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μ_2-Diphosphorus(P—P)-1:2κ^2P,P;1:2κ^2P',P'-bis[η^5-ethoxycarbonylcyclopentadienyl]-bis(carbonyl-1κC)bis(carbonyl-2κC)dimolybdenum(I)(Mo—Mo)]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.035
wR factor = 0.092
Data-to-parameter ratio = 16.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, [$Mo_2(P_2)(CO)_4(C_8H_9O_2)_2$], which was synthesized by refluxing a toluene solution of [(η^5-$CH_3CH_2O_2CC_5H_4)_2Mo_2(CO)_6$] and P_4 under N_2, has a tetrahedral [Mo_2P_2] core with a transverse coordinated P_2 ligand and an [(η^5-$CH_3CH_2O_2CC_5H_4$)Mo(CO)$_2$] moiety. The P—P distance of the coordinated P_2 ligand is 2.089 (2) Å.

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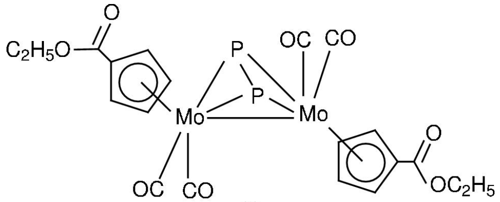
Comment

The study of compounds with substituent-free acyclic and cyclic phosphorus (and homologous ligands) is a new and interesting research area (Davies *et al.*, 2000; Bai *et al.*, 2002). As part of a systematic investigation of the chemistry of cyclopentadienyl-functionalized dimolybdenum compounds, the title compound, (I), has been synthesized (Shi, 2004*a*,*b*) and its crystal structure is reported here (Fig. 1).



(I)

The molecule of (I) has a tetrahedral [Mo_2P_2] core with a transverse coordinated P_2 ligand and an [(η^5-$CH_3CH_2O_2CC_5H_4$)Mo(CO)$_2$] moiety. The Mo—Mo distance in (I) (Table 1) is close to the values [3.022 (1), 3.0161 (8) and 3.0157 (9) Å, respectively] observed in the compounds [(η^5-$C_5H_4R)_2Mo_2(CO)_4(\mu,\eta^2$-P)$_2$] [(II) with R = H (Scherer *et al.*, 1984); (III) with R = CH_3CO and (IV) with R = CH_3O_2C (Shi, 2004*a*)]. The P—P distance in (I) is slightly longer than those in (II) and (III) [2.079 (2) and 2.074 (2) Å, respectively], but close to the value of 2.084 (2) Å in (IV).

As in (II), (III) and (IV), each Mo atom in (I) forms two different Mo—P bonds with two P atoms, and the angles in the bridging region are similar to those in (II), (III) and (IV). However, the dihedral angles between the functional groups and the corresponding C_5H_4 rings are different. The dihedral angles are 4.5 (5) and 4.5 (5)° in (III), and 1.3 (5) and 7.2 (5)° in (IV), while in (I), the values are 4.7 (4) and 6.6 (4)°.

In each of the crystal structures of (I), (III) and (IV), weak C—H···O hydrogen bonding is present, and in each case the C—H donors arise from C_5H_4 rings [see Table 2 for the hydrogen-bond geometry in (I)]. For (III), the hydrogen bonds are of the type C—H···OC [C···O 3.354 (5) and 3.392 (5) Å; C—H···O 139 and 139°], whereas for (IV), C—H···O═C hydrogen bonds are present [C···O 3.455 (7) and 3.394 (8) Å and C—H···O 152 and 149° for one C_5H_4 ring,

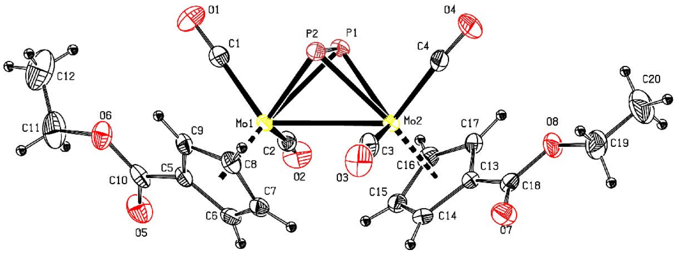


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids.

and C···O 3.438 (8) and 3.348 (8) Å and C—H···O 150 and 156° for the other C_5H_4 ring]. The hydrogen bonding in compound (II) [R = H] is not discussed here, as the H-atom positions are not available in the deposited data.

Experimental

A solution of $[(\eta^5\text{-}CH_3CH_2O_2CC_5H_4)_2Mo_2(CO)_6]$ (1 mmol) and white phosphorus P_4 (1 mmol) in toluene (40 ml) was refluxed under N_2 for 2 h. After evaporation of the solvent *in vacuo*, the resulting residue was chromatographed on silica-gel plates using CH_2Cl_2–petroleum ether (4:1 *v*/*v*) as eluent. The orange band was collected and further recrystallized from deoxygenated CH_2Cl_2–petroleum ether to afford the title compound as red crystals (0.237 g, 37% yield; m.p. 403.5–404.6 K). Spectroscopic analysis: ^{1}H NMR (600 MHz, $CDCl_3$, δ, p.p.m.): 5.69, 5.33 (4H, *t*, 4H, *t*, $2C_5H_4$), 4.28–4.31 (4H, *q*, J = 7.14 Hz, $2OCH_2$), 1.32–1.34 (6H, *t*, J = 7.14 Hz, $2CH_3$); ^{13}C{^{1}H} NMR (600 MHz, $CDCl_3$, δ, p.p.m.): 223.49 (C$\equiv$O), 164.28 (C=O), 90.03, 88.35, 87.75 (C_5H_4), 61.41 (CH_2), 14.23 (CH_3); ^{31}P{^{1}H} NMR (600 MHz, $CDCl_3$, δ, p.p.m.): −30.59; IR (KBr, ν, cm^{-1}): 1995, 1975, 1920 (*vs*, C$\equiv$O), 1708 (*vs*, C=O).

Crystal data

$[Mo_2(P_2)(CO)_4(C_8H_9O_2)_2]$
M_r = 640.16
Monoclinic, $C2/c$
a = 25.705 (9) Å
b = 7.912 (4) Å
c = 24.636 (8) Å
β = 112.742 (8)°
V = 4621 (3) Å^3
Z = 8
D_x = 1.840 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 923 reflections
θ = 2.7–26.3°
μ = 1.27 mm^{-1}
T = 293 K
Block, red
0.14 × 0.12 × 0.10 mm

Data collection

Bruker SMART 1000 CCD area detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.812, T_{max} = 0.874
12 842 measured reflections
4733 independent reflections
3509 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 26.5°
$h = -31 \rightarrow 32$
$k = -8 \rightarrow 9$
$l = -30 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.092$
S = 1.06
4733 reflections
291 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.041P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo1—Mo2	3.0170 (11)	P1—P2	2.089 (2)
Mo1—P1	2.5577 (14)	C1—O1	1.143 (6)
Mo1—P2	2.4700 (14)	C2—O2	1.139 (6)
Mo2—P1	2.4695 (14)	C3—O3	1.146 (6)
Mo2—P2	2.5502 (15)	C4—O4	1.150 (6)
P1—Mo1—P2	49.06 (5)	P2—P1—Mo2	67.44 (5)
P1—Mo1—Mo2	51.79 (3)	Mo1—P2—Mo2	73.86 (4)
P2—Mo1—Mo2	54.29 (4)	P1—P2—Mo1	67.66 (5)
P1—Mo2—Mo1	54.47 (3)	P1—P2—Mo2	63.41 (6)
P2—Mo2—Mo1	51.85 (3)	O1—C1—Mo1	176.3 (5)
P1—Mo2—P2	49.15 (5)	O2—C2—Mo1	175.3 (4)
Mo1—P1—Mo2	73.73 (4)	O3—C3—Mo2	175.8 (5)
P2—P1—Mo1	63.28 (5)	O4—C4—Mo2	175.6 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O5^{i}	0.93	2.59	3.477 (7)	159
C7—H7···O7^{ii}	0.93	2.60	3.441 (7)	151
C14—H14···O7^{ii}	0.93	2.38	3.262 (7)	158

Symmetry codes: (i) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (ii) $-x, y, -z + \frac{1}{2}$.

All H atoms were placed in geometrically idealized positions and were included in a riding-model approximation, with C—H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ [$1.5U_{eq}(C)$ for methyl groups].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1999) ; software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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