J. Am. Chem. Soc. **1980,** *102,* 6989–6992 6989

Organometallic Chemistry. 17. ^{29}Si and ^{13}C NMR Spectroscopic Study of Phenylsilyl Anions. The Question of Si–C $p\pi$–$p\pi$-Electron Delocalization and Comparison with Related Carbanions

George A. Olah* and Ronald J. Hunadi

Contribution from the Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California, 90007. *Received March 24, 1980*

Abstract: A series of phenylsilyl anions, including Ph_3SiLi, $Ph_2MeSiLi$, $PhMe_2SiLi$, and Me_3SiK, has been studied by ^{13}C and ^{29}Si NMR spectroscopy with particular emphasis to determine the effective delocalization of charge away from the silicon atom. The ^{13}C and ^{29}Si data are discussed in this regard and evaluated as indicative of the trend of the delocalization of charge. As compared to the corresponding carbanions, the delocalization is reduced by a factor of about 10 for Ph_3SiLi and 4 for $Ph_2MeSiLi$ and $PhMe_2SiLi$, indicating the substantially decreased degree of Si—C $p\pi$–$p\pi$ interaction and thus Si═C character, as compared to carbanions showing strong C—C $p\pi$–$p\pi$ interaction and thus double-bonded quinoidal character.

Introduction

The question of whether there is Si–C $p\pi$–$p\pi$-electron delocalization in the triphenylsilyl anion, $Ph_3Si^-M^+$ (where M = Li, K, Na), has stimulated studies by different physical methods over the past 15 years.[1-7] The corresponding carbanion analogue has been shown to contain considerable π-electron delocalization as evidenced by UV, ^1H, and ^{13}C NMR spectroscopy.[8-13] Delocalized charges in phenyl-substituted anions and cations tend to produce highly colored species. Our interest in ionic organic intermediates and the highly colored nature of the triphenylsilyl anion, i.e., $Ph_3Si^-M^+$, prompted us to reinvestigate this ion by ^{29}Si and ^{13}C NMR spectroscopy to determine if, indeed, there is delocalization of the charge from silicon into the phenyl rings.

Waack and Doran[1] in 1965 showed that the UV spectrum of (triphenylsilyl)lithium consisted of a strong absorption maximum at 335 nm (log $\epsilon \sim 4.0$). Using valence bond arguments, they concluded that the extent of conjugation in Ph_3SiLi was less than in the corresponding carbon analogue in accordance with the greater tendency of first-row elements to form double bonds. Since d-orbital participation was apparently negligible in the case of Ph_4Si and Ph_3SiH, it was proposed that it is not likely to be significant in Ph_3SiLi. Therefore, the higher energy of d orbitals, compared to p orbitals, should favor $p\pi$ conjugation in Ph_3SiLi. Examination of Ph_3SiLi by ^1H NMR spectroscopy gave additional evidence for electron delocalization since the chemical shifts of (triphenylsilyl)lithium were found to be shielded (by $\sim$0.3–0.6 ppm) from those of its neutral analogues, tetraphenylsilane or triphenylsilane. This observation indicated that there is decreased $p\pi$–$p\pi$ conjugation as compared to Ph_3CLi.

Cox et al.[3] investigated the proton and lithium-7 NMR spectra of triphenyl metal (of group 4) lithium compounds and found that the proton chemical shifts were consistent with electron donation from the group 4 atom into the phenyl rings. Since investigations of the ^1H and ^{13}C NMR spectra of monosubstituted benzenes[14,15] and carbocations[16] have shown that the major factor influencing the para-hydrogen and para-carbon shifts (both shifts exhibit the same trend) was the resonance effect, it has been suggested that these shifts were controlled by the π-electron density at the para-carbon atoms. Noting that, besides resonance and inductive effects, electric field and magnetic anisotropy can strongly influence the meta and ortho shifts,[15] Cox et al. only considered the para shifts in his analysis. He found that the para protons were shielded in the opposite order from that expected solely on the basis of π-bonding trends of the group 4 atoms. His ^7Li NMR data indicated that the degree of electron delocalization into the phenyl rings was controlled by the degree of association between lithium and the group 4 atom and did not follow the established trend for the interaction of the group 4 atoms with a π system. These data, however, did not allow the elucidation of the mechanism of electron delocalization ($d\pi$ or $p\pi$ conjugation).

A. G. Evans[17] argued that the fact that λ_{max} in the UV spectrum decreases markedly from Ph_3CLi to Ph_3SiLi indicated that conjugation between Si and the phenyl groups in Ph_3SiLi is very much less than that between C and the phenyl groups in Ph_3CLi. He concluded that the conjugation between Si and the phenyl groups must be practically zero since the replacement of phenyl by methyl has no effect on the λ_{max}, indicating that the phenyl groups are not conjugated with each other through silicon.

Results

In the present study, we examined the hitherto largely unreported ^{13}C and ^{29}Si NMR parameters of Ph_3SiLi, $Ph_2MeSiLi$, $PhMe_2SiLi$, and Me_3SiK and present unequivocal data supporting the conclusion that the $p\pi$–$p\pi$ delocalization in phenylsilyl anions is greatly reduced compared to their carbanion analogues.[18] This is based on the comparison of the chemical shifts and coupling

---

(1) For part 16, see: Olah, G. A.; Liang, G.; Yu, S. *J. Org. Chem.* **1977**, *42*, 4262.

(2) (a) Waack, R.; Doran, M. A. *Chem. Ind.* **1965**, 564. (b) Evans, A. G.; Hamid, M. A.; Rees, N. H. *J. Chem. Soc.* **1971**, 1110.

(3) Cox, R. H.; Janzen, E. G.; Harrison, W. B. *J. Magn. Reson.* **1971**, *4*, 274.

(4) Glocking, F. *Q. Rev., Chem. Soc.* **1966**, *20*, 45.

(5) Urry, G. "Radical Ions"; Kaiser, E. T., Kevan, L., Eds.; Interscience: New York, 1968; p 275.

(6) Mitchell, K. A. R. *Chem. Rev.* **1969**, *69*, 157.

(7) Eaborn, C. "Organosilicon Compounds"; Butterworths: London, 1960; p 113.

(8) Longuet-Higgins, H. C.; Pople, J. A. *Proc. Phys. Soc., London, Sect. A* **1955**, *68*, 501. Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemist"; Wiley: New York, 1961; p 226. Jaffe, H. H.; Orchin, M. "Theory and Applications of Ultraviolet Spectroscopy"; Wiley: New York, 1962; p 456.

(9) Waack, R.; Doran, M. A.; Baker, E. B.; Olah, G. A. *J. Am. Chem. Soc.* **1966**, *88*, 1272.

(10) Waack, R.; Doran, M. A. *J. Am. Chem. Soc.* **1963**, *85*, 4042.

(11) Waack, R.; Doran, M. A. *J. Am. Chem. Soc.* **1963**, *85*, 1651.

(12) Sandel, V. R.; Freedman, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 2328.

(13) Takahashi, K.; Kondo, Y.; Asami, R.; Inoue, Y. *Org. Magn. Reson.* **1974**, *6*, 580.

(14) Spiesche, H.; Schneider, W. G. *J. Chem. Phys.* **1961**, *35*, 731.

(15) Emsely, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 2; Pergamon Press: New York, 1966; p 752.

(16) (a) Olah, G. A.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 3137. (b) Olah, G. A.; Westerman, P. W.; Forsyth, D. A. *Ibid.* **1975**, *97*, 3419.

(17) Evans, A. G.; Hamid, M. A.; Rees, N. H. *J. Chem. Soc.* **1971**, 1110.

(18) The ^{29}Si NMR chemical shifts of Ph_3SiK and Ph_3SiLi have been reported by Von E. Uhlig et al.,[19] but our value for Ph_3SiLi did not agree with their value. We attribute the difference to a misassignment on Von E. Uhlig's part since our results were consistently reproducible.

(19) Uhlig, Von E.; Hipler, B.; Muller, P. *Z. Anorg. Allg. Chem.* **1978**, *442*, 11.

0002-7863/80/1502-6989$01.00/0 © 1980 American Chemical Society

Table I. ^{13}C and ^{29}Si NMR Shifts of Silyl Anions and Silanes

	^{13}C shifts[a]					coupling const[b] $J_{^{13}C-H}$					
	ipso	ortho	meta	para	other carbon (-Me)	ortho	meta	para	ortho-meta	Me	^{29}Si Shifts[a]
Ph_3SiCl[c]	137.4	135.5	128.0	129.9		159.2	156.9	159.1	7.5		−15.3[c]
$Ph_2MeSiCl$[c]	134.8	134.2	128.2	130.6	0.9	162.0	167.7	159.8	7.2	115	10.0[c]
$PhMe_2SiCl$[c]	136.8	133.7	128.7	130.9	2.5	158.6	162.6	159.9	7.3	120	19.8[c]
Me_3SiCl[c]					3.2[f]					121	29.8[c,i]
$Ph_3Si^-Li^+$ [d]	145.0	136.1	127.5	128.4		155.8	155.8	158.7	7.4		−30.0[d]
$Ph_2MeSi^-Li^+$ [d]	160.3	135.4	126.8	124.0	5.1	153.4	155.0	157.2	7.9	112	−20.5[d]
$PhMe_2Si^-Li^+$ [d]	166.1	134.0	126.8	123.1	8.1	153.7	153.1	155.7	7.8	115	−22.1[d]
$Me_3Si^-K^+$ [g,m]					4.2					115	−34.4[g]
Ph_3SiH[c]	133.7	136.1	128.4	130.1		155.3	157.1	159.8	7.3		−17.7[c]
Ph_2MeSiH[e]	135.2	134.8	127.9	129.5							−18.5[j]
$PhMe_2SiH$[e]	137.3	134.0	127.9	129.2							−17.6[j]
Me_3SiH					−2.6[h]					119	−17.5[j]
$Me_3SiSiMe_3$[g]					−3.3					120[k]	−19.7[g]

[a] Relative to Me_4Si, in ppm. [b] In hertz. [c] In THF, internal Me_4Si as standard. [d] In THF, external Me_4Si as standard. [e] As neat compound, see ref 21. [f] R. Harris reports 3.40, see ref 20. [g] In HMPA. [h] Reference 20. [i] Reference 22 reports 29.8. [j] Reference 23. [k] Reference 32. [m] HMPA used as the internal standard.

Table II. ^{13}C NMR Shifts of Analogue Carbanions[a]

	α	ipso	ortho	meta	para	other (Me–)
Ph_3CH[b,c]	58.2	145.2	129.5	130.7	127.5	
Ph_2CH_2 [b,c]	42.6	142.3	129.2	129.9	126.9	
$PhCH_3$[b,c]	21.5	138.5	129.0	129.7	126.1	
CH_4 [b,d]	−2.3					
Ph_2MeCH[e]	46.1	147.5	128.8	129.6	127.2	23.2
$PhMe_2CH$[f]	34.4	148.6	126.5	128.5	126.0	24.1
$Ph_3C^-Li^+$ [b,c]	91.0	150.5	124.4	128.3	113.3	
$Ph_2CH^-Li^+$ [b,c]	78.8	147.7	117.8	128.4	107.2	
$PhCH_2^-Li^+$ [b,c]	36.9	161.5	117.0	128.6	104.7	
$CH_3^-Li^+$ [b,d]	−15.3					
$Ph_2MeC^-Li^+$ [b,g]	81.4	147.0	116.9	127.8	106.8	19.3

[a] Relative to Me_4Si in ppm. [b] In THF. [c] Reference 13. [d] Reference 24. [e] Reference 25, in $CDCl_3$. [f] Reference 26. [g] Reference 27.

constants of the silyl anions with their neutral precursors, related silanes, and carbon analogues.

^{13}C NMR Studies. The ^{13}C shifts for the silyl anions, their precursors, and related model compounds are summarized in Table I. Carbon shifts for the analogous carbon compounds are given in Table II for comparison. The silyl anions Ph_3SiLi, $Ph_2MeSiLi$, and $PhMe_2SiLi$ were obtained from the corresponding chlorides by treatment with Li in THF while Me_3SiK was prepared by the cleavage of $Me_3SiSiMe_3$ by KO-*t*-Bu in HMPA. Details of the preparation of the ions are given in the Experimental Section.

Specific peak assignments were made with the aid of proton decoupled, as well as proton-coupled, spectra. In the proton-coupled spectra, the ipso carbon was readily identified since it appeared as a broadened singlet. The para carbon was distinguished from the ortho and meta carbons by intensity. Analysis of the ^{13}C NMR spectra of other phenylsilyl compounds[28] has shown that the ortho carbon shifts are generally deshielded from those of the meta carbons. This consideration, along with splitting patterns (in the proton-coupled spectra), was used to assign the ortho and meta carbons. Finally, ^{13}C–H coupling constants were also obtained from the proton-coupled spectra. Table III lists the differences in ^{13}C NMR chemical shifts and ^{13}C-H coupling constants between the phenylsilyl anions and the corresponding neutral silanes and chlorosilanes.

^{29}Si NMR Studies. The ^{29}Si NMR shifts for the silyl anions along with the corresponding silanes and chlorosilanes are given in Table I. The spectra were obtained in THF solution unless otherwise noted.

Discussion

^{13}C NMR Studies. Our group[16] and others[14,15] have shown that in substituted benzenes and carbocations, the para-carbon ^{13}C NMR shift is a quantitatively reliable indicator of charge density at this position (provided there is no steric inhibition of resonance interaction). The ortho-carbon shifts are also sensitive to charge density, but additional shielding (γ-substituent effect) must be taken into effect while the meta carbons are relatively insensitive. On the basis of these considerations, it is expected that the ^{13}C NMR shifts of the para carbon of phenyl-substituted anions should be the best indicator of electron delocalization into the phenyl rings in these systems.

Examination of the data listed in Table IV shows that, besides the α-carbons, the largest change in the chemical shifts of carbanions compared to their neutral precursors occurs in the para carbon, where there is observed a shielding of 14–21 ppm. The ipso-carbon shift differences vary from −23 to 5 ppm, whereas that of the ortho carbons is −5 to −12 ppm and of the meta carbons from −1 to −2 ppm. Based on the discussed assumption that the para ^{13}C chemical shift is the best measure of the electron density of a phenyl substituent, we will base the discussion of the extent of delocalization of charge into the phenyl substituent on the extent of the para chemical shift differences between anions and their precursors. For Ph_3CLi vs. Ph_3CH, Ph_2CHLi vs. Ph_2CH_2, and $PhCH_2Li$ vs. $PhCH_3$, $\Delta\delta_{^{13}C}$ (para) values are −14.3, −19.7, and −21.4, respectively. As the ^{13}C NMR shifts of the cumyl anion have not yet been reported, we are not able to make a direct comparison between $PhMe_2CLi$ and $PhMe_2SiLi$. Nonetheless, the $\Delta^{13}C$(para) value for Ph_2MeCLi vs. Ph_2MeCH is −20.4. This shows that, as the number of phenyl rings attached to the carbon bearing the negative charge is reduced, the delocalization of charge per ring is increased.

Table III shows that Δ(para) values for Ph_3SiLi vs. Ph_3SiCl and Ph_3SiLi vs. Ph_3SiH are −1.5 and −1.7 ppm, respectively. When we compare the change in the para-carbon shifts for Ph_3CLi vs. Ph_3CH, we obtain −14.3 ppm (from Table IV). If, as suggested, the Δ(para) chemical shift is a good indicator of the change in charge density, then it is apparent that the delocalization of the charge in the silyl anion Ph_3SiLi is significantly reduced as compared to the carbanion Ph_3CLi since the Δ(para) for Ph_3SiLi is reduced by a factor of ~9–10. Examination of Δ(ipso) for Ph_3SiLi vs. either Ph_3SiH or Ph_3SiCl shows that there is a large deshielding compared to the corresponding carbanion, indicating a significant charge accumulation on the silicon atom of the silyl anion. This indicates that there is no significant contribution from resonance structures **2**. This observation agrees with other

---

(20) Harris, R. K.; Kimber, B. J. *J. Magn. Reson.* **1975**, *17*, 174.

(21) Rakita, P. E.; Srebo, J. P.; Worsham, L. S. *J. Organomet. Chem.* **1976**, *104*, 27.

(22) Schraml, J.; Nuguyen-Duc-Chuy; Chvalousky, U.; Magi, M.; Lippmaa, E. *J. Organomet. Chem.* **1973**, *51*, C5.

(23) Ernst, C. R.; Spialter, L.; Buell, G. R.; Wilhite, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 5375.

(24) van Dongen, J. P. C. M.; van Dijkman, H. W. D.; de Bie, M. J. A. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 29.

(25) Olah, G. A.; Watkins, M. I., unpublished observation.

(26) Lauer, D.; Motell, E. L.; Traficante, D. D.; Maciel, G. E. *J. Am. Chem. Soc.* **1972**, *94*, 5335.

(27) Bank, S.; Sturges, J. S. *J. Organomet. Chem.*, **1978**, *156*, 5.

(28) Nguyen-Duc-Chuy; Chvalousky, V.; Schraml, J.; Magi, M.; Lippmaa, E. *Collect. Czech. Chem. Commun.* **1975**, *40*, 875.

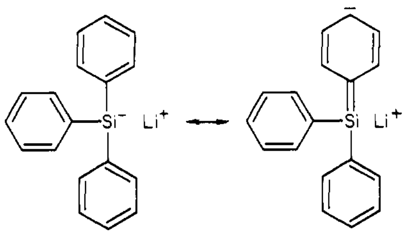
Table III. Changes in Chemical Shifts and Coupling Constants of Silyl Anions vs. Neutral Silanes and Chlorosilanes

	Δ for ^{13}C chem shifts, ppm					Δ for $J_{^{13}C-H}$, Hz				
	ipso	ortho	meta	para	Me	ortho	meta	para	Me	Δ for ^{29}Si
$Ph_3Si^-Li^+$ vs. Ph_3SiCl	+7.6	+0.6	−0.5	−1.5		−4.4	−1.1	−0.4		−14.7
$Ph_3Si^-Li^+$ vs. Ph_3SiH	+11.3	0.0	−0.9	−1.7		+0.5	−1.3	−1.2		−12.3
$Ph_2MeSi^-Li^+$ vs. $Ph_2MeSiCl$	+25.5	+1.2	−1.4	−6.6	+4.2	−8.6	−12.7	−2.6	−3	−30.5
$Ph_2MeSi^-Li^+$ vs. Ph_2MeSiH	+25.1	+0.6	−1.1	−5.4						−2.0
$PhMe_2Si^-Li^+$ vs. $PhMe_2SiCl$	+29.3	+0.3	−1.8	−7.8	+5.5	−4.9	−9.5	−4.2	−6	−41.9
$PhMe_2Si^-Li^+$ vs. $PhMe_2SiH$	+28.8	0.0	−1.0	−6.1						−4.5
$Me_3Si^-K^+$ vs. Me_3SiCl					+1.0				−6	−64.2
$Me_3Si^-K^+$ vs. Me_3SiH					+6.8				−4	−14.7

Table IV. Changes in ^{13}C Chemical Shifts of Carbanions vs. Their Parent Neutral Hydrocarbons

	Δ, ppm					
	α	ipso	ortho	meta	para	Me
$Ph_3C^-Li^+$ vs. Ph_3CH	+32.8	+5.3	−5.1	−2.4	−14.3	
$Ph_2MeC^-Li^+$ vs. Ph_2MeCH	+35.3	−0.5	−11.9	−1.8	−20.4	−3.9
$Ph_2CH^-Li^+$ vs. Ph_2CH_2	+36.2	+5.4	−11.4	−1.5	−19.7	
$PhCH_2^-Li^+$ vs. $PhCH_3$	+15.4	−23.0	−12.0	−1.1	−21.4	
CH_3Li vs. CH_4	−13.0					

spectroscopic determinations of electron delocalization in Ph_3SiLi.[1,3]



1 2

The differences in the para-carbon shifts for $Ph_2MeSiLi$ vs. $Ph_2MeSiCl$, $Ph_2MeSiLi$ vs. Ph_2MeSiH, and Ph_2MeCLi vs. Ph_2MeCH are −6.6, −5.4, and −20.4 ppm, respectively. These $\Delta^{13}C$(para) values indicate that the delocalization for the diphenylmethylsilyl anion $Ph_2MeSiLi$ is reduced by a factor of ~3–4, as compared to the corresponding carbanion. Δ(ipso) values for $Ph_2MeSiLi$ vs. Ph_2MeSiH and $Ph_2MeSiLi$ vs. $Ph_2MeSiCl$ are +25.1 and +25.5, respectively, as compared to −0.5 for Ph_2MeCLi vs. Ph_2MeCH. In the case of $Ph_2MeSiLi$, we would expect the ipso carbon to be more shielded than in Ph_3SiLi since the methyl group is electron donating and does not help in the delocalization of the negative charge so that the two ipso phenyl carbons should effectively experience the effect of more negative charge.

Examination of $PhMe_2SiLi$ vs. $PhMe_2SiCl$ (from Table III) gives Δ(ipso) +29.3, Δ(ortho) +0.3, Δ(meta) −1.8, Δ(para) −7.8, and Δ(Me) +5.5. The ipso carbon is shielded more than the ipso carbon in $Ph_2MeSiLi$ by 3.8 ppm while the para carbon is shielded by 1.3 ppm as compared to that of $Ph_2MeSiLi$. This effect is expected on the basis that in $PhMe_2SiLi$, there are two electron-donating methyl groups, which are causing a larger charge to be built up on the silicon atom. Consequently, there is a larger deshielding of the ipso carbon. Due to the increase in delocalization of negative charge per phenyl ring in the case of $PhMe_2SiLi$, we see a larger shielding of the para-carbon shift. The increase in $\Delta\delta_{^{13}C}$ of the methyl carbon in going from $Ph_2MeSiLi$ to $PhMe_2SiLi$ also substantiates this assumption. Comparison of $PhMe_2SiLi$ vs. $PhMe_2SiH$ gave $\Delta(^{13}C$ ipso) +28.8, Δ(ortho) 0.0, Δ(meta) −1.0, and Δ(para) −6.1.

Since the ^{13}C NMR data for the cumyl anion $PhMe_2CM$, as mentioned, are as of yet unreported, we cannot directly assess the extent of charge delocalization in $PhMe_2SiLi$. Nonetheless, as Δ(para) is −21.4 for $PhCH_2Li$ vs. $PhCH_3$, we can assume that Δ(para) would be ~−20 to −22 ppm. This would indicate that there is decreased delocalization of charge into the phenyl ring of $PhMe_2SiLi$, as compared to $PhMe_2CLi$ by a factor ~3–4.

Examination of the data from Table III shows that Δ(Me) for Me_3SiK vs. Me_3SiCl and Me_3SiK vs. Me_3SiH are +1.0 and +6.8, respectively. As with $Ph_2MeSiLi$ and $PhMe_2SiLi$, the methyl groups are shielded with respect to those of the related chlorosilanes, as expected.

^{29}Si NMR Studies. Although numerous studies using ^{29}Si NMR have appeared in the literature,[21–23,29–31] there are still considerable inconsistancies in the substituent effects on ^{29}Si NMR chemical shifts and coupling constants. Ernst et al.[31] called attention to inconsistencies of ^{29}Si chemical shifts with changes in the substitution of attached phenyl rings in the series, $X-C_6H_4-SiY_3$. Each of the series they studied showed a high degree of linearity to Hammett substituent constants although the slopes were of opposite signs. They concluded, by examination of CNDO/2 calculations vs. the ^{29}Si NMR chemical shifts, that electron densities could not account for the sign changes in the slopes of the Hammett plots. These observations should be kept in mind when the data presented in Tables I and III are examined.

For the chlorosilanes Ph_3SiCl, $Ph_2MeSiCl$, $PhMe_2SiCl$, and Me_3SiCl, there is an increase in the ^{29}Si chemical shifts going from Ph_3SiCl to Me_3SiCl, although the change is not exactly linear. The ^{29}Si shifts of the parent silanes Ph_3SiH through Me_3SiH do not show this effect, and all the chemical shifts are clustered around $\delta_{^{29}Si}$ ~−18 ppm. Thus, no systematic substituent effect is apparent on the sp^2 silicon center. The silyl anions are similar to the silanes in respect to the clustering of their ^{29}Si chemical shifts in the range of $\delta_{^{29}Si}$ −20.5 to −34.5, but the spread is broader. Although the chemical shifts themselves do not follow a linear plot, $\Delta\delta_{^{29}Si}$ of X_3SiM vs. X_3SiCl does follow a nearly linear pattern. $\Delta\delta_{^{29}Si}$ for Ph_3SiLi vs. Ph_3SiCl, $Ph_2MeSiLi$ vs. $Ph_2MeSiCl$, $PhMe_2SiLi$ vs. $PhMe_2SiCl$, and Me_3SiK vs. Me_3SiCl are −14.7, −30.5, −41.9, and −64.2, respectively, indicating that as a methyl group is added (replacing a phenyl group), there is an increase in shielding. This trend does not follow for $\Delta\delta_{^{29}Si}$ of X_3SiM vs. X_3SiH; here the trend is the same for $Ph_2MeSiLi$ through Me_3SiK but $\Delta\delta_{^{29}Si}$ of Ph_3SiLi vs. Ph_3SiH lies much off the line.

Concerning the ^{29}Si NMR shifts themselves, probably the most important factors affecting the chemical shifts are the hybridization of the silicon atom and the presence of a negative charge. The fact that the ^{29}Si NMR shifts of the anions are all in a 14-ppm range seem to indicate that the negative charge is substantially localized on silicon. The trend in chemical shifts indicates that there is only limited delocalization of charge away from silicon even in $Ph_3Si^-Li^+$, the $\delta_{^{29}Si}$ of which is only 4.4 ppm deshielded from that of Me_3SiK (where there is no charge delocalization). As a methyl group is added (i.e., $Ph_2MeSiLi$), there is more delocalization of charge per phenyl group. With two methyl groups added, i.e., in $PhMe_2SiLi$, the inductive effects of the methyl groups may cause more charge to be localized on silicon since only one phenyl group is left to help with the delocalization (this could account for the small $\delta_{^{29}Si}$ shielding observed as compared to that of $Ph_2MeSiLi$). In Me_3SiK, there is no electron

---

(29) Hunter, B. K.; Reves, L. W. *Can. J. Chem.* **1968**, *46*, 1399.

(30) Scholl, R. L.; Maciel, G. E.; Musker, W. K. *J. Am. Chem. Soc.* **1972**, *94*, 6376.

(31) Levy, G. C.; Cargioli, J. D. "NMR Spectroscopy of Nuclei Other than Hydrogen"; Wiley-Interscience: New York, 1974; p 251.

(32) Harris, R. K.; Lemarie, B. *J. Magn. Reson.* **1976**, *23*, 371.

delocalization away from the silicon atom, and, hence, the silicon is shielded as compared to the phenylsilyl anions.

Conclusions

^{13}C NMR spectroscopic studies have shown that the delocalization of charge in phenylsilyl anions is significantly reduced as compared to the corresponding phenyl carbanions. Using the para-carbon shifts as a probe to the electron density in the phenyl rings, we found that the delocalization of charge was reduced by a factor of ~9-10 for Ph_3SiLi. This could be, to a large degree, due to the nonplanarity of the system, which would effectively reduce $p\pi$–$p\pi$ overlap. For $Ph_2MeSiLi$ and $PhMe_2SiLi$, the delocalization is only ~3-4 times less than that in the corresponding carbanion analogues. This is in contrast to the findings of A. G. Evans,[17] who concluded from his UV studies that the conjugation between the silicon center and phenyl groups must be practically zero since replacement of phenyl by methyl has no effect on the λ_{max} of phenylsilyl anions. His conclusions are, however, probably correct in indicating that the phenyl groups are not conjugated with each other through silicon. As in the case of the study by Cox et al.,[3] it is at this time still difficult to elucidate the exact mechanism for the electron delocalization ($d\pi$ or $p\pi$) in phenylsilyl anions although it is most likely $p\pi$–$p\pi$.

The ^{29}Si NMR data are more difficult to interpret than the ^{13}C NMR data. Although $\Delta\delta_{^{29}Si}$ of the chemical shifts for X_3SiM vs. X_3SiCl does follow a nearly linear plot, $\Delta\delta_{^{29}Si}$ for X_3SiM vs. X_3SiH does not (where X = Me, Ph and M = Li or K). The reason for this deviation could not be elucidated. For X_3SiM vs. X_3SiCl, the increase in $\Delta\delta_{^{29}Si}$ indicates that, as a methyl group replaces a phenyl, an increase in shielding is observed. In respect to the ^{29}Si NMR shifts themselves, it is probable that they reflect primarily the amount of charge localized on the silicon atom, being most deshielded for $PhMe_2SiLi$ and $Ph_2MeSiLi$ where there is increased delocalization of charge per phenyl ring and most shielded for Me_3SiK where there is no significant delocalization into the methyl groups.

Experimental Section

Ph_3SiCl, Ph_3SiH, $Ph_2MeSiCl$, $PhMe_2SiCl$, and $Me_3SiSiMe_3$ were commercially available from Peninsular Research Chemicals, Inc. Me_3SiCl was obtained from Aldrich Chemical Co. These silanes were not further purified. Lithium and KO-*t*-Bu were obtained from Alfa-Ventron.

(Triphenylsilyl)lithium[33] was prepared by the treatment of triphenylchlorosilane with 4 equiv of lithium in dry THF, reacting under argon for four days. An aliquot of the solution was transferred by syringe to a dry argon flushed 10-mm NMR tube for spectroscopic study. **(Diphenylsilyl)lithium** and **(methyldiphenylsilyl)lithium**[33] were prepared similarly to (triphenylsilyl)lithium, except that in the case of (methyldiphenylsilyl)lithium, the reaction time was 1 day.

(Trimethylsilyl)potassium[34] was obtained by the treatment of hexamethyldisilane with an equimolar amount of KO-*t*-Bu in HMPA at 0 °C under argon. After the reaction was complete (~1 h at 0 °C), the deep red solution was allowed to warm to room temperature and an aliquot was transferred via syringe and under argon to a dry 10-mm tube for NMR analysis.

Nuclear Magnetic Resonance Studies. ^{13}C NMR studies were carried out by using a Varian FT-80 NMR spectrometer equipped with a broad-band decoupler, variable-temperature probe, and 32K memory capacity computer. Chemical shifts were measured from Me_4Si (internal) in the case of neutral compounds and from solvent THF in the case of the silyl anions (THF, $\alpha = 26.2$, $\beta = 78.0$).

^{29}Si NMR studies were carried out on a Varian FT-80 NMR spectrometer operating at 15.801 MHz by using a variable-temperature probe equipped with a broad-band decoupler. Proton heteronuclear decoupling was performed during these experiments. In the case of neutral silanes, internal Me_4Si was used as reference. For the silicon anions, the spectrometer was zeroed by using a Me_4Si/THF sample and the ^{29}Si NMR of the anion solution was recorded immediately afterwards. Signals deshielded from Me_4Si were considered positive while those shielded were considered negative. Typically, a pulse width of 5 μs, pulse delay of 10-20 s, and sweep width of 8000 Hz were used. The decoupler was turned on during acquisition and off during the pulse delay in order to suppress the negative NOE of silicon-29.

Acknowledgment. Support of our work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

---

[33] George, M. V.; Peterson, P. J.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 403. Gilman, H.; Peterson, D. J.; Wittenberg, P. *Chem. Ind.* **1958**, 1479.

[34] Saburai, H.; Okada, A.; Kira, M.; Yonegawa, K. *Tetrahedron Lett.* **1971**, 1511.

An Electronic Spectroscopic Study of Iron Coordination in Hemerythrin

Joann Sanders Loehr,*[1a] Thomas M. Loehr,[1b] A. Grant Mauk,[1c] and Harry B. Gray

Contribution No. 6217 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California, 91125. *Received April 28, 1980*

Abstract: Electronic spectroscopy in the near-IR region reveals the presence of Fe(III) ligand field bands at 990 nm in oxyhemerythrin, at 970 and 1050 nm in methemerythrin(N_3), and at 935 and 1040 nm in methemerythrin(OH). These bands are assigned as the $^6A_1 \rightarrow {}^4T_1(^4G)$ transitions of octahedrally coordinated high-spin Fe(III) centers. The resolution of two components in the spectra of the methemerythrins is attributed to inequivalent ligation of the two active-site Fe(III) ions by two and three histidines, respectively. The spectrum of deoxyhemerythrin is also characteristic of octahedral iron coordination, with bands at 855 and 1110 nm being associated with a split $^5T_2 \rightarrow {}^5E$ ligand field system of high-spin Fe(II). The near-IR spectrum of the half-reduced hemerythrin(N_3) intermediate exhibits a band at 1190 nm ($\epsilon = 16\ M^{-1}\ cm^{-1}$ per Fe atom); it is proposed that this band arises mainly from Fe(II) ligand field excitation and that the intensity enhancement comes from partial electron delocalization in the [Fe(II)*,Fe(III)] excited state.

Introduction

Hemerythrin is an invertebrate respiratory protein which contains two nonheme iron atoms at each oxygen-binding site.[2,3] In both oxyhemerythrin and methemerythrin, the pair of iron atoms have been identified as antiferromagnetically coupled, high-spin Fe(III) by Mössbauer spectroscopy and magnetic susceptibility measurements.[4] The ligand field (LF) bands in

---

[1] (a) Department of Chemistry, Portland State University, Portland, Oregon 97207. (b) Department of Chemistry and Biochemical Sciences, Oregon Graduate Center, Beaverton, Oregon 97006. (c) Department of Biochemistry, The University of British Columbia, Vancouver, B.C., Canada, V6T 1W5.

[2] Kurtz, D. M., Jr.; Shriver, D. F.; Klotz, I. M. *Coord. Chem. Rev.* **1977**, *24*, 145-178.

[3] Stenkamp, R. E.; Jensen, L. H. *Adv. Inorg. Biochem.* **1979**, *1*, 219-233.

0002-7863/80/1502-6992$01.00/0 © 1980 American Chemical Society