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Tungsten(VI) Fluoride Dimethylhydrazide Complexes: η^2 and η^1 Isomerism

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The reactions of $Me_2N^{15}NH_2$ with the tungsten hexafluoride or oxide tetrafluoride in the presence of NEt_3 in acetonitrile solution have been investigated by multinuclear NMR spectroscopy. The formation of the hydrazido(2–) complex $[WOF_5(NNMe_2)]^-$ and of the complex $[WF_4(NNMe_2)(NHNMe_2)]^-$ containing both hydrazido(1–) and hydrazido(2–) ligands was observed. The last one exists as two isomers which involve the dimethylhydrazido(1–) ligand bound in η^2 (the major isomer) and η^1 forms. The equilibrium between these isomers exists with $K = 4.7$, but no exchange is observed at the temperatures from 248 to 303 K. Complexes $[WF_4(NNMe_2)(\eta^2\text{-}NRNMe_2)]^-$ (R = Me, Et) were obtained by reaction of $[WOF_4(\eta^2\text{-}NRNMe_2)]^-$ with 1,1-dimethylhydrazine and by the reaction of $[WOF_5(NNMe_2)]^-$ with trimethyl- and 1,1-dimethylethylhydrazine, respectively. No isomers were observed for the two last complexes.

Introduction

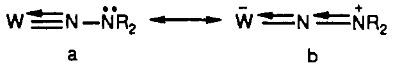
Reaction of substituted hydrazines with tungsten oxide tetrafluoride leads to the formation of the pentagonal bipyramid shaped neutral or anionic complexes with the η^2-coordinated hydrazine (or hydrazido(1–)) ligand lying in the equatorial plane.[1,2] Monosubstituted hydrazines on the same reaction substitute the multiple-bonded oxygen and form η^1-hydrazido(2–) complexes.[3] The same complexes are formed on reaction of WF_6 with monosubstituted hydrazines.[3]

There is the only example of mononuclear complex containing both η^1-hydrazido(2–) and η^2-hydrazido(1–) ligands, listed as follows.

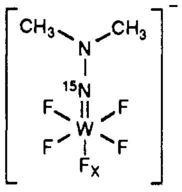
[Mo(NNMePh)(NHNMePh)(S₂CNMe₂)₂][BF₄].[4] The crystal structure reported for this compound shows the presence of the η^2-methylphenylhydrazido(1–) and η^1-methylphenylhydrazido(2–) ligands in a complex having distorted pentagonal bipyramid geometry. We expected that complexes containing both η^1-hydrazido(2–) and η^2-hydrazido(1–) ligands can also be obtained for tungsten(VI). To prove this suggestion we have taken up a multinuclear NMR study of the 1,1-dimethylhydrazine reaction with WOF_4 or WF_6 in CD_3CN. ^{15}N-labeled 1,1-dimethylhydrazine was used to obtain more information about the structure of the complexes formed by ^{15}N NMR.

Results

NMR data at 0 °C for the solution containing WF_6 and $^{15}NH_2N(CH_3)_2$ in molar ratio 1:2 show the formation of complex I. Spectral parameters of I are given in Tables I, II, and III. From analysis of the ^{19}F NMR spectrum (A_4X type) the octahedral geometry of I is evident with four equivalent fluorine atoms occupying the equatorial plane. The fifth fluorine atom (F_X) and nitrogen-containing ligand are in axial positions. The value of the coupling constant $^2J(^{19}F_X\text{–}^{15}N) = 63$ Hz, which is similar to those obtained in *trans*-$[WF(NNH_2)(Ph_2PCH_2CH_2PPh_2)_2][BF_4]$[5] for the trans-(F—W=^{15}N) fragment (58 Hz), indicates the multiplicity of the W=N bond. In addition, in the ^{15}N NMR spectrum of I, the signal of the ^{15}N-labeled nitrogen is shifted 250 ppm downfield vs corresponding signal of free hydrazine and lies in the region of nonprotonated multiple-bonded nitrogen atoms.[6] In the ^1H NMR spectrum, peaks of the methyl groups of I as well as of free hydrazine are split with $^3J(^1H\text{–}^{15}N) = 2$ Hz due to spin coupling through three bonds between protons of methyl groups and nitrogen-15. This coupling shows the presence in I of the W=NN$(CH_3)_2$ fragment, which as follows from equivalence of equatorial fluorine atoms is linear. Proposed linearity is confirmed by the structural data for the hydrazido(2–) ligand, and appears as a result of the contribution of resonance structure b[7]



Thus I can be assigned to the structure



I

Subsequent addition of 1,1-dimethylhydrazine and NEt_3 to the former solution decreases the intensities of I signals, and two new complexes II and III are formed. The NMR parameters of II and III are given in Tables I–III. The ratio of the relative concentrations of II and III, which is equal to 4.7:1, is independent on changes in molar ratio of reacting compounds. This indicates the equilibrium between II and III.

According to the ^{19}F NMR data, anion II has four unequivalent fluorine atoms (ACMX-type spectrum, Figure 1). High values of the $^2J(F_A\text{–}F_C)$ and $^2J(F_A\text{–}F_M)$ in this spectrum, as follows from our earlier considerations,[2] indicate the pentagonal bipyramid geometry of the complex and η^2-coordination of the ligand in equatorial plane.

The peaks of three equatorial fluorine atoms are shifted about 70 ppm upfield vs the corresponding peaks of the common oxofluoro(hydrazido(1–)) complexes. Substantial shielding (~30

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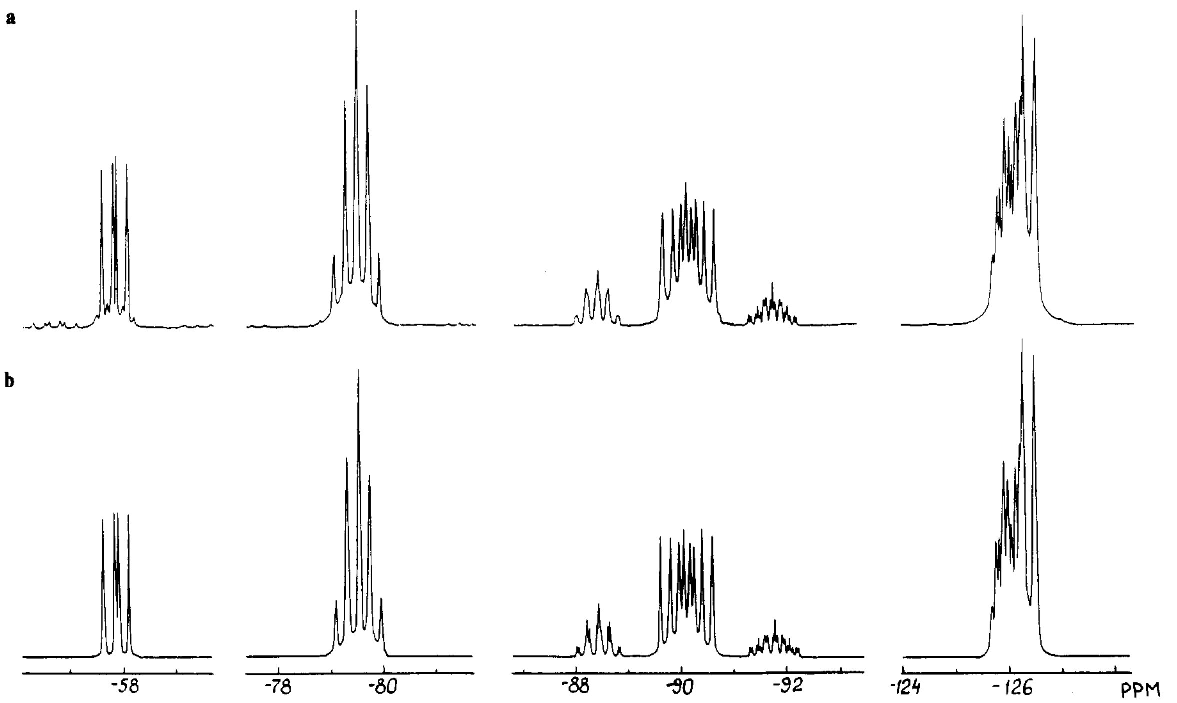


Figure 1. ^{19}F NMR (282.4 MHz) experimental (a) and theoretical (b) spectra of complexes II and III.

Table I. ^{19}F NMR Parameters of $[WF_4XY]^-$ Type Complexes[a]

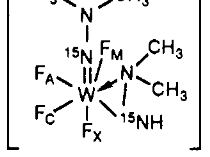
			chem shifts, rel $CFCl_3$, ppm				coupling constants, Hz					
	X	Y	F_A	F_C	F_M	F_X	J_{AC}	J_{AM}	J_{AX}	J_{CM}	J_{CX}	J_{MX}
I	$^{15}NN(CH_3)_2$	F	33.2			-67.5			59.4			
II	$^{15}NN(CH_3)_2$	η^2-$^{15}NHN(CH_3)_2$	-90.2	-126.1	-126.2	-79.6	125.7	96.4	56.8	22.0	63.8	61.0
III	$^{15}NN(CH_3)_2$	η^1-$^{15}NHN(CH_3)_2$	-91.9	-58.3		-88.6	77.6		47.6		59.0	
IV	O	η^2-$NHN(CH_3)_2$	-32.1	-96.0	-105.8	-98.0	126.6	101.4	45.7	33.9	46.4	58.3
V	$NN(CH_3)_2$	η^2-$NCH_3N(CH_3)_2$	-99.9	-126.0	-128.8	-81.8	125.0	84.1	62.3	21.1	53.3	72.2
VI	$NN(CH_3)_2$	η^2-$NC_2H_5N(CH_3)_2$	-101.5	-126.6	-131.4	-82.8	125.7	84.1	63.3	21.4	53.1	71.8

[a] Only F–F coupling constants are given.

ppm) of equatorial fluorine atoms occurs when multiple-bonded oxygen in $[WOF_5]^-$ is substituted by the multiple-bonded nitrogen,[8] so we suggested that in II the axial positions are occupied by the fluorine atom F_x and ${=}N{-}N(CH_3)_2$ or $=NR$ group, respectively. The latter fragment might be formed during the oxidative degradation of 1,1-dimethylhydrazine with cleavage of the N—N bond. Multiplicity of the W═N bond is confirmed as well as in I by the spin coupling with $J = 58$ Hz between the axial fluorine F_x and trans ^{15}N. The proton spectrum of II exhibits splitting of the methyl groups peak to doublet with $^3J(^1H-^{15}N) = 2$ Hz, indicating coordination in the axial position of the ${=}N{-}N(CH_3)_2$ but not $=NR$ ligand.

As follows from the ^1H and ^{13}C NMR spectra, methyl groups of the η^2-coordinated hydrazido(1–) ligand are nonequivalent. The same nonequivalence was observed earlier for the oxofluorohydrazine complexes[1] where it was a result of different substituent orientation of the coordinated hydrazine ligand. When the methyl group was oriented to the axial fluorine F_x, there existed direct spin-coupling through the space between the ^{13}C and ^{19}F nuclei. Such direct coupling is observed in the ^{13}C NMR spectrum of II where the peak corresponding to one of the methyl groups bonded to the nitrogen atom is split to a doublet with $^3J(^{13}C-^{19}F) = 9.6$ Hz. Another nitrogen atom, as follows from $^{15}N\{H\}$ NMR spectrum, is bonded to a proton, however N-H spin-coupling is not observed due to fast proton exchange even at low temperatures. In our previous work[9] it was found that in oxofluorohydrazido(1–) complexes the deprotonated nitrogen atom is a neighbor to the equatorial fluorine atom, which has the highest coupling constant value with F_A. According to this rule and taking into account the values of $J(F_A-F_C)$ and $J(F_A-F_M)$, we may assign the peaks of F_C in the ^{19}F NMR spectrum of II to the fluorine atom lying in the vicinity of the ^{15}NH group. The value of the coupling constant of the ^{15}NH group nitrogen $J(^{15}N-^{19}F_C)$ is about 4 times greater than $J(^{15}N-^{19}F_M)$ and $J(^{15}N-^{19}F_A) = 0$, so it seems likely that the spin-coupling between nitrogen-15 of the ^{15}NH group and equatorial fluorines is mainly contributed by direct coupling through the space.

Thus to II can be assigned the structure with both η^2-hydrazido(1–) and η^1-hydrazido(2–) ligands coordinated in the



II

equatorial plane and in the axial position, respectively. Its formation can be presented as a substitution of the F^- in the equatorial plane of I by the dimethylhydrazido(1–) ligand according to the equation

$$\underset{\text{I}}{[F_5W(NN(CH_3)_2)]^-} + NH_2N(CH_3)_2 \rightarrow$$

$$\underset{\text{II}}{[F_4W(NN(CH_3)_2)(NHN(CH_3)_2)]^-} + HF$$

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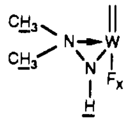
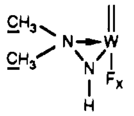
Table II. ^{1}H and ^{13}C NMR Parameters of $[WF_4(^{15}NN(CH_3)_2)X]^-$ Complexes

		^{1}H				^{13}C			
	X	δ, ppm	mult[a]	coupl const	assignment	δ, ppm	mult[a]	coupl const	assignment
I	F	3.2	d	$^3J(NH) = 2$ Hz	$NN(CH_3)_2$	45.3	s		$NN(CH_3)_2$
II	η^2-$^{15}NHN(CH_3)_2$	2.98	d	$^3J(^{15}N\text{–}H) = 2$ Hz	$NN(CH_3)_2$	44.4	s		$NN(CH_3)_2$
		3.34	s			56.0	s		
		3.0	s			48.0	d	$^3J(C\text{–}F_X) = 9.6$ Hz	
		5.33	s						
III	η^1-$^{15}NHN(CH_3)_2$	3.2	d	$^3J(^{15}N\text{–}H) = 2$ Hz	$NN(CH_3)_2$	45.3	s		$NN(CH_3)_2$
		2.51	d	$^3J(^{15}N\text{–}H) = 3.12$ Hz	$NHN(CH_3)_2$	50.3	s		$NHN(CH_3)_2$
		8.9	m	$^1J(^{15}N\text{–}H) = 72.5$ Hz $^3J(H\text{–}F_X) = 11.4$ Hz	$NHN(CH_3)_2$				

[a] Key: s, singlet; d, doublet; m, multiplet.

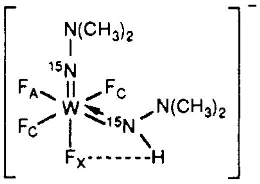
Table III. ^{15}N NMR Parameters of $[WF_4(^{15}NN(CH_3)_2)X]^-$ Complexes

	X	δ, ppm	mult[a]	coupl const	assignment
I	F	349.8	d	$^2J(^{15}N\text{–}F_X) = 62.9$ Hz	$^{15}NN(CH_3)_2$
II	η^2-$^{15}NHN(CH_3)_2$	325.7	d	$^2J(^{15}N\text{–}F_X) = 57.7$ Hz	$^{15}NN(CH_3)_2$
		145.9	m	$^2J(^{15}N\text{–}F_c) = 15.7$ Hz $^2J(^{15}N\text{–}F_M) = 3.8$ Hz $^2J(^{15}N\text{–}F_X) = 2.5$ Hz	$^{15}NHN(CH_3)_2$
III	η^1-$^{15}NHN(CH_3)_2$	338.0	d	$^2J(^{15}N\text{–}F_X) = 58.6$ Hz	$^{15}NN(CH_3)_2$
		298.9	m	$^2J(^{15}N\text{–}F_X) = 36.6$ Hz $^2J(^{15}N\text{–}F_X) = 9.4$ Hz $^1J(^{15}N\text{–}H) = 72.5$ Hz	$^{15}NHN(CH_3)_2$

[a] Key: s, singlet; d, doublet; m, multiplet.

As follows from the ^{19}F NMR spectra (AC_2X type, Figure 1) III has an octahedral geometry with the hydrazido(2–) ligand occupying one of the axial positions. This conclusion follows from the value of the trans $^2J(^{19}F_X\text{–}^{15}N) = 59$ Hz, low-field position of the ^{15}N-labeled nitrogen signal in the ^{15}N NMR spectrum (338 ppm) and from the splitting of the methyl groups peak in the ^{1}H NMR spectrum ($^3J(^{15}N\text{–}H) = 2$ Hz). In the cis position to the $=NN(CH_3)_2$ group lies an organic ligand which, as follows from the relatively small, typical for tungsten(VI) oxide fluoride amide complexes, value of $J(F_A\text{–}F_C) = 78$ Hz, has η^1 coordination. The ^{15}N NMR spectrum of III shows the spin-coupling between ^{15}N of the η^1-coordinated ligand and the trans fluorine with $J(^{15}N\text{–}F_A) = 37$ Hz, and the ^{1}H NMR spectrum shows splitting of the methyl group peak with $^3J(^{15}N\text{–}H) = 3$ Hz. These two splittings indicate the hydrazido-type ligand is coordinated in an equatorial plane by the labeled nitrogen.

In the ^{15}N NMR spectrum recorded without proton decoupling there exists $^1J(^{15}N\text{–}H) = 73$ Hz, indicating that one hydrogen atom is bonded to the labeled nitrogen and no proton exchange occurs. So III can be assigned the structure



III

with four nitrogen atoms and the hydrogen atom of the NH group lying in the axial plane of the complex. In this structure the flat configuration of the equatorial nitrogen atom is a result of the d_π–p_π interaction of the nitrogen lone pair of electrons and tungsten vacant d_{xy} orbital, as it is found in tungsten oxofluoroamide complexes.[10]

Thus II and III are isomeric complexes and differ by the way of coordination of hydrazido(1–) ligand in the equatorial plane of the complex.

Complexes I–III can be obtained also by reaction of the 1,1-dimethylhydrazine (DMH) with WOF_4 according to the equations

$$[WOF_4{\cdot}CD_3CN] + HF \rightleftarrows [WOF_5]^- + H^+ + CD_3CN$$

$$[WOF_5]^- + DMH \rightleftarrows \underset{\text{IV}}{[WOF_4(NHN(CH_3)_2)]^-} + HF$$

$$[WOF_5]^- + DMH \rightleftarrows \underset{\text{I}}{[WF_5(NN(CH_3)_2)]^-} + H_2O$$

$$\text{IV} + DMH \rightleftarrows \underset{\text{II, III}}{[WF_4(NN(CH_3)_2)(NHN(CH_3)_2)]^-} + H_2O$$

$$\text{I} + DMH \rightleftarrows \underset{\text{II, III}}{[WF_4(NN(CH_3)_2)(NHN(CH_3)_2)]^-} + HF$$

It is apparent from the ^{19}F NMR parameters (see Table I) that complex IV is analogous to previously described tungsten oxofluorohydrazido(1–) complexes with η^2-coordinated hydrazido(1–) ligands.[2,9]

According to the equations given above, complexes containing both hydrazido(2–) and hydrazido(1–) ligands formed from the different hydrazines can be obtained. For example, complexes $[WF_4(NN(CH_3)_2)(NRN(CH_3)_2)]^-$ (V, R = CH_3; VI, R = C_2H_5) were obtained by reaction of $[WOF_4(NRN(CH_3)_2)]^-$, analogs of the previously described oxofluorohydrazido complexes,[2,9] with 1,1-dimethylhydrazine. The reaction is to substitute multiple-bonded oxygen by the $=NN(CH_3)_2$ group. The same complexes can be obtained on reaction of I with trimethyl- and 1,1-dimethylethylhydrazine, respectively. In this case the hydrazido(1–) ligand substitutes one of the equatorial fluorine atoms in I. The ^{19}F NMR parameters of V and VI which are given in Table I are close to that of II and indicate that the above complexes are of the same structure. No isomers like III are observed for V and VI.

Discussion

Although complexes containing η^1-coordinated hydrazido(1–) ligand are known,[4,11] and on the basis of the NMR data the η^1,η^2-isomerism of the hydrazido complexes has been proposed,[12] it is only in the present study that reliable experimental evidence of η^1 and η^2 isomerism of hydrazido(1–) complexes is given.

It was shown earlier[13] that complexes of the d^0 transition metals with η^2-coordinated n-donor two-center ligands, such as O_2^{2-}, $R'R''C{=}NO^-$, hydrazido(1–), should be considered as a π complexes in which the central atom accepts the pairs of electrons from both π and π* orbitals of the organic ligand. Such complexes show the hindered internal rotation of organic ligand similar to

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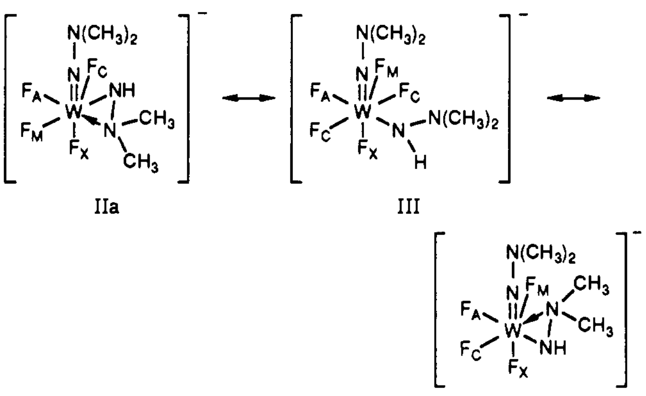
that found in olefin π complexes. Such hindered rotation often is followed by exchange between enantiomers of the complex. The enantiomers by themselves cannot be distinguished by NMR spectroscopy; however exchange between enantiomers can be observed in the ^{19}F NMR spectrum as a specific averaging of some coupling constant and chemical shifts.[13]

Complex II also has the two enantiomeric forms (a and b) which can transfer one to another by the cleavage of one of the metal–ligand bonds with simultaneous rotation around another, i.e. via an intermediate state of η^1 complex (III)



IIa

III

IIb

Due to the short lifetime and relative unstability of η^1-complex, it is usually not observed in the NMR spectra. But in the case of 1,1-dimethylhydrazido complexes, the stability of the η^1 complex is only 3.5 kJ/mol less than that of the η^2 isomer. However no exchange between enantiomers or between II and III was observed in the ^{19}F NMR spectra on raising the temperature to 50 °C, over which the sample decomposes.

Simultaneous presence in solution of the tungsten complexes with η^2- and η^1-coordinated hydrazido(1–) ligands, or in other words π and σ isomers of the hydrazido(1–) complex, appears as a new type of isomerism. Such isomerism for 1,1-dimethylhydrazido complexes becomes possible at the expense of the possible hydrogen bond between the axial fluorine atom F_X and the hydrogen of the hydrazido(1–) NH group and the p_π–d_π interaction. On the other hand the multiple-bonded hydrazido(2–) ligand being a strong π donor lowers the interaction of the hydrazido(1–) ligand orbitals (π^* on η^2 coordination, p on η^1 coordination) with the metal d_{xz} orbital and therefore increases the energy barrier of the transfer between isomers. The energy barrier and, hence, the lifetimes of the complexes are increased also due to the hydrogen bond between the NH hydrogen of the σ isomer and the axial fluorine atom.

Experimental Section

Starting Materials. Tungsten oxide tetrafluoride was sublimed in vacuo prior to use. Tungsten hexafluoride was "pure" grade. The deuterated acetonitrile was dried over 3-Å molecular sieves for several weeks. Triethylamine was distilled 2 times over the solid KOH and was stored over the KOH. 1,1-Dimethylhydrazine (Koch-Light Laboratories) was dried over sodium wire and then distilled. ^{15}N-Labeled 1,1-dimethylhydrazine was prepared according to the method described[15] using sodium nitrite enriched in ^{15}N to 96%. Trimethylhydrazine and 1,1-dimethylethylhydrazine were synthesized by reduction of the formaldehyde and acetaldehyde dimethylhydrazones, respectively, by $LiBH_4$ as described previously.[16] The purity of all starting materials was controlled by NMR spectroscopy.

General Procedures and Instrumentation. All reactions were carried out in NMR tubes under an atmosphere of dry nitrogen on cooling to about –30 °C, by adding certain amounts of organic reagents to the ~30% solution of WOF_4 or WF_6 in CD_3CN.

The ^{19}F NMR spectra were recorded on Bruker WP-80 and MSL-300 spectrometers operating at 75.4 and 282.4 MHz, respectively. ^1H, ^{13}C, and ^{15}N NMR spectra were recorded on a Bruker MSL-300 spectrometer at 300.1, 75.5, and 30.4 MHz, respectively. Chemical shifts are referenced to $CFCl_3$ for ^{19}F, to Me_4Si for ^1H and ^{13}C, and to NH_3(liq) for ^{15}N. All chemical shifts are reported positive to lower shielding. The ^{13}C NMR spectra were recorded using the DEPT technique with $\theta = 3\pi/4$. Correspondence between ^1H, ^{13}C, and ^{15}N NMR spectra was established using the selective polarization transfer from protons to the nucleus observed. All spectral parameters were calculated by iterative simulation using software (PANIC) provided with the Bruker spectrometers.

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