

The crystal structure of dicyclopentadienylmercury[≠]

Bart Fischer, Guido P. M. van Mier, Jaap Boersma* and Gerard van Koten

University of Utrecht, Laboratory for Organic Chemistry, Dept. of Metal-mediated Synthesis, Padualaan 8, 3584 CH Utrecht, The Netherlands

and

Wilberth J. J. Smeets and Anthony L. Spek

Laboratory of Crystal and Structural Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

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Abstract. Crystals of dicyclopentadienylmercury, $\text{Hg}(\eta^1\text{-C}_5\text{H}_5)_2$, are tetragonal, space group $I4_1$, with unit cell dimensions $a = 17.347(5) \text{ \AA}$, $c = 5.810(3) \text{ \AA}$. The low-temperature (100 K) crystal structure was solved using *Patterson* methods and subsequent difference *Fourier* techniques. Anisotropic full-matrix least-squares refinement with 1832 observed reflections and 100 parameters converged at $R = 0.0385$. In the solid state, dicyclopentadienylmercury consists of monomeric units in which the two cyclopentadienyl rings are covalently bonded to the mercury atom.

Introduction

In the course of our investigations on properties and structures of cyclopentadienyl derivatives of Group 12 elements, we recently carried out X-ray analyses of dicyclopentadienylzinc and of the pyridine complex of dicyclopentadienylcadmium, $\text{CdCp}_2 \cdot 2\text{py}^{1,2,3}$.

It is surprising that, although the structure of dicyclopentadienylmercury has been the subject of extensive discussions, no crystal structure determination has been published. Since its first synthesis by *Wilkinson* and *Piper*⁴, a σ -bonded structure has repeatedly been proposed on the basis of spectral properties and chemical behaviour⁴⁻¹⁰. This structure has been questioned by other authors, who have suggested a π -bonded sandwich structure¹¹⁻¹⁸ or allylic and ionic bonding¹⁹⁻²¹.

In 1976, the first crystal structure of a cyclopentadienylmercury compound appeared, *i.e.* that of $[(\text{C}_6\text{H}_5)_3\text{PC}_5\text{H}_4\text{HgI}_2]_2^{22,23}$, which can be readily obtained from the reaction of triphenylphosphonium cyclopentadienylide with mercuric iodide. In the solid state, this compound contains a σ -bonded cyclopentadienyl ring. Pulsed-NMR studies were used by *Campbell* et al. in 1976 to determine the structure of the compound in the solid

state and a σ -bonded structure was proposed²⁴. More recently, in 1980, another X-ray crystal structure was published by *Holy* et al., again of a cyclopentadienylide, *i.e.* $[(\text{CH}_3)_2\text{SC}_5\text{H}_4\text{HgI}_2]_2^{25}$. This structure is similar to that of the phosphine derivative in that it also contains a σ -bonded cyclopentadienyl ring.

The present paper describes the low-temperature crystal-structure determination of dicyclopentadienylmercury.

Results and discussion

Dicyclopentadienylmercury is readily prepared by a modification of the procedure described by *Lorberth*²⁶, *viz.* by reaction of bis[bis(trimethylsilyl)amino]mercury and cyclopentadiene. Although it is not air sensitive in the solid state, it slowly decomposes upon exposure to light. Contrary to comments in the literature²⁷, good quality single crystals can be formed by slow crystallization from non-polar or weakly polar solvents. The best results were obtained by recrystallization from toluene at -30° in the dark. The single crystals thus obtained decomposed on exposure to light but were stable for months when stored at -30° in the dark. At that temperature, decomposition by light was also considerably retarded. Upon exposure to X-rays, however, the crystals were found to decay in the dark within a few hours at room temperature. At a temperature of 100 K, we were able to collect a satisfactory X-ray data set with no significant decay.

[≠] Dedicated to Professor Dr. *G. J. M. van der Kerk* on the occasion of his 75th birthday.

* To whom correspondence should be addressed.

The compound crystallizes in the tetragonal space group $I4_1$, with eight molecules in the unit cell (see Fig. 1). Final atomic coordinates are listed in Table I.

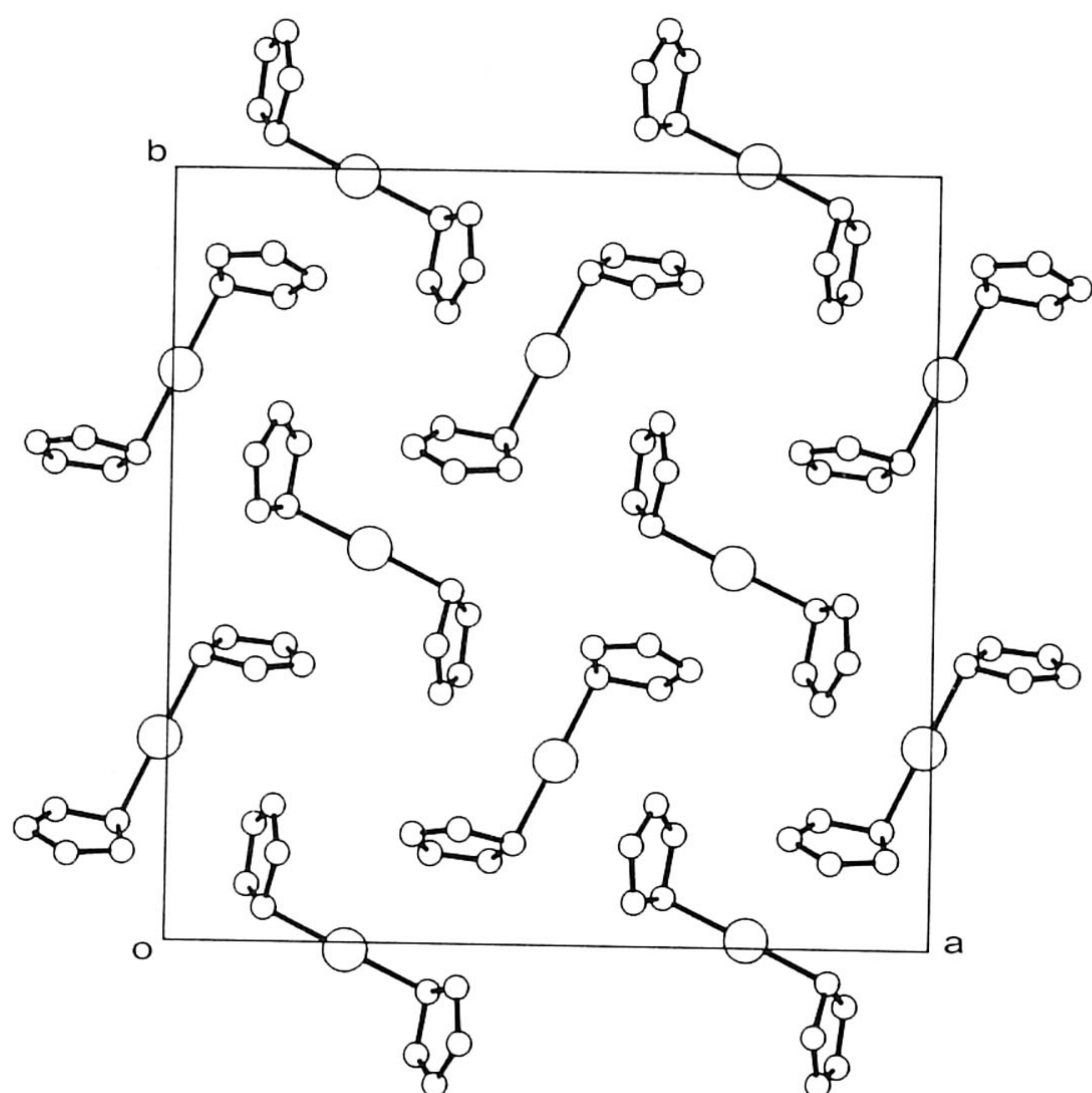


Fig. 1. Projection of the crystal structure of the title compound down the c -axis.

Table I Fractional atomic coordinates and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses for $HgCp_2$.

Atom	x	y	z	$U_{eq} (\text{\AA}^2)^a$
Hg	0.26190(3)	0.50976(3)	0.500(-)	0.0169(2)
C(1)	0.3697(7)	0.4558(8)	0.560(3)	0.020(4)
C(2)	0.3925(8)	0.4259(9)	0.334(3)	0.026(5)
C(3)	0.3835(8)	0.3479(8)	0.332(3)	0.023(4)
C(4)	0.3587(7)	0.3242(8)	0.555(3)	0.025(5)
C(5)	0.3520(8)	0.385(1)	0.694(3)	0.031(5)
C(6)	0.1525(8)	0.5630(8)	0.426(3)	0.021(4)
C(7)	0.1147(8)	0.5569(8)	0.656(3)	0.021(4)
C(8)	0.1104(7)	0.6295(7)	0.750(4)	0.021(4)
C(9)	0.1419(7)	0.6829(8)	0.590(3)	0.017(4)
C(10)	0.1663(8)	0.6446(8)	0.394(3)	0.018(4)

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

The structure consists of monomeric dicyclopentadienylmercury units (see Fig. 2). In these units, two cyclopentadienyl groups are monohapto bonded to mercury. The carbon-mercury-carbon unit in $Hg(\eta^1-C_5H_5)_2$ is linear [$\angle C(1)-Hg-C(6) = 177.9(6)^\circ$], which is in line with sp -hybridization of the Hg centre. The mercury-ring distances are 2.12(1) \AA to C(1) and 2.15(1) \AA to C(6), the other Hg-C distances being much larger. Although each unit is monomeric, there are some rather short intramolecular Hg-C contacts between carbon atoms C(4), C(9) and C(10) and mercury atoms of neighbouring molecules (see Fig. 1). However, these distances, of which the shortest is 3.17(1) \AA , are too large to assume any significant bonding interaction.

Both cyclopentadienyl rings possess appreciable diene character. This diene character had already been established in solution by Mink et al., who carried out reactions of $HgCp_2$ with dienophiles such as maleic anhydride and

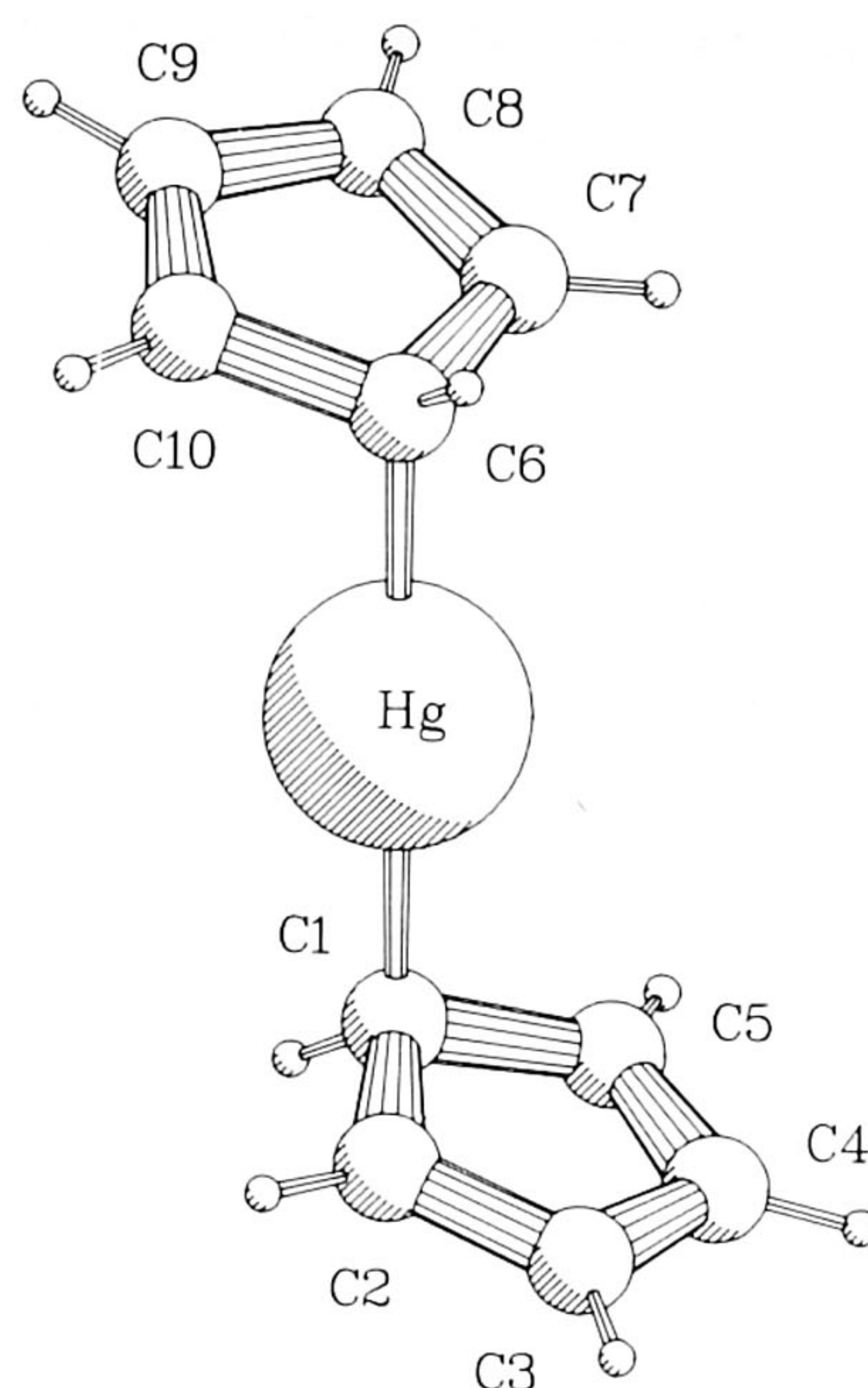


Fig. 2. Pluto drawing of $HgCp_2$ with the adopted atom numbering.

found products resulting from *Diels-Alder* reactions²⁸. The two cyclopentadienyl rings are nearly coparallel, the two ring planes subtending an angle of only $8.0(8)^\circ$.

An indication of the nature of the metal-cyclopentadienyl-ring interaction is given by the variations in the C-C bond distances within the rings. In the case of ionic M-Cp interactions, these differences are very small [see the values for ionic $NaCp(TMEDA)$ and $CdCp_2 \cdot 2py$ in Table II] and increase with the percentage of covalent character. In $HgCp_2$, these distances range from 1.33(2) to 1.49(2) \AA for one ring and from 1.37(2) to 1.49(2) \AA for the other. They alternate even more than in cyclopentadiene²⁹ and silylcyclopentadiene³⁰, indicating a predominant covalent character of the mercury-cyclopentadienyl bonds. Another indication of the covalent nature of the ring-metal interaction is the value of the angle between the ring-plane and the metal-carbon bond. The angles of both ring planes with the Hg-C bond vector are almost the same, *i.e.* $68.1(6)^\circ$ and $68.0(6)^\circ$, which is very close to the value found in covalent SiH_3Cp , *i.e.* 65.6° . In the ionic compounds $NaCp(TMEDA)$ and $CdCp_2 \cdot 2py$, these angles are close to 90° , *i.e.* 88 and 80.1° , respectively (see Table II).

Finally, the covalent character of the mercury-ring interaction is also supported by the values of the bond angles within the cyclopentadienyl rings. Whereas in the case of a pure ionic ring-metal interaction, the negative charge would be fully delocalized and the five-membered ring would be a perfect pentagon with angles of 108° , a more covalent metal-ring interaction would cause the carbon atom bonded to the metal to become sp^3 hybridized, resulting in deviations from 108° . The bond angles of $HgCp_2$ indeed show deviations from 108° which are comparable to those observed in cyclopentadiene itself and in silylcyclopentadiene (see Table II).

Concluding remarks

Although over the last three decades some controversial ideas concerning the structure of $HgCp_2$ have been published, most authors favoured a monohapto bonding mode. The determination of the X-ray crystal structure of $HgCp_2$ proves that this, at least in the solid state, is the correct interpretation. The structure of $HgCp_2$ is quite different

Table II Structural parameters for cyclopentadienyl-metal (MCp_n) compounds.

Compound	Angle C_5-M ($^\circ$) ^a	C-C distances (\AA)					Ref.
		C(1)-C(2)	C(2)-C(3)	C(3)-C(4)	C(4)-C(5)	C(5)-C(1)	
CpH	(54) ^b	1.506	1.352	1.474	(1.352)	(1.506)	29
SiH ₃ Cp	65.6	1.500	1.389	1.43	(1.389)	(1.500)	30
NaCp · TMEDA	88	1.387	1.375	1.402	1.366	1.376	41
CdCp ₂ · 2py	80.1(1) ^c	1.408(6)	1.371(6)	1.382(7)	1.365(7)	1.407(6)	2,3
	80.9(3) ^d	1.373(8)	1.341(8)	1.356(8)	1.331(8)	1.387(7)	
HgCp ₂	68.1(6) ^c	1.47(2)	1.36(2)	1.43(2)	1.33(2)	1.49(2)	
	68.0(6) ^d	1.49(2)	1.37(2)	1.42(2)	1.38(2)	1.45(2)	

	Ring bond angles ($^\circ$)				
	C(1)-C(2)-C(3)	C(2)-C(3)-C(4)	C(3)-C(4)-C(5)	C(4)-C(5)-C(1)	C(5)-C(1)-C(2)
CpH	109.3	109.3	109.3	109.3	102.8
SiH ₃ Cp	112.0	107.9	107.9	112.0	100.3
NaCp · TMEDA	107.3	108.5	108.2	106.8	109.1
CdCp ₂ · 2py	108.8(4) ^c	107.7(4)	109.3(4)	108.1(4)	106.1(4)
	108.8(4) ^d	107.8(5)	109.3(5)	108.0(5)	106.1(4)
HgCp ₂	109(1) ^c	108(1)	110(1)	109(1)	103(1)
	108(1) ^d	108(2)	110(1)	108(1)	105(1)

^a Angle between the least-squares plane of the cyclopentadienyl group and the metal-carbon bond vector. ^b Calculated. ^c Values belong to C(1)-C(5). ^d Values belong to C(6)-C(10).

from that of ZnCp₂. We found the latter to be a coordination polymer consisting of infinite chains of zinc atoms separated by bridging cyclopentadienyl groups. In addition, each zinc atom carries a terminal cyclopentadienyl unit. Although the structure of CdCp₂ is still unknown, we presume that it too is a coordination polymer^{2,3}.

So far, HgCp₂ stands alone as a main-Group metallocene in which the metal atom is *sp* hybridized and does not expand its coordination sphere. A similar retention of *sp* hybridization was observed in ω -functionally substituted organozinc compounds of the type Zn[(CH₂)₃X]₂, where X = OCH₃, SCH₃, N(CH₃)₂ or P(C₆H₅)₂^{31,32}. In these cases, the zinc atom attains four-coordination by intramolecular complexation, but the carbon-zinc-carbon bond angle remains close to 180°, indicating *sp*-*2p* hybridization.

Experimental

General remarks

All experiments were carried out under dry, oxygen-free nitrogen. Solvents were distilled from sodium benzophenone ketyl prior to use. Solutions were handled with syringes. ¹H NMR spectra were recorded on a Bruker AW-80 spectrometer.

Bis[bis(trimethylsilyl)amino]mercury

To a solution of 55 g (341 mmol) of NH(SiMe₃)₂ in 250 ml of diethyl ether was slowly added 213 ml of a 1.6-molar solution of BuLi in hexane (340 mmol). After stirring for 2 h, 113 ml of a 1.5-molar solution of dry HgCl₂ (169 mmol) in diethyl ether was added slowly. After an additional 2 h of stirring, the solution was decanted from the precipitated LiCl and the precipitate was washed once with 100 ml of diethyl ether. The combined ether fractions were evaporated *in vacuo* and the residue was vacuum distilled to yield 70.5 g (135 mmol, 80%) of colourless Hg[N(SiMe₃)₂]₂ (bp. 78°, 0.15 mm Hg).

Dicyclopentadienylmercury

HgCp₂ was prepared by a modification of the method described by Lorberth²⁶. To a solution of 26.9 g (52.8 mmol) of Hg[N(SiMe₃)₂]₂ in 100 ml of diethyl ether, 20 ml (242 mmol) of freshly cracked cyclopentadiene was added at room temperature. On addition, the

mixture immediately turned yellow. After stirring for 30 min, the mixture was stored at -30° with exclusion of light. Yellow crystals were deposited and crystallization was complete after two days. The yellow solution was decanted from the crystals and the product was dried *in vacuo* to yield 14.6 g (44.8 mmol, 85%) of pure, yellow, crystalline HgCp₂; m.p. 83-85°C. ¹H NMR (80 MHz, C₆D₆): δ 5.84 (s, 10H, ²J¹⁹⁹Hg 66 Hz). During and after work-up, HgCp₂ must be protected from light as much as possible.

Structure determination and refinement of HgCp₂

A yellow rod-shaped crystal suitable for an X-ray study was mounted on a glass fibre and transferred into the cold nitrogen stream of the low-temperature unit of an Enraf-Nonius CAD-4F diffractometer for data collection. Crystal data and details of the

Table III Crystal data and details of the structure analysis.

(a) Crystal data (100 K)	
Formula	C ₁₀ H ₁₀ Hg
Mol. wt.	330.78
Crystal system	tetragonal
Space group	I4 ₁ (Nr. 80)
<i>a</i> , <i>c</i> (\AA)	17.347(5), 5.810(3)
<i>V</i> (\AA^3)	1748(1)
<i>Z</i>	8
<i>D</i> _{calc} (g · cm ⁻³)	2.514
<i>F</i> (000)	1200
μ (MoK α) (cm ⁻¹)	175.4
Crystal size (mm)	1.10 × 0.29 × 0.29
(b) Data collection (100 K)	
θ_{\min} , θ_{\max} ($^\circ$)	1.66, 27.49
Radiation	MoK α (Zr-filtered), 0.71073 \AA
$\omega/2\theta$ scan ($^\circ$)	0.60 + 0.35 tan θ
Horizontal and vert. aperture (mm)	3.0, 4.0
Distance crystal to detector (mm)	173
Reference reflections	8 2 2; 0 10 2
Total data	2362
Total unique data	2022
Observed data (<i>I</i> > 2.5 σ (<i>I</i>))	1832
(c) Refinement	
No. of refined parameters	100 (9 × 11 + 1 = 100)
Weighting scheme	$w = 1.0/\sigma^2(F)$
Final R, wR, S	0.0385, 0.0456, 2.33
(Δ/σ) _{av} in final cycle	0.003

structure determination are given in Table III. Unit-cell parameters were determined from a least-squares treatment of the setting angles of 24 reflections in the range $10.1^\circ < \theta < 14.0^\circ$. The I-centred tetragonal unit cell was checked for the presence of higher lattice symmetry³³. Data were collected for two *Bijvoet* related octants (*hkl* and *hk̄l*): $0 \leq h \leq 22$; $0 \leq k \leq 22$; $-7 \leq l \leq 7$. The intensity data were corrected for *Lp*, *absorption* (Gaussian integration: grid $16 \times 16 \times 16$; max. and min. correction: 85.70 and 17.42) and for a linear decay of 0.6% during the $5\frac{1}{2}$ hours of X-ray exposure time. Standard deviations based on counting statistics were increased according to an analysis of the excess variance of the two reference reflections $\sigma^2(I) = \sigma_{cs}^2(I) + (0.021I)^2$ ³⁴. Space group *I4*₁ was determined from the systematic extinctions (*hkl*: $h + k + l \neq 2n$; $4n$) and discriminated from *I4*₁22 during the structure determination process.

The Hg atom was found by *Patterson* methods (SHELXS86³⁵). Other non-hydrogen atoms were located from subsequent difference *Fourier* maps. Refinement was carried out by full-matrix least-squares techniques (on *F*) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced on calculated positions (C–H = 0.96 Å) and included in the refinement riding on their carrier atom with one common isotropic thermal parameter. H atoms of the Hg-bonded carbon atoms C(1) and C(6) were placed on *sp*³ positions. The alternative absolute structure was rejected, based on the resulting higher *R* values (*R* = 0.0396; *wR* = 0.0467) obtained by refinement with negative anomalous-dispersion factor (*-if*). Weights were introduced in the final refinement cycles. Convergence was reached at *R* = 0.0385. A final difference-*Fourier* synthesis reveals maximal densities of 2.34 e/Å³ near Hg, which are interpreted as residual absorption artefacts. Neutral-atom scattering factors were taken from ref. 36 and corrected for anomalous dispersion³⁷. Data collection was carried out using a modified CAD-4F software package³⁸. All calculations were performed with the SHELX76³⁹ and the EUCLID packages⁴⁰ (geometrical calculations and illustrations) on the CDC Cyber-855 of the University of Utrecht.

Supplementary data (anisotropic thermal parameters, all H-atom parameters, complete lists of bond lengths, bond angles, torsion angles and a listing of observed and calculated structure factor amplitudes) are available from one of the authors (A.L.S.).

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