

Fig. 4. Schematic representation of the H bonds involving the water molecules. The coordinate transformations are as follows: (i) $1 + x, y, z$; (ii) $x, y, l + z$; (iii) $-1 + x, y, z$; (iv) $-1 + x, y, l + z$. The standard deviations on distances are: 0.05–0.09 Å for N(O)—H and 0.006–0.009 Å for N(O)—O; on angles, 5–7° where H is apical, 3–5° when it is terminal, and 0.2–0.4° for angles involving no H atoms.

compound might well have been isolated first because it is the most insoluble. Indeed, for the tris-chelates of cobalt, it has been found that the *fac* isomers are systematically less soluble than the *mer* isomers, a peculiarity that can be ascribed to better packing efficiency through van der Waals contacts and H bonding in the *fac* compound. By analogy, among the 24 possible diastereoisomers of the present dihydroxo-alanine complex, other configurations are likely to exist as more soluble species. In this respect, it would be interesting to study corresponding compounds with amino acids bearing bulkier alkyl or aryl substituents

on the asymmetric C atom. In this manner, the influence of the van der Waals forces would become relatively more important and the stereoisomer first isolated might differ from those obtained with the simplest amino acids.

References

- BRYAN, R. F., GREENE, P. T., STOKELY, P. F. & WILSON, E. W. (1971). *Inorg. Chem.* **10**, 1468–1473.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 HERAK, R., PRELESNIK, B. & KRSTANOVIĆ, I. (1978). *Acta Cryst.* **B34**, 91–95.
 HUBERT, J. & BEAUCHAMP, A. L. (1980). *Acta Cryst.* **B36**, 2613–2616.
International Tables for X-ray Crystallography (1969). Vol. I, p. 530. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 LAWTON, S. L. & JACOBSON, R. A. (1965). *The Reduced Cell and Its Crystallographic Application*. Report IS-1141, US Atomic Energy Commission.
 OKI, H. (1977). *Bull. Chem. Soc. Jpn*, **50**, 680–684.
 OKI, H. & OTSUKA, K. (1976). *Bull. Chem. Soc. Jpn*, **49**, 1841–1844.
 PURCELL, K. F. & KOTZ, J. C. (1977). *Inorganic Chemistry*, p. 636. Toronto: Saunders.
 SIMPSON, J. H. & MARSH, R. E. (1966). *Acta Cryst.* **20**, 550–555.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 VEAL, J. T., HATFIELD, W. E., JETER, D. Y., HEMPEL, J. C. & HODGSON, D. J. (1973). *Inorg. Chem.* **12**, 342–346.

Acta Cryst. (1981). **B37**, 1067–1071

Structure of η^5 -Cyclopentadienyl(η^6 -2,4,6-triphenylphosphorin)manganese(I)

BY J. FISCHER AND A. DE CIAN

Institut Le Bel, Université Louis Pasteur, Laboratoire de Cristallographie, 4 rue Blaise Pascal, 67070-Strasbourg CEDEX, France

AND F. NIEF

Equipe CNRS-SNPE, Centre de Recherches du Bouchet, Le Bouchet, 91710 Vert-Le-Petit, France

(Received 11 July 1980; accepted 3 December 1980)

Abstract

$C_{28}H_{22}MnP$, $M_r = 444.4$, triclinic, $P\bar{1}$, $a = 15.843$ (5), $b = 13.665$ (3), $c = 10.155$ (2) Å, $\alpha = 93.89$ (3), $\beta = 102.75$ (3), $\gamma = 89.00$ (3)°, $V = 2139$ Å³, $Z = 4$, $D_c =$

1.38 Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.735$ mm⁻¹. The crystal structure was determined and refined from 4631 diffractometer data to an R value of 0.063. Mn atoms are sandwiched between (η^5 -C₅H₅) and [η^6 -PC₅H₂-(C₆H₅)₃] rings. The difference in C—C bond dis-

0567-7408/81/051067-05\$01.00

© 1981 International Union of Crystallography

tances between $\{(\eta^5\text{-C}_5\text{H}_5)\text{Mn}\{\eta^6\text{-PC}_5\text{H}_2(\text{C}_6\text{H}_5)_3\}\}$ and $\{\text{Cr}(\text{CO})_3\{\eta^6\text{-PC}_5\text{H}_2(\text{C}_6\text{H}_5)_3\}\}$ is related to different π acidities of the phosphorin ligand in each compound.

Introduction

Since several complexes of phosphorins with transition metals have been described in the literature, but only two structural studies of such complexes are currently available (Vahrenkamp & Nöth, 1972, 1973), we decided to undertake the determination of the crystal structure of the recently synthesized title compound (*A*) (Nief, Charrier, Mathey & Simalty, 1980). Compound (*A*) is also interesting because no structural data are available at the present time on sandwich complexes of Mn^I .

Experimental

Suitable single crystals of (*A*) were obtained by slow evaporation of dichloromethane/pentane solutions at 291 K under inert atmosphere. Preliminary precession-camera photographs show that crystals of (*A*) belong to the triclinic system. The unit-cell parameters were refined at room temperature using $\text{Mo K}\alpha$ radiation with the standard method on a Philips PW1100/16 diffractometer.

A parallelepipedal crystal of (*A*) with dimensions $0.06 \times 0.29 \times 0.38$ mm was sealed in a Lindemann-glass capillary and mounted on a rotation-free goniometer head (W. Petter, ETH, Zürich, private communication). All quantitative data were obtained using a Philips PW1100/16 four-circle diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation. Intensity data were collected using the $\theta/2\theta$ flying step-scan technique with a scan rate of $0.016^\circ \text{ s}^{-1}$, θ scan width of $1.20 + (\text{Mo K}\alpha_{1,2} \text{ splitting})^\circ$ and a step width of 0.05° . The intensities of three reflections were monitored throughout the data-collection period at intervals of 2 h; their values did not vary by more than 2% during the data-collection period. All reflections within $0.061 < \sin \theta/\lambda < 0.6510 \text{ \AA}^{-1}$ were measured.

Structure determination and refinement

All computations were conducted on a PDP 11/60 computer using the Enraf-Nonius SDP/V16 package (Frenz, 1978) and local programs for data reduction. The step-scan data were converted to intensities with their standard deviations using the Lehmann-Larsen algorithm (Lehmann & Larsen, 1974). These intensities were then corrected for Lorentz and polarization factors; absorption corrections were applied using a numerical integration method (*A** between 0.88 and

0.97) (Busing & Levy, 1957). Statistical tests on F_o and normalized structure-factor distributions showed that the space group is $P\bar{1}$. The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1970, 1971) and refined with anisotropic temperature parameters for all non-H atoms using 4631 reflections having $I > 3\sigma(I)$. H atoms were introduced with their computed coordinates using a C-H distance of 0.95 Å but not refined.

Final indices are: $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_2 = (\sum w|F_o| - |F_c||^2 / \sum wF_o^2)^{1/2}$ of 0.063 and 0.090 respectively, with $w = 1/[\sigma_{\text{count}}^2 + (pI)^2]$; for $p = 0.08$, the unit-weight observation is equal to 1.49. A final difference map showed no maxima greater than 0.3 e \AA^{-3} .

The positional and thermal parameters of all non-H atoms appear in Table 1.*

Results and discussion

The structure consists of discrete molecules linked only by van der Waals contacts and hydrogen bonds. With $Z = 4$, there are two independent molecules in the asymmetric unit, named (I) and (II). Fig. 1 shows an *ORTEP* plot (Johnson, 1965) of molecule (I) without H atoms; ellipsoids are scaled to enclose 50% of the electronic density. Fig. 2 shows the projection of molecule (I) on the plane containing the cyclopentadienyl ring. Molecule (II) does not differ significantly from molecule (I). Table 2 gives selected bond distances and angles and Table 3 selected mean planes.

The Mn atoms are sandwiched between the cyclopentadienyl rings and the phosphorin rings. The two ring moieties are nearly parallel as indicated by the dihedral angles between mean planes PL1/PL3 and PL2/PL4 in Table 3 (2.2 and 2.0° respectively).

The $\text{Mn} \cdots \text{C}_5\text{H}_5$ ring distances are equal to 1.733 (1) and 1.740 (1) Å for molecules (I) and (II) (PL1 and PL2). These distances are significantly shorter than 1.80 Å found in $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ (Berndt & Marsh, 1963) as are consequently the Mn-C(cyclopentadienyl) bonds: 2.100 (2) Å on average *vs* 2.165 (2) Å.

The distances between phosphorin mean planes PL3/PL4 and Mn(1)/Mn(2) are 1.526 (1) and 1.528 (1) Å respectively, shorter than those found in the only other π complex known with the ligand: $\text{PC}_5\text{H}_2(\text{C}_6\text{H}_5)_3\text{Cr}(\text{CO})_3$ (Vahrenkamp & Nöth, 1972) (*B*). Fig. 2 shows that the projection of the atom on the

* Lists of observed and calculated structure factors, anisotropic thermal parameters, H atom parameters and packing distances less than 3 Å have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35926 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional and thermal parameters and their estimated standard deviations

	x	y	z	B_{eq} (\AA^2)		x	y	z	B_{eq} (\AA^2)
Mn(1)	0.14951 (5)	0.98539 (6)	0.28784 (8)	2.82 (2)	C(27)	0.2786 (4)	0.9471 (6)	0.3633 (7)	5.7 (2)
Mn(2)	0.44183 (6)	0.33514 (7)	0.69780 (10)	3.85 (2)	C(28)	0.2676 (4)	1.0427 (5)	0.4006 (7)	4.9 (2)
P(1)	0.0018 (1)	1.0238 (1)	0.2554 (2)	3.60 (3)	C(29)	0.5635 (4)	0.4031 (4)	0.7019 (6)	3.6 (1)
P(2)	0.4954 (1)	0.4981 (1)	0.7436 (2)	5.16 (5)	C(30)	0.5454 (3)	0.3294 (4)	0.5960 (6)	3.4 (1)
C(1)	0.0338 (3)	0.9086 (4)	0.1957 (5)	3.1 (1)	C(31)	0.4646 (4)	0.3221 (4)	0.4999 (6)	3.9 (1)
C(2)	0.0966 (3)	0.8906 (4)	0.1177 (5)	3.2 (1)	C(32)	0.3875 (3)	0.3883 (3)	0.4896 (6)	3.7 (1)
C(3)	0.1439 (3)	0.9664 (4)	0.0777 (5)	3.0 (1)	C(33)	0.4047 (3)	0.4704 (4)	0.6083 (6)	3.5 (1)
C(4)	0.1306 (3)	1.0656 (4)	0.1148 (5)	3.0 (1)	C(34)	0.6514 (4)	0.4031 (4)	0.7950 (6)	3.9 (1)
C(5)	0.0701 (3)	1.1002 (4)	0.1934 (6)	3.2 (1)	C(35)	0.6658 (5)	0.4267 (5)	0.9346 (7)	5.5 (2)
C(6)	-0.0096 (3)	0.8207 (4)	0.2324 (6)	3.3 (1)	C(36)	0.7490 (5)	0.4291 (6)	1.0130 (8)	6.4 (2)
C(7)	-0.0246 (4)	0.8120 (5)	0.3592 (6)	4.0 (1)	C(37)	0.8183 (5)	0.4068 (6)	0.9553 (8)	6.5 (2)
C(8)	-0.0647 (4)	0.7301 (5)	0.3890 (6)	5.1 (2)	C(38)	0.8054 (4)	0.3826 (5)	0.8191 (7)	5.0 (2)
C(9)	-0.0904 (4)	0.6556 (5)	0.2908 (7)	5.4 (2)	C(39)	0.7221 (4)	0.3811 (4)	0.7396 (6)	4.1 (1)
C(10)	-0.0746 (4)	0.6607 (5)	0.1673 (7)	5.1 (2)	C(40)	0.4516 (4)	0.2393 (5)	0.3954 (6)	4.2 (1)
C(11)	-0.0348 (4)	0.7443 (5)	0.1358 (6)	4.0 (1)	C(41)	0.4925 (4)	0.1495 (5)	0.4190 (7)	4.5 (2)
C(12)	0.2133 (3)	0.9407 (4)	0.0028 (5)	3.3 (1)	C(42)	0.4804 (4)	0.0733 (6)	0.3184 (8)	5.8 (2)
C(13)	0.2606 (4)	0.8551 (5)	0.0213 (6)	4.3 (1)	C(43)	0.4272 (5)	0.0901 (6)	0.1936 (8)	6.9 (2)
C(14)	0.3258 (4)	0.8342 (5)	-0.0463 (7)	5.2 (2)	C(44)	0.3866 (5)	0.1782 (6)	0.1688 (7)	6.7 (2)
C(15)	0.3468 (4)	0.8991 (6)	-0.1325 (7)	5.5 (2)	C(45)	0.3991 (4)	0.2532 (5)	0.2675 (7)	5.3 (2)
C(16)	0.2996 (4)	0.9824 (5)	-0.1527 (6)	5.2 (2)	C(46)	0.3281 (4)	0.5367 (4)	0.6127 (5)	3.4 (1)
C(17)	0.2329 (4)	1.0048 (5)	-0.0879 (6)	4.2 (1)	C(47)	0.2437 (4)	0.5018 (5)	0.5690 (6)	4.1 (1)
C(18)	0.0679 (4)	1.2073 (4)	0.2259 (6)	3.4 (1)	C(48)	0.1742 (4)	0.5656 (5)	0.5573 (7)	4.8 (2)
C(19)	0.1406 (4)	1.2645 (5)	0.2465 (7)	4.4 (2)	C(49)	0.1872 (5)	0.6636 (5)	0.5884 (7)	5.4 (2)
C(20)	0.1360 (5)	1.3663 (5)	0.2629 (7)	5.1 (2)	C(50)	0.2693 (5)	0.6998 (5)	0.6379 (7)	5.3 (2)
C(21)	0.0574 (5)	1.4112 (5)	0.2620 (7)	5.4 (2)	C(51)	0.3396 (4)	0.6371 (4)	0.6491 (6)	4.1 (1)
C(22)	-0.0157 (4)	1.3553 (5)	0.2450 (7)	4.9 (2)	C(52)	0.4489 (5)	0.2914 (5)	0.8959 (7)	6.0 (2)
C(23)	-0.0109 (4)	1.2541 (5)	0.2265 (6)	3.8 (1)	C(53)	0.4654 (4)	0.2104 (5)	0.8121 (7)	5.1 (2)
C(24)	0.2071 (4)	1.0490 (5)	0.4791 (7)	5.4 (2)	C(54)	0.3936 (4)	0.1932 (4)	0.7058 (7)	4.6 (2)
C(25)	0.1806 (4)	0.9511 (6)	0.4897 (6)	5.9 (2)	C(55)	0.3312 (4)	0.2607 (5)	0.7226 (8)	5.6 (2)
C(26)	0.2259 (5)	0.8904 (5)	0.4191 (8)	6.3 (2)	C(56)	0.3642 (5)	0.3231 (5)	0.8384 (7)	6.5 (2)

C_5H_5 ring mean plane lies approximately between two C atoms; thus the rings have a staggered configuration as found in some other sandwich compounds (Mathey, Fischer, Mitschler & Ricard, 1980).

The Mn—P distances have a mean value of 2.361 (2) \AA ; this value is in the same range as the Mn—P bond length found in phosphacymantrene (Mathey, Mitschler & Weiss, 1978), but longer than a normal Mn—P σ bond (Enemark & Ibers, 1967, 1968; Evrard, Thomas, Davis & Bernal, 1976). The Mn—C(phosphorin) bonds have a mean value of 2.136 (2) \AA ; these bonds are longer than the corresponding Mn—C(cyclopentadienyl) distances because the ring is six-membered.

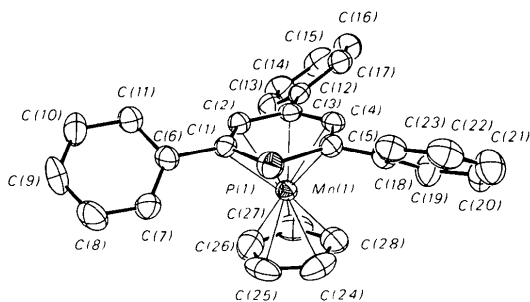


Fig. 1. ORTEP drawing of molecule (I) with the labeling scheme used. H atoms are omitted for clarity.

The overall geometry of the $PC_5H_2(C_6H_5)_3$ moieties is the same as that found in (B); all rings are planar within experimental error as shown by the χ^2 values of mean planes PL3 to PL10 in Table 3. The phenyl rings are rotated around the C(phenyl)—C(phosphorin) bonds by angles between 31.6 and 42.2° to minimize steric interactions; these angles are also in the range found for (B). The mean value of the P—C bonds, 1.764 (3) \AA , is comparable to that found in (B) and in other compounds such as phosphaferrrocene, 1.763 (5), (Mathey, Mitschler & Weiss, 1977) or 1,1'-diphos-

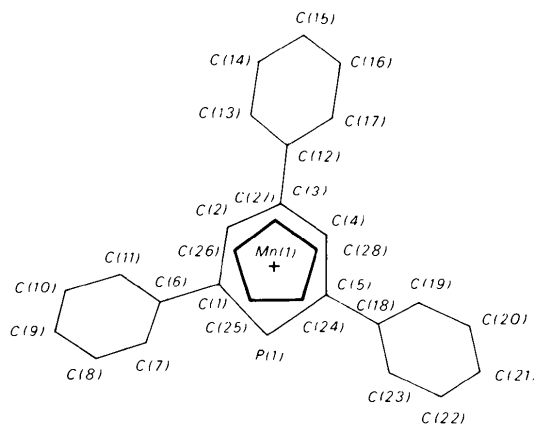


Fig. 2. Projection of molecule (I) on the phosphorin ring.

phaferrocene, 1.767 (2) Å, (de Lauzon, Deschamps, Fischer, Mathey & Mitschler, 1980) and probably not significantly different from what has been found in the complex $\text{PC}_5\text{H}_2(\text{C}_6\text{H}_5)_3\text{Cr}(\text{CO})_5$ (C) or in uncomplexed phosphorins (Fischer, Hellner, Chatzidakis & Dimroth, 1968; Bart & Daly, 1968; Wong & Bartell, 1974).

The C(phosphorin)—C(phosphorin) bond length has a mean value of 1.446 (3) Å, of the same order as that found in complex (B), 1.457 (7) Å, and slightly larger than the mean value found in complex (C) as well as in uncomplexed phosphorins (*ca* 1.40 Å). This bond lengthening has been attributed to π -complexation of the phosphorin ligand in complex (B) and is probably due to decreased electron density on the ligand caused by the $\text{Cr}(\text{CO})_3$ withdrawing group. Since the CpMn moiety is less electropositive than $\text{Cr}(\text{CO})_3$, we expect the phosphorin ligand to be more electron rich in

Table 2. Bond lengths (Å) and angles ($^\circ$) with *e.s.d.*'s

Mn(1)—P(1)	2.346 (2)	P(1)—C(1)	1.755 (5)
Mn(2)—P(2)	2.376 (2)	P(1)—C(5)	1.757 (5)
Mean: 2.361 (2)		P(2)—C(29)	1.763 (6)
		P(2)—C(33)	1.781 (5)
		Mean: 1.764 (3)	
Mn(1)—C(1)	2.124 (5)	C(1)—C(2)	1.410 (7)
Mn(1)—C(2)	2.112 (5)	C(2)—C(3)	1.420 (7)
Mn(1)—C(3)	2.114 (5)	C(3)—C(4)	1.408 (7)
Mn(1)—C(4)	2.097 (5)	C(4)—C(5)	1.432 (7)
Mn(1)—C(5)	2.137 (5)	C(29)—C(30)	1.408 (7)
Mn(2)—C(29)	2.146 (5)	C(30)—C(31)	1.429 (7)
Mn(2)—C(30)	2.122 (5)	C(31)—C(32)	1.495 (7)
Mn(2)—C(31)	2.114 (6)	C(32)—C(33)	1.571 (8)
Mn(2)—C(32)	2.263 (6)		
Mn(2)—C(33)	2.131 (5)		
Mean: 2.136 (2)		Mean: 1.446 (2)	
Mn(1)—C(24)	2.092 (6)	C(1)—C(6)	1.503 (7)
Mn(1)—C(25)	2.083 (6)	C(3)—C(12)	1.494 (7)
Mn(1)—C(26)	2.096 (6)	C(5)—C(18)	1.480 (7)
Mn(1)—C(27)	2.090 (6)	C(29)—C(34)	1.500 (7)
Mn(1)—C(28)	2.100 (6)	C(31)—C(40)	1.483 (8)
Mn(2)—C(52)	2.117 (6)	C(33)—C(46)	1.508 (7)
Mn(2)—C(53)	2.109 (6)	Mean: 1.494 (3)	
Mn(2)—C(54)	2.110 (6)		
Mn(2)—C(55)	2.112 (6)		
Mn(2)—C(56)	2.095 (6)		
Mean: 2.100 (2)			
C(1)—P(1)—C(5)	100.0 (2)	C(1)—P(1)—Mn(1)	60.3 (1)
C(29)—P(2)—C(33)	97.1 (3)	C(5)—P(1)—Mn(1)	60.8 (1)
C(2)—C(1)—P(1)	126.4 (4)	C(29)—P(2)—Mn(2)	60.3 (1)
C(4)—C(5)—P(1)	124.3 (4)	C(33)—P(2)—Mn(2)	59.6 (1)
C(30)—C(29)—P(2)	128.5 (4)	Mean: 60.27 (8)	
C(32)—C(33)—P(2)	132.8 (4)		
Mean C—C phenyl rings			
C(6)—C(11)	1.375 (3)	C(34)—C(39)	1.383 (4)
C(12)—C(17)	1.378 (3)	C(40)—C(45)	1.385 (4)
C(18)—C(23)	1.382 (3)	C(46)—C(51)	1.382 (3)
Mean C—C cyclopentadiene rings			
C(24)—C(28)	1.378 (4)		
C(52)—C(56)	1.399 (4)		

Table 3. Mean planes

Shown are the atoms in the plane, the equation and the distances to the mean plane. Least-squares mean planes are computed according to Blow (1960).

		χ^2
PL 1:	C(24), C(25), C(26), C(27), C(28) $-0.5588x + 0.1275y - 0.8194z = +3.4649$ C(24) 0.000 (7), C(25) 0.003 (7), C(26) -0.006 (8), C(27) 0.005 (7), C(28) -0.002 (7), Mn(1) 1.733 (1)	1
PL 2:	C(52), C(53), C(54), C(55), C(56) $0.5136x + 0.6533y - 0.5563z = +0.0492$ C(52) 0.000 (7), C(53) -0.005 (7), C(54) 0.007 (6), C(55) -0.008 (7), C(56) 0.005 (7), Mn(2) 1.740 (1)	4
PL 3:	P(1), C(1), C(2), C(3), C(4), C(5) $-0.5280x + 0.1190y - 0.8401z = +0.3205$ P(1) 0.001 (2), C(1) -0.009 (5), C(2) 0.001 (5), C(3) 0.006 (5), C(4) -0.001 (5), C(5) -0.009 (5), Mn(1) -1.526 (1)	7
PL 4:	P(2), C(29), C(30), C(31), C(32), C(33) $0.5070x + 0.6337y - 0.5843z = -2.9085$ P(2) -0.003 (2), C(29) 0.016 (6), C(30) -0.001 (6), C(31) -0.010 (6), C(32) -0.002 (5), C(33) 0.016 (6), Mn(2) -1.528 (1)	22
PL 5:	C(6), C(7), C(8), C(9), C(10), C(11) $-0.8417x + 0.4568y - 0.2879z = -4.7884$ C(6) 0.005 (6), C(7) -0.006 (6), C(8) -0.003 (7), C(9) 0.013 (7), C(10) -0.012 (7), C(11) 0.001 (6)	8
PL 6:	C(12), C(13), C(14), C(15), C(16), C(17) $-0.5046x - 0.4188y - 0.7550z = +7.2094$ C(12) -0.009 (5), C(13) 0.002 (6), C(14) 0.012 (7), C(15) -0.013 (7), C(16) 0.000 (7), C(17) 0.010 (6)	12
PL 7:	C(18), C(19), C(20), C(21), C(22), C(23) $0.0710x + 0.1320y - 0.9887z = -0.0031$ C(18) 0.008 (6), C(19) -0.012 (7), C(20) 0.004 (7), C(21) 0.007 (7), C(22) -0.007 (7), C(23) -0.001 (6)	7
PL 8:	C(34), C(35), C(36), C(37), C(38), C(39) $0.1351x + 0.9773y - 0.1629z = -4.7623$ C(34) 0.002 (6), C(35) -0.006 (7), C(36) 0.005 (8), C(37) 0.002 (8), C(38) -0.004 (7), C(39) 0.001 (6)	1
PL 9:	C(40), C(41), C(42), C(43), C(44), C(45) $0.8849x + 0.3414y - 0.3169z = -5.3936$ C(40) -0.006 (6), C(41) 0.003 (6), C(42) 0.000 (7), C(43) 0.001 (8), C(44) -0.007 (8), C(45) 0.009 (7)	4
PL 10:	C(46), C(47), C(48), C(49), C(50), C(51) $0.2712x + 0.2089y - 0.9396z = -3.1830$ C(46) 0.015 (5), C(47) -0.012 (6), C(48) -0.007 (7), C(49) 0.024 (7), C(50) -0.014 (7), C(51) -0.008 (6)	29

(A) than in (B) and the length of the C(phosphorin)—C(phosphorin) bond to be conversely closer to the aromatic value of 1.40 Å in (A) than in (B), which is indeed observed. The C(phosphorin)—C(phenyl) mean bond length has the same value in (A) as in (B) [1.494 (3) vs 1.494 (9) Å].

C—C distances in the phenyl and cyclopentadienyl rings have normal values.

The CPC bond angle has a shorter value in (A) (mean value 98°) or (B) (99°) than in (C) (103°) or uncomplexed phosphorins (ca 102°). The geometry of the P—metal bond is almost the same in (A) and in (B) as indicated by the mean value of the C α —P—metal angle: (A) 60.3, (B) 61.2°. Thus, as the overall geometry of the metal—phosphorin ring bonding appears to be very similar in (A) and (B), the large upfield shift observed in the ³¹P NMR spectrum of (A) compared to (B) (ca 50 p.p.m. shielding) could again be due to overall higher electron density on the phosphorin ring and at the P atom, due to the electron-donating properties of the CpMn group as compared to Cr(CO)₃.

References

- BART, J. C. J. & DALY, J. J. (1968). *Angew. Chem. Int. Ed. Engl.* **7**, 811–815.
- BERNDT, A. F. & MARSH, R. E. (1963). *Acta Cryst.* **16**, 118–123.
- BLOW, D. M. (1960). *Acta Cryst.* **13**, 168.
- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
- ENEMARK, J. H. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 1575–1581.
- ENEMARK, J. H. & IBERS, J. A. (1968). *Inorg. Chem.* **7**, 2339–2344.
- EVARD, G., THOMAS, R., DAVIS, B. R. & BERNAL, I. (1976). *Inorg. Chem.* **15**, 52–57.
- FISCHER, W., HELLNER, E., CHATZIDAKIS, A. & DIMROTH, K. (1968). *Tetrahedron Lett.* pp. 6227–6230.
- FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP. Computing in Crystallography*, edited by H. SCHENK, R. OLTROFF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LAUZON, G. DE, DESCHAMPS, B., FISCHER, J., MATHEY, F. & MITSCHLER, A. (1980). *J. Am. Chem. Soc.* **102**, 994–1000.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- MATHEY, F., FISCHER, J., MITSCHLER, A. & RICARD, L. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2522–2525.
- MATHEY, F., MITSCHLER, A. & WEISS, R. (1977). *J. Am. Chem. Soc.* **99**, 3537–3538.
- MATHEY, F., MITSCHLER, A. & WEISS, R. (1978). *J. Am. Chem. Soc.* **100**, 5748–5755.
- NIEF, F., CHARRIER, C., MATHEY, F. & SIMALTY, M. (1980). *J. Organomet. Chem.* **187**, 277–280.
- VAHRENKAMP, H. & NÖTH, H. (1972). *Chem. Ber.* **105**, 1148–1157.
- VAHRENKAMP, H. & NÖTH, H. (1973). *Chem. Ber.* **106**, 2227–2235.
- WONG, T. C. & BARTELL, L. S. (1974). *J. Chem. Phys.* **61**, 2840–2849.

Acta Cryst. (1981). **B37**, 1071–1075

Structure du Tricarbonyl(indènecarboxylate-2 de méthyle)chrome

PAR RENÉ MERCIER

Laboratoire de Chimie-Physique, Faculté des Sciences et des Techniques, Université de Franche-Comté,
25030 Besançon CEDEX, France

ET JOËL VEBREL

Laboratoire de Chimie-Appliquée, Faculté des Sciences et des Techniques, Université de Franche-Comté,
25030 Besançon CEDEX, France

(Reçu le 4 mars 1980, accepté le 6 novembre 1980)

Abstract

The crystal structure of [Cr(C₁₁H₁₀O₂)(CO)₃] has been determined by a single-crystal X-ray study (Mo K α radiation, $\lambda = 0.7107$ Å, $\mu = 0.95$ mm⁻¹). The unit cell is triclinic, *P*1̄, with $a = 8.244$ (3), $b = 11.240$ (4), $c = 7.103$ (2) Å, $\alpha = 81.17$ (2), $\beta = 81.28$ (2), $\gamma =$

0567-7408/81/051071-05\$01.00

87.77 (3)°, $V = 642.8$ Å³, $Z = 2$, $D_m = 1.60$ (3), $D_x = 1.61$ Mg m⁻³. The structure was solved by Fourier syntheses and refined to an R_w value of 0.030 for 1598 independent reflexions ($\theta \leq 31^\circ$). The staggered conformation of the Cr(CO)₃ group [with C—O lengths close to 1.154 (5) Å] results from interactions with the pentagonal ring and the ester group. The Cr atom is

© 1981 International Union of Crystallography