Crystal Structure of Ferrocenophanyllithium: Absence of an Intramolecular C–H···$^-$C Hydrogen Bond

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The previously inferred intramolecular [C–H–C]$^-$ hydrogen bond in ferrocenophanyllithium from ^{1}H NMR chemical shifts in solution is found to be absent in the solid state.

We report results of an X-ray crystallographic study of ferrocenophanyllithium **1** (Fig. 1), prepared from [1.1]ferrocenophane by abstraction of the C-1 proton by *n*-butyllithium and crystallized from a 2,5-dimethyltetrahydrofuran (DMTHF)–hexane solution. Crystals of **1**† are dark-red needles that decompose rapidly when isolated at ambient temperature, even under inert atmosphere. Special low temperature handling techniques[2] have therefore been employed for isolating, selecting and mounting crystals of **1** for X-ray analysis.

Previously, Mueller-Westerhoff and coworkers have, based on solution ^{1}H NMR studies of the title compound and derivatives in tetrahydrofuran, claimed the 'first evidence for the existence of C–H–C hydrogen bonds'.[3] Now, the solid state structure shows a long distance between the *endo* bridge CH proton [H(122)] and the bridge C$^-$ [C(1)], indicating the absence of an intramolecular hydrogen bond in the solid state. The crystal structure also shows that **1** is monomeric and that the lithium atom is only coordinated to two carbons and two ether molecules. Compound **1**, which undergoes a rapid intramolecular 1,12-proton transfer in solution, as indicated in Scheme 1,[4,5] appears to be a key intermediate in the elucidation of mechanisms of alkali metallations.[6]

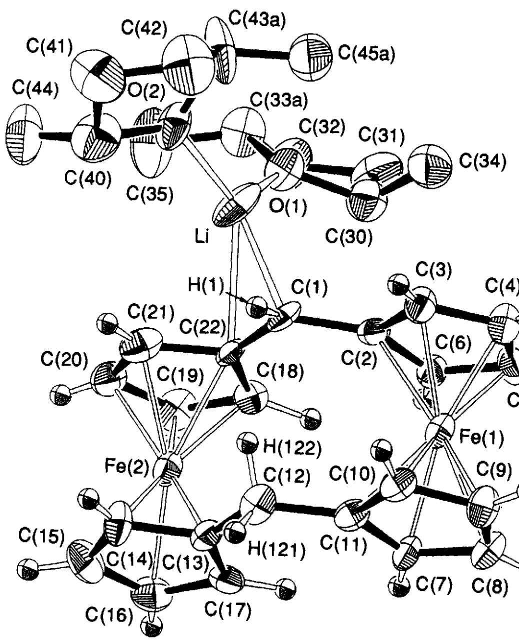
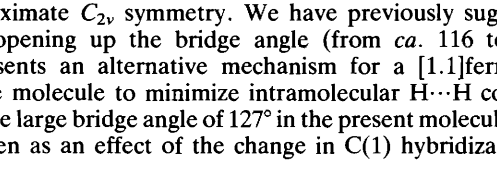


Fig. 1 ORTEP[1] drawing of $C_{34}H_{43}Fe_2LiO_2$, showing the crystallographic numbering. Only the *trans*-dimethyltetrahydrofuran isomers are shown of the disordered solvent molecules which are coordinated to the lithium atom. The solvent hydrogens are omitted for reasons of clarity and disorder. The ferrocenophanyl hydrogens are given the same numeral as the carbon to which they are bonded. Selected bond distances (Å) and angles (°) are as follows: Fe(1)–Fe(2) 4.955(2), Fe(1)–C(2) 2.136(7), Fe(1)–C(4) 2.015(8), Fe(1)–C(9) 2.034(8), Fe(1)–C(11) 2.048(8), Fe(2)–C(13) 2.076(8), Fe(2)–C(15) 2.041(8), Fe(2)–C(20) 2.016(8), Fe(2)–C(22) 2.137(7), Li–O(1) 1.88(2), Li–O(2) 1.94(1), Li–C(1) 2.18(2), Li–C(22) 2.37(2), C(1)–C(2) 1.46(1), C(1)–C(22) 1.43(1), C(2)–C(3) 1.42(1), C(7)–C(11) 1.38(1), C(11)–C(12) 1.52(1), C(12)–C(13) 1.50(1), C(13)–C(14) 1.43(1), C(19)–C(20) 1.39(1), C(21)–C(22) 1.44(1), C(1)–H(1) 0.91(7); C(2)–C(1)–C(22) 127.0(6), C(2)–C(1)–Li 121.3(7), C(2)–C(1)–H(1) 114(4), C(22)–C(1)–H(1) 111(4), Li–C(1)–H(1) 95(4), C(1)–Li–C(22) 36.2(3), C(1)–Li–O(1) 120.1(7), C(1)–Li–O(2) 118.3(7), C(22)–Li–O(1) 109.1(6), C(22)–Li–O(2) 129.2(8), O(1)–Li–O(2) 118.6(8), C(11)–C(12)–C(13) 121.7(6). Selected non-bonded intramolecular contacts (Å) are: H(1)–H(122) 2.39, H(6)–H(18) 2.05, H(7)–H(17) 2.05.

The structural aspects of organolithium complexes and reagents are currently receiving widespread attention and the nature of the Li–C bond is subject to experimental as well as theoretical studies.[7] To our knowledge, **1** represents the first example of a mono-lithiated monomeric organolithium compound which exhibits the lithium atom bridging two carbon atoms (*cf.* Fig. 1). The Li–C(1) bond distance is 2.18(2) Å, which is somewhat, but not significantly longer, than the average Li–C distance (2.16 Å) for monomeric trisolvated alkyllithium compounds.[7] On the other hand, the Li–C(1) distance is significantly shorter than the literature average value of 2.29 Å for sp^3-hybridized carbon atoms bonded to bridging lithium atoms.[7] The longer Li–C(22) (2.37 Å) interaction resembles that seen in dilithiated substituted *ortho*-xylenes,[8] where the lithium atom bridges a benzylic carbon and the C(3) ring carbon. In the present compound, however, bridging takes place from C(1) to the nearest cyclopentadienyl ring carbon [C(22)], which creates the remarkably acute C(1)–Li–C(22) angle of 36.2(3)°. With this in mind, the Li atom can be considered to be distorted tetrahedrally coordinated with Li being 0.20 Å away from the O(1)–O(2)–C(1) trigonal plane. The Li–O bond distances are normal. The two lithium-coordinated DMTHF molecules are disordered, but the disorder can be resolved in a structure model which contains two pairs of solvent molecules, each pair being made up of one *trans* and one *cis* isomer. Refinement of the atom site occupancy indicates a *trans*/*cis* ratio of 1.5; Fig. 1 displays only the *trans* isomers.

The conformational status of a [1.1]ferrocenophane molecule is best described by the four angles in Fig. 2.[9] For **1**, the *twist* angles are 1.8 and 2.4°, the *rotation* angles are 0.5 and 0.8°, the *tilt* angles are 1.2 and 1.6°, and the *bridge* angles are 127.0(6)° [C(2)–C(1)–C(22)] and 121.7(6)° [C(11)–C(12)–C(13)]. As can be seen from the low values of the twist and tilt angles, the four cyclopentadienyl rings are almost coplanar, and in this respect **1** bears a strong resemblance to one of the polymorphs of the parent [1.1]ferrocenophane,[9] which has an approximate C_{2v} symmetry. We have previously suggested[9] that opening up the bridge angle (from *ca.* 116 to 122°) represents an alternative mechanism for a [1.1]ferrocenophane molecule to minimize intramolecular H···H contacts, but the large bridge angle of 127° in the present molecule could be seen as an effect of the change in C(1) hybridization on



Scheme 1

formation of the lithium–carbon bonds. The shortest intermolecular hydrogen contacts in **1** are in the range of 2.3–2.7 Å, and packing effects cannot be disregarded when discussing small conformational changes in flexible molecules like **1**. The Fe(1)–Fe(2) intramolecular distance is 4.955(2) Å, and there is no indication of any metal–metal interaction.

Already the long C(1)–C(12) distance [3.48(1) Å] indicates the possibility of only a weak C(1)···H(122)–C(12) interaction at the most. The non-linear arrangement of C(1)···H(122)–C(12) indicates an even weaker interaction. The C(1)–H(122) distance is 2.7 Å. This is a much longer distance than the sum of the covalent bond radii of H and C, which is 1.07 Å, but close to the sum of the exposed radii (van der Waals radii) of H (1.1 Å) and C (1.7 Å) atoms covalently bonded in molecules, *i.e.* 2.8 Å.[10] This distance similarity indicates that any attraction between CH and $^-$C has not been strong enough to result in bond shortening. Thus, any hydrogen bond seems to be absent in the solid state. However, it could be argued that a carbanionic carbon should have a larger exposed radius than is normally used, since it is negatively charged. Therefore, it might be more reasonable to assume about 20% larger van der Waals radius for the carbanionic carbon, *i.e.* 2.0 Å. Using this radius the sum of the exposed radii is 3.1 Å. This distance is 0.4 Å longer than the experimental C(1)–H(122) distance and could be an indication of a weak CH···$^-$C interaction. However, the shorter experimental distance could be due to the ferrocenophane structure forcing the groups to adopt the observed distance rather than being the consequence of a weak attraction.

In comparison, the O–H distance in the H_2O–H_2O hydrogen bond is about 1.0 Å, but the intermolecular O···H distance is only 1.76 Å, much less than the 2.6 Å expected from summing the two van der Waals radii, but still larger than the covalent distance 1.0 Å.[11]

It is interesting to note that the three covalent bonds to C(1) are not in a single plane, showing that C(1) is not sp^2 hybridized. The hybridization is close to neither sp^2 nor sp^3. The angle between the C(1)–H(1) bond and the plane defined by C(1), C(2) and C(22) is 30°. Furthermore, the 'anion' hybrid is pointing away from H(122).

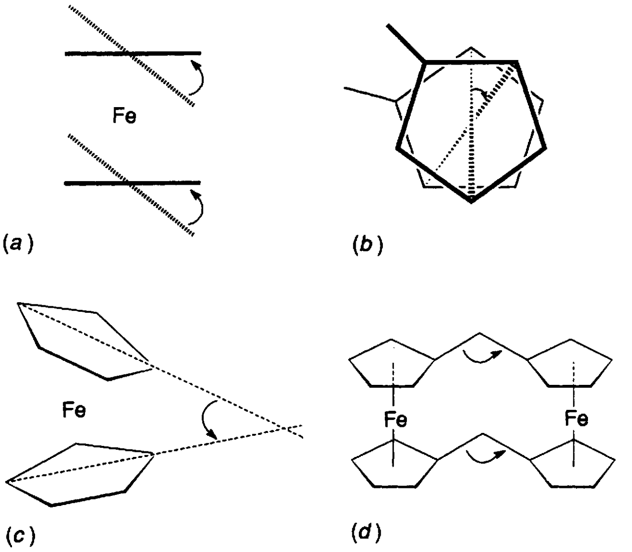


Fig. 2 Showing (*a*) the twist angle, (*b*) the rotation angle, (*c*) the tilt angle and (*d*) the bridge angle

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† *Crystal data* for **1**, $C_{34}H_{43}Fe_2LiO_2$, $a = 11.319(3)$, $b = 11.551(4)$, $c = 11.272(3)$ Å, $\alpha = 93.95(2)$, $\beta = 95.74(2)$, $\gamma = 96.22(3)°$, $V = 1453.1(7)$ Å^3; $D_c = 1.377$ g cm^{-3}, μ(Mo-Kα) = 10.26 cm^{-1} ($\lambda = 0.71069$ Å), $M = 602.35$, triclinic, space group $P\bar{1}$, $Z = 2$. The intensity data were collected at 150 K with ω-2θ scans and $2\theta = 50.0°$. The structure was solved by direct methods and the hydrogens were located from a difference map. Full-matrix least-squares refinement on 2552 [$I > 3\sigma(I)$] reflections and 367 variables resulted in $R = 0.049$ ($R_w = 0.058$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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