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Laurent Brachais, Marc Visseaux. NMR T1-Relaxation Measurements on Paramagnetic Organolanthanides: An Alternative Tool for Structure Determination in Solution. *European Journal of Inorganic Chemistry*, 2005, pp.2486-2492. 10.1002/ejic.200400634 . hal-00106207

HAL Id: hal-00106207

<https://hal.science/hal-00106207>

Submitted on 13 Oct 2006

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NMR T_1 -Relaxation Measurements on Paramagnetic Organolanthanides: an Alternative Tool for Structure Determination in Solution.

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Received (will be filled in by the editorial staff)

T_1 / spin-lattice relaxation times / paramagnetic complexes / lanthanides / ^1H NMR

^1H NMR investigations were conducted on four paramagnetic organolanthanides all bearing the tetraisopropylcyclopentadienyl Cp^{4i} ligand ($\text{Cp}^{4i} = \text{HC}_5\text{iPr}_4$) in order to verify whether or not interactions observed in the solid state were maintained in solution. In some cases, variable temperature experiments were necessary to enhance the resolution and determine the best conditions of study. 1D NMR spectrum could be interpreted in every case. Complementary 2D COSY experiments allowed the full attribution of the signals. T_1 (^1H) relaxation measurements were determined for all the paramagnetic complexes at the most suitable temperature, and compared to those of the diamagnetic KCp^{4i} . The same tendency was observed, with particular features concerning the isopropyl groups. Among the four methyl groups, one exhibits a much higher T_1 value, one a much lower and the two others are intermediate. This was interpreted as the result of a privileged conformation of the Cp^{4i} ligand: the two α -isopropyl groups take a spatial orientation with one methyl in *exo* position, opposite to the metal, whereas the methyl groups of the two β -isopropyl are quite equidistant from the metal. Whatever the nature of the metal (Nd, Sm), the oxidation state (Sm^{II} , Sm^{III}), or the temperature (298, 363 K), this conformation is retained. The structure in solution seems to be different from that previously determined in the solid state.

Introduction

Organolanthanide complexes have recently known a growing interest, due in particular to their performances as catalysts for polymerization. ^[1-4] Investigations about the catalytic mechanisms are conducted starting from their molecular structures usually computed from X-ray diffraction data. However these data reflect a solid-state organization which can be different from the solution structure involved during reactions.

We synthesized recently a series of complexes bearing the voluminous Cp⁴ⁱ ligand (Cp⁴ⁱ = HC₅iPr₄). ^[5,6] X-Ray studies showed a particular behaviour for several of them: one methyl(Cp⁴ⁱ)-lanthanide interaction, possibly agostic, was observed in X-Ray structure of (Cp⁴ⁱ)₂Ln(BH₄) (Ln = Nd, Sm), as well as in divalent (Cp⁴ⁱ)₂Sm, whereas cotLnCp⁴ⁱ (cot = C₈H₈) displayed an unusually short cot-metal distance. We established also that organolanthanides bearing this Cp⁴ⁱ ligand afforded highly *trans*-stereospecific catalysts toward isoprene polymerization upon activation by BuLi, ^[6] which is in accordance with steric hindrance around the metal. ^[7,8] Moreover, (Cp⁴ⁱ)₂Sm was found efficient toward ϵ -caprolactone polymerization whereas it remained unsolvated in the presence of THF. ^[5] It was then of interest to study thoroughly the stereoelectronic environment of the metal in such complexes, and whether or not interactions observed were maintained in solution since molecular complexes of lanthanides often behave differently in solution with respect to the solid state. ^[9]

NMR spectroscopy is a powerful technique which can give additional information, and thus appears as a complementary tool to X-ray diffraction for studying three dimensional structures in solution. ^[10] NMR studies on organolanthanide compounds are still mainly restricted to the diamagnetic derivatives (La, Lu, Y, Sc), ^[11] while the best catalysts are obtained in the more paramagnetic neodymium and samarium series. ^[12-14] However, even if the results usually suffer from the loss of resolution observed on spectra due to the intrinsic properties of lanthanide atom, this paramagnetism is able to give some information concerning the complex geometry. ^[15,16] NMR of paramagnetic molecules has been widely studied and discussed, particularly in terms of chemical shifts^[17] and actually, lanthanide complexes are mainly used as chemical shift reagents. Paramagnetic metals are also involved in a large number of natural compounds like proteins and their presence usually complicates the study of such compounds. Bertini and coworkers recently reviewed the works made in the field of paramagnetic NMR for biological compounds. ^[18] It has been increasingly recognized that, besides contributing to line broadening, the electron-nucleus interactions contain useful structural information. Many of the relevant effects that the presence of paramagnetic metals has on the behaviour of the compound nuclei have to do with the metal magnetic susceptibility. Most of these effects have been well known since the 50s and 60s, but a few have been described more recently. Concerning lanthanide complexes, the effect of

paramagnetism on the spin-lattice relaxation has been studied but they are mostly limited to coordination complexes in aqueous medium. ^[19]

Different techniques have been found to calculate distances from T_1 relaxation rates. ^[20,21] These methods are however complicated to undertake due to the high number of parameters they involve. Particularly, it is admitted that the comparison of T_1 obtained from different compounds can be made at the condition of $T_{1 \text{ min}}$. This is an important problem in the case of paramagnetic compounds because the $T_{1 \text{ min}}$ is usually reached at low temperature which induces an additional loss of resolution. Finally the poor resolution then observed prevents the computation of T_1 .

In the present study, we propose a comparison of the molecular structures of several organolanthanide complexes in solution, based on their paramagnetic ^1H NMR data. Moreover, we chose to examine paramagnetic samarium and neodymium complexes to contest the **general** idea that comprehensive NMR studies are not possible for compounds of those metals.

The choice of these organometallic complexes, presented in table 1, allows the study of different parameters and their influence on the structure. These parameters are: the temperature, the metal, the oxidation state of the metal, the nature of the ligands (cot, Cp^{4i}), the solvent and the temperature.

((Table 1))

Results and Discussion

1. Choice of temperature, assignment:

As a first approach, the chemical shift temperature dependence of the complexes was studied. It is well-known that paramagnetic organolanthanides display temperature-dependent NMR spectra disturbing both chemical shifts and resolution. ^[17]

The goal of this experiment was to determine the best temperature for T_1 measurement, i.e., the temperature at which the spectrum exhibited an enough good resolution with no signal overlaps. For most of the complexes this was reached near the highest temperature of the study, typically a few degrees below the solvent boiling point (near 363K, Fig. 1). This was particularly the case of the neodymium complex (cotNdCp^{4i}) due to the strong paramagnetic character of this metal. In fact this latest complex gave broad lines even at high temperature but it was possible to distinguish all signals with only two recovering lines while at room temperature most of the lines could not be distinguished from the noise.

((Figure 1))

After the temperature had been chosen, it was necessary to complete the assignment. Actually, whatever the complex, there are 4 non equivalent methyls and 2 non equivalent methynes all belonging to the four isopropyl groups attached to the Cp unit. This indicates thus that there are 2 different types of isopropyl groups. According to the symmetry of the Cp⁴ⁱ ligand, two equivalent isopropyls are located in α -position from the Cp methyne (HCp) and the second type is attributed to both isopropyls located in β -position from the HCp (scheme 1).

((Scheme 1))

The presence of 4 non equivalent methyls for 2 non equivalent isopropyls means that both methyls belonging to the same isopropyl are non equivalent (Figure 2). This is explained by the presence of the metal located on one side of the Cp plane. Thus there are two resulting different Cp sides: one *endo* side and one *exo* side. Such a molecular arrangement affords obviously a diastereotopic system of methyls. [22,23]

It is noteworthy that the spectrum of KCp⁴ⁱ displays only two methyl types: one type corresponding to the α isopropyls and the other one to the β isopropyls. Actually, the geometry of this compound is different from that of the complexes under study. KCp⁴ⁱ is an ionic compound, the potassium ion is not linked to the Cp ring as neodymium or samarium can be and in that case, both *endo* and *exo* sides do not exist. The NMR spectrum can be explained in terms of symmetry if the potassium is not coordinated face on to the Cp ring, both sides becoming equivalent, or if it alternatively roams quickly from side to side in THF. [24] Finally, methyls belonging to the same isopropyl group are enantiotopic in the KCp⁴ⁱ complex.

((Figure 2))

The next step in the assignment procedure was to connect methyls with methynes of the same isopropyl. This was done using the 2D-COSY experiment which gives correlations between coupled protons (Figure 3). For some complexes like the cotNdCp⁴ⁱ, no correlation could be observed due to the very fast relaxation occurring in this compound. As a matter of fact, the incrementable delay placed in the 2D sequence to create the second dimension results in a complete relaxation of protons prior to the acquisition step and thus no signal could be detected. The assignment could be achieved for Sm complexes as well as for the potassium salt.

((Figure 3))

Two indecisions still remained at this step of our studies: the identification of the α and the β isopropyls, and of the *exo* and *endo* methyls. The first problem was solved by performing a NOE-difference experiment in which the HCp signal was irradiated. We observed a significant variation of one H(¹Pr) signal intensity. This isopropyl group was thus assigned to the closest α (and α') position. Such an experiment could not be conducted on all complexes due to fast relaxation but was unambiguous for $\text{BH}_4\text{Sm}(\text{Cp}^{4i})_2$. These results were further generalized to the other complexes. The identification of *endo* and *exo* groups was achieved using T_1 measurement experiments (see below).

2. Relaxation study:

The non paramagnetic KCp^{4i} was first studied as reference. As we remarked previously, the potassium cation does not generate an asymmetry on the Cp ring at the origin of both *endo* and *exo* sides noticed in the other complexes. Moreover the metal should have a very poor influence on the Cp^{4i} relaxation rates since it is not paramagnetic in contrast with the other complexes under study. Relaxation times of KCp^{4i} are reported in table 2. These values are in conformity as regards to those usually observed for small organic molecules. α and β methyne signals exhibit relaxation times of 2.77 and 2.11 s, respectively, which are rather different values. However, in such diamagnetic compound, dipolar relaxation is predominant as compared to other relaxation processes and can explain the observed difference. β -methyne protons undergo the influence of methyls belonging to the same isopropyl as well as the one of methyls belonging to both neighbouring isopropyls. In the case of α -methyne protons, there is only one neighbouring isopropyl inducing thus a less efficient dipolar relaxation. α and β methyls display relaxation times of 1.60 and 1.84 s respectively, this small difference seems to be not very significant. Relaxation times measured for KCp^{4i} do not present a structural interest but these values are interesting to be compared to those measured on paramagnetic complexes.

((Table 2))

As expected, all paramagnetic complexes display relaxation times drastically reduced as compared to those reported for KCp^{4i} . This decrease is due to the presence of the paramagnetic metal and distances between protons and the metal may have a strong influence on relaxation times.

Straight lines corresponding to relaxation of cotSmCp^{4i} protons are drawn on figure 4 as an example. Relaxation times of the different complexes under study are reported in table 2.

((Figure 4))

As regards to the variety of complexes under study, the metal nature can be evaluated by comparing both cotSmCp^{4i} and cotNdCp^{4i} . Samarium complexes usually give ^1H spectra which are better resolved than those corresponding to neodymium derivatives which display spectra with very broad lines. [5,6,25] From this consideration, one can expect shorter T_1 for neodymium than for samarium complexes. T_1 values reported in table 2, confirm this. As a matter of fact, cotNdCp^{4i} T_1 values are much shorter than those observed for cotSmCp^{4i} . The ratio $T_1(\text{cotSmCp}^{4i})/T_1(\text{cotNdCp}^{4i})$ takes values included between 10, in the case of the cot protons and 30, in the case of the isopropyl methynes. Nevertheless, it is noteworthy that in both complexes the same tendency in the T_1 distribution is observed. Actually, the HCp proton has the shortest T_1 relaxation in both compounds, followed by the cot protons. Such short HCp T_1 values were not observed for KCp^{4i} . Obviously the diamagnetic character of the compound explains larger T_1 values, but in the case of KCp^{4i} , HCp exhibits the largest T_1 value. As explained previously, dipolar relaxation is the most important relaxation in KCp^{4i} and the HCp is the most distant proton from the other ones, thus explaining the lack of efficiency in its relaxation mechanism. In the cases of both cotSmCp^{4i} and cotNdCp^{4i} complexes, paramagnetic relaxation is dominating and the shorter HCp T_1 values, as compared to those of other nuclei, indicate that HCp is the nearest proton from the metal ion. This remark is valid for all complexes under study since they all display very short HCp T_1 value.

Other interesting T_1 values concern the methyl groups. In all complexes T_1 values corresponding to the four non equivalent methyl group types could be measured leading each time to the same tendency: i) one value is much longer than the others; ii) two methyl group types have intermediate values of the same order; iii) the last methyl type exhibits a T_1 value a little bit smaller than the intermediate value; iv) methyls exhibiting respectively the shortest and longest T_1 belong to the same isopropyl type located in α position to the HCp nucleus and thus methyls with intermediate T_1 values belong to isopropyls in β position to HCp.

These results give important information concerning the complexes geometry. It seems that α isopropyl groups take an orientation in which one methyl group is far from the paramagnetic center while the other one is much closer to the metal. Taking in consideration that the metal is located under the Cp ring plane, this means that α -isopropyl groups take an orientation in which one methyl (with the longest T_1) is located on the *exo* side of the Cp ring plane while the other one (with the shortest T_1) is located on the *endo* side of this plane. The conformation the most likely dispatches the *exo* methyl in the plane perpendicular to the Cp ring. In this situation, this methyl is located as far as possible from the paramagnetic center. It is noteworthy, given the tetrahedral geometry of sp^3 carbons, that in this case *endo* methyls are not as close as possible from the metal. Also, this

conformation dispatches α -isopropyl methynes slightly on the *endo* side but not far from the Cp ring plane (Scheme 2).

Thus, whereas diastereotopy of methyl groups does not give any information about possible free rotation of isopropyls on the basis of chemical shifts, the fact that such a T_1 difference could be observed for methyls belonging to the same isopropyls, clearly indicates a tendency to hindered rotation.

((Scheme 2))

We can notice that β -isopropyl methynes have relaxation times close to those measured for α -methynes. If we consider that paramagnetic relaxation and thus the proximity of the metal is the predominant mechanism of relaxation, this indicates that α - and β -methynes are approximately at the same distance from the metal. Nevertheless, β -methyls adopt a quite different orientation from their α - homologues, since they display relaxation times included between both values observed for α -methyls. Moreover, the difference between both methyls belonging to a same β -isopropyl is rather small as compared to the one measured between α -isopropyl methyls. This suggests an orientation of the β -isopropyls in which methyls have positions probably not far from the plane of the Cp ring. According to the fact that α *endo* methyls have the shortest relaxation time (as compared to other methyls), β methyls might be on the *exo* side due to their longer T_1 (scheme 3).

((Scheme 3))

All these structural considerations are valid for the complete series of paramagnetic complexes under study, whatever the metal nature or its oxidation state. Comparison of cotSmCp^{4i} and $\text{BH}_4\text{Sm}(\text{Cp}^{4i})_2$ shows the influence that other ligands might have on the Cp^{4i} relaxation. In fact, replacing the cyclooctatetraenyle by a borohydride and a second Cp^{4i} induces a small decrease of the T_1 values. This indicates that if the general geometry of Cp^{4i} is the same, the distances between the metal and the Cp^{4i} might be different in both complexes. Actually, the Sm-CP distances have been found at 2.40 Å in cotSmCp^{4i} [51] and 2.44 and 2.47 Å in $\text{BH}_4\text{Sm}(\text{Cp}^{4i})_2$ [61] (CP is the centroid of the Cp^{4i} ring). Although the distance is slightly shorter in the cot complex, T_1 values are higher. But the geometry of the two complexes is different: cotSmCp^{4i} is a metallocene of Sm^{III} , while $\text{BH}_4\text{Sm}(\text{Cp}^{4i})_2$ bears one supplementary ligand.

Also, X-ray diffraction analyses indicated that $\text{BH}_4\text{Sm}(\text{Cp}^{4i})_2$ exhibits one very short **Sm-H(CH₃)** distance (2.50 Å). This could be due to an agostic interaction. A similar feature, though less pronounced, was also detected in the cotLnCp^{4i} complexes (Nd, Sm). According to our NMR

experiments, it comes that such an interaction, which should lead to a much shorter T_1 value, is not retained in solution.

Changing the oxidation state of the metal also has important effects on relaxation times. $\text{Sm}(\text{Cp}^{4i})_2$ has actually much lower relaxation times than $\text{BH}_4\text{Sm}(\text{Cp}^{4i})_2$, while its Sm-CP distances are slightly higher, as expected for Sm^{II} (2.51 Å):^[5] but the more pronounced paramagnetism of Sm^{II} against Sm^{III} is responsible of the important decrease of T_1 values.

As previously noticed these changes do not influence the Cp geometry; the differences in relaxation times are undoubtedly due to different electronic configuration of the metal to which paramagnetism is strongly bound.

Finally, $\text{BH}_4\text{Sm}(\text{Cp}^{4i})_2$ has been submitted to T_1 measurements at two different temperatures (room and high temperatures) while other complexes were generally studied at high temperature only, due to the better resolution in these conditions. This was done mainly to verify that the complexes geometry does not change in the range [298K-373K]. Obviously, some differences are observed by comparing T_1 values measured at both temperatures since temperature influences the motions of the complexes. But whatever the temperature of the study, the same conclusions can be drawn concerning the [Sm]- Cp^{4i} geometry. The most probable conformation of the Cp^{4i} ligand in all the complexes under study is represented figure 5.

((Figure 5))

In order to validate our approach, Ln-H distances computations were investigated from T_1 data. It is well known that relaxation rates are proportional to $1/r^6$ where r can be considered as the metal-H distance since paramagnetic relaxation is the dominant relaxation process^[21]. In our experimental conditions, only relative distances are easily accessible. For each complex under study, we took as reference the Ln-H(Cp) distance found in its X Ray structure. Among all Ln-H distances, the latter is supposed to fluctuate the least from the solid state to the solution due to the Cp rigid plane structure. All other distances were calculated from this reference. The results are gathered in Table 3.

((Table 3))

One can observe that the computed distances fit quite well with those determined from X Ray studies. As expected, a significant difference is found between *endo* and *exo* $\text{CH}_3\alpha\alpha'$. On the other hand, whereas in the solid state the Cp^{4i} ligand displays *endo* and *exo* $\text{CH}_3\beta\beta'$, this seems to be no more the case in solution. The Ln-H($\text{CH}_3\beta\beta'$) distances take values that are quite similar, which corresponds well to methyl groups both located close to the plane of the Cp ring.

Conclusion

Structural information of four paramagnetic organolanthanides could be deduced using ^1H NMR spectroscopy. Despite the paramagnetism, the molecular conformation of the hyperbulky tetraisopropylcyclopentadienyl involved in these complexes was fully resolved, with 1D, 2D COSY and T_1 relaxation experiments.

The specific conformation is retained at high temperature, whatever the other surrounding ligands, the nature (neodymium or samarium) and the oxidation state (divalent or trivalent) of the lanthanide atom. The molecular structure in solution differs from the one precedently observed in the solid state. Such a conclusion could be drawn thanks to T_1 relaxation experiments.

This contribution shows that structural features may not be retained in solution in the case of the bigger early lanthanides; one may take this in consideration at the time of mechanistic studies. And finally, paramagnetism of lanthanide complexes does not necessarily preclude extensive NMR investigations for the determination of conformations in solution.

Experimental Section

General Remarks:

1. Complexes syntheses:

All complexes were prepared as published.^[5,6] The potassium derivative KCp^{4i} was obtained by the classical reaction of KH with HCp^{4i} in THF.

2. NMR study:

All samples were dissolved in toluene- D_8 previously dried on Na/K blend. Toluene was chosen as solvent due to its high boiling point as compared to benzene. Toluene transfer was performed under vacuum distillation in NMR tubes equipped with a teflon valve (Young). After transfer, samples were stored under argon pressure. For the KCp^{4i} compound THF- D_8 was used as solvent due to its non solubility in toluene or benzene. All NMR experiments were recorded on a Bruker Avance 500 spectrometer working at the field of 11 teslas. Initially, several spectra were recorded as a function of the temperature in order to determine the best conditions for the relaxation times measurements. Usually the highest resolution and thus the best conditions were reached at 363 or 373 K, depending on the nature of the complex. Assignment of the proton signals was performed using a 2D COSY experiment. The classical sequence using magnitude correction was used. No gradients were used for the complexes containing a paramagnetic metal because the additional delays involved in the pulse sequence result in a complete loss of magnetization due to the very short relaxation of the compounds under study. Gradient field 2D-COSY pulse sequence was used for the only KCp^{4i} non paramagnetic native complex. In this case, the Z-gradient powers were set to 10 % while the gradient pulse and the delay for gradient recovery were 1 ms and 100 μs , respectively. In order to complete the assignment of the *exo* and *endo* substituents, a 1D NOE-difference experiment was performed; the HCp signal was irradiated to point out the closest α

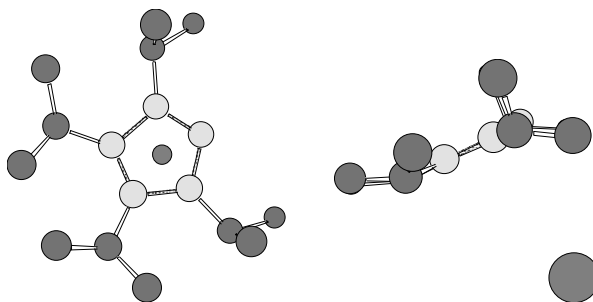
and α' isopropyl groups. Pulse lengths were calibrated prior to each relaxation times measurements. Typically, the 90° proton pulse was $5.6 \mu\text{s}$ at the attenuation of 0 dB. T_1 measurements were performed by using the conventional inversion recovery technique. Several experiments including 256 scans were recorded with 20 different durations between the 180° and the 90° pulses. These experiments were recorded in a random order of the durations to minimize errors due to adjustment drifts occurring as a function of the time. The delay between each scan was chosen to be much larger than 5 times T_1 . After Fourier transformation, intensities of the different signals were collected and the curves $\ln(M_0 - M_z)$ were drawn as a function of the delay between the 180° and the 90° pulses. The constant M_0 was evaluated by averaging 2 experiments involving long delays much larger than 5 times the T_1 . The slopes of the obtained straight lines were then computed and led thus to the T_1 values which are known to be the opposite reverse of the slopes ($-1/T_1$).

Acknowledgments

The authors wish to thank Pr. H. Sitzmann for the gift of the Cp^{4i} ligand and Pr. A. Dormond and Dr. D. Barbier-Baudry for helpful discussions.

Graphical Abstract

Full ^1H NMR (1D, 2D COSY, T1 relaxation) study of paramagnetic organolanthanides bearing the tetraisopropylcyclopentadienyl ligand allowing to determine the conformation in solution.



CAPTIONS

Table 1. Molecular complexes under study

Table 2. T_1 (ms) data of molecular complexes at 298 K

Table 3. Metal-H distances (\AA , calculated from NMR T_1 / determined from X Ray)

Scheme 1. Representation of the Cp^{4i} ligand showing the different types of isopropyl groups and the two different sides of the molecule when a metal is coordinated.

Scheme 2. Conformation of the α -isopropyl group dispatching one methyl as far as possible from the metal.

Scheme 3. Conformation of the β -isopropyl group dispatching the two methyls nearly equidistant to the metal.

Figure 1. Evolution of the ^1H NMR spectrum of cotNdCp^{4i} with temperature (C_7D_8)

Figure 2. 500 MHz ^1H NMR spectrum and assignment of the complex cotSmCp^{4i} recorded at 298 K.

Figure 3. 2D COSY map of the complex cotSmCp^{4i} recorded at 298 K. Assignments of both isopropyl group types are shown.

Figure 4. cotSmCp^{4i} T_1 (^1H) relaxation plots recorded at 298 K

Figure 5. 3D representation of the $[\text{Cp}^{4i}\text{-Sm}]$ moiety of cotSmCp^{4i} orthogonally to the Cp ring (left) and in the Cp ring plane (right).

TABLES

Table 1:

Complex formula ^a	Metal (ox. state)	Ligand 1 (charge)	Ligand 2 (charge)	Ligand 3 (charge)	Temperature for T ₁ measurements
KCp ⁴ⁱ	K (+I)	Cp ⁴ⁱ (-I)			298K
cotSmCp ⁴ⁱ	Sm (+III)	Cp ⁴ⁱ (-I)	cot (-II)		298K
BH ₄ Sm(Cp ⁴ⁱ) ₂	Sm (+III)	Cp ⁴ⁱ (-I)	Cp ⁴ⁱ (-I)	BH ₄ (-I)	298K/363K
cotNdCp ⁴ⁱ	Nd (+III)	Cp ⁴ⁱ (-I)	cot (-II)		363K
Sm(Cp ⁴ⁱ) ₂	Sm (+II)	Cp ⁴ⁱ (-I)	Cp ⁴ⁱ (-I)		373K

^a cot = C₈H₈, Cp⁴ⁱ = HC₅ⁱPr₄

Table 2:

Complex formula	H _{Cp}	CH _α	CH _β	CH ₃ (α,α' <i>exo</i>)	CH ₃ (α,α' <i>endo</i>)	CH ₃ (β,β' <i>exo</i>)	CH ₃ (β,β' <i>endo</i>)	cot/BH ₄
cotSmCp ⁴ⁱ	53.4	212.8	236.4	515.5	208.8	303.0	227.8	73.7
BH ₄ Sm(Cp ⁴ⁱ) ₂	27.5	201.2	152.9	471.7	173.3	- ^c	217.4	3.6
BH ₄ Sm(Cp ⁴ⁱ) ₂ ^a	34.5	244.5	240.4	800.0	248.1	392.2	308.6	2.6
cotNdCp ⁴ⁱ ^a	1.8	7.7	7.1	32.9	9.8	15.3	11.5	6.8
Sm(Cp ⁴ⁱ) ₂ ^b	11.4	37.1	- ^c	176.8	34.0	53.0	37.6	-
KCp ⁴ⁱ	4169	2775	2111	1605 (α, α')		1839 (β, β')		-

^a Recorded at 363K. ^b Recorded at 373 K. ^c Signal overlapped

Table 3:

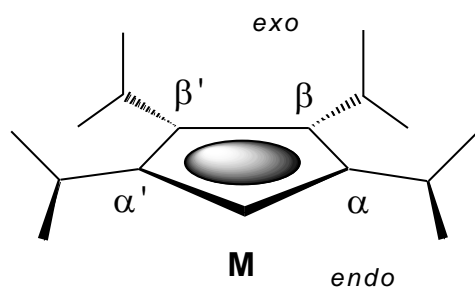
Complex formula	H _{Cp} ^a	CH _α	CH _β	CH ₃ (α,α' <i>exo</i>)	CH ₃ (α,α' <i>endo</i>)	CH ₃ (β,β' <i>exo</i>)	CH ₃ (β,β' <i>endo</i>)	cot/BH ₄
cotSmCp ⁴ⁱ	3.19	4.02/3.87	4.09/3.95	4.65/5.39	4.00/4.11	4.26/5.39	4.06/3.82	3.37/3.29
BH ₄ Sm(Cp ⁴ⁱ) ₂ ^b	3.19	4.45/4.06	4.25/3.90	5.13/5.46	4.34/4.31	- /5.49	4.51/4.13	2.28/2.68
cotNdCp ⁴ⁱ	3.26	4.15/3.95	4.10/4.01	5.29/5.44	4.32/4.10	4.66/5.40	4.44/3.79	4.07/3.32
Sm(Cp ⁴ⁱ) ₂	3.27	3.98/3.92	- /4.04	5.16/5.49	3.92/4.20	4.22/5.43	3.99/3.76	- / -

^a X ray data, used as reference for NMR computed distances. ^b From T₁ recorded at 363K.

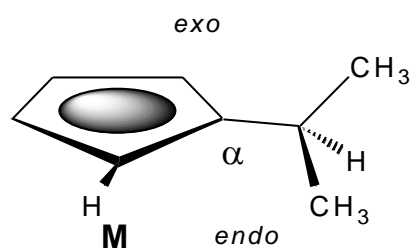
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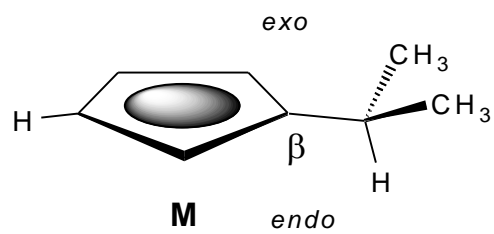
SCHEMES



Scheme 1



Scheme 2



Scheme 3

FIGURES

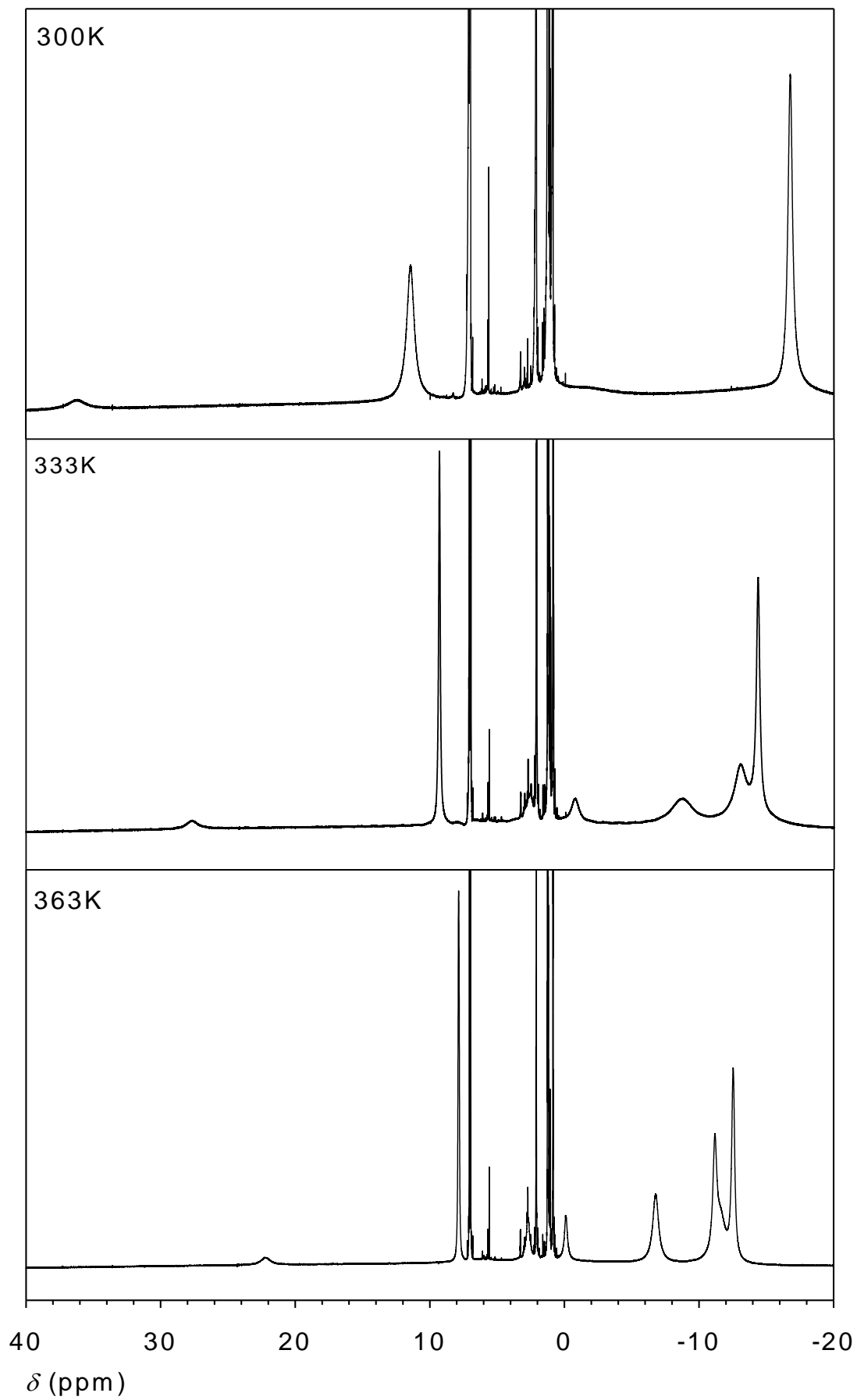


Figure 1

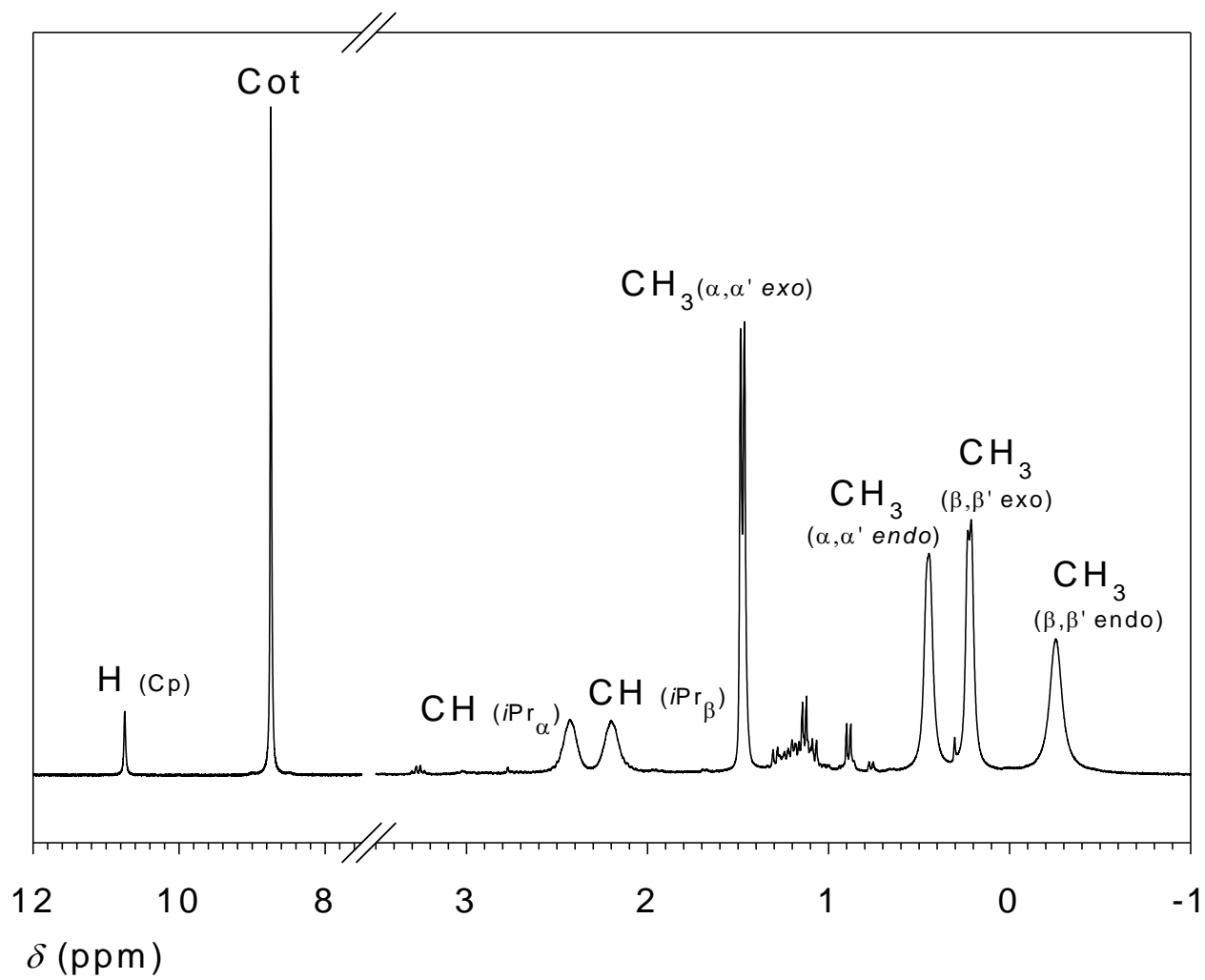


Figure 2

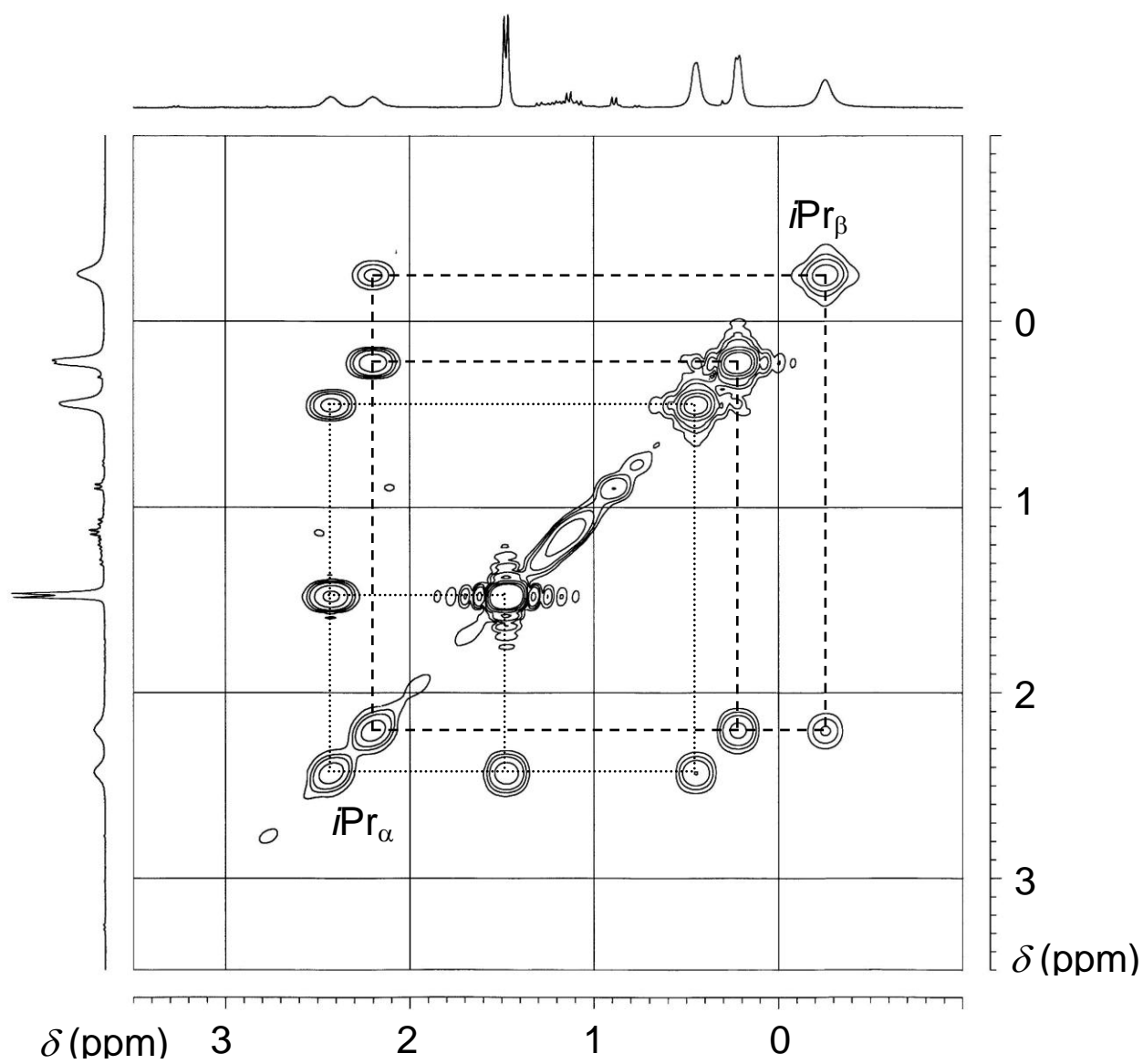


Figure 3

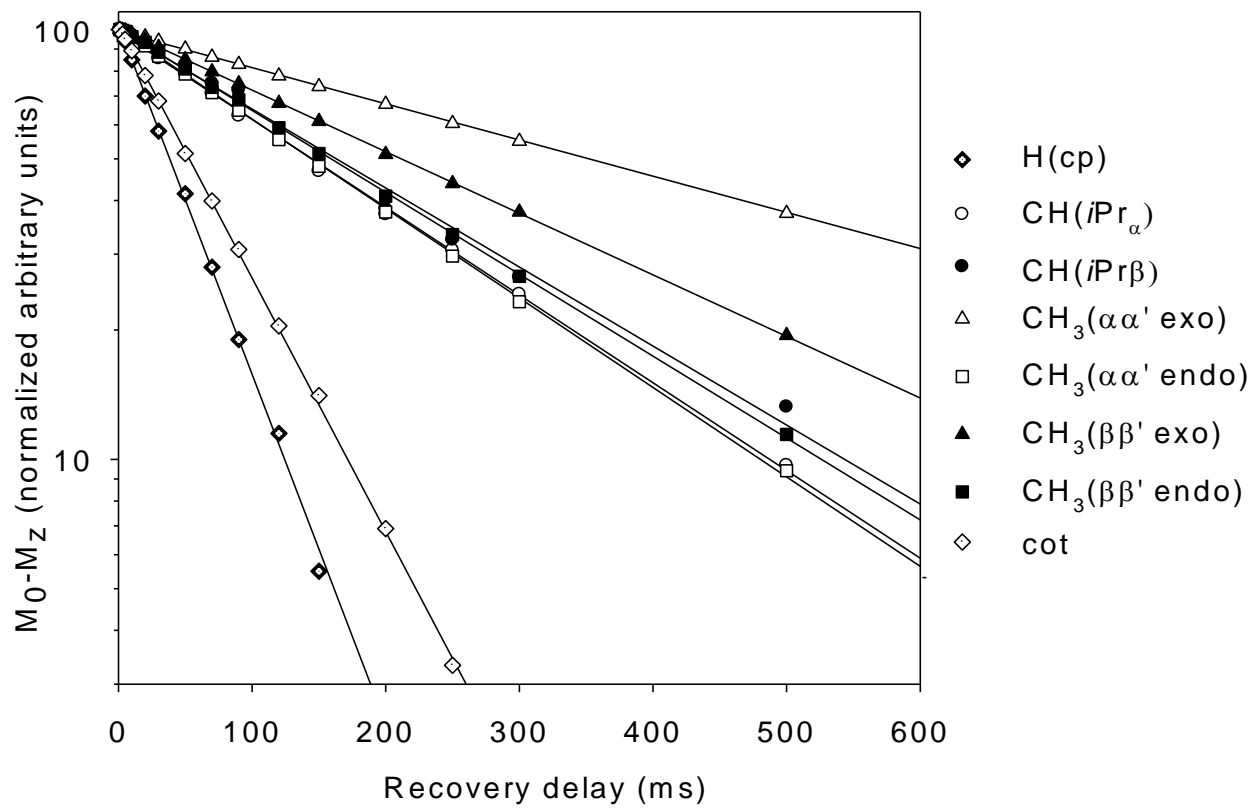


Figure 4

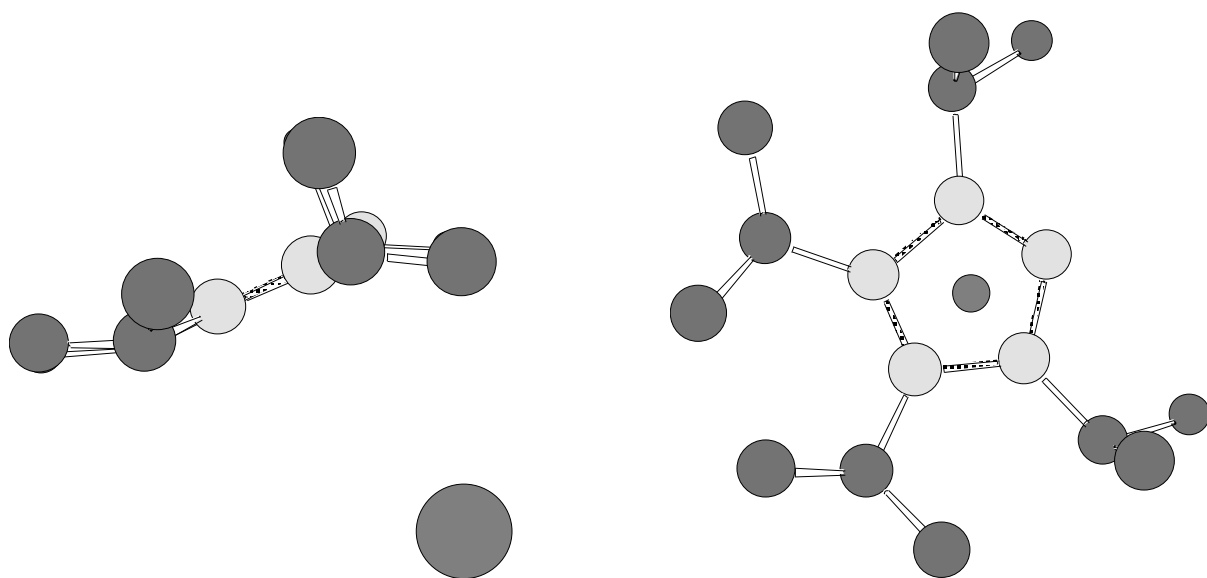


Figure 5