Journal of Organometallic Chemistry, 212 (1981) C35—C38
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PENTAKIS(METHOXYCARBONYL)CYCLOPENTADIENE, A STRONG ORGANIC ACID: CRYSTAL AND MOLECULAR STRUCTURES OF $HC_5(CO_2Me)_5$ AND $Li[C_5(CO_2Me)_5](H_2O)$

MICHAEL I. BRUCE*, JENNIFER K. WALTON, MICHAEL L. WILLIAMS,

Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia 5001 (Australia)

BRIAN W. SKELTON and ALLAN H. WHITE*

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009 (Australia)

(Received February 17th, 1981)

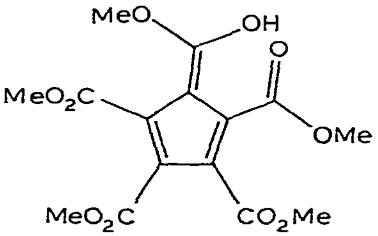
Summary

Contrary to some previously depicted structures, the proton in $HC_5(CO_2Me)_5$ is bonded to two oxygens rather than to carbon; the lithium ion in $Li[C_5(CO_2Me)_5](H_2O)$ is tetrahedrally coordinated by two carbonyl oxygens from one C_5 anion, one from a second anion, and a water molecule.

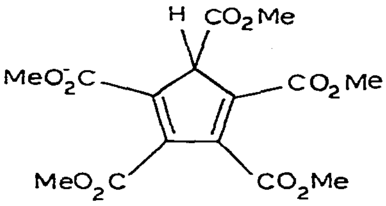
Pentakis(methoxycarbonyl)cyclopentadiene, $HC_5(CO_2Me)_5$(Hcpp) (I) is a strong organic acid, which was first described in 1942 [1,2]. Solutions in D_2O exhibit a sharp singlet for the methyl protons at δ 4.43 ppm, while in C_6D_6, a broad signal at δ 3.50 ppm is observed. The strongly electron-withdrawing nature of the CO_2Me groups suggests that the structure of this diene is better represented as the fulvene derivative (Ia), in agreement with the earlier interpretations of the IR and ^1H NMR spectra of 1,2,3,4-tetrakis(methoxycarbonyl)-cyclopentadiene [3], and of the related di- and tri-carbaldehydes [4]. However, structure Ib, resembling that of the parent cyclopenta-1,3-diene, has often been depicted, and we note that alkylation of the silver(I) derivative occurs at a ring carbon [2,5]. To resolve this structural question, and as a preliminary to a comparison of several transition metal derivatives with their hydrocarbon analogues, we have determined the structure of crystalline I, and find that it corresponds to Ia.

Crystal data: $C_{15}H_{16}O_{10}$, M = 356.3, Triclinic, space group $P\bar{1}$, a 10.944(4), b 10.891(4), c 7.743(3) Å, α 91.32(3), β 101.28(3), γ 113.91(3)°, U 821.9(5) Å^3, Z = 2, D_m 1.44(1), D_c 1.44 g cm^{-3}. 2167 reflections were measured to θ_{max} 25°. Current R value 0.037. Figure 1 shows the molecular

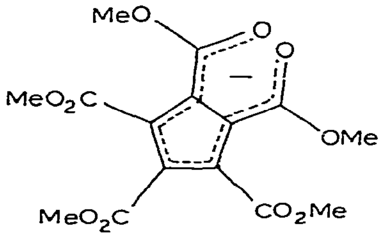
0022-328X/81/0000—0000/$02.50, © 1981, Elsevier Sequoia S.A.



(Ia)



(Ib)



(II)

structure. Significant features include the location of all hydrogen atoms, and the asymmetric C_5 ring, both of which indicate that the acidic hydrogen is placed between two of the carbonyl oxygens of adjacent CO_2Me substituents ($O \cdots H$, 1.12(4), 1.32(4) Å; angle $O \cdots H \cdots O$, 171(3)°). Within the C_5 ring, four C—C distances are essentially equal, (1.396(3)—1.410(5) Å) while the fifth, the bond between the carbons bearing the CO_2Me groups associated with the acidic hydrogen, is significantly longer, at 1.453(5) Å. It is not possible for all five CO_2Me groups to be coplanar with the C_5 ring simultaneously; in I, groups 2, 4 and 5 are almost coplanar, while groups 1 and 3 are almost normal to the ring plane.

Unlike the derivatives of the parent hydrocarbon, the white salts of diene 1, $M(cpp)_n$, with alkali metal ($n = 1$) or alkaline earth cations ($n = 2$), are air-stable and soluble in water. Solutions in D_2O behave as 1/1 or 1/2 electrolytes, respectively, and the CO_2Me resonance of all derivatives examined occurs between δ 4.3—4.4 ppm. The mass spectra of the alkali metal salts show unusual ion association phenomena, with the highest m/e ion corresponding to $[M_2(cpp)]^+$; the spectra of mixtures of these salts contain ions $[MM'(cpp)]^+$. The structure of lithium salt has been determined.

Crystal data: $Li[C_5(CO_2Me)_5](H_2O)$, $C_{15}H_{17}LiO_{11}$, $M = 380.2$, Monoclinic, space group $P2_1/c$, $a = 7.990(2)$, $b = 21.890(3)$, $c = 11.170(3)$ Å, $\beta = 109.99(2)°$, $U = 1835.8(7)$ Å, $Z = 4$, $D_m = 1.37(1)$, $D_c = 1.38$ g cm^{-3}. 3260 reflections were measured to θ_{max} 25°. Current R value 0.044. The molecular structure is shown in Fig. 2. The lithium atom is tetrahedrally coordinated by two oxygens from adjacent CO_2Me groups of one cpp anion, one from a CO_2Me group of a second cpp anion, and the fourth position is occupied by a water molecule. The remaining CO_2Me groups which are not involved in bonding to lithium are normal to the C_5 plane. As found with I, the

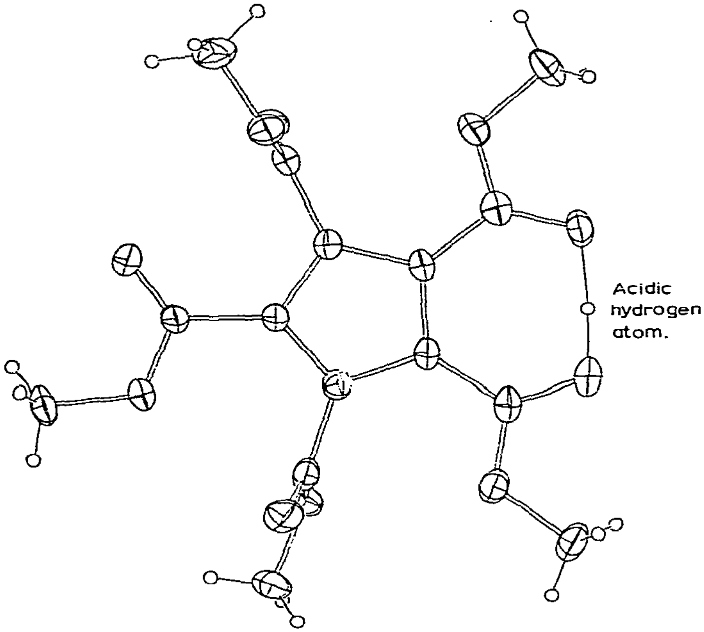


Fig. 1. A single molecule of the free acid I, showing non-hydrogen atoms with 20% thermal ellipsoids and hydrogen atoms with arbitrary radius of 0.1 Å.

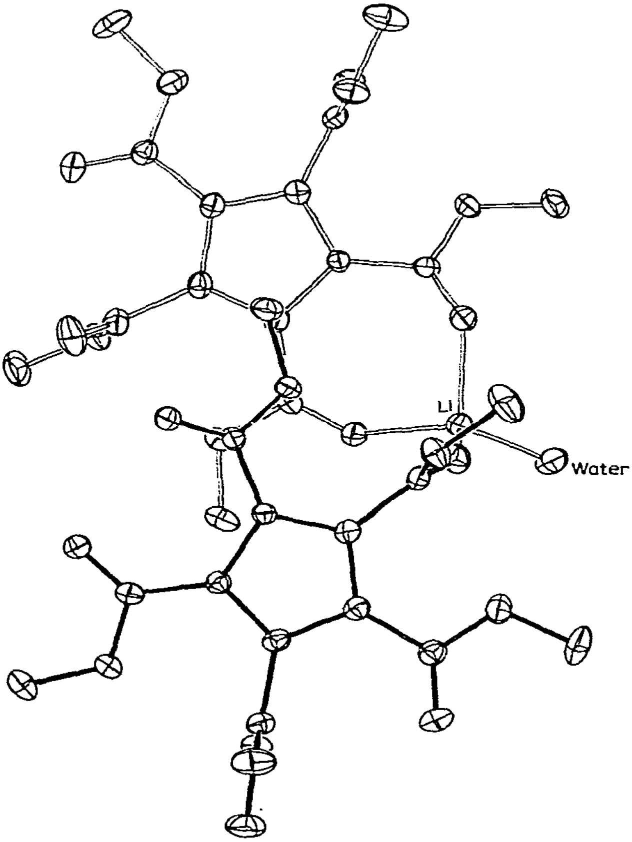


Fig. 2. Fragment of the structure of $Li[C_5(CO_2Me)_5](H_2O)$ showing the association of the lithium atom with two anions and the water molecule.

bond between the two ring carbons bearing the two CO_2Me groups coordinated to lithium is considerably longer (1.447(5) Å) than the other four ring carbon bonds (1.393(5)—1.415(5) Å), showing that the anion has the delocalised structure II (one of five tautomers), rather than the isomeric form with the negative charge localised within the C_5 ring. This contrasts with the behaviour of the $[C_5H_5]^-$ anion, which even in its ionic derivatives, is found associated with the metal ion in a symmetrical manner.

We thank the Australian Research Grants Committee for support of this work. Copies of the atomic coordinates for the two crystal structures determined have been lodged with the Cambridge Crystallographic Data File.

References

1 O. Diels, Chem. Ber., 75 (1942) 1452.
2 E. LeGoff and R.B. LaCount, J. Org. Chem., 29 (1964) 423; R.C. Cookson, J.B. Henstock, J. Hudec and B.R.D. Whitear, J. Chem. Soc. C, (1967), 1986.
3 G. Seitz, Angew. Chem., 78 (1966) 680; Angew. Chem. Internat. Ed., 5 (1966) 670.
4 K. Hafner, H.E.A. Kramer, H. Musso, G. Ploss and G. Schulz, Chem. Ber., 97 (1964) 2066.
5 R.W. Hoffmann and J. Backes, Chem. Ber., 109 (1976) 1928.