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Reviews

High-resolution and cross-polarization magic angle spinning NMR studies of tricarbonylchromium complexes with polycyclic aromatic ligands

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The strategy of investigation of the structures and transformations of organometallic compounds by high-resolution NMR spectroscopy in solutions and in the solid state (cross-polarization magic angle spinning NMR) was considered in relation to tricarbonylchromium complexes with polycyclic aromatic ligands.

Key words: organometallic compounds, NMR, cross-polarization magic angle spinning NMR, reaction mechanisms, adsorption.

Introduction

NMR spectroscopy is an efficient method for investigation of the structures and reactivities of organometallic compounds (OMC).[1—4] The NMR method is successfully used to study intermediates and short-lived states[5] important in catalysis and fast processes (with lifetimes of ~10^{-2}—10^{-5} s), *i.e.*, the dynamic behavior of OMC.[6] The use of NMR parameters such as chemical shifts and spin-spin coupling constants (including those for heavy nuclei detectable by NMR) to study OMC structures is discussed in a number of monographs and reference editions.[1—3,7]

Data on the relaxation times of magnetic nuclei (mainly, ^{13}C and ^{1}H), which represent one more parameter derived from NMR spectra, are used less often. Nevertheless, they, too, provide valuable information on the structures of OMC, in particular, transition metal complexes[8] containing hydride and agostic hydrogen atoms.[9] For example, the relaxation time measurement technique has been used successfully[10] for determining the M—H and H—H bond lengths in hydride and dihydrogen complexes and for investigating agostic systems. Relaxation measurements have also been carried out to study the dynamic behavior of OMC, for example, to estimate the barrier to rotation of the cyclopentadienyl rings in ferrocenes.[11]

Data on the nuclear Overhauser effect (NOE) proved to be valuable for investigation of the OMC structures;[12] the use of NOE data allows determination of the structures of compounds and assignment of NMR signals.[13]

Other types of data useful for interpretation of NMR spectra of organometallic compounds, namely those from the ASIS (aromatic solvent induced shift) effect[14,15] and

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the results of calculations of NMR parameters using additive schemes (in particular, for more precise assignment of NMR signals)[8] are now applied only occasionally to determine the structures of OMC.

The application of two-dimensional NMR techniques [16] for the research into structures and dynamic processes in OMC has not yet become a routine either, apparently, due to appreciable time required for the measurements. However, studies of this type appear in increasing frequency.[17]

Solid-state NMR spectroscopy[18] including the wide-line technique[19] is employed much more rarely for investigation of structure and dynamic behavior of OMC than high-resolution NMR spectroscopy. Nevertheless, in recent years, cross-polarization magic angle spinning (CPMAS) NMR technique has started to gain popularity among the chemists working with organometallic compounds.[20,21]

The CPMAS NMR method proved to be indispensable for the study of complexes that are poorly soluble or unstable in solutions,[22] various inclusion (intercalation) compounds, in which the compound under study (in, particular OMC) occurs within a neutral matrix (for example, graphite[23] or $CdPS_3$ [24]), insoluble metal clusters[25] or organometallic compounds applied onto inorganic oxides or zeolites,[26] and OMC-based catalysts.[5] In addition, this method can be used to study those rearrangements and isomerizations of OMC that cannot be retarded in solution due to low activation barrier. In solids, these processes occur much more slowly due to crystal lattice effects.[27]

The CPMAS NMR method seems to be promising for the investigation of chiral transition metal complexes supported on silica gel modified by grafted chiral reagents (for example, cellulose derivatives[28]). In this case, the support acts as an asymmetric reagent by creating a diastereomeric environment inducing splitting of NMR signals.[29]

This review surveys studies devoted to the structures of transition metal complexes (mainly, tricarbonylchromium complexes) containing polycyclic aromatic ligands and dynamic processes in these complexes by the high-resolution and CPMAS NMR methods. In the case of high-resolution NMR, in addition to recording the ^{1}H, ^{13}C, and ^{2}D NMR spectra (the last-mentioned type of spectra were recorded for deuterium labeled tricarbonylchromium complexes) and NMR spectra for some other nuclei, the homonuclear NOE effect was measured for structure determination and for ^{1}H NMR signal assignment (the NOEDIF technique). In some cases, various 2D spectroscopy techniques were used, for example, COSY [30] and NOESY [31] were used to assign ^{1}H NMR signals, the assignment of ^{13}C NMR signals was done using the HETCOR technique,[32] and selective INEPT was employed to assign signals from quaternary C atoms.[33] A number of complexes both solid and supported on silica gel were studied by ^{13}C and ^{1}H (CP)MAS NMR.

Study of tricarbonylchromium complexes with polycyclic aromatic ligands by high-resolution NMR spectroscopy

Determination of the structure and assignment of ^{1}H NMR signals by NOE measurements. The structures of all complexes were studied using high-resolution ^{1}H, ^{13}C, and ^{2}D NMR spectroscopy. The use of NMR spectroscopy for these and other nuclei having a magnetic moment is rather traditional in the chemistry of OMC,[7] in particular, in the investigation of the tricarbonylchromium complexes with polycyclic aromatic ligands (PAL). The vast experimental material has been arranged in tables.[34] We will only briefly discuss and illustrate these data and will analyze in more detail the scope of applicability of the NOE, double resonance, the ASIS effect, and 2D NMR spectroscopy for determination of the structures of OMC.

The measurement of the nuclear Overhauser effect is among the most convenient and fast methods for identification of spatial proximity of protons[35] (or, to somewhat less extent, of a proton and a different nucleus, for example, ^{13}C).[36] The method is based on direct dipole—dipole coupling of nuclei, which normally has no influence on the spectral pattern for a sample in a liquid isotropic medium. By means of the NOE, one can estimate indirectly the coupling, which is related to internuclear distances and nuclear movement. This effect shows itself as a change in the intensity of one resonance signal on excitation of another signal. This excitation is accomplished by saturating some transition, *i.e.*, by removing the difference between the populations of the corresponding levels by irradiation with a weak radiofrequency field at the frequency of this transition. The magnitude of the NOE is described by the equation

$$\eta_i(\mathrm{S}) = (I - I_0)/I_0, \qquad (1)$$

where I_0 is the signal intensity for nucleus i under usual conditions (without irradiation), I is the intensity of the same signal under irradiation of some other resonance signal (S).

The $\eta_i(\mathrm{S})$ value is often expressed in percent. If relaxation follows mainly a dipole—dipole mechanism (which is typical of small and medium molecules, among which are OMC), the greatest possible increase in intensity is $\eta = \gamma_B/(2\gamma_A)$, where γ_A and γ_B are the gyromagnetic ratios for the observed and irradiated nuclei, respectively. In particular, in a ^{1}H—{^{1}H} NMR spectrum (a proton is observed and a proton is irradiated), η can reach 0.5, while for the ^{13}C—{^{1}H} case, it can be 1.99.

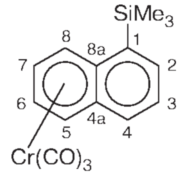
From the dipole—dipole relaxation theory (see, *e.g.*, Ref. 12), it follows that the NOE values rapidly decrease with an increase in the distance between the protons. If the proton Z is irradiated and the protons X and Y are observed, the ratio of the increase in the intensity of the signal from X to the corresponding intensity increase for the signal from Y is described by the equation

$$\eta_{XZ}/\eta_{YZ} = (r_{YZ}/r_{XZ})^6, \qquad (2)$$

where r is the distance between the nuclei.

Experimentally, the NOE is measured by pulse NMR spectroscopy by subtracting the spectrum recorded under irradiation of one proton from the spectrum recorded under the same conditions without irradiation. The spectra are alternately summed up in different computer memory blocks and their difference is found either before or after a Fourier transform. If acquisition to an acceptable signal-to-noise ratio requires N scans, then n scans ($n < N$) are accumulated alternately for each spectrum. This procedure of NOE measurement is quite sensitive to even minor changes in the signal intensity (~1%) because the spectra with and without irradiation are recorded under nearly identical conditions. The NOEDIF program[37] suitable for processing of these data is included in the software support of modern NMR spectrometers. In order to eliminate the influence of the paramagnetic relaxation mechanism (caused by paramagnetic impurities, in particular O_2 contained in the solvent), in some cases, samples are filtered through a silica gel layer and the dissolved O_2 is removed by multiple repeated freezing—thawing—freezing cycle.[38]

The joint use of the NOE and double resonance techniques allows fast and reliable assignment of signals in the ^{1}H NMR spectra of tricarbonylchromium complexes of polycyclic aromatic compounds. As an example, Fig. 1 shows the usual ^{1}H NMR spectrum of (η^6-1-trimethylsilylnaphthalene)tricarbonylchromium (**1**) and the differential NOE spectrum (NOEDIF) recorded with irradiation of the $SiMe_3$ group. The response is detected in the regions of both coordinated and noncoordinated aromatic protons, namely, for doublets at δ 6.42 and 7.75, which were assigned to H(2) and H(8), respectively, relying on their spatial proximity to the $SiMe_3$ group. The increase in the intensity reaches 7.2 and 9.6%, respectively. The intensity increase for any other signal is close to zero.



1

Further assignment was based on the double resonance spectra. For instance, upon irradiation of the doublet for the H(8) proton (δ 6.42), the triplet at δ 5.61 is transformed into a doublet (H(7)), whereas irradiation of the doublet for H(2) at δ 7.75 converts the doublet of doublets at δ 7.43 into a doublet (H(3)). It is noteworthy that correct interpretation of NOE data is possible only

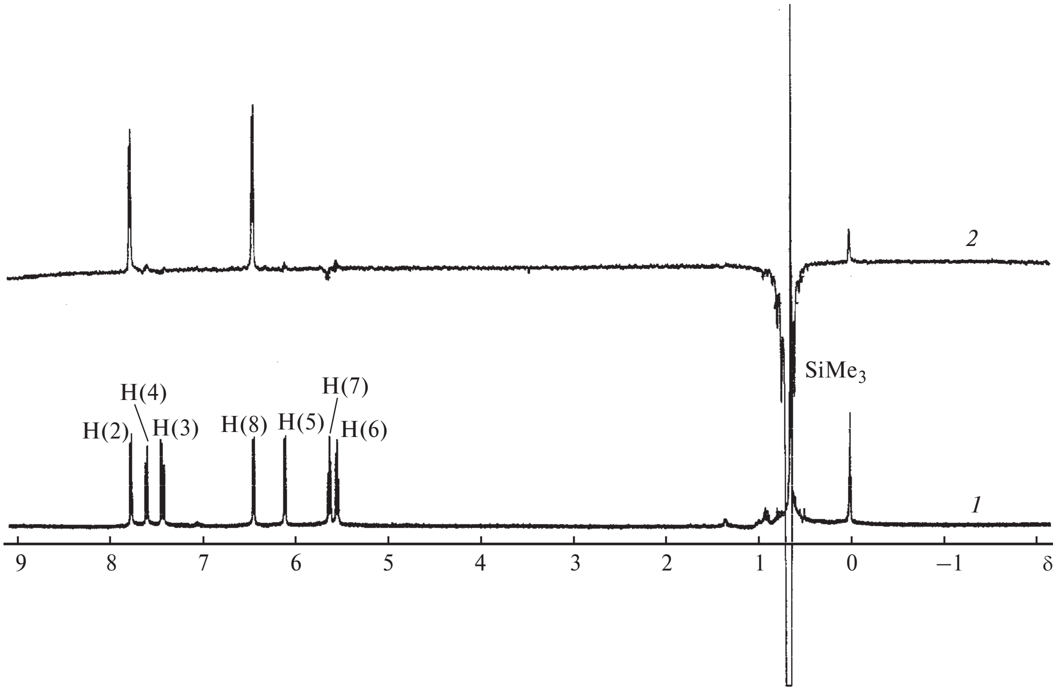
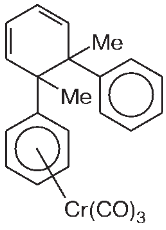


Fig. 1. ^{1}H NMR spectrum of complex **1** (*1*) and NOEDIF spectrum (*2*) recorded upon irradiation of the $SiMe_3$ group at 0.65 ppm (the signal from the irradiated group is directed downwards because the spectrum without irradiation is subtracted from the spectrum in which this signal is saturated).

in the absence of specific interaction between the solvent and the complex. Therefore, more reliable assignment of NMR spectra of (arene)tricarbonylchromium complexes based on the difference NOE spectra (NOEDIF) can be gained using solutions in hexafluorobenzene instead of deuterobenzene.[39] We employed this approach to assign ^{1}H NMR signals for virtually all the tricarbonylchromium PAL complexes that we studied. Several examples are presented below.

The NOEDIF technique was used to establish the orientation of substituents in individual complex **2** prepared from 3-methyl-3-phenylcyclopropene and $(NH_3)_3Cr(CO)_3$ *via* a complex sequence of reactions.[40]



2

The structure of the complex follows unambiguously from the ^{1}H and ^{13}C NMR and mass spectra, while the substituent stereochemistry was proved by NOEDIF.

The methyl groups were assigned based on the signal responses in the regions of noncoordinated and coordinated *ortho*-protons of the Ph groups. The NOE between the Me groups was found to be very low (<1%) and, conversely, a considerable effect was observed between the corresponding *ortho*-protons of the Me and Ph groups of the coordinated and noncoordinated rings (5 and 8%, respectively). Analysis of these data attests to the *trans*-diaxial positions of the Me groups and diequatorial position of the Ph groups. This is consistent with the results of quantum-chemical calculations (HyperChem-AM1), according to which this structure should be thermodynamically most stable for the corresponding noncoordinated ligand (Fig. 2). Other possible structures of the ligands would have a much higher energy, for example, the *cis*-methyl diaxial, phenyl-diequatorial conformation is 3 kcal mol^{-1} higher in energy according to calculations. Structure **2** for the given complex is also in line with the fact that a minor NOE (2.5%) is observed between the *ortho*-protons in the coordinated and noncoordinated rings.

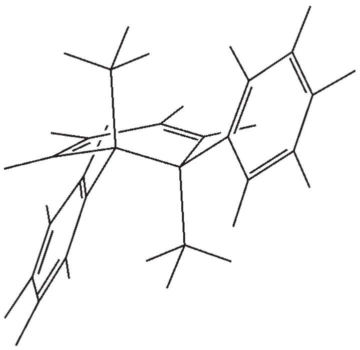
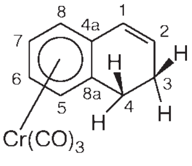


Fig. 2. Structure of the ligand corresponding to complex **2** according to the HyperChem-AM1 calculations.

Yet another interesting example of the use of the homonuclear NOE for the assignment of ^{1}H NMR signals and determination of the structure and stereochemistry of OMC is analysis of the NMR spectra of the 1,4- and 3,4-dihydronaphthalene tricarbonylchromium complexes and their derivatives whose thermal isomerization has been considered previously.[34] For example, the ^{1}H NMR signals of (1,2-dihydronaphthalene)tricarbonylchromium (**3**) were assigned using NOEDIF: irradiation of the doublet in the region corresponding to the coordinated fragment, which is due to the H(5) and H(8) *ortho*-protons, results in the response of a signal in the region typical of the vinyl group (δ 5.62), the highest-field multiplet signal at δ 1.73, and the signal centered at δ 2.10. Since in the anisotropic C_6D_6 solvent, the signal for $H(4)_{exo}$ should be shifted upfield (ASIS effect,[14] see below), we assigned the multiplet at δ 1.73 to $H(4)_{exo}$ and the signal centered at δ 2.10, to $H(4)_{endo}$. This proved to be highly important for the assignment of ^{2}D NMR signals and, finally, for elucidation of the possible mechanism of reversible isomerization of the tricarbonylchromium 1,4- and 1,2-dihydronaphthalene complexes.[34]



3

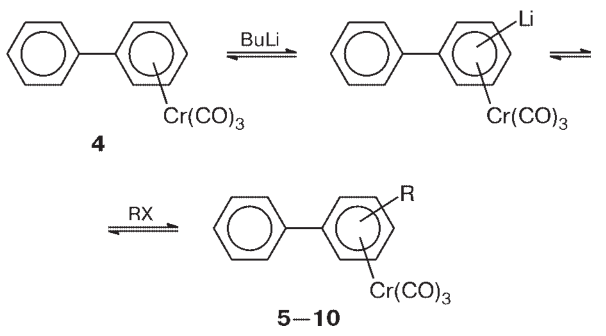
Valuable information can be gained by using the NOE to study the conformational behavior of the tricarbonylchromium complexes of *ortho*-substituted biphenyls. Analysis of the experimental data[41] shows that NOE values for the tricarbonylchromium complexes of *ortho*-substituted biphenyls are much lower than those for the corresponding *para*-derivatives due to the substantial increase in the torsion angle between the rings in the lowest-energy rotamer of these derivatives. This conclusion was additionally confirmed by quantum-chemical calculations and by the fact that inter-ring haptotropic rearrangements (IHR), which consist of migration of the organometallic group from one six-membered ring to the other proceed with difficulty, if at all, for these complexes.

The NOEDIF method is helpful in the analysis of multicomponent mixtures consisting of related complexes formed in a complex process. The chemical shifts and the spin-spin coupling constants for some signals are difficult to determine due to the overlap with the intense signals of other complexes also present in the system. If some signals from different complexes are well resolved and the neighboring signals from other compounds present in the mixture are not saturated upon irradiation of a signal from the complex under interest, then the corresponding signals with close chemical shifts can be distinguished from the superposition of signals from different complexes.

As an example, we will describe interpretation of the ^{1}H NMR spectrum of a complex mixture of tricarbonylchromium complexes of methyl-substituted biphenyls. Metallation of the coordinated nucleus in (η^6-biphenyl)tricarbonylchromium (**4**) takes place in the reaction with BuLi in THF. This reaction involves only the ring linked to the Cr atom, which is activated toward metallation. In the general case, the subsequent reaction with the electrophile RX gives a mixture of *ortho*-, *meta*-, and *para*-isomers. We carried out this reaction with D_2O and methyl iodide.[41]

The reactions of lithium derivatives with D_2O and MeI gave mixtures of deuterated derivatives (**5—7**) (total yield 84%) and methyl derivatives (**8—10**) (total yield 17.5%) (Scheme 1). The *ortho* : *meta* : *para* ratios in the mixtures are 10 : 65 : 25 and 12 : 58 : 30 for deuterated derivatives (^{2}D NMR) and for methyl derivatives (^{1}H NMR), respectively.

Scheme 1



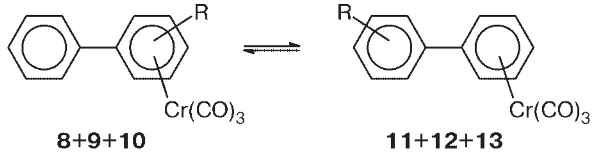
RX = D_2O, R = *o*-D (**5**), *m*-D (**6**), *p*-D (**7**);
RX = MeI, R = *o*-Me (**8**), *m*-Me (**9**), *p*-Me (**10**)

As an example, we will consider analysis of the mixture of methylated complexes **8**, **9**, and **10**. The ^{1}H NMR spectrum contains three singlets corresponding to the Me group at δ 1.62, 1.63, and 1.70, respectively.

The irradiation of the signal at δ 1.70 gives rise to 7% NOE for the signal at δ 4.97 corresponding to H(2) in *meta*-complex **9**. The singlets at δ 1.63 and 1.62 are located too closely for selective irradiation of either of them. On irradiation of the distorted doublet at δ 4.58 (the AA´ part of the AA´BB´ system) coupled with the distorted doublet at δ 5.18 (the BB´ part of the AA´BB´ system), as has been shown by double resonance, an NOE of 7.6% is observed for the Me-group singlet with the shift Δδ 1.62. In view of this fact, the signal at δ 1.62 was ascribed to the Me group of the *para*-complex **10**. Finally, irradiation of the doublet at δ 4.28, which we have assigned to H(3) of *ortho*-complex **8** on the basis of double resonance data and additive calculations, results in a NOE of 6.2% for the methyl-group singlet at δ 1.63. The irradiation of another doublet at δ 4.87 (H(6)) or other doublets in the spectrum of the mixture does not induce NOE at the Me-group signal at δ 1.63. Therefore, the last-mentioned singlet was assigned to *ortho*-complex **8**.

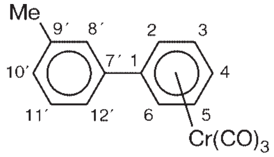
Many-hour heating of a **8**+**9**+**10** mixture in decane (174 °C) results in an inter-ring haptotropic rearrangement (IHR), *i.e.*, migration of the organometallic group from the methylated to nonmethylated ring (Scheme 2), which gives a mixture of complexes **11—13** containing Me groups in both the coordinated and noncoordinated rings. The ^{1}H NMR spectrum of this mixture exhibited only five singlets for the Me groups.

Scheme 2



R = *o*-Me (**8, 11**), *m*-Me (**9, 12**), *p*-Me (**10, 13**)

This means that one complex has not undergone the IHR on heating. The signals of complexes **10** and **13** containing *para*-methyl groups can be readily identified in the mixture because the IHR for pure **10** has been studied. The singlet at δ 2.09, which arose additionally in the spectrum of the reaction mixture, was assigned to the Me group of *meta*-substituted complex **12** containing the tricarbonylchromium fragment in the unsubstituted nucleus. Irradiation of this singlet induces a response of the singlet for H(8) (δ 7.26) and a response of the doublet for H(10) (δ 7.02) in the region of noncoordinated groups of the NOEDIF spectrum; this allows one to confirm more reliably the formation of complex **12** upon the rearrangement without isolating this complex in a pure state.



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These experiments show that the corresponding *ortho*-complex **8** does not undergo the IHR, which may be due to substantial deviation from coplanarity of the Ph rings relative to those in the *meta*- and *para*-complexes.

The NOEDIF technique has been constantly used in our studies, apart from double resonance, for structure determination and for ^{1}H NMR signal assignment for a number of other tricarbonylchromium complexes with polycyclic aromatic ligands, *viz.*, acenaphthene,[42] phenalene,[43] naphthalene derivatives,[13] *etc.*

Proton chemical shifts and spin-spin coupling constants J_{HH} for tricarbonylchromium complexes. The coordination of the tricarbonylchromium group to a six-membered ring of a polyaromatic ligand results in a substantial upfield shift (by 2—3 ppm) of the signals of the corresponding protons. The reason for this fact still remains debatable; however, the following several factors are crucial: (i) the decrease in the ring current due to the electron-withdrawing properties of the tricarbonylchromium group; (ii) the change in the hybridization of carbon atoms; and (iii) the magnetic anisotropy of the $Cr(CO)_3$ group. The spin-spin coupling constant for the coordinated nucleus somewhat decreases (by 15—20%) due to the considerable electron density shift from the ligand to the Cr atom.

In some cases, the COSY(DQ) (phase-sensitive COSY with a two-quantum filter)[44] and NOESY[45] two-dimensional procedures are used to assign ^{1}H NMR signals, in addition to double resonance experiments and NOE measurements. Figure 3 shows the NOESY spectrum for complex **1**. The NOESY method is a 2D analog of the NOEDIF method, *i.e.*, cross peaks arise only between spatially proximate protons. The presence of rather intense cross-peaks between the protons of coordinated and noncoordinated rings allows the corresponding signals to be easily assigned. One more piece of evidence for the assignment of proton signals was gained from the COSY(DQ) spectrum for the same complex (Fig. 4). In this case, cross-peaks arise between the protons having rather high spin-spin coupling constants.

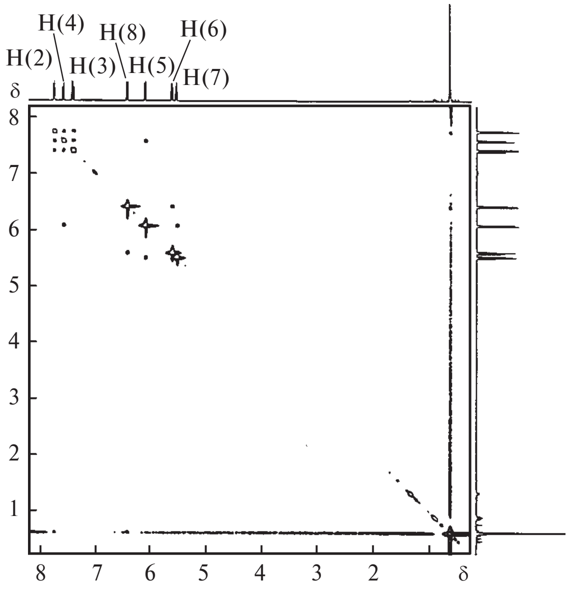


Fig. 3. 2D NOESY spectrum of complex **1**.

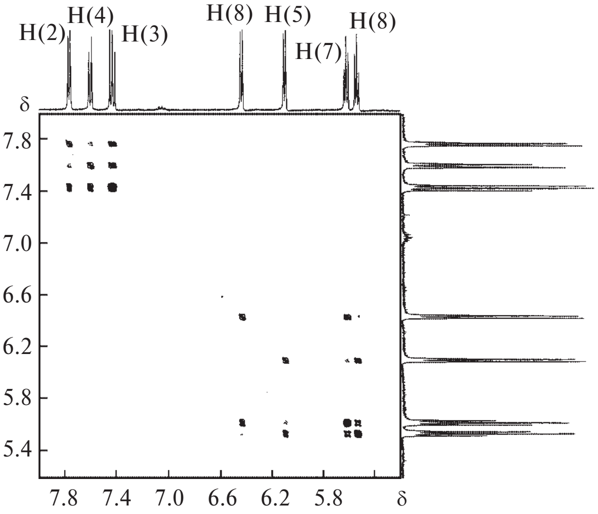
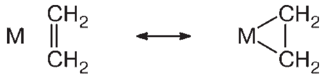


Fig. 4. 2D COSY(DQ) spectrum of complex **1**.

Chemical shifts and spin-spin coupling constants J_{CH} in ^{13}C NMR spectra of tricarbonylchromium complexes. As in the case of ^{1}H NMR spectra, the coordination of the transition metal to the ligand entails upfield shifts of the corresponding ^{13}C signals. An interpretation of this observation proposed previously[16] is based on a scheme that implies the resonance of structures with sp^2- and sp^3-hybridized C atoms (**I** and **II**, respectively).



I **II**

The chemical shift of structure **I** is expected to be close to that of free ethylene (δ 123.3), whereas the chemical shift of **II** should be close to this value found for cyclopropane (δ –2.6). The true shift depends on the ratio of these two canonical structures and is dictated by the nature of the transition metal and the ligand environment. For tricarbonylchromium complexes with polycyclic aromatic ligands, this upfield shift is ~40 ppm. In some cases, the APT, DEPT and HETCOR techniques were also used for signal assignment, and selective INEPT was used for the assignment of quaternary C atoms. Figures 5 and 6 show the HETCOR and selective INEPT spectra for complexes **1** and (η^6-indene)tricarbonylchromium (**14**). Using HETCOR spectroscopy, one can match carbon signals to the signals of protons linked directly to these carbon atoms based on the arising cross-peaks. In the case where the ^{1}H NMR signals have already been assigned (for example, by means of additive schemes, NOEDIF, double resonance or 2D COSY and NOESY procedures), the signals of C atoms bound directly to the corresponding protons can easily be interpreted from the arising cross-peaks. However, this approach does not provide the assignment of signals for quaternary C atoms, which have no direct bonds with protons. In these cases, we used the selective INEPT technique,[46] which implies excitation of the H atom separated from the corresponding C atom by three bonds (the corresponding $^3J_{HC}$ constant should be the highest

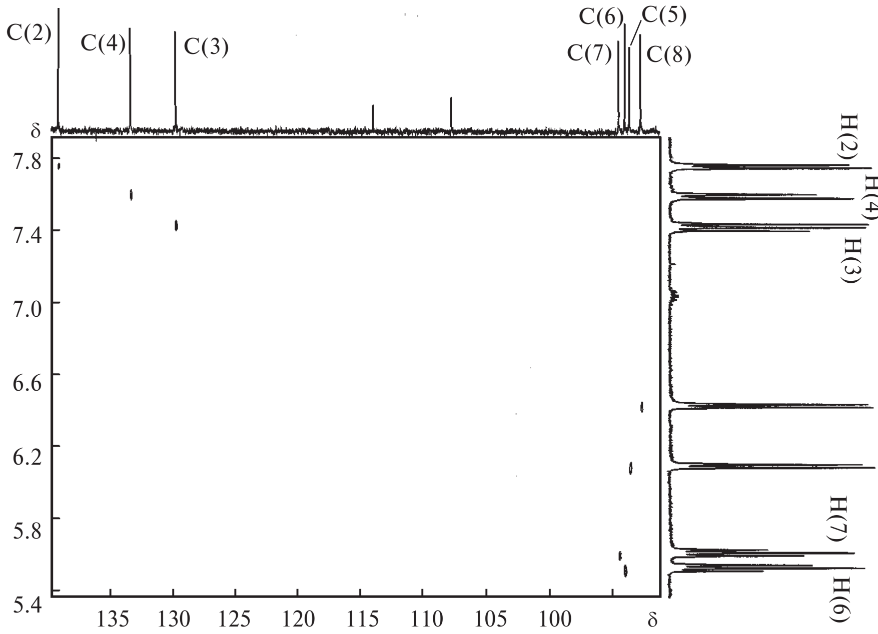


Fig. 5. HETCOR spectrum of complex **1**.

one of the far constants). In this case, the ^{13}C NMR spectrum exhibits only the signal for the quaternary C atom separated by three bonds from the corresponding protons. For example, selective irradiation of the H(6) proton at δ 4.53 results in the signal of the quaternary C atoms being recorded at δ 113.26 in the ^{13}C NMR spectrum of complex **14**, while upon irradiation of the H(5) proton at δ 4.48, a signal at δ 115.43 appears. In view of these results, the above signals were attributed to the C(3a) and C(7a) atoms, respectively (see Fig. 6). It should be mentioned that 2D experiments require rather long instrument time expenditures and they are not always convenient when the corresponding compound is unstable, which is often the case for transition metal complexes with polycyclic ligands.

ASIS study of the structure of tricarbonylchromium complexes with polycyclic aromatic ligands. In a study of the reaction between anionic metal carbonyl complexes of polycyclic aromatic hydrocarbons and the electrophiles RX, the stereochemical outcome of the reaction was shown to depend on the position of the metal carbonyl group. This brings about the need to determine the orientation (either *exo* or *endo*) of the organic group in the resulting neutral complex. For example, upon the reaction with electrophiles of complex fluorenyl anions containing a tricarbonylchromium group in the six-membered (η^6-anion) or five-membered (η^5-anion) ring, the organic group R occupies, due to the stereochemical influence of the bulky tricarbonylchromium group, the *exo*-position for the η^6-anion or the *endo*-position (in

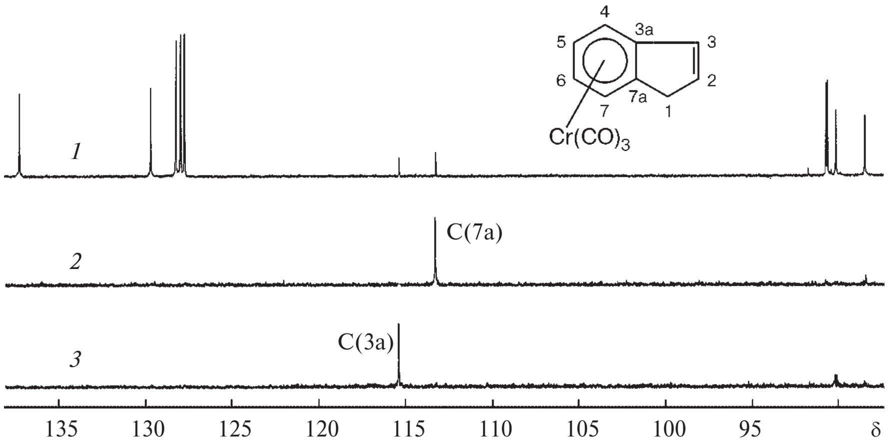
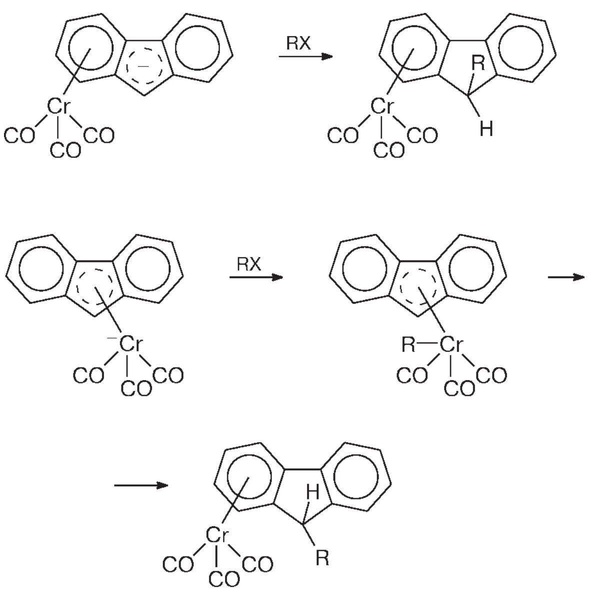


Fig. 6. Selective INEPT spectra for complex **14**: ^{13}C NMR spectrum with broad-band decouping (*1*) and selective excitation of H(6) (*2*) and H(5) (*3*).

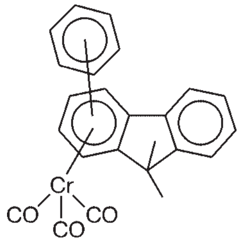
the case of the η^5-anion) *via* the intermediate η^5-complex with localization of the R group on the Cr atom (Scheme 3).

Scheme 3



Previously, other research groups have used various spectral criteria to determine the geometric configurations of substituted complexes of transition metals with polycyclic ligands. The best example[47] is structure determination for substituted tricarbonylchromium complexes of indan. For particular structures, the ^{1}H NMR signals of *exo*-protons or protons of *exo*-substituents were shown to be shifted upfield to a greater extent than the corresponding signals of the *endo*-protons.

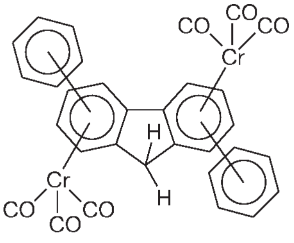
To determine the stereochemistry of α-hydroxy-1,2-tetramethyleneferrocene and (2-hydroxyindan)tricarbonylchromium, the OH stretching frequencies in the IR spectra were analyzed. This was done assuming that the *endo*-isomer is responsible for the lower-frequency vibration due to the presence of a hydrogen bond with the metal atom or the CO group.[48] The stereochemistry was also studied[49] by X-ray diffraction analysis; however, the results were not analyzed in combination with spectroscopic data. In the case of tricarbonylchromium complexes of cyano- and carbomethoxy-substituted indans, the assignment to either *endo*- or *exo*-isomer was based on dipole moments, which are greater for the *endo*-isomers.[50] In determining the configuration (*endo* or *exo*) of 9,10-dihydro-9,10-dimethylanthracene complexes, the relationship between the ^{1}H and ^{13}C NMR chemical shifts was used.[51] In the case of monocyclic π-complexes in which the only substituted sp^3-hybridized C atom is not involved in the bonding with the transition metal (cycloheptatriene, cyclohexadienyl, *etc.* complexes), the most reliable information on configurations is provided by analysis of vicinal spin-spin coupling constants.[52]



15 · C_6D_6

We have proposed[34] a new general approach to determination of the configuration of the substituent at the sp^3 carbon atom. Below we consider the main features of the ^{1}H NMR spectra of tricarbonylchromium complexes of 9-substituted fluorenes and some other molecules containing sp^3 carbon atoms near the coordinated ring (for example, acenaphthene, dihydronaphthalene, phenalene, *etc.* complexes). Anisotropic deuteriobenzene (C_6D_6) proved to be the most suitable solvent for the investigation of these systems. In the case of initial (η^6-fluorene)tricarbonylchromium (**15**), the signals for non-equivalent methylene protons differ appreciably (unlike those in isotropic $CDCl_3$) in chemical shifts and form an AB system in the spectrum. This is due to the ASIS effect.[39,52] This method is widely used to study the structures of organic molecules and to simplify complex and strongly coupled NMR spectra. For fast and reliable determination of the configurations of organic groups at the benzylic C atom in transition metal complexes, we proposed an approach based on evaluation of the change in the chemical shifts of protons of these groups induced by an aromatic solvent, on passing from solutions in $CDCl_3$ to solutions in C_6D_6 ($\Delta\delta(\mathrm{ASIS}) = \Delta\delta(CDCl_3) - \Delta\delta(C_6D_6)$). The molecules in solution can form unstable complexes ("collision complexes") with the aromatic solvent molecules due to the following reasons: (i) formation of hydrogen bonds with the π-electronic system of the solvent molecule, (ii) electrostatic interaction between the polar groups and induced dipoles of aromatic molecules; (iii) the formation of charge transfer associates. Since the lifetime of these complexes is rather short on the NMR time scale, some averaged mutual orientation of the solute and solvent molecules is established. This results in additional shielding for the protons of the solute molecules located near benzene molecules, which have a sixfold axis, due to the influence of their ring current. According to a previous publication,[39] (benzene)tricarbonylchromium can form weak charge transfer complexes with benzene molecules that are located above the plane of the coordinated ligand. Apparently, (fluorene)tricarbonylchromium **15** also forms complexes of this type, and the proton signals of the coordinated six-membered ring are shifted upfield by 0.7—0.8 ppm. This effect is most pronounced, however, for the protons attached to an sp^3-hybridized C atom (position 9). Their diastereotopism is slightly detectable in the ^{1}H NMR spectrum in $CDCl_3$; for example at a resonance frequency of 100 MHz for protons, a singlet with δ 3.94 is recorded (H(9)), *i.e.*, the protons are actually magnetically equivalent. In a benzene solution, $H(9)_{exo}$ and $H(9)_{endo}$ produce an expected AB-type spectrum with the chemical shifts δ 3.10 and 3.35, respectively ($^2J_{HH}$ = 22 Hz). Thus, the ASIS effects for these two protons are 0.84 and 0.59 ppm, respectively. The signal located in a higher field was assigned to the $H(9)_{exo}$ atom, which is closer to the solvent molecule.

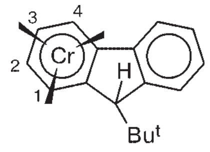
A similar effect was also discovered[53] for (η^6-9,9-dimethylfluorene)tricarbonylchromium (**16**). The induced upfield shift is 0.7—0.8 ppm for the protons of the coordinated nucleus, whereas for the protons of the noncoordinated nucleus, it is only 0.3—0.4 ppm. The signals of the Me groups occur at δ 1.44 and 1.62 ppm in a $CDCl_3$ solution. On gradual addition of benzene, they shift upfield and in pure benzene, they occur at δ 1.02 and 1.42, respectively. The high-field signal in $CDCl_3$ shows a large induced shift Δδ(ASIS) (0.42 ppm) and can be attributed to the Me-group protons in the *exo*-position. The correctness of the above assignments is confirmed by the fact that in the corresponding binuclear complex, *trans*-μ-(η^6,η^6-fluorene)-bis(tricarbonylchromium) (**17**), in which the *trans*-arrangement of the tricarbonylchromium groups is proved by the singlet form of the signal for 9-protons observed for any solvent and any instrument operating frequency, the Δδ(ASIS) value is 0.84 ppm. This value is twice as great as the corresponding value for the mononuclear complex, indicating that both coordinated rings interact efficiently with deuteriobenzene.



17 · C_6D_6

The ASIS effect was also used successfully to establish the configuration of substituents at the sp^3-hybridized C atom in a number of tricarbonylchromium complexes formed by substituted acenaphthenes,[42] dihydronaphthalenes,[34] and phenalenes.[43]

A somewhat less versatile opportunity to distinguish between the *endo*- and *exo*-positions of the substituent R at the sp^3-hybridized C atom in tricarbonylchromium complexes of polycyclic aromatic ligands is provided by analysis of the ^{1}H NMR spectra of pairs of complexes in the spectral range of the coordinated nucleus (δ 4.5—6.0). This was first demonstrated[54] for tricarbonylchromium complexes of singly substituted indans. Later, we confirmed[34] the validity of these rules for the tricarbonylchromium complexes of fluorene and related ligands. Thus in the tricarbonylchromium complexes of *endo*-9-substituted fluorenes, the substituent R points to the same direction as the tricarbonylchromium group. As a result, conformation A is preferred over the corresponding *exo*-complexes, which was confirmed by X-ray diffraction data for the *endo*-tricarbonylchromium complex of 9-benzylfluorene (**18**).[53] As a consequence, the signals of the H(1) and H(3) protons shift downfield compared to those of the H(2) and H(4) protons due to the magnetic anisotropy of the CO groups. This trend is especially pronounced in the case of *exo*- and *endo*-tricarbonylchromium complexes of 9-*tert*-butylfluorene (**19**): the ^{1}H NMR spectrum of *endo*-complexes in the region of coordinated groups (H(1)—H(4) protons) can be easily analyzed in the first-order approximation even with an operating frequency of 100 MHz, unlike the corresponding spectrum of the *exo*-complex. Similar regularities are observed for 9-methyl-, 9-phenyl-, and 9-benzylfluorene complexes.[53]



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The ASIS effect can be used to establish configurations of complexes of other transition metals; however, it should be borne in mind that the coordinating properties of the complexes may change. The formation of "collision complexes" with aromatic molecules of the solvent requires special investigation. Thus in the case of Ir and Rh complexes, the signals of the *exo*-protons occur in a lower field than the signals of the corresponding *endo*-protons.[55] In some cases, the ASIS effect cannot be used, in principle, for determination of *exo*- or *endo*-configurations.[56]

The use of ^{2}H NMR spectroscopy for investigation of the reaction mechanisms of tricarbonylchromium complexes with polycyclic aromatic ligands. The introduction of a deuterium label into an OMC molecule is used fairly extensively to study reactions of these compounds.[57] The mechanisms of hapto- and sigmatropic rearrangements of tricarbonylchromium complexes were studied using regioselective introduction of a deuterium atom in one position of the fluorene,[58] biphenyl,[41] biphenylene,[42] phenalene,[43] or 1,4-dihydronaphthalene[34] ligand. Since the degree of deuteration was usually high (≥90%), ^{2}H{^{1}H} NMR spectra could be recorded for these labeled compounds with reasonable time consumption, although the ^{2}H nucleus is much more difficult to detect by NMR than ^{1}H (the relative sensitivity is 0.015). An additional gain in sensitivity was attained using resonance stabilization for the ^{19}F nucleus (fluorine lock) and broad-band proton decoupling. The combinations of these approaches provided the possibility of investigating the distribution of the deuterium label in the organic ligand. As an example of using ^{2}H{^{1}H} NMR, we will consider rearrangements in the selectively deuterated (1-d-phenalene)tricarbonylchromium (**20**).

Thermal isomerization of complex **20** was studied in a toluene solution at 90, 100, and 110 °C. The concentrations of the resulting products were determined by

$^2H\{^1H\}$ NMR spectroscopy. The spectra were recorded with the fluorine lock using the C_6F_6 signal as the reference. In the study of isomerization in a toluene solution, 10% (v/v) C_6F_6 was specially added to the sample to stabilize the resonance conditions. The samples were thoroughly degassed by the freezing—evacuation—thawing cycle repeated many times at $1 \cdot 10^{-5}$ Torr and sealed under vacuum. Since many signals differing significantly in intensity overlap in the resulting spectra, the standard integration procedure does not ensure the required accuracy in concentration determination. Therefore, quantitative integration was carried out with deconvolution of spectra[38] (representation of the full spectral contour as a sum of Lorentzian lines) with phase and field inhomogeneity corrections. The ^{2}H NMR signals were unambiguously assigned based on the corresponding ^{1}H NMR spectra. Toluene is a convenient solvent for $^2H\{^1H\}$ NMR investigation of thermal isomerization of complex **20** because solubility of the initial complex at room temperature is rather high, and the distances between the signals are large enough for accurate integration, owing to the ASIS effect. The $^2H\{^1H\}$ NMR spectrum of complex **20** itself contains only one signal, irrespective of the chosen solvent. In addition, the singlet for the CH_2D group and three singlets in the range of aromatic protons (corresponding to the three nonequivalent positions of protons in the aromatic nucleus) arising for the natural abundance of deuterium in the solvent can serve as standards for determination of signal positions and for integration.

A drawback of toluene as the solvent is the presence of a side reaction, *viz.*, replacement of the phenalene ligand in complex **20** by toluene. These ligand exchange reactions in arenetricarbonylchromium complexes are well-known and their kinetics has been studied in detail by NMR spectroscopy.[59] However, since these reactions proceed rather slowly at moderate temperatures, they do not preclude quite comprehensive study of the thermal isomerization kinetics. The evolution of the $^2H\{^1H\}$ NMR spectra of complex **20** during heating a toluene solution of **20** at 100 °C is shown in Fig. 7. At an initial step of transformation, a signal due to (phenalene)tricarbonylchtomium deuterated at position 3 (complex **20a**) appears, in addition to the singlet for the initial complex **20**. Complex **20a** is formed upon the [1,5]-sigmatropic shift of the H_{endo} atom of complex **20** (Scheme 4).

Simultaneously, compound **20c** is produced upon the η^6,η^6-haptotropic shift of the $Cr(CO)_3$ group in complex **20** (see Fig. 7, spectra *1* and *2*). Subsequently, a signal of the isotopomer **20b**, formed from compounds **20a** and **20c**, appears in the low field. The intensity of this signal in the ^{2}D NMR spectrum grows faster than that for **20a** (see Fig. 7, spectra *2* and *3*). Detailed analysis of the spectrum reveals also relatively low-intensity signals arising at high degrees of conversion, which correspond to (6a,7-9,9a,9b-η^6-1-*endo*-D-phenalene)tricarbonylchromium (**20e**) and (3a,6a,9b,4-6-η^6-1-*endo*-D-phenalene)tricarbonylchromium (**20d**) (see Fig. 7, spectrum *4*), resulting from the [1,5]-shift of the 1-*exo*-protons in complexes **20a** and **20b**. The whole set of processes occurring in the system is reflected by Scheme 4.

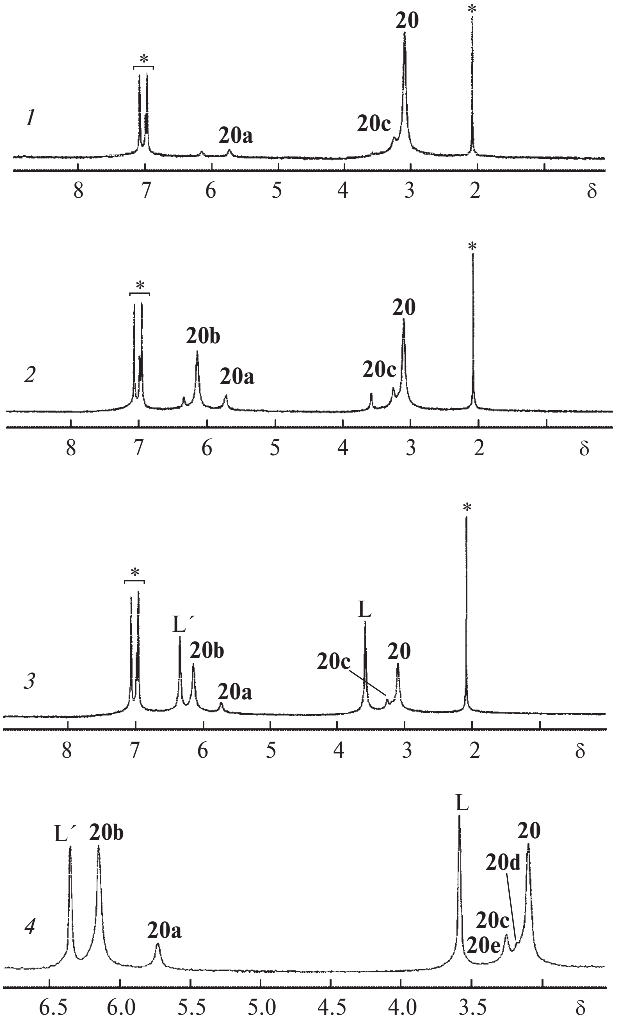
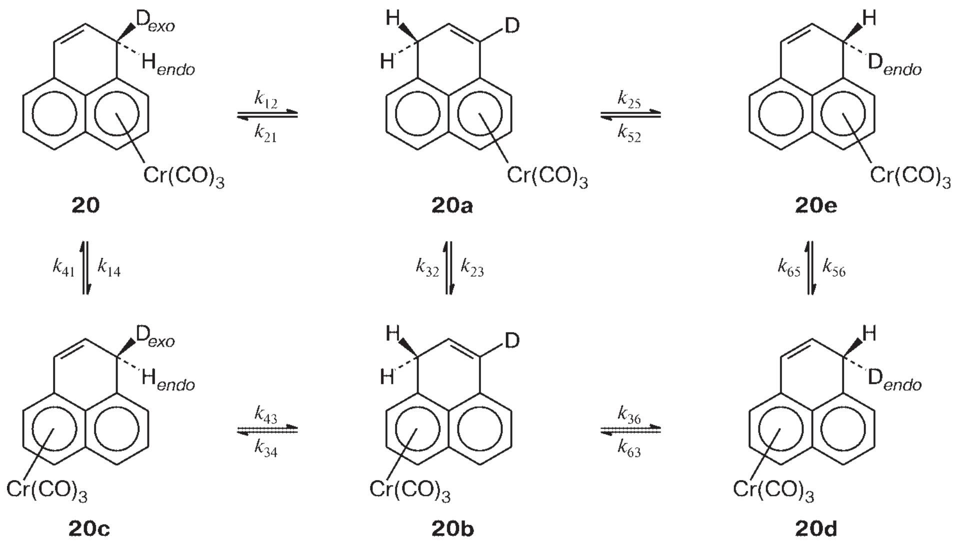


Fig. 7. Variation of the $^2H\{^1H\}$ NMR spectra of complex **20** (the corresponding signals are designated in the Figure by number **20**, and the signals due to the complexes formed from **20** (see Scheme 4) are denoted by numbers **20a—e**) during thermal rearrangement in toluene at 100 °C after heating for 2 (*1*), 12 (*2*), and 110 (*3*) h and the spectral fragment after keeping for 74 h at 100°C (*4*). The asterisks mark the signals for the solvent (toluene) with the natural abundance of deuterium, L and L´ are the phenalene ligand.

The kinetic analysis of the rearrangements described by Scheme 4 carried out using the KINETICS program permitted determination of the thermodynamic parameters of these transformations.[38]

Scheme 4



Study of the structure and dynamic behavior of tricarbonylchromium complexes with polycyclic aromatic ligands by the CPMAS NMR method

In recent years, the solid-state NMR spectroscopy is used more and more frequently to study the structures and the dynamic behavior of organic, inorganic, and organometallic compounds. The substantial technical achievements in the development of instrumentation and the progress in the elaboration of new complicated procedures and pulse sequences provide the possibility of investigating diverse objects that could not be studied previously due to either low solubility or decomposition on passing to the solution. These compounds include polymers, biopolymers, drugs and, in particular, unstable OMC. However, OMC have not yet become popular objects for analysis using the solid-state NMR techniques, although wide-line NMR has previously been used to investigate various rotation and exchange reactions in transition metal complexes and carbonyls.[60]

Solid-state NMR spectroscopy, especially the magic angle spinning (MAS) and cross-polarization (CP) techniques, appears to be a promising method for the investigation of the structures and the dynamic behavior of OMC. Such studies are still few in number. Among them, the pioneering works dealing with the CPMAS NMR study of the dynamic phenomena in metal carbonyls[60,61] and transition metal arene complexes deserve attention.[62,63]

Theoretical foundations of the CPMAS NMR technique. The direct spin-spin coupling mechanism, which does not play any special role in high-resolution NMR spectroscopy is fairly significant for solid-state NMR. This mechanism involves through-space interaction of the nuclear moments (the other name is dipole—dipole interaction). It can be demonstrated (see, for example, Ref. 18) that the dipole Hamiltonian, which causes line broadening for a solid, includes a geometric factor ($3\cos^2\theta - 1$, where θ is the angle between the direction of the internuclear vector and the field B_0). The fast molecular rotation, characteristic of a nonviscous liquid, averages this factor to zero; this accounts for the very narrow lines observed for liquids. An increase in viscosity or orientation effects (*e.g.*, those in liquid crystals) results in line broadening in the NMR spectrum.

Is it possible to create conditions that would represent to an extent this motion for solids? Let us consider spinning of a solid sample at the angle β relative to the axis B_0 (Fig. 8). To estimate the possible effect of this spinning, it is necessary to determine the average value for $3\cos^2\theta - 1$. Averaging is done by rotating the internuclear vector $\mathbf{r}$ about the spinning axis. This implies considering a cone with the aperture angle χ. It can be shown that

$$\langle(3\cos^2\theta - 1)\rangle = 0.5(3\cos^2\beta - 1)(3\cos^2\chi - 1). \qquad (3)$$

The parameter χ for a bulk solid is fixed. However, for a powder, this angle (like the θ angle) can assume any values. Thus, the term $0.5(3\cos^2\beta - 1)$ acts as a scaling factor for the dipole term. The β angle can be varied. If $\beta = 0$ (rotation around the B_0 axis), then $0.5(3\cos^2\beta - 1) = 1$ and this does not have any influence on the spectrum. If $\beta = \pi/2$ (rotation at 90° angle relative to the B_0 axis), then $0.5(3\cos^2\beta - 1) = 0.5$, hence, the spectrum of the powder is scaled by a factor of 2 (is compressed twofold). The most interesting situation arises when $\beta = 54°44'$ because in this case, $3\cos^2\beta - 1 = 0$. Simultaneously, $3\cos^2\theta - 1 = 0$ for any orientation of

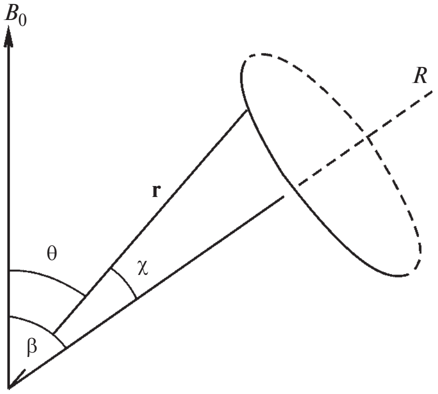


Fig. 8. Spinning of a solid sample at the angle β relative to the B_0 field axis; *R* is the rotation axis.

the internuclear vector (*i.e.*, for any χ). Thus, as in the case of isotropic rotation, the dipole term is averaged to zero and dipole broadening is eliminated, resulting in high spectral resolution. The 54°44′ angle is called magic, while the procedure is referred to as magic angle spinning (MAS). The implementation of this technique, however, is faced with engineering problems because the spinning velocity required for the averaging of the dipole interaction should be greater than the broadening induced by dipole coupling. For instance, in the case of proton—proton coupling, the broadening can reach several tens of thousand hertz; this stipulates the necessity of spinning at a very high velocity, not always attainable.

The magnetic shielding of the corresponding nuclei by the surrounding electrons is also anisotropic and depends on the molecule orientation in the powder or amorphous solid relative to the magnetic field. Actually, a set of resonance frequencies caused by the anisotropy of chemical shift is observed. In a liquid, averaging of this interaction shows itself as the chemical shift. The additional effect of the magic angle spinning is averaging of broadening related to the chemical shift anisotropy.

The next technical breakthrough important for the progress in the quality of solid-state spectra is cross-polarization, *i.e.*, an increase in the signal intensity for nuclei with low concentrations (for example, ^{13}C) upon irradiation of a nuclei with a high concentration (for example, ^{1}H). The heteronuclear Overhauser effect for ^{13}C nuclei and the INEPT, DEPT, and other sequences, which are also associated with polarization transfer from more sensitive to less sensitive spins, are well-known analogs of cross-polarization in high-resolution NMR spectroscopy. The pulse pattern for cross-polarization in a solid is shown in Fig. 9.

At the first stage, the proton magnetization is rotated through 90° along the *y*′ axis of the rotating frame of reference using a high-power radio-frequency pulse directed along the *x*′ axis and then maintained constant using a "locking" radio-frequency pulse directed along the *y*′ axis. At the second stage, the proton spins are fixed along the *y*′ axis for a period *t* (cross-polarization contact time, which is usually optimized against signals from adamantane but can be varied over a rather broad range, from 100 to 5000 μs). During this period, the carbon magnetization is also oriented along the *y*′ axis by means of a high-power radio-frequency pulse. Thus, during this period of time, both spin systems are "locked" and, by choosing appropriate locking pulses $B(^1\mathrm{H})$ and $B(^{13}\mathrm{C})$, it is possible to increase substantially the carbon magnetization, thus bringing spin distribution in the carbon system closer to the favorable spin distribution in the proton system. The pulse amplitudes *B* are chosen from the Hartmann—Hahn relation

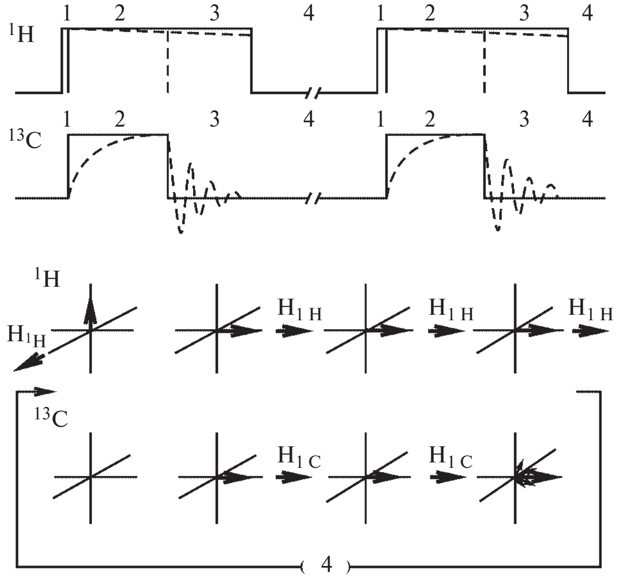


Fig. 9. Pulse sequence used for cross-polarization of "dilute" nuclei (^{13}C).[18]

$$\gamma(^1\mathrm{H})B(^1\mathrm{H}) = \gamma(^{13}\mathrm{C})B(^{13}\mathrm{C}), \quad (4)$$

where $\gamma(^1\mathrm{H})$ and $\gamma(^{13}\mathrm{C})$ are gyromagnetic ratios for the protons and ^{13}C nuclei, respectively.

The maximum increase in the intensity is equal to the ratio of the gyromagnetic ratios of the abundant and sparse nuclei, *i.e.*, it is 4 for cross-polarization from protons to carbon. At the third stage when a stationary value for carbon magnetization is attained during the contact time *t*, the excitation of carbon signals is terminated and the free induction decay (FID) is recorded. The proton irradiation is retained for the H—C dipole—dipole decoupling. At the second stage, a delay is introduced to allow the spins to relax to their equilibrium values. An additional advantage provided by cross-polarization is the substantial decrease in the delay between the pulses because the pulse repetition frequency is determined in this case by the proton relaxation times, which are normally much shorter than the ^{13}C relaxation time. Finally, high-power proton decoupling is an additional factor for the elimination of the dipole—dipole coupling between protons and the sparse nucleus. In the general case, this decoupling removes the information concerning the spin—spin interaction. However, the use of special sequences (such as BR-24 or MREV-8) allows one to retain the information on the J_{CH} spin-spin coupling constants.

The advanced experimental procedures described here permit recording of CPMAS ^{13}C NMR spectra for polycrystalline powders in which the line width does not exceed several tens of hertz. The consecutive use of these methods is described for poly(methyl methacrylate) (Fig. 10).

Until the methods for recording high-resolution spectra for crystalline samples have been developed, chemists used wide-line NMR spectroscopy in which very wide envelope lines devoid of any structure were observed in the spectra. Modern instrumentation allows the sample to be spinned with a frequency of 4—10 kHz during recording the CPMAS NMR spectra. The spinning frequency should be greater, whenever possible, than the chemical shift anisotropy. Otherwise, the spectrum contains a number of spinning-related side bands separated from the basic lines by distances divisible by the spinning frequency. The spinning side bands can be distinguished from the basic lines upon variation of the spinning frequency, because this entails changes in the positions of side bands, the positions of the basic signals remaining the same.

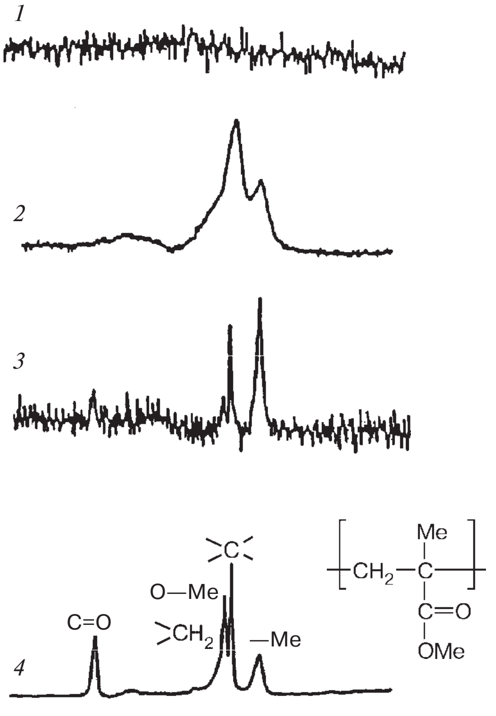
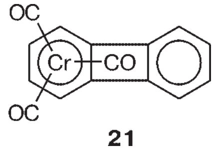


Fig. 10. CPMAS NMR experiment for a "dilute" nucleus (^{13}C):[18] wide-line ^{13}C NMR spectrum (without using additional techniques) (*1*); cross-polarization experiments (*2*); magic angle spinning experiments with broad-band proton decoupling (*3*); combined use of CP, broad-band decoupling, and magic angle spinning (*4*).

The use of CPMAS ^{13}C NMR to study the structures and the dynamic behavior of polycrystalline tricarbonylchromium complexes of aromatic polycyclic compounds. As noted above, CPMAS NMR is a rather new method for the investigation of OMC, which is now used rather rarely. Mention should be made of the use of this technique[60,61] for metal carbonyls, for the study of the dynamic behavior of OMC [62] and rotation of the tricarbonylchromium group in complexes of monocyclic arenes,[64—66] and in our study[67] of transition metal complexes by solid-state NMR spectroscopy. The application of this method to tricarbonylchromium complexes of polycyclic aromatic compounds allowed us to obtain rather well-resolved and informative ^{13}C NMR spectra of these compounds.

A typical CPMAS ^{13}C NMR spectrum is shown in Fig. 11 for (η^6-biphenylene)tricarbonylchromium (**21**). The information that can be derived from this spectrum is approximately the same as that provided by high-resolution spectrum: the ^{13}C NMR signals of the coordinated ring are shifted upfield (δ 90—110) and the C atoms of the noncoordinated ring occur at δ 125—140. Analogous information can be gained from the CPMAS ^{13}C NMR spectrum of polycrystalline (η^6-1,6-methano[10]annulene)tricarbonylchromium (**22**) (Fig. 12).

The signals of the quaternary C atoms can be assigned using the NQS (non-quaternary suppression) pattern[68] (Fig. 13), which allows one to observe the signals of only quaternary C atoms. In most cases, the number of signals in the CPMAS ^{13}C NMR spectra exceeds that expected in view of the molecule symmetry. This finding can be explained by the fact that various fragments of the molecule have asymmetric environments in the crystal lattice. Usually, this complicates substantially interpretation of the spectra. In the high-resolution ^{13}C NMR spectrum for complex **21** only one narrow signal is present in the region characteristic of the CO group, due to the free rotation of the tricarbonylchromium group. Conversely, the CPMAS ^{13}C NMR spectrum of the crystalline sample exhibits three signals at δ 230—240 for the CO groups with an intensity ratio of 1 : 1 : 1. It is significant that the low-field spinning side bands (~315 ppm) are more intense than the basic signals, which is encountered rather frequently and is due to the substantial chemical shift anisotropy for the CO groups.



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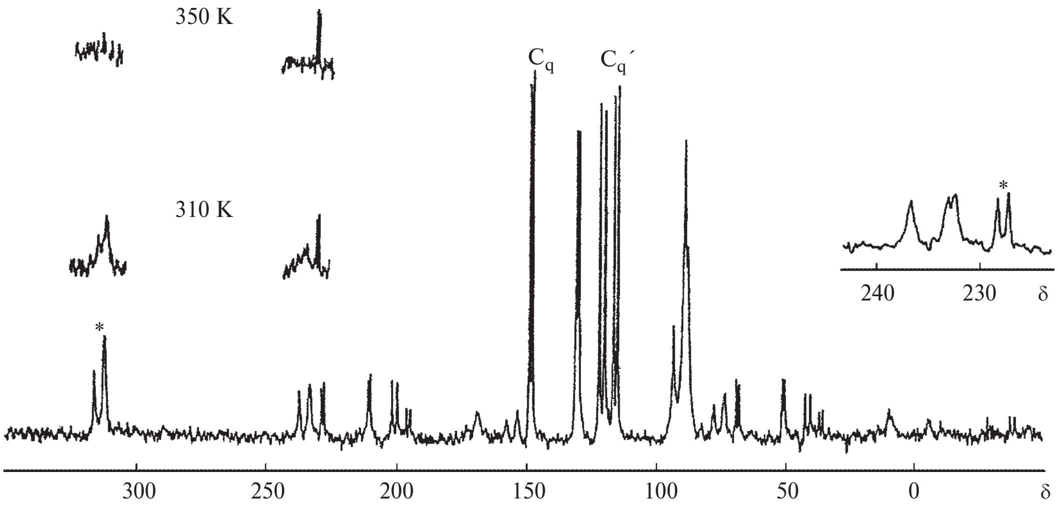

Fig. 11. CPMAS ^{13}C NMR spectrum of a polycrystalline (η^6-biphenylene)tricarbonylchromium (**21**) sample, spinning rate ~6 kHz. The asterisk marks the spinning side bands, C_q and C_q' are the signals for quaternary C atoms linked and not linked to the Cr atom, respectively. The insert shows the CO-group region.

According to X-ray diffraction data,[69] in the crystal structure of complex **21**, two of the three CO groups are equivalent.

The obtained results show that rotation of the $Cr(CO)_3$ group around the axis along which this group is linked to the ligand does not take place in the crystal at room temperature; hence, the activation barrier to this process is rather high. The environment of this group in the crystal lattice is not fully symmetrical. Conversely, the rotation of the $Cr(CO)_3$ group in arene complexes in solution has a very low activation barrier (<3 kcal mol^{-1}), except for few examples, and thus it cannot be frozen.[70] Therefore, high-resolution ^{13}C NMR spectra of tricarbonylchromium complexes of polycyclic arenes exhibit only one signal for the CO group, except for several exotic examples.[71]

Heating of sample **21** results in gradual broadening of the CO signals in the CPMAS ^{13}C NMR spectrum; at 350 K, the signals coalesce. The ^{13}C NMR signals of the aromatic ligand are also somewhat broadened. All these changes in the spectrum are reversible. Determination of the free activation energy for the two-position exchange from the coalescence temperature can be performed using the formula[72]

$$\Delta G^{\#} = RT_c[22.96 + \ln(T_c/\delta\nu)] \text{ (cal mol}^{-1}\text{)}, \qquad (5)$$

where $\delta\nu$ is the difference between the CO chemical shifts, T_c is the coalescence temperature, and

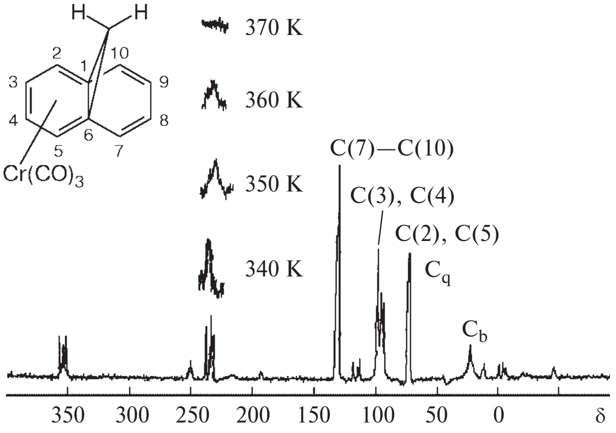

Fig. 12. CPMAS ^{13}C NMR spectrum of a polycrystalline (η^6-1,6-methano[10]annulene)tricarbonylchromium (**22**) sample. The spectral region corresponding to the CO signals is specially designated; C_q and C_b are the signals for quaternary and bridging C atoms, respectively.

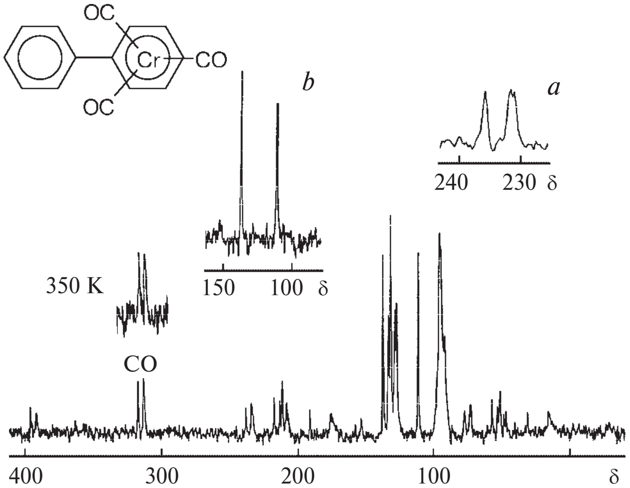

Fig. 13. CPMAS ^{13}C NMR spectrum of a polycrystalline (η^6-biphenyl)tricarbonylchromium (**4**) sample. The inserts show the regions characteristic of CO groups (*a*) and quaternary C atoms identified using the NQS sequence (*b*).

$R = 1.987$ cal mol^{-1}. A rough estimate of the activation barrier to the rotation of the Cr(CO)$_3$ group of complex **21** in the solid state using this relation gives 15.9 kcal mol^{-1}. In a more rigorous approach to the calculation of the activation barrier, the signal shape is simulated using a program for the simulation of dynamic spectra (for example, DISPARDNMR).[73] The calculations for complex **21** based on the coalescence point for a three-position exchange give $\Delta G^{\#} = 16.1$ kcal mol^{-1}, which is in good agreement with the value calculated by simplified relation (5).

The CPMAS ^{13}C NMR spectrum of (η^6-1,6-methano[10]annulene)tricarbonylchromium (**22**) (see Fig. 12) displays[74] the same features as the spectrum of **21**, namely, three signals for the CO groups are present at room temperature, which points to the absence of rotation of the Cr(CO)$_3$ group in the solid state and to an asymmetrical environment of molecule **22** in the crystal lattice. It should be noted that, according to X-ray diffraction analysis,[75] this molecule has a plane of symmetry, and two of the three CO groups are equivalent. The coalescence of these signals takes place at 370 K. Coalescence is also observed in the region of coordinated C atoms, which is also consistent with fast rotation of the Cr(CO)$_3$ group. The $\Delta G^{\#}$ value calculated from the coalescence temperature using the DISPARNMR program is 16.5 kcal mol^{-1}, *i.e.*, it is somewhat greater than that for molecule **21**.

Analogous measurements were carried out for (η^6-biphenyltricarbonyl)chromium (**4**) (see Fig. 13). At room temperature, three signals for the CO group are also recorded; however, the coalescence temperature cannot be reached even on heating to 370 K, which points to a relatively high activation barrier to the rotation of the Cr(CO)$_3$ group. For technical reasons, a MAS probe cannot be operated at temperatures of >370 K due to the efficient oxidation of the probe material. For the same reason, for none of the studied tricarbonylchromium complexes of polycyclic aromatic compounds, were we able to record the singlet for the CO groups indicative of fast exchange.

Nevertheless, we obtained the full picture of spectral changes for (η^6-toluene)tricarbonylchromium (**23**). We found that at 203 K, the CPMAS ^{13}C NMR spectrum of complex **23** contain two signals for the CO ligands with an intensity ratio of ~2 : 1 in the region of spinning side bands (Fig. 14) (unfortunately, we failed to carry out signal acquisition to an appropriate signal-to-noise ratio). However, at room temperature, the signal for the CO group is not manifested at all, *i.e.*, a temperature of 293 K is close to the coalescence temperature (Fig. 15). On further heating to 350 K, a broadened singlet is observed; at 360 K, this signal becomes rather narrow.

In the spectrum of (η^6-diphenylmethane)tricarbonylchromium (**24**) (Fig. 16), the signal for the CO groups is a rather narrow singlet even at room temperature. This indicates that the activation barrier is lower for monocyclic aromatic compounds than for polyaromatic compounds. According to the data obtained by the total line shape analysis (TLSA), the barrier in η^6-toluenetricarbonylchromium equals[61] 15.5 kcal mol^{-1}.

Subsequently, this behavior of tricarbonylchromium complexes of monocyclic arenes was confirmed in other studies.[65,66] A typical behavior of signals of the Cr(CO)$_3$ group in the region of δ 230 is illustrated in Fig. 17 for the Cr(η^6-$C_6H_2Me_4$-1,2,4,5)(CO)$_3$ complex. At 253 K, two signals of the CO groups with 2 : 1 intensity ratio are observed; the signals are broadened and approach each other as the temperature rises and coalesce at 317 K; at 362 K, a narrow singlet appears.

As the temperature rises, the intensity of the side bands in the spectra of all complexes decreases,[67] which was attributed[66] to the decrease in the chemical shift anisotropy of the CO groups. This points to an increase in the rotation velocity of the Cr(CO)$_3$ group but contradicts the theoretical data[76] according to which the rotation barrier for the CO groups in arene complexes is rather high in the solid state due to the packing effects and fast rotation of the Cr(CO)$_3$ group is not expected. In our opinion, the results of our studies[67] and other works[61,64—66] indicate unambiguously that this fast rota-

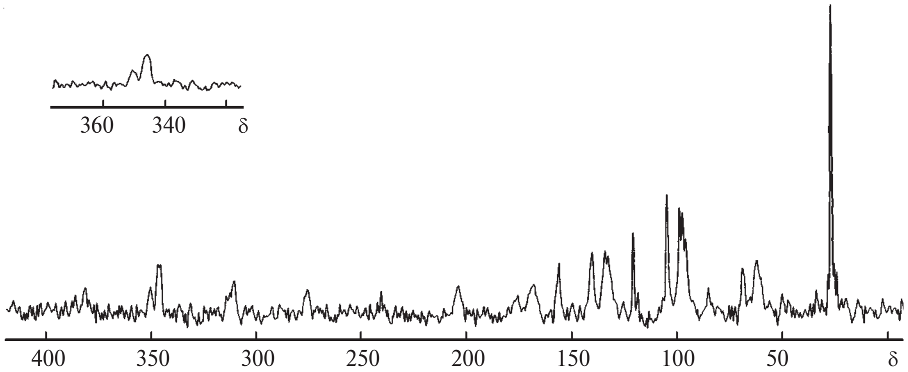

Fig. 14. CPMAS ^{13}C NMR spectrum of a polycrystalline (η^6-toluene)tricarbonylchromium (**23**) sample at 203 K. The insert shows the region of spinning side bands for the signals of the CO groups.

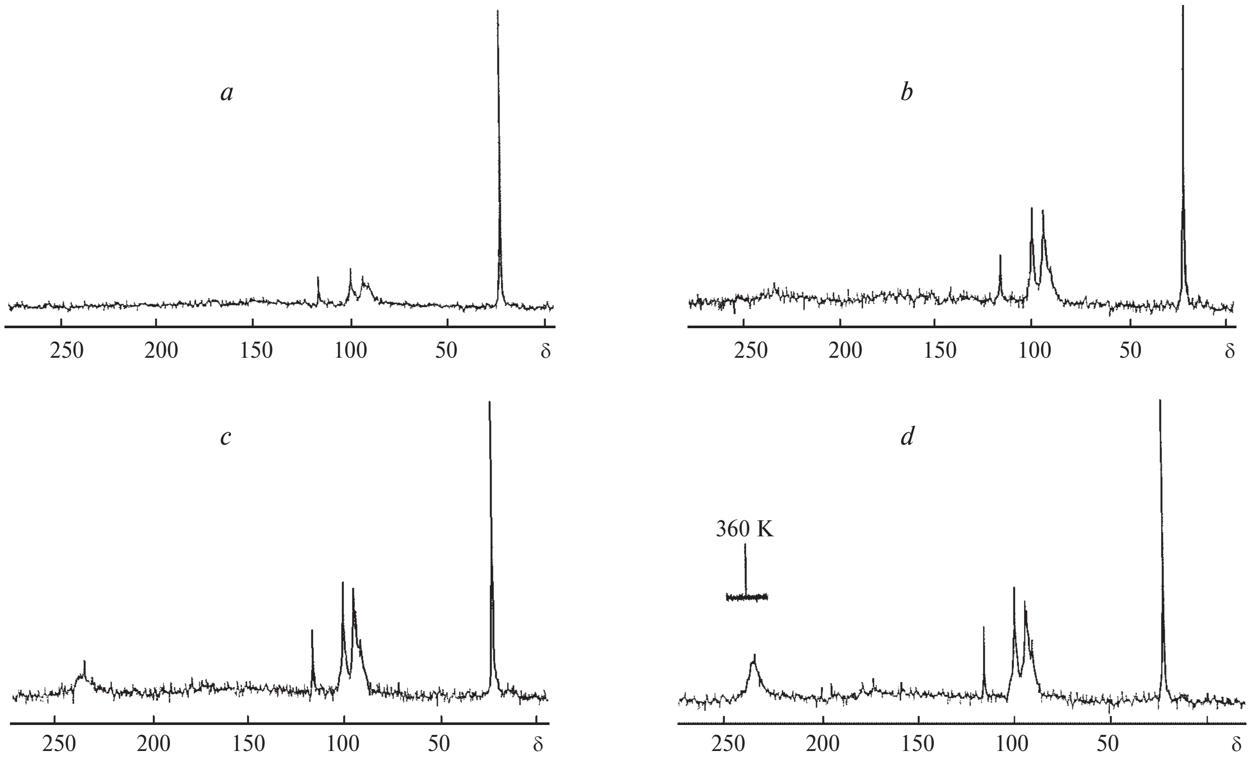

Fig. 15. CPMAS ^{13}C NMR spectrum of a polycrystalline (η^6-toluene)tricarbonylchromium (**23**) sample at 293 (*a*), 340 (*b*), 345 (*c*), and 350 K (*d*).

tion does occur even at rather moderate temperatures. In addition, this is consistent with the X-ray diffraction data**66** obtained for the (η^6-C_6HMe_5)$Cr(CO)_3$ complex over a broad temperature range. A full and correct structure description was possible only at low temperatures (<150 K), which was explained**66** by fast rotation of the $Cr(CO)_3$ group at room temperature.

However, apart from molecular factors, which determine the activation energy for the rotation of the $Cr(CO)_3$ groups, a significant role can be played by the packing of molecules in the crystal cell and the contribution of low-amplitude oscillations of molecular fragments (librations), which can also lead to averaging of the CO signals. This somewhat decreases the significance of the data on the

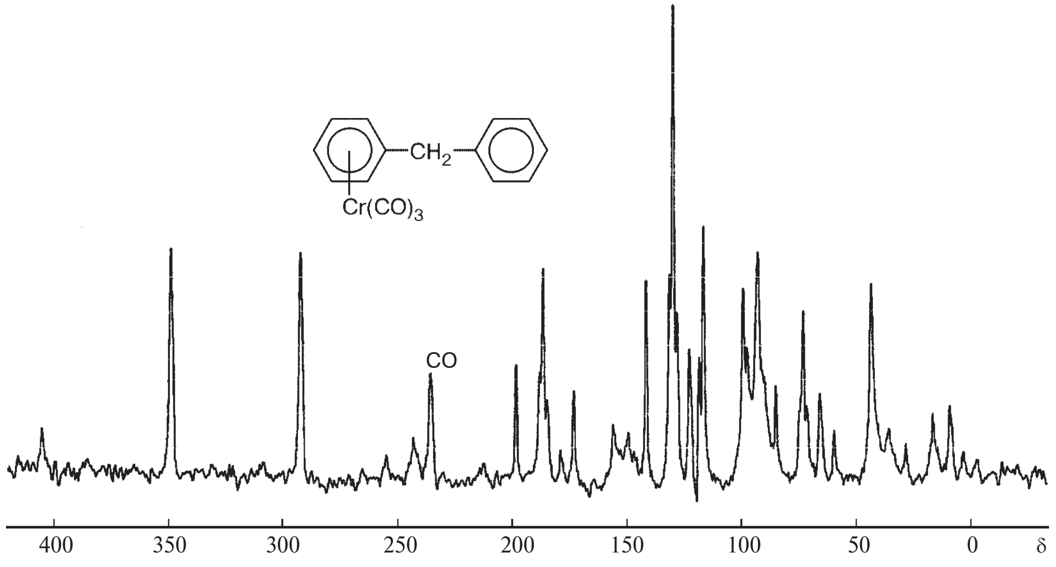

Fig. 16. CPMAS ^{13}C NMR spectrum of a polycrystalline (η^6-diphenylmethane)tricarbonylchromium (**24**) sample.

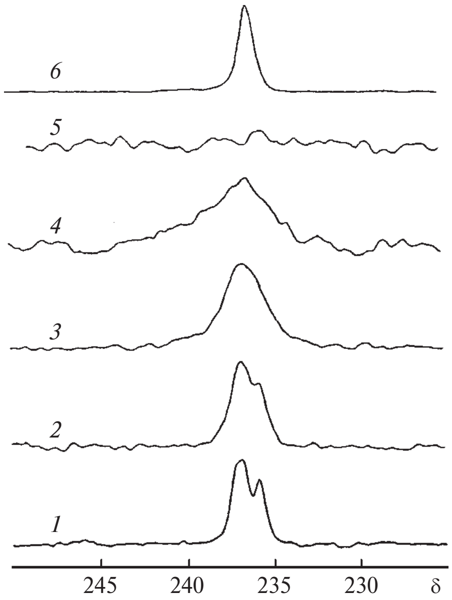

Fig. 17. CPMAS ^{13}C NMR spectrum of a polycrystalline Cr(η^6-$C_6H_2Me_4$-1,2,4,5)$(CO)_3$ sample in the region typical of CO groups[66] at 253 (*1*), 273 (*2*), 283 (*3*), 293 (*4*), 317 (*5*), and 362 K (*6*).

barriers to rotation of the $Cr(CO)_3$ groups in solids, which are still few and far between, because separation of the effects of the purely molecular properties of the system from the packing effects of molecules in the crystal cell appears to be a fairly complicated task.

The CPMAS ^{13}C NMR spectrum of (η^6-naphthalene)tricarbonylchromium (**25**), unlike those of other studied complexes, undergoes interesting irreversible changes (Fig. 18). In the region of CO groups (δ 230) two signals occur at room temperature, pointing to a symmetrical environment of two of the three CO groups in the crystal lattice. This is consistent with X-ray diffraction data.[77] Heating to 370 K results in coalescence of the CO signals ($\Delta G^{\#}$ = 17.3 kcal mol^{-1}), which is manifested most clearly in the region of spinning side bands (δ 320). The signals for the quaternary C atoms also change. Prior to the sample heating, only one signal of this type is recorded, while after the sample has been kept for 1.5 h at 370 K, two more signals for quaternary C atoms appear and grow on further heating. After the sample has been kept at 370 K for 3 h, they become predominant in the spectrum. These spectral changes are irreversible; we assumed that they may be related to a phase transition. The data obtained are in good agreement with the results[77] of a much earlier X-ray diffraction study of complex **25** according to which two types of crystals of compound **25** exist. The whole set of NMR and X-ray diffraction data shows that we are really dealing with a phase transition.

The large potential of the CPMAS NMR method was demonstrated in the investigation of insoluble (in this

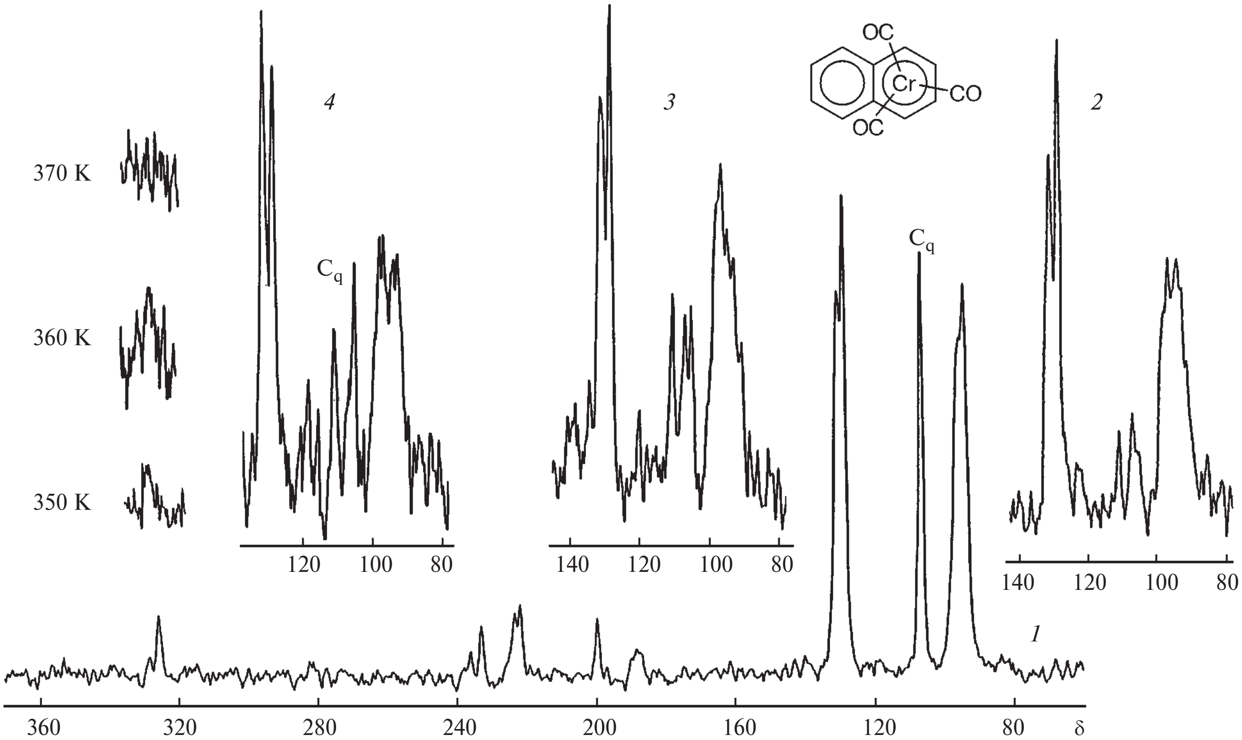

Fig. 18. CPMAS ^{13}C NMR spectrum of a polycrystalline (η^6-naphthalene)tricarbonylchromium (**25**) sample (*1*) and the spectra recorded after keeping the sample at 370 K for 1 (*2*), 1.5 (*3*), and 2 h (*4*); C$_q$ are the signals for the quaternary C atoms.

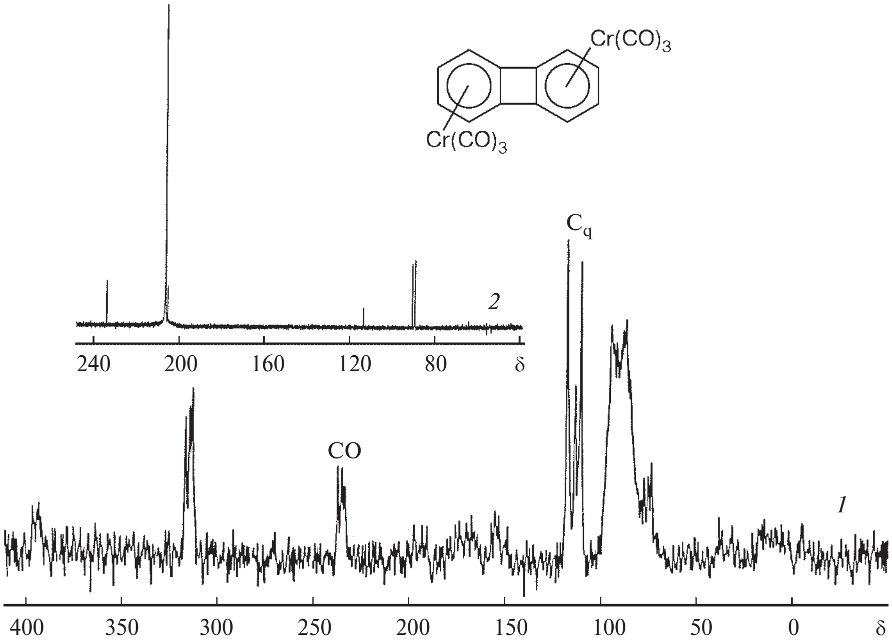

Fig. 19. CPMAS ^{13}C NMR spectrum of a polycrystalline (η^6-biphenylene)bis(tricarbonylchromium) (**26**) sample (*1*) and the ^{13}C NMR spectrum in solution (*2*); C_q are the signals for the quaternary C atoms.

case, this method is irreplaceable) and poorly soluble OMC. Figure 19 shows the high-resolution ^{13}C NMR spectrum of (η^6-biphenylene)bis(tricarbonylchromium) (**26**), whose solubility even in deuterioacetone is so poor that recording of a spectrum with an acceptable signal-to-noise ratio was found to require a ~12-h acquisition for a saturated solution using an instrument operating at 400 MHz. Meanwhile, the CPMAS ^{13}C NMR spectrum was measured over a period of 1 h, and analysis of this spectrum readily makes clear that this is a binuclear tricarbonylchromium complex of biphenylene.

The use of CPMAS ^{13}C NMR for investigation of the structure of tricarbonylchromium complexes with aromatic polycyclic compounds supported on silica gel. Despite the fact that the powder CPMAS NMR spectra are fairly useful for investigation of OMC, especially, complexes and clusters poorly soluble or unstable in solutions, in the case of usual OMC, high-resolution NMR spectroscopy is still used much more often. Apparently, this is due to some problems faced by interpretation of the CPMAS NMR spectra caused by the fact that signals are relatively broad and their number can exceed that expected with allowance for the molecular symmetry.

These problems can be overcome, at least partially, by recording the spectra of substances applied on silica gel. The mobility of substances sorbed on silica gel is known to be markedly higher than that in bulk samples.[78] Therefore, the signals in the CPMAS NMR spectra narrow down (to 10 Hz), and the quality of the obtained information markedly increases. This spectra can already compete with high-resolution spectra in information content. For this reason, we attempted to record the CPMAS spectra for the tricarbonylchromium complexes with polycyclic aromatic ligands applied on silica gel. Previously, this approach has been used[79] to obtain well-resolved spectra of polycyclic hydrocarbons; however, we were the first to use this method for transition metal complexes.

The mere trituration of tricarbonylchromium complexes with silica gel in an agate mortar, unlike a more complex method for application of the complex from a benzene solution, allows one to obtain high-resolution MAS ^{13}C NMR spectra of tricarbonylchromium complexes of polycyclic aromatic compounds. An additional advantage of the trituration method is related to the fact that, when a solvent is used, the solvent signal cannot be completely removed from the spectrum even after drying the sample, and samples obtained by trituration are more stable. However, unlike application from a solution, in some cases, a silica gel sample with a supported complex has to be slightly heated to ~50 °C for 10 min for adsorption to take place.

In the MAS ^{13}C NMR spectrum of complex **4** applied on silica gel (Fig. 20), the signals are rather narrow (<15 Hz) and completely resolved. All information that can be derived from high-resolution spectra can also be gained from this spectrum. It is noteworthy that the use of cross-polarization not only does not improve but even deteriorates the quality of the spectrum, indicating a substantial mobility of adsorbed molecules and a sharp decrease in the ^{1}H and ^{13}C dipole—dipole coupling. Complex **4** applied on silica gel proved to be highly stable; no

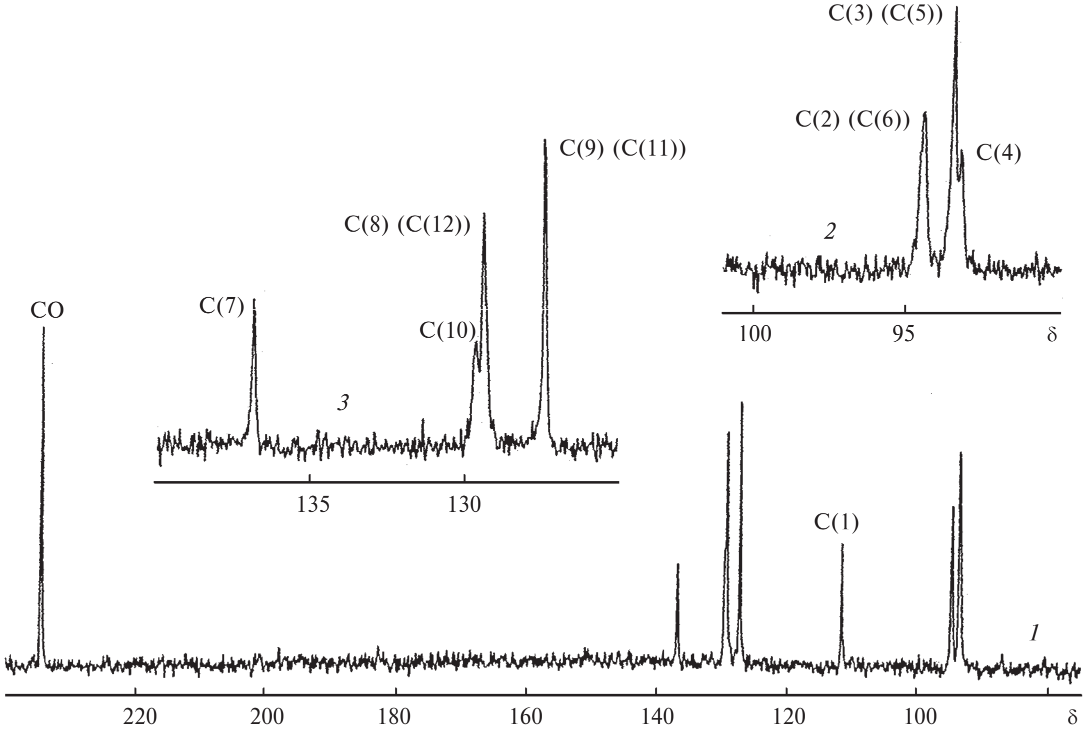

Fig. 20. MAS ^{13}C NMR spectrum of a (η^6-biphenyl)tricarbonylchromium (**4**) sample applied onto silica gel (*1*); the spectral ranges corresponding to the signals of C atoms in coordinated (*2*) and noncoordinated (*3*) rings are also shown.

signs of decomposition were noticed even 24 h after deposition.

Yet another advantage of this procedure is that it does not require the use of expensive deuterated solvents and allows investigation of compounds directly after TLC without preliminary isolation, which may be useful in certain cases.

(η^6-Naphthalene)tricarbonylchromium (**25**) proved to be much less stable and, after application on silica gel, it substantially decomposed even at room temperature. As this took place, signals for naphthalene and $Cr(CO)_6$ (δ 212) appeared and rapidly grew in the spectrum (Fig. 21), which was proved by measuring the spectra of pure naphthalene and chromium hexacarbonyl applied on silica gel.

Complex **21** occupies an intermediate position between very stable compound **4** and unstable compound **25**; in particular, destruction of complex **21** takes place after heating the sample at 50 °C for 1 h. The sample completely decomposes over a period of 8 h to give bi-

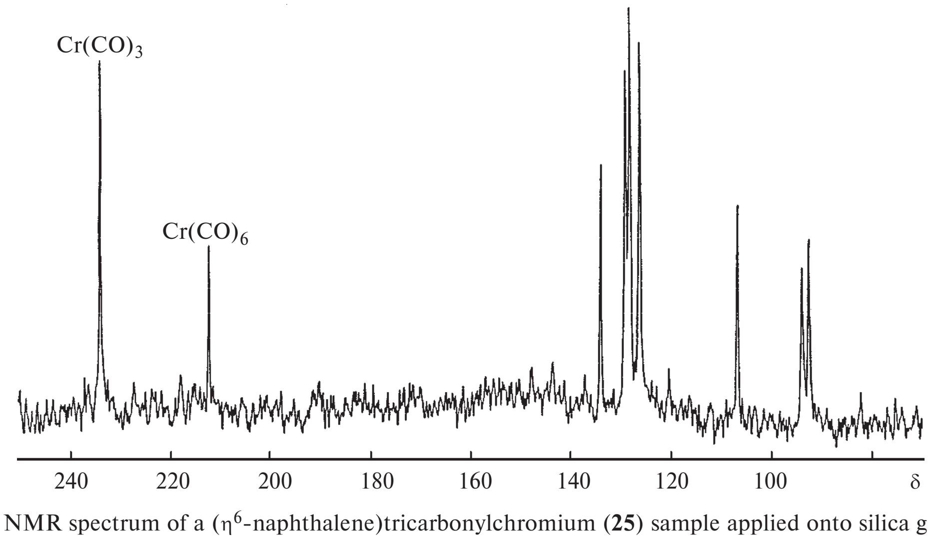

Fig. 21. MAS ^{13}C NMR spectrum of a (η^6-naphthalene)tricarbonylchromium (**25**) sample applied onto silica gel.

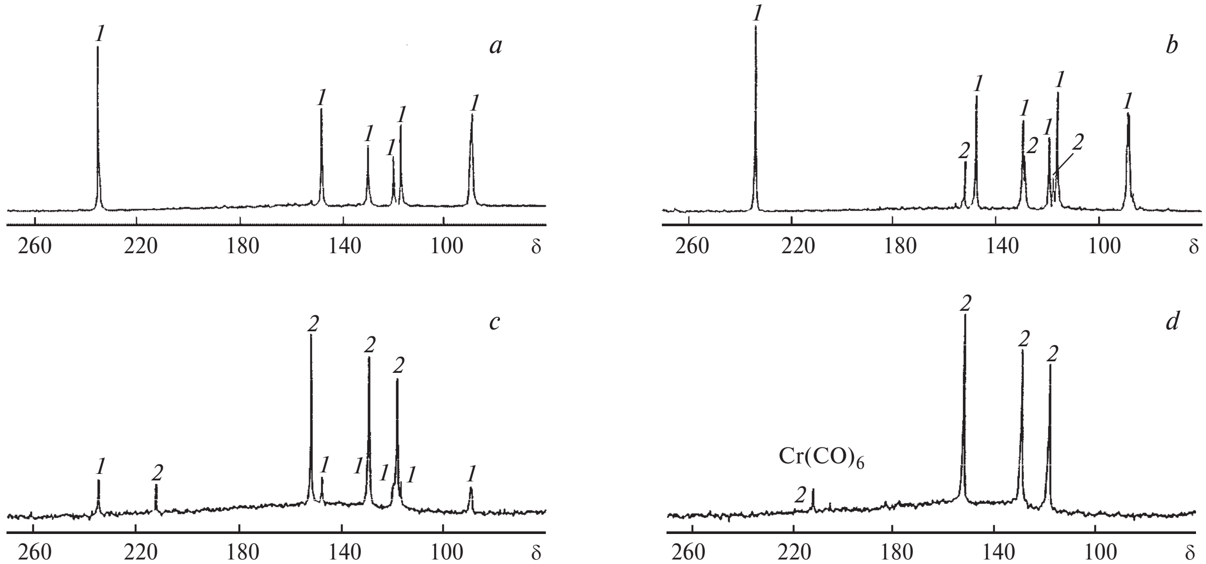

Fig. 22. MAS ^{13}C NMR spectra of a (η^6-biphenylene)tricarbonylchromium (**21**) sample applied onto silica gel (*a*) and kinetics of its decomposition to give free biphenylene and Cr(CO)$_6$ after keeping at 25 °C for 4 (*b*), 12 (*c*), and 24 h (*d*); (*1*) signals of the complex; (*2*) signals of the biphenylene ligand and Cr(CO)$_6$.

phenylene and Cr(CO)$_6$ (Fig. 22) and the reaction kinetics can be followed. Chromium hexacarbonyl is oxidized to give, apparently, Cr$_2$O$_3$, which colors silica gel green. The rate of decomposition of complex **21** depends on the method of silica gel pretreatment; the long-term degassing and storage under argon of silica gel substantially (in some cases, by an order of magnitude) increases the stability of supported complexes. Analogous results were obtained for complexes applied on Al$_2$O$_3$; however, these samples were much less stable.

For silica gel-supported complexes, it is possible to record spectra without broad-band proton decoupling; this provides the possibility of determining the direct J_{CH} constants. As an example, Fig. 23 shows the spectrum of (η^6-toluene)tricarbonylchromium recorded without proton decoupling.

Whereas signal narrowing in the NMR spectra of "dilute" nuclei with the spin $I = 1/2$ (*e.g.*, ^{13}C) is a usual effect for CPMAS NMR spectroscopy, the results for ^{1}H NMR spectra of crystalline samples are less satisfactory due to the strong intra- and intermolecular dipole—dipole interaction. The MAS ^{1}H NMR spectra provide virtually no information. Only in recent years, have the CRAMPS (combined rotation and multipulse sequence) method been developed;[80] this technique combines the MAS and muliple pulse sequence techniques for signal

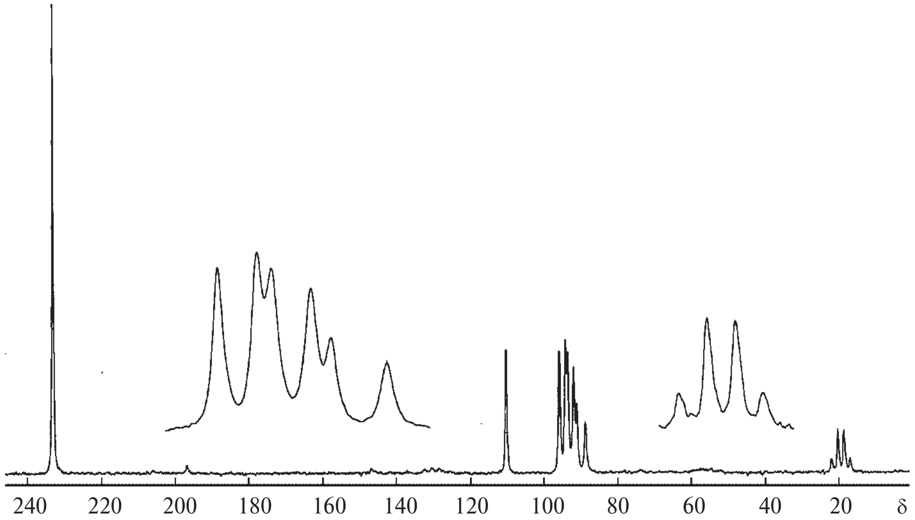

Fig. 23. MAS ^{13}C NMR spectrum of (η^6-toluene)tricarbonylchromium without proton decoupling.

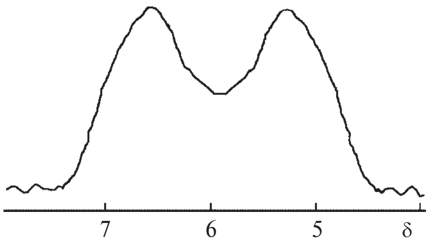

Fig. 24. CRAMPS ^{1}H NMR spectrum of a polycrystalline (η^6-biphenylene)tricarbonylchromium (**21**) sample.

narrowing and allows recording of rather high-quality ^{1}H NMR spectra. This is illustrated by the CRAMPS spectrum for complex **21** (Fig. 24) in which the proton signals from the coordinated and noncoordinated nuclei are resolved, although the $H_{\alpha 1}$ and $H_{\beta 2}$ cannot be resolved for either of the rings.

Unlike crystalline samples, for compound **21** and a number of other complexes supported on silica gel, well resolved MAS ^{1}H NMR spectra were recorded.**34** In the spectrum of complex **21** (Fig. 25), one can see that the H_α and H_β signals are resolved in both coordinated and noncoordinated regions.

The achived resolution made it possible to use 2D spectroscopy for tricarbonylchromium complexes supported on silica gel. Unfortunately, signals in the MAS ^{1}H NMR spectra have no fine structure, and, although the relevant experiments with the use of the COSY sequence known for solutions give the expected cross-peaks, these spectra are not very interesting. The NOESY spectra could not be recorded, apparently, due to fast relaxation and participation of relaxation mechanisms other than the dipole—dipole mechanism (for example, due to the appearance of paramagnetism). The ^{13}C,^{1}H-correlation 2D spectra (HETCOR) proved to provide much more information. This is exemplified in Fig. 26, which shows the corresponding spectrum for complex **21** containing all the expected cross-peaks.

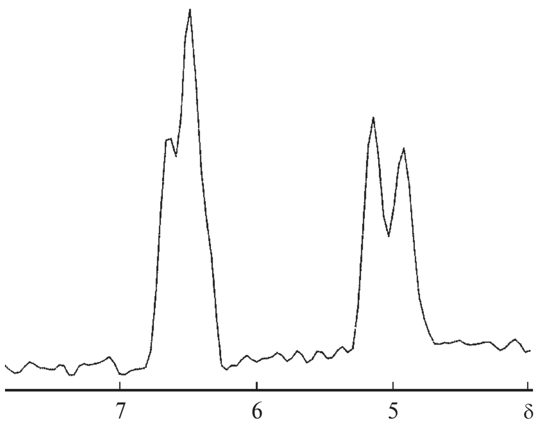

Fig. 25. MAS ^{1}H NMR spectrum of (η^6-biphenylene)tricarbonylchromium (**21**) applied onto silica gel.

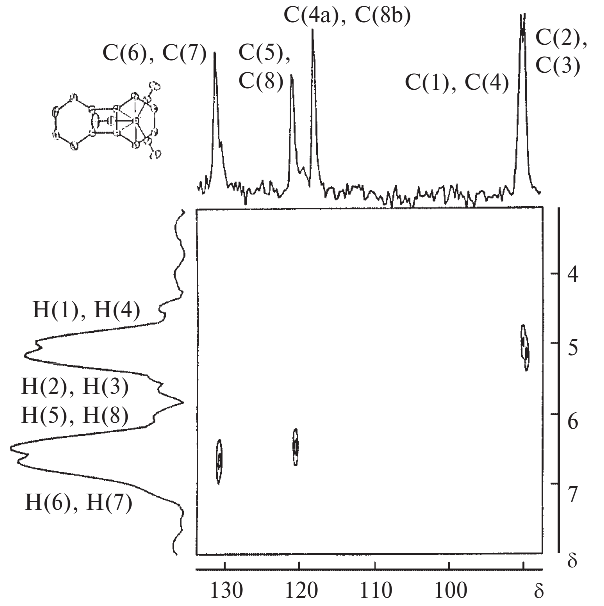

Fig. 26. ^{1}H,^{13}C correlation 2D spectrum (HETCOR) of (η^6-biphenylene)tricarbonylchromium (**21**) applied onto silica gel.

Mention should be made of the prospects opened by this approach in combinatorial chemistry**81** for controlling reactions that proceed on various substrates, in particular, on inorganic oxides.**82**

* * *

Thus, the use of 1D and 2D modes of ^{1}H and ^{13}C NMR spectroscopy including measurement of homonuclear NOE and ASIS effects provides reliable determination of the structure and stereochemistry of OMC, in particular, tricarbonylchromium complexes with polycyclic aromatic ligands.

The use of ^{2}D NMR allows one to analyze efficiently diverse transformations in OMC and to determine the kinetic and thermodynamic parameters of these transformations by investigating the redistribution of a selective deuterium label.

Solid-state high-resolution ^{1}H and ^{13}C NMR spectroscopy for polycrystalline samples is a promising method for investigating the structures, phase transitions, and the dynamic behavior of OMC in the crystalline state.

Solid-state CPMAS NMR spectroscopy of silica gel-supported complexes provides fast and reliable determination of the structures of OMC, including poorly soluble compounds, study of various transformations including chemical reactions, dynamic behavior, *etc*. An additional advantage of this method is the possibility of recording the spectra directly after TLC analysis without isolation of the complex in a pure state or the use of deuterated solvents.

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References

1. *Advanced Applications of NMR to Organometallic Chemistry (Physical Organometallic Chemistry)*, Vol. **1**, Eds. M. Gielen, R. Willem, and B. Wrackmeyer, J. Wiley, New York, 1996.
2. B. E. Mann, *Chem. Soc. Rev.*, 1986, **15**, 167.
3. B. E. Mann, in *Comprehensive Organometallic Chemistry*, Eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, **3**, Ch. 20, 89.
4. K. Schlögl, A. Werner, and M. Widhalm, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1731.
5. *NMR Techniques in Catalysis*, Eds. A. Bell and A. Pines, Marcel Dekker, New York, 1994.
6. F. A. Cotton, in *Dynamic Nuclear Magnetic Resonance*, Eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, Ch. 10, 377.
7. Ch. Elschenbroich and A. Salzer, *Organometallics, an Introduction*, 2nd ed., Wiley-VCH Verlag, Weinheim (Germany), 1992.
8. Yu. N. Luzikov, Yu. F. Oprunenko, Yu. A. Ustynyuk, and N. A. Ustynyuk, *J. Organomet. Chem.*, 1982, **231**, 137.
9. N. S. Hush, *J. Am. Chem. Soc.*, 1997, **119**, 1717.
10. R. H. Crabtree and D. G. Hamilton, *J. Am. Chem. Soc.*, 1986, **108**, 312.
11. B. E. Mann, *J. Chem. Soc.*, *Dalton Trans.*, 1984, 2027.
12. R. A. Bell and J. K. M. Saunders, *Can. J. Chem.*, 1970, **48**, 1114.
13. Yu. F. Oprunenko, S. G. Malyugina, Yu. A. Ustynyuk, N. A. Ustynyuk, and D. N. Kravtsov, *J. Organomet. Chem.*, 1988, **338**, 387.
14. N. A. Ustynyuk, L. N. Novikova, V. K. Bel´skii, Yu. F. Oprunenko, S. G. Malyugina, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 1985, **294**, 31.
15. F. McGlinchey, F. A. Roberts, and P. N. Dodge, *J. Am. Chem. Soc.*, 1993, **115**, 7275.
16. B. E. Mann, *Adv. Organomet. Chem.*, 1988, **28**, 397.
17. I. D. Gridnev, M. E. Gursky, and Yu. N. Bubnov, *Organometallics*, 1996, **15**, 3696.
18. R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*, Pitman, London, 1983.
19. C. S. Yannoni, *Acc. Chem. Res.*, 1982, **15**, 201.
20. R. Benn, R. Mynott, I. Topalovic, and F. Scott, *Organometallics*, 1989, **8**, 2299.
21. A. Stanger, *Organometallics*, 1991, **10**, 2979.
22. G. B. Nagy, *Multinuclear Magnetic Resonance in Liquids and Solids — Chemical Applications*, Eds. B. Granger and R. K. Harris, NATO ASI Ser. C, Springer Verlag, Berlin, 1990, 322; 371.
23. R. Csuk, B. I. Glänzer, and A. Fürstner, *Adv. Organomet. Chem.*, 1988, **28**, 85.
24. H. Estrade-Schwarzkopf and K. H. Müller, *J. Phys. Chem.*, 1985, **89**, 97.
25. P. Styles and N. Soffe, *J. Magn. Reson.*, 1984, **50**, 397.
26. G. Engelhardt and D. Michel, *High Resolution Solid State NMR of Silicates and Zeolites*, J. Wiley, Chichester, 1987.
27. P. G. Gassman and P. A. Deck, *Organometallics*, 1994, **13**, 1934.
28. J. A. Ramsden, C. M. Garner, and J. A. Gladysz, *Organometallics*, 1991, **10**, 1631.
29. E. Yashima, C. Yamamoto, and Y. Okamoto, *J. Am. Chem. Soc.*, 1996, **118**, 4036.
30. D. J. States, R. A. Habekorn, and D. J. Ruben, *J. Magn. Reson.*, 1982, **48**, 286.
31. M. Rance, G. Bodenhausen, G. Wagner, K. Wütrich, and R. R. Ernst, *J. Magn. Reson.*, 1985, **62**, 497.
32. G. A. Morris and K. J. Smith, *J. Magn. Reson.*, 1985, **65**, 506.
33. G. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, 1979, **101**, 760.
34. Yu. F. Oprunenko, Sc.D. Thesis (Chem.), Moscow State University, Moscow, 1999 (in Russian).
35. D. Neuhaus and M. P. Williamson, *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, VCH Edition, Weinheim, 1989.
36. K. E. Kövér and G. Batta, *J. Am. Chem. Soc.*, 1985, **107**, 5829.
37. J. K. M. Saunders and J. D. Mersh, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1982, **15**, 353.
38. Yu. F. Oprunenko, N. G. Akhmedov, S. G. Malyugina, V. I. Mstislavsky, V. A. Roznyatovsky, D. N. Laikov, Yu. A. Ustynyuk, and N. A. Ustynyuk, *J. Organomet. Chem.*, 1999, **583**, 136.
39. W. J. Bland, R. Davis, and J. L. A. Durrant, *J. Organomet. Chem.*, 1984, **234**, C20.
40. Yu. A. Ustynyuk, O. I. Trifonova, and Yu. F. Oprunenko, *Metalloorgan. Khim.*, 1993, **6**, 654 [*Organomet. Chem. USSR*, 1993, **6** (Engl. Transl.)].
41. Yu. F. Oprunenko, I. A. Shaposhnikova, and Yu. A. Ustynyuk, *Metalloorgan. Khim.*, 1991, **4**, 684 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
42. Yu. F. Oprunenko, S. G. Malyugina, O. Ya. Babushkina, Yu. A. Ustynyuk, P. N. Nesterenko, N. A. Ustynyuk, D. N. Kravtsov, and V. A Piven´, *Metalloorgan. Khim.*, 1988, **1**, 384 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].
43. Yu. F. Oprunenko, S. G. Malyugina, O. Ya. Babushkina, Yu. A. Ustynyuk, N. A. Ustynyuk, and D. N. Kravtsov, *Metalloorgan. Khim.*, 1989, **2**, 599 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
44. M. Rance, O. W. Sorensen, G. Bodenhausen, G. Wagner, R. R. Ernst, and R. Wütrich, *Biochem. Biophys. Res. Commun.*, 1983, **117**, 479.
45. D. J. States, R. A. Haberkorn, and D. J. Ruben, *J. Magn. Reson.*, 1982, **48**, 286.
46. R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Oxford University, Oxford, 1987.
47. J. M. Lamarche, J. Vefrel, and B. Laude, *Spectrochim. Acta, A*, 1979, **35**, 673.
48. W. R. Jackson and T. R. B. Mitchell, *J. Chem. Soc., B*, 1969, 1228.
49. B. Caro, E. Gentric, D. Grandjean, and G. Jaouen, *Tetrahedron Lett.*, 1978, 3009.
50. D. E. F. Gracey, W. R. Jackson, C. H. McMullen, and N. Thompson, *J. Chem. Soc., B*, 1969, 2197.
51. R. G. Sutherland, W. J. Pannekoek, and C. C. Lee, *Can. J. Chem.*, 1978, **56**, 1782.
52. E. M. Engler and P. Lazlo, *J. Am. Chem. Soc.*, 1971, **93**, 1317.

53. N. A. Ustynyuk, L. N. Novikova, V. K. Bel´skii, Yu. F. Oprunenko, S. G. Malyugina, O. I. Trifonova, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 1985, **294**, 31.
54. D. E. F. Gracey, W. E. Jackson, W. B. Jennings, S. R. Rehninson, and R. Span, *J. Chem. Soc., B*, 1969, 1210.
55. A. C. Sievert and E. I. Muetterties, *Inorg. Chem.*, 1981, **20**, 2278.
56. B. M. Bandara, A. J. Birch, and W. D. Raverty, *J. Chem. Soc.*, *Perkin Trans. 1*, 1982, 1945.
57. L. A. Paquette and R. Gree, *J. Organomet. Chem.*, 1978, **146**, 319.
58. N. A. Ustynyuk, L. N. Novikova, Yu. F. Oprunenko, S. G. Malyugina, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 1984, **277**, 75.
59. T. G. Traylor and M. J. Goldberg, *Organometallics*, 1987, **6**, 2531.
60. B. E. Hanson, in *Advances in Dynamic Stereochemistry*, Ed. M. Gielen, Freund, London, 1985, 89.
61. G. W. Wagner and B. E. Hanson, *Inorg. Chem.*, 1987, **26**, 2019.
62. R. Benn, R. Mynott, I. Topalovic, and F. Scott, *Organometallics*, 1989, **8**, 2299.
63. A. Stanger, *Organometallics*, 1991, **10**, 2979.
64. A. E. Aliev, K. D. M. Harris, F. Guillaume, and P. J. Barrie, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3193.
65. P. J. Barrie, Ch. A. Mitsopoulou, and E. W. Randall, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2125.
66. P. J. Barrie, Ch. A. Mitsopoulou, M. Motevalli, and E. Randall, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 353.
67. Yu. Oprunenko, M. Ebener, G. von Fircks, and H. Guenther, *XV Intern. Conf. on Organometallic Chemistry, Book of Abstrs.*, Warsaw, 1992, 84.
68. J. S. Opella and M. H. Frey, *J. Am. Chem. Soc.*, 1979, **101**, 5854.
69. R. D. Rogers, J. L. Atwood, T. A. Albright, W. A. Lee, and M. D. Rausch, *Organometallics*, 1984, **3**, 263.
70. M. J. McGlinchey, *Adv. Organomet. Chem.*, 1992, **14**, 285.
71. M. Nambu, D. L. Mohler, K. Hardcastle, K. K. Baldridge, and J. S. Siegel, *J. Am. Chem. Soc.*, 1993, **115**, 6138.
72. H. Günther, *NMR-Spektroskopie*, G. Thieme, Stuttgart, 1992.
73. V. I. Mstislavskii, Ph.D. Thesis (Physics and Mathematics), Moscow State University, Moscow, 1985 (in Russian).
74. Yu. F. Oprunenko, A. S. Batsanov, S. G. Malyugina, M. D. Reshetova, N. A. Ustynyuk, and Yu. A. Ustynyuk, *Organometallics*, 1994, **13**, 2284.
75. P. E. Baikie and O. S. Mills, *J. Chem. Soc., A*, 1969, 328.
76. D. Braga, *Chem. Rev.*, 1992, **92**, 663.
77. V. Kunz and W. Nowacki, *Helv. Chim. Acta*, 1967, **50**, 1052.
78. H. Pfeifer, W. Meiler, and D. Deininger, *Ann. Rep. NMR Spectrosc.*, 1983, **15**, 291.
79. M. Ebener, G. von Fircks, and H. Günther, *Helv. Chim. Acta*, 1991, **74**, 1296.
80. P. Jackson and R. K. Harris, *Magn. Reson. Chem.*, 1988, **26**, 1003.
81. C. R. Anderson, M. A. Jarema, M. J. Shapiro, J. P. Stokes, and M. Ziliox, *J. Org. Chem.*, 1995, **60**, 2650.
82. M. Ebener, V. Francke, and H. Günther, *Fresenius J. Anal. Chem.*, 1997, **357**, 505.

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