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The Structures of Bis[η^5-(1-cyclopentadienyl-2-iodoethane)]diiodomolybdenum and Bis[η^5-(2-cyclopentadienylethyl)]molybdenum

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Abstract

The crystal structures of the title compounds have been determined. (I) $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2I})_2\mathrm{I}_2]$, $\mathrm{C_{14}H_{16}I_4Mo}$, M_r = 787·8, is monoclinic, space group $C2/c$, a = 22·260 (3), b = 7·165 (7), c = 13·155 (4) Å, β = 118·03 (8)°, U = 1852 Å^3, D_c = 2·83 Mg m^{-3} for Z = 4, λ(Mo $K\alpha$) = 0·71069 Å, μ = 7·4 mm^{-1}, $F(000)$ = 1416. (II) $[\overline{\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2}})_2]$, $\mathrm{C_{14}H_{16}Mo}$, M_r = 280·2, is monoclinic, space group $P2_1/a$, a = 12·259 (2), b = 6·372 (6), c = 17·550 (3) Å, β = 126·62 (2)°, U = 1100 Å^3, D_c = 1·69 Mg m^{-3} for Z = 4, λ(Mo $K\alpha$) = 0·71069 Å, μ = 1·1 mm^{-1}, $F(000)$ = 568. The structures were refined to R_w = 0·048 for 1883 reflexions (I) and R_w = 0·033 for 2628 reflexions (II). The molecules have a bent bis(η^5-cyclopentadienyl)–metal complex geometry distorted in the compound (II) to accommodate a σ bond from the alkyl side chain to the metal atom.

Introduction

Cocondensation of Mo with spiro[3.3]heptadiene gives the compound (II) $\overline{\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2}})_2$ which reacts with iodine giving the ring-functionalized compound (I) $\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2I})_2\mathrm{I}_2$.

These reactions can be considered as an example of a general synthetic route towards ring-functionalized bent bis(η^5-cyclopentadienyl)–metal complexes which would make possible the synthesis of many potentially interesting new compounds. A preliminary account of this work has been published (Barretta, Cloke, Feigenbaum, Green, Gourdon & Prout, 1981).

Experimental

The crystals were supplied by A. Barretta, F. G. N. Cloke and M. L. H. Green.

The deep-green (I) (0·7 × 0·4 × 0·15 mm) and red (II) (0·6 × 0·3 × 0·3 mm) crystals were sealed under argon in a glass capillary. After a survey by precession photography, the crystals were set up on a Nonius CAD-4 diffractometer and cell dimensions and orientation matrix obtained from the setting angles of 25 reflexions.

The intensities of reflexions with $\sin\theta/\lambda$ < 0·7 Å^{-1} were measured by an $\omega/2\theta$ scan with a variable scan rate and an ω scan angle of (1·20 + 0·35 tan θ)°. Reflexions with $I < 3\sigma(I)$ were not included in subsequent calculations. Lorentz and polarization and, for (I), empirical absorption corrections (North, Phillips & Mathews, 1968) were applied to the final merged data sets of 1883 (I) and 2631 (II) independent structure amplitudes.

Structure solution and refinement

Both structures were solved by heavy-atom techniques from unsharpened Patterson functions. The subsequent F_o syntheses indicated C atom positions. The refinements were by least squares with a two-block approximation, one from the derivatives of the positional parameters and the other from the temperature factors and the scale factor. Difference syntheses permitted the location of the H atoms in their expected positions. They were, however, positioned geometrically (C—H = 1·0 Å, U_{iso} = 0·05 Å^2), their location being adjusted after each refinement cycle. For (II), the

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three strongest reflexions (110, $\bar{2}02$, $\bar{1}12$) were not included in the final refinement because they were recorded at a count rate for which the dead-time error was very significant.

In the final stages an overall isotropic extinction parameter was introduced (Larson, 1967) and each reflexion was assigned a weight $w = 1/\sum_{r=1}^{n} A_r T_r(x)$ where n is the number of coefficients A_r, for a Chebyshev series, T_r is the polynomial function and x is $|F_o|/|F_o(\text{max.})|$ (Carruthers & Watkin, 1979*a*). Three coefficients, A_r, were used with values $A_1(\text{I}) = 6{\cdot}97 \times 10^4$, $A_2(\text{I}) = 9{\cdot}09 \times 10^4$, $A_3(\text{I}) = 3{\cdot}23 \times 10^4$ and $A_1(\text{II}) = 62{\cdot}4$, $A_2(\text{II}) = 47{\cdot}8$, $A_3(\text{II}) = 8{\cdot}1$.

The refinement converged at $R = 0{\cdot}038$, $R_w = 0{\cdot}048$ for (I) and $R = 0{\cdot}026$, $R_w = 0{\cdot}033$ for (II).

All calculations were performed on the Oxford University ICL 2980 computer with *CRYSTALS* (Carruthers & Watkin, 1979*b*). Neutral atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Results and discussion

The final atomic coordinates* are given in Tables 1 and 2, and bond lengths and angles with e.s.d.'s calculated from the variance–covariance matrix in Tables 3 and 4.

For (I) the unit cell contains four of the molecules shown in Fig. 1. Each has crystallographic twofold symmetry with the Mo atom at $(0,y,\frac{1}{4})$ *etc.* [Wyckoff (*e*)]. The molecule has the geometry characteristic of bent bis(η^5-cyclopentadienyl)–metal complexes.

The two planar cyclopentadienyl rings have an eclipsed configuration. The bending angle of 129° is

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (*mean e.s.d.* 0·004 Å^2) *for* (I)

	x	*y*	*z*	U_{eq} (Å^2)
Mo	0·00000	0·26141 (9)	0·75000	0·0185
I(1)	0·08944 (2)	−0·03199 (6)	0·76175 (4)	0·0306
C(1)	−0·0898 (3)	0·3933 (9)	0·5936 (6)	0·0271
C(2)	−0·0708 (4)	0·2314 (10)	0·5500 (5)	0·0311
C(3)	−0·0050 (4)	0·2534 (12)	0·5645 (6)	0·0344
C(4)	0·0214 (4)	0·4276 (10)	0·6215 (6)	0·0302
C(5)	−0·0327 (4)	0·5141 (8)	0·6335 (6)	0·0261
C(6)	−0·1583 (4)	0·4383 (13)	0·5808 (7)	0·0390
C(7)	−0·2128 (4)	0·4676 (15)	0·4582 (8)	0·0465
I(2)	−0·19406 (3)	0·70623 (10)	0·37567 (6)	0·0548

Table 2. *Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (*mean e.s.d.* 0·004 Å^2) *for* (II)

	x	*y*	*z*	U_{eq} (Å^2)
Mo	0·01477 (2)	−0·01635 (3)	0·24773 (1)	0·0246
C(11)	0·1934 (3)	−0·0146 (5)	0·40627 (19)	0·0357
C(12)	0·1572 (3)	−0·2263 (5)	0·37874 (20)	0·0387
C(13)	0·0208 (4)	−0·2593 (5)	0·34552 (22)	0·0421
C(14)	−0·0263 (3)	−0·0646 (6)	0·35553 (22)	0·0413
C(15)	0·0792 (3)	0·0855 (5)	0·39274 (20)	0·0386
C(16)	0·2976 (3)	0·1013 (7)	0·40332 (23)	0·0475
C(17)	0·2077 (3)	0·1621 (5)	0·29840 (22)	0·0407
C(21)	−0·0846 (3)	−0·0337 (5)	0·08840 (18)	0·0348
C(22)	−0·0534 (3)	0·1788 (5)	0·11491 (20)	0·0369
C(23)	−0·1257 (3)	0·2488 (5)	0·14993 (22)	0·0399
C(24)	−0·2045 (3)	0·0772 (6)	0·14323 (22)	0·0403
C(25)	−0·1801 (3)	−0·0976 (5)	0·10505 (20)	0·0385
C(26)	0·0102 (4)	−0·1842 (6)	0·08903 (24)	0·0483
C(27)	0·0974 (3)	−0·2433 (5)	0·19405 (21)	0·0383

Table 3. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses for* (I)

I(1^{i}) is related to I(1) by the twofold axis.

Mo–I(1)	2·849 (1)	C(2)–C(3)	1·40 (2)
Mo–C(1)	2·293 (6)	C(3)–C(4)	1·43 (2)
Mo–C(2)	2·357 (6)	C(4)–C(5)	1·43 (1)
Mo–C(3)	2·391 (7)	C(5)–C(1)	1·42 (1)
Mo–C(4)	2·293 (6)	C(1)–C(6)	1·49 (1)
Mo–C(5)	2·260 (6)	C(6)–C(7)	1·51 (2)
C(1)–C(2)	1·44 (1)	C(7)–I(2)	2·17 (1)

I(1)–Mo–I(1^{i})	84·90 (3)	C(5)–C(1)–C(2)	104·9 (6)
C(1)–C(2)–C(3)	109·9 (7)	C(5)–C(1)–C(6)	127·0 (7)
C(2)–C(3)–C(4)	108·4 (7)	C(2)–C(1)–C(6)	127·2 (7)
C(3)–C(4)–C(5)	106·1 (7)	C(1)–C(6)–C(7)	114·6 (8)
C(4)–C(5)–C(1)	110·5 (6)	C(6)–C(7)–I(2)	113·4 (6)

Table 4. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses for* (II)

Mo–C(11)	2·295 (3)	C(12)–C(13)	1·420 (5)
Mo–C(12)	2·310 (3)	C(13)–C(14)	1·423 (5)
Mo–C(13)	2·280 (3)	C(14)–C(15)	1·417 (5)
Mo–C(14)	2·251 (3)	C(15)–C(11)	1·424 (4)
Mo–C(15)	2·264 (3)	C(11)–C(16)	1·504 (5)
Mo–C(17)	2·273 (3)	C(16)–C(17)	1·528 (4)
Mo–C(21)	2·292 (3)	C(21)–C(22)	1·409 (4)
Mo–C(22)	2·314 (3)	C(22)–C(23)	1·419 (5)
Mo–C(23)	2·289 (3)	C(23)–C(24)	1·417 (5)
Mo–C(24)	2·250 (3)	C(24)–C(25)	1·421 (5)
Mo–C(25)	2·260 (3)	C(25)–C(21)	1·424 (5)
Mo–C(27)	2·268 (3)	C(21)–C(26)	1·502 (4)
C(11)–C(12)	1·412 (5)	C(26)–C(27)	1·527 (4)

C(17)–Mo–C(27)	82·1 (2)	C(21)–C(22)–C(23)	109·2 (3)
C(11)–C(12)–C(13)	109·6 (3)	C(22)–C(23)–C(24)	107·0 (3)
C(12)–C(13)–C(14)	106·6 (3)	C(23)–C(24)–C(25)	108·6 (3)
C(13)–C(14)–C(15)	108·6 (3)	C(24)–C(25)–C(21)	107·6 (3)
C(14)–C(15)–C(11)	108·1 (3)	C(22)–C(21)–C(25)	107·6 (3)
C(12)–C(11)–C(15)	107·1 (3)	C(22)–C(21)–C(26)	123·7 (4)
C(12)–C(11)–C(16)	123·9 (3)	C(25)–C(21)–C(26)	122·9 (3)
C(15)–C(11)–C(16)	123·0 (4)	C(21)–C(26)–C(27)	98·5 (3)
C(11)–C(16)–C(17)	98·6 (3)	C(26)–C(27)–Mo	100·4 (2)
C(16)–C(17)–Mo	100·3 (2)		

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* Tables of structure factors, anisotropic thermal parameters and H-atom coordinates for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36126 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

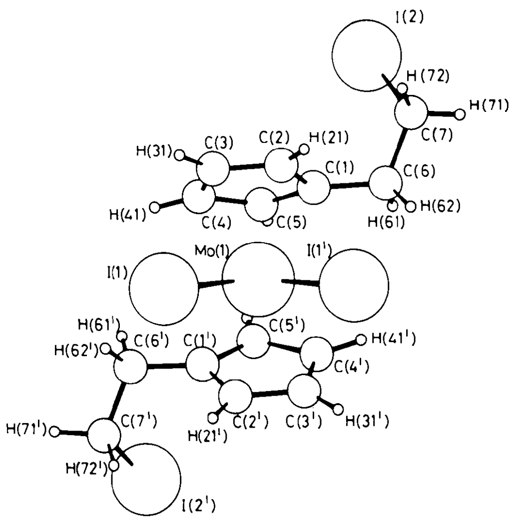

Fig. 1. A perspective view of the molecule $Mo(\eta^5\text{-}C_5H_4\text{-}CH_2CH_2I)_2I_2$. The atoms marked i are related by the twofold axis.

slightly smaller than in $(\eta^5\text{-}C_5H_5)_2MoCl_2$ (130·2 and 130·9°) (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974) perhaps due to a greater ligand-ring repulsion.

In the cyclopentadienyl rings the C—C bond lengths range from 1·40 (2) to 1·44 (1) Å, mean 1·42 Å, very close to the value of 1·43 Å proposed by Wheatley (1967). The rings are slightly 'tilted' (4°) such that the Mo—C distances range from 2·260 (6) to 2·391 (7) Å.

The angle I—Mo—I of 84·90 (3)° is in agreement with the existence of two non-bonding electrons (Prout *et al.*, 1974). The distance between the two I atoms is much smaller [3·846 (1) Å] than the sum of the van der Waals radii (4·30 Å), indicating a strong repulsion between the non-bonding electrons and those of the Mo—I bond.

The distance Mo—I [2·849 (1) Å] is comparable with the distance Zr—I [2·832 (2) Å] in $(\eta^5\text{-}C_5H_5)_2ZrI_2$ (Bush & Sim, 1971) whereas the metal-ring perpendicular distance increases very significantly (1·97 Å in the Mo complex, 2·19 Å in the Zr complex). The similarity in the Mo—I and Zr—I bond lengths can be explained by the repulsion between the electrons of the ψ_A orbital (Green, Green & Prout, 1972) (2 in Mo complex, 0 in Zr complex) and the electrons of the Mo—I bond and by the delocalization of the iodine *p* electrons into the vacant ψ_A orbital in $(\eta^5\text{-}C_5H_5)_2ZrI_2$.

The unit cell of (II) contains four of the molecules shown in Fig. 2 in general positions, with the bent bis(η^5-cyclopentadienyl)–metal complex geometry distorted to permit the formation of the Mo—C σ-bond from the alkyl side chain to the Mo atom. To accommodate the 'chelation', the bending angle is increased to 149°, the angle between the plane containing Mo(1), C(17) and C(27) and the plane defined by the Mo atom and the ring centroids is 77·3° compared with 91° in (I), and C(16) and C(26) of the side chain are pulled 23° away from the plane of the cyclopentadienyl rings. This last feature is common to many strained bent bis(η^5-cyclopentadienyl)–metal complexes such as niobocene (Guggenberger, 1973) and di-μ-(σ:η-cyclopentadienyl)-bis(η-cyclopentadienyl)dimolybdenum(*Mo—Mo*) (Meunier & Prout, 1979).

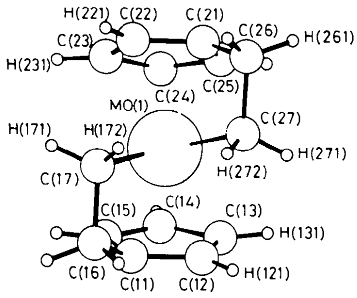

Fig. 2. A perspective view of the molecule $\overline{Mo(\eta^5\text{-}C_5H_4CH_2CH_2)_2}$.

The distances between the Mo atom and the C atoms of the cyclopentadienyl rings range from 2·250 (3) to 2·314 (3) Å, while the C—C distances range from 1·409 (4) to 1·424 (5) Å, mean 1·42 Å.

The angle C(17)—Mo—C(27) of 82·1 (2)° is in agreement with the existence of two non-bonding electrons. The Mo—C(17) and Mo—C(27) distances are 2·273 (3) and 2·268 (3) Å, similar to those found in other molybdenum compounds, *e.g.* $(\eta\text{-}C_5H_5)_2Mo(C_2H_5)Cl$, 2·28 Å (Prout *et al.*, 1974). The difference between the distances Mo—C and Mo—I, 0·57 Å, is the same as the difference in the carbon and iodine covalent radii.

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The Importance of Weak Reflections in Resolving the Centrosymmetric–Noncentrosymmetric Ambiguity: A Cautionary Tale

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Abstract

The weak diffraction intensities are crucially important in determining whether a crystal structure has a real or only an approximate center of symmetry; if these intensities are deleted from the data set, an intelligent conclusion may be impossible. In addition, statistical distribution tests, if based only on the stronger intensities, may be strongly biased toward a noncentrosymmetric indication. In one recently published structure determination [Cotton & Fanwick (1980), *Acta Cryst.* B**36**, 457–459] a distribution test led to the assignment of the noncentrosymmetric space group *Cc* to a structure which can be better described and refined in the centrosymmetric space group *C*2/*c*.

In many, perhaps most, X-ray diffraction laboratories it seems to have become customary to ignore low-intensity reflections, either by dropping them from the data set if they fall below some arbitrary signal-to-noise threshold or by programming the diffractometer to skip them if the counting rate is low. The rationale for this procedure is that the weak reflections, besides being of little importance in Patterson maps and most direct phasing techniques, contribute less than their fair share to the least-squares process since, if there is appreciable background, they must be assigned relatively low weights. A side benefit of ignoring the weak reflections is the cosmetic effect (Hirshfeld & Rabinovich, 1973) of a lower *R* index, which may make the final product more acceptable to some journals.

Hirshfeld & Rabinovich (1973) have pointed out that rejecting, or in any other way biasing, the low-intensity observations introduces systematic errors into the structural parameters, particularly the *B*'s and the scale factor. However, the effect appears to be small, and they remark that 'our limited experience indicates that in real situations the effect of biased data on the structurally interesting parameters is rarely large enough to matter.' I wish to point out that there is one aspect of diffraction crystallography – the determination of the presence or absence of a center of symmetry – where the weak reflections are crucially important, and neglecting them may well lead to an incorrect space-group assignment and severely distorted molecular geometry. I shall cite one example from the recent literature where such an event has almost surely taken place.

There are two areas of a typical crystal-structure analysis where the weak reflections show themselves as vitally important in resolving the centrosymmetric–noncentrosymmetric ambiguity. The more obvious area is during the final least-squares refinement cycles, where it has become popular to carry out a 'significance test' (Hamilton, 1965) on the statistical validity of removing the center and, thereby, increasing the number of structural parameters. Without going into the many pitfalls of such a test as it is usually performed, I wish to emphasize, as has been done in the past (Schomaker & Marsh, 1979), that it is only the weak reflections that can have any importance in distinguishing between a true and an approximate center; tests made on the stronger reflections alone are

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