

THE ^{13}C NMR SPECTRA OF CYCLOPENTADIENYLIDES AND THEIR COMPLEXES WITH THE GROUP VI METAL CARBONYLS

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Summary

The ^{13}C NMR spectra of some cyclopentadienylides including dimethylsulfoniumcyclopentadienylide (I), diphenylphosphoniumcyclopentadienylide (II), dimethylaminofulvene (III), diphenylfulvene (IV) and complexes of the ylides I and II with Group VI metal (Cr, Mo, W) carbonyls are studied. The shielding specificities of the carbon nuclei in the cyclopentadienyl rings of these systems are discussed. Coordination with the transition metal may balance essentially the electron density in the π -cyclopentadienylic fragments of the ylides along with the general enhancement of shielding of the carbon nuclei in these fragments. The degree of shielding depends on the nature of central metal atom varying in the sequence $\text{Cr} > \text{W} > \text{Mo}$.

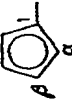


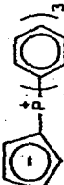
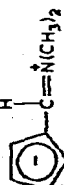


Cyclopentadienylides being rather stable bipolar compounds with the negative charge delocalized over the cyclopentadienyl ring may serve as convenient models in the study of the behaviour of the cyclopentadienyl anion. The syntheses of transition metal complexes with cyclopentadienylides as π -ligands stimulated such investigations. This provided the possibility of elucidating the effect of transition metal coordination upon the properties and reactivity of the cyclopentadienyl anion.

Valuable information on the effect of coordination upon the properties of cyclopentadienylides may be obtained from the ^{13}C NMR spectra. In particular, one may obtain electron density redistribution pattern over the cyclopentadienylide upon its coordination with transition metals.

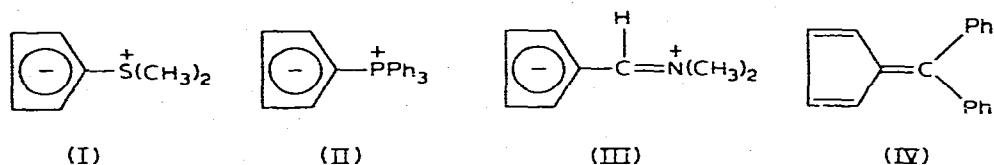
This paper is concerned with the ^{13}C NMR study of some cyclopentadienylides with S-, P- and N-onium atoms: dimethylsulphoniumcyclopentadienylide (I), triphenylphosphoniumcyclopentadienylide (II), dimethylaminofulvene (III), diphenylfulvene (IV, "C-ylide") and complexes of ylides I and II with Group VI metal carbonyls (Va–Vc and VIa–VIc).

Before our investigations only ^{13}C NMR spectral data have been obtained for

TABLE 1
 CHEMICAL SHIFTS OF ^{13}C NUCLEI IN CYCLOPENTADIENYLIDES I-IV IN Cl_2Cl_2 AT 25°C (δ ppm FROM TMS)

Compound			ClI_3	C=			C(p)
	C(1)	C(α (β))			C(β (α))	C(2)	
	83.78	112.60	109.44	35.05	--	--	--
	78.00	116.75	114.48	--	126.70	133.74	132.00
	117.18	124.71 ^b 124.45	119.06 ^b 114.12	43.56	148.75	--	--
	143.95	128.87	124.39	--	152.00	141.35	132.44
	--	102 ^a	--	--	--	--	--

^a See ref. 1. ^b Because of the asymmetry of the molecule the carbon atoms of the Cp-fragment are diastereotopic. This question will be discussed in detail later.



Va, M = Cr; Vb, M = Mo; Vc, M = W

VIa, M = Cr; VIb, M = Mo; VIc, M = W

the P-ylide, II [1] and III, and no information was available on cyclopentadienylide complexes.

Compounds I–IV may be presented by two limiting structures: ylide (A) and ylene (B).



However, the ylide structure is specific for the compounds I and II.

Quantum chemical computations show that there is about 80% of ylidic (A) and only 20% of ylenic (B) structures in the ylides I and II [2,3]. Dimethylaminofulvene III also has a greater quantity of ylidic structure as evident from X-ray analysis [4], whereas the “C-ylide” IV has, generally, a ylenic structure. This conclusion agrees with the dipole moments of compounds I–IV: compound IV possesses a rather small dipole moment (1.3 D) [5], while in I–III the dipole moments are considerable (5.7, 7.0 and 4.5 D respectively) [6–8].

Results and discussion

The ^{13}C (^1H) NMR spectral parameters of compounds I–IV and complexes V and VI are shown in Table 1 and Tables 2–4 respectively.

Ylides

The ^{13}C (^1H) NMR spectra of ylides I–IV (Table 1) contain three signals from the carbon nuclei in the cyclopentadienyl ring: the signal from the key carbon nucleus (C(1)) combined directly with an onium atom and two signals

from the α - and β -carbons. Attention may be drawn to the fact that in the ylides I and II, specified by the ylidic structure, the key carbon C(1)-nuclei are essentially shielded. E.g. the difference between the C(1) carbon chemical shifts in triphenylphosphoniumcyclopentadienylide II and diphenylfulvene IV is about δ 65 ppm (δ 78.00 and 143.95 ppm respectively).

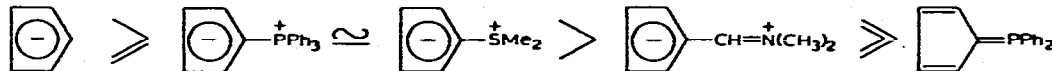
The character of the shielding of the carbon nuclei in the cyclopentadienyl ring in such systems may be elucidated from the data given in Table 1. If in the ylides I and II the α - and β -carbons are considerably less shielded with respect to the key carbons C(1) and their signals are shifted over δ 28–39 ppm downfield, then in ylide III the difference in shielding of the cyclopentadienyl carbons is essentially smaller (δ 3–8 ppm).

An different shielding pattern is observed for cyclopentadienyl ring carbon nuclei in diphenylfulvene IV. In this compound the α - and β -carbons are essentially more shielded than the key C(1)-carbon and their signals are shifted over 15–20 ppm upfield. However, here all the carbon nuclei in the cyclopentadienyl ring are less shielded with respect to those in compounds I–III.

It is interesting to note that the chemical shift of the carbon nuclei in the cyclopentadienyl anion is δ 102 ppm according to Grey [1] which is close to a mean chemical shift of the carbon nuclei in the cyclopentadienyl rings of ylides I and II (ca. δ 105.6 and 108.1 ppm respectively) but different from the value found for IV (δ 130.1 ppm). For ylide III this value is δ 116.7 ppm.

A linear dependence was observed between the mean chemical shifts of the cyclopentadienyl ring carbons and the dipole moments of ylides I–IV (Fig. 1).

These results are in good agreement with the proposed structures of the compounds where the contribution of ylidic structures decreases in the series:



Ylide complexes with metal carbonyls

For elucidating the effect of π -coordination with transition metals upon the shielding of carbon nuclei in the cyclopentadienyl anion, the ¹³C {¹H} NMR

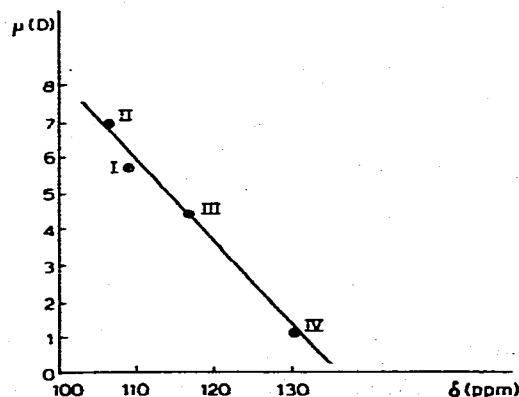


Fig. 1. The mean chemical shifts of the Cp-ring carbon nuclei of ylides versus the dipole moments.

spectra were measured for complexes of S- and P-ylides (I and II) with chromium, molybdenum and tungsten carbonyls. These data are compared to the NMR parameters of the starting ylides I and II (Tables 2 and 3).

(a) *Cyclopentadienyl anion.* It was shown that coordination of ylides I and II with transition metals causes a usual increase in carbon nuclei shielding in the cyclopentadienyl ring. However, there is a difference between the shielding of the C(1) key carbon and the α - and β -carbons. In the α - and β -carbons the signals are shifted more than 20–30 ppm upfield (for complexes Va–Vc and VIa–VIc) while in the key carbon C(1) this value is considerably smaller (δ 2–8 ppm for complexes Va–Vc (Table 2) and 6–10 ppm for VIa–VIc (Table 3)). Thus different shielding of the key and α - and β -carbons upon coordination with transition metals results in significant electron density balancing in the π -cyclopentadienyl fragment of the complexes investigated. For example in the S-ylide (I) the maximum difference in the chemical shifts of the cyclopentadienyl carbons ($\Delta\delta_1 = \delta\alpha_1 - \delta C(1)_1$) attains δ 25.93 ppm while in the same ylide coordinated with Mo(CO)₃ group the value $\Delta\delta_v = \delta\alpha_v - \delta C(1)_v$ is only 8.06 ppm (Table 2, compounds I and Vb respectively). It should be noted that these results agree with the data on hydrogen isotopic exchange in complex Vb [9] in which the rate of hydrogen exchange in the α - and β -positions of the cyclopentadienyl ring was practically the same.

(b) *Substituents at the onium atoms in ylidic ligands.* Analysis of the data given in Tables 2 and 3 shows that the shielding of substituents at the onium atoms changes rather negligibly upon coordination of ylide with the transition metal. Thus the ¹³C NMR signals of methyl groups combined with sulfur atom in Va–Vc are shifted only δ 1–2 ppm upfield (Table 2) with respect to the same signals in the noncoordinated ylide I. A more complex pattern is observed in the case of phenyl groups combined with phosphorus, in complexes VIa–VIc. The signal of the key carbon C(2) in the phenyl ring is shifted over δ 5 ppm upfield upon coordination I with chromium, molybdenum and tungsten. However there was almost no change in the ¹³C signal positions for *o*-, *m*- and *p*-carbons upon their coordination ($\Delta\delta$ 0.3–0.9 ppm for *o*- and *m*- and 2.5 ppm for *p*-) independent of the nature of the central metal atom (Table 3).




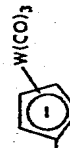
(c) *The effect of the central metal atom.* There is an definite dependence between the shielding of carbon nuclei in the cyclopentadienyl ring and the nature of the central metal atom. Coordination with chromium causes greater shielding relative to molybdenum while tungsten is intermediate, i.e. the α - and β -carbon chemical shifts in the cyclopentadienyl fragments of the ylides change in the following series upon their coordination with the Group VI metals: Cr > W > Mo.

(d) *Carbonylic ligands.* Dependence is also observed in the chemical shifts of the carbonylic ligands of complexes Va–Vc and VIa–VIc. It was shown that the shielding of ¹³C nuclei in the CO ligands is enhanced on passing from chromium to molybdenum and tungsten; the difference in chemical shifts between the metals being about δ 10 ppm. A similar sequence of chemical shifts was observed earlier for the Group VI metal carbonyls [10] and their complexes with cyclooctatetraenic ligands [11]. Table 4 shows the ¹³C NMR data of the Group VI metal carbonyls and some of their derivatives.

It follows from the data given in Table 4 that a replacement of three CO

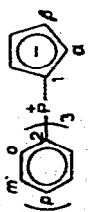
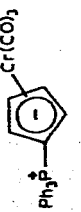
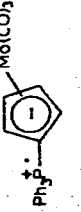

(continued on p. 368)

TABLE 2
 CHEMICAL SHIFTS OF ^{13}C NUCLEI IN YLIDE I AND IN COMPLEXES Va, Vb, Vc IN $(\text{CH}_3)_2\text{SO}$ AT 25°C (δ PPM FROM TMS)

Compound	$\pi\text{-C}_5\text{H}_4$			CH_3			CO		
	C(1)	$\Delta\delta(1)^a$	C($\alpha(\beta)$)	C($\beta(\alpha)$)	$\Delta\delta(2)^a$	δ	$\Delta\delta(3)^a$	δ	$\Delta\delta(4)^b$
	85.44	—	111.37	109.29	—	34.24	—	—	—
	78.62	6.82	86.42	84.26	27.11–22.87	32.03	2.21	241.90	—
	83.36	2.08	91.42	89.40	21.97–17.87	33.07	1.17	231.51	10.39
	77.39	8.06	88.95	87.33	24.04–20.34	32.88	1.36	221.83	9.68

^a $\Delta\delta(1,2,3) = \delta(\text{ylide}) - \delta(\text{complex})$. ^b $\Delta\delta(4) = \delta(\text{CO}_V\text{a}) - \delta(\text{CO}_V\text{b})$ (or $\delta(\text{CO}_V\text{b}) - \delta(\text{CO}_V\text{c})$).

TABLE 3
 CHEMICAL SHIFTS OF ^{13}C NUCLEI IN YLIDES II AND COMPLEXES VIA, VIB, VIC IN CH_2Cl_2 AT 25°C (δ ppm FROM TMS)

Compound	$\pi\text{-C}_5\text{H}_4$				CO		C_6H_5		
	C(1)	$\Delta\delta(1)^a$	C($\alpha(\beta)$)	C($\beta(\alpha)$)	$\Delta\delta(2)^d$	C(2)	C($\alpha(m)$)	C($m(o)$)	C(o)
	78 (112) ^b	--	116.75	114.48	--	126.70 (93)	129.00 (13)	133.74 (12)	132.00
	67.02 (112)	10.98	89.72 (13)	87.25 (13)	29.50-- 24.76	241.02 (93)	129.78 (12)	134.03 (10)	134.52
	71.77 (113)	6.23	94.88 (12)	91.84 (15)	24.91-- 19.60	230.43 (93)	129.78 (13)	134.03 (10)	134.52
	70.3 ^c (109)	7.7	91.47 (12)	89.30 (13)	27.45-- 23.01	220.23 (93)	129.94 (13)	134.23 (10)	134.78

^a $\Delta\delta(1,2) = \delta(\text{ylido II}) - \delta(\text{complex})$, ^b $J(^{13}\text{C}-^{31}\text{P})$ is shown in parentheses (Hz), ^c Spectrum with low signal/noise ratio.

TABLE 4
 ^{13}C NMR DATA OF GROUP VI METAL CARBONYLS

No.	Compound	δ ^{13}C CO ligand (ppm)	$\Delta\delta = \delta(\text{Cr}) - \delta(\text{Mo})$ or $\delta(\text{Mo}) - \delta(\text{W})$ (ppm)	Reference
1	$\text{Cr}(\text{CO})_6$	212.5	—	10
2	$\text{Mo}(\text{CO})_6$	202.0	10.5	10
3	$\text{W}(\text{CO})_6$	192.1	9.9	10
4	$(\text{C}_8\text{H}_8)\text{Cr}(\text{CO})_3$	231.2	—	11
5	$(\text{C}_8\text{H}_8)\text{Mo}(\text{CO})_3$	218.2	13.0	11
6	$(\text{C}_8\text{H}_8)\text{W}(\text{CO})_3$	207.0	11.2	11
7	$(\text{C}_5\text{H}_4\text{S}(\text{CH}_3)_2)\text{Cr}(\text{CO})_3$	241.90	—	This work
8	$(\text{C}_5\text{H}_4\text{S}(\text{CH}_3)_2)\text{Mo}(\text{CO})_3$	231.51	10.49	This work
9	$(\text{C}_5\text{H}_4\text{S}(\text{CH}_3)_2)\text{W}(\text{CO})_3$	221.83	9.68	This work
10	$(\text{C}_5\text{H}_4\text{PPh}_3)\text{Cr}(\text{CO})_3$	241.02	—	This work
11	$(\text{C}_5\text{H}_4\text{PPh}_3)\text{Mo}(\text{CO})_3$	230.43	10.59	This work
12	$(\text{C}_5\text{H}_4\text{PPh}_3)\text{W}(\text{CO})_3$	220.23	10.20	This work

groups in the carbonyls of Group VI metals by π -ylidic ligands causes a downfield shift in the ^{13}C NMR signals of the remaining CO groups (over $\sim \delta$ 30 ppm) while the α - and β -carbon signals in cyclopentadienylic ligands, as was noted, shift over δ 20–30 ppm upfield (Tables 2 and 3). Different shielding of ^{13}C nuclei in CO and π - C_5H_4 ligands in the complexes Va–Vc and VIa–VIc suggests different mechanisms for the electronic effects transmission in the M–CO and M– $\pi(\text{C}_5\text{H}_4)$ fragments of these complexes.

(e) *The spin–spin coupling constants $J(^{13}\text{C}-^{31}\text{P})$.* Important information may be obtained from the experimental values of the spin–spin coupling constants of the ^{13}C and ^{31}P nuclei in ylide II and its complexes with chromium, molybdenum and tungsten carbonyls. A comparison of $J(^{13}\text{C}-^{31}\text{P})$ constants for ylide II and its complexes VIa–VIc (Table 3) shows that these constants change negligibly upon complexation and for the key C(1) carbons they are 112, 112, 113 and 109 Hz respectively. These data indicate that the character of bonds in the ylide does not change considerably upon its coordination with a transition metal.

Thus, analysis of the NMR ^{13}C data of ylides I–IV shows that in compounds I and II, with typical ylide structure, the cyclopentadienyl ring carbons are essentially more shielded in respect to compounds IV with typical ylenic structure. Ylides and ylenes have different patterns of shielding for the carbon nuclei in the cyclopentadienyl fragment. Key carbon nuclei are most shielded in ylides but they are deshielded in ylenic compounds. Linear dependence was established for the mean chemical shifts of the cyclopentadienyl ring carbons and dipole moments of compounds I–IV. The π -coordination of ylides I and II with transition metals not only enhances the shielding of π -ligand carbons but causes considerable balancing of electron density in the π -cyclopentadienyl ring. The degree of shielding is defined by the nature of the central metal atom varying in the order: $\text{Cr} > \text{W} > \text{Mo}$. For triphenylphosphonium cyclopentadienylyde complexes with Cr, Mo and W carbonyls it was shown that the spin–spin coupling constants of the ^{13}C and ^{31}P nuclei practically do not change under complex

formation, and thus the bond character in ylide II with typical ylidic structure does not alter essentially after coordination with a transition metal.

Experimental

Cyclopentadienylides I, II, III and IV were prepared using the methods described [12–15]. Complexes Va–Vc were obtained by method [16] and VIa–VIc as in [17]. All solvents were distilled under argon. The $^{13}\text{C}\{\text{H}\}$ NMR spectra were recorded on a Bruker HX-90 spectrometer at 22.63 MHz with Fourier transform, proton decoupling and noise modulation. The spectra were recorded in ampules (diam. 10 mm) under argon.

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