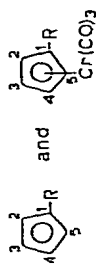




TABLE 1

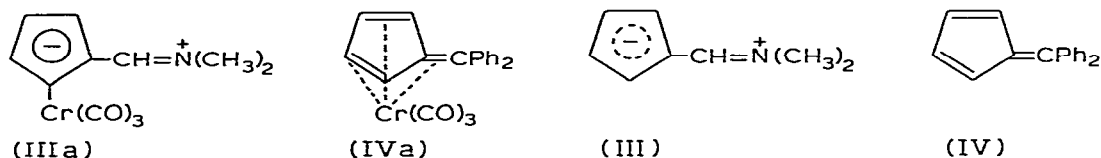
<sup>13</sup>C NMR CHEMICAL SHIFTS (δ ppm from TMS) OF

R	Compound	C <sub>1</sub>	C <sub>2</sub> -O <sub>5</sub>	CO	Substituent R	C <sub>2</sub>		C <sub>p</sub>	C <sub>o(m)</sub>	C <sub>m(o)</sub>	Solvent
						C <sub>exo</sub> <sup>a</sup>	CH <sub>3</sub>				
	IIIa	88.8	89.9	240.3	155.0	47.8					(CH <sub>3</sub> ) <sub>2</sub> CO
	III	117.2	119.1, 124.7, 114.1, 124.5		148.8	49.9					CH <sub>2</sub> Cl <sub>2</sub>
	Δδ	28.4	24.2-34.8		-0.2						
	IVa	107.5	93.9, 89.4	243.3	126.2 <sup>c</sup>		141.0	129.1	128.1	128.3	CH <sub>2</sub> Cl <sub>2</sub>
	IV b	144.0	124.4, 128.9		152.0		141.4	132.5	132.2	127.9	CH <sub>2</sub> Cl <sub>2</sub>
	Δδ b	36.5	30.5-39.5		25.8		0.4	3.4	4.1	-0.4	
	Ia	78.6	86.4, 84.3	241.9		32.1					(CH <sub>3</sub> ) <sub>2</sub> SO
	I	85.5	112.7, 109.4		34.3						(CH <sub>3</sub> ) <sub>2</sub> SO
	Δδ	6.9	23.0-28.4		2.2						
	IIa	67.0	89.7, 87.3	241.0			121.6	134.5	129.8	134.1	CH <sub>2</sub> Cl <sub>2</sub>
	II	78.0	116.8, 114.5				127.0	132.8	129.1	133.8	CH <sub>2</sub> Cl <sub>2</sub>
	Δδ	11.0	24.8-29.5				5.4	-1.7	-0.7	-0.3	

<sup>a</sup> The assignment of the signal was made on the basis of the spectra recorded with or without proton decoupling. <sup>b</sup> Δδ = δ (the starting ylide (ylene) - δ (complex)).  
<sup>c</sup> The ratio signal/noise is small for this signal.

group only 8 ppm. This is in agreement with the results of X-ray analysis of ylide I and its tricarbonylchromium complex which show that the extent of C—C bond equalization in a  $\pi$ -Cp ring of the complex is somewhat higher than in the original ylide I [3]. It seemed therefore to be of great interest to investigate the effect of coordination with a transition metal on the structure and properties of cyclopentadienyl systems in which structure B predominates.

To this end, we studied  $^{13}\text{C}$  NMR spectra of tricarbonylchromium complexes of dimethylaminofulvene (IIIa) and diphenylfulvene (IVa) and compared the results with those obtained earlier for the corresponding non-coordinated fulvenes III and IV [1].



Unlike ylides I and II which are mostly of the ylidic structure, diphenylfulvene (IV) has a typical ylenic structure with dipole moment equal to 1.3 *D* [4]. Dimethylaminofulvene occupies an intermediate position between them (its dipole moment is 4.5 *D* [5]).

## Results and discussion

The  $^{13}\text{C}$  NMR spectra parameters of the complexes IIIa and IVa and the corresponding non-coordinated fulvenes III and IV are given in Table 1, along with the data for ylide I and II and their complexes with a tricarbonylchromium group (Ia and IIa) for comparison.

Analysis of the data in Table 1 shows that coordination with  $\text{Cr}(\text{CO})_3$  in the fulvene IV, which has a typical ylenic structure, and the fulvene III, which has a considerable similarity to the ylidic structure, results in a shifting of the signals from all carbon nuclei of a Cp ring by 25–40 ppm upfield. For ylides I and II this shifting is 22–30 ppm. However, there is a substantial difference in the shielding of the key carbon nuclei ( $\text{C}_1$ ) in these systems. Thus, coordination with a  $\text{Cr}(\text{CO})_3$  group in the fulvenes III and IV shifts the signals from  $\text{C}_1$  in IIIa and IVa by 28 and 36 ppm upfield, respectively, while the corresponding shifts in Ia and IIa are only 7 and 11 ppm. The result is that the difference in the shielding of the  $\text{C}_1$  nuclei in complexes Ia–IVa decreases and becomes equal to about 40 ppm while in free ligands the difference is 66 ppm. Though the degree of shielding of the  $\text{C}_1$  nuclei upon bond formation with the  $\text{Cr}(\text{CO})_3$  fragment increases more in systems with the ylenic structure than in those with the ylidic structure the nuclei remain less shielded in IVa and IIIa as compared with Ia and IIa. It is essential that only in the IVa complex (the original ligand IV has a typical ylenic structure) is the signal from the key carbon  $\text{C}_1$  atom in the Cp ring in a lower field than the signals from the nuclei of other carbons in the ring,  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_4$ , and  $\text{C}_5$ . The reverse is observed in the Ia and IIa complexes where the signals of the key carbon  $\text{C}_1$  nuclei are shifted further upfield than the signals of  $\text{C}_2$ – $\text{C}_5$ . In the complex IIIa (the original ligand III has the ylidic-ylenic structure) the signal of the  $\text{C}_1$  nucleus is shifted only 1.1 ppm upfield with respect to the

center of the multiplet arising from the C<sub>2</sub>—C<sub>5</sub> nuclei of a Cp ring.

As has been mentioned above, bonding with a transition metal atom considerably increases the shielding of the carbon nuclei of a Cp ring in positions 2,5 and 3,4 in all the systems under study. However, shielding is greater in the complexes in which the original ylide (ylene) has a less pronounced ylidic structure. Thus, in the complex Ia the upfield shift of the signals from the C<sub>2</sub>—C<sub>5</sub> nuclei is 22—29 ppm, for the complex IVa it is 30.5—39.5 ppm, while for IIIa the value is intermediate, 29—35 ppm.

A linear dependence proved to exist between the mean values for the chemical shifts of the carbon nuclei in a Cp ring of the original ylides (ylenes) I—IV ( $\bar{\delta}_I$ ,  $\bar{\delta}_{II}$ ,  $\bar{\delta}_{III}$ ,  $\bar{\delta}_{IV}$ ) and the mean change in chemical shifts of the carbon nuclei of the Cp rings in the corresponding complexes Ia—IVa ( $\Delta\delta = \bar{\delta}_I - \bar{\delta}_{Ia\dots}$ ).

The linear dependence (Fig. 1) indicates that greater shielding of the carbon nuclei of a Cp ligand occurs when the Cp ligand is bonded to a transition metal atom in systems with stronger ylenic character with considerable leveling of the electron density in the  $\pi$ -Cp ring in the compounds Ia, IIa, and IIIa.

The <sup>13</sup>C NMR spectral data for the exocyclic carbons C<sub>exo</sub> in the compounds IVa and IIIa should be considered separately. Bonding of the fulvene ligand IV to a chromium atom increases shielding of its C<sub>exo</sub> atom (the signal from the C<sub>exo</sub> nucleus is shifted 26 ppm upfield, while in the compound III such complex formation with the Cr(CO)<sub>3</sub> group results in deshielding of an exocyclic carbon (a shift of the signal from the C<sub>exo</sub> nucleus by 6 ppm downfield).

This difference in the <sup>13</sup>C NMR spectra of the complexes IIIa and IVa is probably due to a specific constitution of the complex IVa in which, according to the X-ray data, the chromium atom is bonded by double bonds of the Cp ring and an exocyclic double bond C<sub>1</sub>=C<sub>exo</sub> [6]. Such coordination results in shifting of the signals from the C<sub>1</sub> and C<sub>exo</sub> nuclei upfield. In the case of the complex IIIa, in which a Cp ring is bound with a Cr(CO)<sub>3</sub> fragment, an increase of the contribution from the ylidic form should result in deshielding of the C<sub>exo</sub> nucleus adjacent to the onium nitrogen and, thus, in an increase of the barrier to rotation of a C<sub>exo</sub>—nitrogen (> C<sub>exo</sub>=N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>) bond. This assumption was supported by an observation of deshielding of the C<sub>exo</sub> nucleus by 6 ppm which took place when the ligand III formed a bond with a Cr(CO)<sub>3</sub> group as well as by the appearance of two signals from methyl groups bonded to a nitrogen atom with chemical shifts of 47.75 and 40.89 in IIIa instead of one signal with a chemical shift of 43.56 in compound III (Table 1).

TABLE 2

MEAN VALUES FOR <sup>13</sup>C NMR CHEMICAL SHIFTS OF THE CARBON NUCLEI IN Cp RINGS IN THE YLIDE-YLENE SYSTEMS AND THEIR COMPLEXES WITH THE Cr(CO)<sub>3</sub> GROUP

Compound	Mean chemical shifts of Cp ring ( $\bar{\delta}$ ) in ppm		
	Non-coordinated (NC)	Coordinated with Cr(CO) <sub>3</sub> (C)	$\bar{\delta} = \bar{\delta}_{NC} - \bar{\delta}_C$
I	105.6	84.0	21.6
II	108.1	84.2	23.9
III	119.9	89.8	30.1
IV	130.1	94.8	35.3

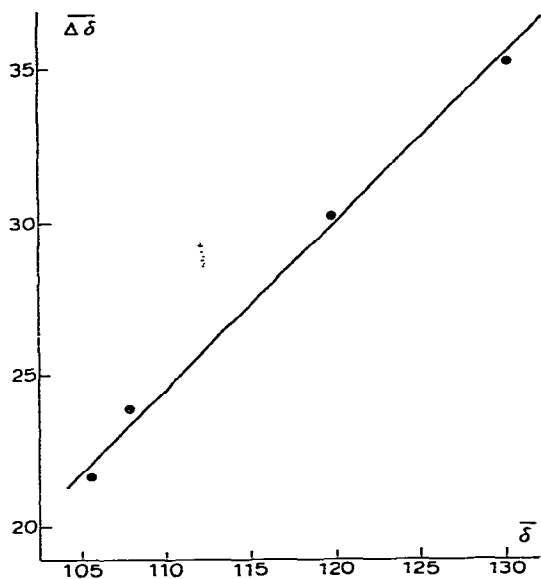


Fig. 1.

Investigation of  $^{13}\text{C}$  NMR spectra of cyclopentadienyl ylide-ylene systems (I–IV) and their  $\pi$ -complexes with the  $\text{Cr}(\text{CO})_3$  group (Ia–IVa) has shown that coordination with a transition metal atom is accompanied by an increase in shielding of all carbon nuclei in cyclopentadienyl fragments which is greater in the systems with a greater contribution from the ylenic structure (compounds III and IV).

In compound III which has an ylide-ylene constitution as well as in compounds I and II with the ylidic structure, coordination with a transition metal atom brings about an increase in the contribution from the ylidic structure, thus causing a leveling of the electron density on all carbon nuclei in the Cp ring as well as an increase in the barrier to rotation about the  $\text{C}_{\text{exo}}-\text{N}(\text{CH}_3)_3$  bond. Coordination with a transition metal atom does not seem to cause changes in the ylenic structure of compound IV which has a typical fulvene structure.

## Experimental

Tricarbonylchromium complexes of dimethylaminofulvene and diphenylfulvene were prepared by following the procedures described in [7] and [8] respectively.

The  $^{13}\text{C}$  NMR spectra were recorded on a Bruker HX-90 spectrometer at 22.635 MHz with Fourier transformations and proton decoupling with noise modulation. The spectra were recorded in ampules with a diameter of 10 mm in argon.

## References

- 1 V.N. Setkina, A.Zh. Zhakaeva, G.A. Panosyan, V.I. Zdanovitch, P.V. Petrovskii and D.N. Kursanov, *J. Organometal. Chem.*, 129 (1977) 361.

- 2 Z. Yoshida, K. Iwata and S. Yoneda, *Tetrahedron Lett.*, (1971) 1519.
- 3 V.G. Andrianov, Yu. T. Struchkov, V.N. Setkina, A. Zh. Shakaeva and V.I. Zdanovitch, *J. Organometal. Chem.*, in press.
- 4 O.A. Osipov and V.I. Minkin, *Handbook on Dipole Moments in Organic compounds (in Russian)*, Vysshaya Shkola Publ. House, Moscow, 1965.
- 5 E.M. Evleth, Jr., J.A. Berson and S.L. Manatt, *Tetrahedron Lett.*, (1964) 3087.
- 6 V.G. Andrianov, Yu.T. Struchkov, V.N. Setkina, V.I. Zdanovitch, A.Zh. Zhakaeva and D.N. Kursanov, *Chem. Commun.*, (1975) 117.
- 7 R.B. King and M.B. Bisnette, *Inorg. Chem.*, 3 (1964) 801.
- 8 R.L. Cooper, E.O. Fischer and W. Semmlinger, *J. Organometal. Chem.*, 9 (1967) 333.