

Cyclosiloxanes as Frameworks for Multimetallic Compounds.¹

2. Synthesis and Characterization of Some Metallocarbonyl-Substituted Cyclosiloxanes

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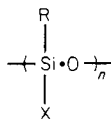
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The compounds $[-\text{Si}(\text{CH}_3)(\text{R})\text{O}-]_n$, 1 (R = $\text{Co}(\text{CO})_4$, $n = 4$ and 5; R = $\text{CpFe}(\text{CO})_2$, $n = 4$), have been prepared by reactions of the appropriate compounds (R = H) with $\text{Co}_2(\text{CO})_8$, 2, and $[\text{CpFe}(\text{CO})_2]_2$, 3, respectively. Reactions of 1 (R = H, $n = 4$ and 5) with a substoichiometric amount of 3 yielded a mixture of partially substituted products, from which were isolated $[-\text{Si}(\text{CH}_3)(\text{H})\text{O}-]_n$ (R = H, $n = 3$ and 4), 4 and 5. Reactions of 4 and 5 with 2 resulted in replacement of the residual Si-H by $\text{Co}(\text{CO})_4$. The new compounds 1 (R = Br, $n = 3$ and 4; R = H, $n = 3$) were also prepared and characterized.

Introduction

The great catalytic efficiency accruing from precise control of the orientation and proximity of reacting and interacting centers is commonplace in biochemistry, most evidently in the function of enzymes. Although our knowledge of enzymes provides clear insights into the general strategies required to tackle the problem of maximizing reaction rates, it does little to guide us in achieving the same ends, but by simpler means than the brute-force method of imitating nature itself. The crux of the problem is to find a family of molecules with the following properties: (i) easily synthesized, (ii) subject to easy and systematic structural modification, (iii) capable of multifunctionalization by substituents of potential catalytic activity, (iv) exhibiting stereochemical properties that can be controlled and systematically modified, and (v) subject to precise structural characterization, preferably in solution. The cyclodextrins³ and the cryptates⁴ satisfy all of these criteria to a greater or lesser degree, but both have serious limitations in terms of the types of chemistry that are necessary for heavy industrial organic synthesis.

The present series of papers explores the synthesis and fundamental properties of some substituted cyclosiloxanes, with a view to assessing their potential for use as frameworks for sterically controlled, multifunctional catalyst systems. Attention will be focussed initially on the simple disubstituted rings of the type 1, where R is an inert alkyl,



or aryl, substituent and X is an organometallic function of potential catalytic activity.⁵ In principle, siloxane systems are amenable to much greater substitutional variability, but as will be seen below, even superficially simple systems can become very complicated in terms of isomeric composition. However, it is this isomeric com-

plexity that provides an important access to stereochemical control, since the orientational and proximal properties of substituents in the different isomers can be quite different.⁶

Other properties of the cyclosiloxanes that recommend them in the present study are (i) their chemical robustness (at least in the absence of strong acids, or bases), (ii) cheapness and ease of synthesis, and (iii) great potential for functionalization. We describe herein the successful synthesis and characterization of some compounds 1 bearing X = $\text{Co}(\text{CO})_4$ and $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2$. These studies together with a number of unsuccessful attempted syntheses give an insight into the general scope of the approach and to some specific advantages and problems that are intrinsic to it.

Results

Synthesis of D^{Co}_n ($n = 4$ and 5) [$\text{Co} = \text{Co}(\text{CO})_4$]. In the reaction of D^{H}_4 with $\text{Co}_2(\text{CO})_8$, all of the SiH functions reacted quite rapidly and full substitution was easily achieved. From spectroscopic data, the reaction was established to proceed in excellent yield ($\sim 90\%$ based on D^{H}_4), but the yield of purified product was considerably reduced by the number of recrystallizations needed to remove colored impurities. Column chromatography was not helpful for purification since columns that effected reasonable separation caused decomposition of the D^{Co}_4 and those that did not decompose the product did not give good separation.

The reaction of D^{H}_5 with $\text{Co}_2(\text{CO})_8$ presented a number of problems that were much less evident in the case of D^{H}_4 . The first was the much slower reaction of the fifth SiH function on D^{H}_5 . The longer reaction time and more severe reaction conditions needed to achieve full substitution led to the accumulation of larger amounts of cobalt carbonyl decomposition byproducts in the reaction mixture. Although IR spectra showed that D^{H}_5 was converted to D^{Co}_5 in high yield, the product's extreme solubility and reluctance to crystallize made isolation of a well-purified sample very difficult. It should be noted, however, that the crude product, isolated in 40% yield, appeared from its spec-

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(5) Throughout this paper we shall use the conventional notation D^{X}_n for such compounds, where D^{X} designates the monosiloxane unit $[-\text{Si}(\text{CH}_3)(\text{X})\text{O}-]$ and n is the number of units in the ring.

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Table I. Infrared Absorptions of Some Cobalt Carbonyl Derivatives in the $\nu(\text{CO})$ Region

products (M = Co(CO) ₄)	frequencies, cm ⁻¹				
	A ₁ (eq)	A ₁ (ax)	E	E	$\nu^{13}\text{CO}$
(CH ₃) ₂ (H) ₂ Si-M ^a	2102 (s)	2043 (s)	2021 (vs)	2015 (vs)	1981 (w) ^e
(C ₆ H ₅) ₂ Si-M ^b	2095 (s)	2031 (s)	2003 (vs)		1975 (w)
[(CH ₃) ₂ (M)SiO] ₂ ^c	2080	2020	2000		1975 (w)
D ^{Co} ₄ (28) ^d	2100 (s)	2040 (s)	2027 (vs)	2011 (vs)	1968 (w)
D ^{Co} ₅ (29) ^d	2101 (s)	2039 (s)	2023 (vs)	2006 (vs)	1966 (w)

^a Reference 9 (gas phase). ^b Reference 10 (*n*-hexadecane solution). ^c Reference 7 (solvent and intensities omitted by authors). ^d This work (hexanes solution). ^e The assignment of $\nu^{13}\text{CO}$ has been discussed in ref 21.

Table II. Major Infrared Absorptions of D^X_n Compounds in the 400–1400 cm⁻¹ Region

compd	absorptions, cm ⁻¹				
	$\nu_{\text{Si-CH}_3}$	$\delta_{\text{Si-CH}_3}$	$\nu_{\text{Si-O}}$	$\delta_{\text{Si-H}}$	$\delta_{\text{M-CO}}$
D ^H ₃	1255 ^a	772 ^a	1025 ^a	888 ^a	
D ^H ₄	1261, ^a 1257 ^b	777, ^a 775 ^b	1096, ^a 1089 ^b	885 ^a	
D ^H ₅	1263 ^a	775 ^a	1097 ^a	879 ^a	
D ^{Co} ₄	1263 ^a	783 ^a	1061 ^a		552 ^a
D ^{Co} ₅	1263 ^a	781 ^a	1073 ^a		552 ^a
D ^{Fp} ₄	1245 ^b	771 ^a	1040 ^b		597 ^b
D ^{Co} ₁ D ^{Fp} ₃	1254, 1247 ^b	771 ^b	1040, 1063 ^b		550, 597 ^b

^a In hexane solution. ^b In CS₂ solution.

troscopic properties to contain very little impurity.

Both D^{Co}_n compounds are white, seemingly microcrystalline solids in the pure state. They exhibit considerable chemical stability, being indefinitely stable under inert atmosphere at <0 °C and being only slowly oxidized in the solid, or in solution, in the presence of air. This is very different from the instability of the tetramethyldisiloxane analogue previously reported by Greene and Curtis.⁷

Since the products D^{Co}₄ and D^{Co}₅ are both mixtures of geometric isomers, it is not surprising that they do not give well-crystallized samples. However, the physicochemical characteristics of the products leave no doubt as to the correct assignment of structure. Mass spectra reveal stepwise losses of 16 and 20 carbonyl groups from the parent ions.¹ ¹H NMR spectra reveal the presence of the appropriate numbers of isomers and the fact that the ratios of these isomers may vary depending on the purification steps.⁸

The infrared spectra of D^{Co}₄ and D^{Co}₅ in the ν_{CO} region correspond to those reported for similar compounds where the degeneracy of the E mode is lifted due to a local symmetry that is less than the ideal *D*_{3h}.^{9,10} The frequencies observed for D^{Co}₄ and D^{Co}₅ in the ν_{CO} region are compared with those of some similar compounds in Table I. The presence of the Co–CO bond system is also indicated by the presence of a pair of peaks at 552 (s) and 515 (w) cm⁻¹ in the D^{Co}₄ spectrum and at 552 (s) and 511 (w) cm⁻¹ in the D^{Co}₅ spectrum. The position and relative intensities of this pair of peaks are characteristic of, and fairly constant for, all compounds of the type X–Co(CO)₄.^{9,10}

While the $\nu_{\text{Si-C}}$ frequency of the Si–CH₃ group remains almost constant in D^{Co}_n relative to D^H_n (see Table II), the $\nu_{\text{Si-O}}$ band is shifted to lower frequency in D^{Co}_n. All of the infrared bands of D^{Co}_n are sharp and show no splittings that might be attributed to the presence of isomers.

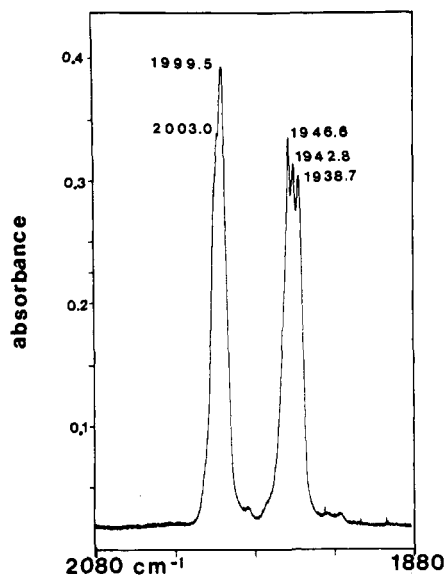


Figure 1. Infrared spectrum of D^{Fp}₄ in the carbonyl region (ca. 1% in cyclohexane; resolution 0.12 cm⁻¹).

Synthesis of D^{Fp}₄ [Fp = (C₅H₅)Fe(CO)₂]. The reaction of Fp₂ with silanes, although generally giving good yields of silyl products, requires much more severe reaction conditions than does the analogous reaction of Co₂(CO)₈.¹¹ In the case of D^H₄ moderate yields of D^{Fp}₄ were obtained only after prolonged reaction (4–5 days) at elevated temperature (170 °C). Even under such vigorous conditions very little decomposition of either the siloxane or Fp₂ occurred and the failure to obtain high yields of the fully substituted product was largely due to the slowness of the final substitution step for the more sterically encumbered isomers. At temperatures above 170 °C, the decomposition of Fp₂ into ferrocene becomes a serious problem.

The D^{Fp}₄ product obtained from a 1:1 SiH to Fp reaction pushed to high conversion is obtained as a pale yellow, apparently crystalline solid that is indefinitely stable in air. The ¹H NMR spectrum of solutions of this material (even of samples appearing to consist of a simple crystal) shows the presence of all four isomers in roughly statistical abundance.⁸ Unlike the D^{Co}_n compounds D^{Fp}₄ is quite stable to most chromatographic materials. Unfortunately, none of the chromatographic techniques used (TLC, HPLC, and flash chromatography) gave a clean fractionation of the isomers. On the other hand, even simple column chromatography gave a sufficient partial fractionation to allow unequivocal assignment of the NMR spectra.⁸ The small amount of D^{Fp}₄ product isolated from a 2:1 Si–H to Fp reaction was found to contain about 80% of the all-trans isomer.

The IR spectrum in the ν_{CO} region of a sample of D^{Fp}₄ containing a roughly statistical distribution of isomers is

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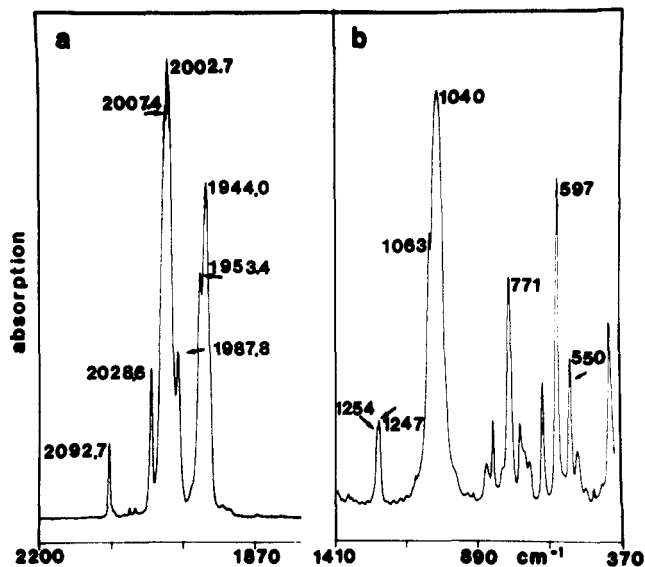


Figure 2. Infrared spectra of $D^{Co_1}D^{Fp_3}$: (a) in the carbonyl region (ca. 1% in cyclohexane); (b) in the 400–1400 cm^{-1} region (ca. 5% in CS_2).

shown in Figure 1. In the absence of special effects, the two modes of the $Fe(CO)_2$ moiety would normally appear as sharp, unsplit bands. Neither the ν_{Si-C} nor ν_{Si-O} bands show any splitting although they are both shifted to lower frequency relative to D^{H_4} (see Table II). The strong sharp band at 597 cm^{-1} , assigned in other $Fp-SiR_3$ compounds to a $Fe-CO$ bending mode,¹⁰ is quite unsplit.

Attempts to prepare D^{Fp_5} were unsuccessful due to the exceptionally low rate for the fifth substitution step.

Synthesis of $D^{Co_1}D^{Fp_3}$ and $D^{Co_1}D^{Fp_4}$. Reaction of D^{H_4} with less than stoichiometric amounts of Fp_2 leads to the formation of a mixture of partially substituted products $D^{H_n}D^{Fp_{4-n}}$. Unreacted D^{H_4} was easily removed by column chromatography, which also yielded a fairly pure fraction corresponding to $D^{H_1}D^{Fp_3}$. The degree of substitution is easily monitored by 1H NMR because of the chemical shift difference between the methyl resonances of $Fp-Si-CH_3$ (average δ 0.85) and $H-Si-CH_3$ (average δ 0.40). Conversion of $D^{H_1}D^{Fp_3}$ to $D^{Co_1}D^{Fp_3}$ was facilitated by the chemical stability of the $Fp-Si$ system and by the ease of reaction of $Si-H$ with $Co_2(CO)_8$. A sample whose analysis and spectroscopic properties corresponded to $D^{Co_1}D^{Fp_3}$ (>95%) was obtained as a light yellow grease. It was air stable in the pure state but decomposed slowly in solution. In the 1H NMR spectrum of the compound, no CH_3-Si-H groups could be detected. Resonances due to C_5H_5 and CH_3 were observed in the appropriate ratio, and 20 separate resonances were evident in the $Si-CH_3$ region (δ 0.75–1.20), indicating the presence of all six possible isomers of $D^{Co_1}D^{Fp_3}$.⁸

The IR spectrum of $D^{Co_1}D^{Fp_3}$ in the ν_{CO} region (Figure 2) confirms the presence of both metallocarbonyl substituents. The peaks at 2092.7 and 2028.6 cm^{-1} are due to the $Co(CO)_4$ group, the other two expected peaks being masked by the strong Fp band at 2002.7 cm^{-1} . The latter band and that at 1944 cm^{-1} are the two modes expected for the Fp group. The small peaks at 1987.8 and 1953.4 cm^{-1} are also attributed to the Fp group and are possibly related to the presence of geometric or conformational isomers. The lower frequency part of the $D^{Co_1}D^{Fp_3}$ spectrum (see Table II) closely resembles that of D^{Fp_4} , with two significant differences. First, the ν_{Si-C} peak, which is a sharp single peak at 1247 cm^{-1} in D^{Fp_4} , is broadened and slightly split (1254 and 1247 cm^{-1}) in $D^{Co_1}D^{Fp_3}$. Second, the ν_{Co-C} mode is evident at 550 cm^{-1} .

Although $D^{H_1}D^{Fp_4}$ can be made in fairly high yield and it reacts readily with $Co_2(CO)_8$ to give $D^{Co_1}D^{Fp_4}$, the workup of the products is much more difficult than in the case of the tetramers since the partially substituted products separate less well by chromatography and the analysis by 1H NMR is much more complicated. Nevertheless, a sample whose analysis and physical properties correspond to $D^{Co_1}D^{Fp_4}$ was prepared. The infrared spectrum of the compound was very similar to that of $D^{Co_1}D^{Fp_3}$ except for the anticipated differences in the relative intensities of bands due to $Co(CO)_4$ and Fp .

Attempted Syntheses of D^{Co_3} and D^{Fp_3} . The trisiloxane D^{H_3} is an elusive compound. The only case where it was probably authentically obtained previous to our study was the very early work of Brewer, who obtained a low yield of a very unstable compound from the thermal cracking of poly(methylhydrosiloxane).¹² Although modern spectroscopic methods were not available at that time, the properties described by Brewer correspond closely to those we have observed for an authentic sample. In the course of the present study we prepared a sample of D^{H_3} by reduction of D^{Br_3} , which was in turn prepared by reaction of the readily available D^{Ph_3} with bromine. Unlike its higher homologues, D^{H_3} spontaneously polymerizes at room temperature, a fact that renders both its isolation as a pure compound and the study of its reaction with $Co_2(CO)_8$ impossible.

Since D^{Co_3} and D^{Fp_3} were unavailable from the H_2 elimination reactions with D^{H_3} , their synthesis by nucleophilic displacement of Br^- from D^{Br_3} by the appropriate metalate anion was attempted. Under all reaction conditions investigated, the competing degradation of the siloxane ring by the metalate reagent prevented the formation of the desired product in isolable amounts.

Attempted Reactions with Other Metal Carbonyls.

A number of other reactions that are known to proceed with monofunctional organosilicon hydrides were attempted with D^{H_4} . The reactions with $Fe(CO)_5$ and $Fe_3(CO)_{12}$ both seemed, by IR spectroscopy, to give conventional products,¹³ but their extreme reactivity prevented successful workup and purification. The thermal reactions of $Mn_2(CO)_{10}$ ¹⁴ and $[C_5H_5Mo(CO)_3]_2$ ¹⁵ both resulted in complete disappearance of the $Si-H$, by IR spectroscopy, but no bands due to the anticipated silylmetallocarbonyls were observed. Workup of the products of the latter reactions by chromatography also gave no silyl-metallo-carbonyl products.

Discussion

The preparations of multifunctional compounds of the kind described in this paper pose several major problems relative to similar preparations of monofunctional species. The first difficulty is that a preparation that gives an $x\%$ yield with a monofunctional reagent will, to a first approximation, give an $x/n\%$ yield with an n functional reagent. For values of $n \geq 4$, this means that only reactions which proceed very cleanly and in good yield will give useful yields of fully substituted products. A second problem is the tendency of polyfunctional compounds to decline with increasing extent of reaction, either because of steric congestion or because collisions between reactants are less likely to bring together the

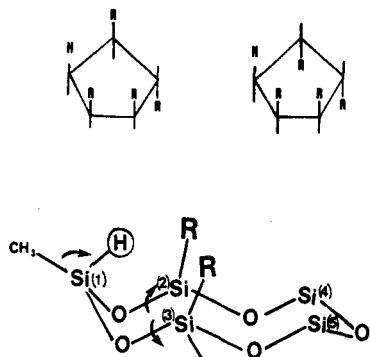
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Chart I. Two Possible Geometric Isomers of Partially Substituted $D^H_1D^R_4$ and the "Double-Chair" Conformation of Isomer II

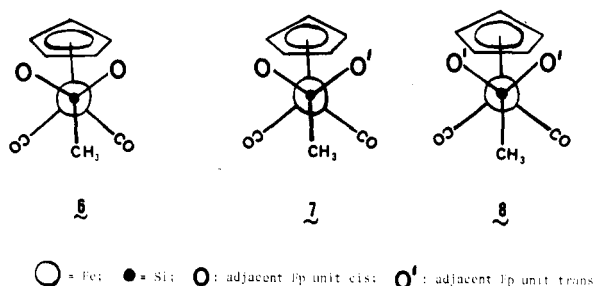


reactive functions. A third problem is the awful complexity of the product mixture when the reaction does not go to completion or when side reactions occur to a significant extent. In all of the cases described above, where the expected products were not obtained, the failure can be ascribed to one or several of the above reasons. The most important side reaction leading to failure seems to be attack on the siloxane ring system. While the reasons for this are obvious for those reactions involving strongly basic metalate anions, they are less obvious for the hydrogen elimination reaction between neutral metal carbonyls and silicon hydrides. The possibility that siloxane ring degradation may result from attack by relatively acidic metal hydrides does not seem likely since the best results are obtained with $Co_2(CO)_8$, which is known to give $HCo(CO)_4$, one of the more acid metal hydrides, on reaction with silicon hydrides.¹⁶

The low reactivity of the fifth hydrogen of D^H_5 is a noteworthy phenomenon. Although the fourth hydrogen of D^H_4 also shows a slightly reduced reactivity, the effect is much less dramatic than is the case for D^H_5 . For example, the residual Si-H of $D^H_1D^{Fp}_3$ reacts readily with $Co_2(CO)_8$ under mild conditions and with Fp_2 under forcing conditions to give fully substituted products. On the other hand, $D^H_1D^{Fp}_4$ reacts with $Co_2(CO)_8$ only slowly and with Fp_2 hardly at all, even under forcing conditions. This behavior could be related to the specific conformational properties of the 10-membered ring. Chart I (upper) shows two examples of $D^H_1D^R_4$ 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 . Chart I (lower) shows a representation of a hypothetical "double-chair" conformation adopted by the pentamer.⁶ 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 favored by large substituents at Si(2) and Si(3) and by the very small size of the hydrogen atom that becomes "hidden" inside the ring between the two adjacent groups. Some large attacking molecules, such as $HCo(CO)_4$ and especially $HFe(CO)_2(\eta^5-C_5H_5)$, would experience major difficulty in reaching the last reaction site. The analogous "hidden conformation" for the unreacted hydrogen is not possible in the tetramer $D^H_1D^R_3$ because the molecule would probably adopt a chair conformation to get the bulky groups away from each other. This conformation is still favorable to the reaction of the last hydrogen.

Although there is no evidence that any of the cyclosiloxanes prepared in this work have their conformational interchange slowed down sufficiently to be evident by

Chart II



NMR methods, there is evidence that steric effects are operative in the D^{Fp}_n compounds. In terms of reactivity this is clearly demonstrated by the isolation of D^{Fp}_4 as mostly the all-trans isomer ($\sim 80\%$) from reactions where there was less Fp_2 than required for complete substitution. In addition to the primary advantage that the all-trans isomer has in being the least sterically encumbered when fully substituted, it also has the advantage that there is only one isomer of the precursor species $D^H_1D^{Fp}_3$. The only other isomers of D^{Fp}_4 that could have a $D^H_1D^{Fp}_3$ precursor containing an Si-H function flanked by two trans Fp substituents is the one with three mutually cis Fp substituents and the fourth one trans. However, at most only one-fourth of the $D^H_1D^{Fp}_3$ precursor would carry the Si-H in the appropriate position (since this position is the least encumbered in $D^H_2D^{Fp}_2$ it is likely to react more readily and will thus be depleted below the statistically determined one quarter). It is well established, though not thus far systematically, that the solid-state structures of cyclosiloxanes show great variability in terms of conformation and Si-O-Si angles in response to varying substitution.⁶

Further indications of the special steric properties of the Fp group emerge from the IR spectra in the ν_{CO} region of compounds containing this substituent. In both D^{Fp}_4 and $D^{Co}_1D^{Fp}_3$ and ν_{CO} bands of the Fp unit show multiplicities that are not evident in those of the $Co(CO)_4$ group. This behavior is reminiscent of that observed originally by Jetz and Graham for $Fp-Si(CH_3)Cl_2$.¹⁵ This phenomenon was attributed to the existence of conformers whose lifetime was very long on the IR time scale but too short on the NMR time scale to be observable by NMR. Since the present compounds consist of a mixture of isomers, the attribution of the phenomenon of conformers is less certain. However, in the case of the D^{Co}_n compounds, where similar isomers are also present, no such splitting of the ν_{CO} bands is observed. In fact, the relative intensities of the three peaks in the 1940 cm^{-1} region for D^{Fp}_4 do vary with varying isomeric composition, but such behavior would be expected if the several peaks were due to either conformational or geometric isomerism, since each geometrical isomer contains different proportions of the three geometrical triads (cis-cis, cis-trans, and trans-trans) and each central group of a triad will have its own special conformational properties. This complicated situation is illustrated in Chart II, from which it can be seen that triads 6 and 8 give two distinct staggered conformers while 7 gives three.

Conclusions

The attachment of organometallic functions of potential catalytic interest to cyclosiloxanes via metal-to-silicon bonds may be achieved, but with less generality than has been established for simple, monofunctional Si-H compounds. Although, in principle, the different isomer structures allow some control over the spatial and angular placement of substituents, the separation of the isomers

is a serious problem that has yet to be resolved. The principle of the attachment of more than one type of organometallic function to the same cyclosiloxane ring has been established in practice, but this limited success also highlights the great isomeric complexity of heterosubstituted $D^x_n D^y_m$ systems. The use of alternative synthetic approaches and the great value of the ^1H NMR spectra of the Si-CH₃ resonances of these compounds for establishing isomeric composition will be the subjects of subsequent papers.

Experimental Section

All solvents were freshly distilled from sodium or Na/K/benzophenone under N₂ immediately prior to use. All organometallic preparations were carried out under oxygen-free conditions by using standard Schlenk techniques. The D^H_n compounds were synthesized by literature methods¹⁷ as were D^{Ph}_n .¹⁸ Reactant metal carbonyl compounds were bought from Strem Chemicals or Alfa-Ventron and were used without further purification. The carbonylate salts NaFp¹⁹ and LiCo(CO)₄²⁰ were prepared according to published procedures.

Reactions were routinely monitored by IR spectroscopy with a Perkin-Elmer 297 spectrometer, using 0.1-mm path length liquid cells. Standard IR spectra of products were recorded on a Nicolet 7000 FTIR instrument. NMR spectra were measured on a Varian XL-200 FT instrument. Details of NMR and mass spectra of all reported compounds are published elsewhere.^{1,3,22}

Preparation of D^{Br}_n ($n = 3$ and 4). 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^{Ph}_3 , purged with N₂, 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 0 °C. 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 N₂ 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^{Br}_3 , as a white crystalline solid. Purity of D^{Br}_3 was estimated to be 99% from ^1H NMR data. The analogous D^{Br}_4 was prepared following the same procedure, using 2.0 g (3.7 mmol) of D^{Ph}_4 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^{Br}_4 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^{Br}_3 : IR (CS₂) 1264 (m), 1031 (vs), 846 (w), 795 (m), 755 (w), 455 (s) cm⁻¹; mp(obsd) 68–70 °C; ^1H NMR (C₆D₆) δ 0.31–0.43 (m); mass spectrum, selected m/e (relative intensity) 402 (M - CH₄⁺, 21), 400 (M - CH₄⁺, 19).

D^{Br}_4 : IR (CS₂) 1266 (m), 1103 (vs), 795 (m), 765 (w), 439 (w) cm⁻¹; mp(obsd) 40 °C; ^1H NMR (C₆D₆) δ 0.29–0.48 (m); mass spectrum, selected m/e (relative intensity) 542 (13), 540 (19), and 538 (11) are the largest peaks of M - CH₄⁺ group.

Preparation of D^{H}_3 . 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^{Br}_3 dissolved in 20 mL of dry diethyl ether, and the solution was cooled to -78 °C. Then, sodium tri-*sec*-butylborohydride/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^H_3 , was only contaminated with a small amount (<5% from IR spectrum) of diethyl ether and pentane. An attempt to purify the product by a microdistillation at atmospheric pressure led to a rapid decomposition of the material. The reduction of D^{Br}_3 to D^H_3 was repeated four times, and crude yields range from 10 to 80% depending on reaction conditions (temperature and time) and isolation techniques. Reagents such as lithium triethylborohydride and lithium tributylborohydride were also found to be efficient in the reduction of D^{Br}_3 at -78 °C, but in both cases the borane residues were too volatile to be separated from the final product.

D^H_3 : IR (hexanes) 2170 (s), 1255 (s), 1025 (vs), 888 (vs), 772 (s) cm⁻¹; bp(obsd) 94–96 °C (lit.¹⁶ 93.8 °C); ^1H NMR (C₆D₆) δ 0.113–0.17 (3 H, m), 4.99–5.04 (1 H, m).

Preparation of D^{Co}_4 . 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. With a small syringe, 2.0 g (0.83 mmol) of D^H_4 was 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 Co₂(CO)₈ and black byproducts, presumed to be Co₄(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^{Co}_4 as a white amorphous solid at ambient temperature.

D^{Co}_4 : IR (hexanes) 2100 (s), 2040 (s), 2027 (sh), 2011 (vs), 1968 (w), 1263 (m) 1061 (s) cm⁻¹; mp(obsd) 95 °C decomp; ^1H NMR (C₆D₆) δ 0.69–1.04 (6 sharp peaks); mass spectrum, selected m/e (relative intensity) 920 (M⁺, <1), 905 (M - CH₃⁺, <1), 892 (M - CO⁺, <1). Anal. Calcd for C₂₀H₁₂O₂₀Si₄Co₄: C, 26.10, H, 1.31. Found: C, 26.14, H, 1.45.

Preparation of D^{Co}_5 . 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^H_5 was added dropwise to the solution. After being warmed to ambient temperature, the solution was stirred for 4 h under a nitrogen atmosphere. A further 12 g (3.47 mmol) of Co₂(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 Co₂(CO)₈ into Co₄(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 column with hexanes. No decomposition was observed, but the separation of red byproducts from the expected $D^{Co(CO)_5}_5$ was not very good. 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 in vacuo. The mother liquor was evaporated to dryness affording 0.4 g (3.5%) of a red viscous residue. The chemical and

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physical properties of the two fractions were essentially identical.

D^{Co_5} : IR (hexanes) 2101 (s), 2039 (s), 2023 (sh), 2006 (vs), 1966 (w), 1263 (m), 1073 (s) cm^{-1} ; mp(obsd) 55 °C decomp; 1H NMR (C_6D_6) δ 0.80–1.25 (m); mass spectrum, selected m/e (relative 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.

Preparation of D^{Fe_4} . 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 $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ and 3.0 g (12.5 mmol) of D^H_4 . 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 $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ was 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, filtered over a layer of Celite, and column chromatographed on silica gel (3 × 40 cm) using pure hexanes as first eluent. The solvent decahydronaphthalene was eluted first and was immediately followed by a yellow-orange band that proved to be ferrocene (0.075 g). 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 $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ (0.40 g). The yellow crude product was redissolved in benzene (12 mL), and a white-beige solid was precipitated by adding a large volume (ca. 100 mL) of cold hexanes; 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^{Fe_4} is a light beige amorphous solid, air stable at ambient temperature.

D^{Fe_4} : IR (CCl_4) 3125 (vw), 2961 (2), 2899 (vw), 2000 (vs), 1943 (vs), 1250 (m), 1064 (sh), 1030 (vs) cm^{-1} ; mp(obsd) 191 °C decomp; 1H NMR (C_6D_6) δ 0.89–0.96 (3 H, m), 4.42–4.48 (5 H, 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.

Preparation of $D^{H_{4-n}}D^{Fe_n}$. Following the above procedure for the preparation of D^{Fe_4} , 3.0 g (12.5 mmol) of D^H_4 were heated at 145 °C in decahydronaphthalene with 6.0 g (8.4 mmol) of $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ for 22 h. The cooled solution was filtered and chromatographed on silica gel. Decalin, ferrocene, and unreacted D^H_4 (traces) were eluted with 300 mL of hexanes. Partially substituted compounds $D^{H_{4-n}}D^{Fe_n}$ 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, and dried in vacuo. Only the third fraction was not entirely soluble in hexanes and afforded 0.27 g (2.3%) of completely substituted D^{Fe_4} . The first fraction afforded 1.35 g of a very

viscous yellow liquid ($n = 2.3$). The second fraction gave 3.04 g of a yellow viscous product ($n = 2.9$) and the third fraction after removal of D^{Fe_4} 1.32 g of a yellow viscous solid ($n = 3.1$). All products were very soluble in hexanes, and attempts to separate by fractional recrystallization at low temperature were unsuccessful. All fractions were air stable when dry but decomposed slowly in solution.

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

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

$D^{H_{4-n}}D^{Fe_n}$ ($n = 3.1$): IR (hexanes) 2140 (m), 2005 (vs), 1950 (sh), 1946 (vs), 1254 (sh), 1249 (s), 1065 (sh), 1049 (vs, br) cm^{-1} ; 1H NMR (C_6D_6) δ 0.39–0.43 (1.0 H, m), 0.84–0.98 (3.1 H, m), 4.29–4.48 (6.7 H, m), 5.2 (0.15 H, 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.

Preparation of $D^{Co_1}D^{Fe_3}$. The fraction $n = 3.1$, 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 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 milligrams 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 of the 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 recooled to –20 °C for 48 h. The red solution was decanted from the precipitated yellow solid, and the product 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 and the red band ($Co_4(CO)_{12}$) afforded 0.21 g (14%) of product as a light yellow wax.

$D^{Co_1}D^{Fe_3}$: 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 0.78–1.14 (3.8 H, m), 4.32–4.48 (5 H, 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).

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