referred to here was conducted with an 2-propanol–hexane mobile phase), we utilize chloroform as a mobile phase for the separation of the enantiomers of **2b** on CSP **1c**. Despite rapid elution of both enantiomers, the same sense of chiral recognition and a large (though reduced) separation factor ($\alpha > 4$) were observed.

In a publication dealing with the separation of enantiomers on CSP **2b**, we show that the presently supported chiral molecular recognition model can be extended to encompass the separation and sense of recognition observed for the 3,5-dinitrobenzoyl derivatives of a large number of chiral amines and alcohols.[10]

We conclude that spectroscopic experiments with soluble analogues of CSPs are a useful adjunct to chromatographic data for establishing the mechanisms by which enantioselectivity occurs. NOE experiments are especially powerful in ascertaining the structure of transient complexes and are capable of providing information regarding conformational preferences in the complex. However, *intermolecular* NOE experiments will not be successful in all cases, since a very high degree of association seems essential. By using chromatographic data to choose analytes for study, it is clear that many other systems suitable for successful intermolecular NOE studies can be found.

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^{7}Li, ^{29}Si, ^{119}Sn, and ^{207}Pb NMR Studies of Phenyl-Substituted Group 4 Anions

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Abstract: The ^{7}Li, ^{29}Si, ^{119}Sn, and ^{207}Pb chemical shifts of phenyl-substituted group 4 anions are reported as a function of solvent and counterion. Generally, upfield shifts are noted on increasing the anion–alkali metal interaction. With additional support from ^{7}Li NMR results, it is argued that the lithium–group 4 atom interaction, including carbon, increases as the size of the group 4 element decreases. However, if the cation solvation is increased, the following order for the anion–cation interaction is obtained: C $\sim$ Pb $<$ Sn $<$ Ge $<$ Si. The increased delocalization upon solvation, which is important for the carbanion only, will thus decrease the electrostatic interaction considerably. A significant interaction between silicon and lithium is also consistent with the existence of scalar Si–Li coupling. ^{207}Pb chemical shifts of plumbyl anions are reported for the first time, and the resonances appear in an extreme low-field range. Large Pb–C scalar couplings are also noted for plumbyl anions. The chemical shifts are discussed by using a simple, relativistic extended Hückel model for PbH_3^- and the relativistic analogue of Ramsey's theory. The Pb 6s atomic orbitals (AO's) are found to be potentially important. The validity of a classical ion pair description of these group 4 anions is illustrated by a multivariate data analysis approach.

The role of covalency in group 4 atom–alkali metal interactions has mostly been studied in carbanion systems,[1] but a few NMR reports exist where both Si–Li and Ge–Li compounds have been examined.[2,3] Considering the ^{29}Si chemical shift data reported earlier, no systematic substituent effects were revealed that could shed light on the Si–Li bonding.[3a] In another study, however, strong resemblances between the C–Li and the Si–Li (Ge–Li) bond have been suggested, based on ^{7}Li chemical shift differences.[3d] It was also found that inversion about the Si (Ge) atom was slow on the ^{1}H NMR time scale, by using diastereotopic groups attached to the silicon atom.[3d] From ^{1}H and ^{7}Li NMR chemical shifts, it was suggested by Cox et al. that the degree of association between the group 4 atom and the lithium increases in the order Pb $<$ Sn $<$ Ge $\sim$ Si.[2a] These authors also suggestd a considerable degree of covalent character in the lithium–group 4 atom bond for the silyl and germyl compounds. An independent study by other workers gave additional support for this trend of interaction between lithium and these group 4 elements.[2b]

Using mainly ^{13}C and $^{6(7)}$Li NMR spectroscopy, we have investigated charge delocalization/polarization in phenyl-substituted group 4 anions,[4a–d] in continuation of our spectroscopic studies of benzylic-type carbanions.[4e–j] Contrary to the situation for the carbanion analogues, it was concluded that the excess charge resides almost exclusively on the group 4 element.[4a,b] The observed ^{13}C chemical shift changes could be satisfactorily explained by π-polarization as the mode of transmission of negative charge. Changing the counterion, or solvent, could modulate this effect to some extent. It was shown that in ethereal solution the silicon–cation interaction was equal or greater than that for the C–Li bond in Ph_3CLi in diethyl ether (DEE).[4a] Both ^{13}C chemical shift data and ^{7}Li chemical shifts supported this conclusion. A major contribution from tight ion pairing was also indicated for the

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Table I. ^{29}Si, ^{119}Sn, and ^{207}Pb NMR Chemical Shifts and J Couplings of Phenyl-Substituted Group 4 Anions[a]

	MTHF		THF		DME		DMPU	
	Li	K	Li	K	Li	K	Li	K
$Ph_3Si^-X^+$[b]	-9.2	-7.5	-9.0	-7.5	-8.7	-8.0	(-9.0)[e]	(-8.4)[f]
$Ph_2MeSi^-X^+$[b]			-20.6	-18.5				
$PhMe_2Si^-X^+$[b]			-27.8	-22.7				
$Ph_3Sn^-X^+$[c]	-116.2	-114.7	-106.7	-108.4	-105.8	-107.9	-107.6	-108.0
$^1J[^{119}Sn,^{13}C]$	165	237	260	257	285		290	
$^2J[^{11}Sn,^{13}C]$	48	52	53	52	54		54	
$Ph_3Pb^-X^+$[d]	1036.6	1045.7	1062.6	1045.0	1060.1	1055.1	1047.3	1048.1
$^1J[^{207}Pb,^{13}C]$	1020	1021	1030	1030	1038		1030	
$^2J[^{207}Pb,^{13}C]$	60	57	59	56	59		59	
$^3J[^{207}Pb,^{13}C]$	29	29	31	25	31		31	

[a] Abbreviations for solvents: MTHF, 2-methyltetrahydrofuran; THF, tetrahydrofuran; DME, 1,2-dimethoxyethane; DMPU, 1,3-dimethyl-3,4,5,6-tetrahydro-2(*H*)-pyrimidinone. [b] Referenced relative to internal tetramethylsiline (TMS). [c] Referenced relative to internal tetramethyltin. [d] Referenced relative to external hexaphenyldilead/CS_2/benzene = -73.2. [e] THF/12-crown-4. [f] THF/18-crown-6.

stannyllithium compound, but only in solvents less polar than tetrahydrofuran (THF).[4c]

Further support for a significant Si–Li interaction was afforded by the observation of Si–Li coupling at low temperatures.[4b] The bimolecular exchange process that caused coalescence of the splitting was found to increase with increasing temperature, with increasing degree of phenyl substitution, or with increasing coordinating ability of the solvent. Such scalar coupling could be caused by a minor, covalent contribution to the Si–Li bonding, or possibly by a through-space effect. As evidenced by the signal multiplicity, the silyl anion species exist as monomers in ether solution.

The purpose of the present study is to increase our understanding of group 4 element–alkali metal interactions by observing the group 4 element chemical shifts as a function of solvent and counterion and also to monitor the ^7Li chemical shift changes in various media. One would expect these parameters to be more sensitive and more directly probe changes in group 4 atom–alkali metal bonding than ^1H and ^{13}C NMR parameters. It could also be of interest to determine whether the scalar couplings between the negatively charged group 4 atom and the phenyl carbons will be affected by ion pair effects or increased orbital overlap between the alkali metal and the negative group 4 atom.

Results and Discussion

Evidence from ^{29}Si, ^{119}Sn, and ^{207}Pb Chemical Shifts. The effects of solvent and cation on the group 4 element chemical shifts of $Ph_3M^-X^+$ (M = Si, Sn, Pb) are presented in Table I. The ^{29}Si chemical shifts of $Ph_2MeSi^-X^+$ and $PhMe_2Si^-X^+$ are also included since anion–cation interactions, if existent, would be more pronounced in these substrates.[4b] The frequency range and the sensitivity (in ppm) to structural effects, such as ion pairing, are expected to increase in the order Si < Sn < Pb, an assumption based on the observed substituent effects found in neutral tetracoordinated species.[5] As can be seen from the shift data obtained in 2-methyltetrahydrofuran (MTHF), the shift differentials between the lithium and potassium salts are found in approximately that order on going from Si to Pb. Hence, changes in alkali metal radius are most easily observed when the ^{207}Pb resonance is studied.

If one considers such systems or solvents that are known to favor aggregation or cation–anion interactions, it is seen from Table I that the group 4 element resonance of the lithium group 4 anions is shifted slightly upfield relative to the values obtained for the potassium species. In contrast, when such systems are considered where the anion–cation interaction can be expected to be small or insignificant, the group 4 element shift occurs downfield for the lithium compounds (Table I). This observation is consistent with established ion pair theory, where lithium salts are claimed to form solvent-separated ion pairs (SSIP) more easily. In Table I, such conditions are fullfilled for the lithium salts of Ph_3Sn^- and Ph_3Pb^- in solvents more polar than MTHF. One can conclude, therefore, that increased anion–cation interaction generally yields upfield shifts of the group 4 atom. As expected, this observation is most apparent for the lithium compounds.

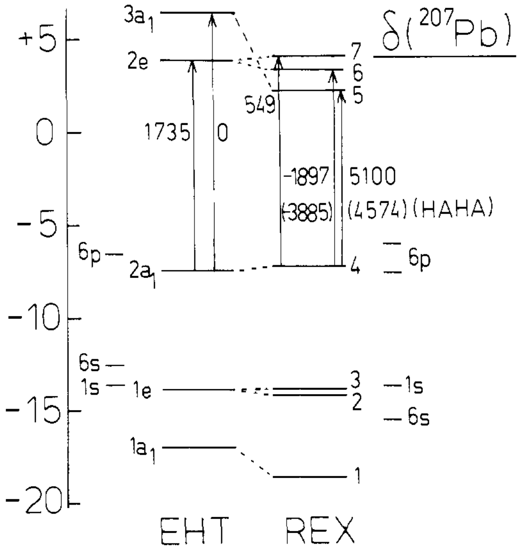

Figure 1. Paramagnetic contributions (in ppm) to the ^{207}Pb chemical shift ($\delta = -\sigma$) in a PbH_3^- model according to relativistic (REX) and nonrelativistic (EHT) parametrizations. The contributions from Pb 6s orbitals are given in parentheses.

A pronounced chemical shift change is observed for Ph_3SnLi when the medium is changed from MTHF to THF. This is interpreted as a change in equilibrium from contact ion pairs (CIP) toward solvent-separated ion pairs (SSIP). Additional support is given by the observation that the shift differences between lithium and potassium salts decrease as the cation solvation or polarity of the medium increases. The solvation radius of the lithium and potassium cations will then be rather similar. In the higherly polar *N*,*N*-dimethylpropyleneurea (DMPU) solvent, there is virtually no dependence of the group 4 element chemical shifts on the nature of the cation.

Although the observed ion pair effects on changing the cation or solvent are significant and systematic, they are small in magnitude. Taking sensitivity effects and the absence of resonance interactions into account, the shift differential noted for $Ph_3SiLi \rightarrow Ph_3SiK$ is quite comparable to the value found for the carbanion analogue ($\Delta\delta = +4.0$ in THF under CIP conditions).[6] Hence, there is no evidence to suggest that changes in anion–cation orbital overlap should be more important for the other group 4 anions (Si to Pb). The larger downfield shifts noted for the Ph_2MeSiX and $PhMe_2SiX$ systems by changing the cation are also consistent with the results obtained for a carbanion analogue, $Ph_2CHLi \rightarrow Ph_2CHK$ ($\Delta\delta = +8$, THF, CIP).[6]

The chemical shift range for the ^{119}Sn signal of Ph_3SnX, -116 (MTHF) to -106 (DMPU), is similar to the values obtained for Me_3SnLi: $\delta = -185$ (MTHF), $\delta = -186$ (THF), and $\delta = -162$ (hexamethylphosphoric triamide, HMPA).[7,8] However, on the

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basis of the ^{119}Sn chemical shifts and assuming a proportionality between ^{119}Sn and ^{207}Pb as noted for the tetracoordinated derivatives [$\delta(\mathrm{Pb}) = 2.424\ \delta(\mathrm{Sn}) + 74.8$; $r = 0.975$], one would expect the Pb signal to appear close to −350 ppm.[5] Quite on the contrary, the resonance of $\mathrm{Ph_3Pb^-}$ appears at an extreme low-field shift, ca. +1040 to +1060 ppm. Possible reasons are discussed below.

Triphenylplumbyllithium is the most stable of the group 4–alkali metal compounds investigated, and the solution could be kept for days at room temperature on exclusion of moisture and oxygen. Chemical evidence for the existence of $\mathrm{Ph_3PbLi}$ was provided by a quenching experiment with use of benzyl bromide, which afforded benzyltriphenyllead in almost quantitative yield.

Theoretical Discussion of ^{207}Pb Chemical Shifts. The extreme low-field shifts of ca. +1040 to +1060 ppm observed here for $\mathrm{Ph_3Pb^-}$ are of interest though they have precedents. Wrackmeyer[9] observed a record $\delta(^{207}\mathrm{Pb})$ of 4916 ppm relative to $\mathrm{Me_4Pb}$ for $\mathrm{Pb[N(SiMe_3)_2]_2}$, while Björgvinsson et al.[10] also report for $\mathrm{Pb_2Ch_3^{2-}}$ (Ch = Se, Te) cluster anions (tbp symmetry with axial lead atoms) δ(Pb) values ranging from +3290 for all Ch = Se to +1727 ppm for all Ch = Te. It is common to all three cases that they have lone pair orbitals at lead.

The relativistic analogue of Ramsey's theory of chemical shifts[11] has recently been implemented[12] with use of relativistic extended Hückel ("REX") wave functions. Taking a simple $\mathrm{PbH_3^-}$ model system (pyramidal geometry, HPbH = 109.47°, R = 175.3 pm; REX parameters from ref 13, $\zeta_\mathrm{H} = 1.2$; hyperfine parameters from ref 12 and 14), we find the main contributions to the paramagnetic shift as given in Figure 1. The contributions arising from the Pb 6s AO's (zero in Ramsey's theory!) are given in parentheses.

While the nonrelativistic paramagnetic shift arises mostly from a single, $2a_1$(HOMO)-to-2e(LUMO) excitation, the relativistic one has large contributions of opposite sign from both the 4 → 5 ($2a_1 \rightarrow 3a_1$) and the 4 → (6, 7) ($2a_1 \rightarrow 2e$) excitations.

We showed in ref 12 how to interpret the "heavy-atom shift" on a neighboring atom through spin–orbit-induced changes in the wave function. We now find a similar "heavy-atom shift of the heavy atom" (HAHA).[15]

Due to the cancellations it is difficult to estimate the HAHA reliably. Our estimate provides, in any case, a plausible interpretation, with the correct sign, for the qualitatively different behavior of $\mathrm{Ph_3Sn^-}$ and $\mathrm{Ph_3Pb^-}$. $\mathrm{SnH_3^-}$ is qualitatively similar to the EHT $\mathrm{PbH_3^-}$ case. The $2a_1 \rightarrow 2e$ and $2a_1 \rightarrow 3a_1$ contributions to $\delta(^{119}\mathrm{Sn})$ are +1376 and −151 ppm, respectively.

Caution should be exercised in taking the above figures too rigorously, since a change in parameters such as from $\alpha_\mathrm{H} = -10$ to −13.6 eV will strongly affect the results. The anion geometries are also hypothetical. However, the qualitative picture, especially the HAHA, remains unaltered.

The large ^1J(PbC) value for $\mathrm{Ph_3Pb^-}$ (ca. 1030 Hz) remains unexplained at this time. In the neutral $\mathrm{Ph_4Pb}$ the value is only 481 Hz. In the earlier study of tetrahedral $\mathrm{MX_4}$ vs. pyramidal $\mathrm{MX_3^-}$, the latter always had a *smaller* ^1J(MX) coupling constant, due to opposed $1a_1 \rightarrow 3a_1$ and $2a_1 \rightarrow 3a_1$ contributions[14] (terminology of Figure 1). We have explained earlier the very small, or even negative, ^1J(PbC) of some lead organometallics as a frontier orbital effect.[16] More data are needed to explain why the ^1J(PbC) of the present plumbyl anions should be so large, such as if significant changes have occurred in the geometry of the plumbyl anion.

Scalar Coupling between Group 4 Elements and Phenyl Carbons. The one-bond scalar coupling observed for $\mathrm{Ph_3SnLi}$ in MTHF ($^1J[^{119}\mathrm{Sn},^{13}\mathrm{C}]$ = 165 Hz) is of similar magnitude to the value reported earlier for $\mathrm{Me_3SnLi}$ in THF ($^1J[^{119}\mathrm{Sn},^{13}\mathrm{C}]$ = 155 Hz).[9] A change from phenyl to methyl substitution is expected to increase the Sn–Li interaction, by analogy with the corresponding silyl anion and carbanion derivatives. This Sn–C coupling increases to 260 Hz on going to the better solvating THF, which can be compared with the corresponding value for $\mathrm{Me_3SnLi}$ in HMPA ($^1J[^{119}\mathrm{Sn},^{13}\mathrm{C}]$ = 220 Hz).[7] It is possible that the steric demand upon contact ion pairing could cause changes in bond angles, an assumption that is supported by an even lower observed value in diethyl ether ($^1J[^{119}\mathrm{Sn},^{13}\mathrm{C}]$ = 119 Hz). A covalent contribution to the Sn–Li bond might also change the observed scalar coupling in this direction.

The plumbyl anion does not show such changes in the scalar coupling. The $^1J[^{207}\mathrm{Pb},^{13}\mathrm{C}]$ value is exceptionally large and rather constant throughout the solvent series. It is noted that the order $^1J > {}^2J > {}^3J$ is different from that reported for neutral species such as $\mathrm{Ph_4Pb}$, where $^1J > {}^3J > {}^2J$.[17] The coupling constants for the plumbyl potassium salts could not be obtained due to the limited solubilities of these salts. Sensitivity limitations were also the reason for not obtaining the Si–C coupling constants in all media. The stability of silyl anions is limited in polar media, and the one-bond scalar coupling ($^1J[^{29}\mathrm{Si},^{13}\mathrm{C}]$ = 10 Hz) could only be obtained in MTHF.

Ion Pair Effects Experienced by ^{7}Li NMR Chemical Shifts. It was also felt that the shielding of the quadrupolar ^{7}Li nucleus should be sensitive to ion pairing, i.e., to the structure of the first cation solvation shell. Earlier studies have shown that measurements of the ^{7}Li signal provided valuable information of the cation–anion interaction, which could not easily be obtained by other methods.

The measured ^{7}Li shifts are expected to reflect the nature of the anion, the solvent, and the degree of association. In the present systems, shift changes could occur by ring currents from the phenyl rings, electrostatic polarization of the ^{7}Li atom, and orbital interaction between lithium and the anion/solvent. Polarization and orbital overlap will both induce downfield shifts, which are modulated by interionic distances. One also has to account for the actual position of the cation when the ring current effects are estimated.

Therefore, covalent or CIP systems are known to give rise to resonances downfield of aqueous LiCl.[2,3d] However, going to SSIP, the electrostatic polarization and/or overlap as well as ring current effects will decrease. The first solvation sphere of the lithium cation will now be entirely composed of solvent molecules, and shielding differences in various solvents will mostly reflect differences in solvent–lithium orbital overlap.

In Table II, we have listed the observed ^{7}Li chemical shifts for $\mathrm{Ph_3MLi}$ using the same solvents as earlier. In addition, we have included shift values in DEE to allow comparisons with the data for the corresponding carbanions. It is noted that low-field shifts relative to LiCl, indicative of CIP, are obtained for the silyl and germyl compounds as well as for the stannyl anion in the less polar ethers. In MTHF and DEE, where CIP structures are suggested, the ^{7}Li NMR chemical shift of $\mathrm{Ph_3SnLi}$ is close to the value obtained for $\mathrm{(CH_3)_3SnLi}$ in MTHF ($\delta(^7\mathrm{Li}) = 0.75$) and THF ($\delta(^7\mathrm{Li}) = 0.70$)[8]. An additional observation is that the observed shift range for the lithium resonances is quite similar to the range observed for structurally similar carbanions (~2 ppm). In this context, one should mention that triphenylmethyllithium is known to exist as CIP in MTHF solution at room temperature.[6] The present results are therefore consistent with those obtained from the ^{29}Si, ^{119}Sn, and ^{207}Pb NMR measurements.

The observed data can be explained as follows. Under tight ion pair conditions, i.e., in diethyl ether solution, the charge *localization* on the group 4 element is optimized, and therefore the group 4 atom–cation interaction increases as the size of the group 4 atom decreases, i.e., Pb < Sn < Ge < Si < C. However, increasing cation solvation toward solvent-separated ion pairs will

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Table II. Solvent Effects on ^7Li NMR Chemical Shifts of Group 4 Metal Anions[a]

	DEE	MTHF	THF	DME	DMPU
Ph_3CLi	+1.35	−0.57	−0.35		
Ph_3SiLi	+1.00	+0.49	+0.66	+0.43	
Ph_3GeLi	+1.23	+0.66	+0.88	+0.09	+0.20
Ph_3SnLi	+0.95	+0.37	−0.56	−1.58	−0.06
Ph_3PbLi		−0.75	−0.71	−1.69	−0.04
$Ph_1MeSiLi$		+0.58	+0.61	+0.23	
$PhMe_2SiLi$			+0.53	+0.32	

[a] External referencing 1 M $LiCl/H_2O$. See Experimental Section.

increase the charge *delocalization*, which will then be by far the most significant for the carbanionic species. On simple electrostatic basis, the order for the anion–cation interaction will then be C ∼ Pb < Sn < Ge < Si. Hence, the group 4 element (Si to Pb) anion–alkali metal cation interaction can be found within the same range as for the carbon–lithium bond, having Ph_3CLi/DEE (CIP) and Ph_3CLi/THF (SSIP) as extremes. After magnetic susceptibility correction, the ^7Li values obtained for Ph_3SnLi and Ph_3PbLi in DME and DMPU are in close agreement with the values reported for the SSIP structure of Ph_3CLi with 1,2-dimethoxyethane (DME) and HMPA as solvents.[18] Consequently, it seems reasonable to suggest that under CIP conditions, the covalent contribution to the C–Li bond for Ph_3CLi/DEE is of a comparable magnitude as that found for the silyl and germyl anions. This view is further supported by recent ab initio calculations on silyllithium species.[19] The similarity of Si–Li and C–Li bond strength is also supported by the existence of Si–Li scalar coupling which quenches in a similar temperature range as has been observed for the localized alkyl–lithium systems.[1]

Multivariate Data Analysis of the Multinuclear NMR Chemical Shifts. Although traditionally it has been common to discuss structural effects by examining one experimental variable at a time, we have found score plots resulting from multivariate data analysis to be extremely powerful in illustrating similarities or dissimilarities in experimental data, as in the present case.[20] Therefore, a shift matrix was initially constructed composed of 22 anion/solvent objects described by 5 shift variables. The ortho, meta, and para ^{13}C chemical shifts were used in addition to the ^7Li chemical shifts. The ipso carbon was omitted due to the expected dominance of direct bonding effects to the various group 4 elements. The group 4 element NMR descriptor was obtained by subtracting the observed shift value from the calculated mean shift value for that specific group 4 anion series. To allow comparisons, this value was then divided by the expected sensitivity factors derived from studies of tetracoordinated compounds. Missing values will occur for the germyl anions and for the potassium salts. The shift data in DMPU were omitted after the initial analysis since both ^{13}C and ^7Li shift "continuity" will be "poisoned" by an unsaturated non-ether solvent. A principal components data analysis package, SIMCA, was used for the multivariate data analysis.[20] A two-dimensional window in this M-dimensional space showed significant grouping in the expected CIP and SSIP classes. However, three objects, SnLi/DEE, SnLi/MTHF, and SnK/THF, showed comparable distances to both classes. Consequently, these values were omitted from the modelling of the separate CIP and SSIP classes in the next classification step.

The residual standard deviations S_p (class) for the two classes were stored on a multiple classification result file (MCL) and thereafter plotted in a Coomans manner[21] (Figure 2). In this figure, the X axis represents the distance to the SSIP class while the Y axis represents the distance to the CIP class. The PbLi/DME value represents the most extreme SSIP structure, while SiLi/DEE is the system where anion–cation interaction is most significant. Comparable contributions from CIP and SSIP are expected for the SnLi/MTHF and SnK/THF systems. Hence, the conclusions based on the multivariate analysis parallel those derived from the use of separate variables.

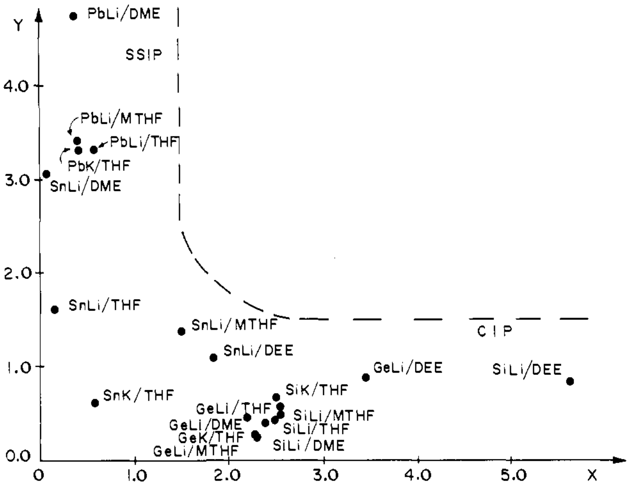

Figure 2. A class–distance plot for the group 4 anion–alkali metal compounds, where X is the distance to the SSIP class and Y is the distance to the CIP class.

Concluding Remarks

The multinuclear NMR studies of phenyl-substituted group 4 anions show that the structure in solution can be described by a classical ion pair model. The degree of orbital interaction between elements most prone to overlap, i.e., between silicon and lithium, is comparable to the carbon–lithium interaction found for triphenylmethyllithium in diethyl ether. According to the ^7Li NMR results, the differences in anion–cation interactions for all Si-to-Pb ion pairs are also found within the range observed for triphenylmethyllithium on changing the solvent from diethyl ether (CIP) to tetrahydrofuran (SSIP). While in poorly solvating ethers the anion–cation interaction increases on decreasing the group 4 atom size, the order of interaction in more polar media was found to be C ∼ Pb < Sn < Ge < Si. The increased delocalization upon cation solvation, significant for the carbanion only, will thus decrease the electrostatic interaction between the anion and cation considerably. In agreement with ab initio MO calculations, the degree of ionic character of the Si–Li bond seems to be equal or somewhat greater than that of the C–Li bond, a condition that will favor contact ion pairs. The similarity in the interaction between lithium and silyl and localized alkyl anions is strongly supported by the existence of Si–Li and C–Li scalar couplings which collapse at very similar temperature ranges.

Experimental Section

The phenyl-substituted group 4 anions were prepared by alkali metal cleavage of the corresponding hexasubstituted R_3MMR_3 neutral species, as previously described.[4a] The procedure for transferring the anion solution to NMR tubes is given elsewhere. All spectra were obtained on a Bruker WM 250 instrument with use of tunable broad-banded probes. The relaxation times for the ^{29}Si nuclei were unexpectedly short, and normal spectral parameters for pulse width and delay, being $\pi/4$ and 20 s, respectively, were used throughout the investigation. Solutions were 0.2–0.3 M in all cases, and the reported chemical shifts are accurate within 0.1 ppm.

In the quenching experiment, 2.1 mM of hexaphenyldilead was cleaved with use of potassium metal in dry THF. After addition of $PhCH_2Br$ in excess, the solution was hydrolyzed and evaporated, yielding a semisolid residue in quantitative yield. Recrystallization from ethanol yielded long shiny needles of Ph_3PbCH_2Ph (76%) as identified by NMR and IR, mp 87 °C (lit. 92 °C).[22]

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