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Molecular structures of tris(methylcyclopentadienyl)-scandium and -ytterbium as studied by gas phase electron diffraction and molecular mechanics calculations: the scandium atom is too small to accommodate three pentahapto cyclopentadienyl rings *

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Abstract

The syntheses and spectroscopic properties (IR and ^{1}H and ^{13}C NMR spectra) of tris(methylcyclopentadienyl)-scandium and -ytterbium are described. The vapour pressure of Yb(MeCp)$_3$ has been determined over the range 70–90°C. The gas phase electron diffraction data for M(MeCp)$_3$ (M = Sc or Yb) have been recorded with nozzle temperatures of about 160°C. The data for M = Yb are consistent with a model containing three pentahapto cyclopentadienyl rings; Yb(η^5-MeCp)$_3$, a mean Yb to ring-centre distance of Yb–Z = 236.6(6) pm, and a mean Yb–C bond distance of 265.5(7) pm. The gas phase electron diffraction data for M = Sc are incompatible with models containing three η^5-MeCp rings, but consistent with models containing two η^5 rings and one ring with a hapticity of 2 or 3; $\eta^{2/3}$-MeCp. The distance from Sc to the centres of the two η^5-MeCp rings is 222.3(6) pm, corresponding to a mean Sc–C(η^5) bond distance of 253.0(6) pm. The third ring is at a greater distance from the Sc atom, Sc–Z($\eta^{2/3}$) = 252(5) pm, but is tilted, the angle between the Sc–Z($\eta^{2/3}$) vector and the ring normal being 22(4)°. As a result two or three carbon atoms of the ring are in a position to form strong bonds to the metal atom. Molecular mechanics calculations indicate that interligand interactions in M(η^5-C$_5$H$_4$)$_3$ or M(η^5-MeCp)$_3$ molecules are strongly repulsive when M-Z(η^5) is less than 225 pm, and that the strain is eliminated on rearrangement to M(η^5-C$_5$H$_5$)$_2$($\eta^{2/3}$-C$_5$H$_5$) or M(η^5-MeCp)$_2$($\eta^{2/3}$-MeCp) configurations.

1. Introduction

The syntheses of the tricyclopentadienyl derivatives of scandium, yttrium, lanthanum, and several rare earth metals, M(C$_5$H$_5$)$_3$ or MCp$_3$, were reported by Birmingham and Wilkinson in 1956 [1], and over the years the crystal structures of ScCp$_3$ [2], YCp$_3$ [3], LaCp$_3$ [4], PrCp$_3$ [5], SmCp$_3$ [6], ErCp$_3$ and TmCp$_3$ [7], YbCp$_3$ [8] and LuCp$_3$ [9] have been determined by X-ray diffraction. The structure of SmCp$_3$ in crystals containing an undetermined but chemically significant amount of diethyl-ether, has also been determined [10], but is not considered in the following discussion.

In each of the neat MCp$_3$ structures the molecular unit may be recognized in the crystalline phase. Each metal atom is pentahapto-bonded to two cyclopentadienyl rings, which may be described as terminal, since there are no short contacts between the C or H atoms of these rings and the metal atoms of other molecular units. The third ring may be η^5, *i.e.* pentahapto, or η^1, *i.e.* monohapto, bonded, and may be described as

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* Dedicated to Professor Michael F. Lappert on the occasion of his 65th birthday.

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bridging, since there are secondary interactions between two or three C atoms of the ring and the metal atom of another molecular unit. The length, and presumably the strength, of the secondary interactions vary within wide limits; the shortest contact is only 5 pm longer than the average of the 10 bond distances from the metal atom to the terminal η^5 bonded rings, M–C(η^5), the longest is more than 100 pm longer.

These structures have been discussed by Raymond and Eigenbrot [11], by Hammel and coworkers [12,13], and by R.D. Fischer and coworkers [14]. All agree that the crystal structure adopted is determined by the size of the metal atom (or ion) and the coordination space around it.

The largest of the metal atoms under consideration is lanthanum. In crystalline $LaCp_3$ each metal atom is surrounded by three η^5-Cp rings. The average of the 15 La–C(η^5) bond distances is 286 pm and the average of the three angles $\measuredangle$ZLaZ, where Z denotes the centre of a Cp ring, is 114.3°. In the direction perpendicular to the Z_3 plane the La atom interacts with two C atoms in another molecular unit at a distance of $La \cdots C = 303$ pm. As one goes along the series of rare earth metals from La to Yb, the size of the metal atom decreases and the angles $\measuredangle$ZMZ increase, presumably as a consequence of increased repulsion between ligand rings. At the same time the $M \cdots C$ interaction distances between molecular units increase, again presumably as a result of increased interligand repulsion. In the last member of the series, $YbCp_3$, the sum of the three $\measuredangle$ZMZ angles is 359.8°; the Yb atom and the three ring centres are very nearly coplanar. At the same time the fourth ring has been effectively squeezed out of the coordination space around the metal, the shortest $Yb \cdots C$ interactions being 414 pm. The crystal structures of $LaCp_3$, $PrCp_3$, $SmCp_3$, $ErCp_3$, $TmCp_3$ and $YbCp_3$ may be described as polymeric $[(\eta^5\text{-Cp})_2M(\mu\text{-}\eta^5:\eta^x\text{-Cp})]$, where $x = 1$ or 2, or as Type **A**. The size of the yttrium atom is similar to the sizes of Er or Tm atoms, and the structure of YCp_3 is very similar to those of $ErCp_3$ and $TmCp_3$.

On going to the last and smallest of the rare earth metals, lutetium, there is an abrupt change of structure. The two terminal Cp rings remain pentahapto bonded to the metal atom, but the bridging Cp ring is now monohapto, or η^1, bonded to both metals, and seems to interact strongly with both at relatively short M–C distances of 252 and 265 pm. The first of these distances is shorter and the second longer, than the mean of the ten Lu–C(η^5) distances. The scandium atom is smaller than the Lu atom, and the structure of $ScCp_3$ is similar to that of $LuCp_3$. The shortest distances from the bridging ring to the two metal atoms are respectively 252 and 263 pm compared with a mean Sc–C(η^5) distance of 249 pm. The crystal structures of $LuCp_3$ and $ScCp_3$ may be described as $[(\eta^5\text{-Cp})_2M(\mu\text{-}\eta^1:\eta^1\text{-Cp})]$ or Type **B**.

At the ionic limit these crystalline substances may be regarded as consisting of M^{+3} cations and Cp^- anions. Raymond and Eigenbrot [11] suggested that since the cyclopentadienide ion may be regarded as a six electron ligand, coordination of a η^5-Cp^- ligand should be regarded as increasing the coordination number of the metal atom by three.

Whatever the actual charge on the metal atoms, the mean M–C(η^5) bond distance in each of these compounds is strongly correlated with the radius of the tripositive metal ion with $CN = 9$ as given by Shannon [15]. The mean M–C(η^5) bond distance in all the MCp_3 compounds under consideration may be calculated to within 2 pm by adding the radius of the appropriate metal ion to an effective C(η^5) radius of 162 pm.

The smallest of those metal atoms that coordinate three η^5 rings in the solid state is Yb, with an ionic radius ($CN = 9$) of 104.2 pm [15]. Lu and Sc, with ionic radii ($CN = 9$) of 103.2 and 94 pm, respectively, crystallize with only two η^5-Cp rings. What molecular structures would be expected for these compounds in the gas phase? $M(\eta^5\text{-Cp})_3$ structures cannot be ruled out, since the energy release accompanying the establishment of strong bridging interactions might be sufficient to compensate for rearrangements from $M(\eta^5\text{-Cp})_3$ to $M(\eta^5\text{-Cp})_2(\eta^1\text{-Cp})$ configurations.

Neither $LuCp_3$ or $ScCp_3$ are amenable to studies by gas electron diffraction. When heated both compounds undergo thermal decomposition before the vapour pressure reaches 1 torr [1]. It is known, however, that introduction of a methyl group into the rings of a metal cyclopentadienyl compound generally increases both the vapour pressure and the thermal stability. We decided, therefore, to synthesize tris(methylcyclopentadienyl)scandium in order to determine the molecular structure in the gas phase.

When studying structural anomalies by gas electron diffraction, we have often found it useful to carry out a parallel investigation of a related compound where no structural anomaly is expected. In this case we chose to use $Yb(MeCp)_3$. The crystal structure of this compound is known [13]. The structure is of Type **A**, with three η^5 rings around the metal atom, and with M–C(η^5) and $M \cdots C(\eta^x)$ distances and $\measuredangle$ZMZ angles very similar to those observed in unsubstituted $YbCp_3$.

The molecular structure determinations were accompanied by molecular mechanics calculations. Such calculations have been found to provide useful information on interligand interactions in organometallic compounds [16].

2. Syntheses and spectroscopy

The air- and moisture-sensitive compounds described below were handled under purified nitrogen or argon by use of Schlenk or high vacuum techniques. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from sodium benzophenone ketyl prior to use. The metal trihalides, $YbCl_3$ (Venthron Gmbh, 99.9%) and $ScCl_3$ (Aldrich, 99.999%) were dried with thionyl chloride [17]. All glassware was heated *in vacuo* to remove traces of oxygen and water. Infrared spectra were recorded on a Perkin Elmer PE 283 or PE 684. The intense colours of $Yb(MeCp)_3$ and $Sc(MeCp)_3$ prevented us from obtaining Raman spectra.

2.1. $K(C_5H_4CH_3)$

Metallic potassium (41.85 g, 1.07 mol) and about 500 ml DME were placed in a three-necked round bottom flask fitted with a reflux condenser, a nitrogen inlet and a funnel. The mixture was heated with stirring until the potassium melted to form spherical droplets. The heating was stopped and 105 ml (1.06 mol) of freshly-cracked methylcyclopentadiene were added dropwise at such a rate that the mixture continued to reflux gently. The mixture was stirred for one hour and cooled to room temperature. The clear solution was used for further syntheses.

On cooling of the solution to 5°C, K(MeCp) · DME crystallized as needles up to 5 cm in length. Solvent-free K(MeCp) (m.p. 254–255°C) of high purity was obtained by heating the crystals under high vacuum.

2.2. $Yb(C_5H_4CH_3)_3$

Anhydrous $YbCl_3$ (14.0 g, 50 mmol) was placed in a three-necked round bottom flask fitted with a reflux condenser, a nitrogen inlet, a funnel and a Teflon stirring bar. 300 ml of THF was added slowly with cooling. The cooling was stopped and 75.3 ml K(MeCp)/DME solution ($c = 2.19$ mol l^{-1}, 165 mmol) was added dropwise to the stirred solution. The occurrence of a stepwise reaction was indicated by changing colours: blue violet, dark red, and finally green. After about 5 h the solvent was removed *in vacuo*, leaving a mixture of $Yb(MeCp)_3$ · THF and KCl. The coordinated THF was removed by heating *in vacuo* at 50–60°C for 4 h. The remaining light green solid mixture was transferred to a sublimation apparatus and heated under high vacuum ($< 10^{-4}$ torr). $Yb(MeCp)_3$ started to sublime at 60°C. The temperature was raised slowly to 90–100°C, and 19.1 g (93%) of dark green plates of $Yb(C_5H_4CH_3)_3$ was obtained. M.p. 117°C, slow decomposition. Anal. Calc. for $YbC_{18}H_{21}$: Yb, 42.16. Found 42.2%. NMR-spectra in benzene-d_6, 297 K, halfwidths in parentheses: ^{1}H δ −131.2 (560 Hz, 6H, ring), −38.1 (620 Hz, 6H, ring) 58.9 (520 Hz, 9H, CH_3). ^{13}C δ −118.3 (205 Hz, C1), −80.3 (195 Hz) and −150.5 (220 Hz) C2/5 and C3/4 respectively, 47.2 (170 Hz, CH_3).

IR-spectra in Nujol/Hestaflon mulls between CsI plates: 3105m and 3075m (ν_{CH} ring); 2960sh, 2930ms and 2905sh (ν_{CH} CH_3); 2870m; 2740w; 1625w m br; 1590sh; 1550w m; 1495w m (ν_{CC}); 1450w m br (δ_{asCH} CH_3); 1385m (δ_{sCH} CH_3); 1355w (ν_{CC}); 1245w m (ν_{C-CH3}); 1068w m sh (δ_{CH} $\parallel$); 1030m s (ring breathing); 1015w m (δ_{C-CH3} wag); 932w m (δ_{CH} $\parallel$); 882m (δ_{CC} $\parallel$); 850s, 785sh, 765vs and 720sh (δ_{CH} $\perp$); 622m (δ_{CC} $\perp$); 325m (δ_{C-CH3} $\parallel$).

2.3. $Sc(C_5H_4CH_3)_3$

The scandium compound was prepared in the way described for the Yb analogue. The sublimation yielded 5.4 g (82%) orange-red crystals of base free $Sc(C_5H_4CH_3)_3$. Analysis. Calc. for $ScC_{18}H_{21}$: Sc, 15.92. Found 16.0%. NMR-spectra in toluene-d_8: ^{1}H (295 K) δ 5.99 (m, 6H, ring), 5.87 (m, 6H, ring), 1.88 (s, 9H, CH_3); ^{1}H (193 K) δ 5.93 (s, broad, ring), 5.75 (s, broad, ring), 1.87 (s, sharp, CH_3); ^{13}C (295 K) δ 122.0 (ring), 117.7 (ring), 130.7 (C1?), 19.4 (CH_3); ^{13}C (295 K) δ 122.5 (ring), 117.2 (ring), 128.8 (C1?), 19.5 (CH_3).

IR-spectra in Nujol/Hestaflon mulls between CsI plates: 3095m and 3075m (ν_{CH} ring); 2960sh, 2925s (ν_{CH} CH_3); 2860m s; 2735w; 1550w br; 1495m (ν_{CC}); 1460w br (δ_{asCH} CH_3); 1378m w (δ_{sCH} CH_3); 1355w (ν_{CC}); 1240w (ν_{C-CH3}); 1070sh, 1052m (δ_{CH} $\parallel$); 1040m s (ring breathing); 1018sh (δ_{C-CH3} wag); 933w m (δ_{CH} $\parallel$); 895sh, 887m br (δ_{CC} $\parallel$); 852s, 775vs and 720sh (δ_{CH} I); 688w; 673w m; 615m (δ_{CC} $\perp$); 375w, br; 325m (δ_{C-CH3} $\parallel$).

2.4. Determination of vapour pressure of $Yb(MeCp)_3$

Since $Yb(MeCp)_3$ may find use in Metal-Organic Vapour Phase Epitaxy (MOVPE) we determined the vapour pressure over the range 70 to 90°C using a method [18] similar to the "saturation method" described previously [19]. The vapour pressures were consistent with the equation $\log P[Pa] = -A/T[K] + B$, where $A = 5985 + 87$ and $B = 16.12 + 0.25$. The vapour pressure is compared with that of $YbCp_3$ [20] in Fig. 1.

3. Molecular mechanics calculations

The calculations were based on a simple model for π-complexes suggested by Timofeeva and coworkers [21]. According to this model the coordination geometry about the metal is governed by van der Waals interactions between the ligands. Ligands are regarded as rigid or semi-rigid; *i.e.* bond stretching, angle bending, and out of plane deformation energies are regarded as harmonic and assigned very large force constants. Metal to ligand bond distances are fixed, and the valence angles at the metal and the relative orientation of the ligands varied to determine the minimum energy geometry.

Van der Waals interaction energies between nonbonded atoms X, Y where X and Y are C or H were calculated from the equation $U_{vdW}(XY) = A\ \exp(-B\ r_{XY}) - C(r_{XY})^{-6}$ where r_{XY} is the interatomic distance. The values used for the constants A, B and C for CC and HH interactions, see Table 1, were taken from ref. 22. The constants for CH interactions were taken to be the geometric mean of the corresponding constants for CC and HH interactions [22]. Total van der Waals energies were obtained as sums over all nonbonded atom pairs.

The first calculations were performed on models with three pentahapto bonded rings, $M(\eta^5\text{-Cp})_3$. The length and stretch force constants assigned to C–C and C–H bonds, the bending force constants, and the out of plane force constants of the η^5-Cp rings are listed in Table 1. The planes of the ligand rings were assumed to be perpendicular to the M–Z vectors (Z = ring centre), and the conformational energies were calculated for fixed M–Z distances ranging from 210 to 250 pm in steps of 10 pm. The resulting conformational energies are displayed in Fig. 2. The energy is positive, and interligand interactions are strongly repulsive when M–Z is less than 225 pm. The calculations were then repeated with an M–Z distance equal to 217 pm, the mean M–Z distance in $[(\eta^5\text{-Cp})_2Sc(\mu\text{-Cl})_2]_2$ [23] and an M–Z force constant of 1000 N m^{-1}; see Table 2.

We then turned our attention to models with two η^5- and one η^1-Cp ring. The η^5 rings were treated as described in the preceding paragraphs. The η^1 ring was assigned an M–C(1) distance equal to the Sc–C(Me) bond distance in $(CH_3)Sc(\eta^5\text{-}C_5Me_5)_2$ [24] and a force constant of 700 N m^{-1}. The C(1) carbon atom was assumed to be tetrahedral. Other force constants of the η^1 ring are listed in Table 1. Energy minimization yielded the parameters listed in Table 2. It is seen that inter-ligand van der Waals interactions favour the $Sc(\eta^5\text{-Cp})_2(\eta^1\text{-Cp})$ model over the $Sc(\eta^5\text{-Cp})_3$ model by more than 40 kJ mol^{-1}.

TABLE 1. Force field parameters used for molecular mechanics calculations on MCp_3 and $M(MeCp)_3$.

	Bond distances/ pm	Force constants/ (N m^{-1})	
$M(\eta^5\text{-Cp})$ and $M(\eta^5\text{-MeCp})$ fragments:			
M–Z	217	1000	
C(Cp)–C(Cp)	142	700	
C(Cp)–H	109	700	
C(Cp)–C(Me)	151	700	
C(Cp)–Z	119	700	
$M(\eta^1\text{-Cp})$ and $M(\eta^1\text{-MeCp})$ fragments:			
M–C(sp^3)	224	700	
C=C	136	700	
C(sp^2)–C(sp^2)	144	700	
C(sp^2)–C(sp^3)	147	700	
	Bond angle/deg	Force constant/ (nN rad^{-1})	
$Z(\eta^5)MZ(\eta^5)$	120	0	
$C(\eta^5)Z(\eta^5)M$	90	25	
$Z(\eta^5)MC(sp^3)$	120	0	
C(Cp)C(Cp)C(Cp)	108	5	
C(Cp)C(Cp)C(Me)	126	5	
C(Cp)C(Cp)H	126	5	
C(Cp)C(Me)H	110	3	
MC(Cp)C(Cp)	109	5	
MC(Cp)H	109	3	
	Out of plane deformation	Force constant/ (nN rad^{-1})	
CCCC		25	
CCCH		25	
van der Waals parameters:			
	A/(kJ mol^{-1})	B/(10^{-5} pm^{-1})	C/(10^{10} pm^6 kJ mol^{-1})
CC	2358	3882	1178
HH	3623	4529	718

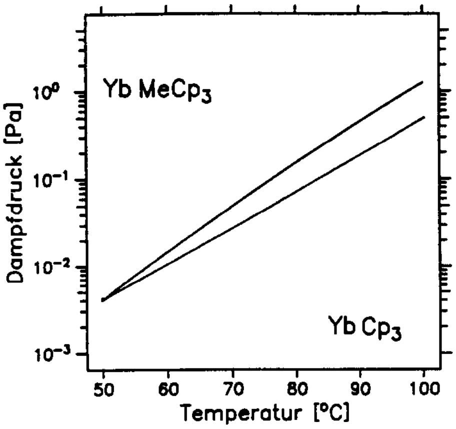

Fig. 1. The vapour pressures (in Pa) of $YbCp_3$ [20] (below) and $Yb(MeCp)_3$ (above) from 50 to 100°C.

Calculations on $M(MeCp)_3$ required the introduction of additional force constants to describe the MeCp ligand, as indicated in Table 1. Energy minimization of $M(\eta^5\text{-MeCp})_3$ models with M–Z = 217 pm was carried out with two or three methyl groups on the same side of the MZ_3 plane. Several minima with approximately the same energy but with different orientations of the three MeCp rings were located. The conformational

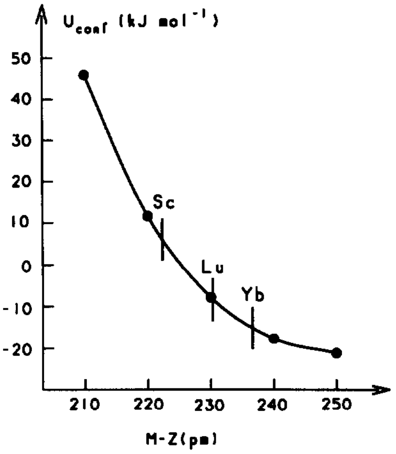

Fig. 2. The conformational energy, U_{conf}, obtained by molecular mechanics calculations on a $M(\eta^5\text{-}Cp)_3$ molecule as a function of the metal to ring centre distance M–Z. Vertical bars indicate the average $M\text{–}Z(\eta^5)$ distances in gaseous $M(MeCp)_3$ M = Sc or Yb (this work) and in crystalline $LuCp_3$ [3].

energy appears insensitive to the orientations of the η^5-MeCp rings as long as the angles between the C(Cp)–C(Me) bonds and the MZ_3 plane are larger than *ca.* 60°.

The conformational energies obtained by energy minimization of $M(\eta^5\text{-}MeCp)_3$ and $M(\eta^5\text{-}MeCp)_2(\eta^1\text{-}MeCp)$ models are listed in Table 2.

The determination of the structure of $Sc(MeCp)_3$ by gas phase electron diffraction shows that while two rings are η^5 bonded to the metal, the third is bonded in a less symmetric fashion, with a Sc–Z distance of 252 pm and an angle between the Sc–Z vector and the ring normal of 22(4)°. The final molecular mechanics calculations were therefore carried out with two η^5-MeCp ligands fixed at the experimental distance of 222 pm and the third ring at an $M\text{–}Z(\eta^x)$ distance of 252 pm. The angle between the $M\text{–}Z(\eta^x)$ vector and the ring normal (the tilt), the angles ∡ZScZ and the orientations of the three ligand rings with respect to rotation about the ring centres were varied during energy minimization.

TABLE 2. Conformational energies and main geometrical parameters obtained by molecular mechanics calculations on $ScCp_3$ and $Sc(MeCp)_3$

	$Sc(\eta^5\text{-}Cp)_3$	$Sc(\eta^5\text{-}Cp)_2(\eta^1\text{-}Cp)_2$
U_{conf} /(kJ mol^{-1})	20.0	−23.3
$Sc\text{–}Z(\eta^5)$/pm	218	217
$Sc\text{–}C(\eta^1)$/pm	–	224
$< Z(\eta^5)ScZ(\eta^5)$/deg	120	132
$< Z(\eta^5)ScC(\eta^1)$/deg	–	110
	$Sc(\eta^5\text{-}MeCp)_3$	$Sc(\eta^5\text{-}MeCp)_2(\eta^1\text{-}MeCp)_2$
U_{conf} /(kJ mol^{-1})	4.3	−37.8
$Sc\text{–}Z(\eta^5)$/pm	218	217
$Sc\text{–}C(\eta^1)$/pm	–	224
$< Z(\eta^5)ScZ(\eta^5)$/deg	120	132
$< Z(\eta^5)ScC(\eta^1)$/deg	–	109

Calculations were performed with the MOLBD 3 program [25] on an IBM PC/386 computer. Energy minimization was continued untill the root mean square atom deviations became less than 0.5 pm.

4. Gas electron diffraction

Data were recorded on a Balzers KDG-2 instrument with nozzle to plate distances of about 50 and 25 cm and nozzle temperatures of 160 ± 10° (Sc) and 165 ± 10° (Yb). Four photographic plates from each of the four sets were microphotometered and the optical densities processed by standard procedures [26].

Atomic scattering factors, f′(s) exp[i η(s)], were taken from standard sources [27*]. Backgrounds were drawn as polynomials to the difference between total experimental and calculated molecular intensities. The final modified molecular intensity curves calculated with increments $\Delta s = 2.00$ nm^{-1} extended from $s =$ 16.0 to 150.0 (50 cm plates) and from 40.0 to 300.0 nm^{-1} (25 cm) for Sc and from 16.0 to 150.0 and from 5.0 to 250.0 nm^{-1} for Yb. Experimental radial distribution curves calculated by Fourier inversion of modified molecular intensity curves are shown in Fig. 3.

Molecular structures were refined by least-squares calculations on the molecular intensity with diagonal matrices using a program written by Rankin [28].

Two main molecular models were considered. In Model I all three methylcyclopentadienyl rings are η^5 bonded to the metal as in the solid state structure of $Yb(MeCp)_3$ [13]. In model II two rings continue to be η^5 bonded, while the third is allowed to slip sideways into a mode of lower hapticity.

The molecules $M(MeCp)_3$ (M = Sc or Yb) are too large to allow complete structure determination by gas phase electron diffraction, and assumptions must be made in order to reduce the number of parameters that have to be refined. The following assumptions were made for both models: (i) the structures of the three MeCp ligands are equal; (ii) MeCp fragments could be constructed from cyclopentadienyl rings of C_{5h} symmetry by substituting a H atom by a methyl group (the methyl group was allowed to move out of the C_5H_4 plane); (iii) CCH_3 fragments are constrained to C_{3v} symmetry, with a CCH angle of 110° and one C–H bond pointing away from the metal. (iv) The MC_5 frame of each $M(\eta^5\text{-}MeCp)$ fragment has C_{5v} symme-

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* Reference number with an asterisk indicates a note in the list of references.

try. (v) The metal atom and the three ring centres (Z) are coplanar.

Considering model I, several refinements on both molecules made it clear that the data give no information on the orientation of the MeCp ligands with respect to rotation about the M–Z axes. The final refinements were therefore made on a model based on the solid state structure of Yb(η^5-MeCp)$_3$ [13] in which the methyl groups are found on the same side of the MZ$_3$ plane and the C(Cp)–C(Me) bonds are approximately perpendicular to the same plane (see Fig. 4a). The model was constrained to overall C_{3v} symmetry and described by four independent parameters; the M to ring distance M–Z; the mean C–C bond distance (the difference between the C(Cp)–C(Me) and C(Cp)–C(Cp) bond distances was fixed at 8.0 pm); the mean C–H bond distance (the difference between the C(Me)–H and C(Cp)–H bond distances was fixed at 2.0 pm); and finally the angle between the C(Cp)–C(Me) bond and the C$_5$ ring plane, which we denote by $\sphericalangle$C$_5$, C–C and define as positive when the methyl group is displaced *towards* the metal atom.

In Model II one of the three rings was allowed to slide sideways into a bonding mode of lower hapticity, η^x. The metal atom and the three ring centres remained coplanar. Both the C$_5$ ring planes and the C(Cp)–C(Me) bonds remained perpendicular to the MZ$_3$ plane. Even so, four independent structure parameters had to be added to those of Model I; the distance from the metal atom to the centre of the η^x bonded ring, M–Z(η^x) = P(5); the tilt of the η^x ring defined as the angle between the M–Z(η^x) vector, and the ring normal = P6; the angle defined by the metal atom at the apex and the centres of the two η^5 bonded rings, $\sphericalangle$Z(η^5)–M–Z(η^5) = P7; and finally the angle $\sphericalangle$Z(η^5)–M–Z(η^x) = P8, see Fig. 4b.

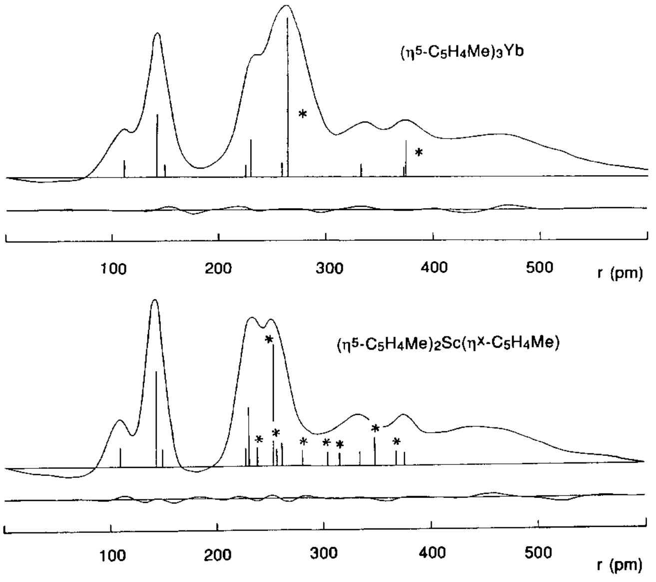

Fig. 3. Calculated (full lines) and experimental (dots) radial distribution curves for M(MeCp)$_3$ M = Yb or Sc, with difference curves shown below. MC distances (marked by *) and major intraligand CC and CH distances are indicated by bars of height approximately proportional to the area under the corresponding peak. Artificial damping constant k = 20 pm^2.

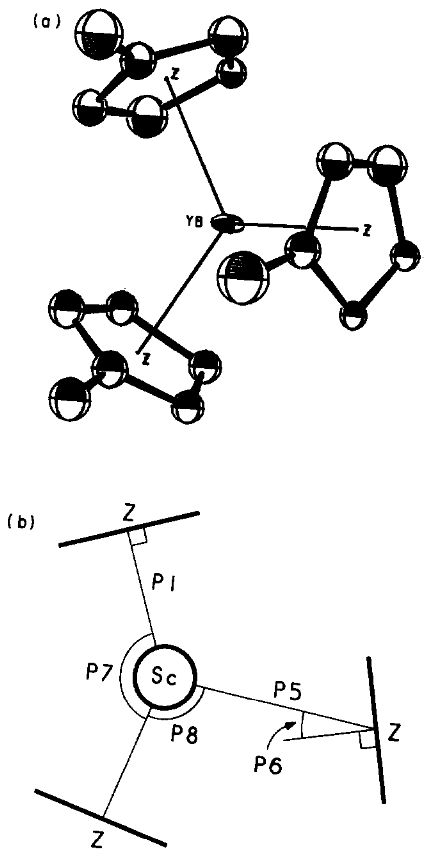

Fig. 4. Left; Molecular model of Yb(η^5-MeCp)$_3$ [13]. Right; schematic representation of molecular model of Sc(η^5-MeCp)$_2$(η^x-MeCp) with definition of the structure parameters P5 to P8.

5. Results and discussion

5.1. *Yb(MeCp)$_3$*

Refinement of models with three η^5-bonded rings led to satisfactory agreement between experimental and calculated molecular intensities. Refinement of models differing only in the orientation of the ligand rings with respect to rotation about the metal to ring axes M–Z led to equally good agreement, and indistinguishable values for structure parameters and vibrational amplitudes. The data clearly give no information on the orientation of the rings. This is hardly surprising, since the molecular mechanics calculations on

M(MeCp)$_3$ indicated the existence of several low energy conformers.

The final refinements were made on a model based on the crystal structure of Yb(MeCp)$_3$ [13]; in the solid state all the methyl groups are found at the same side of the MZ$_3$ plane and with all C(Cp)–C(Me) bonds approximately perpendicular to the same plane (see Fig. 4a). Refinements of a model of overall C_{3v} symmetry, Model I, yielded the structural parameters listed in Table 3. Experimental and calculated radial distribution curves are compared in Fig. 2.

Introduction of the four additional parameters needed to characterize a less symmetric Yb(η^5-MeCp)$_2$(η^x-MeCp) model, did not improve the fit, and the refinements failed to converge. We conclude that the three MeCp rings, which are already known to be η^5 bonded in the solid phase [13], remain η^5-bonded in the gas phase.

The mean Yb–C(η^5) bond distance in gaseous Yb(MeCp)$_3$ is not significantly different from that found by the low temperature X-ray diffraction study of the crystal, and indeed no difference was expected, in view of the length of the intermolecular Yb $\cdots$ C contacts in the solid phase. The ionic radius of tripositive Yb with CN = 9 is 104.2 pm, the ionic radius of dipositive Yb with CN = 6 is 102 pm [15] and the mean M–C bond distance in gaseous Yb(η^5-MeCp)$_3$ is found to be about 2 pm greater than the mean Yb–C bond distance in gaseous Yb(η^5-C$_5$Me$_5$)$_2$ [29].

5.2. *Sc(MeCp)$_3$*

The most significant contribution to the conformational energies obtained in molecular mechanics calculations, U_{conf}, is the sum of the van der Waals interactions between the C and H atoms at different ligands.

Figure 2 shows the conformational energy of a M(η^5-Cp)$_3$ molecule as a function of the metal to ring distance M–Z. For distances of less than 225 pm the conformational energy is positive and strongly repulsive. Comparison with experimental M–Z distances indicate that ligand–ligand repulsion is negligible in Yb(η^5-Cp)$_3$ and simple derivatives, but may be significant in Sc(η^5-Cp)$_3$ and derivatives.

TABLE 3. Structure parameters, P1 to P8, of Yb(MeCp)$_3$ and Sc(MeCp)$_3$ obtained by gas electron diffraction; bond distances, nonbonded distances and root-mean-square vibrational amplitudes (l). Distances and amplitudes in pm, angles in degrees. Estimated standard deviations in parentheses in units of the last digit [a]

	Yb(η^5-MeCp)$_3$ Symmetry C_{3v}		Sc(η^5-MeCp)$_2$(η^x-MeCp) Symmetry C_1	
P1 = M–Z(η^5)	236.6(6)		222.3(6)	
P2 = mean C–C	143.3(3)		143.4(2)	
P3 = mean C–H	107.6(15)		107.8(8)	
P4 = < C$_5$,C–C	–8(3)		–1(2)	
P5 = M–Z(η^x)	–		252(5)	
P6 = tilt	–		22(4)	
P7 = < Z(η^5)MZ(η^5)	[120]		139(7)	
P8 = < Z(η^5)MZ(η^x)	–		105(8)	
Bond distances and vibrational amplitudes:				
M–C(η^5)	265.5(7)	14.1(7)	253.0(6)	12.1(5)
M–C(η^x)	–	–	237 to 316	11 to 15
C(Cp)–C(Cp)	141.6(8)	4.6(8)	142.0(2)	5.0(4)
C(Cp)–C(Me)	151.6(8)	5.3(8)	150.0(2)	5.8(4)
C(Cp)–H	107(2)	8(2)	107(1)	[7.8]
C(Me)–H	109(2)	8(2)	109(1)	[7.8]
Nonbonded distances and vibrational amplitudes:				
M $\cdots$ C(Me)	373(3)	[20]	348 and 368	[18]
Intraligand distances:				
C $\cdots$ C	229.1(4)	5.8(8)	229.8(3)	[6.1]
C $\cdots$ C	260.8(6)	11(4)	260.3(3)	[6.6]
C $\cdots$ C	375.4(8)	[7]	375.4(4)	[7.0]
R-factors [b]				
50 cm	0.061			0.041
25 cm	0.091			0.069
Total	0.068			0.053

[a] Nonrefined parameters in square brackets. [b] $R = [\Sigma W(I_{\mathrm{obs}} - I_{\mathrm{calc}})^2/\Sigma W I_{\mathrm{obs}}^2]^{1/2}$

Calculations on an $M(\eta^5\text{-Cp})_3$ model with M–Z = 217 pm, corresponding to the experimental distance in $[(\eta^5\text{-Cp})_2Sc(\mu\text{-Cl})]_2$ [18], yields a conformational energy of 20 kJ mol^{-1}, with −23 kJ mol^{-1} for a model with two η^5- and one η^1-bonded ring. Van der Waals interactions between ligand rings thus favour a $M(\eta^5\text{-Cp})_2(\eta^1\text{-Cp})$ over a $M(\eta^5\text{-Cp})_3$ model by more than 40 kJ mol^{-1}.

Molecular mechanics calculations on $M(MeCp)_3$ add little to the picture. Introduction of the methyl groups does not lead to additional strain as long as the C(Cp)–C(Me) bonds form angles of 60° or more with the MZ_3 plane. A $M(\eta^5\text{-MeCp})_2(\eta^1\text{-MeCp})$ model is favoured over a $M(\eta^5\text{-MeCp})_3$ model by about 42 kJ mol^{-1}.

Least squares refinements of the structure of $Sc(MeCp)_3$ based on models with three η^5 ligand rings did not lead to satisfactory agreement between experimental and calculated molecular intensities. Refinements on Model I yielded an overall *R*-factor of 0.080 as compared to 0.068 for the Yb analogue. Since Sc is a much lighter element than Yb (atomic numbers 21 and 70, respectively) the better agreement is expected for $Sc(MeCp)_3$.

Refinements based on Model II which contains one ring bonded in a less symmetric η^x fashion, proceeded without difficulty to yield an overall *R*-factor of 0.053. The values obtained for the four additional structural parameters were significantly different from the values assigned to them in Model I. We conclude that gaseous $Sc(MeCp)_3$ contains not more than two η^5 bonded rings, with the third ring having a lower hapticity.

In solid $ScCp_3$ each Sc atom interacts with two bridging $\eta^1:\eta^1$ rings at M–C distances of 252 and 263 pm. The metal atom (or more precisely, the projection of the metal atom onto the ring plane) is *outside* the periphery of both rings. The angles between the Sc–C (bridge) bonds and the ring planes are 61 and 71°, respectively, reasonably close to the 55° expected for idealized η^1 interactions. In gaseous $Sc(MeCp)_3$ the bridging ring at the greater distance may be regarded as lost, while the nearest of the two rings has pivoted some 50° about an axis through the nearest C atom in the direction of an η^5 configuration. As a result the metal atom is now *inside* the ring periphery, 94(16) pm from the ring centre. Since we have been unable to determine the orientation of the ligand rings with respect to orientation about the ring centres, we are unable to give a unique set of distances from the metal atom to the C atoms in the η^x ring. In reality the η^x ring probably undergoes large amplitude libration about the ring centre.

Whatever the orientation of the ring, there will, however, always be two or three $Sc–C(\eta^x)$ distances shorter than 275 pm, *i.e.* no more than 10% longer than the $Sc–C(\eta^5)$ distances. We therefore choose to describe the structure as asymmetric polyhapto, $\eta^{2/3}$.

The crystal structure of $ScCp_3$ was determined at room temperature [2], and $M–C(\eta^5)$ distances are expected to be systematically shortened by 2 or 3 pm due to librational motion in the crystal. Comparison with the bond distances in gaseous $Sc(MeCp)_3$ indicate, therefore, that $Sc–C(\eta^5)$ bond distances are essentially unaffected by evaporation and geometrical rearrangement.

Finally molecular mechanics calculations carried out on a model of $Sc(\eta^5\text{-MeCp})_2(\eta^x\text{-MeCp})$ with the three M–Z distances fixed at their experimental values. The three angles $\sphericalangle ZScZ$ and the tilt of the η^x ring were varied to minimize the energy. The optimal values thus obtained were in qualitative agreement with the experimental values: tilt = 17°, $P7 = \sphericalangle Z(\eta^5)ScZ(\eta^5) = 127°$, and $P8 = \sphericalangle Z(\eta^5)ScZ(\eta^x) = 108°$. The conformational energy was 37 kJ mol^{-1} lower than for a $Sc(\eta^5\text{-MeCp})_3$ model, indicating that interligand strain has been eliminated.

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