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Photochemical Reactions of Transition Metal Organyl Complexes with Olefins.
18.† Dicarboxylbis(η⁵-cyclopentadienyl)-
(μ-1,4-η:4,5-η-1,4-pentadien-1,4-diyl)-
oxoditungsten(W—W)‡

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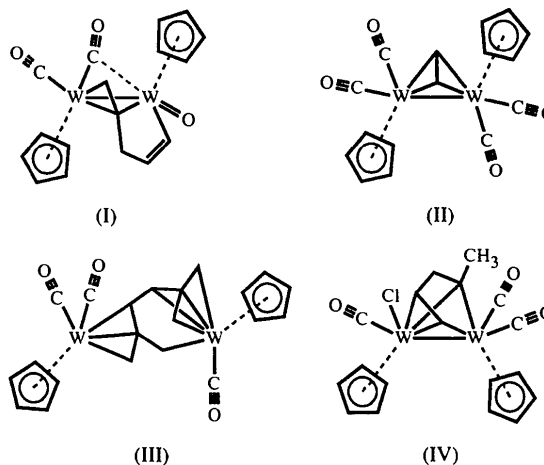
Abstract

In the binuclear title complex, [W₂O(C₅H₅)₂(C₅H₆)(CO)₂], the W centres are bridged by a 1,4-pentadien-1,4-diyl ligand. The W—W distance of 2.9426 (5) Å is in accord with a W—W single bond, the W—O distance of 1.678 (5) Å corresponds to a W=O double bond.

Comment

When irradiated with UV light, (μ-η^{2:2}-acetylene)-tetracarbonylbis(η⁵-cyclopentadienyl)ditungsten(W—W), (II), and ethylene react to give predominantly (μ-η^{1:4}-1,3-butadien-1-yl)tricarbonylbis(η⁵-cyclopentadienyl)hydridoditungsten(W—W), (μ-η^{1:3}-2-butene-1,1-diyl)tetracarbonylbis(η⁵-cyclopentadienyl)ditungsten(W—W) and thermolabile (η⁴-1,3-butadiene)tricarbonylbis(η⁵-cyclopentadienyl)hydridoditungsten(W—W). The three different C₄ ligands of these compounds are formed by insertion of ethylene into a W—C bond of the tetrahedral W₂C₂ core of (II) and successive metal-mediated H shifts (Kern, 1992; Kreiter, Kern, Wolmershäuser & Heckmann, 1997). When conjugated or cumulated dienes are used instead of ethylene, the longer carbon chains and the additional double bonds of these hydrocarbons should lead to a different reaction behaviour (Würtz, 1988). Somewhat unexpectedly, upon UV irradiation in the presence of a large excess of allene, complex (II) in THF (tetrahydrofuran) at 223 K forms the title complex, (I), in reasonable yield (23%). Dark-red crystals of the compound are obtained from the reaction mixture after successive column chromatography on alumina (Schwarz, 1996). Orange crystals of tricarbonylbis(η⁵-cyclopentadienyl)(μ-1-3,1',6-η:4,5,1''-η-2,5-dimethylenehexa-1,3,4,6-tetrayl)ditungsten(W—W), (III), and yellow needles of tricarbonylchlorobis(η⁵-

cyclopentadienyl)(μ-1,4-η:1,2,4-η-1-penten-4-yliden-1-yl)ditungsten(W—W), (IV), are minor by-products. The latter is formed during chromatography with methylene chloride as eluent.



Several examples of oxo complexes generated from metal carbonyls have been observed (Herrmann, Serrano & Bock, 1984; Klahn-Oliva & Sutton, 1984; Herrmann, 1988; Bottomley & Sutin, 1988; Bottomley, 1992). Sources for the oxo ligands are water, oxygen or hydroperoxide. Although all the preparative manipulations during the photochemical synthesis of (I) were conducted under dry argon in thoroughly dried solvents, obviously there must have been traces of water in the system (probably in the allene), from which the oxo ligand was generated.

In oxo complexes, M—O single and double bonds have been observed with bond lengths of 1.78–2.22 Å for single and 1.59–1.71 Å for double bonds (Carroll, Green, Orpen, Schaverien, Williams & Welch, 1986; Herrmann, 1988; Bottomley & Sutin, 1988); thus the W—O bond length of 1.678 (5) Å in complex (I) indicates a W=O double bond. The W—W distance of 2.9426 (5) Å is in accord with a W—W single bond (Adams, Collins & Cotton, 1974; Ginley, Bock, Wrighton, Fischer, Tipton & Bau, 1978). By simple electron counting, 17 electrons result for W1, but only 15 electrons for W2. The formal oxidation number for W1 is +1 and for W2 +5. The electron deficiency at W2 results in reduced back-bonding to the cyclopentadienyl (Cp) ligand, reflected by the greater distance of W2 to the plane of its Cp ring [2.069 (4) Å] in comparison with the corresponding distance at W1 [1.991 (4) Å]. One carbonyl ligand of W1 is semi-bridging (Cotton, 1976) to W2 with W1—C2—O2 169.5 (7), W2—W1—C2 70.2 (2)° and W2—C2 2.955 (7) Å. In this way, some electron density is transferred to W2. As is to be expected from the different coordination modes of the two carbonyl ligands, C1—O1 [1.135 (10) Å] is slightly shorter than C2—O2 [1.152 (10) Å]. The W—C single

† Part 17: Kreiter & Eckert (1997).

‡ Alternative name: dicarbonyl-1κ²C-1,2-bis(η⁵-cyclopentadienyl)oxo-2κO-μ-1-pentene-1,4,4,5-tetrayl-1κ²C⁴,C⁵:2κ²C¹,C⁴-ditungsten(W—W).

bond lengths, the C—C bond lengths within the penta-dienediyl ligand and the distorted η^2 coordination geometry at W1 are as expected, taking into account the special bonding situation of (I).

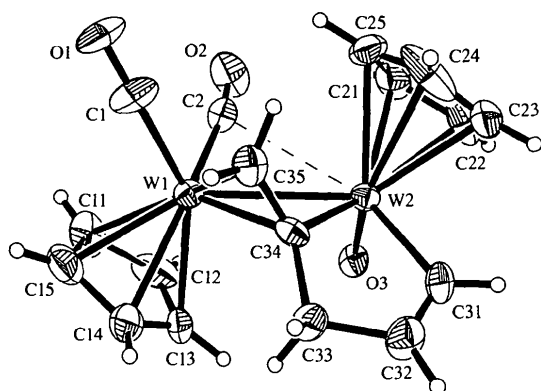


Fig. 1. Structure of compound (I) in the crystal showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level; H-atom labels have been omitted for clarity.

Experimental

The air-sensitive title compound was synthesized according to Schwarz (1996). Red crystals were grown from *n*-pentane/diethyl ether (1:3) at room temperature. The crystal used for the structure determination was mounted in a nitro-gen-filled capillary.

Crystal data

[W₂O(C₅H₅)₂(C₅H₆)(CO)₂]
 $M_r = 636.01$
 Monoclinic
 $P2_1/c$
 $a = 8.6460(11) \text{ \AA}$
 $b = 10.8490(13) \text{ \AA}$
 $c = 15.9600(2) \text{ \AA}$
 $\beta = 95.48(2)^\circ$
 $V = 1490.2(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 2.835 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 9.22\text{--}12.54^\circ$
 $\mu = 15.435 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Nearly isometric with broken edge
 $0.34 \times 0.30 \times 0.26 \text{ mm}$
 Red

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
 ω/θ scans
 Absorption correction: by integration, transmission factors calculated using *SHELX76* (Sheldrick, 1976)
 $T_{\min} = 0.041$, $T_{\max} = 0.082$
 5433 measured reflections
 2625 independent reflections

2446 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\max} = 25.05^\circ$
 $h = -10 \rightarrow 10$
 $k = -12 \rightarrow 12$
 $l = 0 \rightarrow 18$
 2 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.075$
 $S = 1.136$
 2625 reflections
 205 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 3.8P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.083$
 $\Delta\rho_{\max} = 2.237 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.958 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

W1—W2	2.9426 (5)	W2—C22	2.304 (8)
W1—C1	1.982 (9)	W2—C23	2.394 (9)
W1—C2	1.964 (8)	W2—C24	2.492 (10)
W1—C11	2.292 (7)	W2—C25	2.441 (8)
W1—C12	2.319 (7)	W2—C31	2.125 (8)
W1—C13	2.347 (8)	W2—C34	2.121 (7)
W1—C14	2.331 (8)	O1—C1	1.135 (10)
W1—C15	2.323 (8)	O2—C2	1.152 (10)
W1—C34	2.196 (7)	C31—C32	1.325 (12)
W1—C35	2.289 (7)	C32—C33	1.495 (11)
W2—O3	1.678 (5)	C33—C34	1.491 (10)
W2—C2	2.955 (7)	C34—C35	1.406 (11)
W2—C21	2.319 (8)		
C1—W1—C2	82.6 (3)	C31—C32—C33	116.4 (7)
C2—W1—W2	70.9 (2)	C32—C33—C34	105.4 (6)
W1—C1—O1	179.3 (8)	W2—C34—C33	116.6 (5)
W1—C2—W2	70.2 (2)	W2—C34—C35	118.8 (5)
W1—C2—O2	169.5 (7)	C33—C34—C35	121.1 (7)
C32—C31—W2	119.7 (6)		

The orientations of the H atoms at C35 were refined with C—H restrained to 0.96 \AA within a standard deviation of 0.02; the other H atoms were refined as riding in idealized positions. The remaining electron-density maxima higher than 1 e \AA^{-3} are located near the W atoms.

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, 1990). 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1195). Services for accessing these data are described at the back of the journal.

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Di- μ -chloro-bis[chloro(6,7,8,9,10,11,18,19-octahydro-5H,17H-dibenzof[*f*,*o*][1,5,9,13]-dioxadiazacyclohexadecane)copper(II)][†]

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Abstract

The title complex, [CuCl₂(C₂₀H₂₆N₂O₂)]₂, has a centrosymmetrical dimeric structure linked by a pair of chloride bridges. Each Cu atom has the five-coordinated geometry of a distorted square pyramid. The axial sites are occupied by the bridging chlorides which are bound asymmetrically to Cu at distances of 2.8288 (14) and 2.2963 (12) Å. The Cu...Cu distance of 3.4294 (13) Å is too long to suggest a Cu—Cu bond in the dimeric unit.

[†] Alternative name: di- μ -chloro-bis{chloro[2,6-dioxo-14,18-diazatricyclo[18.4.0.0^{7,12}]]tetracos-1(20),7(12),8,10,21,23-hexaene-*N,N'*-copper(II)}.

Comment

In recent years, various macrocyclic ligands have been the subject of an intense research effort because of their high selectivity towards metal ions. From the investigation of the interaction of N₂O₂-donor macrocycles with Cu^{II} and high-spin Ni^{II}, Andereg, Ekstrom, Lindoy & Smith (1980) reported that one of the major parameters affecting the metal-ion specificity for Ni^{II} is the hole size in the macrocyclic ligand. It has been confirmed by X-ray studies of Ni^{II} analogues (Adam *et al.*, 1979) that the nickel ion sits in the hole of the macrocycle and a clear correlation between macrocyclic hole size and thermodynamic stability has been observed. In contrast, such a correlation was not observed for Cu^{II} complexes (Adam *et al.*, 1980). In an effort to elucidate the difference in behaviour for Cu^{II} complexes, we have determined the structure of title complex, (I).

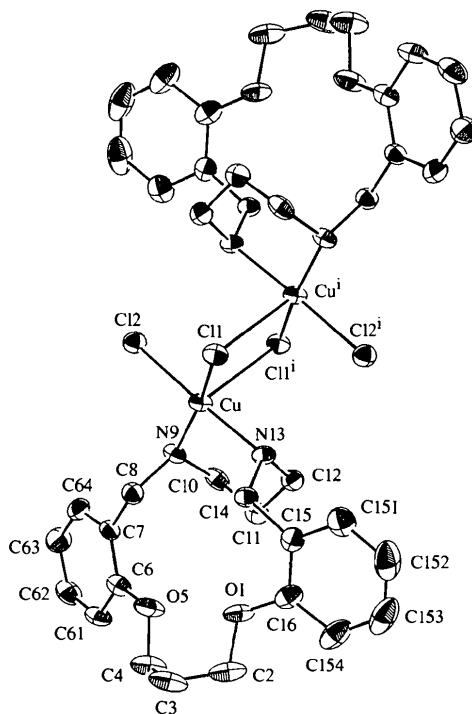
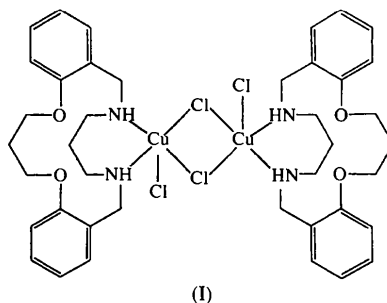


Fig. 1. Displacement ellipsoid plot (50% probability level) for the title complex with the atom-numbering scheme. H atoms have been omitted for clarity.