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Weak hydrogen bonds from Cp donors to C≡C acceptors

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Abstract

In the crystal structure of **1**, pairs of molecules are connected by mutual C(Cp)–H···C≡C interactions which have a geometry suggestive of weak hydrogen bonding ($1 = [(\eta^5\text{-}C_5H_5)Fe(C{\equiv}C - C_7H_7\text{-}2,4,6)(CO)_2]$). The shorter of the H···C distances is only 2.59 Å, which is a distance that is typically observed for C–H···C≡C hydrogen bonds of stronger donors such as chloroform or alkyne groups. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Hydrogen bonds; Cp donors; C≡C acceptors

1. Introduction

In contrast to the vast literature on hydrogen bonding in organic and biological structures, the hydrogen bond functions of organometallic compounds have only recently come into the focus of structural research. This is largely due to the circumstance that the periphery of typical organometallic compounds is not formed by classical hydrogen bond functionalities, but by various kinds of C–H groups, carbonyl ligands, and other moieties which were formerly regarded as more or less inert to hydrogen bond effects. Today, however, it is well established that most kinds of C–H groups can donate [1,2], and that carbonyl ligands can accept weak hydrogen bonds [3]. In a database analysis, it could be shown that C–H···O hydrogen bonding is a very common phenomenon in organometallic solids [4]; this includes the observation that η^5-cyclopentadienyl (Cp) ligands frequently donate C–H···O hydrogen bonds. In addition, Cp has been observed as acceptor of O–H···π(Cp) hydrogen bonds donated by hydroxyl groups [5]. The global interpretation of short intermolecular C–H···O/N contacts as 'hydrogen bonds' is not unchallenged [6], but in view of the vast experimental material that is today available, and in particular of the distance- and angular statistics analysed by several groups of authors [1,2,7–9], the hydrogen bond donor capacities of suitably polarized C–H groups can be no more questioned.

Whereas it seems to be generally accepted that Cp can donate hydrogen bonds to O and N, related hydrogen bonds with π-acceptors have hardly ever been discussed. Of interest is a structure report suggesting hydrogen bond-like C–H···π interactions between Cp groups, i.e. C(Cp)–H···π(Cp) [10]. Closer examination of this and related phenomena has not been performed as yet, although it is known that the π-bonded moieties C≡C [11,12], Ph [13], and C=C [14] may in principle accept hydrogen bonds from sufficiently polarized C–H groups.

In the course of our work on ligands containing cycloheptatrienyl rings [15–19], we have synthesized

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and crystallized compound **1** as a precursor for the preparation of allenylidene complexes [18]. Unexpectedly, we find an example of short C(Cp)–H···π(C$\equiv$C) contacts which can be interpreted as weak hydrogen bonds. Because this donor/acceptor combination has not been discussed in the context of hydrogen bonding before, more detailed discussion is appropriate.

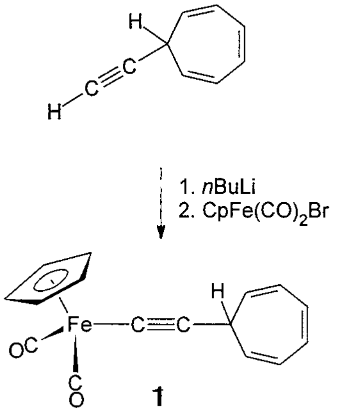
2. Experimental

Compound **1**, dicarbonyl(η^5-cyclopentadienyl)(2,4,6-cycloheptatrienylethynyl) iron(II), [(η^5-C_5H_5)Fe(C$\equiv$C–C_7H_7-2,4,6)$(CO)_2$], was obtained by lithiation of 7-ethynyl-1,3-5-cycloheptatriene followed by treatment with [(η^5-C_5H_5)Fe$(CO)_2$Br], Scheme 1. After chromatographic work-up and recrystallization from diethyl ether, **1** was isolated as yellow crystals in 46% yield. Further experimental details and spectroscopic data will be presented elsewhere in a different context [20].

X-ray diffraction data were collected at room temperature on an Enraf–Nonius Turbo CAD4 diffractometer (Cu–Kα radiation with $\lambda = 1.54176$ Å, room temperature). The structure was solved and refined with standard methods [21,22] (anisotropic refinement on F^2 for non-H atoms, H-atoms treated in the riding model with U allowed to vary, empirical absorption correction). Refinement converged with $R = 0.060$ (for observed reflections). Because all H-atom displacement parameters refine to realistic values (i.e. about 1.2–1.5 times larger than U of the carrier atom), the riding model can be considered as realistic and appropriate. Relevant crystallographic data are given in Table 1, the fractional atomic coordinates of the structure model are given in Table 2.

3. Results

The molecular conformation of **1** as observed in the crystal structure is shown in Fig. 1, a selection of bond distances and angles is listed in Table 3. The C$\equiv$C–Fe moiety is characterized by bond distances of C–Fe=1.907(4) and C$\equiv$C=1.215(6) Å, and a bond angle of 177.5(4)°. In a brief search through the organometallic crystal structures archived in the Cambridge Structural Database [23] (January 1998 update), it is found that this is a very typical geometry (search fragment C–C$\equiv$C–Fe, $n = 24$, mean C–Fe=1.907(6) and mean C$\equiv$C=1.204(4) Å, mean C$\equiv$C–Fe angle = 176.5°). The Cp ring of **1** does not show significant deviations from ideal geometry, and the seven-membered ring is found in the expected boat conformation with localized double bonds [C=C distances between 1.334(7) and 1.348(7) Å].



Scheme 1.

Table 1
Crystallographic data for 1

Formula	$C_{16}H_{12}O_2Fe$
Formula weight	292.1
Crystal system	Monoclinic
Space group	$P2_1/n$ (Number 14)
a (Å)	6.4272(9)
b (Å)	11.855(1)
c (Å)	17.885(2)
β (deg).	96.97(1)
V (Å^3	1352.6(3)
Z	4
D_c (g cm^{-3})	1.434
μ (mm^{-1})	8.89
Crystal size (mm)	0.66 × 0.30 × 0.20
Measured reflections	2345
Unique reflections	2009
Unique with $I > 2\sigma(I)$	1986
R [for $I > 2\sigma(I)$]	0.060
R_w [for all data]	0.179

The intermolecular interactions of crystalline **1** contain an unexpected feature that deserves closer discussion. To our surprise, the far shortest intermolecular contacts do not involve the CO ligands, but the C$\equiv$C moiety: pairs of molecules, which are related by the crystallographic inversion center, are connected mutual C(Cp)–H···C$\equiv$C interactions as shown in Fig. 2. With a H···C separation of only 2.59 Å, Table 4, the contact is far shorter than the sum of the H and C van der Waals radii (1.20 and 1.70 Å, respectively [24]). The distance of H to the center of the triple bond is even slightly shorter, 2.58 Å. The contact geometry closely resembles the C$\equiv$C–H···C$\equiv$C interactions in organic alkynes, for which we could repeatedly show hydrogen bond nature [13,25]. Furthermore, it must be considered that the acceptor potential of C$\equiv$C moieties bonded to metal atoms exceeds that in purely organic alkynes [26]. On this basis, it is concluded that the discussed contact is in nature not of the van der Waals type, but a directional hydrogen bond-like interaction. Because X–H···π hydrogen bonds have very soft geometries even with the

Table 2
Fractional atomic coordinates of **1** ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}^{a}
Fe	328(1)	−2273(1)	165(1)	59(1)
C(1)	2955(7)	−1230(4)	332(3)	77(1)
C(2)	3016(7)	−1843(5)	−334(3)	76(1)
C(3)	3061(7)	−2986(5)	−155(3)	78(1)
C(4)	3046(8)	−3101(5)	634(3)	75(1)
C(5)	3006(8)	−2005(4)	924(3)	78(1)
C(1′)	−3657(6)	−809(4)	−1910(2)	62(1)
C(2′)	−2332(7)	−239(4)	−2425(2)	74(1)
C(3′)	−3135(8)	529(5)	−2926(3)	84(1)
C(4′)	−5304(9)	780(5)	−3077(3)	86(2)
C(5′)	−6882(9)	53(5)	−3060(2)	86(2)
C(6′)	−6671(7)	−1116(5)	−2882(3)	85(2)
C(7′)	−5135(7)	−1570(4)	−2393(2)	73(1)
C(8′)	−2427(7)	−1369(4)	−1267(2)	68(1)
C(9′)	−1321(7)	−1730(4)	−720(2)	63(1)
O(100)	−2188(6)	−977(3)	1096(2)	98(1)
C(100)	−1211(7)	−1504(4)	723(3)	72(1)
O(101)	−2306(6)	−4258(3)	24(2)	95(1)
C(101)	−1246(7)	−3470(4)	91(2)	69(1)
H(1)	2890(7)	−432(4)	374(3)	107(18)
H(2)	3026(7)	−1533(5)	−824(3)	105(18)
H(3)	3095(7)	−3589(5)	−503(3)	101(17)
H(4)	3061(8)	−3785(5)	911(3)	114(20)
H(5)	3012(8)	−1817(4)	1441(3)	74(13)
H(1′)	−4481(6)	−243(4)	−1711(2)	51(10)
H(2′)	−887(7)	−426(4)	−2396(2)	92(16)
H(3′)	−2194(8)	932(5)	-3199(3)	79(14)
H(4′)	−5667(9)	1539(5)	−3202(3)	79(14)
H(5′)	−8264(9)	340(5)	-3177(2)	143(25)
H(6′)	−7692(7)	−1615(5)	−3126(3)	98(16)
H(7′)	−4986(7)	−2366(4)	−2354(2)	80(15)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond distances and angles of 1

Bond lengths (Å)	
Fe–C(1)	2.085(5)
Fe–C(2)	2.102(5)
Fe–C(3)	2.091(5)
Fe–C(4)	2.089(5)
Fe–C(5)	2.083(5)
Fe–C(9′)	1.907(4)
Fe–C(100)	1.746(5)
Fe–C(101)	1.738(5)
C(1)–C(2)	1.400(7)
C(1)–C(5)	1.400(7)
C(2)–C(3)	1.392(7)
C(3)–C(4)	1.420(7)
C(4)–C(5)	1.401(7)
C(1′)–C(2′)	1.490(5)
C(1′)–C(7′)	1.504(6)
C(1′)–C(8′)	1.472(6)
C(2′)–C(3′)	1.337(7)
C(3′)–C(4′)	1.419(7)
C(4′)–C(5′)	1.334(7)
C(5′)–C(6′)	1.426(7)
C(6′)–C(7′)	1.348(7)
C(8′)–C(9′)	1.215(6)
O(100)–C(100)	1.153(5)
O(101)–C(101)	1.154(5)
Bond angles (°)	
C(8′)–C(1′)–C(2′)	113.2(4)
C(8′)–C(1′)–C(7′)	114.8(4)
C(2′)–C(1′)–C(7′)	106.6(3)
C(3′)–C(2′)–C(1′)	121.4(4)
C(2′)–C(3′)–C(4′)	124.1(5)
C(5′)–C(4′)–C(3’)	126.4(5)
C(4′)–C(5′)–C(6′)	125.5(5)
C(7′)–C(6′)–C(5′)	125.1(5)
C(6′)–C(7′)–C(1′)	119.7(5)
C(9′)–C(8′)–C(1′)	173.6(5)
C(8′)–C(9′)–Fe	177.5(4)

strong O–H and N–H donors [13,27–29], the bending of the angles at H in **1** is to be regarded as a normal case (Table 4). It was not attempted to support the above interpretation with IR absorption experiments. This is because the presence of five C(Cp)–H oscillators and further six cycloheptatrienyl $C(sp^2)$–H oscillators in **1** must lead to a very complex spectrum of overlapping C–H stretching bands with little hope for unambiguous band assignment.

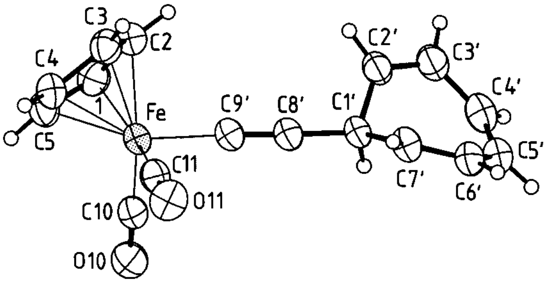


Fig. 1. Molecular structure and atomic numbering scheme of **1**.

To see if the present observation has precedents, a search through the Cambridge Structural Database was performed (June 1997 update with 167797 entries [23]). It is found that C(Cp)–HC≡C–M contacts are relatively common with H···C distances typically in the range 2.6–2.9 Å, occasionally down to 2.55 Å. Interpretation of such contacts is in most cases not straightforward, but the example of the C–H···C≡C interactions in crystalline $[(\eta^5\text{-}C_5H_5)W(C{\equiv}C-C_3H_5)(PMe_3)(CO)_2]$ is very helpful for discussion, Scheme 2.

In this compound [30], a tungsten bonded C≡C moiety accepts two short contacts from C–H groups, one from a dichloromethane molecule and one from a Cp ligand. The contact of the dichloromethane molecule, which is known to be one of the strongest C–H hydrogen bond donors [1,2], is only slightly shorter than that of the Cp ligands, suggesting that both interactions are similar in nature. The arrangement as a whole strongly

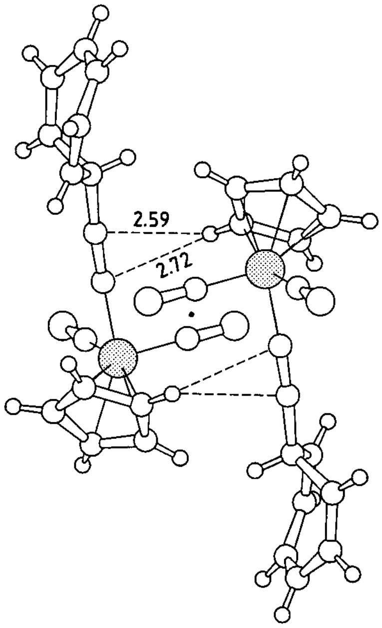


Fig. 2. The pair of molecules linked by mutual C(Cp)–H···C$\equiv$C interactions.

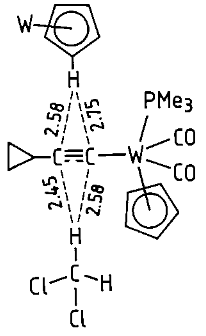
resembles that of the dual Cl_3C–H···C$\equiv$C···H–CCl_3 interactions for which C–H···C$\equiv$C–M hydrogen bonding has been characterized for the first time [11] (with H···C=2.33 and 2.42 Å). The interpretation that C(Cp)–H···C$\equiv$C contacts can in principle represent weak hydrogen bonds is thereby supported.

The present work strengthens the view [3,4] that directional interactions are of substantial importance in organometallic solids, even if the molecules carry no conventional hydrogen bond functionalities. The question whether the described C(Cp)–H···C$\equiv$C contacts deserve the classification as 'hydrogen bonds' is more of semantic than of chemical nature, as is also the case for the weaker types of directional C–H···O interactions [9]. More important is the observation that they do occur in crystal structures, and do contribute to determine the intermolecuar architecture.

Table 4
Geometry of the C(Cp)–H···C$\equiv$C interaction given in Å and degrees (for C–H=1.09 Å)

	H···X	C···X	C–H···X
Compound **1**			
C1–H···C8′	2.59	3.541(7)	146
C1–H···C9′	2.72	3.751(7)	157
C1–H···*M*	2.58	3.597(7)	154
Compound **2** [22]			
C(Cp)–H···C1	2.75	3.73	151
C(Cp)–H···C2	2.53	3.52	152
C(Cp)–H···*M*	2.57	3.58	154
Cl_2C(H)–H···C1	2.58	3.65	167
Cl_2C(H)–H···C2	2.45	3.35	140
Cl_2C(H)–H···*M*	2.44	3.45	154

M denotes the midpoint of the C$\equiv$C bond. For compound **2**, the atoms are labelled W–C1$\equiv$C2



Scheme 2.

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