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# THE REARRANGEMENT MECHANISM OF $\eta^3$-ALLYLIRON TRICARBONYL HALIDES

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## Summary

Spin saturation transfer and lanthanide shift reagent studies demonstrate that the *endo* conformer is stable in solution. The predominant mode of conformer interconversion is proven to be rotation rather than a $\sigma$—$\pi$ interconversion.

## Introduction

Allyl complexes of transition metals often exist in two conformations because of the shape of the $\pi$-bonded ligand [1,2]. Thus, in $\eta^5$-$(C_5H_5)M(CO)_n$ ($\pi$-allyl) complexes (where $n$ =2, M = Mo or W [3,4], and $n$ = 1, M = Fe [5—7]), two isomers are seen which differ in the orientation of the allyl with respect to the cyclopentadienyl ligand. The stereochemistry, relative stabilities of conformations and interconversion processes for these compounds have been investigated previously. Two conformations are also observed in the compounds $\eta^3$-allyl-$Fe(CO)_3X$ (where X = halide); however, before the work reported here, the identity of the most stable conformer in these compounds was uncertain because of conflicting assignments of NMR spectra. Furthermore the nature of the isomer interconversion process had not been investigated because decomposition above 30°C prevented the normal use of the NMR line-broadening method. The NMR technique of spin saturation transfer, however, allows measurement of much slower rates than the line broadening method [8,9]. Although it is generally less accurate, it does allow for measurement of barriers in processes such as these, which are not accessible by other means. Spin saturation transfer also provides important mechanistic details because the site to which transfer occurs may be determined, as well as the rate.

Earlier work on the $\eta^3$-allyliron tricarbonyl halides revealed that their proton NMR spectra were more complex than would be expected for a single symmetrical allyl [10,11]. Nesmeyanov et al. rationalized these spectra in terms of two symmetrical isomers which differed in the orientation of the allyl with respect

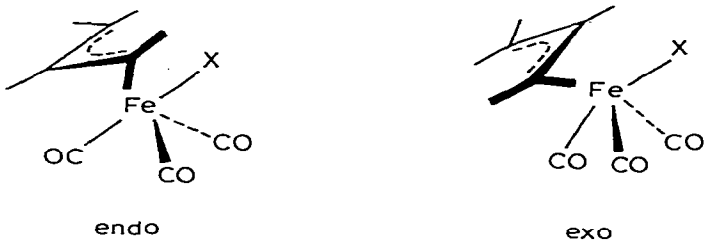


Fig. 1. The *endo* and *exo* conformation of $\eta^3$-allylFe(CO)$_3$X.

to the halide [12]. An X-ray crystal structure of the iodide [13] demonstrated that the isomer which crystallized was the one in which the central proton of the allyl points away from the halogen (Fig. 1) and which we designate as the *endo* isomer *. By analogy with other allyl complexes, it follows that the second stable conformer should have the *exo* configuration shown in Fig. 1. Nesmeyanov was able to show that the properties of the complexes, in particular their proton NMR, followed a regular trend with variation of halide substituent. He assigned the major isomer for all the halide complexes on the basis of comparison of chemical shift to the magnetic anisotropy of the halogens to the same conformation as that found in the crystal structure. A more recent $^{13}$C NMR study of $\eta^3$-allyliron tricarbonyl iodide by Randall et al. [14] assigned the major isomer to the opposite structure of that assigned by Nesmeyanov [12]. Both assignments were based on assumptions about chemical shift changes and neither of these groups were able to investigate the interconversion process of the isomers.

Because of the conflicting assignments, we undertook a study of a series of the allyliron tricarbonyl halide and pseudohalide compounds to determine unequivocally the correct assignment and to investigate the mechanism and barrier for isomer interconversion. The assignment of isomer stereochemistry for these compounds was accomplished with the isocyanate analog, which we show possesses the same isomer stereochemistry as the halide complexes and allows binding to lanthanide shift and relaxation reagents. The isomer interconversion process has been investigated using proton NMR spin saturation transfer.

## Results

The series of compounds investigated are $\eta^3$-allylFe(CO)$_3$X, where X = I, Br, Cl, NCO. In the series all physical properties vary smoothly from iodide to chloride and isocyanate. The iodide is a very dark brown.

The chemical shifts for this series of compounds are summarized in Table 1. The *syn* and *anti* protons * of the minor isomer appear upfield of the corresponding protons of the major isomer in all the compounds studied. As the halide

* Nomenclature by analogy to that of ref. 6.

* *Syn* and *anti* refer to the orientation of the terminal allyl protons relative to the central proton. The *syn* proton is on the same side of the C—C bond as the central proton, i.e., effectively "*cis*" to it. *Syn* protons are readily identified by their smaller coupling to the central proton (6—8 Hz) compared to that of the *anti* proton (10—14 Hz).

TABLE 1

CHEMICAL SHIFTS AND ISOMER RATIOS OF $\eta^3$-$C_3H_5Fe(CO)_3X$ DERIVATIVES

Chemical shifts (δ) ppm downfield from TMS observed at 100 MHz.

| X | Solvent | *syn* | | *anti* | | central | | isomer ratio |
|---|---|---|---|---|---|---|---|---|
| | | major | minor | major | minor | major | minor | major/minor |
| I | $CDCl_3$ | 4.24 | 3.68 | 3.78 | 2.39 | 4.71 | 5.83 | 1.3 |
| | acetone-$d_6$ | 4.43 | 3.83 | 3.72 | 2.64 | 4.98 | 5.81 | 2.6 |
| Br | $CDCl_3$ | 4.37 | 4.05 | 3.43 | 2.60 | 4.92 | 5.38 | 6.6 |
| | acetone-$d_6$ | 4.63 | 4.14 | 3.60 | 2.86 | 5.33 | 5.3 [b] | 11. |
| Cl | $CDCl_3$ | 4.58 | 4.32 | 3.28 | 2.73 | 5.20 | [b] | 25. |
| | acetone-$d_6$ | 4.71 | 4.26 | 3.11 | 2.92 | 5.44 | [b] | 36. |
| NCO | $CDCl_3$ | 4.47 | 4.32 | 3.05 | 2.65 | 5.15 | 5.05 [c] | 24. |
| | acetone-$d_6$ | 4.68 | 4.38 | 2.90 | 2.90 [a] | 5.42 | [b] | 32. |

[a] The *anti* proton resonance of the minor isomer is hidden under the *anti* resonance of the major isomer. [b] Obscured by the central proton resonance of the major isomer. [c] Resonance position determined by INDOR.

is varied from iodide to chloride and isocyanate, the chemical shift differences between the isomers decrease. The *syn* protons for both isomers move downfield along the series, but those of the minor isomer move to a greater extent, with the net result that the shift difference between isomers shrinks to 0.26 ppm for the chloride. The *anti* proton resonances, meanwhile, move toward each other. The *anti* resonance of the major isomer moves upfield, while that of the minor isomer moves downfield. These trends suggest that the major isomers for all complexes are consistently of the same configuration. Thus, one characteristic feature that distinguishes the isomers is that the *syn* and *anti* resonances of the less stable configurations are always at higher field than the corresponding resonances of the more stable configurations.

The shift differences between the isomers appear to be determined by the electronegativity or polarizability of the X group, which changes systematically from one compound to the next in the series. Furthermore, in the series from iodide to chloride, the changes in chemical shift are accompanied by an isomer ratio change in favor of the major isomer. An increase in solvent polarity causes a similar change in chemical shift and isomer ratio for each member of the series. It is important to note that the isomer ratio for each compound changes in the same sense when the solvent polarity is changed; that is, increased solvent polarity increases the proportion of the major isomer in all of the complexes. These trends and the correlation of isomer population with chemical shift can be readily seen by plotting the data presented in Table 1, as shown in Fig. 2. The isocyanate complex (indicated by arrows in Fig. 2) also follows the trends. Thus, as suggested previously by chemical shift variations, the isomer ratio trends and the solvent effects upon them provide further evidence that the major isomers for all of the compounds have the same configuration. Therefore, an assignment of stereochemistry for the isomers of the isocyanate complex will determine the stereochemistry for the entire series.

The actual assignment of structure for the isocyanate complex was made with the use of a combination of shift and relaxation reagents. Throughout this work,

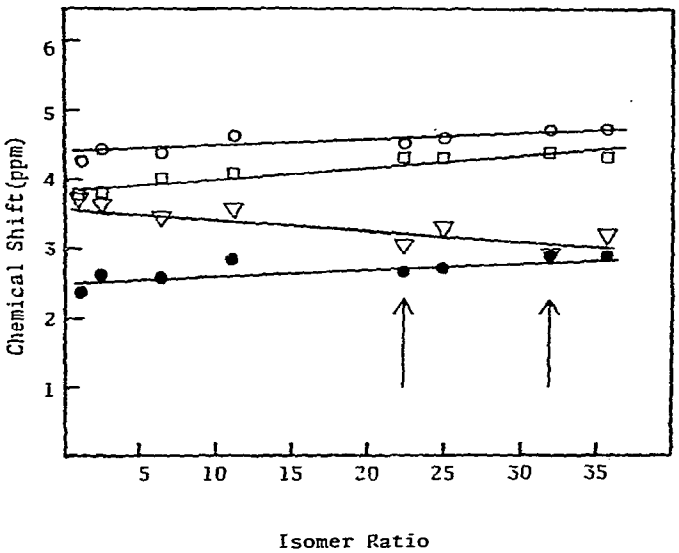


Fig. 2. The trends in chemical shift vs. isomer ratio for $\eta^3$-allylFe(CO)$_3$X complexes in $CDCl_3$ and $(CD_3)_2CO$. Arrows indicate the data for X = NCO. This is a graphical presentation of the data in Table 1. The halide and the solvent for each vertical set of shifts can be identified by the isomer ratio given in Table 1. ○, *syn* major isomer; □, *syn* minor isomer; ▽, *anti* major isomer; ●, *anti* minor isomer.

the NCO moiety was assumed to be N-bonded as is usually observed for transition metal organometallic compounds of this type [15,16]. Addition of Pr(fod)$_3$ * to a $CDCl_3$ solution of the isocyanate complex resulted in upfield shifts of the proton resonances. The lanthanide induced shifts relative to the *anti* resonance are compared in Table 2 to values calculated from geometric factors for both isomers. Spectra were also taken in the presence of Eu(fod)$_3$ which produced downfield shifts. The relative shifts paralleled those of Pr(fod)$_3$. However, the praseodymium shifts were larger and are, therefore, used for comparison to geometric calculations. Dipolar relaxation from an axially symmetric anisotropic magnetic dipole was assumed. The symmetry axis was taken as a vector from the iron atom through the NCO oxygen atom to the praseodymium atom and values of $(3\cos^2\theta - 1)/r^3$ determined relative to the assumed position of the praseodymium atom (see experimental). The calculated shifts are sufficiently insensitive to angle variations that qualitatively one expects nuclei nearest the Pr—OCN bond to shift the most. The approximations made here are justified by the internal consistency of the results and the correlations with the relaxation data discussed below. The observed lanthanide induced shifts (LIS) are summarized in Table 2. In the major isomer, the *anti* resonance is observed to shift the most, followed by the *syn* and then the central resonance. In the minor isomer, the pattern is reversed. The shift patterns for both isomers correspond with calculated values assuming the major isomer has the *endo* configuration and the minor isomer the *exo* configuration.

A somewhat more straightforward approach to geometry determinations by

* fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione.

TABLE 2

LANTHANIDE INDUCED SHIFTS FOR $\eta^3$-$C_3H_5Fe(CO)_3NCO$

In $CDCl_3$ produced by $Pr(fod)_3$; relative to *anti* proton.

| | Major | | | Minor | | |
|---|---|---|---|---|---|---|
| | *anti* | *syn* | central | *anti* | *syn* | central |
| Obs. | 1 | 0.52 | 0.44 | 1 | 1.9 | — |
| Calcd. | 1 | 0.42 | 0.36 | 1 | 1.2 | 1.7 |

NMR is through the use of relaxation reagents [17,18]. This method is not beset with the practical and theoretical [19] difficulties of shift reagents. The relaxation reagent $Gd(fod)_3$ produces a dominant relaxation mechanism which is proportional to $1/r^6$ where $r$ is the distance from the gadolinium to the atom in question. The $T_1$ relaxation times were measured by the inversion recovery method [9,20] at 270 MHz on a degassed $CDCl_3$ solution of the isocyanate which was 0.1 $M$ in $Gd(fod)_3$. The $T_1$ values are given in Table 3 along with the ratio of values compared to those calculated from distances of the protons to the gadolinium. The chemical shift of the central proton of the minor isomer is coincident with that of the major isomer. Since the central proton of the minor isomer would be the closest to the gadolinium and therefore have the broadest signal, as well as the lowest intensity, it could not be observed and its $T_1$ could not be determined. A large uncertainty exists for the $T_1$ values for several reasons. First, the short relaxation times require the use of very short pulse delays (<0.01 s), which we have found to be less reliable. Secondly, the minor isomer *syn* and *anti* resonances overlap partially with the corresponding resonances of the major isomer, which makes accurate determinations of their height difficult. Finally, the isocyanate complex is the least stable of all of the compounds studied and, even though the measurements were carried out at ca. 5°C, a small amount of paramagnetic decomposition products may have been present, thus producing an alternate source of relaxation. In spite of these limitations, the results are completely satisfactory, not only from a qualitative view, but also from the correlation of calculated and observed ratios in Table 3. The *anti* proton has the shortest relaxation time in the major isomer whereas, in the minor

TABLE 3

$T_1$ VALUES FOR $\eta^3$-$C_3H_5Fe(CO)_3NCO$ WITH $Gd(fod)_3$

In $CDCl_3$, ±0.005 s.

| | Major | | | Minor | |
|---|---|---|---|---|---|
| | *anti* | *syn* | central | *anti* | *syn* |
| $T_1$ | 0.035 | 0.081 | 0.099 | 0.089 | 0.062 |
| Ratios [a] | | | | | |
| Obs. | 1 | 0.43 | 0.35 | 1 | 1.4 |
| Calcd. | 1 | 0.31 | 0.16 | 1 | 1.8 |

[a] Relative to *anti* proton.

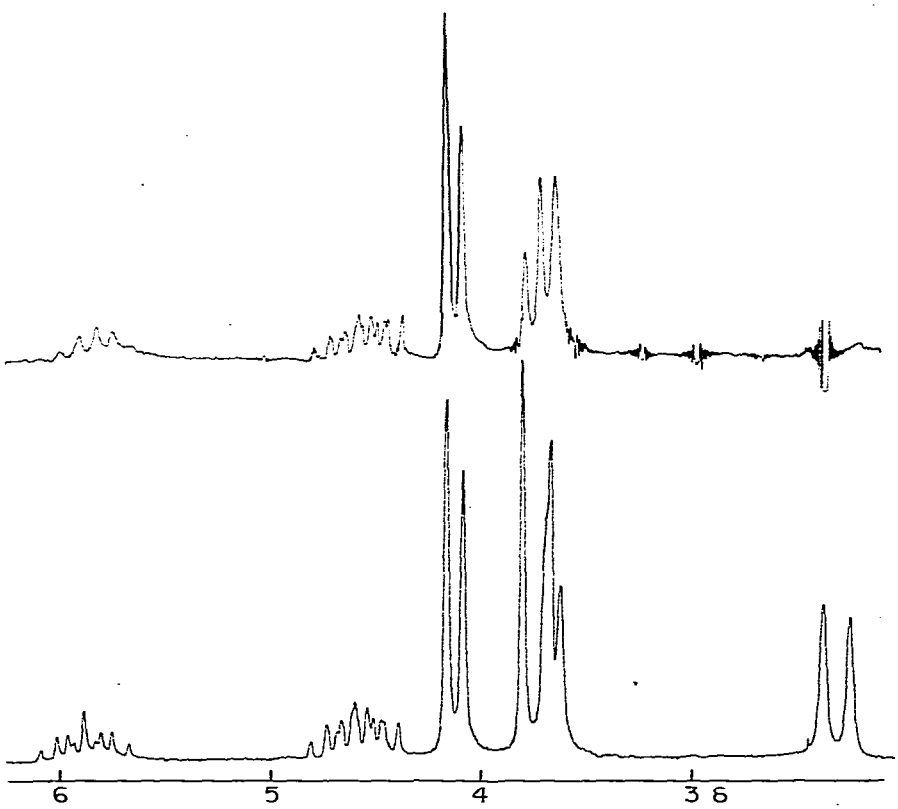


Fig. 3. A 100 MHz $^1$H CW saturation transfer experiment at 25°C. Saturation of the 2.39 δ *anti* resonance of the minor isomer of $\eta^3$-allylFe(CO)$_3$I decreases the intensity of only the 3.78 δ *anti* resonance of the major isomer. No significant intensity is lost from the 4.24 *syn* resonance of the major isomer as required for a $\pi$—$\sigma$ rearrangement. Note also the partial decoupling effects in the resonances of the minor isomer.

isomer, the *syn* proton is more efficiently relaxed. Again, the data for the major isomer correspond with that calculated for the *endo* configuration.

The mechanism and rate of isomer interconversion was determined using spin saturation transfer. The method was used in both CW mode at 100 MHz and FT mode at 270 MHz. In the CW mode, the *anti* proton of the minor isomer of allyliron tricarbonyl iodide was saturated with a strong RF field centered on the low field component of the doublet, while a weak observing field was swept through the remainder of the spectral region (Fig. 3). In the FT mode, a long (10 s) RF pulse centered on the *anti* proton resonance of the minor isomer was applied and after a 0.1 s delay a 90° observing pulse was applied and the FID immediately accumulated *. In both experiments, saturation was transferred only to the *anti* protons of the major isomer. To determine the rate of transfer, the $T_1$ relaxation times were measured by the inversion recovery method *. The *syn* and *anti* protons of both isomers have the same relaxation time of 2.87 s. The shorter relaxation time for the *syn* and *anti* protons can be attributed to the relative proximities of other protons. The change in intensity of the major isomer

* The spectra were reproduced previously [9].

*anti* signal can be used with the $T_1$ value for the site to calculate the rate of exchange between isomers. Equation 1 gives the relation between the observed intensity change and the lifetime of the saturated site which is the reciprocal of the first order rate constant out of that site (7). The rate constant for intercon-

$$\frac{I_\infty^A}{I_0^A} = \frac{\tau_A}{\tau_A + T_1} \quad (1)$$

version of the major isomer to the minor at 25°C is 0.85 $s^{-1}$. Only minor variations in rate, which are consistent with isomer ratio changes, appear to occur on changing the solvent.

## Discussion

The *endo* isomer as shown in Fig. 1 has the *anti* protons directed toward the halogen and would, therefore, be the closest to the bound lanthanide in the isocyanate compound. In the *exo* isomer, it is the central proton which is closest. The lanthanide induced shift (LIS) is proportional to the well known geometric factor $(1 - 3\cos^2\theta)/r^3$ [21—23] in which $r$ is the distance from the atom to the lanthanide and $\theta$ is the angle between the magnetic axis of the lanthanide (i.e., the lanthanide to binding site vector) and the vector from the lanthanide to the atom in question. The relaxation effect from the isotropic gadolinium complex is proportional to $1/r^6$ [17,18]. Thus, for both techniques, the greatest effect from the lanthanide will be for those atoms that are the closest *. The results clearly show that the major isomer is *endo* for the isocyanate compound since the *anti* protons have the largest LIS in the presence of $Pr(fod)_3$ and their relaxation time is reduced the most by addition of $Gd(fod)_3$. The minor isomer also can be assigned to the *exo* isomer since a greater effect is seen for the *syn* protons than the *anti* (the central proton is not seen for the minor isomer). The isocyanate complex also fits nicely into the complete series of compounds. Its properties of all the compounds are similar enough to imply that in the entire series, the major isomers have the same configuration. The chemical shift variation down the series of both isomers is gradual and is consistent with a smooth transition in properties. One would, therefore, not expect a sudden drastic change in isomer ratio. The change in isomer ratio upon changing the solvent from $CDCl_3$ to acetone-$d_6$ is in the same direction for each compound as are the accompanying chemical shift changes. We believe that this along with the correlation shown in Fig. 2 is conclusive evidence that we can assign the major isomers for the whole series to the *endo* isomer. This assignment corresponds to that of Nesmeyanov et al. [12] and not to that of Randall et al. [14].

### *Isomer interconversion*

A qualitative MO analysis of the allyliron tricarbonyl halide system suggested to previous workers [12] that the barrier to interconversion of the two isomers, if it occurred by rotation, would be lowest for the iodide. This would arise from

* In certain cases it is possible for the angular dependence of the LIS to compensate for changes in distance. If large variations in $\theta$ are not involved, the relative LIS for each proton tends to be determined by $r^{-3}$.

the increased donating ability of the iodide which weakens the allyl—metal interaction. There are, of course, other means of *exo* → *endo* interconversion in allyl isomers [1]. The spin saturation transfer experiment allows a straightforward solution to the problem of mechanism. The interconversion of isomers via a $\sigma$—$\pi$ mechanism would involve *syn*—*anti* interchange as would several other mechanisms [1]. The $\sigma$—$\pi$ mechanism is most often seen in cases in which added bases are able to coordinate to the $\sigma$-bonded allyl intermediate to complete the metal's coordination sphere. The $\sigma$—$\pi$ mechanism is also observed in a few cases without added bases, but these are usually systems of high coordination numbers [24]. If any mechanism which interconverted *syn* and *anti* protons were occurring, than saturation at an *anti* site would transfer saturation to both *syn* and *anti* sites of the other isomer. This experiment demonstrates, however, that isomer interconversion occurs by a rotation mechanism since saturation at the *anti* site of the minor isomer is transferred only to the *anti* site of the major isomer (Fig. 3). The iodide complex was the only one of the complexes in which saturation transfer occurred under 30°C thus showing it has the lowest barrier in the series as predicted [12]. The free energy barrier calculated for the iodide complex at 25°C is 17.4 kcal/mol. This value is similar to the activation barrier for the allyl isomer interconversion of the $\eta^5$-cyclopentadienyl-$\eta^3$-allyl-molybdenum and -tungsten dicarbonyl complexes which have free energies of 14—17 kcal/mol [4]. These compounds also interconvert by a rotation (or pseudorotation) mechanism. The similarity of barrier for the rotation mechanism in two different series of compounds plus the fact that the barrier for the iodide is less than that for the bromide and chloride indicate that the barrier to rotation is mainly electronic. The barrier is considerably less, however, than for the $\eta^5$-cyclopentadienyl-$\eta^3$-allyliron monocarbonyl complex which has the free energy barrier of 24 kcal/mol [6]. The higher barrier for the cyclopentadienyliron complex has been proposed to be due to a $\sigma$—$\pi$ mechanism based on the fact that terminal substitution in the *anti* position results in a somewhat more rapid *endo* to *exo* isomer interconversion than when substituted *syn* [6]. This does not unequivocally prove a $\sigma$—$\pi$ mechanism and the simple orbital diagram used to rationalize the mechanism could be applied to the system studied here. The higher barrier for the cyclopentadienyliron complex cannot readily be attributed to simple steric arguments, but further experimentation will be needed to determine the origin of these larger barrier differences.

## Experimental

NMR spectra were recorded using a Varian HA-100 and a Bruker HX-270 spectrometer. Routine spectra were recorded at temperatures below 10°C because of thermal instability of the compounds. The temperatures for the spin saturation transfer studies were calibrated using methanol sample. Infrared spectra were recorded with a Perkin—Elmer 421 spectrometer calibrated with DCl. Chemical analyses were performed by the Baron Consulting Analytical Laboratory, Milford, Connecticut.

The FT saturation transfer experiments were performed on a Bruker HX-270 spectrometer operated in the "gated-decoupling" mode. The details of measuring rates by this method have been discussed elsewhere [8,9].

The allyliron tricarbonyl iodide [25], bromide [26], and chloride [26] were prepared according to literature methods. All physical properties correspond to those reported previously. Crude reaction mixtures were chromatographed on silica gel with benzene, the solvent removed and the solids stored at −40°C and sublimed at 0.1 torr just prior to use. The formulation of the isocyanate complex was confirmed by NMR, IR and a satisfactory chemical analysis.

*Synthesis of $\eta^3$-$C_3H_5Fe(CO)_3NCO$*

The isocyanate complex was prepared from the iodide by metathesis with silver cyanate.

The iodide (3.0 g) and AgOCN (2.0 g) were added to 150 ml of degassed $CH_2Cl_2$ under a nitrogen atmosphere. The mixture was stirred for 3 h in the dark. The reaction can be monitored readily by the CO stretch of the cyanate at 2209.5 $cm^{-1}$. The mixture was then filtered through layers of Celite and silica to remove metallic silver and silver salts. The material was then chromatographed on silica gel. Removal of solvent yielded a yellow solid. The compound is thermally unstable and required vacuum sublimation just prior to use for a well resolved NMR spectrum. Considerable decomposition accompanied sublimation. Yields varied from 60 to 80%. M.p.: 76—77°C (dec.); IR: $\nu$(CO) 2051.3, 2016.7, 2095.5 $cm^{-1}$; $\nu$(NCO) 2209.5 (br) $cm^{-1}$.

*Geometry calculations*

To calculate the relative values of the LIS and the relaxation change due to the gadolinium, the reported crystal structure of the iodide complex was used [13] with other crystal structure data [15,27] to construct the geometry of the isomers for the isocyanate compound complexed to a lanthanide atom. The molecule was assumed to possess $C_s$ symmetry in solution and any variations in the two halves of the molecule were averaged. The bond length and angle data were used to construct atomic coordinates for each atom in both isomers. A summary of the basic bond lengths and angles employed is found in Table 4. The atomic coordinates were then used to calculate the necessary distances and angles.

TABLE 4

ASSUMED BOND LENGTHS AND BOND ANGLES

| Bond lengths (Å) | | Bond angles [a] (deg.) | |
|---|---|---|---|
| Fe—C (central allyl) | 2.30 | C—C—C (allyl) | 131 |
| Fe—C (terminal allyl) | 2.09 | H—C—C (*syn* and *anti*) | 120 |
| Fe—N | 1.80 | C—Fe—N (terminal allyl carbons) | 90 |
| N—C | 1.12 | C—Fe—C (equivalent carbonyls) | 109 |
| C—O (isocyanate) | 1.19 | C—Fe—C (nonequivalent carbonyls) | 91 |
| O—Gd | 2.60 | I—Fe—C (carbonyl carbon) | 82 |
| C—C (allyl | 1.40 | | |
| C—H | 1.08 | | |

[a] The iron—isocyanate—lanthanide linkage was assumed to be linear for the purpose of these calculations, although it is probably bent.

## Acknowledgments

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