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^{13}C CHEMICAL SHIFTS AND C—H COUPLING CONSTANTS OF MAIN GROUP ELEMENT CYCLOPENTADIENYL DERIVATIVES; A CRITICAL SURVEY

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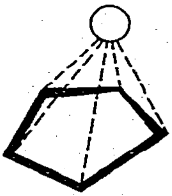
Summary

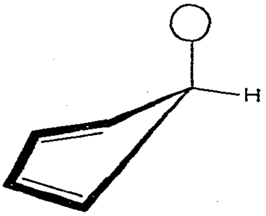
For a series of cyclopentadienyl derivatives of Group IA, IIA and IIIB elements, δ_C, ^1J(C—H) and $^{2,3}J$(C—H) values are reported. The results indicate that neither the ^{13}C chemical shift nor the primary C—H coupling constant may be used as a criterion for assigning a π- or σ-bonded structure to a given cyclopentadienyl compound. The "high resolution" ^{13}C spectrum of lithium cyclopentadienide is fully analyzed; for (C_5H_5)BeBr, a ^{13}C—^{9}Be coupling has been observed.

Introduction

Since the discovery of ferrocene, the question of cyclopentadienyl (Cp) bonding structure has continued to pose intriguing problems to synthetic chemists and spectroscopists. For organometal derivatives of cyclopentadiene, the two extreme types of Cp bonding are represented by the symmetrical π-complex with a *pentahapto* (h^5) C_5H_5 ring, and by a σ-bonded structure incorporating a *monohapto* (h^1) cyclopentadienyl moiety [1] which may also be reduced to C_{5v} symmetry by rapid migration of the metallic ligand around the C_5-perimeter.



π-complex (h^5)



σ-complex (h^1)

TABLE 1

^{13}C NMR DATA FOR MAIN GROUP ELEMENT CYCLOPENTADIENYL DERIVATIVES $(C_5H_5)MR_n$ [δ (ppm) relative to TMS, J (Hz)] [a]

M(etal)	$R_{(n)}$	C_5H_5		α-C(R)		β-C(R)		Internal reference [c]	
		δ_C	J [b]	δ_C	^1J	δ_C	^1J		
Tl(I) [d]		107.52	[e]					C_6D_6	128.25
In [f]	$(C_2H_5)_2$	111.54	163.3	9.74 [g]	? [h]	13.02	122.0	C_6D_6	128.25
			7.0						
Ga [f]	$(C_2H_5)_2$	111.98	164.7	6.83 [g]	120.0	10.60	123.0	C_6H_{12}	27.51
			6.8					(C_6D_6	128.24)
	$(CH_3)_2$	112.72	165.1	? [i]	?			C_6H_{12}	27.51
			6.8					(C_6D_6	128.26)
Al [f]	$(C_2H_5)_2$	111.67	168.3	2.40 [g]	~113	9.64	124.0	C_6D_6	128.25
			6.7						
	$(CH_3)_2$	111.64	167.6	? [i]	?			C_6H_{12}	27.51
			6.6					(C_6D_6	128.27)
Mg [f] [11]	(C_5H_5)	108.02	167.5					C_6D_6	128.25
			6.9						
Be [f] [15]	Br	105.52	179.1					C_6H_{12}	27.51
			6.3					(C_6D_6	128.32)
Be [k] [15]	(σ)-C_6H_5	104.68	[$^1J(^{13}C-^9Be)$ 1.1]	C(1) ? [i]		C(2,6) 140.00		C_6H_{12}	27.51
			177.4			C(3,5) 127.24		($CDCl_3$	77.60)
			6.7			C(4) 127.35			
K [l]		104.78	155.9					C_6H_{12}	27.51
			6.9					(C_6D_6	128.39)
Na [l]		103.35	156.5					C_6H_{12}	27.51
			7.0					(C_6D_6	128.36)
Li [l]		103.59	159.4					C_6H_{12}	27.51
			6.9					(C_6D_6	128.31)

[a] For details of the PFT measurements see Experimental section. [b] The first coupling constant given for the cyclopentadienyl partial spectrum is ^1J(C—H), the second represents the mean spacing of the five prominent lines of each subspectrum ($^{2,3}J$, see text). [c] As TMS has been shown to influence the signal position of metal-bonded carbon atoms [13], cyclohexane was used throughout as internal reference; the δ_C values were then converted to the TMS scale with $\delta(C_6H_{12})$ 27.51 ppm [14]. The chemical shift of hexadeuterobenzene, C_6D_6, is given as a secondary standard; for those instances where it served as primary internal standard, $\delta(C_6D_6)$ was set at 128.25 ppm relative to TMS. [d] Solvent $C_6D_6/(CD_3)_2SO$ (1 : 3). [e] Not determined because of very low solubility. [f] Solvent C_6D_6. [g] Severely broadened lines. [h] Evaluation not feasible due to extreme line broadening. [i] The corresponding resonance cannot be identified in the spectrum. [k] Solvent $CDCl_3$. [l] Solvent dimethoxyethane/C_6D_6 (3 : 1).

Even under fast exchange conditions for the σ-complex, NMR spectroscopy would, in principle, be an excellent tool for differentiating between these two extreme structures. For ^1H NMR, however, shifts due to anisotropic magnetic and/or electric field gradients (based, for instance, on the metal atom) or to solvent effects are of the same order of magnitude as those induced by the change in bond hybridization inherent in going from π- to σ-complex. Thus, the rather small δ_H differences observed for the various cyclopentadienyl compounds do not provide clear evidence for one or the other structural alternative.

Carbon-13 spectra, on the other hand, are expected to provide much more cogent information on the Cp bonding type for a given compound since an aliphatic carbon atom, especially when directly bonded to an electropositive metallic substituent, appears better shielded by 50—100 ppm relative to olefinic or aromatic ^{13}C nuclei. So even under fast exchange conditions the average chemical shift for a σ-complex molecule should differ significantly from that for a true π-complex (with five sp_2 carbons), i.e. $\delta_C(\pi) > \delta_C(\sigma)$. While δ_C values for ferrocene and related compounds have been known for some time, true σ-bonded structures were established only recently when $(CH_3)_3M$ migration around the C_5-perimeter could be frozen out for the trimethylcyclopentadienyl derivatives of Group IVB elements (M = Si, Ge, Sn) [2—4]. The chemical shift argument set forth above was shown to be invalid, however, since for all these σ-complex compounds, the cyclopentadienyl ^{13}C shifts appear at appreciably lower field than for established π-complexes. Nevertheless, Sergeyev was able to classify about a dozen cyclopentadienyl derivatives from their Cp carbon shifts as either π- or σ-bonded [5]; for each type, he gives limiting δ_C shift ranges [6] as follows (only transition metal compounds listed in the case of π-complexes):

σ-complexes	113—118 ppm	[$(CH_3)_3Ge(C_5H_5)$	116.7 ppm]
π-complexes	70— 93 ppm	[ferrocene	69.2 ppm]

Thus, we turned to ^{13}C NMR spectroscopy in the hope of obtaining definite evidence for the cyclopentadiene bonding structure in the dialkyl cyclopentadienyl derivatives of Group IIIB elements [7], independent from that given by the vibration spectral analysis reported in the preceding paper [8]. The attempt to fit the δ_C values for these compounds into Sergeyev's general scheme met with difficulties. The investigation was therefore extended to include a number of alkali and earth-alkali metal cyclopentadienides, and the results represent a fairly comprehensive survey of ^{13}C NMR spectral properties of Cp derivatives of elements of the first three Main Groups.

^{13}C Shift data

For these Main Group element cyclopentadienyls, the ^{13}C chemical shift data (Table 1) do not yield any relevant structural information. Within each main group, i.e. for the alkali cyclopentadienides as well as for the Group IIIB derivatives, the δ_C variance is little more than 1 ppm; the deviation for the thallium compound has probably to be attributed to its being a thallium(I) monoligand derivative. The only trend which appears from the values compiled in Table 1 is a distinct low-field shift with increasing electronegativity of the central atom when one goes along a given period.

	NaCp	→	CpMgCp	→	$(CH_3)_2AlCp$	→	$(CH_3)_3SiCp$
δ_C(ppm)	103.35		108.02		111.64		115.8 [4]
	KCp	→		→	$(CH_3)_2GaCp$	→	$(CH_3)_3GeCp$
δ_C(ppm)	104.78		?		112.72		116.7 [4]

(The values for trimethylsilyl and -germyl cyclopentadiene are those reported in the literature [4] for fast exchange conditions.)

Despite the rather narrow range of carbon shifts, the above compounds comprise the full range of cyclopentadienyl bonding structure. Thus, Na and K cyclopentadienide are definitely ionic species while dicyclopentadienylmagnesium has been shown by both crystal structure analysis [9] and electron diffraction [10] to possess a sandwich structure with more or less covalent character. The Si and Ge derivatives, on the other hand, are *monohapto* σ-cyclopentadienyl compounds; this has been established unequivocally by ^1H and ^{13}C NMR in cases in which the silyl and germyl migration can be frozen out [3,4]. For dialkylcyclopentadienyls of Group IIIB elements, such a true σ-bonded structure was ruled out from an analysis of the vibration (IR, Raman) spectra [8], but we were not able to assign to these compounds either a *pentahapto* (π-complex) or a *polyhapto* (h^2/h^3) configuration. From an electron diffraction study of $(CH_3)_2AlCp$, Haaland has deduced a h^2/h^3-structure for this compound [11].

In terms of the standard ranges given by Sergeyev [6], both $MgCp_2$ and the Group IIIB derivatives must be assigned a σ-bonded rather than a π-complex configuration, contrary to all other spectral evidence. Furthermore, in compiling his list of cyclopentadienyl derivatives, Sergeyev omitted two π-complexes, $(\pi\text{-}C_5H_5)_2TiCl_2$ and $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_6H_5)_2$ [12], whose chemical shifts (121.3 and 116.8 ppm, respectively) definitely fall within his limits for genuine σ-bonded structures. From this and from the δ_C values in Table 1, it is apparent that ^{13}C chemical shift data do not warrant a structural type assignment, at least not for cyclopentadienyl compounds of Main Group elements.

$^{13}C—^1H$ Coupling constants

For *monohapto* σ-cyclopentadienyls, the $^1J(C—H)$ values determined experimentally under fast exchange conditions is an average value given by:

$$^1\bar{J} = 1/5[2\,{}^1J(C^{1,4}_{sp_2}—H) + 2\,{}^1J(C^{2,3}_{sp_2}—H) + {}^1J(C^{5}_{sp_3}—H)]$$

Because of the smaller ^1J coupling for the sp_3 carbon C(5), one would expect the mean value of ^1J for rapidly fluctuating σ-cyclopentadienyls to be significantly smaller than that for π-complexes where the C_5H_5 ligand is made up by five sp_2 carbons. Hence, Sergeyev [6] has set the following limits for *mono-* and *penta-hapto* Cp species, respectively:

π-complex	175—180 Hz	[ferrocene	174.8 Hz]
σ-complex	153—162 Hz	[cyclopentadiene	159.0 Hz ($\bar{J}$)]

(The ^1J value for C_5H_6 represents the arithmetical mean of the one sp_3 and the four sp_2 C—H couplings.)

With 156—159 Hz, the coupling constants for the alkali metal cyclopentadienides (Table 1) fall within the σ-complex range even though they may safely be assumed to exist as ionic species in dilute solution (<0.1 molar for our measurements); in our solvent system, benzene/dimethoxyethane, they are probably in the form of fairly tight ion pairs. Since Cp partial structure and C—H bond hybridization should be closely alike for the C_5H_5 anion and the π-complexes, the ^1J values for Li, Na, and K cyclopentadienide clearly violate the coupling constant criterion as set forth by Sergeyev. For Cp_2Mg, on the other hand, the double π-complex (sandwich) structure of which has been established in the gas phase [11] and may reasonably be assumed also for dilute solutions, the 167.5 Hz coupling constant lies appreciably lower than Sergeyev's limiting value for π-complexes, the 174.8 Hz for ferrocene being a typical value for a sandwich molecule. Taken together, these results render the ^1J coupling constant untenable as a means for classifying cyclopentadienyl bonding structure.

However, closer inspection of the alkali cyclopentadienide coupling constants reveals that the value of ^1J decreases with the electronegativity of the metal atom. (The effect is small but outside the experimental error as determined by computer resolution as well as by the constancy of signal position for the secondary standard C_6D_6 (Table 1).) If one assumes fairly close contact between cation and C_5H_5 anion in a kind of charge transfer complex, a smaller electron affinity of the metal cation would mean enhanced negative charge density for the Cp anion.

It has been shown that upon introduction of a cationic center in α-position, ^1J(C—H) for the neighbouring carbon increases by 7—10 Hz [16]; the ^1J value for a carbon atom itself bearing a positive charge, on the other hand, is reduced if the charge can be delocalized, for example into an aromatic π-system [17]. Data for the converse effect, i.e. the decrease of ^1J with an increase in negative charge density, are scarcer, and the effect is by no means firmly established [18]. Within our set of data (Table 1), this trend appears twice, however, once for the ionic alkali cyclopentadienides, and again for the homologous series of dialkyl cyclopentadienyl derivatives of Al, Ga and In for which identical basic structures have been confirmed by vibration spectral analysis [8]. (In the following compilation the ^1J values from Table 1 have been rounded to the nearest 0.5 Hz.)

	LiCp	→	NaCp	→	KCp		
^1J(Hz)	159.5		156.5		156.0		
			$(C_2H_5)_2AlCp$	→	$(C_2H_5)_2GaCp$	→	$(C_2H_5)_2InCp$
^1J(Hz)			168.5		165.0		163.5

Since the cyclopentadienyl bonding type is identical within each of these two series, we think that, for the Cp derivatives of elements of a given group, the decrease of the cyclopentadienyl ^1J(C—H) value with higher atomic number of the metallic counterpart may be rationalized for an otherwise unchanged structure in terms of increasing charge density in the C_5H_5 moiety.

For $MgCp_2$, we find ^1J 10 Hz larger than for the alkali cyclopentadienides; the two beryllium compounds included in this investigation [15] exhibit a direct C—H coupling increased by an additional 10 Hz. This may once more be understood in terms of the charge density concept since, taken as a molecular subunit, both $[BeBr]^+$ and $[Be—C_6H_5]^+$ should exert a considerably higher electron affinity than $[Mg \cdots C_5H_5]^+$.

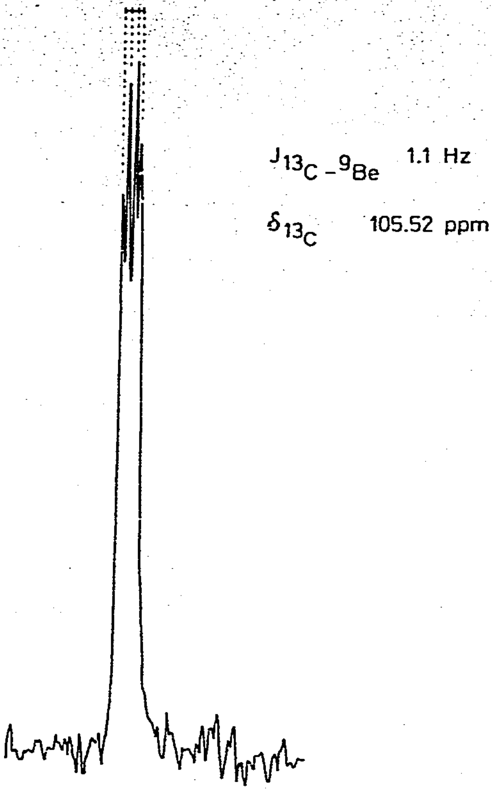


Fig. 1. Cyclopentadienyl carbon-13 resonance of $(C_5H_5)BeBr$ (proton noise-decoupled; in C_6D_6, 30°C).

In the proton noise-decoupled spectrum of $BrBe(C_5H_5)$, the cyclopentadienyl carbon line appears split into a quadruplet of almost equal intensity (Fig. 1); in a high resolution ^{13}C—^{1}H trace, each of the characteristical five lines which constitute the fine structure of the $^{1}J(C—H)$ doublet again displays this extra multiplicity, though not experimentally resolved in each case into all four resonances. We attribute the additional splitting to a coupling between the ^{13}C nuclei and the metal (I_{Be} 3/2); with 1.1 Hz, it can just be resolved under optimum conditions. Final confirmation will have to come from a triple resonance $^{13}C—\{^{1}H, ^{9}Be\}$ experiment. For the corresponding phenyl derivative, $CpBe(C_6H_5)$, we failed to resolve an analogous C(Cp)—Be coupling.

As mentioned above, the ^{1}J doublets of all the cyclopentadienyls investigated in this study exhibit additional fine structure due to long range coupling to protons on neighbouring carbon atoms. For the alkali metal cyclopentadienides, the resonances of the primary doublet are each split into a complex multiplet pattern which is dominated, though, by five prominent lines (Fig. 2a). In the case of the Group IIIB derivatives, these main lines are broadened to such an extent by the quadrupolar metal nuclei ($\nu_{1/2}$ 1.5—2.5 Hz) that their "hyperfine structure" is completely obscured; also, the smaller satellites are buried under the broad bases of the larger resonances. The long range coupling given in Table 1 is therefore not a value arrived at by computational analysis of the

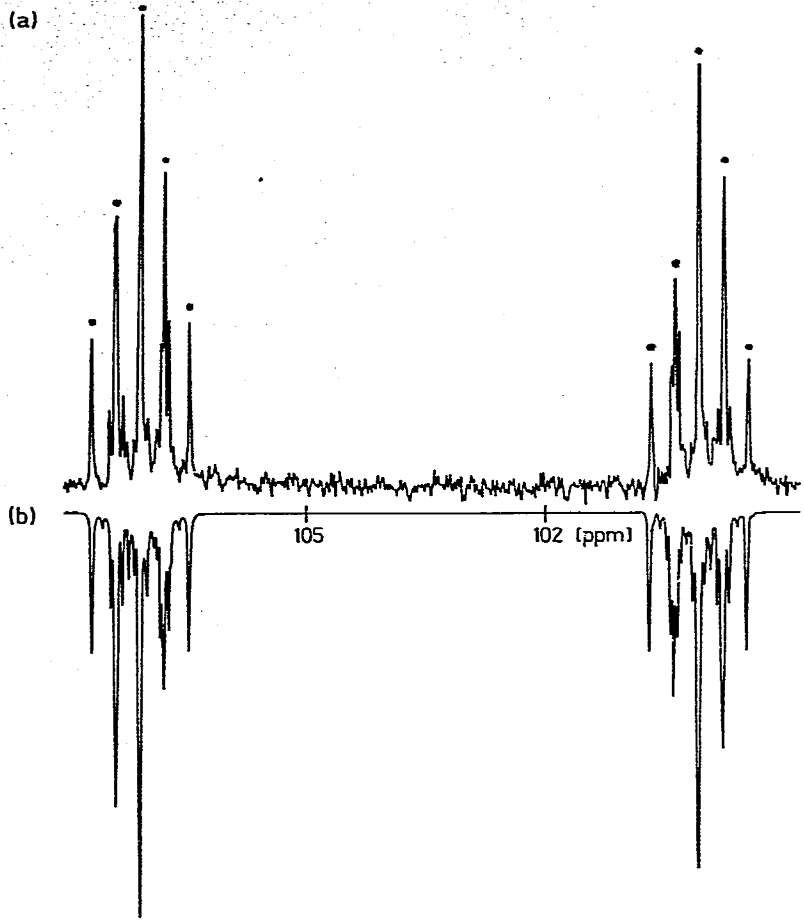


Fig. 2. Fully ^{1}H-coupled ^{13}C NMR spectrum of lithium cyclopentadienide: (a) experimental trace (~0.1 *M* in dimethoxyethane/C_6D_6 (3 : 1), 30°C) obtained with a computer resolution of ±0.2 Hz (2976.1904 Hz sweep width, 16 k interferogram); (b) theoretical spectrum calculated with the ^{13}C—^{1}H and ^{1}H—^{1}H coupling constant values given in the text (line width 0.5 Hz).

fully coupled spectra but rather the mean spacing of the five major lines of each doublet resonance. However, within the limit of experimental error, the apparent $^{2,3}J$ is identical, for all the compounds (6.8 ± 0.2 Hz).

For LiCp, a representative example of the alkali cyclopentadienides for which fully coupled spectra could be obtained with excellent resolution ($\nu_{1/2} < 0.5$ Hz, see Fig. 2a), we attempted to calculate the high resolution ^{13}C spectrum and thus achieve a separation of the two and the three bond ^{13}C—H coupling from the apparent $^{2,3}J$ value. The literature values for ferrocene [19] were used for the ^{13}C isotope shifts of the cyclopentadienyl ring protons. The calculation was started with the three and four bond proton—proton couplings reported for ferrocene [19] which were then iterated for best fit with the experimental trace; likewise, all ^{13}C—^{1}H couplings were optimized for closest fit. Fig. 2b gives the theoretical spectrum calculated with the final numerical values (line width 0.5 Hz):

${}^1J$(C—H)	159.1 Hz	${}^3J$(H—H)	2.40 Hz
${}^2J$(C—H)	5.65 Hz	${}^4J$(H—H)	1.43 Hz
${}^3J$(C—H)	8.20 Hz		

As far as the hyperfine-structure of each doublet resonance is concerned, the fully coupled ^{13}C NMR traces of Na and K cyclopentadienide as well as of $Mg(Cp)_2$ and C_6H_5—Be(Cp) are fully superimposable upon that of the Li compound as shown in Fig. 2a. This represents final and conclusive evidence for an identical structure, both geometrically and electronically, of the cyclopentadienyl moiety in the derivatives of Group IA and IIA elements.

Incidentally, no ^{13}C signal can be detected for the (σ-bonded) methyl groups of both $CpAl(CH_3)_2$ and $CpGa(CH_3)_2$ (see Table 1); for the corresponding diethyl derivatives, the methylene carbon signals are markedly broadened. Likewise, the lines of the aryl carbons C(2) to C(6) of $CpBeC_6H_5$ are sharply defined while no signal appears for C(1) which is σ-bonded to the quadrupolar Be nucleus. Thus one would expect that fixation of a nucleus with $I > 1/2$ to a cyclopentadienyl carbon would so broaden the ^{13}C resonance as to render it practically indetectable. The Cp multiplet fine structure of $CpBeC_6H_5$, though, is as well resolved as, and practically superimposable upon, that for the ionic species LiCp and KCp, which is consistent only with a π-complex structure or with very rapid migration of the BeC_6H_5 moiety around the C_5 ring. For the Al and Ga dimethyl- and diethyl-cyclopentadienyls, low temperature ^{1}H and ^{13}C NMR spectra (toluene-d_8 —80° C; CD_2Cl_2 —100° C) failed to give any evidence of approach to the slow exchange limit for such a process: except for a general line broadening due to the increased viscosity of the samples, no significant change in the spectra was observed which could be interpreted in terms of incipient freezing-out of a sigmatropic metal shift.

Conclusions

^{13}C spectra provide no useful guide to the Cp bonding structure of dialkylcyclopentadienyl derivatives of the Group IIIB elements. For a differentiation between *mono-* and *penta-hapto* compounds, i.e. between σ- and π-complex, neither the ^{13}C shift criterion nor that of the primary ${}^1J$(C—H) coupling stand up to a critical scrutiny in the case of Main Group element cyclopentadienyls. Despite the considerable number of transition metal cyclopentadienyls which conform to Sergeyev's criteria, we believe they should be used with great care even for these compounds: the overwhelming influence of the paramagnetic term for the ^{13}C screening tensor makes any straightforward comparison between transition metal complexes which have either different configuration about the central atom or where the metals belong to different groups of the periodic table a rather risky enterprise since for such complexes the differences in average excitation energy may become very large.

The hypothesis that a careful analysis of the ${}^1J$ data can give an estimate of the relative negative charge density in the C_5H_5 ring for the derivatives of elements of the same group must be tested for a larger ensemble of Main Group as well as for a series of transition metal compounds. Furthermore, for complexes which are markedly associated at higher concentrations, a careful investigation will be needed to show whether there is a significant dependence upon solute concentration for either δ_C or ^1J(C—H) (or both).

Experimental

The ^{13}C NMR spectra were run on a Bruker HX 90 E/Nicolet BNC 12 system (15″ magnet, B-SV 3 PM pulse unit equipped with B-GD1 multipulser, B-SV 3B broad band decoupler, 20 k computer), at 22.63 MHz nominal frequency. Pulse width was 2 μsec (15° tip angle), dwell time/address 168 μsec corresponding to a spectral width of 2976.1904 Hz; with 8 k computer space being utilized for interferogram storage and Fourier transformation, this gives a resolution of 0.7266 Hz or 0.03 ppm per address. For the Cp derivatives of Groups IA and IIA where no quadrupolar line broadening was observed, IF and FT were extended to 16 k thus improving computer resolution by a factor of 2. Decoupling power for proton noise decoupling was set at ~15 W.

The coupling constants were taken from fully ^{13}C—^{1}H coupled spectra obtained by gated decoupling technique. The gated traces were run with 5 μsec pulse width (35° tip angle), the repetition time between consecutive scans (3.0—7.0 sec) being adjusted to about 1.5 times the total acquisition time. Since the J values listed in Table 1 represent average values for multiplet spacings, they should be correct to ±0.2 Hz for 8 k and ±0.1 Hz for 16 k interferograms.

Solutions were 0.1 M in the respective solvents indicated in Table 1 (mostly C_6D_6), the samples being kept protected from air and moisture by dry nitrogen or argon. The temperature was kept at 30°C.

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