

## Multinuclear NMR Study of the Structure and Intramolecular Dynamics of ( $\eta^2$ -Acetone phenylhydrazonato)tetrafluorooxotungsten(VI)

Sergei G. Sakharov\* and Yuri A. Buslaev

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 117907 Russia

Ivan Tkáč

Magnetic Resonance Unit, Derer Hospital, 833 05 Bratislava, Slovakia

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Using one- and two-dimensional techniques of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{19}\text{F}$  NMR spectroscopy, it was proved that acetone phenylhydrazone (H-aph) acts as a two-center N,N-donor ligand in the complex  $[\text{WOF}_4(\text{aph})]^-$ . As a result of the coordination to tungsten, the ligand conformation changes from *E* to *Z*, and at the same time the phenyl ring is turned out of the  $>\text{N}-\text{N}=\text{C}<$  plane. At low temperatures ( $-30\text{ }^\circ\text{C}$ ), the equatorial plane of the pentagonal-bipyramidal tungsten polyhedron comprises two donor nitrogen atoms of hydrazone and three fluoro ligands. At elevated temperatures, stereoisomeric interconversion caused by hindered intramolecular rotation of the aph<sup>-</sup> ligand occurs. The mechanism of this process was elucidated on the basis of the dynamic effects in  $^{19}\text{F}$  spectra and line-shape analysis of the *trans*- $\text{CH}_3$  resonance in  $^{13}\text{C}$  spectra split due to direct “through-space” coupling with the proximate fluoro ligand.

### Introduction

The late transition metals form, due to their favorable electronic structure, a wide range of coordination compounds where the coordination numbers higher than 6 are rather common. Group V and VI  $d^0$  transition-metal fluorides usually form pentagonal-bipyramidal  $\eta^2$ -complexes with two-center n-donor ligands (containing  $-\text{O}-\text{O}-$ ,  $-\text{O}-\text{N}-$ ,  $\text{N}-\text{N}$ , and other similar groupings).<sup>1–3</sup> These ligands (oximes, hydrazones, hydrazine, hydroxylamine, hydrogen peroxide, and their derivatives) have two contiguous n-donor centers (directly bonded) in contrast to bidentate ligands, where coordinating centers are separated by at least one noncoordinating bridging atom. Complexes of  $\text{WOF}_4$  with two n-donor atoms in the equatorial plane are normally stable only at low temperatures. At elevated temperatures intramolecular dynamic processes involving two-center donors occur.<sup>4,5</sup> NMR spectroscopy, especially  $^{19}\text{F}$  NMR, is a very efficient method for monitoring these processes.<sup>6–8</sup>

Complexes with two-center ligands,<sup>9</sup> as well as olefin  $\pi$ -complexes,<sup>10</sup> are often the intermediates in a number of

catalytic and biochemical processes. The analogy is not accidental, since it results from the similarity of the structures of these types of compounds. Indeed, two features are typical of the olefin  $\pi$ -complexes, as well as of the complexes with n-donor two-center ligands. (1) An organic ligand is coordinated by the central atom in an  $\eta^2$  fashion.<sup>1,11</sup> (2) This  $\eta^2$ -coordinated ligand experiences hindered internal rotation (we were the first to reveal this phenomenon for the two-center ligands<sup>4,12</sup>). As we showed,  $d^0$  transition-metal complexes containing n-donor two-center ligands should be considered specific  $\pi$ -complexes where the central atom functions as an acceptor of the electrons from the  $\pi$ -bonding and  $\pi$ -antibonding MOs of the two-center ligand.<sup>2</sup> A systematic study of the coordination ability and reactivity of two-center ligands, as well as conditions of formation, structure and dynamic behavior of their complexes, and a comparison of their properties with those of olefin  $\pi$ -complexes will allow us not only to enlarge the scope of traditional notions about the role of  $\pi$ -complexes in metal–complex catalysis but also to develop a new synthetic strategy for organic compounds.

In this study, we intend to show that acetone phenylhydrazone reacts with  $\text{WOF}_4$  to give, among other compounds, a tungsten complex with a  $\eta^2$ -coordinated ligand. Using multinuclear NMR spectroscopy, we focused on studying the character of the metal–ligand bond, conformation, stereochemical arrangement, and dynamic changes at elevated temperatures, which was the primary goal of our investigation.

### Experimental Section

**Starting Materials.** Tungsten oxide tetrafluoride was prepared by a reaction of  $\text{WF}_6$  with  $\text{WO}_3$  at  $300\text{ }^\circ\text{C}$ .  $\text{WOF}_4$  was sublimated under vacuum prior to use. Tungsten hexafluoride and  $\text{WO}_3$  were “pure” grade. The deuterated acetonitrile was dried over  $3\text{ \AA}$  molecular sieves for several weeks. Triethylamine was distilled two times over solid KOH.

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Acetone phenylhydrazone was synthesized by reaction of phenylhydrazine with a small excess of acetone in the ether in the presence of a trace of hydrochloric acid as a catalyst. This method is a combination of different published methods.<sup>13,14</sup>

The purity of all starting materials was determined by NMR spectroscopy.

**Preparation of the Samples.** WOF<sub>4</sub> is rather sensitive to traces of moisture; therefore, the reaction mixture was prepared in a drybox under an argon atmosphere using dry reagents kept above 3 Å molecular sieves. The samples for the NMR study were prepared by combining a 35% WOF<sub>4</sub> solution in deuterated acetonitrile (CD<sub>3</sub>CN) and acetone phenylhydrazone (H-aph) in 1:1, 1:2, and 1:3 molar ratios. Triethylamine (NEt<sub>3</sub>) was used as a buffer to bind the protons released in the reaction.

**NMR Measurements.** The <sup>1</sup>H, <sup>13</sup>C, and natural-abundance <sup>15</sup>N NMR spectra were recorded on a Bruker AM 300 spectrometer operating at 300.13, 75.45, and 30.42 MHz, respectively. Some <sup>13</sup>C NMR spectra were obtained on a JEOL FX-100 spectrometer operating at 25.15 MHz. <sup>19</sup>F NMR spectra were recorded on a Bruker WP-80 spectrometer operating at 75.26 MHz. The <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to internal TMS. The NMR measurements were performed in the temperature range -30 to +40 °C.

**<sup>1</sup>H NOE Difference Spectra.** Presaturation of the chosen CH<sub>3</sub> resonance up to 90% was achieved by selective irradiation ( $\gamma_{H_2}/2\pi = 2.5$  Hz) for 8 s prior to a nonselective 90° reading pulse. A total of 34 scans (2 dummy scans, 8 scans, 4 cycles) for each irradiating frequency were acquired. Direct subtraction of FIDs (on- and off-resonance) and subsequent Fourier transform were performed.

**<sup>1</sup>H Homonuclear 2D J-Resolved Spectrum.** For the 2D J-resolved experiment a spectral width of 512 Hz (1.7 ppm, aromatic part) was used in F<sub>2</sub> and ±16 Hz in F<sub>1</sub>; 4 scans (2 dummy) were acquired for each of 64 t<sub>1</sub> increments. Digital resolution was 2 Hz per point in F<sub>2</sub> and 0.25 Hz per point in the F<sub>1</sub> domain; zero filling was used.

**<sup>13</sup>C-<sup>1</sup>H Heteronuclear Correlation 2D NMR Spectra.** The aliphatic and aromatic parts of the spectra were measured separately in two 2D experiments. Standard conditions were used, and the fixed evolution delays were set to correspond to the averaged <sup>1</sup>J(C,H) values of 125 and 160 Hz for the aliphatic and aromatic protons, respectively. For each of 64 t<sub>1</sub> increments 32 scans (2 dummy) were acquired. Data processing with zero filling results in 256 × 128 and 512 × 128 matrices. The final digital resolution was 2.6–4.8 Hz per point in F<sub>1</sub> and 3.5 Hz per point in F<sub>2</sub>.

**Selective INEPT <sup>13</sup>C Spectra.** The soft <sup>1</sup>H pulses ( $\gamma_{H_2}/2\pi = 25$  Hz, i.e. 10 ms pulse duration for 90° flip angle) were applied in the selective INEPT<sup>15</sup> pulse sequence. The delays were optimized for the polarization transfer via long-range couplings with an average value of 8 Hz for <sup>3</sup>J(C<sub>ar</sub>-C<sub>ar</sub>-C<sub>ar</sub>-H) and <sup>2</sup>J(=C-C<sub>met</sub>-H).

**<sup>15</sup>N NMR Spectra.** The absolute <sup>1</sup>H frequency of TMS was used to calculate the resonance frequency of nitromethane ( $\delta(^{15}\text{N})$  0.0 ppm), to which the <sup>15</sup>N chemical shifts are referenced ( $\Xi(^{15}\text{N})$  = 10.136 783 MHz).<sup>16</sup>

The INEPT technique with polarization transfer from the directly bonded proton and with refocusing was used for the measurement of the N(1) nitrogen in free H-aph. The evolution and refocusing delays were set to 5.6 ms. Acquisition of 256 scans provided an adequate signal-to-noise ratio.

Various versions of 1D and 2D INEPT methods with selective polarization transfer from protons to nitrogen via three-bond couplings were used for the measurement of non-proton-bearing nitrogens. Soft proton pulses in the pulse sequences were applied ( $\gamma_{H_2}/2\pi = 25$  Hz, i.e., 10 ms pulse duration for a 90° flip angle). For selective INEPT<sup>15,17</sup> it was desirable to use polarization transfer from the protons of the *trans*-CH<sub>3</sub> group and their coupling to N(2), because the coupling constant <sup>3</sup>J(<sup>15</sup>N,<sup>1</sup>H(*trans*-CH<sub>3</sub>)) is twice as large as <sup>3</sup>J(<sup>15</sup>N,<sup>1</sup>H(*cis*-

**Table 1.** <sup>1</sup>H and <sup>13</sup>C Chemical Shifts of the Free Ligand H-aph and the Ligand Bound in [WOF<sub>4</sub>(aph)]<sup>-</sup> at -30 °C

chemical shift	$\delta(^1\text{H})/\text{ppm}$			$\delta(^{13}\text{C})/\text{ppm}$		
	H-aph	complex	$\Delta\delta_{\text{coord}}$	H-aph	complex	$\Delta\delta_{\text{coord}}$
<i>ipso</i> Ph				147.4	150.3	+2.9
<i>ortho</i> Ph	7.05	6.89	-0.18	113.0	120.2	+6.9
<i>meta</i> Ph	7.16	7.35	+0.19	129.7	128.7	-1.0
<i>para</i> Ph	6.72	6.92	+0.20	119.3	125.4	+6.1
<i>cis</i> -CH <sub>3</sub>	1.80	2.03	+0.23	16.5	24.9	+8.7
<i>trans</i> -CH <sub>3</sub>	1.94	2.59	+0.65	25.4	21.9 <sup>a</sup>	-3.3
=C<				144.8	162.4	+17.7

<sup>a</sup> Doublet with  $J(^{19}\text{F}, ^{13}\text{C}) = 6.2$  Hz.

CH<sub>3</sub>)).<sup>18,19</sup> The dephasing and refocusing delays were set to 100 and 30 ms, respectively. For free H-aph it was sufficient to collect 256 scans. In the case of the [WOF<sub>4</sub>(aph)]<sup>-</sup> complex, the number of scans was increased to 6000 because of a higher resonance multiplicity due to <sup>15</sup>N-<sup>19</sup>F coupling. To measure the <sup>3</sup>J(<sup>15</sup>N,<sup>1</sup>H) values, we used INEPT with selective <sup>1</sup>H decoupling of the *cis*-CH<sub>3</sub> group.<sup>20</sup>

The long-range couplings of N(1) with protons in *ortho* positions of the phenyl ring were obtained by a selective INEPT 2D technique<sup>21</sup> that suppresses all  $J(^{15}\text{N}, ^1\text{H})$  couplings except for the coupling with the proton active in the polarization transfer. In this method, 64 t<sub>1</sub> increments with 128 scans each (2 dummy) were sampled for a spectral width of 300 Hz in 512 time domain data points. The t<sub>1</sub> increment was set to 31 ms, giving an F<sub>1</sub> spectral width of ±8 Hz. The final digital resolution in F<sub>1</sub> after data processing was 0.125 Hz per point.

**<sup>19</sup>F NMR Spectra.** The <sup>19</sup>F chemical shifts were referred to CFCl<sub>3</sub>. Typical conditions for recording <sup>19</sup>F spectra were as follows: spectral width 21 700 Hz, digital resolution 2.6 Hz per point, number of scans 100–500. The values of <sup>2</sup>J(<sup>19</sup>F,<sup>19</sup>F) coupling constants were refined by spectral simulation using the PANIC program (Bruker software).

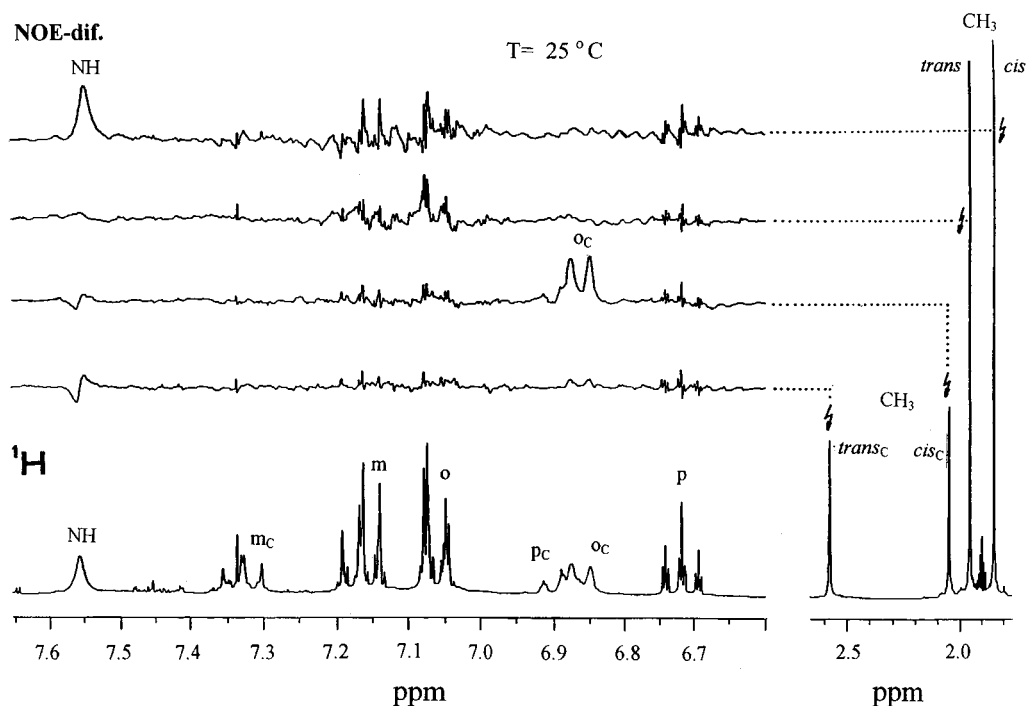
**Dynamic NMR.** Calculations of a NMR line shape were performed by a modified version of the program for dynamic NMR spectra simulations<sup>22</sup> using the classical formalism. The temperature was measured with a precision of ±1°. The Eyring equations were used to evaluate activation parameters of the dynamic process from rate constants ( $k = 1/\tau$ ).<sup>23a</sup> Errors in determining the activation parameters were estimated by the methods reported in ref 23b.

## Results and Discussion

**<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Free H-aph.** The <sup>1</sup>H and <sup>13</sup>C chemical shifts of free H-aph in CD<sub>3</sub>CN at low temperature are given in Table 1. These shifts are virtually temperature-independent: in the range from -30 °C to +40 °C,  $\Delta\delta_{\text{max}}(^1\text{H}) = 0.02$  ppm and  $\Delta\delta_{\text{max}}(^{13}\text{C}) = 0.2$  ppm. However, they are rather sensitive to medium acidity due to the protonation of the electron lone pair of the N(2) imino nitrogen. A sufficiently high concentration of NEt<sub>3</sub> makes it possible to keep the proton concentration at a low level. Methyl groups of H-aph are magnetically nonequivalent, and the corresponding CH<sub>3</sub> signals were assigned by <sup>1</sup>H NOE difference spectroscopy (Figure 1). Selective presaturation of the signal of a more shielded CH<sub>3</sub> group ( $\delta$  1.80 ppm) resulted in +4% NOE on the NH proton. On the other hand, presaturation of the CH<sub>3</sub> signal at 1.94 ppm provided no NOE. Therefore, the signal at 1.80 ppm corresponds to the CH<sub>3</sub> group in the *cis* position relative to the N(1) amino nitrogen. The carbon and nitrogen atoms of acetone

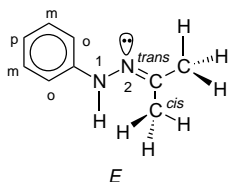
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**Figure 1.**  $^1\text{H}$  NMR spectra of the reaction mixture at 25 °C (NOE difference spectroscopy). The  $o_c$ ,  $m_c$ ,  $p_c$  and  $\text{CH}_3$  ( $cis_c$ ,  $trans_c$ ) resonances correspond to the tungsten complex.

hydrazone are coplanar, and the H-aph molecule has an *E* conformation relative to  $>\text{N}=\text{N}$  bond:



The  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear correlation 2D NMR technique was used to unambiguously assign the signals of protonated carbons. Quaternary carbons were assigned by the selective INEPT technique.<sup>15</sup>

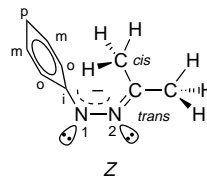
#### Complexes of Acetone Phenylhydrazone with $\text{WOF}_4$ .

When dissolved in acetonitrile, oxotungsten(VI) tetrafluoride forms an adduct ( $\text{WOF}_4 \cdot \text{CD}_3\text{CN}$ ) with the acetonitrile molecule in a *trans* position relative to the oxygen atom.<sup>24</sup> The  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra indicate that increasing the H-aph concentration in the reaction mixture results in the formation of several types of mono- and binuclear complexes; specifically  $[\text{WOF}_4(\text{H-aph})]$ ,  $[\text{WOF}_3(\text{aph}) \cdot \text{CD}_3\text{CN}]$ ,  $[\text{W}_2\text{O}_2\text{F}_9]^-$ ,  $[\text{W}_2\text{O}_2\text{F}_8(\text{aph})]^-$ , and  $[\text{W}_2\text{O}_2\text{F}_7(\text{aph})_2]^-$  were observed in the systems with oximes, amines, ketimines, and substituted hydrazines.<sup>24-27</sup> If  $\text{WOF}_4$ , H-aph, and  $\text{NEt}_3$  are combined in a 1:3:2 molar ratio, the complex anion  $[\text{WOF}_4(\text{aph})]^-$  is the predominant product. In this paper, we aimed our structural study on just this latter complex species.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts of this complex  $[\text{WOF}_4(\text{aph})]^-$  are summarized in Table 1. In addition, the difference between the corresponding values of the coordinated and free ligand are also presented in this table. To assign

superimposed  $^1\text{H}$  multiplets, the homonuclear 2D *J*-resolved technique was used (Figure 2). The projections of the spectra of the phenyl *ortho*, *meta*-, and *para* protons of the complex are presented on the right-hand side of the figure. The signals at 7.11 ppm are the "artifacts" due to folding in of lines outside the spectral width.<sup>28</sup>

The signals of methyl groups were unambiguously assigned by NOE difference spectroscopy (Figure 1). Signal presaturation of the more shielded  $\text{CH}_3$  group ( $\delta$  2.03 ppm) results in a 5% NOE on the phenyl *ortho* protons. This effect is measurable over the entire temperature range studied. The signal at 2.03 ppm evidently corresponds to the  $\text{CH}_3$  group *cis* to N(1). In addition, when it is coordinated to  $\text{WOF}_4$ , the ligand adopts the *Z* conformation. Such a conformation change is possible only if the phenyl ring is turned out of the  $>\text{N}=\text{N}=\text{C}<$  plane:



To unambiguously assign the signals of protonated carbon atoms in the  $^{13}\text{C}$  NMR spectra,  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear correlation 2D NMR experiments were performed. The signals of quaternary carbons were assigned by selective INEPT<sup>15</sup> with polarization transfer from *meta*  $^1\text{H}$  to *ipso*  $^{13}\text{C}$  and from *cis*- $\text{CH}_3$  to  $=\text{C}<$ . The  $^{13}\text{C}$  signal of the *trans*- $\text{CH}_3$  group is a doublet. The  $^{13}\text{C}$  NMR spectra recorded on two spectrometers operating at different frequencies (25.15 and 75.45 MHz) indicated that the splitting is due to spin-spin coupling with one fluoro ligand, and  $J(^{19}\text{F}, ^{13}\text{C})$  is 6.2 Hz. Taking into account the number of bonds separating these nuclei, this spin-spin coupling can be rationalized from a direct "through-space" mechanism<sup>29</sup> via nonbonding orbital overlap due to a spatial proximity of these nuclei.

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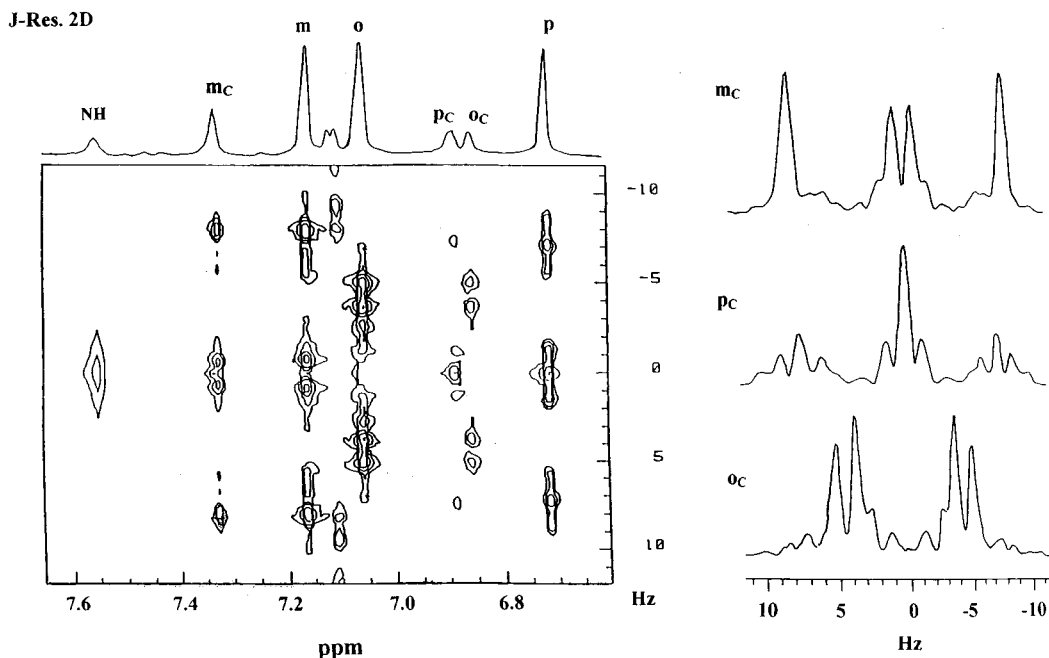
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**Figure 2.** (Left) Aromatic part of the 2D *J*-resolved spectrum of the reaction mixture at 25 °C. The *oc*, *mC*, and *pc* resonances correspond to the tungsten complex. (Right) Projections of *meta*, *para*, and *ortho* protons of the phenyl group of the  $[\text{WOF}_4(\text{aph})]^-$  complex.

**Table 2.**  $^{15}\text{N}$  Chemical Shifts and Coupling Constants of the Free Ligand H-aph and of the Ligand Bound in  $[\text{WOF}_4(\text{aph})]^-$  at -30 °C

chem shift	$\delta(^{15}\text{N})/\text{ppm}$			coupling constant	$^3J(^{15}\text{N}, ^1\text{H})/\text{Hz}$ , H-aph
	H-aph	complex	$\Delta\delta_{\text{coord}}$		
N(1)	-248.6 <sup>a</sup>	<i>b</i>		N(1)- $^1\text{H}(o\text{-Ph})$	2.7 <sup>c</sup>
N(2)	-69.5 <sup>d</sup>	-107.7	-38.2	N(2)- $^1\text{H}(trans\text{-CH}_3)$	4.0 <sup>e</sup>

<sup>a</sup> INEPT with refocusing. <sup>b</sup> Not successfully measured at the natural-abundance level. <sup>c</sup> Selective INEPT 2D.<sup>21</sup> <sup>d</sup> Selective INEPT<sup>17</sup> with polarization transfer from  $^1\text{H}(trans\text{-CH}_3)$  and broad-band  $^1\text{H}$  decoupling. <sup>e</sup> Selective INEPT<sup>20</sup> with polarization transfer from  $^1\text{H}(trans\text{-CH}_3)$  and selective decoupling of  $^1\text{H}(cis\text{-CH}_3)$ .

The  $^{15}\text{N}$  NMR data for free H-aph and for the ligand incorporated in the  $[\text{WOF}_4(\text{aph})]^-$  complex are given in Table 2. Strong shielding of the N(2) imino nitrogen ( $\Delta\delta$  -38.2 ppm) gives evidence for direct participation of the nitrogen electron lone pair in nitrogen-metal bonding.<sup>30,31</sup> This conclusion follows from the fact that the local paramagnetic term (which is negative) for the screening of the nucleus ( $\sigma_{\text{loc}}^p$ ) is inversely proportional to the electronic excitation energy between low-lying states:<sup>32</sup>  $\sigma_{\text{loc}}^p \propto 1/\Delta E$ .

When the lone electron pair of nitrogen is removed as a result of its coordination,  $\sigma \rightarrow \pi^*$  electron transitions occur instead of  $n \rightarrow \pi^*$ . The  $\Delta E$  value grows, and the screening of the nucleus increases. The signal is rather broad ( $\Delta\nu_{1/2} \approx 30$  Hz) due to unresolved spin-spin coupling with four nonequivalent fluoro ligands.

We failed to measure the  $^{15}\text{N}$  NMR signal of the N(1) amino nitrogen in the coordinated ligand. We suggest that the reason is the splitting of the  $^{15}\text{N}$  resonance by four nonequivalent fluoro ligands. Further, for the registration of the  $^{15}\text{N}$  signal, selective transfer of polarization from *ortho* protons of phenyl through three bonds to the observed nucleus was used. For the successful accumulation of the  $^{15}\text{N}$  signal by this method it is necessary to know the precise value of  $^3J(^1\text{H}-^{15}\text{N})$ . The same constant value (2.7 Hz) as in the free hydrazone was used in the experiment. It is apparent that the value of  $^3J(^1\text{H}-^{15}\text{N})$

changed as well, due to the change of hydrazone conformation from *E* to *Z* upon coordination, which made this method less efficient.

The  $^{19}\text{F}$  NMR spectrum of  $[\text{WOF}_4 \cdot \text{CD}_3\text{CN}]$  is represented by a singlet at 68.5 ppm.<sup>24</sup> Equatorial fluoro ligands of  $[\text{WOF}_5]^-$ , which is also formed in the reaction mixture, have similar chemical shifts:  $\delta(^{19}\text{F}_d)$  55 ppm. The quintet of the axial fluorine ( $\text{F}_y$ ) at -89 ppm lies just in the range of chemical shifts for  $[\text{WOF}_4(\text{aph})]^-$ . The  $^{19}\text{F}$  NMR spectra of  $[\text{WOF}_4(\text{aph})]^-$  at two different temperatures are presented in Figure 3, and the  $^{19}\text{F}$  chemical shifts and coupling constants are summarized in Table 3.

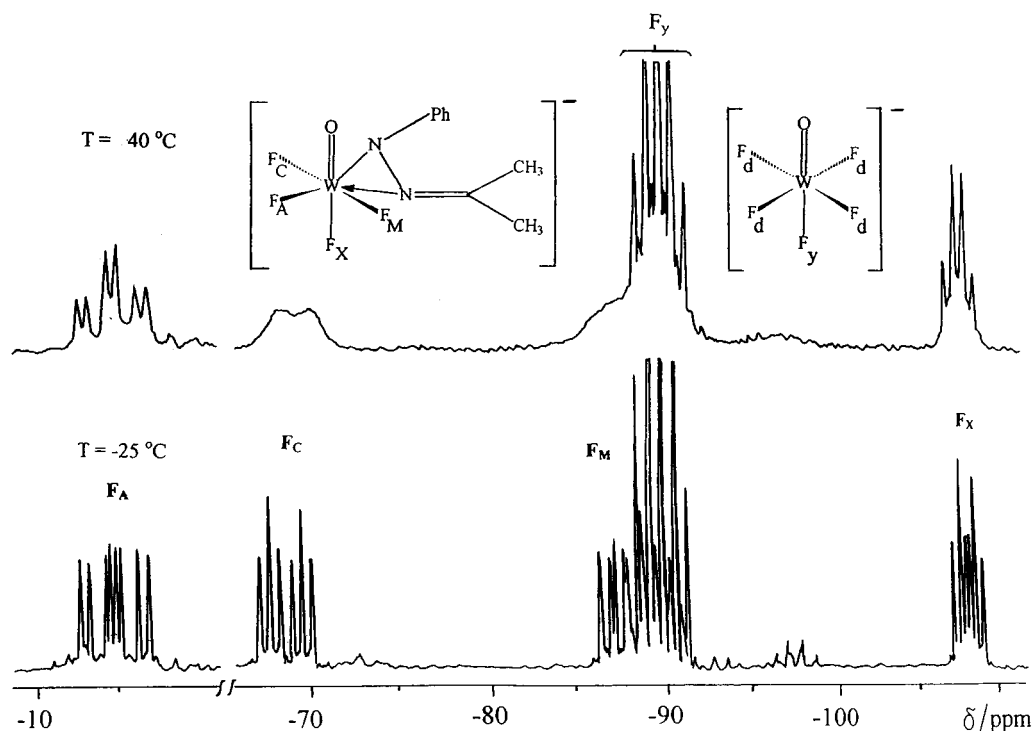
It is evident that at low temperature (-25 °C) fluorine atoms occupy four nonequivalent positions in the coordination sphere. A considerable increase of shielding of all four fluoro ligands compared to that in neutral tungsten fluoro complexes with simple hydrazones<sup>8</sup> indicates that the deprotonated molecule *aph*<sup>-</sup> is the coordinating species. The asymmetry of the complex characterized by non equivalence of the fluoro ligands and a considerable change of  $\delta(^{15}\text{N})$  of the imino nitrogen unambiguously demonstrate that *aph*<sup>-</sup> is incorporated in the tungsten complex as a  $\eta^2$  ligand via the two hydrazone nitrogens. Taking into account the NMR data of analogous complexes with oximes,<sup>4,24,33</sup> hydrazones,<sup>8</sup> and hydrazine derivatives,<sup>5</sup> one can assign the signals at -14.6 and -108.2 ppm to fluorines in positions *trans* to *aph*<sup>-</sup> and oxygen, respectively. The increased values of spin-spin coupling between neighboring equatorial

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**Figure 3.** Parts of the  $^{19}\text{F}$  NMR spectra of the reaction mixture with the resonances of the  $[\text{WOF}_4(\text{aph})]^-$  complex at low ( $-25\text{ }^\circ\text{C}$ ) and increased ( $+40\text{ }^\circ\text{C}$ ) temperatures. The fluorine  $\text{F}_\text{M}$  signal from the  $[\text{WOF}_4(\text{aph})]^-$  complex is superimposed on the resonance of the axial fluorine atom ( $\text{F}_\text{y}$ ) from  $\text{WOF}_5^-$ .

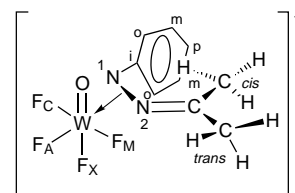
**Table 3.** Temperature Dependence of  $^{19}\text{F}$  Chemical Shifts and Coupling Constants of  $[\text{WOF}_4(\text{aph})]^-$

chem shift	$\delta(^{19}\text{F})/\text{ppm}$		coupling constant	$^2J(^{19}\text{F}, ^{19}\text{F})/\text{Hz}$	
	$T = -25\text{ }^\circ\text{C}$	$T = +40\text{ }^\circ\text{C}$		$T = -25\text{ }^\circ\text{C}$	$T = +40\text{ }^\circ\text{C}$
$\text{F}_\text{A}$	-14.6	-14.0	$\text{F}_\text{A}-\text{F}_\text{C}$	138.3	$130.0^a$
$\text{F}_\text{C}$	-68.6	-69.3	$\text{F}_\text{A}-\text{F}_\text{M}$	118.8	$130.0^a$
$\text{F}_\text{M}$	-87.8	$\sim -88$	$\text{F}_\text{A}-\text{F}_\text{X}$	42.8	45.8
$\text{F}_\text{X}$	-108.2	-107.7	$\text{F}_\text{C}-\text{F}_\text{M}$	43.3	$b$
			$\text{F}_\text{C}-\text{F}_\text{X}$	41.8	$51.9^a$
			$\text{F}_\text{M}-\text{F}_\text{X}$	63.7	$51.9^a$

<sup>a</sup> Splitting constant (dynamic averaged coupling). <sup>b</sup> Not observable due to line broadening.

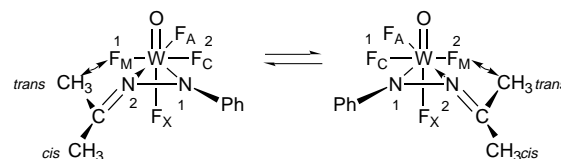
fluorine atoms is characteristic of complexes with  $\eta^2$  ligands.<sup>3,5,34</sup> This increase is probably caused by a closer arrangement of fluorine ligands in the equatorial plane due to coordination of the two-center ligand. In addition, the methyl group *trans* to the  $\text{N}(1)$  amino nitrogen is in close spatial proximity to one of the equatorial fluorines. Since steric effects are mainly accompanied by deshielding (van der Waals effect),<sup>35</sup> the deshielding of *trans*- $\text{CH}_3$  protons is in accordance with this proposal. As a result of the van der Waals interaction, C-H bond polarization takes place, and an expressive shielding of  $^{13}\text{C}$  in the *trans*- $\text{CH}_3$  group is observed analogously to the  $\gamma$ -effect.<sup>36</sup> Therefore, it could be supposed that the  $^{19}\text{F}$  NMR signal at  $-69$  ppm corresponds to this fluorine ( $\text{F}_\text{M}$ ). On the other hand, we previously showed<sup>27</sup> that the deprotonated nitrogen atom of the  $\eta^2$ -coordinated ligand in tungsten oxo fluoro hydrazido complexes is in close spatial proximity to whichever of the two equatorial fluorine atoms ( $\text{F}_\text{C}$  or  $\text{F}_\text{M}$ ) has a greater constant of spin-spin coupling with the third atom ( $\text{F}_\text{A}$ ). This also seems to be valid for this tungsten oxo fluoro hydrazonato complex.<sup>8</sup> As in this case  $J(\text{F}_\text{A}-\text{F}_\text{C}) > J(\text{F}_\text{A}-\text{F}_\text{M})$ , we are inclined to

believe that the deprotonated nitrogen atom ( $\text{N}_1$ ) is in close spatial proximity to the  $\text{F}_\text{C}$  fluorine atom:



**Intramolecular Dynamics.** Increasing the temperature leads to principal changes in the  $^{19}\text{F}$  NMR parameters of the  $\text{F}_\text{C}$  and  $\text{F}_\text{M}$  ligands (Table 3). The resonances of the  $\text{F}_\text{C}$  and  $\text{F}_\text{M}$  fluoro ligands are considerably broadened, and the splitting of  $\text{F}_\text{A}$  and  $\text{F}_\text{X}$  resonances due to  $^2J(^{19}\text{F}, ^{19}\text{F})$  coupling with  $\text{F}_\text{C}$  and  $\text{F}_\text{M}$  is averaged. At the same time in  $^{13}\text{C}$  NMR spectra, a signal from the *trans*- $\text{CH}_3$  carbon gradually transforms from a doublet to a triplet (Figure 4). These changes in NMR spectra indicate intramolecular dynamic processes in the tungsten coordination sphere.

The  $[\text{WOF}_4(\text{aph})]^-$  complex can exist in two stereoisomeric forms, which cannot be directly distinguished by NMR spectroscopy:

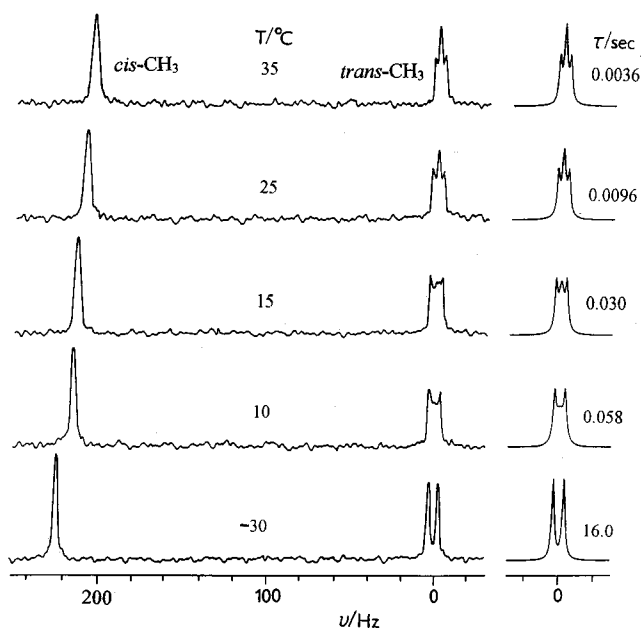


At higher temperatures, intramolecular transformation from one isomer to its mirror image occurs. The residence time of the complex in each of the stereoisomeric forms (between two successive interconversions) decreases with increasing temperature. It is reasonable to assume that the spin states of each

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**Figure 4.** Temperature dependence of the methyl resonances in  $^{13}\text{C}$  NMR spectra of the coordinated  $\text{aph}^-$  complex anion: (left) experimental spectra; (right) theoretical line-shape behavior of the  $\text{trans-CH}_3$  resonance calculated as a function of the lifetime  $\tau$ .

fluorine nucleus in one molecule of the complex are unchanged on the NMR time scale.

With regard to the nuclear spin states of the equatorial fluoro ligands  $F_C$  and  $F_M$ , two types of  $[\text{WOF}_4(\text{aph})]^-$  complexes (or spin isomers) of equal probability are possible. On the one hand, if the spin states of  $F_C$  and  $F_M$  are the same, the dynamic process has no influence on the  $^{13}\text{C}$  NMR spectrum, and a doublet is observed for  $\text{trans-CH}_3$  group.

On the other hand, in complexes with opposite spin states of equatorial fluorine nuclei  $F_C$  and  $F_M$ , dynamic averaging takes place. As a result, in the limit of fast exchange the doublet of the  $\text{trans-CH}_3$  group should transform to a singlet. The real experimental  $^{13}\text{C}$  NMR spectrum of the  $\text{trans-CH}_3$  group is the superposition of these subspectra. Calculated NMR spectra for this type of dynamic exchange with the values of averaged lifetime  $\tau$  is presented in Figure 4. The following values of activation parameters of intramolecular rotation of the  $\text{aph}^-$  ligand in the coordination sphere of  $\text{WOF}_4$  are derived from the line-shape analysis:

$$\Delta H^\ddagger = 78.5 \pm 0.5 \text{ kJ/mol}$$

$$\Delta S^\ddagger = 56.78 \pm 1.84 \text{ J/(mol K)}$$

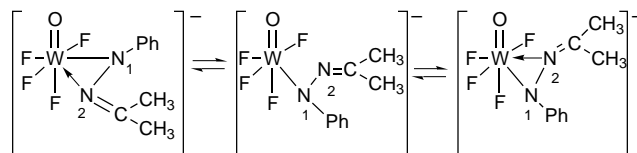
$$\Delta G_{284(\text{average temperature})}^\ddagger = 62.34 \pm 0.25 \text{ kJ/mol}$$

$$\Delta G_{313}^\ddagger = 60.71 \pm 0.25 \text{ kJ/mol}$$

Since the coalescence temperature depends on a frequency difference of exchanging sites, we roughly evaluated that the coalescence of  $F_C$  and  $F_M$  signals should be attained at approximately  $60^\circ\text{C}$ . However, the stability of  $[\text{WOF}_4(\text{aph})]^-$  above  $40^\circ\text{C}$  rapidly decreases, and irreversible degradation of the complex occurs.

As for olefin  $\pi$ -complexes, two paths of isomerization are possible here: (a) with retention of  $\eta^2$  coordination in the intermediate state and (b) via the  $\sigma$ - $\pi$  rearrangement, i.e. via the intermediate formation of a complex with an open structure. We obtained indirect data testifying to the fact that for hydrazido complexes the process takes place the second way.<sup>6,27</sup> Considering the question of the paths of isomerization of  $[\text{WOF}_4(\text{aph})]^-$ , it should be mentioned that in  $^{13}\text{C}$  NMR spectra the width of the signal of the phenyl *ortho* carbon atoms in the complex decreases with increasing temperature. With the help of the scaled model, we showed that in the  $\eta^2$ -coordinated ligand free rotation of the phenyl group around the N-C bond is hindered due to spatial proximity of the protons of the *cis*-methyl group and the *ortho* protons of the phenyl ring. This may lead to magnetic nonequivalence of the *ortho* carbon atoms in the first place and, consequently, to their broadening in the low-temperature  $^{13}\text{C}$  NMR spectrum. With increasing temperature, the signals narrow, which might result from free rotation of the phenyl group of the coordinated ligand. With allowance for isomerization to occur through the breakage of the W-N<sub>2</sub> bond and intermediate formation of  $\sigma$ -complexes, internal rotation of the ligand around the N-N bond becomes possible. There also is realized a conformation of the ligand in which free rotation of the phenyl group around the C-N bond will occur due to sufficient remoteness of the methyl groups.

Thus, we believe that the most probable mechanism of isomerization of the complex with  $\eta^2$ -coordinated hydrazonate ion occurs via breakage and subsequent formation of the W-N<sub>2</sub> bond with simultaneous rotation of the ligand around the W-N<sub>1</sub> bond, i.e. through the intermediate formation of the  $\sigma$ -complex:



The high positive value of entropy of activation of the process that is obtained is also in accordance with this conclusion.

## Conclusion

The analysis of NMR experimental data indicates that  $\text{aph}^-$  is coordinated to  $\text{WOF}_4$  as a  $\eta^2$  ligand. Both donor nitrogen atoms occupy equatorial positions in a pentagonal bipyramid, and the coordinated ligand adopts the Z conformation. Due to charge-density transfer from the ligand to the central atom, a deshielding of the majority of the  $^1\text{H}$  and  $^{13}\text{C}$  nuclei is observed (Table 1). The carbon atom attached to the imino nitrogen and the methyl groups is strongly deshielded. The only apparent exception,  $\Delta\delta(^{13}\text{C})$  for the  $\text{trans-CH}_3$  group, was rationalized in terms of C-H bond polarization due to the steric effect of the equatorial fluoro ligand  $F_M$ . This interaction is confirmed by direct "through-space" coupling with the value of  $J(^{19}\text{F}, ^{13}\text{C}) = 6.2 \text{ Hz}$ . Increasing the temperature leads to stereoisomer interconversion due to a hindered intramolecular rotation of the  $\text{aph}^-$  ligand. All activation parameters of this dynamic process were determined from complete line-shape analyses of the  $^{13}\text{C}$  NMR spectra of the complex at various temperatures.

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