

| | | | | |
|-----|-------------|-------------|-------------|-----------|
| C54 | 0.151 (2) | -0.4236 (9) | 0.3609 (9) | 0.093 (3) |
| C55 | 0.0486 (9) | -0.3518 (8) | 0.3561 (8) | 0.073 (3) |
| C56 | 0.0511 (8) | -0.2443 (7) | 0.3044 (8) | 0.064 (2) |
| C61 | -0.2531 (6) | 0.0461 (6) | -0.2080 (5) | 0.032 (2) |
| C62 | -0.3509 (6) | -0.0415 (7) | -0.2045 (5) | 0.040 (2) |
| C63 | -0.4779 (7) | -0.0079 (9) | -0.2029 (6) | 0.057 (2) |
| C64 | -0.4983 (8) | 0.118 (2) | -0.2022 (7) | 0.069 (3) |
| C65 | -0.4033 (9) | 0.2075 (9) | -0.2059 (7) | 0.066 (2) |
| C66 | -0.2812 (7) | 0.1734 (7) | -0.2091 (6) | 0.045 (2) |
| C71 | -0.0081 (6) | 0.1185 (6) | -0.2636 (5) | 0.031 (2) |
| C72 | -0.0666 (7) | 0.1461 (6) | -0.3651 (6) | 0.042 (2) |
| C73 | -0.0110 (8) | 0.2333 (7) | -0.4209 (6) | 0.049 (2) |
| C74 | 0.1086 (8) | 0.2957 (7) | -0.3725 (7) | 0.056 (2) |
| C75 | 0.1695 (7) | 0.2703 (7) | -0.2728 (7) | 0.056 (2) |
| C76 | 0.1127 (7) | 0.1825 (7) | -0.2157 (6) | 0.045 (2) |
| C81 | 0.0608 (6) | -0.2053 (6) | -0.3295 (6) | 0.033 (2) |
| C82 | 0.1279 (7) | -0.1356 (7) | -0.3911 (6) | 0.045 (2) |
| C83 | 0.2509 (7) | -0.1675 (8) | -0.4045 (7) | 0.059 (2) |
| C84 | 0.3022 (7) | -0.2665 (8) | -0.3614 (7) | 0.060 (2) |
| C85 | 0.2386 (7) | -0.3369 (7) | -0.2979 (7) | 0.055 (2) |
| C86 | 0.1148 (7) | -0.3060 (7) | -0.2831 (7) | 0.053 (2) |

Table 2. Selected geometric parameters (Å, °)

| | | | |
|--------------|------------|--------------|-----------|
| Mn1—C1 | 1.793 (7) | P1—O4 | 1.603 (5) |
| Mn1—C2 | 1.814 (7) | P1—O3 | 1.606 (5) |
| Mn1—N2 | 2.050 (5) | P2—P3 | 2.245 (2) |
| Mn1—N1 | 2.053 (5) | P3—N5 | 1.588 (6) |
| Mn1—P1 | 2.210 (2) | P3—N3 | 1.621 (5) |
| Mn1—P2 | 2.362 (2) | P4—N3 | 1.556 (5) |
| Cl1—P4 | 1.979 (3) | P4—N4 | 1.566 (7) |
| Cl2—P4 | 2.008 (2) | P5—N4 | 1.569 (6) |
| Cl3—P5 | 2.004 (3) | P5—N5 | 1.579 (6) |
| Cl4—P5 | 2.000 (3) | O1—C1 | 1.141 (7) |
| P1—O5 | 1.581 (5) | O2—C2 | 1.139 (7) |
| C2—Mn1—N2 | 171.4 (3) | O4—P1—Mn1 | 122.4 (2) |
| C1—Mn1—N1 | 173.8 (3) | O3—P1—Mn1 | 111.3 (2) |
| C1—Mn1—P1 | 86.2 (2) | P3—P2—Mn1 | 120.1 (1) |
| C2—Mn1—P1 | 88.9 (2) | N5—P3—N3 | 115.5 (3) |
| N2—Mn1—P1 | 87.2 (2) | N3—P4—N4 | 119.2 (3) |
| N1—Mn1—P1 | 93.6 (2) | Cl1—P4—Cl2 | 101.0 (2) |
| C1—Mn1—P2 | 91.5 (2) | N4—P5—N5 | 118.5 (3) |
| C2—Mn1—P2 | 86.0 (2) | Cl4—P5—Cl3 | 100.0 (2) |
| N2—Mn1—P2 | 98.2 (2) | P4—N3—P3 | 121.1 (3) |
| N1—Mn1—P2 | 89.2 (2) | P4—N4—P5 | 120.3 (4) |
| P1—Mn1—P2 | 174.3 (1) | P5—N5—P3 | 122.8 (3) |
| O5—P1—Mn1 | 115.8 (2) | | |
| N2—Mn1—P2—P3 | -24.5 (2) | Mn1—P2—P3—N3 | 47.7 (2) |
| N1—Mn1—P2—P3 | -102.6 (2) | | |

Data were collected (Enraf–Nonius, 1989) with profile analysis over all reflections (Lehmann & Larsen, 1974; Grant & Gabe, 1978). Friedel pairs were measured from 0 to 20° (θ). Standard drift corrections were applied. Cell refinement was performed using *DIRDIF CRYSDA* (Beurskens *et al.*, 1992). *DATAR* (Van der Maelen Uría, 1991) was used for data reduction. The structure was completed by the *DIRDIF* phase-expansion procedure. Isotropic least-squares refinement used a local version of *SHELX76* (Sheldrick, 1976; Van der Maelen Uría, 1991). Final refinement used *SHELXL93* (Sheldrick, 1993). The absolute configuration was checked with a new version of the *BIJVOET* program (Beurskens, Noordik & Beurskens, 1980) giving a Bijvoet coefficient of 0.933 (2) for the strongest 100 Friedel pairs. Further geometrical calculations were made with *PARST* (Nardelli, 1983) and Fig. 1 was produced using the *EUCLID* package (Spek, 1982).

We thank the Spanish DGICYT for support (project PB91-0664).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and hydrogen-bonding geometry have been deposited with the IUCr (Reference: HR1019). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Allcock, H. R., Manners, I., Mang, M. N. & Parvaez, M. (1990). *Inorg. Chem.* **29**, 522–529.
- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., García-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, Univ. of Nijmegen, The Netherlands.
- Beurskens, G., Noordik, J. H. & Beurskens, P. T. (1980). *Cryst. Struct. Commun.* **9**, 23–28.
- Carriedo, G. A., Crespo, C., Riera, V., Valín, M. L., Moreiras, D. & Solans, X. (1986). *Inorg. Chim. Acta.* **121**, 191–198.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Grant, D. F. & Gabe, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.
- Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–589.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Orpen, G. A., Brammer, L., Allen, H. F., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* p. S55.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Spek, A. L. (1982). *The EUCLID Package. Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.
- Van der Maelen Uría, J. F. (1991). PhD thesis, Univ. of Oviedo, Spain.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1995). **C51**, 23–26

[MoH₄(dppe)₂].thf (dppe = Ph₂PCH₂CH₂PPh₂; thf = Tetrahydrofuran)

ARMANDO J. L. POMBEIRO

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa codex, Portugal

ADRIAN HILLS, DAVID L. HUGHES AND RAYMOND L. RICHARDS

AFRC IPSR Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, England

(Received 19 May 1994; accepted 28 June 1994)

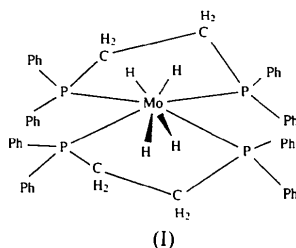
Abstract

The structure of tetrahydridobis[1,2-bis(diphenylphosphino)ethane-*P,P'*]molybdenum(IV). [MoH₄(dppe)₂] (dppe = Ph₂PCH₂CH₂PPh₂), is reported as

the tetrahydrofuran solvate. The molecule has dodecahedral geometry with the four P atoms in the *B* sites and the hydrides in the *A* sites. Mean Mo—P and Mo—H distances are 2.420 (3) and 1.67 (2) Å, respectively.

Comment

The tetrahydride [MoH₄(dppe)₂], (I), (dppe = Ph₂-PCH₂CH₂PPh₂) can be prepared either by hydric reduction of a halide complex such as [MoCl₄(dppe)] in the presence of dppe or, more conveniently, by treatment of *trans*-[Mo(N₂)₂(dppe)₂] with H₂ (Archer, George & Noble, 1981). Apart from H₂, a number of species can act as hydrogen-transfer agents to *trans*-[Mo(N₂)₂(dppe)₂], to give the tetrahydride complex; these include 2-propanol, tetrahydrofuran (thf), pyrrolidene or indoline (Tatsumi, Tominaga, Hidai & Uchida, 1977), 1-alkynes (which we have also shown to give alkynyl-hydride complexes) (Pombeiro, Hills, Hughes & Richards, 1990) and, as observed in this work, even EtPh₃PNH₂ or acrylonitrile. The last reagent was the source of the crystals of [MoH₄(dppe)₂] used in this study.



Treatment of *trans*-[Mo(N₂)₂(dppe)₂] under argon in tetrahydrofuran (thf) solution for 2 d with 2.2 mol equivalents of acrylonitrile gave a dark brown solution. Addition of hexane gave a mixture of a brown amorphous solid (which could be removed by rapid washing with dichloromethane) and brown rectangular prisms. The yield of crystalline material was about 15% and the compound, which was yellow when crushed, had bands in its infrared spectrum at 1725 cm⁻¹ (broad, Mo—H stretch) and 1090 cm⁻¹ (CO stretch of thf).

The molecular structure of [MoH₄(dppe)₂].thf is shown with the atom-numbering scheme in Fig. 1. The structure is well resolved and the hydride atoms are clearly identified and refined. The molecule lies about a twofold symmetry axis and shows typical dodecahedral coordination (Hoard & Silverton, 1963), with the four P atoms in the pseudo-equatorial *B* sites and the hydrides in the *A* sites. The mean Mo—P and Mo—H distances are 2.420 (3) and 1.67 (2) Å, respectively. The Mo—P distances are among the shortest recorded for dodecahedral phosphine complexes of *M* (*M* = Mo or W) and the

pseudo-*trans* P—Mo—P angles [157.70 (2) and 160.20 (2)°] are among the largest (Guggenberger, 1973; Cloke, Gibson, Green, Mletwa & Prout, 1988; Lobkovskii, Makhaev, Borisov & Semenenko, 1979, 1980; Lobkovskii, Borisov, Makhaev & Semenenko, 1980*a,b*).

The shape and size of the diphosphine ligands strongly influence the dimensions in this type of complex. Our molecule is very similar to [MoH₄(dippe)₂] (dippe = 'Pr₂PCH₂CH₂P'Pr₂) and [CrH₄(dmpe)₂] (dmpe = Me₂PCH₂CH₂PMe₂), which, as far as we are aware, are the only other tetrahydride bis(diphosphine) complexes to have been structurally characterized (Cloke, Gibson, Green, Mletwa & Prout, 1988; Salt *et al.*, 1985). In both the Mo molecules, there is relatively little steric crowding and the four P atoms take up positions close to the equatorial plane and close to the Mo atom. For the analogous tetrahydride monophosphine complexes, the Mo—P distances often range widely, *e.g.* 2.433 (2) and 2.512 (2) Å in [MoH₄(PMePh₂)₄] (Guggenberger, 1973); the pseudo-*trans* P—Mo—P angles of [MoH₄(PMePh₂)₄], at 141.5 (1) and 144.1 (1)°, are also rather smaller than in the diphosphine complexes.

In the crystal of [MoH₄(dppe)₂].thf, the complex molecules are discrete moieties, separated from each other and from the unresolved molecules of thf by normal van der Waals distances.

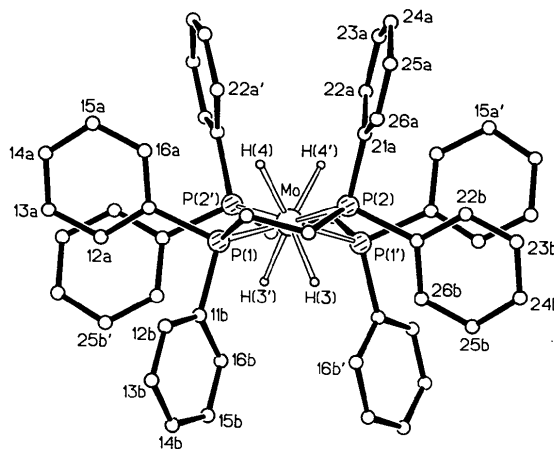


Fig. 1. The molecular structure of [MoH₄(dppe)₂], showing the atom-numbering scheme; C atoms are shown as *e.g.* 22*a* for C(22*a*).

Experimental

Crystal data

[MoH₄(C₂₆H₂₄P₂)₂].C₄H₈O
M_r = 968.9

Mo Kα radiation
λ = 0.71069 Å

| | |
|---|--|
| Monoclinic | Cell parameters from 25 reflections |
| $P2/n$ | $\theta = 10-11^\circ$ |
| $a = 15.743 (1) \text{ \AA}$ | $\mu = 0.42 \text{ mm}^{-1}$ |
| $b = 10.300 (1) \text{ \AA}$ | $T = 293 \text{ K}$ |
| $c = 15.830 (1) \text{ \AA}$ | Rectangular prisms |
| $\beta = 104.638 (7)^\circ$ | $0.55 \times 0.45 \times 0.20 \text{ mm}$ |
| $V = 2483.5 \text{ \AA}^3$ | Brown-yellow |
| $Z = 2$ | |
| $D_x = 1.295 \text{ Mg m}^{-3}$ | |
| <i>Data collection</i> | |
| Enraf-Nonius CAD-4 diffractometer | $R_{\text{int}} = 0.005$ |
| ω - θ scans | $\theta_{\text{max}} = 25^\circ$ |
| Absorption correction: empirical | $h = 0 \rightarrow 18$ |
| $T_{\text{min}} = 0.99, T_{\text{max}} = 1.00$ | $k = 0 \rightarrow 12$ |
| 4573 measured reflections | $l = -18 \rightarrow 18$ |
| 4373 independent reflections | 2 standard reflections |
| 3882 observed reflections | frequency: 167 min |
| $[I > 2\sigma(I)]$ | intensity variation: steady decrease to 86.3% of starting values |
| <i>Refinement</i> | |
| Refinement on F | $\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$ |
| $R = 0.032$ | $\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$ |
| $wR = 0.040$ | Extinction correction: none |
| $S = 2.13$ | Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV) |
| 4373 reflections | |
| 330 parameters | |
| $w = 1/\sigma^2(F)$ | |
| $(\Delta/\sigma)_{\text{max}} = 1.33$ (in parameters of disordered solvent atoms) | |

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

U_{iso} for H and thf atoms; $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ for others.

| Occupancy | x | y | z | U_{eq} | |
|-----------|-----|-------------|-------------|-----------------|------------|
| Mo | 1.0 | 1/4 | 0.14111 (2) | 1/4 | 0.0325 (1) |
| C(11a) | 1.0 | 0.0086 (1) | 0.1101 (2) | 0.2120 (1) | 0.0448 (7) |
| C(12a) | 1.0 | -0.0432 (2) | 0.1792 (3) | 0.2540 (2) | 0.064 (1) |
| C(13a) | 1.0 | -0.1076 (2) | 0.1171 (3) | 0.2862 (2) | 0.081 (1) |
| C(14a) | 1.0 | -0.1192 (2) | -0.0144 (4) | 0.2753 (2) | 0.082 (1) |
| C(15a) | 1.0 | -0.0684 (2) | -0.0837 (3) | 0.2342 (2) | 0.083 (1) |
| C(16a) | 1.0 | -0.0038 (2) | -0.0226 (3) | 0.2033 (2) | 0.064 (1) |
| C(11b) | 1.0 | 0.0585 (1) | 0.3547 (2) | 0.1555 (1) | 0.0430 (7) |
| C(12b) | 1.0 | -0.0237 (2) | 0.3805 (2) | 0.1022 (2) | 0.0549 (9) |
| C(13b) | 1.0 | -0.0534 (2) | 0.5065 (3) | 0.0849 (2) | 0.066 (1) |
| C(14b) | 1.0 | -0.0013 (2) | 0.6081 (3) | 0.1199 (2) | 0.070 (1) |
| C(15b) | 1.0 | 0.0814 (2) | 0.5858 (3) | 0.1709 (2) | 0.075 (1) |
| C(16b) | 1.0 | 0.1111 (2) | 0.4598 (2) | 0.1889 (2) | 0.0606 (9) |
| P(1) | 1.0 | 0.09885 (3) | 0.18650 (5) | 0.17609 (3) | 0.0366 (2) |
| C(1) | 1.0 | 0.0805 (1) | 0.1269 (2) | 0.0625 (1) | 0.0450 (7) |
| C(2) | 1.0 | 0.1592 (1) | 0.1644 (2) | 0.0284 (1) | 0.0457 (8) |
| P(2) | 1.0 | 0.26071 (3) | 0.10064 (5) | 0.10217 (3) | 0.0368 (2) |
| C(21a) | 1.0 | 0.2640 (1) | -0.0670 (2) | 0.0627 (1) | 0.0424 (7) |
| C(22a) | 1.0 | 0.2966 (2) | -0.1646 (2) | 0.1208 (2) | 0.076 (1) |
| C(23a) | 1.0 | 0.3018 (3) | -0.2909 (3) | 0.0935 (2) | 0.097 (2) |
| C(24a) | 1.0 | 0.2733 (2) | -0.3225 (3) | 0.0077 (2) | 0.074 (1) |
| C(25a) | 1.0 | 0.2410 (2) | -0.2283 (3) | -0.0514 (2) | 0.070 (1) |
| C(26a) | 1.0 | 0.2360 (2) | -0.1008 (3) | -0.0245 (2) | 0.0595 (9) |
| C(21b) | 1.0 | 0.3459 (2) | 0.1802 (2) | 0.0593 (1) | 0.0464 (8) |
| C(22b) | 1.0 | 0.3976 (2) | 0.1169 (3) | 0.0152 (2) | 0.077 (1) |
| C(23b) | 1.0 | 0.4640 (2) | 0.1801 (4) | -0.0108 (3) | 0.095 (2) |
| C(24b) | 1.0 | 0.4792 (2) | 0.3063 (4) | 0.0055 (3) | 0.099 (2) |

| | | | | | |
|--------|-----|--------------|-------------|-------------|------------|
| C(25b) | 1.0 | 0.4294 (3) | 0.3732 (3) | 0.0511 (3) | 0.115 (2) |
| C(26b) | 1.0 | 0.3632 (2) | 0.3107 (3) | 0.0765 (2) | 0.088 (2) |
| H(3) | 1.0 | 0.2597 (12) | 0.2758 (20) | 0.1954 (12) | 0.044 (5) |
| H(4) | 1.0 | 0.1871 (14) | 0.0070 (23) | 0.2220 (13) | 0.057 (7) |
| O(50) | 0.4 | -1/4 | 0.4228 (14) | 1/4 | 0.146 (4) |
| C(51) | 0.4 | -0.1817 (18) | 0.5066 (32) | 0.3132 (15) | 0.176 (9) |
| C(52) | 0.4 | -0.2194 (22) | 0.6196 (26) | 0.3281 (15) | 0.175 (9) |
| C(53) | 0.4 | -0.1911 (17) | 0.4812 (28) | 0.2361 (22) | 0.184 (9) |
| C(54) | 0.4 | -0.1633 (16) | 0.5776 (33) | 0.2770 (24) | 0.193 (9) |
| O(55) | 0.4 | -1/4 | 0.6888 (20) | 1/4 | 0.215 (8) |
| C(61) | 0.2 | -0.2353 (45) | 0.6470 (40) | 0.1902 (33) | 0.149 (13) |
| C(62) | 0.2 | -0.2517 (29) | 0.4990 (33) | 0.1846 (20) | 0.135 (9) |
| C(63) | 0.2 | -0.1897 (36) | 0.6335 (40) | 0.2897 (33) | 0.153 (13) |
| C(64) | 0.2 | -0.1995 (36) | 0.6108 (62) | 0.2084 (41) | 0.144 (19) |
| C(65) | 0.2 | -0.1883 (18) | 0.4614 (28) | 0.2816 (28) | 0.102 (7) |

Table 2. Selected geometric parameters ($\text{\AA}, ^\circ$)

| | | | |
|----------------------------------|------------|--------------------|------------|
| About the Mo atom | | | |
| Mo—P(1) | 2.417 (1) | Mo—H(3) | 1.661 (20) |
| Mo—P(2) | 2.424 (1) | Mo—H(4) | 1.692 (23) |
| P(1)—Mo—P(1') | 157.70 (2) | P(2)—Mo—H(3) | 66.7 (7) |
| P(1)—Mo—P(2) | 82.30 (2) | P(2)—Mo—H(3') | 133.1 (7) |
| P(1)—Mo—P(2') | 101.56 (2) | P(2)—Mo—H(4) | 77.6 (7) |
| P(1)—Mo—H(3) | 78.2 (7) | P(2)—Mo—H(4') | 86.2 (7) |
| P(1)—Mo—H(3') | 83.2 (7) | H(3)—Mo—H(3') | 66.8 (9) |
| P(1)—Mo—H(4) | 65.9 (7) | H(3)—Mo—H(4) | 132.1 (10) |
| P(1)—Mo—H(4') | 136.4 (7) | H(3)—Mo—H(4') | 133.9 (9) |
| P(2)—Mo—P(2') | 160.20 (2) | H(4)—Mo—H(4') | 70.6 (10) |
| In the dppe ligands | | | |
| P(1)—C(1) | 1.852 (2) | P(2)—C(2) | 1.845 (2) |
| P(1)—C(11a) | 1.835 (2) | P(2)—C(21a) | 1.841 (2) |
| P(1)—C(11b) | 1.845 (2) | P(2)—C(21b) | 1.841 (2) |
| Mo—P(1)—C(11a) | 120.8 (1) | Mo—P(2)—C(21a) | 120.2 (1) |
| Mo—P(1)—C(11b) | 121.3 (1) | Mo—P(2)—C(21b) | 120.9 (1) |
| Mo—P(1)—C(1) | 107.4 (1) | Mo—P(2)—C(2) | 106.8 (1) |
| C(11a)—P(1)—C(11b) | 101.5 (1) | C(21a)—P(2)—C(21b) | 101.9 (1) |
| C(11a)—P(1)—C(1) | 102.4 (1) | C(2)—P(2)—C(21a) | 102.3 (1) |
| C(11b)—P(1)—C(1) | 100.2 (1) | C(2)—P(2)—C(21b) | 101.8 (1) |
| Torsion angle in the dppe ligand | | | |
| P(1)—C(1)—C(2)—P(2) | 55.7 (2) | | |

Symmetry code: (i) $\frac{1}{2} - x, y, \frac{1}{2} - z$.

All non-H atoms of the Mo complex were allowed anisotropic displacement parameters; H atoms in the dppe ligands were included in idealized positions with isotropic displacement parameters and refined freely. The two distinct hydride atoms were located in difference maps and refined independently. A single molecule of solvent, thf, lies disordered over several orientations about a twofold symmetry axis. Eleven partially occupied atom sites were included in the refinement process but total resolution of the disorder has not proved feasible. Computer programs used in this analysis include *SHELX76* (Sheldrick, 1976) and others have been listed in Table 4 of Anderson, Richards & Hughes (1986) and were run on the DEC MicroVAX II machine in the Nitrogen Fixation Laboratory.

This work was partially supported by JNICT, INIC (Portugal) and the British Council.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Anderson, S. N., Richards, R. L. & Hughes, D. L. (1986). *J. Chem. Soc. Dalton Trans.* pp. 245–248.
- Archer, L. J., George, T. A. & Noble, M. E. (1981). *J. Chem. Educ.* **58**, 727–728.
- Cloke, F. G. N., Gibson, V. C., Green, M. L. H., Mtetwa, V. S. B. & Prout, K. (1988). *J. Chem. Soc. Dalton Trans.* pp. 2227–2229.
- Guggenberger, L. J. (1973). *Inorg. Chem.* **12**, 2295–2304.
- Hoard, J. L. & Silvertown, J. V. (1963). *Inorg. Chem.* **2**, 235–243.
- Lobkovskii, E. B., Borisov, A. P., Makhaev, V. D. & Semenenko, K. N. (1980a). *Zh. Strukt. Khim.* **21**, 126–130.
- Lobkovskii, E. B., Borisov, A. P., Makhaev, V. D. & Semenenko, K. N. (1980b). *J. Struct. Chem.* **21**, 100–104.
- Lobkovskii, E. B., Makhaev, V. D., Borisov, A. P. & Semenenko, K. N. (1979). *Zh. Strukt. Khim.* **20**, 944–946.
- Lobkovskii, E. B., Makhaev, V. D., Borisov, A. P. & Semenenko, K. N. (1980). *J. Struct. Chem.* **20**, 812–813.
- Pombeiro, A. J. L., Hills, A., Hughes, D. L. & Richards, R. L. (1990). *J. Organomet. Chem.* **398**, C15–C18.
- Salt, J. E., Girolami, G. S., Wilkinson, G., Motevalli, M., Thornton-Pett, M. & Hurhouse, M. B. (1985). *J. Chem. Soc. Dalton Trans.* pp. 685–692.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Tatsumi, T., Tominaga, H., Hidai, M. & Uchida, Y. (1977). *Chem. Lett. (Chem. Soc. Jpn)*, pp. 37–38.

both complexes, O—C bonds of the coordinated ring are shorter than those of the uncoordinated ring.

Comment

The title complexes were synthesized, following a previously described procedure (Sutherland, Piórko, Gill & Lee, 1982), by the reaction of catechol with (η^5 -1,2-dichlorobenzene)(η^5 -Cp)iron(II) hexafluorophosphate and with (η^6 -2,3-dichlorotoluene)(η^5 -Cp)iron(II) hexafluorophosphate to give (1) and (2), respectively. Crystals of both complexes were grown from acetone–dichloromethane–diethyl ether solutions at ca 255 K. Crystals of complex (2) contain molecules of diethyl ether in the complex:solvent ratio 2:1. Results obtained in the course of this study add to earlier studies on the synthesis, reactivity and, in particular, the structure of tricyclic heterocycles complexed with an FeCp moiety. It had been noted earlier that the effect of complexing iron, the presence of substituents on the heterocycle and the packing forces in the crystal all may influence the overall geometry of the heterocycle. Our results provide additional information on the influence of the above factors on the structure of the heterocycle.

Acta Cryst. (1995). **C51**, 26–29

Hexafluorophosphate Salts of Cyclopentadienyliron(II) Complexes of Dibenzodioxin and 1-Methyldibenzodioxin

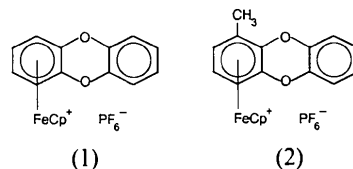
ADAM PIÓRKO,* SEAN CHRISTIE AND
MICHAEL J. ZAWOROTKO

*Department of Chemistry, Saint Mary's University,
Halifax, Nova Scotia, Canada B3H 3C3*

(Received 27 September 1993; accepted 5 April 1994)

Abstract

The structures of (η^5 -cyclopentadienyl)[(1,2,3,4,4a,10a- η^6)-dibenzo[*b,e*][1,4]dioxin]iron(II) hexafluorophosphate (1), [Fe(C₅H₅)(C₁₂H₈O₂)]PF₆, and (η^5 -cyclopentadienyl)[(1,2,3,4,4a,10a- η^6)-1-methyldibenzo[*b,e*][1,4]-dioxin]iron(II) hexafluorophosphate diethyl ether solvate (2), [Fe(C₅H₅)(C₁₃H₁₀O₂)]PF₆·0.5C₄H₁₀O, have been determined. The dihedral angle between the outer rings of dibenzodioxin was found to be 175.8 (2)° in (1) and 177.55 (19)° in (2). The planes of the coordinated arene and cyclopentadienyl (Cp) rings are nearly parallel for both complexes. The Fe atom is centered above the Cp ring while Fe—C distances involving the quaternary C atoms of the coordinated arene rings are slightly longer than those involving the other aromatic C atoms, particularly for complex (2). In the central dioxin ring of



Many of the structural features of complexes (1) and (2) resemble those reported for the FeCp complex of 2-methyldibenzodioxin (Abboud, Simonsen, Piórko & Sutherland, 1991). The Fe atom is centered above the Cp ring in both complexes, while bonding to the benzene ring is asymmetrical. The longest Fe—C distances are found for the quaternary C atoms [average 2.107 (6) versus 2.091 (6) Å for the other Fe—C distances in (1) and 2.104 (5) versus 2.079 (5) Å for the other Fe—C distances in (2)]. This phenomenon has been reported earlier for similar complexes (Abboud, Simonsen, Piórko & Sutherland, 1991; Simonsen, Lynch, Sutherland & Piórko, 1985; Sutherland, Piórko, Lee, Simonsen & Lynch, 1988; Lynch, Thomas, Simonsen, Piórko & Sutherland, 1986). The C—C distances within the coordinated rings are slightly longer than those of the uncoordinated rings [average 1.411 (10) versus 1.380 (11) Å in (1) and 1.410 (7) versus 1.383 (12) Å in (2)]. Asymmetry of the central dioxin ring, exemplified by the shortening of the O—C bonds of the coordinated ring, was noted earlier for the FeCp complex of 2-methyldibenzodioxin (Abboud, Simonsen, Piórko & Sutherland, 1991) and is also evident in (1) and (2) [average 1.364 (7) Å for O—C(coordinated) versus 1.399 (7) Å for the others in (1) and 1.367 (6) Å for O—C(coordinated) versus 1.393 (6) Å for the others in