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trans-$[Mo_2(CO)_8(\mu\text{-dppp}_e)_2]$ $[\text{dppp}_e = Ph_2P(CH_2)_5PPh_2]$

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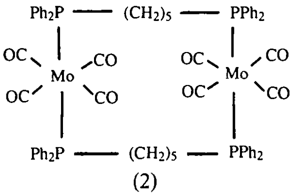
Abstract

The dppp_e-bridged bimetallic complex, *trans*-bis[μ-1,5-bis(diphenylphosphino)pentane-*P*:*P'*]bis[tetracarbonylmolybdenum(0)], was prepared thermolytically from $[Mo(CO)_6]$ and dppp_e and identified from IR, ^{1}H and ^{31}P NMR, and elemental analysis. It has a *trans* bridged 16-membered-ring structure; the *trans* geometry may be the result of the steric effect of the diphenylphosphino groups during the thermolytic substitution reaction. The molybdenum coordination sphere is a slightly distorted octahedron with Mo—P bonds of 2.478 (2) and 2.488 (2) Å, and Mo—CO bonds ranging from 2.01 (1) to 2.030 (9) Å. A crystallographic inversion centre coincides with the molecular centroid.

Comment

There are several reports concerning reactions between α,ω-diphosphines and Group 6B metal carbonyls: the monobridged dinuclear complexes $[(CO)_5M\{Ph_2P(CH_2)_5PPh_2\}M(CO)_5]$ were prepared from $[M(CO)_6]$ and 0.5 molar equivalent of dppp_e either in $EtOCH_2CH_2OCH_2CH_2OH$ under reflux (*M* = Mo; Dietsche, 1966) or with Me_3NO as initiator in CH_3CN (*M* = Cr, Mo and W; Hor, 1989). The dpph-bridged bimetallic complex *trans*-$[Mo_2(CO)_8(\mu\text{-dpph})_2]$ [dpph = $Ph_2P(CH_2)_6PPh_2$] (1) was prepared thermolytically from $[Mo(CO)_6]$ and dpph under reflux in toluene (Ueng & Hwang, 1991). The present report describes the synthesis and spectroscopic characterizations of the unusual 16-membered-ring complex *trans*-$[Mo_2(CO)_8(\mu\text{-dppp}_e)_2]$, (2), and the determination of its crystal structure.



(2)

The title compound (2) was synthesized from $[Mo(CO)_6]$ and dppp_e in a similar fashion to the synthesis of (1), except that the reflux time was 6 instead of 4 h. Elemental analysis found: C 61.65, H 4.81% ($C_{66}H_{60}Mo_2O_8P_4$ requires C 61.14, H 4.63%). The IR spectrum (Jasco FT/IR-5300 spectrophotometer) in the carbonyl stretching region included absorptions at 2018*w*, 1944*w* and 1873*s* cm^{-1} (KBr pellet) which coincide with the CO stretching modes of *trans*-$[ML_2(CO)_4]$ (Cotton & Kraihanzel, 1962; Ueng & Hwang, 1991). Solutions in C_6D_6 show a singlet resonance in the ^{31}P NMR spectrum (Bruker 300 MHz spectrophotometer) at δ 40.30 p.p.m., which is lower than that of the corresponding singly bridged complexes (Hor, 1989). The signals in the ^{1}H NMR spectrum (Bruker 300 MHz spectrophotometer, C_6D_6) are at δ 2.38–2.50 (20 Hz, *m*, 10-CH_2) and 7.28–7.49 p.p.m. (40 Hz, *m*, 8-C_6H_5).

There is a crystallographic inversion centre at the molecular centroid for both the title compound (2) and compound (1) (Ueng & Hwang, 1991). The title compound (Fig. 1) consists of two Mo atoms, each bonded to four equatorial carbonyls and two P atoms from different diphosphine ligands. The coordination polyhedron around each metal is a distorted octahedron with bond angles at Mo in the ranges 176.4 (3)–177.7 (3) and 86.7 (3)–93.8 (2)°. The distortion from ideal octahedral coordination at Mo is smaller than for compound (1). As a result of the *trans* geometry and the presence of the inversion centre, a *trans* bis(dppp_e)-bridged rectangular 16-membered-ring structure is formed with two P—Mo—P axes and two dppp_e groups as the four sides.

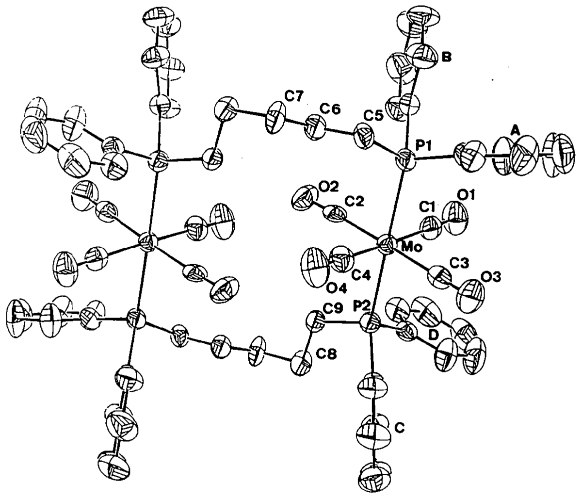


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecular structure of *trans*-$[Mo_2(CO)_8(\mu\text{-dppp}_e)_2]$. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

The Mo—P(1) bond length is slightly shorter than Mo—P(2), while the four Mo—CO lengths are almost equal [2.007 (9)–2.030 (9) Å]. The orientations of the four phenyl groups (*A*–*D*) in the unique molecule are different, with $A\wedge B$ and $C\wedge D$ inter-ring dihedral angles of 79.0 (4) and 63.6 (4)°, respectively.

The P—C [1.829 (8)–1.842 (8) Å] and C—C bond lengths [C_{sp^3}—C_{sp^3} 1.50 (1)–1.55 (1), C_{sp^2}—C_{sp^2} 1.33 (2)–1.40 (1) Å] are reasonable and there are no intermolecular contacts of structural significance. Unlike compound (1), there are no solvent molecules in the crystals.

Experimental

Crystal data

$[Mo_2(C_{29}H_{30}P_2)_2(CO)_8]$
M_r = 1296.96
Triclinic
$P\overline{1}$
a = 9.4528 (14) Å
b = 11.4874 (18) Å
c = 15.4943 (23) Å
α = 72.056 (13)°
β = 87.550 (12)°
γ = 74.118 (12)°
V = 1538.0 (4) Å^3
Z = 1
D_x = 1.400 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9–12°
μ = 0.55 mm^{-1}
T = 298 K
Prismatic
0.20 × 0.15 × 0.10 mm
Light greenish yellow
Crystal source: toluene at 258 K

Data collection

CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{\min}$ = 0.890, $T_{\max}$ = 0.995
4194 measured reflections
4013 independent reflections
2515 observed reflections [$I > 2.5\sigma(I)$]

$\theta_{\max}$ = 22.45°
$h = -9 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = -15 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity variation: 6%

Refinement

Refinement on F
R = 0.041
wR = 0.044
S = 1.99
2515 reflections
361 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.50 e Å^{-3}
$\Delta\rho_{\min}$ = −0.37 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Mo	0.16339 (8)	0.13723 (7)	0.29357 (5)	2.68 (3)
P1	0.3654 (2)	−0.0444 (2)	0.2784 (1)	2.9 (1)
P2	−0.0457 (2)	0.3191 (2)	0.3029 (1)	2.9 (1)
O1	0.0509 (7)	0.1832 (6)	0.0921 (4)	5.7 (4)
O2	−0.0296 (6)	−0.0496 (5)	0.3861 (5)	5.2 (4)
O3	0.3712 (7)	0.3184 (6)	0.2187 (5)	6.5 (4)
O4	0.2911 (7)	0.0805 (7)	0.4917 (4)	6.2 (5)
C1	0.0896 (9)	0.1671 (8)	0.1656 (6)	3.5 (5)
C2	0.0407 (8)	0.0181 (8)	0.3501 (6)	3.2 (4)
C3	0.2942 (9)	0.2543 (8)	0.2441 (6)	3.8 (5)
C4	0.2436 (9)	0.1018 (8)	0.4202 (6)	3.9 (5)
C5	0.4633 (8)	−0.1533 (7)	0.3851 (5)	3.2 (4)
C6	0.3634 (8)	−0.2226 (7)	0.4478 (5)	3.3 (4)
C7	0.4279 (8)	−0.2942 (8)	0.5424 (6)	3.9 (4)
C8	−0.3243 (8)	0.3624 (7)	0.3959 (5)	3.9 (4)
C9	−0.1838 (8)	0.2647 (7)	0.3807 (5)	3.4 (4)
C1*A*	0.5113 (8)	0.0031 (8)	0.2058 (6)	3.4 (4)
C2*A*	0.6449 (9)	−0.0016 (8)	0.2417 (6)	4.4 (5)
C3*A*	0.748 (1)	0.042 (1)	0.1830 (8)	5.7 (6)
C4*A*	0.718 (1)	0.089 (1)	0.0913 (7)	6.0 (6)
C5*A*	0.585 (1)	0.097 (1)	0.0564 (6)	6.4 (7)
C6*A*	0.482 (1)	0.0549 (9)	0.1150 (6)	5.3 (6)
C1*B*	0.3265 (9)	−0.1578 (7)	0.2277 (5)	3.4 (4)
C2*B*	0.186 (1)	−0.1513 (9)	0.2035 (6)	4.7 (5)
C3*B*	0.159 (1)	−0.240 (1)	0.1666 (7)	6.6 (7)
C4*B*	0.266 (2)	−0.336 (1)	0.1539 (8)	7.3 (8)
C5*B*	0.407 (2)	−0.344 (1)	0.1788 (8)	7.2 (8)
C6*B*	0.439 (1)	−0.2569 (9)	0.2154 (7)	5.7 (6)
C1*C*	−0.0100 (9)	0.4470 (7)	0.3379 (5)	3.4 (4)
C2*C*	0.1202 (9)	0.4304 (8)	0.3814 (6)	4.3 (5)
C3*C*	0.146 (1)	0.5250 (9)	0.4106 (7)	5.5 (6)
C4*C*	0.043 (1)	0.6362 (9)	0.3985 (7)	5.4 (6)
C5*C*	−0.090 (1)	0.6574 (8)	0.3547 (7)	5.4 (6)
C6*C*	−0.1181 (9)	0.5627 (8)	0.3244 (7)	4.6 (5)
C1*D*	−0.1495 (8)	0.4054 (7)	0.1944 (5)	3.1 (4)
C2*D*	−0.2585 (9)	0.3641 (8)	0.1674 (6)	4.2 (5)
C3*D*	−0.324 (1)	0.423 (1)	0.0800 (8)	6.0 (6)
C4*D*	−0.282 (1)	0.521 (1)	0.0209 (7)	6.8 (7)
C5*D*	−0.172 (1)	0.561 (1)	0.0480 (8)	7.0 (7)
C6*D*	−0.107 (1)	0.5043 (9)	0.1343 (6)	5.3 (6)

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

C7′ and C8′ are the symmetry equivalents of C7 and C8, respectively.

Mo—P1	2.478 (2)	P2—C1*C*	1.829 (8)
Mo—P2	2.488 (2)	P2—C1*D*	1.831 (8)
Mo—C1	2.026 (9)	O1—C1	1.16 (1)
Mo—C2	2.007 (9)	O2—C2	1.16 (1)
Mo—C3	2.030 (9)	O3—C3	1.15 (1)
Mo—C4	2.01 (1)	O4—C4	1.14 (1)
P1—C5	1.837 (8)	C5—C6	1.53 (1)
P1—C1*A*	1.835 (8)	C6—C7	1.50 (1)
P1—C1*B*	1.834 (8)	C7—C8′	1.54 (1)
P2—C9	1.842 (8)	C8—C9	1.55 (1)
P1—Mo—P2	177.38 (8)	C5—P1—C1*A*	104.4 (4)
P1—Mo—C1	89.0 (2)	C5—P1—C1*B*	100.8 (4)
P1—Mo—C2	90.0 (2)	C1*A*—P1—C1*B*	100.1 (4)
P1—Mo—C3	89.4 (2)	Mo—P2—C9	111.5 (3)
P1—Mo—C4	88.7 (2)	Mo—P2—C1*C*	119.6 (3)
P2—Mo—C1	88.6 (2)	Mo—P2—C1*D*	112.9 (2)
P2—Mo—C2	89.3 (2)	C9—P2—C1*C*	104.8 (4)
P2—Mo—C3	91.5 (2)	C9—P2—C1*D*	104.0 (4)
P2—Mo—C4	93.8 (2)	C1C—P2—C1*D*	102.6 (4)
C1—Mo—C2	93.4 (3)	Mo—C1—O1	178.4 (7)
C1—Mo—C3	90.1 (3)	Mo—C2—O2	177.1 (7)
C1—Mo—C4	177.7 (3)	Mo—C3—O3	177.7 (8)
C2—Mo—C3	176.4 (3)	Mo—C4—O4	178.9 (7)
C2—Mo—C4	86.7 (3)	P1—C5—C6	111.9 (5)
C3—Mo—C4	89.8 (3)	C5—C6—C7	114.3 (6)
Mo—P1—C5	115.5 (3)	C6—C7—C8′	113.1 (6)
Mo—P1—C1*A*	113.8 (3)	C7′—C8—C9	110.7 (6)
Mo—P1—C1*B*	119.9 (3)	P2—C9—C8	120.1 (5)

The computer program package used was *NRCVAX* (Larson, Lee, Le Page, Webster, Charland & Gabe, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1095). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(η^5-Cyclopentadienyl)[(1,2,3,4,4a,10a-η^6)-2-methylthianthrene]iron(II) Hexafluorophosphate

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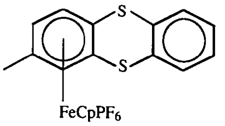
Abstract

The structure of the title compound, [$Fe(C_5H_5)(C_{13}H_{10}S_2)$].$PF_6$, (I), has been studied. The dihedral angle between the outer benzene rings of the ligand is 137.7 (3)°; the benzene and Cp rings are nearly parallel to each other [dihedral angle 3.5 (5)°]. The Fe atom, which is located inside the fold of the heterocyclic ligand, is closer to the benzene ring [1.548 (3) Å] than the Cp ring [1.668 (7) Å].

Comment

The title complex was synthesized following the described procedure (Sutherland, Piórko, Gill & Lee, 1982) by the reaction of 1,2-benzenedithiol with (η^6-3,4-dichlorotoluene)(η^5-Cp)iron(II) hexafluorophosphate. Crystals were grown from acetone–dichloromethane–diethyl ether solution at *ca* 255 K. Results obtained in the course of this study add to earlier data on the structure of thianthrenes and their FeCp complexes.



(I)

The Fe atom is centered above the Cp ring while the longest Fe—C distances to the arene ring are found for the quaternary C atoms [Fe—C2 = 2.111 (6), Fe—C4a = 2.111 (5) and Fe—C10a = 2.109 (5) Å]. Similar results have been noted for the isomeric 2-methylthianthrene complex (Simonsen, Lynch, Sutherland & Piórko, 1985) but not for both 'in'- and 'out'-FeCp–thianthrene complexes [FeCp moiety inside or outside the fold of the heterocyclic ligand (Abboud, Lynch, Simonsen, Piórko & Sutherland, 1990)]. The C—C distances of the coordinated rings also show a tendency to be longer than those of the uncoordinated rings. The distances between Fe and the Cp ring plane [1.668 (7) Å] and between Fe and the coordinated arene ring plane [1.548 (3) Å] are within the range reported for FeCp complexes of arenes (Zaworotko, Sturge & White, 1990; Houlton, Roberts, Silver, Wells & Frampton, 1992). The planes of the coordinated benzene ring and the Cp ring are nearly parallel [3.5 (5)°]; the dihedral angle is within the range of values reported for similar complexes.

It has been observed earlier that complexation with the FeCp moiety flattens the thianthrene (TT) molecule [the dihedral angle between the outer benzene rings of the ligand is 136.3 (2) for TT–out-FeCp and 143.1 (2)° for TT–in-FeCp (Abboud, Lynch, Simonsen, Piórko & Sutherland, 1990)]. For the isomeric 2-methyl-TT complex however, the folding was actually of the same magnitude as for TT itself [127.14 (3)° (Larson, Simonsen, Martin, Smith & Puig-Torres, 1984); for isomeric 2-MeTTFeCp, 127.4 (3)° (Simonsen, Lynch, Sutherland & Piórko, 1985)]. The dihedral angle for (I) was found to be 137.7 (3)°, which is between the values found for TT–in-FeCp and isomeric 2-MeTT-FeCp. The FeCp moiety in (I) is located inside the heterocyclic fold.

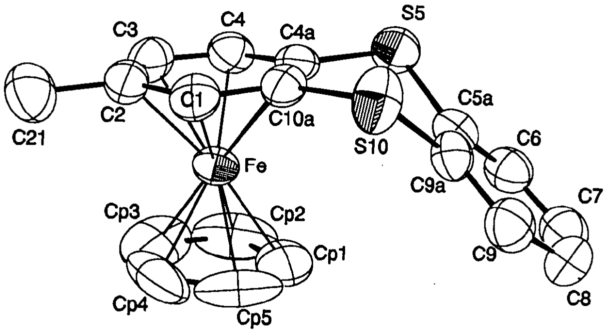


Fig. 1. Molecular structure of the cation of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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