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Hexacarbonyl($\eta^{5:1}$ -2-cyclopentadienediylethyl)(μ - $\eta^{1:3}$ -1-ethoxy-2-propenylidene)molybdenumtungsten

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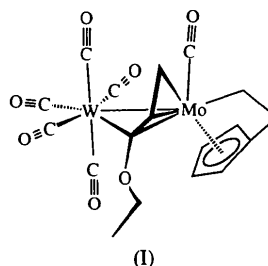
Abstract

The crystal structure of the title compound [alternative nomenclature: hexacarbonyl-1 κ^5 C, 2 κ C-2(η^5)-2-cyclopentadienediylethyl-2 κ C¹- μ -2(η^2)-1-ethoxy-2-propenylidene-1:2 κ^2 C¹-2-molybdenum-1-tungsten(Mo—W)], [(C₅H₄C₂H₄)(CO)Mo(C₃H₃OC₂H₅)W(CO)₅], (I), has been determined from single-crystal X-ray diffraction data. Geometry and bond lengths of (I) are in accord with its description as a 1-molybdena-5-tungstenatri-cyclo[2.1.0.0^{1,3}]pentane or, even better, as an *arachno*-pentagonal bipyramid with an Mo atom at the apex.

Comment

Transition metal complexes with α,β -unsaturated carbene or propenylidene ligands coordinate to 14-electron complex fragments, *e.g.* tetracarbonyl tungsten or tricarbonyl iron, in a comparable fashion to 1,3-butadiene. In the resulting dinuclear complexes the $\eta^{1:3}$ -propenylidene ligands are in bridging positions (Parlier, Rose, Rudler & Rudler, 1982; Parlier, Rudler, Rudler & Daran, 1987; Macomber, Liang & Rogers, 1988; Macomber, Liang, Madhukar & Verma, 1989; Alvarez-Toledano *et al.*, 1987).

Tricarbonyl($\eta^{1:5}$ -2-cyclopentadienediylethyl)molybdenum (Eilbracht, 1976) was shown to form photochemically stable η^2 - and η^4 -diene complexes with conjugated dienes (Kreiter, Michels & Wenz, 1986; Kreiter, Wenz & Bell, 1990) and is, therefore, a promising candidate for the coordination of propenylidene complexes. As pentacarbonyl(1-ethoxy-2-propenylidene)tungsten, (II) (Macomber *et al.*, 1989), is decomposed photochemically, tricarbonyl($\eta^{1:5}$ -2-cyclopentadienediylethyl)molybdenum, (III), was first irradiated in THF in order to obtain the reactive compound dicarbonyl($\eta^{1:5}$ -2-cyclopentadienediylethyl)-(tetrahydrofuran)molybdenum, which reacts readily with the title compound, (I), primarily to give orange heptacarbonyl($\eta^{1:5}$ -2-cyclopentadienediylethyl)(μ -2,3- η -1-ethoxy-2-propenylidene)molybdenum-tungsten, (IV). Even at 248 K (IV) loses carbon monoxide, forming the green title compound, (I) (Schufft, 1992).



Crystals of (I) contain discrete dinuclear complexes. The Mo atom with its carbonyl and its $\eta^{5:1}$ -chelating cyclopentadienediylethyl ligand is connected to a tungsten pentacarbonyl fragment by an Mo—W bond and the propenylidene part of the ethoxypropenylidene ligand. The Mo—W distance corresponds well with known Mo—W single bonds (Delgado, Garcia, Jeffery, Sherwood & Stone, 1988).

The propenylidene unit C1—C3, with essentially equal C—C bond lengths [C1—C2 1.396 (7) and C2—C3 1.399 (7) Å], is η^3 -coordinated to Mo and η^1 -coordinated to W. The corresponding Mo—C distances are somewhat shorter than those found for the allyl ligand in (η^3 -allyl)dicarbonyl(η^5 -cyclopentadienyl)molybdenum (Faller, Chodosh & Katahira, 1980) or for the butadiene ligand in (η^4 -1,3-butadiene)-carbonylmethyl(η^5 -pentamethylcyclopentadienyl)molybdenum, (V) (Kreiter, Wendt & Sheldrick, 1987), whereas the Mo—C17 single bond [2.313 (7) Å] is significantly longer than the Mo—methyl carbon distance [2.24 (2) Å] in (V). The coordination sphere of tungsten is distorted pentagonal bipyramidal or distorted octahedral if Mo and C(1) together are considered to occupy one coordination site. In comparison with the corresponding W—alkyl group bond in [(CO)₅WCH(OCH₃)(C₆H₅)][−] (2.34 (1) Å; Casey, Polichnowski, Tuinstra, Albin & Calabrese, 1978), the W—C1 bond is considerably shorter [2.282 (6) Å].

The CO ligand approximately *trans* to the Mo atom has a shorter W—C bond than the other four W-bonded carbonyl ligands, as one would expect for a CO ligand with a greater degree of tungsten-carbon π^* -back-bonding.

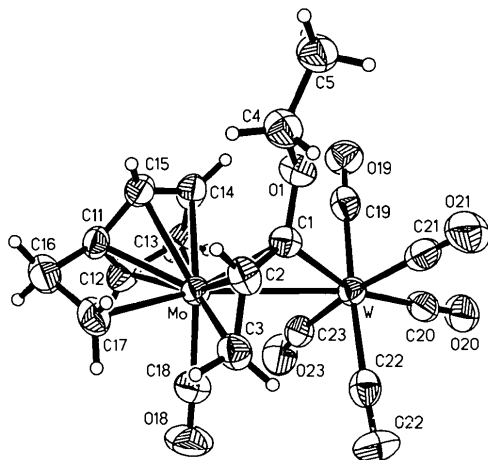


Fig. 1. Diagram of (I) showing the atom-numbering scheme (displacement ellipsoids at the 50% probability level; H atom labels are omitted for clarity; the H atom at C12 is covered by C17)

Experimental

The air-sensitive compound was synthesized according to the procedure given by Schufft (1992). Dark green plates were grown from pentane at room temperature.

Crystal data

[MoW(C ₇ H ₈)(C ₅ H ₈ O)(CO) ₆]	Mo $K\alpha$ radiation
$M_r = 624.110$	$\lambda = 0.71069 \text{ \AA}$
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	$\theta = 9.37\text{--}12.24^\circ$
$a = 8.708 (2) \text{ \AA}$	$\mu = 6.867 \text{ mm}^{-1}$
$b = 9.047 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 12.961 (3) \text{ \AA}$	Plate
$\alpha = 72.40 (3)^\circ$	$0.3 \times 0.1 \times 0.05 \text{ mm}$
$\beta = 84.61 (3)^\circ$	Dark green
$\gamma = 77.36 (3)^\circ$	
$V = 949.28 (42) \text{ \AA}^3$	
$Z = 2$	
$D_x = 2.1835 \text{ Mg m}^{-3}$	

Data collection

Enraf-Nonius CAD-4 four-circle diffractometer	$\theta_{\max} = 24.97^\circ$
ω/θ scans	$h = -10 \rightarrow 10$
Absorption correction: ψ scan	$k = -10 \rightarrow 10$
$T_{\min} = 0.484$, $T_{\max} = 0.730$	$l = 0 \rightarrow 12$
3005 measured reflections	3 standard reflections
3005 independent reflections	frequency: 60 min
2685 observed reflections	intensity decay: none
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.125$
$R[F^2 > 2\sigma(F^2)] = 0.0240$	$\Delta\rho_{\max} = 1.101 \text{ e \AA}^{-3}$
$wR(F^2) = 0.0495$	$\Delta\rho_{\min} = -0.732 \text{ e \AA}^{-3}$
$S = 1.625$	Extinction correction:
2894 reflections	SHELXL93 (Sheldrick, 1993)
286 parameters	Extinction coefficient:
All H atoms refined together with the corresponding C atoms as rigid groups, with one common isotropic U for the H atoms of each group	0.00114 (14)
$w = 1/\sigma^2(F_o^2)$	Atomic scattering factors for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
W	0.05681 (3)	0.48662 (3)	0.24110 (2)	0.04367 (10)
Mo	0.27032 (6)	0.73929 (6)	0.22053 (4)	0.04281 (15)
O1	0.3969 (5)	0.3612 (5)	0.3106 (3)	0.0530 (11)
C1	0.2815 (7)	0.4866 (7)	0.3186 (5)	0.0465 (14)
C2	0.2986 (8)	0.5734 (7)	0.3882 (5)	0.052 (2)
C3	0.1751 (8)	0.6989 (8)	0.3936 (5)	0.057 (2)
C4	0.5180 (9)	0.3005 (8)	0.3893 (6)	0.065 (2)
C5	0.6068 (8)	0.1449 (8)	0.3774 (7)	0.072 (2)
C11	0.4731 (7)	0.8553 (7)	0.1302 (5)	0.051 (2)
C12	0.3505 (8)	0.8958 (9)	0.0591 (6)	0.066 (2)
C13	0.3265 (9)	0.7581 (11)	0.0400 (6)	0.071 (2)
C14	0.4346 (9)	0.6308 (10)	0.1004 (6)	0.066 (2)
C15	0.5246 (7)	0.6900 (8)	0.1571 (6)	0.055 (2)
C16	0.5006 (9)	0.9495 (8)	0.2004 (7)	0.068 (2)
C17	0.3824 (9)	0.8997 (8)	0.2875 (6)	0.065 (2)
O18	-0.0286 (7)	1.0050 (6)	0.2036 (5)	0.104 (2)
C18	0.0786 (8)	0.9063 (8)	0.2100 (6)	0.064 (2)
O19	0.2780 (6)	0.3241 (6)	0.0812 (4)	0.0748 (14)
C19	0.2039 (8)	0.3835 (8)	0.1406 (6)	0.055 (2)
O20	-0.2016 (6)	0.3673 (6)	0.1546 (5)	0.082 (2)
C20	-0.1083 (8)	0.4109 (7)	0.1885 (6)	0.058 (2)
O21	0.1047 (7)	0.1655 (6)	0.4297 (5)	0.097 (2)
C21	0.0884 (7)	0.2815 (9)	0.3617 (6)	0.060 (2)
O22	-0.2163 (6)	0.6446 (6)	0.3755 (4)	0.083 (2)
C22	-0.1110 (8)	0.5885 (8)	0.3309 (6)	0.058 (2)
O23	-0.0628 (6)	0.7851 (6)	0.0464 (4)	0.085 (2)
C23	-0.0077 (7)	0.6840 (8)	0.1177 (6)	0.057 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

W—Mo	3.1862 (10)	O1—C4	1.436 (7)
W—C1	2.282 (6)	C1—C2	1.400 (8)
Mo—C1	2.241 (6)	C2—C3	1.396 (9)
Mo—C2	2.237 (6)	C4—C5	1.496 (9)
Mo—C3	2.268 (7)	C11—C12	1.391 (9)
Mo—C18	1.975 (7)	C11—C15	1.406 (8)
W—C19	2.026 (8)	C11—C16	1.487 (9)
W—C20	1.975 (7)	C12—C13	1.402 (11)
W—C21	2.017 (8)	C13—C14	1.394 (11)
W—C23	2.016 (7)	C14—C15	1.405 (9)
W—C22	2.020 (8)	C16—C17	1.488 (10)
Mo—C11	2.296 (6)	O18—C18	1.132 (7)
Mo—C12	2.289 (7)	O19—C19	1.141 (7)
Mo—C13	2.307 (7)	O20—C20	1.148 (7)
Mo—C14	2.308 (7)	O21—C21	1.139 (8)
Mo—C15	2.286 (6)	O22—C22	1.143 (7)
Mo—C17	2.313 (7)	O23—C23	1.141 (7)
O1—C1	1.364 (6)		

C20—W—C21	87.4 (3)	C18—Mo—W	89.7 (2)
C20—W—C23	84.1 (3)	C3—Mo—W	77.7 (2)
C21—W—C23	171.0 (3)	C17—Mo—W	153.4 (2)
C20—W—C22	88.4 (3)	C1—O1—C4	118.9 (5)
C21—W—C22	90.7 (3)	O1—C1—C2	119.8 (5)
C23—W—C22	86.3 (3)	O1—C1—Mo	125.8 (4)
C20—W—C19	85.1 (3)	C2—C1—Mo	71.6 (3)
C21—W—C19	91.2 (3)	O1—C1—W	110.9 (4)
C23—W—C19	90.9 (3)	C2—C1—W	127.7 (4)
C22—W—C19	173.2 (3)	Mo—C1—W	89.6 (2)
C20—W—C1	161.0 (2)	C3—C2—C1	116.9 (6)
C21—W—C1	76.6 (2)	C3—C2—Mo	73.2 (4)
C23—W—C1	112.3 (2)	C1—C2—Mo	71.9 (3)
C22—W—C1	101.8 (2)	C2—C3—Mo	70.7 (4)
C19—W—C1	85.1 (2)	O1—C4—C5	108.0 (6)
C20—W—Mo	152.0 (2)	C12—C11—C15	107.3 (6)
C21—W—Mo	120.6 (2)	C12—C11—C16	125.9 (7)
C23—W—Mo	68.1 (2)	C15—C11—C16	122.4 (6)
C22—W—Mo	92.7 (2)	C13—C12—C11	108.9 (7)
C19—W—Mo	92.0 (2)	C14—C13—C12	107.7 (7)
C1—W—Mo	44.69 (14)	C13—C14—C15	107.9 (7)
C18—Mo—C2	111.7 (3)	C11—C15—C14	108.2 (6)
C18—Mo—C1	123.6 (3)	C17—C16—C11	97.4 (5)
C18—Mo—C3	76.0 (3)	C16—C17—Mo	101.9 (5)
C18—Mo—C17	84.7 (3)	O18—C18—Mo	178.0 (7)
C2—Mo—C17	84.6 (3)	O19—C19—W	175.4 (6)
C1—Mo—C17	118.8 (2)	O20—C20—W	177.7 (6)
C3—Mo—C17	75.7 (3)	O21—C21—W	179.3 (6)
C12—Mo—C17	81.7 (3)	O22—C22—W	173.4 (6)
C11—Mo—C17	58.0 (2)	O23—C23—W	169.4 (6)

Scattering factors, dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Tables 6.1.1.4, 4.2.6.8 and 4.2.4.2).

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *XCAD4* (Harms & Wocadlo, 1993). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1070). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(*N*¹-isopropyl-2-methylpropane-1,2-diamine)diisothiocyanatocadmium(II)

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Abstract

In the complex [Cd(NCS)₂(C₇H₁₈N₂)₂], the Cd atom lies on an inversion centre and has a distorted octahedral environment consisting of four amine N atoms from two bidentate *N*¹-isopropyl-2-methylpropane-1,2-diamine (*N*-*N*) ligands [Cd—N(primary) = 2.362 (3) Å, Cd—N(secondary) = 2.400 (3) Å] and two N atoms from two isothiocyanato groups [Cd—N = 2.378 (5) Å]. The conformation of the diamine chelate rings is δλ. Molecules are linked by N—H···S hydrogen bonds (N···S 3.665 Å).

Comment

The coordination geometry around a complexed metal ion is greatly influenced by the variation of substituents on the ethane-1,2-diamine as well as counteranions. The crystal structure of the title compound, (I), as found by X-ray analysis, clearly depicts the pattern of coordination and bonding in the molecule.