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THE ^{1}H AND ^{13}C NMR SPECTRA OF *sym*-METHYLCOBALTICINIUM HEXAFLUOROPHOSPHATES

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Summary

The NMR spectra of *sym*-methylcobalticinium hexafluorophosphates have been investigated and a comparison with the spectra of the ferrocene analogs made. It was assumed for both series of the compounds that the spatial interactions of the vicinal metallocene methyl substituents are of a similar nature. The trends in the signal shifts of all the ligand nuclei in both series of compounds are discussed.

Introduction

After studying the interaction of methyl groups with a non-classical aromatic metallocene system [1,2,3], we have turned to the consideration of the homologous methylcobalticinium hexafluorophosphate series of the form $[(CH_3)_nC_5H_{5-n}]_2CoPF_6$, the analogs of the methylferrocenes described earlier [1,2]. The electronic system of these compounds is the closest to that of ferrocene and its homologs. It enables us to trace the nature of methyl group conformational interactions in both series and to propose a method of predicting the positions of the ^{13}C(Me) nuclei signals in the NMR spectra for each member of the series of ferrocene methyl homologs, the cobalticinium cation and, probably, other diamagnetic methylmetallocenes.

On the other hand, the transition from ferrocene to the cobalticinium cation makes it possible to consider the perturbation effects introduced by the unit positive charge into the closed electron shell of the parent metallocene. Comparison of the data for both the series of compounds gives additional information on the electronic interactions of the central metal atom with various ligand types: ring, key (the substituted ring C atom), methyl C atoms, hydrogen atoms of the Cp ring and of the methyl groups.

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Results

The form of the ^{1}H NMR spectra of both series of compounds, $(Me_nC_5H_{5-n})_2$-Fe and $[(Me_nC_5H_{5-n})_2Co]PF_6$, is represented schematically in Fig. 1; the ^{13}C NMR spectra are shown in Fig. 2. The coupling constants of ^{1}H signals of

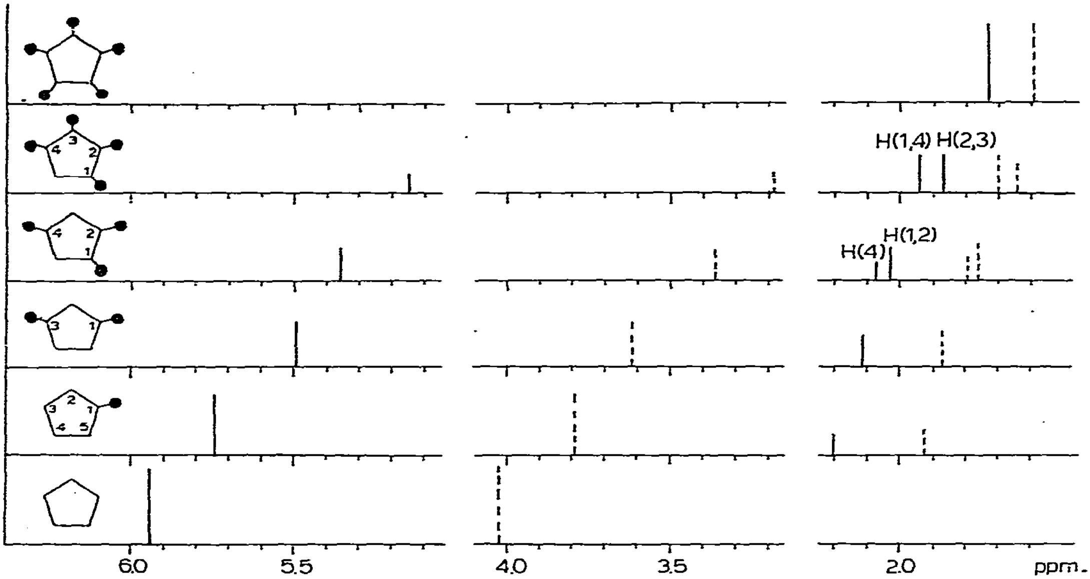


Fig. 1. Schematic form of ^{1}H NMR spectra of the series of *sym*-methylcobalticinium hexafluorophosphates (solid line) and *sym*-methylferrocenes (broken line).

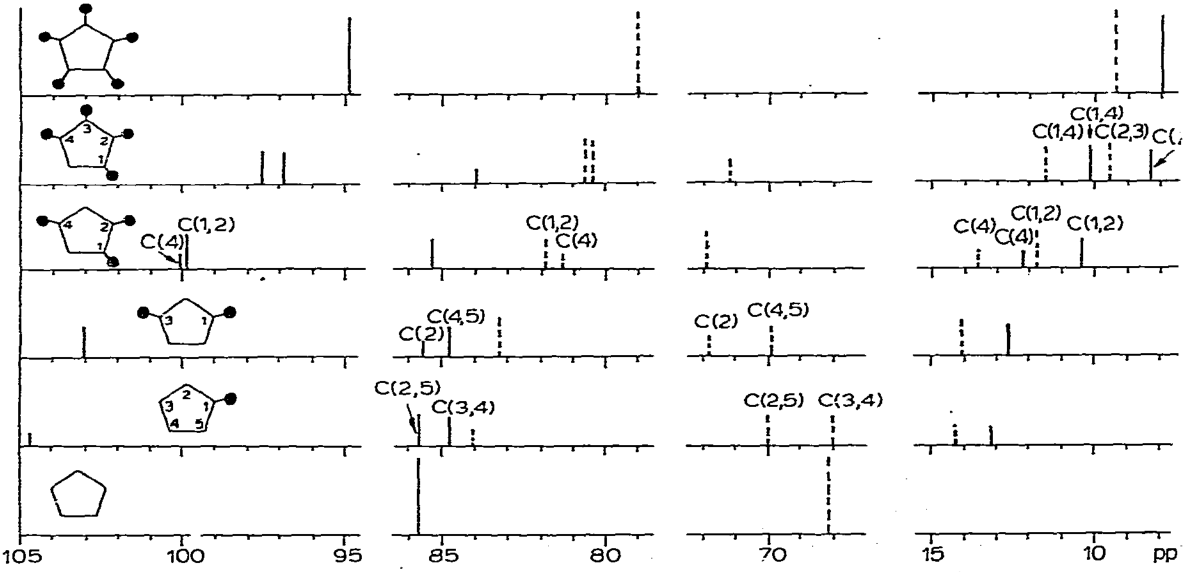


Fig. 2. Schematic form of ^{13}C NMR spectra of the series of *sym*-methylcobalticinium hexafluorophosphates (solid line) and *sym*-methylferrocenes (broken line).

TABLE 1

CHEMICAL SHIFTS OF ^{1}H NMR SIGNALS OF *sym*-METHYLCOBALTICINIUM HEXAFLUOROPHOSPHATES (THE SOLVENT IS ACETONE)

Cation	H(Cp) (ppm)	H(Me) (ppm)
$(Cp_2Co)^+$	5.95	
$[(MeC_5H_4)_2Co]^+$	5.75	2.20
$[(1,3\text{-}Me_2C_5H_3)_2Co)]^+$	5.50	2.12
$[(1,2,4\text{-}Me_3C_5H_2)_2Co]^+$	5.37	2.08(1) [a]
		2.04(2)
$[(Me_4C_5H)_2Co]^+$	5.15	1.95
		1.87
$[(Me_5C_5)_2Co]^+$		1.74

[a] Figures in brackets show the relative intensities of the signals.

methylcobalticinium hexafluorophosphates are given in Table 1. Table 2 shows the chemical shifts of the ^{13}C NMR signals and the coupling constants $^1J(^{13}C{-}^1H)$ for C(Me) nuclei. A signal assignment was made by analogy with the compounds of the ferrocene series [1]. The data for the 1,1'-dimethyl homolog coincide quite closely with those given previously [4].

Discussion

1. *Conformational interactions of methyl groups*

Since in the course of the study of the homologous methylferrocene series by X-ray analysis [2,3] we obtained unambiguous evidence for steric hindrance in the "overcrowded" methylferrocenes and the corresponding ferrocinium cations, it was of great interest to follow the effects of this hindrance in the NMR spectra. The arrangement of the ^{13}C(Me) signals in the spectra of methylferrocenes and methylcobalticinium cations seemed to differ only slightly from the position of the analogous methylbenzene signals. This enabled us to

TABLE 2

CHEMICAL SHIFTS OF SIGNALS AND COUPLING CONSTANTS $^1J(^{13}C{-}^1H)$ OF C(Me) IN ^{13}C NMR SPECTRA OF *sym*-METHYLCOBALTICINIUM HEXAFLUOROPHOSPHATES (THE SOLVENT AND INTERNAL STANDARD IS ACETONE)

Cation	C(Key) [b] (ppm)	C(Cp) (ppm)	C(Me) (ppm)	$^1J(^{13}C{-}^1H)$Me (Hz)
$(Cp_2Co)^+$		85.72		
$[(MeC_5H_4)_2Co]^+$	104.63	85.66	13.08	129.699
		84.68		
$[(1,3\text{-}Me_2C_5H_3)_2Co]^+$	103.01	85.59	12.69	129.394
		84.68		
$[(1,2,4\text{-}Me_3C_5H_2)_2Co]^+$	100.09(1) [a]	85.27	12.17(1)	130.004
	99.89(2)		10.42(2)	129.394
$[(Me_4C_5H)_2Co]^+$	97.55	83.90	10.16	128.784
	96.90		8.27	128.784
$[Me_5C_5)_2Co]^+$	94.88		7.88	

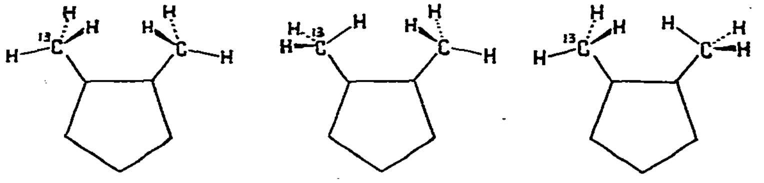
[a] Figures in brackets show the number of carbon atoms. [b] C(Key) is the substituted C atom.

assume, following Grant and his colleagues [5,6], that in this case a conformational interaction of the neighbouring methyl groups is observed, which manifests itself through the electronic effects. It was possible to obtain a set of equations corresponding to the number of unknown parameters. Namely, for the series $(Me_nC_5H_{5-n})_2Fe$ at specified n, the chemical shifts δ of C(Me) nuclei are expressed in the following way

$$\begin{array}{lll}
n=1 & \delta & =\delta_0 \\
n=2(1,3): & \delta & =\delta_0+\Delta\delta_m \\
n=3(1,2,4): & \delta_{(4)} & =\delta_0+2\Delta\delta_m \\
 & \delta_{(1,2)} & =\delta_0+\Delta\delta_{22}+\Delta\delta_m \\
n=4: & \delta_{(1,4)} & =\delta_0+0.33\Delta\delta_{22}+0.67\Delta\delta_{12}+2\Delta\delta_m \\
 & \delta_{(2,3)} & =\delta_0+0.67\Delta\delta_{22}+\Delta\delta_{21}+0.33\Delta\delta_{12}+\Delta\delta_m \\
n=5: & \delta & =\delta_0+0.67\Delta\delta_{22}+\Delta\delta_{21}+0.33\Delta\delta_{22}+2\Delta\delta_m
\end{array}$$

where $\Delta\delta_i$ are the contributions from the main [5] conformations of the $^{13}CH_3$ group to the chemical shift of a given ^{13}C nucleus (Fig. 3). Numbers in brackets show the position of this CH_3 group in a methylferrocene molecule. The chemical shift δ_0 of the nucleus C(Me) of 1,1′-dimethylferrocene was taken as the origin.

In this way we succeeded in calculating the increments of the chemical shifts of signals for three main conformations of vicinal methyl groups of methylferrocenes and for the CH_3 group in the *meta* (*m*) position. The schemes and notations of the conformations are represented in Fig. 3, the conformational population factors are given in Table 3 and the values of the increments are given in Table 4. In accordance with Grant and Woolfenden, the conformations are denoted according to the number of hydrogen atoms of the indicator $^{13}CH_3$ group, which interacts with a neighbouring $^{12}CH_3$ group. As is seen from studying the model, the most stable [5] is the 22 conformation (the two hydrogen atoms of the indicator group interact with the two hydrogen atoms of a neighbouring group). It is also necessary to take into account the 21 and 12 conformations and the electronic effect of *meta* CH_3 groups. The population factors reflect the time of interaction of the indicator group with the other methyl groups for each conformation under study.



22 21 12

Fig. 3. Schemes and notations of the three main conformations of vicinal methyl groups of methylmetallocenes.

TABLE 3

POPULATION FACTORS (P) OF CONFORMATIONS OF *sym*-METHYLFERROCENES ($(Me_nC_5H_{5-n})_2Fe$)

n	CH_3 group position	P_{22}	P_{21}	P_{12}	P_m	Notes
1	1,1′	—	—	—	—	
2	1,3	—	—	—	1	
3	4	—	—	—	2	
	1,2	1	—	—	1	
4	1,4	0.33	—	0.67	2	
	2,3	0.67	1	0.33	1	
5	1—5	—	1	1	2	According to ref. 5 No agreement with experiment
	1—5	0.67	1	0.33	2	

As might be expected, the presence of the unit positive charge does not noticeably affect the conformational hindrance in the methylcobalticinium cations isostructural to the methylferrocenes. Increments found for the neutral compounds predict the values of chemical shifts of the signals in methylcobalticinium cations within experimental errors (Table 5).

We have not restricted ourselves to measuring the ^{13}C NMR chemical shifts only, but we also measured the corresponding coupling constants $^1J(^{13}C—^1H)$. This made it possible, by analogy with the previous case, to find the increments ΔJ_{22}, ΔJ_{21}, ΔJ_{12} and ΔJ_m from the data for di-, tetra-, hexa- and octamethylferrocenes and to use them for predicting the coupling constants in the corresponding methylcobalticinium salts. The values thus obtained agree with the experiment within experimental error (Table 5). These increments $\Delta\delta_i$ and ΔJ_i make it possible to obtain values which are in a good agreement with the experimental chemical shifts and coupling constants for the decamethyl homologs of ferrocene and cobalticinium cation (Table 5) and to perform a more detailed analysis of the conformational state of the CH_3 groups in the decamethyl compounds.

If during this analysis conformational states are used which are similar to the postulated ones for hexamethylbenzene [5], a $^1J(^{13}C—^1H)$ value is obtained which is underestimated by 3.3 Hz. This indicates convincingly that there is another compromise possible for overcoming steric hindrances in overcrowded

TABLE 4

INCREMENTS OF CHEMICAL SHIFTS ($\Delta\delta$, ppm) AND COUPLING CONSTANTS ($\Delta ^1J(^{13}C—^1H)_{Me}$, Hz), CALCULATED FOR *sym*-METHYLFERROCENES

Increment	Conformation			
	22	21	12	m
$\Delta\delta$	—2.24	—2.19	—2.29	—0.23
ΔJ	—0.764	—0.360	—1.874	0.016

TABLE 5

COMPARISON OF THE EXPERIMENTAL AND CALCULATED CHEMICAL SHIFTS δ AND CONSTANTS $^{1}J(^{13}C—^{1}H)$ FOR $^{13}C(Me)$ NUCLEI

Compound	CH_3 group position	δ (ppm)		^{1}J (Hz)	
		experim.	calcd.	experim.	calcd.
$[(MeC_5H_4)_2Co]PF_6$	1,1'	13.08		129.699	
$[(1,3\text{-}Me_2C_5H_3)_2Co]PF_6$	1,3	12.69	12.85	129.394	129.715
$[(1,2,4\text{-}Me_3C_5H_2)_2Co]PF_6$	4	12.17	12.62	130.004	129.732
	1,2	10.42	10.61	129.394	128.951
$[(Me_4C_5H)_2Co]PF_6$	1,4	10.16	10.35	128.784	128.224
	2,3	8.27	8.40	128.784	128.218
$[(Me_5(C_5)_2Co]PF_6$	1—5	7.88	8.17		
$(Me_5Cp)_2Fe$	1—5	9.48	9.41	125.74	125.026

metallocene structures. In hexamethylbenzene the C(Ph)—C(Me) bonds are situated in the benzene ring plane. The rotation of all CH_3 groups is completely equivalent, which masks steric hindrance and shift the C(Me) signals to low fields compared with the C(Me) signal of pentamethylbenzene. In contrast to the planar hexamethylbenzene, a decamethylmetallocene molecule has a greater choice of possible conformations without decreasing the total molecular symmetry. The most favourable conformation, 22, is retained, and a displacement of the CH_3 groups from the Cp ring planes to the outside of a molecule additionally occurs [7]. This allows for independent rotation of the two Cp rings of the molecule and yet does not lead to the necessity of a consistent rotation of

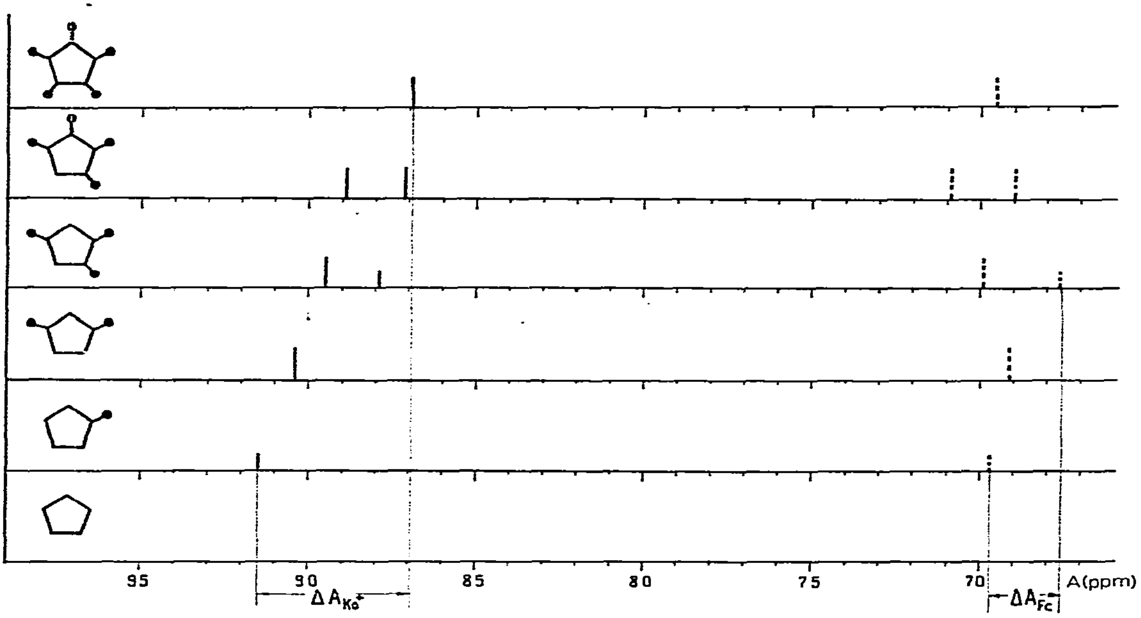


Fig. 4. A plot of the change in the difference of chemical shifts, δ(C(Key)) — δ(C(Me)) = A, in the series of *sym*-methylcobalticinium hexafluorophosphates (solid lines) and *sym*-methylferrocenes (broken lines).

the CH_3 groups belonging to the same ring because the angle between the adjacent methyl groups in the C_5 cycle is greater than that in the C_6 cycle. As a result, the steric interactions of the CH_3 groups are not masked, and the C(Me) signals are in a higher field region compared with the similar signals of octamethylmetallocenes. It is likely that such a picture of the conformational interactions of the adjacent methyl groups will be true for any metallocene of the first transition series due to the similar C(Cp)—C(Cp), C(Cp)—C(Me) and C(Cp)—M distances in these molecules.

2. *Differences in the electronic interaction of the central metal atom with ligands in both series of compounds*

The most appreciable difference in the NMR spectra of both series of compounds is observed for the signals of the C(Cp) nuclei. The position of this signal turned out to correlate with the changes in the difference of the chemical shifts $\delta(C(Key)) - \delta(C(Me)) = A$ (C(Key) is the substituted ring C atom) for the same compound (Fig. 4) (compare Fig. 4 with Fig. 2). This difference reflects the contribution of electronic density of the C(Cp) atom to the C(Cp)—C(Me) bond and may be taken as a measure of this contribution. The maximum shifts towards a smaller difference (ΔA) is a measure of the electron-donating effect of the methyl groups in the series of compounds considered, which is evaluated by the values observed in the NMR spectra.

It is characteristic that the fraction of this displacement per CH_3 group, $\Delta A/A_{n=1}$, is one and a half times greater in the methylcobalticinium series than in the ferrocene series. This shows a greater conductivity of the electron density in the H(Me)—C(Me)—C(Key)—M fragments of a metallocene system with the central atom M having an electron reservoir or a "capacity" (the positive charge of cobalticinium cation). Two other arguments supporting this conclusion are i) the larger upfield shift of the C(Key) signals of methylcobalticinium cations with increasing number of CH_3 groups in the molecule and ii) the weaker perturbation (downfield shift) of the signal of the C(Cp) atom adjacent to C(Key) (i.e. the difference $\delta(C(Cp)_\alpha - \delta(C(Cp)_\beta)$ is smaller) in the methylcobalticinium series. It should be noted that these arguments point to the predominant location of a positive charge on the metal atom.

Deshielding of the ligand nuclei under the effect of a positive cationic charge is seen in the ^1H and ^{13}C NMR spectra of the cobalticinium salts in the form of a downfield shift of the signals of all ^{13}C and ^1H nuclei, except C(Me), compared with the signals of ferrocene analogs. This single exception is related to the stronger release of electron density from the electron-donating methyl substituents in the methylcobalticinium salt series. As a result, a larger displacement electron cloud of the C(Me)—H(Me) bond in the direction of C(Me) occurs, which leads to a stronger shielding of the C(Me) nuclei.

In comparison with the ^{13}C NMR spectra, the arrangement of signals in the ^1H NMR spectra is less characteristic for any series of compounds. This reflects the indirect character of the interaction of hydrogen atoms with a central metal atom. Yet it is clear from Fig. 1 that the electron density is drawn off less from the H(Me) atom in the methylferrocene series and that the upfield shift of the H(Cp) signal, with increasing numbers of CH_3 groups is almost two times more than the H(Me) shift for the both series of compounds. The reason for this phenomenon is clear: the chain for the indirect action of the central metal atom with the H(Cp) atoms is half as long.

Although in considering NMR chemical shifts of diamagnetic molecules we deal with a many-electron parameter and in the NMR of paramagnetic molecules with essentially a monoelectron one, nevertheless for the paramagnetic analogs of methylferrocenes and methylcobalticinium salts (methylferrocinium cations [8,9]) we also can observe not only a mutual effect of the vicinal methyl groups, but also a dominating role of the central metal atom (more than 90% of the unpaired electronic density is concentrated in the nonbonding orbitals of iron). Thus, from the consideration of ^1H and ^{13}C NMR data of all three series of metallocenes it follows that the dominating role in the distribution of the electron density over a metallocene molecule belongs to the central metal atom.

Experimental

Synthesis of methylcobalticinium hexafluorophosphates was described in our previous publication [10]. The IR absorption spectra of these salts were registered with a UR-20 apparatus in KBr pellets in the 600—4000 cm^{-1} region. Spectra of $[(Me_nC_5H_{5-n})_2Co]^+$ cations contain the following absorption bands (in cm^{-1}) for the specified n (numbers in brackets denote the location of the CH_3 group in the cycle).

$n = 0$: 890m, 905m, 940w, 1010m, 1060w, 1417s, 3129s.

$n = 1$: 915s, 940m, 995w, 1042s, 1065w(sh), 1205w, 1243w, 1378w, 1422w, 1445m(sh), 1465s, 1485s, 2875w, 2910w, 2943w, 2980w, 3128s.

$n = 2$ (1,3): 911s, 955m, 1035s, 1048s, 1345w, 1387s, 1440s, 1459s, 1490s, 2870w, 2935w, 2975w, 2990w, 3100m(sh), 3113m.

$n = 3$(1,2,4): 913s, 960m, 980w, 1005m, 1040s, 1120w, 1137w, 1145w, 1200w, 1305w, 1317w, 1340w, 1377s, 1392s, 1421m, 1452s, 1470s, 1493s, 1575w, 2875w, 2935m, 2970w, 2995w, 3010w, 3098s.

$n = 4$: 908s, 990w, 1055s, 1094w, 1117w, 1220w, 1325w, 1370m(sh), 1389s, 1428m, 1458s, 1478s, 1630w, 2870w, 2928m, 2978m, 3104w.

$n = 5$: 1040m, 1090m, 1397s, 1404s, 1443m, 1493s, 2890w, 2937m, 2985m, 3005m.

The ^1H NMR spectra were obtained with a Hitachi-Perkin-Elmer R-20 apparatus with a working frequency of 60 MHz at 34°C, with acetone-d_6 as a solvent; internal standard HMDS. ^{13}C NMR spectra were registered with a Bruker HX-90 apparatus at 22.653 MHz frequency at 30°C; the solvent and the internal standard was acetone.

References

1 R.B. Materikova, V.N. Babin, I.R. Lyatifov, T.Kh. Kurbanov, E.I. Fedin, P.V. Petrovskii and A.I. Lutsenko, J. Organometal. Chem., 142 (1977) 81.
2 Yu.T. Struchkov, V.G. Andrianov, T.N. Sal'nikova, I.R. Lyatifov and R.B. Materikova, J. Organometal. Chem., 145 (1978) 213.
3 V.G. Andrianov, Yu.T. Struchkov, I.R. Lyatifov and R.B. Materikova, Coordinatsionnaya chimiya, in press.
4 A.N. Nesmeyanov, E.V. Leonova, E.I. Fedin, N.S. Kochetkova, P.V. Petrovskii and A.I. Lutsenko, Dokl. Acad. Nauk SSSR, 237 (1977) 143.
5 W.R. Woolfenden and D.M. Grant, J. Amer. Chem. Soc., 88 (1966) 1496.
6 D.M. Grant and B.V. Cheney, J. Amer. Chem. Soc., 89 (1967) 5315.
7 A. Almenningen, A. Haaland, S. Samdal, J. Brunvoll, J.L. Robbins and J.S. Smart, J. Organometal. Chem., 173 (1979) 293.
8 I.R. Lyatifov, S.P. Solodovnikov, V.N. Babin and R.B. Materikova, Z. Naturforsch., 34b (1979) 863.
9 R.B. Materikova, V.N. Babin, S.P. Solodovnikov, I.R. Lyatifov, P.V. Petrovskii and E.I. Fedin, Z. Naturforsch., 35b (1980) 1415.
10 A.N. Nesmeyanov, R.B. Materikova, I.R. Lyatifov, T.Kh. Kurbanov, E.V. Leonova and N.S. Kochetkova, J. Organometal. Chem., 136 (1977) C55.