

were identified and indexed with an optic goniometer, and their respective distance  $d$  to the origin of the crystal was carefully measured with a microscope. In all three cases, absorption corrections of a Gaussian integration type were applied to the intensity data. The introduction of the corrected data files after refinement of the isotropic model led to an improved fit between observed and calculated structure factors.

**Solution and Refinement of the Structures.** All calculations were performed on a MicroVAX 3400 computer by using combinations of the following program files: SDP,<sup>41</sup> SHELXS-86,<sup>42</sup> and SHELX-76.<sup>43</sup> Neutral atomic scattering factors were taken from the standard sources.<sup>44</sup> Anomalous dispersion corrections were applied to Ru atoms. The structures were solved by direct methods (SHELXS-86) and subsequently refined by combinations of full-matrix least-squares and electron density calculations (SHELX-76).

All non-hydrogen atoms were refined with anisotropic thermal parameters, except for [PPN][4c]. Due to the high number of variable parameters in the latter case, the eight phenyl rings of [PPN][4c] were treated as rigid groups including the hydrogen atoms in idealized positions ( $D_{6h}$  symmetry; C-C = 1.395 Å, C-H = 0.95 Å). The methyl hydrogens of 6d were located on a Fourier

(41) *Structure Determination Package*, 4th ed.; B. A. Frenz & Associates: College Station, TX 77840, and Enraf-Nonius: Delft, The Netherlands, 1981.

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map and could be refined. The phenyl hydrogens of 10c were entered in idealized positions but were not refined.

Crystal and intensity data for [PPN][4c], 6d, and 10c are summarized in Table I. Perspective views of the three complexes are provided in Figure 1 for [PPN][4c], in Figures 2 and 3 for the two independent cluster units of 6d, and in Figure 4 for 10c. The final atomic coordinates, selected interatomic distances, and bond angles for [PPN][4c], 6d, and 10c are listed respectively in Tables II-IV, V-VII, and VIII-X. Whenever possible, these data have been listed according to the noncrystallographic symmetry of the molecules: in a given table, the distances and the angles corresponding to "equivalent" atoms are given on the same line. Tables of anisotropic thermal parameters, hydrogen coordinates, and observed and calculated structure factor amplitudes are provided as supplementary material.

**Acknowledgment.** Financial support from the CNRS is acknowledged. We are also grateful to Johnson-Matthey for generous loans of ruthenium trichloride.

**Registry No.** [PPN][1], 110487-55-3; [PPN][2], 117308-22-2; [PPN][3], 134153-77-8; [PPN][4a], 123640-66-4; [PPN][4b], 123640-68-6; [PPN][4c], 123640-70-0; [PPN][4d], 123640-72-2; 5c, 134153-78-9; 6c, 123640-74-4; [PPN][7b], 123640-76-6; [PPN][8c], 123640-79-9; 9c, 56802-15-4; 10c, 39531-19-6; Ru<sub>3</sub>(C-O)<sub>12</sub>, 15243-33-1; PhC≡CPh, 501-65-5; CH<sub>3</sub>C≡CCH<sub>3</sub>, 503-17-3; PhC≡CH, 536-74-3; HC≡CH, 74-86-2.

**Supplementary Material Available:** Listings of anisotropic thermal parameters for [PPN][4c], 6d, and 10c and calculated hydrogen coordinates for [PPN][4c] and 10c (5 pages); structure factor tables (86 pages). Ordering information is given on any current masthead page.

## Pentacoordinate Hydridosilicates: Synthesis and Some Aspects of Their Reactivity

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Pentacoordinate hydridosilicates [HSi(OR)<sub>4</sub>]<sup>-</sup> (where R = Me, Et, *n*-Bu, *i*-Pr, Ph) as their K<sup>+</sup> salts are obtained from reactions of trialkoxy- (or phenoxy-) silanes with the respective alkoxide (or phenoxide). Compared to HSi(OEt)<sub>3</sub>, [HSi(OEt)<sub>4</sub>]K exhibits a wide range of reactivities: (1) it undergoes facile displacement reactions at silicon with Grignard reagents and PhLi; (2) it acts as a base and leads to proton abstraction in the case of PhC≡CH and Ph<sub>3</sub>CH; (3) it is able to reduce carbonyl compounds to the related alcohols; (4) it reacts with primary organic halides through an ionic mechanism (a SET process can be invoked in the case of benzylic halides (RX), which afford the dimer RR in addition to the alkane RH); (5) the ability to donate one electron is confirmed in reactions with oxidizing agents (Cu<sup>+</sup>, Ag<sup>+</sup>, Cp(CO)<sub>2</sub>Fe<sup>+</sup>) and by direct ESR observation of stable radical intermediates.

### 1. Introduction

Since the pioneering work carried out in the 1960s by Frye,<sup>1</sup> Müller,<sup>2</sup> and Muettterties,<sup>3</sup> numerous pentacoordinate anionic organosilicon derivatives have been reported<sup>4</sup> and structurally characterized.<sup>5</sup> They have been

invoked as intermediates in nucleophilic displacements at silicon,<sup>6</sup> and moreover, they have recently received much

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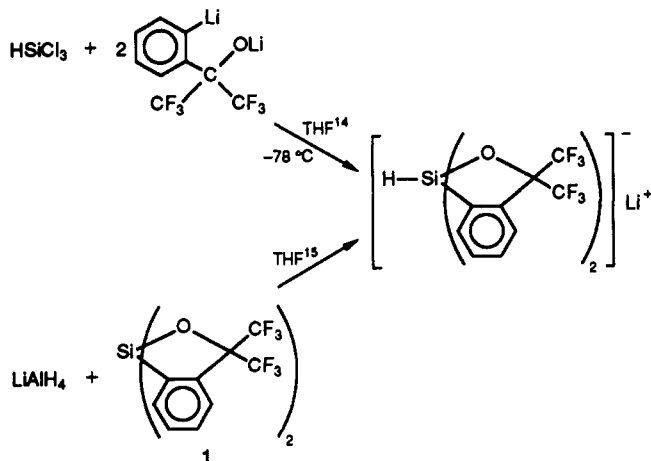
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Table I.  $^{29}\text{Si}$  NMR Data<sup>a</sup> for  $\text{HSi}(\text{OR})_3$  Silanes and  $[\text{HSi}(\text{OR})_4]^- \text{K}^+$  Silicates

silane	$\delta$ , ppm	$^1J_{\text{Si-H}}$ , Hz	silicate anion	$\delta$ , ppm	$^1J_{\text{Si-H}}$ , Hz	$\Delta\delta$	$\Delta J$
$\text{HSi}(\text{OMe})_3$	-62.6	290	$[\text{HSi}(\text{OMe})_4]^-$	-82.5	223	19.9	67
$\text{HSi}(\text{OEt})_3$	-59.6	285	$[\text{HSi}(\text{OEt})_4]^-$	-86.2	218	26.6	68
			$[\text{HSi}(\text{OEt})_4]^-^b$	-87.5	215	27.9	71
			$[\text{HSi}(\text{OEt})_4]^-^c$	-85.8	223	26.2	63
$\text{HSi}(\text{O}-n\text{-Bu})_3$	-59.2	286	$[\text{HSi}(\text{O}-n\text{-Bu})_4]^-$	-86.1	219	26.9	67
$\text{HSi}(\text{O}-i\text{-Pr})_3$	-63.4	285	$[\text{HSi}(\text{O}-i\text{-Pr})_4]^-$	-90.5	215	27.1	70
			$[\text{HSi}(\text{O}-i\text{-Pr})_4]^-^b$	-92.0	209	28.6	76
$\text{HSi}(\text{OPh})_3$	-71.3	320	$[\text{HSi}(\text{OPh})_4]^-$	-112.6	296	41.3	24

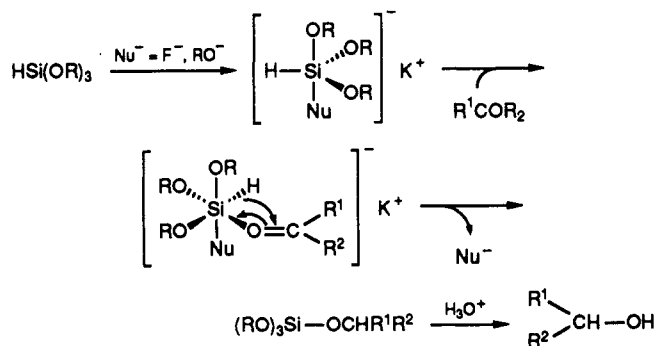
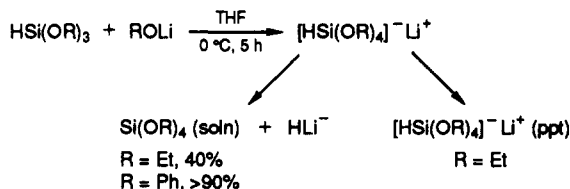
<sup>a</sup> All spectra were recorded at room temperature in THF. <sup>b</sup> As the  $[\text{K}^+(18\text{-crown-6})]$  salt. <sup>c</sup> As the sodium salt.

Scheme I



attention from the mechanistic point of view, including intramolecular ligand exchange,<sup>5d,7</sup> enhanced reactivity toward nucleophiles,<sup>8</sup> and activation of the silicon-carbon bonds.<sup>9</sup> At the same time, a number of synthetic methods have been reported that involve the intermediacy of pentacoordinate silicon.<sup>10</sup>

In this context and as a part of our systematic investigation of hypervalent organosilicon species,<sup>4b,8c,11</sup> we became interested in pentacoordinate anionic hydrido-

Scheme II. Reduction of Aldehydes or Ketones by  $\text{HSi}(\text{OR})_3$  Catalyzed by  $\text{F}^-$  or  $\text{RO}^-$ Scheme III. Reaction of  $\text{HSi}(\text{OR})_3$  with  $\text{ROLi}$ 

silicates,<sup>12</sup>  $[\text{HSi}(\text{OR})_4]^-$ , for two main reasons.

(1) No general synthetic route to these derivatives has been developed. The bis(1,2-benzenediolato)hydrosilicate has been obtained in solution.<sup>13</sup> The only compound that has been isolated up to now in this series resulted either from the reaction between trichlorosilane and the dithio derivative of the hexafluorocumyl alcohol<sup>14</sup> or from the reaction of the spiro-silane 1 with lithium aluminum hydride<sup>15</sup> (Scheme I).

(2) Pentacoordinate hydrosilicates have been suggested to be the reactive intermediates in the reduction of aldehydes and ketones by tetravalent hydrosilanes catalyzed by fluoride<sup>16</sup> and alkoxides<sup>13,17</sup> (Scheme II).

We have now established the formation of several  $[\text{HSi}(\text{OR})_4]^-$  species (where  $\text{R} = \text{Me}, \text{Et}, n\text{-Bu}, i\text{-Pr}, \text{Ph}$ ) as  $\text{K}^+$  salts. In the present paper, we shall describe our synthetic route and focus on some aspects of their chemistry.

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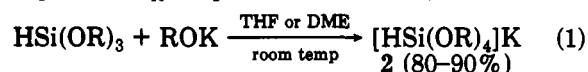
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## 2. Results and Discussion

**2.1. Formation of the  $[\text{HSi}(\text{OR})_4]^-$  Anions.** We have found that the direct reaction of alkoxy- (or aryloxy-) hydrosilane with the corresponding potassium alkoxide (or aryloxide) affords the anionic five-coordinate hydrosilicate  $[\text{HSi}(\text{OR})_4]^-$  (eq 1). For instance, treatment of



R = Me, Et, *n*-Bu, *i*-Pr, Ph

triethoxysilane with 1 equiv of potassium ethoxide as a suspension in a large excess of THF at room temperature yielded 2 (R = Et), which was isolated as a white powder by removal of the solvent (see the Experimental Section for details). This reaction, which is general for other potassium alkoxides (R = Me, *i*-Pr, *n*-Bu) or aryloxide (R = Ph) has been carried out in either THF or dimethoxyethane (DME), and the yields have been optimized up to 80–90%. In a similar manner, the hydrosilicate anions have been obtained as the sodium (2, R = Et) or potassium 18-crown-6 (2; R = Et, *i*-Pr) salts. However, the stability of these species in solution seems to depend on the nature of the cation. In the reaction of EtOLi with  $[\text{HSi}(\text{OEt})_4]^-$  in THF at room temperature, we observed competitive formation of  $\text{Si}(\text{OEt})_4$  in 40% yield as the isolated product in addition to  $[\text{HSi}(\text{OEt})_4]^- \text{Li}^+$ , which precipitated from the reaction mixture (Scheme III). Treatment of  $[\text{HSi}(\text{OPh})_4]^-$  with PhOLi led exclusively to  $\text{Si}(\text{OPh})_4$ .

Scheme III represents a likely mechanism for the formation of  $\text{Si}(\text{OR})_4$ , which corresponds to a nucleophilic displacement of the Si–H bond by  $\text{RO}^-$ . A two-step pathway is suggested, with the first step involving nucleophilic addition of  $\text{RO}^-$ , resulting in  $[\text{HSi}(\text{OR})_4]^- \text{Li}^+$ . The hydrosilicate formed then precipitates (R = Et). When it remains in solution, it undergoes elimination of ionic LiH; the formation of the latter compound is the driving force for the process.

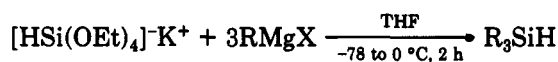
The ready hydrolysis of these salts made both their analysis and subsequent NMR study difficult. Nevertheless, when extreme care was taken, NMR studies could be carried out and the hydrosilicates 2 gave satisfactory spectroscopic data (see Experimental Section for details). In particular, the  $^{29}\text{Si}$  NMR chemical shifts were in the usual range of neutral or anionic pentacoordinate silicon compounds<sup>5,18</sup> (Table I). Similar values were reported recently for the anionic pentaosilicates  $[\text{Si}(\text{OR})_5]^-$  and  $[\text{R}'_n\text{Si}(\text{OR})_{5-n}]^-$ .<sup>5e,8d</sup> As expected, upfield shifts of the  $^{29}\text{Si}$  NMR resonances relative to those of the corresponding alkoxy- (or phenoxy-) silanes were observed. The use of EtOK or *i*-PrOK and 18-crown-6 does not significantly alter the  $^{29}\text{Si}$  NMR spectrum. The  $^{29}\text{Si}$ – $^1\text{H}$  coupling constants are smaller for the five-coordinate silicates than for the corresponding neutral species, as expected from the decrease of the proportion of s character of the orbital for the Si–H bond.

**2.2. Chemical Reactivity.** Recent work clearly indicated that pentacoordinate silicon species have a varied chemistry, significantly different from that of their tetravalent counterparts. Furthermore, data emphasized their enhanced reactivity as compared to that observed with the latter compounds.<sup>4b</sup> From this point of view, the hydrosilicate  $[\text{HSi}(\text{OEt})_4]^-$  reported here has, in fact, such a wide range of reactivities. As will be shown, it can undergo facile nucleophilic attack at silicon by strong

nucleophiles such as Grignard reagents and organolithiums. The high reactivity of the Si–H bond is illustrated both in reactions where the hydrosilicate will act as a base and in the ready reduction of carbonyl derivatives. Finally, evidence will be given of the possibility for  $[\text{HSi}(\text{OEt})_4]^-$  to donate one electron to suitable substrates.

**Reactions with Grignard Reagents and Phenyllithium.** We have reported recently the high reactivity of pentacoordinate anionic *o*-arenediolato<sup>18</sup> and fluoro- and alkoxosilicates<sup>8d</sup> toward strong nucleophiles, such as Grignard reagents or organolithiums relative to the tetraordinated species. Analogous reactions with nucleophiles were performed in the case of  $[\text{HSi}(\text{OEt})_4]^-$  as the potassium salt. For instance, this silicate reacts readily with a slight excess of the Grignard reagent  $\text{R}'\text{MgX}$  at low temperature. Whatever the nature of  $\text{R}'\text{MgX}$  ( $\text{R}' = n\text{-Bu, Ph, PhCH}_2$ ), the triorganosilane  $\text{R}'_3\text{Si-H}$  was obtained in high yield (Scheme IV), and the formation of such compounds provides sound chemical evidence for the nature of the hydrosilicate. Moreover, the displacement of the Si–H bond was not detected.

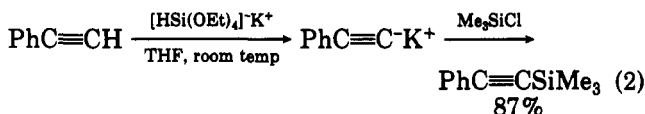
### Scheme IV. Reactivity of $[\text{HSi}(\text{OEt})_4]^-$ toward Grignard Reagents



R = Ph, 66%; R = *n*-Bu, 62%; R =  $\text{PhCH}_2$ , 70%

Treatment of the anionic silicate (R = Et) with 4 molar equiv of phenyllithium in THF or ether at 0 °C for 2 h led to the tetrasubstituted silane,  $\text{Ph}_4\text{Si}$  (85% yield). Under mild conditions, i.e., –78 °C for 1 h with only 3 equiv of the organolithium reagent, a mixture of  $\text{Ph}_4\text{Si}$  (35%) and  $\text{Ph}_3\text{SiH}$  (42%) as major products was obtained.

**Reactions with  $\text{PhC}\equiv\text{CH}$  and  $\text{Ph}_3\text{CH}$ :**  $[\text{HSi}(\text{OEt})_4]^- \text{K}^+$  as a Base. The ready hydrolysis of  $[\text{HSi}(\text{OEt})_4]^- \text{K}^+$  on exposure to air moisture is consistent with a high hydridic character of the Si–H bond. Thus, we investigated the reactions with the weak acids triphenylmethane and phenylacetylene. When phenylacetylene reacted with 1 equiv of  $[\text{HSi}(\text{OEt})_4]^- \text{K}^+$  in THF, deprotonation was observed. The metalation was complete within 4 h at room temperature and led to the potassium acetylide, which was trapped with  $\text{Me}_3\text{SiCl}$  (eq 2). In a



similar manner, the reaction of  $\text{Ph}_3\text{CH}$  with  $[\text{HSi}(\text{OEt})_4]^- \text{K}^+$  resulted in the formation of  $\text{Ph}_3\text{CK}$ . Upon deuteration,  $\text{Ph}_3\text{CD}$  was obtained in 35% yield.

**Reduction of Carbonyl Derivatives.** The reduction of aldehydes and ketones with hydrosilanes has been recognized as a useful synthetic method for a number of years.<sup>10a</sup> This reaction was shown to be catalyzed by fluoride ion<sup>16,20</sup> or alcoholate<sup>17</sup> ions (Scheme II). It was clearly demonstrated that the reducing properties of hydrosilanes are enhanced by intramolecular pentacoordination.<sup>21</sup> Furthermore, either the in situ generated

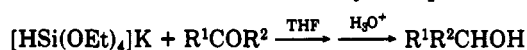
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Table II. Reduction of Carbonyl Compounds



R <sup>1</sup> COR <sup>2</sup>	t, °C	reacn time, h	R <sup>1</sup> R <sup>2</sup> C- HOH, %
PhCHO	0	3	90
p-BrC <sub>6</sub> H <sub>4</sub> CHO	0	4	84
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CHO	0	4	80
PhCOPh	room temp	4	73
PhCOMe	room temp	15	53

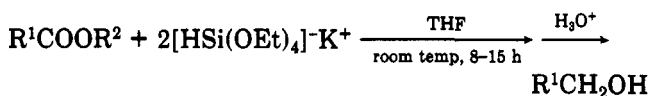
$[\text{HSi}-\text{o}-\text{OC}_6\text{H}_4\text{O}]_2^{-13}$  or the isolated  $[\text{HSi}-\text{o}-\text{C}_6\text{H}_4\text{C}(\text{CF}_3)_2\text{O}]_2^{-}$  in the presence of the related spiroasilane<sup>15</sup> has been found to be an effective reducing agent toward aldehydes and ketones.

As indicated in Scheme II, the results summarized in the literature support the notion that the reduction catalyzed by F<sup>-</sup> or RO<sup>-</sup> takes place by in situ generated pentacoordinate silicon hydrides related to  $[\text{HSi}(\text{OEt})_4]^-$ . The isolation of the hydrido silicates 2 should be a good model for examining the proposed mechanism (Scheme II), and as summarized in Table II, the isolated  $[\text{HSi}(\text{OEt})_4]\text{K}$  was found to reduce ketones and aldehydes effectively in the absence of a catalyst at room temperature.

Yields of primary and secondary alcohols were generally excellent (up to 90%); the lower yield in the case of acetophenone could be attributed to partial enolization of the starting material due either to ethoxide anions liberated during the reaction or to the hydridosilicate itself, the basic behavior of which was demonstrated above. The presence of the enolate derived from PhCOCH<sub>3</sub> was demonstrated with Me<sub>3</sub>SiCl as a trapping agent. The enol silyl ether PhC(OSiMe<sub>3</sub>)=CH<sub>2</sub> was recovered in 40% yield in addition to PhCH(OSiMe<sub>3</sub>)CH<sub>3</sub> resulting from H<sup>-</sup> addition to the carbonyl group. Reduction of benzophenone gave only benzhydrol. No trace of the blue ketyl radical anion was detected during the reaction, and no benzpinacol was recovered. Furthermore, a dilute mixture of  $[\text{HSi}(\text{OEt})_4]$  and benzophenone was found to be ESR inactive.

The efficiency of  $[\text{HSi}(\text{OEt})_4]\text{K}$  as a hydride-transfer agent also is illustrated by its reactions with ethyl benzoate and ethyl dodecanoate. Whereas no reduction was observed with dilithium bis(1,2-benzenediolato)hydridosilicate,<sup>13</sup> the alcohols were obtained in good yield in the reactions with the potassium hydridosilicate (Scheme V).

#### Scheme V. Reduction of Esters by $[\text{HSi}(\text{OEt})_4]^- \text{K}^+$



R<sup>1</sup> = Ph, R<sup>2</sup> = Et, 86%; R<sup>1</sup> = CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>,

R<sup>2</sup> = Et, 65%

From a mechanistic point of view, the present data demonstrate the inherent high reactivity of the Si-H bond in the pentacoordinate hydridosilicates. In sharp contrast, under similar experimental conditions, the analogous hydrosilane HSi(OR)<sub>3</sub> is unreactive toward carbonyl compounds. Furthermore, the data strongly support the notion that the anionic silicates should be the reactive species toward the ketones and aldehydes in the one-pot reaction, as summarized in Scheme I. It is also assumed that the hydride transfer should arise in a hexacoordinate intermediate generated by coordination of the carbonyl derivative to silicon.

**Reactivity toward Organic Halides.** In recent years, numerous studies concerning the reduction of organic halides by metal hydrides have appeared in the literature.

Table III. Reduction of Organic Halides



RX	t, °C	reacn time, h	RH, % <sup>a</sup>	RR, % <sup>a</sup>
C <sub>12</sub> H <sub>25</sub> Cl	45	48	33	
C <sub>12</sub> H <sub>25</sub> Br	room temp	15	47	
PhCH <sub>2</sub> Cl	room temp	40	16	14
PhCH <sub>2</sub> Br	room temp	20	37	34
Ph <sub>2</sub> CHCl	room temp	15	12	40
Ph <sub>3</sub> CBr	room temp	15	47	22 <sup>b</sup>

<sup>a</sup> Yields refer to the percentage of the R radical recovered in RH and RR. The only other product is the unreacted starting material. <sup>b</sup> RR = (4-tritylphenyl)diphenylmethane.<sup>26</sup>

In particular, the occurrence of either a direct nucleophilic substitution or an initial single-electron-transfer pathway (SET) in these reactions has been discussed in detail.<sup>22</sup> Furthermore, the pentavalent anion formed in situ from phenyldimethylsilane and fluoride anion has been reported previously to be a SET reagent,<sup>20a</sup> and thus we investigated the reactions of  $[\text{HSi}(\text{OEt})_4]\text{K}$  with organic halides.

The hydridosilicate reacted smoothly with alkyl halides in THF to give the corresponding alkanes in 30–35% yields after 2 days. The bromides were more reactive than the chlorides. Moreover, concomitant formation of Si(OEt)<sub>4</sub> was observed (Table III). Under similar experimental conditions, HSi(OEt)<sub>3</sub> was found to be unreactive.

Since it is known that the 5-hexen-1-yl radical cyclizes to the cyclopentylmethyl radical, 6-bromo-1-hexene can serve as a probe for the detection of a SET process.<sup>23</sup> Thus, if the 5-hexen-1-yl radical is produced in the reduction by  $[\text{HSi}(\text{OEt})_4]^-$ , then the occurrence of a single-electron transfer would be confirmed by the observation of methylcyclopentane. In fact, the rearranged cyclic product was obtained in less than 5% yield, in addition to 1-hexene, suggesting a polar hydride-transfer process in the reduction of primary alkyl halides instead of a SET mechanism. The latter would require that the 5-hexen-1-yl intermediate radical would be intercepted by  $[\text{HSi}(\text{OEt})_4]^-$  generated from the initial electron-transfer step before it can cyclize into methylcyclopentane.

We have also investigated other reactions with organic halides that might produce stable radical intermediates. Reaction of a slight excess of  $[\text{HSi}(\text{OEt})_4]\text{K}$  with 1 equiv of PhCH<sub>2</sub>Cl, PhCH<sub>2</sub>Br, or Ph<sub>2</sub>CHCl gave the dimer in addition to the expected toluene and diphenylmethane, respectively (Table III). In the case of Ph<sub>3</sub>CBr, an intense red color developed immediately when the bromide was added to a THF solution of the silicate anion at room temperature. After hydrolysis of the reaction mixture, Ph<sub>3</sub>CH and (4-tritylphenyl)diphenylmethane<sup>24</sup> were recovered as the main organic compounds (Table III). Moreover, the reaction solution was found to be EPR active and showed an ESR spectrum consistent with that of

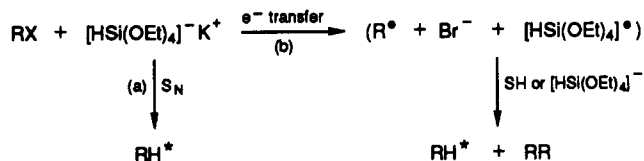
(22) For instance: (a) Ashby, E. C.; Goel, A. B.; De Priest, R. N. *Tetrahedron Lett.* 1981, 22, 3729. (b) Ashby, E. C.; De Priest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* 1984, 49, 3545. (c) Ashby, E. C.; Pham, T. N. *J. Org. Chem.* 1986, 51, 3598. (d) Park, S.-U.; Chung, S.-K.; Newcomb, M. *J. Org. Chem.* 1987, 52, 3275.

(23) Review: Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* 1988, 21, 206.

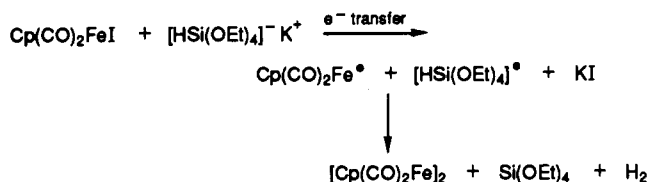
(24) (4-Tritylphenyl)diphenylmethane results from the rearrangement of 1-(diphenylmethylene)-4-tritylcyclohexa-2,5-diene, i.e., the dimer of the triphenylmethyl radical,<sup>25,26</sup> under our experimental conditions (Scheme VII).

(25) For instance: (a) Lankamp, H.; Nauta, W. Th.; MacLean, C. *Tetrahedron* 1968, 249. (b) Guthrie, R. D.; Weisman, G. R. *J. Chem. Soc. D* 1969, 1316. (c) Volz, H.; Lotsch, W.; Schnell, H.-W. *Tetrahedron* 1970, 26, 5343.

(26) Huszthy, P.; Lempert, K.; Simig, G.; Tamas, J.; Hegedüs-Vajda, J.; Toth, G. *J. Chem. Soc., Perkin Trans. 2* 1985, 491.

**Scheme VI.<sup>a</sup> Reduction of Organic Halides with  
[HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup>**


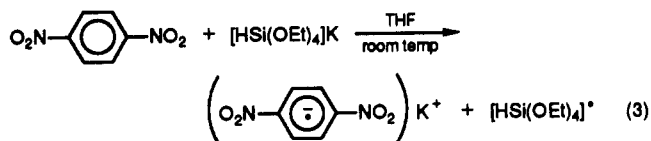
<sup>a</sup> For R = alkyl, RH results from path a; for R = PhCH<sub>2</sub>, Ph<sub>2</sub>CH, Ph<sub>3</sub>C, RH may result from path a or / and b.

**Scheme VII**


the trityl radical<sup>22a,27</sup> generated by one-electron transfer from [HSi(OEt)<sub>4</sub>]<sup>-</sup> to Ph<sub>3</sub>CBr. Additionally, the red color of the reaction mixture did not decay with time and so is indicative of the presence of some Ph<sub>3</sub>C<sup>-22a</sup> resulting from the reaction from Ph<sub>3</sub>CH with [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> (vide supra). Thus, (i) the detection of the dimers, i.e. (PhCH<sub>2</sub>)<sub>2</sub> and (Ph<sub>2</sub>CH)<sub>2</sub>, respectively, in the case of PhCH<sub>2</sub>X (X = Cl, Br) and Ph<sub>2</sub>CHCl, resulting from a radical coupling and (ii) the radical Ph<sub>3</sub>C<sup>•</sup> observed with use of ESR spectroscopy indicate that a SET process can be invoked in the reduction of benzylic halides. However, we cannot exclude that a part of the RH that was formed (PhCH<sub>3</sub>, Ph<sub>2</sub>CH, or Ph<sub>3</sub>CH) results from direct nucleophilic substitution and we propose Scheme VI for the reactions above.

**[HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> as a Single-Electron-Transfer Reagent.** The aptitude of the pentacoordinate hydrosilicates to donate one electron was confirmed with substrates such as Cu<sup>+</sup> and Ag<sup>+</sup> cations and Cp(CO)<sub>2</sub>FeI. In both cases, Si(OEt)<sub>4</sub> was the major organosilicon product (up to 90%). In the case of the iron iodide complex, the reaction gave the iron dimer [Cp(CO)<sub>2</sub>Fe]<sub>2</sub> quantitatively (Scheme VII).

Additionally, a THF solution of [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> with added *p*-dinitrobenzene (DNB) turned green, indicating the formation of the radical anion. Si(OEt)<sub>4</sub> was recovered in 75% yield. A dilute aliquot of this mixture showed an ESR spectrum which was identified as that (*g* = 2.002) of the radical anion of *p*-dinitrobenzene.<sup>20a,28</sup> [HSi(OEt)<sub>4</sub>]<sup>-</sup> itself did not produce the radical anion when treated with *p*-dinitrobenzene. Thus, it was apparent that the electron transfer was due to the interaction of the pentavalent silyl anion with DNB (eq 3).



[HSi(OEt)<sub>4</sub>]<sup>-</sup> was also added to another electron acceptor, i.e., 2,6-di-*tert*-butylbenzoquinone. The solution was found again to be ESR active and showed a three-line spectrum (*a* = 1.256, *g* = 1.999), assigned to the radical anion of the benzoquinone.<sup>20a,29</sup>

**3. Conclusion**

The present investigation has provided a general route to a new series of pentacoordinate hydrosilicates, [HSi(OR)<sub>4</sub>]<sup>-</sup>K<sup>+</sup>, isolated as stable crystalline products.

From a mechanistic point of view, the data clearly indicate that these five-coordinate species exhibit a wide range of reactivities. (i) The silicon atom acts as an electrophilic center and undergoes fast nucleophilic displacement reactions with Grignard reagents and organolithiums. (ii) The hydrosilicates exhibit basic properties in deprotonation reactions of weakly acidic compounds such as PhC≡CH and Ph<sub>3</sub>CH. (iii) They are reducing agents toward carbonyl derivatives. In the reaction, hydride transfer occurs through a hexacoordinate intermediate, resulting from the coordination of the carbonyl species to silicon. The data also confirm unambiguously the intermediacy of such species in the reduction of aldehydes and ketones with trialkoxysilanes catalyzed by F<sup>-</sup> or RO<sup>-</sup> anions. (iv) The reduction of alkyl halides results from a direct attack of the hydride at silicon via an S<sub>N</sub>2-type mechanism. However, a SET process can be invoked in the case of benzylic halides (RX), which afford the dimer RR in addition to the expected alkane RH. (v) Finally, this ability to donate an electron is confirmed in reactions with oxidizing agents (Cu<sup>+</sup>, Ag<sup>+</sup>, Cp(CO)<sub>2</sub>FeI). This is a new kind of reactivity that was never observed with tetra-coordinate silanes.

The varied chemical behavior of the pentacoordinate hydrosilicates is of special interest, and generalization of the above observations to other models is now in progress.

**4. Experimental Section**

All reactions were carried out under argon by using a vacuum line and Schlenk tubes. Solvents were dried and distilled before use. All carbonyl compounds and organic halides used are commercial products. Triethoxysilane (Fluka) and trimethoxysilane (Aldrich) were used as received. Other alkoxysilanes were prepared from trichlorosilanes and the corresponding alcohols.<sup>30</sup> Potassium and lithium alcoholates or phenates were prepared by reaction of potassium hydride (Aldrich) or butyllithium, respectively, with the corresponding alcohols and phenol.

<sup>1</sup>H NMR spectra were obtained on a Bruker AW-60, AW-80, or AC-250 instrument and <sup>29</sup>Si NMR spectra on a Bruker AC-200 or AC-250 spectrometer (chemical shifts are relative to Me<sub>4</sub>Si). <sup>29</sup>Si NMR spectra in THF were taken by using an internal capillary tube with C<sub>6</sub>D<sub>6</sub> to lock the instrument or a THF-C<sub>6</sub>D<sub>6</sub> (90:10) mixture and are referenced to Me<sub>4</sub>Si taken under the same conditions. IR spectra were recorded on a Perkin-Elmer 298 or Perkin-Elmer 1600 instrument. ESR spectra were obtained on a Bruker ER 200 D instrument. Melting points were taken under vacuum with a Gallenkamp melting point apparatus and are uncorrected. Gas chromatography analyses were performed with a 1.40-m Chromosorb W, DMCS, 10% SE30 column, with hexadecane as internal standard.

**4.1. Preparation of Hydrosilicates [HSi(OR)<sub>4</sub>]<sup>-</sup>K<sup>+</sup>.** The following procedure is given as an example.

**[HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup>.** A solution of triethoxysilane (3.27 g, 20 mmol) in THF (20 mL) was added dropwise to a slurry of potassium ethoxide (1.68 g, 20 mmol) in THF (60 mL) at room temperature, and the mixture was stirred for 2 h. The reaction mixture was filtered to remove traces of potassium ethoxide, and the solvent was evaporated under vacuum to give a white powder (4.18 g, 16.8 mmol, 85% yield). This crude product was recrystallized from ether at -20 °C and gave the title compound as white crystals (3.67 g, 14.8 mmol, 75% yield): mp 127–134 °C dec; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 4.24 (s, 1 H, SiH), 4.00 (q, 8 H, CH<sub>2</sub>), 1.36 (t, 12 H, CH<sub>3</sub>); <sup>29</sup>Si NMR (THF) δ -86.2 ppm (dh), *J*(Si-H) = 218 Hz, <sup>3</sup>*J*(Si-H) = 6 Hz. Anal. Calcd for C<sub>8</sub>H<sub>21</sub>KO<sub>4</sub>Si: C, 38.67; H, 8.52;

(27) Adam, F. C.; Weisman, S. I. *J. Am. Chem. Soc.* **1958**, *80*, 2057.

(28) Freed, J. H.; Fraenkel, G. K. *J. Chem. Phys.* **1964**, *40*, 1815.

(29) Chen, K. S.; Foster, T.; Wan, J. K. S. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1288.

(30) Eaborn, C. In *Organosilicon Compounds*; Butterworths: London, **1960**.

Si, 11.30. Found: C, 37.86; H, 8.74; Si, 11.53.

**[HSi(OPh)<sub>4</sub>]K<sup>+</sup>**. This compound was prepared by the same procedure as for [HSi(OEt)<sub>4</sub>]K<sup>+</sup> with triphenoxysilane (1.98 g, 6.44 mmol) and potassium phenoxide (0.85 g, 6.44 mmol) in 20 mL of THF; a clear, colorless solution was obtained after 1-h reaction, and removal of the solvent gave the title compound quantitatively as a white powder: mp 298–299 °C; <sup>1</sup>H NMR (THF-*d*<sub>6</sub>) δ 6.8 (m, 20 H, Ph), 4.6 (s, 1 H, SiH); <sup>29</sup>Si NMR (THF) δ -112.6 ppm (d), *J*(Si-H) = 296 Hz. Anal. Calcd for C<sub>24</sub>H<sub>21</sub>KO<sub>4</sub>Si: C, 65.42; H, 4.81; Si, 6.37. Found: C, 65.36; H, 4.67; Si, 6.43.

**[HSi(O-*i*-Pr)<sub>4</sub>]K<sup>+</sup>**. This compound was prepared by the same procedure as for [HSi(OEt)<sub>4</sub>]K<sup>+</sup> with triisopropoxysilane (9.41 g, 45.7 mmol) and potassium isopropoxide (4.48 g, 45.7 mmol) in 100 mL of THF. The title compound was obtained as a white powder (12.3 g, 40.4 mmol, 89% yield): mp 120–130 °C dec; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 4.41 (m, 4 H, CH), 3.64 (s, 1 H, SiH), 1.30 (d, 24 H, *J* = 6 Hz, CH<sub>3</sub>); <sup>29</sup>Si NMR (THF) δ -90.5 ppm (d), *J*(Si-H) = 215 Hz.

**[HSi(OMe)<sub>4</sub>]K<sup>+</sup>**. This compound was prepared by the same procedure as for [HSi(OEt)<sub>4</sub>]K<sup>+</sup> with trimethoxysilane (3.10 g, 25.4 mmol) and potassium methoxide (1.78 g, 25.4 mmol) in THF (30 mL). The title compound was obtained as a white powder (4.20 g, 21.9 mmol, 86% yield): mp 260 °C dec; <sup>29</sup>Si NMR (THF) δ -82.5 ppm (d), *J*(Si-H) = 223 Hz. Anal. Calcd for C<sub>4</sub>H<sub>13</sub>KO<sub>4</sub>Si: C, 24.98; H, 6.81; Si, 14.60. Found: C, 23.84; H, 6.51; Si, 15.00. This compound is extremely air and moisture sensitive; this fact explains why we did not obtain a good <sup>1</sup>H NMR spectrum or a better analysis.

**[HSi(O-*n*-Bu)<sub>4</sub>]K<sup>+</sup>**. This compound was prepared by the same procedure as for [HSi(OEt)<sub>4</sub>]K<sup>+</sup> with tributoxysilane (8.43 g, 34.0 mmol) and potassium butoxide (3.80 g, 34.0 mmol) in THF (50 mL). The title compound was obtained as a white powder (10.0 g, 27.7 mmol, 82% yield): mp 115–125 °C dec; <sup>1</sup>H NMR δ 4.0 (m, 9 H, CH<sub>2</sub>, SiH), 1.65–1.13 (m, 28 H, CH<sub>2</sub>, CH<sub>3</sub>); <sup>29</sup>Si NMR (THF) δ -86.1 ppm (d), *J*(Si-H) = 219 Hz.

**[HSi(OEt)<sub>4</sub>]Na<sup>+</sup>**. This compound was prepared by the same procedure as for [HSi(OEt)<sub>4</sub>]K<sup>+</sup> with triethoxysilane (0.57 g, 3.5 mmol) and sodium ethoxide (0.24 g, 3.5 mmol) in THF (20 mL) (reaction time 4 h). The title compound was obtained as a white sticky powder (0.77 g, 3.3 mmol, 95% yield): <sup>29</sup>Si NMR (THF) δ -85.8 ppm (d), *J*(Si-H) = 223 Hz.

**Reaction of HSi(OEt)<sub>3</sub> with LiOEt.** A solution of HSi(OEt)<sub>3</sub> (2.0 g, 12 mmol) was added to a slurry of LiOEt (0.62 g, 12 mmol) in THF (20 mL) cooled to 0 °C, and the mixture was stirred for 4 h at room temperature. The reaction mixture was filtered, giving a solid residue and a solution. <sup>29</sup>Si NMR spectroscopy of the solution gave a single peak at -81.6 ppm, which corresponds to Si(OEt)<sub>4</sub>. Distillation of the solution gave Si(OEt)<sub>4</sub> (0.96 g, 4.6 mmol, 40% yield). The solid residue was treated with 30 mmol of PhMgBr at room temperature for 15 h and gave, after the usual workup and preparative silica gel plate purification (eluent CH<sub>2</sub>Cl<sub>2</sub>) a 30% yield (0.92 g, 3.5 mmol) of Ph<sub>3</sub>SiH (identical with an authentic sample).

**Reaction of HSi(OPh)<sub>3</sub> with LiOPh.** The same procedure as for HSi(OEt)<sub>3</sub> and LiOEt was used. Treatment of HSi(OPh)<sub>3</sub> (1.23 g, 4.0 mmol) with LiOPh (0.40 g, 4.0 mmol) in THF (50 mL) gave a clear colorless solution, the <sup>29</sup>Si NMR spectrum of which showed a major peak at δ -100.1 ppm corresponding to Si(OPh)<sub>4</sub>. The solution was treated with PhMgBr (10 mmol) to give a 5% yield (0.05 g, 0.2 mmol) of Ph<sub>3</sub>SiH (identical with an authentic sample).

**4.2. Reactions of [HSi(OEt)<sub>4</sub>]K<sup>+</sup> with Nucleophiles.** The following example is given as a general procedure.

**PhMgBr.** A solution of PhMgBr (28.5 mmol) in THF was added dropwise to a stirred solution of [HSi(OEt)<sub>4</sub>]K<sup>+</sup> (2.35 g, 9.5 mmol) in THF (30 mL) stirred at 0 °C. After it was stirred at -78 °C for 2 h, the reaction mixture was hydrolyzed with a saturated solution of ammonium chloride. Standard workup gave Ph<sub>3</sub>SiH in 66% yield (1.64 g, 6.3 mmol) after recrystallization from benzene (identical with an authentic sample).

**PhCH<sub>2</sub>MgBr.** This procedure was the same as for PhMgBr. (PhCH<sub>2</sub>)<sub>3</sub>SiH was obtained in 70% yield after recrystallization from diethyl ether (identical with an authentic sample).

***n*-BuMgBr.** This procedure was the same as for PhMgBr. *n*-Bu<sub>3</sub>SiH was obtained in 62% yield after distillation (bp<sub>15</sub> 95–100 °C; lit.<sup>36</sup> bp<sub>20</sub> 104 °C) (identical with an authentic sample).

**PhLi.** A solution of PhLi (32.5 mmol) in diethyl ether was added dropwise to a solution of [HSi(OEt)<sub>4</sub>]K<sup>+</sup> (2.0 g, 8.06 mmol) in THF (20 mL) at -78 °C. The reaction mixture was warmed up to 0 °C and stirred for 2 h. The mixture was hydrolyzed with a saturated solution of ammonium chloride and extracted from toluene to give Ph<sub>4</sub>Si in 87% yield (2.35 g, 7.0 mmol) (identical with an authentic sample). With 3 equiv of PhLi (i.e. 21.6 mmol) and 7.2 mmol (1.8 g) of [HSi(OEt)<sub>4</sub>]K<sup>+</sup>, the same procedure gave Ph<sub>3</sub>SiH in 42% yield (0.79 g, 3.0 mmol) and Ph<sub>4</sub>Si in 35% yield (0.84 g, 2.5 mmol) after separation on a preparative silica gel plate (eluent toluene-hexane, 1:1).

**4.3. Reduction of Carbonyl Compounds with [HSi(OEt)<sub>4</sub>]K<sup>+</sup>.** The following example is given as a general procedure. All products are known and identified by comparison with authentic samples.

**PhCHO.** A solution of PhCHO (0.80 g, 7.5 mmol) in THF (10 mL) was added dropwise to a stirred solution of [HSi(OEt)<sub>4</sub>]K<sup>+</sup> (1.8 g, 7.5 mmol) in THF (10 mL) at 0 °C. After 3 h at that temperature, the reaction mixture was hydrolyzed with a 2 N solution of HCl. Standard workup followed by purification on a preparative silica gel plate (eluent CHCl<sub>3</sub>) gave PhCH<sub>2</sub>OH in 90% yield (0.73 g, 6.8 mmol).

**CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>CHO.** This procedure was the same as for PhCHO. The corresponding alcohol CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>OH was obtained in 80% yield.

***p*-BrC<sub>6</sub>H<sub>4</sub>CHO.** This procedure was the same as for PhCHO. The corresponding alcohol was isolated in 84% yield.

**PhCOPh.** This procedure was the same as for PhCHO (reaction conditions: 4 h at room temperature). PhCHOHPh was obtained as crystals in 73% yield without chromatographic purification (no Ph<sub>2</sub>C(OH)C(OH)Ph<sub>2</sub> was observed).

**PhCOCH<sub>3</sub>.** This procedure was the same as for PhCHO (reaction conditions: 15 h at room temperature). PhCH(OH)CH<sub>3</sub> was obtained in 53% yield together with 28% of PhCOCH<sub>3</sub> obtained from hydrolysis of the enolate. The presence of PhC(O)CH=CH<sub>2</sub> was demonstrated by its reaction with Me<sub>3</sub>SiCl, which was added to the preceding reaction mixture before the hydrolysis step. Distillation gave a 30% yield of PhC(OSiMe<sub>3</sub>)=CH<sub>2</sub>; bp<sub>0.2</sub> 50–60 °C. The <sup>1</sup>H NMR spectrum was identical with that in the literature.<sup>31</sup>

**PhCOOEt.** This procedure was the same as for PhCHO. A mixture of PhCOOEt (2.3 g, 15 mmol) and [HSi(OEt)<sub>4</sub>]K<sup>+</sup> (3.7 g, 15 mmol) in THF (45 mL) was stirred at room temperature for 4 h. After hydrolysis a mixture of PhCH<sub>2</sub>OH (0.62 g, 5.7 mmol, 38% yield) and starting material (0.93 g, 6.2 mmol) were obtained. No PhCHO was found. With a 1:2 ratio of PhCOOEt-[HSi(OEt)<sub>4</sub>]K<sup>+</sup>, PhCH<sub>2</sub>OH was obtained in 86% yield after stirring at room temperature for 8 h and the usual workup.

**CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>COOEt.** This procedure was the same as for PhCHO. A mixture of CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>COOEt (0.77 g, 3.40 mmol) and [HSi(OEt)<sub>4</sub>]K<sup>+</sup> (1.70 g, 6.85 mmol) in THF (20 mL) was stirred at room temperature for 15 h to give, after hydrolysis, a 65% yield (0.41 g, 2.2 mmol) of CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH.

**4.4. Reduction of Organic Halides.** The following example is given as a general procedure.

**C<sub>12</sub>H<sub>25</sub>Br.** A solution of C<sub>12</sub>H<sub>25</sub>Br (1.1 g, 4.4 mmol) in THF (5 mL) was added via a syringe to a stirred solution of [HSi(OEt)<sub>4</sub>]K<sup>+</sup> (1.4 g, 5.6 mmol) in THF (15 mL) at room temperature and stirred for 15 h. A gas chromatographic analysis indicated 55% C<sub>12</sub>H<sub>26</sub>, 45% C<sub>12</sub>H<sub>25</sub>Br, and 31% Si(OEt)<sub>4</sub>. Filtration and distillation gave a 45% yield (0.35 g, 2.1 mmol) of C<sub>12</sub>H<sub>26</sub>.

**C<sub>12</sub>H<sub>25</sub>Cl.** This procedure was the same as for C<sub>12</sub>H<sub>25</sub>Br. The reaction was performed at 45 °C for 48 h. Gas chromatographic analysis gave 33% C<sub>12</sub>H<sub>26</sub>, 67% C<sub>12</sub>H<sub>25</sub>Cl, and 28% Si(OEt)<sub>4</sub>.

**PhCH<sub>2</sub>Cl.** This procedure was the same as for C<sub>12</sub>H<sub>25</sub>Br. The reaction was performed at room temperature for 40 h. Gas chromatographic analysis gave 16% toluene, 7% PhCH<sub>2</sub>CH<sub>2</sub>Ph, and 70% starting material.

**PhCH<sub>2</sub>Br.** This procedure was the same as for C<sub>12</sub>H<sub>25</sub>Br. After the reaction mixture was stirred at room temperature for 20 h, gas chromatographic analysis indicated 37% toluene and 55% Si(OEt)<sub>4</sub>. A silica gel plate purification (eluent hexane) yielded

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PhCH<sub>2</sub>CH<sub>2</sub>Ph (34% calculated from PhCH<sub>2</sub>Br).

**Ph<sub>2</sub>CHCl.** This procedure was the same as for C<sub>12</sub>H<sub>22</sub>Br. The mixture was stirred at room temperature for 15 h, filtered, and concentrated to give crystals of Ph<sub>2</sub>CHCHPh<sub>2</sub> in 40% yield (calculated from Ph<sub>2</sub>CHCl). The filtrate was distilled (bp<sub>0.4</sub> 70–80 °C) to give 12% Ph<sub>2</sub>CH<sub>2</sub>.

**Ph<sub>3</sub>CBr.** A solution of Ph<sub>3</sub>CBr (2.9 g, 9.0 mmol) was added dropwise to a stirred solution of [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> (2.3 g, 9.2 mmol) in THF (60 mL) at room temperature. After it was stirred for 15 h, the reaction mixture was hydrolyzed with a saturated solution of NH<sub>4</sub>Cl and extracted with toluene to give a white powder after removal of the solvents. Addition of diethyl ether gave a solution (A) and left a solid (B). Solution A was concentrated to give Ph<sub>3</sub>CH as colorless crystals (1.03 g, 4.2 mmol) in 47% yield. Dissolution of the solid B into CCl<sub>4</sub> followed by preparative TLC (eluent CCl<sub>4</sub>) gave *p*-Ph<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>CPh<sub>3</sub><sup>24</sup> in 22% yield (0.48 g, 0.99 mmol): mp 215–235 °C (lit.<sup>32</sup> mp 226–227 °C); <sup>1</sup>H NMR spectrum identical with that in the literature.<sup>33</sup>

**4.5. Miscellaneous. Reaction of [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> with PhC≡CH.** A solution of PhC≡CH (0.55 g, 5.4 mmol) in 10 mL of THF was added to a solution of [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> (1.34 g, 5.4 mmol) in the same solvent (10 mL), and the mixture was stirred at room temperature for 4 h. Me<sub>3</sub>SiCl (0.65 g, 6 mmol) was added, and the reaction mixture was stirred for 4 h. Hydrolysis with a saturated solution of NH<sub>4</sub>Cl, followed by standard workup, gave an oil, which was purified by TLC (silica, eluent hexane) to give PhC≡CSiMe<sub>3</sub> in 87% yield (0.82 g, 4.7 mmol): <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 7.0–7.5 (m, 5 H, Ar), 0.1 (s, 9 H, SiMe<sub>3</sub>); IR (neat) ν(C≡C) 2159 cm<sup>-1</sup>.

**Reaction of [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> with Ph<sub>3</sub>CH.** A solution of Ph<sub>3</sub>CH (0.60 g, 2.5 mmol) in 10 mL of THF was added dropwise to the solution of [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> (0.80 g, 3.2 mmol) in 15 mL of THF. The solution turned red. After 48 h of stirring, the <sup>1</sup>H NMR spectrum of the reaction mixture showed the presence of Ph<sub>3</sub>C-

(about 35%, <sup>1</sup>H NMR spectrum analogous to that in the literature<sup>34</sup>) and Ph<sub>3</sub>CH. After deuteration, a mixture of Ph<sub>3</sub>CD and Ph<sub>3</sub>CH (35:65) was determined by <sup>1</sup>H NMR spectroscopy.

**Reaction of [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> with Copper and Silver Salts. With AgBPh<sub>4</sub>.** A solution of [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> (1.6 g, 6.4 mmol) in 20 mL of THF was added to a suspension of AgBPh<sub>4</sub> (2.2 g, 6.4 mmol) in 10 mL of the same solvent. After 4 h of stirring at room temperature, Ag and KBPh<sub>4</sub> were eliminated by filtration. The filtrate was concentrated and distilled, giving Si(OEt)<sub>4</sub> in 83% yield (1.1 g, 5.3 mmol) (bp<sub>10</sub> 55–60 °C).

**With CuI.** This procedure was the same as for AgBPh<sub>4</sub> with [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> (1.75 g, 7 mmol) and CuI (1.3 g, 7 mmol) in 30 mL of THF. Distillation gave an 81% yield of Si(OEt)<sub>4</sub> (1.2 g, 5.7 mmol) (bp<sub>10</sub> 55–60 °C).

**Reaction of [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> with Cp(CO)<sub>2</sub>FeI.** A solution of Cp(CO)<sub>2</sub>FeI (0.70 g, 2.3 mmol) in 15 mL of THF was added dropwise to a solution of [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> (0.80 g, 3.2 mmol) in 15 mL of THF at 0 °C. After 4 h of stirring at room temperature, the IR spectrum of the reaction mixture showed only the presence of [Cp(CO)<sub>2</sub>Fe]<sub>2</sub>. Elimination of the solvent under vacuum followed by recrystallization from hexane gave [Cp(CO)<sub>2</sub>Fe]<sub>2</sub> in 81% yield (0.33 g, 0.94 mmol).

**4.6. EPR Experiments.** The following procedure is given as an example. One milliliter of a dilute solution (5–10 mg in 3 mL of THF) of Ph<sub>3</sub>CBr was added via a cannula under argon to 1 mL of a dilute solution of [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> (5–10 mg in 3 mL of THF) in a 5- or 2-mm-diameter glass tube, which was then put in the field of the instrument: *g* = 1.977; *a* = 1.256 G (spectrum analogous to that in the literature<sup>22a</sup>). [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> with 2,5-di-*tert*-butyl-*p*-quinone: *g* = 1.999; *a* = 1.256 G (spectrum analogous to that in the literature<sup>20a,29</sup>). [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> with *p*-dinitrobenzene gave a nonsymmetrical signal centered at *g* = 2.002 (see refs 20a and 28). A solution of pure [HSi(OEt)<sub>4</sub>]<sup>-</sup>K<sup>+</sup> in THF gave no ESR signal under similar conditions.

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## NMR Structural and Dynamic Study of a Carbenium Ion with a Steroidal Substituent, [Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>(μ-HC≡CC<sub>19</sub>H<sub>24</sub>O)]<sup>+</sup>BF<sub>4</sub><sup>-</sup>

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<sup>13</sup>C and <sup>1</sup>H NMR evidence for the fluxional behavior of a carbenium ion with a steroidal substituent, [Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>(μ-HC≡CC<sub>19</sub>H<sub>24</sub>O)]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, is presented. In solution, the NMR spectra are highly temperature dependent. We propose the existence of diastereomers of this ion in solution, one of these being very similar to the solid-state structure previously determined by X-ray diffraction.

### Introduction

It is well-known that the organometallic derivatives of ethynylestradiol recognize the estradiol receptor. In the case of a Co<sub>2</sub>(CO)<sub>8</sub> derivative, the interaction with the receptor is irreversible, while for a Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub> derivative

a reversible bond is formed.<sup>1</sup> This result has been attributed to the formation of a carbenium ion, which is stabilized by the presence of a bimetallic cluster coordinated to the position adjacent to the carbenium ion.<sup>2–5</sup>

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