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Preliminary communication

HINDERED ROTATION AND STRUCTURE IN μ-ALLYLBIS(η-CYCLOPENTADIENYLDICARBONYLIRON) CATIONS

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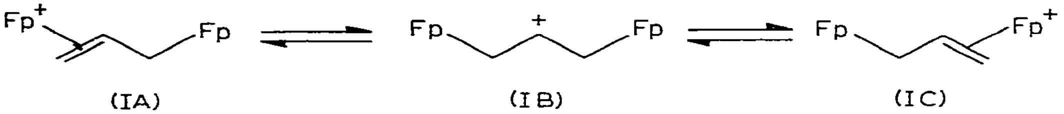
Summary

Studies of four μ-allylbis(η-cyclopentadienyldicarbonyliron) cations by IR and variable temperature ^{1}H and ^{13}C NMR indicate unsymmetrical hybrid structures. Rotation about the C—C bonds of the μ-allyl moiety requires about 12 kcal ($\Delta G^{\ddagger}_c$); interconversion of nonequivalent iron groups was not frozen out at —90°C.

In 1967, King and Bisnette [1] reported generation of the stable cation I by β-hydride removal from μ-(1,3-propanediyl)bis(η-cyclopentadienyldicarbonyliron). Cation I was represented as being in dynamic equilibrium between forms IA, IB, and IC**. The possibility of I having a static hybrid structure has also been raised [2]. We report here some new data which show interesting dynamic properties of I and related compounds, and which bear upon the still-active general question of structure of β-metallocarbonium ions [3].



IR and ^{1}H NMR data for I, related compounds II—IV, and some model compounds are given in Table 1.

The solution IR spectra generally show four carbonyl stretching bands, qualitatively as expected for IA or IC. However, the actual frequencies deviate systematically from those of normal π- and σ-complexes.

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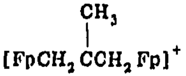
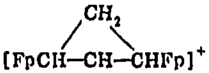
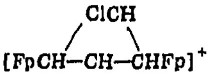
[**] Fp symbolizes the η-cyclopentadienyldicarbonyliron group.

TABLE 1

IR AND ^{1}H NMR DATA FOR THE COMPOUNDS I—IV

Compound			ν(CO) (cm^{-1})	^{1}H NMR spectrum (δ, ppm)			
				Cp	α-CH$_2$	β-CH	other
$[\mathrm{FpCH_2CHCH_2Fp}]^+$	$\mathrm{BF_4}^-$	I	2053, 2017, 1962 ^{a} 2048, 2019, ? ^{b} ca. 2030, 2010, 1990(all v.br) ^{c}	5.21 ^{d}	2.48d	6.53quint	—
 $[\mathrm{FpCH_2\overset{CH_3}{\overset{\vert}{C}}CH_2Fp}]^+$	$\mathrm{PF_6}^-$	II	2044, 2020, 1996, 1968 ^{a} 2041, 2024, 1993, 1977 ^{b} 2028, 2012, 1966 br ^{c}	5.30 ^{d} 5.32 ^{a}	2.82s 2.81s	— —	2.23s (CH$_3$) 2.18s
 $[\mathrm{FpCH{-}\overset{CH_2}{CH}{-}CHFp}]^+$	$\mathrm{BF_4}^-$	III	2060, 2020, 2010, 1953 ^{a} 2059, 2020 br, 1959 ^{b} 2053, 2014, 2000, 1950(sh), 1940 ^{c}	5.24 ^{d}	3.95dt	6.38quint	2.27dt (CH$_2$)
 $[\mathrm{FpCH{-}\overset{ClCH}{CH}{-}CHFp}]^+$	$\mathrm{PF_6}^-$	IV	2068, 2032, 2015, 1959 ^{a} 2070, 2034, 2020, 1962 ^{b}	5.14 5.51 ^{d}	3.38, 4.45	6.48t	4.83 (CHCl)

^{a}Acetone solution. ^{b}Methylene chloride solution. ^{c}Hexachlorobutadiene mull. ^{d}Nitromethane-d_3 solution.

The ^1H NMR spectra of I—III all show single, sharp cyclopentadienyl resonances and equivalence of both ends of the bridging allyl ligands, at least on a time-average. The *trans* geometry of the Fp groups in III is shown by the equivalence of the two protons of the methylene group [7]. These protons are coupled to the α-CH protons by a 2.1 Hz coupling constant and to the β-CH at δ 6.38 ppm by 0.7 Hz; the latter is also coupled to the α-CH protons by 0.7 Hz. In IV, two cyclopentadienyl resonances and two α-CH resonances are observed due to the lowered symmetry relative to III, one Fp group is necessarily *cis* to the Cl and the other *trans*. That I—IV all have qualitatively the same structure follows, however, from the IR and ^{13}C NMR data (vide infra). The cations I, III, and IV all show the β-CH proton at low field, ca. δ 6.5 ppm. This is lower than expected for pure σ,π-structures like IA, the protons on the complexed double bond of Fp^+-cyclobutene resonate at δ 5.75 ppm, for example. A role for structures like IB may be suggested.

Most important, the ^1H NMR spectra of I and II change significantly as the temperature is lowered. The 4-proton singlet at δ 2.81 ppm due to the CH_2 groups of II gradually broadens on cooling and resolves (coalescence temperature —60°C) into a doublet with a separation of 6.4 Hz at —90°C. However, the cyclopentadienyl resonance remains a single, sharp peak even at —90°C. The nature of the temperature-dependent process becomes clearer from the spectra of I. At room temperature, the β-proton appears as a quintet and the α-protons as a broad doublet, with J of 10.2 Hz. On cooling to —35°C, one observes three sets of lines for these protons, a triplet of triplets (J = 14.2, 6.0 Hz) at δ 6.64 ppm, a doublet of doublets (J 6.0, 3.0 Hz) at δ 2.85 ppm, and a doublet of doublets (J = 14.2, 3.0 Hz) at δ 2.23 ppm. No further changes occur on cooling to —70°C, again, the cyclopentadienyl resonance remains a single, sharp peak. What is being frozen out is therefore not a σ,π-interconversion but rather a hindered rotation about the carbon—carbon bond of I and II. This is consistent with the invariance of the ^1H NMR spectrum of III down to —85°C [7]. Assuming for I a coalescence temperature of 0°C and a $\Delta\nu$ of 49.5 Hz, a $\Delta G_c^\ddagger$ of 13 kcal for the rotation can be deduced. Similarly, a $\Delta G_c^\ddagger$ of 11 kcal results for II.

We have also used ^{13}C NMR to study the structures of these cations. Chemical shifts (ppm downfield from internal tetramethylsilane) are reported in Table 2. Assignments were confirmed, when necessary, by proton off-resonance noise decoupling; otherwise fully decoupled spectra were obtained.

As in the ^1H NMR spectra, only single, sharp cyclopentadienyl resonances are observed in I—III, even at —90°C in the case of II. The resonances of the various μ-allyl ligands are quite instructive. For comparison, the α-C of $CH_2=CHCH_2Fp$ (V), resonates at 32.7 ppm [8]; π-complexation of the double bond as in IA should little affect this chemical shift. The γ-carbon of V resonates at 134.9 ppm; π-complexation with an Fp^+ normally shifts an unsubstituted alkene carbon upfield by 60 ppm [9], giving about 75 ± 5 ppm as the predicted chemical shift for this carbon in the static structure IA. Rapid equilibration of the two Fp groups would average the two CH_2 groups to a predicted chemical shift of 54±7 ppm. This is quite disparate from the observed 24 ppm in I; similar disparities are found for II—IV. Another extraordinary

TABLE 2

^{13}C NMR SPECTRA OF Fp COMPOUNDS (δ, ppm)

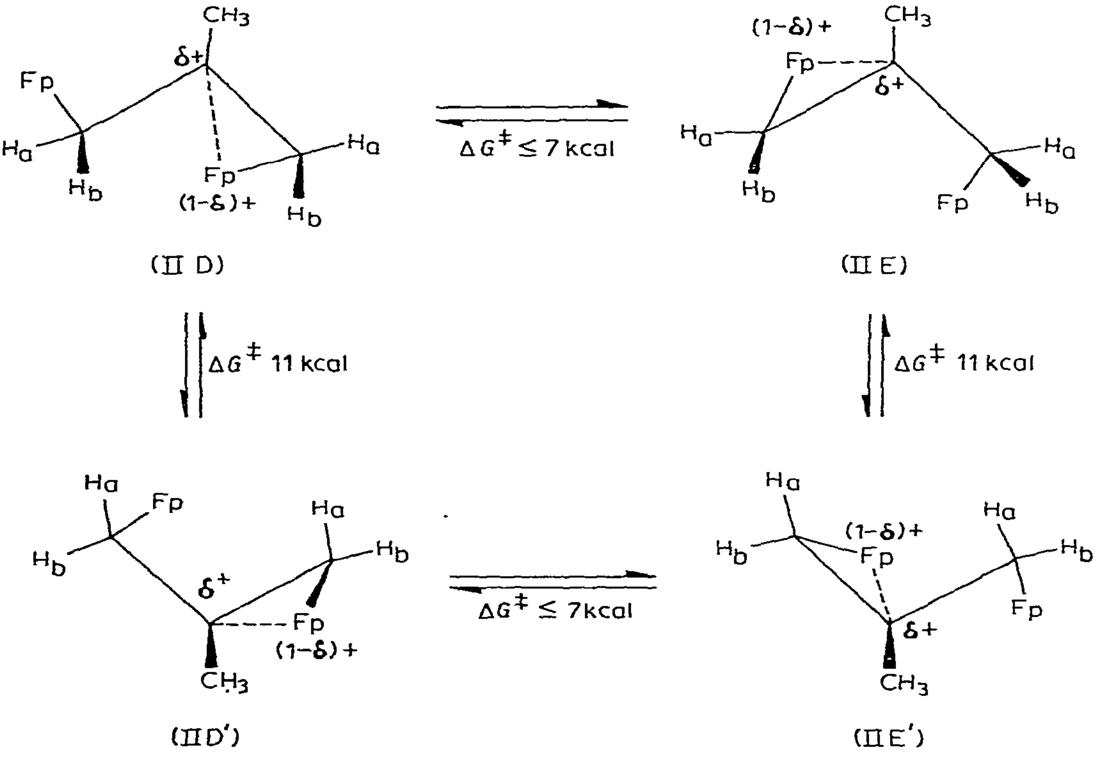
Compound	Solvent	δ(CO)	δ(Cp)	δ(α-C) [a]	δ(β-C) [b]	other
I	CD_3NO_2	—	88.0	24.1	128.9	—
II	CD_3NO_2	215.5	88.2	26.8	192.0	28.9 (CH_3)
	$CD_3\overset{\overset{O}{\|}}{C}CO_3$, −60°C	—	88.2	26.4	186	28.5
III	CD_3NO_2	216.0	88.4	48.6	112.8	42.2 (CH_2)
IV	CD_3NO_2, −20°C [c]	—	87.6, 90.2	68.4, 69.1	109.7	44.6 (CHCl)
$[FpCH_2C(CH_3)_2]^+$ BF_4^-	CD_3NO_2, −20°C [c]	—	90.5	54.5	87.2	29.6 (CH_3)
	CD_2Cl_2	—	89.3	55.2	85.7	29.2
	D_2O [d]	212.7	91.3	57.1	87.9	30.7
$[FpCH_2CHC_6H_5]^+$ BF_4^-	CD_2NO_2, −20°C [c]	209	91.0	48.9	85.8	129.0, 131.0, 132.1
	$CD_3\overset{\overset{O}{\|}}{C}CD_3$	—	90.6	49.5	86.7	128.7, 130.3, 131.3

[a] Less substituted carbon in case of alkene complexes. [b] More substituted carbon in case of alkene complexes. [c] Run at −20°C to avoid sample decomposition.

datum is the very large downfield shift of the β-C, 63 ppm, caused by replacing the β-H of I by CH_3 to form II. This far exceeds the normal "methyl effect" of ca. 8 ppm on sp^2 carbon [10]. A similar effect has been noted for the α-carbons of ferrocenylcarbonium ions [3c]. Olah and Forsyth [10] have found that "the deshielding α-effect of the methyl group increases as methyl hyperconjugation becomes more important because of increased π-charge at C_α." The anomalously high field α-carbon chemical shifts, the anomalously low field β-carbon shifts, and this large methyl effect can all be interpreted in terms of structures with strong bonds from the irons to the α-carbons and weak (or non-existent) bonds to the β, with substantial charge development on the β-C. This would also allow ready interpretation of the rotation barrier as being due to loss of hyperconjugative interaction involving the C—Fe bonds on rotation [3a].

Unfortunately, the IR data do not allow the structures to be interpreted simply as IB with only hyperconjugative charge delocalization, since the two Fp groups do appear to be non-equivalent on the infrared time scale. The IR data are consistent with discrete rotamers of IB and IIB, but such rotamers are impossible for the cyclic compounds.

We conclude that these cations are best represented as having fluxional structures ID and IE. From the observed $\nu_{(CO)}$ for the carbonyl groups in the IR spectrum of II and the correlation of Cutler, Raghu, and Rosenblum [11], one can calculate ^{1}H NMR chemical shifts for the IID cyclopentadienyl rings of ca. 5.45 and 5.05 ppm, or a relative shift of 32 Hz at 80 MHz. From their



apparent equivalence in the ^{1}H NMR spectrum at −90°C, then, the barrier to interconversion of IID and IIE cannot exceed 7 kcal. We interpret our observations on hindered rotation in terms of the interconversion IID$\rightleftharpoons$IID′, a double rotation, to avoid creating a sterically very congested isomer with both Fp groups on the same side of the bridging allyl ligand, an isomer for which no evidence exists.

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