (3)	0.023 (1)
C	0.3846 (3)	0.1288 (2)	0.3169 (2)	0.021 (1)
C(1)	0.3522 (3)	0.1170 (2)	0.4712 (2)	0.026 (1)
O(1)	0.4309 (3)	0.0955 (2)	0.5443 (2)	0.036 (1)
C(2)	0.2225 (3)	0.0000 (2)	0.3241 (2)	0.024 (1)
O(2)	0.2337 (3)	-0.0866 (2)	0.3139 (2)	0.036 (1)
C(3)	0.3434 (4)	0.3551 (2)	0.4084 (2)	0.032 (2)
O(3)	0.2934 (3)	0.4118 (2)	0.4423 (2)	0.055 (2)
C(4)	0.3902 (4)	0.3865 (3)	0.2660 (3)	0.037 (2)
O(4)	0.3641 (4)	0.4574 (2)	0.2177 (2)	0.055 (2)
C(5)	0.1381 (4)	0.0840 (3)	0.1407 (2)	0.030 (1)
O(5)	0.0594 (4)	0.0185 (2)	0.1021 (2)	0.046 (1)
C(6)	0.3974 (5)	0.1845 (3)	0.1607 (2)	0.037 (2)
O(6)	0.4908 (4)	0.1794 (3)	0.1399 (2)	0.065 (2)
C(7)	0.1290 (4)	0.2940 (3)	0.1509 (2)	0.030 (1)
O(7)	0.0441 (3)	0.3585 (2)	0.1178 (2)	0.046 (2)
Cp(11)	0.0247 (3)	0.2758 (3)	0.3273 (3)	0.033 (2)
Cp(21)	0.0682 (4)	0.2270 (3)	0.4106 (3)	0.035 (2)
Cp(31)	0.0257 (4)	0.1206 (3)	0.3950 (3)	0.041 (2)
Cp(41)	-0.0465 (4)	0.1074 (3)	0.3003 (3)	0.040 (2)
Cp(51)	-0.0472 (3)	0.2026 (3)	0.2591 (3)	0.032 (2)
Cp(12)	0.6976 (4)	0.2105 (4)	0.3904 (4)	0.050 (3)
Cp(22)	0.6988 (4)	0.3146 (4)	0.3751 (3)	0.049 (3)
Cp(32)	0.6795 (5)	0.3681 (4)	0.4409 (4)	0.053 (3)
Cp(42)	0.6668 (5)	0.2935 (7)	0.4992 (3)	0.054 (3)
Cp(52)	0.6789 (4)	0.1970 (5)	0.4654 (4)	0.051 (3)

Table 2. Selected bond distances (\AA) and bond angles ($^\circ$) with their *e.s.d.*'s for (μ_3 -CH)CoMo₂(CO)₇(η^5 -C₅H₅)₂

Mo(1)—Mo(2)	2.9849 (3)	Mo(1)—Co(1)	2.7169 (3)
Mo(2)—Co(1)	2.7679 (4)	Mo(1)—C	2.069 (3)
Mo(2)—C	2.087 (3)	Co(1)—C	1.933 (3)
C—H(C)	0.975 (35)	Co(1)—C _(CO) (av)	1.792
Mo(1)—C _(CO) (av)	1.974	Mo(2)—C _(CO) (av)	1.959
C—O (av)	1.146	Mo(1)—Cp (av)	2.34
Mo(2)—Cp (av)	2.33	C—C _(Cp) (av)	1.391
Mo(2)—Mo(1)—Co(1)	57.85 (1)	Mo(1)—Mo(2)—Co(1)	56.21 (1)
Mo(1)—Co(1)—Mo(2)	65.93 (1)	Mo(1)—C—Mo(2)	91.8 (1)
Mo(1)—C—Co(1)	85.4 (1)	Mo(1)—C—H(C)	133.0 (21)
Mo(2)—C—Co(1)	87.0 (1)	C(1)—Mo(1)—C(2)	84.6 (1)
Mo(2)—C—H(C)	123.2 (21)	Co(1)—C—H(C)	122.8 (21)
Mo(1)—C(1)—O(1)	175.8 (3)	Mo(1)—C(2)—O(2)	178.6 (3)
Mo(2)—C(3)—O(3)	168.6 (3)	Mo(2)—C(4)—O(4)	171.3 (3)
Co(1)—C(5)—O(5)	178.4 (3)	Co(1)—C(6)—O(6)	176.2 (4)
Co(1)—C(7)—O(7)	177.9 (3)		

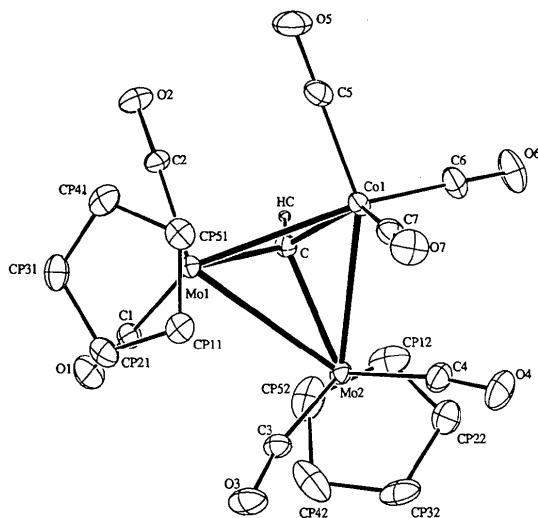


Fig. 1. The molecular structure of (μ_3 -CH)CoMo₂(CO)₇(η^5 -C₅H₅)₂ and the numbering scheme used (*ORTEPII*).

Discussion. The structure consists of two molybdenum atoms and a cobalt atom forming a metal triangle which is capped by an alkylidyne unit. The structure is similar to that of the methyl analogue, (μ_3 -CCH₃)CoMo₂(CO)₇(η^5 -C₅H₅)₂, (2), recently prepared by Vahrenkamp (Blumhofer *et al.*, 1986), with several minor variations.

The metal triangle in (1) is slightly distorted in that the two Mo—Co distances are different at [Mo(1)—Co(1)], 2.7169 (3) \AA , and [Mo(2)—Co(1)], 2.7679 (4) \AA , compared to the value of 2.712 (2) \AA listed for (2). This unexpected variation in the metal

triangle is reflected in variations of the other bonds and angles associated with the molybdenum atoms as shown in Table 2. The longer Mo—Co bond is that associated with the molybdenum whose cyclopentadienyl ring is on the upper, or capped, face of the metal triangle, *i.e.* Mo(2). Normally this lengthening would be assumed to be a mechanism to reduce the steric interactions between the cyclopentadienyl group and the other atoms on the upper face. However, the closest contact on this upper face is between the alkyldiene carbon and C(2) and Mo(1), at 2.36 Å, yet this causes no marked distortions around Mo(1). The Mo—C_{ap} [Mo(1)—C_{ap} 2.069 (3) Å, Mo(2)—C_{ap} 2.087 (3) Å] distances are slightly shorter than in (2), and are also slightly shorter than in the related compound (μ_3 -CPh)Co₂Mo(CO)₈(η^5 -C₅H₅), (3) (Beurich & Vahrenkamp, 1982), but not significantly so. These other two structures have Mo—C_{ap} distances of 2.11 (1) and 2.10 (1) Å respectively. The Co—C_{ap} distances are essentially identical in all three structures [1.933 (3) Å in (1), 1.94 (1) Å in (2) and 1.93 (1) Å in (3)].

The carbonyl groups on the cobalt atom are all as expected with no unusual variations in bond lengths or angles. The carbonyl groups on the molybdenum atoms, on the other hand, show deviations from the expected norm. The main deviation of note for the carbonyl groups is that those attached to Mo(2) show marked deviations from linearity. The Co(1) and Mo(1) carbonyls all have angles close to the expected 180° [range 175.8 (3)–178.6 (3)°], whereas those on Mo(2) show angles of 168.6 (3)° [C(3)—O(3)] and 171.3 (3)° [C(4)—O(4)]. The closest contact for carbonyl C(3)—O(3) is H(Cp11) at 2.6 Å, while the closest contact for C(4)—O(4) is C(3) at 2.63 Å.

These distances are similar to those found for all the other carbonyl groups except for the close interaction of the alkyldiene carbon with C(2) (2.36 Å) and so presumably the distortion is due to subtle interactions, both intra- and intermolecular.

A further point of note is the tilting of the cyclopentadienyl ligands with respect to the metal. The metal—(η^5 -C₅H₅) distances range from 2.367 to 2.299 Å for ring 2 [on Mo(2)] and from 2.378 to 2.306 Å for ring 1 [on Mo(1)]. This tilting appears to be a common feature of metal—cyclopentadienyl interactions and this range of distances is as expected.

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Structure of (*N,N'*-Bissalicylidene-1,5-diamino-3-azapentane)dioxouranium(VI) Ethanol Solvate

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Abstract. [*N,N'*-(3-Aza-1,5-pentanediy)bis(salicylideneiminato)]dioxouranium(VI) ethanol solvate, C₁₈H₁₉N₃O₄U·C₂H₆O, *M_r* = 625.466, orthorhombic, *Pca*2₁, *a* = 9.912 (10), *b* = 11.438 (19), *c* = 19.599 (38) Å, *V* = 2222.2 Å³, *Z* = 4, *D_x* = 1.869 g cm⁻³, λ(Mo *Kα*) = 0.71069 Å, μ = 69.29 cm⁻¹, *F*(000) = 1191.7, room temperature,

final *R* = 0.069 for 1654 unique observed reflexions. The ethanol molecules are not coordinated to the uranium but occupy channels running through the lattice. They cause distortion of the molecules of the complex in which the angles between the planes of the benzene rings and the equatorial coordination plane of the uranium are decreased.