The Crystal and Molecular Structures of Bent Bis-π-cyclopentadienyl–Metal Complexes:
(a) Bis-π-cyclopentadienyldibromorhenium(V) Tetrafluoroborate,
(b) Bis-π-cyclopentadienyldichloromolybdenum(IV),
(c) Bis-π-cyclopentadienylhydroxomethylaminomolybdenum(IV) Hexafluorophosphate,
(d) Bis-π-cyclopentadienylethylchloromolybdenum(IV),
(e) Bis-π-cyclopentadienyldichloroniobium(IV),
(f) Bis-π-cyclopentadienyldichloromolybdenum(V) Tetrafluoroborate,
(g) μ-Oxo-bis[bis-π-cyclopentadienylchloroniobium(V)] Tetrafluoroborate,
(h) Bis-π-cyclopentadienyldichlorozirconium

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The molecular structure and chemical bonding in bent bis-π-cyclopentadienyl–metal complexes is discussed with reference to known structures and to the crystal and molecular structures of the title compounds which were determined by X-ray diffraction techniques from diffractometer intensity measurements. (a) [(π-C$_5$H$_5$)$_2$ReBr$_2$]BF$_4$, orthorhombic, $a=9\cdot50$, $b=9\cdot38$, $c=7\cdot03$ Å, space group *Pmmn*, 690 reflexions, $R=0\cdot068$; (b) (π-C$_5$H$_5$)$_2$MoCl$_2$, monoclinic, $a=13\cdot29$, $b=12\cdot09$, $c=12\cdot99$ Å, $\gamma=106\cdot9°$, space group *P2$_1$/b*, 2101 reflexions, $R=0\cdot068$; (c) [(π-C$_5$H$_5$)$_2$Mo(OH)NH$_2$CH$_3$]PF$_6$, monoclinic, $a=9\cdot98$, $b=13\cdot07$, $c=10\cdot88$ Å, $\gamma=100\cdot4°$, space group *P2$_1$/n*, 2138 reflexions, $R=0\cdot049$; (d) (π-C$_5$H$_5$)$_2$Mo(C$_2$H$_5$)Cl, monoclinic, $a=8\cdot66$, $b=13\cdot87$, $c=10\cdot94$ Å, $\gamma=120\cdot1°$, space group *P2$_1$/b*, 1560 reflexions, $R=0\cdot050$; (e) (π-C$_5$H$_5$)$_2$NbCl$_2$, monoclinic, $a=13\cdot74$, $b=12\cdot21$, $c=13\cdot16$ Å, $\gamma=107\cdot7°$, space group *P2$_1$/b*, 2832 reflexions, $R=0\cdot068$; (f) [(π-C$_5$H$_5$)$_2$MoCl$_2$]BF$_4$, orthorhombic, $a=9\cdot55$, $b=9\cdot34$, $c=6\cdot79$ Å, space group *Pmmn*, 639 reflexions, $R=0\cdot026$; (g) {[(π-C$_5$H$_5$)$_2$NbCl]$_2$O}(BF$_4$)$_2$, orthorhombic, $a=11\cdot15$, $b=8\cdot12$, $c=12\cdot93$ Å, space group *Pnn2*, 1293 reflexions, $R=0\cdot030$; (h) (π-C$_5$H$_5$)$_2$ZrCl$_2$, triclinic, $a=14\cdot06$, $b=8\cdot09$, $c=13\cdot15$ Å, $\alpha=113\cdot7$, $\beta=117\cdot9$, $\gamma=99\cdot5°$, space group *P$\bar{1}$*, 3478 reflexions, $R=0\cdot095$.

There are two apparently conflicting descriptions of the electronic structure and bonding in bent (twisted) bis-π-cyclopentadienyl–metal complexes, particularly with reference to the role of the non-bonding d electrons. The earlier model of Ballhausen & Dahl (1961) was conditioned by the need to explain the acid-base properties of the bis-π-cyclopentadienyl metal hydrides. A hybridization scheme was postulated with nine mutually orthogonal hybrid orbitals in three sets of three. Two of these sets interact with the bis-π-cyclopentadienyl ligands and the third is in a plane at right-angles to that containing the normals to the cyclopentadienyl rings at the metal atom [Fig. 1(*a*)]. It is this third set that is said to be available for bonding to further ligands. If a group of complexes, say (π-C$_5$H$_5$)MX$_2$ (M = Zr, Nb, Mo), is considered, then the orbitals $\psi_{A'}$ and $\psi_{C'}$ [Fig. 1(*a*)] presumably engage in bonding to the ligands X and the 0, 1 or 2 non-bonding electrons are accommodated in $\psi_{B'}$ which lies between the ligands. The occupancy or use of the Ballhausen $\psi_{B'}$ is

consistent with a variety of properties of this class of compound, including the formation of (π-C$_5$H$_5$)$_2$TaH$_3$ and (π-C$_5$H$_5$)$_2$MoH$_3^+$, and the occurrence of metal–metal bonds in, for example, (π-C$_5$H$_5$)$_2$Ti(μ-SCH$_3$)$_2$Mo(CO)$_4$ (Davies & Kilbourn, 1971).

A later model proposed by Alcock (1967) and conditioned by the observation of a 75° CH$_3$–Re–CH$_3$ angle in (π-C$_5$H$_5$) (C$_5$H$_5$–CH$_3$)Re(CH$_3$)$_2$, which was believed to be inconsistent with the occupancy of the Ballhausen $\psi_{B'}$, did not amend the proposals for bonding to the π-cyclopentadienyl ligands but formed, with only those orbitals that made up Ballhausen & Dahl's $\psi_{A'}$, $\psi_{B'}$ and $\psi_{C'}$, a new orbital $\psi_{C''}$ with equal lobes in the $+y$ and $-y$ directions. The remaining orbitals formed two hybrids $\psi_{B''}$ and $\psi_{A''}$ orthogonal to each other and to $\psi_{C''}$, directed between x and $-y$ and x and y [Fig. 1(*b*)]. This model places the non-bonding electrons outside ligands X in (π-C$_5$H$_5$)$_2$MX$_2$ complexes as required by the observed small angles between the methyl ligands and the formation of chelate complexes such as those formed with amino acids, but does not satisfy the needs of the hydride chemistry.

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Recently there has been an attempt based on crystallographic and spectroscopic evidence (Green, Green & Prout, 1972) to combine these two approaches to give a unified model. Here we present the crystallographic evidence in support of this unified model based on studies of the structures of complex molecules or ions of the form $(\pi\text{-}C_5H_5)_2MX_2$ where M = Zr, Nb, Mo, Re, and X is a monodentate ligand. The crystal structures of eight new compounds are reported.

Experimental

Preparation

Crystalline samples of all compounds were supplied by Dr M. L. H. Green and were prepared by the methods described in the following references:
$(\pi\text{-}C_5H_5)_2ReBr_2BF_4$ and $(\pi\text{-}C_5H_5)_2MoCl_2BF_4$: Cooper & Green (1967) (as the hexafluorophosphates), $(\pi\text{-}C_5H_5)_2MoCl_2$: Cooper & Green (1967), $(\pi\text{-}C_5H_5)_2Mo(OH)NH_2CH_3PF_6$: Benfield & Green (1974a), $(\pi\text{-}C_5H_5)_2Mo(C_2H_5)Cl$: Benfield & Green (1974b), $(\pi\text{-}C_5H_5)_2NbCl_2$ and $[(\pi\text{-}C_5H_5)_2NbCl]_2O(BF_4)_2$: Douglas & Green (1972). $(\pi\text{-}C_5H_5)_2ZrCl_2$ was obtained commercially from Alfa Products.

X-ray diffraction measurements

For each compound a survey of the X-ray diffraction pattern was made by oscillation, Weissenberg and precession techniques. For all compounds except $(\pi\text{-}C_5H_5)_2ZrCl_2$ the cell parameters were refined and X-ray intensities measured on a Hilger and Watts linear diffractometer which had been modified so that in the automatic mode the moving-crystal stationary-counter method was used for both peak and background. All measurements were made with Mo $K\alpha$ radiation and balanced filters. Reflexions with $I < 3\sigma$ were assumed to be 'unobserved' and those with very unequal backgrounds were not included in the structure analysis. The X-ray intensities were corrected for Lorentz and polarization effects but not for absorption or extinction.

A Hilger & Watts four-circle automatic diffractometer was used for $(\pi\text{-}C_5H_5)_2ZrCl_2$. The cell dimensions
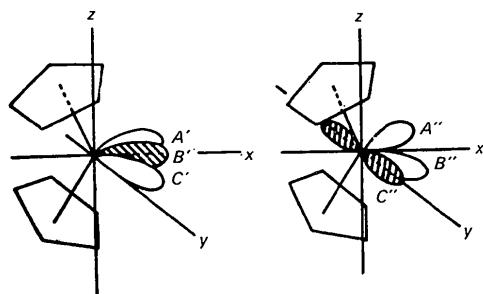
were refined by a least-squares best fit to 30 reflexions, and X-ray intensities were observed by the balanced filter technique with ordinate analysis. The intensities were corrected for Lorentz and polarization effects, and for absorption by the empirical method of North, Phillips & Mathews (1968).

Structure determination

All the structures were determined by the heavy-atom method using the unsharpened Patterson function to locate the metal atoms.

Refinement was by the least-squares method with either the full normal matrix or a large block approximation when computer limitations made this necessary. When a large block approximation was used the division was into blocks of derivatives of space parameters of chemically identifiable units and similar blocks of derivatives of temperature parameters. All refinements began with unit weights which were replaced by analytical weighting schemes designed to stabilize $\sum w\Delta^2$ with respect to ranges in F_o. The criteria for a satisfactorily completed analysis were (i) the ratio of the parameter shifts to standard deviations all less than 0·5, (ii) no significant features in the final difference map, (iii) no anomalous values of F_c for unobserved or invalid reflexions.

Calculations

Rollett & Ford's Algol system (Ford, 1969) for the English Electric KDF9 computer was used for all calculations except those for (c) and (d). Of these two analyses the latter used a system devised by Sheldrick (1972) and the former the X-RAY 70 system of Stewart, Kundell & Baldwin (1970) both suitably adapted for an ICL 1906A computer. Calculations with Rollett & Ford's program and X-RAY 70 used atomic scattering factors from *International Tables for X-ray Crystallography* (1962), and Sheldrick's program those of Cromer & Waber (1965). All calculations included a correction for the real part of the anomalous dispersion.

Crystal data, results and description of crystal structures

For each complex, copies of the observed structure amplitudes and structure factors calculated from the final atomic parameters are available.*

(a) *Bis-π-cyclopentadienyldibromorhenium*(V) *tetrafluoroborate* (B.D.)†

$[(\pi\text{-}C_5H_5)_2ReBr_2]BF_4$, $C_{10}H_{10}BBr_2F_4Re$, $M = 563\cdot0$, orthorhombic, $a = 9\cdot50$ (1), $b = 9\cdot38$ (1), $c = 7\cdot03$ (1) Å,

Fig. 1. Bent bis-π-cyclopentadienyl–metal systems: metal hybrid orbitals available for bonding to monodentate ligands according to (a) Ballhausen & Dahl (1961) and (b) Alcock (1967).

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* These tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30477 (104 pp., 2 microfiches). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† The initials following the compound name indicate the author largely associated with the practical work.

$U = 626$ Å^3, systematic extinctions, $hk0$: $h + k = 2n + 1$, space group $Pmmn$ (D_{2h}^{13}, No. 59, second setting) from the structure analysis, $D_m = 2\cdot98$ g cm^{-3} (by flotation), $D_c = 2\cdot98$ g cm^{-3} (for $Z = 2$), $F(000) = 532$, Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å), $\mu = 169$ cm^{-1}, linear diffractometer data, layers $hk0$ to $hk6$, 690 independent reflexions significantly above background. Although these crystals are isomorphous with (π-C$_5$H$_5$)$_2$MoCl$_2$BF$_4$ the two structure determinations were carried out independently from the respective Patterson functions. The rhenium bromide was refined by full-matrix least-squares, first with isotropic, then with anisotropic temperature factors, to a final R of 0·054 with the weighting scheme $w = \{1 + [(|F_o| - 36)/18]^2\}^{-1}$.

The final atomic parameters are given in Table 1 and the bond distances and angles in Table 2. The crystals are isostructural with those of bis-π-cyclopentadienyl-dichloromolybdenum(V) tetrafluoroborate and the molecular dimensions similar except for details discussed below.

(b) Bis-π-cyclopentadienyldichloromolybdenum(IV) (G.V.R.)

(π-C$_5$H$_5$)$_2$MoCl$_2$, C$_{10}$H$_{10}$Cl$_2$Mo, $M = 297\cdot0$, monoclinic, $a = 13\cdot29$ (2), $b = 12\cdot09$ (2), $c = 12\cdot99$ (2) Å, $\gamma = 106\cdot9$ (1)°, $U = 1996$ Å^3, systematic extinctions, $hk0$: $k = 2n + 1$, $00l$: $l = 2n + 1$, space group $P2_1/b$ (C_{2h}^5, No. 14, 1st setting), $D_m = 1\cdot96$ g cm^{-3} (by flotation), $D_c = 1\cdot97$ g cm^{-3} (for $Z = 8$), $F(000) = 1168$, Mo $K\alpha$ ($\lambda = 0\cdot7107$ Å) radiation, $\mu = 17$ cm^{-1}, crystal size $0\cdot2 \times 0\cdot1 \times 0\cdot6$ mm, linear diffractometer data, layers $hk0$ to $hk15$, 2101 independent reflexions significantly above background.

A complete trial structure was obtained from a Fourier synthesis phased on the molybdenum atom positions deduced from an unsharpened Patterson function. The trial structure was refined by 'large block matrix' least-squares first with isotropic then with anisotropic temperature factors. The matrix was divided into five blocks, one for the derivatives of the scale factor and dummy overall temperature factor, one for those of the space parameters and one each for those of the temperature parameters of the heavy atoms and of the two pairs of π-cyclopentadienyl rings. The refinement terminated at an R of 0·068 with the weighting scheme $w = (65/|F_o|)^2$ if $|F_o| > 65$, otherwise $w = 1$.

Table 2. Bis-π-cyclopentadienyldibromorhenium(V) tetrafluoroborate: bond lengths (Å) and angles (°)

Re–Br	2·565 (5)	Re–C(2)	2·259 (10)
Re–C(1)	2·207 (13)	Re–C(3)	2·283 (11)
Br–Re–Br'	82·05 (12)		
C(1)–C(2)	1·42 (3)	C(1)–C(2)–C(3)	108 (2)
C(2)–C(3)	1·34 (3)	C(2)–C(3)–C(3')	110 (2)
C(3)–C(3')	1·43 (3)	C(2)–C(1)–C(2')	107 (2)
B–F(1)	1·36 (3)	F(1)–B–F(2)	109·5 (1·5)
B–F(2)	1·37 (4)	F(1)–B–F(1')	109·8 (1·5)

The final atomic parameters are listed in Table 3 and the bond distances and angles in Table 4. The crystal structure (Fig. 2) is built up from discrete molecules. Each asymmetric unit contains two such independent molecules at general positions in the cell each of virtually identical dimensions but differing in conformation. One at Mo(1) is eclipsed and the other at Mo(2) is staggered. In the crystal the independent molecules form discrete layers parallel to the bc plane, those at Mo(1) in the layer at height a and at Mo(2) in the layer at height $a/2$ (Fig. 2). The general stereo-
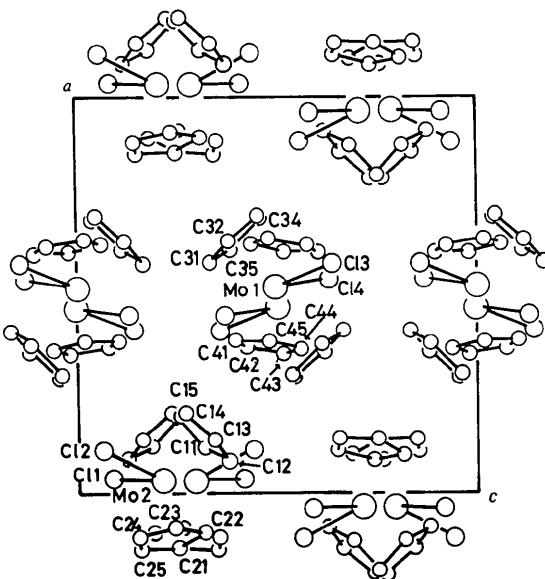
Fig. 2. The structure of bis-π-cyclopentadienyldichloromolybdenum(IV) in projection down b.

Table 1. Bis-π-cyclopentadienyldibromorhenium(V) tetrafluoroborate: fractional atomic coordinates and temperature factors

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Re	0·25	0·25	0·1951 (1)	0·009 (1)	0·023 (1)	0·017 (1)	0	0	0
Br	0·25	0·4292 (2)	−0·0802 (3)	0·034 (1)	0·045 (1)	0·035 (1)	0·033 (1)	0	0
C(1)	0·4970 (17)	0·25	0·1427 (38)	0·002 (6)	0·116 (18)	0·044 (13)	0	0·003 (11)	0
C(2)	0·4500 (19)	0·3723 (17)	0·2567 (33)	0·031 (7)	0·048 (7)	0·093 (15)	0·024 (13)	0·051 (14)	−0·043 (11)
C(3)	0·4028 (20)	0·3262 (20)	0·4245 (33)	0·028 (7)	0·090 (10)	0·039 (13)	−0·053 (17)	−0·017 (13)	0·016 (12)
B	0·25	0·75	0·3918 (46)	0·034 (12)	0·034 (11)	0·023 (15)	0	0	0
F(1)	0·25	0·6312 (15)	0·4979 (36)	0·069 (10)	0·042 (6)	0·109 (16)	0·045 (15)	0	0
F(2)	0·3665 (17)	0·75	0·2740 (29)	0·031 (7)	0·132 (13)	0·054 (11)	0	0·025 (12)	0

chemical features of the molecule are typical of a $(\pi\text{-}C_5H_5)_2MX_2$ system and are discussed in relation to the other complexes in a subsequent section.

(c) Bis-π-cyclopentadienylhydroxomethylaminomolybdenum(IV) hexafluorophosphate (S.R.C.)

$[(\pi\text{-}C_5H_5)_2Mo(OH)NH_2CH_3]PF_6$, $C_{11}H_{16}F_6MoNOP$, $M = 419\cdot2$, monoclinic, $a = 9\cdot98$ (1), $b = 13\cdot07$ (1), $c = 10\cdot88$ (1) Å, $\gamma = 100\cdot4$ (1)°, $U = 1398$ Å³, systematic extinctions, $hk0$: $h+k = 2n+1$, $00l$: $l = 2n+1$, space group $P2_1/n$ [C_{2h}^5, No. 14, non-standard setting, general positions $\pm(x,y,z; \frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}+z)$], $D_c = 1\cdot99$ (for $Z = 4$), $F(000) = 872$, Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å), $\mu = 8$ cm⁻¹, crystal size $0\cdot25 \times 0\cdot25 \times 0\cdot1$ mm, linear diffractometer data, layers $hk0$–$hk11$,2138 reflexions significantly above background. The position of the molybdenum atom was deduced from an unsharpened Patterson synthesis, and the remaining non-hydrogen atoms located from F_o and difference syntheses. The trial structure was refined by full-matrix least-squares methods, first with isotropic then with anisotropic temperature factors for all atoms. The normal matrix was divided into five blocks, one for the derivatives of the scale and dummy overall isotropic temperature parameters and one each for those of the parameters of the π-cyclopentadienyl rings, the molybdenum atom plus remaining ligand atoms and the anion. After two cycles with unit weights, each reflexion was assigned a weight calculated from the expression $w = \{1 + [(|F_o| - 36)/55]^2\}^{-1}$ (F on an absolute scale), and then two further cycles led to a final R of $0\cdot049$.

The final atomic parameters are given in Table 5 and bond distances and angles in Table 6. The structure consists of discrete $(\pi\text{-}C_5H_5)_2Mo(OH)NH_2CH_3^+$

cations and PF_6^- anions at general positions in the cell (Fig. 3), but to a good approximation the cation has C_{2v} symmetry and the anion O_h. The planar π-cyclo-

Table 4. *Bis-π-cyclopentadienyldichloromolybdenum*(IV):
bond lengths (Å) and angles (°)

Mo(1)–Cl(3)	2·464 (6)	Cl(3)–Mo(1)–Cl(4)	82·0 (0·2)
Mo(1)–Cl(4)	2·470 (5)		
Mo(1)–C(31)	2·27 (3)	Mo(1)–C(41)	2·30 (3)
Mo(1)–C(32)	2·32 (3)	Mo(1)–C(42)	2·29 (3)
Mo(1)–C(33)	2·38 (3)	Mo(1)–C(43)	2·30 (3)
Mo(1)–C(34)	2·32 (3)	Mo(1)–C(44)	2·25 (3)
Mo(1)–C(35)	2·27 (3)	Mo(1)–C(45)	2·27 (3)
C(31)–C(32)	1·43 (3)	C(41)–C(42)	1·44 (6)
C(32)–C(33)	1·36 (4)	C(42)–C(43)	1·24 (6)
C(33)–C(34)	1·25 (5)	C(43)–C(44)	1·35 (6)
C(34)–C(35)	1·47 (4)	C(44)–C(45)	1·40 (5)
C(35)–C(31)	1·40 (5)	C(45)–C(41)	1·30 (5)
C(35)–C(31)–C(32)	107 (2)	C(45)–C(41)–C(42)	107 (3)
C(31)–C(32)–C(33)	107 (2)	C(41)–C(42) C(43)	108 (4)
C(32)–C(33)–C(34)	112 (3)	C(42)–C(43)–C(44)	111 (4)
C(33)–C(34)–C(35)	110 (3)	C(43)–C(44)–C(45)	107 (3)
C(34)–C(35)–C(31)	104 (2)	C(44)–C(45)–C(41)	107 (3)
Mo(2)–Cl(1)	2·473 (5)	Cl(1)–Mo(2)–Cl(2)	82·0 (0·2)
Mo(2)–Cl(2)	2·477 (5)		
Mo(2)–C(11)	2·26 (2)	Mo(2)–C(21)	2·28 (3)
Mo(2)–C(12)	2·32 (3)	Mo(2)–C(22)	2·27 (3)
Mo(2)–C(13)	2·30 (3)	Mo(2)–C(23)	2·30 (3)
Mo(2)–C(14)	2·34 (3)	Mo(2)–C(24)	2·37 (3)
Mo(2)–C(15)	2·27 (3)	Mo(2)–C(25)	2·34 (3)
C(11)–C(12)	1·41 (4)	C(21)–C(22)	1·52 (6)
C(12)–C(13)	1·41 (4)	C(22)–C(23)	1·41 (5)
C(13)–C(14)	1·35 (4)	C(23)–C(24)	1·30 (5)
C(14)–C(15)	1·34 (4)	C(24)–C(25)	1·39 (5)
C(15)–C(11)	1·41 (4)	C(25)–C(21)	1·33 (5)
C(15)–C(11)–C(12)	105 (2)	C(25)–C(21)–C(22)	105 (3)
C(11)–C(12)–C(13)	107 (2)	C(21)–C(22)–C(23)	102 (3)
C(12)–C(13)–C(14)	109 (3)	C(22)–C(23)–C(24)	113 (3)
C(13)–C(14)–C(15)	109 (3)	C(23)–C(24)–C(25)	107 (3)
C(14)–C(15)–C(11)	110 (3)	C(24)–C(25)–C(21)	112 (3)

Table 3. *Bis-π-cyclopentadienyldichloromolybdenum*(IV): *fractional atomic coordinates and temperature factors*

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Mo(2)	0·0336 (1)	0·2820 (1)	0·2091 (1)	0·018 (1)	0·032 (1)	0·026 (1)	−0·006 (1)	−0·001 (1)	0·015 (1)
Cl(1)	0·0369 (3)	0·1267 (4)	0·0864 (4)	0·045 (2)	0·034 (2)	0·031 (2)	−0·012 (3)	−0·005 (4)	0·034 (3)
Cl(2)	0·1109 (3)	0·4058 (4)	0·0604 (4)	0·038 (2)	0·044 (3)	0·043 (3)	0·014 (4)	0·006 (4)	0·028 (4)
C(11)	0·1183 (18)	0·1909 (18)	0·3152 (18)	0·062 (14)	0·056 (12)	0·047 (13)	0·002 (19)	−0·072 (22)	0·030 (21)
C(12)	0·0852 (16)	0·2691 (26)	0·3780 (20)	0·041 (11)	0·122 (22)	0·061 (16)	−0·019 (31)	−0·051 (21)	0·062 (25)
C(13)	0·1368 (19)	0·3812 (23)	0·3412 (21)	0·064 (14)	0·091 (18)	0·073 (19)	−0·108 (31)	−0·096 (27)	0·101 (27)
C(14)	0·2044 (18)	0·3730 (22)	0·2663 (25)	0·052 (13)	0·067 (15)	0·106 (24)	0·080 (31)	−0·096 (28)	−0·065 (23)
C(15)	0·1936 (15)	0·2610 (24)	0·2479 (17)	0·030 (9)	0·127 (21)	0·042 (12)	−0·050 (26)	−0·049 (16)	0·073 (24)
C(21)	−0·1376 (14)	0·1877 (23)	0·2477 (29)	0·004 (9)	0·098 (18)	0·164 (31)	0·095 (39)	0·050 (25)	0·029 (20)
C(22)	−0·0988 (17)	0·2958 (33)	0·3134 (20)	0·037 (11)	0·191 (33)	0·048 (15)	−0·006 (35)	0·030 (20)	0·111 (33)
C(23)	−0·0843 (18)	0·3846 (24)	0·2402 (28)	0·047 (13)	0·093 (19)	0·125 (28)	−0·029 (37)	−0·058 (31)	0·079 (27)
C(24)	−0·1080 (18)	0·3459 (28)	0·1470 (24)	0·037 (12)	0·136 (23)	0·094 (21)	0·134 (38)	0·025 (26)	0·101 (28)
C(25)	−0·1407 (17)	0·2262 (30)	0·1523 (28)	0·030 (12)	0·149 (27)	0·133 (27)	−0·168 (46)	−0·074 (29)	0·098 (30)
Mo(1)	0·5265 (1)	0·2579 (1)	0·4980 (1)	0·022 (1)	0·035 (1)	0·026 (1)	−0·002 (1)	−0·003 (1)	0·018 (1)
Cl(3)	0·5843 (4)	0·3961 (4)	0·6407 (4)	0·054 (3)	0·042 (3)	0·042 (3)	−0·018 (4)	−0·001 (4)	0·006 (4)
Cl(4)	0·5466 (4)	0·1196 (4)	0·6308 (4)	0·047 (2)	0·042 (3)	0·040 (3)	0·008 (4)	−0·014 (4)	0·037 (4)
C(31)	0·5862 (16)	0·2684 (17)	0·3334 (15)	0·062 (12)	0·054 (12)	0·027 (10)	0·025 (17)	−0·002 (17)	0·033 (19)
C(32)	0·6388 (16)	0·3766 (20)	0·3807 (20)	0·044 (11)	0·071 (15)	0·076 (17)	0·047 (26)	0·079 (23)	0·007 (21)
C(33)	0·7041 (16)	0·3542 (24)	0·4534 (19)	0·037 (11)	0·104 (18)	0·051 (14)	−0·039 (26)	0·045 (20)	−0·001 (22)
C(34)	0·6949 (14)	0·2486 (29)	0·4613 (23)	0·022 (9)	0·143 (24)	0·092 (20)	0·111 (38)	0·012 (22)	0·053 (24)
C(35)	0·6189 (15)	0·1829 (17)	0·3847 (18)	0·041 (11)	0·055 (11)	0·066 (15)	−0·037 (21)	0·099 (21)	0·025 (17)
C(41)	0·3896 (14)	0·2732 (32)	0·3960 (17)	0·016 (9)	0·208 (32)	0·036 (12)	0·034 (33)	−0·022 (15)	0·070 (28)
C(42)	0·3714 (16)	0·1539 (31)	0·4241 (35)	0·023 (11)	0·126 (24)	0·175 (38)	−0·184 (51)	−0·046 (34)	0·020 (27)
C(43)	0·3555 (18)	0·1452 (21)	0·5185 (33)	0·042 (12)	0·045 (13)	0·182 (35)	0·115 (37)	−0·043 (35)	−0·022 (20)
C(44)	0·3673 (14)	0·2500 (33)	0·5614 (17)	0·014 (8)	0·221 (33)	0·037 (12)	0·007 (32)	0·015 (15)	0·086 (27)
C(45)	0·3877 (16)	0·3299 (20)	0·4808 (20)	0·043 (11)	0·092 (15)	0·074 (17)	0·078 (27)	−0·004 (21)	0·099 (22)

Table 5. *Bis-π-cyclopentadienylhydroxomethylaminomolybdenum(IV) hexafluorophosphate:*
fractional atomic coordinates and temperature factors

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Mo	0·1730 (1)	−0·0978 (1)	0·1489 (1)	0·024 (1)	0·021 (1)	0·039 (1)	0·005 (1)	−0·006 (1)	0·000 (1)
O(1)	0·0174 (5)	−0·1250 (4)	0·0234 (6)	0·037 (3)	0·032 (2)	0·056 (4)	0·000 (4)	−0·032 (4)	0·000 (4)
N(1)	0·0367 (6)	0·0123 (4)	0·1855 (6)	0·039 (3)	0·031 (3)	0·043 (4)	0·004 (4)	−0·010 (4)	0·018 (4)
C(1)	0·0756 (10)	0·0988 (6)	0·2752 (9)	0·065 (5)	0·033 (4)	0·059 (6)	−0·016 (6)	−0·018 (8)	0·026 (6)
C(11)	0·2829 (8)	−0·0388 (7)	−0·0394 (9)	0·036 (4)	0·060 (5)	0·051 (6)	−0·018 (8)	−0·018 (6)	0·000 (6)
C(12)	0·2758 (8)	0·0433 (6)	0·0395 (10)	0·044 (4)	0·038 (4)	0·074 (7)	0·040 (3)	0·036 (8)	0·002 (6)
C(13)	0·3499 (8)	0·0324 (6)	0·1483 (10)	0·045 (4)	0·044 (4)	0·060 (6)	−0·020 (8)	0·010 (8)	−0·032 (6)
C(14)	0·3994 (7)	−0·0589 (7)	0·1354 (10)	0·028 (3)	0·061 (4)	0·061 (6)	0·028 (8)	0·008 (6)	−0·002 (6)
C(15)	0·3552 (8)	−0·1056 (7)	0·0206 (9)	0·041 (4)	0·052 (4)	0·053 (6)	0·000 (8)	0·020 (8)	−0·020 (6)
C(21)	0·2241 (10)	−0·1530 (6)	0·3467 (10)	0·072 (6)	0·047 (4)	0·049 (6)	0·042 (8)	−0·010 (10)	0·010 (8)
C(22)	0·2472 (9)	−0·2243 (6)	0·2586 (10)	0·046 (4)	0·046 (4)	0·078 (7)	0·054 (8)	0·000 (8)	0·026 (8)
C(23)	0·1236 (9)	−0·2671 (5)	0·1969 (9)	0·062 (5)	0·024 (4)	0·064 (6)	0·026 (6)	0·002 (8)	0·012 (6)
C(24)	0·0276 (8)	−0·2160 (6)	0·2552 (10)	0·036 (4)	0·041 (4)	0·074 (7)	0·060 (8)	0·016 (8)	−0·006 (6)
C(25)	0·0886 (10)	−0·1499 (6)	0·3455 (10)	0·080 (6)	0·042 (4)	0·050 (5)	0·042 (8)	0·026 (10)	0·044 (8)
P	0·1889 (2)	0·3977 (2)	0·0970 (2)	0·036 (1)	0·037 (1)	0·047 (1)	−0·010 (2)	0·004 (2)	0·008 (2)
F(1)	0·1290 (7)	0·4929 (4)	0·1401 (9)	0·097 (4)	0·043 (3)	0·138 (7)	−0·018 (8)	0·030 (10)	0·040 (6)
F(2)	0·0473 (5)	0·3261 (4)	0·1227 (7)	0·052 (3)	0·060 (3)	0·106 (6)	−0·014 (6)	0·046 (6)	−0·016 (4)
F(3)	0·2473 (6)	0·3001 (4)	0·0596 (8)	0·068 (4)	0·058 (3)	0·127 (6)	−0·044 (8)	0·036 (8)	0·044 (6)
F(4)	0·3300 (6)	0·4669 (5)	0·0720 (8)	0·055 (3)	0·079 (4)	0·110 (6)	0·004 (8)	0·008 (8)	−0·038 (6)
F(5)	0·2332 (7)	0·3807 (5)	0·2339 (7)	0·100 (5)	0·100 (5)	0·059 (5)	0·002 (6)	−0·030 (8)	0·026 (8)
F(6)	0·1477 (7)	0·4135 (6)	−0·0405 (7)	0·075 (4)	0·127 (5)	0·059 (4)	−0·026 (8)	0·028 (6)	0·004 (8)

Table 6. *Bis-π-cyclopentadienylhydroxomethylamino-*
molybdenum(IV) hexafluorophosphate:
bond lengths (Å) and angles (°)

Mo–N	2·188 (6)	N—C(1)	1·491 (10)
Mo–O	2·050 (5)	Mo–N–C(1)	120·7 (0·5)
N---Mo–O	72·2 (0·2)		
Mo–C(11)	2·39 (1)	Mo–C(21)	2·36 (1)
Mo–C(12)	2·28 (1)	Mo–C(22)	2·27 (1)
Mo–C(13)	2·22 (1)	Mo–C(23)	2·24 (1)
Mo–C(14)	2·23 (1)	Mo–C(24)	2·24 (1)
Mo–C(15)	2·31 (1)	Mo–C(25)	2·35 (1)
C(11)–C(12)	1·39 (2)	C(21)–C(22)	1·39 (2)
C(12)–C(13)	1·42 (2)	C(22)–C(23)	1·43 (2)
C(13)–C(14)	1·38 (2)	C(23)–C(24)	1·41 (2)
C(14)–C(15)	1·43 (2)	C(24)–C(25)	1·38 (2)
C(15)–C(11)	1·39 (2)	C(25)–C(26)	1·36 (2)
C(15)–C(11)–C(12)	107 (1)	C(25)–C(21)–C(22)	108 (1)
C(11)–C(12)–C(13)	110 (1)	C(21)–C(22)–C(23)	111 (1)
C(12)–C(13)–C(14)	106 (1)	C(22)–C(23)–C(24)	102 (1)
C(13)–C(14)–C(15)	109 (1)	C(23)–C(24)–C(25)	111 (1)
C(14)–C(15)–C(11)	107 (1)	C(24)–C(25)–C(26)	109 (1)
P–F(1)	1·55 (1)	P–F(4)	1·55 (1)
P–F(2)	1·57 (1)	P–F(5)	1·58 (1)
P–F(3)	1·55 (1)	P–F(6)	1·58 (1)
F(1)–P–F(2)	89·3 (0·3)	F(2)–P–F(6)	91·1 (0·4)
F(1)–P–F(3)	177·4 (0·5)	F(3)–P–F(4)	89·8 (0·3)
F(1)–P–F(4)	91·6 (0·4)	F(3)–P–F(5)	88·6 (0·4)
F(1)–P–F(5)	89·2 (0·5)	F(3)–P–F(6)	90·2 (0·4)
F(1)–P–F(6)	92·0 (0·5)	F(4)–P–F(5)	90·0 (0·4)
F(2)–P–F(3)	89·3 (0·3)	F(4)–P–F(6)	89·3 (0·4)
F(2)–P–F(4)	179·1 (0·4)	F(5)–P–F(6)	178·6 (0·4)
F(2)–P–F(5)	89·6 (0·4)		

pentadienyl ligands have a staggered conformation (Fig. 9). The Mo–O (2·05 Å) and Mo–N (2·19 Å) distances are comparable with the corresponding distances and angles in bis-π-cyclopentadienylmolybdenum amino acid complexes (Prout, Allison, Delbaere & Gore, 1972). The carbon atom of the N-methyl group lies only 0·2 Å out of the N–Mo–O plane; presumably much greater deviations than this would result in un-acceptedly close contacts between the hydrogen atoms of the methyl group and those of one of the rings.

There are no short intermolecular contacts corresponding to O–H···N, or N–H···O hydrogen bonds; however, the possibility of an intramolecular hydrogen bond at the short (2·50 Å) intramolecular O···N contact cannot be ruled out, although the possible hydrogen atom positions are geometrically unsatisfactory.

(d) Bis-π-cyclopentadienylethylchloromolybdenum(IV)
(R.A.F.)

$(\pi\text{-}C_5H_5)_2Mo(C_2H_5)Cl$, $C_{12}H_{15}ClMo$, $M = 290\cdot6$, monoclinic, $a = 8\cdot66(1)$, $b = 13\cdot87(1)$, $c = 10\cdot94(2)$ Å, $\gamma = 120\cdot1(2)°$, $U = 1137$ Å³, systematic extinctions, $hk0: k = 2n+1$, $00l: l = 2n+1$, space group $P2_1/b$ (C^5_{2h}, No. 14, 1st setting), $D_m = 1\cdot70$ g cm⁻³ (by flotation), $D_c = 1\cdot70$ g cm⁻³ (for $Z = 4$), $F(000) = 584$, Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å), $\mu = 13$ cm⁻¹, crystal size $0\cdot2 \times 0\cdot6 \times 0\cdot2$ mm, linear diffractometer data, layers $h0l$–$h14l$, 1560 reflexions significantly above background.

The position of the molybdenum atom was deduced from an unsharpened Patterson function and the re-
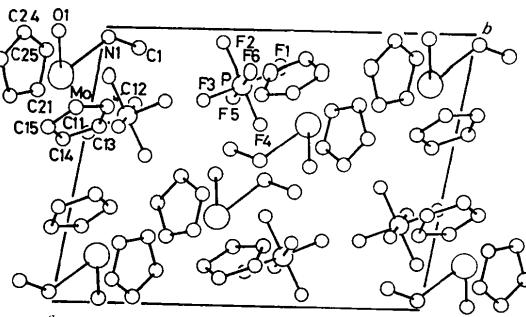

Fig. 3. The structure of bis-π-cyclopentadienylhydroxomethyl-aminomolybdenum(IV) hexafluorophosphate in projection down c.

maining non-hydrogen atoms from F_o and difference syntheses. The trial structure was refined by the full-matrix least-squares method first with isotropic, then with anisotropic temperature factors and the weighting scheme $w = (20 + |F_o|)^{-1}$. The final R was 0·050.

The final atomic parameters are given in Table 7 and bond distances and angles in Table 8. The crystal structure consists of discrete $(\pi\text{-}C_5H_5)_2Mo(Cl)C_2H_5$ units at general positions in the cell (Fig. 4) but the symmetry of the metal coordination sphere approximates to C_{2v}. The planar π-cyclopentadienyl rings have the staggered conformation. The molybdenum–chlorine bond (2·50 Å) is not greatly different in length from that found in the dichloride [2·47 Å (mean)] and the molybdenum–carbon σ-bond length (2·28 Å) is similar to those found in other molybdenum compounds, e.g. $(\pi\text{-}C_5H_5)_2Mo(NO)$ $(\pi\text{-}C_5H_5)$ 2·29 Å (Calderon, Cotton & Legzdins, 1969), $(\pi\text{-}C_5H_5)_2Mo(CO)_3C_2H_5$ 2·40 Å (Bennett & Mason, 1963), $(\pi\text{-}C_5H_5)Mo(CO)_3CH_2COOH$ 2·36 Å (Ariyaratne, Bierrum, Green, Ishaq, Prout & Swanwick, 1969). The difference in the Mo–C and Mo–Cl bond lengths is approximately the same as the difference in the carbon and chlorine covalent radii.
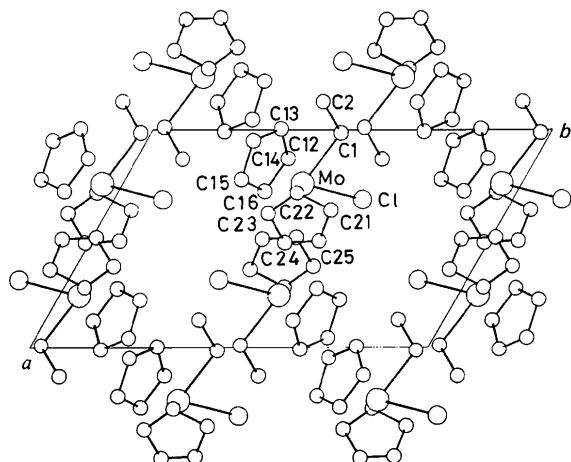

Fig. 4. The structure of bis-π-cyclopentadienylethylchloro-molybdenum(IV) in projection down c.

Table 8. *Bis-π-cyclopentadienylethylchloromolyb-denum*(IV): *bond lengths* (Å) *and angles* (°)

Mo–Cl	2·500 (5)	C(1)–C(2)	1·54 (2)
Mo–C(1)	2·284 (10)	C(2)–C(1)–Mo	117 (1)
Cl—Mo–C(1)	78·9 (0·4)		
Mo–C(11)	2·30 (1)	Mo–C(21)	2·29 (1)
Mo–C(12)	2·36 (1)	Mo–C(22)	2·30 (1)
Mo–C(13)	2·36 (1)	Mo–C(23)	2·29 (1)
Mo–C(14)	2·27 (1)	Mo–C(24)	2·30 (2)
Mo–C(15)	2·25 (1)	Mo–C(25)	2·28 (1)
C(11)–C(12)	1·42 (2)	C(21)–C(22)	1·40 (2)
C(12)–C(13)	1·38 (2)	C(22)–C(23)	1·38 (2)
C(13)–C(14)	1·37 (2)	C(23)–C(24)	1·37 (3)
C(14)–C(15)	1·45 (2)	C(24)–C(25)	1·20 (4)
C(15)–C(11)	1·42 (2)	C(25)–C(21)	1·40 (3)
C(15)–C(11)–C(12)	105 (1)	C(25)–C(21)–C(22)	105 (2)
C(11)–C(12)–C(13)	111 (1)	C(21)–C(22)–C(23)	105 (1)
C(12)–C(13)–C(14)	109 (1)	C(22)–C(23)–C(24)	108 (2)
C(13)–C(14)–C(15)	107 (1)	C(23)–C(24)–C(25)	110 (2)
C(14)–C(15)–C(11)	109 (1)	C(24)–C(25)–C(21)	112 (2)

(*e*) *Bis-π-cyclopentadienyldichloroniobium*(IV) (G.V.R.)

$(\pi\text{-}C_5H_5)_2NbCl_2$, $C_{10}H_{10}Cl_2Nb$, $M = 294\cdot0$, monoclinic, $a = 13\cdot74$ (2), $b = 12\cdot21$ (2), $c = 13\cdot16$ (2), $\gamma = 107\cdot7$ (1)°, $U = 2103$ Å³, systematic extinctions, $hk0$: $k = 2n + 1$, $00l$: $l = 2n + 1$, space group $P2_1/b$ (C_{2h}^5, No. 14, 1st setting), $D_m = 1\cdot84$ g cm⁻¹ (by flotation), $D_c = 1\cdot86$ g cm⁻¹ (for $Z = 8$), $F(000) = 1160$, Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å), $\mu = 16$ cm⁻¹, crystal size $0\cdot2 \times 0\cdot1 \times 0\cdot4$ mm, linear diffractometer data, layers $hk0$–$hk15$, 2832 reflexions significantly above background.

Although the crystals were isomorphous with the corresponding molybdenum compound, the structure was determined independently by the heavy-atom method from the Patterson function. The refinement used the 'large block matrix' least-squares method with the same blocking scheme as for the dichloride. The anisotropic refinement converged at an R of 0·068 with the weighing scheme $w = \{(1 + [(|F_o| - 65)/26]^2\}^{-1}$.

The final atomic parameters are given in Table 9 and the bond distances and angles in Table 10. The crystals are isostructural with those of the molybdenum dichloride and the molecular dimensions differ only in the fine detail discussed later.

Table 7. *Bis-π-cyclopentadienylethylchloromolybdenum*(IV): *fractional atomic coordinates and temperature factors*

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	0·24352 (8)	0·44985 (5)	0·20747 (5)	0·0515 (4)	0·0425 (4)	0·0415 (3)	−0·0006 (3)	−0·0089 (3)	0·0206 (3)
Cl	0·3154 (4)	0·6229 (2)	0·0919 (2)	0·092 (2)	0·057 (1)	0·082 (2)	0·017 (1)	−0·009 (1)	0·033 (1)
C(1)	0·0116 (13)	0·4744 (10)	0·2646 (10)	0·075 (6)	0·071 (7)	0·091 (7)	−0·007 (5)	−0·004 (5)	0·042 (5)
C(2)	−0·1319 (16)	0·3847 (13)	0·3475 (13)	0·086 (7)	0·116 (11)	0·109 (9)	−0·001 (8)	0·022 (7)	0·046 (7)
C(11)	0·2766 (15)	0·3652 (9)	0·0366 (9)	0·093 (7)	0·070 (7)	0·066 (6)	−0·025 (5)	0·004 (5)	0·028 (6)
C(12)	0·1276 (18)	0·3783 (11)	0·0124 (9)	0·123 (9)	0·089 (8)	0·056 (5)	−0·026 (5)	−0·038 (6)	0·047 (7)
C(13)	−0·0069 (15)	0·3188 (11)	0·0955 (11)	0·087 (7)	0·091 (9)	0·084 (7)	−0·041 (6)	−0·032 (6)	0·034 (6)
C(14)	0·0471 (14)	0·2661 (8)	0·1761 (10)	0·089 (7)	0·040 (5)	0·089 (7)	−0·012 (4)	−0·006 (6)	0·012 (5)
C(15)	0·2239 (15)	0·2912 (9)	0·1377 (11)	0·090 (7)	0·061 (6)	0·099 (8)	−0·019 (5)	−0·017 (6)	0·034 (5)
C(21)	0·3633 (25)	0·5591 (12)	0·3768 (13)	0·184 (14)	0·086 (9)	0·091 (8)	−0·051 (7)	−0·089 (9)	0·084 (9)
C(22)	0·2822 (15)	0·4484 (12)	0·4155 (8)	0·091 (7)	0·125 (11)	0·046 (5)	0·015 (5)	−0·021 (4)	0·048 (7)
C(23)	0·3784 (29)	0·4057 (14)	0·3598 (16)	0·184 (16)	0·114 (11)	0·117 (12)	−0·039 (9)	−0·103 (11)	0·105 (12)
C(24)	0·5117 (32)	0·4894 (40)	0·2931 (21)	0·114 (14)	0·425 (55)	0·092 (13)	−0·053 (23)	−0·035 (11)	0·166 (26)
C(25)	0·5042 (29)	0·5729 (24)	0·3021 (21)	0·092 (13)	0·208 (23)	0·102 (16)	0·078 (16)	−0·063 (12)	−0·065 (14)

Table 9. *Bis-π-cyclopentadienyldichloroniobium*(IV): *fractional atomic coordinates and temperature factors*

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Nb(1)	0·5274 (1)	0·2562 (1)	0·4997 (1)	0·0266 (4)	0·0423 (5)	0·0303 (5)	−0·0015 (8)	−0·0022 (8)	0·0195 (7)
Nb(2)	0·0360 (1)	0·2847 (1)	0·2030 (1)	0·0250 (4)	0·0386 (5)	0·0289 (4)	−0·0064 (8)	−0·0003 (8)	0·0245 (7)
Cl(1)	0·0366 (3)	0·1257 (3)	0·0875 (2)	0·051 (2)	0·037 (2)	0·037 (2)	−0·021 (2)	−0·007 (3)	0·035 (3)
Cl(2)	0·1092 (2)	0·4123 (3)	0·0579 (2)	0·045 (2)	0·043 (2)	0·044 (2)	−0·025 (3)	−0·006 (3)	0·025 (3)
Cl(3)	0·5750 (3)	0·3992 (3)	0·6375 (3)	0·078 (3)	0·044 (2)	0·042 (2)	−0·023 (3)	0·004 (3)	−0·0011 (3)
Cl(4)	0·5439 (3)	0·1156 (3)	0·6289 (3)	0·051 (2)	0·049 (2)	0·040 (2)	−0·017 (3)	0·004 (3)	0·044 (3)
C(11)	0·1306 (12)	0·1981 (13)	0·3118 (13)	0·065 (10)	0·053 (9)	0·074 (11)	0·030 (15)	−0·050 (17)	0·053 (15)
C(12)	0·0945 (12)	0·2660 (21)	0·3717 (11)	0·041 (8)	0·162 (19)	0·030 (8)	0·040 (19)	−0·009 (12)	0·050 (20)
C(13)	0·1339 (17)	0·3787 (20)	0·3430 (17)	0·101 (16)	0·102 (15)	0·091 (16)	−0·121 (26)	−0·123 (26)	0·122 (27)
C(14)	0·2048 (15)	0·3788 (22)	0·2674 (18)	0·067 (12)	0·127 (19)	0·100 (17)	0·101 (29)	−0·128 (22)	−0·087 (25)
C(15)	0·1981 (11)	0·2682 (18)	0·2478 (13)	0·028 (7)	0·124 (15)	0·055 (9)	−0·035 (19)	−0·020 (13)	0·064 (18)
C(21)	−0·1384 (12)	0·1890 (17)	0·2314 (30)	0·024 (8)	0·068 (12)	0·264 (35)	0·114 (32)	0·087 (29)	0·026 (16)
C(22)	−0·1075 (14)	0·2730 (38)	0·3011 (14)	0·043 (11)	0·343 (46)	0·041 (9)	0·068 (34)	0·064 (17)	0·219 (39)
C(23)	−0·0876 (16)	0·3661 (29)	0·2619 (36)	0·053 (12)	0·147 (28)	0·252 (42)	−0·313 (62)	−0·060 (42)	0·086 (31)
C(24)	−0·1053 (14)	0·3558 (25)	0·1652 (30)	0·043 (10)	0·128 (19)	0·241 (39)	0·224 (45)	0·115 (33)	0·131 (25)
C(25)	−0·1363 (12)	0·2423 (26)	0·1447 (15)	0·033 (8)	0·173 (24)	0·073 (12)	−0·084 (27)	−0·035 (15)	0·101 (25)
C(31)	0·5968 (10)	0·2796 (16)	0·3311 (10)	0·038 (7)	0·104 (14)	0·029 (7)	0·019 (14)	0·006 (10)	0·018 (15)
C(32)	0·6432 (16)	0·3787 (17)	0·3831 (19)	0·074 (13)	0·094 (14)	0·119 (19)	0·094 (26)	0·138 (27)	0·046 (22)
C(33)	0·7036 (13)	0·3527 (27)	0·4584 (17)	0·038 (9)	0·201 (27)	0·070 (13)	−0·090 (32)	0·033 (17)	−0·026 (24)
C(34)	0·6949 (14)	0·2398 (24)	0·4573 (15)	0·057 (11)	0·203 (24)	0·072 (12)	0·127 (29)	0·080 (19)	0·197 (30)
C(35)	0·6266 (14)	0·1878 (16)	0·3804 (15)	0·073 (11)	0·081 (12)	0·086 (14)	−0·024 (20)	0·119 (21)	0·018 (19)
C(41)	0·3905 (12)	0·2729 (24)	0·3974 (15)	0·032 (8)	0·193 (23)	0·060 (11)	0·063 (26)	0·005 (15)	0·097 (24)
C(42)	0·3743 (13)	0·1586 (27)	0·4106 (26)	0·043 (10)	0·167 (25)	0·205 (27)	−0·266 (46)	−0·112 (28)	0·135 (28)
C(43)	0·3556 (11)	0·1367 (22)	0·5113 (26)	0·022 (8)	0·129 (18)	0·184 (28)	0·198 (39)	−0·041 (25)	−0·017 (20)
C(44)	0·3596 (11)	0·2357 (28)	0·5580 (14)	0·024 (7)	0·226 (28)	0·059 (11)	−0·039 (28)	−0·008 (14)	0·078 (24)
C(45)	0·3782 (13)	0·3183 (17)	0·4844 (19)	0·052 (9)	0·084 (12)	0·127 (18)	−0·007 (25)	−0·009 (21)	0·086 (18)

Table 10. *Bis-π-cyclopentadienyldichloroniobium*(IV): *bond lengths* (Å) *and angles* (°)

Nb(1)–Cl(3)	2·464 (5)	Cl(3)–Nb(1)–Cl(4)	85·7 (0·2)
Nb(1)–Cl(4)	2·475 (4)		
Nb(1)–C(31)	2·40 (3)	Nb(1)–C(41)	2·37 (3)
Nb(1)–C(32)	2·38 (3)	Nb(1)–C(42)	2·39 (3)
Nb(1)–C(33)	2·41 (3)	Nb(1)–C(43)	2·37 (3)
Nb(1)–C(34)	2·44 (3)	Nb(1)–C(44)	2·37 (3)
Nb(1)–C(35)	2·39 (3)	Nb(1)–C(45)	2·40 (3)
C(31)–C(32)	1·37 (3)	C(41)–C(42)	1·36 (4)
C(32)–C(33)	1·39 (4)	C(42)–C(43)	1·36 (4)
C(33)–C(34)	1·35 (5)	C(43)–C(44)	1·34 (4)
C(34)–C(35)	1·40 (4)	C(44)–C(45)	1·37 (5)
C(35)–C(31)	1·46 (3)	C(45)–C(41)	1·31 (5)
C(35)–C(31)–C(32)	107 (2)	C(45)–C(41)–C(42)	109 (3)
C(31)–C(32)–C(33)	108 (2)	C(41)–C(42)–C(43)	107 (3)
C(32)–C(33)–C(34)	111(3)	C(42)–C(43)–C(44)	108 (2)
C(33)–C(34)–C(35)	108 (3)	C(43)–C(44)–C(45)	107 (3)
C(34)–C(35)–C(31)	106 (2)	C(44)–C(45)–C(41)	109 (3)
Nb(2)–Cl(1)	2·468 (4)	Cl(1)–Nb(2)–Cl(2)	85·5 (0·1)
Nb(2)–Cl(2)	2·476 (3)		
Nb(2)–C(11)	2·39 (2)	Nb(2)–C(21)	2·36 (3)
Nb(2)–C(12)	2·40 (3)	Nb(2)–C(22)	2·33 (4)
Nb(2)–C(13)	2·36 (2)	Nb(2)–C(23)	2·35 (4)
Nb(2)–C(14)	2·41 (3)	Nb(2)–C(24)	2·41 (3)
Nb(2)–C(15)	2·37 (2)	Nb(2)–C(25)	2·39 (3)
C(11)–C(12)	1·34 (3)	C(21)–C(22)	1·35 (6)
C(12)–C(13)	1·37 (4)	C(22)–C(23)	1·20 (7)
C(13)–C(14)	1·39 (4)	C(23)–C(24)	1·30 (6)
C(14)–C(15)	1·35 (4)	C(24)–C(25)	1·35 (5)
C(15)–C(11)	1·35 (3)	C(25)–C(21)	1·31 (5)
C(15)–C(11)–C(12)	107 (2)	C(25)–C(21)–C(22)	105 (4)
C(11)–C(12)–C(13)	111 (2)	C(21)–C(22)–C(23)	111 (4)
C(12)–C(13)–C(14)	105 (2)	C(22)–C(23)–C(24)	110 (5)
C(13)–C(14)–C(15)	108 (2)	C(23)–C(24)–C(25)	107 (4)
C(14)–C(15)–C(11)	110 (2)	C(24)–C(25)–C(21)	107 (3)

(*f*) *Bis-π-cyclopentadienyldichloromolybdenum*(V)
tetrafluoroborate (T.S.C. *and* B.D.)

[(π-C₅H₅)₂MoCl₂]BF₄, C₁₀H₁₀BCl₂F₄Mo, $M = 383·8$,
orthorhombic, $a = 9·55$ (1), $b = 9·34$ (1), $c = 6·79$ (1) Å,

$U = 606$ Å³, systematic extinctions, $hk0$: $h + k = 2n + 1$,
space group $Pmmn$ (D_{2h}^{13}, No. 59, 2nd setting; from the
structure analysis), $D_m = 2·06$ g cm⁻³ (by flotation), $D_c = 2·06$ g cm⁻³ (for $Z = 2$), $F(000) = 374$, Mo $K\alpha$ radiation
($\lambda = 0·7107$ Å), $\mu = 17$ cm⁻¹, linear diffractometer data,
layers $hk0$–$hk6$, 539 independent reflexions significantly above background.

The structure was determined from the Patterson
function. Each cation, sited at the intersection of a pair
of orthogonal mirror planes in the space group $Pmmn$,
has crystallographic mm symmetry (Fig. 5). The π-cy-
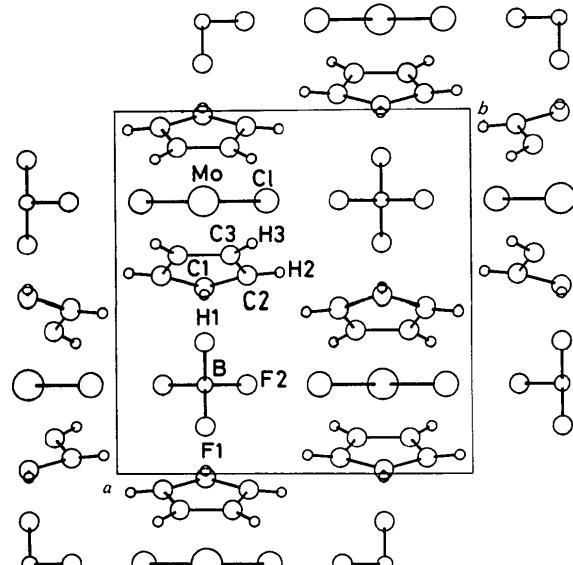
Fig. 5. The structure of bis-π-cyclopentadienyldichloromolybdenum(V) tetrafluoroborate in projection down c.

clopentadienyl ligands are therefore necessarily equivalent and in the eclipsed conformation. Each possesses a mirror plane at right angles to the ligand plane with the carbon atom in the mirror pointing towards the chlorine ligands [*i.e.* opposite to the arrangement in (π-C_5H_5)$_2$MoH$_2$ (Mason & Gerloch, 1965)]. The BF$_4^-$ ions also have *mm* crystallographic symmetry but do not differ significantly from $\overline{4}3m$.

The trial structure was refined by the full-matrix least-squares method first with isotropic, then with anisotropic temperature factors to $R = 0.031$. At this stage, peaks attributed to hydrogen atoms were clearly defined in the difference synthesis but were closer to the carbon sites than expected in X-ray work. The hydrogen atoms were placed at 0.95 Å (Cotton & Takats, 1970) from the carbon atoms (notwithstanding the known internuclear separation of 1.1 Å) and refined with Waser (1963) type constraints (Rollett, 1969). The hydrogen atoms were given an isotropic temperature factor of 0.06 Å^2 which was not refined. The final R was 0.026 for the weighting scheme $w = \{1 + [(|F_o| - 73/52]^2\}^{-1}$.

The final atomic parameters are given in Table 11 and the bond distances and angles in Table 12. The crystals are isostructural with those of the rhenium dibromide salt and the molecular dimensions differ only in the fine detail discussed later.

(*g*) *μ-Oxo-bis[bis-π-cyclopentadienylchloroniobium*(V)] *tetrafluoroborate* (B.D.)

$\{[(\pi$-$C_5H_5)_2NbCl]_2O\}(BF_4)_2$, $C_{20}H_{20}B_2Cl_2F_8Nb_2O$, $M = 706.7$, orthorhombic, $a = 11.55$ (1), $b = 8.12$ (1), $c = 12.93$ (1) Å, $U = 1364$ Å^3, systematic extinctions, 0*kl*: $k + l = 2n + 1$, *h*0*l*: $h + l = 2n + 1$, space group *Pnn*2 (C_{2v}^{10}, No. 34) from the structure analysis, $D_m = 1.835$ g cm^{-3} (by flotation), $D_c = 1.837$ g cm^{-3} (for $Z = 2$), $F(000) = 692$, Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), $\mu = 11$ cm^{-1}, linear diffractometer data, layers *hk*0–*hk*12, 1293 independent reflexions significantly above background.

The niobium atoms were located from an unsharpened Patterson function. The heavy-atom-phased F_o map, which had *Pnnm* symmetry, exhibited a number of large peaks, one of which could be interpreted as a chlorine atom if the space group were *Pnn*2. Proceed-

Table 12. *Bis-π-cyclopentadienyldichloromolybdenum*(V) *tetrafluoroborate*: *bond lengths* (Å) *and angles* (°)

Mo–Cl	2·382 (4)	Mo–C(1)	2·296 (9)
Cl—Mo–Cl'	87·9 (1)	Mo–C(2)	2·329 (6)
		Mo–C(3)	2·305 (6)
C(1)–C(2)	1·392 (11)		
C(2)–C(3)	1·364 (9)	C(1)–C(2)–C(3)	106·8 (6)
C(3)–C(3')	1·394 (9)	C(2)–C(3)–C(3')	108·6 (5)
		C(2)–C(1)–C(2')	109·0 (5)
B–F(1)	1·356 (12)		
B–F(2)	1·365 (12)	F(1)–B–F(2)	108·9 (8)
		F(1)–B–F(1')	111·0 (8)

ing on this assumption, the remaining atoms other than hydrogen were located from successive F_o syntheses. The trial model was refined by full-matrix least-squares methods with isotropic then anisotropic temperature factors. A difference synthesis calculated at $R = 0.032$ showed clearly defined peaks indicative of hydrogen atom positions but too close to the carbon atoms. Hydrogen atoms were introduced in calculated positions and refined with Waser (1963) type constraints (Rollett, 1969). The final R was 0.030 with the weighting scheme $w = \{1 + [(|F_o| - 80)/79]^2\}^{-1}$.

The final atomic parameters are given in Table 13 and bond distances and angles in Table 14. In the crystal (Fig. 6) the BF$_4^-$ anions lie on twofold axes at Wyckoff (*a*) and (*b*) (*International Tables for X-ray Crystallography*, 1962) and approximate to regular tetrahedra. The cations also have twofold symmetry with the bridging oxygen atom at Wyckoff (*a*) roughly halfway between the anions. The Nb–O–Nb bridge is significantly non-linear (169°), and the Nb–O bonds (1·876 Å) shorter than the expected single-bond value 2·10–2·15 Å but larger than the terminal double bond Nb=O ~ 1·70 Å. The length is comparable with the niobium–ethoxy-oxygen bond (1·87 Å) in (dipy)Nb(O)(OEt)Cl$_2$ (Prout & Kamenar, 1970). The relatively short bond must indicate a certain degree of π-bonding and it might be assumed that the lowest-energy vacant orbital of the apparently 16*e* complex must have the symmetry required for π-bonding. In this case the Cl–Nb–O–Nb–Cl system would be non-coplanar with a 90° angle between the two Cl–Nb–O

Table 11. *Bis-π-cyclopentadienyldichloromolybdenum*(V) *tetrafluoroborate*: *fractional coordinates and temperature factors*

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Mo	0·2500	0·2500	0·1830 (1)	0·015 (1)	0·023 (1)	0·019 (1)	0	0	0
Cl	0·2500	0·4272 (2)	−0·0696 (2)	0·045 (1)	0·050 (1)	0·038 (1)	0·041 (1)	0	0
C(1)	0·4890 (7)	0·2500	0·1468 (13)	0·017 (3)	0·123 (6)	0·035 (4)	0	0·012 (4)	0
C(2)	0·4565 (6)	0·3714 (5)	0·2565 (9)	0·034 (2)	0·053 (2)	0·072 (4)	0·027 (4)	−0·040 (5)	−0·040 (4)
C(3)	0·3994 (5)	0·3245 (6)	0·4293 (9)	0·024 (2)	0·081 (3)	0·049 (3)	−0·054 (5)	−0·033 (4)	0·013 (3)
B	0·2500	0·7500	0·3862 (15)	0·027 (4)	0·034 (4)	0·039 (5)	0	0	0
F(1)	0·2500	0·6310 (4)	0·5005 (10)	0·085 (4)	0·048 (2)	0·091 (4)	0·047 (4)	0	0
F(2)	0·3678 (4)	0·7500	0·2727 (8)	0·040 (3)	0·129 (4)	0·047 (3)	0	0·029 (4)	0
H(1)	0·509 (14)	0·2500	0·034 (26)	0·06*					
H(2)	0·449 (8)	0·037 (7)	0·194 (13)	0·06*					
H(3)	0·367 (9)	0·114 (7)	0·519 (15)	0·06*					

* Not refined.

Table 13. *μ-Oxo-bis[bis-π-cyclopentadienylchloroniobium(V)] tetrafluoroborate*:
fractional coordinates and temperature factors

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Nb	0·1591 (1)	0·0411 (1)	0	0·031 (1)	0·031 (1)	0·043 (1)	0	0	-0·001 (2)
Cl	0·1993 (2)	-0·1874 (4)	0·1083 (3)	0·068 (2)	0·060 (3)	0·076 (3)	0·043 (3)	-0·031 (6)	0·017 (9)
O	0	0	-0·0135 (8)	0·027 (7)	0·044 (8)	0·058 (13)	0	0	0
C(1)	0·1960 (7)	0·3329 (9)	0·0222 (7)	0·078 (9)	0·035 (12)	0·045 (11)	-0·008 (13)	0·008 (13)	-0·030 (12)
C(2)	0·0881 (9)	0·3020 (12)	0·0596 (11)	0·067 (8)	0·039 (7)	0·103 (5)	-0·063 (10)	0·004 (12)	0·005 (10)
C(3)	0·0967 (9)	0·2034 (13)	0·1458 (10)	0·076 (7)	0·058 (7)	0·077 (10)	-0·070 (18)	0·022 (13)	-0·015 (12)
C(4)	0·2166 (10)	0·1655 (16)	0·1660 (11)	0·071 (8)	0·075 (8)	0·087 (11)	-0·070 (15)	-0·044 (14)	-0·048 (14)
C(5)	0·2729 (8)	0·2459 (15)	0·0874 (12)	0·046 (6)	0·081 (9)	0·113 (13)	-0·053 (18)	-0·033 (14)	-0·038 (12)
C(6)	0·3229 (9)	-0·0578 (21)	-0·0921 (16)	0·057 (7)	0·124 (14)	0·106 (15)	-0·051 (21)	0·024 (14)	0·021 (16)
C(7)	0·2361 (12)	-0·1560 (16)	-0·1179 (14)	0·111 (10)	0·050 (8)	0·119 (16)	-0·044 (16)	0·083 (20)	0·039 (15)
C(8)	0·1594 (9)	-0·0700 (16)	-0·1718 (9)	0·062 (6)	0·106 (12)	0·045 (7)	-0·064 (13)	0·044 (11)	-0·038 (15)
C(9)	0·1952 (13)	0·0950 (18)	-0·1754 (12)	0·104 (10)	0·104 (12)	0·063 (11)	0·065 (16)	0·096 (16)	0·045 (2)
C(10)	0·3029 (11)	0·0930 (19)	-0·1275 (13)	0·064 (9)	0·099 (11)	0·107 (14)	-0·065 (20)	0·104 (17)	-0·110 (17)
B(1)	0·5000	0·5000	-0·0787 (15)	0·083 (8)	0·062 (13)	0·060 (13)	0	0	0
B(2)	0·5000	0	0·2686 (20)	0·087 (6)	0·041 (9)	0·112 (18)	0	0	0
F(1)	0·4899 (6)	0·6347 (17)	-0·0248 (15)	0·099 (30)	0·170 (33)	0·296 (17)	-0·236 (12)	-0·014 (7)	0·042 (8)
F(2)	0·5980 (9)	0·5149 (14)	-0·1346 (10)	0·127 (13)	0·144 (16)	0·164 (17)	-0·074 (12)	0·136 (8)	-0·094 (11)
F(3)	0·5027 (8)	0·1359 (20)	0·2200 (16)	0·129 (25)	0·185 (32)	0·282 (19)	0·314 (16)	0·047 (7)	-0·004 (10)
F(4)	0·5968 (9)	-0·0041 (16)	0·3243 (11)	0·119 (16)	0·168 (19)	0·182 (19)	-0·094 (14)	-0·157 (14)	0·066 (15)

Table 14. *μ-Oxo-bis[bis-π-cyclopentadienylchloronio-bium(V)] tetrafluoroborate*: *bond lengths (Å) and angles (°)*

Nb-O	1·88 (1)	Cl—Nb-O	96·2 (9)
Nb-Cl	2·370 (4)	Nb-O—Nb	169·3 (8)
Nb-C(1)	2·43 (1)	Nb-C(6)	2·38 (2)
Nb-C(2)	2·40 (1)	Nb-C(7)	2·38 (2)
Nb-C(3)	2·41 (1)	Nb-C(8)	2·40 (1)
Nb-C(4)	2·46 (2)	Nb-C(9)	2·35 (2)
Nb-C(5)	2·40 (2)	Nb-C(10)	2·38 (2)
C(1)-C(2)	1·36 (2)	C(6)—C(7)	1·33 (3)
C(2)-C(3)	1·39 (2)	C(7)—C(8)	1·30 (3)
C(3)-C(4)	1·43 (2)	C(8)—C(9)	1·40 (2)
C(4)-C(5)	1·39 (2)	C(9)—C(10)	1·41 (2)
C(5)-C(1)	1·41 (2)	C(10)—C(6)	1·30 (3)
C(1)-C(2)-C(3)	108 (1)	C(6)—C(7)—C(8)	110 (2)
C(2)-C(3)-C(4)	110 (1)	C(7)—C(8)—C(9)	109 (1)
C(3)-C(4)-C(5)	103 (1)	C(8)—C(9)—C(10)	103 (1)
C(4)-C(5)-C(1)	112 (1)	C(9)—C(10)-C(6)	109 (2)
C(5)-C(1)-C(2)	107 (1)	C(10)-C(6)—C(7)	109 (1)
B(1)-F(1)	1·30 (2)	B(2)-F(3)	1·27 (3)
B(1)-F(2)	1·36 (3)	B(2)-F(4)	1·34 (3)
F(1)-B(1)-F(2)	107 (2)	F(3)-B(2)-F(4)	106 (2)
F(1)-B(1)-F(1')	116 (2)	F(3)-B(2)-F(3')	111 (2)
F(2)-B(1)-F(2')	114 (2)	F(4)-B(2)-F(4')	114 (2)

planes, enabling one oxygen p-lone pair, say p_x, to form a π-bond to one niobium and the other, say p_y, to form a similar π-bond to the second niobium atom. The torsional angle Cl-Nb···Nb'-Cl' is 72·5°.

(*h*) *Bis-π-cyclopentadienyldichlorozirconium* (G.V.R.)

(π-C$_5$H$_5$)$_2$ZrCl$_2$, C$_{10}$H$_{10}$Cl$_2$Zr, $M = 292\cdot3$, triclinic, $a = 14\cdot06$ (1), $b = 8\cdot09$ (1), $c = 13\cdot15$ (1) Å, $\alpha = 113\cdot7$ (1), $\beta = 117\cdot9$ (1), $\gamma = 99\cdot5$ (1)°, $U = 1089$ Å^3. Crystals frequently twinned, space group $P\bar{1}$ (C_i^1, No. 2) from structure determination, $D_m = 1\cdot76$ g cm^{-3}, $D_c = 1\cdot74$ g cm^{-3} (for $Z = 4$), $F(000) = 576$, Cu $K\alpha$ radiation ($\lambda = 1\cdot5418$ Å), $\mu = 124\cdot6$ cm^{-1}, crystal size $0\cdot6 \times 0\cdot3 \times 0\cdot2$ mm, 4-circle diffractometer data, 3478 reflexions significantly above background.

The zirconium atoms of the two independent molecules in the cell were located from an unsharpened Patterson function and a trial structure containing all atoms but hydrogen was obtained from subsequent F_o syntheses. After three cycles of 'large block matrix' least-squares refinement with isotropic thermal parameters it was found that the thermal parameters of the π-cyclopentadienyl rings associated with Zr(2) were much higher than those of the rings associated with
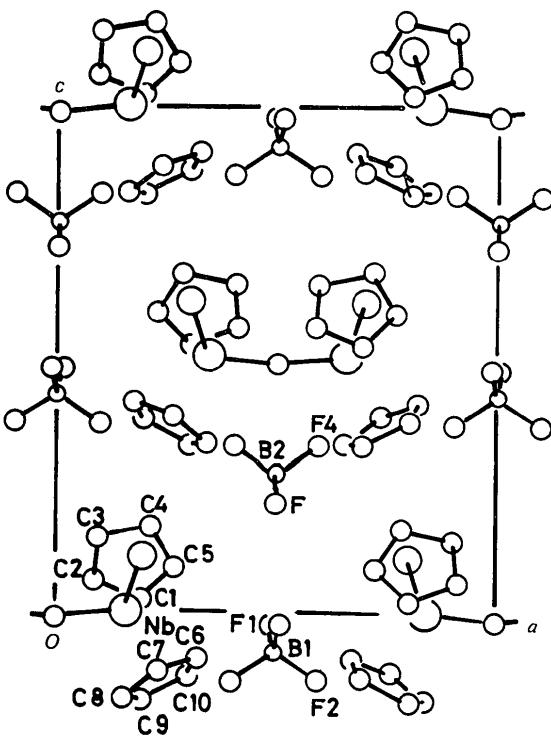

Fig. 6. The structure of *μ*-oxo-bis[bis-π-cyclopentadienylchloroniobium(V)] tetrafluoroborate in projection down **b**.

Zr(1). F_o and difference syntheses indicated that there was some disorder associated with the rings at Zr(2) and it proved possible to set up a second trial structure with two different arrangements of the bis-π-cyclopentadienylzirconium group at Zr(2) with occupation parameters S and $1 - S$. In the subsequent refinement, neighbouring carbon atoms within each of the disordered π-cyclopentadienyl rings were constrained to lie within $1\cdot41 \pm 0\cdot01$ Å of each other (thought with hindsight to have been somewhat too large a value) by the method of Waser (1963) (Rollett, 1969), anisotropic temperature factors were assigned to all atoms other than the carbon atoms of the disordered rings which retained individual isotropic temperature factors, and the site occupation number was refined. The normal matrix was divided into four blocks, one for the derivatives of the scale factor and dummy overall temperature factor, one each for those of the space and temperature parameters of the ordered molecule and one for those of the parameters describing the disordered molecule. The refinement converged at an R of 0·095 with the final weighting scheme $w = \{1 + [(|F_o| - 11)/20]^2\}^{-1}$.

The final atomic parameters are given in Table 15 and the bond distances and angles in Table 16. In the projection of the crystal structure given in Fig. 7 only

the disordered system with the higher occupation number is shown at Zr(2). The two crystallographically independent molecules in the asymmetric unit show no significant differences in shape or dimensions and, except in the details discussed later, are essentially similar to other systems described above.

Discussion

All monomeric complexes of the type $(\pi\text{-}C_5H_5)_2MX_2$ have the same general stereochemistry. The complexes may be thought of as derived from ferrocene by bending the molecule until the planes of the cyclopentadienyl rings are inclined to each other at about 50° and then placing the ligands X in a plane perpendicular to that of the normals to the rings at the metal atom so that the line bisecting the approximately 90° X–M–X angle also bisects the angle between the ring normals as in Fig. 8. The details of the $(\pi\text{-}C_5H_5)_2MX_2$ stereochemistry depend on the nature and valence state of M and the nature of X. These details, which shed light on the electronic structures of the complexes, appear to be best described by the parameters defined in Fig. 8 and enumerated in Table 17.

For those complexes reported here, an examination of the carbon–carbon bond lengths in the π-cyclopen-

Table 15. *Bis-π-cyclopentadienyldichlorozirconium: fractional coordinates and temperature factors*

	x/a	y/b	z/c	U_{11} or U_{iso}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$	Occupation number
Zr(1)	0·7382 (1)	0·4566 (1)	0·3447 (1)	0·036 (1)	0·025 (1)	0·037 (1)	0·035 (1)	0·038 (1)	0·025 (1)	
Cl(1)	0·5787 (3)	0·4106 (5)	0·1326 (3)	0·051 (2)	0·069 (2)	0·054 (2)	0·072 (3)	0·038 (3)	0·051 (3)	
Cl(2)	0·8758 (3)	0·4210 (6)	0·2834 (4)	0·069 (2)	0·083 (2)	0·093 (3)	0·120 (4)	0·119 (4)	0·095 (4)	
C(11)	0·6200 (13)	0·0834 (17)	0·2202 (14)	0·080 (9)	0·028 (5)	0·062 (8)	0·045 (11)	0·083 (15)	0·024 (11)	
C(12)	0·5739 (14)	0·1774 (22)	0·2881 (20)	0·074 (9)	0·053 (8)	0·117 (14)	0·097 (18)	0·133 (20)	0·051 (14)	
C(13)	0·6603 (21)	0·2835 (21)	0·4265 (21)	0·176 (20)	0·037 (7)	0·119 (15)	0·080 (17)	0·237 (32)	0·079 (20)	
C(14)	0·7658 (16)	0·2576 (21)	0·4483 (18)	0·102 (12)	0·045 (7)	0·093 (12)	0·101 (17)	0·102 (21)	0·041 (16)	
C(15)	0·7378 (15)	0·1351 (21)	0·3219 (16)	0·090 (11)	0·048 (7)	0·072 (9)	0·070 (14)	0·094 (17)	0·074 (15)	
C(21)	0·7457 (13)	0·7998 (18)	0·4348 (15)	0·063 (8)	0·038 (6)	0·071 (9)	0·060 (13)	0·059 (14)	0·035 (11)	
C(22)	0·8533 (13)	0·8226 (17)	0·4521 (14)	0·075 (9)	0·031 (5)	0·068 (8)	0·050 (11)	0·082 (15)	0·032 (11)	
C(23)	0·9157 (13)	0·7792 (21)	0·5529 (17)	0·048 (7)	0·042 (7)	0·074 (10)	0·023 (14)	0·000 (14)	0·016 (12)	
C(24)	0·8393 (18)	0·7279 (20)	0·5885 (15)	0·120 (14)	0·037 (7)	0·049 (8)	0·028 (12)	0·073 (18)	0·044 (16)	
C(25)	0·7328 (15)	0·7361 (19)	0·5114 (17)	0·099 (11)	0·036 (6)	0·081 (10)	0·044 (13)	0·121 (19)	0·054 (14)	
Zr(2)	0·2345 (1)	0·4521 (1)	0·1220 (1)	0·035 (1)	0·028 (1)	0·036 (1)	0·028 (1)	0·038 (1)	0·025 (1)	
Cl(3)	0·0777 (3)	0·4366 (6)	0·1563 (4)	0·051 (2)	0·077 (2)	0·068 (2)	0·078 (4)	0·077 (3)	0·061 (3)	
Cl(4)	0·3565 (4)	0·3815 (6)	0·2902 (4)	0·083 (2)	0·091 (3)	0·064 (2)	0·105 (4)	0·092 (4)	0·121 (4)	
C(31)	0·3592 (38)	0·7221 (61)	0·1287 (49)	0·053 (12)						0·34 (4)
C(32)	0·2565 (46)	0·7507 (57)	0·1057 (38)	0·052 (11)						0·34 (4)
C(33)	0·2616 (23)	0·8067 (74)	0·2250 (48)	0·054 (13)						0·34 (4)
C(34)	0·3673 (45)	0·8133 (49)	0·3225 (39)	0·049 (11)						0·34 (4)
C(35)	0·4274 (30)	0·7615 (67)	0·2626 (39)	0·053 (11)						0·34 (4)
C(41)	0·0816 (42)	0·0979 (57)	−0·0785 (39)	0·050 (11)						0·28 (4)
C(42)	0·1956 (30)	0·1015 (60)	−0·0298 (31)	0·041 (11)						0·28 (4)
C(43)	0·2560 (31)	0·2297 (59)	−0·0492 (50)	0·051 (11)						0·28 (4)
C(44)	0·1747 (39)	0·2895 (56)	−0·1223 (25)	0·039 (10)						0·28 (4)
C(45)	0·0719 (24)	0·2246 (62)	−0·1279 (46)	0·042 (11)						0·28 (4)
C(51)	0·3009 (21)	0·7232 (27)	0·0929 (14)	0·051 (5)						0·66 (4)
C(52)	0·2462 (13)	0·7843 (32)	0·1585 (25)	0·054 (6)						0·66 (4)
C(53)	0·3162 (23)	0·8206 (30)	0·2913 (21)	0·053 (5)						0·66 (4)
C(54)	0·4164 (17)	0·7859 (35)	0·3078 (18)	0·061 (6)						0·66 (4)
C(55)	0·4058 (18)	0·7212 (30)	0·1845 (26)	0·054 (6)						0·66 (4)
C(61)	0·1319 (22)	0·0770 (24)	−0·0481 (20)	0·054 (5)						0·72 (4)
C(62)	0·2402 (16)	0·1485 (34)	−0·0310 (20)	0·058 (5)						0·72 (4)
C(63)	0·2333 (19)	0·2724 (29)	−0·0825 (24)	0·060 (6)						0·72 (4)
C(64)	0·1216 (23)	0·2790 (29)	−0·1301 (20)	0·062 (6)						0·72 (4)
C(65)	0·0585 (12)	0·1568 (35)	−0·1096 (21)	0·059 (5)						0·72 (4)

Table 16. *Bis-π-cyclopentadienyldichlorozirconium*(IV): *bond lengths* (Å) *and angles* (°)

Zr(1)–Cl(1)	2·446 (5)	Cl(1)–Zr(1)–Cl(2)	97·1 (2)
Zr(1)–Cl(2)	2·436 (5)		
Zr(1)–C(11)	2·53 (2)	Zr(1)–C(21)	2·50 (2)
Zr(1)–C(12)	2·51 (3)	Zr(1)–C(22)	2·51 (2)
Zr(1)–C(13)	2·48 (3)	Zr(1)–C(23)	2·50 (2)
Zr(1)–C(14)	2·46 (2)	Zr(1)–C(24)	2·48 (3)
Zr(1)–C(15)	2·49 (2)	Zr(1)–C(25)	2·48 (2)
C(11)–C(12)	1·40 (3)	C(21)–C(22)	1·39 (3)
C(12)–C(13)	1·36 (4)	C(22)–C(23)	1·43 (3)
C(13)–C(14)	1·44 (4)	C(23)–C(24)	1·42 (3)
C(14)–C(15)	1·35 (3)	C(24)–C(25)	1·39 (3)
C(15)–C(11)	1·40 (3)	C(25)–C(21)	1·37 (3)
C(11)–C(12)–C(13)	109 (2)	C(21)–C(22)–C(23)	105 (2)
C(12)–C(13)–C(14)	108 (2)	C(22)–C(23)–C(24)	107 (2)
C(13)–C(14)–C(15)	107 (2)	C(23)–C(24)–C(25)	109 (2)
C(14)–C(15)–C(11)	110 (2)	C(24)–C(25)–C(21)	106 (2)
C(15)–C(11)–C(12)	107 (2)	C(25)–C(21)–C(22)	113 (2)
Zr(2)–Cl(3)	2·442 (5)	Cl(3)–Zr(2)–Cl(4)	97·2 (2)
Zr(2)–Cl(4)	2·439 (5)		
Zr(2)–C(31)	2·51 (6)	Zr(2)–C(41)	2·52 (4)
Zr(2)–C(32)	2·49 (5)	Zr(2)–C(42)	2·50 (4)
Zr(2)–C(33)	2·50 (7)	Zr(2)–C(43)	2·44 (5)
Zr(2)–C(34)	2·53 (6)	Zr(2)–C(44)	2·54 (4)
Zr(2)–C(35)	2·53 (6)	Zr(2)–C(45)	2·48 (4)
Zr(2)–C(51)	2·48 (3)	Zr(2)–C(61)	2·52 (3)
Zr(2)–C(52)	2·50 (3)	Zr(2)–C(62)	2·52 (3)
Zr(2)–C(53)	2·51 (3)	Zr(2)–C(63)	2·48 (3)
Zr(2)–C(54)	2·52 (3)	Zr(2)–C(64)	2·47 (4)
Zr(2)–C(55)	2·49 (4)	Zr(2)–C(65)	2·50 (3)
C(31)–C(32)	1·41 (4)	C(41)–C(42)	1·41 (8)
C(32)–C(33)	1·41 (4)	C(42)–C(43)	1·41 (8)
C(33)–C(34)	1·41 (5)	C(43)–C(44)	1·41 (9)
C(34)–C(35)	1·41 (4)	C(44)–C(45)	1·41 (8)
C(35)–C(31)	1·41 (4)	C(45)–C(41)	1·41 (8)
C(51)–C(52)	1·41 (5)	C(61)–C(62)	1·41 (9)
C(52)–C(53)	1·41 (5)	C(62)–C(63)	1·41 (9)
C(53)–C(54)	1·41 (4)	C(63)–C(64)	1·41 (9)
C(54)–C(55)	1·41 (5)	C(64)–C(65)	1·41 (9)
C(55)–C(51)	1·41 (5)	C(65)–C(61)	1·41 (9)
C(31)–C(32)–C(33)	108 (3)	C(41)–C(42)–C(43)	108 (5)
C(32)–C(33)–C(34)	108 (3)	C(42)–C(43)–C(44)	108 (5)
C(33)–C(34)–C(35)	107 (3)	C(43)–C(44)–C(45)	108 (5)
C(34)–C(35)–C(31)	109 (3)	C(44)–C(45)–C(41)	108 (5)
C(35)–C(31)–C(32)	108 (3)	C(45)–C(41)–C(42)	108 (5)
C(51)–C(52)–C(53)	109 (3)	C(61)–C(62)–C(63)	107 (6)
C(52)–C(53)–C(54)	107 (3)	C(62)–C(63)–C(64)	108 (6)
C(53)–C(54)–C(55)	108 (3)	C(63)–C(64)–C(65)	108 (5)
C(54)–C(55)–C(51)	107 (3)	C(64)–C(65)–C(61)	108 (5)
C(55)–C(51)–C(52)	108 (3)	C(65)–C(61)–C(62)	108 (5)

Occupation numbers

C(31–35)	0·71
C(41–45)	0·28
C(51–55)	0·66
C(61–65)	0·34

tadienyl rings shows that for a given complex the spread of values is not in excess of 3σ in any particular ring, but when all the complexes are considered together, the overall range of values is very large. In any given complex the shorter mean carbon–carbon bond length is associated with the ring with the greater apparent thermal motion as indicated by the anisotropic thermal parameters. However, the failure of these temperature parameters to be adequately represented by rigid-body T and ω tensors prevented bond-length corrections and suggested that the problem might be

better considered as one of disorder rather than of thermal motion. The difficulty in the interpretation is further aggravated in some cases by the lack of an absorption correction to the primary X-ray intensity measurements. These factors combine to make the study of mean carbon–carbon bond lengths unrewarding. However, it does appear that in the better analyses, where the π-cyclopentadienyl rings are well defined, the mean C–C bond lengths are in general longer and, intuitively, might be extrapolated to a value of about 1·41 Å in the ideal situation. It is believed therefore that the observed values are not significantly at variance with the value of 1·43 postulated by Wheatley (1967). Unfortunately, consequent upon the geometry of the system, the errors in the positions of the carbon atoms are reflected in the carbon–metal bond lengths to give some apparent correlation of shorter mean carbon–metal contacts with shorter mean carbon–carbon bond lengths. Therefore we have chosen the length of the normal to the π-cyclopentadienyl ring from the metal
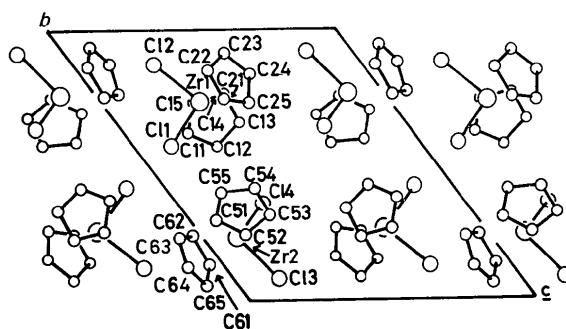

Fig. 7. The structure of bis-π-cyclopentadienyldichlorozirconium(IV) in projection down **a**.
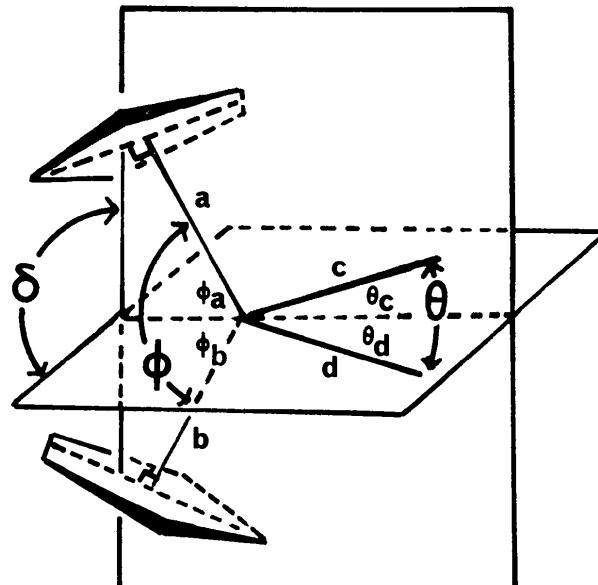
Fig. 8. Definition of the molecular structure parameters used in Table 17.

Table 17. Summary of molecular dimensions of $(\pi\text{-}C_5H_5)_2MX_2$ systems

The column headings when not self-explanatory refer to Fig. 8.

Cp_2MX_2 $Cp\equiv\pi\text{-}C_5H_5$	d-Electron configuration	Point symmetry	a	b	c	d	δ	φ	φ_a	φ_b	θ	θ_c	θ_d	Ring configuration	$x_a{}^*$	x_b	d(M–C) mean a	b	d(C–C) mean a	b
$Cp_2ReBr_2BF_4$	d^2	C_{2v}	1·924†		2·563		90·0	139·5	69·7		82·0	41·0		e‡	0·08		2·26		1·39	1·35
Cp_2MoCl_2 at Mo(1)	d^2	C_1	1·98	1·97	2·46	2·47	89·4	130·9	64·1	66·8	82·0	39·5	42·4	s	0·15	0·06	2·31	2·28	1·38	1·39
Cp_2MoCl_2 at Mo(2)	d^2	C_1	1·97	1·98	2·47	2·48	89·0	130·2	66·8	63·4	82·0	43·2	38·8	e	0·08	0·15	2·30	2·31	1·38	1·39
$Cp_2MoCl(C_2H_5)$	d^2	C_1	1·97	1·98	2·50	2·28	89·2	133·9	65·5	68·4	78·9	33·2	45·7	s	0·13	0·04	2·31	2·29	1·41	1·35
$Cp_2Mo(OH)(NH_2CH_3)PF_6$	d^2	C_1	1·94	1·96	2·05	2·19	88·1	133·1	65·5	67·6	72·2	35·2	37·0	s	0·16	0·15	2·29	2·29	1·40	1·39
Cp_2NbCl_2 at Nb(1)	d^1	C_1	2·09	2·09	2·46	2·48	89·4	130·9	64·3	66·6	85·7	42·8	43·0	s	0·06	0·02	2·40	2·38	1·39	1·35
Cp_2NbCl_2 at Nb(2)	d^1	C_1	2·08	2·09	2·47	2·48	90·0	129·6	66·0	63·6	85·5	44·3	41·2	e	0·01	0·08	2·38	2·36	1·36	1·30
$Cp_2MoCl_2BF_4$	d^1	C_{2v}	1·99		2·39		90·0	131·5	65·8		87·9	44·0		e	0·00		2·32		1·38	
$([Cp_2NbCl]_2O)(BF_4)_2$	d^0	C_1	2·11	2·08	2·37	1·88	88·1	129·7	65·9	63·8	96·2	51·7	44·5	s	0·03	0·05	2·42	2·38	1·39	1·35
Cp_2ZrCl_2 at Zr(1)	d^0	C_1	2·20	2·19	2·45	2·44	89·6	126·6	62·9	63·7	97·1	47·2	49·9	s	0·07	0·03	2·49	2·49	1·39	1·40
Cp_2ZrCl_2 at Zr(2)	d^0	C_1	2·19	2·21	2·44	2·44	88·4	128·3	63·7	64·6	97·2	48·6	48·6	s	0·04	0·04	...constrained...		...constrained...	
Cp_2ZrCl_2 at Zr(2)	d^0	C_1	2·19	2·19	2·44	2·44	89·9	126·0	63·1	62·9	97·2	47·9	49·4	s	0·04	0·06	...constrained...		...constrained...	
$Cp_2Mo(NO)(\sigma\text{-}C_5H_5)^a$	d^4	C_1	2·14	2·15	1·75	2·29	87·5	137·6	68·4	69·2	84·2	40·6	43·6	e	0·34	0·43	2·47	2·49	1·40	1·40
$Cp(\pi\text{-}CH_3C_5H_4)Re(CH_3)_2{}^b$	d^2	C_1	1·89	1·90	2·23	2·25		135·3	68·1	67·3	75·8			s						
$Cp_2MoBr(SnBr_3)^c$	d^2	C_s	1·99		2·60	2·69	90·0	128·3	64·1		80·2	38·7	41·5	e	0·24		2·32		1·38	
$Cp_2MoD_2{}^d$	d^2	C_s	1·96		1·96		87·7	148·2	74·1		83·2	41·6		e	0·15		2·32		1·44	
$(\pi\text{-}(CH_3)_3C_5H_4)_2TiCl_2{}^e$	d^0	C_1	2·06	2·06	2·37	2·37	89·7	133·6	66·5	67·1	93·8	45·2	48·6	e	0·02	0·04	2·39	2·38	1·40	1·39
$Cp_2ZrF_2{}^f$	d^0	C_{2v}	2·20		1·97		90·0	131·1	65·5		96·2	48·1		e	0·08		2·49		1·36	
$Cp_2ZrI_2{}^f$	d^0	C_{2v}	2·19		2·83		89·7	126·0	63·0		96·2	48·1		e	0·10		2·48		1·35	
$Cp_2ZrCl(Si(C_6H_5)_3)^g$	d^0	C_1	2·21	2·18	2·43	2·81	88·0	130·5	63·5	67·0	93·9	38·8	55·2	e	0·02	0·06	2·50	2·48	1·38	1·39

References

(a) Calderon, Cotton & Legzdins (1969); (b) Alcock (1967); (c) Cameron & Prout (1972); (d) Cheetham (1974); (e) Davis & Bernal (1971); (f) Bush & Sim (1971); (g) Muir (1971).

* x_a and x_b are the distances from the ring centroid to the point of intersection of the ring normal.
† When two quantities are equal by crystal symmetry only the first is given.
‡ $e\equiv$eclipsed, $s\equiv$staggered.

atom to represent the comparative sizes of the metal atoms when bonding with the π-cyclopentadienyl groups. When the ligands X are approximately equal in size, this normal intersects the π-cyclopentadienyl ring close to its centroid and has less tendency to contain a component of the ring shrinkage from disorder/ thermal motion than the carbon–metal distance. The lengths of the ring normals indicate that the metal radii with respect to the π-cyclopentadienyl rings (a) increase from the first to the second transition series, cf. [π-(CH$_2$)$_3$(C$_5$H$_4$)$_2$]TiCl$_2$, 2·06 Å (Davies & Bernal, 1971), (π-C$_5$H$_5$)$_2$ZrCl$_2$, 2·19 Å; (b) remain almost constant from the second to the third transition series, cf. (π-C$_5$H$_5$)$_2$MoCl$_2$, 1·98 Å, (π-C$_5$H$_5$)$_2$W(μSPh)$_2$M(CO)$_4$, M = Cr, Mo, W, 1·99 Å (Cameron et al., 1971); (c) decrease across a transition series, cf. (π-C$_5$H$_5$)$_2$ZrCl$_2$, 2·19, (π-C$_5$H$_5$)$_2$NbCl$_2$, 2·09, (π-C$_5$H$_5$)$_2$MoCl$_2$, 1·98 Å; and (d) are little affected by the oxidation state of the metal atom, cf. (π-C$_5$H$_5$)$_2$MoCl$_2$, 1·98, (π-C$_5$H$_5$)$_2$MoCl$_2^+$, 1·99 Å. The angles between the ring normals vary over only a relatively small range and are in general less than 135°, the minimum considered by the Ballhausen or Alcock models for the electronic structures of the complexes. The general trend is that the longer the ring normal lengths the smaller the angles between the normals, suggesting the angle may be to some extent controlled by the mutual repulsions of the hydrogen atoms of the π-cyclopentadienyl ligands at the end of the molecule away from the ligands X. The conformations of the bis-π-cyclopentadienyl systems from this and other work are given in Fig. 9, as projections onto the MX$_2$ plane. It has been reported that the repulsion of the rings by the ligands X and interaction between the hydrogen atoms of the π-cyclopentadienyl groups determined whether the conformation of the rings was eclipsed or staggered (Knox & Prout, 1969), but later it was shown that the conformation was counter-ion dependent and the choice of conformation was attributed to crystal packing effects (Prout, Allison, Delbaere & Gore, 1972). Further confirmation of this belief is gained from the present work, where examples of the staggered and eclipsed conformations are to be found in the same crystal in both (π-C$_5$H$_5$)$_2$NbCl$_2$ and (π-C$_5$H$_5$)$_2$MoCl$_2$, and in (π-C$_5$H$_5$)$_2$ZrX$_2$ systems the fluoride and iodide are eclipsed but the chloride is staggered.

The ligands X lie in a plane that is almost or exactly at right angles to that of the ring normals. The line of intersection of the ring-normal plane and the MX$_2$ plane roughly bisects the ring-normal and MX$_2$ angles, but all the molecules are significantly skew except when the point symmetry of the metal site in the crystal requires an exact bisection. The skewness of the molecule does not obviously relate to the nature of M or X and is presumed to be a function of the crystal packing.

From the values recorded in Table 17, the size of the X–M–X angle is related to the number of non-

bonding electrons in the complex rather than to the nature of the central metal atom. As the number of non-bonding electrons of the metal atom increases so the X–M–X angle decreases. The MX$_2$ angles fall into fairly discrete, non-overlapping groups according to the number of non-bonding electrons: d^0 94–97°, d^1 85–88°, d^2 76–82°, but with a slightly anomalous (too low) value in (π-C$_5$H$_5$)$_2$Mo(OH)NH$_2$CH$_3$, 72·2°, comparable to that found in certain amino acid chelates (Prout et al., 1972) and possibly due to O–H$\cdots$N hydrogen bonding. The M–X bond lengths present a remarkable picture when contrasted with the lengths of the ring normals. If the bonds to chlorine are considered, then for the series of complexes (π-C$_5$H$_5$)$_2$MCl$_2$ with M = Zr, Nb, and Mo the M–Cl bond length increases marginally with atomic number from 2·44 to
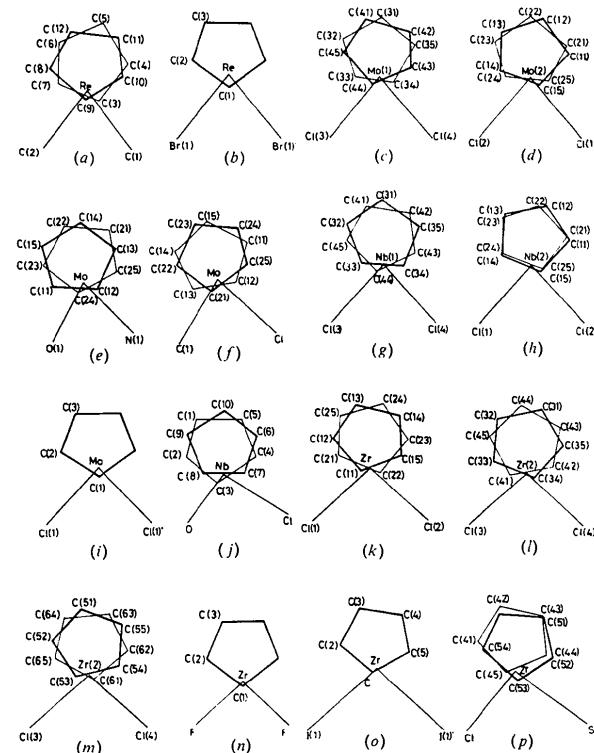
Fig. 9. Projections of (πC$_5$H$_5$)$_2$MX$_2$ and related systems on to their MX$_2$ planes. (a) π-Cyclopentadienyl(methylcyclopentadiene)dimethylrhenium (Alcock, 1967), (b) bis-π-cyclopentadienyldibromorhenium(V) tetrafluoroborate, (c) bis-π-cyclopentadienyldichloromolybdenum(IV) at Mo(1), and (d) at Mo(2), (e) bis-π-cyclopentadienylhydroxomethylaminomolybdenum(IV) hexafluorophosphate, (f) bis-π-cyclopentadienylethylchloromolybdenum(IV), (g) bis-π-cyclopentadienyldichloroniobium(IV) at Nb(1), and (h) at Nb(2), (i) bis-π-cyclopentadienyldichloromolybdenum(V) tetrafluoroborate, (j) μ-oxo-bis[bis-π-cyclopentadienylchloroniobium(V)] tetrafluoroborate, (k) bis-π-cyclopentadienyldichlorozirconium (IV) at Zr(1), (l) at Zr(2) (minor component), and (m) at Zr(2) (major component), (n) bis-π-cyclopentadienyldifluorozirconium(IV) (Bush & Sim, 1971), (o) bis-π-cyclopentadienyldiiodozirconium(IV) (Bush & Sim, 1971), (p) bis-π-cyclopentadienylchlorotriphenylsilylzirconium(IV) (Muir, 1971).

2·47 Å, whereas the lengths of the ring normals decrease very significantly from 2·19 to 1·98 Å.

The elements zirconium, niobium, and molybdenum have almost identical (Allred & Rochow, 1958) electronegativities; therefore in the absence of other factors the M–Cl bond lengths might indicate that the metal radii with respect to the M–X bonds are about equal. However, if the Mo–C and Zr–Si bonds in $(\pi\text{-}C_5H_5)_2MoCl(C_2H_5)$ and $(\pi\text{-}C_5H_5)_2ZrClSi(C_6H_5)_3$ (Muir, 1971) respectively are examined, and if it is assumed that for both bonds the lengths can be represented as the sums of the respective covalent radii with an appropriate electronegativity correction, then the radius of Zr appears to be about 0·2 Å greater than that of Mo, consistent with the differences in radii derived from the lengths of the ring normals in these complexes. Further, the covalent radius of Mo for Mo–X bonds is the same when derived from the Mo–C, Mo–N, Mo–Cl, Mo–Br and Mo–Sn bonds taking into account electronegativity differences, although the Mo–O bond in $(\pi\text{-}C_5H_5)_2Mo(OH)NH_2CH_3$ is rather shorter than would be predicted on this basis. It is inferred therefore that the apparent contraction of the Zr–Cl bond (and the similar but possibly lesser contraction in the Ti–Cl bond, Table 17) cannot be adequately accounted for in terms of electronegativity differences alone, although within the Zr–halogen complexes the contraction in the apparent radius of the metal in its bonds to fluorine relative to those to chlorine and iodine may be due to the increased electronegativity difference, which results in the Zr–F bond having greater ionic character, as suggested by Bush & Sim (1971).

If an electron is withdrawn from the $(\pi\text{-}C_5H_5)_2MoCl_2$ complex to give $(\pi\text{-}C_5H_5)MoCl_2^+$, then the radius of the Mo atom in its bonding with the π-cyclopentadienyl system remains unchanged but the Mo–Cl bond length shortens significantly by 0·1 Å. The minimal implication of this observation and the similar observations for the Nb(IV) and Nb(V) complexes is that the non-bonding electrons are intimately associated with the MX_2 system and have little or no association with the π-cyclopentadienyl groups.

There are two possible interpretations of the overall stereochemistry of these complexes, one based entirely on steric repulsions and the other taking into account the directional properties of the non-bonding electrons.

First, if it is assumed that the non-bonding electrons have no stereochemical role the idealized structure might be seen as ferrocene-like with a near-linear MX_2 system parallel with the cyclopentadienyl rings. This structure is perturbed by steric repulsions between the ligands X and the cyclopentadienyl groups so that the ferrocene-like part bends back and the ligands X are forced forward. The equilibrium position is determined by repulsions (a) between the ligands X, (b) between the ligands X and the cyclopentadienyl rings, and (c) at the opposite end of the molecule to the ligand X, between the hydrogen atoms of the two rings. Thus

greater metal atom to ring distances for a given ligand X [$(\pi\text{-}C_5H_5)_2MoCl_2$, $(\pi\text{-}C_5H_5)_2NbCl_2$, $(\pi\text{-}C_5H_5)_2ZrCl_2$, Table 17] lead to reduced ligand–ring and ring–ring repulsions and consequently to smaller ring–normal angles and larger MX_2 angles. Shorter M–X bonds for a given ligand X [see $(\pi\text{-}C_5H_5)_2MoCl_2$ and $(\pi\text{-}C_5H_5)_2MoCl_2^+$] lead to increased ligand–ligand and ligand–ring repulsions and hence to larger MX_2 angles. Smaller ligands X [see $(\pi\text{-}C_5H_5)$ $(\pi\text{-}CH_3C_5H_5)Re(CH_3)_2$ and $(\pi\text{-}C_5H_5)_2MoH_2$] reduce ligand–ligand and ligand–ring repulsions giving smaller MX_2 angles and larger ring–normal angles. All the data in Table 17 are consistent with this steric constraint approach except perhaps the 20e $(\pi\text{-}C_5H_5)_2Mo(NO)$ ($\sigma\text{-}C_5H_5$) with long metal–ring contacts and unchanged metal–σ-carbon bond length, suggesting that the additional electrons are associated with anti-bonding metal–ring orbitals rather than with the MX_2 system. In this complex, although the metal–ring contact is increased to about the value found in the Zr complexes (thus reducing ring–ligand repulsions), the MX_2 angle remains within the range expected for the Mo(IV) d^2 complexes and does not expand to the values found in Zr(IV) d^0 complexes. This could reflect the steric role of the non-bonding pair of electrons. It is also perhaps a little surprising that the MX_2 angles are little perturbed by the bulky ligands in $(\pi\text{-}C_5H_5)_2Zr(Cl)Si(C_6H_5)_3$ (Muir, 1971) and $(\pi\text{-}C_5H_5)_2MoBr(SnBr_3)$ (Cameron & Prout, 1972).

If the non-bonding electrons have directional properties, there is an immediate conflict between the interpretation of these properties in relation to the chemistry (Ballhausen & Dahl, 1961) and the stereochemistry (Alcock, 1967) (Fig. 1).

The evidence of the MX_2 bond angle in $(\pi\text{-}C_5H_5)_2MX_2$ systems is consistent only with sterically significant non-bonding electrons occupying an Alcock-type orbital lying outside the MX_2 angle and is quite contrary to the occupancy of a Ballhausen-type orbital. If it is assumed that the primary stereochemical feature of the molecule is the MX_2 angle, determined by the lone-pair bond-pair repulsions between the non-bonding electrons and those of the M–X bonds, then the less significant details can be explained as steric consequences of these angles using arguments similar to those outlined above. This non-bonding electron approach to the stereochemistry is thought to be the more satisfactory because of (1) the small non-overlapping ranges of MX_2 angle, (2) the general observation that non-bonding electrons without steric significance are rarities in covalent molecules. Green, Green & Prout (1972) have attempted to reconcile the apparent conflict between chemistry and stereochemistry to give a unified approach to the electronic structure. From the strong similarities between the photoelectron spectrum of ferrocene and $(\pi\text{-}C_5H_5)_2MoH_2$ it seemed to them reasonable to generate the M.O.'s for the bent hydride system by 'bending' ferrocene to C_{2v} symmetry. The resulting M.O. diagram shows that the essentially

non-bonding e_{2g} and a_{1g} orbitals of ferrocene become the $3a$, $2b$ and $4a$ orbitals of the bent system. If the $4a$ and $3a$ orbitals, essentially $d_{x^2-y^2}$ and d_{z^2} in character, can mix to give two orbitals ψ_A and ψ_B (Fig. 1), ψ_A resembling the $\psi_{C''}$ of Alcock and ψ_B the $\psi_{B'}$ of Ballhausen in their localization, it can then be argued that in $(\pi\text{-}C_5H_5)_2MX_2$ complexes it is ψ_B together with the $2b_1$ orbital that are engaged in the bonding to X, and it is ψ_A which, as the next lowest energy orbital, accommodates the non-bonding electrons. In a complex with three ligands (e.g. $(\pi\text{-}C_5H_5)MoH_3^+$ or a metal–metal bonded dimer of the form $(\pi\text{-}C_5H_5)M(\mu\text{-}X_2)M'L_n$ where X and L are ligands and M and M' are the same or different metals) ψ_A, ψ_B and $2b_1$ all form bonding M.O.'s.

In describing the $[(\pi\text{-}C_5H_5)_2NbCl]_2O^{2+}$ cation it was necessary to invoke the concept of π-bonding between metal and oxygen. Now that the symmetry of the vacant low-energy orbital in the MX_2 plane of the d^0 complexes is defined, it can be seen that it would permit a bonding interaction with the oxygen p-lone pairs and that the observed torsion angle about the Nb–O–Nb bond is very close to the value expected from the proposed model.

The π-acceptor nature of ψ_A may also be involved in the apparent contraction of the metal radius, as deduced from the metal–halogen bonds, in $(C_5H_5)_2MCl_2$, M = Mo, Nb, Zr. The smaller electron–electron repulsion which is associated with a vacant ψ_A orbital will be reinforced by delocalization of the halogen p-lone pairs into that orbital, resulting in a shortening and strengthening of the metal–halogen bond across the series $(C_5H_5)_2MoCl_2$, $(C_5H_5)_2NbCl_2$, $(C_5H_5)_2ZrCl_2$. These effects will be in addition to the shortening noted by Bush & Sim (1971) in the series $(\pi\text{-}C_5H_5)_2ZrX_2$, X = I, Cl, F, attributed to the increasing ionic character of the bond.

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