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Spin Order Transfer from a Parahydrogen Molecule to a Cyanide Ion in the Iridium Complex under the SABRE Conditions

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Abstract—A possibility of generating a high degree of spin polarization of ^{13}C and ^{15}N nuclei in the cyanide ion, which forms the coordination bond with the metal ion, using parahydrogen is demonstrated for the first time for the new iridium carbene complex as an example. The spin–spin interaction constants in the synthesized complex and the structure of the hydride intermediate are determined by an analysis of the ^{13}C NMR spectra detected using broadband and selective heteronuclear decoupling. The cyanide ion is shown to coordinate to the metal ion by the carbon atom in one of two equatorial positions, and two pyridine molecules are arranged in the axial and equatorial positions. The signal amplification factors for ^{13}C and ^{15}N nuclei of the cyanide anion (5665 and –49555, respectively) are estimated by NMR spectroscopy of the polarized substrate using the SABRE method from an ultralow magnetic field of 0.5 μT. This amplification corresponds to 15.5% polarization of nitrogen nuclei achieved within several seconds at room temperature.

Keywords: NMR spectroscopy, parahydrogen, hyperpolarization, iridium complexes, carbene ligands, signal enhancement, parahydrogen-induced nuclear hyperpolarization

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INTRODUCTION

Low sensitivity is the main drawback of nuclear magnetic resonance (NMR) spectroscopy and restricts its application in chemistry [1], biology [2], and medicine [3]. This restriction is caused by a very low difference in populations of nuclear spin states (also named polarization) at thermal equilibrium at room temperature [4]. The known methods for solving this problem associated with the generation of nonequilibrium populations of these spin states (hyperpolarization) are often based on the transfer of the spin order from the particles the polarization of which is simpler. For example, the spin order can be transferred from electrons in the form of dynamic nuclear polarization [5, 6] or photons in the form of optical pumping of noble gases [7–9]. However, these approaches, are a rule, require the use of very expensive equipment.

Another version of the solution of the problem implies the spin order transfer from a molecule of parahydrogen. This compound can easily be prepared by the *ortho–para* conversion of hydrogen that occurs at low temperatures in the presence of the paramagnetic catalysts [10]. The presence of molecular parahydrogen does not result in the appearance of signals in the NMR spectra [11]. However, when parahydrogen is attached to the analyzed substrates during hydrogenation [12] or reversible exchange upon the coordination of the hydrogen molecule with the iridium complex [11], the products are formed in which the nonequilibrium distribution of populations of nuclear levels results in a significant increase in the signal intensity in the NMR spectrum [10, 13]. The case of reversible exchange, the so-called SABRE approach [11] ("Signal Amplification by Reversible Exchange," i.e., signal enhancement due to reversible exchange), is of special interest since allows polarization transfer between two types of molecules capable of coordinating with the chosen metallocenter. Thus, polarization can be transferred from parahydrogen to such a coligand as pyridine [14] or other heterocyclic compounds [15, 16].

The predominant number of the SABRE catalysts is presented by the charged iridium complexes containing a weakly coordinated counterion [16, 17]. We have previously [18] demonstrated the possibility of the polarization transfer to outer-sphere tetrafluoroborate and hexafluorophosphate anions.

In this work, we synthesized the new iridium complex Ir(SIMes)(COD)(CN) with the inner-sphere cyanide anion and studied the polarization transfer from the parahydrogen molecule to the ^{13}C and ^{15}N nuclei of this anion at the natural content of isotopes and to the ^{13}C and ^{15}N nuclei of the exchangeable pyridine coligand under the SABRE conditions at the natural isotope content in pyridine enriched in ^{15}N.

EXPERIMENTAL

All procedures associated with the synthesis and isolation of the complex were carried out under a nitrogen atmosphere in a glove box. 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride (SIMes·HCl) was used as received (Sigma-Aldrich), and $(IrCODCl)_2$ and IrCl(COD)(SIMes) were synthesized using a described procedure [19, 20]. Elemental analyses to carbon, nitrogen, and hydrogen were conducted on a Carlo Erba (model 1106) microanalyzer. SABRE spectra were recorded on a Bruker Ascend 400 MHz spectrometer (Larmor frequency for protons was 400.13 MHz) in methanol-d_4.

Synthesis of complex IrCl(COD)(SIMes) ([1,3-bis[2,4,6-trimethylphenyl]-2-imidazolidenylidene]-chloro[(η^4)-1,5-cyclooctadiene] iridium(I)). The dimer of η^4-cycloocta-1,5-diene iridium(I) chloride $[Ir(Cl)(COD)]_2$ (537 mg, 0.80 mmol) and ^{t}BuOK (80 mg, 0.80 mmol) were mixed in a 20-mL vial in a glove box, and the mixture was stirred for 10 min. Anhydrous THF (10 mL) was added, and the resulting dark red solution was stirred at room temperature for 10 min. Then SIMes·HCl (544 mg, 1.60 mmol) was added as one portion, and the color of the solution changed from dark red to dark yellow. The obtained reaction mixture was stirred for 16 h and evaporated in vacuo. The dry residue was purified using column flash chromatography eluting the yellow fraction with a dichloromethane–acetone (8 : 1) mixture as an eluent. The yield was 875 mg (86%).

^{1}H NMR (400 MHz; $CDCl_3$; δ, ppm): 6.94 (d, $^3J_{H-H}$ = 14.1 Hz, 4H, ArH), 4.08 (d, $^3J_{H-H}$ =2.9 Hz, 2H, COD CH), 3.88 (s, 4H, NCH_2–CH_2N), 3.06 (d, $^3J_{H-H}$ = 1.7 Hz, 2H, COD CH), 2.54 (s, 6H, CH_3), 2.33 (s, 6H, CH_3), 2.30 (s, 6H, CH_3), 1.60 (m, 4H, COD CH_2), 1.25 (m, 4H, COD CH_2). ^{13}C NMR ($CDCl_3$; 100 MHz; δ, ppm): 207.4, 138.2, 138.0, 136.4, 135.4, 130.0, 128.6, 83.9, 52.0, 51.7, 33.6, 29.9, 21.3, 20.1, 18.7.

For $C_{30}H_{38}N_3Ir$

Anal. calcd., %	C, 56.94	H, 6.05	N, 6.64
Found, %	C, 57.10	H, 6.17	N, 6.66

Synthesis of complex Ir(SIMes)(COD)(CN). A weighed sample of [IrCl(COD)(SIMes)] (269 mg, 0.40 mmol) was dissolved in acetone (10 mL), and AgCN (54 mg, 0.40 mmol) was added. The resulting suspension was stirred at room temperature for 2 h. The formed precipitate of silver chloride was filtered off, and the mother liquor was evaporated on a rotary evaporator and dried in deep vacuum. The prepared product was used without further purification. The yield was 246 mg (93%).

^{1}H NMR (400 MHz; $CDCl_3$; δ, ppm): 7.00 (s, 2H, ArH), 6.92 (s, 2H, ArH), 4.16–4.04 (m, 2H, COD CH), 3.94 (d, ^3J = 2.8 Hz, 4H, NCH_2–CH_2N), 3.67 (s, 2H, COD CH), 2.59 (s, 6H, CH_3), 2.31 (s, 12H, CH_3), 1.56–1.47 (m, 8H, COD CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ, ppm): 207.41, 137.98, 137.67, 137.08, 135.64, 134.89, 129.99, 128.36, 76.57, 72.53, 51.64, 31.63, 30.40, 21.05, 19.61, 18.28.

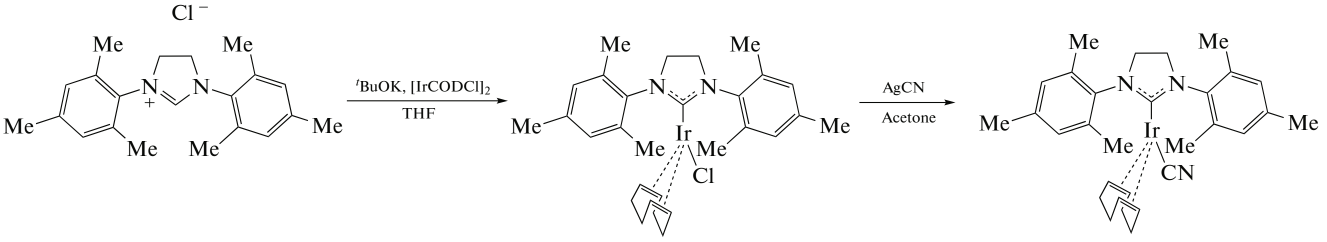
For $C_{29}H_{38}N_2ClIr$

Anal. calcd., %	C, 54.23	H, 5.96	N, 4.36
Found, %	C, 54.40	H, 5.77	N, 4.38

NMR spectroscopy and SABRE. During the experiment, parahydrogen was passed through the sample placed inside a standard cylindrical 5-mm NMR tube under a pressure of 5 bar for 10 s prior to recording ^{1}H NMR spectra and for 30 s prior to recording ^{13}C and ^{15}N NMR spectra using the automated gas system made at the International Tomography Center (Siberian Branch, Russian Academy of Sciences) [21]. After bubbling in a specified magnetic field, the sample was rapidly transferred to the sensor of the spectrometer and NMR spectra were recorded. The magnetic field intensity was specified by an electromagnet mounted at the center of the magnetic shield fixed coaxially above the main cryomagnet. The setup with swift magnetic field switching was described in detail [22, 23].

RESULTS AND DISCUSSION

Iridium complex Ir(SIMes)(COD)(CN) was synthesized from the starting 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (SIMes·HCl) by the in situ generation of carbene in the presence of potassium *tert*-butylate and dimer of η^4-cycloocta-1,5-diene iridium(I) chloride $(Ir(Cl)(COD))_2$ followed by the replacement of the counterion under the action of silver cyanide in acetone (Scheme 1). The ^{1}H and ^{13}C NMR spectra of the synthesized complex completely corresponded to the expected spectra. However, we failed to detected this signal even upon a very prolong acquisition because of very long relaxation times of the ^{13}C nuclei in the cyanide anion. This signal was detected in the ^{13}C SABRE spectra.



Scheme 1.

To study the polarization transfer from the parahydrogen molecule under the SABRE conditions, the corresponding NMR spectra were recorded with parahydrogen bubbling through solutions of the indicated complexes in methanol-d_4 in the presence of pyridine. The appearance of intense signals of the hydride intermediates in the negative spectral range was observed (Fig. 1) in addition to the signal of gaseous parahydrogen (chemical shift $\delta = 4.57$ ppm). The antiphase nature of the most part of the indicated signals in a strong magnetic field is characteristic of the hydride intermediates generated under the SABRE conditions [24, 25] and differs in the number and coordination mode of the pyridine and methanol molecules present in the solution. For instance, an analogous NMR spectrum recorded for the classical SABRE catalyst Ir(COD)(Imes)Cl contained one signal in the hydride range indicating the chemical and magnetic equivalence of the hydride protons [26]. The activation of the catalysts is accompanied by cyclooctadiene hydrogenation, and the spectrum of the synthesized Ir(COD)(SIMes)(CN) complex exhibits several antiphase doublets with splitting about 6–7 Hz, which corresponds to the spin–spin interaction constant between two hydride protons. Several intermediates with nonequivalent hydride protons that simultaneously exist in the solution indicate that pyridine (present in excess) does not displace the cyanide anion from the coordination sphere of the metal ion. Otherwise only signals of the symmetric complex with three coordinated pyridine molecules would be observed. Remarkably, prolong parahydrogen bubbling through the sample leads to a gradual decrease in the relative intensity of signals of the hydride protons, due to which only doublets with $\delta = -9.33$ and -22.89 ppm and a singlet with $\delta = -22.35$ ppm are observed. The latter was absent from the polarized spectra and underwent a partial splitting to a doublet with a constant of 20 Hz upon the addition of pyridine-^{15}N. This makes it possible to assign the compound to the hydride complex with three coordinated pyridine molecules for which no hyperpolarization was observed.

For an efficient polarization transfer to the heteronuclei in the Ir(COD)(SIMes)(CN) complex and nuclei of the pyridine coligand, this process was carried out in ultralow magnetic fields in which the difference in frequencies (taking into account chemical shifts of the nuclei in the complex) is considerably lower than the spin–spin interaction constant between them [27]. For this purpose, the setup was used for the automated dislocation of the sample between the NMR spectrometer sensor [28] and magnetic shield and inductive coils that make it possible to obtain ultralow magnetic fields from 5 nT and higher by the magnetic field variation in the shield placed above a warm hole of the superconducting magnet of the spectrometer [29].

Significant changes in the signal intensity in the ^{13}C NMR spectra were observed depending in the chosen magnetic field strength, which indicated the polarization transfer to the corresponding nuclei (Fig. 2). The most part of the indicated signals corresponded to the ^{13}C nuclei of pyridine. However, the ^{13}C NMR spectrum also exhibits a signal with $\delta = 149.2$ ppm that was assigned to the ^{13}C nucleus of the coordinated cyanide anion. Although this signal was not observed in the ^{13}C NMR spectrum at thermal equilibrium, the efficient polarization transfer from the parahydrogen molecules made it possible to significantly enhance its intensity. The assignment of this signal is also indirectly confirmed by its absence in the spectra of similar iridium complex Ir(Imes)(COD)Cl bearing no cyanide anion [28].

A detailed analysis of the ^{13}C spectral range in which the signal of the cyano group of the cyanide anion is observed (Fig. 2) indicated a possible overlapping of two signals in the range of the group of peaks with $\delta = 149.6$ ppm. The complete assignment of the ^{13}C signals was performed due to a comparative analysis of the ^{13}C NMR spectra recorded using broadband and selective heteronuclear proton decoupling after conducting SABRE experiments under similar conditions in the ultralow field (Fig. 3).

The use of selective suppression of the interaction with the hydride protons led to the simplification of the multiplet structure of the cyano group signal (Figs. 3b, 3c, 3e) and observation of multiplets with constants of 36.5 and 4.0 Hz corresponding to its interaction with the *trans*- ($\delta = -9.33$ ppm) and *cis*-hydride protons ($\delta = -22.89$ ppm), respectively [30]. The full structure of this multiplet was observed for the selective suppression of the spin–spin interaction of the *ortho*-carbon atoms of pyridine with the aromatic protons (Fig. 3d), and the use of the broadband proton decoupling made it possible to get rid of overlapping of

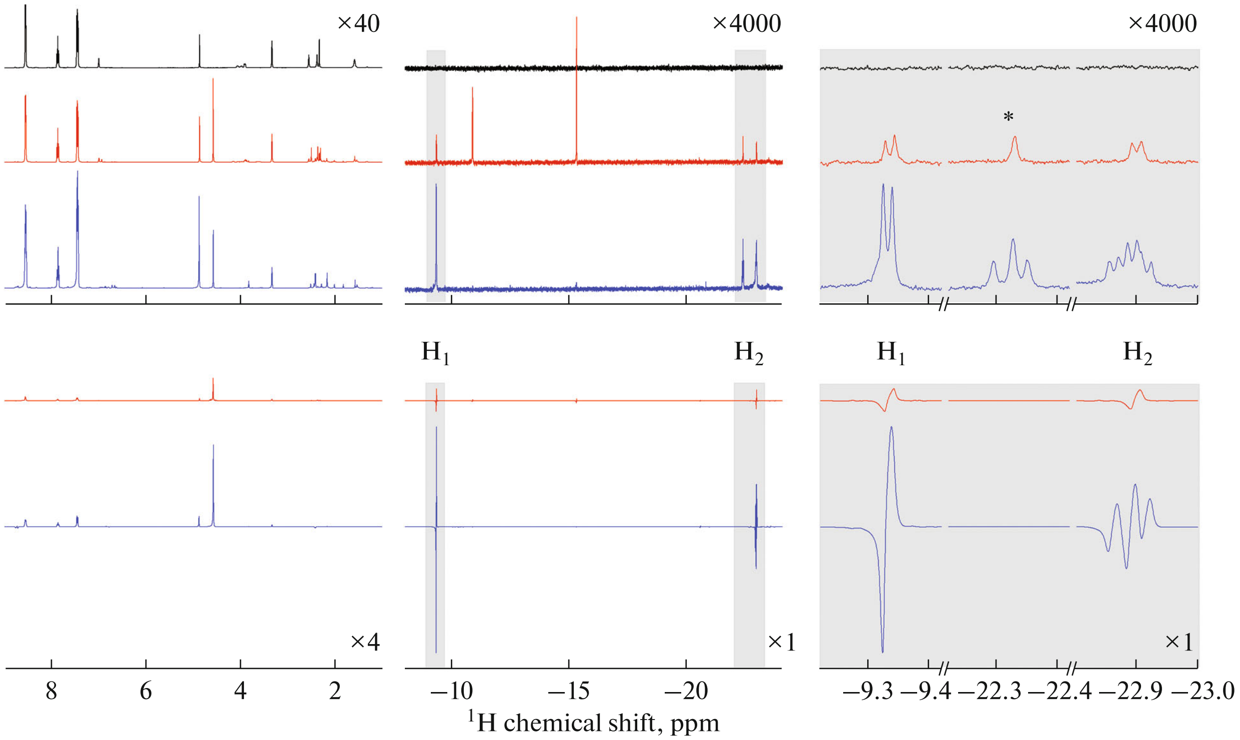


Fig. 1. ^{1}H NMR spectra of the Ir(SIMEs)(H_2)$(Py)_2$(CN) complex thermally polarized (top) and parahydrogen-polarized in the strong magnetic field (bottom). Thermal spectra (top): the black spectrum was obtained immediately after a solution of 3.8 mM Ir(SIMes)(COD)(CN) and 100 mM pyridine-^{14}N was prepared in deuterated methanol before bubbling with parahydrogen, the red spectrum was detected after a prolong interaction of the solution with parahydrogen after a delay for hyperpolarization relaxation, and the blue spectrum was obtained after 100 mM pyridine-^{15}N was added to the solution. The parahydrogen-induced polarization spectra (bottom) were obtained using a 45-deg radio frequency pulse immediately after bubbling of the solutions: (red) 3.8 mM Ir(SIMes)(COD)(CN) and 100 mM pyridine-^{14}N in deuterated methanol and (blue) 3.8 mM Ir(SIMes)(COD)(CN), 100 mM pyridine-^{14}N, and 100 mM pyridine-^{15}N in deuterated methanol. The assignments of the hydride protons indicated on the structural formula in Fig. 4 are shown on the spectra, and asterisk marks the signal of the hydride protons in the complex with three pyridine molecules.

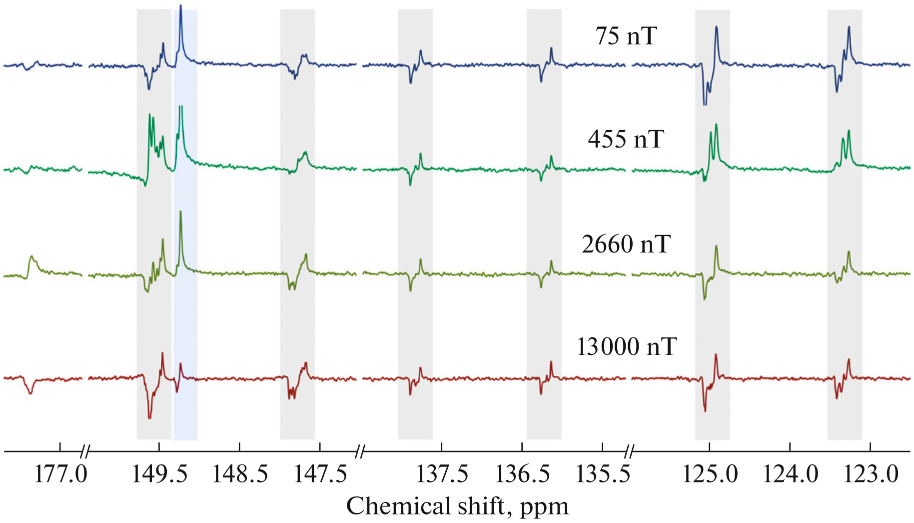


Fig. 2. ^{13}C NMR spectra of the Ir(COD)(SIMes)(CN) complex (3.8 mM) in deuterated methanol in the presence of pyridine (100 mM) detected by swift field switching in the SABRE experiment in the ultralow magnetic fields generated by the system of coils inside the magnetic shield arranged above the superconducting magnet of the NMR spectrometer. Gray color marks the ^{13}C signals of free pyridine having high splitting constants on the corresponding protons, and blue color marks the right component of the signal of the cyano group of the cyanide anion.

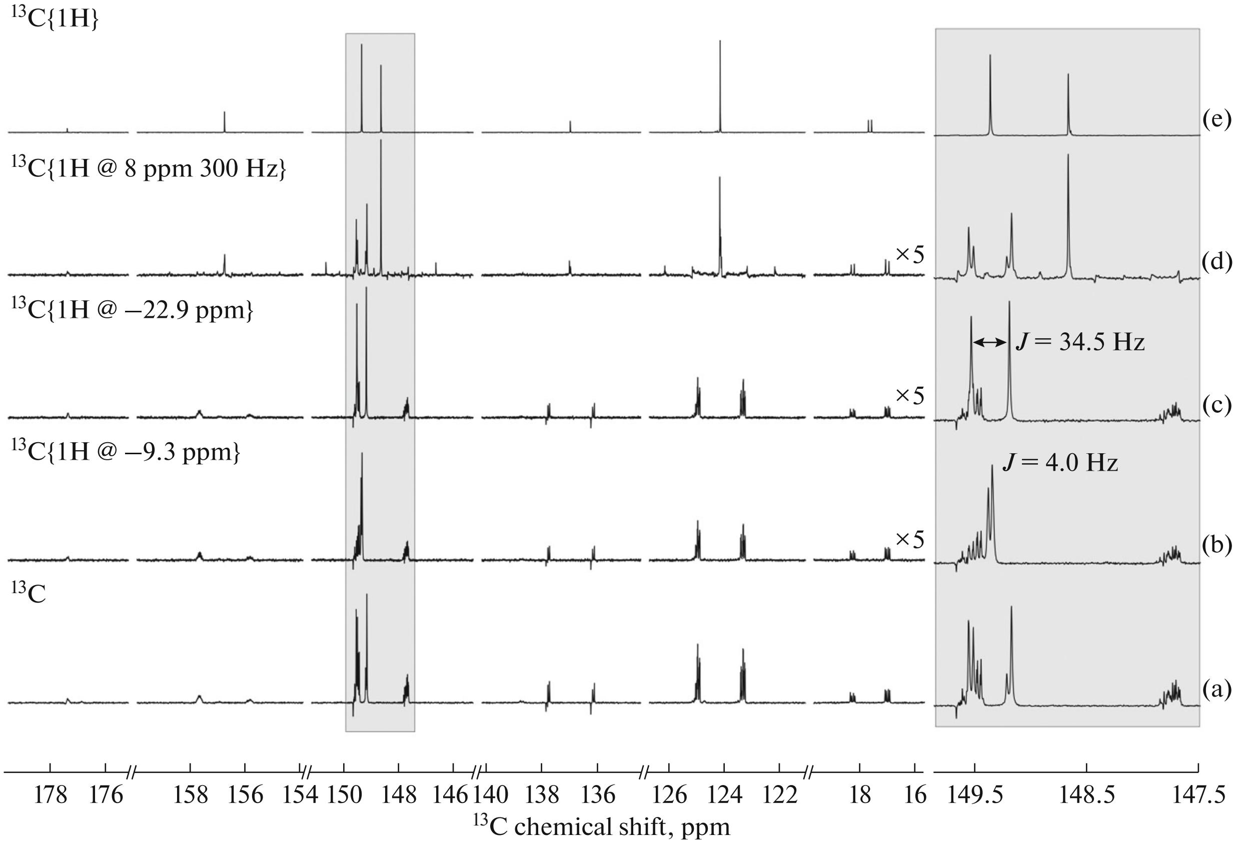


Fig. 3. ^{13}C NMR spectra (100.6 MHz, 9.4 T, 25°C) of the Ir(SIMes)(COD)(CN) complex (3.8 mM) in deuterated methanol in the presence of pyridine (100 mM) after bubbling parahydrogen (95%, 5 atm) in a field of 0.5 μT (a) without heteronuclear decoupling, with the selective suppression of the spin–spin interaction with the hydride protons at (b) $\delta = -9.33$ ppm and (c) –22.89 ppm, (d) with the selective suppression of the spin–spin interaction with the aromatic protons, and (e) with broadband heteronuclear decoupling. The spectral range with the signals of the polarized cyano group is shown at the right.

the multiplets attributed to the ^{13}C nuclei of the cyano group and pyridine ligand (Fig. 3e).

The chemical nonequivalence of the hydride protons indicates the coordination of the cyano group of the cyanide anion in the equatorial position of the hydride complex. For the final confirmation of its structure, we recorded the ^{15}N NMR spectra for the SABRE experiment in the ultralow magnetic field. In spite of using pyridine with the natural content of this isotope, the obtained spectra had a good signal to noise ratio (Fig. 4). The disappearance of the multiplet structure of the signal with $\delta = -261.5$ ppm of the cyano group (doublet with a constant of 5 Hz) upon the suppression of the spin–spin interaction with the hydride protons with $\delta = -9.33$ ppm unambiguously indicates that the signal can be assigned to the ^{15}N nucleus of the cyano group coordinated to the iridium ion by the carbon atom.

A further increase in the intensity of the magnetic field (in which the polarization transfer was performed) due to the transition of the sample from the magnetic shield to the region of the residual field of the NMR spectrometer did not result in an increase in the signal to noise ratio (Fig. 5) in spite of an increase in the thermal difference in populations of the spin levels split by the magnetic field. This “resonance” behavior confirms that an efficient coherent polarization transfer requires an anticrossing of the levels in a very weak magnetic field [31].

A standard approach to the estimation of the polarization transfer efficiency and signal amplification factor is a comparison of the integral intensities of identical signals for the polarized substance and a sample with thermal polarization. Since the signal for the thermally polarized sample could not be detected because of very long relaxation times of the ^{13}C and ^{15}N nuclei of the cyano group and a low natural content of these isotopes, the signal amplification factors were determined using the signals of methanol and pyridine as intermediate standards. The obtained values of polarization (4.4 and 15.5%) and signal amplification coefficients for the ^{13}C and ^{15}N nuclei of the cyano group (5665 and –49 555, the difference in signs of the signal amplification coefficient is caused by the negative gyromagnetic ratio for ^{15}N) are very high,

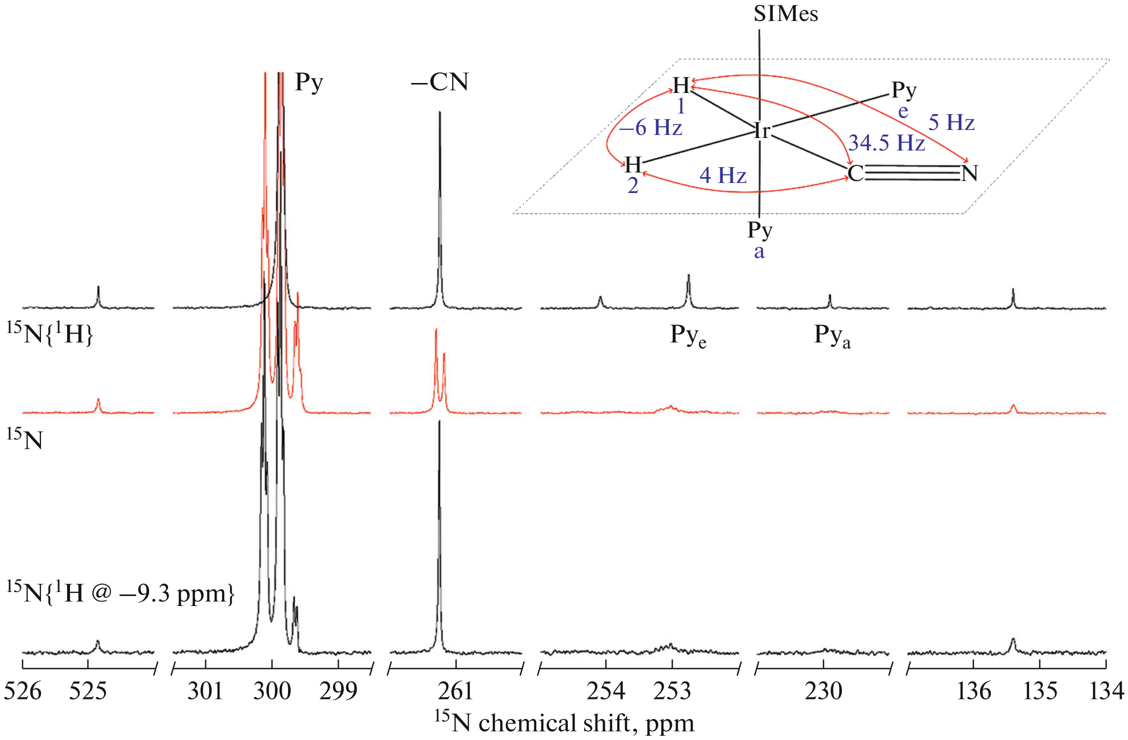


Fig. 4. ^{15}N NMR spectra (40.6 MHz, 9.4 T, 25°C) detected after bubbling parahydrogen (95%, 5 atm) through a solution of the Ir(SIMes)(COD)(CN) complex (3.8 mM) and pyridine (100 mM) in deuterated methanol in a magnetic field of 0.3 μT for 30 s. The spectra were detected using broadband heteronuclear decoupling (top), without suppression of spin–spin interactions with protons (midst), and using selective suppression with the hydride protons at $\delta = -9.33$ ppm (bottom). Inset: the structure of the active hydride complex stabilized by the cyanide ion and two pyridine molecules in the axial and equatorial positions according to the NMR spectroscopy data.

which indirectly indicates the coherent mechanism of the spin order transfer from the parahydrogen molecule to the integral polarization of heteronuclei in the ultralow field. In the hydride complex, one of the equatorial positions is occupied by the cyano group of the cyanide anion containing no magnetic nuclei. For this reason, the ^{15}N nuclear spin of pyridine that occupies another equatorial position forms a strongly bound three-spin system with the hydride protons, where only one anticrossing of levels exists in the region of which the maximum efficiency of the polarization transfer is formed. Another anticrossing exists in the zero field and does not result in the generation of polarization of the heteronucleus. The very high signal amplification factors found in the synthesized Ir(COD)(SIMes)(CN) complex provide wide possibilities for controlling the spin dynamics of the system by the directed action of adiabatic switching of the magnetic field or radio frequency pulses for the controlled polarization transfer to the heteronuclei.

To conclude, the spin polarization transfer from the parahydrogen molecule to organic molecules using the iridium-containing catalysts under the SABRE conditions makes it possible to reliably enhance NMR spectroscopy sensitivity. Although the majority of works in this area is devoted to studying the polarization transfer to the nuclei of the exchangeable ligand (e.g., pyridine), the presence of such a coordinately bound counterion as cyanide anion in the molecular complex can also result in the polarization transfer to the nuclei. The present study of the [Ir(SIMes)(COD)(CN)] complex allowed us to demonstrate for the first time the spin order transfers from parahydrogen molecules to the ^{13}C of ^{15}N nuclei of the cyanide anion under the SABRE conditions. The choice of another anion capable of partially dissociating from the metallocenter or the selection of the conditions under which the cyanide anion is capable of chemical exchanging with inorganic cyanide excess in the solution can result in the formation of hyperpolarized cyanide under the SABRE conditions. The high reactivity of cyanides, the possibility of preparing from them organic compounds of different nature, and the slow magnetic relaxation of their nuclei combined with the possibility of generating long-lived spin states for $^{13}C^{15}N$-labeled cyanides can result in the preparation of efficient hyperpolarized labels for magnetic resonance tomography.

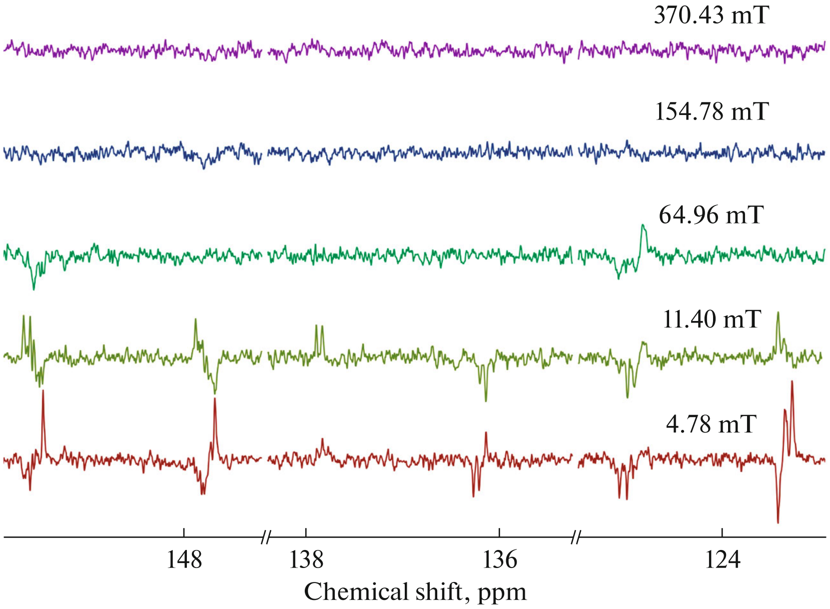


Fig. 5. ^{13}C NMR spectra of the Ir(COD)(SIMes)(CN) complex (3.8 mM) in deuterated methanol in the presence of pyridine (100 mM) for the polarization transfer from parahydrogen (~95% *para*-H_2) to the substrates in the residual field of the NMR spectrometer magnet with different intensities.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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