The Structure of Pentachlorocyclopentadienylphenylmercury(II) in the Solid State and in Solution; the Effect of *X*-Ray Absorption and Crystal Decay on Molecular Geometry Parameters†

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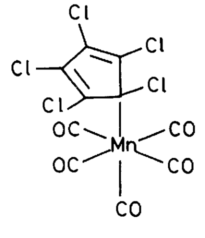
The structure of pentachlorocyclopentadienylphenylmercury(II), $Hg(C_5Cl_5)Ph$, has been determined by single-crystal *X*-ray diffraction. The cyclopentadienyl ring is σ bonded, and the ring and the vinylic chlorine atoms are essentially coplanar. The structure provides no evidence for secondary Cl→Hg bonding. The ^{13}C n.m.r. spectrum shows that, in solution, the cyclopentadienyl ring is fluxional; the sequence of mobilities is $Hg(C_5H_5)_2 > Hg(C_5H_5)Cl \sim Hg(C_5Cl_5)Ph > Hg(C_5Me_5)_2$.

Pentachlorocyclopentadienylphenylmercury(II), **(1)** was prepared by Wulfsberg and West in 1971.[1] The u.v., i.r., and n.q.r. spectra were interpreted to imply that the cyclopentadienyl ring was σ bonded,[2,3] with significant σ–π hyperconjugation between the phenyl–metal bond and the diene double bonds.[4] The splitting in the n.q.r. spectra, and its temperature dependence, were taken to indicate that secondary Cl→Hg bonding occurred,[3,4] probably intermolecularly.[5]

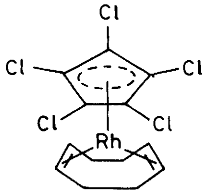
We have been using pentachlorocyclopentadienylphenylmercury as a photolytic source of $C_5Cl_5^{\bullet}$ radicals, and have taken the opportunity of determining its structure by single-crystal *X*-ray diffraction, and by ^{13}C n.m.r. spectroscopy of solutions. One σ- and one η^5-pentachlorocyclopentadienyl metallic compound have previously been reported [compounds (2)[6],‡ and (3)[7],§ respectively], but the only cyclopentadienylmercury compounds which have been studied by *X*-ray diffraction are the ylides (4; X = PPh_3[8] or SMe_2[9]), in which the mercury is four-co-ordinate.

$Cl_5C_5HgC_6H_5$

(1)



(2)



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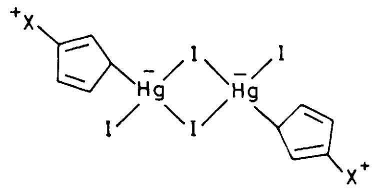

(4)

Discussion

X-Ray Diffraction.—The structure of the molecule is shown in Figure 1, and the bond lengths and angles are listed in Table 1. The cyclopentadienyl ring is σ bonded, at sp^3-hybridised carbon. The two bonds at the mercury centre are collinear [178.3(7)°] as they are in the vast majority of diorganomercury compounds.[10] The length of the Ph–Hg bond is 2.052(20) Å [*cf.* 2.085(7) Å in $HgPh_2$],[11] and the aromatic ring has the normal geometry, with mean carbon–carbon bond length of 1.418 Å. In diphenylmercury the C(*ipso*)–C(*para*) vector of the phenyl ring makes an angle of less than 180° with the Ph–Hg bond, so that the mercury atom is displaced by 0.1 Å from the mean plane of the phenyl ring;[11] no such distortion is apparent in pentachlorocyclopentadienylphenylmercury.

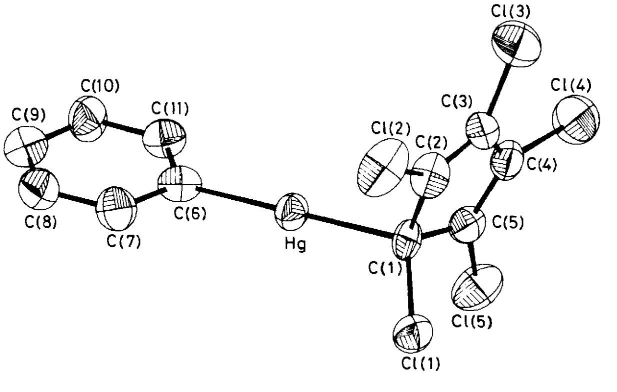

Figure 1. The structure of pentachlorocyclopentadienylphenylmercury(II). The thermal ellipsoids are drawn to include 50% probability (E. K. Davies, SNOOPI program for drawing molecular structures, University of Oxford, 1983)

The length of the $Hg–C_5Cl_5$ bond is 2.135(16) Å, typical for an alkyl–mercury bond. The cyclopentadienyl ring is essentially planar, with the carbon atoms deviating from the mean plane by not more than 0.046 Å. The four vinylic chlorine atoms lie close to the main plane of the ring, deviating by not more than four times the maximum deviation of the carbon atoms. The plane

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† *Supplementary data available* (No. SUP 56108, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, pp. xvii—xix. Structure factors are available from the editorial office.

‡ The cyclopentadienyl ring has two C–C bonds of 1.351 Å and three of 1.487 Å, and four C–Cl bonds of 1.693 Å and one of 1.798 Å.

§ The cyclopentadienyl ring has two short (1.399 Å) and three long (1.436 Å) C–C bonds, suggesting an appreciable contribution from a bonding model where the ring is bonded to the metal by two olefinic π bonds and one σ bond.

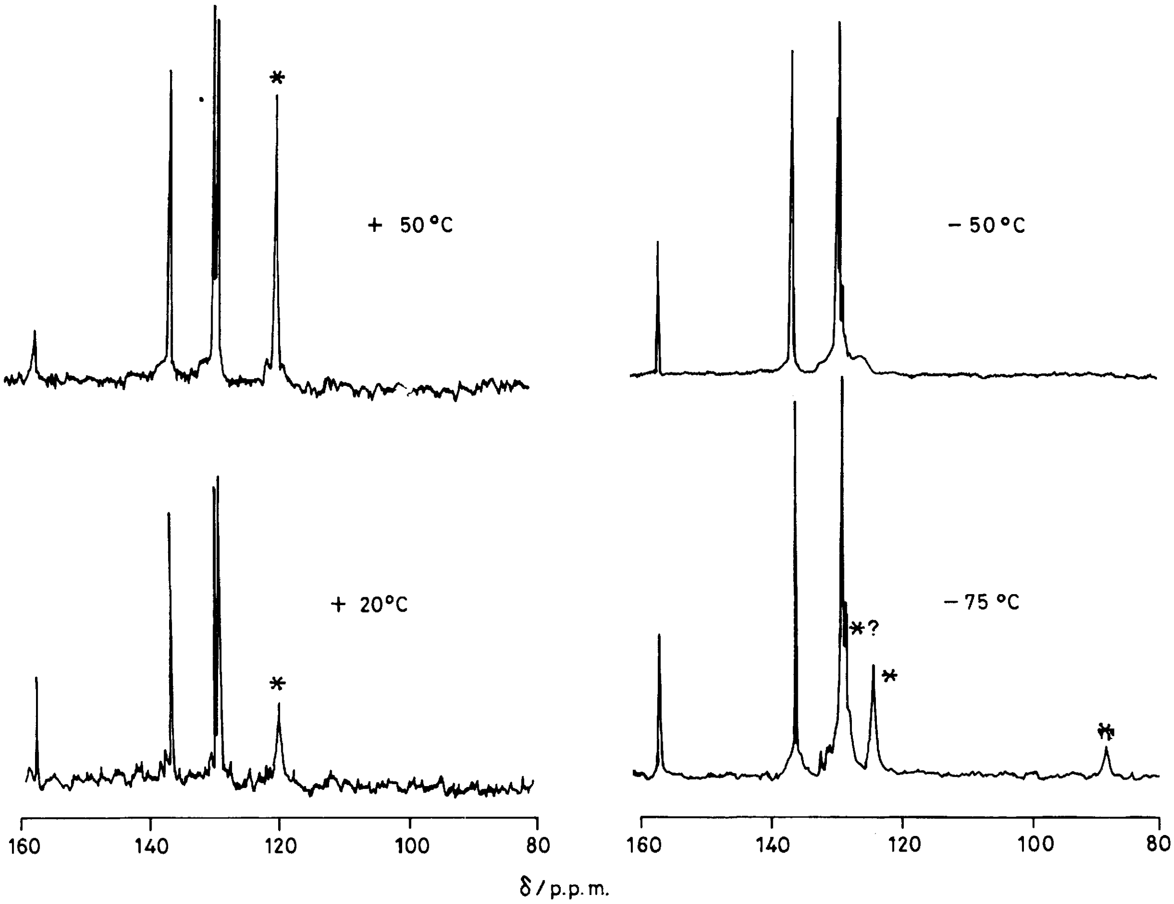

Figure 2. ^{13}C N.m.r. spectrum of $Hg(C_5Cl_5)Ph$ at different temperatures. Signals associated with the cyclopentadienyl ring are denoted by an asterisk. Details are given in the Experimental section

which bisects the cyclopentadienyl ring and Cl(1) makes an angle of 39.5° with the plane of the phenyl ring.

The nearest approach of mercury and chlorine atoms intramolecularly is 3.236 Å [to Cl(1)], and intermolecularly is 3.526 Å [to Cl(5)], whereas the sum of the van der Waals radii is 3.3—3.53 Å, and the covalent Hg–Cl bond length is *ca.* 2.30 Å.

None of the bond lengths or angles is distorted from the normal value (see Experimental section), and the structure does not appear to provide any evidence for Cl→Hg secondary bonding or σ–π hyperconjugation; indeed the single and double bonds in the cyclopentadienyl ring are more localised than those found in related compounds.[6,7] The alternative suggestion[3,12] that the splitting of the n.q.r. spectrum results from an electrostatic polarisation of the chlorine electrons by the mercury, rather than from a covalent interaction, merits further consideration. Secondary Cl–Hg bonding has also been invoked to account for the splitting in the n.q.r. spectra of pentachlorophenylmercury(II) derivatives, but the crystal structure of none of these compounds has been determined.[13]

^{13}C *N.M.R. Spectra.*—A number of studies have been reported of the proton n.m.r. spectra of cyclopentadienyl mercury compounds at variable temperatures.[14] For example, cyclopentadienylmercury chloride in tetrahydrofuran shows a singlet down to −27 °C; this then broadens until, at −100 °C, it shows one signal for CH(1) and one for CH(2,3,4,5). The ring is therefore fluxionally σ bonded.[15] On the other hand, dicyclopentadienylmercury shows a singlet spectrum down to −100 °C,[15] but bis(pentamethylcyclopentadienyl)mercury showed three separate signals even at room temperature.[16]

The only ^{13}C n.m.r. study appears to be that by Cotton *et al.*[17] Cyclopentadienylmercury chloride in 2-methyltetrahydrofuran at 22 °C showed a single ^{13}C signal at 116.3 p.p.m., which at −122 °C resolved into separate signals at 60.0 [C(1)], 128.1 [C(3) and C(4)], and 131.3 p.p.m. [C(2) and C(5)] (weighted mean 115.8 p.p.m). The sequence of broadening of the lines as the temperature was raised indicated a [1,5] sigmatropic mechanism for the rearrangement.

The ^{13}C n.m.r. spectra of our pentachlorocyclopentadienylphenylmercury in $CDCl_3$ and $CDCl_3$–CH_2Cl_2 are shown in Figure 2. By comparison with other phenylmercury compounds, the signals for the phenyl group can be identified at δ 129.2 [C(4)], 129.7 [C(3) and C(5)], 136.7 [C(2) and C(6)], and 157.7 p.p.m. [C(1)]. At +50 °C, the cyclopentadienyl ring shows a sharp singlet at 119.8 p.p.m. As the temperature is reduced, this signal broadens until it is no longer detectable between −20 and −50 °C, then at −75 °C it re-emerges as signals at 88.5 and 124.8 p.p.m. with relative areas *ca.* 1:3. The signal at higher field can be assigned to C(1); the larger signal at lower field may be assigned to C(2)—C(5), in which case the weighted mean would be 117.5 p.p.m., or more probably it is to be assigned to C(3) and C(4), the signal for C(2) and C(5) being obscured by that for the benzene ring at 129 p.p.m., in which case the weighted mean would be 119.2 p.p.m. In either case, the pentachlorocyclopentadienyl group is clearly fluxional, with a mobility lying in the sequence $Hg(C_5H_5)_2 > Hg(C_5H_5)Cl \sim Hg(C_5Cl_5)Ph > Hg(C_5Me_5)_2$.

Experimental

Pentachlorocyclopentadienylphenylmercury was prepared by treating phenylmercury hydroxide with pentachlorocyclopentadiene as described in ref. 2 (Found: C, 25.65; H, 1.00. Calc. for $C_{11}H_5Cl_5Hg$: C, 25.65; H, 1.00%).

Crystallography.—Crystal data. $C_{11}H_5Cl_5Hg$, $M = 514.9$, orthorhombic, $a = 6.849(1)$, $b = 10.570(2)$, $c = 19.220(2)$ Å, $U = 1\,391.4$ Å^3, space group $P2_12_12_1$, D_m not measured. $Z = 4$, $D_c = 2.46$ g cm^{-3}, $F(000) = 944$, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 115.3 cm^{-1}.

Data collection. Unit-cell parameters were determined and intensity data collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation and an ω–2θ scan procedure.[18] The crystal used was a tablet measuring 0.4 × 0.25 × 0.1 mm cut from a much larger plate. 2 469 Data ($1.5 \leqslant \theta \leqslant 30°$) were measured of which 2 343 were unique and 1 704 considered observed [$I \geqslant 1.5\sigma(I)$]. Three intensity-control reflections measured every hour during data collection showed a non-uniform reduction in diffracted intensity ranging from 10% (for two) to 22%, indicating the presence of anisotropic decay. A linear correction, with respect to time, was applied to the data using the lower estimate of intensity fall-off. A semi-empirical absorption correction using normalised and averaged ψ-scan measurements[19] from three reflections was applied to the data; the maximum and minimum transmission was 99.8 and 21.1%, respectively.

Structure solution and refinement. The heavy-atom method was used to solve the structure, and refinement of all non-hydrogen atoms with isotropic thermal parameters gave an R value ($\Sigma|\Delta F|/\Sigma|F_o|$) of 0.140 which reduced to 0.058 when anisotropic thermal parameters were used. However, inspection of the bond lengths showed that there were significant deviations both from idealised lengths and, more importantly, between assumed equivalent bonds in the pentachlorocyclopentadienyl and phenyl rings, see Table 2. Consequently, an empirical method of absorption correction (DIFABS[20]) was applied after refinement using semi-empirically 'corrected' data and isotropic thermal parameters for the atoms. Isotropic refinement with these data produced a residual of 0.072 which fell to 0.047 with the use of anisotropic thermal parameters. Furthermore, Table 2 shows that this correction produced a significant improvement in the bond lengths although the final R value was only lowered by 0.011. The sizeable reduction in the R factor from 0.140 to 0.072 with isotropic parameters indicates that previous anisotropic refinement had transferred these errors into the thermal parameters. The DIFABS method, in addition to providing a more rigorous absorption correction, may have removed systematic errors in the data due to anisotropic decay during data collection. The final full-matrix least-squares refinement was carried out with unit weights and omitted one strong low-angle reflection and gave $R = 0.044$ and $R' = (\Sigma|\Delta F|^2/\Sigma|F_o|^2)^{\frac{1}{2}} = 0.049$. The correct absolute configuration was determined since the inverted structure produced $R = 0.061$ and $R' = 0.067$.

All computations were made using the SHELX 76[21] program on a DEC VAX-11/750. Final bond lengths and angles are given in Table 1, and fractional atomic co-ordinates in Table 3.

^{13}C *N.M.R. Spectroscopy.*—Spectra were recorded using a Varian XL200 instrument. The pentachlorocyclopentadienylphenylmercury was dissolved in $CDCl_3$ for measurements down to −50 °C, or in a $CDCl_3$–CH_2Cl_2 mixture for measurements at lower temperatures, and chromium(III) acetylacetonate (0.03 mol dm^{-3}) was added to reduce the relaxation time of the carbon atoms of the cyclopentadienyl ring.

Table 1. Bond lengths (Å) and angles (°) for $Hg(C_5Cl_5)Ph$

C(1)–Hg	2.14(2)	C(6)–Hg	2.05(2)
C(1)–Cl(1)	1.76(2)	C(2)–Cl(2)	1.72(2)
C(3)–Cl(3)	1.72(2)	C(4)–Cl(4)	1.69(2)
C(5)–Cl(5)	1.72(2)	C(2)–C(1)	1.52(3)
C(5)–C(1)	1.50(3)	C(3)–C(2)	1.29(3)
C(4)–C(3)	1.45(3)	C(5)–C(4)	1.31(2)
C(7)–C(6)	1.41(2)	C(11)–C(6)	1.43(3)
C(8)–C(7)	1.41(3)	C(9)–C(8)	1.45(4)
C(10)–C(9)	1.35(3)	C(11)–C(10)	1.39(3)

C(6)–Hg–C(1)	178.3(7)	Cl(1)–C(1)–Hg	112.0(9)
C(2)–C(1)–Hg	106(1)	C(2)–C(1)–Cl(1)	114(1)
C(5)–C(1)–Hg	112(1)	C(5)–C(1)–Cl(1)	113(1)
C(5)–C(1)–C(2)	98(2)	C(1)–C(2)–Cl(2)	119(2)
C(3)–C(2)–Cl(2)	129(2)	C(3)–C(2)–C(1)	111(2)
C(2)–C(3)–Cl(3)	127(2)	C(4)–C(3)–Cl(3)	123(2)
C(4)–C(3)–C(2)	111(2)	C(3)–C(4)–Cl(4)	125(2)
C(5)–C(4)–Cl(4)	128(2)	C(5)–C(4)–C(3)	106(2)
C(1)–C(5)–Cl(5)	120(1)	C(4)–C(5)–Cl(5)	127(2)
C(4)–C(5)–C(1)	113(2)	C(7)–C(6)–Hg	120(1)
C(11)–C(6)–Hg	122(1)	C(11)–C(6)–C(7)	119(2)
C(8)–C(7)–C(6)	120(2)	C(9)–C(8)–C(7)	119(2)
C(10)–C(9)–C(8)	120(2)	C(11)–C(10)–C(9)	121(2)
C(10)–C(11)–C(6)	120(2)		

Table 2. Changes in selected bond lengths (Å) during the refinement procedure. The estimated standard deviations, where shown, are in parentheses

Systematic correction applied*	Type of thermal parameter	R factor	C(1)–C(2)	C(1)–C(5)	C(2)–C(3)	C(4)–C(5)	C(2)–Cl(2)	C(3)–Cl(3)	C(4)–Cl(4)	C(5)–Cl(5)
Isotropic decay	Isotropic	0.201	1.72	1.04	1.25	1.58	1.70	1.71	1.49	1.96
Semi-empirical absorption correction[19]	Isotropic	0.140	1.56	1.45	1.29	1.40	1.73	1.75	1.63	1.67
	Anisotropic	0.058	1.56(4)	1.42(4)	1.29(4)	1.40(4)	1.70(3)	1.71(3)	1.64(3)	1.72(3)
DIFABS empirical absorption correction[20]	Isotropic	0.072	1.51	1.49	1.28	1.28	1.75	1.74	1.67	1.73
	Anisotropic	0.047	1.51(3)	1.50(3)	1.30(3)	1.32(3)	1.74(2)	1.72(2)	1.68(2)	1.72(3)

* Corrections are applied on a cumulative basis down the Table.

Table 3. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Hg	304(1)	2 211(1)	1 625
Cl(1)	−1 778(10)	−388(5)	2 115(3)
Cl(2)	−4 611(8)	2 254(6)	2 261(3)
Cl(3)	−3 328(15)	3 368(7)	3 859(4)
Cl(4)	855(13)	1 949(6)	4 346(3)
Cl(5)	2 319(9)	18(6)	3 044(4)
C(1)	−973(25)	1 089(16)	2 428(8)
C(2)	−2 569(27)	1 894(19)	2 747(10)
C(3)	−2 089(30)	2 280(18)	3 359(10)
C(4)	−250(39)	1 719(16)	3 573(8)
C(5)	308(30)	990(15)	3 057(9)
C(6)	1 451(23)	3 305(16)	844(9)
C(7)	582(35)	3 285(19)	180(9)
C(8)	1 340(40)	4 048(21)	−356(11)
C(9)	3 089(40)	4 792(21)	−227(12)
C(10)	3 826(34)	4 862(20)	424(11)
C(11)	3 101(30)	4 106(18)	960(10)

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