SYNTHESIS AND CHARACTERIZATION OF A NEW CLASS OF SILYL-TRANSITION METAL COMPOUNDS

by

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ABSTRACT

PhD Emilien Pelletier Chemistry

SYNTHESIS AND CHARACTERIZATION OF A NEW CLASS OF SILYL-TRANSITION METAL COMPOUNDS

Some new inorganic and organometallic derivatives of methylcyclosiloxanes have been prepared and characterized by IR, MS and ^{1}H NMR. Compounds, $[CH_3(Br)SiO]_3$ and $[CH_3(Br)SiO]_4$ were prepared by cleavage of silicon-phenyl bond with bromine at low temperature. The reaction of $[CH_3(Br)SiO]_3$ with Na(sec-butyl)$_3$BH at low temperature produced the highly reactive trimer, $[CH_3(H)SiO]_3$. Compounds $[CH_3(Co(CO)_4)SiO]_4$, $[CH_3(Fe(CO)_2\eta^5-C_5H_5)SiO]_4$, and $[CH_3(Co(CO)_4)SiO]_5$ were prepared by the hydrogen elimination reaction of $[CH_3(H)SiO]_n$, n = 4 and 5 with $Co_2(CO)_8$ and $[Fe(CO)_2\eta^5-C_5H_5]_2$. It was also possible to isolate the compound $[CH_3(Co(CO)_4)SiO]_1[CH_3(Fe(CO)_2\eta^5-C_5H_5)SiO]_3$ by reacting $[CH_3(H)SiO]_1[CH_3(Fe(CO)_2\eta^5-C_5H_5)SiO]_3$ with a stoichiometric amount of $Co_2(CO)_8$. A detailed study of mass spectra of $[CH_3(R)SiO]_n$, where R = H, (n = 4, 5, and 6), R = C_6H_5, (n = 3 and 4), R = Br, (n = 3 and 4), R = $Co(CO)_4$, (n = 4 and 5) and R = $Fe(CO)_2\eta^5-C_5H_5$, (n = 4) was achieved. Compounds R = $Co(CO)_4$ show stepwise loss of all CO groups from ions $[M]^{+\cdot}$, $[M-Co(CO)_4]^+$, and also $[M]^{++}$. A simple empirical approach based on the chemical environment of

methyl protons was used to assign ^1H NMR spectra of geometric isomers of substituted methylcyclosiloxanes. The total assignment of ^1H NMR spectra allowed the determination of the isomeric composition of most new compounds mentioned above.

RÉSUMÉ

PhD Emilien Pelletier Chimie

SYNTHÈSE ET CARACTÉRISATION D'UNE NOUVELLE CLASSE DE COMPOSÉS SILICIUM-MÉTAL DE TRANSITION

Plusieurs nouveaux dérivés inorganiques et organométalliques du méthylcyclosiloxane ont été préparés et caractérisés par i.r., s.m. et r.m.n. de proton. Les composés $[CH_3(Br)SiO]_3$ et $[CH_3(Br)SiO]_4$ furent obtenus par clivage du lien silicium-phényle avec le brome à basse température. La réaction du $[CH_3(Br)SiO]_3$ en présence de Na(*sec*-butyle)$_3$BH à basse température produisit le trimer hautement réactif $[CH_3(H)SiO]_3$. Les composés $[CH_3(Co(CO)_4SiO]_4$, $[CH_3(Fe(CO)_2\eta^5\text{-}C_5H_5)SiO]_4$, et $[CH_3(Co(CO)_4SiO]_5$ furent préparés pour élimination d'hydrogène entre $[CH_3(H)SiO]_n$, n = 4 et 5, et $Co_2(CO)_8$ et $[Fe(CO)_2\eta^5\text{-}C_5H_5]_2$. Il fut aussi possible d'isoler le composé $[CH_3(Co(CO)_4)SiO]_1[CH_3(Fe(CO)_2\eta^5\text{-}C_5H_5)SiO]_3$ en réagissant $[CH_3(H)SiO]_1[CH_3(Fe(CO)_2\eta^5\text{-}C_5H_5SiO]_3$ avec une quantité stoichiométrique de $Co_2(CO)_8$. Les spectres de masse de $[CH_3(R)SiO]_n$ où R = H, (n = 4, 5 et 6), R = C_6H_5, (n = 3 et 4), R = Br, (n = 3 et 4), R = $Co(CO)_4$, (n = 4 et 5) et R = $Fe(CO)_2\eta^5\text{-}C_5H_5$, (n = 4) furent étudiés en détail. Les composés R = $Co(CO)_4$ décomposent par la perte successive de tous leurs groupes CO à partir des ions $[M]^{+\cdot}$, $[M\text{-}Co(CO)_4]^+$, et aussi $[M]^{++}$. Une approche empirique

simple basée sur l'environnement chimique des protons méthyliques fut utilisée pour assigner les spectres r.m.n. des isomères géometriques des méthylcyclosiloxanes substituées. L'assignation complète des spectres r.m.n. a permis la détermination de la composition isomérique de la plupart des nouveaux composés mentionnés ci-dessus.

à Arlette et Sarah

Le savant dit: "Si vous saviez...
Si vous saviez mon ignorance
Le metier de la connaissance
Est mal connu et journalier."
Mais ne fais pas un militaire...

Les beaux metiers
Gilles Vigneault

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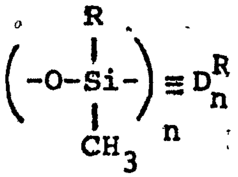
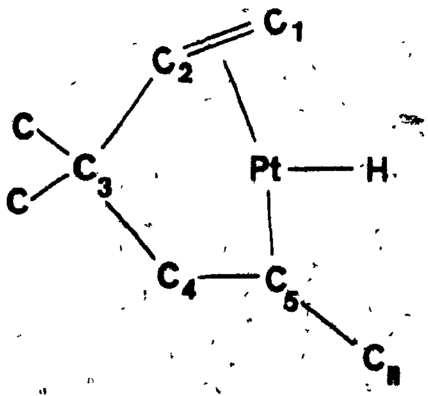
LIST OF ABBREVIATIONS

A or R	organic, inorganic or organometallic substituent at silicon
Co	cobalt tetracarbonyl group, $Co(CO)_4$ in D_n^{Co}
Cp	cyclopentadienyl, C_5H_5
D	methylcyclosiloxane unit, such as  $\left(-O-\overset{R}{\underset{CH_3}{Si}}-\right)_n \equiv D_n^R$
Et	ethyl, CH_2CH_3
Fp	cyclopentadienyl iron dicarbonyl group, $Fe(CO)_2$ $\eta^5-C_5H_5$ in D_n^{Fp}
M	transition metal
Me	methyl group
n	number of siloxane units in the ring, such as D_n^R
Ph	phenyl, C_6H_5
R_f	in chromatography, distance from center of spot to origin over distance of solvent front from origin
<u>sec</u>-bu	<u>sec</u>-butyl, $CH(CH_3)C_2H_5$
t-bu	<u>ter</u>-butyl, $C(CH_3)_3$
THF	tetrahydrofuran, C_4H_8O

PREFACE

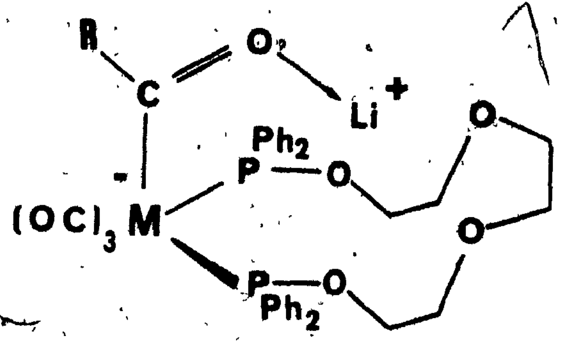
The aim of the present project is the preparation and the full characterization of a new class of silyl-transition metal compounds with potential for multifunctional catalytic activity.

The extraordinary activities and selectivities of many enzymes depend on the precise placement of several different active functions on the catalyst, with respect to active centers of the substrate. Very few examples of simple metal-based synthetic catalytic systems, where the rate depends strongly on the spacial disposition of substrate with respect to active centre(s), are known in the literature. A few years ago, a homogeneous platinum(II)-catalyzed hydrogen-deuterium exchange at a saturated carbon atom was reported[1]. The proposed mechanism involved a five metallocycle intermediate (1). The H-D exchange occurs in a highly regiospecific manner at carbon 5 because that carbon is in a



(1)

particularly favorable position to bond to the platinum nucleus. Powell et al.[2] recently reported a system (2) where a coordinated carbon monoxide is activated with respect to

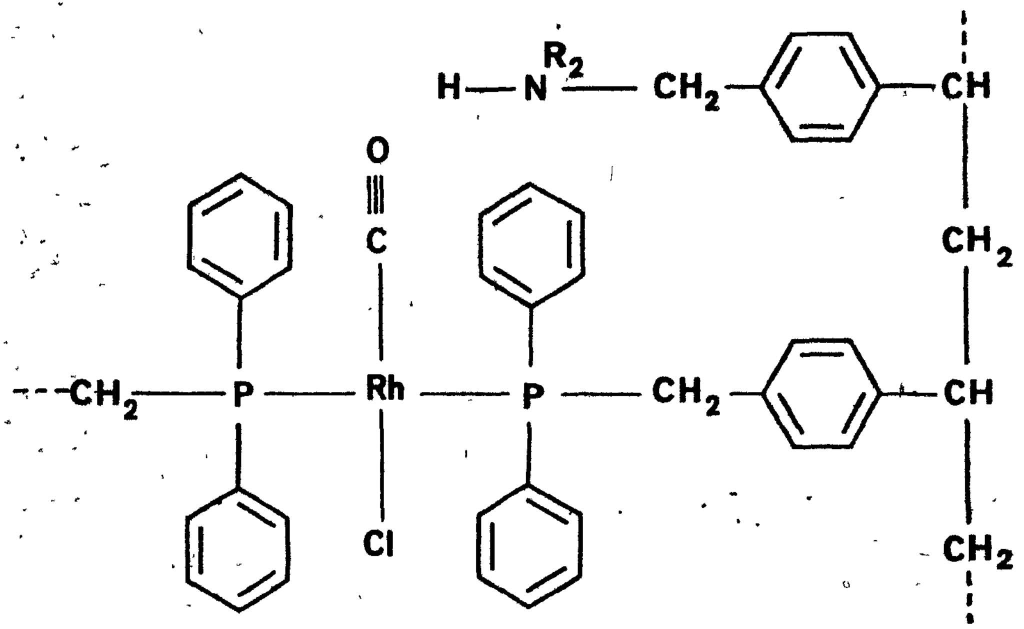


(2)

M = Cr, Mo, W

R = Me, Ph, *t*-Bu, Et_2N

nucleophilic addition by coordination to a transition metal through carbon and to a Lewis acid (Li^+) through oxygen. The reactivity of the CO with respect to attack by hydride ion is extremely sensitive to the distance of the Li^+ ion from the O. These two 'academic' examples of relatively simple homogeneous systems contrast strongly with the 'magic' heterogeneous systems currently used in industrial catalytic processes. Joseph Haggin[3] recently pointed out: "The advances in computer software and surface science are enabling scientists to design industrial catalysts using highly organized procedures, such as combining specific chemical and physical functions." One of the examples cited by Haggin shows a new catalyst (3) designed for producing 2-ethyl hexanol (Aldox process) using a solid polymer containing a metal function (rhodium) and a base function (amine). Bruce C. Gates, a designer of new catalysts (Director of the Center for Catalytic Science and Technology at the University of Delaware) states: "Assuming that the catalyst functions are identifiable, it is, in principle, possible to combine them into a prescribed multifunctional catalyst"[3].



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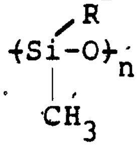
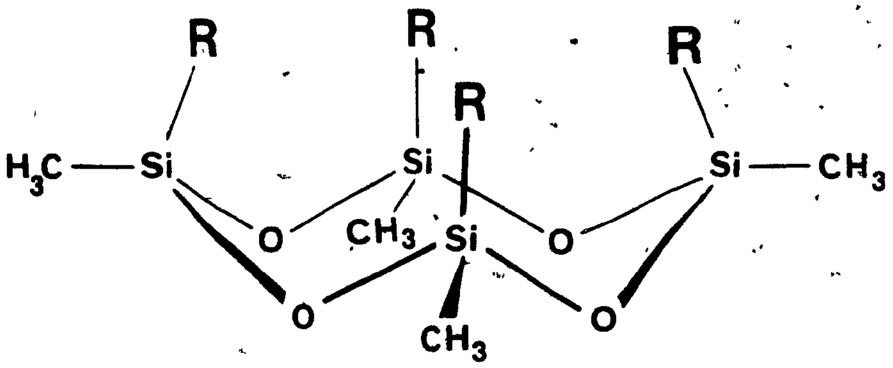
The present project deals with the design of new potential catalysts combining advantages of homogeneous systems (chemical simplicity and selectivity) and heterogeneous systems (efficiency and low cost). One avenue for such designed catalysts could be to attach several catalytic functions (transition metal moieties, organic bases or acids, redox pairs) to a single framework small enough and flexible enough to get convenient spacial placement of active functions and to remain practicable as a homogeneous system. The present work explores a new family of polyfunctional molecules where small ring methylcyclosiloxanes (e.g. 4) serve as a supporting framework for organometallic functions of potential catalytic interest. The synthesis of some molecules of the general formula,  $\left(\underset{\mathrm{CH_3}}{\overset{\mathrm{R}}{\mathrm{Si}}}-\mathrm{O}\right)_n$, will be described together with their characterization by infrared and mass spectrometry. The methyl substituents in these molecules provide a useful probe for estimating the various possible geometric isomers by ^1H NMR spectroscopy. The assignments of NMR spectra for all of the reactant and product methylcyclosiloxanes will be discussed.



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1. GENERAL INTRODUCTION

1.1 History of organosilicon compounds

The first organosilicon compound, tetraethylsilane, was discovered by the famous French-American team of chemists, Charles Friedel and James Crafts[4] in 1863. A few years later, the same authors[5] reported the preparation of tetramethylsilane by the action of dimethylzinc on tetrachlorosilane. From the preparation of tetramethoxysilane, the authors[5] mentioned a secondary product called disilicate hexaméthylique having the empirical formula, $[2Si,6CH_3,7O]$. It was probably the first isolation of a disiloxane which we would formulate today as $[(CH_3O)_3Si]_2O$. In two subsequent papers[6,7], hexaethyl- and hexachlorodisiloxane were isolated and properly identified. Studying properties of ethylphenyldichlorosilane, Kipping[8] observed the formation of "a viscous, colourless oil when phenyl ethyl silicon dichloride is decomposed with water." Kipping did not identify this product but a few years later, he prepared and formulated very accurately, and for the first time, some polyphenylcyclosiloxanes[9] from the hydrolysis of $(C_6H_5)_2SiCl_2$ and also from the condensation of $(C_6H_5)_2Si(OH)_2$.

Fundamental progress in the chemistry of silicon came 40 years after the first report of Friedel and Crafts by the application of the newly-discovered Grignard reagents to the synthesis of a wide variety of alkyl, aryl and halogeno substituted silanes (eq. 1.1)[8-11]. By the end of the Second World War, Rochow[12] reported that vapors of many

$$R_nSiX_{4-n} + R'MgBr \longrightarrow R_nR'SiX_{3-n} + MgBrX \qquad \text{(eq. 1.1)}$$

alkyl and aryl halides react directly with heated solid silicon producing a mixture of organosilicon halides. '<u>The direct method</u>' is still today the main industrial route for commercial scale synthesis of organosilicon compounds. The most efficient application is the production of methylchlorosilanes in ton quantities by the direct reaction of methylchloride with silicon at high temperature in the presence of copper[13] (eq. 1.2). Hydrolysis of organodichlorosilane leads to a variety of cyclosiloxanes used in the manufacturing of silicones.

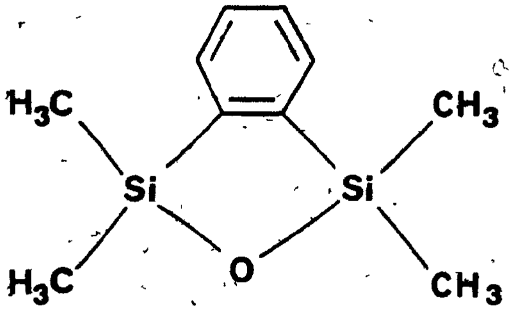
$$CH_3Cl + Si \xrightarrow[\Delta]{Cu} (CH_3)_2SiCl_2 + CH_3SiCl_3 + (CH_3)_3SiCl \qquad \text{(eq. 1.2)}$$

1.2 Chemistry of siloxanes

To date, cyclosiloxanes have not been investigated as multidentate ligands, able to coordinate one or many transition metal centers but the physical and chemical features of linear and cyclic siloxanes have been extensively studied in the last two decades mostly by workers in the Soviet Union[14].

1.2.1 Some physical and structural features

In valence bond terms, the Si-O bond in tetravalent silicon compounds is described as a σ bond from the overlap of hybridized s and p orbitals of oxygen with sp^3 hybrids of Si. An additional (p→d)π interaction of the unshared p electrons of oxygen with the empty 3d orbitals of Si is often postulated to explain the extra stability of the siloxane bond and the great variability of Si-O-Si and Si-O-C angles[13-14]. In most organosilicon compounds the lengths of Si-O bonds are in the range 1.61 ± 0.03 Å compared to 1.83 Å calculated from covalent radii of Si and O atoms. The Si-O-Si angle varies from 105° in very strained rings like 5 to 150-180° in halogenodisiloxanes, such as $(Cl_3Si)_2O$. Siloxane angles in



(5)

D_n (n = 3, 4 and 5) are respectively 131.6°, 144.8°, and 146.5° which correspond to relatively unstrained structures[14]. The siloxane bond is one of the more stable bonds formed by silicon. The energy of the Si-O bond, estimated from heat of combustion, ranges from 420 to 500 kJ/mole. The value of 451 kJ/mole for D_4 accords with the relatively unstrained ring of the cyclotetrasiloxane. Furthermore it may be assumed that the energy of the Si-O bond is the same in all isomers of a given cyclosiloxane since the equilibrium ratio of cyclosiloxane stereoisomers is always close to the statistical ratio[15,16].

The intensities of Si-O-Si vibrational bands in infrared and Raman spectra are several times greater than those of C-O-C bands but their absorption regions practically coincide[17]. The fundamental vibration frequencies of the siloxane grouping lie in the regions 450-630 cm^{-1} (ν_{sym}) and 930-1170 cm^{-1} (ν_{as}).

For silicon atoms bonded to only one oxygen, the ^{29}Si NMR chemical shifts (δ) are downfield relative to tetramethylsilane (TMS), but for silicon attached to more than one oxygen atom the ^{29}Si δ values are upfield. In the D_n series, ^{29}Si δ values are -9.2 ppm for n = 3, -20.0 for n = 4, and about -23.0 for n > 6. This trend suggests that a substantial difference exists between the bonding state of silicon atoms in the near planar D_3 and large distorted D_n, n > 4[14,18].

1.2.2 Chemical reactivity of siloxanes

The high energy and the ionicity of the siloxane bond are responsible for the high thermal stability of siloxanes[14]. For example, the thermal degradation of D_4 occurs in the gas phase only at 450°C and gives only D_3 as a thermal decomposition product[19]. The redistribution, or equilibration of siloxane linkages is catalyzed by acids and bases. Under these conditions a continuous cleavage and reformation of siloxane bonds occurs until the system reaches an equilibrium[13].

Strong bases cleave the siloxane bond. Alkali metal hydroxides react readily to form silanolates by successive nucleophilic attacks at silicon (eqs. 1.3 and 1.4) followed

$$OH^{-} + Si{-}O{-}\overset{*}{Si} \longrightarrow Si{-}O^{-} + \overset{*}{Si}{-}OH \qquad \text{(eq. 1.3)}$$

$$Si{-}O^{-} + Si{-}O{-}\overset{**}{Si} \longrightarrow Si{-}O{-}Si + \overset{**}{Si}{-}O^{-} \qquad \text{(eq. 1.4)}$$

$$\overset{*}{Si}{-}OH + \overset{*}{Si}{-}OH \rightleftharpoons \overset{*}{Si}{-}O{-}\overset{*}{Si} + H_2O \qquad \text{(eq. 1.5)}$$

by condensation of silanols (eq. 1.5) formed in equation 1.3. The final composition of the mixture of siloxanes is thus a true thermodynamic equilibrium[13,14].

Anhydrous HCl is known as an effective reagent for either the cleavage, or the redistribution of siloxane linkages. As in the alkali-catalyzed process, the silanols produced in the first reaction (eq. 1.6) can condense together giving a new siloxane linkage and water (eq. 1.5). The organosilicon chloride from eq. 1.6 is thus easily hydrolyzed (eq. 1.7) giving another siloxane bond and regenerating HCl[13].

$$\text{Si-O-Si} + \text{HCl} \rightleftharpoons \text{Si-OH} + \text{SiCl} \qquad \text{(eq. 1.6)}$$

$$\text{Si-Cl} + H_2O \rightleftharpoons \text{Si-OH} + \text{HCl} \qquad \text{(eq. 1.7)}$$

Cleavage of the siloxane bond by other covalent halides also occurs under mild conditions and is sometimes useful in the preparation of organohalogenosilanes (eq. 1.8)[20].

$$(Et_3Si)_2O + AlBr_3 \longrightarrow {}^{2}Et_3SiBr + AlOBr \qquad \text{(eq. 1.8)}$$

Finally, siloxane linkages can also be cleaved by Grignard reagents and, more readily, by organolithium compounds[14,21].

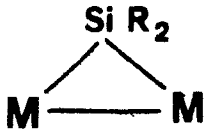
1.3 Synthesis of transition metal silyl complexes

Silyl-transition metal chemistry is of relatively recent vintage beginning in 1956 with the preparation of the first organosilyl derivative of ironcyclopentadienyldicarbonyl, $(CH_3)_3SiFe(CO)_2\eta^5\text{-}C_5H_5$, by Wilkinson et al.[22]. Interest in this new field grew explosively in the second half of the 1960's. The main lines of research[23] derived from: (i) comparative studies with the corresponding complexes of alkyl- and other group IV B elements, particularly with respect to the role of π-back-bonding from filled d_π orbitals of transition metals into empty d_π orbitals of silicon; (ii) expectation of useful catalytic properties from such heteronuclear derivatives. A number of relevant reviews[23-28] on the topic have been published up to 1974 but only one general review has been published very recently[29]. Some other surveys of certain aspects have appeared in the last four years[30-33].

Most silyl-transition metal complexes reported up to now can be classified according to the following schematic structural types where M stands for the transition metal atom

monosilyl ligands:

(6)



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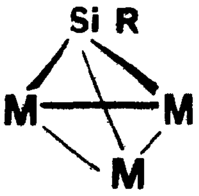
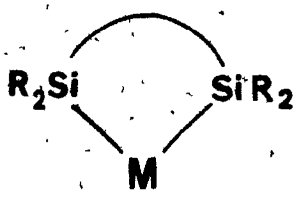


(8)

polysilyl ligands:



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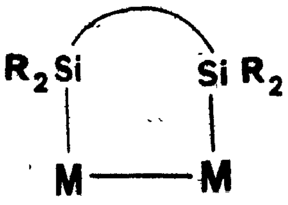

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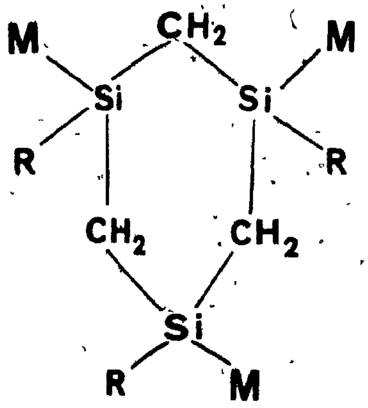


(11)

and R for substituent at silicon, other ligands at the transition metal atom are omitted for simplicity. In the category of monosilyl ligand, types 6 and 7 represent about 90 to 95% of all silyl-complexes reported whereas compounds of the type 8 are still a rarity[36,37]. Some complexes with polysilyl ligands, types 9 and 10, have been reported recently by Curtis and Greene[38,39]. The category 11 is also very recent[34,35].

All three major synthetic routes to silyl-transition metal complexes were discovered before 1970.

1.3.1 Salt elimination (metathesis)

The reaction of a transition metal anion with an organosilicon halide provided the first compound with a Si–M bond (eq. 1.9)[22]. The same procedure has been used to prepare many

$$Na[\eta^5\text{-}C_5H_5Fe(CO)_2] + (CH_3)_3SiCl \longrightarrow (CH_3)_3SiFe(CO)_2\eta^5\text{-}C_5H_5 + NaCl \qquad \text{(eq. 1.9)}$$

silyl derivatives from anions like $[Co(CO)_4]^-$, $[\eta^5\text{-}C_5H_5Mo(CO)_3]^-$, $[Mn(CO)_5]^-$, and $[\eta^5\text{-}C_5H_5Cr(CO)_3]^-$ [23,40,41]. The reaction of an alkali metal silyl with a transition metal halide has also been used with some success (eq. 1.10)[42,43] but some inherent limitations have been pointed out[23,28] for both types of salt elimination reactions: (i) the expected silyl-transition metal complex may be difficult to separate from the alkali

$$H_3SiK + [\eta^5\text{-}C_5H_5Fe(CO)_2]Br \xrightarrow{(43)}$$

$$H_3SiFe(CO)_2\eta^5\text{-}C_5H_5 + KBr \qquad \text{(eq. 1.10)}$$

metal halide, (ii) difficulties may arise through metal-halogen exchange[44], (iii) problems have been found in the preparation of some reactants, especially alkali metal silyls, and (iv) carbonylate anions have a tendency to attack the silicon via the oxygen of the carbonyl group[45].

1.3.2 Hydrogen elimination

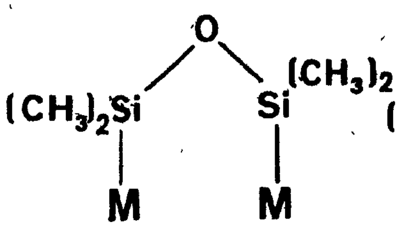
Chalk and Harrod[46,47] reported that the highly reactive, dicobalt octacarbonyl, is rapidly cleaved at room temperature by a variety of silicon hydrides to give hydrogen and new silyl-cobalt complexes. They described a two-step mechanism (eqs. 1.11 and 1.12) where R is an organic substituent and in

$$R_3SiH + Co_2(CO)_8 \longrightarrow R_3SiCo(CO)_4 + HCo(CO)_4 \qquad \text{(eq. 1.11)}$$

$$R_3SiH + HCo(CO)_4 \longrightarrow R_3SiCo(CO)_4 + H_{2(g)} \qquad \text{(eq. 1.12)}$$

which the production of $HCo(CO)_4$ in the first step (eq. 1.11) is thought to be responsible for the catalytic activity of $Co_2(CO)_8$ in the hydrosilation of olefins[48]. This now classical approach has been used extensively for the preparation of silyl-metal complexes by cleavage of a variety of metal-

metal bonded dimers[23]. Of particular interest to the present study is the recent preparation[38,39] of some siloxanyl-transition metal derivatives. The linear disiloxane, $[(CH_3)_2HSi]_2O$, was used in reaction with metal complexes and three groups of products were isolated (e.g. 12, 13, 14):



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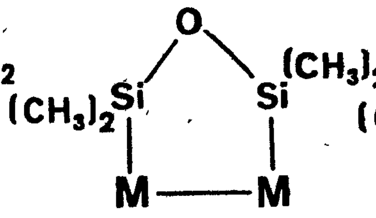

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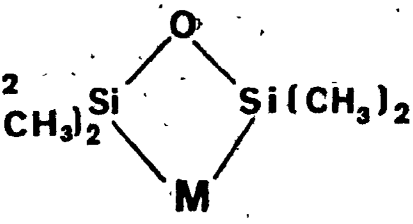


(14)

where M stands for the transition metal moiety. Such complexes have many features in common with the cyclosiloxane compounds to be described in this thesis and their properties will be discussed in more detail in the following chapter.

1.3.3 Oxidative addition and elimination

Oxidative addition with or without elimination of a neutral ligand has been extensively used for the formation of transition metal bonds to all of the elements of group IV A[49-52]. Typical reactions involve five and four coordinate d^8 complexes, or three and four coordinate d^{10} complexes with silanes (eq. 1.13). Although d^6-d^4 reactions are rare, there are examples. An unusual rhodium(V) complex, $[(\eta^5\text{-}C_5(CH_3)_5)Rh(H)_2(Si(C_2H_5)_3)_2]$, was recently prepared[58] by the addition of $(C_2H_5)_3SiH$ to the Rh(III)dimer $[(\eta^5\text{-}C_5(CH_3)_5)_2Rh_2Cl_4]$.

$$((C_6H_5)_3P)_2Ir(CO)Cl + R_3SiH \xrightarrow{50} R_3SiIr(CO)(H)(P(C_6H_5)_3)_2 \qquad \text{(eq. 1.13)}$$

Attempts to extend the application of the oxidative addition route to some light metals (Fe, Co, Mn, or Ni) were only partially successful due to the generally high reactivity of silyl-transition metal hydrides[53-56]. The best results have been obtained with metal carbonyls (eq. 1.14)[53] which react photochemically with silanes to form silyl metal hydrides and eliminate one carbon monoxide.

$$\eta^5\text{-}C_5H_5Rh(CO)_2 + (C_6H_5)_3SiH \xrightarrow{h\nu} (C_6H_5)_3SiRh(CO)(H)\eta^5\text{-}C_5H_5 + CO \qquad \text{(eq. 1.14)}$$

These oxidative addition reactions are often reversible and Si-M adducts (where M = Rh, Pt, Ir) tend to be more stable when there are electron-withdrawing groups on silicon[48,58]. Oxidative additions of Si-H are normally assumed to be concerted reactions[59].

1.4 Chemistry of transition metal silyl complexes

1.4.1 General reactivity

In addition to classical routes of synthesis mentioned above, many silyl-transition metal complexes have been prepared by substitution reactions both at silicon and at the transition metal[23]. For example, the progressive chlorination at the silicon center of $H_3SiMn(CO)_5$ by HCl has been reported by Aylett and Campbell[60]. Many substitution reactions at the transition metal involving displacement of a neutral ligand such as CO by another neutral ligand (eq. 1.15), with or without UV irradiation, have been reported for many

$$R_3SiMn(CO)_5 + (C_6H_5)_3P \xrightarrow{h\nu} R_3SiMn(CO)_4((C_6H_5)_3P) + CO \qquad \text{(eq. 1.15)}$$

metals (Mn, Fe, Re, ...)[28]. Sometimes cyclometalation occurs when phosphorus ligands, such as phosphines or phosphites, are reacted with silyl-transition metal complexes under UV irradiation[61].

Silyl-transition metal hydrides can show remarkably high acidities, which makes possible the formation of ionic species and adducts. Thus the complex $Cl_3SiFe(CO)(H)(\eta^5\text{-}C_5H_5)$ is a strong acid in acetonitrile ($pK_a = 2.6$) and gives the tetraphenylarsenium salt of the corresponding anion in acetone by loss of a proton[62] (eq. 1.16).

$$[(C_6H_5)_4As]Cl + Cl_3SiFe(CO)(H)\eta^5\text{-}C_5H_5 \longrightarrow$$

$$[(C_6H_5)_4As][Cl_3SiFe(CO)\eta^5\text{-}C_5H_5] \qquad \text{(eq. 1.16)}$$

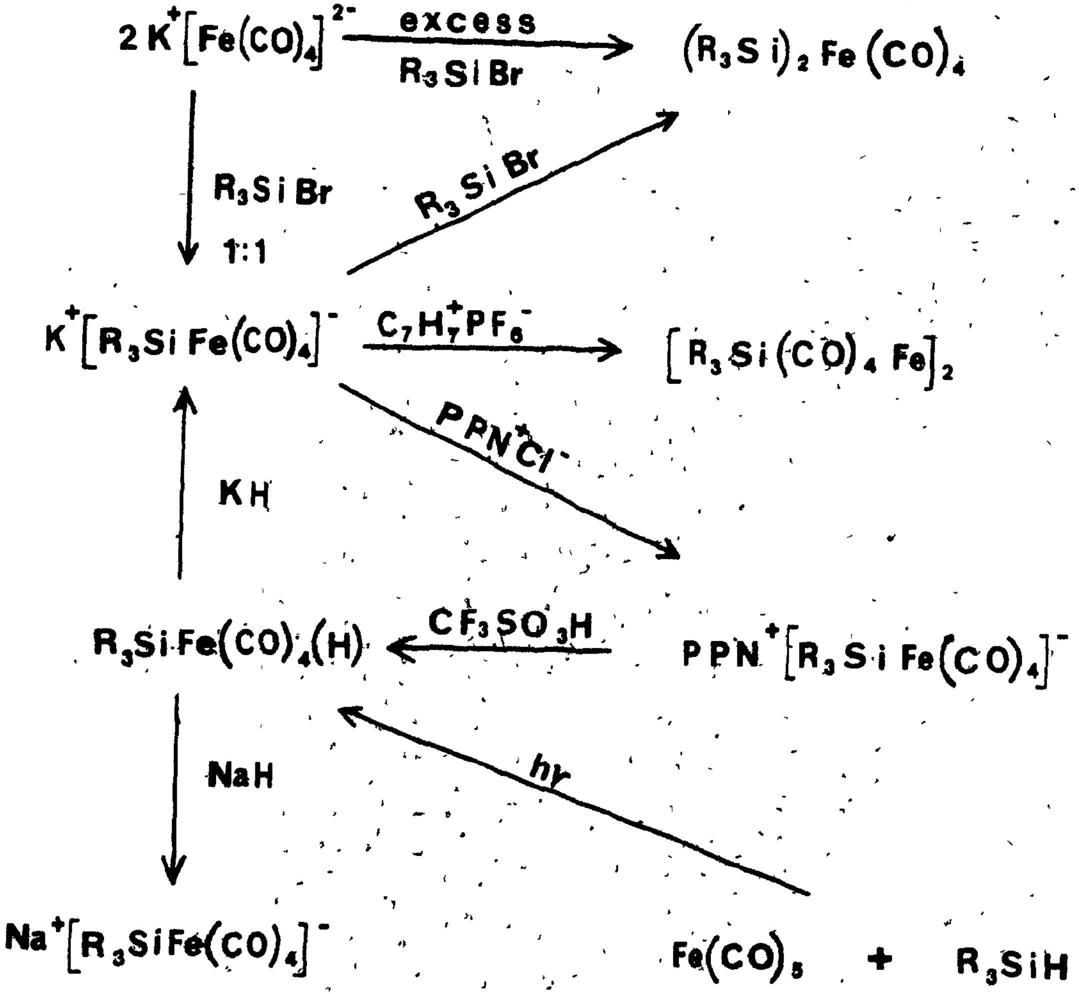
Analogous hydrides of Mn, Co, and Cr have also been found to be deprotonated with amines[55,60,62].

Recently, Gladysz and coworkers[63] reinvestigated synthetic routes to, and reactivity of, trimethylsilyl-iron tetracarbonyls. Some syntheses and interconversions of such trimethylsilyl derivatives are shown in Scheme 1.1. This is one of the best examples of the rich chemistry involving trialkylsilyl-transition metal complexes. An earlier comparative study of the reactions of some analogous $(CH_3)_3Si$-metal carbonyl complexes was published by MacDiarmid et al.[64-66]. The complexes $(CH_3)_3SiCo(CO)_4$ and $(CH_3)_3SiMn(CO)_5$ are cleaved by reagents, such as H_2O, MeOH, and amines, whereas $(CH_3)_3SiFe(CO)_2\eta^5\text{-}C_5H_5$ is much more resistant to nucleophilic attack. Nevertheless, a rapid reaction occurs in the presence of anhydrous hydrogen chloride (eq. 1.17) even at very low temperature[64]. It was suggested that the high rate of

$$(CH_3)_3SiFe(CO)_2\eta^5\text{-}C_5H_5 + HCl_{(g)} \longrightarrow$$

$$(CH_3)_3SiCl + HFe(CO)_2\eta^5\text{-}C_5H_5 \qquad \text{(eq. 1.17)}$$

Scheme 1.1: Syntheses and interconversions of trimethylsilyliron derivatives (from ref. 63)



PPN = $[(C_6H_5)_3P]_2N^+$ R = CH_3

reaction with HCl indicates that the rate-controlling step in the cleavage might involve an electrophilic attack at the iron center analogous to the silicon-phenyl bond which undergoes electrophilic attack by HCl[67a]. It was also observed that the silicon-cobalt bond is easily cleaved by covalent halides and iodine[65]. Few attempts to insert carbon monoxide into the silicon-metal bond[67b], as $M-\overset{O}{\overset{\|}{C}}-SiR_3$, were successful even at high pressure. The lack of easy insertion of a carbon atom can be due to the loss of $(d \rightarrow d)\pi$ bonding energy between the transition metal and the silicon which would result[68].

The chemistry of group IV B elements (Si, Ge and Sn) with platinum and iridium has been investigated by Glockling et al.[69] and many interesting features have been shown. Among those, the hydrogenolysis of the $(CH_3)_3Si-Pt$ bond was shown to proceed readily at 1 atm. H_2 and ambient temperature (eq. 1.18). Furthermore, the second $(CH_3)_3Si-Pt$ bond is hydrogenated at 70°C and 1 atm. H_2 giving the second $(CH_3)_3SiH$ and a platinum cluster[69]. The reversibility of the oxidative addition of R_3SiH to $(R_3P)_2PtHCl$ has also been demonstrated[69].

$$(R_3P)_2Pt(Si(CH_3)_3)_2 \xrightarrow{H_2\ (1\ atm)} (R_3P)_2Pt(H)Si(CH_3)_3 + (CH_3)_3SiH \qquad \text{(eq. 1.18)}$$

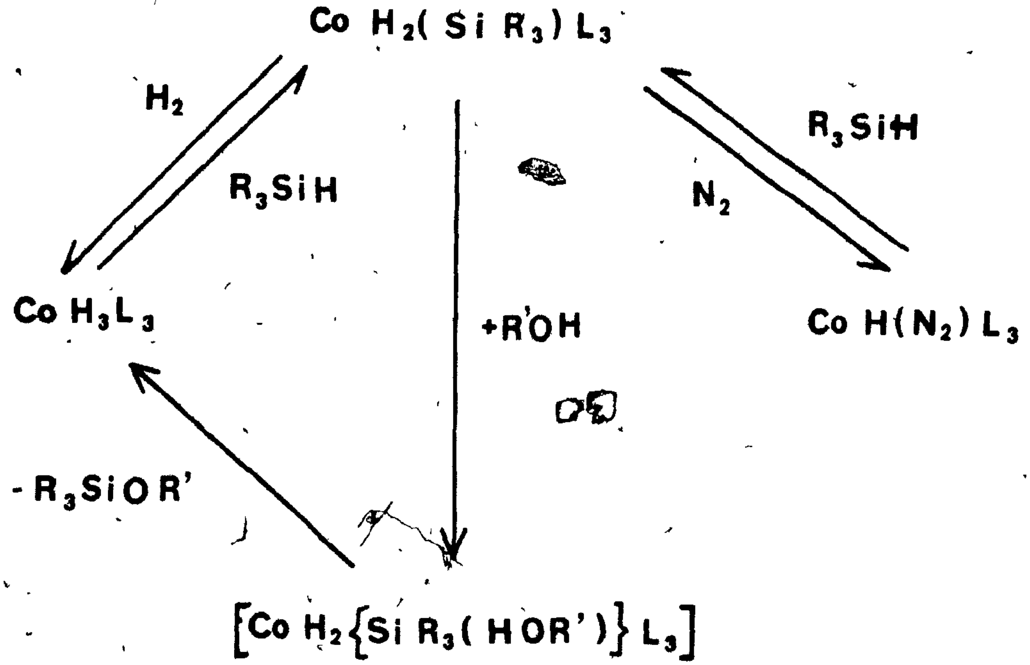
1.4.2 Silyl-transition metal complexes in catalysis

One of the more interesting fields of silyl-transition metal chemistry is the use of these complexes in catalysis. Hydrosilation, the addition of a silicon hydride to an olefin (eq. 1.19), became an important industrial route for the

$$R_3SiH + CH_2 = CHR' \xrightarrow{\text{catalyst}} R_3SiCH_2CH_2R' \qquad \text{(eq. 1.19)}$$

formation of silicon-carbon bonds with the discovery of the exceptional catalytic activities of chloroplatinic acid by Speier et al.[24,70]. A general comprehensive mechanism has been proposed for the catalysis of hydrosilation by group VIII complexes[47,48,52]. The mechanism proposed for platinum is a reversible oxidative addition of Si-H to the platinum-olefin complex followed by insertion of olefin into Pt-H and reductive elimination of hydrosilated olefin[48]. In addition to platinum complexes some other group VIII metal complexes have been found to be effective catalysts for hydrosilation and other reactions with silanes[48]. Recently, Haszeldine and coworkers[71] reported homogeneous catalysis of deuteriation of R_3SiH ($R = OC_2H_5, C_2H_5, CH_3F$), hydrosilation of $C_4H_9CH=CH_2$, and O-silylation of simple alcohols by silyl-cobalt(III) complexes. The proposed mechanism for the catalytic O-silylation (scheme 1.2) shows that the reaction can be inhibited by the presence of molecular hydrogen and nitrogen. The polymerization of silacyclobutane is another example of

Scheme 1.2: Catalysis of O-silylation of ethanol (from ref. 71).



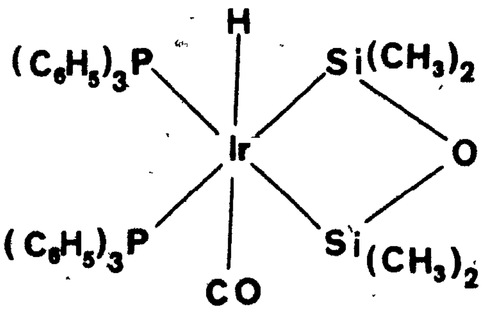
$R = OC_2H_5$ $R' = CH_3\ ,\ C_2H_5$

the participation of silyl-metal compounds in a catalytic cycle[70,72].

1.4.3 Siloxanyl-metal complexes

Monomeric metal complexes with siloxanyl-metal bonds have been very rarely mentioned in the literature. Although Harrod and Chalk[47] reported the infrared spectrum of tetrakis-(tetracarbonylcobalt)tetramethylcyclotetrasiloxane, no other property of the compound was described. Eaborn[73] reported, in a short communication, the formation of a poorly characterised 4-membered ring metallocycle, $(C_6H_5)_3P)_2Pt(Si_2(CH_3)_4O)$, from the reaction of the disiloxane $[(CH_3)_2HSi]_2O$ with $((C_6H_5)_3P)_2Pt(C_2H_4)$ in benzene.

The reactivity of some linear siloxanes toward metal complexes has been clearly shown in a recent study of Curtis and coworkers[38,39,74,75]. They reported the formation of some small metallocycles (9 and 10) by the reaction of tetramethyldisiloxane (TMDS) with $Fe(CO)_5$, $Ru_3(CO)_{12}$, $(C_6H_5)_3P)_2PdCl_2$, and $(C_6H_5)_3P)_2Ir(CO)Cl$. The reaction of TMDS with $CO_2(CO)_8$ gave the complex (12) without metal-metal linkage.



(15)

All of these siloxane-metal complexes were reported to be of low stability[38].

The most interesting metallodisiloxane prepared[74-76] (15) was the 4-membered ring $((C_6H_5)_3P)_2(CO)(H)Ir[Si_2(CH_3)_4O]$ which was found to be active in the catalytic oligomerization of linear siloxanes. The strain present in this metallocycle compresses the Si-Ir-Si angles by 25° from the ideal octahedral 90°, whilst the Si-O-Si angle of 99.8° represents a 30-50° compression from the normal 130-150° found in cyclic siloxanes[14]. Similar redistribution reactions of a variety of hydrogen-substituted siloxanes were also reported to be catalyzed by various transition metal complexes of iridium and rhodium[76].

1.5 Geometric isomers and ring conformation of cyclosiloxanes

One of the most interesting features of cyclosiloxanes is the presence of many geometrical isomers in each ring size. Figure 1.2 shows the schematic representation of these isomers and their statistical abundance at equilibrium. In all figures (triangle, lozenge and pentagon), each straight line joining two corners represents a siloxane bond and each corner stands for a silicon atom bonded to one methyl group and one other substituent R (fig. 1.1a). The subsequent R can be an organic, inorganic or organometallic group. The notation of one isomer of a given cyclosiloxane is done by

Figure 1.1a: The triangular representation of one geometric isomer of 1,3,5-trimethylcyclotrisiloxane

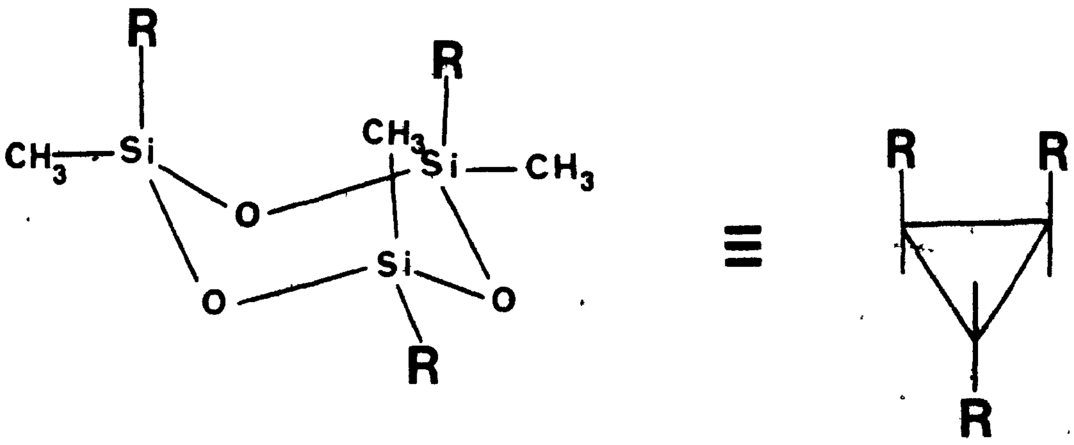


Figure 1.1b: Two classical conformers of the geometric isomer $D_3^R(I)$

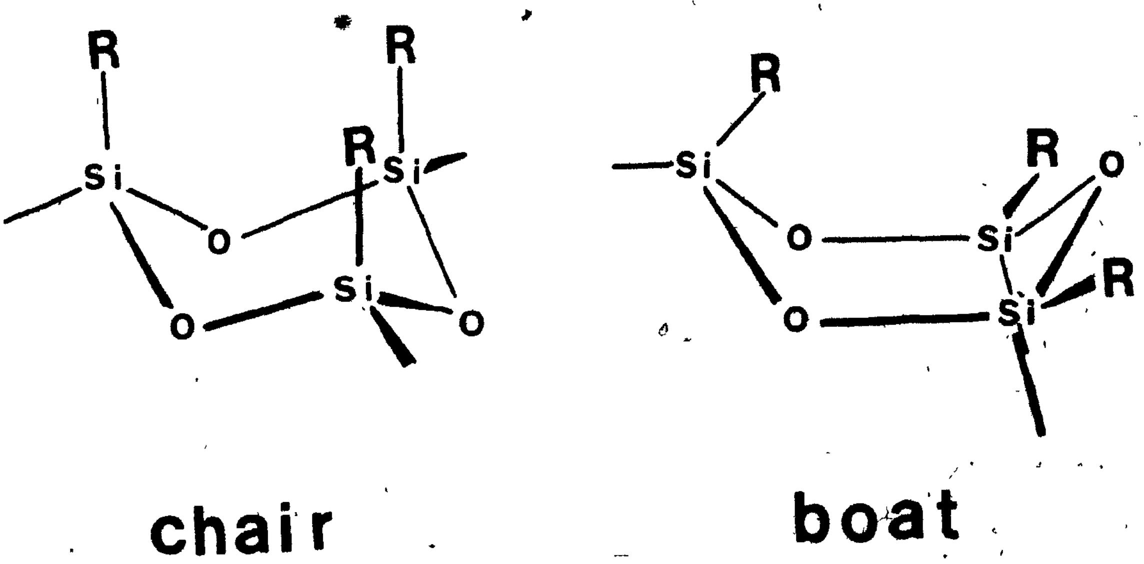
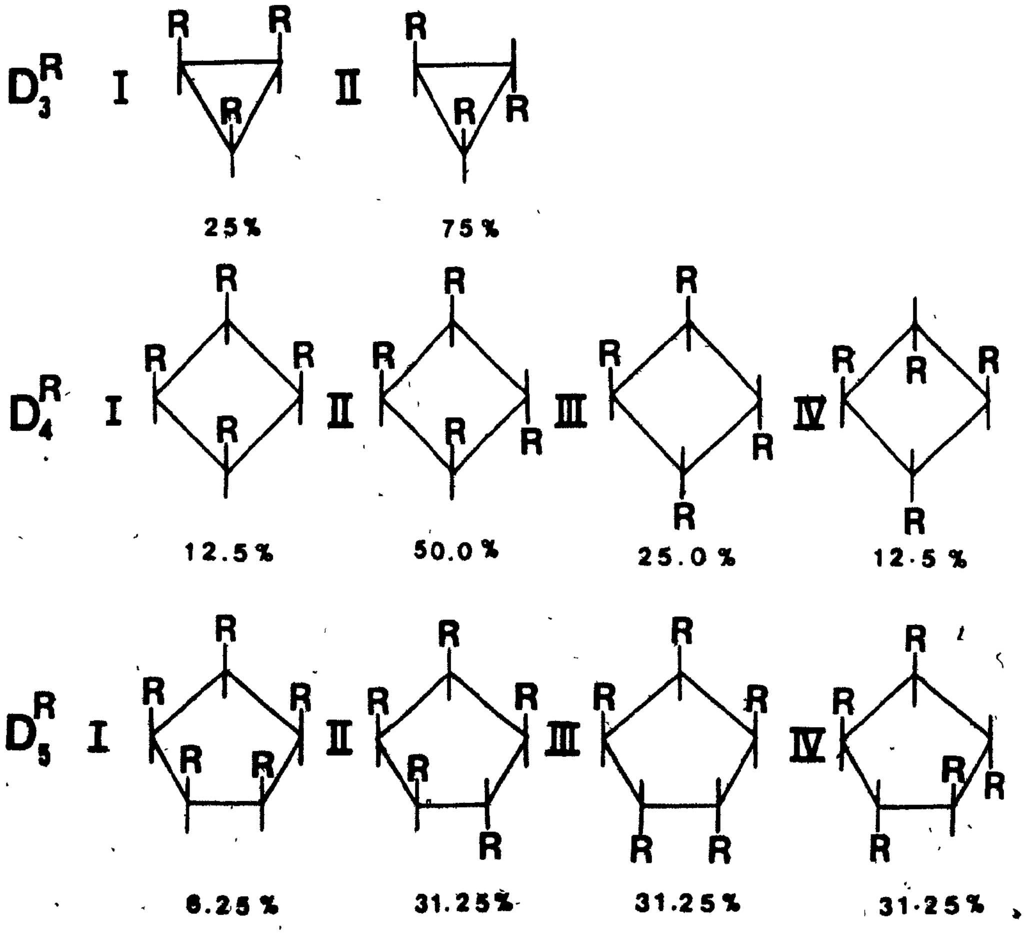


Figure 1.2: Schematic representation of geometric isomers of D_n^R (n = 3, 4, and 5) and their statistical abundances



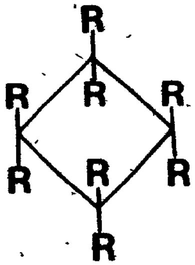
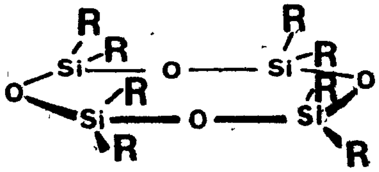
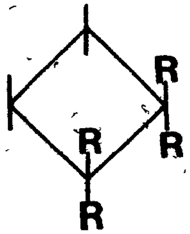
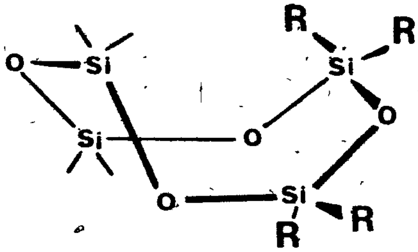
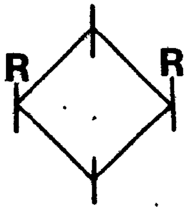
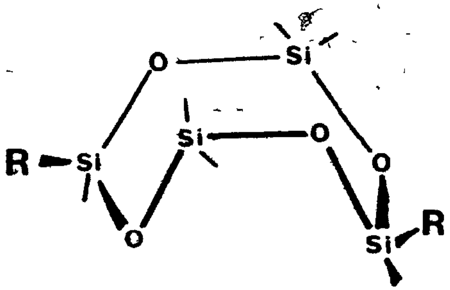
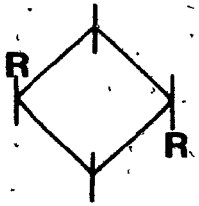
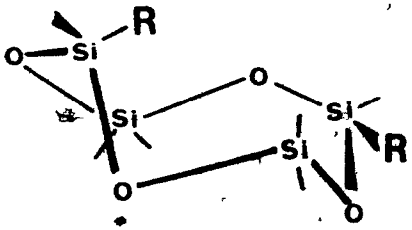
mentioning the ring symbol D_n^R, followed by the Roman number in brackets, assigned to that isomer in Figure 1.2. Thus the notation D_4^H(III) refers to the third isomer (from left to right in Figure 1.2) of the tetramethylcyclotetrasiloxane. The notation $D_{4-n}^A D_n^R$ (n = 1 to 3) will be used to describe methylcyclotetrasiloxanes bearing two different substituents, A and R , on the same molecule.

By analogy with carbocycles, one can draw many different conformations for cyclosiloxanes. The simplest example is illustrated in Figure 1.1b. Point groups and the corresponding conformations of the cyclotetrasiloxane ring have been discussed by Andrianov and coworkers[77]. Conformers are probably in fast fluxional equilibrium and have never been observed by NMR spectroscopy[14]. Two recent studies of the D_n series (n= 3 to 6) using vibrational spectroscopy[78,79] indicate that these rings have a fairly flat geometry in the gas phase and in solution. A planar structure using D_{nh} symmetry was found to be a good approximation for assignment of vibrational spectra of all members of D_n series. In the solid state, recent crystal structure studies[80] of both isomers D_3^{Ph}(I) and (II) confirm the nearly flat structure of this trimer with Si-O-Si angle at 132°. Many cyclotetrasiloxanes have also a flat ring in the solid state[81] with Si-O-Si angle ranging from 142° to 168° contrasting with analogous cyclotetrasilazanes which show distorted structures in the solid state with a Si-N-Si angle ranging from 120° to 130°[82].

In contrast with the silazane bond, that of the siloxane is extremely flexible and the siloxane ring accommodates conformational and steric strains. The conformation of a cyclosiloxane can be totally modified by changing the nature and the relative position of substituents[83]. That unique property is illustrated by the conformations of four analogous molecules (Fig. 1.3). The octaphenylcyclotetrasiloxane (16) is almost planar with Si-O-Si angles ranging from 153° to 168° and a maximum deviation of 0.1 Å from the average plane of the ring[81]. By contrast the compound 17 has the boat conformation with the bow and stern bent at angles of 27.5° and 31.0° to the bottom. The deviation over the average plane of the bottom is as much as 0.45 Å[77]. The compounds 18 and 19 are two geometric isomers of the same molecule. The *cis* isomer 18 adopts a boat conformation with a maximum deviation of 0.4 Å from the average plane[84] whereas the *trans* isomer 19 shows a chair conformation with a deviation of 0.3 Å from the average plane of Si and O atoms[85]. The interest and the importance of these two isomeric structures (18 and 19) have been noted by biologists[86] who found a very marked estrogen-like activity for the *cis* form (18) but no pronounced biological activity for the *trans* form (19).

From these few examples, it becomes evident that the conformation of the cyclosiloxane molecules must be regarded as the result of a compromise between the repulsion of the

Figure 1.3: Conformations of some cyclotetrasiloxanes (in all cases $R = C_6H_5$)

Compound		Si–O–Si	Conformation	
	16	153-168°		CROWN
	17	144-156°		BOAT
	18	142-147°		BOAT
	19	144-147°		CHAIR

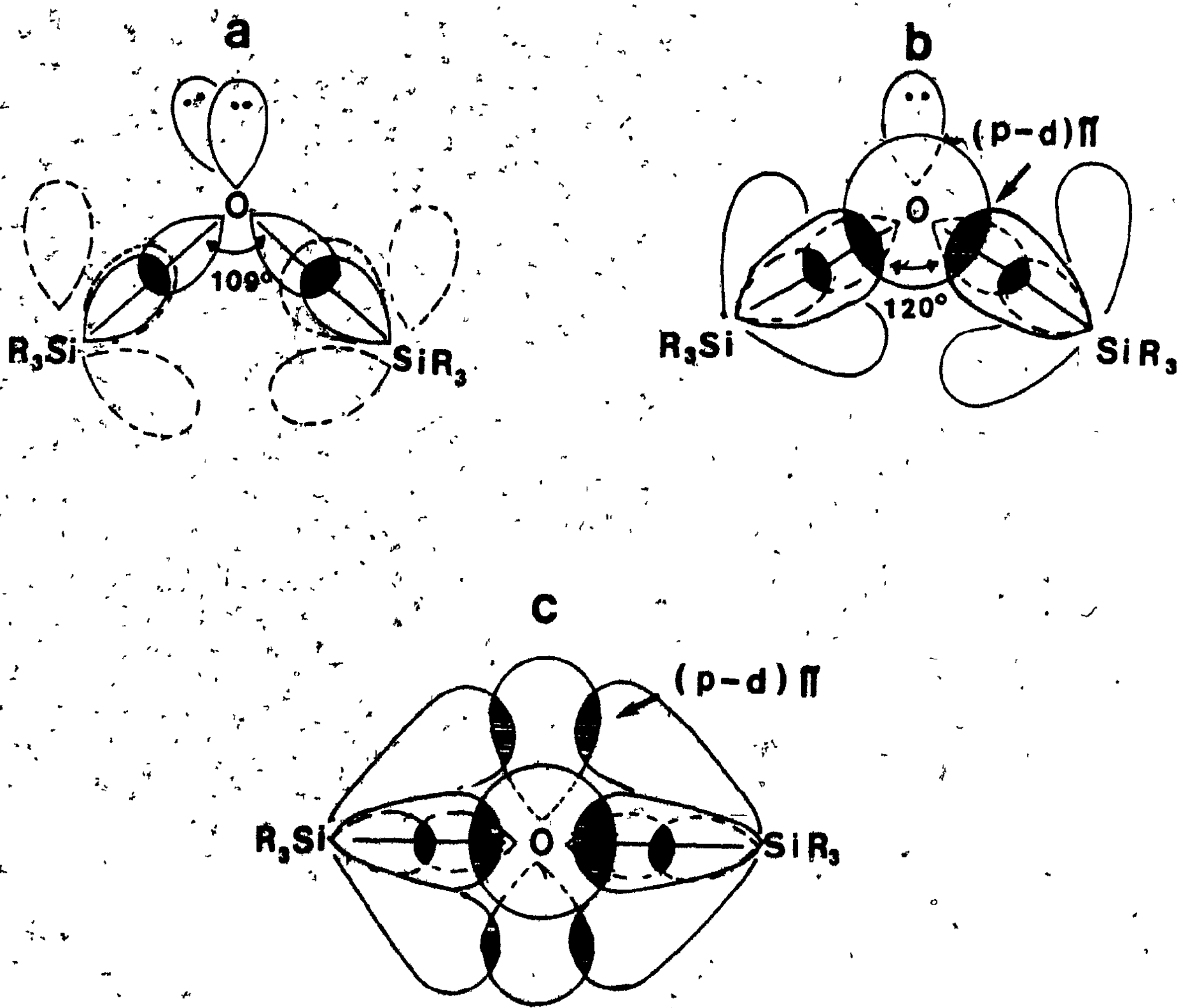
nonbonded groups (adjacent groups) and the requirement for maximum orbital interaction[14,77]. Oxygen when it is bonded with two silicon atoms has a hybridization that is an average between sp^3, sp^2 and sp hybridization. In the limiting case, an increase in the Si-O-Si angle, associated with the transition from the sp^3 hybridization of the oxygen atom to sp^2 and to sp, probably favors the formation of common mutually perpendicular $(p\rightarrow d)\pi$ orbitals of both unshared pairs of the oxygen with the d orbitals of both of the silicon atoms bonded to it[14]. Thus the loss of sigma contribution (sigma bonding is maximum at 109.4°) is compensated by gain of $(p\rightarrow d)\pi$ contribution (Fig. 1.4). This feature explains the extraordinary stability of the siloxane bond in various organosilicon compounds where the Si-O-Si angle ranges from 105° to 180°[14].

1.6 Methylcyclosiloxane as framework

The major requirement in the building of multifunctional catalysts mentioned in the preface, is to get some control over the spacial relationship of substituents. Small methylcyclosiloxanes offer some of the sought-for properties:

1) The ring sizes are variable ($n = 3$ to ∞).
2) Many geometric isomers are present in all ring sizes.
3) The Si-O-Si bond is highly flexible.
4) By steric effects on substituents, it becomes possible to modify strongly the conformation of the ring.

Figure 1.4: Overlapping of electronic orbitals of oxygen atom in sp^3 (a), sp^2 (b), and sp (c) hybridization with orbitals of silicon atoms in disiloxane grouping (from ref. 14)



5) All known methylcyclosiloxanes are readily soluble in protic and aprotic solvents (except water), a desirable situation in homogeneous catalysis.

6) The methyl group attached to the silicon provides an excellent ^1H NMR probe for characterization of geometric isomers.

7) Many silicon-transition metal bonds are stable, strong and nonreactive which reduces the likelihood of loss of the catalytic functions from the frame.

8) Silicon-carbon bond is also strong[13,14] which offers opportunity to attach other different organic functions onto the ring besides the organometallic moiety (e.g. 3).

9) Dichlorosilanes, $RR'SiCl_2$, from which all cyclosiloxanes can be prepared, are cheap and commercially available.

10) The Si-H bond, e.g. in D_4^H, offers an interesting reaction site for the H_2 elimination reaction with organometallic complexes.

After that exhaustive list of advantages we should mention at least two disadvantages:

1) The Si-O bond is very sensitive to strong bases and quite sensitive to strong acids.

2) A major problem of separation of multiple products can arise from substitution reactions where the reactants have been only partially reacted.

Finally, it should be noted that some other known cyclic compounds present major disadvantages:

1) Carbocycles (including cyclic ethers) are expected to be much less flexible than cyclosiloxanes due to the absence of $(p \rightarrow d)\pi$ bonding.
2) The sigma carbon-transition metal bond is reactive and easily cleaved[87].
3) Heterocycles containing phosphorus or nitrogen atoms (i.e. cyclophosphanes, cyclosilazanes) present little interest due to the strong chelating properties of N and P.
4) Cyclosilanes could present some interest but they are much less known than cyclosiloxanes and not readily available.
5) Cyclocarbosilanes recently used by Houle and Schneriny[35] have extremely complex ^1H NMR spectra and are difficult to characterize.

2. SYNTHESIS AND PROPERTIES OF SOME NEW METHYL SUBSTITUTED CYCLOSILOXANES

As mentioned in the preface, the goal of this work was to synthesize and characterize some new large organometallic complexes involving methylcyclosiloxanes as frameworks. In the present chapter, the synthesis, some physicochemical properties, and the infrared spectra of this new class of polynuclear organometallic complexes are described in detail. In the course of this work, compound 1,3,5-trimethylcyclotrisiloxane (D^H_3) has been prepared by a new route and two new methylbromocyclosiloxanes have been isolated. The preparations and characterizations of these compounds are also included.

Some ^{1}H NMR and MS data are briefly presented to support the correct formulation of the isolated products. The full characterization of complexes by MS and ^{1}H NMR will be separately presented and discussed in Chapters 3 and 4.

2.1 Materials and methods

All procedures involving air-sensitive compounds were performed in Schlenk-type glassware interfaced to a moderate vacuum (10^{-2} torr) line using normal bench-top Schlenk techniques[88]. Nitrogen (Matheson, prepurified) was passed through a Drierite ^{R} column (1 x 20 cm) prior to use. Petroleum ether, n-hexane, hexanes, cyclohexane, pentane and decahydronaphthalene were deoxygenated by bubbling N_2 for a few minutes before use. Toluene, benzene, and tetrahydrofuran were dried over Na/K/benzophenone and freshly distilled before each experiment. All alkali trialkylborohydride/THF solutions were purchased from Aldrich and used as received. In experiments where THF was not desired, it was pumped off under moderate vacuum (10^{-2} torr) and replaced volume by volume with anhydrous diethyl ether, syringed through a rubber septum from the commercial container. All halogenosilanes were purchased from Silar, Petrarch, and Aldrich and used without further purification. Dicobalt octacarbonyl and triiron dodecacarbonyl were purchased from Strem Chemicals and Alfa-Ventron. Air sensitive compounds were transferred to Schlenk tubes and kept under N_2 at -20°C until used. The salt $NaFe(CO)_2\,\eta^5\text{-}C_5H_5$ was prepared from $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and sodium amalgam by the standard procedure using dry THF[89]. Lithium tetracarbonylcobaltate was prepared by reacting $Co_2(CO)_8$ with $Li(CH_3CH_2)_3BH$/THF following the procedure of Gladysz et al.[90].

2.2 Physical and analytical measurements

Most reactions were routinely monitored by infrared spectroscopy using a Perkin Elmer 297 spectrophotometer with a pair of liquid cells (NaCl windows, 0.1 mm path length) calibrated with a polystyrene film at 1601 cm^{-1}. Many infrared measurements were also measured on a Nicolet 6000 FTIR instrument using a liquid cell (KBr windows, 0.1 mm path length), or a gas cell for samples in gas phase (NaCl windows, 10 cm path length). The resolution is 4 cm^{-1} for all spectra except those specifically mentioned. Since most of the prepared compounds were amorphous solids or viscous liquids at ambient temperature, KBr pellets for infrared measurements were found to be very difficult to prepare and in most cases gave poor spectra.

^1H NMR spectra were recorded on a Varian XL200 (200-MHz, FT mode) spectrometer and all chemical shifts are reported in ppm relative to internal $(CH_3)_4Si$. Full descriptions of instrumental specifications and procedures for mass spectroscopy measurements and NMR spectroscopy are given in Chapters 3 and 4.

Gas chromatographic separations were performed on a Hewlett-Packard 5730A gas chromatograph equipped with a flame ionization detector and a programmable temperature oven. A two-meter Chrom WHP (OV-101 5%) packed column was used with argon as the carrier gas. Chromatographic separations by gravity were processed using air-free glass columns equipped with a nitrogen inlet at the top and a stopcock with a 19/26 outer member joint at the bottom. Columns were filled with a slurry of Florisil ^{R} (60-100 mesh), or silica gel (60-200 mesh) or activated alumina (80-200 mesh) prepared with deoxygenated hexanes. TLC separations were performed on precoated aluminum oxide 15 F 254 neutral on aluminum sheets (Type T from Merck) or on silica gel precoated on flexible sheets (Kodak Chromagram #13179).

Elemental analyses were carried out by Guelph Chemical Laboratories Ltd, Guelph, Ontario. Melting points were measured with a Thomas Hoover capillary melting point apparatus, and are uncorrected.

2.3 Synthetic procedures

Preparation of D_n^H (n = 4, 5, and 6) - The hydrolysis of CH_3SiHCl_2 and isolation of methylcyclosiloxanes have already been reported, and the following procedure is adapted from literature procedures[13,91]. A three-necked, 2-L flask with a Teflon stopcock on the bottom was equipped with a 500 mL dropping funnel and a large magnetic stirring bar. The flask was filled with 500 mL of a water-ice slurry and 250 mL of diethyl ether. A mixture of 500 g of CH_3SiHCl_2 and an equal amount of diethyl ether was added dropwise to the water-ice-ether mixture with moderate stirring. When half of the silane-ether solution had been added, the hydrolysis medium was vigorously stirred for a few minutes and then 15 minutes were allowed for a good phase separation to occur. The lower phase was drained off by the bottom stopcock and a fresh 500 mL water-ice slurry was added to the flask. The second half of the silane-ether solution was hydrolyzed by the same procedure. The ether layer was transferred to a 2-L separatory funnel, washed with 5 x 1-L distilled water and carefully dried over

$MgSO_4$. The solvent was distilled off on a rotary evaporator, leaving 220 g of a transparent and viscous mixture of methylcyclosiloxanes. A fractional distillation at atmospheric pressure was carried out using standard distillation apparatus with a 30 cm Vigreux column. The first fraction afforded 49 g of D_4^H (99.7%) giving a yield of 19% and the second fraction, 33 g of D_5^H (97.5%) giving a yield of 13%. Percentages of purity were calculated from GC traces and the retention time of D_4^H was checked against an authentic sample purchased from Petrarch Systems. The D_5^H sample was only contaminated by D_6^H as shown by GC-MS analysis and was used in chemical reactions without further purification.

D_4^H: 1,3,5,7-tetramethylcyclotetrasiloxane (m.w. 240). IR (gas) 2955 (m), 2179 (s), 1267 (s), 1105 (vs, br), 890 (s), 781 (m) cm^{-1}. Boiling point observed: 134-135°C, lit.: 133.0°C[91]. ^1H NMR (C_6D_6) δ 0.11 to 0.17 (3H, m), 4.98 to 5.04 (1H, m). Mass spectrum, selected m/e (rel. intensity %), 239 ($M-H^+$, 65), 225 ($M-CH_3^+$, 100). Anal. calcd for $C_4H_{16}O_4Si_4$: C, 19.98; H, 6.71. Found: C, 19.81; H, 6.68. Compound <u>20</u>.

D_5^H: 1,3,5,7,9-pentamethylcyclopentasiloxane (m.w. 300). IR (gas) 2950 (m), 2175 (s), 1267 (m), 1105 (vs, br), 883 (s), 774 (m) cm^{-1}. Boiling point observed: 167-169°C, lit.: 168.7°C[91]. ^1H NMR (C_6D_6) δ 0.12 to 0.20 (3H, m), 4.97 to 5.05 (1H, m). Mass spectrum, selected m/e (rel. intensity %), 299 ($M-H^+$, 25), 285 ($M-CH_3^+$, 91). Anal. calcd for $C_5H_{20}O_5Si_5$: C, 19.98, H. 6.68. Found: C, 19.63, H, 6.50. Compound 21.

D_6^H: 1,3,5,7,9,11-hexamethylcyclohexasiloxane (m.w. 360). This compound was identified in the second fraction by the gas chromatography-mass spectrometry analysis. Mass spectrum, selected m/e (rel. intensity %), 359 ($M-H^+$, 9), 345 ($M-CH_3^+$, 38). Compound 22.

Preparation of D_n^{Ph} (n = 3 and 4) The synthesis of methylphenylcyclosiloxanes was performed as described in the literature[17,92,93]. Methylphenyldichlorosilane (500 g) was hydrolyzed following the procedure described above for D_n^H. The fractional distillation was performed at low pressure (2×10^{-2} torr) with an insulated 30 cm Vigreux column. The first fraction afforded 100 g (28%) of D_3^{Ph}, as a transparent viscous liquid which crystallized after a few hours into a white solid at ambient temperature. The second fraction afforded 75 g (21%) of D_4^{Ph}, as a transparent viscous liquid which became cloudy on standing at ambient temperature for many weeks. The purities of D_3^{Ph} (99.5%) and D_4^{Ph} (98%) were estimated from their ^1H NMR spectra and both were used without further purification. Attempts to distill a higher boiling-point fraction (assumed to be D_5^{Ph}) by slowly increasing the temperature of the distillation flask were unsuccessful and led to thermal decomposition of the residue (white fumes and darkening residue). The isolation of D_5^{Ph} has not been reported in the literature.

D_3^{Ph}: 1,3,5-trimethyltriphenylcyclotrisiloxane (m.w. 408). IR (hexanes) 1261 (m), 1126 (m), 1034 (s), 1018 (vs), 997 (s), 795 (s), 782 (m), 730 (m), 698 (m), 486 (m), 436 (m), 416 (m) cm^{-1}. Boiling point observed: 147°C/8×10^{-2} torr, lit.: 149°C/10^{-1} torr[17]. Melting point observed: 97.5°C, lit.: 99.5°C[17]. ^1H NMR (C_6D_6) δ 0.41 to 0.57 (3H, m), 7.0 to 7.6 (5H, br, m). Mass spectrum, selected m/e (rel. intensity %), 408 (M^+, 10), 393 ($M-CH_3^+$, 78). Anal. calcd for $C_{21}H_{24}O_3Si_3$: C, 61.72, H, 5.92. Found: C, 61.76, H, 5.82. Compound <u>23</u>.

D_4^{Ph}: 1,3,5,7-tetramethyltetraphenylcyclotetrasiloxane (m.w. 544). IR (hexanes) 1261 (m), 1127 (s), 1081 (vs) 1025 (s), 995 (m), 730 (m), 699 (m), 487 (m), 435 (m) cm^{-1}. Boiling point observed: 168°C/8×10^{-2} torr, lit.: 190°C/1.5 torr[92]. ^1H NMR (C_6D_6) δ 0.26 to 0.55 (3H, m), 7.12 to 7.69 (5H, br, m). Mass spectrum, selected m/e (rel. intensity %), 544 (M^+, 8), 529 ($M-CH_3^+$, 100). Anal. calcd for $C_{28}H_{32}O_4Si_4$: C, 61.72, H, 5.92. Found: C, 61.77, H, 5.98. Compound <u>24</u>.

<u>Preparation of D_n^{Br} (n = 3 and 4)</u>. A 100-mL three-necked round-bottom flask equipped with a nitrogen inlet and a

50-mL dropping funnel was charged with 2.0 g (4.8 mmol) of D_3^{Ph}, purged with N_2 and cooled to -50°C in an acetone-dry ice bath. Bromine (20 mmol) was then added dropwise to the solid with vigorous stirring over a period of 1 h. The reaction mixture was stirred for a further 30 min. at -50°C and then allowed to warm slowly to zero. After 3 h, all volatiles were slowly pumped off (10^{-2} torr) leaving a light yellow viscous slurry. Pentane (10 mL) was syringed into the flask, the solution was filtered under N_2 and transferred into a dry Schlenk tube (50-mL). The product was then recrystallized twice from a minimum amount of pentane at -78°C affording 0.92 g (45%) of D_3^{Br}, as a white crystalline solid. Purity of D_3^{Br} was estimated to be 99% from ^1H NMR data. The analogous D_4^{Br} was prepared following the same procedure, using 2.0 g (3.7 mmol) of D_4^{Ph} and 3.2 g (20 mmol) of bromine. Recrystallization from cold pentane afforded a white amorphous solid. The yield was 1.47 g (72%). Purity of D_4^{Br} was estimated to be 95-97% from the ^1H NMR spectrum. As both compounds are quite volatile, further purification can be achieved by sublimation *in vacuo* under rigorously dry conditions.

D_3^{Br}: 1,3,5-trimethyltribromocyclotrisiloxane (m.w. 417). IR (CS_2) 1264 (m), 1031 (vs), 846 (w), 795 (m), 755 (w), 455 (s) cm^{-1}. Melting point observed: 68-70°C. ^1H NMR (C_6D_6) δ 0.31 to 0.43 (m). Mass spectrum, selected m/e (rel. intensity %), 402 (M-CH_4^+, 21), 400 (M-CH_4^+, 19). Anal. calcd for $C_3H_9O_3Si_3Br_3$: C, 8.64, H, 2.17. Found: C, 10.70, H, 2.52. Compound 25.

D_4^{Br}: 1,3,5,7-tetramethyltetrabromocyclotetrasiloxane (m.w. 556). IR (CS_2) 1266 (m), 1103 (vs), 795 (m), 765 (w), 439 (w) cm^{-1}. Melting point observed: 40°C. ^1H NMR (C_6D_6) δ 0.29 to 0.48 (m). Mass spectrum, selected m/e (rel. intensity %), 542 (13), 540 (19), and 538 (11) are the largest peaks of M-CH_4^+ patch. Anal. calcd for $C_4H_{12}O_4Si_4Br_4$: C, 8.64, H, 2.17. Found; C, 11.96, H, 2.56. Compound 26.

Preparation of D_3^H A 200-mL three-necked round-bottom flask with a nitrogen inlet and a rubber septum was charged with 2.0 g (4.8 mmol) of D_3^{Br} dissolved in 20-mL of dry diethyl ether and the solution was cooled to -78°C. Then, sodium tri-sec-butyl borohydride/diethyl ether solution (20.0 mmol) was introduced dropwise with a syringe through the rubber septum. Following the addition, the solution was allowed to react at -78°C for 0.5 h, with vigorous stirring. The progress of the reaction was monitored by IR (the growth of Si-H peak at 2170 cm^{-1}). Many successive trap-to-trap transfers at low temperature (between 0 and -20°C) and under moderate vacuum (10^{-2} torr) afforded 0.55 g (63%) of a transparent volatile liquid. This product, D_3^H, was only contaminated with a small amount (< 5% from IR spectrum) of diethyl ether. An attempt to purify the product by a microdistillation at atmospheric pressure led to a rapid decomposition of the material. The reduction of D_3^{Br} to D_3^H was repeated four times and crude yields range from 10 to 80% depending on reaction conditions (temperature and time) and isolation techniques. D_3^H was found to be too sensitive to thermal rearrangement and was not submitted to mass spectral analysis. Reagents such as lithium tri-ethyl borohydride and lithium tri-butyl borohydride were also found to be efficient in the reduction of D_3^{Br} at -78°C but both borane residues were too volatile to be separated from the final product.

D_3^H: 1,3,5-trimethylcyclotrisiloxane (m.w. 180). IR (hexanes) 2170 (s), 1255 (s), 1025 (vs), 888 (vs), 772 (s) cm^{-1}. Boiling point observed: 94-96°C, lit.: 93.8°C[94]. ^1H NMR (C_6D_6) δ 0.13 to 0.17 (3H, m), 4.99 to 5.04 (1H, m). Compound <u>27</u>.

<u>Preparation of D_4^{Co}</u> A single-necked, 100-mL round-bottom flask with a Teflon stopcock side-arm was flushed with nitrogen and charged with 30 mL of deoxygenated pentane. Dicobalt octacarbonyl (7.0 g, 2.00 mmol) was dissolved in the pentane and the solution was cooled to 0°C in a water-ice bath. Using a small syringe, 2.0 g (0.83 mmol) of D_4^H were added dropwise through a rubber septum to the solution with vigorous stirring. After 0.5 h, the solution was allowed to warm to ambient temperature and the reaction was continued

for an additional 4 h. The completion of the reaction was verified by following the disappearance of the Si-H peak at 2170 cm^{-1}. The solution was stored for 48 h at -20°C and then cooled to -78°C for 4 h to complete the precipitation of excess $Co_2(CO)_8$ and black by-products, presumed to be $Co_4(CO)_{12}$. The supernatant red solution was syringed into a dry Schlenk round-bottom flask and evaporated to 10-12 mL under suction. The flask was slowly cooled to -78°C and pink crystals were precipitated. The crude yield gives 6.3 g (82%). Many successive recrystallizations in a minimum amount of dry pentane at -78°C afforded 2.72 g (35%) of pure D_4^{Co}, as a white amorphous solid at ambient temperature.

D_4^{Co}: 1,3,5,7-tetrakis[tetracarbonyl cobalt(I)] tetramethylcyclotetrasiloxane (m.w. 920). IR (hexanes) 2100 (s), 2040 (s), 2027 (sh), 2011 (vs), 1968 (w), 1263 (m) 1061 (s) cm^{-1}. Melting point observed: 95°C (decomposition). ^1H NMR (C_6D_6) δ 0.69 to 1.04 (6 sharp peaks). Mass spectrum, selected m/e (rel. intensity %), 920 (M^+, < 1), 905 ($M-CH_3^+$, < 1), 892 ($M-CO^+$, < 1). Anal. calcd for $C_{20}H_{12}O_{20}Si_4Co_4$: C, 26.10, H, 1.31. Found: C, 26.14, H, 1.45. Compound <u>28</u>.

<u>Preparation of D_5^{Co}</u> A single-necked, 100-mL round-bottom flask with a Teflon stopcock side-arm was flushed with nitrogen and charged with 30 mL of deoxygenated petroleum ether.

Dicobalt octacarbonyl (9.0 g, 2.60 mmol) was dissolved in the petroleum ether, the solution was cooled to 0°C, and 3.0 g (1.00 mmol) of D_5^H was added dropwise to the solution. After warming to ambient temperature, the solution was stirred for 4 h under a nitrogen atmosphere. A further 12 g (3.47 mmol) of $Co_2(CO)_8$ was added and the mixture was stirred for an additional period of 48 h at room temperature to complete the reaction. The solution was warmed to 40°C for 2 h to convert excess $Co_2(CO)_8$ into $Co_4(CO)_{12}$ for easier precipitation. The solution was then cooled to -20°C for 48 h followed by 4 h at -78°C. The supernatant red solution was transferred into a Schlenk round-bottom flask and evaporated by suction, leaving a sticky red solid. The residue was redissolved in a small amount of n-hexane and the solution was cooled slowly to -78°C. After 10 h, a red amorphous solid was isolated by decantation and dried in vacuo. Crude yield: 4.6 g (40%). Due to the extreme solubility of the product in all organic solvents (including cold petroleum ether), it was impossible to isolate a pure product (expected to be white) by successive fractional recrystallization. Nevertheless, 1.5 g of the crude red product was partially purified by passing it through a 30 cm Florisil^R column with hexanes. No decomposition was observed but we got very poor separation of red by-products from the expected D_5^{Co}. A reddish fraction (∿ 25 mL) was collected before the elution of the more intense red band.

The sticky residue (0.54 g) from this fraction was redissolved in 7 mL of hexanes and stored under nitrogen at -20°C for 5 days. A white amorphous solid (0.10 g, < 1%) was precipitated, isolated and dried <u>in vacuo</u> (compound <u>29</u>). The mother liquor was evaporated to dryness affording 0.4 g (3.5%) of a red viscous residue (compound <u>30</u>). Total yield of <u>30</u> = 10.2%.

D_5^{Co} (compound <u>29</u>): 1,3,5,7,9-pentakis[tetracarbonyl cobalt(I)] pentamethylcyclopentasiloxane (m.w. 1150). IR (hexanes) 2101 (s), 2039 (s), 2023 (sh), 2006 (vs), 1966 (w), 1263 (m), 1073 (s) cm^{-1}. Melting point observed: 55°C (decomposition). ^1H NMR (C_6D_6) δ 0.80 to 1.25 (m). Mass spectrum, selected m/e (rel. intensity %), 1094 ($M-2CO^+$, < 1), 1066 ($M-3CO^+$, < 1), 1038 ($M-4CO^+$, 1). Anal. calcd for $C_{25}H_{15}O_{25}Si_5Co_5$: C, 26.10, H, 1.31. Found: C, 26.20, H, 1.46. Total yield of <u>29</u> = 2.6%.

Compound <u>30</u> exhibits an infrared spectrum very similar to that of compound <u>29</u>, but also shows some extra peaks in the CO stretching region (2100 to 1850 cm^{-1}) attributed to a contamination by $Co_2(CO)_8$ and $Co_4(CO)_{12}$. Some differences in ^1H NMR spectra are reported and discussed in Chapter 4.

<u>Preparation of D_4^{Fp}</u> A 200-mL three-necked round-bottom flask equipped with a condenser, a nitrogen inlet at the condenser top, and a nitrogen outlet on the flask was charged with 25 mL of deoxygenated decahydronaphthalene. The apparatus was

purged with N_2 prior to the addition of 5.0 g (14.1 mmol) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and 3.0 g (12.5 mmol) of D_4^H. The N_2 outlet was closed and the slurry was heated to 160°C with a wax bath for 70 h with vigorous stirring and a slight positive pressure of N_2. At the end of this time, 3.0 g (8.4 mmol) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ were added and the bath temperature was increased to 170°C for the next 50 h in order to complete the reaction. The solution was cooled to ambient temperature and filtered over a layer of Celite^R. The solution was column chromatographed on silica gel (3 x 40 cm) using pure hexanes as first eluent. The solvent decahydronaphthalene was eluted first and was immediately followed by a yellow-orange band. The yellow solid (0.075 g) was isolated and identified as pure ferrocene. The expected product was then eluted with 500 mL of a mixture of hexanes and benzene (3:1). The yellow solution was evaporated to dryness leaving 7.2 g of yellow crude product. An intense red band was also eluted with a mixture of hexanes/benzene (1:1) and was characterized as the pure starting material, $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ (0.40 g). The yellow crude product was redissolved in benzene (12 mL) and a white-beige solid was precipitated from this benzene solution by adding a large volume (ca. 100 mL) of cold hexanes. The product was washed with hexanes and dried in vacuo. Yield: 3.54 g (30%). An appreciable amount (∿ 3 g) of partially substituted product was isolated from the mother liquor as a viscous yellow residue. The product D_4^{Fp}

is a white-beige amorphous solid, air stable at ambient temperature.

D_4^{Fp}: 1,3,5,7-tetrakis[cyclopentadienyl dicarbonyliron(II)]-tetramethylcyclotetrasiloxane (m.w. 944). IR (CCl_4) 3125 (vw), 2961 (w), 2899 (vw), 2000 (vs), 1943 (vs), 1250 (m), 1064 (sh), 1030 (vs) cm^{-1}. Melting point observed: 191°C (decomposition). ^1H NMR (C_6D_6) δ 0.89 to 0.96 (3H, m), 4.42 to 4.48 (5H, m). Anal. calcd for $C_{32}H_{32}O_{12}Si_4Fe_4$: C, 40.70, H, 3.42. Found: C, 40.68, H, 3.45. Compound 31.

Preparation of $D^H_{4-n}D^{Fp}_n$ Following the above procedure described for D_4^{Fp}, 3.0 g (12.5 mmol) of D_4^H were heated at 145°C in decahydronaphthalene with 6.0 g (8.4 mmol) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ for 22 h. The cooled solution was filtered and chromatographed on silica gel (2 x 42 cm). Decalin, ferrocene and unreacted D_4^H (traces) were eluted with 300 mL of pure hexanes. Partially substituted compounds, $D^H_{4-n}D^{Fp}_n$, were slowly eluted with 250 mL of hexanes/benzene (5:2), followed by 200 mL with the ratio 3:2. The long tailing yellow band was collected as three fractions (*ca.* 150 mL each) and solvents were evaporated to dryness. Each residue was redissolved in 10 mL of hexanes, filtered through Celite^R, and dried *in vacuo*. Only the third fraction was not entirely soluble in hexanes and afforded 0.27 g (2.3%) of the completely substituted D_4^{Fp} (32). The first fraction afforded

1.35 g of a very viscous yellow liquid (compound 33). The second fraction gave 3.04 g of a yellow viscous product (compound 34) and the third fraction, 1.32 g of a yellow viscous solid (compound 35). All products are very soluble in hexanes and attempts to separate some of them by fractional recrystallization at low temperature were unsuccessful. All fractions are air stable when dry but decompose slowly in solution.

$D^{H}_{4-n}D^{Fp}_{n}$ n = 1.4: IR (hexanes) 2150 (s), 2006 (vs), 1950 (sh), 1944 (vs), 1254 (sh), 1249 (m), 1065 (vs, br) cm^{-1}. ^{1}H NMR (C_6D_6) δ 0.30 to 0.42 (1.7H, m), 0.77 to 0.92 (2.3H, m), 4.19 to 4.41 (3.8H, m), 5.2 (0.5H, m). Compound 33.

$D^{H}_{4-n}D^{Fp}_{n}$ n = 2.6: IR (hexanes) 2146 (m), 2006 (vs), 1950 (sh), 1946 (vs), 1254 (sh), 1248 (m), 1065 (sh), 1060 (vs, br) cm^{-1}. ^{1}H NMR (C_6D_6) δ 0.39 to 0.43 (1.1H, m), 0.79 to 0.96 (2.9H, m), 4.29 to 4.48 (4.8H, m), 5.2 (0.3H, m). Compound 34.

$D^{H}_{4-n}D^{Fp}_{n}$ n = 3.1: IR (hexanes) 2140 (m), 2005 (vs), 1950 (sh), 1946 (vs), 1254 (sh), 1249 (s), 1065 (sh), 1049 (vs, br) cm^{-1}. ^{1}H NMR (C_6D_6) δ 0.39 to 0.43 (1.0H, m), 0.84 to 0.98 (3.1H, m), 4.29 to 4.48 (6.7H, m), 5.2 (0.15H, m). Anal. calcd for $C_{25}H_{28}O_{10}Si_4Fe_3$: C, 39.73, H, 3.57. Found: C, 40.79, H, 3.64. Compound 35.

Preparation of $D_1^{Co}D_3^{Fp}$ Compound 35, prepared above (1.2 g), was redissolved in dry deoxygenated hexanes (25 mL) and filtered. This solution was transferred by syringe into a 100-mL round-bottom flask with a nitrogen inlet and cooled to 0°C. With vigorous stirring, 0.4 g (1.2 mmol) of $Co_2(CO)_8$ was added in portions of a few mg and the reaction was monitored by IR. When the reaction was almost complete, the solution was warmed to 30°C for 1 h to convert most excess $Co_2(CO)_8$ into $Co_4(CO)_{12}$. The solution was stored at -20°C. The black precipitate formed overnight was filtered off. The red solution was partially evaporated to ca. 10 mL and re-cooled to -20°C for 48 h. The red solution was decanted and the yellow solid formed overnight was dried in vacuo. Crude yield: 0.57 g (39%). The yellow residue was purified by passing through a 25-cm silica gel column eluted with pure hexanes. The fraction collected just before the red band ($Co_4(CO)_{12}$) afforded 0.21 g (14%) of a light yellow viscous solid, air stable when dry.

$D_1^{Co}D_3^{Fp}$: 1-[tetracarbonylcobalt(I)],3,5,7-tris[cyclopentadienyldicarbonyliron(II)]-tetramethylcyclotetrasiloxane (m.w. 938). IR (hexanes) 2092 (w), 2031 (m), 2006 (vs), 1944 (vs), 1260 (m), 1252 (sh), 1063 (sh), 1035 (s, br) cm^{-1}. ^1H NMR (C_6D_6) δ 0.78 to 1.14 (3.8H, m), 4.32 to 4.48 (5H, m). Anal. calcd for $C_{29}H_{27}O_{14}Si_4Co_1Fe_3$: C, 37.12, H, 2.90. Found: C, 34.7, H, 2.7 ($Co_4(CO)_{12}$ contamination). Compound 36.

Reaction of D_4^{Fp} with $Co_2(CO)_8$ A 100-mL three-necked round-bottom flask equipped with a nitrogen inlet was charged with 0.10 g (0.11 mmol) of D_4^{Fp} dissolved in 20 mL of dry benzene. Dicobaltoctacarbonyl (0.20 g, 0.59 mmol) was added slowly at ambient temperature and the solution was stirred for 4 h. Infrared monitoring of the carbonyl stretching region did not show any evidence for the formation of new Si-$Co(CO)_4$ bonds. The benzene was evaporated to dryness. The black residue was extracted with 30 mL of hexanes. The insoluble yellow material was filtered, dried and weighed (0.08 g). The infrared spectrum of this product was found to be identical to pure D_4^{Fp}.

2.4 Results and discussion

2.4.1 The classical route to D_n^H and D_n^{Ph}

The hydrolysis of organodichlorosilanes, known for many decades[13,92,93,95-97], leads to the formation of a complex mixture of small and medium-sized cyclosiloxanes:

$$CH_3(R)SiCl_2 \xrightarrow[0°C]{H_2O/(CH_3CH_2)_2O} D_n^R \text{ for } n \geq 3 \qquad \text{(eq. 2.1)}$$

The isolation of the smaller rings (n = 3 to 6) has usually been performed by fractional distillation under reduced pressure[17,91]. The hypothetical dimer, D_2^R, has never been observed regardless of the nature of the organic groups attached to silicon[13,79].

The composition of the reaction products from the hydrolysis of RR'$SiCl_2$ has been discussed by Andrianov and coworkers[98-100]. Some determining factors were pointed out:

a) When the reaction is run with an excess of water, the size of the rings formed is governed by the size of the organic substituent at silicon. The hydrolysis of $(CH_3)_2SiCl_2$ gives D_3 (3%), D_4 (82%), and D_5 (12%), whereas the hydrolyzate of $C_6H_5(CH_3)SiCl_2$ contains D_3^{Ph} (16%), D_4^{Ph} (56%), and D_n^{Ph} (28%) for n > 4[98].

b) The composition is also dependent on the concentration and the nature of the solvent used. In general, a low concentration of the silane in ether favours the formation of small rings and decreases the yield of long chain products.

c) High temperature and a highly acidic aqueous solution (due to the formation of HCl during the hydrolysis) are both responsible for intermolecular rearrangements increasing the molecular weight of products.

Keeping in mind all of these factors, attempts were made to improve upon published methods in order to maximize the yield of the small rings to be used in the present project. The method described in the experimental section was particularly successful with the hydrolysis of $C_6H_5(CH_3)SiCl_2$ where the composition of the hydrolyzate was D_3^{Ph} (29%), D_4^{Ph} (52%), and D_n^{Ph} (19%) for n > 4. The actual yield of pure D_3^{Ph} is greater than that of D_4^{Ph} because a significant portion of D_4^{Ph} was lost by thermal rearrangement (or decomposition) during the distillation. The hydrolyzate from $CH_3(H)SiCl_2$ gave the distribution: D_4^H (20%), D_5^H (44%), and D_6^H (15%). Unfortunately, no trace of D_3^H was found and all attempts to prepare that compound by hydrolysis were unsuccessful.

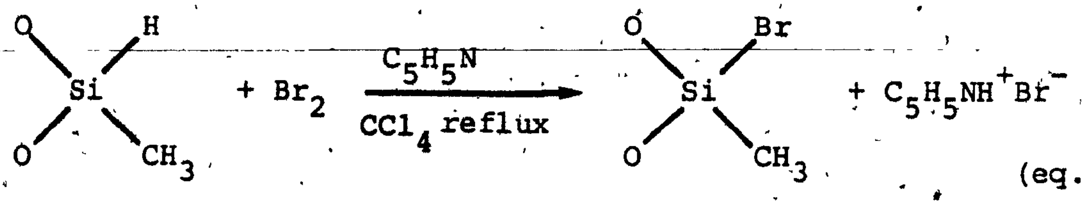
The isolation of the trimer, D_3^H, was claimed by Brewer[94] who prepared ca. 7 g of a "highly unstable light product" (b.p. 93.8°C) from the thermal cracking of 1.2 kg of a polymeric material obtained from hydrolysis of $CH_3(H)SiCl_2$[101]. Examining hydrolyzates from $CH_3(H)SiCl_2$, $(CH_3)_2SiCl_2$, and $CH_3CH_2(H)SiCl_2$, Okawara and coworkers[91,102] found no evidence for trimers, such as $D_2D_1^H$, $D_1D_2^H$, and D_3^H. Nevertheless, they isolated a small amount of unstable triethylcyclotrisiloxane. The infrared spectrum showed two medium peaks at 1260 and 1240 cm^{-1} (both attributed to the CH_3-CH_2-Si≡ group) and a very characteristic absorption band at 1023 cm^{-1} associated with the siloxane stretching vibration[102]. From these examples, it seems that the stability and obviously the yield of the six-membered ring increase with the size of the organic substituent. The D_3^{Ph} is obtained in 29% yield, and sometimes the trimer becomes the major product[100], e.g. $[CH_3(n\text{-}C_8H_{17})SiO]_3$ (38%), and $[CH_3(n\text{-}C_8H_{17})SiO]_4$ (18%), when the substituent is very large.

Infrared data listed in the experimental section for products D_4^H, D_5^H, D_3^{Ph}, and D_4^{Ph} are in accordance with literature values[17,103-107].

In the series D_n^H, ^1H NMR spectra always show two multiplets in the ratio 3:1 confirming the presence of CH_3 (0.2 ppm) close to TMS, and the hydrogen atom at low field (ca. 5 ppm). Similarly, the series D_n^{Ph} always shows two groups of multiplets in the ratio 5:3. The methyl groups are close to TMS (0.5 ppm) and the phenyl protons appear as a group of multiplets at low field (ca. 7.3 ppm). In mass spectrometry, molecular ions are observed for D_3^{Ph} and D_4^{Ph} whereas ions $[M-1]^+$ and $[M-15]^+$ are observed for all D_n^H products (detailed study in Chapter 3).

2.4.2 The synthesis of two new bromocyclosiloxanes

In the course of this project, it became important to obtain halogenocyclosiloxanes as starting materials to carry out the salt elimination reaction (eq. 1.9) with transition metal anions. Surprisingly, it seems that little attention has been paid to methylhalocyclosiloxanes before the present work. The synthesis of D_4^{Cl} was mentioned by Sokolov et al.[108] using the photochlorination (Cl_2 ~~gas~~) of D_4^H. This chlorinated cyclosiloxane was subsequently mentioned twice in the literature[109,110]. In 1965, Sakiyama and coworkers[111] reported the preparation of some linear and cyclic halosiloxanes, including D_4^{Br}, by the bromination of methylhydropolysiloxanes in the presence of pyridine (eq. 2.2):



(eq. 2.2)

The products were very poorly characterized and only the m.p. (97-98°C), the b.p. (112°C/4 torr) and the analysis % Br-Si (56.8%) are cited for D_4^{Br}. The authenticity of these products is doubtful since in the present study it was found that neither D_3^{Br} nor D_4^{Br} exhibit any boiling point when heated under low pressure, but sublime quite easily and form white crystals. As the methods of Sokalov[108] and Sakiyama[111] were not promising, we decided to extend the well-known bromination reaction of aryl silanes[12,112] (eq. 2.3) to the methylphenylcyclosiloxanes (eq. 2.4):

$$C_6H_5Si(CH_3)_3 + Br_2 \longrightarrow (CH_3)_3SiBr + C_6H_5Br \qquad \text{(eq. 2.3)}$$

$$D_n^{Ph} + nBr_2 \xrightarrow[-50^\circ C]{} D_n^{Br} + nC_6H_5Br \qquad \text{(eq. 2.4)}$$

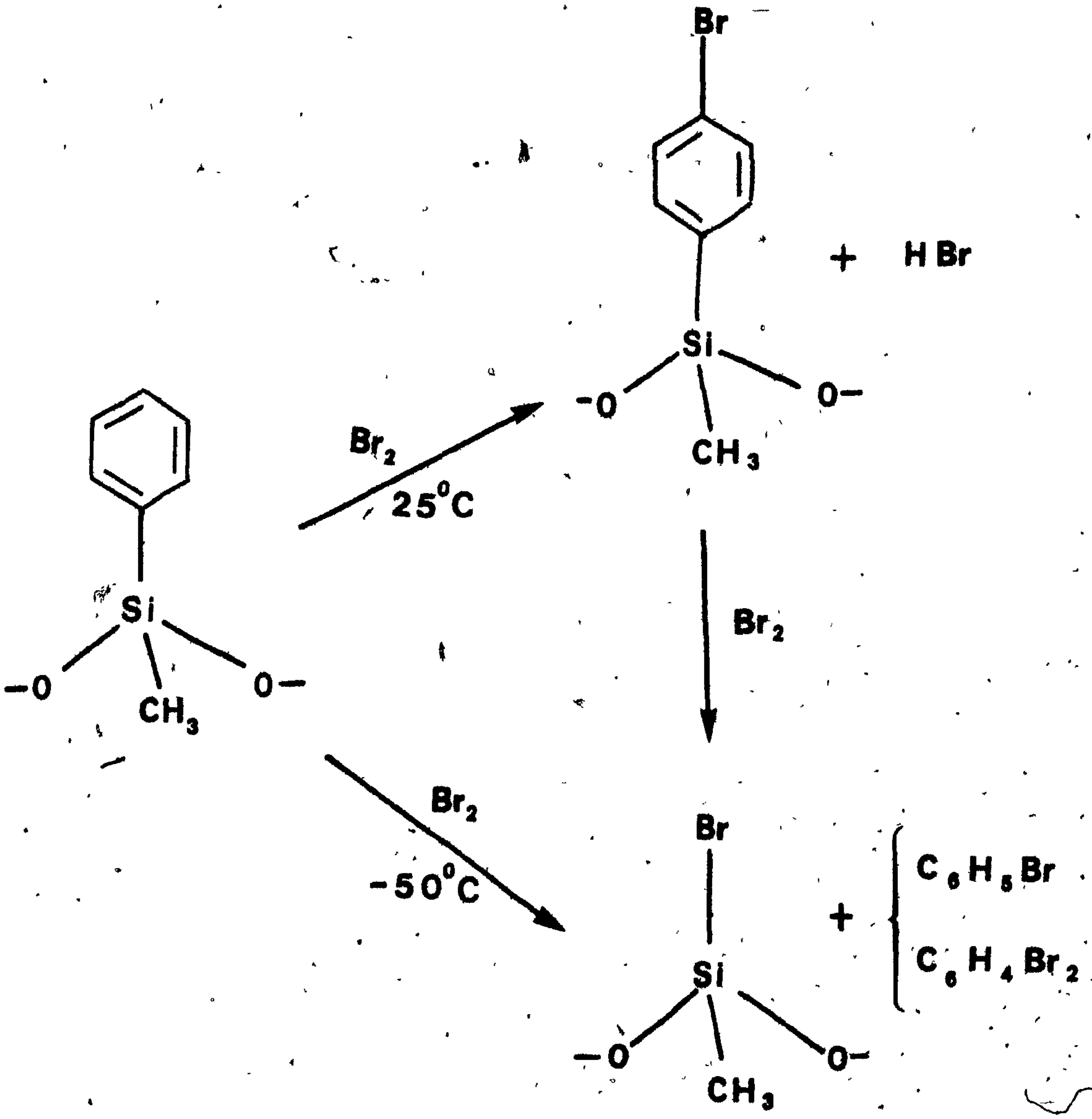
Other bromination agents, such as $AlBr_3$ and HBr, have been avoided because they are all known to cleave the siloxane bond under mild conditions (eq. 1.8)[20]. When a slight excess of bromine is added dropwise to D_3^{Ph} or D_4^{Ph} at -50°C in the absence of solvent, the product D_3^{Br} (25) or D_4^{Br} (26) is formed in essentially quantitative yield. The bromobenzene formed in the reaction prevents the precipitation of products from cold pentane and must be evaporated in vacuo before recrystallization. Unfortunately, D_3^{Br} is quite volatile and an appreciable amount is lost with the bromobenzene decreasing the yield of the isolated pure product. D_4^{Br} is less volatile and therefore much easier to isolate in good yield. In addition, both products can be purified by slow sublimation (ca. 50°C at 10^{-3} torr).

When the same bromination is run at ambient temperature an additional reaction occurs:

$$D_3^{Ph} \xrightarrow[25°C]{Br_2} D_3^{Br} + C_6H_5Br + p\text{-}C_6H_4Br_2 + PBM + HBr \qquad \text{(eq. 2.5)}$$

where PBM = polymeric brominated material. The presence of para-dibromobenzene was easily detected by infrared and ^1H NMR (one sharp singlet at 6.80 ppm). The yellow PBM (over 60% yield in some cases) was very viscous and exhibited an extremely complex pattern of some dozen peaks in the methyl region (0.3 to 0.8 ppm) of the ^1H NMR spectrum. This undesired behavior is attributed to a bromination at the para position of the phenyl before the expected cleavage at the silicon center (Scheme 2.1). The HBr produced in the reaction could be responsible for the siloxane bond cleavage and rearrangement (eqs. 1.6 and 1.7) observed in the PBM. At low temperature, the attack at the para position of the phenyl

Scheme 2.1: Two possible reactions of Br_2 with methylphenylcyclosiloxane



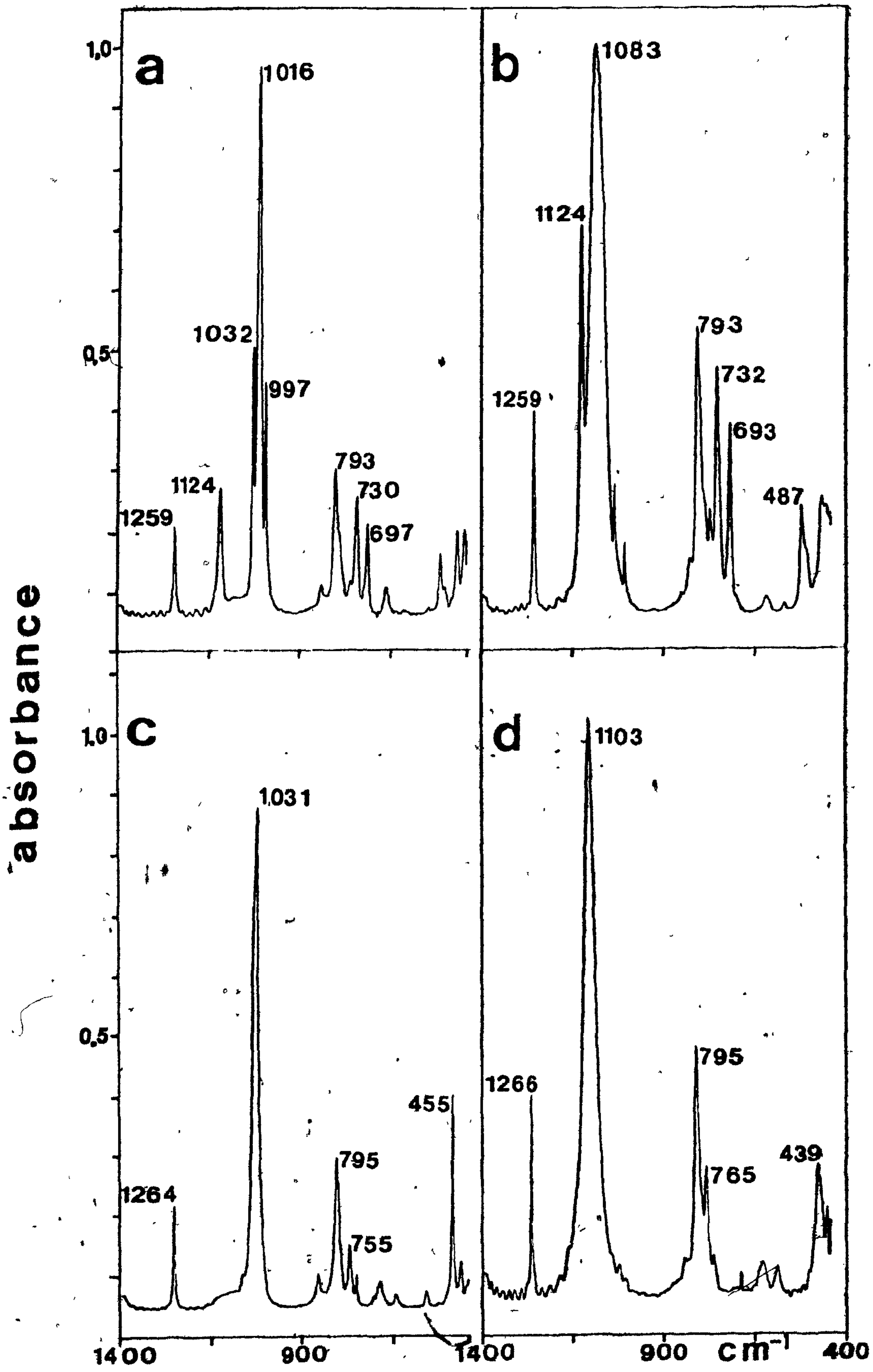
group is completely suppressed and only the cleavage at silicon takes place selectively.

The comparative study of infrared spectra (region 400-1400 cm^{-1}) of D_n^{Ph} and D_n^{Br} presented in Figure 2.1 shows two characteristic features of silicon halide compounds and supports the formulation of the new bromosiloxanes[103,113]:

a) Peaks at 455 cm^{-1} and 439 cm^{-1} for D_3^{Br} and D_4^{Br} respectively, are tentatively assigned to the vibration of a direct Si-Br bond. The valence Si-Br stretching frequencies in methylbromosilanes are observed in the range 360-430 cm^{-1} [113]. The Si-Br stretching observed in siloxanes should be higher than in silanes due to the presence of two oxygens bonded to the silicon, which increase the vibrational frequency of attached substituents by an electronegativity effect[113].

b) Similarly, the replacement of the phenyl group by the bromine induces an upward shift of stretching frequencies of the $Si-CH_3$ bond (from 1259 cm^{-1} in D_n^{Ph} to about 1265 cm^{-1} in D_n^{Br}) and of the siloxane (from 1016 to 1031 cm^{-1} in the trimer and from 1083 to 1103 cm^{-1} in the tetramer). This effect seems to be caused by a withdrawal of electrons from the silicon by the new, more electronegative substituent. This redistribution of electrons presumably induces a shortening of the Si-O and $Si-CH_3$ bonds and increases the vibrational frequency[105]. It ~~should~~ be

Figure 2.1: Infrared spectra of: a) D_3^{Ph} (23), b) D_4^{Ph} (24), c) D_3^{Br} (25), and d) D_4^{Br} (26) measured in CS_2 solution (*ca*. 5%) in the region 400-1400 cm^{-1}


absorbance
1,0
0,5
a
1016
1032
997
1124
1259
793
730
697
b
1083
1124
793
732
1259
693
487
1,0
0,5
c
1031
455
795
1264
755
d
1103
795
1266
765
439
1400
900
1400
900
cm⁻¹
400

noted that the frequency 1103 cm^{-1} in D_4^{Br} is probably the highest value reported up to now for a cyclotetrasiloxane stretching frequency measured in solution[103].

2.4.3 A new route to D_3^H

Our great interest in D_3^H as a precursor for organometallic synthesis was for practical reasons. Only three reactive sites are available for hydrogen elimination reactions (eq. 1.11) and only two geometric isomers exist for the trisiloxane system (Fig. 1.2). The preparation and isolation of D_3^{Br} opened up a new route to the synthesis of the elusive D_3^H.

The reduction of organosilicon halides by classical reducing agents such as $LiAlH_4$ and $NaBH_4$, is a known process for the preparation of many organosilicon hydrides[13]:

$$4R_3SiBr + LiAlH_4 \longrightarrow 4R_3SiH + AlBr_3 + LiBr \qquad \text{(eq. 2.6a)}$$

In most cases, reactions are fast and clean, and the organosilicon hydrides are easy to separate from inorganic salt by-products[13]. However, the reduction of halogenosiloxanes has never been reported because the reaction (eq. 2,6a) produces highly acidic inorganic salts which are able to cleave rapidly the siloxane bond (eq. 1.8). These features led us to explore the reactivity toward siloxanes of recently available trialkyl borohydride salts as powerful and sometimes selective reducing agents[114]. A successful reaction (eq. 2.6b) was carried out at -78°C using an ethereal solution of sodium

$$D_3^{Br} + 3[R_3B/NaH] \xrightarrow[-78\,°C]{(C_2H_5)_2O} D_3^{H} + 3R_3B + 3NaBr \qquad \text{(eq. 2.6b)}$$

tri-sec-butyl borohydride. The reaction (monitored by IR) is fast, quantitative and selective toward Si-Br reduction as long as no excess of reducing agent is present and the temperature is kept at less than -50°C. When the same reaction is run at ambient temperature a destructive reaction toward the siloxane linkage takes place leaving no trace of siloxane material in solution (complete disappearance of the siloxane stretching peak in infrared). Major problems were encountered with the isolation and purification of the new product, 27. It was found to be very sensitive to thermal rearrangement and attempts at a distillation at atmospheric pressure (b.p. 94-96°C) led to a total decomposition giving only a viscous, transparent material. (^{1}H NMR monitoring of the thermal decomposition will be presented in Chapter 4). This behavior confirms the observations of Brewer[94] about the instability of the same product as well as the observations of Okawara et al.[91] about the instability of the analogous triethylcyclotrisiloxane. It should be noted that another trimer, $[(C_6H_5)(H)SiO]_3$ was claimed to be a stable compound and was distilled at 168°C/2 x 10^{-3} torr[115]. Nevertheless, this preparation has never been successfully repeated, even though the tetramer, $[(C_6H_5)(H)SiO]_4$ is stable and often cited in the literature. The hexamethylcyclotrisiloxane, D_3, is known as a stable compound but is, however, much more easily polymerized than D_4[14]. The relative instability of trimers seems to be related to the ring strain but the very high reactivity of D_3^H (the ring strain is probably less than for D_3) could be due to the low steric effect of Si-H which exposes the siloxane bond to facile electro- and nucleophilic attack and easy initiation of polymerization.

2.4.4 Hydrogen elimination reactions

The hydrogen elimination reaction, already known to occur with silanes[46,47] (eq. 1.11) and linear disiloxanes[38,39], was applied successfully to methylhydrogencyclosiloxanes (eq. 2.7):

$$D_n^H + n/2Co_2(CO)_8 \longrightarrow D_n^{Co} + n/2H_2 \qquad \text{(eq. 2.7)}$$

where n = 4 and 5

The reaction was fast and near quantitative with D_4^H but was much more difficult to push to completion with D_5^H. As both products, D_4^{Co} (<u>28</u>) and D_5^{Co} (<u>29</u>), were very soluble in hydrocarbons (even in pentane at -78°C) and decomposed on chromatographic material, it was fairly difficult to isolate the pure white solids in reasonable yields. Both compounds were found to be stable under nitrogen at ambient temperature in the solid state and also in solution with dry and oxygen-free solvents. They have been preserved as solids or in solution at -20°C for months without decomposition. The analogous complexes, 1,3-bis(cobalttetracarbonyl)tetramethyldisiloxane and digermoxane, reported by Greene and Curtis[38] were described as "exceedingly thermolabile, decomposing slowly at -78°C, under nitrogen atmosphere". The authors suggested that the decreased stability compared to mononuclear silylcobalt carbonyls[47] may be due to "the proximity of the two metallic centers". Surprisingly, the D_n^{Co} compounds have respectively four and five metallic centers very close together and appear to be as stable as the simple $R_3Si\text{-}Co(CO)_4$ (R = H, Cl, F, CH_3, C_6H_5). D_4^{Co} was exposed to air and moisture at ambient temperature without evidence of decomposition but it turned blue-green when heated at 100°C in an open capillary tube. The great stability of silylcobalt carbonyls in contrast to the analogous alkylcobalt carbonyls has been attributed to the $(d \rightarrow d)\pi$ partial double bond between the silicon and the metal[47,116,117]. Furthermore, it has been suggested that the presence of strong electronegative substituents at silicon increases the π bonding character of the Si-M bond and improves the stability of the complex[118]. Each silicon atom in the cyclic siloxane framework can be considered to be in a moderately electronegative environment, being bonded to a CH_3 group and two oxygens (shared with another silicon). It was therefore not surprising to find easily prepared and stable cobalt carbonyl derivatives.

The infrared spectra of D_4^{Co} and D_5^{Co} in the carbonyl stretching region are consistent with the C_{3v} symmetry usually observed for complexes with the general formula R-Co(CO)$_4$ (Table 2.1) Symmetry rules predict three infrared-active ^{12}CO stretching modes ($A_1 + A_1 + E$) as observed in $(C_6H_5)_3Si-Co(CO)_4$. In the case of $(CH_3)(H)_2SiCo(CO)_4$ as well as of D_4^{Co} and D_5^{Co}, the degeneracy of the E band has been removed, presumably because of the unsymmetrical nature of the silyl group[116]. The geometry at the cobalt center of silylcobalt tetracarbonyls has been shown to be trigonal bipyramidal (substituent Si lying in the C_{3v} axis) and the equatorial carbonyl groups are slightly displaced toward the silicon[118]. The similarity of D_n^{Co} infrared spectra with analogous silylcobalt carbonyl complexes (Table 2.1) confirms the trigonal bipyramidal geometry at the cobalt center and excludes any possibilities of adjacent metal-metal bonds and bridging carbonyls over the siloxane ring.

The comparative study of infrared spectra (region 400-1400 cm^{-1}) of D_n^H and D_n^{Co} (Fig. 2.2) highlights two characteristic features of the new siloxanyl-cobalt complexes:

a) The new pair of peaks at 552 (s) and 515 (w) cm^{-1} for D_4^{Co} and 552 (s) and 511 (w) cm^{-1} for D_5^{Co} are assigned to the valence vibration of Co-CO. The position and the relative intensities of this pair of peaks are characteristic and constant in all R-Co(CO)$_4$ complexes[117,118].

Table 2.1: Infrared absorptions of some cobalt carbonyl derivatives in the $\nu(CO)$ region

Products	Frequencies (cm^{-1})				
M = $Co(CO)_4$	A_1(eq)	A_1(ax)	E	E	$\nu(^{13}CO)$
$(CH_3)(H)_2Si-M$[a]	2102 (s)	2043 (s)	2021 (vs)	2015 (vs)	1981 (w)[e]
$(C_6H_5)_3Si-M$[b]	2095 (s)	2031 (s)	2003 (vs)	--	1975 (w)
$[(CH_3)_2(M)SiO]_2$[c]	2080	2020	2000	--	1960 (vw)
D_4^{Co} (28)[d]	2100 (s)	2040 (s)	2027 (vs)	2011 (vs)	1968 (w)
D_5^{Co} (29)[d]	2101 (s)	2039 (s)	2023 (vs)	2006 (vs)	1966 (w)

[a] Ref. 116 (gas phase).

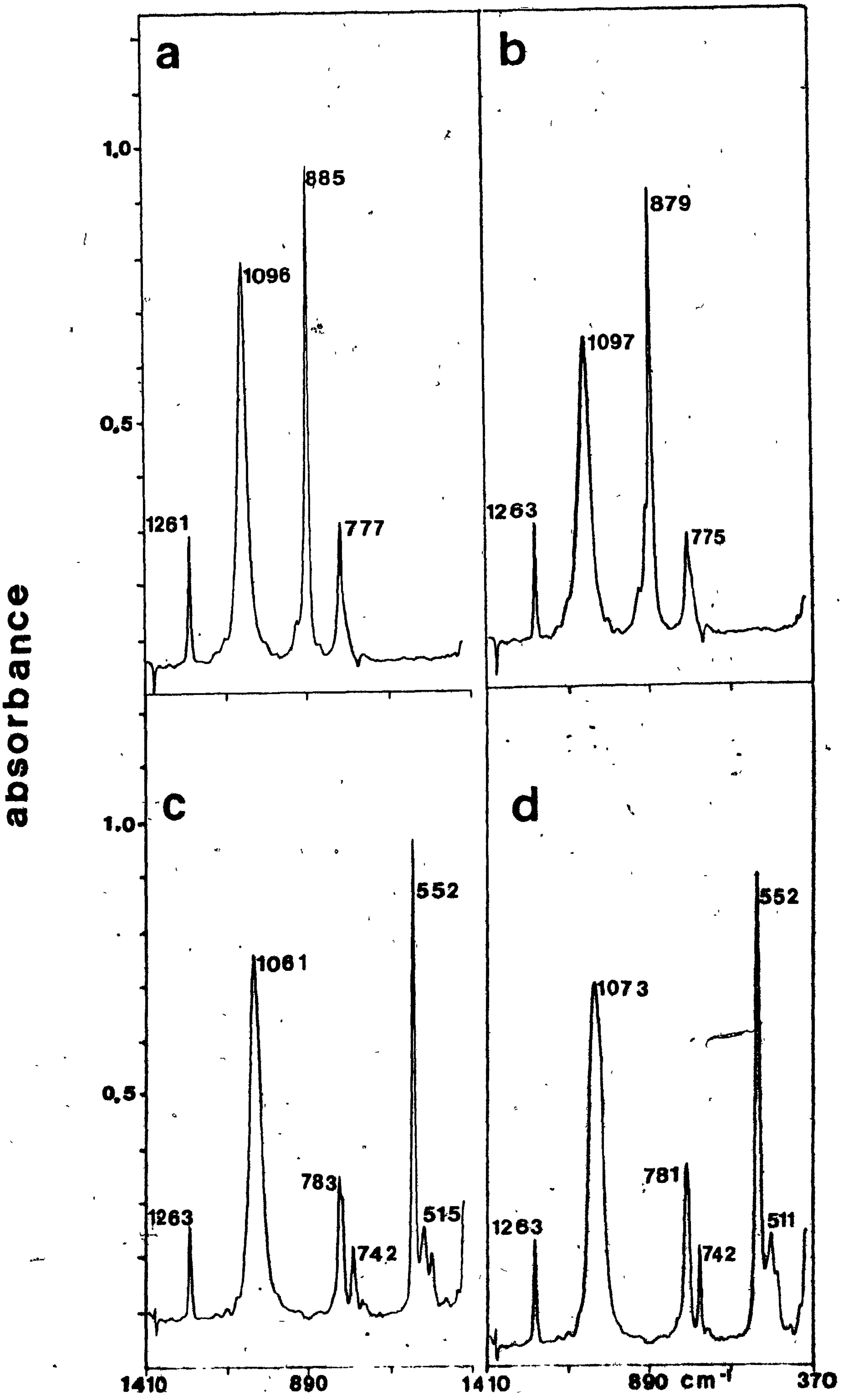
[b] Ref. 117 (n-hexadecane solution).

[c] Ref. 38 (solvent and intensities omitted by authors).

[d] This work (hexanes solution).

[e] The assignment of $\nu(^{13}CO)$ has been discussed by ref. 60.

Figure 2.2: Infrared spectra of: a) D_4^{H} (20), b) D_5^{H} (21), c) D_4^{Co} (28), and d) D_5^{Co} (29) measured in hexanes solution (ca. 5%) in the region 400-1400 cm^{-1}


a
b
c
d
absorbance
1,0
0,5
1261
1096
885
777
1263
1097
879
775
1263
1061
783
742
552
515
1263
1073
781
742
552
511
1410
890
1410
890
cm-1
370

b) The stretching frequency of Si-CH_3 has not been significantly changed from D_n^H to D_n^{Co} which could be an indication of only a very small change in the electronegativity of the substituent from hydrogen to the $Co(CO)_4$ group. However, the siloxane stretching frequency has been shifted downward by 25 to 35 cm^{-1} which may be due to the large steric requirement of the new substituent. The presence of a single siloxane band in both cases is a good indication of the monomeric nature of the compound. A polymeric material or a series of rearranged rings would give rise to more than one band in the siloxane stretching region. The monomeric nature of D_n^{Co} is also supported by ^1H NMR spectra detailed in Chapter 4.

The hydrogen elimination reaction is also known with the dimer $[Fe(CO)_2\eta^5\text{-}C_5H_5]_2$[62,119] and was successfully applied to D_4^H (eq. 2.8):

$$D_4^H + 2[Fe(CO)_2\eta^5\text{-}C_5H_5]_2 \longrightarrow D_4^{Fp} + 2H_2 \qquad \text{(eq. 2.8)}$$

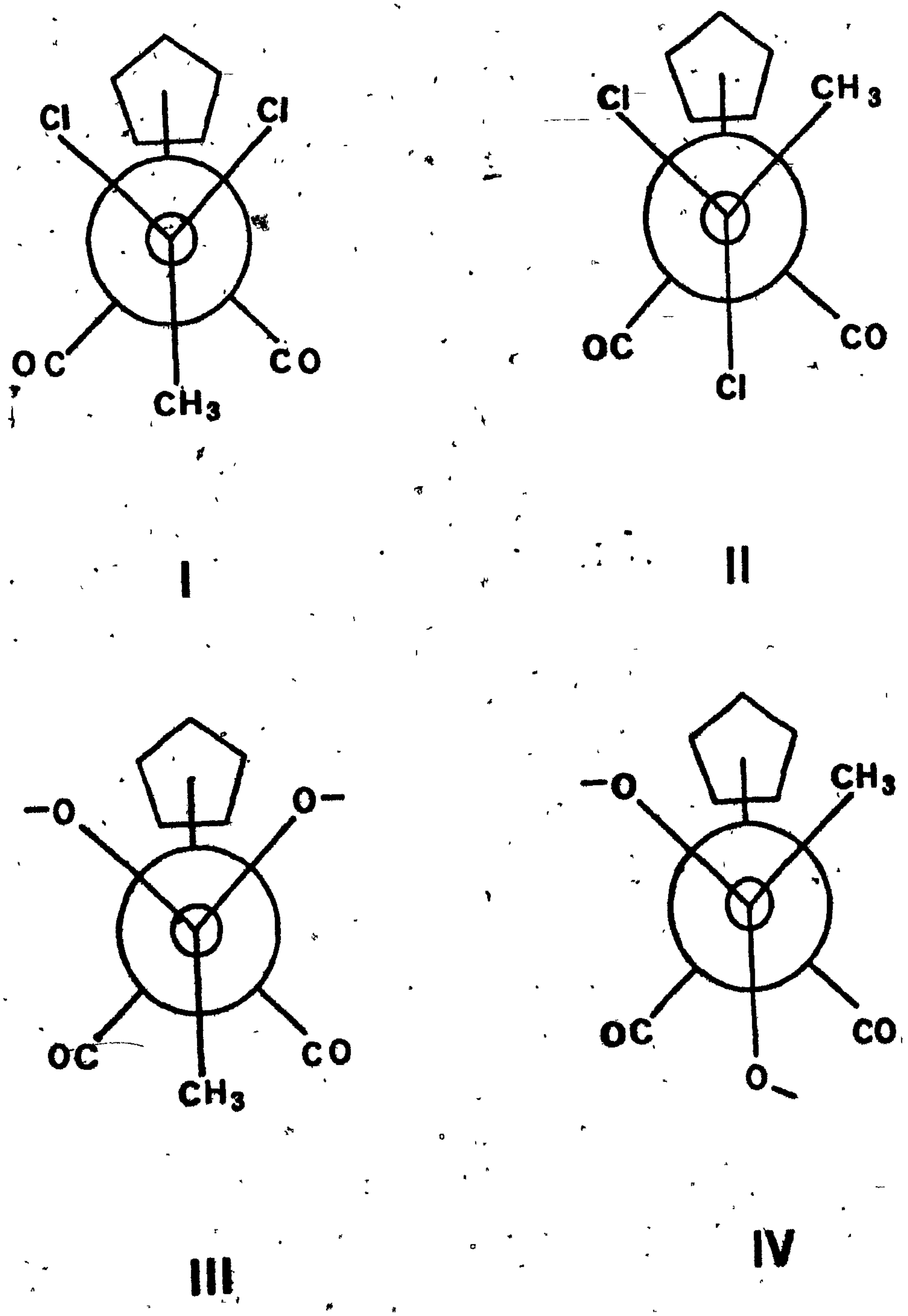
The dimer $[Fe(CO)_2\eta^5\text{-}C_5H_5]_2$, being much less reactive than $Co_2(CO)_8$, required more severe conditions (160-180°C) to complete the reaction and to get fully substituted D_4^{Fp}. Attempts to prepare the analogous D_5^{Fp} were unsuccessful even upon heating the reactants in a sealed tube at 180°C for several days. The latter conditions gave only partially substituted compounds,

$D^{H}_{5-n}D^{Fp}_{n}$, $5 > n \geqslant 1$, following workup by column chromatography. Any increase in the temperature and the time of the reaction did not increase the yield of D^{Fp}_{n} but seemed only to increase the thermal decomposition of reactants (the amount of ferrocene increased). The compound D^{Fp}_{4}, was found to be very stable in air at ambient temperature but decomposed slowly when heated above 190°C in an open capillary tube. D^{Fp}_{4} is also stable in solution with dry and deoxygenated solvents.

For silyl (also germyl and stannyl) complexes containing π-cyclopentadienyl metal carbonyl substituents, structural assignments from infrared are difficult[27]. In general, the number of carbonyl stretching frequencies can be used to deduce the number of carbonyl groups present in the complexes. Complexes of the formulae $[M(CO)_3\eta^5\text{-}C_5H_5]$, $[M(CO)_2\eta^5\text{-}C_5H_5]$ and $[M(CO)\eta^5\text{-}C_5H_5]$ (M = transition metal moiety) exhibit three, two and one bands[27], respectively, in the region 1800-2100 cm^{-1}. However, some exceptional cases have been reported. The compounds $[(CH_3)_2ClSiFe(CO)_2\eta^5\text{-}C_5H_5]$[119] and $[(CH_3)Cl_2SiFe(CO)_2\eta^5\text{-}C_5H_5]$[120] have two pairs of CO absorptions. The extra bands have been rationalized in terms of the presence of two conformational isomers (Scheme 2.2, structures I and II). Rapid interconversion could account for the simple ^1H NMR signal[62,119].

A very similar structure can be drawn for the compound D^{Fp}_{4}, where both chlorine atoms are replaced with oxygen atoms (Scheme 2.2, structures III and IV). The high resolution

<u>Scheme 2.2</u>: Newman projections along the Si-Fe axis of $[(CH_3)Cl_2SiFe(CO)_2\eta^5\text{-}C_5H_5]$ (structures I and II) and D_4^{Fp} (<u>31</u>) (structures III and IV)



infrared spectrum of D_4^{Fp} in the carbonyl stretching region is shown in Figure 2.3. The sample 31 used for this measurement was a mixture of all geometric isomers (as determined by ^1H NMR). Spectra measured with samples containing different isomer distributions (e.g. 32) show the same general pattern but the relative intensities of the shoulder at left (2003.0 cm^{-1}) and the first peak (1946.6 cm^{-1}) in the group at right vary significantly. The spectrum of D_4^{Fp} (Fig. 2.3) is quite different from those observed for $[(CH_3)Cl_2SiFe(CO)_2\eta^5\text{-}C_5H_5]$ and analogous compounds[120,121] and could be due not only to conformers as expected but also to geometric isomers of the cyclotetrasiloxane. As will be detailed by ^1H NMR studies, each Fp group bonded to a siloxane ring can have three different combinations of nearest neighbors. These three environments could be responsible for the three peaks (1946.6, 1942.8 and 1938.7 cm^{-1}) in the lower frequency band but they are not completely resolved in the higher frequency band (Fig. 2.3). It is also possible that the rotation of the Fp group along the Fe-Si bond axis (Scheme 2.2) could be strongly affected by steric hindrance and one of the two conformers (III or IV) could be present in considerable excess. This hypothesis is supported by the observation of only two 'normal' peaks for compounds $(C_6H_5)_2ClSi\text{-}Fp$ and $(C_6H_5)Cl_2Si\text{-}Fp$[122] where the rotation could be locked by the phenyl groups. Much remains to be learned of the structural behavior of silyl-$Fe(CO)_2\eta^5\text{-}C_5H_5$ complexes in solution.

Figure 2.3: Infrared spectrum of the carbonyl stretching region of D_4^{Fp} (<u>31</u>) measured in cyclohexane solution (<u>ca</u>. 1%). The resolution is 0.12 cm^{-1}

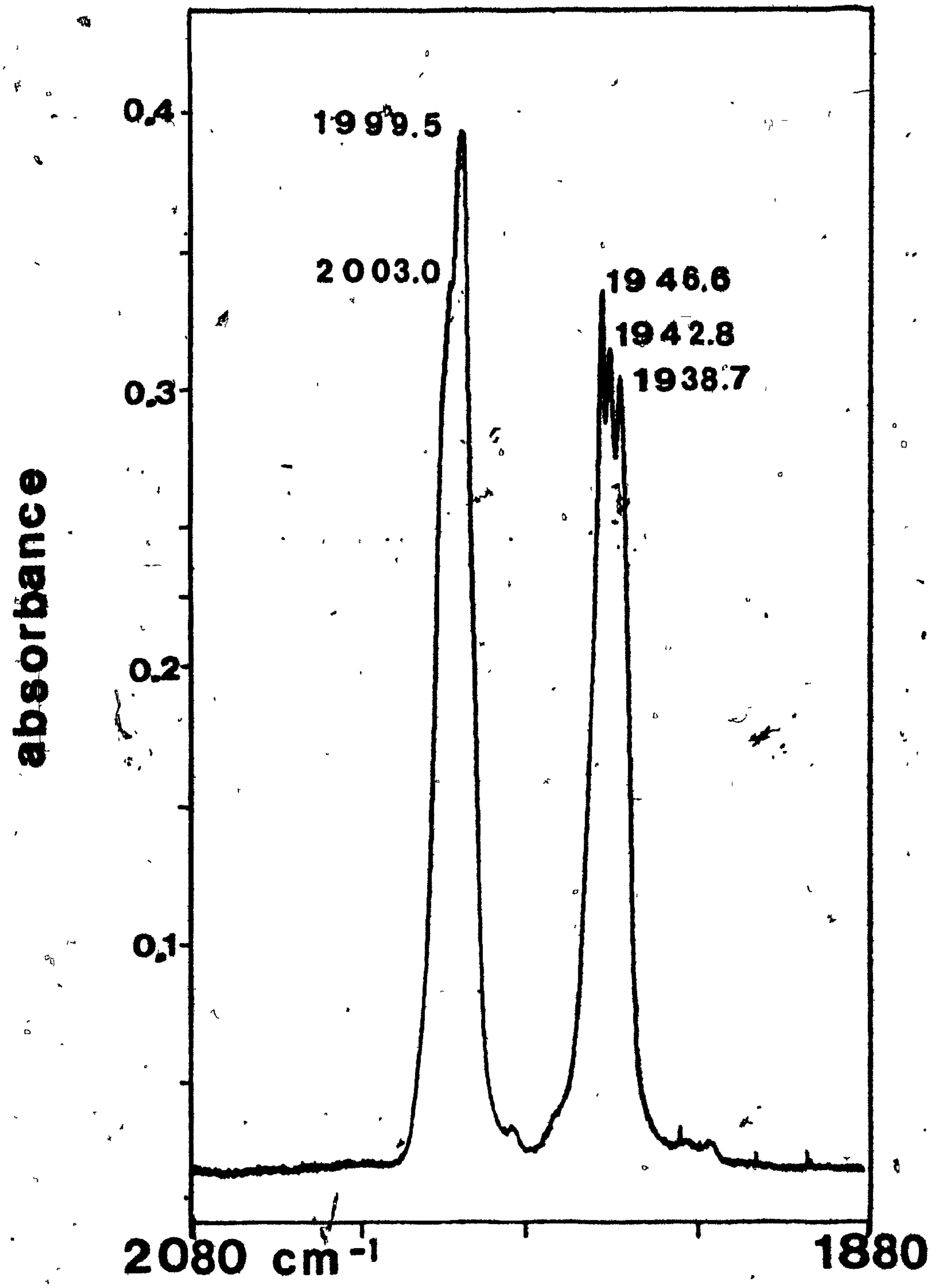


Figure 2.4 shows the infrared modification when all single hydrogens of D_4^H are replaced by Fp groups with perfect preservation of the cyclotetrasiloxane framework:

a) Si-H bending at 885 cm^{-1} in D_4^H disappears completely in D_4^{Fp}.

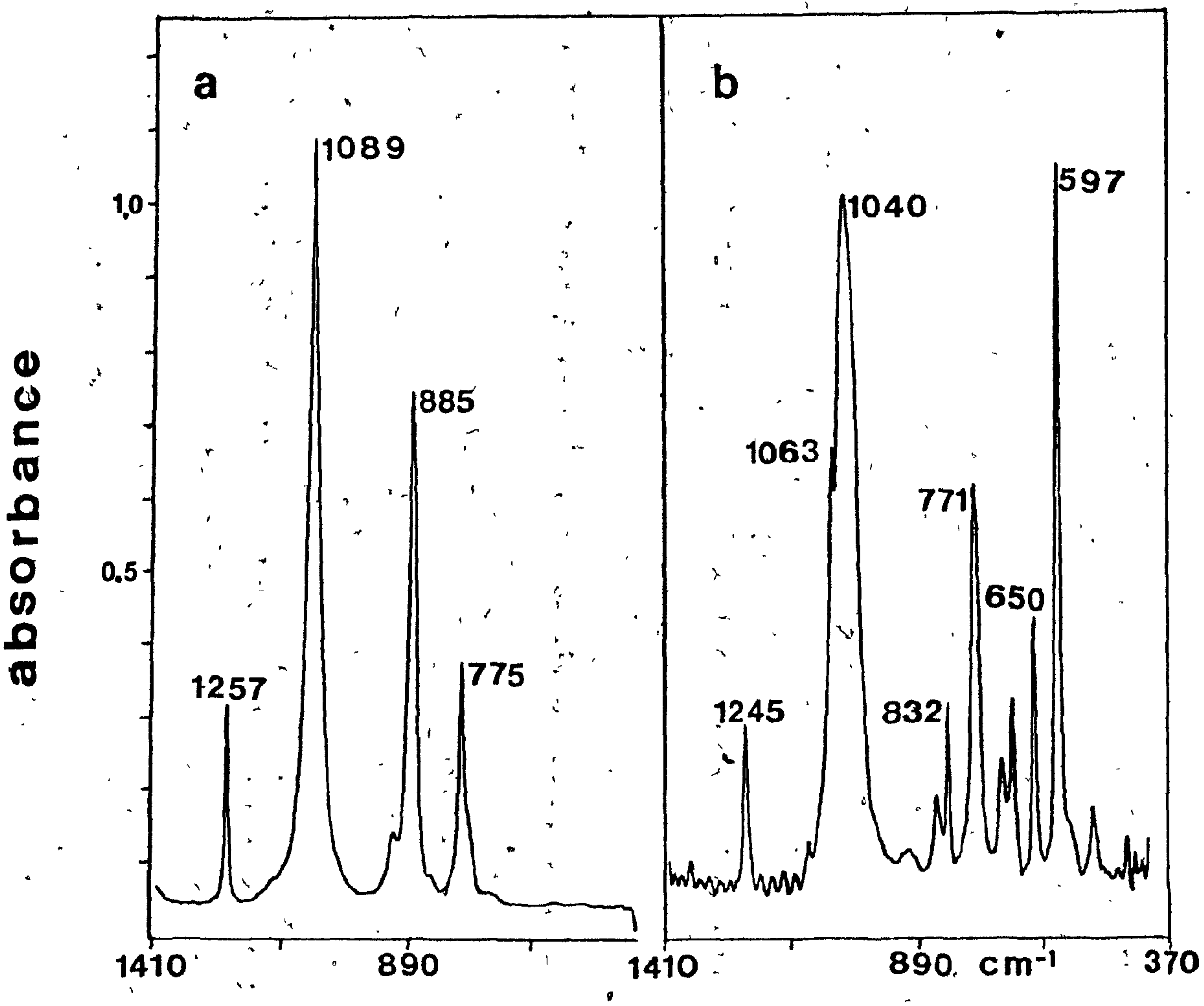
b) $Si-CH_3$ bands at 1257 and 775 cm^{-1} and Si-O-Si stretching at 1089 cm^{-1} in D_4^H are all strongly shifted to lower frequency in the new compound due to the presence of a large substituent which tends to lengthen the Si-O-Si bond and even the $Si-CH_3$ bond. Note that the sharp peak at 1063 cm^{-1} belongs to the cyclopentadienyl ring[90].

c) Following analogous assignments by Kahn and Bigorgne[117], the new and strong peak at 597 cm^{-1} in the D_4^{Fp} spectrum has been assigned to a Fe-CO bending vibration. This vibration is a function of the transition metal (ranges from 550 to 630 cm^{-1} for iron) and is usually independent of the nature of the substituent at the metal center[117].

The proposed formulation of D_4^{Fp} is supported by the presence of only one peak at 1245 cm^{-1} for $Si-CH_3$ and at 1040 cm^{-1} for Si-O-Si. As for the case of D_4^{Co}, polymeric and/or rearranged siloxanes should give a broader and more complex siloxane stretching band.

Elemental analysis is also perfectly consistent with the formula: $C_{32}H_{32}O_{12}Si_4Fe_4$.

Figure 2.4: Infrared spectra of: a) D_4^H (20) and b) D_4^{Fp} (31) measured in CS_2 solution (ca. 5%) in the region 400-1400 cm^{-1}



2.4.5 A new series of heteronuclear complexes

Very few heteronuclear silyl complexes are known[123]. Some recent examples were published by Malish and coworkers[124]. The complexes $[\eta^5\text{-}C_5H_5(CO)_2Fe\text{-}SiCl_2\text{-}Co(CO)_4]$, $[\eta^5\text{-}C_5H_5(CO)_2\text{-}P(CH_3)_3W\text{-}Si(CH_3)\text{-}Co_2(CO)_7]$, and $[\eta^3\text{-}C_5H_5(CO)_2Fe\text{-}Si\text{-}Co_3(CO)_9]$ were prepared by hydrogen elimination reactions and characterized by infrared and ^{29}Si NMR.

As the preparation of D_4^{Co} and D_4^{Fp} were successful, with acceptable yields, it was decided to try to synthesize and isolate at least one cyclosiloxane complex containing simultaneously $\text{-}Co(CO)_4$ and $\text{-}Fe(CO)_2\eta^5\text{-}C_5H_5$ groups. The synthetic approach to heteronuclear derivatives, $D_{4-n}^{Co}D_n^{Fp}$ where n = 1, 2, 3), was divided into two steps.

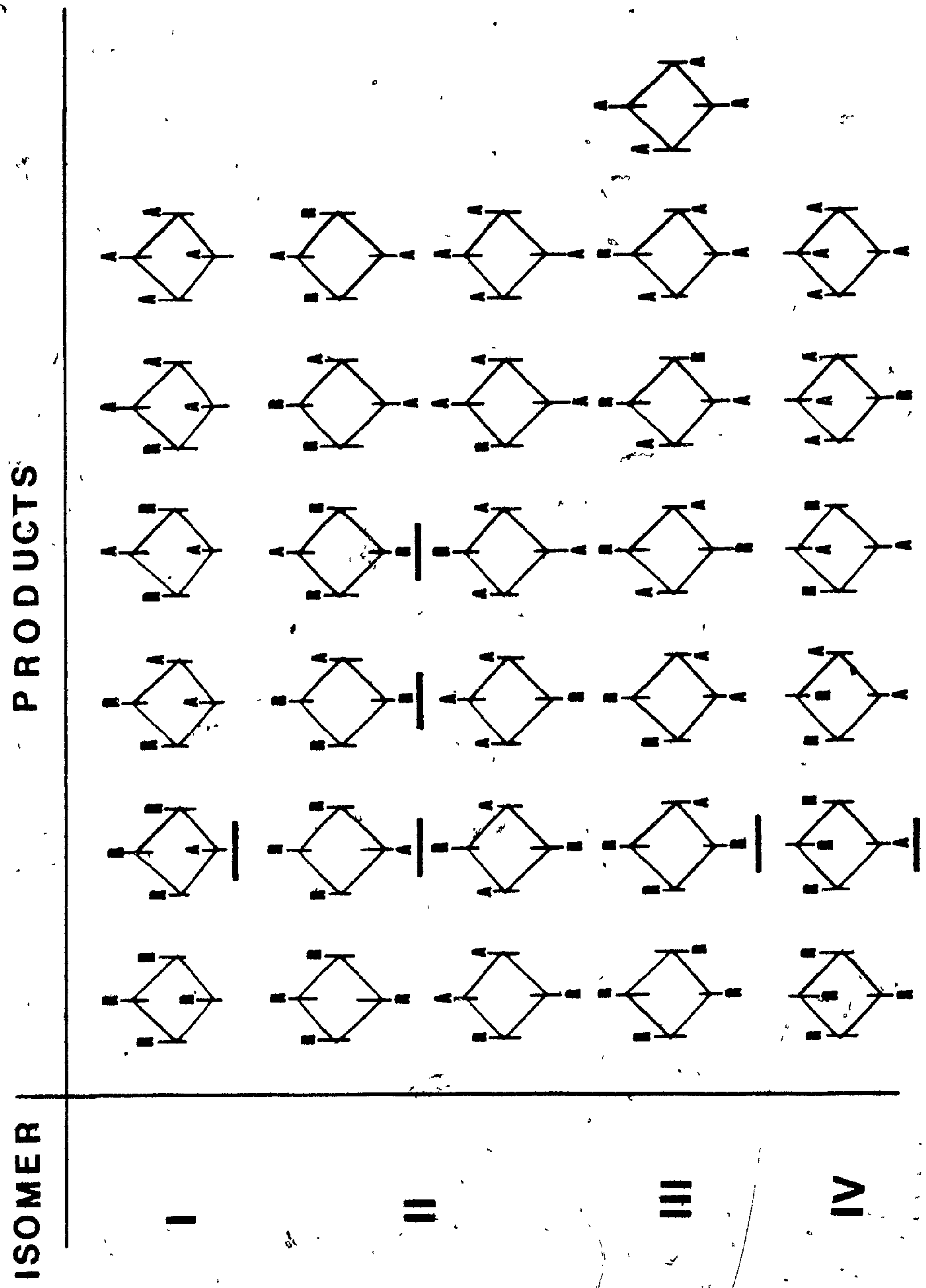
1) The preparation of partially substituted compounds: $D_{4-n}^{H}D_n^{Fp}$:

When D_4^H was reacted with a deficiency of $[Fe(CO)_2\eta^5\text{-}C_5H_5]_2$ under mild conditions, a very complex mixture of partially substituted cyclotetrasiloxanes was formed (eq. 2.9):

$$D_4^H \xrightarrow[145°C/23\ h]{[Fe(CO)_2\eta^5\text{-}C_5H_5]_2} D_{4-n}^{H}D_n^{Fp} + n/2H_2 \qquad \text{(eq. 2.9)}$$

The mixture can contain as much as 31 different geometric isomers (Scheme 2.3) which makes very difficult the complete separation and isolation of the products. Nevertheless, a simple workup can simplify greatly a portion of the mixture.

Scheme 2.3: Geometric isomers of $D^{A}_{4-n}D^{R}_{n}$ (where n = 0 to 4) formed by the partial substitution of D^{R}_{4} isomers by the substituent A



The unreacted isomers of D_4^H can be easily separated by an elution on a silica gel column with pure hexanes. Partially substituted compounds begin to migrate only when benzene is gradually mixed with hexanes for the elution. It was not possible to get a clean separation of some specific isomers. A large yellow mixture migrated as a long tailing band and was collected into three equal fractions (150 mL). The fully substituted D_4^{Fp} was easily removed by washing each fraction with pure hexanes. A small amount of the insoluble D_4^{Fp} (0.23 g, 2% yield) was found only in the last fraction. The particular isomeric composition of compound <u>32</u> is discussed in Chapter 4. The isomeric composition of each fraction can be estimated from ^1H NMR spectra because a CH_3 group attached to a substituted silicon resonates at a lower field (<u>ca</u>. 0.85 ppm) than a CH_3 attached to an unsubstituted silicon (<u>ca</u>. 0.40 ppm) and they can be integrated separately. The first and second fractions (<u>33</u> and <u>34</u>) had relatively low values for n (1.4 and 2.6) but the third fraction (<u>35</u>), with a calculated value of n = 3.1, appeared to be a much more simple mixture. Assuming that D_4^{Fp} is virtually absent, the sample is a mixture of six geometric isomers of the same compound $D_1^H D_3^{Fp}$. These isomers are identified in Scheme 2.3. The sample <u>35</u> was used as starting material for the preparation of $D_1^{Co} D_3^{Fp}$.

2) Preparation of the heteronuclear complex $D_1^{Co}D_3^{Fp}$:

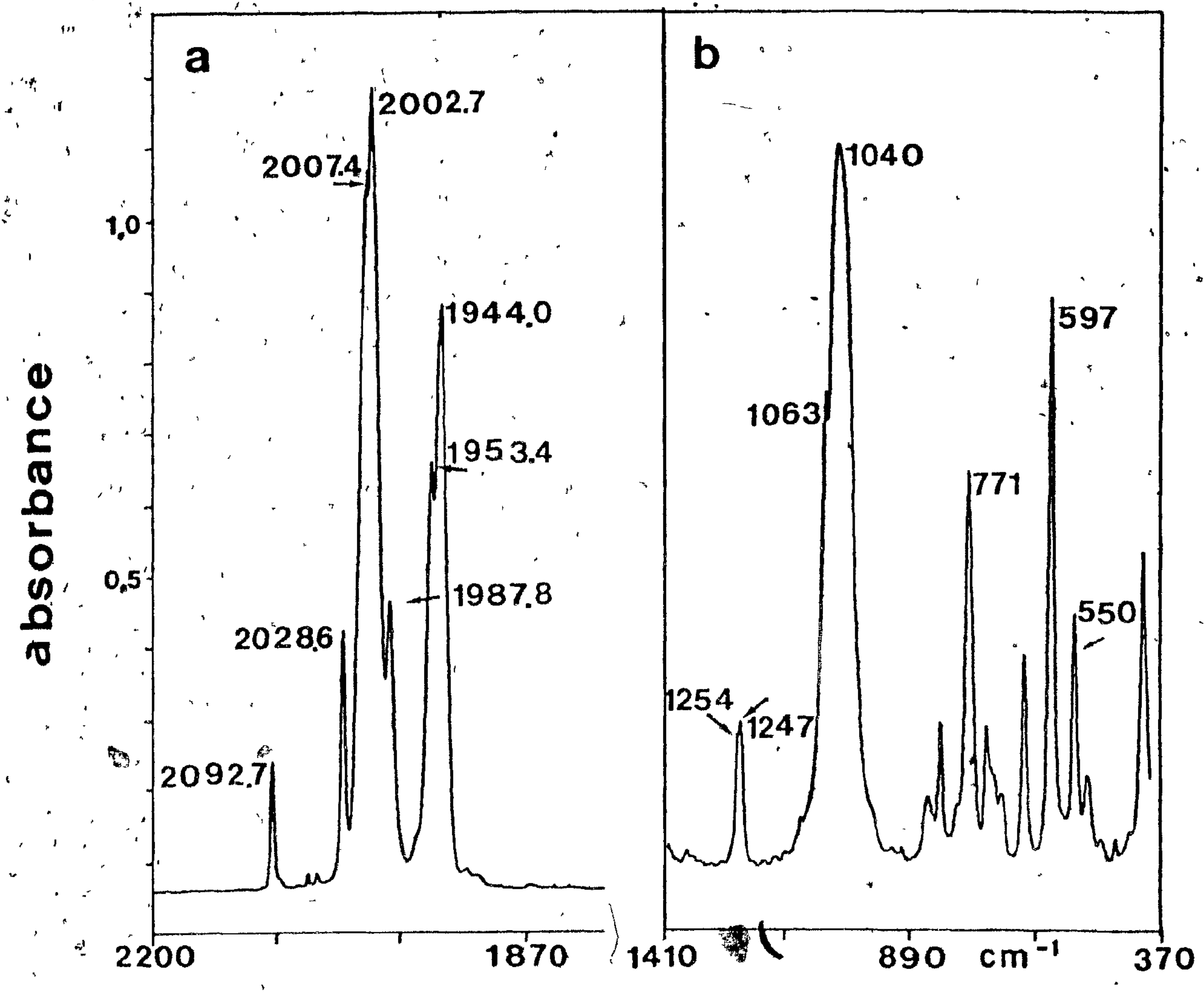
The reaction of $D_1^{H}D_3^{Fp}$ with $Co_2(CO)_8$ in hexanes (eq. 2.10) under conditions similar to the preparation of D_4^{Co} was rapid

$$D_1^{H}D_3^{Fp} + 1/2Co_2(CO)_8 \xrightarrow[25°C]{\text{hexanes}} D_1^{Co}D_3^{Fp} + 1/2H_2 \quad \text{(eq. 2.10)}$$

and quantitative. Several purification steps by precipitation and column chromatography afforded a light yellow grease. The compound was air stable but decomposed slowly in solution. The ^1H NMR spectrum shows the complete disappearance of the multiplet at ca. 0.4 ppm and the formation of a large and complex multiplet at ca. 0.9 ppm corresponding to the resonance of a CH_3 attached to ≡Si-M where M = Fp or $Co(CO)_4$. A detailed study of the ^1H NMR spectrum of the cyclopentadienyl region is given in Chapter 4 and helps to support the proposed formulation of the compound. Indeed, the elemental analysis also supports this formulation.

The high resolution infrared spectrum in the carbonyl stretching region for $D_1^{Co}D_3^{Fe}$ (Fig. 2.5a) confirms the presence of both organometallic groups. The $Co(CO)_4$ grouping shows peaks at 2092.7, 2028.6 and probably 2007.4 cm^{-1} but the expected fourth peak is hidden by absorptions from the Fp group. The $Fe(CO)_2\eta^5-C_5H_5$ moiety shows strong peaks at 2002.7 and 1944.0 cm^{-1}. The small peaks at 1987.8 and 1953.4 cm^{-1} are also attributed to $Fe(CO)_2\eta^5-C_5H_5$ and are possibly related to the presence of geometric isomers as

Figure 2.5: Infrared spectra of $D_1^{Co}D_3^{Fp}$ (36): a) carbonyl stretching region measured in cyclohexane solution (ca. 1%) with a resolution of 0.12 cm^{-1}, b) the region 400-1400 cm^{-1} measured in CS$_2$ solution (ca. 5%)



proposed in the case of pure D_4^{Fp}.

The lower frequency part of the $D_1^{Co}D_3^{Fp}$ spectrum in CS_2 (Fig. 2.5b) is quite similar to the spectrum of D_4^{Fp} shown in Figure 2.4. However, two major and significant differences are evident:

a) The peak at 1247 cm^{-1} in the D_4^{Fp} spectrum (assigned to Si-CH_3 stretching) is split (1254 and 1247 cm^{-1}) in the spectrum of $D_1^{Co}D_3^{Fe}$ due to the presence of two different substituents on the silicon atoms.

b) The presence of a new peak at 550 cm^{-1} in the spectrum of $D_1^{Co}D_3^{Fe}$, compared to that of D_4^{Fp} confirms the presence of a cobalt carbon stretching mode as observed in D_4^{Co} (Fig. 2.2).

The similarity of the siloxane regions of D_4^{Fp} and $D_1^{Co}D_3^{Fp}$ supports the formulation of the new product. The new heteronuclear complex consists of a cyclosiloxane molecule containing three $Fe(CO)_2\eta^5$-C_5H_5 groups but only one $Co(CO)_4$ group, giving a siloxane ring stretching frequency very close to that of D_4^{Fp} (actually the same in CS_2 solution).

The absence of reactivity of $Co_2(CO)_8$ toward D_4^{Fp} confirms the extraordinary stability of the Si-$Fe(CO)_2\eta^5$-C_5H_5 bond[64] and above all makes sure that the product from the reaction of $D_{4-n}^{H}D_n^{Fp}$ with $Co_2(CO)_8$ is only due to hydrogen elimination from a Si-H reaction center and not due to a metal substitution at a Si-Fe center.

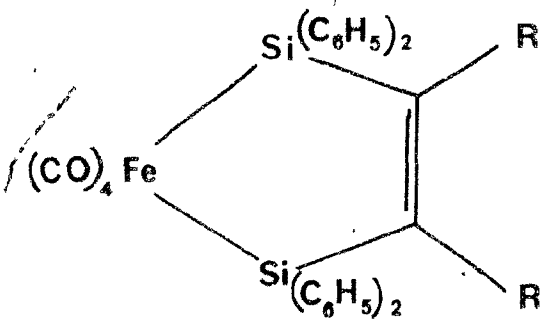
The Appendix 1 describes a small scale preparation of the analogous pentamer, $D_{5-n}^{Co}D_{n}^{Fe}$. Infrared and ^1H NMR evidence for the formation of the mixture of heteronuclear complexes are given. The mixture becomes so complex with the pentamer that it seems unrealistic to try to isolate some compounds with the usual separation methods.

2.4.6 Anomalous reactions of D_4^H with some metal carbonyls

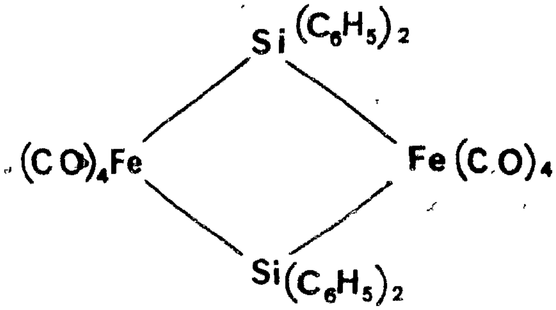
Hydrogen elimination is a fairly general reaction and many reports have mentioned the thermal reactivity of simple silanes with the dimers, $Mn_2(CO)_{10}$[40,66,119,125-127], $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2$[119] and even with the trimer, $Fe_3(CO)_{12}$[117,128-130]. Reactions of D_4^H will all of these compounds gave poor results (see Appendix 1). The reaction of D_4^H with $Mn_2(CO)_{10}$ was performed in a sealed tube under rigorously dry and anaerobic conditions[40,119]. The infrared of the crude solution after the reaction showed that ca. 95% of the Si-H had reacted. In spite of this, only traces (< 1% yield) of presumably $D_4^{Mn(CO)_5}$ were isolated. The infrared of this compound in the ν(CO) region is in good accordance with the C_{4v} symmetry generally observed for $R_3Si\text{-}Mn(CO)_5$[60,66]. In the reaction of $Mn_2(CO)_{10}$ with polysilanes, Nicholson and Simpson[40] observed a low yield (10 to 40%) of expected polynuclear complexes and mentioned the production of siloxane species. The oxygen for the siloxane formation must be presumed as the result of the attack on silicon by oxygen of coordinated carbonyl groups[29,40]. Very similar behavior seems to be present in the reaction with D_4^H where a silicone grease-like material was isolated by chromatography (see Appendix 1). In addition, the strong tendency of $(CH_3)_3Si\text{-}Mn(CO)_5$ to homolytic cleavage and the subsequent formation of silyloxy-alkyl complexes by attacking the oxygen of many aldehydes and ketones has recently been studied and a mechanism was proposed[131].

The formation of $Cl_3SiMo(CO)_2\eta^5\text{-}C_5H_5$ from the reaction of Cl_3SiH with $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2$ has been reported by Jetz and Graham[119]. A similar reaction with D_4^H led to a complex mixture from which it was impossible to extract any recognizable products. The presence of a complex pattern of carbonyl peaks and a very broad band in the Si-O-Si region of the IR spectrum of the crude solution indicated that polymerization of the siloxane and formation of some unknown molybdenum carbonyl derivatives had taken place.

The thermal reaction of $Fe_3(CO)_{12}$ with Cl_3SiH has been reported[119] to give a di-silyl derivative: $(Cl_3Si)_2Fe(CO)_4$. When $Fe_3(CO)_{12}$ was slowly added to D_4^H solution under rigorously anaerobic conditions, all Si-H was reacted after a few hours in hexanes under reflux. The product was a mixture of extremely air-sensitive compounds showing a complex pattern in the $\nu(CO)$ region. A small amount of one of the products, isolated by chromatography, had an infrared spectrum consistent with a silyl-Fe(CO)$_4$ derivative[37,62,128,132]. The compound was found to be very unstable. A recent report by Carré and Moreau[133] mentioned the good stability of a chelating di-silyl complex (37) compared to the high reactivity of a



(37)



(38)

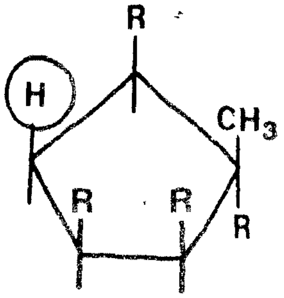
non-chelating analog (38). The apparent instability of the expected complex with D_4^H where Fe(CO)$_4$ is coordinated to two adjacent (or trans-annular) silicons on the same cyclosiloxane molecule can be due to an unfavorable strain as observed in 38. It was also reported[134] that the complex cis-(CO)$_4$Fe[Si(CH$_3$)$_3$]$_2$ attacks the oxygen of a variety of acyclic ethers to form new siloxane bonds (eq. 2.11). A similar reaction at the oxygen of a siloxane bond of D_4^H would open the ring and give a new siloxane product.

$$(CO)_4Fe[Si(CH_3)_3]_2 + CH_3OSi(CH_3)_3 \longrightarrow (CH_3)_4Si + [(CH_3)_3Si]_2O + \ldots \quad \text{(eq. 2.11)}$$

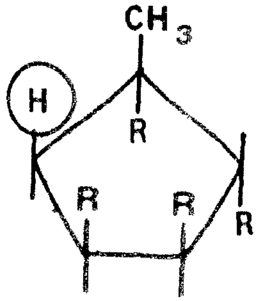
2.4.7 The low reactivity of $D_1^HD_4^R$

It was previously mentioned in this chapter that the reactivity of the pentamer, D_5^H, toward $Co_2(CO)_8$ and $[\eta^5-C_5H_5Fe(CO)_2]_2$ was much lower than expected from analogous reactions with D_4^H. It was impossible to prepare the fully substituted D_5^{Fp} and very difficult to get D_5^{Co} in even very low yield. This behavior could be related to the conformation of the molecule when four sites have been substituted and only one hydrogen is still unreacted. Scheme 2.4 (top) shows two examples of $D_1^HD_4^R$ isomers where the unreacted hydrogen is surrounded by two adjacent bulky groups (R = Fp or $Co(CO)_4$) or by one bulky group and one CH_3. Scheme 2.4 (bottom) shows the representation of a hypothetical "double chair" conformation adopted by the pentamer. The motion of Si(1) toward the inside of the ring (as indicated by the arrow) induces an outward motion of Si(2) and Si(3) but has little effect on Si(4) and Si(5). Such a motion is favoured by the large size of substituents at Si(2) and Si(3) and by the very small size of the hydrogen atom which becomes "hidden" inside the ring between the two adjacent groups. Some large attacking molecules, such as $HCo(CO)_4$ and above all, $HFe(CO)_2\eta^5-C_5H_5$, would have major difficulties in

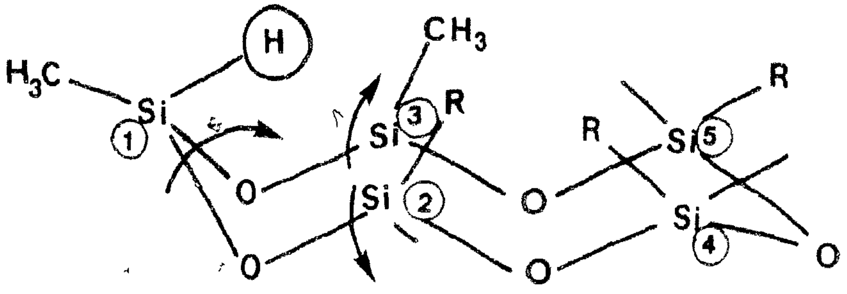
Scheme 2.4: Two possible geometric isomers of partially substituted $D_1^H D_4^R$. The "double chair" conformation of isomer III is shown (bottom)



ISOMER II.



ISOMER III



ISOMER III

reaching the last reaction site. It should be noted that the analogous "hidden conformation" for the unreacted hydrogen is not possible in the tetramer $D_1^HD_3^R$. The molecule would probably tend to adopt a "chair conformation", (e.g. Fig. 1.3, bottom) to get the bulky groups away from each other. This conformation is still favorable to the reaction of the last hydrogen.

In addition, the statistical effect should be mentioned as an important factor in the substitution of the last hydrogen. As five reaction sites are present on the same molecule, which is not a common feature in synthesis, the attacking reagent finds it more and more difficult to be in the right place at the right time as the level of substitution increases up to five.

2.4.8 Salt elimination reactions

The salt elimination reaction was the original route used by Piper and Wilkinson[22] to prepare silyl-Fe(CO)$_2$-η^5-C_5H_5 complexes. The major interest in the present work for this approach was the possibility of preparing D_3^{Co} and D_3^{Fp} from D_3^{Br} and the appropriate alkali-transition metal salts.

The reaction of D_3^{Br} with $LiCo(CO)_4$ in THF even at low temperature gave an unexpected but already known methinyl-tricobalt enneacarbonyl[135], identified by ^1H NMR and mass spectrometry (Appendix 1) as $HO(CH_2)_4CCo_3(CO)_9$. Tricobalt carbonyls are common in reactions with $Co(CO)_4^-$ and the present product is formed by the cleavage of the THF[135]. The expected D_3^{Co} was not isolated. Many anomalous reactions between silicon compounds and cobalt carbonyl anions have been reported[45,135,136]. The electrophilic attack by the silicon compound on oxygen atoms of coordinated carbonyl groups was observed[45] (eq. 2.11) to give siloxane products.

$$(C_6H_5)_3SiCl + Co(CO)_4^- \xrightarrow{THF} [(C_6H_5)Si]_2O + \ldots\ldots \qquad \text{(eq. 2.11)}$$

Reactions of both D_3^{Br} and D_4^{Br} with $NaFe(CO)_2\eta^5\text{-}C_5H_5$ in THF were also unsuccessful. The reaction was also carried out in dry toluene but the unknown products decomposed on the column (Appendix 1). Many reactions of halogenated silanes, polysilanes and cyclic carbosilanes with $[Fe(CO)_2\eta^5\text{-}C_5H_5]^-$ were successful[29]. Reactions were run in THF and stable products were isolated by column chromatography in reasonable yields (30 to 75%)[40,120]. Silicon chlorides are usually used for the reaction but at least one series of successful reactions has been reported with bromosilanes[137]. Nevertheless, it should be noted that no successful reaction was reported with halogenated siloxane. It seems that the siloxane ring does not resist to the reaction conditions and polymerization probably occurs.

2.5 Conclusion

The following conclusions can be drawn from the synthetic work reported above:

- The yields of small rings, D_3^{Ph} and D_4^{H}, can be improved by hydrolyzing the corresponding dichlorosilane slowly at 0°C in a large volume of ether/ice.
- The new compounds, D_3^{Br} and D_4^{Br}, have been prepared by the cleavage of the phenyl group by Br_2 in the corresponding methylphenylcyclosiloxanes.
- The reduction of D_3^{Br} at low temperature with trialkylborohydride salts led to the formation of the elusive D_3^{H}. This compound was found to be very unstable toward polymerization.
- The reaction of D_n^{H} with $Co_2(CO)_8$ and $[Fe(CO)_2\eta^5\text{-}C_5H_5]_2$ led to the formation of the new compounds, D_4^{Co}, D_5^{Co}, and D_4^{Fp}. These heavy organometallic complexes were characterized by infrared. It was also possible to synthesize the heteronuclear complex, $D_1^{Co}D_3^{Fp}$ by reacting the partially substituted $D_1^{H}D_3^{Fp}$ with $Co_2(CO)_8$.
- The reactions of D_4^{H} with $Mn_2(CO)_{10}$, $[Mo(CO)_2\eta^5\text{-}C_5H_5]_2$ and $Fe_3(CO)_{12}$ did not lead to the formation of isolable and recognizable products.
- The salt elimination reactions of D_3^{Br} and D_4^{Br} with alkali-transition metal salts were also unsuccessful.

3. MASS SPECTRA OF SOME METHYL SUBSTITUTED CYCLOSILOXANES*

3.1 Introduction

In this chapter the results of a systematic investigation of the mass spectra of some methyl substituted cyclosiloxanes will be presented and interpreted. Despite the fact that methyl siloxanes have been and are still of prime interest in the silicone industry, very little has been published on the characterization by mass spectrometry of small and monomeric methylcyclosiloxanes[138]. Linear as well as cyclic methylsiloxanes are characterized by an intense $[M-15]^+$ ion and, like most organosilicon compounds, exhibit no molecular ion. Two important contributions to the mass spectrometry of methylcyclosiloxanes were published in recent years[139,140]. These authors proposed an elegant transannular methyl migration/ring contraction mechanism to account for the observed spectra of dimethylcyclosiloxanes (D_n $n > 5$). To our knowledge, this mechanism has not been investigated with an analogous series of compounds where one methyl on each silicon is replaced by another substituent. In the present chapter, a detailed discussion of fragmentation patterns of most of the substituted methylcyclosiloxanes described in Chapter II will be presented.

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*Some results presented in this chapter have been published in Can. J. Chem. (The Leo Yaffe Issue), April, 1983.

3.2 Experimental and instrumentation

The spectra of D_n^H (n = 4, 5, and 6) and D_n^{Co} (n = 4 and 5) were measured at the McGill University Mass Spectrometry Unit (Dr. O.A. Mamer) on a LKB 9000 instrument (electron energy 70 eV, source temperature 270°C). D_4^H was introduced directly as a pure compound at an inlet temperature of 100°C whereas D_5^H and D_6^H together in a mixture were separated on a coupled GLC using a two meter glass column of 6% OV-101 at 135°C. Samples of D_4^{Co} and D_5^{Co} were introduced directly at probe temperatures of 46° and 50°C respectively.

The spectra of D_n^{Ph} and D_n^{Br} (n = 3 and 4) were measured on a Dupont 21-492B instrument (electron energy 70 eV, source temperature 250°C) at the Department of Chemistry (Dr. John Finkenbine). Compounds D_3^{Ph} and D_4^{Ph} were introduced directly at probe temperatures of 55° and 80°C respectively. Both D_3^{Br} and D_4^{Br} compounds were sufficiently volatile to be introduced directly at ambient temperature.

The high resolution spectrum of D_5^H was measured on an AEI MS 902 spectrometer (at 70 eV ionizing energy and source temperature 250°) at the Laboratoire de spectrométrie de masse, Université de Montréal (Dr. Michel Bertrand).

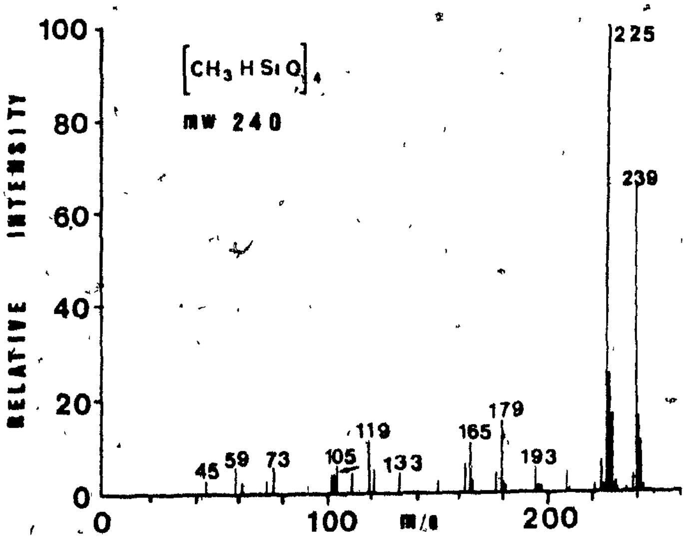
3.3 Results

3.3.1 The methylhydrogencyclosiloxanes

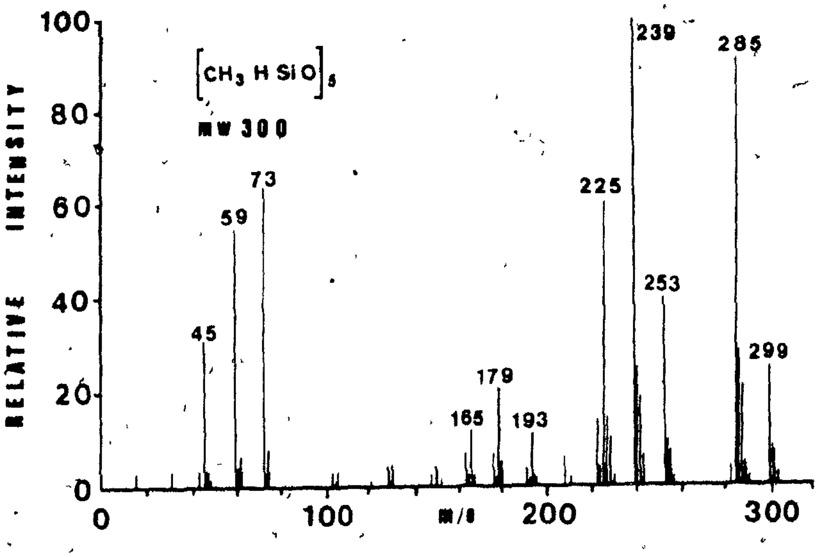
In each spectrum of D_n^H (n = 4, 5, 6) the heaviest ions are $[M-1]^+$ and $[M-15]^+$ and the relative intensities of these ions diminish with increasing ring size (Fig. 3.1). The absence of $[\dot{M}]^{+\cdot}$ is a common feature of methylsiloxane fragmentation due to the facile loss of $\dot{C}H_3$ from the parent ions[139,140]. Another evident feature of the spectra is the high intensity of the peaks m/e 73, 59 and 45 in D_5^H and D_6^H compared to D_4^H.

The spectra of D_n^H are considerably richer in lines than those of D_n. For example, the spectrum of D_5^H (Fig. 3.1) shows eleven peaks of relative intensity > 10 per cent, whilst D_5 shows only three major peaks at $[M-15]^+$, $[M-103]^+$ and m/e 73[138-140]. The two groupings of lines at $[M-47]^+$, $[M-61]^+$ and $[M-75]^+$, and at $[M-107]^+$, $[M-121]^+$ and $[M-135]^+$, consistently present in D_n^H, are separated by a characteristic mass increment of 60 amu. Exact mass measurements on D_5^H show this increment to be in fact due to two processes: loss of SiO_2 and also of $(CH_3)HSiO$ (Table 3.1b). The separation between the lines of these two groups, as well as that between the light ions at m/e 73, 59 and 45, all correspond to a mass increment of 14 amu. Contrary to the case of D_n, no evidence for significant currents of doubly charged ions was observed, except in D_6^H where ion m/e 179 can be attributed to $[M-2]^{++}$.

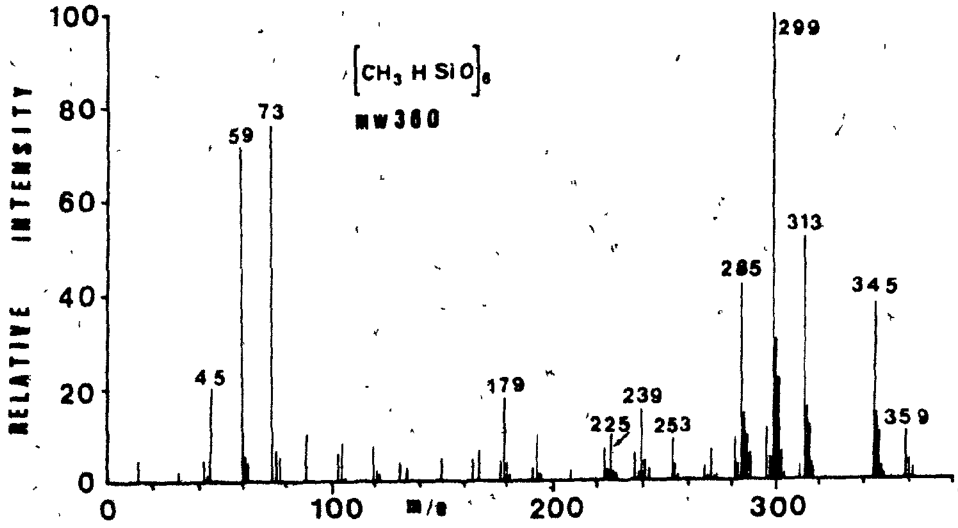
Figure 3.1: Mass spectra of the methylhydrogencyclosiloxanes, D_n^H (n = 4, 5, and 6)



$[CH_3HSiO]_4$
mw 240
RELATIVE INTENSITY
100
80
60
40
20
0
225
239
45
59
73
105
119
133
165
179
193
0
100
m/e
200



$[CH_3HSiO]_5$
mw 300
RELATIVE INTENSITY
100
80
60
40
20
0
239
285
225
73
59
253
45
299
179
165
193
0
100
m/e
200
300



$[CH_3HSiO]_6$
mw 360
RELATIVE INTENSITY
100
80
60
40
20
0
299
73
59
313
285
345
45
179
239
225
253
359
0
100
m/e
200
300

Table 3.1a: Some metastable ions observed in spectra of D_n^H series

Metastable ions	Observed	Calculated
in D_4^H	142	$(179)^2/225 = 142.4$
D_5^H	201	$(239)^2/285 = 200.4$
D_6^H	259	$(299)^2/345 = 259.1$

Table 3.1b: High resolution mass measurements on D_5^H

Ions$^+$	m/e	Observed	Calculated
$[M-47]^+$	253	252.988	252.984 ($C_4H_{13}Si_4O_5$)
$[M-61]^+$	239	238.965	238.968 ($C_3H_{11}Si_4O_5$)
$[M-75]^+$	225	224.951	224.953 ($C_2H_9Si_4O_5$)
$[M-107]^+$	193	192.958	192.981 ($C_3H_9Si_3O_4$)
$[M-121]^+$	179	178.999	179.002 ($C_3H_{11}Si_3O_3$)
		178.964	178.965 ($C_2H_7Si_3O_4$)
$[M-135]^+$	165	164.984	164.986 ($C_2H_9Si_3O_3$)
		164.947	164.949 ($C_1H_5Si_3O_4$)

3.3.2 The methylphenyl- and methylbromocyclosiloxanes

The mass spectra of D_n^{Ph} (n = 3 and 4) are shown in Figure 3.2. Both compounds show the molecular ion at low intensity on the oscillograms. The major peaks in both spectra occur at $[M-15]^+$ and $[M-93]^+$. It is clear that the distribution of peaks in these two compounds is quite different from that in D_n and D_n^H and reflects a very different fragmentation mechanism.

The spectra of D_3^{Br} and D_4^{Br} are notable for their simplicity (Fig. 3.3). In neither case is $[M]^{+\bullet}$ observed, and the strongest peaks are due to $[M-CH_4]^{+\bullet}$ and $[M-HBr]^{+\bullet}$. Apart from these peaks, the only others with relative abundance > 10 per cent are those at m/e 128 and 129 (D_3^{Br}) and at m/e 197, 198 and 199 (D_4^{Br}) attributed to doubly charged $[M-2Br]^{++}$. As expected, HBr^+ (m/e 80, 82) and Br^+ (m/e 79, 81) are present in both spectra.

3.3.3 The tetracarbonylcobalt(I)methylcyclosiloxanes

The expanded spectra of D_4^{Co} and D_5^{Co} are shown in Figures 3.4 and 3.5. The presence of geminate series of lines is highlighted. The first series (noted a_1, a_2, a_3,...), beginning at the highest mass corresponds to the stepwise loss of all CO ligands from $[M]^{+\bullet}$. The second series (noted b_1, b_2, b_3,..., starting at $[M-171]^+$, corresponds to the stepwise loss of all CO ligands from $[M-Co(CO)_4]^+$. Also quite important in terms of total ion current are the series

Figure 3.2: Mass spectra of the methylphenylcyclosiloxanes, D_n^{Ph} (n = 3 and 4)

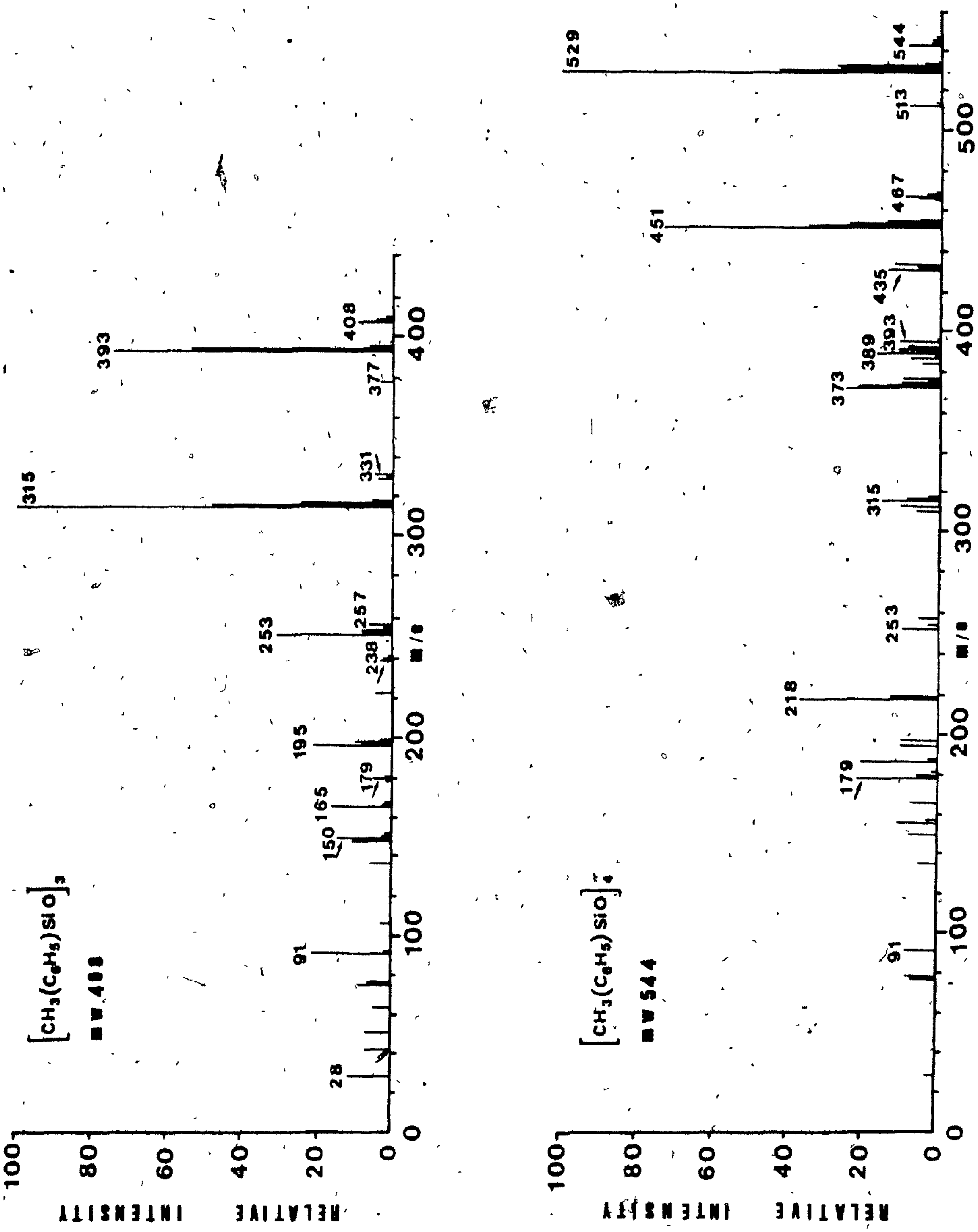


Figure 3.3: Mass spectra of the methylbromocyclosiloxanes, D_n^{Br} (n = 3 and 4)

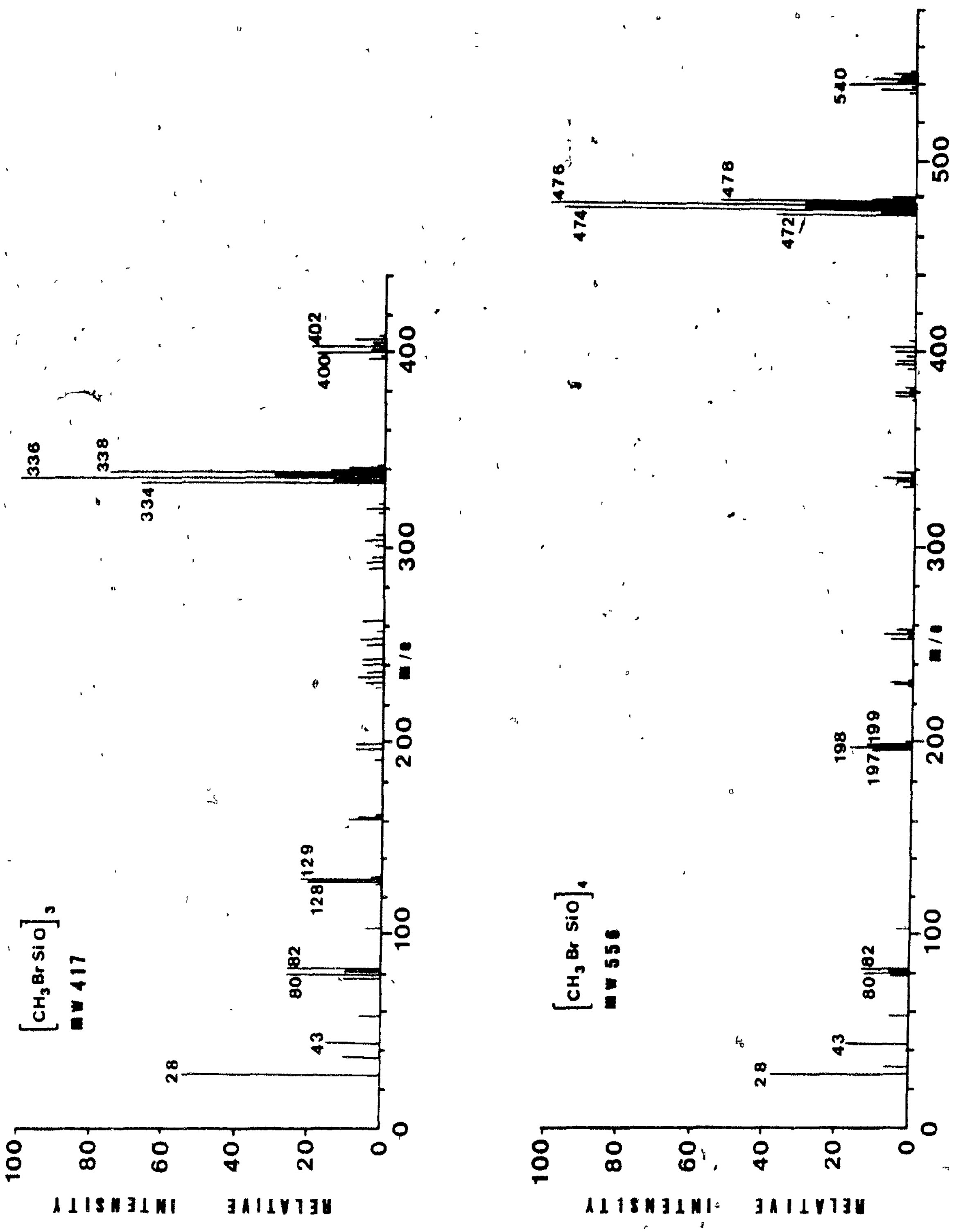


Figure 3.4: Mass spectrum of the tetracarbonylcobalt(I)-methylcyclotetrasiloxane, D_4^{Co}. Peak noted b^+ stands for the ion $[M-171]^+$ m/e 749

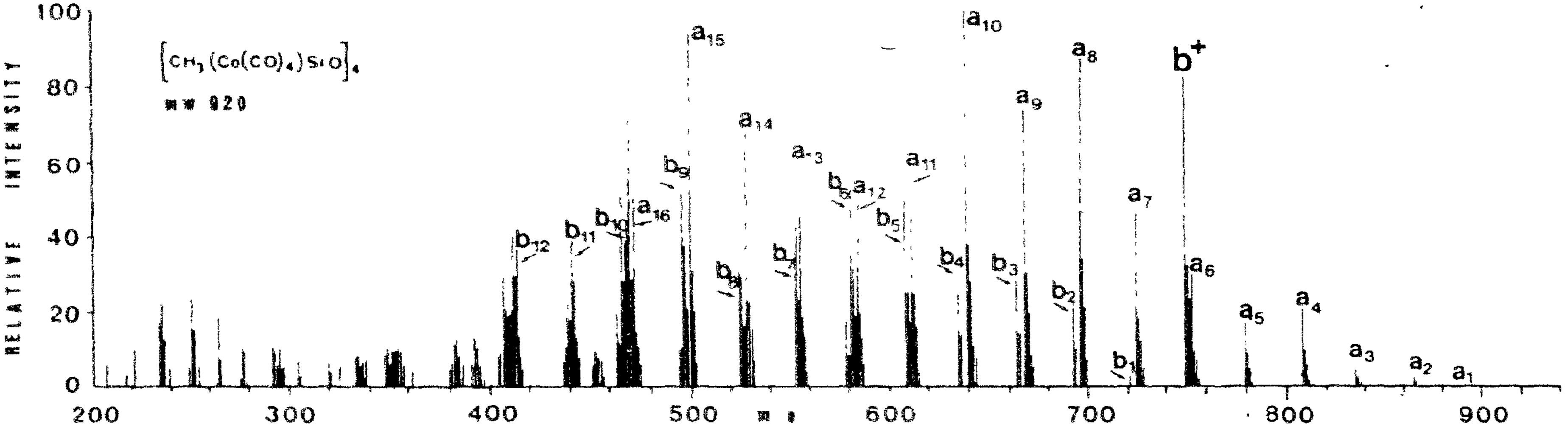
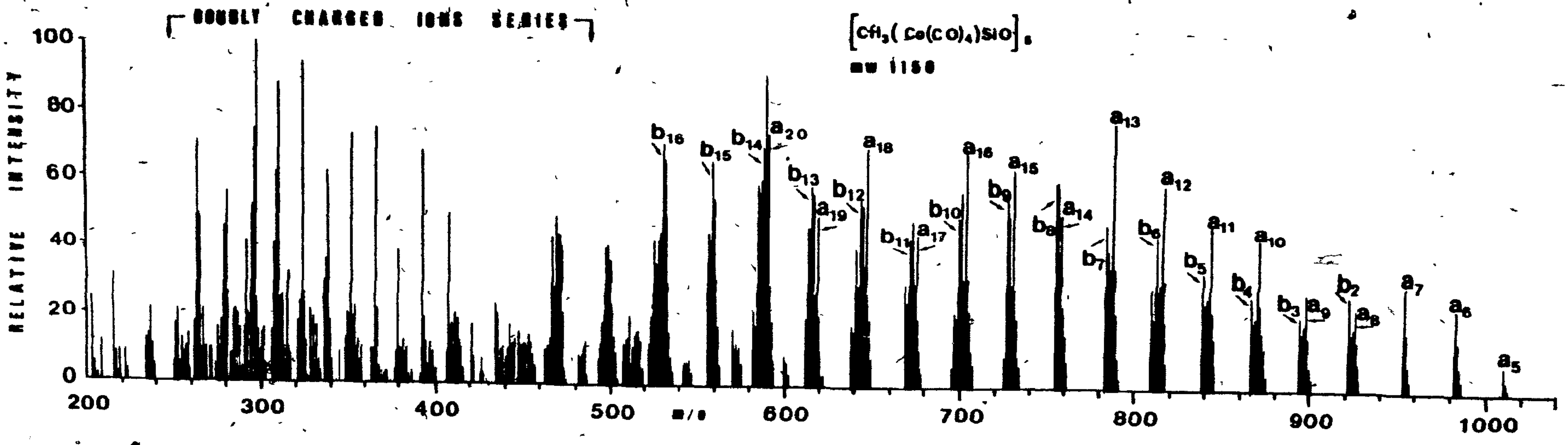

$[CH_3(Co(CO)_4)SiO]_4$
MW 920
RELATIVE INTENSITY
0
20
40
60
80
100
200
300
400
500
600
700
800
900
a_{15}
a_{10}
a_8
b^+
a_9
a_{14}
a_{13}
a_{11}
b_9
b_6
a_{12}
a_{16}
b_{10}
b_{11}
b_{12}
b_5
a_7
b_8
b_7
b_4
b_3
a_6
b_2
a_5
a_4
b_1
a_3
a_2
a_1

Figure 3.5: Mass spectrum of the tetracarbonylcobalt(I)-methylcyclopentasiloxane, D_5^{Co}


DOUBLY CHARGED IONS SERIES
[CH3(Co(CO)4)SiO]5
mw 1150
RELATIVE INTENSITY
100
80
60
40
20
0
200
300
400
500
m/e
600
700
800
900
1000
b16
b15
b14
a20
b13
b12
a19
a18
b11
a17
b10
a16
b9
a15
b8
a14
b7
a13
b6
a12
b5
a11
b4
a10
b3
a9
b2
a8
a7
a6
a5

of CO dissociations from doubly charged ions, evidenced by the large number of peaks separated by 14 amu in the m/e 200 to 500 region of the spectrum of D_5^{Co} (Fig. 3.5).

3.3.4 The cyclopentadienyldicarbonyliron(II)methylcyclotetrasiloxane

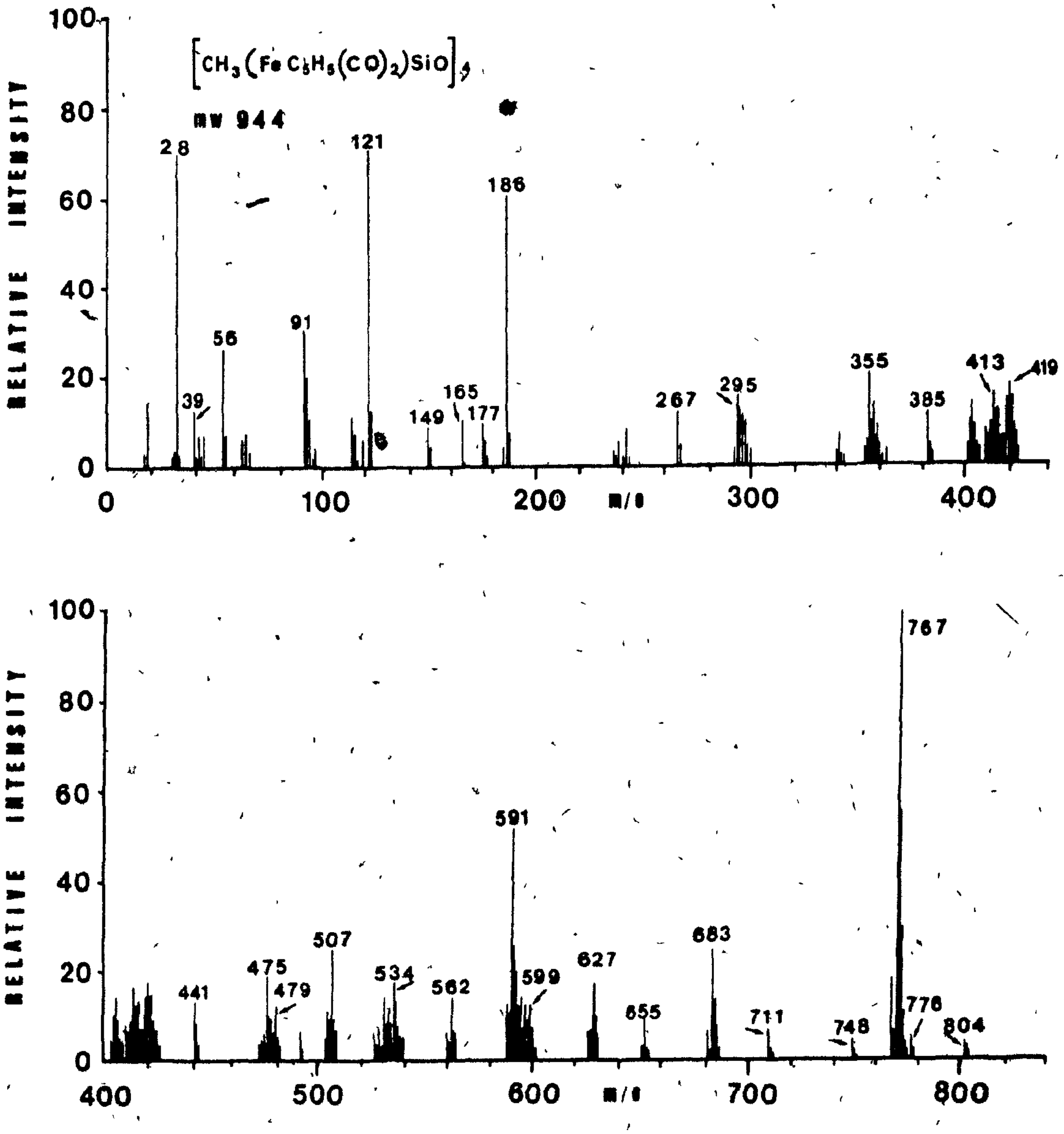
The details of the mass spectrum of D_4^{Fp} are reported in Figure 3.6. In contrast to the analogous D_4^{Co}, this complex does not show the successive loss of carbonyl groups from the parent ion as the dominant pathway. The major fragmentation route seems to be the facile loss of the whole group Fp from the molecular ion giving rise to the ion $[M-177]^+$ m/e 767. The multiple loss of CO and cyclopentadienyl groups are observed from ion $[M-177]^+$, $[M-353]^+$, and $[M-531]^+$. The presence of unexpected fragments such as $(C_5H_5)_2Fe^+$ (m/e 186), $C_7H_7^+$ (m/e 91) and $C_3H_3^+$ (m/e 39) will be discussed below.

3.4 Discussion

3.4.1 The methylhydrogencyclosiloxanes

Previous studies of mixed methylhydrogensiloxanes have been summarized by Coutant and Robinson[138]. The fragmentation pathway of the cyclopentasiloxanes, $D_nD^H_{5-n}$ (n = 1 to 5) shows that the initial cleavage happens at either substituent H or CH_3 and is followed by the loss of a neutral fragment $(CH_3)_4Si$ or $(CH_3)_3SiH$. In the fragmentation of the linear siloxane, $(CH_3)_2HSiO(Si(CH_3)_2-O)_2Si(CH_3)_3$, the dominant process is

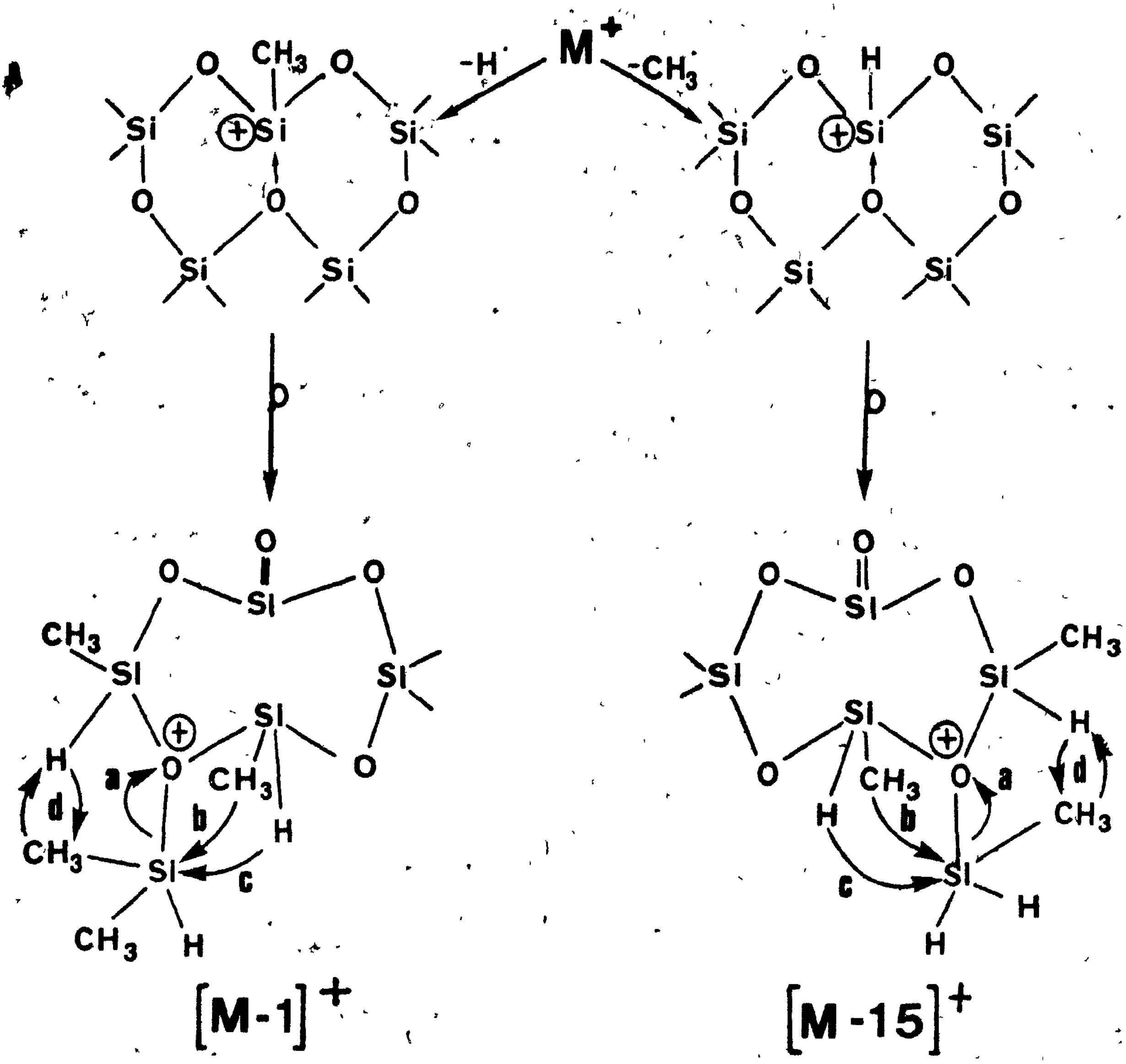
Figure 3.6: Mass spectrum of the cyclopentadienyldicarbonyliron(II)methylcyclosiloxane, D_4^{Fp}



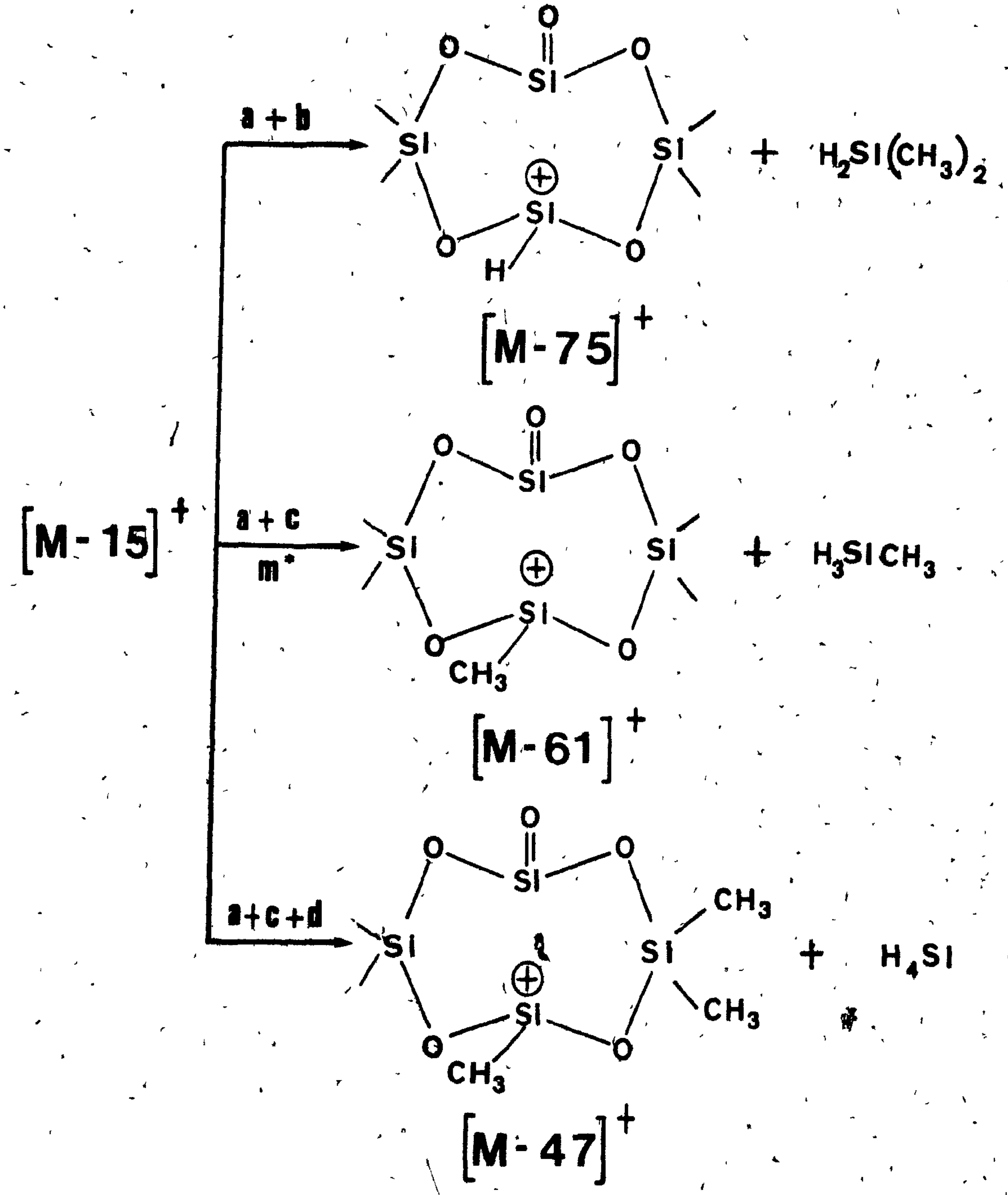
the formation of the ion $[M-89]^+$ by loss of $(CH_3)_3SiH$ from the initial $[M-CH_3]^+$ ion. Either hydrogen, or methyl migration could give rise to these products but methyl migration giving the neutral fragment $(CH_3)_4Si$ and the ion $[M-103]^+$ is much less important[138].

Mass spectra of polymethylcyclosiloxanes (D_n) have been studied by Van den Heuvel et al.[139] and a fragmentation mechanism has been proposed for the spectra of D_5 and larger rings[140]. The key step of this mechanism is the formation of the bicyclized ion $[M-15]^+$. Such transannular interactions have been proposed to account for the mass spectra of trimethylsilylethers[141] and also for medium-sized organosilicon heterocycles[142]. A similar scheme for D_n^H, where it is assumed that either $CH_3^\bullet$ or $H^\bullet$ can be lost to form the initial cation fragment, and either $CH_3^\bullet$ or $H^\bullet$ can participate in the subsequent migrations accompanying ring contraction, is shown in Scheme 3.1. The ring contraction is followed by elimination of light fragments, $(CH_3)_nSiH_{4-n}$, as exemplified by the ion $[M-15]^+$ in Scheme 3.2. This pathway is supported by the observation of metastable ions corresponding to $[M-15]^+ \rightarrow [M-61]^+ + MeSiH_3$ in all spectra of D_n^H (Table 3.1). After their first fragmentation, heavy ions $[M-47]^+$, $[M-61]^+$, and $[M-75]^+$ are charged cyclosiloxanone species which can easily eliminate a neutral fragment as SiO_2 or $(CH_3)HSi{=}O$ (both corresponding to 60 amu) and give rise to the series of ions $[M-107]^+$, $[M-121]^+$, and $[M-135]^+$. Scheme 3.3 shows

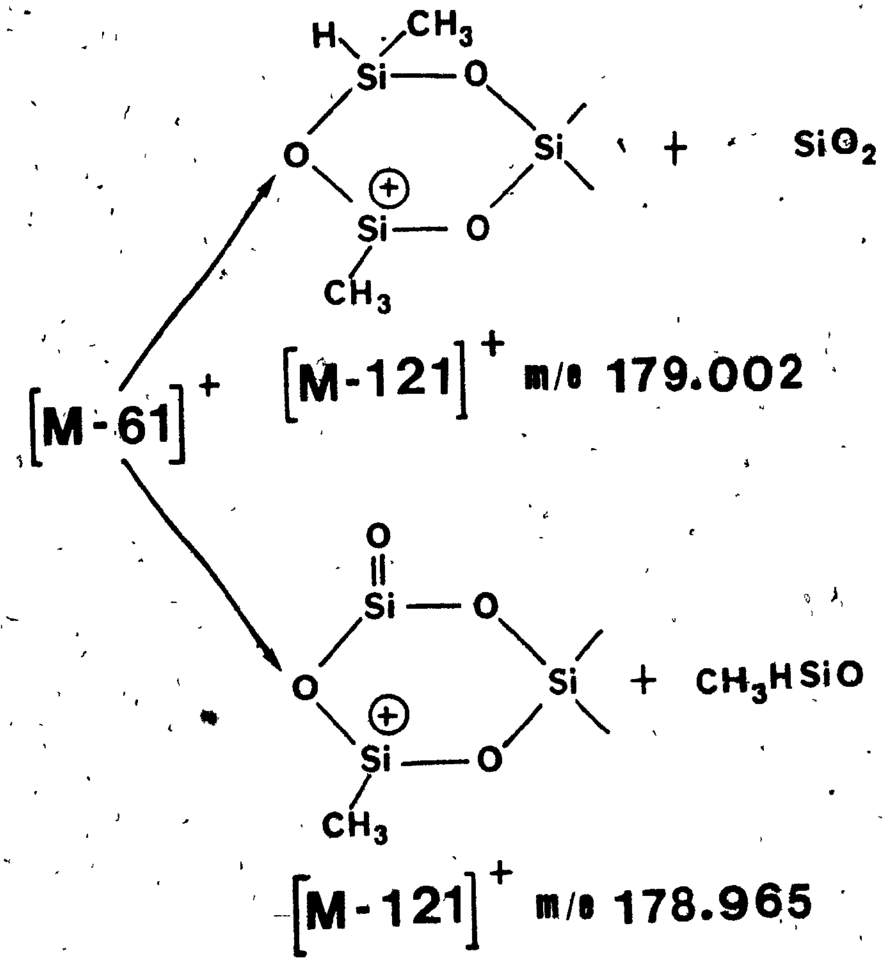
Scheme 3.1: Transannular migration and ring contraction of D_5^H. Small arrows show different possible mechanisms for elimination of silanes



Scheme 3.2: Fragmentation of $[M-15]^+$ ion



Scheme 3.3: Fragmentation of $[M-61]^+$ ion



two possible fragmentations of ion $[M-61]^+$ giving two very similar $[M-121]^+$ ions. This part of the mechanism is supported by the determination of a high resolution mass spectrum on a D_5^H sample. Observed and calculated results reported in Table 3.1 (bottom) show unequivocally the presence of a pair of peaks fully resolved at m/e 179 and 165 due to the elimination of SiO_2 and/or $(CH_3)HSi=O$ from both $[M-61]^+$ and $[M-75]^+$ ions. The identity of lighter ions m/e = 73, 59 and 45 is also confirmed by the high resolution spectrum and corresponds to expected fragments $(CH_3)_3Si^+$, $(CH_3)_2SiH^+$, and $CH_3SiH_2{}^+$.

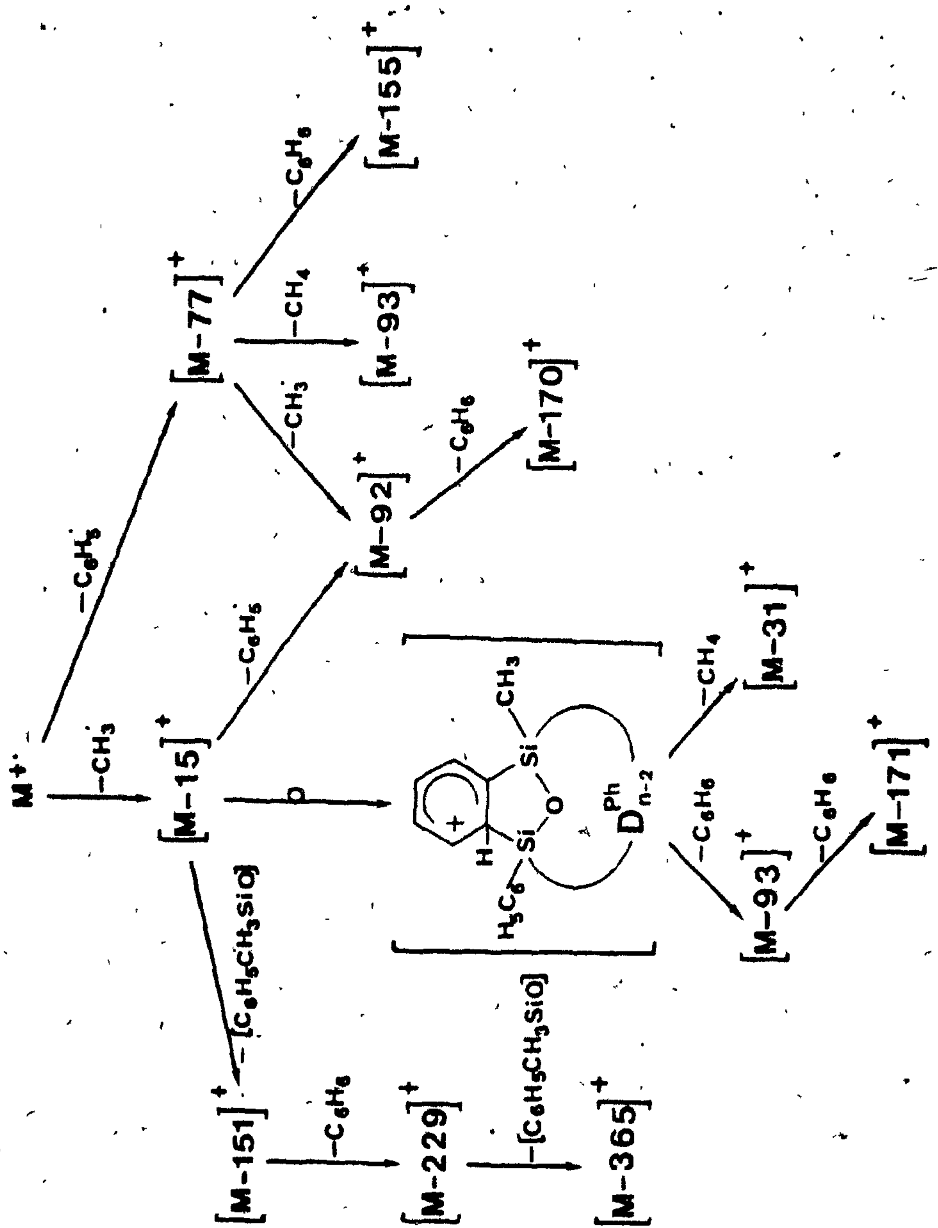
In the case of D_n, the smaller rings D_3 and D_4 do not undergo the ring contraction as easily as D_5 and D_6[139]. The most intense peaks in their mass spectra are ions $[M-15]^+$, whilst the m/e 73 peak is unimportant. In the cases of D_5 and D_6, the m/e 73 peak is the most important. A similar trend is observed with D_n^H where the features associated with ring contraction are much more evident in D_5^H and D_6^H than in D_4^H.

3.4.2 The methylphenylcyclosiloxanes

The fragmentation of some linear and cyclic methylphenylsiloxanes was first studied by Chernyshev et al.[143-145]. The formation of a bridged benzenonium ion was proposed but no complete fragmentation mechanism was presented. A recent study of mass spectra of methylarylpolysiloxanes[146] proposed the formation of the same benzenonium ion followed by loss of benzene and methane as the main fragmentation pathway for the linear siloxane $[C_6H_5(CH_3)_2Si]_2O$. All pathways were supported by observation of numerous metastable peaks. The same essential features are evident in the spectra of D_n^{Ph} (Fig. 3.2.), where siliconium ions $[M-15]^+$, $[M-93]^+$, and $[M-155]^+$ are quite abundant in both cases. A fragmentation pathway is proposed in Scheme 3.4 involving the formation of an intramolecularly binding benzenonium ion from $[M-15]^+$ followed by either loss of benzene, or to a much lesser degree methane. The same mechanism is also consistent with the presence of the ions $[M-77]^+$, $[M-92]^+$, $[M-93]^+$, $[M-155]^+$, and $[M-170]^+$. The initial loss of the phenyl group seems much less favorable probably because the fragmentation of an aryl group attached to a group IV metal requires a larger amount of energy than the fragmentation of an alkyl group[147]. The second major aspect of the mechanism (Scheme 3.4) is the possible elimination of the phenylmethyl silanone from ions $[M-15]^+$, $[M-77]^+$, $[M-171]^+$, $[M-93]^+$ and $[M-229]^+$. These hypotheses account for most of the important observed heavier ions in D_n^{Ph}. The presence, in both spectra, of $C_7H_7^+$ (m/e 91) probably results from the insertion of a methyl group into a silicon-phenyl bond, followed by a β-elimination of the tropylium ion, $C_7H_7^+$, as is commonly observed in aryl compounds[148].

The rather intense $[M-155]^+$ (m/e 253) and $[M-213]^+$ (m/e 195) peaks in the D_3^{Ph} spectrum (weaker in D_4^{Ph}) suggest a relatively important initial fragmentation by loss of $C_6H_5^{\bullet}$

Scheme 3.4: Fragmentation pattern of the methylphenylcyclosiloxanes, D_n^{Ph}



followed by losses of either benzene, or the elements of phenylmethylsilanone, analogous to the reactions of $[M-CH_3]^+$.

On the other hand, the formation of the ion $[M-151]^+$ from $[M-15]^+$ followed by loss of benzene giving ion $[M-229]^+$ seems to be a more favorable process in D_4^{Ph} than in D_3^{Ph}. This behavior could be related to the ring size stability because it would be easy for the siliconium ion $[M-151]^+$ from D_4^{Ph} to rearrange into a stable charged cyclic trimer, whereas it would be difficult to form the hypothetical cyclic dimer ion, $[(CH_3)_2(C_6H_5)_2Si_2O_2]^+$, from D_3^{Ph}. Finally, doubly charged ions are not important in either spectrum, in contrast to those observed for most aryl substituted linear siloxanes[146]. The total absence of peaks at $[M-237]^+$ and $[M-289]^+$ indicates that ring contraction of ion $[M-CH_3]^+$ by loss of $(C_6H_5)_2Si(CH_3)_2$ and $(C_6H_5)_3SiCH_3$, such as occurs with D_n and D_n^H, does not occur with D_n^{Ph}. The more likely transannular migration of methyl group from $[M-C_6H_5]^+$ leading to the formation of ions $[M-165]^+$ and $[M-227]^+$ is also not observed. It is possible that decreased flexibility of the ring due to increased steric demands of the phenyl group[149] contributes directly to this effect. The phenyl migration from oxygen[150], or carbon[151], or nitrogen[152] to the adjacent silicon has been described, but a migration through a siloxane ring would be a function of the flexibility of the ring and has never been demonstrated for a phenyl group.

Even if such a process is not favorable[149], we should point out that a ring opening at the beginning of the fragmentation is not impossible and can be an alternative way to explain the major fragmentation pathway of cyclic siloxanes which is so similar to the one of linear siloxanes, specifically that of the phenylmethylderivatives.

3.4.3 The methylbromocyclosiloxanes

The behavior of halogenosilanes under electron impact is relatively well-known and quite simple[138,149-154] but very little has been published on halogenosiloxanes[138,155]. In most cases the molecular ion shows a very low intensity in contrast to polyhalogenated aromatic compounds which give an intense M^{+}[156a]. The migration of a chlorine atom has been observed in $(CH_3)_3Si-O(Si(CH_3)Cl)_2O-Si(CH_3)_3$, where the loss of $(CH_3)_3SiCl$ from $[M-15]^+$ is the main pathway. Nevertheless, no migration of fluorine or methyl group was observed in fragmentation of $[(CH_3)_3SiO]_2Si(CH_3)F$[156b]. In the present study, no ring contraction, either by transannular migration or by loss of silanone fragment, was observed with D_n^{Br}. The major ions in both spectra, $[M-CH_4]^{+\cdot}$ and $[M-HBr]^{+\cdot}$, are formed by the abstraction either by a CH_3 group or a bromine atom of a hydrogen atom from an adjacent or transannular methyl group. The elimination of HX from organosilicon halides is quite common[149,157] and is sometimes the major process of fragmentation[158]. The elimination of CH_4 is much less favorable but has been observed in the fragmentation of many cyclosiloxanes[159] and some cyclocarbosilanes[160]. In the case of D_n^{Br}, the elimination of CH_4 and HBr seems to be favoured by the spatial disposition of substituents on the siloxane rings. The loss of substituents to form doubly charged ions is particularly evident in D_n and D_n^{Br} ($n = 3$ and 4) compared to D_n^{Ph} and D_n^{H}. Apparently the absence of alternative facile fragmentation pathways is responsible for such behavior in these cases.

3.4.4 The tetracarbonylcobalt(I)methylcyclosiloxanes

Metal carbonyls and their derivatives undergo stepwise loss of CO ligands under mass spectrometry conditions[157]. It is usual for such compounds to show a stepwise loss of all CO groups to produce the base metal ion, or the metal ion plus original substituents other than CO. The low ionization potentials of transition metal atoms also result in the common appearance of multiply-charged ions in carbonyl mass spectra. To our knowledge, one of the heaviest clusters for which a complete mass spectrometric analysis has been reported is $Ru_6C(CO)_{17}$. This compound shows a stepwise loss of seventeen CO groups from both the singly and doubly charged ions[161].

The mass spectra of several simple silylcobalttetracarbonyls have been reported and they show the typical stepwise loss of CO[162]. The spectra of the compounds reported in the present study have a number of novel features. The most striking aspect of the spectra is the fact that one can observe the stepwise loss of such a large number of CO groups. Unlike the fragmentation of carbonyl clusters, where breakup of the metal cluster does not usually occur under mass spectrometer operating conditions, the D_n^{Co} compounds do show loss of metal fragments. Thus, the most obvious feature of the spectra is the presence of the two series corresponding to stepwise loss of 4nCO molecules from $[M]^{+\cdot}$ and 4(n-1)CO molecules from $[M-Co(CO)_4]^+$. A more careful scrutiny of the spectra also shows the presence of a series corresponding to stepwise loss of 4nCO molecules from $[M]^{++}$ (Fig. 3.5). As well, $[M-15]^+$ was detected at low abundance for both n = 4 and 5, and CO loss series was detected for this ion.

3.4.5 The cyclopentadienyldicarbonyliron(II)methylcyclosiloxane

Earlier work on mass spectra of the simple mononuclear cyclopentadienyl metal carbonyls[163,164] shows that the successive loss of CO before the cleavage of C_5H_5 is observed in most cases. Ions of the type $(C_5H_5)_2M^+$ have been observed in the spectra of many complexes which contain only one cyclopentadienyl ring bonded to a metal atom[165,166]. King[166] has observed the ion $(C_5H_5)_2Fe^+$ in the spectra of a number of mononuclear derivatives. The spectrum of $CH_3COFe(CO)_2\eta^5-C_5H_5$ was recorded in two instruments having source temperatures of 70° and 200°C, respectively, and the large differences observed in spectra were attributed to the production of ferrocene by pyrolysis within the instruments[167]. In a subsequent paper, King and coworkers[120] reported the mass spectra of some (permethylpolysilanyl)iron cyclopentadienyl derivatives. The molecular ion, always evident in the spectra, undergoes the usual stepwise loss of the two carbonyl groups. However, loss of methyl groups by cleavage of $Si-CH_3$ bonds competed effectively with the stepwise carbonyl loss.

Most features reported in the previously cited studies are also observed in the mass spectrum of D_4^{Fp} (Fig. 3.6). Table 3.2 lists and assigns all ions clearly discernible from the background. The major pathway appears to be the cleavage of a whole Fp group from the parent ion to give the ion $[(C_5H_5)_3Fe_3(CO)_6Si_4O_4(CH_3)_4]^+$ (m/e 767). The apparently facile Fe-Si cleavage observed in this spectrum was not observed by King et al.[120] and is suspicious. Physical and chemical properties of D_4^{Fp} show the great stability of that bond (Chapter 2) and one can suspect a contribution of thermal decomposition to the total intensity of the peak m/e 767. The presence of thermal degradation is also supported by the presence of a large peak for ion $(C_5H_5)_2Fe^+$ (m/e 186) as previously mentioned[166].

The molecule seems also to break down <u>via</u> successive losses of carbonyl groups to give the monocarbonyl ion $[(C_5H_5)_4Fe_4COSi_4O_4(CH_3)_4]^+$ (m/e 748). No competitive side pathway is observed for this minor process.

Table 3.2: Assignments of ions observed in the D_4^{Fp} spectrum

m/e	Assignments	m/e	Assignments
929*	$[(C_5H_5)_4Fe_4(CO)_8Si_4O_4(CH_3)_3]^+$	655	$[(C_5H_5)_3Fe_3(CO)_2Si_4O_4(CH_3)_4]^+$
916*	$[(C_5H_5)_4Fe_4(CO)_7Si_4O_4(CH_3)_4]^+$	627	$[(C_5H_5)_3Fe_3(CO)Si_4O_4(CH_3)_4]^+$
888*	$[(C_5H_5)_4Fe_4(CO)_6Si_4O_4(CH_3)_4]^+$	591	$[(C_5H_5)_2Fe_2(CO)_4HSi_4O_4(CH_3)_4]^+$
860*	$[(C_5H_5)_4Fe_4(CO)_5Si_4O_4(CH_3)_4]^+$	562	$[(C_5H_5)_2Fe_2(CO)_3Si_4O_4(CH_3)_4]^+$
832*	$[(C_5H_5)_4Fe_4(CO)_4Si_4O_4(CH_3)_4]^+$	534	$[(C_5H_5)_2Fe_2(CO)_2Si_4O_4(CH_3)_4]^+$
804	$[(C_5H_5)_4Fe_4(CO)_3Si_4O_4(CH_3)_4]^+$	507	$[(C_5H_5)_2Fe_2(CO)HSi_4O_4(CH_3)_4]^+$
776	$[(C_5H_5)_4Fe_4(CO)_2Si_4O_4(CH_3)_4]^+$	479	$[(C_5H_5)_2Fe_2HSi_4O_4(CH_3)_4]^+$
767	$[(C_5H_5)_3Fe_3(CO)_6Si_4O_4(CH_3)_4]^+$	475	$[(C_5H_5)_2Fe_2(CO)_2Si_3O_3(CH_3)_3]^+$
748	$[(C_5H_5)_4Fe_4(CO)Si_4O_4(CH_3)_4]^+$	441	$[(C_5H_5)Fe_2(CO)Si_4O_4(CH_3)_4]^+$
711	$[(C_5H_5)_3Fe_3(CO)_4Si_4O_4(CH_3)_4]^+$	419	$[(C_5H_5)_2Fe_2Si_3O_3(CH_3)_3]^+$
683	$[(C_5H_5)_3Fe_3(CO)_3Si_4O_4(CH_3)_4]^+$	413	$[(C_5H_5)Fe(CO)_2Si_4O_4(CH_3)_4]^+$

Table 3.2: (cont'd)[a]

m/e	Assignments	m/e	Assignments
405	$[(C_5H_5)_2FeHSi_3O_3(CH_3)]^+$	121	$[(C_5H_5)Fe]^+$
385	$[(C_5H_5)Fe(CO)Si_4O_4(CH_5)_4]^+$	115	$[C_9H_7]^+$
357	$[(C_5H_5)FeSi_4O_4(CH_3)_4]^+$	91	$[C_7H_7]^+$
355	$[(C_5H_5)Fe(CO)Si_4O_4(CH_3)_2]^+$	65	$[C_5H_5]^+$
295	$[(C_5H_5)Fe(CO)_2Si_2O_2(CH_3)_2]^+$	39	$[C_3H_3]^+$
267	$[(C_5H_5)Fe(CO)Si_2O_2(CH_3)_2]^+$		
241	$[(C_5H_5)_2Fe_2]^+$		
186	$[(C_5H_5)_2Fe]^+$		
177	$[(C_5H_5)Fe(CO)_2]^+$		
165	$[C_{13}H_9]^+$		
149	$[(C_5H_5)Fe(CO)]^+$		

*Small peaks observed on the oscillogram only.

The most interesting feature of the D_4^{Fp} spectrum is the formation of what appears to be $[(C_5H_5)_2Fe_2(CO)_4HSi_4O_4(CH_3)_4]^+$ (m/e 591). An analogous ion $[C_5H_5Fe(CO)_2HSi(CH_3)_2]^+$ was observed in the spectrum of $(CH_3)_5Si_2Fe(CO)_2\eta^5\text{-}C_5H_5$ but was not explained[120]. It seems the origin of the extra hydrogen can be rationalized by a hydride migration from a $\eta^5\text{-}C_5H_5$ group to an adjacent or transannular siliconium ion. The proposed rearrangement is shown in Scheme 3.5.

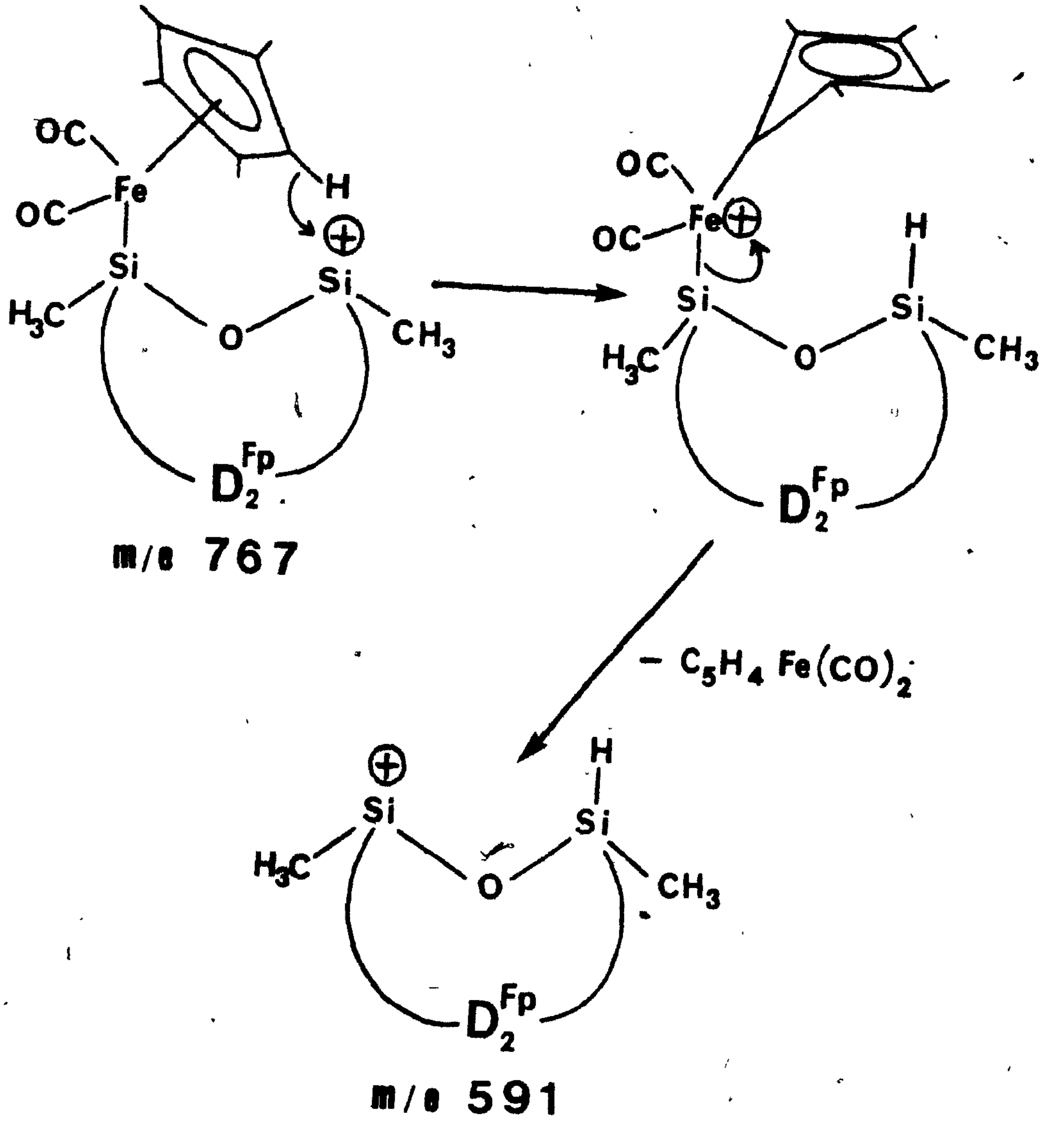
The ion $C_3H_3^+$ (m/e 39) present in most spectra of cyclopentadienyl iron carbonyl derivatives[163] has been attributed to the extrusion of the elements of acetylene (C_2H_2) from $C_5H_5M^+$ [166]. The formation of ion $C_7H_7^+$ is less often observed and can be formed by the coupling of a C_5H_5 ring with the acetylene elements.

3.5 Conclusion

In conclusion, it is evident that the different series of methyl(oligo)cyclosiloxanes studied have very little in common and it is possible to draw out characteristic behaviors for each of them:

- mass spectra of the D_n^H series show all the features associated with the ring contraction mechanism previously proposed for D_n. The characteristic pattern of peaks m/e 45, 59 and 73 could be useful for identification of methyl hydrogen siloxane units in complex mixtures of methyl(oligo)cyclosiloxanes.

Scheme 3.5: Hydride migration during the fragmentation of D_4^{Fp}



- mass spectra of the D_n^{Ph} series show the formation of a bridged benzenonium ion as the major pathway, even though the formation of such an intermediate ion probably introduces a much more severe strain in the siloxane ring than in the analogous linear methylphenylsiloxanes.
- mass spectra of the D_n^{Br} series show the loss of CH_4 and HBr from the molecular ion instead of $CH_3^{\bullet}$ and $Br^{\bullet}$ as observed for most halogenosiloxanes. This unexpected behavior is attributed to favorable spatial disposition of substituents on the siloxane rings.
- mass spectra of the D_n^{Co} series show successive losses of carbonyl ligands from the ions $[M]^{+\bullet}$, $[M-Co(CO)_4]^+$, and $[M]^{++}$. Since the D_n^H rings of $n > 5$ are easily obtainable (Chapter 2), and there is no reason to believe that they cannot be converted to the appropriate D_n^{Co} analogues, one could envisage molecules with many more than the reported twenty CO ligands for D_5^{Co}. The relatively high volatility of these compounds, together with their high molecular weights, suggests that they may have some value as mass markers.
- the mass spectrum of D_4^{Fp} shows, in addition to the usual stepwise loss of CO and cleavage of the $Fe-C_5H_5$ bond, an interesting hydrogen migration from a cyclopentadienyl ring to an adjacent siliconium ion. Such a rearrangement is highly favoured by the ring structure of the D_4^{Fp} molecule.

4. ^{1}H NMR SPECTRA OF SOME METHYL SUBSTITUTED CYCLOSILOXANES

4.1 Introduction

This chapter describes the characterization by nuclear magnetic resonance of the methylcyclosiloxanes prepared and isolated as described in Chapter 2. While infrared spectroscopy 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, proton magnetic resonance spectroscopy was found to be the most useful tool for the investigation of isomeric structure and composition. The ^{1}H NMR method provides new information about the natures and the distributions of geometric isomers of most methylcyclosiloxanes reported here.

The first successful separation of geometric isomers of methylphenylcyclosiloxanes (D_n^{Ph}) by distillation and fractional crystallization, and their characterization by infrared spectroscopy, were reported by Lewis[92] and by Young et al.[93]. In the early 60's, the advent of NMR spectroscopy allowed the complete assignment of the ^{1}H NMR spectrum of a natural mixture (close to the statistical distribution) of D_4^{Ph} isomers[16]. Later, it was shown that the methyl group attached to the silicon atom in linear and cyclic siloxanes is an excellent NMR probe[168]. The methyl chemical shift was found to depend on the ring size and upon the nature and orientation of neighboring groups[169,170]. Silicon-29 NMR, with proton noise decoupling has recently been used for structural studies of oligo- and polymeric siloxanes[171,172].

4.2 Experimental and instrumentation

4.2.1 NMR measurements

All ^{1}H and ^{29}Si NMR spectra were recorded on a Varian XL-200 (200-MHz, FT) spectrometer. Deuterated solvents were used as received. All chemical shifts are reported relative to internal $Si(CH_3)_4$. Principal instrumental parameters used are given in Table 4.1. The special ^{29}Si-INEPTR sequence[172] is described in Appendix II.

4.2.2 Separation of isomers of D_3^{Br}

Crude, freshly prepared D_3^{Br} (1.02 g) was dissolved in 6 mL of dry pentane, filtered and cooled to -20°C for 24 h. The supernatant solution was then carefully decanted by syringe and transferred to a second round-bottom flask under a stream of nitrogen and the white crystalline residue was washed, filtered and dried (compound 39). The solution was cooled to -78°C in an acetone-dry ice bath for 8 h. More crystals were formed (compound 40). The mother liquor was syringed into a third flask and evaporated to dryness leaving a light yellow solid residue (0.26 g). The crystalline fractions 39 and 40 were dried under moderate vacuum, weighed and analyzed by ^{1}H NMR. Data are reported in

Table 4.1: Instrumental parameters for NMR measurements

Parameters	^{1}H coupled	^{1}H decoupled	^{29}Si-INEPTR
Transmitter nucleus	1.700	1.700	29.000
Spectral width (Hz)	2000.0	2000.0	2000.0
Acquisition time (sec)	4.0	4.0	4.0
Number of points	1600	1600	1600
Pulse width (μ sec)	5.0	5.0	50.0
Number of transients	from 16 to 400	from 16 to 400	600
Transmitter offset (Hz)	0	0	-700
Presequence delay DI (sec)	-	-	5.0
Excitation transfer delay D2 (sec)	-	-	3.84×10^{-3}
Refocusing delay D3 (sec)	-	-	3.84×10^{-3}
Coupling constant J(Si-H)(Hz)	-	-	130.0
Proton 90° pulse (μ sec)	-	-	50.0
Decoupler nucleus	-	1.700	1.700
Decoupler power level	-	low (0 to 60 dB)	high
Decoupler mode	-	YYY	NY
Probe temperature (°C)	19.5	19.5	20.0
Resolution (ppm)	0.001	0.001	0.001

Table 4.5. The yellowish residue contained hydrolyzed siloxanes and some D_3^{Br}.

4.2.3 Separation of isomers of D_4^{Fp}

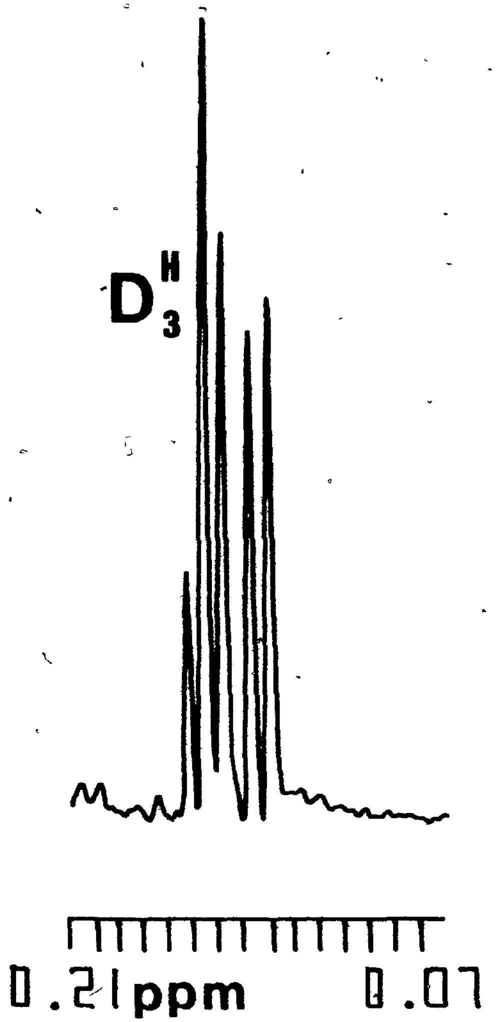
A sample of compound 31 (0.159 g) was dissolved in 1.5 mL of dry benzene and charged onto a silica gel chromatographic column (1 x 60 cm). The column was slowly eluted with ca. 200 mL of 4:1 hexanes/benzene mixture. A transparent fraction (ca. 100 mL) containing only the solvent was first collected. A yellow band (10 cm long) migrated slowly and was collected as eight small fractions (7 to 12 mL each). The fractions were evaporated to dryness and the residues were weighed and analyzed by ^1H NMR. Data are reported in Table 4.6. Attempts to separate D_4^{Fp} isomers by TLC and flash chromatography are reported in Appendix III.

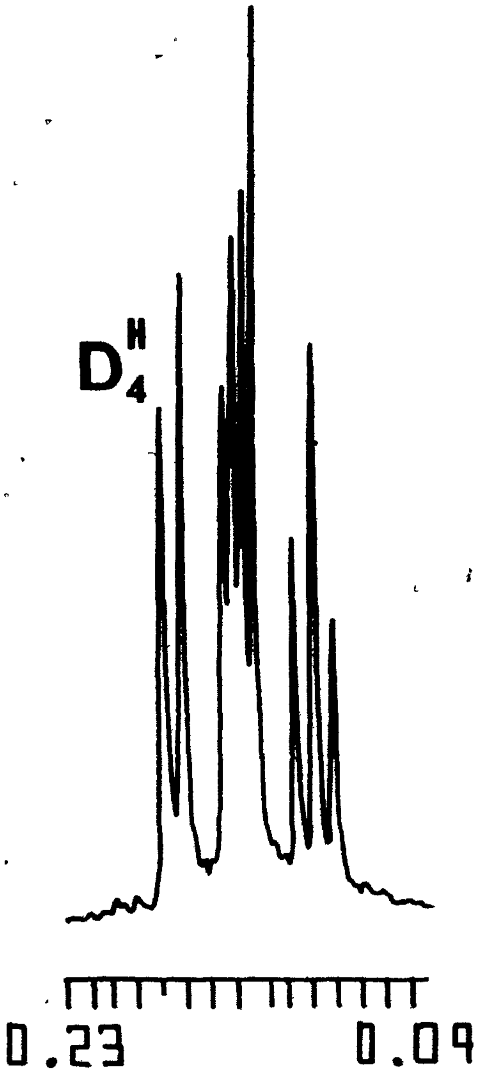
4.3 Results

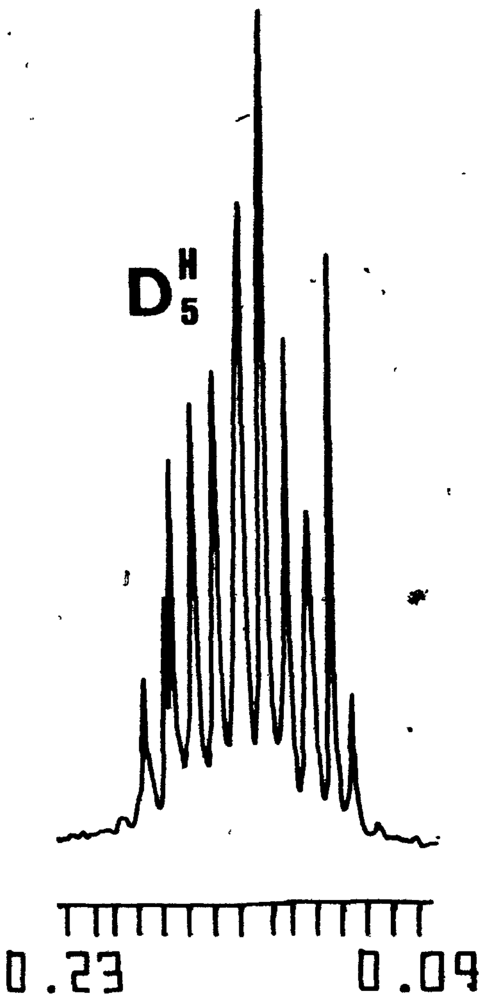
4.3.1 The methylhydrogencyclosiloxanes

The ^1H NMR spectra of methylhydrogencyclosiloxanes exhibit resonances in the region δ 4.9-5.1 for Si-H protons and δ 0.1-0.2 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-CH_3 region shows the superposition of many doublets for D_3^H and D_4^H and a complicated cluster of overlapping peaks for D_5^H (Fig. 4.1). The complexity of the D_n^H spectra is partially due to the

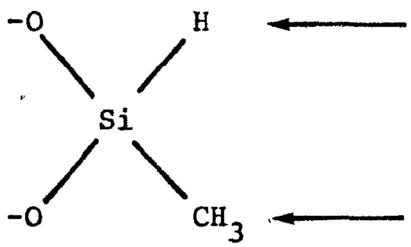
<u>Figure 4.1</u>: Coupled ^{1}H NMR spectra of D_3^H, D_4^H, and D_5^H in the methyl region, measured in C_6D_6 (<u>ca</u>. 5%) at 20°C


D^H_3
0.21ppm
0.07


D^H_4
0.23
0.09


D^H_5
0.23
0.09

three-bond-coupling between the hydrogen bonded to the silicon and the protons of the geminal methyl group:



gives a quartet (*ca.* 5 ppm)

gives a doublet (*ca.* 0.15 ppm)

The coupling constant ranges from 1.45 Hz in D_3^H to 1.55 Hz in D_4^H as determined in spectra shown in Figure 4.1. Decoupled spectral data for the methyl region are given in Table 4.2 for D_3^H and D_4^H and in Table 4.3 for D_5^H. Decoupled spectra appear as three independent singlets for D_3^H, two pseudo-doublets and one singlet for D_4^H and a cluster of nine poorly resolved singlets for D_5^H. The decoupled spectrum for the hydrogen region of D_4^H also gives five peaks: 4.986, 5.010, 5.014, 5.031, and 5.037 ppm. The decoupled spectrum in the Si-H region is the mirror image of that of the methyl region.

4.3.2 The methylphenylcyclosiloxanes

The ^1H NMR spectra of D_3^{Ph} and D_4^{Ph} in the methyl region have been reported and assigned previously[170]. The results of the present work listed in Table 4.2, do not differ significantly from published results. The spectrum of D_3^{Ph} shows three independent singlets whereas D_4^{Ph} looks like two pseudo-doublets and two singlets. The coupling between

Table 4.2: ^{1}H NMR data for CH_3 resonances of D_n^R (n = 3 and 4) recorded in C_6D_6 at ambient temperature. The relative intensities are given in parentheses.

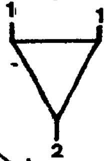
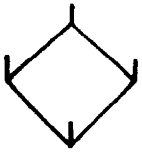
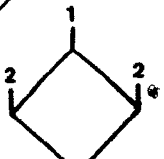
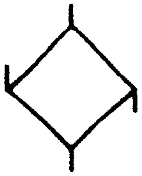
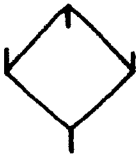
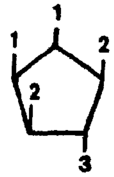
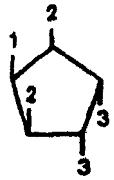
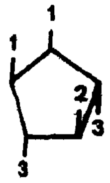
Isomer	Notation		δ(ppm)				
			H	C_6H_5	Br	$Co(CO)_4$	Fe(~~CO~~)$_2\eta^5$-C_5H_5
	D_3^R (I)		0.136 (8.5)	0.572 (4.1)	0.299 (4.4)	- -	- -
	D_3^R (II)	1	0.154 (10.0)	0.489 (10.0)	0.376 (10.0)	- -	- -
		2	0.161 (5.0)	0.420 (5.0)	0.426 (5.0)	- -	- -
	D_4^R (I)		0.113 (4.1)	0.553 (6.8)	0.289 (7.7)	0.693 (5.7)	0.885 (3.9)
	D_4^R (II)	1	0.120 (4.8)	0.487 (5.0)	0.330 (2.8)	0.763 (5.2)	0.918 (3.2)
		2	0.143 (10.0)	0.475 (10.0)	0.412 (6.0)	0.858 (10.0)	0.936 (6.0)
		3	0.170 (8.8)	0.264 (4.9)	0.483 (3.0)	1.040 (5.2)	0.945 (3.2)
	D_4^R (III)		0.146 (10.0)	0.390 (8.0)	0.427 (10.0)	0.918 (8.8)	0.957 (10.0)
	D_4^R (IV)		0.170 (8.8)	0.358 (4.9)	0.471 (2.6)	1.002 (3.0)	0.957 (10.0)

Table 4.3: ^{1}H NMR data for CH_3 resonances of D_5^R recorded in C_6D_6 at ambient temperature. The relative intensities are given in parentheses.

Isomer	Notation		δ (ppm)		
			H	$Co(CO)_4$ (29)	$Co(CO)_4$ (30)
	D_5^R (I)		0.123 (2.5)	- -	- -
	D_5^R (II)	1	0.131 (5.2)	- -	0.804 (3.0)
		2	0.149 (5.2)	- -	0.953 (10.0)
		3	0.195 (2.7)	- -	1.097 (4.5)
	D_5^R (III)	1	0.141 (3.2)	0.843 (4.7)	0.851 (2.3)
		2	0.159 (10.0)	0.953 (10.0)	0.953 (10.0)
		3	0.169 (5.9)	0.997 (9.0)	0.998 (4.0)
	D_5^R (IV)	1	0.159 (10.0)	0.953 (10.0)	0.953 (10.0)
		2	0.176 (2.7)	1.067 (0.8)	1.063 (1.0)
		3	0.186 (5.2)	1.100 (1.4)	1.097 (4.5)

methyl and phenyl protons is too weak to be observed. As expected, the phenyl regions (from 7.0 to 7.6 ppm) of both compounds are too complicated to be interpreted and will not be mentioned in the discussion.

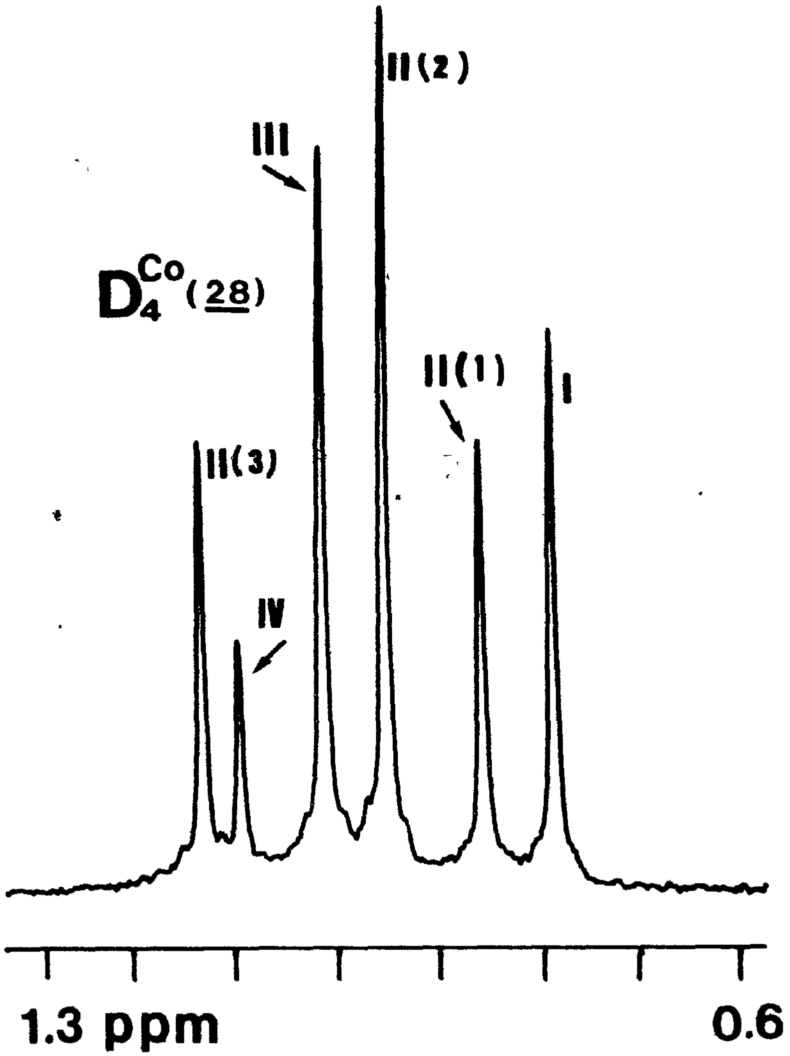
4.3.3 The methylbromocyclosiloxanes

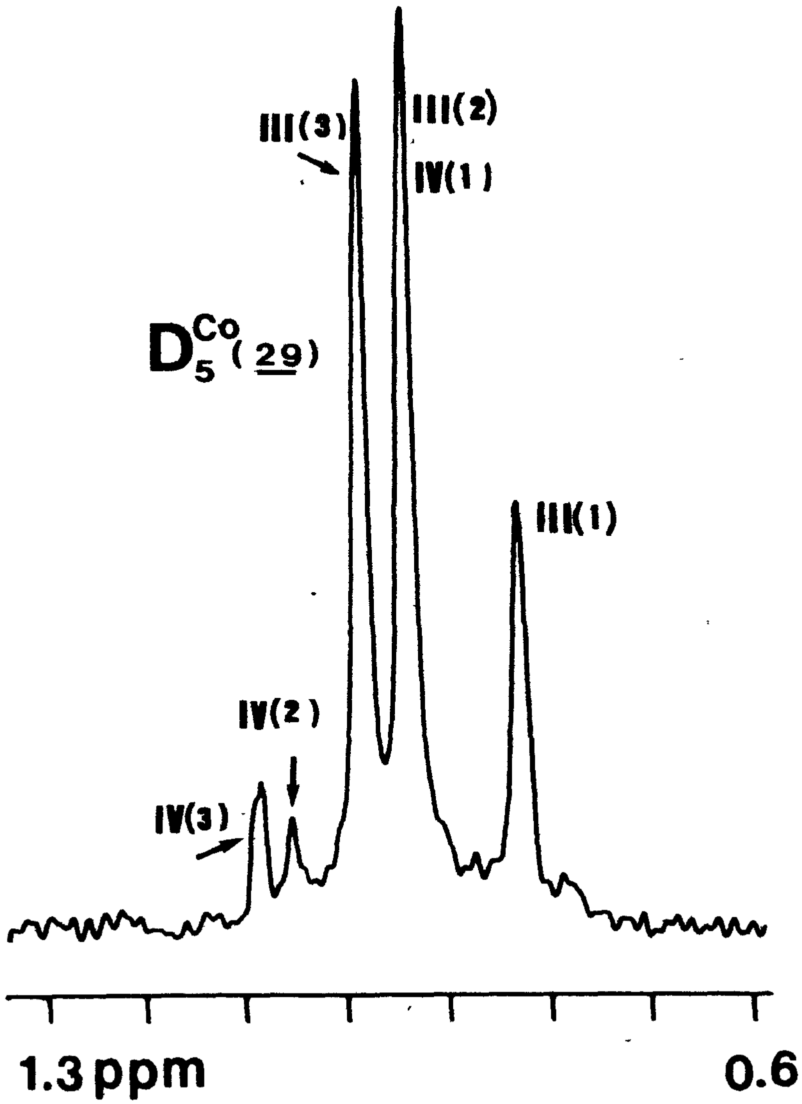
The ^1H NMR spectra of the two new products, D_3^{Br} and D_4^{Br}, are fairly simple (listed in Table 4.2). The spectrum of D_3^{Br} appears as a series of three independent singlets and that of D_4^{Br} consists of three groups of two peaks each. The chemical shifts of D_n^{Br} are in a region between those of D_n^H and D_n^{Ph}. The several peaks are spread over ranges of 25.4 and 30.4 Hz for D_3^{Br} and D_3^{Ph} respectively, compared to the very small 5.0 Hz range for D_3^H.

4.3.4 The tetracarbonylcobalt(I)methylcyclosiloxanes

The ^1H NMR spectra of the two new compounds D_4^{Co} and D_5^{Co} are shown in Figure 4.2 and chemical shifts are listed in Tables 4.2 and 4.3 respectively. The spectrum of D_4^{Co} shows three groups of well-resolved peaks as expected from analogous D_4^{Br} and D_4^{Ph}. Surprisingly, the spectrum of D_5^{Co} (29) was much simpler than expected from the decoupled spectrum of D_5^H (Table 4.3). Furthermore, data from two different samples (29 and 30) 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

Figure 4.2: ^{1}H NMR spectra of D_4^{Co} and D_5^{Co} in the methyl region, measured in C_6D_6 (*ca.* 5%) at 20°C


D_4^{Co}(<u>28</u>)


D_5^{Co}(<u>29</u>)

crystallization. Assignments given in Figure 4.2 will be discussed in the next section. Methyl proton shifts observed for D_n^{Co} are the highest of any of the cyclosiloxanes discussed in this work. The ^1H NMR spectrum of the previously reported compound, $[(CH_3)_2SiCo(CO)_4]_2O$, gives a single peak at 0.6 ppm[38].

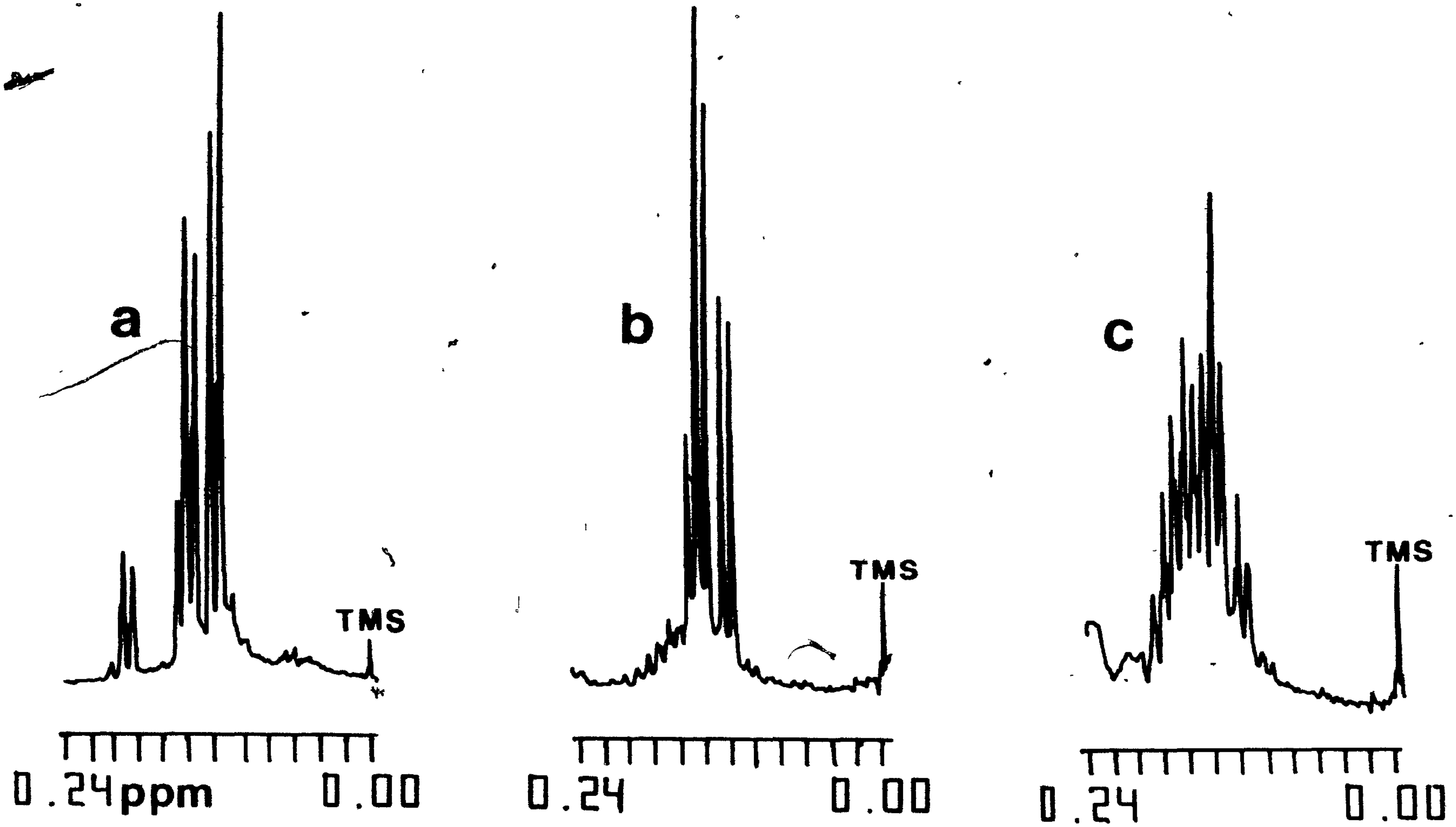
4.3.5 The tetrakis(cyclopentadienyldicarbonyliron(II))tetramethylcyclotetrasiloxane

The ^1H NMR spectrum of D_4^{Fp} (<u>31</u>) in the methyl region is listed in Table 4.2. The cyclopentadienyl resonances appear as a group of peaks in the region, 4.4 to 4.5 ppm.
The range covered by methyl proton shifts in D_4^{Fp} (15 Hz) is about 5 times smaller than in D_4^{Co} which results in problems with the resolution of all of the peaks. In somewhat similar compounds (methyl polysilane derivatives) reported by King[116], the η^5-C_5H_5 proton shifts ranged from 4.4 to 4.8 ppm and CH_3-SiFe proton shifts were observed in the region 0.5 to 0.9 ppm.

4.3.6 Decomposition of D_3^H

As mentioned in Chapter 2, the slow decomposition of D_3^H (<u>ca</u>. 1% in C_6D_6) was monitored by ^1H NMR over a 20 h period. The spectra (Fig. 4.3) show the disappearance of D_3^H characteristic peaks and the formation of a symmetrical cluster possibly due to the formation of polymeric material.

Figure 4.3: Monitoring of the decomposition of D_3^H (27) in C_6D_6 (ca. 1%) at 20°C. ^1H NMR spectra in the methyl region were recorded: a) 15 min, b) 2 h and c) 20 h after the isolation of the product

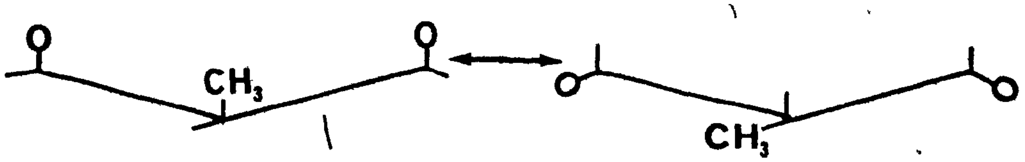

a
b
c
TMS
TMS
TMS
0.24ppm
0.00
0.24
0.00
0.24
0.00

4.4 Discussion

4.4.1 Assignment of ^1H NMR spectra of isomers

The problem of methyl NMR shift-structure correlations in methylphenylcyclosiloxanes has been studied[170] and a simple empirical equation was used to predict accurately the methyl proton shifts in different geometric isomers. The methyl shifts were found to be dependent upon the ring size of the siloxane and chiefly upon the position and the spacial orientation of all other methyl and phenyl groups in the molecule. Application of this approach allowed the complete assignment of methyl ^1H NMR spectra of cyclopolysiloxanes, $[(CH_3)_2SiO]_n[(C_6H_5)CH_3SiO]_{\ell-n}$ where $n = 0$ to 5 and $\ell = 3$ to 5[170].

The study of analogous methylhydrogencyclosiloxanes (D_n^H) is slightly complicated by the proton-proton coupling occurring between the methyl group and the hydrogen bonded to the same silicon. Some methylhydrogencyclotetrasiloxanes, $D_{4-n}D_n^H$ for $n = 0$ to 4, have been studied[169]. The best reported coupled spectrum for D_4^H 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 δ 4.8 for the Si-H hydrogen[169]. The assignments presented for the coupled spectrum in the methyl region[169] are based on the presence in the molecule of three different environments for each methyl group. The presence of two peaks for each environment was curiously attributed to the flipping of the observed groups (<u>cis</u> ↔ <u>trans</u>) rather than to the

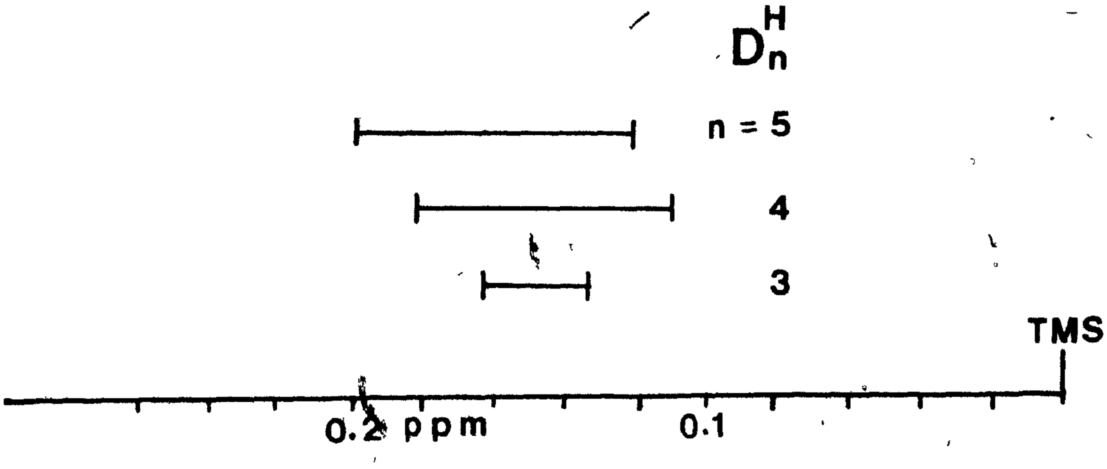


simple coupling with the geminal hydrogen! Furthermore, these authors totally neglected the through-space-shielding-effect due to geometric isomers discussed below. To our knowledge, no detailed proton decoupled spectrum has yet been published for D_n^H (n = 3, 4, and 5). All other compounds (except D_n^{Ph}) reported in the present work are new and thus have never been studied by ^{1}H NMR spectroscopy.

An analysis of the ^{1}H chemical shifts given in Tables 4.2 and 4.3 reveals a clear dependence of the shifts upon the nature and the spacial position of the substituent R. The methyl proton shifts seem to be mainly correlated to the simultaneous interplay of two factors:

1) The through-bond-shielding-effect controlled by the ring size and the nature of the substituent R on each silicon.
2) The through-space-shielding-effect controlled by the nature and the spacial orientation of neighbors (geometric isomerism).

An examination of ^{1}H shift ranges in decoupled D_n^H spectra (Tables 4.2 and 4.3) does not reveal a clear relationship between the ring size and the chemical shift:



This observation is also true for all other series reported here. Thus, it seems that the shielding effect due to the ring is roughly constant whatever the size. This lack of simple correlation is also observed in the D_n series where D_3, D_4, and D_5 give, respectively, one singlet at 0.12, 0.07 and 0.06 ppm[93]. The D_n system is free of isomeric population effects (all CH_3 have a similar environment in the same ring) and should give a true picture of the ring effect. The effect seems to be relatively small and not directly correlated to the number of siloxane units in the ring.

The nature of the substituent R is clearly much more important in the variation of the chemical shift. The through-bond-shielding-effect should be related to the electron donor/acceptor ability of the substituent. A good electron-donor (an electron-rich substituent) will increase the electron density around the silicon atom and thus increase the shielding of methyl protons. Highly shielded protons will resonate up-field and the chemical shift expressed in ppm from TMS will tend toward zero and eventually become negative for strongly shielded protons. On the other hand, a good electron withdrawing substituent will decrease the shielding of methyl protons. Such protons will resonate down-field and the shift (δ) will tend to increase. It is difficult to estimate the electronegativities of complex substituents, but organic chemists have developed sets of substituent constants[174] from kinetic data and structural considerations which allow empirical calculations of the electronegativity[175]. Such calculations give the following electronegativity trend:

$$C_6H_5 \simeq Br > CH_3 \simeq H$$

Transition metal atoms, such as iron and cobalt, could be regarded as electron-rich substituents due to their electropositive character, but when the cobalt(I) atom is coordinated to four carbonyl groups, and the iron(II) to one η^5-C_5H_5 and two carbonyls, they become strongly electronegative substituents toward silicon because CO is a strong π acceptor ligand and there is a net withdrawal of electrons away from the metal. The cyclopentadienyl ligand is amphoteric (acceptor and donor) and can become a good acceptor when competing with carbonyls[87]. A strong electrophilic character has been attributed to the ion $[Fe(CO)_2\eta^5\text{-}C_5H_5]^-$ by King[176]. Available data from some trimethylsilyl derivatives (Table 4.4) shows that organometallic substituents have a deshielding effect comparable to and even greater than Br and the phenyl group. If a similar trend persists in the cyclosiloxane derivatives, the through-bond-shielding-effect of the substituent R should be

$$Co(CO)_4 > Br \simeq Fe(CO)_2\eta^5 C_5H_5 \simeq C_6H_5 > CH_3 \simeq H$$

where $Co(CO)_4$ should have the strongest deshielding effect (methyl protons observed down-field) and CH_3 should have the weakest effect (CH_3 protons up-field). The observed values for D_4^R (Table 4.4) are in reasonable agreement with this hypothesis. The observed trend clearly shows three groups

$$Co(CO)_4 \simeq Fe(CO)_2\eta^5 C_5H_5 > C_6H_5 \simeq Br > CH_3 \simeq H$$

of substituents. Both organometallic groups have the strongest deshielding effect, C_6H_5 and Br have the intermediate position, and CH_3 and H have a relative shielding effect. Nevertheless, the $Fe(CO)_2\eta^5\text{-}C_5H_5$ group seems to have a stronger deshielding effect in cyclic siloxanes than in simple trimethylsilanes. This supplementary effect seems

Table 4.4: ^1H NMR data for CH_3 resonances of some trimethylsilyl and cyclotetrasiloxanyl derivatives

Substituent	δ(ppm)	
R	$(CH_3)_3Si-R$	D_4^R
H	0.02[177]	0.14[a]
CH_3	0.00[b]	0.07[93]
C_6H_5	0.24[177]	0.41[a]
Br	0.52[177]	0.39[a]
$Co(CO)_4$	0.59[32]	0.89[a]
$Fe(CO)_2n^5-C_5H_5$	0.36[57]	0.92[a]

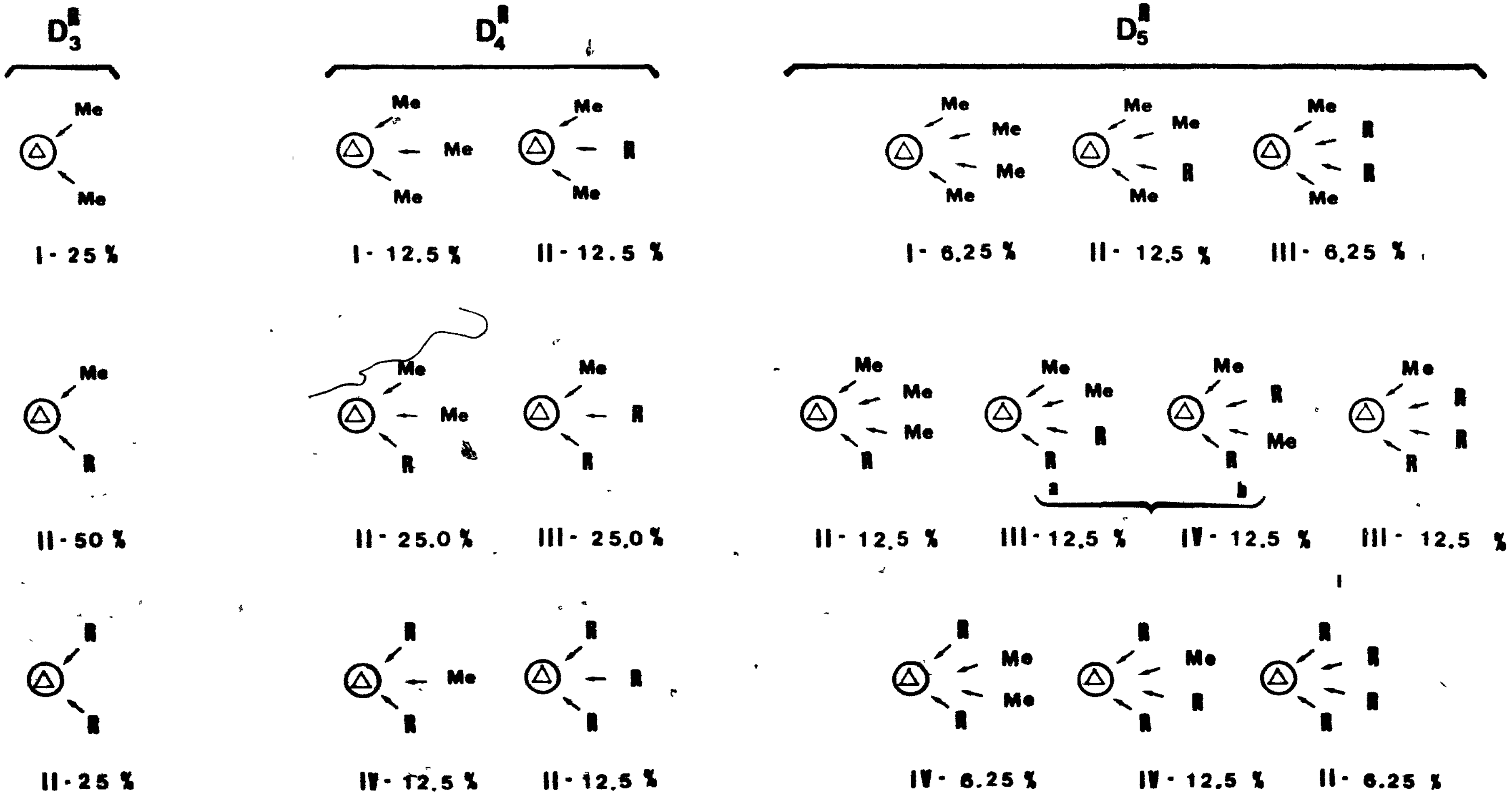
[a] The median value of the cluster of peaks has been calculated from the data of Table 4.2.

[b] TMS is taken as reference.

related to the structure of the cyclosiloxane itself and will be discussed later in this chapter.

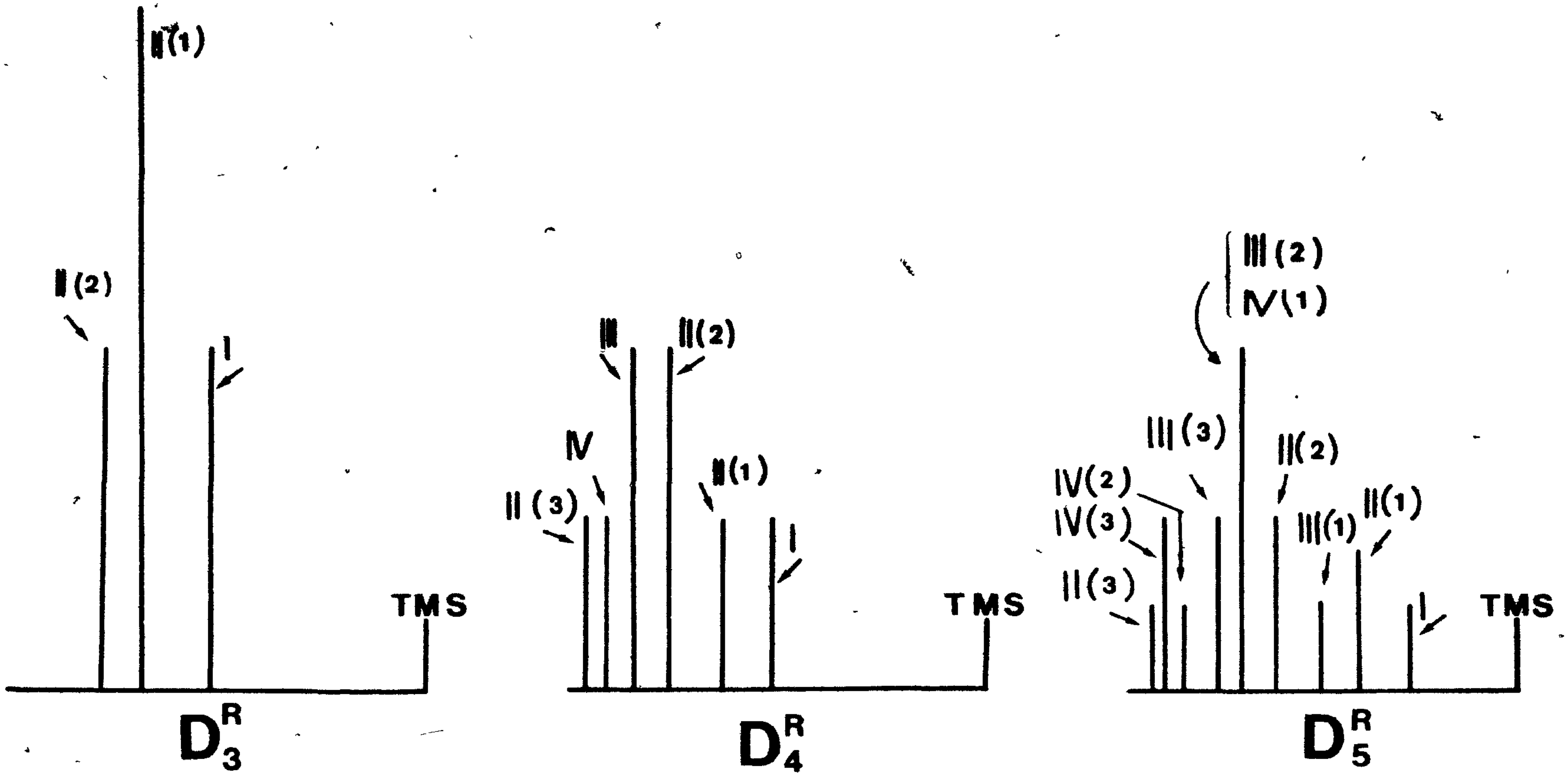
The through-space-shielding-effect on methyl protons is due to the nature of the substituent but is above all related to its spacial position toward the methyl group. On the initial assumption that the isomers have similar conformations (or fast interconversion of different conformers), it has been proposed[16] 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 the different methyl groups in D_n^R (n = 3 to 5) are shown in Scheme 4.1. 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 Scheme 4.1) 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. Scheme 4.1 gives also the statistical abundance of each environment calculated from the statistical abundance of each isomer given in Figure 1.2. Using information given in Scheme 4.1, three theoretical spectra can be drawn, as shown in Figure 4.4, where the through-space-shielding-effect of the substituent R on neighboring CH_3 protons is assumed to

<u>Scheme 4.1</u>: Chemical environments of methyl groups and their statistical abundances in D_n^R (n = 3, 4, and 5). The symbol $\textcircled{\triangle}$ stands for the observed CH_3



D3R
D4R
D5R
Me
R
a
b
I - 25 %
II - 50 %
II - 25 %
I - 12.5 %
II - 12.5 %
II - 25.0 %
III - 25.0 %
IV - 12.5 %
II - 12.5 %
I - 6.25 %
II - 12.5 %
III - 6.25 %
II - 12.5 %
III - 12.5 %
IV - 12.5 %
III - 12.5 %
IV - 6.25 %
IV - 12.5 %
II - 6.25 %

Figure 4.4: Theoretical ^{1}H NMR spectra for CH_3 resonances of D_n^R (n = 3, 4 and 5) where the through-space-shielding-effect of R group is smaller than the effect of CH_3 itself



II(2)
II(1)
I
TMS
D_3^R
II (3)
IV
III
II(2)
II(1)
I
TMS
D_4^R
III(2)
IV(1)
III(3)
IV(2)
IV(3)
II(3)
II(2)
III(1)
II(1)
I
TMS
D_5^R

be smaller than the effect of the methyl group itself. If the opposite case is considered, the mirror image spectrum results. Assignments of methyl resonances for the cyclotrisiloxane isomers are unambiguous and provide basic information about chemical shift effects of adjacent substituents. In the decoupled spectrum of D_3^H (Table 4.2), 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_3^{Br} has a deshielding effect but the phenyl group has the reverse effect. It seems reasonable to attribute this unexpected effect to the ring current induced in the phenyl ring by an applied field. When the plane of an aromatic ring is oriented perpendicularly to an applied field, B, a molecular circulation of electrons is induced[178]. The small magnetic field produced by the ring current adds to the applied field B (down-field shift) when protons are held in the plane of the ring but opposes the field B (up-field shift) when protons are held above the plane of the ring. Such effects are illustrated for the case of a methylphenylsiloxane in Figure 4.5a. The CH_3 in a cis-position toward the adjacent phenyl group experiences an upfield chemical shift.

Figure 4.5a: Illustration of the ring current effect of the phenyl group upon the shift of methyl protons in a methylphenylsiloxane unit. B is the applied magnetic field

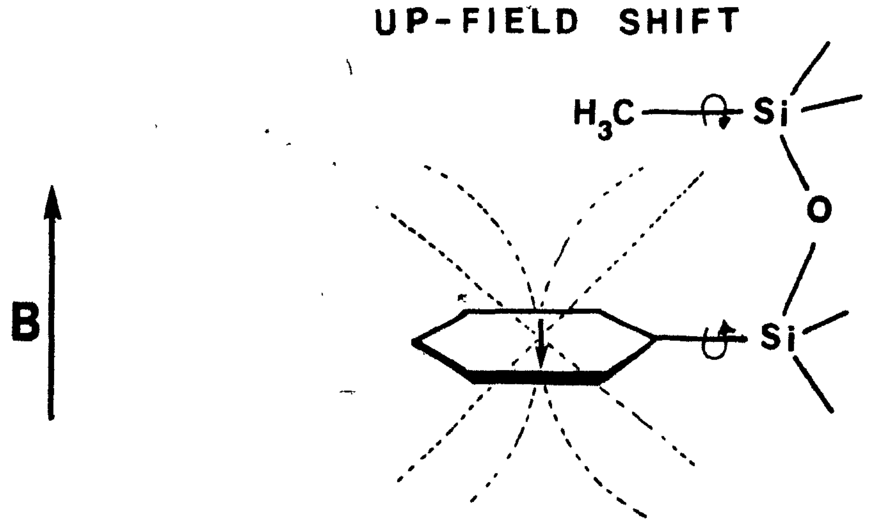
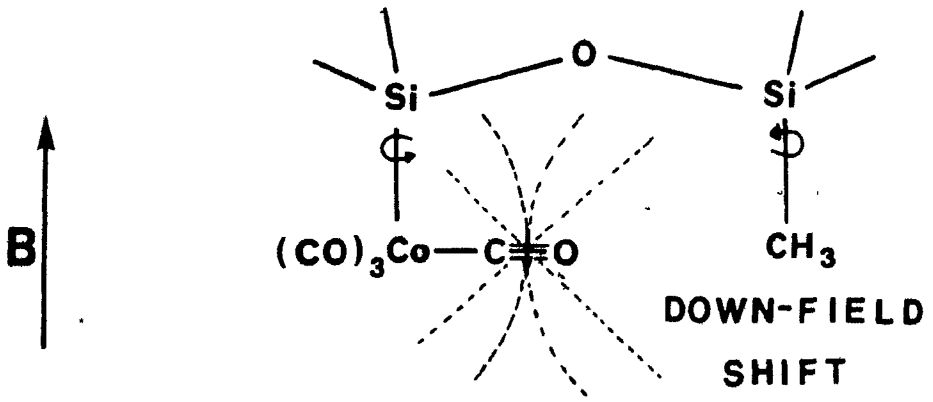


Figure 4.5b: Illustration of the anisotropic effect of carbonyls upon the shift of adjacent cis-methyl protons



Assuming that the effects observed in D_3^R (R = H, C_6H_5, and Br) are also present in larger rings, it is possible, by using the chemical environment arguments discussed above and in Scheme 4.1, to assign the observed peaks of the tetramers D_4^R (R = H, C_6H_5, and Br) (see Table 4.2) and D_5^H (see Table 4.3). Peak #3 of isomer D_4^H(II) and the lone peak of isomer D_4^H(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(IV) alone.

Since D_3^{Co} has not been synthesized, the assignment of D_4^{Co} has to be established directly from the tetramer. The spectrum of a mixture of isomers of D_4^{Co}, <u>28</u>, (Figure 4.2 left) shows six well-resolved peaks and strongly suggests an assignment similar to the theoretical spectrum of Figure 4.4 (center). The second peak at the extreme right of the spectrum (Fig. 4.2), 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_4^{Co}(II). Other peaks are then assigned following the hypothesis of chemical environments as used for D_4^H and D_4^{Br}. Thus peak #3 of isomer D_4^{Co}(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_4^{Co}(I) because they are all surrounded by methyl groups only (Fig. 1.2).

The spectrum of D_5^{Co} (<u>29</u>) shown in Figure 4.2 can be tentatively assigned following the same basic hypothesis. The isomer D_5^{Co}(I) is probably absent due to the low natural abundance (5.8%) of the corresponding D_5^{H}(I) in the starting material and the very low final yield of the product (2.6%). The isomer D_5^{Co}(II), if present, should show the peak pattern 1:2:2 according to the theoretical spectrum of Figure 4.4. This pattern does not seem to be present in the spectrum of compound <u>29</u> but a pattern 2:2:1 is clearly observed and is assigned to the isomer D_5^{Co}(III), the most abundant isomer in the mixture. The pattern 2:1:2, due to isomer D_5^{Co}(IV), is also present in a small amount, but is partially hidden by the large peaks of D_5^{Co}(III). The spectrum of compound <u>30</u>, also reported in Table 4.3, shows one extra peak at 0.804 ppm which could belong to isomer D_5^{Co}(II) but the poor quality of the sample (contaminated with $Co_2(CO)_8$) resulted in a spectrum of poorer quality, with respect to resolution, than that obtained from compound <u>29</u>.

The above assignments for D_4^{Co} and D_5^{Co} suggest an exceptionally strong deshielding effect for the $Co(CO)_4$ group on adjacent and transannular methyl protons. This special effect is attributed to the anisotropic effect of carbonyl groups lying in the plane of neighboring methyl protons (Fig. 4.5b). In a manner similar to that of aromatic rings, the free circulation of electrons in linear molecules such as RC≡CH and MC≡O gives rise to diamagnetic effects when the axis of the molecule is parallel to an applied field[179]. In the case of carbonyl groups, the anisotropy causes deshielding of protons lying inside a cone whose axis is along the C≡O bond and shielding outside this cone[179] (Fig. 4.5b). Furthermore, the rotation of the three equatorial carbonyls about the C_3 axis (Si-Co(CO)$_4$ has near perfect C_{3v} symmetry[117]) and perpendicular to B induces a deshielding, doughnut shaped area, around the cobalt center. Thus, methyl protons lying in this deshielding area resonate at very low field. For this reason, the peak observed at lowest field for D_4^{Co} (1.040 ppm) is assigned to the methyl #3 of isomer D_4^{Co}(II) (Table 4.2).

The spectrum of D_4^{Fp} in the methyl region shows only five peaks, relatively close together (Table 4.2) and cannot be assigned directly by using a strategy similar to D_4^{Co}. An alternative strategy is to get a separation (even partial) of some isomers and compare spectra from different isomeric compositions.

4.4.2 Separation of geometric isomers of D_3^{Br} and D_4^{Fp}

The separation of D_3^{Ph} isomers by recrystallization from methanol is relatively easy and gives a good yield of both isomers[16]. The separation of D_4^{Ph} isomers was achieved previously by a crude chromatography on silica gel, followed by successive recrystallizations on eluted fractions[16]. The method is laborious, requires a large amount of crude mixture and gives poor yields. The separation of isomers of D_n^H has never been reported.

The data in Table 4.5 show the relatively good separation of one D_3^{Br} isomer by recrystallization from a non-polar solvent. The isomer D_3^{Br}(II) can be isolated at near 95% purity (by NMR) after one recrystallization from the reaction mixture. Nevertheless, the less abundant isomer, D_3^{Br}(I), probably the most interesting one from the point of view of catalyst design, seems to be much more difficult to isolate from its companion.

The partial separation of D_4^{Fp} isomers was achieved by column chromatography on silica gel (Table 4.6). Many attempts at selective recrystallization of some isomers from the normal mixture using polar solvents at low tempera- were unsuccessful. In most cases, D_4^{Fp} decomposed slowly in solution. Unsuccessful attempts at separation of these isomers by TLC and flash chromatography are described in Appendix III. 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 (Table 4.6 and Fig. 4.6) 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. The isomer (III) is a centrosymmetric molecule and should have a near zero dipole moment.

Table 4.5: Data from the separation of isomers of D_3^{Br} by recrystallization

Compound	Weight (mg)	^{1}H NMR shifts δ(ppm) (intensity)	Isomeric composition (%)
		0.300 (1.0)	D_3^{Br} (I) = 6
39	470	0.375 (10.0)	D_3^{Br} (II) = 94
		0.424 (5.1)	
		0.298 (10.0)	D_3^{Br} (I) = 56
40	210	0.375 (5.3)	D_3^{Br} (II) = 44
		0.426 (2.6)	

Total = 680 mg; D_3^{Br} (I), 140 mg (20%); D_3^{Br} (II), 540 mg (80%).

Table 4.6: Data from the separation of isomers of D_4^{Fp} by column chromatography

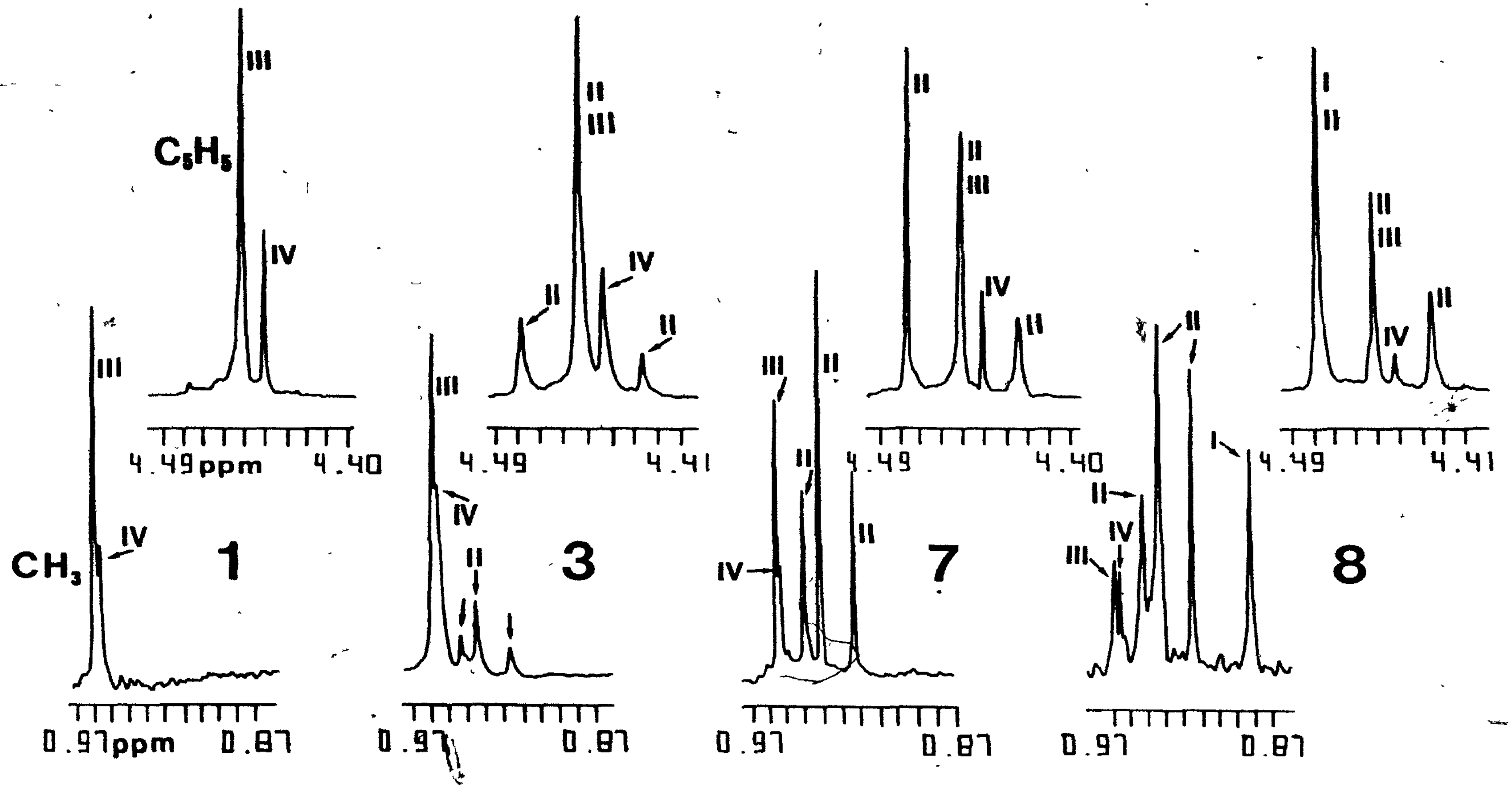
Fraction	Weight (mg)	^{1}H NMR shifts δ(ppm) (intensity)		Isomeric composition (%)
		CH_3 protons	n^5-C_5H_5 protons	
1	8	0.95 (10.0)	4.442 (3.2)	(IV) = 24
		0.96 (10.0)	4.453 (10.0)	(III) = 76
2	7	0.918 (0.3)	4.426 (0.7)	(II) = 16
		0.936 (0.7)	4.442 (4.6)	(IV) = 29
		0.942 (0.4)	4.453 (10.0)	(III) = 55
		0.957 (10.0)	4.477 ((1.3)	
		0.960 (10.0)		
3	14	0.917 (0.8)	4.426 (1.1)	(II) = 26
		0.935 (1.9)	4.443 (3.5)	(IV) = 22
		0.943 (0.9)	4.454 (10.0)	(III) = 53
		0.956 (10.0)	4.478 (2.2)	
		0.958 (10.0)		
4	29	0.915 (1.8)	4.426 (1.7)	(II) = 43
		0.932 (3.9)	4.442 (2.5)	(IV) = 16
		0.941 (1.9)	4.453 (10.0)	(III) = 41
		0.952 (10.0)	4.477 (3.4)	
		0.955 (10.0)		
5	22	0.918 (4.3)	4.426 (3.3)	(II) = 64
		0.936 (7.8)	4.443 (2.0)	(IV) = 13
		0.945 (4.2)	4.454 (10.0)	(III) = 23
		0.959 (10.0)	4.479 (6.7)	

Table 4.6: (cont'd)

Fraction	Weight (mg)	^{1}H NMR shifts δ(ppm) (intensity)		Isomeric composition (%)
		CH$_3$ protons	n^5-C$_5$H$_5$ protons	
6	26	0.916 (3.6)	4.426 (3.6)	(II) = 60
		0.935 (7.6)	4.443 (2.9)	(IV) = 13
		0.943 (3.5)	4.453 (10.0)	(III) = 27
		0.956 (10.0)	4.479 (8.0)	
		0.958 (10.0)		
7	19	0.914 (5.0)	4.425 (4.8)	(II) = 74
		0.932 (10.0)	4.443 (1.7)	(IV) = 6
		0.941 (4.9)	4.452 (10.0)	(III) = 20
		0.953 (7.1)	4.478 (9.0)	
		0.956 (7.1)		
8	29	0.885 (4.2)	4.426 (3.7)	(I) = 15
		0.917 (5.1)	4.442 (1.4)	(II) = 71
		0.935 (10.0)	4.452 (5.1)	(III) = 7
		0.944 (4.7)	4.478 (10.0)	(IV) = 7
		0.956 (4.1)		
		0.959 (4.1)		

Total: 154 mg; D_4^{Fp} (I) 4.3 mg (3%), D_4^{Fp} (II) 81.7 mg (53%),
D_4^{Fp} (III) 81.7 mg (30%), D_4^{Fp} (IV) 21.2 mg (14%).

<u>Figure 4.6</u>: ^{1}H NMR spectra of CH_3 and η^5-C_5H_5 groups of selected fractions from the chromatographic separation of geometric isomers of D_4^{Fp}, measured in C_6D_6 (<u>ca</u>. 5%) at 20°C


C$_5$H$_5$
CH$_3$
I
II
III
IV
4.49ppm
4.40
4.49
4.41
0.97ppm
0.87
0.97
1
3
7
8

The isomer (IV) is the most symmetrical and should have a smaller dipole moment than the isomers (II) and (I)[82]. The two peaks observed in the spectrum of fraction 1 are attributed to isomers D_4^{Fp}(III) and D_4^{Fp}(IV). As the theoretical abundance of isomer (III) is twice the abundance of isomer (IV), the largest peak has been assigned to isomer D_4^{Fp}(III) and the smallest to D_4^{Fp}(IV). The separate integration of peaks is possible in the cyclopentadienyl region and allows the calculation of isomeric composition (Table 4.6).

b) The 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 4.6, clearly shows the presence of isomer D_4^{Fp}(II) which makes the assignment easy. The fractions 4, 5, and 6 show only a relative increase in the abundance of the isomer (II). The fraction 7 (Fig. 4.6) is 75% isomer D_4^{Fp}(II).

c) The most polar isomer, D_4^{Fp}(I), is well separated and appears only in the last fraction. The fraction 8 (Fig. 4.6) is the tail of the yellow band. It contains very little D_4^{Fp}(III) and (IV) but a large percentage of D_4^{Fp}(II) is still present. As a supplementary support for the proposed assignments, calculations of total composition of unfractionated D_4^{Fp} (shown at the bottom of Table 4.6) agree well with theoretical statistically determined abundances. The exceptionally low abundance of D_4^{Fp}(I) 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} spectrum (methyl region of fraction 8 in Fig. 4.6) is significantly different from the assignment proposed for the analogous D_4^{Co} (Fig. 4.2). Methyl protons of D_4^{Fp}(III) and (IV) resonate at lower field than expected from analogous D_4^{Co}(III) and (IV). The hypothesis of chemical environments (Scheme 4.1), used up to now, fails to explain this behavior.

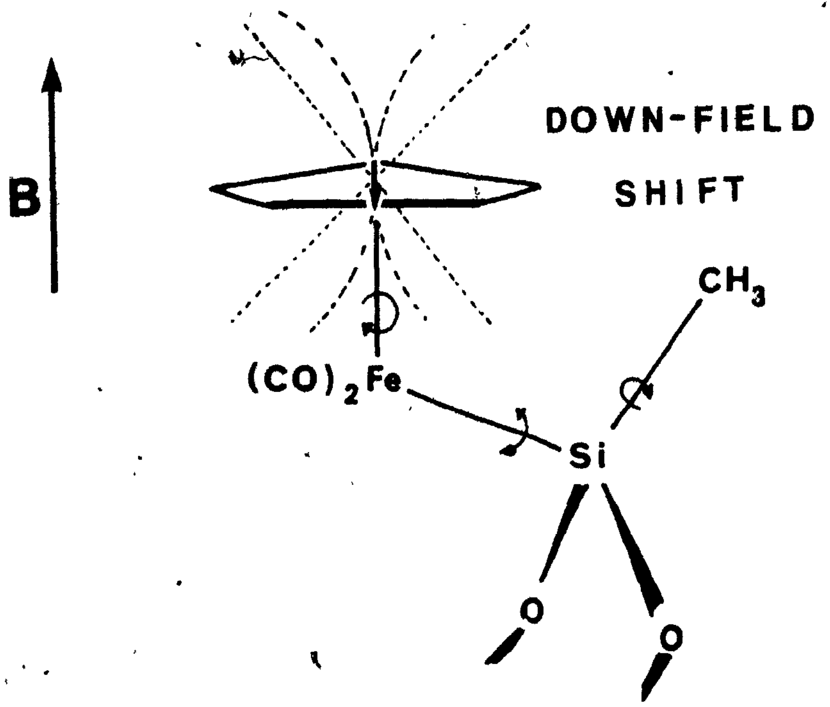
At this point, three relevant experimental observations should be recalled and summarized:

1) As noted in Chapter II, the high resolution infrared spectrum (Fig. 2.3) in the carbonyl stretching region showed an unexpectedly large number of peaks and a restricted rotation of the Fp group along the Si-Fe axis was proposed to explain the result.
2) In this chapter, it was noted that methyl protons of D_4^{Fp} resonate at abnormally low field when compared to analogous monosilyl-Fp (Table 4.4).
3) Finally, the assignment of methyl proton resonances cannot be rationalized by the usual chemical environment approach.

In the absence of more sophisticated studies (i.e. X-ray structure), the following hypothesis is proposed: if the rotation of the Fp group is not free, as suggested by observation (1) above, the cyclopentadienyl group, the largest substituent at Fe, will tend to spend most of its time as far away as possible from the siloxane ring and thus will lie in the vicinity of the methyl group attached to the same silicon (Fig. 4.7). Just as for the phenyl group, a ring current can also be induced in the cyclopentadienyl ring. Figure 4.7 shows how the methyl protons experience a down-field shift effect from the η^5-C_5H_5 ring. Whatever the geometry of the isomer, this effect is always present. For this reason, the methyl protons of all isomers of D_4^{Fp} are observed at lower field than expected from analogous $(CH_3)_3$Si-Fp where rotation along the Si-Fe axis is probably free.

A basic assumption for all peak assignments made above was the averaging of individual conformers of a same geometric isomer (^{1}H 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_4^{Fp} as suggested by observation (3) above. An attempt to "observe" the individual conformers by means of a ^{1}H NMR variable temperature experiment on compound 31 was unsuccessful (Appendix IV). Spectra at -70°C and +20°C are virtually the same. This observation may have three interpretations:

<u>Figure 4.7</u>: Illustration of the ring current effect of the cyclopentadienyl group upon the shift of vicinal methyl protons



1) The interconversion energy of conformers is very low and the flipping cannot be stopped in the range of temperatures studied.
2) All rings are flat and have no conformers.
3) The conformers are frozen even at +40°C due to the very bulky substituent Fp.

Unfortunately, the available data does not allow us to go any further into the structure elucidation of D_4^{Fp} in solution.

The abundance of geometric isomers of D_n^R (listed in Table 4.7) was calculated from the assignment and the relative intensity of all ^{1}H NMR spectra reported in Tables 4.2 and 4.3. 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_4^{Co} (Fig. 4.2) is easily integrated and gives very accurate results whereas the spectra of D_4^{Fp} (Fig. 4.6) gave serious difficulties in resolution and integration. All compounds have an isomeric composition not significantly different from the statistical composition, except for D_5^{Co} (29) and D_4^{Fp}, as previously mentioned in the discussion.

Finally, it should be mentioned that the compound 32, isolated from the partial substitution of D_4^H, has the isomeric composition (by ^{1}H NMR): D_4^{Fp}(III) and D_4^{Fp}(IV) 70% D_4^{Fp}(II) 30%. As expected, the dimer $[Fe(CO)_2\eta^5\text{-}C_5H_5]_2$ shows good selectivity toward the less hindered isomers (III)

Table 4.7: Abundance of geometric isomers of D_n^R (n = 3, 4, and 5) given in %

Isomer	Statistical	Substituents				
		H	C_6H_5	Br	$Co(CO)_4$	$Fe(CO)_2n^5$-C_5H_5
D_3^R (I)	25.0	36	21	23	-	-
(II)	75.0	64	79	77	-	-
D_4^R (I)	12.5	11	17	24	15	3[a]
(II)	50.0	52	50	36	54	53
(III)	25.0	27	20	31	23	30
(IV)	12.5	10	13	9	8	14
D_5^R (I)	6.25	6	-	-	-	-
(II)	31.25	31	-	-	-	-
(III)	31.25	35	-	-	86[b]	-
(IV)	31.25	28	-	-	14	-

[a] Data from Table 4.6.

[b] Data from compound 29.

and (IV) in a Fp deficient reaction.

4.4.3 An approach to the interpretation of ^{1}H NMR spectra of heteronuclear compounds

The chemical environment approach used above for the assignment of ^{1}H NMR spectra of isomers of most homonuclear substituted compounds can be extended to the spectra of some heteronuclear compounds already described in Chapter 2. The discussion will be later restricted to substituted methylcyclotetrasiloxanes of the type $D^{A}_{4-n}D^{R}_{n}$ (n = 0 to 4). All possible geometric isomers of the later compound for n ranging from zero to four have been drawn in Scheme 2.3. Surprisingly, only 18 chemical environments are generated by the 31 geometric isomers of $D^{A}_{4-n}D^{R}_{n}$ (Scheme 4.2). It is evident that many environments are common to many isomers and thus it seems virtually impossible to assign all isomers possibly present in a crude mixture of $D^{A}_{4-n}D^{R}_{n}$ (n = 0 to 4). In order to predict ^{1}H NMR spectra and assign some isomers, it is necessary to know:

a) The relative through-bond-shielding-effect of the substituents A and R.

b) The relative through-space-shielding-effect of A and R, and of CH_3.

Some hypothetical cases can be proposed:

1) If the through-bond-shielding-effect is the same for A and R (i.e. same electronegativity) but the through-space-shielding-effect of A is different from R, one cluster of a maximum of 36 peaks is expected in the methyl region.
2) If the through-space-effect is the same for A and R but the through-bond-effect is different, two symmetrical clusters of a maximum of 18 peaks each are expected.
3) If both through-bond and through-space-effects are different for A and R, two unsymmetrical clusters of 18 peaks each are expected.

To illustrate these general considerations, it is interesting to look at the spectra of compounds 35 and 36. The spectrum of 35, a partially-substituted $D^{H}_{4-n}D^{Fp}_{n}$ (n = 3.1) shows the presence of two clusters of peaks in the methyl region in the ratio 3:1 (Fig. 4.8). The spectrum illustrates the hypothetical case (3) above, where the through-bond-shielding-effect of the hydrogen (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 eighteen as expected. The spectrum of $D^{Co}_{1}D^{Fp}_{3}$ (36) (Fig. 4.9) shows only one group of peaks in the methyl region illustrating the first hypothetical case above where the through-bond-effects of Fp and $Co(CO)_4$ are roughly the same, but their through-space-effects are different. The model predicts 14

Figure 4.8: ^1H NMR spectrum of compound 35, measured in C_6D_6 at 20°C. The C_5H_5 region is enlarged.

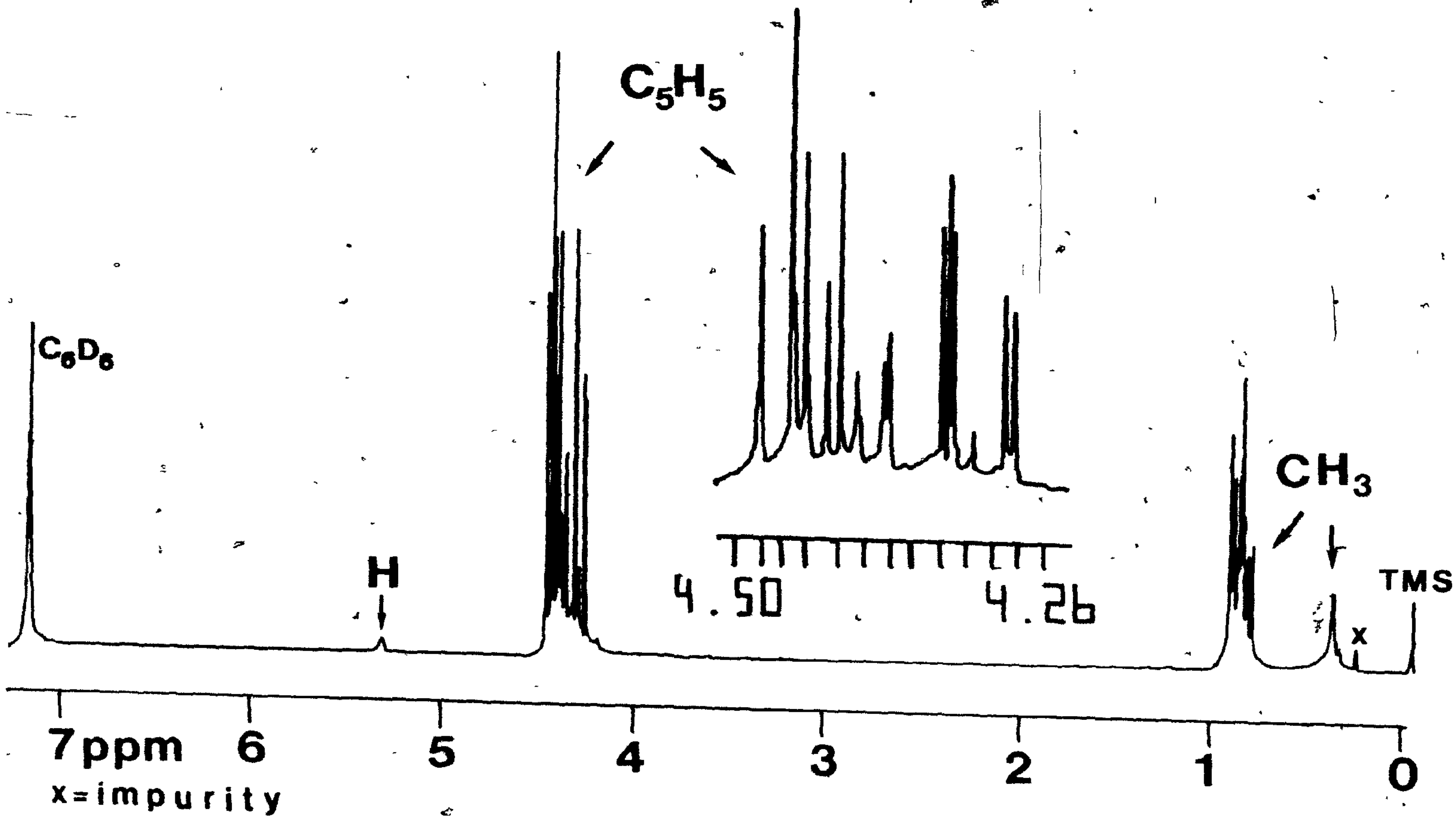
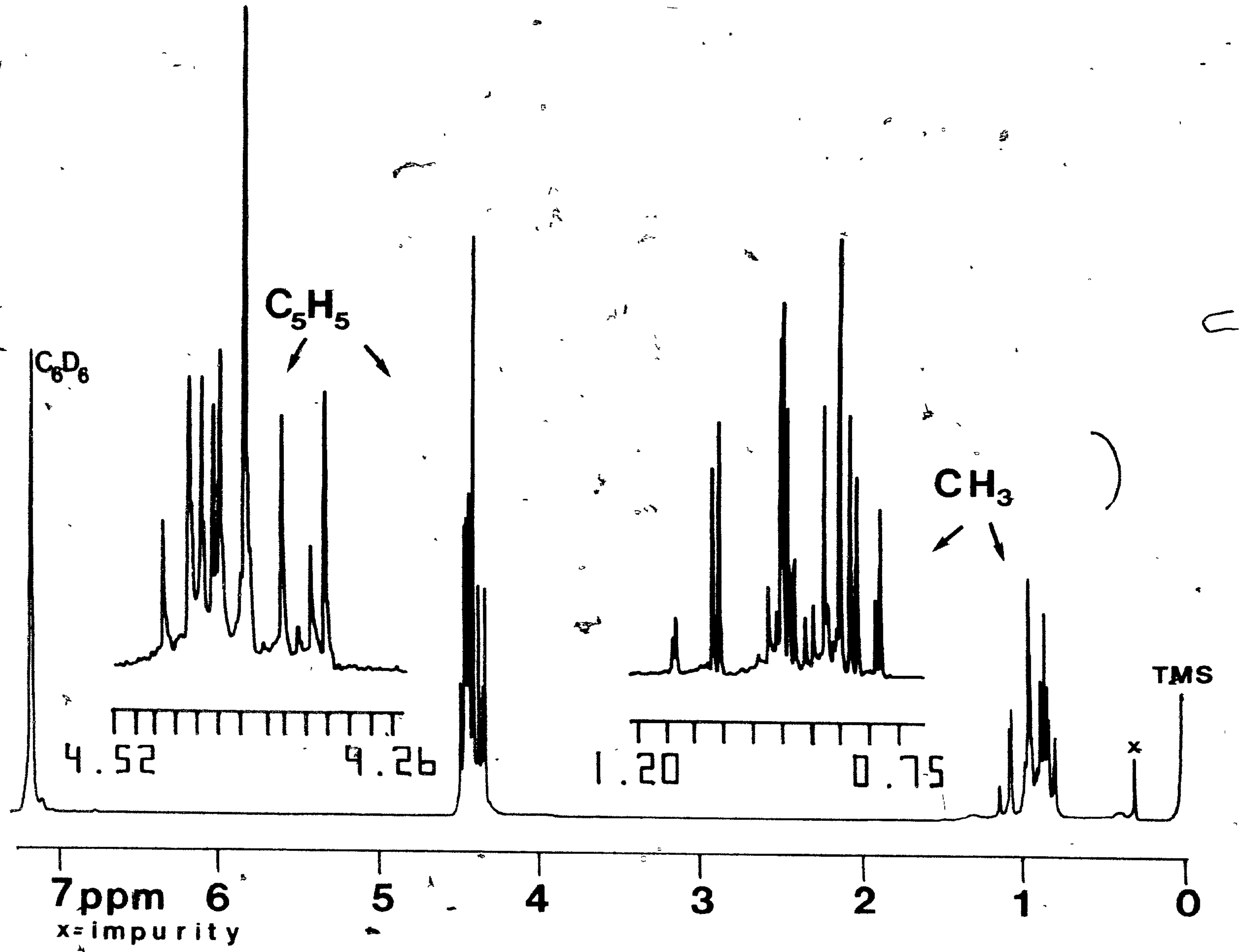
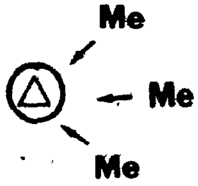
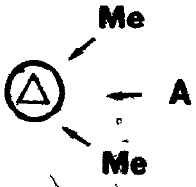

C$_6$D$_6$
H
C$_5$H$_5$
4.50
4.26
CH$_3$
TMS
x
7ppm
6
5
4
3
2
1
0
x=impurity

Figure 4.9: ^{1}H NMR spectrum of compound $D_1^{Co}D_3^{Fp}$ (<u>36</u>), measured in C_6D_6 at 20°C. The CH_3 and C_5H_5 regions are enlarged


C$_6$D$_6$
C$_5$H$_5$
4.52
4.26
1.20
0.75
CH$_3$
x
TMS
7ppm
6
5
4
3
2
1
0
x=impurity

Scheme 4.2: Chemical environments of methyl groups in $D^A_{4-n}D^R_n$ (n = 0 to 4). The symbol (△) stands for the observed CH_3


Me
Me
Me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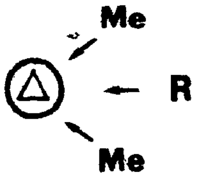
A
Me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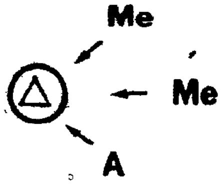
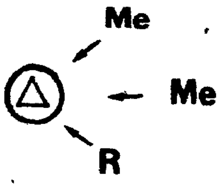
R
Me


Me
Me
A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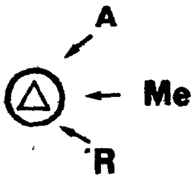
Me
R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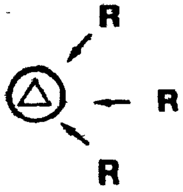
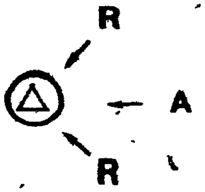
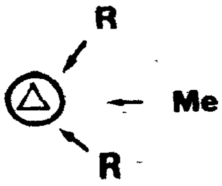
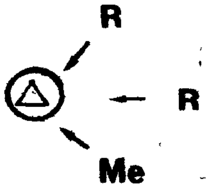
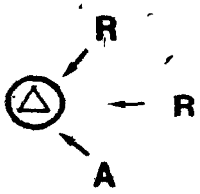
Me
R

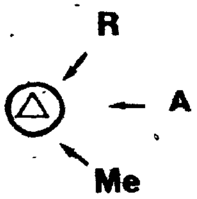

R
R
R

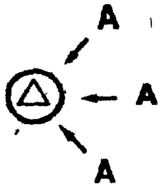

R
A
R

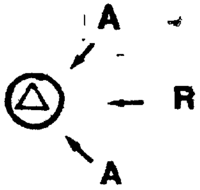

R
Me
R

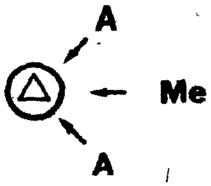

R
R
Me

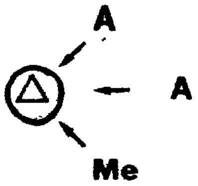

R
R
A

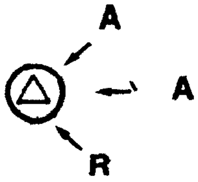

R
A
Me

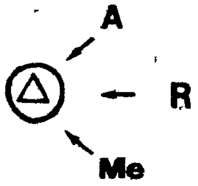

A
A
A


A
R
A

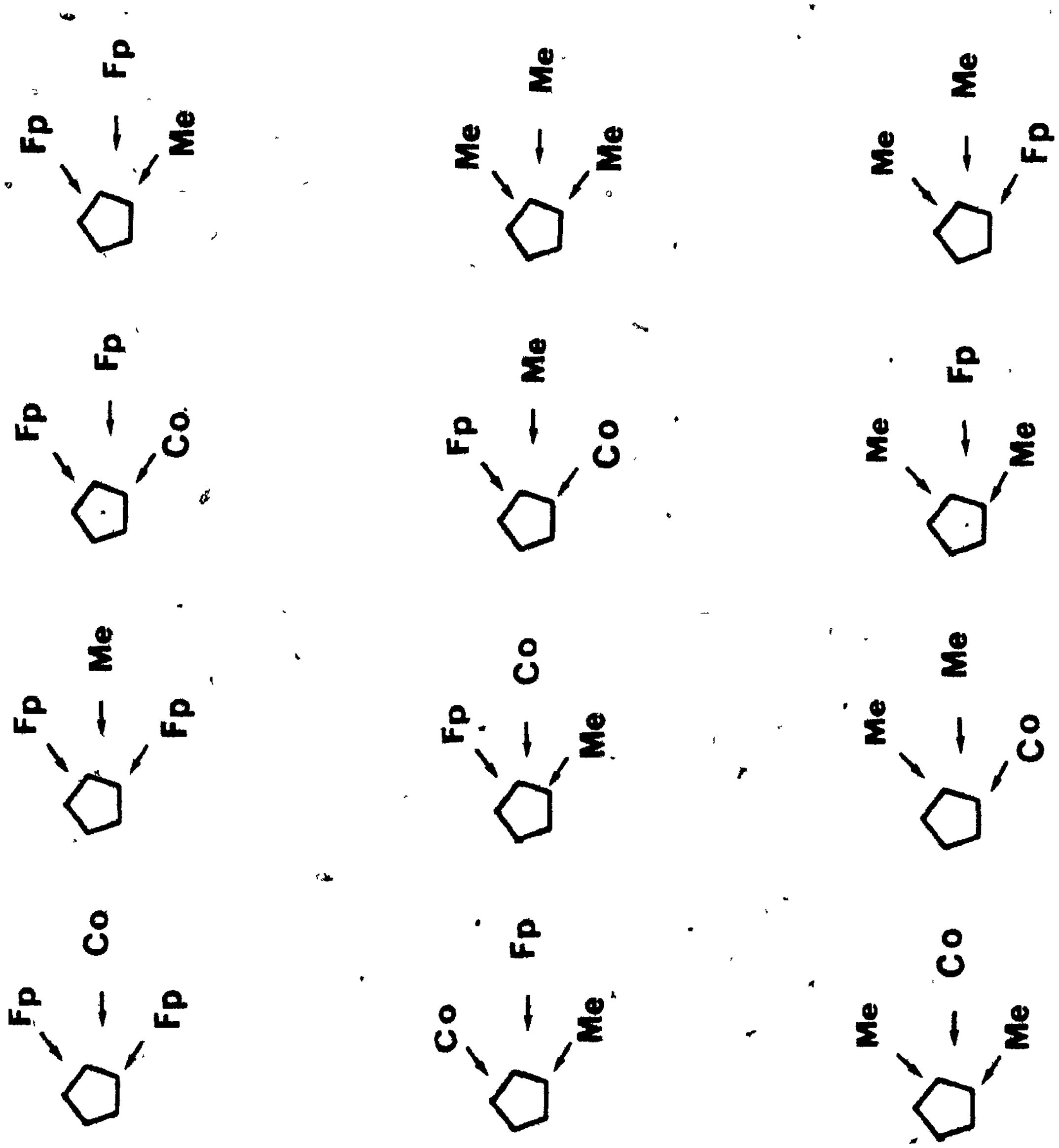

A
Me
A


A
A
Me


A
A
R


A
R
Me

Scheme 4.3: Chemical environments of the cyclopentadienyl groups in the compound $D_1^{Co}D_3^{Fp}$ (36). The symbol ⬠ stands for the observed C_5H_5



peaks for CH_3-Si-R groups and 6 peaks for CH_3-Si-A when only the compound $D_1^A D_3^R$ is present. The observed spectrum of $D_1^{Co} D_3^{Fe}$ shows 20 peaks in the methyl region. Nevertheless, 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 (Scheme 4.3). 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 $D_1^{Co} D_3^{Fp}$ could be possible by means of a partial separation of these isomers as used successfully for D_4^{Fp}. Compound 36 was only prepared on a small scale and such a separation was not attempted.

4.5 Conclusion

A simple empirical approach based on the chemical environment of the resonating protons was used to assign most ^1H NMR spectra of isomers of substituted methylcyclosiloxanes. The CH_3 group attached to the silicon served as a NMR probe. 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 spacial orientation of neighbors. The assignment and the integration of ^1H NMR spectra allowed for the first time (except D_n^{Ph}) the determination of the isomeric composition of all reported fully-substituted compounds. A partial separation of D_4^{Fp} isomers was carried out and the assignment was done by comparing spectra from different isomeric compositions. The chemical environment approach is also valuable for the interpretation of the complex spectra of heteronuclear compounds.

CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

Some new inorganic and organometallic derivatives of methylcyclosiloxanes have been prepared, isolated and characterized by IR, MS, and ^1H NMR. The 1,3,5-tribromotrimethylcyclotrisiloxane, $[CH_3BrSiO]_3$, and the 1,3,5,7-tetrabromotetramethylcyclotetrasiloxane, $[CH_3BrSiO]_4$, were prepared by the cleavage of the phenyl group by Br_2, at low temperature in the corresponding methylphenylcyclosiloxanes. The infrared spectra of these new halogenocyclosiloxanes show the characteristic Si-Br valence stretching frequency at 455 and 439 cm^{-1} for D_3^{Br} and D_4^{Br}, respectively.

The reaction of D_3^{Br} with sodium tri-sec-butyl borohydride at low temperature was selective toward Si-Br reduction and produced the elusive D_3^H. This compound, previously prepared by a different route, was confirmed to be very sensitive to thermal rearrangement.

The hydrogen elimination reaction of D_n^H with $Co_2(CO)_8$, and $[Fe(CO)_2\eta^5\text{-}C_5H_5]_2$ led to the formation and the isolation of three new homonuclear compounds: 1,3,5,7-tetrakis-[tetracarbonylcobalt(I)]tetramethylcyclotetrasiloxane, $[CH_3(Co(CO)_4)SiO]_4$, 1,3,5,7-tetrakis[cyclopentadienyldicarbonyliron(II)]tetramethylcyclotetrasiloxane, $[CH_3(Fe(CO)_2\eta^5\text{-}C_5H_5)SiO]_4$, and 1,3,5,7,9-pentakis[tetracarbonylcobalt(I)]pentamethylcyclopentasiloxane, $[CH_3(Co(CO)_4)SiO]_5$. The infrared spectra of these compounds in the ν(CO) region show the characteristic pattern of peaks already observed for monosilyl derivatives. It was also possible to prepare and isolate the new heteronuclear compound, $[CH_3(Co(CO)_4SiO]_1[CH_3(Fe(CO)_2\eta^5\text{-}C_5H_5)SiO]_3$ by reacting the partially substituted compound $D_1^HD_3^{Fp}$ with $Co_2(CO)_8$.

As very little was previously published on the mass spectrometry of substituted methylcyclosiloxanes, a detailed study of mass spectra of D_n^R, where R = H (n = 4, 5 and 6), R = C_6H_5 (n = 3 and 4), R = Br (n = 3 and 4), R = $Co(CO)_4$ (n = 4 and 5), and R = $Fe(CO)_2\eta^5\text{-}C_5H_5$ (n = 4) was carried out. The compounds R = H fragment by transannular migration and ring contraction mechanisms as previously reported for the compounds R = CH_3 but also by the losses of SiO_2 and methylhydrogensilanone. The compounds R = C_6H_5 fragment by loss of of benzene and methane from an intra-molecularly bridging benzenonium ion, and also by losses of the phenylmethylsilanone fragments. The compounds R = Br only undergo HBr and CH_3 losses without evidence for a ring fragmentation. The compounds R = $Co(CO)_4$ show stepwise loss of all CO groups from $[M]^{+\bullet}$, $[M\text{-}Co(CO)_4]^+$, and also $[M]^{++}$. The compound R = $Fe(CO)_2\eta^5\text{-}C_5H_5$ fragments by loss of one whole $Fe(CO)_2\eta^5\text{-}C_5H_5$ group followed by losses of CO groups.

A simple empirical approach based on the chemical environment of the resonating protons was used to assign the ^1H NMR spectra of isomers of substituted methylcyclosiloxanes. The chemical shifts of the methyl protons have been correlated to the nature of the substituent R at the silicon and to the nature and the spacial orientation of all neighbors. The total assignment and the integration of ^1H NMR spectra of D_n^R, where R = H (n = 4 and 5), R = C_6H_5 (n = 3 and 4), R = Br (n = 3 and 4), R = $Co(CO)_4$ (n = 4 and 5), and R = $Fe(CO)_2\eta^5-C_5H_5$ (n = 4) were achieved. These results allowed for the first time (except for the previously reported D_n^{Ph}) the determination of the isomeric composition of all of the above compounds. The chemical environment approach was also found to be suitable for the general interpretation of the complex spectra of heteronuclear compounds, such as $D_1^{Co}D_3^{Fp}$.

All of these results point to the possibility of using methylcyclosiloxanes as a framework for organometallic functions of potential catalytic interest. Compounds with more than one function, such as $D_{4-n}^{Co}D_n^{Fp}$, can also be prepared and isolated. Nevertheless, two limitations should be mentioned: 1) problems in the separation of products and 2) undesired reactivity of the siloxane toward ionic reagents. The former problem could be partially resolved by using a ter-butyl group instead of a methyl group attached at silicon. The bulky $C(CH_3)_3$ will reduce the flexibility of the ring (i.e. reduce the solubility) but it will retain its characteristic as an NMR probe as with the CH_3 group.

APPENDIX I

Reaction of D_5^H with $[Fe(CO)_2\eta^5\text{-}C_5H_5]_2$ Following the procedure described for the preparation of D_4^{Fp}, 1.5 g (5 mmol) of D_5^H was reacted with 12.9 g (37.7 mmol) of $[Fe(CO)_2\eta^5\text{-}C_5H_5]_2$. After 3 days at 160°C, the mixture was chromatographed on silica gel. Examination of all fractions eluted with a hexanes/benzene mixture did not reveal the presence of fully substituted D_5^{Fp}. The yellow viscous product present in all fractions (overall yield: 2.9 g) was identified as a complex mixture of partially substituted products. The last fraction (30 mL) eluted with hexanes/benzene (2:1), collected before the usual red band afforded 0.2 g of a yellow product showing infrared and ^1H NMR properties of a highly substituted product described hereafter.

$D_{5-n}^H D_n^{Fp}$ (where n is mainly 3 and 4): IR (hexanes) 2138 (m) 1995 (vs), 1936 (vs), 1255 (m), 1248 (sh), 1045 (vs, br) cm^{-1}. ^1H NMR (C_6D_6) δ 0.30 to 0.53 (3H, m), 0.70 to 1.02 (9H, m), 4.16 to 4.68 (14H, m), 5.3 (1H, m).

Reaction of $D_{5-n}^H D_n^{Fp}$ with $Co_2(CO)_8$ The above sample of $D_{5-n}^H D_n^{Fp}$ (n = 3 and 4) (0.2 g) was treated with 0.15 g (0.44 mmol) of $Co_2(CO)_8$ at 0°C in hexanes. Following the procedure described for the preparation of $D_1^{Co}D_3^{Fp}$, a pink-red very viscous oil (0.2 g) was isolated. This crude product (impossible to recrystallize at low temperature) shows spectroscopic properties of a $D^{Co}_{5-n}D^{Fe}_{n}$ mixture slightly contaminated by the usual $Co_4(CO)_{12}$ by-product.

$D^{Co}_{5-n}D^{Fp}_{n}$ (where n is mainly 3 and 4): IR (hexanes) 2095 (m), 2060 (w), 2050 (m), 2040 (w), 2028 (m), 2000 (vs), 1950 (vs), 1865 (w), 1855 (sh, w), 1258 (m), 1246 (w), 1040 (vs, br) cm^{-1}. Underlined wave-numbers belong to $Co_4(CO)_{12}$. ^1H NMR (C_6D_6) δ 0.76 to 1.08 (3H, m), 4.20 to 4.71 (5H, m).

Reaction of D^{H}_{4} with $Mn_2(CO)_{10}$ A toluene slurry (ca. 3 mL) containing 0.88 g (4.50 mmol) of $Mn_2(CO)_{10}$ and 0.30 g (1.25 mmol) of D^{H}_{4} was introduced into a heavy-walled tube (15 mm I.D. x 250 mm length) and sealed under vacuum (10^{-3} torr). The tube was heated in an oil bath at 140°C for 48 h and then at 160°C for a further 30 h. After cooling in liquid nitrogen, the tube was opened and the black slurry was extracted with 10 mL of toluene. An infrared examination of the crude material showed that *ca*. 95% of the Si-H had been reacted but a large amount of $Mn_2(CO)_{10}$ was still present. The toluene solution was evaporated to dryness and the black viscous residue was column chromatographed on Florisil^R. The first yellow band eluted by 120 mL of hexanes was due to $Mn_2(CO)_{10}$ (*ca*. 0.4 g). The second fraction eluted with 150 mL of hexanes/benzene (1:1) was 0.7 g of a silicone-grease like siloxane species showing no absorption band in the ν(CO) region of IR spectrum. Finally, ca. 200 mL of pure benzene afforded a trace amount of a white solid which exhibited IR peaks characteristic of an $\equiv$Si-Mn(CO)$_5$ compound. Most of the material left at the head of the column was not displaced by benzene, toluene or ethyl acetate.

$D_4^{Mn(CO)_5}$ (uncertain): IR (hexanes) 2100 (m), 2030 (sh) 2015 (vs), 2005 (vs), 1970 (w), 1946 (m), 1270 (sh), 1260 (m), 1050 (s, br), 665 (s) cm^{-1}.

Reaction of D_4^H with $Fe_3(CO)_{12}$ A 200-mL three-necked round-bottom flask equipped with a Soxhlet extractor and a nitrogen inlet was charged with 150 mL of n-hexane and 0.96 g (4.0 mmol) of D_4^H. The apparatus was purged with nitrogen, 1.7 g (3.3 mmol) of $Fe_3(CO)_{12}$ was placed in the extractor thimble and the hexane solution was brought to reflux over an oil bath at 85°C. The extraction was continued for 19 h until the complete disappearance of the Si-H band in IR. The solution was filtered at ambient temperature over a thick layer of Celite ^{R} on a fritted glass filter. The greenish solution was cooled to -78°C for 2 h and then filtered cold over Celite ^{R}. The last filtration left a brown-yellow solution free of $Fe_3(CO)_{12}$. A brown-black solid was slowly precipitated from this solution upon standing under nitrogen atmosphere at ambient temperature. The solution was concentrated to ca. 5 mL in vacuo, and filtered again (more insoluble brown material present) and chromatographed on silica gel, eluted with n-hexane. Despite evidence for decomposition on the column, (color changes, bubble formation), traces of a viscous yellow solid were isolated from one of the fractions collected. The compound was unstable in n-hexane at ambient temperature. IR (hexanes) 2055 (w), 2030 (s), 2000 (vs), 1968 (vw), 1268 (m), 1260 (m), 1105 to 1020 (vs, br) cm^{-1}. The compound decomposed rapidly in C_6D_6 in the NMR tube.

<u>Reaction of D_4^H with $[Mo(CO)_2\eta^5-C_5H_5]_2$</u> Following the procedure described for the preparation of D_4^{Fp}, 0.51 g (2.12 mmol) of D_4^H and 3.81 g (8.8 mmol) of $[Mo(CO)_2\eta^5-C_5H_5]_2$ were heated together in decahydronaphthalene solution (25 mL) at 175°C for 5 h. The IR examination of the crude solution showed the complete disappearance of the Si-H peak, the presence of a complex pattern in the carbonyl stretching region (2010 to 1850 cm^{-1}) and the formation of a very broad band in the siloxane stretching region (1150 to 990 cm^{-1}). The black solution was filtered and column chromatographed on silica gel using successively hexanes, benzene, toluene, tetrahydrofuran and acetonitrile as eluents. A red band corresponding to starting material $[Mo(CO)_2\eta^5-C_5H_5]_2$ was eluted but no molybdenum-siloxane compound was found in successive fractions.

Reaction of D_3^{Br} with LiCo(CO)$_4$ A 200-mL three-necked round-bottom flask fitted with a nitrogen inlet and a rubber septum was charged with 2.0 g (4.8 mmol) of D_3^{Br} dissolved in 25 mL of dry THF and the solution was cooled to -50°C. A solution of 3 g (16.8 mmol) of LiCo(CO)$_4$ in 25 mL of dry THF was added dropwise by syringe through the rubber septum. The solution was slowly warmed to ambient temperature with vigorous stirring and allowed to react for a total period of 2 h. The solution was filtered over Celite ^{R} and the solvent was pumped off slowly to dryness. The black residue was redissolved in 25 mL of hexanes and the solution filtered again. The solution was cooled to -78°C for 3 h without formation of any precipitate. The solution was warmed up, evaporated to *ca.* 10 mL and column chromatographed on Florisil ^{R} using successively hexanes, hexanes/toluene, and toluene as eluents Small amounts of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ were first eluted with 150 mL of hexanes, followed by a fraction (*ca.* 200 mL) containing 300 mg of a transparent viscous material having infrared peaks characteristic of "silicone grease" but no signal in the ν(CO) region. The last fraction (420 mL) eluted with toluene contained a dark violet solid which was redissolved in a minimum amount of hexanes (15 mL). The solution was stored at -20°C for two weeks and afforded 12 mg of red-black needles. The product was filtered and dried under vacuum. The air stable compound was identified as a methinyltricobalt enneacarbonyl complex (see Discussion, Section 2.4.8). Proposed formula: $HO(CH_2)_4CCo_3(CO)_9$ (m.w. 514), IR (cyclohexane) ν(CO) 2100 (s), 2050 (s), 2030 (s), and 2016 (w). Melting point observed: 92°C. ^1H NMR (C_6D_6) δ 0.89 (1H, d), 1.35 (2H, m), 1.84 (2H, m), 3.22 (2H, m), 3.48 (2H, m). Mass spectrum, selected m/e (rel. intensity %), 514 (1.0), 486 (10.9), 458 (88.5), 430 (99.0), 402 (100.0), 374 (84.6), 346 (82.7), 318 (80.6), 290 (33.1), 262 (34.8), 258 (27.9), 229 (7.6), 193 (13.5), 176 (7.9), 142 (8.1).

Reaction of D_4^{Br} with $NaFe(CO)_2\eta^5$-C_5H_5 A 200-mL three-necked round-bottom flask fitted with a nitrogen inlet and a rubber septum was charged with 1.50 g (2.7 mmol) of D_4^{Br} dissolved in 30 mL of dry THF and the solution was cooled to -78°C. A solution (11.3 mmol) of $NaFe(CO)_2\eta^5$-C_5H_5 in THF (75 mL; 0.151 M) was slowly added to the reaction solution by syringe. The solution was stirred at -78°C for 30 min and then warmed slowly to ambient temperature (ca. 1 h) and stirred overnight. After evaporation of solvent in vacuo, the residue was extracted with 50 mL of benzene. The extract was filtered through Celite ^{R} and the volume of the solution reduced to 5 mL. The concentrated solution was chromatographed on a silica gel column prepared with hexanes. A small amount of ferrocene (5-7 mg) was first eluted with 150 mL hexanes and ca. 10 mg of $[Fe(CO)_2\eta^5$-$C_5H_5]_2$ was also eluted with the benzene/hexanes (1:1) (150 mL). A golden band was slowly eluted with pure benzene and collected into one fraction

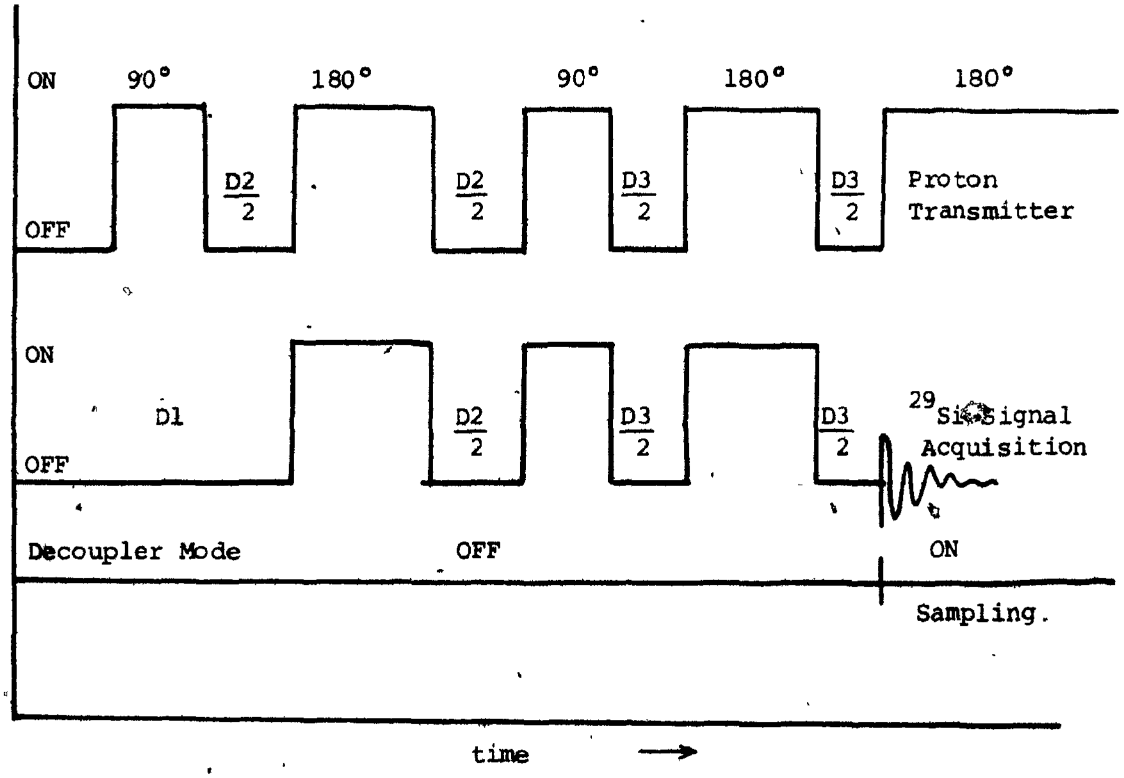
(300 mL). The evaporation of the solvent left a viscous yellow-brown residue (0.5 g). Attempts to recrystallize the product from a hexanes/benzene mixture led to a slow decomposition of the material. IR (hexanes) 2000 (vs), 1955 (vs), 1920 (w), 1265 (m), 1245 (w), 1010 (sh), 1068 (s, br), 820 (w), 780 (m), 645 (w), 630 (w), 597 (s). ^{1}H NMR (C_6D_6) 0.25 to 0.50 (2H, m), 0.75 to 0.95 (1.7H, m), 4.10 to 4.45 (4H, m).

Reaction of D_3^{Br} with NaFe(CO)$_2\eta^5$-C_5H_5 The reaction was run under conditions similar to that of D_4^{Br}, using 1.5 g (3.6 mmol) of D_3^{Br} dissolved in 30 mL of dry THF. A solution of 11.3 mmol of NaFe(CO)$_2\eta^5$-C_5H_5 in THF (75 ml, 0.151 M) was slowly added. The work up afforded a viscous yellow-brown residue (0.27 g) very similar to the product obtained with D_4^{Br} which was also very unstable.

The reaction was also repeated under the same conditions as previously, using 1.5 g (3.6 mmol) of D_3^{Br} dissolved in 30 mL of dry toluene instead of THF. The THF from the preparation of NaFe(CO)$_2\eta^5$-C_5H_5 was pumped off to dryness and replaced by an equal volume of dry toluene before the addition to D_3^{Br} solution. The heterogeneous mixture was stirred an additional 24 h at ambient temperature. The solution was filtered over Celite ^{R} and the volume was reduced to ca. 10 mL. The solution was filtered over glass wool (viscous black material present) and chromatographed on silica gel. Attempts to elute products with hexanes under nitrogen were unsuccessful due to strong decomposition at the head of the column (bubbles and color changes).

APPENDIX II

<u>^{29}Si-NMR measurements of D_4^H and D_5^H</u> The ^{29}Si-NMR spectra of D_4^H and D_5^H were obtained using a Varian XL-200 NMR spectrometer operating in the special INEPTR* sequence[172]. This sequence can be described as follows:



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*Insensitive Nucleus Enhance by Polarization Transfer with Refocusing.

Delay times (D1, D2, and D3) are given in Table 4.1. The ^{29}Si chemical shifts measured by this method are listed in Table A-II. The results are in accordance with previously published results and do not show a significant improvement toward the classical ^{29}Si NMR proton noise decoupling experiment used by Harris et al.[172].

Table A-II: ^{29}Si chemical shifts for D_4^H and D_5^H

D_4^H		D_5^H	
δ(Si) (ppm)		δ(Si) (ppm)	
Reference 172[a]	This work[b]	Reference 172[a]	This work[b]
-32.39	-32.53	-34.45	-33.61
-32.41	-32.57	-34.55	-33.71
-32.68	-32.87	-34.61	-33.78
-32.69	-32.88	-34.68	-33.84
-33.02	-33.23	-34.73	-33.90
		-34.75	-33.92
		-34.83	-33.94
		-34.85	-34.00
			-34.02
			-34.03

[a] Obtained from a mixture of D_4^H and D_5^H in C_6D_6 with internal TMS at ambient temperature.

[b] Obtained from isolated D_4^H and D_5^H, 20% in C_6D_6 with internal TMS at ambient temperature.

APPENDIX III

Separation of D_4^{Fp} isomers

1) by Thin Layer Chromatography

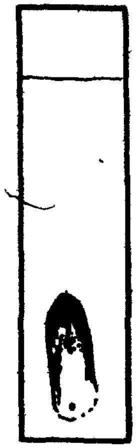
Many attempts to separate the geometric isomers of D_4^{Fp} (31) were made by means of Thin Layer Chromatography on silica gel plates (described in the Experimental Section of Chapter 2). Many combinations of polar and non-polar solvents were unsuccessful in achieving an acceptable separation of one or more of these isomers. Some of the chromatograms are reproduced in Figure A-IIIa. No clean separation was achieved but the "best results" were obtained with the solvent system: benzene/hexanes.

2) by Flash Chromatography

Following the method developed by Still et al.[180], the compound 31 was chromatographed on silica gel using a low viscosity solvent system. The solvent system (hexanes/ethyl acetate, 10:1) was adjusted to put the midpoint of the spot at Rf = 0.35 on analytical TLC (Fig. A-IIIa, bottom) in accordance with author specifications to get maximum efficiency of the column. A glass column (2 x 80 cm) fitted with a nitrogen inlet at the top, was filled with *ca*. 17 cm of dry 40-63 µm silica gel (E. Merck no. 9385). The column was filled completely with the solvent mixture chosen above and nitrogen gas (2 to 5 psi) was used to rapidly push all the air from the silica gel. The sample (231 mg of <u>31</u>) was dissolved in 2 mL of solvent and carefully applied on the column with a syringe. The column was refilled with solvent and eluted at a flow rate of 5 cm/min by applying a nitrogen pressure (2 to 10 psi). The light yellow band was collected as 10 small fractions (1 to 3 mL each). The solvent was pumped off and the residues weighed. The analysis by ^{1}H NMR revealed a very poor separation of isomers (Fig. A-IIIb). The spectra in the cyclopentadienyl region of fractions 1 and 10 show little change in their isomeric compositions. The method was found to be less efficient than the standard gravity method reported in Section 4.4.2, possibly due to the use of a too polar solvent (ethyl acetate).

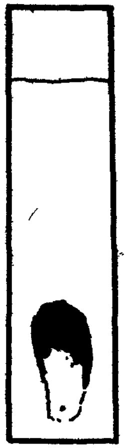
Figure A-IIIa: Thin Layer Chromatograms of D_4^{Fp} (31). Solvent systems and Rf are indicated below each plate (actual size)

2

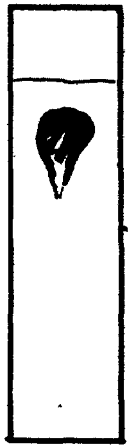


cyclohexane

Rf = 0.35

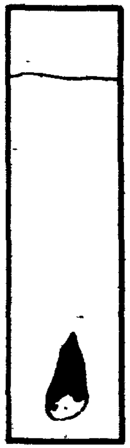


cyclohexane 1
hexanes 1
0.30

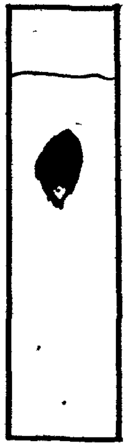


cyclohexane 5
benzene 4
0.80

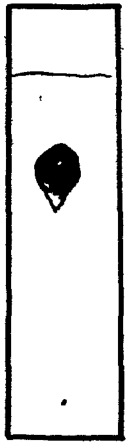
cyclohexane 5
chloroform 1
0.60



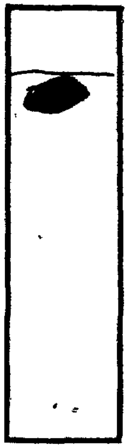
cyclohexane 5
CCl_4 2
(decomposition)



toluene 1
hexanes 1
Rf = 0.75

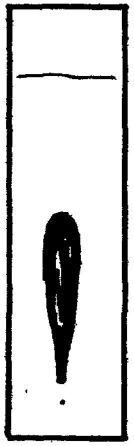


xylene 1
hexanes 1
0.70

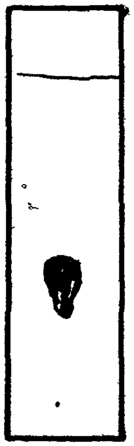


benzene

0.95



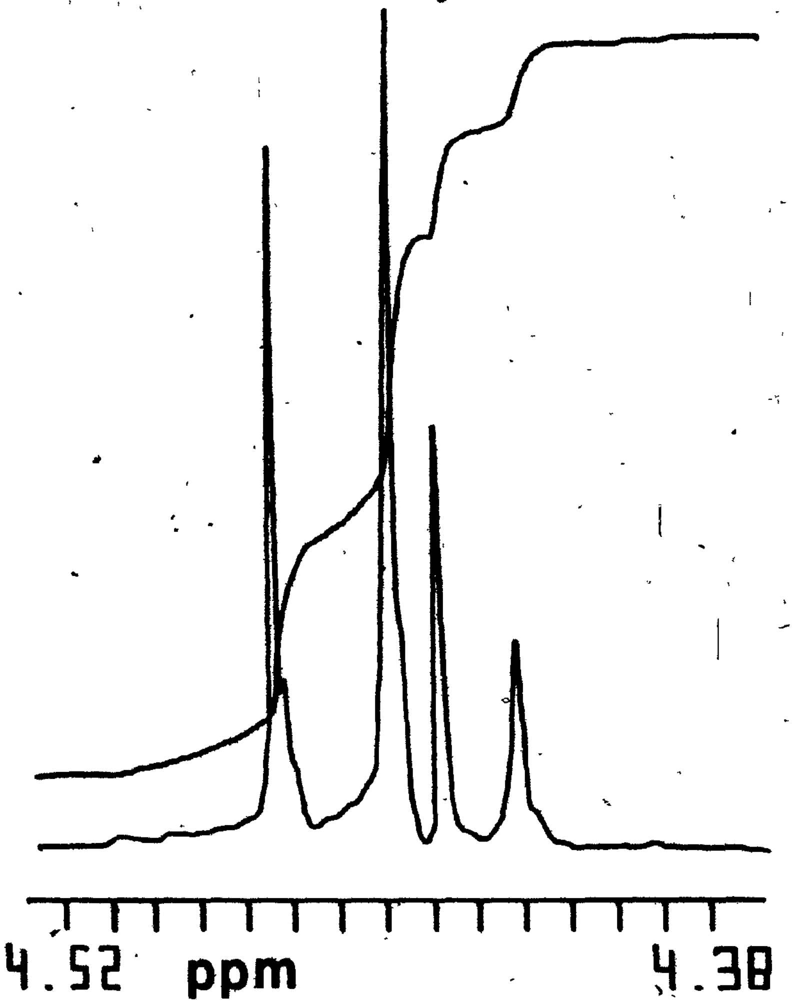
benzene 1
hexanes 3
0.50



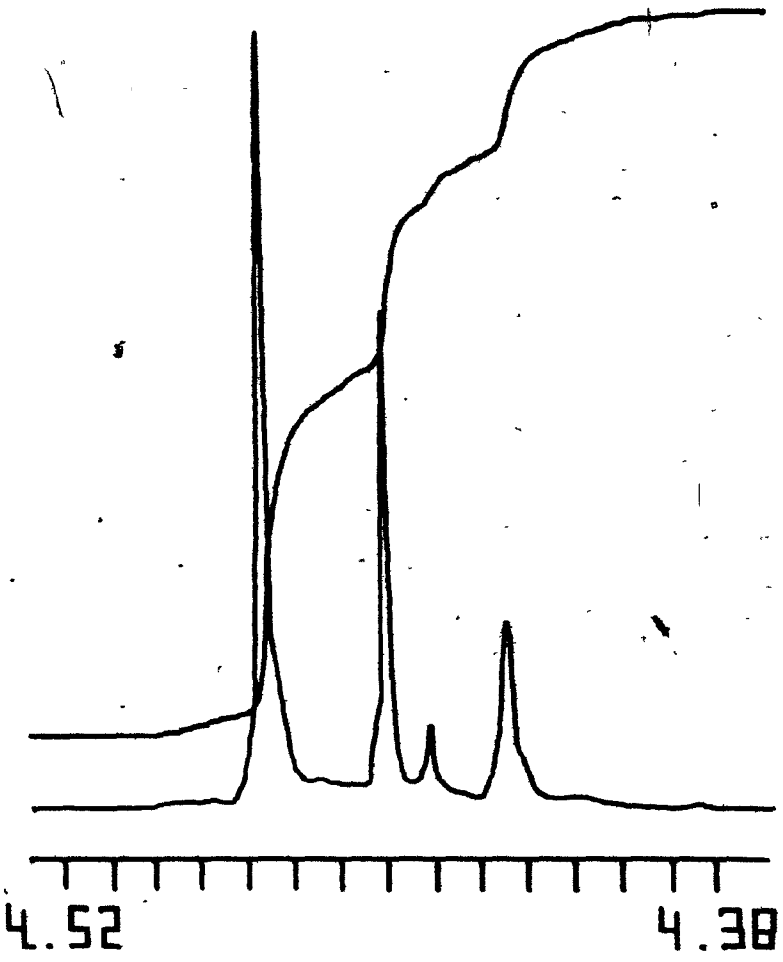
acetate 1
hexanes 10
0.35

Figure A-IIIb: ^1H NMR spectra of fractions one and ten from the separation of D_4^{Fp} isomers by Flash Chromatography in the cyclopentadienyl region (C_6D_6 at 20°C)

1



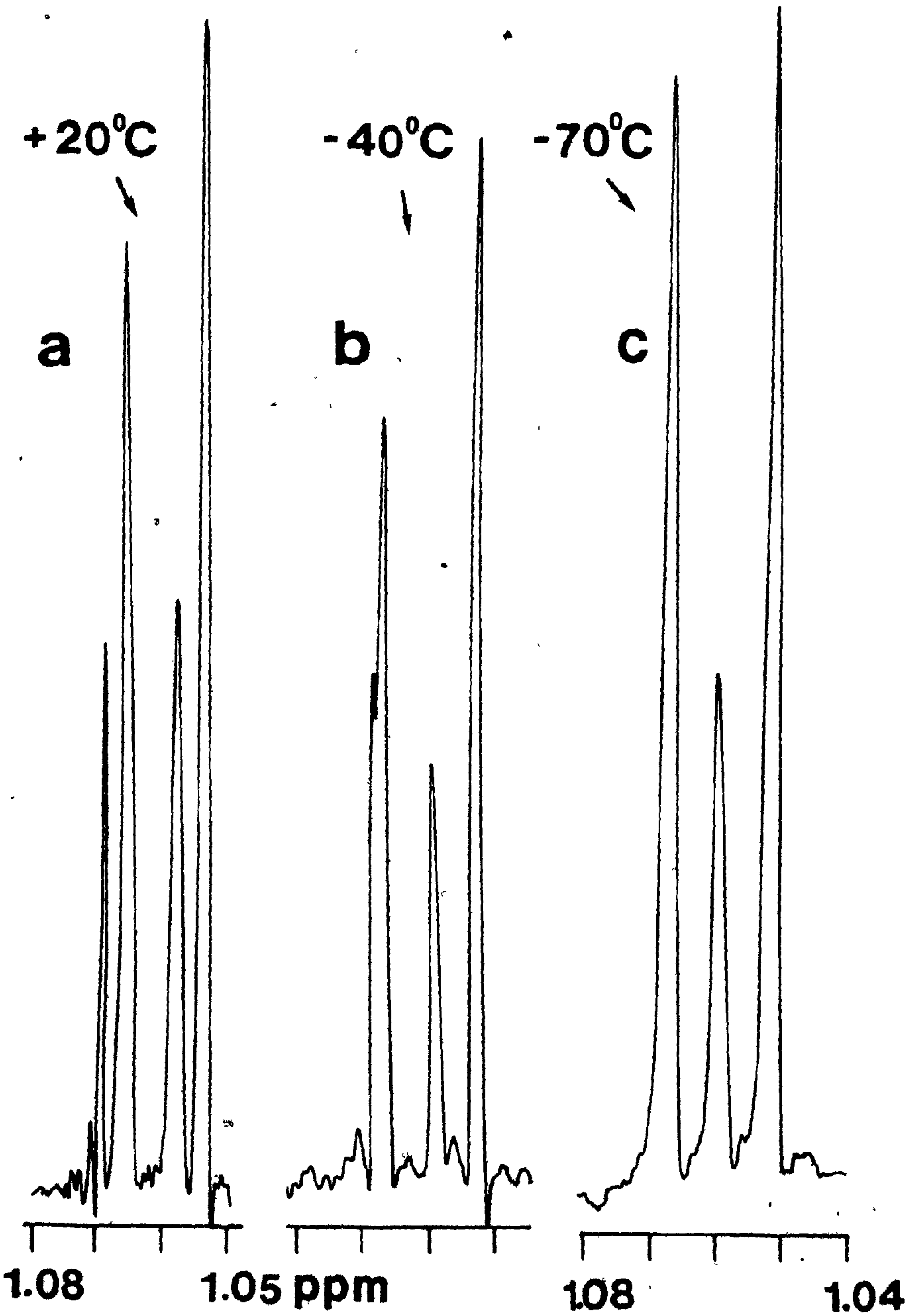
10



APPENDIX IV

<u>^{1}H NMR variable temperature experiment</u> Compound <u>31</u> (<u>ca.</u> 10 mg) was dissolved in 2 mL of dry toluene-d_8 and syringed into a 5 mm NMR tube with TMS. The Varian XL-200 Spectrometer was set on the Variable Temperature Mode, using liquid nitrogen as cold source, and spectra were recorded in the usual way at +20°C, 0°C, -20°C, -40°C, and -70°C successively. The sample was then warmed to ambient temperature and a last spectrum was measured at +20°C and was found to be identical to the first one. Spectra of the methyl region recorded at +20°C, -40°C and -70°C, are shown in Figure A-IV. Spectra show very little changes and only the peak at left (in spectrum a) is slightly displaced upfield in the low temperature spectra b and c. It should be noted that the general pattern of the spectra is different from the usual pattern found in C_6D_6 (Fig. 4.6) due to the use of a more polar solvent, toluene-d_8.

Figure A-IV: ^{1}H NMR spectra of the methyl region of D_4^{Fp} (31) in C_7D_8 solution recorded at 20°C, -40°C, and -70°C


+20°C
-40°C
-70°C
a
b
c
1.08
1.05 ppm
1.08
1.04

REFERENCES

1. P.A. KRAMER and C. MASTERS. *J. Chem. Soc., Dalton Trans.*, 849 (1975).
2. J. POWELL, A. KUKSIS, C.J. MAY, S.C. NYBURG, and S.J. SMITH. *J. Am. Chem. Soc.*, **103**, 5941 (1981).
3. J. HAGGIN. *Chem. Eng. News*, **60**, 11 (1982).
4. C. FRIEDEL and J.M. CRAFTS. *C.R. Acad. Sci., Paris*, **56**, 590 (1863).
5. C. FRIEDEL and J.M. CRAFTS. *Bull. Soc. Chim. Paris*, **3**, 356 (1865).
6. C. FRIEDEL and J.M. CRAFTS. *Ann. Chim. (Phys.)*, **19**, 334 (1870).
7. C. FRIEDEL and A. LADENBURG. *Ann. Chim. (Phys.)*, **19**, 390 (1880).
8. F.S. KIPPING. *J. Chem. Soc.*, **91**, 209 (1907).
9. F.S. KIPPING. *J. Chem. Soc.*, **101**, 2108 (1912).
10. F.S. KIPPING. *Proc. Chem. Soc. London*, **20**, 15 (1904).
11. W. DILTHEY and F. EDUARDOFF. *Ber. dtsch. chem. Ges.*, **37**, 1139 (1904).
12. E.G. ROCHOW. *J. Am. Chem. Soc.*, **67**, 963 (1945).
13. C. EABORN. *Organosilicon Compounds*, Butterworths Scientific Publ., London (1960).
14. M.G. VORONKOV, V.P. MILESHKEVICH, and Yu.A. YUZHELEVSKI. *The Siloxane Bond, Physical Properties and Chemical Transformations*, Consultants Bureau, Plenum Publ. Corp., New York (1978).
15. C.B. MORE and H.A. DEWHURST. *J. Org. Chem.*, **27**, 693 (1962).
16. H.J. HICKTON, A. HOLT, J. HOMER, and A.W. JARVIE. *J. Chem. Soc.*, C149 (1966).
17. R.E. RICHARDS and H.W. THOMPSON. *J. Chem. Soc.*, 124 (1949).

18. G. ENGELHARDT and H. JANEKE. *J. Organomet. Chem.*, **28**, 293 (1971).

19. J.M.T. DAVIDSON and J.F. THOMPSON. *J. Chem. Soc., Chem. Commun.*, 251 (1971).

20. M.G. VORONKOV, B.N. DOLGOV, and N.A. DMITRIEVA. *Dokl. Akad. Nauk SSSR*, **84**, 959 (1952).

21. W.C. SCHUMB and C.M. SAFFER. *J. Am. Chem. Soc.*, **61**, 363 (1969).

22. T.S. PIPER, D. LEMAL, and G. WILKINSON. *Naturwissenschaften*, **43**, 129 (1956).

23. C.S. CUNDY, B.M. KINGSTON, and M.F. LAPPERT. In: *Advances in Organometallic Chemistry*, (F.G.A. Stone and R. West, eds), Vol. II, p. 253, Academic Press, New York (1973).

24. C. EABORN. In: *Organometallic Compounds of Group IV Elements* (A.G. MacDiarmid, ed.), Vol. I, Part I, p. 213, Marcel Dekker, New York (1968).

25. F.G.A. STONE. In: *New Pathways in Inorganic Chemistry* (E.A.V. Ebsworth, A.G. Maddock, and A.G. Sharpe, eds), Cambridge Univ. Press, London and New York (1968).

26. A.G. MacDIARMID, Y.L. BAAY, S.F. BALD, Jr., A.D. BERRY, S.K. GONDAL, A.P. HAGEN, M.A. NASTA, F.E. SAALFELD, and M.V. McDOWELL. *Pure Appl. Chem.*, **19**, 431 (1969).

27. H.G. ANG and P.T. LAU. *Organometal. Chem. Rev.*, Sect. **A8**, 235 (1972).

28. F. HOFLER. In: *Topics in Current Chemistry*, Vol. 50, p. 129, Springer-Verlag, New York (1974).

29. B.J. AYLETT. *Adv. Inorg. Chem. Radiochem.*, **25**, pp. 1-133 (1982) (over 450 references cited).

30. B.J. AYLETT. *Organometallic Compounds*, 4th ed., Vol. I, Part 2, Chapman and Hall, London (1979).

31. B.J. AYLETT. *J. Organomet. Chem. Libr.*, **9**, 327 (1980).

32. E. COLOMER and R.J.P. CORRIU. *Topics in Current Chemistry*, (F.L. Boschke ed.), Vol. 96, p. 79, Springer-Verlag, Berlin (1981).

33. P.G. HARRISON. *Coord. Chem. Revs.*, **40**, 179 (1982).

34. G. FRITZ and K. HOHENBERGER. *Z. Anorg. Allg. Chem.*, **464**, 107 (1980).

35. W. HONLE and H.G. SCHNERING. *Z. Anorg. Allg. Chem.*, **464**, 139 (1080).

36. G. SCHMID, V. BATZEL, and G. ETZROOT. *J. Organomet. Chem.*, **112**, 345 (1976).

37. D.J. PATMORE and W.A.G. GRAHAM. *Inorg. Chem.*, **5**, 2222 (1966).

38. J. GREENE and M.D. CURTIS. *Inorg. Chem.*, **17**, 2324 (1978).

39. M.D. CURTIS and J. GREENE. *J. Am. Chem. Soc.*, **100**, 6362 (1978).

40. B.K. NICHOLSON and J. SIMPSON. *J. Organomet. Chem.*, **72**, 211 (1974).

41. A.P. HAGEN, C.R. HIGGINS, and P.S. RUSSO. *Inorg. Chem.*, **10**, 1657 (1971).

42. M.C. BAIRD. *J. Inorg. Nucl. Chem.*, **29**, 367 (1967).

43. E. AMBERGER, E. MÜHLOFER, and H. STERN. *J. Organomet. Chem.*, **17**, P5 (1969).

44. H.R.H. PATIL and W.A.G. GRAHAM. *Inorg. Chem.*, **5**, 1401 (1966).

45. M.D. CURTIS. *Inorg. Chem.*, **11**, 802 (1972).

46. A.J. CHALK and J.F. HARROD. *J. Am. Chem. Soc.*, **87**, 1133 (1965).

47. A.J. CHALK and J.F. HARROD. *J. Am. Chem. Soc.*, **89**, 1640 (1967).

48. J.F. HARROD and A.J. CHALK. In: *Organic Synthesis via Metal Carbonyls*, Vol. II, p. 673 (I. Wender and P. Pino, eds), John Wiley and Sons, New York (1973).

49. J.P. COLLMAN and W.R. ROPER. *Adv. Organomet. Chem.*, **7**, 54 (1968).

50. A.J. CHALK and J.F. HARROD. *J. Am. Chem. Soc.*, **87**, 16 (1965).

51. R.N. HASZELDINE, R.V. PARISH, and D.J. PARRY. *J. Chem. Soc.*, A683 (1971).

52. J.E. BENTHAM, S. CRADOCK, and E.A.V. EBSWORTH. J. Chem. Soc., A587 (1971).

53. A.J. OLIVER and W.A.G. GRAHAM, Inorg. Chem., 10, 1 (1971).

54. A.M. CARDOSO, R.J.H. CLARK, and S. MOORHOUSE. Can. J. Chem., 48, 870 (1970).

55. W. JETZ and A.G. GRAHAM. Inorg. Chem., 10, 1647 (1971).

56. D.F. DONG, J.K. HAYANO, and W.A.G. GRAHAM. Can. J. Chem., 59, 1455 (1981).

57. J.F. HARROD, D.F.R. GILSON, and R. CHARLES. Can. J. Chem.; 48, 870 (1970).

58. M.J. FERNANDEZ and P.M. MAITLIS. J. Chem. Soc., Chem. Commun., 310 (1982).

59. J.F. HARROD and C.A. SMITH. J. Am. Chem. Soc., 92, 2699 (1970).

60. B.J. AYLETT and J.M. CAMPBELL. J. Chem. Soc., A1910 and A1916 (1969).

61. G. CERVEAU, G. CHAVIERE, E. COLOMER, and R.J.P. CORRIU. J. Organomet. Chem., 210, 343 (1981).

62. W. JETZ and W.A.G. GRAHAM. Inorg. Chem., 10, 1159 (1971).

63. A.J. BLAKENEY, D.L. JOHNSON, P.D. DONOVAN, and J.A. GLADYSZ. Inorg. Chem., 20, 4415 (1981).

64. M.A. NASTA and A.G. MacDIARMID. J. Organomet. Chem., 18, p. 11 (1969).

65. Y.L. BAAY and A.G. MacDIARMID. Inorg. Chem., 8, 986 (1969).

66. A.D. BERRY and A.G. MacDIARMID. Inorg. Nucl. Chem. Letters, 5, 601 (1969).

67. a) G. FRITZ and D. KUMER. Z. Anorg. Allg. Chem., 305, 105 (1961): b) S. MURAI and N. SONORA. Angew. Chem. Int. Ed. Engl., 18, 837 (1979).

68. B.J. AYLETT and J.M. CAMPBELL. Inorg. Nucl. Chem. Letters, 3, 137 (1967).

69. A.F. CLEMMIT and F. GLOCKLING. J. Chem. Soc., A1164 (1971) and references therein.

70. J.L. SPEIER. *Adv. Organomet. Chem.*, **17**, 407 (1979).

71. N.S. ARCHER, R.N. HASZELDINE, and R.V. PARISH. *J. Chem. Soc.*, *Dalton Trans.*, 695 (1979).

72. C.S. CUNDY, C. EABORN, and M.F. LAPPERT. *J. Organomet. Chem.*, **44**, 291 (1972).

73. C. EABORN, T.N. METHAM, and A. PIDCOCK. *J. Organomet. Chem.*, **54**, C3 (1973).

74. M.D. CURTIS, J. GREENE, and W.M. BUTLER. *J. Organomet. Chem.*, **164**, 371 (1979).

75. J. GREENE and M.D. CURTIS. *J. Am. Chem. Soc.*, **99**, 5176 (1977).

76. W.A. GUSTAVSON, P.S. EPSTEIN, and M.D. CURTIS. *J. Organomet. Chem.*, **238**, 87 (1982).

77. V.E. SHKLOVER, A.E. KALININ, *et al.* *Zh. Strukt. Khim.*, **14**, 692 (1973).

78. G. FOGARASI, H. HACKER, V. HOFFMANN, and S. DOBOS. *Spectrochim. Acta*, **30A**, 692 (1974).

79. D.M. ADAMS and W.S. FERNANDO. *J. Chem. Soc.*, *Dalton* Trans., 410 (1973).

80. V.E. SHKLOVER, N.G. BOKII, *et al.* *Zh. Strukt. Khim.*, **15**, pp. 90-98 and pp. 841-849 (1974).

81. D. BRAGA and G. ZANOTTI. *Acta Cryst.*, **B36**, 950 (1980) and references therein.

82. V.E. SHKLOVER, Yu.T. STRUCHKOV, B.A. ASTAPOV, and K.A. ANDRIANOV. *Zh. Strukt. Khim.*, **20**, 102 (1979).

83. V.A. PALYULIN, N.S. ZEFIROV. V.E. SHKLOVER, and Yu.T. STRUCHLOV. *J. Mol. Struct.*, **70**, 65 (1981).

84. D. CARLSTROM and G. FALKENBERG. *Acta Chem. Scand.*, **27**, 1203 (1973).

85. M. SODERHOLM and D. CARLSTROM. *Acta Chem. Scand.*, **B31**, 193 (1977).

86. D.R. BENNET and B. ABERG. *Acta Pharmacol. Toxicol.*, **36** (1975), Suppl. III.

87. F.A. COTTON and G. WILKINSON. *Advanced Inorganic Chemistry*, third ed., Intersicence Publ., New York (1972).

88. D.F. SHRIVER. *The Manipulation of Air-sensitive Compounds*, McGraw-Hill Book Co., New York (1969).

89. R.B. KING. *Organometallic Synthesis. V. 1. Transition-Metal Compounds* (J.J. Eisch and R.B. King, eds), Academic Press, New York (1965).

90. J.A. GLADYSZ, G.M. WILLIAMS, W. TAN, D.L. JOHNSON, D.W. PARKER, and J.C. SELOVER. *Inorg. Chem.*, **18**, 553 (1979).

91. R. OKAWARA, V. TAKAHASHI, and M. SAKIYAMA. *Bull. Chem. Soc. Jpn*, **30**, 608 (1957).

92. R.N. LEWIS. *J. Am. Chem. Soc.*, **70**, 1115 (1948).

93. C.W. YOUNG, P.C. SERVAIS, C.C. CURRIE, and J. HUNTER. *J. Am. Chem. Soc.*, **70**, 3758 (1948).

94. S.D. BREWER. *J. Am. Chem. Soc.*, **70**, 3962 (1948).

95. R.O. SAUER. *J. Am. Chem. Soc.*, **66**, 1707 (1944).

96. W. PATNODE and D.F. WILCOCK. *J. Am. Chem. Soc.*, **68**, 358 (1946).

97. E.G. ROCHOW. *Introduction to the Chemistry of the Silicones*, John Wiley and Sons, New York, NY (1946).

98. K.A. ANDRIANOV. *Metalorganic Polymers*, in: *Polymer Reviews*, Vol. 8 (H.F. Mark and E.H. Immergut, eds), John Wiley and Sons, New York (1965).

99. K.A. ANDRIANOV and L.M. KHANANASHVILI. *Organomet. Chem. Rev.*, **2**, 141 (1967).

100. K.A. ANDRIANOV and B.A. IZMAYLOV. *J. Organomet. Chem.*, **8**, 443 (1967).

101. R.O. SAUER, W.J. SCHEIBER, and S.D. BREWER. *J. Am. Chem. Soc.*, **68**, 962 (1946).

102. R. OKAWARA, E. ASADA, and T. WATASE. *Bull. Chem. Soc. Jpn*, **26**, 141 (1953).

103. D.A. ANDERSON. In: *Analysis of Silicones*, (A.L. Smith, ed.), John Wiley and Sons, New York (1974), Chap. 10.

104. E. WIBERG and E. AMBERGER. *Hydrides of the Elements of Main Group I-IV*, Elsevier Publ. Amsterdam (1971).

105. A.L. SMITH and N.C. ANGELOTTI. *Spectrochim. Acta*, **15**, 412 (1959).

106. T. ALVIK and J. DALE. *Acta Scand.*, **25**, 2124 (1971).

107. H. KRIEGSMANN. *Pure Appl. Chem.*, **13**, 203 (1966).

108. N.N. SOKOLOV, K.A. ANDRIANOV, and S.M. AKIMOVA. *Zh. Obshch. Khim.*, **26**, 933 (1956).

109. E.P. LEBEDEV, A.D. FEDOROV, V.D. REIKHFEL'D, and L.~~Z.~~ ZAKIROVA. *Zh. Obshch. Khim.*, **45**, 2645 (1975).

110. A.V. TOMADZE, V.A. YABLOKOV, N.V. YABLOKOVA, and Yu.A. ALEKSANDROV. *Zh. Obshch. Khim.*, **47**, 2549 (1977).

111. M. SAKIYAMA, Y. NISHIZAWA, and R. OKAWARA. *Bull. Chem. Soc. Jpn*, **38**, 2182 (1965).

112. B.O. PRAY, L.H. SOMMER, G.M. GOLDBERGER, G.T. KERR, P.D. GEORGE, and F.C. WHITMORE. *J. Am. Chem. Soc.*, **70**, 433 (1948).

113. A.L. SMITH. *Spectrochim. Acta*, **19**, 849 (1963).

114. H.C. BROWN and S. KRISHWAMURTHY. *J. Am. Chem. Soc.*, **99**, 1669 (1973).

115. M.C. HARVEY, W.H. NEBERCALL, and J.S. PEAKE. *J. Am. Chem. Soc.*, **79**, 1437 (1957).

116. A.P. HAGEN and A.G. MacDIARMID. *Inorg. Chem.*, **6**, 686 and 1941 (1967).

117. O. KAHN and M. BIGORGNE. *J. Organomet. Chem.*, **10**, 137 (1967).

118. A.D. BERRY, E.R. COREY, A.P. HAGEN, A.G. MacDIARMID, F.E. SAALFELD, and B.B. WAYLAND. *J. Am. Chem. Soc.*, **92**, 1940 (1970).

119. W. JETZ and W.A.G. GRAHAM. *J. Am. Chem. Soc.*, **89**, 2773 (1967).

120. R.B. KING, K.H. PANNELL, C.R. BENNETT, and M. ISHAQ. *J. Organomet. Chem.*, **19**, 327 (1969).

121. T. SAWAI. Ph.D. thesis, McGill University, Quebec, Canada (1972).

122. A.N. NESMEYANOV, K.M. ANISIMOV, N.E. KOLOBOVA, and V.V. SKRIPKIN. *Akad. Nauk SSSR Ser. Khim.*, 2364 (1967).

123. S.A.R. KNOX and F.G.A. STONE. J. Chem. Soc., A3147 (1970).

124. W. MALISCH, H.U. WEKEL, I. GROB, and F.H. KOHLER. Z. Naturforsch, 37b, 601 (1982).

125. B.K. NICHOLSON and J. SIMPSON. J. Organomet. Chem., 32, C29 (1971).

126. G.D. DOBSON, R.T. JERNIGEN, and E.P. ROSS. J. Inorg. Nucl. Chem., 33, 3375 (1971).

127. W. JETZ, P.B. SIMONS, J.A.J. THOMPSON, and W.A.G. GRAHAM. Inorg. Chem., 5, 2217 (1966).

128. R.K. POMEROY and K.S. WIJESEKERA. Inorg. Chem., 19, 3729 (1980).

129. E.H. BROOKS, M. ELDER. W.A.G. GRAHAM, and D.J. HALL. J. Am. Chem. Soc., 90, 3587 (1966).

130. W. FINK. Helv. Chim. Acta, 58, 1464 (1975) and 59, 606 (1976).

131. D.L. JOHNSON and J.A. GLADYSZ. Inorg. Chem., 20, 2508 (1981).

132. L. VANCEA and W.A.G. GRAHAM. Inorg. Chem., 13, 511 (1974).

133. F.H. CARRE and J.J.E. MOREAU. Inorg. Chem., 21, 3099 (1982).

134. A.J. BLAKENEY and J.A. GLADYSZ. J. Organomet. Chem., 210, 303 (1981).

135. B.K. NICHOLSON, B.H. ROBINSON, and J. SIMPSON. J. Organomet. Chem., 66, C3 (1974).

136. B.K. NICHOLSON and J. SIMPSON. J. Organomet. Chem., 155, 237 (1978).

137. W. MALISCH and M. KUHN. Chem. Ber., 107, 979 (1974).

138. J.E. COUTANT and R.J. ROBINSON. In: Analysis of Silicones (A.L. Smith, ed.), J. Wiley and Sons, New York (1974), Chap. 12, pp. 338-375.

139. W.J.A. VAN DEN HEUVEL, J.L. SMITH, R.A. FIRESTONE, and J.L. BECK. Anal. Letters, 5, 285 (1972).

140. G.R. PICKERING, C.J. OLLIFF, and K.J. RUTT. Org. Mass Spectrom., 10, 1035 (1975).

141. E. WHITE, V.S. TSUBOYAMA, and J.A. McCLOSKEY. J. Am. Chem. Soc., 93, 6340 (1971).

142. W.P. WEBER, R.A. FELIX, A.K. WILLARD, and H.G. BOETTGER. J. Org. Chem., 36, 4060 (1971).

143. V.N. BOCHKAREV, A.N. POLIVANOV, N.P. TELEGINA, and E.A. CHERNYSHEV. J. Gen. Chem. USSR, 44, 920 (1974).

144. V.N. BOCHKAREV, A.N. POLIVANOV, N.P. TELEGINA, A.G. KUZNETSOVA, and E.A. CHERNYSHEV. J. Gen. Chem. USSR, 44, 1021 (1974).

145. V.N. BOCHKAREV, A.N. POLIVANOV. L.V. SOBOLEVSKAYA, L.M. BLEKH, M.V. SOBOLEVSKII, and E.A. CHERNYSHEV. J. Gen. Chem. USSR, 44, 1174 (1974).

146. R.E. SWAIM, W.P. WEBER, H.G. BOETTGER, M. EVANS, and F.M. BOCKHOFF. Org. Mass Spectrom., 15, 304 (1980).

147. M. GIELEN and G. MAYENCE. J. Organomet. Chem., 12, 1759 (1967).

148. H.C. HILL. Introduction to Mass Spectroscopy, in Spectroscopy in Education, V. 3 (T. Cairns, ed.), Heyden and Son Ltd., London (1966).

149. B.Y.K. HO, L. SPIALTER, and L.D. SMITHSON. Org. Mass Spectrom., 10, 361 (1975).

150. J. DIEKMAN, J.B. THOMPSON, and C. DJERASSI. J. Org. Chem., 34, 3147 (1969).

151. W.P. WEBER, R.A. FELIX, and A.K. WILLARD. Tetrahedron Lett., 907 (1970).

152. B.Y.K. HO, L. SPIALTER, and L.D. SMITHSON. Inorg. Nucl. Chem. Letters, 10, 795 (1974).

153. R.R. SCHRIEKE and B.D. WEST. Aust. J. Chem., 22, 49 (1969).

154. C.R. BETTER, J.C. SEWDRA, and G. URRY. Inorg. Chem., 9, 1060 (1969).

155. C.H. MIDDLECAMP. W. WOJNOWSKI, and R. WEST. J. Organomet. Chem., 140, 133 (1977).

156. a) J.Y.K. HSIEH and C.M. BUESS. Org. Mass Spectrom., 16, 189 (1981).

b) A.D. BRITT and W.B. MONIZ. J. Am. Chem. Soc., 91, 6204 (1969).

157. M.R. LITZOW and T.R. SPALDING. Mass Spectrometry in Inorganic and Organometallic Compounds, (M.F. Lappert, ed.), Elsevier Scientific, Amsterdam (1973), chap. 7.

158. G.V. VAN MOURIK and F. BICKELHAUPT. Rec. Trav. Chim., 88, 868 (1969).

159. V. Yu. ORLOV. J. Gen. Chem. USSR, 37, 2188 (1967).

160. V. Yu. ORLOV, N.S. NAMETKIN, L.E. GUSEL'NIKOV, and T.H. ISALAMOV. Org. Mass Spectrom., 4, 195 (1970).

161. B.F.G. JOHNSON, R.D. JOHNSTON, and J. LEWIS. J. Chem. Soc., A2865 (1968).

162. F.E. SAALFELD, M.V. McDOWELL, A.G. MacDIARMID, and R.E. HIGHSMITH. Int. J. Mass Spectrom. Ion Phys., 9, 197 (1972) and references therein.

163. R.E. WINTERS and R.W. KISER. J. Organomet. Chem., 4, 190 (1965).

164. S. PIGNATARO and F.P. LOSSING. J. Organomet. Chem., 11, 571 (1968).

165. E. SCHUMACHER and R. TAUBENEST. Helv. Chim. Acta, 49, 1447 (1966).

166. R.B. KING. J. Am. Chem. Soc., 90, 1417 (1968).

167. B.F. HALLAM and P.L. PAUSON. J. Chem. Soc., 3030 (1956).

168. J. HOMER, A.W. JARVIE, A. HOLT, H.J. HICKTON. J. Chem. Soc., B67 (1967).

169. H. JANCKE, G. ENGELHARDT, R. RADEGLIA, and H. KRIEGSMANN. Spectrochim. Acta, 25A, 85 (1969).

170. D.E. WILLIAMS, G.M. RONK, and D.E. SPIELVOGEL. J. Organomet. Chem., 69, 69 (1974).

171. R.K. HARRIS and B.J. KIMBER. J. Organomet. Chem., 70, 43 (1974).

172. R.K. HARRIS, B.J. KIMBER, M.D. WOOD, and A. HOLT. J. Organomet. Chem., 116, 291 (1976).

173. G.A. MORRIS and R. FREEMAN. J. Am. Chem. Soc., 101, 760 (1979) and 102, 428 (1980).

174. C.G. SWAIN and E.C. LUPTON. J. Am. Chem. Soc., 90, 4328 (1968).

175. J.E. HUHEEY. Inorganic Chemistry, Principles of Structure and Reactivity. Harper and Row Publishers, New York (1972), Chaps. 4 and 6.

176. R.B. KING. Acc. Chem. Res., 3, 417 (1970).

177. D.E. WILLIAMS. In: Analysis of Silicones (A. Smith, ed.), J. Wiley and Sons, New York (1974), Chap. 11.

178. E.D. BECKER. High Resolution NMR, Theory and Chemical Applications. Academic Press, New York (1980), Chap. 4.

179. R.J. ABRAHAM and P. LOFTUS. Proton and Carbon-13 NMR Spectroscopy, Heyden and Son, Great Britain (1978), Chap. 2.

180. W.C. STILL, M. KHAN, and A. MITRA. J. Org. Chem., 43, 2923 (1978).