Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

The structure of dicyclopentadienylmercury

J. MINK, L. BURSICS and G. VÉGH
Institute of Isotopes of the Hungarian Academy of Sciences, Budapest (Hungary)

(Received October 11th, 1971)

The structure of dicyclopentadienylmercury has been the subject of extensive discussions. Thus, on the basis of spectral properties and chemical behaviour a σ-structure has been repeatedly proposed [1-7], although this has been questioned by other authors who have suggested the possible existence of a π-bonded sandwich structure [8-15]. In addition π-allylic [17] and ionic [16,18] bonding have also been considered.

The σ-structure was first proposed by Wilkinson and Piper [1,2]. In the present paper we wish to report some evidence in favour of this structure resulting from a comparison of the infrared spectra of 'light' and perdeutero dicyclopentadienylmercury, and also on the basis of preparative results.

As shown in Table 1, four CD stretching vibrational bands are found in the infrared spectra of $Hg(C_5D_5)_2$ when the latter is dissolved in CS_2 or CCl_4. The observed frequency shifts ν(CH)/ν(CD) are in good agreement with those found (between 1.328 and 1.359) for C_5H_6 and C_5D_6 [19,20]. As a rule, frequencies above 3000 cm^{-1} may be assigned to the 'olefinic' CH stretching vibrations. A medium band observed in the infrared spectrum of $Hg(C_5H_5)$ at 2970 cm^{-1} has been interpreted in a variety of ways. It may be treated as a combination band, perhaps 1530 + 1427 cm^{-1}, as well as a fundamental. If it were a combination band, it should have appeared in the infrared spectrum of $Hg(C_5D_5)_2$ at 1518 + 1380 = 2898 cm^{-1} which is considerably higher than the observed band at 2218 cm^{-1}. For this reason the suggestion that this band is a fundamental appears to be more reasonable, and in this study we have assigned the bands at 2970 cm^{-1} and 2218 cm^{-1} to fundamental 'aliphatic' CH and CD stretching vibrations (Table 1).

TABLE 1

VIBRATIONAL FREQUENCIES OF $Hg(C_5H_5)_2$ AND $Hg(C_5D_5)_2$ DEMONSTRATING THE EXISTENCE OF A σ-BONDED DIENE STRUCTURE

Frequency (cm^{-1})[a]			
$Hg(C_5H_5)_2$[b]	$Hg(C_5D_5)_2$	ν(CH)/ν(CD)	Assignment
3090 s	2318 s	1.333	'Olefinic' CH (CD) stretching
3088 s	(2318 s)	1.332	
3076 (sh)	2285 s	1.346	
3040 (sh)	2275 (sh)	1.336	
2970 m	2218 w	1.339	'Aliphatic' CH (CD) stretching
1530 vw	1518 vw		C=C stretching
348 s	329 s		CHg stretching

[a] Band intensities: s, strong; m, medium; sh, shoulder; w, weak; vw, very weak. [b] Frequencies from Ref. 6.

As expected the C=C stretching bands appear to be only slightly sensitive to deuterium substitution (Table 1).

The vibrational data of a series of dialkylmercury compounds and some perdeutero derivatives have been extensively investigated previously [21-25], and the CHg asymmetric stretching frequencies of some of these compounds are shown in Table 2. If a simplified calculation is performed on a linear XY_2 model, assuming that the alkyl groups are single atoms, their estimated 'effective' masses may be determined. In this way a value of 1.7 mdyn/Å may be obtained for the CHg stretching force constant in cyclopentadienylmercury derivatives (Table 2). This value appears to be very reasonable in comparison with those obtained for methyl [25] and ethyl [23] mercury compounds and it may be related to the unusually low frequencies of the CHg stretching vibrations and the weakness of the CHg bond in $Hg(C_5H_5)_2$ and $Hg(C_5D_5)_2$.

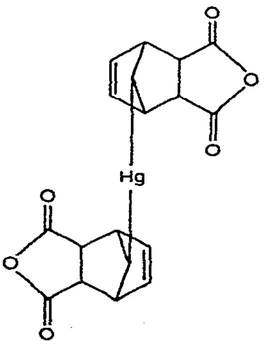
TABLE 2

CARBON–MERCURY ASYMMETRIC STRETCHING FREQUENCIES FOR LIGHT AND HEAVY HgR_2

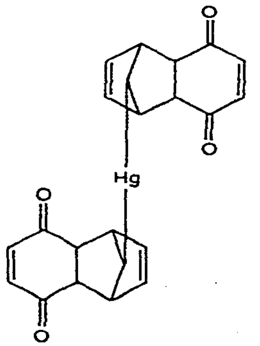
Compound	CHgC asymmetric stretching frequency (cm^{-1})	Alkyl 'effective' masses (a.m.u.)	CHg stretching force constant (mdyn/Å)	References
$Hg(CH_3)_2$	546.3 (gas)	16	2.40	22, 25
$Hg(CD_3)_2$	497.7 (gas)	19		
$Hg(C_2H_5)_2$	517.5 (gas)	20	2.65	21, 23, 25
$Hg(C_2D_5)_2$	465.3 (gas)	25		
$Hg(C_5H_5)_2$	348 (solution)	31	1.70	
$Hg(C_5D_5)_2$	329 (solution)	36		

It should also be mentioned that the out-of-plane skeletal bending frequency in C_5H_6 was found to occur at 350 cm^{-1}, but that in C_5D_6 this band would be expected to appear at a considerably lower frequency, at about 270 cm^{-1} [20]

Reactions with dienophiles may be considered as further evidence of the diene structure of dicyclopentadienylmercury. A Diels–Alder reaction with maleic anhydride in ether–dioxane solution at room temperature resulted in a white crystalline product. This compound has been prepared earlier by Wilkinson and Piper[1]. From its principal infrared bands and a chemical analysis (Found: C, 40.96; H, 2.77; Hg, 37.75; O, 18.32. $C_{18}H_{14}HgO_6$



(I)



(II)

calcd.: C, 41.02; H, 2.68; Hg, 38.07; O, 18.22 %) it is reasonable to assume that the probable structure for this compound may be witten as (I). A crystalline dark brown adduct was also formed with *p*-benzoquinone in dioxane solution after gentle heating. The structure of this compound on the basis of infrared spectra and chemical analysis (Found: C, 46.96; H, 3.41; Hg, 37.22; O, 11.93. $C_{22}H_{18}HgO_4$ calcd.: C, 48.29; H, 3.32; Hg, 36.67; O, 11.70 %) is most probably as depicted in (II).

From the observed frequency shifts of infrared bands of $Hg(C_5H_5)_2$ and $Hg(C_5D_5)_2$ and on the basis of chemical behaviour, it may be concluded that the assignment first proposed by Maslowsky and Nakamato[6] which demonstrated the existence of a σ-bonded diene structure seems to be correct.

REFERENCES

1 G. Wilkinson and T.S. Piper, *J. Inorg. Nucl. Chem.*, 2 (1956) 32.
2 T.S. Piper and G.W. Wilkinson, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.
3 J.M. Birmingham, *Advan. Organometal. Chem.*, 2 (1964) 365.
4 H.P. Fritz, *Advan. Organometal. Chem.*, 1 (1964) 239.
5 E. Maslowsky and K. Nakamato, *Chem. Commun.*, 5 (1968) 257.
6 E. Maslowsky and K. Nakamato, *Inorg. Chem.*, 8 (1969) 1108.
7 W. Kitching and B.F. Hegarty, *J. Organometal. Chem.*, 16 (1969) P49.
8 E.O. Fisher and H.P. Hofman, *Angew. Chem.*, 69 (1957) 639.
9 S. Shibata, L.S. Bartell and R.M. Gavin, *J. Chem. Phys.*, 47 (1964) 717.
10 A.N. Nesmeyanov, G.G. Dvoryantseva, N.S. Kochetkova, R.B. Materikova and Yu.N. Sheinker, *Doklady Akad. Nauk SSSR*, 159 (1964) 847.
11 G.G. Dvoryantseva, K.F. Turchin, R.B. Materikova, Yu.N. Sheinker and A.N. Nesmeyanov, *Doklady Akad. Nauk SSSR*, 166 (1966) 868.
12 A.N. Nesmeyanov, R.B. Materikova, E.I. Fedin, N.S. Kochetkova, P.V. Petrovsky, L.A. Fedorov and E.V. Leonova, *Doklady Akad. Nauk SSSR*, 177 (1967) 586.
13 A.N. Nesmeyanov, L.A. Fedorov, R.B. Materikova, E.I. Fedin and N.S. Kochetkova, *Tetrahedron Lett.*, (1968) 3753.
14 A.N. Nesmeyanov, L.A. Fedorov, R.B. Materikova, E.I. Fedin and N.S. Kochetkova, *Chem. Commun.*, (1969) 105.
15 A. Almenningen, A. Haaland and T. Matzfeld, *J. Organometal. Chem.*, 7 (1967) 97.
16 F.A. Cotton and L.T. Reynolds, *J. Amer. Chem. Soc.*, 80 (1958) 269.
17 F.A. Cotton, *Proc. 9th Robert A. Welch Foundation Conf. Chem. Res. (Organometallic Compounds)*, Nov. 15–17, 1965, p. 213.
18 M.D. Rausch and J.M. Birmingham, *Ann. N. Y. Acad. Sci.*, 125 (1965) 43.
19 H.P. Fritz and L. Schäfer, *Spectrochim. Acta*, 21 (1965) 211.
20 K.E. Blick, J.W. deHaan and K. Niedenzu, *Spectrochim. Acta*, 26A (1970) 2319.
21 J. Mink and Yu.A. Pentin, *J. Organometal. Chem.*, 23 (1970) 293.
22 J. Mink and L. Nemes, *J. Organometal. Chem.*, 28 (1971) C39.
24 J. Mink, Yu.A. Pentin, G. Végh and L. Bursics, *5th Intern. Conf. Organometal. Chem.*, Moscow, 1971. Abstr. Paper 143.
25 J. Mink and Yu.A. Pentin, *Vibrational spectra and molecular structure of organomercury compounds. (Advances in Phys. Chem.)*, Moscow State Univ. Vol. 7, 1972, in the press.