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Acta Cryst. (1996). C**52**, 2701-2703

Photochemical Reactions of Transition Metal Organyl Complexes with Olefins. 15.† Tricarbonyl(η^4-1,3-butadiene)-μ-hydrido-(μ-$\eta^{1:5}$-indene-1,1-diyl)(η^5-indenyl)dimolybdenum(*Mo—Mo*)

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(*Received 10 April 1996; accepted 19 June 1996*)

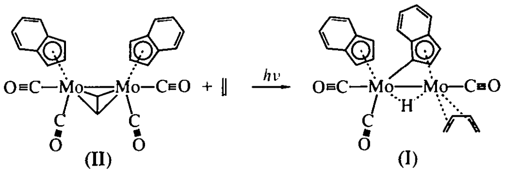
Abstract

The Mo centres of the dinuclear title complex, [1(η^4)-1,3-butadiene]tricarbonyl-1κC,2$\kappa^2 C$-μ-hydrido-[2(1,2,3,3a,7a-η)-indenyl][μ-1(1,2,3,3a,7a-η):2κC^1-indenylidene]dimolybdenum(*Mo—Mo*), [$Mo_2(H)(C_9H_6)(C_9H_7)(C_4H_6)(CO)_3$], are bridged by a μ-$\eta^{1:5}$-indene-1,1-diyl and a hydrido ligand. The Mo—Mo distance of 3.2024 (7) Å is normal for an Mo—Mo single bond.

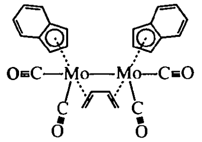
Comment

When tetracarbonylbis(η^5-cyclopentadienyl)(μ-$\eta^{2:2}$-ethyne)dimolybdenum, (III), is UV irradiated in the presence of ethene, the stable products (η^4-butadiene)tricarbonylbis(η^5-cyclopentadienyl)dimolybdenum, (η^4-butadiene)tetracarbonylbis(η^5-cyclopentadienyl)dimolybdenum and (μ-$\eta^{1:3}$-2-buten-1-ylidene)tetracarbonylbis(η^5-cyclopentadienyl)dimolybdenum (Kern, 1992; Kreiter & Kern, 1993) are formed. The butadiene and 2-buten-1-ylidene ligands are formed by insertion of ethene into an Mo—C bond of the tetrahedral Mo_2C_2 core of compound (III) and successive metal-mediated hydride shifts.

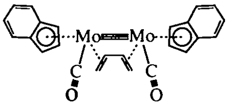
η^5-Indenyl complexes often show a different reaction behaviour from the corresponding η^5-cyclopentadienyl compounds because of the ability of the indenyl ligand to change its hapticity. In order to study the differences caused by indenyl ligands, tetracarbonyl(μ-$\eta^{2:2}$-ethyne)bis(η^5-indenyl)dimolybdenum, (II), was reacted photochemically with simple mono-olefins (Meuser, 1993). Compound (II) when reacted with ethene forms three butadiene complexes, namely, the title compound, (η^4-1,3-butadiene)tricarbonyl-μ-hydrido-(μ-$\eta^{1:5}$-indene-1,1-diyl)(η^5-indenyl)dimolybdenum, (I), (μ-$\eta^{2:2}$-1,3-butadiene)tetracarbonylbis(η^5-indenyl)dimolybdenum, (IV), and (μ-$\eta^{2:2}$-1,3-butadiene)dicarbonylbis(η^5-indenyl)dimolybdenum, (V). The variability of the products reflects the different possibilities of coordination for the butadiene ligand at complex fragments with metal–metal single or triple bonds. In contrast to (η^4-butadiene)tricarbonylbis(η^5-cyclopentadienyl)dimolybdenum, where the electron deficiency of the binuclear 32-electron complex is compensated for by a μ-$\eta^{2:1}$-CO ligand, the comparable indenyl complex (I) is stabilized by the oxidative addition of a C—H bond of one indenyl ligand to the Mo1 atom.



(II) (I)



(III)



(IV)

Compound (I) (Fig. 1) contains three terminal carbonyl, an *S-cis*-η^4-1,3-butadiene, a η^5-indenyl, a bridging μ-$\eta^{5:1}$-indene-1,1-diyl and a bridging hydrido ligand. The Mo—Mo distance of 3.2024 (7) Å is in agreement with the Mo—Mo single-bond distance found in hexacarbonyldi(η^5-cyclopentadienyl)dimolybdenum (Adams, Collins & Cotton, 1974). In order to fulfil the 18-electron rule for both metal centres, the hydrido ligand could be bonded terminally to the Mo1 atom. In fact,

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† Part 14: Kreiter, Eckert, Frank & Reiß (1996).

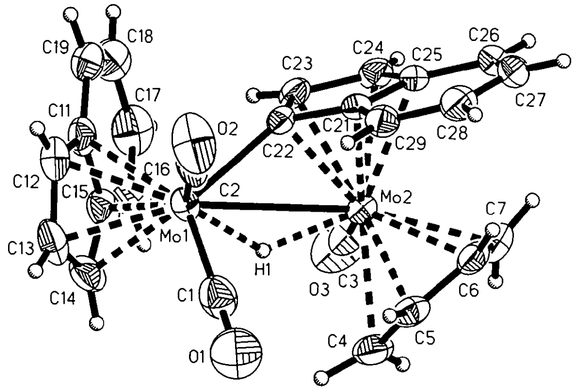

Fig. 1. Diagram of compound (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and with the exception of the label of the H1 atom, H-atom labels have been omitted for clarity.

H1 is nearly equidistant from both Mo atoms and the Mo—H—Mo angle is 122 (3)°. The core of compound (I) is thus represented by an Mo—H—Mo three-centre–two-electron bond.

Comparable bonding features to those observed for the μ-$\eta^{5:1}$-indene-1,1-diyl ligand are also found for the μ-$\eta^{5:1}$-cyclopentadienediyl ligands in 'dimeric molybdenocene' and in tricarbonyl(μ-$\eta^{5:1}$-cyclopentadienediyl)di(η^5-cyclopentadienyl)dimolybdenum (Green, Poveda, Bashkin & Prout, 1982; Bashkin, Green, Poveda & Prout, 1982).

Both the η^5-indenyl and the μ-$\eta^{5:1}$-indene-1,1-diyl ligands show a slight 'ring slippage' (Faller, Crabtree & Habib, 1985). The distances between the Mo1 atom and the C12, C13 and C14 atoms are on average 0.16 Å shorter than those to atoms C11 and C15. Similarly, the distances between Mo2 and C22, C23 and C24 are on average 0.14 Å shorter than those to C21 and C25. The dihedral angle between the planes of the five- and six-membered rings is 5.2° for the η^5-indenyl and 1.6° for the indenediyl ligand. The Mo1—C22 bond length [2.146 (3) Å] lies in the range of Mo—C single bonds. The angle between the corresponding direction and the plane of the C21–C25 ring is 20.3°.

Experimental

The air-sensitive title compound was synthesized according to the procedure of Meuser (1993). Crystals were grown from an *n*-pentane/diethyl ether (2:1) solution at room temperature.

Crystal data

$[Mo_2(H)(C_9H_6)(C_9H_7)(C_4H_6)(CO)_3]$
$M_r = 560.29$
Triclinic
$P\bar{1}$
$a = 9.558 (2)$ Å
$b = 10.454 (2)$ Å
$c = 11.009 (2)$ Å
$\alpha = 80.29 (2)°$
$\beta = 87.94 (2)°$
$\gamma = 75.43 (2)°$
$V = 1049.4 (4)$ Å^3
$Z = 2$
$D_x = 1.773$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 50 reflections
$\theta = 28.0$–$30.0°$
$\mu = 1.219$ mm^{-1}
$T = 291 (2)$ K
Needle
$0.6 \times 0.2 \times 0.1$ mm
Dark red

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
ω/θ scans
Absorption correction: ψ scans (*CAD*-4 *Software*; Enraf–Nonius, 1989)
$T_{min} = 0.82$, $T_{max} = 0.89$
3698 measured reflections
3641 independent reflections
3331 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0184$
$\theta_{max} = 24.97°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections frequency: 60 min intensity decay: 7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0221$
$wR(F^2) = 0.0501$
$S = 1.875$
3533 reflections
352 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0056P)^2 + 0.4262P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.013$
$\Delta\rho_{max} = 0.347$ e Å^{-3}
$\Delta\rho_{min} = -0.431$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0147 (4)
Atomic scattering factors from *International Tables 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* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mo1	0.94785 (3)	0.76004 (3)	0.73003 (2)	0.03679 (9)
Mo2	0.65329 (3)	0.66667 (2)	0.73107 (2)	0.03273 (9)
O1	1.0972 (3)	0.4878 (3)	0.6548 (4)	0.1017 (12)
O2	1.0450 (3)	0.8336 (4)	0.4607 (2)	0.0844 (10)
O3	0.5478 (4)	0.6405 (3)	1.0016 (3)	0.0901 (10)
C1	1.0389 (4)	0.5896 (4)	0.6833 (4)	0.0602 (10)
C2	1.0051 (4)	0.8088 (4)	0.5604 (3)	0.0556 (9)
C3	0.5900 (4)	0.6443 (3)	0.9023 (3)	0.0544 (9)
C4	0.7651 (5)	0.4387 (3)	0.7914 (4)	0.0540 (9)
C5	0.7422 (4)	0.4716 (3)	0.6634 (3)	0.0445 (8)
C6	0.5994 (4)	0.5246 (3)	0.6207 (3)	0.0435 (8)
C7	0.4851 (5)	0.5444 (4)	0.7024 (4)	0.0531 (9)
C11	0.9506 (4)	0.9312 (3)	0.8604 (3)	0.0462 (8)
C12	1.0754 (4)	0.9019 (4)	0.7871 (4)	0.0548 (9)
C13	1.1530 (4)	0.7703 (4)	0.8280 (4)	0.0599 (10)
C14	1.0716 (4)	0.7095 (4)	0.9160 (4)	0.0562 (10)
C15	0.9461 (4)	0.8107 (3)	0.9418 (3)	0.0480 (8)
C16	0.8344 (5)	0.8121 (5)	1.0284 (4)	0.0628 (11)
C17	0.7357 (5)	0.9301 (5)	1.0353 (4)	0.0687 (12)
C18	0.7413 (5)	1.0487 (4)	0.9554 (4)	0.0652 (11)
C19	0.8443 (4)	1.0503 (4)	0.8684 (4)	0.0556 (9)
C21	0.6630 (3)	0.8213 (3)	0.5475 (3)	0.0334 (6)
C22	0.7355 (3)	0.8444 (3)	0.6520 (3)	0.0332 (6)
C23	0.6213 (3)	0.8877 (3)	0.7364 (3)	0.0384 (7)
C24	0.4882 (3)	0.8771 (3)	0.6934 (3)	0.0438 (8)

C25	0.5112 (3)	0.8416 (3)	0.5733 (3)	0.0388 (7)
C26	0.4149 (4)	0.8250 (3)	0.4856 (4)	0.0502 (9)
C27	0.4692 (4)	0.7885 (3)	0.3782 (4)	0.0556 (10)
C28	0.6182 (4)	0.7616 (3)	0.3539 (3)	0.0509 (9)
C29	0.7139 (4)	0.7764 (3)	0.4354 (3)	0.0416 (7)
H1	0.826 (3)	0.653 (3)	0.798 (3)	0.052 (9)

Table 2. *Selected geometric parameters (Å, °)*

Mo1—Mo2	3.2024 (7)	C4—C5	1.405 (5)
Mo1—C1	1.921 (4)	C5—C6	1.403 (5)
Mo1—C2	1.948 (4)	C6—C7	1.387 (5)
Mo1—C11	2.481 (3)	C11—C19	1.408 (5)
Mo1—C12	2.315 (4)	C11—C12	1.414 (5)
Mo1—C13	2.306 (3)	C11—C15	1.427 (5)
Mo1—C14	2.316 (3)	C12—C13	1.396 (6)
Mo1—C15	2.475 (3)	C13—C14	1.391 (6)
Mo1—C22	2.146 (3)	C14—C15	1.441 (5)
Mo1—H1	1.87 (3)	C15—C16	1.404 (5)
Mo2—C3	1.954 (4)	C16—C17	1.363 (6)
Mo2—C4	2.345 (3)	C17—C18	1.406 (6)
Mo2—C5	2.243 (3)	C18—C19	1.350 (6)
Mo2—C6	2.233 (3)	C21—C22	1.449 (4)
Mo2—C7	2.351 (3)	C21—C25	1.437 (4)
Mo2—C21	2.380 (3)	C21—C29	1.420 (4)
Mo2—C22	2.229 (3)	C22—C23	1.443 (4)
Mo2—C23	2.264 (3)	C23—C24	1.409 (4)
Mo2—C24	2.344 (3)	C24—C25	1.428 (5)
Mo2—C25	2.460 (3)	C25—C26	1.418 (4)
Mo2—H1	1.80 (3)	C26—C27	1.349 (5)
O1—C1	1.159 (4)	C27—C28	1.405 (5)
O2—C2	1.158 (4)	C28—C29	1.358 (5)
O3—C3	1.149 (4)		
C1—Mo1—C2	77.0 (2)	O1—C1—Mo1	178.2 (3)
C1—Mo1—C22	112.84 (13)	O2—C2—Mo1	176.9 (3)
C1—Mo1—*IN*1†	119.4	O3—C3—Mo2	175.2 (3)
C2—Mo1—C22	82.11 (13)	C23—C22—C21	104.9 (2)
C2—Mo1—*IN*1	118.3	C23—C22—Mo1	116.5 (2)
C22—Mo1—*IN*1	126.7	C21—C22—Mo1	133.0 (2)
C3—Mo2—C22	120.09 (12)	C23—C22—Mo2	72.6 (2)
C3—Mo2—*IN*2†	115.4	C21—C22—Mo2	77.5 (2)
C3—Mo2—*BU*†	98.9	Mo1—C22—Mo2	94.09 (11)
C22—Mo2—*BU*	140.0	Mo1—H1—Mo2	122 (3)
*IN*2—Mo2—*BU*	135.6		

† *IN*1, *IN*2 and *BU* are the unweighted centroids of the C11–C15 ring, the C21–C25 ring and the C4–C7 butadiene chain, respectively.

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

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *XCAD*4 (Harms & Wocadlo, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1134). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2703-2705

Bis[(1,2,5,6-η)-1,5-cyclooctadiene]-di-μ-ethoxo-dirhodium(I)

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(*Received 14 March 1996; accepted 18 June 1996*)

Abstract

The solvent-free title compound, $[Rh_2(C_2H_5O)_2(C_8H_{12})_2]$, was obtained by reaction of $[(cod)Rh(OH)]_2$ (cod is cyclooctadiene) with $Ti(OC_2H_5)_4$. The coordination of the Rh atoms is essentially square planar. The Rh and O atoms form a folded four-membered ring.

Comment

The reaction of the halide derivative $[(cod)RhCl]_2$ (cod is cyclooctadiene) with Na_2CO_3/ethanol or KOH/ethanol led to $[(cod)Rh(OC_2H_5)]_2$, *i.e.* bis(1,5-cyclooctadiene)-di-μ-ethoxo-dirhodium(I), (1). Such reactions may result, however, in hydrated (1) (Green & Meek, 1989) and the solvate water is not removable in these cases. Pure (1) is accessible from $[(cod)_2Rh_2O_2]$ by reaction with ethanol (Sakurai, Suzuki, Moro-oka & Ikawa, 1980). We have found that solvent-free (1) can also be formed by subsequent ion metathesis reaction of $[(cod)Rh(OH)]_2$ with $Ti(OC_2H_5)_4$