Crystal Structure of Dicarbonyl-η-cyclopentadienyl[(3-dimethylarsino)-propyl]molybdenum

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The crystal structure of the title compound has been determined from *X*-ray diffractometer data by the heavy-atom method and refined by least squares to *R* 0.060 for 2 013 observed reflections. Crystals are orthorhombic, space group *Pcab*, a = 15.903(5), b = 13.297(2), c = 12.925(2) Å, Z = 8. Mo–As is 2.533(2), and the Mo–C(alkyl) 2.35(1) Å. The η^5-cyclopentadienyl group occupies an apical position in the pseudo-square-pyramidal complex.

THE preparation of unusual σ-bonded cyclo-alkyl-, -aryl-, and -benzyl-arsine complexes of molybdenum by the reductive cyclisation of compounds of the type $[Mo(\eta\text{-}C_5H_5)(CO)_2(L)I]$ (where L is a suitable halogen-substituted tertiary arsine) with sodium amalgam has been described recently.[1] We present here details of the molecular stereochemistry of $[Mo(\eta\text{-}C_5H_5)(CO)_2\{(CH_2)_3AsMe_2\}]$ as determined by *X*-ray diffraction.

EXPERIMENTAL

A prismatic crystal section 0.18 × 0.28 × 0.18 mm was used for the crystallographic work. Cell dimensions were obtained from a least squares fit of the angular parameters of 15 reflections with 2θ *ca.* 20° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer; a unique data set was gathered in the range $2\theta < 50°$ yielding 2 412 independent reflections, of which 2 013 with $I > 2\sigma(I)$ were considered observed and used in the structure solution and refinement, after absorption correction.

Crystal Data.—$C_{12}H_{17}AsMoO_2$, $M = 364.1$, Orthorhombic, $a = 15.903(5)$, $b = 13.297(2)$, $c = 12.925(2)$ Å, $U = 2\,733(2)$ Å^3, $D_m = 1.77(1)$, $Z = 8$, $D_c = 1.771$ g cm^{-3},

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[1] M. Mickiewicz, K. P. Wainwright, and S. B. Wild, *J.C.S. Dalton*, 1976, 262.

$F(000) = 1\,440$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å (monochromatic), μ(Mo-K_α) = 34.9 cm^{-1}. Space group *Pcab* (alternative setting of No. 61, *Pbca*). Neutral atom scattering factors,[2,3] those for Mo and As being corrected for anomalous dispersion effects ($\Delta f'$, $\Delta f''$).[4]

Computation was carried out on a CDC 6200 machine using a local version of the '*X*-ray '72' program system.[5] Results are given in Tables 1 and 2, with the exception of the structure amplitudes which are deposited as Supplementary Publication No. SUP 21664 (5 pp., 1 microfiche).*

TABLE 1

Atomic fractional cell (Mo and As × 10^5, C and O × 10^4, and H × 10^3) and thermal parameters ($U \times 10^3$ Å^2), with least-squares estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	27 975(6)	41 612(7)	39 106(8)	32(3)	34(3)	38(2)	−3(1)	−2(1)	3(1)
Cyclopentadiene ligand									
C(1)	1 762(9)	3 100(12)	4 590(12)	51(9)	71(11)	65(11)	−21(8)	−6(8)	18(9)
H(1)	177(8)	268(10)	518(11)	100(−)					
C(2)	1 393(9)	4 042(13)	4 355(14)	40(9)	95(14)	80(12)	−18(9)	10(8)	−19(11)
H(2)	134(8)	439(10)	479(10)	100(−)					
C(3)	1 442(8)	4 197(12)	3 305(13)	43(9)	69(11)	76(12)	−1(8)	−23(8)	18(10)
H(3)	131(8)	482(10)	292(10)	100(−)					
C(4)	1 790(8)	3 344(12)	2 848(11)	36(8)	79(12)	61(10)	−22(8)	−7(7)	−19(10)
H(4)	192(8)	335(10)	213(11)	100(−)					
C(5)	2 022(8)	2 681(10)	3 629(13)	46(9)	39(8)	84(12)	−13(6)	−10(8)	−9(8)
H(5)	218(8)	201(10)	344(11)	100(−)					
Arsine ligand									
As	41 277(8)	31 813(9)	42 913(11)	39(3)	47(3)	54(3)	7(1)	−7(1)	−3(1)
C(6)	4 871(9)	3 274(15)	3 081(12)	50(10)	161(19)	54(11)	36(11)	13(8)	−8(12)
C(7)	4 526(9)	4 132(16)	2 425(14)	37(9)	176(20)	78(12)	−10(12)	11(9)	2(14)
C(8)	3 608(9)	4 113(12)	2 390(10)	74(10)	80(11)	33(8)	3(9)	−1(7)	18(8)
H(81)	347(8)	341(11)	209(11)	100(−)					
H(82)	327(8)	454(11)	199(11)	100(−)					
C(9)	3 984)10)	1 717(10)	4 511(18)	70(10)	35(10)	193(21)	5(8)	−21(13)	12(11)
C(10)	4 853(10)	3 489(13)	5 445(14)	55(10)	80(12)	62(10)	8(9)	−21(9)	0(10)
H(10)	509(11)	396(12)	533(15)	100(−)					
H(102)	545(10)	304(11)	552(11)	100(−)					
Carbonyls									
C(a)	3 025(8)	5 546(10)	3 518(10)	59(9)	50(9)	47(9)	−8(7)	−6(7)	−5(7)
O(a)	3 116(7)	6 376(8)	3 288(9)	123(10)	44(7)	97(9)	−20(6)	−31(8)	24(6)
C(b)	3 119(7)	4 789(9)	5 212(9)	45(8)	24(7)	56(9)	−4(5)	6(7)	2(6)
O(b)	3 305(6)	5 199(7)	5 971(7)	80(8)	60(7)	52(7)	−5(6)	−8(6)	−15(6)

The structure was solved by the heavy-atom method and refined by least squares in two blocks, the parameters of the $C_5M(CO)_2AsC_3$ molecular skeleton being refined as a single block (with the parameters of the remaining atoms in a second block) in order to approximate to a full-matrix procedure. Anisotropic thermal parameters employed for the non-hydrogen atoms were of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{23}klb^*c^*)]$. Hydrogen atoms of the cyclopentadienyl ring were located in a difference map, as were those associated with C(8) and C(10), and were refined positionally with isotropic thermal parameters constrained to 0.10 Å^2. The thermal motion of C(6), C(7), and C(9) was much higher and the corresponding hydrogen atoms could not be successfully located and refined in the above manner. The positional parameters of the methylene hydrogen atoms were thus estimated geometrically (r_{C-H}, 1.0 Å) and included as invariants. In the final refinement cycle, no parameter shift exceeded 0.2σ; R was 0.060, R' $[= \Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ being 0.066; the weighting scheme $w = (\sigma^2|F_o| + n \times 10^{-4}|F_o|^2)^{-1}$ was appropriate for $n = 3$.

Unit-cell contents are shown in Figure 1, atomic labelling and thermal ellipsoids in Figure 2.

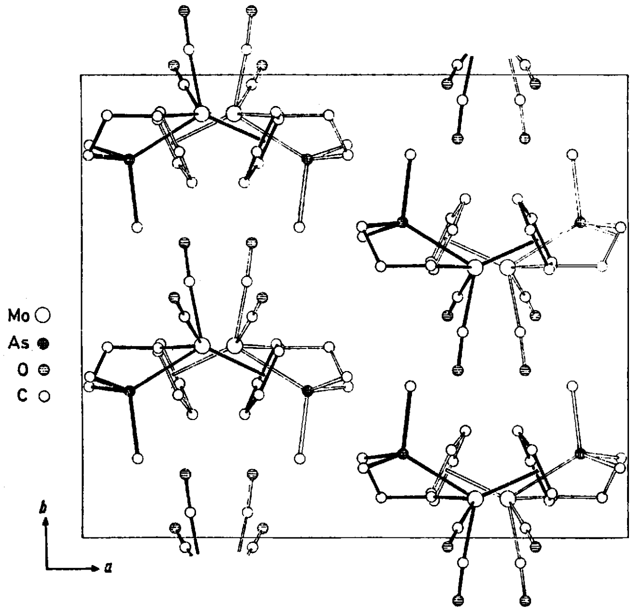

FIGURE 1 Unit-cell contents projected down *c*; molecules in the upper half of the cell are shown with solid bonds

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* For details, see Notice to Authors No. 7, *J.C.S. Dalton*, Index issue, 1975 (items less than 10 pp. are supplied as full-size copies).

[2] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 7.

[5] '*X*-Ray' program system, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., June, 1972.

TABLE 2

Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses

(*a*) The Mo environment			
Mo–C(1)	2.34(2)	C(2)–Mo–C(8)	137.3(8)
Mo–C(2)	2.31(1)	C(3)–Mo–C(4)	34.7(5)
Mo–C(3)	2.29(1)	C(3)–Mo–C(5)	58.1(5)
Mo–C(4)	2.37(1)	C(2)–Mo–c(a)	93.8(6)
Mo–C(5)	2.35(1)	C(2)–Mo–C(b)	122.2(5)
Mo–C(a)	1.94(1)	C(2)–Mo–As	149.5(4)
Mo–C(b)	1.95(1)	C(2)–Mo–C(8)	103.3(5)
Mo–As	2.533(2)	C(4)–Mo–C(5)	34.2(5)
Mo–C(8)	2.35(1)	C(4)–Mo–C(a)	114.1(6)
C(1)–Mo–C(2)	35.5(6)	C(4)–Mo–C(b)	150.9(5)
C(1)–Mo–C(3)	58.6(5)	C(4)–Mo–As	116.2(4)
C(1)–Mo–C(4)	57.7(5)	C(5)–Mo–C(8)	82.8(5)
C(1)–Mo–C(5)	85.3(5)	C(5)–Mo–C(a)	148.3(5)
C(1)–Mo–C(a)	143.2(5)	C(5)–Mo–C(b)	129.1(5)
C(1)–Mo–C(b)	96.9(5)	C(5)–Mo–As	92.1(3)
C(1)–Mo–As	101.8(4)	C(5)–Mo–C(8)	97.8(5)
C(1)–Mo–C(8)	133.1(5)	C(a)–Mo–C(b)	76.7(5)
C(2)–Mo–C(3)	34.7(6)		
C(2)–Mo–C(4)	57.3(5)	C(a)–Mo–As	112.5(4)
C(2)–Mo–C(5)	58.3(6)	C(a)–Mo–C(3)	72.9(5)
C(2)–Mo–C(a)	108.0(6)	C(b)–Mo–As	80.4(3)
C(2)–Mo–C(b)	93.9(6)	C(b)–Mo–C(8)	126.2(5)
C(2)–Mo–As	136.4(4)	As–Mo–C(8)	72.0(4)
(*b*) Carbonyls			
C(a)–O(a)	1.15(2)	Mo–C(a)–O(a)	176(1)
C(b)–O(b)	1.16(2)	Mo–C(b)–O(b)	177(1)
(*c*) Cyclopentadiene ligand			
C(1)–C(2)	1.42(2)	C(2)–C(1)–C(5)	106(1)
C(2)–C(3)	1.37(2)	C(1)–C(2)–C(2)	109(1)
C(3)–C(4)	1.39(2)	C(2)–C(2)–C(4)	109(1)
C(4)–C(5)	1.39(2)	C(2)–C(4)–C(5)	108(1)
C(5)–C(1)	1.42(2)	C(4)–C(5)–C(1)	108(1)
C(i)–H(i)	0.7—1.0(1)	H(i)–C(i)–C(i ± 1)	115—135(10)
(*d*) Arsine ligand			
As–C(a)	1.98(1)	Mo–As–C(8)	115.9(5)
As–C(10)	1.93(2)	Mo–As–C(10)	122.7(5)
As–C(6)	1.96(2)	Mo–As–C(6)	108.4(5)
C(6)–C(7)	1.52(3)	C(9)–As–C(10)	99.6(8)
C(7)–C(8)	1.46(2)	C(9)–As–C(6)	104.2(8)
As–C(6)–C(2)	106(1)	C(10)–As–C(6)	104.0(7)
C(6)–C(2)–C(8)	111(1)	Me–C(8)–C(7)	121(1)

(*e*) Least-squares plane through the cyclopentadienyl ring [C(1)—(5)] ($X = ax$, $Y = by$, $Z = cz$):

$$0.8970X + 0.4328Y + 0.0897Z = 4.832$$

Atomic deviations (Å): C(1) 0.00, C(2) −0.01, C(3) 0.02, C(4) −0.02, C(5) 0.02 (σ 0.02); Mo 2.01

DISCUSSION

The unit-cell contents comprise discrete molecules of the complex, there being no significant intermolecular contacts at distances shorter than the sum of the van der Waals radii. The molecular geometry is pseudo-square-pyramidal with the η^5-cyclopentadienyl ring occupying the position at the apex of the pyramid. The *X*-ray determination confirms the structure suggested for the complex on the basis of ^{1}H n.m.r. spectroscopy.[1] The molybdenum–cyclopentadienyl carbon distances are expected, ranging from 2.29(1) to 2.37(1) Å, indicating that the molybdenum atom is slightly off the ring axis, the ring being slightly tilted with respect to the molybdenum. The molybdenum–carbonyl geometries are as expected. The molybdenum–arsenic distance [2.533(2) Å] is significantly shorter than previously reported values (2.57—2.65 Å),[6] and probably reflects the association of the latter with phenyl rings or fluorinated alkyl chains. Two examples have been established for molybdenum–alkyl-carbon distances: in [Mo(η-C_5H_5)(CO)$_3$Et],[7] it is 2,397(19) Å, while the distance in the perfluorinated alkyl derivative, [Mo(η-C_5H_5)(CO)$_3$(C_3F_7)],[8] is considerably less, 2.288(9) Å. In the present case, the distance is 2.35(1) Å, probably between the two previously found values, and certainly much longer than the second of the two. The remainder of the geometry within the chelate ligand is as expected.

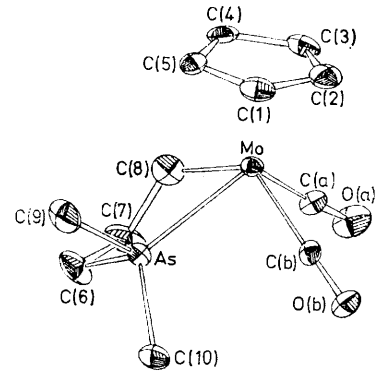

FIGURE 2 Molecular diagram showing atom labelling and 20% thermal ellipsoids

[5/1762 *Received*, 15*th September*, 1975]

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[6] P. J. Roberts and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 1501; I. W. Nowell and J. Trotter, *ibid.*, p. 2922; M. G. B. Drew, *J.C.S. Dalton*, 1972, 626; I. W. Nowell, S. Rettig, and J. Trotter, *ibid.*, p. 2381; M. G. B. Drew and J. D. Wilkins, *ibid.*, 1973, 2664; J. C. Dewan, K. Henrick, D. L. Kepert, K. R. Trigwell, and A. H. White, *ibid.*, 1975, 546.

[7] M. J. Bennett, Ph.D. Thesis, Sheffield University, 1965, quoted in ref. 7.

[8] M. R. Churchill and J. P. Fennessy, *Inorg. Chem.*, 1967, **6**, 1213.