

Carbanion mechanisms

XX. [☆] Is there charge delocalization in phenyl-substituted Group 4 anions? Evidence from electronic absorption spectroscopy

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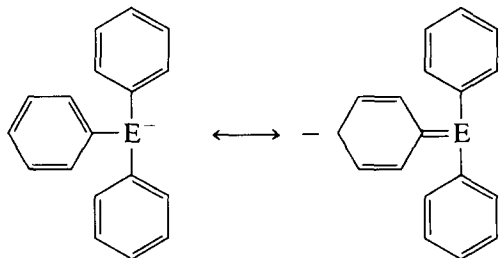
Abstract

From the electronic absorption spectra of the triphenyl silyl, germyl, stannyl and plumbyl anions Ph_3E^- (E = Si, Ge, Sn or Pb), it is concluded that there exists in these species almost no conjugation between the Group 4 element and the phenyl group substituents, contrasting with the Ph_3C^- carbanion. A similar conclusion can be drawn from the near constancy of λ_{max} values in the series Ph_3Si^- , Ph_2SiH^- and PhSiH_2^- .

Keywords: Silicon; Germanium; Tin; Lead; Anions

1. Introduction

The mechanism of electronic charge transmission in phenyl-substituted Group 4 anions has been of considerable interest. While there is abundant evidence to show that in the carbanion system Ph_3E^- (E = C) charge is delocalized through resonance (albeit steric inhibition reduces the conjugation when three phenyl groups are present relative to the benzyl anion) [2], with the heavy metal anions Ph_3E^- (E = Si, Ge, Sn or Pb) the situation is by no means clear.



The results of an early study by Waack and Doran [3] of the electronic absorption spectrum of Ph_3SiLi in tetrahydrofuran (THF) were interpreted as consistent

with transitions ($\pi \rightarrow \pi^*$) of conjugated π electrons. However, $p_\pi-p_\pi$ conjugation was considered to be less than that in the carbon analogue Ph_3CLi , in accord with the lesser tendency of second-row elements to form double bonds. Subsequently, a more extensive UV–visible study by Evans et al. [4a] of the series Ph_3SiLi , Ph_2MeSiLi and PhMe_2SiLi was interpreted as providing evidence of almost zero conjugation between Si and the phenyl groups. ¹H and ¹³C NMR studies of silyl anions have also received varied interpretations [5–7]. As part of our continuing studies on the generation and structure–reactivity relationships of Group 4 anions, we recently reported novel methods of preparation of the anions R_3E^- (E = Si, Ge, Sn or Pb) [1,8]. In this paper we report a spectroscopic study of these anions.

2. Results and discussion

We present the results of a UV–visible study of triphenyl germyl, stannyl and plumbyl anions which, together with the previous data for the triphenyl silyl anion, provides very strong evidence for the absence of $p_\pi-p_\pi$ -type conjugation in the series Ph_3E^- (E = Si, Ge, Sn or Pb). Corroborating evidence was obtained from study of the silyl anions Ph_2SiH^- and PhSiH_2^- , and the comparison with Ph_2CH^- and PhCH_2^- .

[☆] For Part XIX, see [1].

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The UV–visible spectral characteristics of the lithium and potassium compounds in THF at 20°C are given in Table 1 which also includes results for the silyl anions as well as carbanions. The triphenyl germyl, stannyl and plumblyl anions in this work were generally prepared by cleavage of the hexaphenyl compounds Ph_3EPh_3 with potassium metal or with *n*-butyllithium, or from the triphenyl hydrides Ph_3EH by reaction with K or *n*-BuLi. The silyl anions Ph_2SiH^- and PhSiH_2^- were generated from the corresponding hydrides and potassium.

The contrast between the λ_{max} values for the carbanion Ph_3C^- and the other Group 4 anions Ph_3E^- (E = Si, Ge, Sn or Pb) is striking and has to be interpreted as resulting from different types of electronic transition, namely $\pi \rightarrow \pi^*$ for Ph_3CM and $n \rightarrow \pi^*$ for the remaining Ph_3E^- series (i.e. from an unconjugated lone pair on Si, Ge, Sn or Pb, rather than a conjugated $p\pi$ pair on C, to a π^* molecular orbital of the phenyl group(s)). The large hypsochromic shift in λ_{max} as one goes along the carbanion series $\text{Ph}_3\text{C}^- \rightarrow \text{Ph}_2\text{CH}^- \rightarrow \text{PhCH}_2^-$ is in agreement with the decreased possibility of resonance in this series, as reflected by the order of acidities (Ph_3CH , 31.4; Ph_2CH_2 , 33.4, PhCH_3 , 40.9) [2]. In direct contrast is the almost constancy in λ_{max} values for the silyl anions Ph_3Si^- , Ph_2SiH^- and PhSiH_2^- , providing further evidence for the virtual absence of $p_\pi-p_\pi$ type of conjugation in these anions.

In a previous study [11] of the solvent and cation dependence of the electronic absorption spectra of triphenylmethyl anions, it was found that λ_{max} varied with the type of ion pair present, i.e. contact ion pair (CIP) and solvent-separated ion pair (SSIP) [12,13]. In diethyl ether, both Ph_3CLi ($\lambda_{\text{max}} = 446$ nm) and Ph_3CK ($\lambda_{\text{max}} = 467$ nm) were found to exist predominantly as CIP but in THF the λ_{max} values (Table 1) were taken as indicative of 95% SSIP formation for Ph_3CLi , and 65% SSIP formation for Ph_3CK [11]. Similarly, for the silyl anions it was concluded by Evans et al. [4b] that in THF Ph_3SiK exists as CIP but that for Ph_3SiLi there is some

degree of SSIP formation. Thus the results in Table 1 for the triphenyl germyl, stannyl and plumblyl anions, particularly the bathochromic shift on going from Li to K, are indicative of CIP formation for this series of Group 4 anions. A similar situation probably holds for the silyl anions Ph_2SiH^- and PhSiH_2^- .

3. Conclusions

The conclusions of the present study using electron absorption spectroscopy, regarding the nature of transmission of electronic charge and the type of ion pair present for the phenyl-substituted Group 4 anions, are in complete accord with the conclusions drawn from our detailed multinuclear NMR studies of these species, including a multivariate data analysis [14].

4. Experimental section

Hexaphenyldistannane, hexaphenyldiplumbane, triphenylgermane and triphenylstannane were purchased from Organometallics Inc. Triphenylsilane was obtained from Aldrich. Hexaphenyldisilane and hexaphenyldigermane were prepared according to literature procedures [15]. Diphenylsilane and phenylsilane were prepared by LiAlH_4 reduction of Ph_2SiCl_2 and PhSiCl_3 respectively. THF (Fluka) was treated with sodium wire overnight and distilled under argon into a vessel containing freshly cut shiny potassium metal and distilled again under argon. The distillation from potassium metal was repeated once more and the final distillate was kept over sodium wire in a 250 ml cylindrical reservoir vessel fitted with a Rotaflo stopcock and an O-ring for connection to a vacuum line.

The reaction vessel used in the spectrophotometric studies is shown in Fig. 1. It consists of a cylindrical tube of capacity about 120 ml, made of Pyrex brand glass, and equipped with one side arm to which a 1 mm

Table 1
Electronic absorption data for Group 4 anion alkali metal compounds in THF at 20°C

	Li		K	
	λ_{max} (nm)	$10^{-3} \epsilon$ ($\text{M}^{-1} \text{cm}^{-1}$)	λ_{max} (nm)	$10^{-3} \epsilon$ ($\text{M}^{-1} \text{cm}^{-1}$)
Ph_3CM [11a]	500	28.5	486	21.3
Ph_3SiM [4b]	335	10.3	363	12.0
Ph_3GeM	308	9.8	352	15.0
Ph_3SnM	298 (sh)	^b	350 (sh)	^b
Ph_3PbM	298 (sh)	^b	348	11.4
Ph_2CHM ^a [11b]	418	30.8	440	43.0
Ph_2SiHM			349	12.3
PhCH_2M	330 [9]	9.5	355 ^c [10]	12.0
PhSiH_2M			350	5.4 ^b

^a Corresponds to externally solvated contact ion pairs.

^b Reaction incomplete.

^c Corresponds to benzylium ($\text{M} = \text{Na}$).

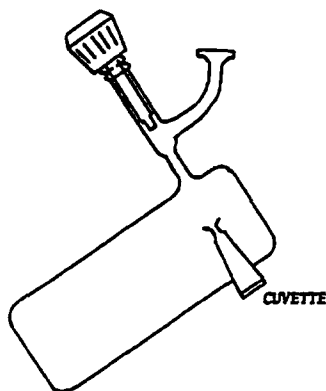


Fig. 1. Reaction vessel for preparation and spectrophotometric study of Group 4 anions in an inert atmosphere.

or 10 mm quartz UV cell is attached via a graded seal and a second side arm consisting of a greaseless RotaFlo stopcock attached to an O-ring joint. The reaction vessel is made to fit into the cell compartment of the Beckman Acta IV UV–visible spectrophotometer (a modification to the cover of the cell compartment is needed with some models to increase its effective height).

The triphenyl anions were prepared by reaction of the hexaphenyl compounds Ph_3EPh_3 , with lithium or potassium metal or with *n*-butyllithium, or from the triphenyl hydrides Ph_3EH and ${}^n\text{BuLi}$. (However, Ph_3SiH reacts with ${}^n\text{BuLi}$ to give $\text{Ph}_3\text{Si}^n\text{Bu}$ instead). The silyl anions Ph_2SiH^- and PhSiH_2^- were obtained from Ph_2SiH_2 and PhSiH_3 by reaction with K. A typical experiment is described below.

The substrate (about 5 mg) was introduced into the reaction vessel inside an argon-filled glove-box following which the vessel was attached to the vacuum line through the O-ring joint assembly. The vessel was evacuated, cooled in liquid nitrogen and solvent (20–25 ml) from the reservoir flask was transferred under vacuum to the pre-weighed vessel. The reaction vessel was then replaced inside the argon glove-box and a septum was attached to the O-ring joint. The *n*-butyllithium solution (1.6 M in hexane, Fluka) was syringed in through the septum and the stopcock was closed, following which the vessel was removed from the glove-box and shaken or stirred with a magnetic stirrer bar prior to the spectrophotometric study. In preparation of the potassium derivatives, Na–K alloy kept under xylene was used and syringed through the septum under argon while simultaneously opening the stopcock of the reaction cell. Any unreacted (excess) metal was removed by filtration through a fritted disk into a second reaction vessel similarly fitted with a cuvette for the spectrophotometric study. Spectra were taken over the range 200–700 nm for several hours until a maximum absorption developed. The heterogeneous reactions with Li or K metal were generally slower than the homogeneous systems involving ${}^n\text{BuLi}$ as the metallating agent.

The Group 4 anions were characterized by multinuclear NMR studies [7,14] and in some cases by product-forming reactions. For instance, Ph_3SiLi on quenching with D_2O and extraction with ether yielded Ph_3SiD (melting point, 44–45°C). ${}^1\text{H}$ NMR (CDCl_3): δ 7.2–7.4 ppm (mult, Ph). Ph_3SiK on reaction with CO_2 yielded Ph_3SiCOOH , and Ph_3GeLi similarly yielded Ph_3GeCOOH . Also, Ph_3SnK when reacted with PhCH_2Br produced $\text{Ph}_3\text{SnCH}_2\text{Ph}$, while Ph_3PbK similarly gave $\text{Ph}_3\text{PbCH}_2\text{Ph}$.

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