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CYCLOPENTADIENYL–METAL COMPLEXES

III. THE INTRAMOLECULAR 1,5-TRANSFER AND THE EQUILIBRIUM BETWEEN THE POSITIONAL ISOMERS OF σ-(TRIMETHYLSILYL)CYCLOPENTADIENE

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SUMMARY

In the course of a series of thermochemical studies on gaseous cyclopentadienyl–metal complexes we have investigated the intramolecular 1,5-transfer of hydrogen and the $Si(CH_3)_3$ group and the composition of equilibrated mixtures of the x-(trimethylsilyl)cyclopentadiene (=x-TSCP) isomers. For the equilibria

$$\text{5-TSCP} \underset{2}{\overset{1}{\rightleftarrows}} \text{1-TSCP} \underset{4}{\overset{3}{\rightleftarrows}} \text{2-TSCP}$$

the following Van 't Hoff relationships have been derived: $\log K_{1,2} = (0.193 \pm 0.014) - (1.56 \pm 0.03)/\theta$ and $\log K_{3,4} = (0.09 \pm 0.03) - (0.84 \pm 0.05)/\theta$ where θ equals $4.58 \cdot 10^{-3}\ T$ (°K). In contrast to the carbon analogues, the 5-isomer is thermodynamically the most stable isomer. The data are used to derive intrinsic differences in incremental data for entropy and enthalpy contributions in specific carbon–silicon compounds. Vapour pressure measurements on equilibrated isomer mixtures yielded $\log p(\text{mm}) = (7.79 \pm 0.10) - (2029 \pm 31)/T$ (°K) resulting in a heat of vaporization ΔH_v of 9.28 ± 0.14 kcal/mole.

INTRODUCTION**

Cyclopentadienyl–metal complexes have received a great deal of attention, primarily directed towards the relationship between reactivity and structure in such compounds. It is well documented[1-7] that metal centers σ-bonded to cyclopentadiene rings undergo concerted intramolecular migration reactions similar to the sigmatropic 1,5-hydrogen shifts in cyclopentadiene and its derivatives[8]. Both, 1,3-[3,9] and 1,5-transfers[1-3,7b,9] have been proposed for the metal transfer, depending on the structure of the complex.

There are in principle two possible intramolecular isomerization reactions in $R_x(H)M\text{-}\sigma\text{-}C_5H_5$ complexes, (accepting that the cyclopentadiene ring be flat[10,11]):

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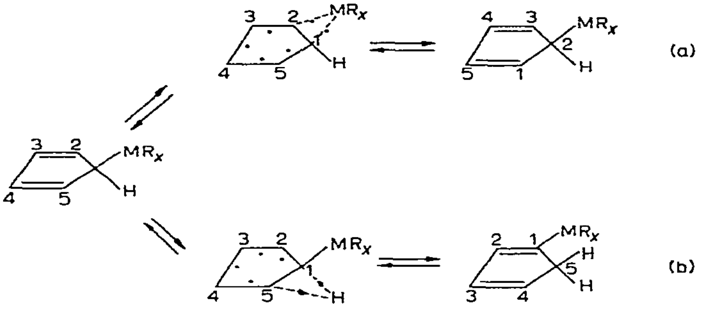
** Throughout this paper cal = 4.184 J, atm = 101.325 kN·m^{-2}, torr = mm Hg = 101.325/760 kN·m^{-2}.



For cyclopentadiene itself, the 1,5-hydrogen transfer reaction requires about 25 kcal of activation energy[10] compared to more than 40 kcal/mole postulated* for the intramolecular transfer of a methyl group in methylcyclopentadienes[12].

In contrast, the transfer of $-Si(CH_3)_3$ groups in 5-(trimethylsilyl)cyclopentadiene as that of metalcentered groups in general requires very little activation energy ($\lesssim$ 9 kcal/mole)[9], leading in the liquid phase** to a very fast equilibration and PMR-equivalency of the ring protons. The activation parameters for this intramolecular isomerization process are apparently of the same order of magnitude as that expected for a hindered rotation about the σ-C_5H_5–MR_x bond! Such a fast continuous intramolecular MR_x-transfer (halflife $10^{-6\pm1}$ sec), not leading to any net chemical change does not result in any "stabilizing" effect on the structure of the compound nor does it inhibit energetically feasible competitive reactions like (b).

Using the concept of single bond dissociation energies we have demonstrated in earlier papers[13,14] that gas phase kinetics can be a valuable tool in determining the type of metal–carbon bonding involved in cyclopentadienyl compounds. This work was prompted by our interest in the prospect of using the intramolecular hydrogen transfer reaction (b) as a criterion for discriminating between σ- or π-M–C_5H_5 bonding. If a 5-metal σ-cyclopentadienyl compound is sufficiently stable towards pyrolysis up to temperatures of 100 to 150° it should undergo consecutive 1,5-hydrogen transfers into the corresponding 1-metal– and 2-metal–cyclopentadiene isomers, exhibiting M–C=C-bonding. Based on the concept of bond dissociation energies outlined previously[13,15] the C=C–M bond should be much more stable than the corresponding $\rangle$C–M bond in the starting 5-isomer.

During our investigation of the intramolecular isomerizations involved in $(CH_3)_3SiC_5H_5$ and $Hg(C_5H_5)_2$ several papers appeared on this same subject[7,9,16–18]. Ashe[16] investigated the kinetics of the 1,5-hydrogen migration in 5-TSCP using PMR-spectroscopy and reported $k_1(\text{sec}^{-1}) = 2 \times 10^{13} \exp(-26.2\ \text{kcal}\cdot\text{mole}^{-1}/RT)$. Ustynyuk and co-workers[9,17–19] reported on PMR spectra of the title compound[17] and of 5-(methyldichlorosilyl)cyclopentadiene[9,18], for which they reported an activation energy of 9 ± 1 kcal/mole for the metallotropic rearrangement compared with an earlier rough estimate of Fritz and Kreiter[20] of ~3 kcal/mole. We restrict ourselves in this paper to the equilibrium measurements and thermodynamic aspects

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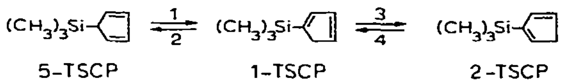
* The observed first-order activation parameters for the isomerization of 1,5,5-trimethylcyclopentadiene into the 1,2,5-isomer[12] are also consistent with a free radical process.

** In solid state intermolecular forces lead to "locked" or "instantaneous"[1] σ-structures in which no further MR_x-shifts can be observed.

of the rearrangement



(c)

Results obtained with $Hg(C_5H_5)_2$ will be reported separately[21].

EXPERIMENTAL

1. *Materials*

The Grignard method was used to prepare (5-trimethylsilyl)cyclopentadiene, (5-TSCP) reacting $(CH_3)_3SiCl$ with C_5H_5MgBr following a recipe of Frisch[22]. Attempts to prepare 5-TSCP by direct reaction of $Tl(C_5H_5)$[23] with $(CH_3)_3SiC_5H_5$ in tetrahydrofuran in analogy to the preparation[24] of $Hg(C_5H_5)_2$ from $HgCl_2$, failed.

Based on the integration of $(CH_3)_3Si$-groups the PMR-analysis of the starting material (in benzene solution) gave 82.1% 5-(trimethylsilyl)cyclopentadiene, 15.7% 1- and 0.6% of the 2-isomer, besides 2.0% of an impurity, probably $ClSi(CH_3)_3$.

The ring protons in the starting material resulted in a total relative hydrogen count of 5.04 compared to 8.95 for the methyl-hydrogens. The same starting material was used for all the experiments.

2. *Procedures*

The reaction was carried out in a static reaction system described previously[25], using a pyrex-glass reaction cell of 1050 ml volume. The connecting leads were kept at ~55±2°. This way premature condensation in the deadspace could be prevented and at the same time the temperature was still low enough, to minimize continued reaction during quenching of the product mixture.

Between 5 and 7 sec were required to condense 90% or more of the product mixture.

Based on the kinetic data for the hydrogen migration in 5-TSCP given by Ashe[16] and a quenching time of 5 sec one can conclude that up to temperatures of

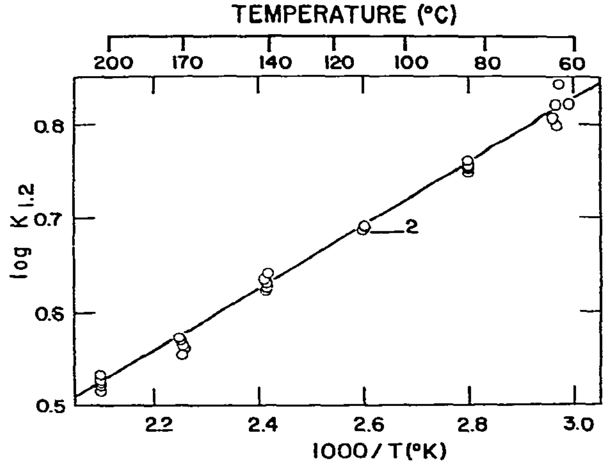


Fig. 1. Van 't Hoff relationship of the equilibrium constant $K_{1,2}=[\text{1-TSCP}/\text{5-TSCP}]_{eq}$. The number 2 indicates overlapping points.

~ 140°, no measurable conversion should take place upon condensing the reaction product. The observed isomer ratio for reaction products obtained at 265° evidently do not represent equilibrium mixtures at this temperature, but correspond to a significantly lower, non defined temperature. In contrast the isomer ratios observed at ~200° fall onto the "best" lines shown in Figs. 1 and 2 and drawn through the experimental points for the temperature range 64 to 170°. This then implies, that the quenching procedure was fast enough to allow for reliable measurements of the equilibrium concentrations up to about 200°.

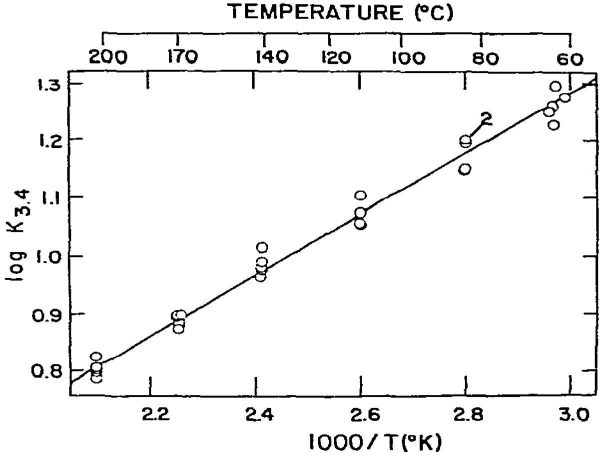


Fig. 2. Van 't Hoff relationship of the equilibrium constant $K_{3,4}$=[2-TSCP/1-TSCP]$_{eq}$. The number 2 indicates overlapping points.

At 200° we could certainly expect to be at the limits of the experimental procedures considering that the halflife of the 5-isomer is expected to be less than 0.1 sec at this temperature. Another important condition for reproducible equilibrium data was the immediate PMR analysis of the collected product mixture. If the material was stored for several days at 0° prior to analysis, as was the case for the first set of experiments, (compare Table 1) the observed isomer ratios deviated in a consistent manner, suggesting that the products underwent further isomerization upon storage and handling.

3. *Analysis*

Proton magnetic resonance spectra (PMR) were recorded using a Varian HA60 instrument. Tetramethylsilane as an internal standard and field-sweep integration were used.

The PMR spectra of the TSCP-isomers showed the expected appearance, chemical shifts, coupling constants and relative H-counts[16-18,20]. Benzene solutions were used throughout, allowing complete separation of the absorptions of the $-Si(CH_3)_3$-groups of 5-TSCP (τ 10.116 ppm), 1-TSCP (9.858 ppm) and 2-TSCP (9.812 ppm), which served as a basis for the quantitative analyses of the isomer mixtures.

The reliability of the quantitative PMR analyses was checked by analysing test mixtures made up by mixing weighed aliquots of purified samples of CH_3Si-

TABLE 1

TEST OF THE RELIABILITY OF THE QUANTITATIVE PMR-ANALYSES

Test mixture	Components[a]	Mole %		Δ in % of (I) or (II)
		Weight	NMR	
A	(I)	57.60	57.81	0.37
	(II)	42.40	42.19	0.50
B	(I)	16.44	16.27	1.05
	(II)	83.56	83.73	0.20
C	(I)	89.15	89.82	0.75
	(II)	10.85	10.12	6.15

[a] (I) stands for $CH_3Si(OC_2H_5)_3$ and (II) for $CH_3Si(H)(C_6H_5)_2$.

$(OC_2H_5)_3$ (τ 9.86 ppm) and $CH_3Si(H)(C_6H_5)_2$ (τ 9.52 ppm). The PMR absorptions of the $SiCH_3$ groups (given in parentheses) again served as a quantitative measure of the relative concentrations. The results are summarized in Table 1 below.

As can be seen from the results listed in Table 1, the PMR absorptions of Si–CH_3-groups is a reliable quantitative measure for the concentrations of CH_3SiR_3 compounds. The error limits for the ratios of the (trimethylsilyl)cyclopentadiene isomers are expected to be cumulative with respect to those attributed to the individual isomers, as the analysis is based on the assumption that the PMR-integrations for the three isomers add up to 100%.

A negative error in one of the compounds then necessarily results in a positive error in one of the other isomers.

Attempts were made to separate the three TSCP-isomers by gas–liquid partition chromatography (GLC). Various GLC procedures and column materials were tested but the TSCP-isomers always interconverted on the column during analysis, resulting in overlapping and asymmetrical peaks. We were unsuccessful in deriving workably "smooth" GLC conditions that would have enabled quantitative separation without isomerization.

RESULTS

Gaseous samples of the TSCP-starting material were thermally equilibrated in a static reaction system and the quenched reaction products analyzed by PMR. Experiments have been carried out between 61.2 and 265.6°, with initial pressures ranging from 18.4 to 86.1 torr.

The results of these experiments are listed in Table 2, using the notation given in equation (c). For reasons of continued reaction during prolonged storage and handling of the samples prior to analysis (compare experimental section) the first set of experiments carried out at 265, 138 and 84° has been found to be unreliable with respect to the proper temperatures involved. These data, then, have not been used in computing the Van 't Hoff relationships, shown in Figs. 1 and 2 and given below (with standard errors):

$$\log K_{1,2} = \log\left(\frac{\text{1-TSCP}}{\text{5-TSCP}}\right) = (0.193 \pm 0.014) - (1.56 \pm 0.03)/\theta(^{\circ}\text{K})$$

$$\log K_{3.4} = \log\left(\frac{2\text{-TSCP}}{1\text{-TSCP}}\right) = (0.09 \pm 0.03) - (0.84 \pm 0.05)/\theta(^\circ\text{K})$$

where θ equals $4.58 \times 10^{-3}\ T(^\circ\text{K})$.

For an average temperature of 400° K this results in

$$\Delta H_{1.2} = \Delta H_f^0(1\text{-TSCP}) - \Delta H_f^0(5\text{-TSCP}) = 1.56 \pm 0.03 \text{ kcal/mole}$$
$$\Delta H_{3.4} = \Delta H_f^0(2\text{-TSCP}) - \Delta H_f^0(1\text{-TSCP}) = 0.84 \pm 0.05 \text{ kcal/mole}$$
$$\Delta S_{1.2} = S^0(1\text{-TSCP}) - S^0(5\text{-TSCP}) = 0.89 \pm 0.06 \text{ cal/}^\circ\text{mole}$$
$$\Delta S_{3.4} = S^0(2\text{-TSCP}) - S^0(1\text{-TSCP}) = 0.43 \pm 0.12 \text{ cal/}^\circ\text{mole}$$

Considering that very small differences in heat capacities between the various isomers are to be expected, the above data are equally valid for room temperature.

The reproducibility of experiments was reasonably good. As can be seen from the listings in Table 2, the *maximum deviations* of the equilibrium constants $K_{1.2}$ at a given temperature are ±2% except for 65°, where ±4.9% has been measured. For $K_{1.2}$ the maximum error ranges between ±1.5 and ±5.7%. The scatter of the equi-

TABLE 2

COMPOSITION OF EQUILIBRATED MIXTURES OF x-(TRIMETHYLSILYL)CYCLOPENTADIENE ISOMERS[a,b]

Temp.[c] (°C)	Time (min)	P_0 (mm)	Prod. mix.[a]		Temp.[c] (°C)	Time (min)	P_0 (mm)	Prod. mix.[a]	
			$\frac{5\text{-TSCP}}{1\text{-TSCP}}$	$\frac{1\text{-TSCP}}{2\text{-TSCP}}$				$\frac{5\text{-TSCP}}{1\text{-TSCP}}$	$\frac{1\text{-TSCP}}{2\text{-TSCP}}$
265.6*	10	70.0	3.58	1.88	203.4	10	29.5	3.41	1.80
265.3*	40	86.1	2.97	1.88	203.4	3	23.5	3.34	1.90
137.6*	5	29.5	4.51	3.00	203.4	1	27.3	3.36	1.99
138.9*	1	20.4	4.94	2.40	203.4	7	20.5	3.32	1.90
138.8*	30	28.9	5.15	2.39	203.4	5	26.0	3.27	1.96
138.4*	15	28.2	4.88	2.44	140.9	2	27.3	4.28	2.29
138.7*	10	27.4	5.02	2.38	141.6	5	24.0	4.32	2.14
83.9*	60	25.8	6.24	2.50	141.2	10	19.2	4.20	2.27
84.1*	40	31.7	6.20	2.67	140.7	1	22.4	4.23	2.27
83.9*	90	34.5	6.20	2.53	140.5	15	35.0	4.38	2.37
84.1*	20	21.2	6.18	2.52	84.0	882	18.4	5.80	2.70
84.2*	10	28.0	6.11	2.76	84.0	45	26.5	5.61	2.53
111.1	30	27.7	4.90	2.59	84.0	10	25.0	5.67	2.79
111.3	20	25.9	4.91	2.42	84.1	20	28.7	5.72	2.46
111.3	3	26.8	4.88	2.46	84.1	30	31.1	5.77	2.75
111.5	20	33.3	4.82	2.38	64.6	79	30.3	6.40	2.79
169.5	5	30.0	3.68	2.14	64.0	120	26.8	6.60	2.76
170.4	1	31.4	3.58	2.09	61.2	972	22.1	6.61	2.85
170.9	30	37.7	3.73	2.09	63.7	393	23.5	6.29	2.69
171.3	15	30.6	3.74	2.11	63.2	2616	25.2	6.95	2.85
170.2	10	28.0	3.67	2.08					

[a] 5-, 1- and 2-TSCP stand for the 5-, 1- and 2-(trimethylsilyl)cyclopentadiene isomers respectively. [b] Listed in sequential order of experiments. [c] The first set of experiments, marked with asterisks, have not been used in calculating the Van 't Hoff relationship and they are not incorporated in Figs. 1 and 2. In these experiments the reaction temperature is not defined, due to continued reaction upon storage and handling of the quenched isomer mixtures prior to analyses. Compare text experimental section.

librium constants is only slightly larger than the experimental error limits. The reproducibility of duplicate PMR analyses for four experiments ranged between ±0.4 and ±1.1% (max. deviations) for $K_{1.2}$ and between ±0.7 and ±4.7% for $K_{3.4}$.

Vapour pressure measurements carried out using a regular isoteniscope arrangement gave $\log p(\text{torr}) = (7.787 \pm 0.095) - (2029 \pm 31)/T(°\text{K})$ resulting in a heat of vaporization of $\Delta H_v \sim 9.28 \pm 0.14$ kcal/mole. The extrapolated boiling point is 140.4° and Trouton's constant 22.4.

DISCUSSION

The consistency of the data, listed in Table 2 and the fact that equilibrium was approached from both sides* show, that equilibrium concentrations were indeed established. Care was taken, not to introduce any systematic errors with the handling or analytical procedures.

No indication of the formation of any dimeric materials could be observed except in the products recovered after the vapor-pressure measurements showing a yellow residue upon distillation.

The data quoted in reference 16 for $K_{1.2}$ at 30° of 0.126 (0.120) and at 50° of 0.150 (0.132) are in reasonable agreement with our own values, shown in parentheses. Combining our data on $K_{1.2}$ with those reported by Ashe[16] for k_1 results in k_2 $(\text{sec}^{-1}) = 10^{13.1} \cdot 10^{-24.6/\theta}$ which appears to be reasonable.

In Table 3 the enthalpy and entropy differences obtained in this work are compared with those for the corresponding carbon analogues.

TABLE 3

THERMODYNAMIC DIFFERENCES AT 300°K BETWEEN THE POSITIONAL ISOMERS OF $(CH_3)_3X\text{-}\sigma\text{-}C_5H_5$ WHERE X EQUALS Si OR C

X	$\Delta H_{1.2}$ (kcal/mole)	$\Delta S_{1.2}$ (cal/°mole)	$\Delta H_{3.4}$ (kcal/mole)	$\Delta S_{3.4}$ (cal/°mole)	$K_{1.2}$ (400°K)	$K_{3.4}$ (400°K)
Si	1.56±0.03	0.89±0.06	0.84±0.05	0.43±0.12	0.221	0.441
C[a]	−0.21±0.5	+1.21±0.5	0.35±0.5	−0.31±0.5	2.40	0.550

[a] Calculated on the basis of the concept of direct additivity of incremental ΔH_f^0, S^0 and C_p^0-properties[26], using for the group $C(C)(C_d)_2(H)$ the values $\Delta H_f^0 = -1.15$ and $S^0 = -11.3$[27].

The data listed in Table 3 show, that the relative stabilities of the positional isomers are reversed in the silicon analogue compared to the hydrocarbon. While, in the hydrocarbon case, the 1-isomer is thermodynamically most stable; of the (trimethylsilyl)cyclopentadienes it is the 5-isomer.

The observed differences can be attributed to differences in the respective group-increment[26] properties.

Applying the concept of direct additivity of ΔH_f^0, S^0 and C_p^0 group increment properties and using the notation and hydrocarbon increments listed in reference 27

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* The initial ratio $[\text{5-TSCP}/\text{1-TSCP}]_0 = 5.23$ is smaller than the corresponding equilibrium values for the experimental temperatures of 61° and 84°. For all other temperatures, $[\text{5-TSCP}/\text{1-TSCP}]_{eq.} < 5.23$.

TABLE 4

Increments[a]	$\Delta\Delta H_f^0$ (kcal/mole)	ΔS (cal/° mole)
$C_d(Si)(C_d) - C_d(Si)(C)$	-1.0 (-1.46)[b]	-1.2 (-1.9)[b]
$C_d(Si)(C) - C(Si)(C_d)_2(H) + Si(C)_3(C_d) - Si(C)_4$	14.4 (12.67)[b]	-1.3 (-1.0)[b]
$Si(C)_3(C_d) - Si(C)_4$[c]	2.95 (1.18)[b]	0.06 (+0.38)[b]
$Si(C)_4$[d]	14.32 (0.5)[b]	-22.2 (-35.1)[b]
$Si(C)_3(C_d)$[d]	17.3 (1.68)[b]	-22.1 (-34.7)[b]

[a] C and Si stand for singly bonded carbon and silicon, C_d for doubly bonded carbon etc. [b] The data for the carbon analogues are given in parentheses. *c* Based on the similarity demonstrated above for increments with carbon centers attached to carbons or to carbon and silicon atoms at the same time we can set $[C_d(Si)(C) - C(Si)(C_d)_2(H)] = [C_d(C)_2 - C(C)(C_d)_2(H)]$. [d] Using the data for ΔH_f^0 and S^0 listed in ref. 27 for $Si(CH_4)_4$ and assigning $C(H)_3(Si) \equiv C(H)_3(C)$.

we derive from our data (for 300° K and 1 atm) the intrinsic differences in incremental data for entropy and enthalpy contributions compiled in Table 4.

Thermochemical data like heats of combustion, heats of hydrogenation or isomerization of silicon containing compounds are so few and largely inconsistent that to date no reliable group-increment values for ΔH_f^0, S^0, C_p^0 [26] of organosilicon compounds can be derived. In order to get at least some useful intrinsic thermodynamic values that would allow predictions of relative stabilities in silanes and related compounds, O'Neal and Ring[28] used the much less reliable bond additivity principle. Their data however are not borne out by our experiment. Using the simplified concept of direct linear additivity of incremental bond values[29], we would predict the difference $\Delta H_f^0(\text{1-TSCP}) - \Delta H_f^0(\text{5-TSCP}) = \Delta H_{1,2}$ to be equal to $[Si{-}C] + [C_d{-}H] - [Si{-}C_d] - [C{-}H]$. Using literature data[29] for $[C_d{-}H]$ and $[C{-}H]$ this would then result in $[Si{-}C] - [Si{-}C_d] = -8.59$ kcal/mole, compared to $+11.9$ kcal/mole, using the data given in ref. 28.

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