Synthesis of 1,1-Bis(n-butyl, t-butyl)-2,3,4,5-Tetraphenyl-1-Silacyclopentadiene and NMR Study of Their 2,5-Carbodianions

Jang-Hwan Hong

Abstract

1,1-Bis(n-butyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene (3) and 1,1-bis(t-butyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene (4) are synthesized from the reaction of the versatile silole dianion (2) with n-butyl bromide and t-butyl bromide. Reduction of (3) and (4) with an excess of lithium to give 1,1-bis(n-butyl)-2,5-dilithio-2,3,4,5-tetraphenyl-1-silacyclopenta-3-enide (6) and 1,1-bis(t-butyl)-2,5-dilithio-2,3,4,5-tetraphenyl-1-silacyclopenta-3-enide (7). 13C-NMR study of two 2,5-carbodianions (6 and 7) shows tert-carbanion at 73.18 and 78.12 ppm respectively. Two bulky tert-butyl groups in (7) increase the inversion barrier at the tert-carbanion, line broadenings of tert-butyl groups in 1H and 13C-NMR spectrum are observed.

Key words: Silole, tert-Carbanion, 2,5-Carbodianion, Inversion

1. Introduction

In last decades a lot of group 14 metalloles have been prepared[1-6]. Especially their anions/dianions have been reported to be aromatic systems in experimental[7-23] and theoretical studies[20-31] except trimethylsilyl group substituted silole and germole anions[10,18]. Cα, Cβ, Cαi, Cβi atoms of 2,3,4,5-tetraphenyl substituted group 14 metallole anions/dianions are participate in π-delocalization of the negative charge on Si atom to give chemical shift changes ongoing from group 14 metalloles to their anions/dianions[9,10,12]. Lately siloles have been attracted by the unique electronic structures[22] and novel aggregation-induced emission (AIE) characteristics[23]. Recently the reduced silole species of 2,5-dilithio-1-silacyclopenta-3-ene have been utilized as a new route to synthesize a silole-containing hyperbranched poly(silylenevinylene)[34,35]. However there are few reports for the reduction of siloles to 2,5-carbodianion species since W.H. Atwell and coworkers had reported for silole anions and dianions[30]. Herein we report NMR study of 1,1-bis(n-butyl/1-t-butyl)-2,5-dilithio-2,3,4,5-tetraphenyl-1-silacyclopenta-3-enide.

2. Experimental Section

2.1. General Procedures

All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Air sensitive reagents were transferred in a nitrogen-filled glove box. THF and ether were distilled from sodium benzophenone ketyl under nitrogen. Hexane and pentane were stirred over concentrated H2SO4 and distilled from CaH2. NMR spectra were recorded on JEOL GSX270 and GSX400 spectrometers. GC-MS and solid sample MS data were obtained on a Hewlett-Packard 5988A GC-MS system equipped with a methyl silicon capillary column. Elemental analyses were done by Desert Analytics (Tucson, AZ, USA).

2.2. 1,1-bis(n-butyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene (3)

1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene (0.57 g, 1.25 mmol) was sonicated with an excess of lithium for 2 hr. Then the remaining lithium was removed by filtration to give the red purple solution of the silole dianion. The solution was added to THF solution of 1-bromo-butane with stirring at room temperature for 2 hrs to give yellow solution. After removing solvent under vacuum the remained yellow solid was extracted with hexane. The concentrated solution was kept in refrigerator for couple of days to
provide yellow crystals. Yield: 0.56 g (90%); mp 85 °C (lit.[43], mp 81 °C).

2.3. 1,1-Bis(t-butyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene (4).

1,1-dichloro-TPSCp (0.55 g, 1.21 mmol) was sonicated with an excess of lithium in THF for 2 hr. Then the remaining lithium was removed by filtration to give the red purple solution of (2). The solution was added to THF solution of t-butylbromide with stirring at room temperature for 5 hrs to give yellow solution. After removing solvent under vacuum the remained yellow solid was extracted with ether. The concentrated solution was kept in refrigerator for couple of days to provide pale yellow crystals of 1,1-bi(1-t-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene) (5). The filtrated solution was concentrated under vacuum, then it was kept in refrigerator for couple of days to provide pale yellow crystals of 1,1-bis(t-butyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene (4). Yield: 0.33 g (54%); mp 169-171 °C.

2.4. NMR Study of the Reduction of (3) and (4) with Lithium in THF-d8.

The respective 1,1-bis(n-butyl)-TPSCp (3) (0.025 g, 0.05 mmol) and 1,1-bis(t-butyl)-TPSCp (4) (0.025 g, 0.05 mmol) was transferred into 5 mm NMR tube, they were sonicated with an excess of lithium in THF-d8 for 1.5 hr to give red-purple solution. Then 1H, 13C, and 29Si-NMR spectroscopic study was performed. 1,1-Bis (n-butyl-2,5-dilithio-2,3,4,5-tetraphenyl-1-silacyclopenta-3-enide) (6); 1H-NMR (THF-d8, ref; ext. TMS = 0.00 ppm), 0.83 (t, CH3, 6H), 0.90 (m, CH2, 4H), 1.36 (sept, CH2, 4H), 1.52 (m, CH2, 4H), 6.68-7.15 (m, 20H), 1,1-Bis (t-butyl-2,5-dilithio-2,3,4,5-tetraphenyl-1-silacyclopenta-3-enide) (7); 1H-NMR (THF-d8, ref; ext. TMS = 0.00 ppm), 1.21 (brd s, Me, 18H), 6.68-7.15 (m, 20H).

3. Results and Discussion

3.1. Preparation of 1,1-bis(n-butyl/t-butyl)-2,3,4,5-tetraphenyl-silacyclopentadiene

1,1-Bis(n-butyl)-2,3,4,5-tetraphenyl-silacyclopentadiene [1,1-bis(n-butyl)-TPSCp] (3) is prepared from the reaction of 2,3,4,5-tetraphenyl-1-silacyclopentadiene dianion (2) with n-bromobutane in good yield. The silole dianion (2) is generated by the sonication of 1,1-dichloro-TPSCp (1) in THF with lithium[11]. However, in the case of tert-butyl bromide, 1,1-bis(t-butyl)-TPSCp (4) is provided with 1,1-bi(1-t-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene) (5) Yield: 0.19 g (18%)[8].

J. Chosun Natural Sci., Vol. 6, No. 2, 2013
3.2. Reduction of 1,1-bis(n-butyl/t-butyl)-2,3,4,5-tetraphenyl-silacyclopentadiene and NMR Study of their Reduced Species

1,1-Bis(n-butyl)-TPSCp (3) and 1,1-bis(t-butyl)-TPSCp (4) are sonicated in THF-d8 with lithium in the 5mm NMR tube for 1.5 hr. Then the color of the mixture becomes red and/or purple. The NMR study of the species in THF-d8 clearly indicates that the only one species is generated in there. The respective 13C-NMR spectrum of (6) and (7) shows ten peaks, consistent with C₂-symmetry, and the respective 29Si-NMR spectrum shows only one resonance. In 1H-NMR spectra of them there are two kinds of protons, 20 phenyl protons and 18 butyl protons. Even if they are sonicated further, they show the same peaks with no change. They have been characterized to be 2,5-carbodianions of 1,1-bis(n-butyl)-TPSCp (3) and 1,1-bis(t-butyl)-TPSCp (4) respectively.

![Diagram of 1,1-bis(n-butyl)-TPSCp and 1,1-bis(t-butyl)-TPSCp reduction](image)

3.3. NMR Study of their Reduced Species (6 and 7) of 1,1-bis(n-butyl/t-butyl)-2,3,4,5-tetraphenyl-silacyclopentadiene

Upon lithiation of (4) to (7) the chemical shifts of Cα in (4) are shifted far upfield from 141.69 ppm to 78.12 ppm [Δ(α) = -63.57 ppm] and the chemical shifts of Cβ in (4) are shifted far upfield from 157.22 ppm to 130.34 ppm [Δ(β) = -26.88 ppm]. The chemical shifts of Cω and Cτ in (7) are observed at 152.59 ppm and 147.36 ppm, those are shifted far downfield from 142.88 and 138.94 ppm in (4) [Δ(ω) = 9.71 ppm (Δ(τ) = 8.42 ppm)]. The chemical shifts of two Cp in (7) are shifted from 124.94 and 125.70 ppm to 110.87 and 120.25 ppm [Δ(ω) = -14.07 ppm (Δ(τ) = -5.45 ppm)]. The chemical shifts of two Cω are shifted downfield slightly, but those of Cτ are shifted upfield slightly. Polarization of these phenyl groups in (7) is observed due to their bulkiness and congestion of four phenyl groups. Thus no phenyl group is able to be planar with 5-membered ring, there is no π-conjugation between phenyl groups and 5-membered ring[37].

The 13C-NMR chemical shift changes of 2,5-carbodianion species of (6) in the ring and phenyl groups are similar to those of (7); the chemical shifts of Cω and Cτ are 73.18 ppm and 128.06 ppm, the chemical shifts of Cω and Cτ are 147.68 ppm and 151.51 ppm, and the chemical shifts of Cω and Cτ are 108.49 ppm and 120.80 ppm. The sum of 13C-NMR chemical shifts [sum(Cω+Cτ)] is 201.24 ppm for (6) and 208.46 ppm for (7) and the sum of 13C-NMR chemical shifts [sum(Cω+Cτ)] is 69.90 ppm for (6) and 68.83 ppm for (7).

Both 13C-NMR chemical shifts of two tert-carbodianion in (6) and (7) are consistent with those of the 2,5-carbodianions of 1,1-R,R-TPSCp (R₁=R₂=Me [38]; R₁=Me, R₂=H [39]) and those of 2-carbodianions of 1,1-

Table 1. 13C-NMR chemical shifts

<table>
<thead>
<tr>
<th></th>
<th>(4)</th>
<th>(6)</th>
<th>(7)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
</tr>
<tr>
<td>Cα</td>
<td>141.69</td>
<td>73.18</td>
<td>78.12</td>
</tr>
<tr>
<td>Cβ</td>
<td>157.22</td>
<td>128.06</td>
<td>130.34</td>
</tr>
<tr>
<td>Sum(Cα+Cβ)</td>
<td>298.91</td>
<td>201.24</td>
<td>208.46</td>
</tr>
<tr>
<td>Ci</td>
<td>142.88</td>
<td>138.94</td>
<td>151.51</td>
</tr>
<tr>
<td>Co</td>
<td>127.63</td>
<td>129.32</td>
<td>123.58</td>
</tr>
<tr>
<td>Cm</td>
<td>126.86</td>
<td>130.19</td>
<td>125.93</td>
</tr>
<tr>
<td>Cp</td>
<td>124.94</td>
<td>125.70</td>
<td>120.80</td>
</tr>
<tr>
<td>Sum(Ci+Cp)</td>
<td>31.19</td>
<td>69.90</td>
<td>68.83</td>
</tr>
<tr>
<td>Cω=n-butyl</td>
<td>20.79</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₂</td>
<td>-</td>
<td>14.70, 18.88, 27.34</td>
<td>-</td>
</tr>
<tr>
<td>CH₃</td>
<td>29.01</td>
<td>29.08</td>
<td>31.5, 33.3 (brd d)</td>
</tr>
</tbody>
</table>

*In CDCl₃, reference; external TMS as standard; *b*In THF-d8, reference = 25.30 ppm.
Upon lithiation of (4) to (7) the chemical shift of $^{29}$Si-$\text{NMR}$ in (4) does not change much, but it depends on the substituent of Si atom.

3.4. Inversion of tert-carbanions in (6) and (7)

Before lithiation two tert-butyl groups of (4) in $^1$H-NMR are observed as a sharp singlet at 1.16 ppm, but unexpectedly those of (7) are observed as broad singlet at 1.21 ppm. Moreover the tert-butyl groups of (7) in $^{13}$C-NMR are observed as broad doublet at 31.5 ppm and 33.3 ppm with no tert-carbon peak to be assigned, those of (4) are observed sharp singlet at 20.79 ppm for tert-C and 29.01 ppm for methyl groups. This may be to the slow inversion rate at two tert-carbanions in (7) due to the bulkiness of two tert-butyl groups substituted on Si atom. However in the case of (6) with two $n$-butyl groups it seems to be fast inversion at two tert-carbanions since there is no observable line broadening $^1$H and $^{13}$C-NMR of (6). In the cases of (6) and (7) there are two tert-carbanions with no tetravalence bonds at 5-position, those lower the inversion barriers each other. Even though two bulky tert-butyl groups in (7) increase the barrier, they still do slow inversion to broaden the lines of tert-butyl groups in $^1$H and $^{13}$C-NMR spectrum.

On the contrary no inversion at 2-carbanion for 1,1-$R_1$-$R_2$-2-lithio-2,3,4,5-tetraphenyl-1-silacyclopenta-3-enide ($R_1$=Me, $R_2$=H; $R_1$=N(SiMe$_3$)$_2$, $R_2$=H) was reported. They have one tert-carbanion with tetravalence bonds at 5-position, which increases the barrier to prevent the inversion.

4. Conclusions

1,1-Bis($n$-butyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene (3) and 1,1-bis(tert-butyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene (4) are synthesized from the reaction of the versatile silole dianion (2) with $n$-butyl bromide and tert-butyl bromide. Reduction of (3) and (4) with an excess of lithium in THF-$d_8$ by sonication gives the respective 1,1-Bis($n$-butyl)-2,5-dilithio-2,3,4,5-tetraphenyl-1-silacyclopenta-3-enide (6) and 1,1-Bis(tert-butyl)-2,5-dilithio-2,3,4,5-tetraphenyl-1-silacyclopenta-3-enide (7). Two bulky tert-butyl groups in (7) increase the inversion barrier at the tert-carbanions, line broadenings of tert-butyl groups in $^1$H and $^{13}$C-NMR spectrum are observed.

---

Table 2. $^{13}$C-NMR chemical shifts

<table>
<thead>
<tr>
<th>$R_1$, $R_2$</th>
<th>$M'$</th>
<th>$M$</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$=Me, $R_2$=Me</td>
<td>Li</td>
<td>Li</td>
<td>77.4</td>
</tr>
<tr>
<td>$R_1$=Me, $R_2$=n-Bu</td>
<td>Li</td>
<td>Li</td>
<td>76.42</td>
</tr>
<tr>
<td>$R_1$=n-Bu, $R_2$=Me</td>
<td>Li</td>
<td>Li</td>
<td>73.18</td>
</tr>
<tr>
<td>$R_1$=n-Bu, $R_2$=t-Bu</td>
<td>Li</td>
<td>Li</td>
<td>78.12</td>
</tr>
<tr>
<td>$R_1$=n-Bu, $R_2$=H</td>
<td>K</td>
<td>K</td>
<td>77.78</td>
</tr>
<tr>
<td>$R_1$=n-Bu, $R_2$=Me</td>
<td>Na</td>
<td>Na</td>
<td>86.20</td>
</tr>
<tr>
<td>$R_1$=H, $R_2$=Me</td>
<td>Na</td>
<td>Na</td>
<td>89.77</td>
</tr>
</tbody>
</table>

Table 2. $^{29}$Si-NMR chemical shifts

<table>
<thead>
<tr>
<th>$R_1$, $R_2$</th>
<th>(4)</th>
<th>(6) ($R_1$=n-Bu)</th>
<th>(7) ($R_1$=t-Bu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$16.49$</td>
<td>$-0.27$</td>
<td>$13.69$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$In CDCl$_3$, reference; external TMS as standard; $^b$In THF-$d_8$, reference; external TMS as standard.

In THF-$d_8$, reference = 25.30 ppm.

---

Scheme 1. Inversion of tert-carbanions
Acknowledgments

The author acknowledges the advice provided by Professor Sung-Jun Cho (Pai Chai University, Daejon, S. Korea).

References


[23] J.-H. Hong, “Dissociation of the disilatricyclic diallylic dianion [(C\textsubscript{4}Ph\textsubscript{4}SiMe\textsubscript{2})\textsubscript{2}]\textsuperscript{-} by halide ion coordination or halide ion nucleophilic substitution at the silicon atom”, Molecules, Vol. 16, pp. 8451-8462, 2011.


[27] B. Goldfuss and P.v.R. Schleyer, “The siloyl anion C\textsubscript{4}H\textsubscript{4}SiH\textsuperscript{-} is aromatic and the lithium silolide C\textsubscript{4}H\textsubscript{4}SiLi even more so”, Organometallics, Vol. 14, pp. 1553-1555, 1995.


[42] P. Jutzi and A. Karl, “Synthese und reaktionen einiger 1R,1R\textsuperscript{`},2,3,4,5-tetraphenyl-1-silacyclopenta-