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A ^{13}C NMR Study of Several Perphenylated Polysilanes and Cyclo-1,1-bis(h^5-cyclopentadienyl)titana-2,2,3,3,4,4,5,5-octaphenylpentasilane*

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The ^{13}C NMR spectra of decaphenylcyclopentasilane, (I), 1,1,2,2,3,3,4,4-octaphenyltetrasilane, (II), 1,1,2,2,3,3,4,4-octaphenyl-1-chlorotetrasilane, (III) and the metallocycle, cyclo-1,1-bis(h^5-cyclopentadienyl)titana-2,2,3,3,4,4,5,5-octaphenylpentasilane, (IV), were obtained and assignments based on the ^{13}C–^{1}H coupled ^{13}C NMR spectra of (I) and (III). For compounds (I) and (III) both one bond, J_1, and three bond, J_3, ^{1}H–^{13}C coupling constants were observed and found to be 159 and 6.8 Hz respectively. The ^{13}C NMR spectra of (III) and (IV) were assigned based on a comparison of the spectra to those of (I) and (II).

Introduction

Previous ^{13}C NMR data for phenylsilane species has been limited to reports of the spectra of monosilane species [1–3], and references therein. As part of a continuing series of investigations in the laboratory* [4, 5] concerning the interactions of various polysilanes with transition metal compounds, we have had occasion to examine the heretofore unreported ^{13}C NMR spectra of a series of perphenylated polysilanes, both linear and cyclic, and of a cyclometallopolysilane.

Results and Discussion

The ^{13}C–^{1}H coupled and decoupled NMR spectra for decaphenylcyclopentasilane (I) and 1-hydrido-4-chlorooctaphenyltetrasilane, (III), were recorded as well as the ^{13}C{^{1}H} NMR spectra of 1,4-dihydrido-octaphenyltetrasilane (II) and the metallocycle, cyclo-1,1-bis(h^5-cyclopentadienyl)titana-2,2,3,3,4,4,5,5-octaphenylpentasilane(IV). The ^{13}C NMR spectrum of octaphenylcyclotetrasilane was not obtained due to its insolubility in all solvents other than benzene derivatives.

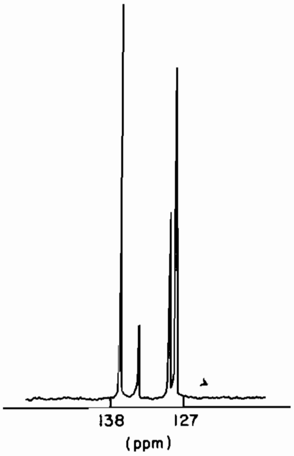
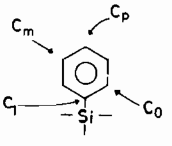


Fig. 1. ^{13}C{^{1}H} NMR spectrum of $Si_5(C_6H_5)_{10}$ in $CDCl_3$.

^{13}C assignments for (I) and (II) were based on first order analysis of the proton coupled and decoupled NMR spectra. ^{13}C assignments for (III) and (IV) were based on a comparison of the ^{13}C{^{1}H} spectra of (III) and (IV) with those of (I) and (II).

Decaphenylcyclopentasilane, (I)

The ^{13}C{^{1}H} NMR spectrum of (I), in $CDCl_3$, is shown in Fig. 1. Four resonances are seen at 137.8, 134.5, 128.5, and 127.4 ppm downfield from TMS and have been assigned to the carbon *ortho* to C_1, where C_1 denotes the carbon bonded directly to silicon, to C_1, to C_p, where C_p is the carbon *para* to C_1, and to C_m, which is the carbon *meta* to C_1, respectively.



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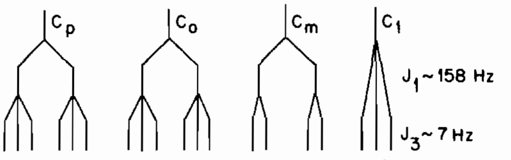

Fig. 2. Expected one and three bond ^{13}C–^{1}H couplings for $Si_5(C_6H_5)_{10}$.

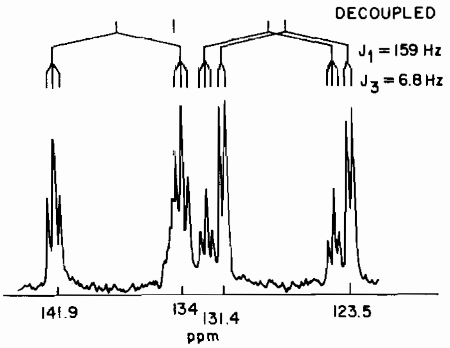

Fig. 3. ^{13}C–^{1}H NMR spectrum of $Si_5(C_6H_5)_{10}$ in $CDCl_3$.

For (I) all of the phenyl groups are equivalent and the molecule is considered as a monosubstituted benzene, where C_1, C_O, C_m, and C_p refer to the carbons of the phenyl ring identified in the drawing. These designations will hold throughout the discussion. In ^{13}C NMR spectroscopy of these types of systems, three types of spin couplings are observed, one, two, and three bond ^{1}H–^{13}C couplings, where J_1, J_2, and J_3 refer to the couplings, respectively. In general the magnitude of these couplings is $J_1 >> J_3 > J_2$ [6]. J_2 typically is ~1Hz for monohalobenzenes [7] and is usually not observed, except under high resolution conditions. All carbons in (I) except C_1 have H bonded directly to them; therefore, all one bond ^{13}C–^{1}H couplings yield doublets, except for C_1. In addition to the one-bond ^{13}C–^{1}H interaction, a three-bond ^{13}C–C–C–^{1}H coupling is expected, with $J_1 >> J_3$. Thus each component of the three doublets expected for C_O, C_m, and C_p will be further split. A three-bond coupling involving C_1 is also expected, but since C_1 is a quaternary carbon with low intensity, such coupling may not have sufficient intensity to be observed. The expected one- and three-bond couplings for (I) are summarized in Fig. 2. The triplet for C_1 arises from the coupling of the two protons bound to the C_m's three bonds away. Thus since no one-bond coupling is expected, one should observe a triplet of 1:2:1 intensity for C_1 in the coupled spectrum. For the *ortho* carbon, C_O, the three-bond coupling will be between C_O and the H bound to the other C_O, three bonds away, and to the proton bound to the *para* carbon, C_p, three bonds away. Thus if the two three-bond interactions have similar coupling constants, one expects each component of the doublet arising from J_1 to be split into a 1:2:1 triplet by the three-bond interaction. The *meta* carbon, C_m, can couple only to the proton on the other *meta* carbon three bonds away. The *para* carbon would show a three-bond coupling to the protons bound to the two *ortho* carbons, leading to a 1:2:1 triplet for each component of the doublet arising from the one-bond interaction. In summary, one expects, for (I), a triplet for C_1, a doublet of triplets for C_O, a doublet of doublets for C_m, and a doublet of triplets for C_p. The observed proton coupled ^{13}C NMR spectrum of (I) is reproduced in Fig. 3 and matches the expected pattern. Superimposed above the spectrum is a stick diagram indicating the positions of the four resonances observed in the decoupled spectrum and the observed one- and three-bond spin interactions leading to the observed spectrum. All one-bond coupling constants, J_1, were found to be 159 Hz, and all three-bond coupling constants, J_3, were found to be 6.8 Hz. These values are consistent with those observed for monohalogenated benzenes [7]. The doublet of doublets is assigned to the *meta* carbon, C_m, therefore one may clearly assign the resonance at 127.4 ppm, Fig. 1, to the *meta* carbons of (I). The smaller doublet of triplets is due to the para carbon, C_p, while the larger is due to the *ortho* carbon, C_O, on the basis of their intensities. Because there are two C_Os for each C_p, the larger doublet of triplets is assigned to C_O. Therefore the absorption at 128.5 ppm, Fig. 1, is assigned to C_p, while that at 137.8 ppm is attributed to C_O. The expected signal for C_1 is not observed in the coupled spectrum because it is obscured by the one-bond coupling of the *ortho* carbon. The assignment of the resonance at 134.5 ppm to C_1, in the decoupled spectrum, is therefore made by elimination. The assignment is confirmed by examination of the relative intensities of the ^{13}C absorbances, Fig. 1. The resonance assigned to C_1 is the least intense and this is expected because C_1 is a quaternary carbon and, as such, should appear with lowest intensity [7]. Thus all of the resonances observed have been unambiguously assigned and the coupling constants, $J_1 = 159$ and $J_3 = 6.8$ Hz, determined.

1,4-Dihydridooctaphenyltetrasilane, II

In order to determine if significant differences exist in the ^{13}C NMR spectra of cyclic and linear perphenylated polysilanes, the ^{13}C NMR spectrum of two linear polysilanes were examined. The $^{13}C\{^{1}H\}$ NMR spectrum of the linear polyphenylated tetrasilane, $1\text{-}4H_2Si_4Ph_8$, is reproduced in Fig. 4. Eight resonances are observed between 127 and 137 ppm downfield from TMS in $CDCl_3$. For this linear tetrasilane there are two distinct sets of phenyl rings, four equivalent terminal phenyl moieties and a second set of four equivalent internal phenyl rings. One would expect to observe eight resonances in the

TABLE I. Comparison Spectral Data for the $^{13}C\{^1H\}$NMR Spectrum of $Si_5(C_6H_5)_{10}$, (I), and $H_2Si_4(C_6H_5)_8$, (II).

$Si_5(C_6H_5)_{10}$			$H_2Si_4(C_6H_5)_8$		
Chemical Shift (PPM)	Relative Intensity	Assignment	Chemical Shift (PPM)	Relative Intensity	Assignment
137.8	5.2	C_0	137.0	7.4	C_0-internal
			136.3	7.8	C_0-terminal
134.5	1.0	C_1	134.5	1.0	C_1-internal
			133.4	1.4	C_1
			133.2	1.6	
			129.0	4.8	C_p-terminal
128.5	2.4	C_p	128.7	4.4	C_p-internal
127.4	4.3	C_m	127.7	13.0	C_m

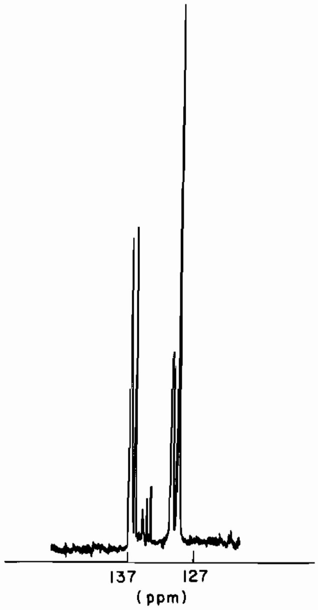

Fig. 4. $^{13}C\{^1H\}$ NMR spectrum of $H_2Si_4(C_6H_5)_8$ in $CDCl_3$.

decoupled spectrum, two each for C_0, C_1, C_m, and C_p. A comparison between the observed $^{13}C\{^1H\}$ spectrum of 1,4-H_2-Si_4Ph_8, (II), and the previously discussed spectrum of (I), is shown in Table I and forms the basis for the tentative assignments. The ^{13}C NMR spectrum of (II) contains two resonances at 137.0 and 136.3 ppm of nearly equal intensity and are assigned to C_0, based on comparison of these chemical shifts to that of C_0 of (I). In like manner the two resonances at 129.0 and 128.7 ppm are assigned to C_p of (II). The very intense resonance at 127.7 coincides with the C_m resonance of (I) and is assigned as such. Although two resonances are expected for C_m, only one is observed and, from its intensity, it seems likely that this resonance is for both sets of C_ms of (II); *i.e.*, the *meta* carbons either are magnetically equivalent or have chemical shifts too close to each other to be resolved into the expected two resonances. There remain three resonances of low intensity, 134.5 133.4, and 133.2 ppm that have yet to be explained. Their low intensity, relative to the other resonances, indicate they belong to quaternary carbons (C_1). However, only two such resonances should be observed. One may infer from molecular models of (II) that the molecule is extremely crowded and a high barrier to rotation about the C–Si bonds probably exists. This may favor certain very specific orientations of the phenyl rings which would be felt most by those carbons bound directly to the silicon backbone. This may account for what appears to be an extra ^{13}C resonance.

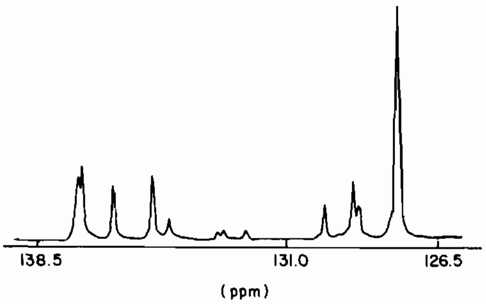

Fig. 5. $^{13}C\{^1H\}$ NMR spectrum of $HSi_4(C_6H_5)_8Cl$ in $CDCl_3$.

Assignment of the two C_p ^{13}C resonances of (II) to internal and terminal C_p is possible by comparison of the C_p resonances to that of (I). This assigns the C_p at 128.7 ppm of (II) to an internal C_p and the 129.0 ppm C_p resonance of (II) to a terminal phenyl ring because the chemical shift of the internal C_p should be similar to that observed for the C_p of (I). By a similar comparison the C_0s of (II) are assigned as 137.0 ppm to C_0 internal with 136.3 ppm to C_0 terminal. Finally, the C_1 resonance of (II) as 134.5 ppm corresponds to an internal C_1.

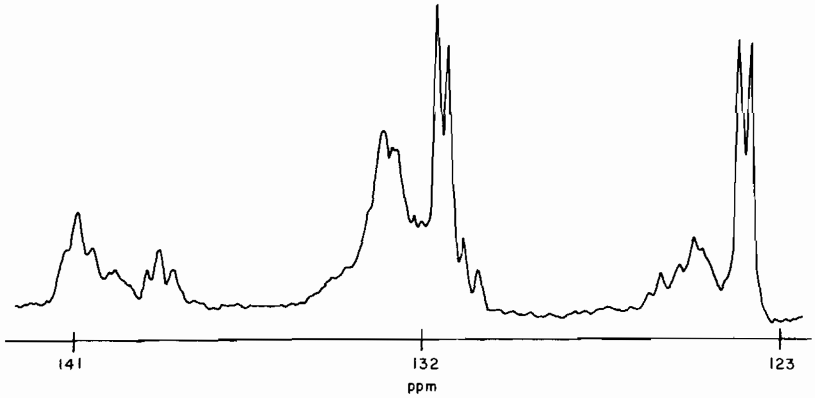

Fig. 6. ^{13}C–^{1}H NMR spectrum of $HSi_4(C_6H_5)_8Cl$ in $CDCl_3$.

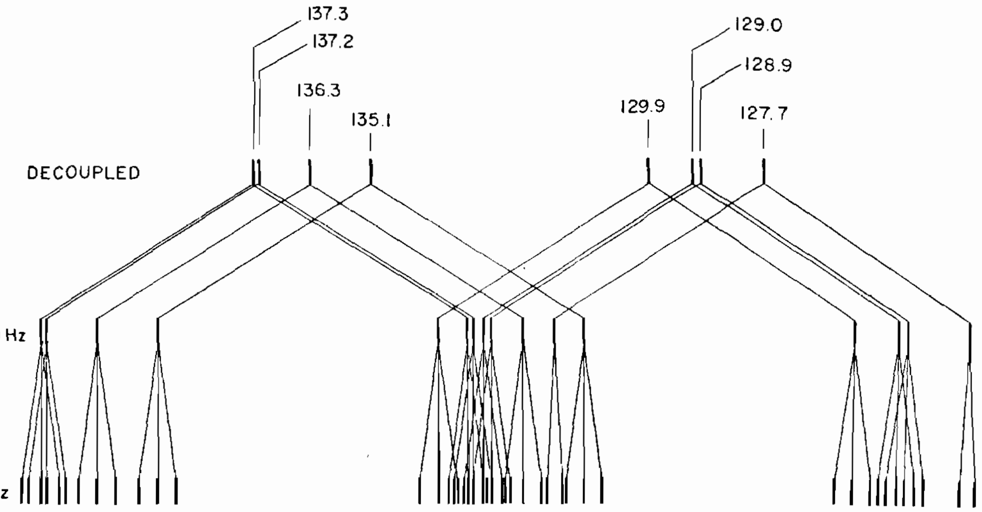

Fig. 7. Expected pattern for ^{1}H coupled ^{13}C NMR spectrum of $HSi_4(C_6H_5)_8Cl$.

TABLE II. $^{13}C\{^{1}H\}$ NMR Spectral Data for $HSi_4(C_6H_5)_8Cl$, (III).

Chem. shift (PPM)	Relative Intensity	Assignment
137.3	7.5	C_0-internal
137.2	9	C_0-internal
136.3	6.8	C_0-H terminal
135.1	8.0	C_0-Cl terminal
134.6	2.5	C_1-internal
133.1	1.0	C_1internal
132.9	1.2	C_1-internal
132.3	1.2	C_1-internal
129.9	4.5	C_p-Cl terminal
129.0	7.5	C_p-internal
128.9	4.2	C_p-H terminal
127.7	28.5	C_m

1-Hydrido-4-chlorooctaphenyltetrasilane, (III)

The $^{13}C\{^{1}H\}$ NMR spectrum of (III) is shown in Fig. 5, summarized in Table II, and consists of twelve distinct resonances between 138 and 127 ppm downfield from TMS in $CDCl_3$. The first four resonances at 137.3, 137.2, 136.3, and 135.1 ppm are assigned as C_0 resonances. There are four such resonances because there are four dinstict sets of phenyl rings in the molecule: a H-terminal set, a Cl-terminal set, and two different sets of internal rings. Thus the twelve observed resonances may be grouped into four sets: one set of four resonances for C_0, one set of four C_1 resonances, one set of three C_p resonances and a single resonance for C_m. A comparison of the spectrum of (III) to the previously discussed spectra of (I) and (II) allow tentative assignments to be made. Resonances at 137.3 and 137.2 ppm represent C_0s in a similar environment and are assigned as C_0s of internal phenyls. This assignment is supported

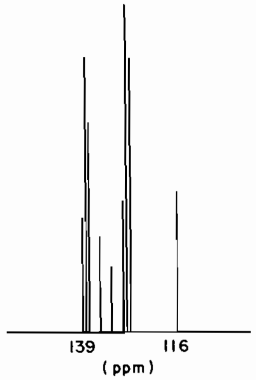

Fig. 8. $^{13}C\{^1H\}$ NMR spectrum of $(h^5\text{-}C_5H_5)_2\overline{TiSi(C_6H_5)_2\text{-}[Si(C_6H_5)_2]_2Si}(C_6H_5)_2$ in d_6-acetone.

TABLE III. $^{13}C\{^1H\}$ NMR Spectral Data for $(h^5\text{-}C_5H_5)_2\text{-}\overline{TiSi(C_6H_5)_2[Si(C_6H_5)_2]_2Si}(C_6H_5)_2$, (IV)

Chemical Shift (PPM)	Relative Intensity	Assignment
139.6	1.7	C_p
138.7	4.1	C_0
138.3	3.1	C_0
135.4	1.4	C_1
132.0	1.0	C_1
129.5	1.9	C_p
128.4	4.9	C_m
127.9	4.1	C_m
116.4	2.1	Cyclopentadienyl

by comparison of these resonances to the internal C_0s of (II) found at 137.0 ppm. The resonance at 136.3 ppm, for (III), corresponds to a H-terminal resonance of (II) at 136.3 ppm and is assigned to the C_0 of the H-terminal phenyls of (III). The remaining C_0 resonance of (III) at 135.1 ppm is assigned to Cl-terminal phenyls. The intense resonance at 127.7 ppm in (III) is assigned to C_ms of the molecule. As in the case of (II) all the C_ms of (III) are equivalent. Within the C_p set of (III) there are three resonances: one for H-terminal, one for Cl-terminal and one for all internal C_ps of the phenyl rings of (III). The 129.0 ppm C_p of (III) is assigned to all internal C_ps of (III) while the 128.9 ppm resonance is assigned to H-terminal C_ps and the resonance at 129.9 is assigned to Cl-terminal C_ps. These assignments are based on several factors. First, the 129.0 ppm resonance is about twice the area as the other C_ps and should correspond to twice the number of nuclei. Because internal C_ps should have nearly the same environment, this resonance was assigned to internal C_ps. Four terminal C_ps should be in an environment similar to terminal rings found in (II). Thus, the 128.9 ppm resonance should correspond to H-terminal C_ps while C_ps on terminal Cl phenyls should be a different chemical shift than all the others. As a result the 129.9 ppm resonance of (III) is assigned to C_ps of Cl terminal phenyls. Finally the C_1 resonances must be assigned. Resonances at 133.1 and 132.9 ppm are probably internal C_1s because their environments are more nearly the same. C_1s at 134.6 and 132.3 ppm are assigned to terminal C_1s. Assignment of these to Cl- and H-terminal phenyls is not easy because the H-terminal C_1 of (II) could not be unambiguously assigned.

In an effort to confirm these assignments, the ^1H–^{13}C coupled spectrum of (III) was examined and is reproduced in Fig. 6. As in the case of (I), C_0s and C_ps yield doublets of triplets, C_ms yield doublets of doublets and coupling of C_1s is not observed. The spectrum is a series of overlapping doublets of triplets from C_0 and C_p carbons and a prominent doublet of doublets from C_ms. J_1 and J_3 values, calculated from the doublet of doublets, are 159 and 6.8 Hz respectively and confirm the assignment of the 127.7 ppm resonance as the C_m resonance. The values of J_1 and J_3 in the spectrum of (III) are identical to those observed for J_1 and J_3 in (II). A stick diagram using the decoupled spectrum of (III) and the observed J_1 and J_3 values was constructed and is shown in Fig. 7. Its appearance corresponds closely to that of the experimental spectrum and confirms the assignment of the resonances for C_0, C_p and C_m carbons.

Using these polysilane systems as models, the ^{13}C NMR spectrum of the metallocyclosilane, (IV), was examined.

1,1-Bis(h⁵-cyclopentadienyl)titana-2,2,3,3,4,4,5,5-octaphenyltetrasilane, (IV)

The $^{13}C\{^1H\}$ NMR spectrum of (IV) is reproduced in Fig. 8. This spectrum, obtained after 80000 scans in d_6-acetone, contains nine distinct resonances, as one would expect for a cyclic structure. One resonance will result from the ten equivalent carbons of the cyclopentadienyl ligands bonded to Ti, one set of four resonances should arise from the carbons of the phenyl rings bound to the silicon attached to Ti and a second set of four resonances from the remaining phenyl rings. The nine resonances observed, tabulated in Table III, are in accord with this expectation. Tentative assignments of the observed resonances are based on the trends established for the ^{13}C NMR data obtained for (I) and (II). Due to the limited solubility of (IV) in acetone, and its decomposition in other potential solvents, it was not possible to obtain the ^{13}C–^1H coupled NMR spectrum.

The resonance appearing at 116.4 ppm may be assigned with confidence to the resonance of the cyclopentadienyl carbons. Such carbons almost always occur upfield from phenyl resonances [6], with the resonance for Cp_2TiCl_2 occurring at 120 ppm [8]. Neither (I) nor (II) have resonances below 127 ppm. The remaining eight absorptions occur between 127 and 139 ppm and are in the range observed for phenyl on silicon. If one assumes that the spectrum of (IV) follows the pattern observed for (I) and (II) tentative assignments for the remaining resonances are possible. The absorptions at 135.4 and 132.0 ppm are the least intense and of similar chemical shift as the C_1 of (I) and (II). Based on the chemical shift, and intensities, these two absorptions are C_1 resonances of (IV). Assignment of the remaining six lines is more difficult. For (IV) there are twice as many C_0 and C_m as C_p, therefore, assuming similar relaxation times, the resonances for C_0 and C_m should be about twice as intense as those for C_p. Comparing chemical shifts of the resonances of (I), (II), and (IV), and their relative intensities, the resonances at 128.4 and 127.9 ppm are assigned to C_ms of (IV) and those at 138.7 and 138.3 ppm to C_0s. The remaining absorptions at 139.6 and 129.5 ppm are assigned to the C_ps of (IV). One immediately notes the large difference in chemical shifts for the two C_ps. The C_p at 129.5 ppm compares well with that of (I) and (II) in terms of chemical shift and intensity while the C_p assigned at 139.6 does not. It matches a C_p in relative intensity but not in chemical shift, being deshielded almost 10 ppm from the other C_p resonances. The 129.5 ppm resonance is probably for C_ps furthest from the Ti. Their chemical environment is more like that of C_ps in (I) and (II), and they should have a comparable chemical shift. The C_p at 139.6 ppm would therefore correspond to C_ps closest to Ti. The downfield shift of these carbons could be the result of either steric or electronic effects. Steric effects seem unlikely because the cyclopentadienyl ligands bound to Ti would have to approach the *para* carbons for deshielding to occur. Molecular models of (IV) indicate that these ligands are not in close proximity to the C_ps of the phenyl rings. An electronic effect, however, may explain the observed deshielding. Appropriate overlap of the empty 3d orbitals on Ti and Si with the filled pπ orbitals of phenyls is possible [4]. Such an interaction would allow redistribution of electron density in the molecule from the phenyl rings through the Si3d orbital towards the Ti 3d orbitals. This pπ–dπ interaction could act to add stability to the Ti–Si bond and to deshield C_p. Wirthlin [7] has observed that chemical shifts of C_ps correlate well with the total charge density, calculated by CNDO, while C_0 s shows no such correlation. C_ps, therefore, are more sensitive to changes in electron density than C_0 and C_m.

Experimental

Equipment

^{13}C Fourier Transform NMR spectra were obtained at 20 MHz using a Bruker WP80 spectrometer as solutions in 10 mm OD tubes from Wilmad Glass. Unless otherwise stated all spectra were run using deuterated solvents with TMS as an internal reference.

Reagents-Decaphenylcyclopentasilane, $Si_5(C_6H_5)_{10}$, was prepared from diphenyldichlorosilane (PCR Inc., Gainesville, FL), according to the literature [9]. *1-Hydrido-4-chlorooctaphenyltetrasilane,* $HSi_4(C_6H_5)_8Cl$, was prepared from octaphenylcyclotetrasilane and dry HCl according to the literature [10]. *1,1,2,2,3,3,4,4-octaphenyltetrasilane,* $HSi_4(C_6H_5)_8H$, was prepared by the hydride reduction of 1,4-dichlorooctaphenyltetrasilane by an adaptation of the method reported for the synthesis of 1,1,2,2,3,3,4,4-octamethyltetrasilane [11].

To a stirred suspension of a fourfold excess of $LiAlH_4$ in dry THF, under dry N_2, a dry THF solution of 4 g, 5 mmol, of 1,4-dichlorooctaphenyltetrasilane was added dropwise. The reaction was exothermic and external heating was not required to maintain reflux. After the addition of the silane was complete, heat was applied and the reaction mixture was refluxed for two hours. The solution was then cooled to room temperature, still under dry N_2 and then filtered in air to remove undissolved $LiAlH_4$; 15 mL of ethanol was added slowly to the filtrate to destroy any remaining $LiAlH_4$. The filtrate was then evaporated to dryness and the residue dissolved in warm benzene, filtered and petroleum ether added until the filtrate became cloudy whereupon the solution was chilled overnight. The white crystalline product was collected by filtration and dried *in vacuo*. The yield was 2.9 g (80%) with a melting point of 160–162 °C (lit. 161°) [12]. *1,1-Bis(h^5-cyclopentadienyl)titana-2,2,3,3,4,4,5,5-octaphenyltetrasilane,* $(h^5\text{-}C_5H_5)_2Ti\text{-}Si(C_6H_5)_2[Si(C_6H_5)_2]_2Si\text{-}(C_6H_5)_2$, was prepared according to a previously reported procedure [13].

Acknowledgement

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