Study of allylic rearrangement in $(\mu\text{-H})Os_3(\mu\text{-O=CNRCH}_2\text{CH=CH}_2)(CO)_{10}$ (R = H or CH_3) clusters

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The migration of the double bond in the allylcarboxamide ligands of $(\mu\text{-H})Os_3(\mu\text{-O=CNRCH}_2\text{CH=CH}_2)(CO)_{10}$ (R = H (**1**) or CH_3 (**2**)), $(\mu\text{-D})Os_3(\mu\text{-O=CNDCH}_2\text{CH=CH}_2)(CO)_{10}$, and $(\mu\text{-H})Os_3(\mu\text{-O=CNHCD}_2\text{CH=CH}_2)(CO)_{10}$ clusters was studied by ^1H, ^2H, and ^{13}C NMR spectroscopy. Neither μ-D nor ND groups in the deuterated complexes are directly involved in prototropic processes of allylic rearrangement. Initially, the deuterium atom of the CD_2 group migrates to the γ-carbon atom of the allyl fragment to form the $-CD=CH-CH_2D$ propenyl moiety, in which the deuterium and hydrogen atoms are gradually redistributed between the γ- and β-carbon atoms. The triosmium cluster complexes containing the bridging carboxamide ligands O=CNRR′ catalyze the allylic rearrangement of *N*-allylacetamide. Based on the data obtained, the probable scheme of the allylic rearrangements in clusters **1** and **2** was proposed.

Key words: triosmium clusters, isotopically labeled complexes, allylic rearrangement, ^1H, ^2H, and ^{13}C NMR spectroscopy, catalysis.

Previously[1] we reported on the rearrangement of the allylic fragment in the $(\mu\text{-H})Os_3(\mu\text{-O=CNRCH}_2\text{CH=CH}_2)(CO)_{10}$ (R = H (**1**) and CH_3 (**2**)) clusters.[1,2] The rearrangement of cluster **1** was found to give *cis*- and *trans*-isomers of the cluster $(\mu\text{-H})Os_3(\mu\text{-O=CNHCH=CHCH}_3)(CO)_{10}$ relative to the C=C bond; each of them exists as *Z*- and *E*-isomers relative to the N=C(O) bond. The rearrangement of **2**, unlike that of cluster **1**, occurs stereospecifically, giving *trans,Z*- and *trans,E*-isomers of the $(\mu\text{-H})Os_3(\mu\text{-O=CNRCH=CHCH}_3)(CO)_{10}$ complex.[2] The resulting pair of isomers is stable at room temperature or on moderate heating, unlike the isomeric clusters formed upon the rearrangement of **1**, which undergo interconversion at 20 °C. Unlike the rearrangements of complexes of allylamines and *N*-allylamides with similar structures, which occur only at elevated temperatures[3–5] in the presence of rhodium and iron complexes,[6] the rearrangement of the allylic fragment in **1** and **2** proceeds at ~20°C. Analysis of the structure of $(\mu\text{-H})Os_3(\mu\text{-O=CNHCH}_2\text{CH=CH}_2)(CO)_{10}$ with the aid of Dreiding models indicates that intramolecular coordination of the allylic fragment to one metal atom is impossible without rupture of the Os—O or Os—C bond for steric reasons. Intermolecular replacement of one CO group in the cluster by an allylic ligand of another molecule to give a π-complex able to rearrange at room temperature is also unlikely.

In the present work, we studied the reasons for isomerization of the allylic fragment in the $(\mu\text{-H})Os_3(\mu\text{-O=CNRCH}_2\text{CH=CH}_2)(CO)_{10}$ clusters (R = H (**1**), Me(**2**)) under mild conditions.

Results and Discussion

In view of the discovered allylic rearrangement in **1** and **2**, in this study we analyzed the IR and ^1H NMR spectra of the $(\mu\text{-H})Os_3(\mu\text{-NHCH}_2\text{CH=CH}_2)(CO)_{10}$, $(\mu\text{-H})M_3(\mu\text{-SCH}_2\text{CH=CH}_2)(CO)_{10}$ (M = Os, Ru), and $(\mu\text{-H})Os_3(\mu\text{-OCH}_2\text{CH=CH}_2)(CO)_{10}$ clusters prepared previously,[7] which contain allylic groups in the bridging ligands. Analysis of the spectral data showed that in none of these complexes does migration of the double bond in the allylic fragment of the ligand occur. Therefore, the rearrangement of clusters **1** and **2** evidently cannot be explained only by electronic effects of the $[(\mu\text{-H})Os_3(\mu\text{-O=CNR—})]$ fragment, attached to the allylic group, because a similar influence of the corresponding fragments in other clusters considered should be equally significant.

Experimental data confirmed the important role of the N(R)=C=O fragment in the rearrangement of clusters **1** and **2**. It was found that unless the complexes have been isolated from the reaction medium containing an excess of free allylamine, the rearrangement does not occur even over a period of several months. In the presence of other amines, the rearrangement does not occur either. It was found that the double bond migration in the allylic groups of clusters **1** and **2** is substan-

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tially retarded in the presence of Brønsted acids. The carbamoyl fragment N(R)=C=O in the bridging ligand is the most reactive group in the clusters considered. The inhibition of the rearrangement is, apparently, due to the interaction of the NH group, containing an active hydrogen atom and a lone electron pair, with acids and bases. The possibility of protonation of the oxygen atom of the bridging ligand also cannot be ruled out.[8] Therefore, the participation of hydrogen of the NH group in the prototropic processes involved in the rearrangement of cluster **1** was verified experimentally. For this purpose, the $(\mu\text{-D})Os_3(\mu\text{-O=CNDCH}_2\text{CH=CH}_2)(CO)_{10}$ complex, containing deuterium at the nitrogen atom and in the metal-containing ring (the initial content of deuterium in each position was ~85%), was synthesized by a known procedure.[9]

It was found that only deuterium contained in the ND group is replaced during the rearrangement by hydrogen atoms from impurities, which are always present in solutions in amounts comparable with the complex concentrations ($\sim 10^{-3}$ mol L^{-1}). This is indicated by the ratio of the integral intensities and splitting of the signals corresponding to the propenyl group in the ^{1}H NMR spectra of the resulting isomeric clusters $(\mu\text{-D})Os_3(\mu\text{-O=CNHCH=CHCH}_3)(CO)_{10}$. The ^{13}C NMR spectrum of the propenyl fragment of this complex recorded in the INVGATE mode exhibits only three singlets, whereas partial deuteration of any carbon atom in this radical should change the chemical shift and, hence, bring about additional signals. These data also indicate that the bridging deuterium atom is not involved in the rearrangement.

In order to study the migration of hydrogen atoms within the allylic fragment during the rearrangement, the $(\mu\text{-H})Os_3(\mu\text{-O=CNH—CD}_2\text{CH=CH}_2)(CO)_{10}$ cluster (**3**), deuterated at the α-carbon atom of the organic ligand, was synthesized. The rearrangement of complex **3** was carried out under previously described conditions.[1] Chromatography of the reaction mixture yielded two pairs of inseparable isomers, $(\mu\text{-H})Os_3\{\mu\text{-O=CNHCD=C(H/D)CH}_2\text{(D/H)}\}(CO)_{10}$ (**4a,c** and **4b,d**), for which ^{1}H NMR spectra were recorded; for one isomer pair (**4a,c**), the ^{2}H and ^{13}C NMR spectra were also recorded (see Experimental and Fig. 1). The regions of the ^{1}H NMR spectra corresponding to the deuterated propenyl ligands of isomeric clusters **4a,c** and **4b,d** contain two complex multiplets, whose character is determined by the overlap of signals due to two types of molecules differing in the deuterium distribution in the propenyl group. The ^{2}H NMR spectrum exhibits three broad singlets with chemical shifts of 6.61, 4.89, and 1.69 (—NH—C<u>D</u>=, =C<u>D</u>—, and —CH_2<u>D</u>, respectively) with an intensity ratio of about 4 : 1 : 3. Analysis of the spectral data showed that the rearrangement yields two types of deuterated clusters for each isomer, $(\mu\text{-H})Os_3(\mu\text{-O=CNHCD=CHCH}_2\text{D})(CO)_{10}$ and $(\mu\text{-H})Os_3(\mu\text{-O=CNHCD=CDCH}_3)(CO)_{10}$. Initially, the mixture contains only several percent of the cluster deuterated at the β-carbon atom. However, the concentrations of complexes deuterated at the β- and γ-positions of the propenyl group gradually become equal. Simultaneously, interconversion of the *cis*- (**4a,c**) and *trans*-isomers (**4b,d**) occurs. These data suggest that the mechanisms of the allylic rearrangement, the interconversion of the *cis*- and *trans*-isomers, and the redistribution of deuterium and hydrogen atoms in a propenyl fragment have a common step.

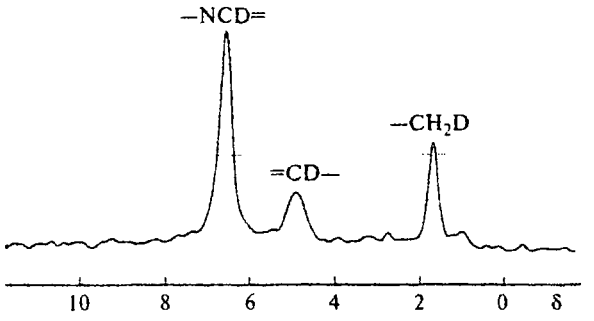
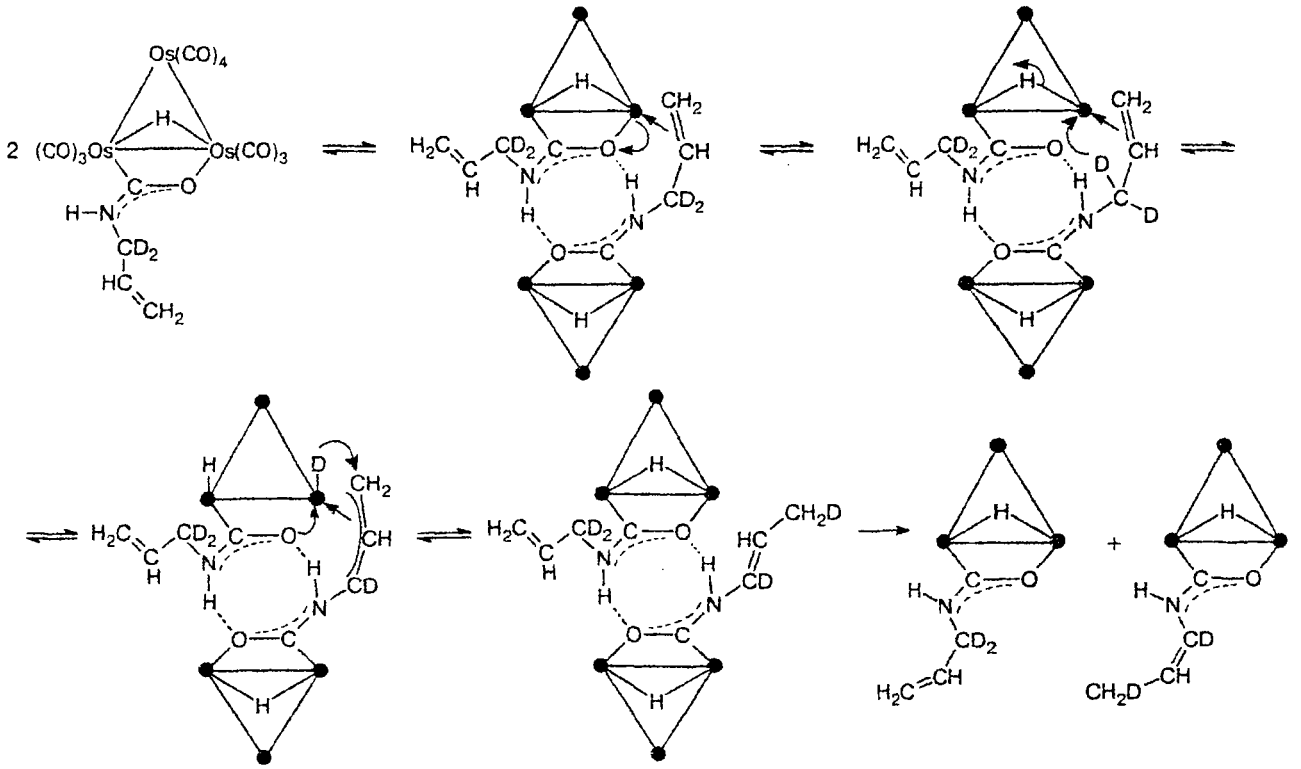


Fig. 1. ^{2}H NMR spectrum ($CDCl_3$, 61 MHz) of the *Z,E*-isomers of $(\mu\text{-H})Os_3\{\mu\text{-O=CNHCD=C(H/D)—CH}_2\text{(D/H)}\}(CO)_{10}$ (**4a,c**) after keeping in a benzene solution for ~15 days

An attempt was made to perform rearrangement of allyl-containing organic compounds in the presence of clusters containing a bridging allylcarboxamide ligand. This was done using the $(\mu\text{-H})Os_3(\mu\text{-O=CNHCH}_2\text{CH=CH}_2)(CO)_{10}$ (**1**) complex and unsaturated compounds $NH_2CH_2CH=CH_2$, $S(CH_2CH=CH_2)_2$, and $CH_3C(O)—NHCH_2CH=CH_2$. The course of the process was monitored based on the decrease in the intensity of the N—CH_2-group signal in the allylic group and the increase in the intensity of the signal for the CH_3 group in the resulting propenyl fragment. Allylamine and diallyl sulfide were found to remain unchanged for two months in a $CDCl_3$ solution containing cluster **1**. *N*-Allylacetamide slowly isomerized under these conditions to give *N*-propenylacetamide. Isomerization does not stop after the allylic rearrangement of the cluster has been completed, *i.e.*, it does not depend on the position of the double bond in the ligand. It should be noted that the reaction involves ~6 moles of *N*-allylacetamide per mole of the cluster, pointing to a catalytic character of this process. *N*-Allylacetamide differs from allylamine and diallyl sulfide in that it, like the cluster, contains an NH=C=O group. *N*-Allylacetamide is known[6] to rearrange only in the presence of metal-complex catalysts at elevated temperatures. It is beyond doubt that the triosmium metallacycle acts as the catalyst in the above-described reaction. The rearrangement of *N*-allylacetamide taken in an excess proceeds at approximately the same rate in the presence of the $(\mu\text{-H})Os_3(\mu\text{-O=CNHCHRCO}_2\text{Et})(CO)_{10}$ clusters (R = H, Me),

Scheme 1



Note. For compactness, the Os atoms and carbonyl ligands are designated in the scheme by filled circles.

which contain neither an allylic nor propenyl fragment in the ligand but do contain the NH=C=O group.

Organic carboxamides are known to exist in solutions and in condensed phases as associates formed as cyclic dimers or linear polymers due to hydrogen bonds between the —NHR and —C=O groups.[10] In the case of cluster **1**, in which hydrogen of the N—H group occupies the *cis*-position relative to the oxygen atom of the bridging carbonyl group, as for lactams,[10] the formation of cyclic dimers is more likely, although the formation of linear associates also cannot be ruled out due to steric reasons hampering the cyclization of the bulky clusters. For cluster **2**, having no N—H hydrogen atom, the formation of cyclic dimers due to dipole—dipole interaction is possible, as in the case of *N,N*-disubstituted amides.[11] Based on analysis of experimental data and those available from the literature on the cyclization of organic amides in solution, a scheme for the rearrangement of the allylic fragments in clusters of types **1** and **2** can be proposed (Scheme 1).

This scheme complies with the main experimental data described above; acids and bases should hamper the formation of dimeric complexes due to interaction with the NH group of the bridging ligand; clusters in which allylamine, allylthiol, or allylic alcohol are coordinated as one-atom bridges cannot be activated by the above scheme; the deuterium atom of the ND group in the $(\mu\text{-D})Os_3(\mu\text{-O=CNDCH}_2\text{CH=CH}_2)(CO)_{10}$ cluster is not expected to pass into the hydrocarbon group, and deuterium of the $-NHCD_2$ group can be redistributed among the carbon atoms during the allylic rearrangement and the subsequent *cis,trans*-isomerization of the arising propenyl fragment.

The key step of the rearrangement shown in the scheme is apparently rupture of the Os—O bond, which occurs after the formation of associates. Therefore, it can be expected that not only amides but other compounds forming associates with clusters containing the RR'N=C=O bridging ligand would undergo catalyzed isomerization. Meanwhile, it can be suggested that clusters whose dimerization or formation of associates with organic compounds such as amides could result in the cleavage of the bonds between the metallacycle and the bridging ligand and appearance of a vacant coordination site would also catalyze the allylic rearrangement. Elucidation of the range of clusters and organic compounds possessing these properties is the purpose of the next stage of the research.

Experimental

IR spectra were recorded on a Specord IR-75 spectrometer in hexane or cyclohexane. ^{1}H NMR spectra were run on Bruker SXP 4-100 (100 MHz), Bruker DPX-250 (250 MHz),

and Bruker AM-400 (400 MHz) instruments in $CDCl_3$ using tetramethylsilane as the internal standard; ^2H NMR spectra were measured on Bruker CPX-300 (46 MHz) and Bruker MSL-400 (46 MHz) instruments in CCl_4 using $CDCl_3$ as the internal standard; and ^{13}C NMR spectra were obtained on Bruker DPX-250 (62 MHz) and Bruker AM-400 (100 MHz) instruments in $CDCl_3$ or CCl_4 using tetramethylsilane as the internal standard.

All the reactions were carried out in freshly distilled solvents under argon. Analysis of the reaction mixtures and isolation of the reaction products were performed by TLC on Silufol UV_{254} plates.

$NH_2CD_2CH{=}CH_2$ was synthesized by a procedure similar to that described previously[11] (the degree of deuteration was 100%). Allylamine deuterated at the amino group ($ND_2CH_2CH{=}CH_2$) was prepared by keeping $NH_2CH_2CH{=}CH_2$ in D_2O containing some D_2SO_4 for 24 h. $ND_2CH_2CH{=}CH_2$ was evaporated from the aqueous solution using an efficient vacuum fractionationg column and collecting the fraction with b.p. 52 °C (the content of deuterium in the amino group of allylamine was ~95%).

$(\mu\text{-D})Os_3\{\mu\text{-O}{=}CN(D/H)CH_2CH{=}CH_2\}(CO)_{10}$. The synthesis was carried out by a known procedure[1] using the allylamine $ND_2CH_2CH{=}CH_2$ prepared previously. Initially, the content of deuterium in the ND and μ-D groups of the cluster was ~85%. Upon dissolution of the complex in C_6H_6 or CH_2Cl_2, the content of deuterium in the ND group decreased and, after two days, deuterium was completely replaced by hydrogen. The content of the bridging deuterium atom remained constant. The IR spectrum of the complex was virtually identical to that of **1**. ^1H NMR ($CDCl_3$), δ: 5.86 (m, NH); 5.68 (m, 1 H, $-C\underline{H}{=}CH_2$); 5.12 (m, 2 H, $-CH{=}C\underline{H}_2$); 3.72 (m, 2 H, NCH_2); −14.25 (s, 1 H, μ-H).

$(\mu\text{-D})Os_3(\mu\text{-O}{=}CNHCH{=}CHCH_3)(CO)_{10}$. The complex $(\mu\text{-D})Os_3\{\mu\text{-O}{=}CNDCH_2CH{=}CH_2\}(CO)_{10}$ was dissolved in benzene and kept for two days. The resulting isomeric clusters were separated by a known procedure.[1] The IR spectra of these clusters in the region of stretching vibrations of the NH and CO groups were virtually identical to the corresponding spectra of the complexes obtained upon the rearrangement of cluster **1**.[1] The ^1H NMR spectrum for the *cis*-isomers ($CDCl_3$), δ: 7.30 (br.d, 1 H, NH); 6.50 (m, 1 H, $N-C\underline{H}{=}CH-$); 4.70 (m, 1 H, $N-CH{=}C\underline{H}-$); 1.61 (dd, 3 H, CH_3, ^3J = 6.82 Hz, ^4J = 1.60 Hz); −14.17 (s, μ-H); 7.72 (br.d, 1 H, NH); 6.55 (m, 1 H, $N-C\underline{H}{=}CH-$); 4.99 (m, 1 H, $N-CH{=}C\underline{H}-$); 1.54 (dd, 3 H, CH_3, ^3J = 7.10 Hz, ^4J = 1.70 Hz); −13.96 (s, μ-H).

The ^1H NMR spectrum for the *trans*-isomers ($CDCl_3$), δ: 7.17 (br. d, 1 H, NH); 6.54 (m, 1 H, $N-C\underline{H}{=}CH-$); 5.18 (m, 1 H, $N-CH{=}C\underline{H}-$); 1.60 (dd, 3 H, CH_3, ^3J = 7.40 Hz, ^4J = 2.00 Hz); −14.19 (s, μ-H); 7.63 (br.d, 1 H, NH); 6.41 (m, 1 H, $N-C\underline{H}{=}CH-$); 4.85 (m, 1 H, $N-CH{=}C\underline{H}-$); 1.70 (dd, 3 H, CH_3, ^3J = 7.00 Hz, ^4J = 1.71 Hz); −13.98 (s, μ-H).

The $^{13}C\{^1H\}$ NMR of the *cis*-isomer (recorded using the INVGATE technique; 6 : 1 CCl_4 : $(CD_3)_2CO$)), δ: 183.50, 183.34, 182.37, 179.19, 176.05, 175.96, 175.89, 175.68, 174.54, 173.49, 173.46 (carbonyl region); 121.61 ($N-\underline{C}H{=}CH-$); 107.49 ($N-CH{=}\underline{C}H-$); 12.60 ($\underline{C}H_3$).

$(\mu\text{-H})Os_3(\mu\text{-O}{=}CNHCD_2CH{=}CH_2)(CO)_{10}$ (3). Complex **3** was prepared by a known procedure[1] using the previously synthesized allylamine $NH_2CD_2CH{=}CH_2$. The IR spectrum of **3** in the stretching region of NH and CO groups was virtually identical to the corresponding spectrum of cluster **1**.[1] ^1H NMR ($CDCl_3$), δ: 5.87 (m, H, NH); 5.69 (m, 1 H, $-C\underline{H}{=}CH_2$); 5.13 (m, 2 H, $-CH{=}C\underline{H}_2$); −14.25 (s, 1 H, μ-H).

$(\mu\text{-H})Os_3\{\mu\text{-O}{=}CNHCD{=}C(H/D)CH_2(D/H)\}(CO)_{10}$ (4a—d). Complex **3** was dissolved in CH_2Cl_2 or C_6H_6 and kept for four days. The resulting isomeric clusters were separated by a known procedure.[1] The IR spectra of the isomeric clusters in the stretching region of the NH and CO groups were virtually identical to those of the isomeric complexes obtained by the rearrangement of cluster **1**.[1] The NMR spectrum of each isomer was a superposition of the spectra of isotopomers **4** deuterated at the α,β- and α,γ-carbon atoms of the propenyl fragment.

^1H NMR, **4a** ($CDCl_3$), δ: 7.14 (br.s, 1 H, NH); 4.79 (m, $N-CD{=}C\underline{H}-$); 1.60 (m, CH_3, CH_2D); −14.16 (s, 1 H, μ-H).

^2H NMR, **4a** (CCl_4), δ: 6.57 (br.s, 1 D, N—CD=); 4.89 (br.s, =CD—); 1.68 (br.s, CH_2D).

$^{13}C\{^1H\}$ NMR, **4a** ($CDCl_3$), δ: 186.10, 183.16, 181.77, 178.44, 175.64, 175.54, 175.22, 175.12, 174.03, 174.00, 172.89 (carbonyl region); 107.53 ($N-CH{=}\underline{C}H-$, $N-CH{=}\underline{C}D-$); 10.68 ($\underline{C}H_3$, $\underline{C}H_2D$).

^1H NMR, **4b** ($CDCl_3$), δ: 7.22 (br.s, 1 H, NH); 5.19 (m, $N-CD{=}C\underline{H}-$); 1.60 (m, $CH_3 + CH_2D$); −14.25 (s, 1 H, μ-H).

^2H NMR, **4b** (CCl_4), δ: 6.61 (br.s, 1 D, N—CD=); 5.24 (br.s, =CD—); 1.68 (br.s, CH_2D).

^1H NMR, **4c** ($CDCl_3$), δ: 7.71 (br.s, 1 H, NH); 4.98 (m, $N-CD{=}C\underline{H}-$); 1.55 (m, $CH_3 + CH_2D$); −13.95 (s, 1 H, μ-H).

^1H NMR, **4d** ($CDCl_3$), δ: 7.67 (br.s, 1 H, NH); 5.21 (m, $N-CD{=}C\underline{H}-$); 1.70 (m, $CH_3 + CH_2D$); −13.97 (s, 1 H, μ-H).

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