

Cyclosiloxanes as Frameworks for Multimetallic Compounds. 3. ¹H NMR Spectra of Some Substituted Methylcyclosiloxanes¹

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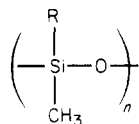
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A simple empirical approach based on the chemical environment of the resonating protons is used to assign ¹H NMR spectra of isomers of some substituted methylcyclosiloxanes of general structure -Si(CH₃)(R)O-_n (R = H, Br, Ph, Co(CO)₄, and CpFe(CO)₂). The CH₃ group attached to the silicon served as a useful NMR probe of isomeric structure. The chemical shifts of the methyl protons are correlated to the through-bond shielding effect governed by the nature of the substituent R at the silicon and to the through-space shielding effect controlled mainly by the nature and the spatial orientation of neighbors. The assignment and the integration of ¹H NMR spectra allowed the determination of the isomeric composition of all reported fully substituted compounds. A partial separation of D^{Fp}₄ isomers was carried out, and the assignment was done by comparing spectra from different isomeric compositions.

Introduction

This paper describes the characterization by proton nuclear magnetic resonance of a variety of methylcyclosiloxanes of the general formula 1. While infrared spec-



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- R = CH₃, D_n
 R = C₆H₅, D^{Ph}_n
 R = Br, D^{Br}_n
 R = Co(CO)₄, D^{Co}_n
 R = Fe(CO)₂Cp, D^{Fp}_n
 R = H, D^H_n

troscopy gives important information about the nature of substituents and the mode of bonding and mass spectrometry provides critical insight into the molecular weight and the mode of decomposition of the whole molecule under electron impact,¹ proton magnetic resonance spectroscopy was found to be the most useful tool for the investigation of isomeric structure and composition.

The first successful separation of geometric isomers of methylphenylcyclosiloxanes (D^{Ph}_n) by distillation and fractional crystallization, and their characterization by infrared spectroscopy, were reported by Lewis³ and by Young et al.⁴ In the early 1960s, the advent of NMR spectroscopy allowed the complete assignment of the ¹H spectrum of a natural mixture of D^{Ph}₄ isomers.⁵ Later, it was shown that the methyl group attached to the silicon atom in linear and cyclic siloxanes is an excellent NMR probe.⁶ The methyl chemical shift was found to depend on the ring size and upon the nature and orientation of neighboring groups.

Experimental Section

NMR Measurements. All ¹H NMR spectra were recorded on a Varian XL-200 (200-MHz, FT) spectrometer. Deuterated

(1) For earlier papers in the series see: Pelletier, E.; Harrod, J. F. *Can. J. Chem.* 1983, 61, 762. Harrod, J. F.; Pelletier, E. *Organometallics*, preceding paper in this issue.

(2) Present address: INRS-Océanologie, Rimouski, Québec G5L 3A1, Canada.

(3) Lewis, R. N. *J. Am. Chem. Soc.* 1948, 70, 1115.

(4) Young, C. W.; Servais, P. C.; Currie, C. C.; Hunter, J. J. *Am. Chem. Soc.* 1948, 70, 3758.

(5) Hickton, H. J.; Holt, A.; Homer, J.; Jarvis, A. W. *J. Chem. Soc.* 1966, C149.

(6) Homer, J.; Jarvis, A. W.; Holt, A.; Hickton, H. J. *J. Chem. Soc.* 1967, B67.

solvents were used as received. All chemical shifts are reported relative to internal Si(CH₃)₄. The number of transients ranged from 16 to 400 using an acquisition time of 4 s and a pulse width of 5 μs. Except where otherwise stated the probe temperature was 20 ± 1 °C.

Synthesis of New D^R_n Compounds. The synthesis of all of the compounds used in the present study is described elsewhere.¹

Partial Separation of Isomers of D^{Fp}₄. A sample of an isomeric mixture of D^{Fp}₄ (0.159 g) was dissolved in 1.5 mL of dry benzene and charged onto a silica gel column (1 × 60 cm). The column was slowly eluted with ca. 200 mL of 4:1 hexanes/benzene mixture. A transparent fraction (ca. 100 mL) containing only the solvent was first collected. A yellow band (10 cm long) migrated slowly and was collected as eight small fractions (7-12 mL each). The fractions were evaporated to dryness, and the residues were weighed and analyzed by ¹H NMR.

Results

The ¹H NMR spectra of methylhydrogenocyclosiloxanes (D^H_n) exhibit resonances in the region 4.9-5.1 ppm for Si-H protons and 0.1-0.2 ppm for the methyl groups. In coupled spectra, the Si-H region appears as an unresolved, complicated cluster of overlapping peaks in all spectra, whereas the Si-CH₃ region shows the superposition of several doublets for D^H₃ and D^H₄ and a complicated cluster of overlapping peaks for D^H₅. The complexity of the D^H_n spectra is partially due to the three-bond coupling between the hydrogen bonded to the silicon and the protons of the geminal methyl group. The coupling constant ranges from 1.45 Hz in D^H₃ to 1.55 Hz in D^H₄. Decoupled spectral data for the methyl region are given in Table I for D^H₃ and D^H₄ and in Table II for D^H₅. Decoupled spectra in the methyl region appear as three independent singlets for D^H₃, two pseudodoublets, and one singlet for D^H₄ (Figure 1) and a cluster of nine poorly resolved singlets for D^H₅. The decoupled spectrum for the Si-H region of D^H₄ also gives five peaks: 4.986, 5.010, 5.014, 5.031, and 5.037 ppm.

The ¹H NMR spectra of D^{Ph}₃ and D^{Ph}₄ in the methyl region have been reported and assigned previously.⁷ The results of the present work are listed in Table I and do not differ significantly from published results. The coupling between methyl and phenyl protons is too weak to be observed. As expected, the phenyl region (from 7.0 to 7.6 ppm) of both compounds is too complicated to be interpreted and will not be mentioned in the discussion.

The ¹H NMR spectra of the methylbromocyclosiloxanes (D^{Br}₃ and D^{Br}₄) are fairly simple (listed in Table I). The spectrum of D^{Br}₃ appears as a set of three peaks and that

(7) Williams, D. E.; Ronk, G. M.; Spielvogel, D. E. *J. Organomet. Chem.* 1974, 69, 69.

Table I. ^1H NMR Chemical Shift Data for CH_3 Resonances of D^{R}_n ($n = 3$ and 4) Recorded in C_6D_6 at Ambient Temperature^a

isomer	notatn	δ				
		H	C_6H_5	Br	$\text{Co}(\text{CO})_4$	$\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$
	$\text{D}^{\text{R}}_3(\text{I})$	0.136 (36)	0.572 (21)	0.299 (23)		
	$\text{D}^{\text{R}}_3(\text{II})$	1 2 0.154 } (64) 0.161 }	0.489 } (79) 0.420 }	0.376 } (77) 0.426 }		
	$\text{D}^{\text{R}}_4(\text{I})$	0.113 (11)	0.553 (17)	0.289 (24)	0.693 (15)	0.885 (10)
	$\text{D}^{\text{R}}_4(\text{II})$	1 2 0.120 } (52) 0.143 } 3 0.170 }	0.487 } (50) 0.475 } 0.264 }	0.330 } (36) 0.412 } 0.483 }	0.763 } (54) 0.858 } 1.040 }	0.918 } (34) 0.936 } 0.945 }
	$\text{D}^{\text{R}}_4(\text{III})$	0.146 (27)	0.390 (20)	0.427 (31)	0.918 (23)	0.957 (28)
	$\text{D}^{\text{R}}_4(\text{IV})$	0.170 (11)	0.358 (13)	0.471 (9)	1.002 (8)	0.957 (28)

^a The isomer abundances calculated from peak integrals are given in parentheses (%).

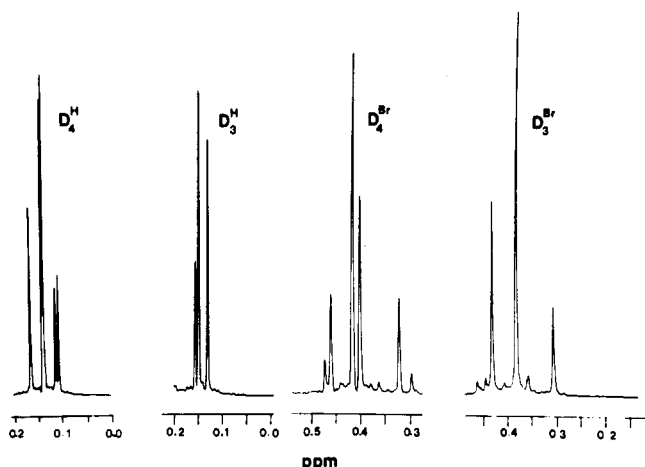


Figure 1. ^1H NMR spectra in the methyl region of D^{H}_3 and D^{H}_4 (in Si-H decoupled mode) and D^{Br}_3 and D^{Br}_4 . All spectra are measured in C_6D_6 (ca. 5%) at 20 °C.

of D^{Br}_4 consists of three groups of two peaks each (Figure 1). The chemical shifts of D^{Br}_n are in a region between those of D^{H}_n and D^{Ph}_n . The several peaks are spread over ranges of 25.4 and 30.4 Hz for D^{Br}_3 and D^{Ph}_3 , respectively, compared to the very small 5.0 Hz range for D^{H}_3 .

The ^1H NMR spectra of the two new compounds D^{Co}_4 and D^{Co}_5 are shown in Figure 2, and chemical shifts are listed in Tables I and II, respectively. The spectrum of D^{Co}_4 shows six well-resolved peaks as expected from analogous D^{Br}_4 and D^{Ph}_4 . Surprisingly, the spectrum of D^{Co}_5 was much simpler than expected from the decoupled spectrum of D^{H}_5 . Furthermore, data from two different samples show that slightly different purification techniques may lead to a variation in the isomeric composition of the product, probably as a result of fractionation during the crystallization. The ^1H NMR spectrum of a previously reported compound, $[(\text{CH}_3)_2\text{SiCo}(\text{CO})_4]_2\text{O}$, gives a single peak at 0.6 ppm.⁸

The ^1H NMR spectrum of D^{Fe}_4 in the methyl region is listed in Table I. The cyclopentadienyl resonances appear

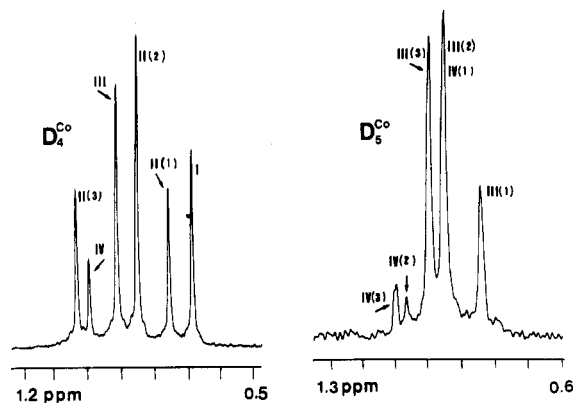


Figure 2. ^1H NMR spectra of D^{Co}_4 and D^{Co}_5 , measured in C_6D_6 (ca. 5%) at 20 °C.

Table II. ^1H NMR Chemical Shift Data for CH_3 Resonances of D^{R}_5 Recorded in C_6D_6 at Ambient Temperature^a

isomer	notatn	δ	
		H	$\text{Co}(\text{CO})_4$
	$\text{D}^{\text{R}}_5(\text{I})$	0.123 (6)	
	$\text{D}^{\text{R}}_5(\text{II})$	1 2 0.131 } (31) 0.149 } 3 0.195 }	
	$\text{D}^{\text{R}}_5(\text{III})$	1 2 0.141 } (35) 0.159 } 3 0.169 }	0.843 } (86) 0.953 } 0.997 }
	$\text{D}^{\text{R}}_5(\text{IV})$	1 2 0.159 } (28) 0.176 } 3 0.186 }	0.953 } (14) 1.067 } 1.100 }

^a The isomer abundances are given in parentheses.

as a group of peaks in the region 4.4–4.5 ppm. The range covered by methyl proton shifts in D^{Fe}_4 (15 Hz) is about 5 times smaller than in D^{Co}_4 which results in problems with

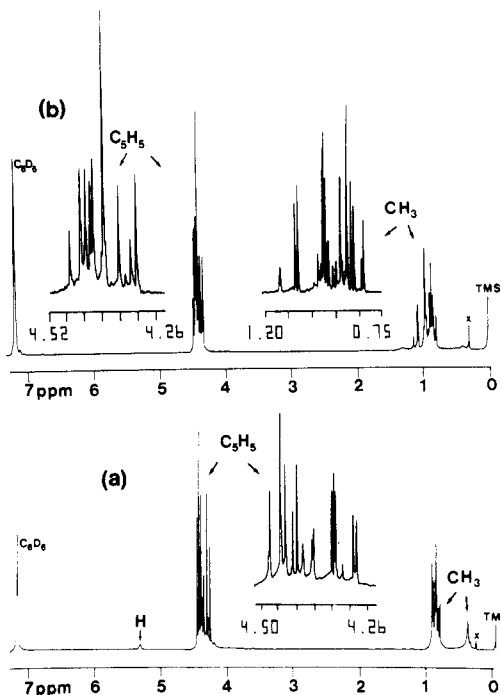


Figure 3. ^1H NMR spectra of the mixed compounds (a) $\text{D}^{\text{H}}_1\text{D}^{\text{Fp}}_3$ and (b) $\text{D}^{\text{Co}}_1\text{D}^{\text{Fp}}_3$ measured in C_6D_6 (ca. 5%) at 20°C . X is an impurity.

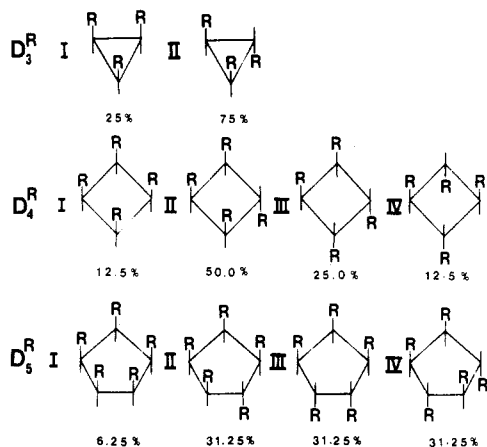


Figure 4. Schematic representation of geometric isomers of D^{R}_n ($n = 3, 4,$ and 5) and their statistical abundances.

the resolution of all of the peaks. In somewhat similar compounds (methyl polysilane derivatives) reported by King⁹ the $\eta^5\text{-C}_5\text{H}_5$ proton shifts ranged from 4.4 to 4.8 ppm and $\text{CH}_3\text{-SiFe}$ proton shifts were observed in the region 0.5–0.9 ppm.

The ^1H NMR spectra of $\text{D}^{\text{H}}\text{D}^{\text{Fp}}_3$ and $\text{D}^{\text{Co}}\text{D}^{\text{Fp}}_3$ are shown in Figure 3. In addition to the clear presence of CH_3 resonances due to each of the relevant D^{R} groups, the appropriate number of lines also appears, as will be discussed below.

Discussion

One of the most interesting features of cyclosiloxanes is the presence of several geometrical isomers in each ring size. Figure 4 shows a schematic representation of these isomers and their statistical abundance at equilibrium. In each of the figures (triangle, square, and pentagon), a side represents a siloxane bond and a corner stands for a silicon atom bonded to one methyl group and one other substit-

Table III. ^1H NMR Chemical Shift Data for CH_3 Resonances of Some Trimethylsilyl and Cyclotetrasiloxanyl Derivatives

substituent	δ	
	$(\text{CH}_3)_3\text{Si-R}$	D^{R}_4
H	0.02 ^a	0.14 ^e
CH_3	0.00 ^b	0.07 ^f
C_6H_5	0.24 ^a	0.41 ^e
Br	0.52 ^a	0.39 ^e
$\text{Co}(\text{CO})_4$	0.59 ^c	0.89 ^e
$\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$	0.36 ^d	0.92 ^e

^a Reference 12. ^b $\text{Si}(\text{CH}_3)_4$ is taken as reference. ^c Reference 13. ^d Reference 14. ^e The median value of the cluster of peaks has been calculated from the data of Table I. ^f Reference 4.

uent R, which can be an organic, inorganic, or organometallic group. The isomers will be identified according to chemical composition (D^{R}_n) and the appropriate Roman numeral given in Figure 4.

Assignment of ^1H NMR Spectra of Isomers. The problem of methyl NMR shift–structure correlations in methylphenylcyclosiloxanes has been studied,⁷ and a simple empirical equation was derived to predict the methyl proton shifts in different geometric isomers. The methyl shifts were found to be slightly dependent on the ring size of the siloxane and more strongly upon the position and the spatial orientation of all other methyl and phenyl groups in the molecule.

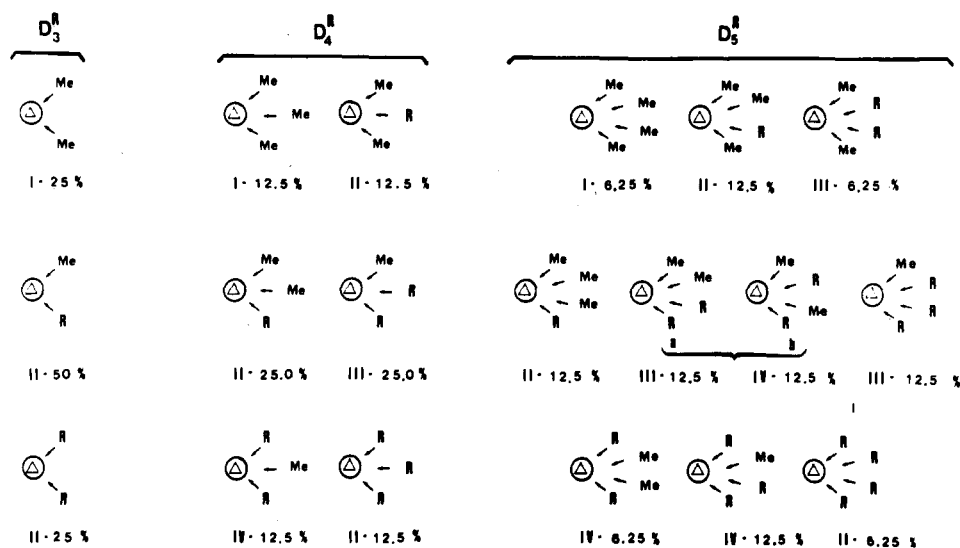
The study of analogous methylhydrocyclosiloxanes (D^{H}_n) is slightly complicated by the proton–proton coupling occurring between the methyl group and the hydrogen bonded to the same silicon. Some methylhydrocyclo-tetrasiloxanes, $\text{D}_{4-n}\text{D}^{\text{H}}_n$ for $n = 0\text{--}4$, have been studied.¹⁰ The best reported coupled spectrum for D^{H}_4 at 100 MHz (20% in CCl_4) seemed to consist of three poorly resolved doublets at 0.22, 0.23, and 0.25 ppm for methyl protons and one quartet at 4.8 ppm for the Si–H hydrogen. In their attempts to assign the spectrum, the authors neglected the through-space shielding effect due to geometric isomers discussed below and arrived at an incorrect assignment. To our knowledge, no detailed proton decoupled spectra have yet been published for D^{H}_n ($n = 3, 4,$ and 5). All other compounds (except D^{Ph}_n) reported in the present work are new and thus have never been studied by ^1H NMR spectroscopy.

Assignments of methyl resonances for the cyclo-trisiloxane isomers are unambiguous and provide basic information about chemical shift effects of adjacent substituents. In the decoupled spectrum of D^{H}_3 (Table I), the methyl protons in a cis relation to two adjacent methyls resonate at higher field (0.136 ppm) than methyl protons that are cis to two hydrogens (0.161 ppm). Methyl protons adjacent to one cis methyl and one cis hydrogen resonate at an intermediate frequency (0.154 ppm). Hydrogen has a net through-space deshielding effect when compared to the methyl group itself. Similarly, bromine in D^{Br}_3 has a deshielding effect but the phenyl group has the reverse effect. It seems reasonable to attribute this unexpected effect of the ring current induced in the phenyl ring by an applied field.¹¹

(10) Jancke, J.; Engelhardt, G.; Radeglia, R.; Kriegsmann, H. *Spektrochim. Acta, Part A* 1969, 25A, 85.

(11) Becker, E. D. "High Resolution NMR, Theory and Chemical Applications"; Academic Press: New York, 1980; Chapter 4. Abraham, R. J.; Loftus, P. "Proton and Carbon-13 NMR spectroscopy"; Heyden and Son: Great Britain, 1978; Chapter 2.

(12) Williams, D. E. In "Analysis of Silicones"; Smith, A., Ed.; Wiley: New York, 1974; Chapter 11.

Chart I. Chemical Environments of Methyl Groups and Their Statistical Abundances in D_n^R ($n = 3, 4, \text{ and } 5$)^a

^a The symbol \triangle indicates the observed CH_3 .

An examination of the ^1H chemical shifts given in Tables I and II reveals a clear dependence of the shifts upon the nature and the spatial position of the substituent R. The methyl proton shifts are mainly governed by the simultaneous interplay of (1) the through-bond shielding effect, controlled mainly by the nature of the substituent R on each silicon, and (2) the through-space shielding effect, controlled mainly by the spatial orientation of neighbors (geometrical isomerism).

(1) **Through-Bond Shielding Effects.** Available data from some trimethylsilyl derivatives (Table III) show that organometallic groups of the type used in this study have a deshielding effect comparable to the Br and phenyl groups. Our results for the D_n^R compounds exhibit the following trend $\text{Co}(\text{CO})_4 \approx \text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5) > \text{C}_6\text{H}_5 \approx \text{Br} > \text{CH}_3 \approx \text{H}$.

(2) **Through-Space Shielding Effects.** On the assumption that the isomers have similar conformations or rapid interconversion of different conformers, it has been proposed⁵ that methyl group shift assignments can be made on the basis of a comparison of their environments and on the assumption that the adjacent substituents have the greatest influence. The environments of different methyl groups in D_n^R ($n = 3-5$) are shown in Chart I. All three methyl groups in D_3^R (I) are equivalent, and all protons should resonate at the same frequency. Two different environments are possible for the isomer D_3^R (II), and two peaks should be observed in the ratio 2:1. Six different environments are possible for all isomers of D_4^R and ten for those of D_5^R . Two very similar environments in D_5^R (noted a and b in Chart I) will give only one peak if the average conformation of the ring in each isomer, D_5^R (III) and D_5^R (IV), is not changed by the size of the substituent. Chart I gives also the statistical abundance of each environment calculated from the statistical abundance of each isomer given in Figure 4. With use of the information from Chart I, three theoretical spectra can be drawn, as shown in Figure 5, where the through-space shielding effect of the substituent R on neighboring CH_3 protons is assumed to be smaller than the effect of the methyl group itself. If the opposite case is considered, the mirror-image spectrum results.

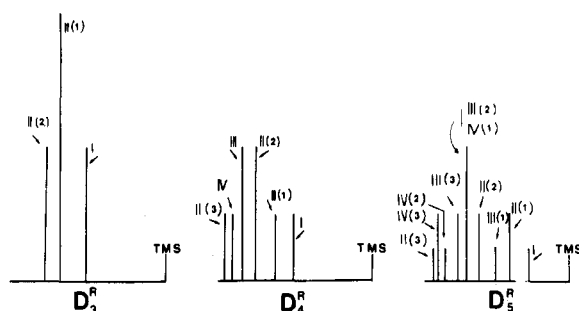


Figure 5. Theoretical ^1H NMR spectra for CH_3 resonances of D_n^R ($n = 3, 4, \text{ and } 5$) where the through-space shielding effect of the R group is smaller than the effect of CH_3 itself. The digits in parentheses correspond to peak numbers used in Tables I and II.

Assuming that the effects observed in D_3^R ($R = \text{H}, \text{C}_6\text{H}_5$, and Br) are also present in larger rings, it is possible, by using the chemical environment arguments to assign the observed peaks of the tetramers D_4^R ($R = \text{H}, \text{C}_6\text{H}_5$, and Br) (see Table I) and D_5^R (see Table II). Peak 3 of isomer D_4^R (II) and the lone peak of isomer D_4^R (IV) overlap, but this is not prejudicial to the total assignment of the spectrum since the integration value of peak 1 (equal to peak 3) can be subtracted to get the value for isomer D_4^R (IV) alone.

Since D^{Co_3} has not been synthesized, the assignment of D^{Co_4} has to be established directly from the tetramer. The spectrum of a mixture of isomers of D^{Co_4} (Figure 2 left) shows six well-resolved peaks and strongly suggests an assignment similar to the theoretical spectrum of Figure 5 (center). The second peak at the extreme right of the spectrum (Figure 2), the largest one in the center, and the last one at the extreme left are in perfect correlation 1:2:1 and are attributed to isomer D^{Co_4} (II). Other peaks are then assigned following the hypothesis of chemical environments as used for D_4^R and D_5^R . Thus peak 3 of isomer D^{Co_4} (II), the lowest shift observed, corresponds to the methyl protons completely surrounded by cobalt carbonyl groups whereas the peak at the extreme right, the highest shifted, is due to the methyl protons of isomer D^{Co_4} (I) because they are all surrounded by methyl groups only (Figure 4).

The spectrum of D^{Co_5} shown in Figure 2 can be tentatively assigned following the same basic hypothesis. The

(13) Colomber, E.; Corriu, R. J. P. *Top. Curr. Chem.* 1981, 96, 79.

(14) Jetz, W.; Graham, A. G. *Inorg. Chem.* 1971, 10, 1647.

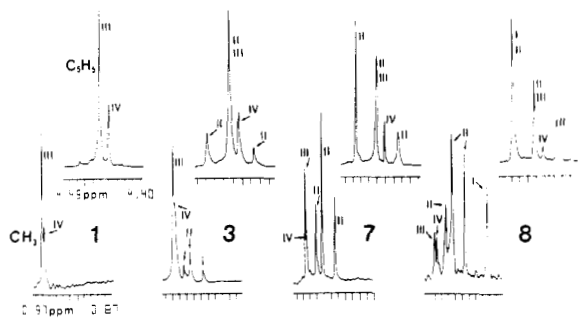


Figure 6. ^1H NMR spectra of CH_3 and $\gamma^2\text{-C}_5\text{H}_5$ groups of selected fractions from the chromatographic separation of geometric isomers of D^{Fp}_4 , measured in C_6D_6 (ca. 5%) at 20°C .

isomer $\text{D}^{\text{Co}}_5(\text{I})$ is probably absent due to the low natural abundance (5.8%) of the corresponding $\text{D}^{\text{H}}_5(\text{I})$ in the starting material and the very low final yield of the product (ca. 3%).¹ The isomer $\text{D}^{\text{Co}}_5(\text{II})$, if present, should show the peak pattern 1:2:2 according to the theoretical spectrum of Figure 5 (from left to right). This pattern does not seem to be present in the spectrum, but a pattern of 2:2:1 is clearly observed and is assigned to the isomer $\text{D}^{\text{Co}}_5(\text{III})$, the most abundant isomer in the mixture. The pattern 2:1:2, due to isomer $\text{D}^{\text{Co}}_5(\text{IV})$, is also present in a small amount but is partially hidden by the large peaks of $\text{D}^{\text{Co}}_5(\text{III})$.

The above assignments for D^{Co}_4 and D^{Co}_5 suggest an exceptionally strong deshielding effect for the $\text{Co}(\text{CO})_4$ group on adjacent and transannular methyl protons. This special effect is attributed to the anisotropic deshielding effect of carbonyl groups lying in the plane of neighboring methyl protons.¹¹ Thus, methyl protons lying in this deshielding area resonate at very low field. For this reason, the peak observed at lowest field for D^{Co}_4 (1.040 ppm) is assigned to the methyl 3 of isomer $\text{D}^{\text{Co}}_4(\text{II})$ (Table I).

Assignment of ^1H NMR Spectrum of D^{Fp}_4 . The spectrum of D^{Fp}_4 in the methyl region shows only five peaks, which are relatively close together and cannot be assigned directly by using a strategy similar to D^{Co}_4 . An alternative approach was to get a separation (even partial) of some isomers and compare spectra from different isomeric compositions.

The partial separation of D^{Fp}_4 isomers was achieved by column chromatography on silica gel. Many attempts at selective recrystallization of isomers from the crude mixture using polar solvents at low temperature were unsuccessful. Although separation on a silica gel column with benzene/hexanes is poor, it was possible, by comparing successive fractions, to assign all observed peaks. These assignments (Figure 6) are based on the following considerations.

(a) Isomers having low polarity should have a weaker interaction with the column and should migrate faster than polar isomers. Isomer III is a centrosymmetric molecule and should, depending on conformation, have a low dipole moment. Isomer IV is the most symmetrical and should have a smaller dipole moment than isomers II and I.¹⁵ The two peaks observed in the spectrum of fraction 1 are attributed to isomers $\text{D}^{\text{Fp}}_4(\text{III})$ and $\text{D}^{\text{Fp}}_4(\text{IV})$. As the theoretical abundance of isomer III is twice the abundance of isomer IV, the larger peak has been assigned to isomer $\text{D}^{\text{Fp}}_4(\text{III})$ and the smaller to $\text{D}^{\text{Fp}}_4(\text{IV})$. The separate integration of peaks is possible in the cyclopentadienyl region and allows the calculation of isomeric composition.

(b) Isomer II should be eluted third and should be easily distinguishable by virtue of its very characteristic peak pattern 1:2:1. The fraction 3, illustrated in Figure 6, clearly shows the presence of isomer $\text{D}^{\text{Fp}}_4(\text{II})$ that makes the assignment easy. The fractions 4, 5, and 6 (not illustrated) show only a relative increase in the abundance of isomer II. The fraction 7 is 75% isomer $\text{D}^{\text{Fp}}_4(\text{II})$.

(c) The most polar isomer $\text{D}^{\text{Fp}}_4(\text{I})$ is well separated and appears only in the last fraction. Fraction 8 (Figure 6) is the tail of the yellow band. It contains very little $\text{D}^{\text{Fp}}_4(\text{III})$ and $\text{D}^{\text{Fp}}_4(\text{IV})$, but a large percentage of $\text{D}^{\text{Fp}}_4(\text{II})$ is still present. The exceptionally low abundance of $\text{D}^{\text{Fp}}_4(\text{I})$ (4%) in the collected fraction is probably an experimental artifact. This isomer seems to migrate much more slowly than other isomers and was probably not completely collected in fraction 8.

The assignment proposed for the D^{Fp}_4 spectrum (methyl region of fraction 8 in Figure 6) is significantly different from the assignment proposed for the analogous D^{Co}_4 (Figure 2). The methyl protons of $\text{D}^{\text{Fp}}_4(\text{III})$ and $\text{D}^{\text{Fp}}_4(\text{IV})$ resonate at lower field than expected from the analogous $\text{D}^{\text{Co}}_4(\text{III})$ and $\text{D}^{\text{Co}}_4(\text{IV})$. The first-order hypothesis of chemical environments (Chart I), which works well with the other D^{R}_n compounds, fails to explain this behavior.

The anomalous ordering of the D^{Fp}_4 resonances may be explained by the fact that the rotation of the Fp group is probably not free.¹⁶ Since the bulky cyclopentadienyl group will tend to spend most of its time as far away as possible from the siloxane ring, it will lie in the vicinity of methyl group attached to the same silicon. Just as for the phenyl group, a ring current can also be induced in the cyclopentadienyl ring. Whatever the geometry of the isomer, this effect is always present. For this reason, the methyl protons of all isomers of D^{Fp}_4 are observed at lower field than expected from analogous $(\text{CH}_3)_3\text{Si-Fp}$ where rotation along the Si-Fe axis is probably free (Table III).

The basic assumption for all peak assignments made above was the averaging of individual conformers of a given geometric isomer (^1H NMR signal is averaged by fast flipping of conformers, or the rings are essentially planar and give simple NMR signals). This hypothesis seems to be questionable in the specific case of D^{Fp}_4 . An attempt to observe the individual conformers by means of an ^1H NMR variable-temperature experiment on an isomeric mixture was unsuccessful.¹⁷

The abundances of the geometric isomers of D^{R}_n , listed in Tables I and II, were calculated directly from the assignments and peak integrals. The values listed for D^{Fp}_4 were for an unfractionated product. The accuracy of these calculations is variable and is a function of the quality of the spectrum obtained for the individual compound. For example, the spectrum of D^{Co}_4 (Figure 2) is easily integrated and gives very accurate results whereas the spectra of D^{Fp}_4 gave serious difficulties in resolution and integration. All compounds have an isomeric composition not significantly different from the statistical composition, except for D^{Co}_5 .

An Approach to the Interpretation of ^1H NMR Spectra of Heteronuclear Compounds. The chemical

(16) The high-resolution infrared spectrum in the carbonyl stretching region showed an unexpectedly large number of peaks.¹ A restricted rotation of the Fp group along the Si-Fe axis may be partly responsible for this effect.

(17) Spectra in toluene at -70 and $+20^\circ\text{C}$ are virtually the same. This observation may have three interpretations: The interconversion energy of conformers is very low, and the flipping cannot be stopped in the range of temperature studied. All rings are flat and have no conformers. The conformers are frozen even at $+40^\circ\text{C}$ due to the very bulky substituent Fp.

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environment approach used above for the assignment of ^1H NMR spectra of isomers of homonuclear substituted compounds, in principle, can be extended to the spectra of the heteronuclear compounds $\text{D}^{\text{H}}_1\text{D}^{\text{Fp}}_3$ and $\text{D}^{\text{Co}}_1\text{D}^{\text{Fp}}_3$ (Figure 3).

In order to predict the ^1H NMR spectra of these compounds and assign the isomers, it is necessary to know the relative through-bond shielding effect of the two metallic substituents and the relative through-space shielding effect of the two metallic substituents and of CH_3 .

The following limiting cases yield to analysis: (1) If the through-bond shielding effect is the same for both metallic silicon substituents, but their through-space shielding effects are different, a single cluster of peaks is expected in the methyl region. (2) If the through-space effect is the same for the two substituents but the through-bond effect is different, two symmetrical clusters of peaks are expected. (3) If both through-bond and through-space effects of the two substituents are different, two unsymmetrical clusters of peaks are expected.

The spectrum of a partially-substituted $\text{D}^{\text{H}}_{4-n}\text{D}^{\text{Fp}}_n$ ($n = 3, 1$) (Figure 3a) shows the presence of two clusters of peaks in the methyl region in the ratio 3:1. The spectrum illustrates the limiting case 3 above, where the through-bond shielding effect of the Si-H (at right) is clearly different from the effect of the Fp group (at left). The cyclopentadienyl region is very complex and cannot be assigned, but the total number of peaks does not exceed 18, as expected. The spectrum of $\text{D}^{\text{Co}}_1\text{D}^{\text{Fp}}_3$ (Figure 3b) shows only one group of peaks in the methyl region illustrating the first limiting case above where the through-bond effects

of Fp and $\text{Co}(\text{CO})_4$ are roughly the same, but their through-space effects are different. The model predicts 14 peaks for $\text{CH}_3\text{-Si-Fp}$ groups and six peaks for $\text{CH}_3\text{-Si-Co}$ when only the compound $\text{D}^{\text{Co}}_1\text{D}^{\text{Fp}}_3$ is present. The observed spectrum of $\text{D}^{\text{Co}}_1\text{D}^{\text{Fp}}_3$ shows 20 peaks in the methyl region. The assignment of these peaks is impossible because the precise shielding effects of each substituent are unknown. The model also predicts 12 peaks in the cyclopentadienyl region. The spectrum shows only 11 peaks, but it seems reasonable to assume that the large central peak results from the overlap of two peaks. The assignments of the ^1H NMR spectrum of isomers of $\text{D}^{\text{Co}}_1\text{D}^{\text{Fp}}_3$ could be possible by means of a partial separation of these isomers as used successfully for D^{Fp}_4 . This was not attempted due to the difficulty involved in preparing a large enough sample of pure $\text{D}^{\text{Co}}_1\text{D}^{\text{Fp}}_3$.

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Registry No. $\text{D}_3^{\text{H}}(\text{I})$, 89887-17-2; $\text{D}_3^{\text{Ph}}(\text{I})$, 3424-57-5; $\text{D}_3^{\text{Br}}(\text{I})$, 89887-18-3; $\text{D}_3^{\text{H}}(\text{II})$, 89887-19-4; $\text{D}_3^{\text{Ph}}(\text{II})$, 6138-53-0; $\text{D}_3^{\text{Br}}(\text{II})$, 89887-20-7; $\text{D}_4^{\text{H}}(\text{I})$, 89887-21-8; $\text{D}_4^{\text{Ph}}(\text{I})$, 4885-37-4; $\text{D}_4^{\text{Br}}(\text{I})$, 89887-22-9; $\text{D}_4^{\text{Co}}(\text{I})$, 89885-87-0; $\text{D}_4^{\text{Fp}}(\text{I})$, 89887-14-9; $\text{D}_4^{\text{H}}(\text{II})$, 89887-23-0; $\text{D}_4^{\text{Ph}}(\text{II})$, 5131-04-4; $\text{D}_4^{\text{Br}}(\text{II})$, 89887-24-1; $\text{D}_4^{\text{Co}}(\text{II})$, 89885-88-1; $\text{D}_4^{\text{Fp}}(\text{II})$, 89887-15-0; $\text{D}_4^{\text{H}}(\text{III})$, 89887-25-2; $\text{D}_4^{\text{Ph}}(\text{III})$, 15331-54-1; $\text{D}_4^{\text{Br}}(\text{III})$, 89887-26-3; $\text{D}_4^{\text{Co}}(\text{III})$, 89887-16-1; $\text{D}_4^{\text{Fp}}(\text{III})$, 89885-89-2; $\text{D}_4^{\text{H}}(\text{IV})$, 89887-27-4; $\text{D}_4^{\text{Ph}}(\text{IV})$, 4885-39-6; $\text{D}_4^{\text{Br}}(\text{IV})$, 89887-28-5; $\text{D}_4^{\text{Co}}(\text{IV})$, 89885-90-5; $\text{D}_4^{\text{Fp}}(\text{IV})$, 89885-91-6; $\text{D}_5^{\text{H}}(\text{I})$, 89887-29-6; $\text{D}_5^{\text{H}}(\text{II})$, 89887-30-9; $\text{D}_5^{\text{H}}(\text{III})$, 89887-31-0; $\text{D}_5^{\text{Co}}(\text{III})$, 89885-92-7; $\text{D}_5^{\text{H}}(\text{IV})$, 89887-32-1; $\text{D}_5^{\text{Co}}(\text{IV})$, 89885-93-8.

Chirality Transfer in the Coordination Sphere of Iron

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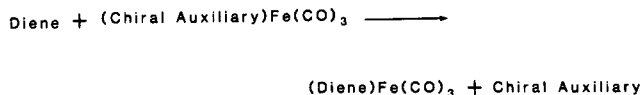
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Transfer of chirality between a chiral donor complex and an unsymmetrical diene ligand gives rise to optically active tricarbonyliron complexes with enantiomeric excesses as high as 40%.

To achieve a high degree of asymmetric induction in an irreversible reaction, considerable kinetic discrimination between two diastereomeric transition states is required. In this paper we describe the application of this concept to the asymmetric synthesis of diene complexes by chirality transfer during a ligand exchange reaction between the metal complex of a chiral auxiliary and a prochiral diene (Scheme I). Our results indicate a much higher degree of asymmetric induction than is obtained² when a chiral auxiliary is directly attached to the ligand, as is anticipated because of the more intimate involvement of the chiral component when linked within the coordination sphere of the metal.

Scheme I



In view of the synthetic utility³ of enone complexes as a source of the tricarbonyliron group in ligand exchange reactions, we selected a range of chiral enone complexes as donors for this study. Reports have indicated that

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