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^{13}C NMR Studies of the Complexes $[\eta^5\text{-}C_5H_5Fe(CO)_2(\text{olefin})]BF_4$

DAVID E. LAYCOCK and MICHAEL C. BAIRD*

Department of Chemistry, Queen's University, Kingston, Ont. K7L 3N6 Canada

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The ^{13}C nmr spectra of a series of eighteen complexes of the type $[\eta^5\text{-}C_5H_5Fe(CO)_2(\text{olefin})]BF_4$ are presented. It is suggested that there is a correlation between bond strengths and coordination shifts, both of which are affected by both steric and electronic factors.

Introduction

Numerous ^{13}C nmr data are available in the literature for η^2-olefin complexes of the transition metals [1–3]. While many attempts have been made to correlate olefinic carbon chemical shifts with, for instance, the relative strengths of σ and π bonding [4–7], as well as non-bonding paramagnetic shielding effects [8], there appeared by 1976 to be a concensus that attempts to rationalize ^{13}C chemical shifts in terms of any one factor are not justified and must await greater understanding of both the nature of metal–ligand bonding and the factors affecting carbon chemical shifts [2, 3]. Very recent publications have indeed drawn attention to the complexities involved in understanding ^{13}C chemical shifts of both free [9] and coordinated [10] olefins.

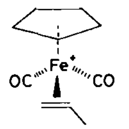
We have recently reported the preparation of a series of complexes of the type $[\eta^5\text{-}C_5H_5Fe(CO)_2\text{-}(\text{olefin})]BF_4$ [11]; many of the compounds were new, and very few ^{13}C nmr data for the series were available [7, 12, 13]. The opportunity was thus presented to investigate a variety of subtle effects of olefin substitution on ^{13}C nmr parameters while holding the metal substituent constant. We report herein the results of this study; the moiety $[\eta^5\text{-}C_5H_5Fe(CO)_2]$ will hereafter be designated Fp.

Experimental

All compounds of the type $[Fp(\text{olefin})]BF_4$ were prepared as previously reported [11]; the compounds studied are listed in Table I. All ^{13}C nmr spectra were obtained on a Bruker HX 60 spectrometer.

Results and Discussion

Complexes of the type $(Fp(\text{olefin}))^+$ assume a pseudotetrahedral structure about the iron, the preferred conformation of the olefin being parallel to the Cp plane [12, 13], *i.e.*



Barriers to rotation about the olefin–metal axis are about 8 kcal mol^{-1} Where possible, olefinic substituents prefer the orientation away from the Cp ring, as shown, consistent with known large stereochemical requirements of the Cp group [14].

The ^{13}C nmr parameters for the compounds studied are listed in Table I along with relevant data from the literature. In each case, only a single set of olefinic resonances was observed, consistent with the expected low barriers to rotation and/or the expected strong preference for a particular conformation. As previously reported [12, 13], complexes of prochiral olefins each exhibit two carbonyl resonances, arising from the diastereotopic carbonyl groups.

As noted previously [7, 12, 13] and shown in Table II, olefinic carbon resonances shift upfield on coordination to the Fp$^+$ moiety. The upfield shift is largest for ethylene (65.6 ppm, compound *1*), and is about 10 ppm larger for C_1 of unbranched terminal olefins than for C_2 (59.5 ± 2.5 ppm *vs.* 49.5 ± 2.8 ppm, compounds *2–7, 9*). The η^2-butadiene complex, *10,* is also comparable to the latter group.

In contrast, the methylene resonances of 2,2-disubstituted olefins shift to a lesser extent on coordination (54.7 ± 1.5 ppm, compounds *12–15*), while the C_2 resonances seem relatively unperturbed (19.8 ± 5.6 ppm). Smaller coordination shifts are also observed for the complexes of *trans*-2-butene (compound *16*), *cis*-2-butene (compound *17*) and *cis*-2-heptene (compound *18*).

Noting that negative coordination shifts in effect move the olefinic resonances upfield towards the positions of saturated aliphatic carbons, Aris *et al.* [7] have suggested that the upfield shifts are a result of π back bonding. While not wishing to add to this

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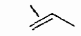
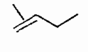
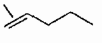
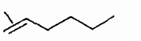
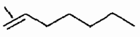
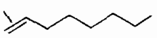
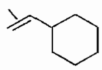
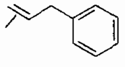
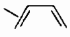
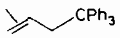
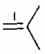
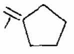
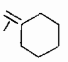
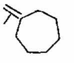
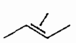
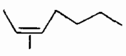
*Author to whom correspondence should be addressed.

TABLE I. ^{13}C Chemical Shifts for the Complexes [Fp(olefin)]$^{+}$.[a]

No.	Complexes as [Fp-‖]$^{+}$	Vinyl Carbon Chemical Shifts			δ(CO)	δ(Cp)	Other
		δ (= CH_2)	δ (= CHR)	δ (= CR_2)			
1		57.2			209.9	90.3	
2 [13]		55.8	85.7		211.0, 209.2	90.0	22.1(CH_3)
3		54.2	91.1		211.2, 209.4	90.2	30.5(C_3), 17.0(C_4)
4		55.3	89.5		211.4, 209.5	90.2	39.7(C_3), 26.7(C_4), 13.8(C_5)
5		55.2	~90.3[b]		211.4, 209.6	90.3	37.6(C_3), 35.9(C_4), 23.2(C_5), 14.2(C_6)
6		54.9	89.6		211.2, 209.4	89.6	37.5(C_3), 33.1(C_4), 32.0(C_5), 23.2(C_6), 14.3(C_7)
7		55.0	89.8		211.2, 209.4	90.2	37.6(C_3), 29.6(C_4), 32.4(C_5), 33.5(C_6), 23.4(C_7), 14.4(C_8)
8		51.6	97.2		211.8, 209.2	90.3	45.1(C_3), 36.7, 36.1, 27.0 (ring CH_2)
9		55.1	86.9		210.9, 209.1	90.1	43.2(C_3), 141.3, 130.1, 129.8, 128.5 (phenyl)
10		52.8	88.5		211.1, 208.8	90.3	125.5, 137.6 (free olefin)
11		60.8	85.0		211.4, 208.4	90.2	48.1(C_3), 58.8(C_4), 147.0, 130.3, 129.4, 127.8(phenyl)
12 [13]		54.3		122.8	210.8	89.9	28.9(CH_3)
13		51.7		127.8	211.4	90.3	38.6(C_3), 27.0(C_4)
14		52.5		130.9	211.4	90.3	42.3(C_3), 35.6(C_4), 26.9(C_5)
15		55.2		135.3	211.3	90.0	41.9(C_3), 31.1(C_4), 28.4(C_5)
16 [12],[c]			89.2		204.9, 201.3	88.0	21.2(CH_3)
17			79.1		210.8	90.0	16.1(CH_3)
18			78.7(C_2) 84.0(C_3)		d	90.2	33.6(C_4), 31.6(C_5), 23.6(C_7), 14.2(C_8)

[a] δ (ppm) relative to TMS, in CD_3NO_2; positive shifts downfield. [b] Obscured by Cp resonance. [c] In CD_3CN. [d] Not observed.

controversy, we suggest a possible correlation between strength of the olefin–iron bonding interaction(s) and the magnitude of the coordination shift. On this basis, we note that the relative coordination shifts listed in Table II suggest that the bonding interaction is the strongest for ethylene, and is somewhat stronger for C_1 than for C_2 of unbranched terminal olefins. In the cases of 2,2-disubstituted terminal olefins, the methylene carbon appears to interact with the metal much more strongly than does C_2,

TABLE II. Comparisons of ^{13}C NMR Data for Free and Coordinated Olefins.

Compound	Δδ^a		
	$= CH_2$	$= CHR$	$= CR_2$
1	−65.6		
2	−62.0	−52.3	
3	−58.6	−49.1	
4	−58.2	−48.1	
5	−58.3	~−47.5	
6	−59.3	−49.5	
7	−59.1	−49.2	
9	−60.7	−50.9	
10	−63.8	−48.7	
12	−55.5		−18.4
13	−53.2		−25.4
14	−54.4		−18.9
15	−55.6		−16.6
16		−36.8	
17		−44.2	
18		−44.8(C_2) −46.8(C_3)	

^{a}Change in chemical shift on coordination.

but somewhat less strongly than does C_1 of unbranched terminal olefins. Furthermore, *trans*-2-butene would appear to interact less strongly than the two *cis*-2-olefins studied, and the two olefinic carbons of *cis*-2-heptene appear to be comparable in their coordinating abilities.

While the suggested correlation between coordination shifts and, in effect, metal–olefin bond strengths may seem rather tenuous, it is known that stability constants for olefin complex formation generally decrease in the order ethylene > 1-olefins > *cis*-2-olefins > *trans*-2-olefins [15]. If back donation is generally important in stabilizing metal–olefin bonds, then it is reasonable that substitution of olefinic hydrogens by alkyl groups should have a destabilizing effect, thus explaining the apparent correlation between coordination shifts and complex stabilities.

However, steric effects may also play an important role in determining the strength of bonding in the iron system under consideration here. As mentioned above, the preferred conformation of the coordinated olefins is that in which the C=C axis is parallel to the Cp ring. Where possible, substituents on the olefin prefer to be oriented away from the bulky Cp ring, and indeed, it would seem that the C=C axis of coordinated unbranched terminal olefins is actually tilted such that C_2 is further away from the Cp ring than is C_1 [1]. If the substituted olefinic carbon were also at a longer bonding distance to the iron, perhaps because of steric interactions with a carbonyl group [16], then bonding between the iron and C_2 would be weaker than that with C_1, consistent with the chemical shift data of Table II.

The data for the complexes of the 2,2-disubstituted olefins are also consistent with this hypothesis. In these cases, it is impossible for the olefin to assume a conformation containing parallel C=C axis and Cp ring without having an alkyl substituent interacting with the Cp ring. The methylene coordination shifts suggest that the bonding in these complexes is weaker than in the terminal olefin complexes already discussed but, more importantly, the data suggest that in each case the bonding of the disubstituted carbon is very weak. Asymmetry in olefin–metal bond lengths has been discussed previously [17].

The internal olefins would be expected to be even more sensitive to steric destabilization, the effect being greater for *trans*- than for *cis*-2-butene because both methyl groups can be oriented away from the Cp ring in the latter case, but only one in the former. It is interesting that the coordination shifts of *cis*-2-butene and C_2 of *cis*-2-heptene are almost identical, suggesting similar degrees of steric destabilization, and are both larger than that of *trans*-2-butene.

A search of the literature reveals very few systems where the coordination shifts of a large series of olefins have been determined. For the compounds *trans*-$PtCl_2$(olefin)($NC_5H_4CH_3$), the coordination shifts do decrease in the order C_2H_4(47.4) > propylene (43.5, 36.1) ≈ 1-butene (42.9, 34.2) ≈ 1-hexene (44.5, 35.8) > *cis*-2-butene (33.0) > *trans*-2-butene (30.4) [17]. While the significance of the differences between the platinum and iron systems is at present unknown, it is gratifying to note that both series of compounds exhibit the same trends. Furthermore, we note that the spread of the coordination shifts in the platinum series (~ 17 ppm), for which steric hindrance to coordination of substituted olefins would be at a minimum, is only half that of the iron series (~ 29 ppm).

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