The same crystal specimen was used for the two structure determinations. Enraf-Nonius cooling apparatus and liquid nitrogen were used for collecting the low-temperature data. The integrated intensities were measured using a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. Corrections for Lorentz and polarization effects and corrections for absorption [spherical specimen, $\mu R = 0.21$; *International Tables for X-ray Crystallography* (1992), Vol. C, Table 6.3.3.4] were applied to both sets of data. No corrections for extinction were found to be necessary. The structure at 293 K was solved initially using the Patterson method of *SHELXS*86 (Sheldrick, 1985). All of the H atoms were found in a final $\Delta\rho$ map and refined isotropically. The results of the 293 K refinement were used as starting data for the refinement at 113 K. Both structures were refined on F^2 using *SHELXL*92 (Sheldrick, 1993). The thermal-motion analysis was carried out using the *THMV* (Trueblood, 1984) program. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) The calculations were carried out on the Gould Powernode-6040 and ENCORE-91 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma). Data collection: local programs. Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Data reduction: local programs. Program(s) used to solve structure: *SHELXS*86. Program(s) used to refine structure: *SHELXL*92. Molecular graphics: *ORTEP* (Johnson, 1965); *PLUTO* (Motherwell & Clegg, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983); *PARSTCIF* (Nardelli, 1992).

Financial support by Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexacarbonylcyclopentadienyl-bis-μ-diphenylphosphanido-manganesetungsten, $[MnW(C_{12}H_{10}P)_2(C_5H_5)(CO)_6]$

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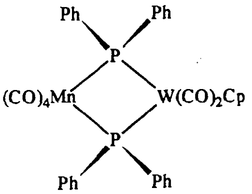
Abstract

Two metal centres in the title compound [hexacarbonyl-$1\kappa^2C,2\kappa^4C$-1(η^5)-cyclopentadienyl-bis(μ-diphenylphosphido-1:$2\kappa^2P$)manganesetungsten], Mn and W, are linked *via* two bridging diphenylphosphanido groups. This new four-membered ring, $MnWP_2$, is folded with a large dihedral angle of 27.5 (2)°.

Comment

The title compound, (I), is the first example of a heterometallic $MM'P_2$ ring with Mn and W as metal centres. The Mn atom has four CO groups and the two bridging P atoms as ligands. Its coordination sphere is a slightly distorted octahedron; the sum of the bond angles at the Mn atom in the ring plane is 360°. Regarding the centre of the cyclopentadienyl group (Cp) as the locus of the W—Cp bond, this Cp ligand, two CO groups and the two bridging P atoms surround the W atom with distorted square-pyramidal coordination with the Cp as the apex of the pyramid.



(I)

The Mn···W distance of 3.919 Å is non-bonding, as expected from the electron saturation of the metals: both satisfy the EAN (effective atomic number) rule with 18 valence electrons. The obtuse endocyclic ring angles W—P—Mn [104.9 (1) and 105.5 (1)°] and the acute P—M—P angles [69.6 (1) at W, 75.0 (1)° at Mn] are in accordance with the absence of a metal-metal bond. Similar values are known for a great variety of M_2P_2 ring structures (Flörke & Haupt, 1994). The Mn—P distances of 2.384 (4) and 2.390 (4) Å compare well with those found in homometallic Mn_2P_2 rings as in, *e.g.* $[Mn_2(CO)_8(\mu\text{-}PHPh)_2]$, with an average value of 2.358 (2) Å (Flörke

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& Haupt, 1993), or $[Mn_2(CO)_8(\mu\text{-}PPh_2)_2]$, with an average of 2.388 (2) Å (Masuda, Taga, Machida & Kawamura, 1987). The W—P bond lengths of 2.539 (3) and 2.550 (3) Å are somewhat larger than those found for WMP_2 rings with metal-metal bonds, *e.g.* 2.481 Å (average) in $[W_2(CO)_8(\mu\text{-}PPh_2)_2]$ (Shyu, Calligaris, Nardin & Wojcicki, 1987) or 2.473 (3) Å in $[WRe(CH_3)(CO)_7(\mu\text{-}PPh_2)_2]$ (Mercer, Geoffroy & Rheingold, 1984), but shorter than in the anion $[W(CO)_8(\mu\text{-}PPh_2)_2]^{2-}$ [average 2.599 (2) Å] where no metal-metal bond is present (Shyu *et al.*, 1987).

The most interesting geometrical feature is the considerable deviation from planarity of the $MnWP_2$ ring. In contrast to other structures with W_2P_2 or WMP_2 rings (*e.g.* Breen, Geoffroy, Rheingold & Fultz, 1983; Breen, Shulman, Geoffroy, Rheingold & Fultz, 1984; Mercer *et al.*, 1984; Morrison, Harley, Marcelli, Geoffroy, Rheingold & Fultz, 1984; Shyu *et al.*, 1987; Targos, Rosen, Whittle & Geoffroy, 1985) where planar geometries are formed, the title compound has a dihedral angle W—P(1)—Mn/W—P(2)—Mn of 27.5 (2)°. Accordingly, the centres of the phenyl groups 2 and 3 (on the Cp side of the molecule) are 8.04 Å apart and those of the groups 1 and 4, only 5.82 Å. Obviously, this folding of the ring is caused by the steric requirement of the Cp group which forces the PPh_2 groups out of the plane; the C—P—C angles are not affected and remain at common values of 99.2° (average). In the title structure, the shortest non-bonding intramolecular H···H distance between the Cp and Ph ligands is 2.76 Å, but in a corresponding molecular model with a planar $MnWP_2$ ring, these contacts would be as short as 2.2 Å. The positions of the phenyl groups are rather critical and rotation around the P—C axis is not sufficient to avoid short contacts in the planar model but leads to new collisions of the phenyl groups next to each other. A similar ring deformation due to intramolecular repulsion forces has been observed recently for $[Re_2(C_6H_{11}IP)_2(CO)_8]$ (Flörke & Haupt, 1994).

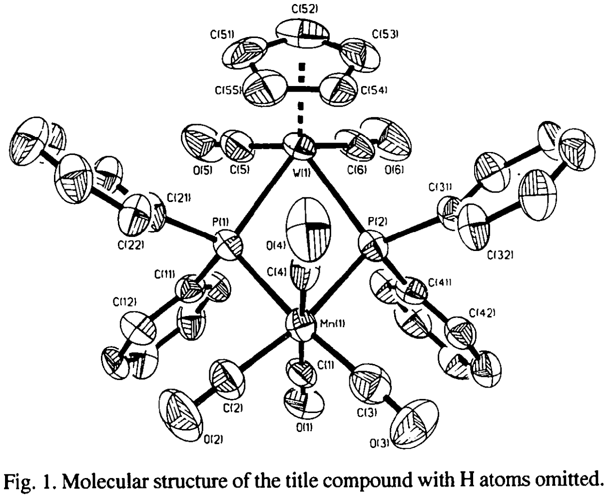

Fig. 1. Molecular structure of the title compound with H atoms omitted.

Experimental

The title compound was synthesized by the reaction of $Mn_2(CO)_{10}$, $[W(CO)_3Cp]_2$ and $HP(C_6H_5)_2$ (molar ratio 1:1:2) in xylene solution at 450 K for 15 h in a glass tube. Recrystallization was from dichloromethane.

Crystal data

$[MnW(C_{12}H_{10}P)_2(C_5H_5)(CO)_6]$
$M_r = 842.28$
Tetragonal
$I4_1/a$
$a = 18.6720\ (10)$ Å
$c = 40.104\ (7)$ Å
$V = 13982.0\ (27)$ Å^3
$Z = 16$
$D_x = 1.601$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 37 reflections
$\theta = 6\text{-}15°$
$\mu = 3.782$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.46 × 0.20 × 0.13 mm
Orange

Data collection

Siemens *R*3*m/V* diffractometer
ω-2θ scans
Absorption correction: empirical *via* ψ-scans
$T_{\min} = 0.423$, $T_{\max} = 0.506$
8588 measured reflections
8099 independent reflections
3902 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.059$
$\theta_{\max} = 27.57°$
$h = 0 \rightarrow 24$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 52$
3 standard reflections monitored every 400 reflections intensity variation: 5%

Refinement

Refinement on F^2
$R(F) = 0.0684$
$wR(F^2) = 0.1447$
$S = 1.176$
8092 reflections
398 parameters
H-atom parameters not refined
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0758P)^2 + 15.6463P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 1.242$ e Å^{-3}
$\Delta\rho_{\min} = -0.714$ e Å^{-3}
Extinction correction: none
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)

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

	x	y	z	$U_{\rm eq}$
W1	0.90509 (3)	0.57819 (3)	0.119610 (13)	0.0416 (2)
Mn1	0.70429 (10)	0.61727 (9)	0.14152 (5)	0.0396 (5)
P1	0.7800 (2)	0.5897 (2)	0.09539 (8)	0.0365 (7)
P2	0.8115 (2)	0.5706 (2)	0.16578 (8)	0.0365 (7)
C1	0.6697 (6)	0.5243 (7)	0.1401 (3)	0.044 (3)
O1	0.6464 (5)	0.4675 (5)	0.1408 (2)	0.061 (3)
C2	0.6306 (8)	0.6465 (8)	0.1145 (3)	0.056 (4)
O2	0.5842 (6)	0.6676 (7)	0.0988 (3)	0.092 (4)
C3	0.6553 (8)	0.6329 (8)	0.1801 (4)	0.060 (4)
O3	0.6229 (6)	0.6432 (6)	0.2038 (3)	0.084 (4)
C4	0.7438 (8)	0.7058 (7)	0.1443 (3)	0.048 (3)
O4	0.7679 (7)	0.7630 (5)	0.1464 (3)	0.085 (4)
C5	0.9131 (7)	0.5142 (8)	0.0814 (4)	0.059 (4)
O5	0.9217 (5)	0.4751 (7)	0.0584 (3)	0.087 (4)

C6	0.9428 (7)	0.4954 (7)	0.1420 (4)	0.057 (4)
O6	0.9719 (6)	0.4469 (6)	0.1550 (4)	0.104 (4)
C11	0.7418 (6)	0.5113 (6)	0.0732 (3)	0.039 (3)
C12	0.6844 (7)	0.5248 (7)	0.0524 (3)	0.051 (3)
C13	0.6495 (8)	0.4649 (9)	0.0373 (3)	0.063 (4)
C14	0.6713 (9)	0.3957 (7)	0.0430 (3)	0.062 (4)
C15	0.7289 (8)	0.3854 (7)	0.0641 (3)	0.060 (4)
C16	0.7630 (6)	0.4424 (6)	0.0790 (3)	0.043 (3)
C21	0.7842 (7)	0.6543 (7)	0.0606 (3)	0.049 (3)
C22	0.7611 (7)	0.7246 (7)	0.0629 (3)	0.051 (3)
C23	0.7745 (8)	0.7729 (8)	0.0377 (4)	0.065 (4)
C24	0.8094 (9)	0.7539 (9)	0.0096 (4)	0.073 (5)
C25	0.8311 (8)	0.6823 (9)	0.0065 (3)	0.068 (4)
C26	0.8195 (8)	0.6334 (7)	0.0320 (3)	0.055 (4)
C31	0.8481 (7)	0.6174 (7)	0.2031 (3)	0.043 (3)
C32	0.8200 (8)	0.6802 (6)	0.2158 (3)	0.050 (3)
C33	0.8530 (9)	0.7141 (8)	0.2423 (3)	0.063 (4)
C34	0.9141 (8)	0.6875 (8)	0.2566 (3)	0.059 (4)
C35	0.9407 (8)	0.6254 (8)	0.2450 (3)	0.064 (4)
C36	0.9074 (7)	0.5897 (7)	0.2181 (3)	0.056 (4)
C41	0.7901 (6)	0.4844 (6)	0.1854 (3)	0.040 (3)
C42	0.7526 (7)	0.4838 (7)	0.2142 (3)	0.047 (3)
C43	0.7287 (8)	0.4225 (8)	0.2298 (4)	0.061 (4)
C44	0.7446 (9)	0.3557 (8)	0.2139 (5)	0.075 (5)
C45	0.7843 (8)	0.3560 (8)	0.1843 (4)	0.067 (4)
C46	0.8041 (7)	0.4197 (6)	0.1698 (4)	0.052 (4)
C51	0.9722 (7)	0.6598 (6)	0.0897 (3)	0.083 (6)
C52	1.0170 (6)	0.6257 (6)	0.1130 (4)	0.075 (5)
C53	0.9944 (6)	0.6457 (6)	0.1451 (3)	0.070 (4)
C54	0.9356 (6)	0.6922 (5)	0.1417 (3)	0.056 (4)
C55	0.9219 (6)	0.7009 (6)	0.1075 (3)	0.071 (5)

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

W1—Cp	2.002 (10)	Mn1—P1	2.384 (4)
W1—P1	2.539 (3)	Mn1—P2	2.390 (4)
W1—P2	2.550 (3)		
C6—W1—C5	81.1 (6)	Cp—W1—C5	116.6 (6)
C6—W1—P1	125.7 (4)	Cp—W1—C6	115.9 (6)
C5—W1—P1	79.7 (4)	P1—Mn1—P2	74.98 (12)
Cp—W1—P1	118.1 (4)	C21—P1—C11	99.8 (6)
C6—W1—P2	82.4 (5)	Mn1—P1—W1	105.47 (12)
C5—W1—P2	126.1 (4)	C41—P2—C31	98.5 (5)
Cp—W1—P2	116.9 (4)	Mn1—P2—W1	104.95 (12)
P1—W1—P2	69.64 (10)		

Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1073). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Effects of Halogen Substitution in Nucleic Acid Components. Structure of Sodium 5-Bromocytidine 5′-Phosphate Hydrate

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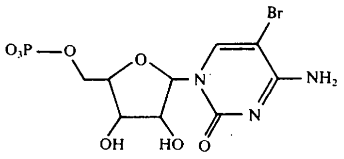
Abstract

The conformation of 5-bromocytidine 5′-monophosphate in the title compound, $Na^+.C_9H_{11}BrN_3O_8P^-.1.25H_2O$, is *anti*, C(3′)-*endo* and *gauche-gauche*, similar to that in analogous non-halogenated nucleosides/nucleotides. The Na ion coordinates directly with phosphate O atoms and base atoms. Br is not involved in any stacking interaction.

Comment

Although there have been a number of crystallographic studies on halogenated nucleosides, only a few structures of halogenated nucleotides have been reported. We report here the crystal structure of the sodium salt of 5-bromocytidine monophosphate (I); this is the first halogenated pyrimidine mononucleotide to be determined. Cytosine with bulky substituents such as bromine and iodine at the 5 position is found to be a good substrate for human DNA (cytosine-5) methyltransferase (Hardy, Barker, Newman, Sowers, Goodman & Smith, 1987). The presence of monovalent sodium in the present structure is also of interest in view of the fact that earlier



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