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Chemical shift effects in the ^{13}C-NMR spectra of [$(C_5H_5)(CO)_2Fe^{II}$]-substituted cyclohexanes, dioxanes and tetrahydropyrans

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This manuscript is dedicated to Professor Myron Rosenblum on the occasion of his 75th birthday. Both the field and the authors have benefited greatly from his contributions and inspiration

Abstract

A set of empirically derived ^{13}C-NMR chemical shift additivity constants have been calculated for the Fp-substituent on cyclohexane, tetrahydropyran and dioxane rings. These were tested against a series of alkyl substituted Fp-complexes. These parameters prove to be highly reliable; the calculated and experimental chemical shifts are within ± 1 ppm. The parameters vary greatly between ring systems. One explanation for the differences relates to changes in conformation about the bond connecting the Fp-group to the various rings. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyclohexanes; Chemical shift parameters; Dioxanes

1. Introduction

Organometallic fragments which activate bound organic ligands toward unusual reactions have become a major field of study. The application of such groups as $(C_5H_5)Co$ [1], $Cr(CO)_3$ [2] and $[PdCl]_2$ [3] to organic synthesis is well established. We have been interested in the use of $(C_5H_5)(CO)_2Fe$ (henceforth Fp [4]) in this fashion [5]. Activation of organic molecules by Fp has been used in the synthesis of β-lactams [6], hydroazulenes [7] and other cyclization reactions [8], and natural products [9] and in the stereocontrolled reactions of ester enolates [10]. One problem that may occur in the use of these complexes is in the characterization of metal-containing intermediates by NMR. The coordinated metal ions induce unusual chemical shift effects that may be quite large. For example, the carbon adjacent to the iron in $(O)C(CH_2)_4CHCH_2CH(CN)–Fp$ is shifted upfield to -10.8 ppm [11] and the CH_2= carbon in the complex $Fp(CH_2{=}CHOCH_3)^+BF_4^-$ is shifted upfield to 27.3 ppm [12]. To assist in the assignment of NMR spectra of Fp-complexes we have undertaken the study of a series of Fp-substituted cyclohexanes, tetrahydropyrans (THP) and dioxanes. As a result of this study we wish to report a set of empirically derived chemical shift parameters for the Fp-group as an equatorial substituent on these six-membered rings.

2. Results and discussion

2.1. Syntheses

Reaction of NaFp with bromocyclohexane and a series of alkyl substituted cyclohexyl *p*-toluenesulfonate esters **1b**–**f** produced the corresponding cyclohexyl Fp-complexes **2a**–**f** in low to fair yield. The major product was most likely the alkyl substituted cyclohexene, resulting from Fp-induced elimination. Fp_2 was recovered in varying amounts from all reactions. Attempts to prepare the *cis*- and *trans*-2-methyl compounds yielded only elimination products.

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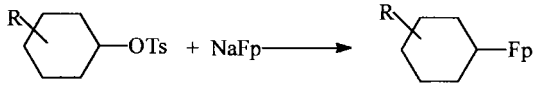
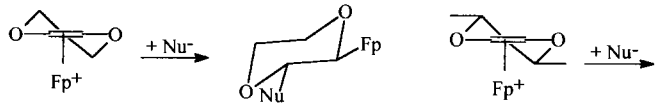
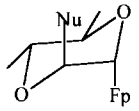


1	R	2	R
		a	H
b	*t*-4-Me	b	*c*-4-Me
c	*c*-4-Me	c	*t*-4-Me
d	*t*-3-Me	d	*c*-3-Me
e	*c*-3-Me	e	*t*-3-Me
f	*t*-4-Et	f	*c*-4-Et

The Fp-dioxane complexes **3a–d** and Fp-5,6-dimethyldioxane complexes **4a–e** were prepared from the corresponding Fp salts by addition of the appropriate nucleophile as previously reported [5c].



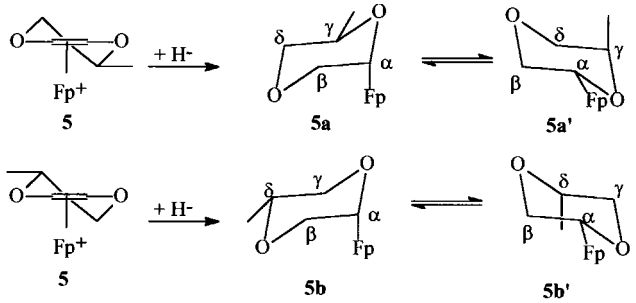
3a Nu = H
3b Nu = Me
3c Nu = CN
3d Nu = Ph



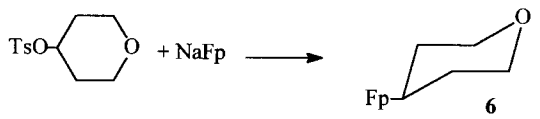
4a Nu = H
4b Nu = Me
4c Nu = CN
4d Nu = Ph
4e Nu = $CH{=}CH_2$

Trans-2-Fp-6-methyldioxane (**5a**), and *cis*-2-Fp-5-methyldioxane (**5b**), were prepared by addition of $NaBH_4$ to a mixture of the diastereomeric salts, **5**. The resulting neutral compounds **5a** and **5b** were separated chromatographically. Low-temperature ^{13}C-NMR spectra revealed the presence of two conformers in solution (the minor conformers are designated **5a′** and **5b′**).

The predominate position of the Fp-groups (equatorial or axial) in each **2–4** is supported by their ^1H-NMR spectra. For the Fp–dioxane complexes (**3**), (equatorial Fp) the coupling constants for the protons adjacent to the Fp and the nucleophile are in the range of 6–9 Hz, while for the Fp–dimethyldioxane complexes (**4**) and Fp-methyldioxane complexes (**5**) (axial Fp) they are less than 1 Hz. Both are in good agreement with the established values for proton couplings in dioxanes [13].

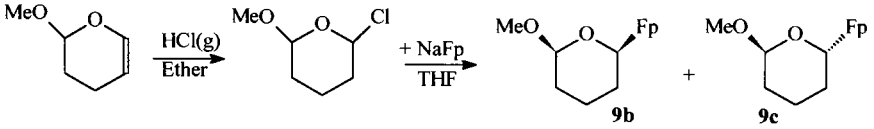


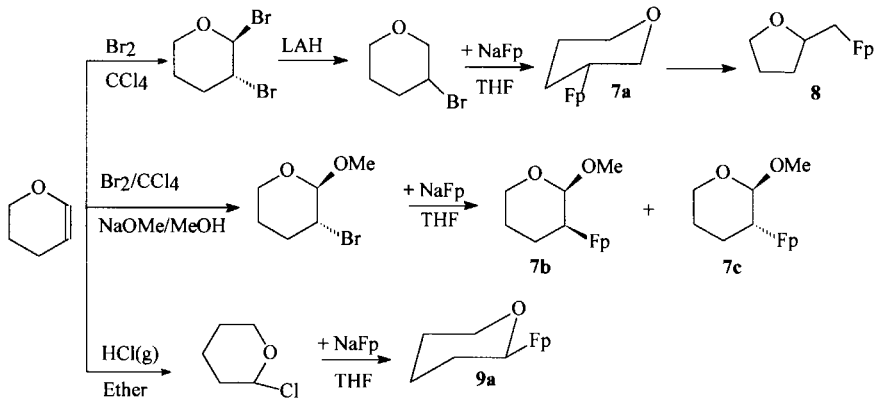
The Fp–THP complexes were prepared by treatment of the appropriate tetrahydropyranyl tosyl ester or halide (purchased or prepared from dihydropyran according to literature procedures) to generate the corresponding Fp-alkyl. Reaction of 4-tetrahydropyranyl *p*-toluenesulfonate with Na^+Fp^- in THF gave compound **6** in 15% yield.



Similarly, treatment of 3-bromotetrahydropyran with Na^+Fp^- gave (3-tetrahydropyranyl)-Fp (**7a**), in low yield (23%). On standing, even at 0 °C after one week, or in the presence of catalytic acid, the compound rearranges to the corresponding tetrahydrofuran (**8**). The same type of process has been observed in the isomerization of Fp-substituted dioxanes to dioxolanes [5c]. Addition of Na^+Fp^- to 3-bromo-2-methoxytetrahydropyran gave a 5:1 mixture of the *cis*- and *trans*-substituted compounds **7b** and **7c** in 28% overall yield. Reaction of Na^+Fp^- with 2-chlorotetrahydropyran in THF at −70 °C gave the 2-substituted complex (**9a**), in 56% yield (see Scheme 1). The relatively high yield of this reaction at low temperature suggests that α-haloethers may be particularly good substrates for nucleophilic attack by Fp^-.

The 2,6-disubstituted THPs **9b** and **9c** were prepared by a similar route to that used to make **9a**, starting with 6-methoxydihydropyran. Attempts to separate the mixed *cis*- and *trans*-isomers of the intermediate chloromethoxytetrahydropyran by vacuum distillation resulted in pyrolysis, so the crude product was treated with Na^+Fp^- at −78 °C resulting in a 46% yield of a nearly 1:1 mixture of **9b** and **9c**. Repeated attempts to separate the isomers by column chromatography were unsuccessful. As was seen in the synthesis of **9a**, the α-chloroether seems to be a particularly good substrate for Fp^- nucleophilic substitutions.





Scheme 1.

2.2. ^{13}C-NMR data

Interpretation of ^{13}C-NMR data indicates that the majority of the Fp-alkyl complexes obtained result from inversion of stereochemistry at carbon. Juaristi and Glass also observed inversion of stereochemistry in the synthesis of the 4-*tert*-butyl and 4-phenylcyclohexyl-Fp complexes [14]. Although Krusic and co-workers [15] have demonstrated the intermediacy of free radicals in the reaction of Fp^- with alkyl halides, Whitesides and co-workers have shown that an S_N2 mechanism is preferred for reactions with alkyl sulfonates [16]. Winstein and Holness [17] clearly demonstrated that, in solvolysis reactions of cyclohexyl tosylates, only an S_N2 mechanism leads to direct substitution products. In the case of the only alkyl halide used in this investigation, bromocyclohexane, the stereochemical outcome is inconsequential since the product is mono-substituted. Thus, the observed stereochemistries were the expected ones for all reactions.

^{13}C-NMR spectra for all complexes were obtained and assigned by a combination of chemical shifts and either APT, or INEPT [18] pulse sequence ^{13}C-NMR experiments to distinguish methyl and methine carbons from methylene carbons. In addition, in most cases homonuclear decoupling experiments allowed for unambiguous assignment of the ^{1}H-NMR spectra and then single-frequency proton decoupling experiments confirmed the ^{13}C-NMR assignments. ^{13}C-NMR data for cyclohexyl-Fp are given in Table 1, along with the derived chemical shift parameters ($\Delta\delta$ values) for an equatorial Fp-group.

This assignment agreed with the general observation that carbons β to a substituent lie downfield from carbons γ to the substituent in mono-substituted cyclohexanes [19]. $\Delta\delta$ values were then calculated relative to cyclohexane at 27.7 ppm. Assignment of the Fp in the equatorial position of compounds **2a**–**g** was made based upon a number of arguments. The chemical shift of the methyl carbons in substituted methylcyclohexanes is diagnostic of their conformation. Axial methyl carbons resonate near 17.5 ppm while equatorial methyl carbons resonate near 22.5 ppm [20]. In **2b**, *cis*-4-methylcyclohexyl-Fp, the methyl carbon is observed at 17.6 ppm while in the *trans*-isomer **2c** the methyl carbon occurs at 22.8 ppm. No change in the ^{13}C-NMR spectrum of either cyclohexyl-Fp (**2a**) or *cis*-4-methylcyclohexyl-Fp (**2b**) was observed in CD_2Cl_2 between 300 and 190 K. It is apparent from the chemical shift of the methyl carbon that the major conformer of **2b** at room temperature is that with the methyl substituent axial, and therefore the Fp-group equatorial. Because the enthalpy of activation for the inversion of cyclohexane is about 10.8 kcal mol^{-1}, and the rate of conformational inversion does not change substantially with ring substitution [21], our inability to observe a change in the ^{13}C-NMR spectrum at 190 K implies that the minor conformer must be present in an amount of much less than 5%. Even when cyclohexane is substituted by the very bulky (benzene)chromium tricarbonyl moiety, individual conformers are completely resolved at 173 K [22]. Taking the conformational energy for a methyl group as 1.7 kcal mol^{-1} [23] and assuming an equilibrium constant between the two conformers of 20 at 190 K, we estimated a lower limit for the conformational bias energy of the Fp-group as 2.8 kcal mol^{-1}. This is in agreement with the value of 3.7 kcal mol^{-1} reported by Juaristi and co-workers [14]. This value implies that at room temperature the structure of cyclohexyl-Fp itself should have greater than a 99% contribution from the Fp-equatorial conformer. Thus comparison of ^{13}C-NMR resonances in cyclohexyl-Fp with those in cyclohexane yields $\Delta\delta$ val-

Table 1
^{13}C-NMR chemical shift parameters for Fp-group[a]

Compound	Cα	Cβ	Cγ	Cδ
Cyclohexane	27.7	27.7	27.7	27.7
Cyclohexyl-Fp (**2a**)	28.2	44.1	31.8	27.4
$\Delta\delta$	+0.5	+16.4	+4.1	−0.3

[a] Chemical shifts in ppm relative to $CDCl_3$ at 77.0.

Table 2
Calculated and observed ^{13}C-NMR chemical shifts for substituted Fp–cyclohexanes (Fp-eq)

Compound		C1	C2	C3	C4	C5	C6
2b 4-Me-ax [a]	Calc.	28.2	37.7	37.2	28.1	37.2	37.7
	Obs.	28.4	37.6	36.4	27.8	36.4	37.6
2c 4-Me-eq	Calc.	28.0	44.1	40.8	33.4	40.8	44.1
	Obs.	27.3	43.6	40.2	33.4	40.2	43.6
2d 3-Me-ax	Calc.	21.8	49.5	33.2	32.7	25.4	44.1
	Obs.	21.7	49.4	32.4	31.7	25.6	44.2
2e 3-Me-eq	Calc.	28.2	53.1	37.8	36.4	31.8	43.9
	Obs.	27.1	53.0	37.5	35.8	31.0	43.3
2f 4-Et-ax	Calc.	28.3	38.5	34.8	35.9	34.8	38.5
	Obs.	28.6	38.1	34.7 [b]	35.4 [b]	34.7	38.1
2g 4-^{t}Bu-eq	Calc.	27.4	44.8	32.0	48.4	32.0	44.8
	Obs.	28.1	44.1	32.4	48.6	32.4	44.1

[a] Assignments confirmed by single-frequency proton decoupling.
[b] Assignments of these pairs of signals may be inverted.

Table 3
^{13}C-NMR chemical shift parameters for Fp-substituted dioxanes

Compound	Cα	Cβ	Cγ	Cδ
Dioxane	67.6	67.6	67.6	67.6
Dioxanyl-Fp-eq (**3a**)	77.0	78.3	71.4	67.5
$\Delta\delta$	+9.4	+10.7	+3.8	−0.1
2,3-dimethyldioxane	67.4	67.4	80.1	80.1
Dioxanyl-Fp-ax (**4a**)	75.5	76.8	71.6	77.0
$\Delta\delta$	+8.1	+9.4	−8.5	−3.1

Table 4
Calculated and observed ^{13}C-NMR chemical shifts for substituted Fp-dioxanes (Fp-eq)

Compound		Cα	Cβ	Cγ	Cδ
(3-Me-eq) (**3b**)	Calc.	83.5	81.8	71.4	67.5
	Obs.	83.3	82.5	71.4	67.9
(3-CN-eq) (**3c**)	Calc.	77.5	76.8	69.4	65.4
	Obs.	76.0	75.3	69.5	66.9
(3-Ph-eq) (**3d**)	Calc.	81.7	93.2	69.1	66.5
	Obs.	81.2	89.8	71.2	67.9

Table 5
Calculated and observed ^{13}C-NMR chemical shifts for substituted Fp-5,6-dimethyldioxanes (Fp-ax)

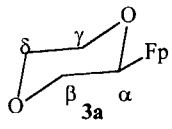
Compound		Cα	Cβ	Cγ	Cδ
(3-Me) (**4b**)	Calc.	81.1	78.4	71.6	70.6
	Obs.	79.2	78.2	71.6	68.8
(3-CN) (**4c**)	Calc.	74.7	77.0	70.6	70.0
	Obs.	73.8	74.1	71.8	72.6
(3-Ph) (**4d**)	Calc.	78.1	85.0	71.6	70.9
	Obs.	75.2	83.2	72.0	69.7
(3-CH=CH2) (**4e**)	Calc.	78.3	85.7	71.2	70.6
	Obs.	77.1	83.5	71.6	69.7

ues for an equatorial Fp-substituent. Using the $\Delta\delta$ values so obtained, the chemical shifts of the ring carbons in **2b**–**g** were calculated. Theoretical chemical shifts for the cyclohexyl carbons were calculated by addition of the literature parameters [24] for the alkyl substituents (axial or equatorial, as appropriate). Then the chemical shift values for the Fp-substituent presented in Table 1 were added to give the calculated values for the molecule in question. The calculated and experimental values are shown in Table 2. The agreement between these values is excellent; the difference never exceeds 1.1 ppm and is generally much less.

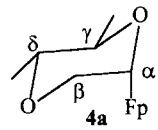
In similar fashion, ^{13}C-NMR data for Fp-substituted dioxanes **3a** and **4a** were made and are given in Table 3, along with the derived chemical shift parameters ($\Delta\delta$ values) for both the equatorial and axial Fp-group (all designations α, β, etc. are given relative to the Fp-substituent). Using the $\Delta\delta$ values so obtained, the chemical shifts of the ring carbons in the remaining compounds **3**–**5** were calculated. Corrections were made for *gauche* effects of −2.5 ppm for carbons bearing *trans–gauche* substituents and −3.4 for the carbon bearing the axial substituent and −2.9 for the carbon bearing the equatorial substituent in the case of *cis–gauche* interactions [24a]. Although these corrections were derived for methyl groups, they provide good agreement with the current compounds as well. Calculated and observed chemical shifts for the Fp-equatorial compounds **3b**–**d** and the Fp-axial compounds **4b**–**e** are given in Tables 4 and 5, respectively. Calculated chemical shifts for the conformers of **5a** and **5b** and the observed values for each at 180 K are given in Table 6.

The chemical shift parameters for the α and β positions, relative to the Fp moiety, are comparable for both axial and equatorial substitution. The large differences seen in the parameters for the carbons γ and δ to the Fp between axial (−8.5, −3.1 ppm) and equato-

Table 6
Calculated and observed ^{13}C-NMR chemical shifts for Fp-substituted 5- or 6-methyldioxanes



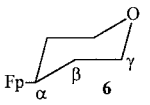
3a



4a

Compound	Cα	Cβ	Cγ	Cδ	
(6-Me, Fp-ax) (**5a**)	Calc.	75.7	76.8	65.1	73.5
	Obs.	75.9	76.9	66.2	72.4
(6-Me, Fp-eq) (**5a′**)	Calc.	70.6	78.2	72.8	72.9
	Obs.	68.0	78.2	70.5	71.6
(5-Me, Fp-ax) (**5b**)	Calc.	75.5	77.0	68.1	70.5
	Obs.	74.5	77.6	67.2	70.5
(5-Me, Fp-eq) (**5b′**)	Calc.	76.9	71.9	76.8	68.9
	Obs.	78.8	71.4	75.6	68.1

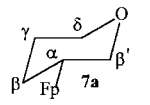
Table 7
C-NMR chemical shift parameters for Fp-substituted tetrahydropyrans



6

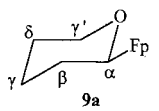
Compound	Cα	Cβ	Cγ	Cδ
Tetrahydropyran	23.6	26.8	68.8	*
4-Tetrahydropyranyl-Fp	21.5	43.7	71.6	*
Δδ	2.1	+16.9	+2.8	*

* No δ-carbon



7a

Compound	Cα	Cβ	Cβ'	Cγ	Cδ
Tetrahydropyran	26.8	23.6	68.8	26.8	68.8
3-Tetrahydropyranyl-Fp	23.2	39.6	79.8	32.2	68.9
Δδ	-3.6	+16.0	+11.0	+5.4	0.1



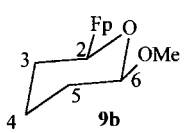
9a

Compound	Cα	Cβ	Cγ	Cγ'	Cδ
Tetrahydropyran	68.8	26.8	23.6	68.8	26.8
2-Tetrahydropyranyl-Fp	79.8	43.5	27.9	72.5	27.2
Δδ	+11.0	+16.7	+4.3	+3.7	+0.4

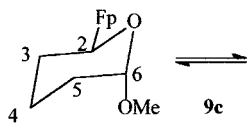
rial (+ 3.8, − 0.0 ppm) agree with the normal observation of moderate to large upfield shifts in these positions for axial substituents due to steric compression. As can be seen in Tables 4–6, calculated chemical shifts based upon these $\Delta\delta$ values are in good agreement with the observed spectroscopic data; the calculated values are generally within 2 ppm of the observed values and more often are within 1 ppm.

In a similar fashion, chemical shift parameters for an equatorial Fp-substituent on a THP ring were calculated from the observed values for compounds **6**, **7a** and **9a** (see Table 7).

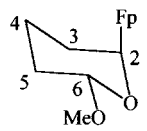
There are three unique positions for the Fp-group on the THP ring, unlike cyclohexane and dioxane, and so three different sets of parameters are shown. The dependence of ^{13}C-NMR chemical shift parameters upon a substituent's position relative to the heteroatom in THP, piperidine and other saturated monoheterocyclic rings is well established [25]. The axial conformers of these compounds were not detected down to 180 K.



9b

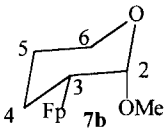


9c

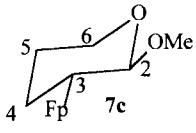


The values for the 2- and 3-Fp substituted THPs were tested by comparison of the calculated and observed chemical shifts for the methoxy compounds **7b** and **7c**, and **9b** and **9c**. The chemical shift values for the 4-Fp substituted THP were not tested for lack of a suitable compound (Tables 8 and 9).

Table 8
Chemical shifts for 2-methoxytetrahydropyran [a] and calculated and observed ^{13}C-NMR chemical shifts for *cis*- and *trans*-3-(2-methoxy)tetrahydropyranyl-Fp



7b



7c

Compound		C2	C3	C4	C5	C6
2-MeO-THP	(MeO-ax)	97.7	29.6	17.6	25.2	59.3
	(MeO-eq)	103.0	31.4	22.2	25.2	66.3
cis-**7b**	Calc.	107.1	23.7	33.6	29.6	59.4
	Obs.	106.8	24.0	34.2	31.3	59.4
trans-**7c**	Calc.	111.5	25.3	38.2	29.6	66.4
	Obs.	111.9	24.5	39.0	31.4	66.2

[a] Values taken from Ref. [24e].

2.3. Correlation of chemical shift parameters

A summary of the chemical shift parameters for the Fp-group as a substituent on the three ring systems is given in Table 10 for comparison. In cyclohexane, an equatorial Fp-substituent induces a small chemical shift change at the α carbon, but a pronounced deshielding effect at the β carbon. The small α carbon effect may reflect the nature of the Fe–C bond as a non-polar bond, similar to certain C–C bonds, since the α effects of substituents such as –C≡N and –C≡CH on cyclohexane are similarly small. The magnitude of the α effect depends on the polarity of the bond formed between the ring carbon and the substituent. The more polar the bond is, the bigger the α effect [19]. The chemical shifts induced on the β carbon are strongly dependent of the nature of the substituent. However, the origin of the β effect is not completely clear [26] making it hard to interpret its difference from the α effect.

Table 9
Calculated and observed ^{13}C-NMR chemical shifts for *cis*- and *trans*-2-(6-methoxy)tetrahydropyranyl-Fp[a]

Compound	C2	C3	C4	C5	C6	
cis-**9b**	Calc.	77.3	41.9	26.5	31.8	106.7
	Obs.	74.3	41.8	26.2	31.8	105.6
trans-**9c** (Fp-eq)	Calc.	70.3	41.9	21.9	30.2	101.4
trans-**9c** (Fp-ax) [b]	Calc.	74.6	34.4	13.7	28.3	94.5
	Obs.	74.3	41.8	17.3	29.8	98.3

[a] Values for 2-methoxytetrahydropyran (Table 8) were used in the calculation.

[b] Chemical shift parameters for the axial Fp-group from dioxane were used.

Table 10
Summary of chemical shift parameters for Fp on cyclohexane, tetrahydropyran (THP) and dioxane

Compound	Cα	Cβ	Cβ′ [a]	Cγ	Cγ′ [a]	Cδ
Cyclohexane (Fp-eq)	+0.5	+16.4		+4.1		−0.3
Dioxane (Fp-eq)	+9.4	+10.7		+3.8		−0.1
Dioxane (Fp-ax)	+7.9	+9.2		−8.5		−3.2
2-THP (Fp-eq)	+11.0	+16.7		+4.3	+3.7	+0.4
3-THP (Fp-eq)	−3.6	+16.0	+11.0	+5.4		+0.1
4-THP (Fp-eq)	−2.1	+16.9		+2.8		[b]

[a] The notations Cβ′ and Cγ′ refer to the β or γ carbons adjacent to the O in THP.
[b] No δ carbon.

The β effect of the Fp-group in cyclohexane is unusually high (about 16 ppm), compared with the deshielding range of 3–14 ppm found for most substituents on cyclohexane [19]. Another striking feature is the significant (+4.8) γ deshielding effect of the Fp-group. For most substituents, this parameter is negligible to slightly shielding. A reasonable explanation of this effect is that the γ carbon lies in the deshielding cone of the Fe–cyclopentadienide system. This will be discussed in more detail shortly.

In dioxane, both equatorial and axial Fp configurations induce a larger α effect and a smaller β effect when compared to cyclohexane. This notable change in the α parameter may imply that the Fe–C bond is not non-polar in dioxane. A large difference in the γ effect is also observed between the equatorial and axial Fp positions for dioxane. The axial Fp-group shows a large γ shielding (−8.5 ppm) which is only slightly larger than that usually observed for axial substituents in cyclohexane [19]. The γ deshielding effect seen for equatorial Fp in dioxane (+3.8 ppm) is comparable to that found for cyclohexane. This difference may arise from a difference in conformation about the Fe–C bond when the Fp is in an equatorial position as opposed to an axial one. This difference in conformation may be clearly seen in the crystal structures of the cyano adduct **4c** [5c] (Fp axial) and 3-(2-oxocyclohexyl)-2-Fp–dioxene (Fp equatorial). Work by Rosenblum and co-workers [27] has shown that protons which lie near, or along the Fe–Cp central axis are strongly shielded while protons lying adjacent to the Fe atom, perpendicular to the Fe–Cp axis, are strongly deshielded. It is reasonable to extend this observation to ^{13}C-NMR chemical shifts. When the Fp-group is in the axial orientation on a dioxane ring, the γ carbon lies in the shielding area along the Fe–Cp axis, and an upfield shift is observed. When the Fp-group is in an equatorial position, the γ carbon is within the deshielding region and a downfield shift is observed.

The α chemical shift parameters for the Fp-group as a substituent on THP differ significantly depending on the position of the Fp on the ring. The equatorial Fp at the 2-position behaves very much the same as it does in dioxane, with a large deshielding effect for the α carbon (+11.0). The equatorial Fp-substituent at both the 3- and 4-positions exhibits very different chemical shift parameters. The small shielding values at the α carbon (−3.5, −2.1 ppm, respectively) are much closer to the value of +0.5 observed for cyclohexane than to those observed for either 2-Fp THP or dioxane. This wide range suggests that the Fe–C bond may be quite polarizable and therefore the α effect is dependent upon the electron density at the ring carbon. In addition, in THP the shorter carbon–oxygen distance will make the ring geometry somewhat different from that of cyclohexane, particularly in the region of C-2, O-1 and C-6. Since carbons at the 2-position of THP are in an environment similar to that of dioxane, it is not unreasonable that they would have comparable chemical shift parameters, while carbons C-3 and C-4 in the THP ring would be in environments more closely resembling cyclohexane.

One additional feature of the chemical shift parameters for THP is the observation of two different γ shifts for the 2-Fp complex and two different β shifts for the 3-Fp complex. In both cases, the chemical shift induced by the Fp-substituent is smaller at the carbon adjacent to the ring O-atom (γ for 2-Fp, $\Delta\delta = +4.3$ at C4, 3.7 at C6; β for 3-Fp, $\Delta\delta = +11.0$ at C2, and +16.0 at C4). This may be explained by saturation of polarizability, the idea that an atom that has already been substantially polarized by one substituent cannot be as effectively polarized by a second one [28]. For example, compare the deshielding effects of a methoxy group on cyclohexane (+52.9 ppm) with that for the methoxy group in the 2-position of THP (+31.1 ppm). The correlation between the β effects for cyclohexane (+16.4) and the cyclohexane like positions in THP (+16.7, +16.0 and +16.9 for the 2-, 3- and 4-Fp substituted compounds) as well as between dioxane (+10.7) and Cβ′ in 3-Fp-THP (**7a**), the dioxane-like position, (+11.0) seems to corroborate this idea.

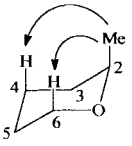
2.4. Conformational bias energy on dioxane

The conformational bias energy (*A*-value) for the Fp-group has been previously shown to be 3.8 kcal mol^{-1} [14]. The isolation of the 5- and 6-methyl-2-

Fp-dioxane complexes **4a** and **4b** allow for determination of the conformational bias energy of the Fp-substituent on a dioxane ring.

At 180 K, individual conformers were observed in both the ^{1}H- and ^{13}C-NMR spectra of both **5a**/**5a′** and **5b**/**5b′**. The different conformers were easily characterized by the chemical shifts of the signals in question; the proton adjacent to an axial Fp-group on dioxane occurs lower field than its Fp-equatorial counterpart [5c]. The same is true for the carbon frequencies of the Cp ring. The Fp–CH proton and the Cp ring carbons were fully resolved between the conformers and thus were used for calculation of the relative concentrations of the two conformers of each compound. The ratios of their relative areas by each method were: **5a′**/**5a** = 1.4 (^{1}H-NMR) 1.2 (^{13}C-NMR); **5b′**/**5b** = 1.11 (^{1}H-NMR) 1.14 (^{13}C-NMR). There is good agreement between the different compounds and different techniques.

We find no measurement of the *A*-value of a methyl group on dioxane in the literature, and so a value was adapted from the reported constant of 2.9 kcal mol^{-1} measured for 2-methyltetrahydropyran [29]. There are two different 1,3-diaxial interactions apparent for an axial 2-methyl substituent on THP. The interaction between the methyl group and the 4-proton may be classed as cyclohexane like, while that between the methyl and the 6-proton (greater due to the shorter C–O bond lengths) should resemble the interaction in dioxane. Assuming the interaction between the methyl group and the 4-proton is comparable to cyclohexane (0.85 kcal mol^{-1} per axial proton) [23], the contribution from the 6-proton may be estimated at 2.05 kcal mol^{-1}. Using the equilibrium values given above, the free energy difference between the two conformers may be estimated at 0.07 kcal mol^{-1} and thus the *A*-value for the Fp-substituent on the dioxane ring is 2.1 ± 0.2 kcal mol^{-1}.



This value is substantially lower than the 3.8 kcal mol^{-1} established for the *A*-value of the Fp-group on cyclohexane. There is also a substantial difference between the values for Fp (3.8 kcal mol^{-1}) and methyl (1.7 kcal mol^{-1}) in cyclohexane. By contrast, there is virtually no difference between the values for Fp (2.1 kcal mol^{-1}) and methyl (estimated at 2.05) on dioxane. While this latter value is questionable due to the need to estimate an *A*-value for the methyl group, the near unity value of the equilibrium constant for both **5a** and **5b** confirms the fact that their *A*-values are nearly identical. This reduction in the *A*-value for the Fp-group in dioxane relative to cyclohexane is truly unexpected since most alkyl substituents at the 2-position show a greater preference for the equatorial orientation in 1,3-dioxane or THP relative to cyclohexane [29]. The decreased C–O bond length (relative to the C–C bond) brings an axial 2-alkyl group into closer contact with the *syn*-axial hydrogens at the 6-position (THP) or the 4- and 6-positions (1,3-dioxane) [30]. We believe there are two possible explanations for this observation.

One possibility is an anomeric effect [31]. While the Fp-group is not normally considered a polar substituent, and therefore unlikely to exhibit anomeric stabilization, the strong π-acid character of the carbonyl substituents allows for great variability in the electron density at the iron atom. The substantially larger α-chemical shift parameter seen for Fp in dioxane, relative to cyclohexane, supports the idea that the Fp–C bond in dioxane is substantially more polar than in cyclohexane.

A second possibility is a transannular interaction between the carbonyls of the Fp-moiety and the remote oxygen of the dioxane ring. When the Fp-group is in the axial position, the geometry allows for a stabilizing overlap between the O lone pair orbital and the π* orbital of one of the carbonyl groups. Such an interaction is geometrically similar to that found in 5-hydroxy-1,3-dioxane in which the OH-axial conformation is preferred [32]. Here, this conformation is favored because of a transannular hydrogen bond which can form only when the hydroxyl group is in the axial position. It is possible that a combination of both of these effects are involved in these complexes. There is no substitution position on the 1,4-dioxane ring where both explanations are not possible and thus such compounds cannot be used to distinguish the two explanations. The Fp-substituted THP compounds do present such a possibility, however. With the Fp-group in the 2-position, only anomeric stabilization would be possible while in the 3-position only the transannular interaction could occur. Neither route is available in 4-Fp THPs. Unfortunately, no changes were observed in the spectra of **6**, **7a** or **9a** down to 180 K.

3. Conclusions

A series of chemical shift parameters for the Fp-group in cyclohexane, dioxane and THP have been derived and tested. The good agreement between the calculated and observed values shows the validity of the parameters which will serve as practical tools for the characterization of organoiron complexes. The Fp-group also exhibits very different preferences for equatorial versus axial positions in dioxane relative to cyclohexane. This difference can be accounted for via either anomeric or transannular stabilization, but these cannot be distinguished with the materials available at present. Work is in progress to prepare substituted

THP, and 1,3-dioxane complexes suitable for determining the extent to which each may be involved.

4. Experimental

Reactions were carried out under Ar or nitrogen atmosphere using standard Schlenk technique. Solvents were distilled under nitrogen from Na–benzophenone (ether and THF) or CaH_2 (CH_2Cl_2 and hexane). Alumina refers to Basic Alumina Activity IV. Cyclohexanols and cyclohexanones were purchased from Aldrich Chemical Company or K and K Laboratories and used without further purification. IR spectra were recorded on a PE-1330 spectrophotometer and are calibrated against a polystyrene standard. ^{1}H- and ^{13}C-NMR FT spectra were taken on a Bruker AC-200 Spectrometer (courtesy of the Worcester NMR Consortium) at 25 °C in $CDCl_3$ and referenced to Me_4Si (^{1}H) or solvent (^{13}C). Elemental analyses were performed by MultiChem Laboratories, Lowell, MA, USA, or University Instrumentation Center, University of New Hampshire, Durham, NH, USA.

*4.1. trans-4-Ethylcyclohexyl 4-methylbenzenesulfonate [33] (**1f**)*

Trans-4-ethylcyclohexanol (4.2 g, 33 mmol) was dissolved in 25 ml of dry Py and cooled to 5 °C. 4-Methylbenzenesulfonyl chloride (12.6 g, 66 mmol, 100% excess) was added, the mixture was stirred for 30 min to effect solution and then was placed in the freezer (-5 °C) for 2–3 days. The resulting mixture was then poured into 600 ml of ice and water. After stirring briefly a white solid formed which was filtered, washed with cold water and allowed to air dry to yield 8.2 g (90%). Anal. Found: C, 63.65; H, 7.81. Calc. for $C_{15}H_{22}O_3S$: C, 63.60; H, 7.77%. IR (KBr, cm^{-1}): 1355, 1180 (S=O). ^{1}H-NMR: $\delta = 7.71$, 7.25 (two d, $J = 8.0$ Hz, 2H each, Ar–H), 4.30 (t of t, $J = 11.1$, 4.5 Hz, 1H, OCH), 2.36 (s, 3H, Ar–CH_3), 1.95–1.80, 1.75–1.65 (two broad m, 8H, ring CH_2s), 1.38 (q of d, $J = 9.0$, 3.0 Hz,), 1.06 (q of d, $J = 7.2$ Hz [doublet coupling not resolved], 2H, CH_3–CH_2), 0.85 (m, unresolved, overlaps Me triplet), 0.76 (t, $J =$ 7.2 Hz, 3H, CH_2–CH_3). ^{13}C-NMR: $\delta = 144.2$, 134.6, 129.6, 127.4 (Ar), 82.4 (O–C), 37.6 (Et–*C*), 32.2, 30.3, 28.6 (CH_2s), 21.4 (Ar–CH_3), 11.4 (CH_2CH_3). The remaining 4-methylbenzenesulfonates **1b**–**e** were prepared by the same procedure on the same scale (33 mmol) and have been reported previously. Yields (%) of isolated product were: **1b**, 96; **1c**, 97; **1d**, 92; **1e**, 90.

4.2. Synthesis of cyclohexyl-Fp complexes from the sulfonate esters

Sodium metal (0.30 g, 13 mmol) was added slowly to 3 ml of mercury in a 100 ml three-necked, round-bottomed flask equipped with a stopcock at the base of the flask (*Caution:* highly exothermic process). Once the amalgam had cooled to room temperature (r.t.), 30 ml of THF was added followed by Fp_2 (1.3 g, 3.7 mmol). After 45 min, the amalgam was drained from the flask and the dark red solution of NaFp was cooled to 0 °C. The 4-methylbenzenesulfonate was then added and the mixture stirred for 1 h. The resulting solution was then transferred via cannula and filtered through a fritted glass funnel containing alumina, the alumina was washed with 20 ml of Et_2O and the solvent removed from the combined organics in vacuo. The residue was then chromatographed on alumina with 10% Et_2O–petroleum ether, collecting all yellow fractions. Small amounts of ferrocene were frequently seen as by-products, along with substantial amounts of Fp_2. The yields of purified product (all are bright yellow oils), along with their spectroscopic and analytical data are presented below. Complete assignment of the ^{13}C-NMR spectra are made in the text.

*4.3. Cyclohexyl-η^5-cyclopentadienyldicarbonyliron(II) (**2a**)*

Yield: 12%. Anal. Found: C, 60.41; H, 6.55. Calc. for $C_{13}H_{16}FeO_2$: C, 60.03; H, 6.20%. IR (cm^{-1}, neat): 2000, 1940 (C≡O). ^{1}H-NMR: $\delta = 4.62$ (s, 5H, Cp), 2.59 (m, 1H, Fp–CH), 1.90 (m, 4H, Fp–CHCH_2CH_2s), 1.62 (m, 4H, Fp–CHCH_2s), 1.27 (m, 2H, Fp–CHCH_2CH_2CH_2s). ^{13}C-NMR: $\delta = 218.4$ (C≡O), 85.7 (Cp), 44.1, 31.8, 27.4 (CH_2s), 28.2 (Fp–CH). (*Note:* this compound was prepared by the procedure above using bromocyclohexane, instead of the sulfonate ester.)

*4.4. cis-4-Methylcyclohexyl-η^5-cyclopentadienyldicarbonyliron(II) (**2b**)*

Yield: 17%. IR (cm^{-1}, neat): 1990, 1930 (C≡O). ^{1}H-NMR: $\delta = 4.68$ (s, 5H, Cp), 2.63 (apparent t, $J =$ 11 Hz, 1H, Fp–CH), 1.85 (m, 3H, Fp–CH–C*H*s and CH_3C*H*), 1.8–1.4 (m, 6H, remaining cyclohexane Hs), 0.94 (d, $J = 7.0$ Hz, 3H, CH_3). ^{13}C-NMR: $\delta =$ 218.1 (C≡O), 85.7 (Cp), 37.6, 36.6 (CH_2s), 28.4, 27.8 (CHs), 17.6 (CH_3).

*4.5. trans-4-Methylcyclohexyl-η^5-cyclopentadienyldicarbonyliron(II) (**2c**)*

Yield: 15%. Anal. Found: C, 61.62; H, 6.90. Calc. for $C_{14}H_{18}FeO_2$: C, 61.34; H, 6.62%. IR (cm^{-1}, neat):

1990, 1930 (C≡O). ^{1}H-NMR: $\delta = 4.68$ (s, 5H, Cp), 2.48 (m, 1H, Fp–CH), 1.98 (m, 1H, CH_3CH), 1.9–1.2 (m, 8H, CH_2s), 0.90 (d, $J = 7.4$ Hz, 2H, CH_3). ^{13}C-NMR: $\delta = 218.0$ (C≡O), 85.7 (Cp), 43.6, 40.2 (CH_2s), 33.3, 27.3 (CHs), 22.8 (CH_3).

4.6. cis-3-Methylcyclohexyl-η^5-cyclopentadienyldicarbonyliron(II) (2d)

Yield: 18%. IR (cm^{-1}, neat): 1995, 1935 (C≡O). ^{1}H-NMR: $\delta = 4.68$ (s, 5H, Cp), 2.58 (m, 1H, Fp–CH), 2.0–1.2 (m, 9H, CH_2s and CH_3CH), 0.82 (d, $J = 6.0$ Hz, 3H, CH_3).

^{13}C-NMR: $\delta = 218.1$ (C≡O), 85.7 (Cp), 53.0, 43.3, 35.8, 31.0 (CH_2s), 37.5 (CH_3C), 27.0 (Fp–CH), 22.9 (CH_3).

4.7. trans-3-Methylcyclohexyl-η^5-cyclopentadienyldicarbonyliron(II) (2e)

Yield: 6%. IR (cm^{-1}, neat): 1995, 1940 (C≡O). ^{1}H-NMR: $\delta = 4.69$ (s, 5H, Cp), 2.96 (m, 1H, Fp–CH), 1.9–1.0 (m, 9H, CH_2s and CH_3CH), 0.86 (d, $J = 11$ Hz, 3H, CH_3). ^{13}C-NMR: $\delta = 218.2$ (C≡O), 85.8 (Cp), 49.4, 44.1, 32.8, 25.4 (CH_2s), 32.4 (CH_3C), 21.7 (Fp–CH), 17.8 (CH_3).

4.8. trans-4-tert-Butylcyclohexyl-η^5-cyclopentadienyldicarbonyliron(II) (2g)

Yield: 11%. IR (cm^{-1}, neat): 1990, 1935 (C≡O). ^{1}H-NMR: $\delta = 4.68$ (s, 5H, Cp), 2.50 (m, 1H, Fp–CH), 2.01 (m, 1H, ^{t}Bu–C*H*), 1.9–0.9 (m, 8H, CH_2s), 0.80 (s, 9H, CH_3s). ^{13}C-NMR: $\delta = 218.1$ (C≡O), 85.7 (Cp), 48.5 (^{t}Bu–*C*H), 44.1, 32.4 (CH_2s), 32.4 [$(CH_3)_3C$], 28.0 (Fp–CH), 27.3 (CH_3).

4.9. cis-4-Ethylcyclohexyl-η^5-cyclopentadienyldicarbonyliron(II) (2f)

Yield: 8%. IR (cm^{-1}, neat): 2000, 1940 (C≡O). ^{1}H-NMR: $\delta = 4.72$ (s, 5H, Cp), 2.68 (m, 1H, Fp–CH), 2.1–1.25 (m, 11H, other ring Hs), 1.2 (m, 2H, CH_2CH_3), 0.93 (app. d, 3H, $J = 6.2$ Hz, CH_3). ^{13}C-NMR: $\delta = 218.1$ (C≡O), 85.7 (Cp), 38.1, 34.7 (ring CH_2s), 35.4 (Et–*C*H), 28.6 (Fp–CH), 23.8 (CH_3CH_2), 12.5 (CH_3).

4.10. trans-2-(6-Methyl-1,4-dioxanyl)-η^5-cyclopentadienyldicarbonyliron(II) (5a) and cis-2-(5-methyl-1,4-dioxanyl)-η^5-cyclopentadienyldicarbonyliron(II) (5b)

NaOMe (0.075 g, 1.4 mmol) and a 1:1 mixture of *syn*- and *anti*-(5,6-dihydro-5-methyl-dioxene)-cyclopentadienyl-dicarbonyliron(II) tetrafluoroborate (**5**) (0.45 g, 1.27 mmol) were combined in 15 ml of THF and cooled to −50 °C. $NaBH_4$ (0.048 g, 1.27 mmol) was then added to the slurry. The mixture was stirred for 30 min at −50 °C, allowed to warm to r.t. and stirred for an additional 30 min. The precipitate was removed via filtration through a fritted disc packed with a short plug of alumina. The alumina was washed with 30 ml of ether, the solvent removed from the combined filtrate and washings, and the residue was chromatographed on an alumina column using 50% ether–petroleum ether as solvent. The second fraction (light brown) contained a mixture of **5a** and **5b** (0.17 g, 50%). The third fraction (bright yellow) was characterized as 2-Fp-acetaldehyde (0.06 g, 21%). The residue of the second fraction was rechromatographed on an alumina column using an ether–petroleum ether gradient elution. The first fraction (light brown) gave 0.075 g of **5b**, while the second fraction (yellow) gave 0.070 g of **5a**.

5a: IR (cm^{-1}, neat): 2000, 1945 (C≡O). ^{1}H-NMR (acetone-d_6): $\delta = 5.59$ (d of d, $J = 6.0$ Hz, 2.4 Hz, 1H, FpCH), 4.94 (s, 5H, Cp), 3.80–3.39 (m, 5H OCH_2s overlapped with CH_3CH), 1.19 (d, $J = 6.4$ Hz, 3H, CH_3). ^{13}C-NMR (acetone-d_6): $\delta = 217.9$ (C≡O), 86.5 (Cp), 77.4 (FpCH) 73.8, 71.4 (OCH_2s), 69.7 (CH_3CH), 16.1 (CH_3).

5b: IR (cm^{-1}, neat): 1995, 1935 (C≡O). ^{1}H-NMR (acetone-d_6): $\delta = 5.88$ (d of d, $J = 7.8$ Hz, 2.8 Hz, 1H, FpCH), 4.93 (s, 5H, Cp), 3.74–3.52 (m, 5H OCH_2s overlapped with CH_3CH), 1.14 (d, $J = 6.4$ Hz, 3H, CH_3). ^{13}C-NMR (acetone-d_6): $\delta = 217.8$, 217.4 (C≡O), 86.5 (Cp), 78.1, 71.9 (OCH_2s), 72.4 (FpCH), 69.1 (CH_3CH), 16.7 (CH_3).

4.11. 4-Tetrahydropyranyl-η^5-cyclopentadienyldicarbonyliron(II) (6)

A solution of NaFp (7.4 mmol) in 30 ml of THF was cooled to 0 °C with stirring and a solution of 4-tetrahydropyranyltosylate (1.8 g, 7.3 mmol) in THF added slowly. The mixture was stirred for 1 h and then filtered through a plug of alumina. The alumina was washed with 40 ml of ether and the solvent removed in vacuo from the combined filtrate and washings. The residue was chromatographed on an alumina column with 50% ether–petroleum ether and the yellow fraction collected and the solvent removed to give a yellow oil, 0.30 g (15%). IR (cm^{-1}, neat): 2000, 1955 (C≡O). ^{1}H-NMR: $\delta = 4.72$ (s, 5H, Cp), 3.81–3.72 [m, 2H, OCH_2(eq)], 3.42–3.30 [m, 2H, OCH_2(ax)], 2.64 (m, 1H, FpCH), 1.98–1.61 (m, 4H, CH_2s) [34]. ^{13}C-NMR: $\delta = 217.5$ (C≡O), 85.7 (Cp), 71.7 (OCH_2), 43.7 (CH_2), 21.5 (Fp–C).

4.12. 3-Tetrahydropyranyl-η^5-cyclopentadienyldicarbonyliron(II) (**7a**)

A solution of NaFp (7.4 mmol) in 30 ml of THF was cooled to 0 °C and 3-bromotetrahydropyran (1.12 g, 7.4 mmol, prepared according to the procedure of Hurd and Jenkins [35] and treated with 5 mol% NaOMe in THF to remove traces of acid) was added and the mixture stirred for 1 h. The reaction was worked up as for **6** to give a light brown oil, 0.40 g (20%). IR (cm^{-1}, neat): 1998, 1936 (C≡O). ^{1}H-NMR: $\delta = 4.71$ (s, 5H, Cp), 3.86–3.27 (m, 4H, OCH_2s), 2.64 (m, 1H, FpCH), 1.90–1.32 (m, 4H, $OCH_2CH_2CH_2$). ^{13}C-NMR: $\delta =$ 216.5 (C≡O), 85.2 (Cp), 79.8 (OCH_2CH), 68.9 (OCH_2CH_2), 39.6 ($FpCHCH_2$), 32.2 (OCH_2CH_2), 23.1 (FpCH).

4.13. cis-3-[η^5-Cyclopentadienyldicarbonyliron(II)]-2-methoxytetrahydropyran (**7b**) and trans-3-[η^5-cyclopentadienyldicarbonyliron(II)]-2-methoxytetrahydropyran (**7c**)

To a solution of NaFp (7.4 mmol) in 30 ml of THF at 0 °C was added *trans*-3-bromo-2-methoxytetrahydro-pyran [36] (1.44 g, 7.4 mmol) with stirring. The mixture was stirred for 1 h and then worked up as for **6**. ^{13}C-NMR showed the product to be a mixture of the *cis*- and *trans*-diastereomers ($\sim$5:1), 0.60 g (28%). The mixture was rechromatographed on alumina by gradient elution using petroleum ether–ether and the *cis*-isomer was recovered as a yellow oil, 0.20 g (33% recovery). The minor *trans*-isomer was lost during the separation, most likely due to decomposition. Its NMR spectroscopic parameters were determined by comparison of the spectra for the mixture to that for the purified *cis*-compound.

7b: IR (cm^{-1}, neat): 2000, 1940 (C≡O). ^{1}H-NMR: $\delta = 4.72$ (s, 5H, Cp), 4.44 (d, $J = 3$ Hz, 1H, OCH), 3.85 [m, 1H, OCH_2(eq)], 3.51 [m, 1H, OCH_2(ax)], 3.32 (s, 3H, OCH_3), 2.77 (m, 1H, FpCH), 2.11–1.51 (m, 4H, CH_2s). ^{13}C-NMR: $\delta = 217.2$ (C≡O), 106.8 (OCH), 85.4 (Cp), 59.4 (OCH_2), 54.9 (OCH_3), 34.2 ($FpCHCH_2$), 31.3 (OCH_2CH_2), 24.0 (FpCH).

7c: ^{1}H-NMR: $\delta = 4.70$ (s, Cp), 4.22 (d, $J = 8.6$ Hz, 1H, OCH), 4.11–3.52 (m, OCH_2), 2.34 (m, FpCH). Remaining signals overlap those of the *cis*-isomer. ^{13}C-NMR: $\delta = 217.15$ (C≡O), 111.9 (OCH), 85.4 (Cp), 66.2 (OCH_2), 55.8 (OCH_3), 39.0 ($FpCHCH_2$), 31.4 (OCH_2CH_2), 24.5 (FpCH).

4.14. 2-[(η^5-Cyclopentadienyldicarbonyliron(II))-methyl]-tetrahydrofuran (**8**)

If the synthesis of **7a** is carried out without the addition of NaOMe–THF to remove traces of acid, compound **8** is isolated instead as a bright yellow oil and characterized by NMR. ^{1}H-NMR: $\delta = 4.78$ (s, 5H, Cp), 3.89–3.32 (m, 3H, OCH and OCH_2), 1.96–1.29 (m, 6H, remaining CH_2s). ^{13}C-NMR: $\delta = 217.2$ (C≡O), 86.1 (OCH), 85.2 (Cp), 67.4 (OCH_2), 34.6, 26.5 ($OCH_2CH_2CH_2$), 6.4 ($FpCH_2$). *Note:* a ^{13}C-NMR INEPT experiment showed the only methine carbon was the ring carbon 2 at 86.1 ppm and the Fp–CH_2 occurred at the unusually high field shift of 6.4 ppm as expected [37], confirming our assignment for compound **8**.

4.15. 2-Tetrahydropyranyl-η^5-cyclopentadienyldicarbonyliron(II) (**9a**)

To a solution of NaFp (7.4 mmol) in 30 ml of THF was slowly added with stirring at −70 °C, 2-chlorotetrahydropyran (0.88 g, 7.4 mmol) which had been freshly prepared by treatment of dihydropyran with dry HCl [38]. The mixture was stirred for 1 h, allowed to warm to r.t. and then worked up as for **6** to give a bright yellow oil, 1.18 g (56%). IR (cm^{-1}, neat): 2000, 1960 (C≡O). ^{1}H-NMR: $\delta = 5.13$ (d, $J = 10.3$ Hz, 1H, FpCH), 4.75 (s, 5H, Cp), 3.84 [d, $J = 11$ Hz, 1H, OCH_2 (eq)], 3.33 [d of d, $J = 11.2$, 10.2 Hz, 1H, OCH_2 (ax)], 2.01–1.48 (m, 6H, CH_2s). ^{13}C-NMR: $\delta = 218.3$, 217.8 (C≡O), 86.4 (Cp), 79.8 (FpCH), 72.5 (OCH_2), 43.5 ($FpCHCH_2$), 27.9 ($OCH_2CH_2CH_2$), 27.2 (OCH_2CH_2).

4.16. cis-2-[η^5-Cyclopentadienyldicarbonyliron(II)]-6-methoxytetrahydropyran (**9b**) and trans-2-[η^5-cyclopentadienyldicarbonyliron(II)]-6-methoxytetrahydropyran (**9c**)

To a solution of NaFp (7.4 mmol) in 30 ml of THF was slowly added with stirring at −70 °C, 2-chloro-6-methoxytetrahydropyran (0.88 g, 7.4 mmol, 1:1 mixture of diastereomers) [39]. The mixture was stirred for 1 h, allowed to warm to r.t. and then worked up as for **6** to give a 1:1 mixture of **7b** and **7c** as a brown oil, 0.99 g (46%). Attempted separation by gradient elution with ether–petroleum ether on alumina failed and the product was recovered as a nearly 1:1 mixture. Small changes in the relative intensities of one set of ^{13}C-NMR resonances after chromatography were used to distinguish which peak belonged to each isomer. IR (cm^{-1}, neat): 1995, 1935 (C≡O). 1H-NMR: $\delta = 5.58$ (d of d, $J = 10.8$, 2.0 Hz, 1H, FpCH), 5.06 (broad, 1H, FpCH), 4.78, 4.76 (two s, 10H, Cps), 4.54–4.12 (m, 2H, OCHOs), 3.44, 3.37 (2 s, 6H, OCH_3s), 2.13–1.25 (m, 12H, CH_2s). ^{13}C-NMR: $\delta = 218.2$, 216.8 (C≡O), 105.6, 98.3 (OCHO), 86.3, 85.6 (Cp), 74.3, 74.3 (FpCH), 57.9, 55.6 (OCH_3), 41.8, 41.8 ($FpCHCH_2$), 31.8, 29.8 ($MeOCHCH_2$), 26.2, 17.3 ($FpCHCH_2CH_2$).

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