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Synthesis and reactivity of 1,1,2,2-tetraphenyl 1,2-digermyldilithium

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Abstract

The new 1,1,2,2-tetraphenyl 1,2-digermyldilithium compound (**2**) is prepared in high yield by metallation of the corresponding aryldihydrodigermane (**1**) with t-BuLi in THF. It is characterized by ^{13}C NMR spectroscopy and by alkylation with methyl iodide. Some nucleophilic substitution reactions are reported: compound **2** reacts with MesCOCl to give a new digermyldiketone $[Ph_2(MesCO)Ge]_2$ (**8**). Its germylation reaction with several alkyl methoxygermanes or -digermanes constitute a convenient way for synthesizing cyclopolygermanes (3,4 or 6 rings). Its reaction with *trans*-$Cl_2Pt(PEt_3)_2$ leads to a mixture of the expected cyclic complex **12** and its corresponding oxide **13**.

Introduction

Recently, we have reported the preparation and properties of the organohydrogermyllithium compounds: R_2HGeLi [1] and RH_2GeLi [2] (R = Ph, Mes). It is interesting to extend this study to digermyldilithium derivatives of the type $R_2LiGeGeLiR_2$ which might behave as useful intermediates in the synthesis of organometallic heterocycles.

We have already postulated the existence of such species in our study of poly(1,1,2,2-tetraphenyl digermylmercuric) compounds [3] $(Ph_4Ge_2Hg)_n$. In fact, cleavage of Ge–Hg bonds by Li gave dilithium intermediates which we could not isolate but however characterized *in situ* by alkylation reaction.

In this paper, we report a better way of obtaining such derivatives, their physical properties and several reactions.

Experimental

General procedures

All manipulations were performed under an inert atmosphere of nitrogen or argon by using standard Schlenk and high-vacuum-line techniques. NMR spectra were recorded on Bruker AC 80 (^1H) and AC 200 (^{13}C and ^{31}P) spectrometers, IR spectra on a Perkin-Elmer 1600 spectrometer and mass spectra on a Ribermag R10-10H spectrometer operating in the chemical ionization mode (CH_4), and on a Hewlett Packard 5989 spectrometer in the electron impact mode at 70 eV. Gas-phase chromatography was done with an HP 5890 series II apparatus using nitrogen as the carrier gas. Elemental analyses were performed by the Ecole National Supérieure de Chimie de Toulouse, France.

Synthesis of $Ph_2LiGeGeLiPh_2$ (2)

A solution of 1.2 ml (2 mmol) of t-BuLi (1.7 M) in pentane was added to a solution of $Ph_2HGeGeHPh_2$ (**1**) [4] (0.44 g, 1 mmol) in THF (2 ml) at −40 °C. The mixture was stirred for 40 min at −40 °C. Analysis by ^{13}C NMR spectroscopy showed that **2** had formed exclusively. **2** was treated with an excess of MeI at −40 °C. The solution was allowed to warm to ambient temperature. After 30 min at 20 °C, hydrolysis, extraction and concentration under vacuum, analysis of the residue showed the formation of $Ph_2MeGeGeMePh_2$ (**3**) [5]. After recrystallization in 4 ml of pentane, 0.37 g (77%) of pure **3** were obtained. ^1H NMR (C_6D_6): δ CH_3 0.77(s), δ C_6H_5 7.12–7.45(m) ppm. Mass spectrum: $[M^+]$ m/z 484.

Stability of 2 at 20 °C

A solution of **2** (0.5 mmol) in 2 ml of THF was stirred for 1 h at 20 °C and then treated with an excess of MeI, as above. Analysis of the residue by ^1H NMR spectroscopy showed the presence of **3** (53%), **1** (13%), Ph_2GeH_2 (traces) and $(Ph_2Ge)_n$ (34%).

Attempts to prepare $Ph_2HGeGeLiPh_2$

(1) A solution of 0.36 ml (0.62 mmol) of t-BuLi (1.7 M) in pentane was added to a solution of **1** (0.28 g, 0.62 mmol) in THF (1.5 ml) at −40 °C. The mixture

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was stirred for 30 min at −40 °C then treated with an excess of MeI. Using the same work-up procedure as described above, the residue was analyzed by ^1H NMR spectroscopy which showed the formation of: $Ph_2HGeGeMePh_2$ (**5**) (36%), **3** (25%) and $(Ph_2Ge)_n$ (~40%). **5**: ^1H NMR (C_6D_6): δ CH_3 0.79(s), δ GeH 5.53(s), δ C_6H_5 7.12–7.45(m) ppm. Mass spectrum: $[M^+]$ m/z 470, $[M-CH_3]$ 455.

(2) When a deficiency of t-BuLi 0.15 ml (0.25 mmol) was mixed with **1** (0.22 g, 0.50 mmol) we obtained: **1** (50%), **5** (13%), Ph_2GeH_2 (15%), $(Ph_2Ge)_n$ (20%) and Ph_2HGeMe [1] (traces).

Reaction of 2 with $Br(CH_2)_3Br$

A solution of 1,3-dibromopropane (0.11 g, 0.55 mmol) in THF (0.5 ml) was added drop by drop to a solution of **2** (0.5 mmol) in THF (2 ml) at −40 °C. The mixture was heated to ambient temperature and stirred for 4 h at 20 °C. After hydrolysis with HCl (5%), extraction and concentration under vacuum, the residue was crystallized from a mixture of ether/pentane (1/5) at −30 °C. The white powder which precipited was isolated after decantation and dried *in vacuo*, giving **6**: yield 0.10 g (26%). **6** was identified by comparison with a sample prepared by a different route (see below).

Synthesis of 6

Preparation of $Ph_2HGe(CH_2)_3GeHPh_2$ *(7)*

A solution of 1,3-dibromopropane (0.32 g, 1.60 mmol) in THF (1 ml) was slowly added to a solution of Ph_2HGeLi [1] (4 mmol) in THF (2 ml) at −40 °C. After 10 min at −40 °C, the mixture was heated to ambient temperature. After 3 h of stirring at 20 °C, it was hydrolyzed, extracted, dried over anhydrous sodium sulfate and concentrated *in vacuo*. Analysis of the residue by ^1H NMR and GC methods showed the presence of **7** (80%), **1** (8%), Ph_2GeH_2 (4%) and Ph_2HGeBr (8%). **7**: ^1H NMR ($CDCl_3$): δ CH_2Ge 1.52(m), δ CH_2 1.77(m), δ GeH 5.04(m), δ C_6H_5 7.10–7.70(m) ppm. IR (pure, KBr): ν(GeH) 2027 cm^{-1}. Mass spectrum: $[M^+]$ m/z 498, $[M-2H]$ 496, $[M-PhH]$ 420.

Reaction of 7 with Bu_2Hg

A solution of (0.42 g, 0.84 mmol) of **7** and (0.27 g, 0.87 mmol) of Bu_2Hg in C_6H_6 (5 ml) was stirred for 4 h at 40 °C in the dark. The mercuric compound so obtained was heated in a Carius tube for 12 h at 120 °C. After elimination of Hg and concentration, the residue was recrystallized in a 1:5 ether/pentane mixture. After decantation and drying under vacuum, a white powder was obtained. **6**: 0.10 g (26%), m.p. 80–82 °C. ^1H NMR ($CDCl_3$): δ CH_2Ge 1.61(m), δ CH_2 2.20(m), δ C_6H_5 7.15–7.40(m) ppm. Mass spectrum: $[M^+]$ m/z 496, $[M-C_6H_5]$ 419. *Anal.* Calc. for $C_{27}H_{26}Ge_2$: C, 65.43; H, 5.25. Found: C, 66.60; H, 6.50%.

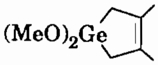
Reaction of 2 with α,α′-dibromoorthoxylene

A solution of (0.26 g, 1 mmol) of α,α′-dibromo-orthoxylene in THF (3 ml) was added to a solution of **2** (1 mmol) in 4 ml of THF at −78 °C. The mixture was stirred for 30 min at this temperature then heated to 20 °C. After 2 h at 20 °C, it was hydrolyzed, extracted, dried and concentrated under vacuum. Analysis of the residue by ^1H NMR showed the only significant predominant product was $(Ph_2Ge)_n$ δ C_6H_5 7.20(m) ppm.

Reaction of 2 with MesCOCl

A solution of **2** (0.5 mmol) in THF (1 ml) was added to a solution of MesCOCl (0.18 g, 1 mmol) in 1.5 ml of ether at −70 °C. After 30 min at −70 °C, the mixture was heated to ambient temperature. After 2 h of stirring at 20 °C, it was hydrolyzed ($NaHCO_3$/H_2O), extracted, dried over anhydrous sodium sulfate, and concentrated under vacuum. The residue was crystallized from a mixture of ether (0.5 ml) and methanol (1.5 ml) at −30 °C. The yellow solid which precipitated was isolated after decantation and dried *in vacuo*, giving **8**: 0.16 (45%), m.p. 175–177 °C. ^1H NMR (C_6D_6): δ p-CH_3 1.94(s), δ o-CH_3 1.92(s), δ C_6H_2 6.39(s), δ C_6H_5 7.05–7.65(m) ppm. ^{13}C NMR ($CDCl_3$): δ p-CH_3 21.05, δ o-CH_3 19.20, δ C_6H_5 128.17, 128.49, 135.50, 138.42; δ C_6H_2 129.97, 138.54, 142.52, δ CO 241.82 ppm. IR (C_6D_6): ν(CO) 1639 cm^{-1}. Mass spectrum (DCI, CH_4): $[M+29]$ 777, $[M+29-C_2H_6]$ 747, $[M-Me]$ 733, $[M-Ph]$ 671. *Anal.* Calc. for $C_{44}H_{42}Ge_2O_2$: C, 70.65; H, 5.66. Found: C, 70.00; H, 5.76%.

Reaction of 2 with



A solution of 1,1-dimethoxygermacyclopentene [6] (0.09 g, 0.45 mmol) in THF (0.5 ml) was added to a solution of **2** (0.50 mmol). The mixture was stirred for 12 h, then hydrolyzed (HCl 5%) extracted, dried and concentrated *in vacuo*. The residue was treated with a 1:5 ether/pentane mixture giving a white powder which was isolated after decantation and dried *in vacuo*. **9**: 0.15 g (56%), m.p. 103–105 °C. ^1H NMR ($CDCl_3$): δ CH_3 1.40(s), δ CH_2 1.62(s), δ C_6H_5 6.90–7.40(m) ppm. Mass spectrum: $[M^+]$ m/z 608. $[M-CH_3]$ 593.

Reaction of 2 with $Et_2Ge(OMe)_2$

A solution of $Et_2Ge(OMe)_2$ (0.09 g, 0.45 mmol) in THF (0.5 ml) was added to a solution of **2** (0.5 mmol) at −40 °C. The mixture was heated to ambient temperature and stirred for 4 h. After hydrolysis (HCl 5%), extraction, drying and concentration under vacuum, the residue was crystallyzed from a mixture of ether (0.5 ml) and pentane (4 ml) at −30 °C, giving a white powder identified as **10**: 0.07 g (22%), m.p. 170–172 °C. ^1H NMR ($CDCl_3$): δ $CH_2 = \delta$ CH_3 0.85–0.95(m), δ C_6H_5 7.10–7.30(m) ppm. Mass spectrum (DCI, CH_4): [$M-$Ph] 1091, [$M-Ph_2Ge$] 942.

Reaction of 2 with $Et_2(MeO)GeGe(OMe)Et_2$

A solution of $Et_2(MeO)GeGe(OMe)Et_2$ [7] (0.15 g, 0.58 mmol) in THF (1 ml) was added to a solution of **2** (0.65 mmol) at −40 °C. Using the same procedures as described above (8 h at 20 °C), a white powder was obtained and identified as **11**: 0.20 g (49%), m.p. 140–145 °C. ^1H NMR ($CDCl_3$): δ $CH_3 = \delta$ CH_2 1.10–1.25(m), δ C_6H_5 7.14–7.34(m) ppm. Mass spectrum: [M^+] *m/z* 716, [$M-2C_2H_5$] 658, [$M-4C_2H_5$] 600. We also observed the presence of $(Et_2Ge)_4$ [8] [M^+] 524.

Reaction of 2 with $Cl_2Pt(PEt_3)_2$

A solution of **2** (0.48 mmol) was added to a suspension of $Cl_2Pt(PEt_3)_2$ (0.24 g, 0.48 mmol) in 15 ml of ether at −40 °C. The mixture was stirred for 20 min at −40 °C then heated to ambient temperature. After 4 h at 20 °C, concentration under vacuum, the residue was extracted with 10 ml of toluene then filtered to remove LiCl. The solvent was removed under vacuum and the remaining oil extracted by 5 ml of ether. After concentration and drying under vacuum, a yellow powder was obtained, 0.40 g. Analysis by ^{31}P NMR showed the formation of **12** (60%) and **13** (40%).

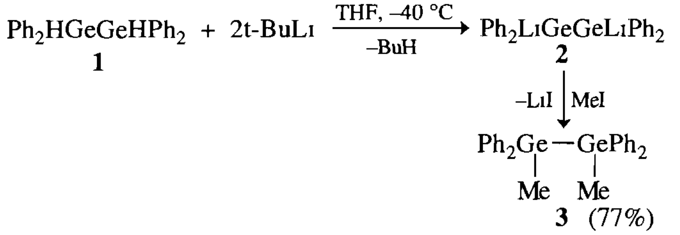
12: ^1H NMR (C_6D_6): δ CH_3 0.80(m), δ CH_2P 1.50(m), δ C_6H_5 6.90–8.10(m) ppm. ^{31}P NMR (C_6D_6): δ 9.33 ppm (s, ^1J(Pt–P) = 2171 Hz). Mass spectrum (DCI, CH_4): [$M+29$] 915, [$M-$PhGe] 735, [$M-Ph_2Ge$] 658.

13: ^{31}P NMR (C_6D_6): δ 8.85 ppm (s, ^1J(Pt–P) = 2180 Hz). Mass spectrum (DCI, CH_4): [M^+] *m/z* 902, [$M-C_6H_6$] 824. IR (nujol): ν(GeOGe) 836 cm^{-1}.

When air is present the proportion of **13** in the mixture of **12** and **13** increases. In addition to the oxidation of the transition-metal complex, oxygen also causes degradation of the complex.

Results and discussion

The reaction of two equivalents of t-BuLi with 1,1,2,2-tetraphenyl 1,2-digermane easily gives the expected digermyldilithium in high yield:



$$\underset{\mathbf{1}}{Ph_2HGeGeHPh_2} + 2\,t\text{-}BuLi \xrightarrow[-BuH]{THF,\,-40\,°C} \underset{\mathbf{2}}{Ph_2LiGeGeLiPh_2} \xrightarrow[-LiI]{MeI} \underset{\mathbf{3}\ (77\%)}{Ph_2(Me)Ge{-}Ge(Me)Ph_2} \quad (1)$$

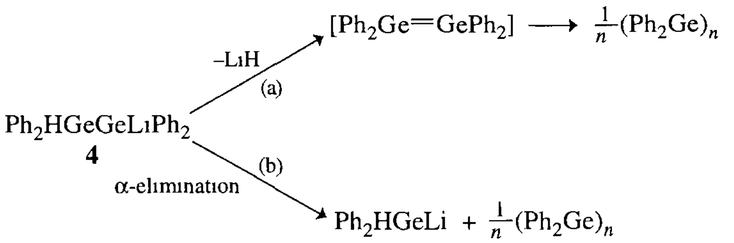
Compound **2** was characterized by its reaction with methyl iodide. Although perfectly stable at low temperature, it decomposes slowly at room temperature forming polygermanes (eqn. (2)).

$$Ph_2LiGeGeLiPh_2 \xrightarrow[(2)\ MeI,\ H_2O]{(1)\ 1\ h\ at\ 20\ °C} \underset{\mathbf{3}\ (53\%)}{Ph_2MeGeGeMePh_2} + \underset{(13\%)}{Ph_2HGeGeHPh_2} + \underset{(34\%)}{\frac{1}{n}(Ph_2Ge)_n} + \underset{(traces)}{Ph_2GeH_2} \quad (2)$$

However, reaction of **1** with one equivalent of t-BuLi gives a mixture of mono- and di-lithiated compounds, which in turn produces a mixture of polygermanes:

$$\underset{\mathbf{1}}{Ph_2HGeGeHPh_2} + t\text{-}BuLi \xrightarrow[-BuH]{THF,\,-40\,°C} \underset{\mathbf{4}}{Ph_2HGeGeLiPh_2} + Ph_2LiGeGeLiPh_2 \xrightarrow[-LiI]{MeI} \underset{\mathbf{5}\ (35\%)}{Ph_2HGeGeMePh_2} + \underset{\mathbf{3}\ (25\%)}{Ph_2MeGeGeMePh_2} + \underset{(40\%)}{\frac{1}{n}(Ph_2Ge)_n} \quad (3)$$

The formation of polygermanes can be explained by the instability of the arylhydrodigermyllithium intermediate **4**.



(4)

Compound **4** can decompose either by intramolecular elimination of LiH or by an α-elimination [8]. We have been able to verify this weak stability by using a deficiency of t-BuLi, making the formation of digermyldilithium less favorable.

$$Ph_2HGeGeHPh_2 + 0.5t\text{-}BuLi \xrightarrow[(2)\ MeI,\ H_2O]{(1)\ THF,\ -40\,^{\circ}C} \underset{\mathbf{1}\ (50\%)}{Ph_2HGeGeHPh_2} + \underset{\mathbf{5}\ (13\%)}{Ph_2HGeGeMePh_2} + \underset{(traces)}{Ph_2HGeMe} + \underset{(15\%)}{Ph_2GeH_2} + \underset{(20\%)}{\frac{1}{n}\,(Ph_2Ge)_n} \qquad (5)$$

We have effectively observed the presence of compound **1** and of a small percentage of monolithiated digermane **5**, diphenylgermane and polygermanes. The formation of Ph_2GeH_2 in amounts slightly less than those of the polygermanes $(Ph_2Ge)_n$ seems to suggest two competitive decomposition reactions (eqn. 4(a) and (b)) with, however a predominance of α-elimination, eqn. 4(a).

It is noteworthy that in all of these reactions, contrary to those which have been reported for distannanes (eqn. (6)) [9], cleavage of the Ge–Ge bond in the initial digermane could not be detected.

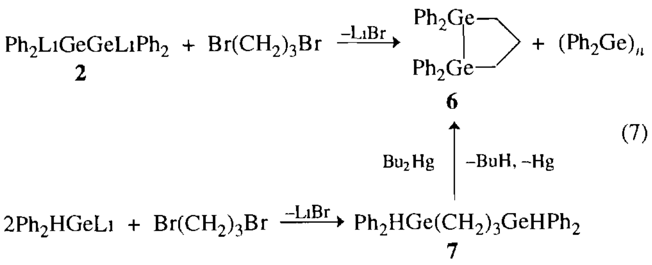
$$Ph_3SnSnPh_3 + PhLi \longrightarrow Ph_3SnLi + Ph_4Sn \qquad (6)$$

The ^{13}C NMR chemical shifts are given in Table 1. In the ^{13}C NMR spectrum the *ipso* carbon of the phenyl group undergoes a large deshielding which is characteristic of this type of structure [1, 10–12].

The digermyldilithium was then combined with various organic halides. 1,3-dibromopropane gave the expected cyclization reaction.

TABLE 1. ^{13}C NMR spectra of 1,1,2,2-tetraphenyl 1,2-digermyldilithium and of the corresponding digermane

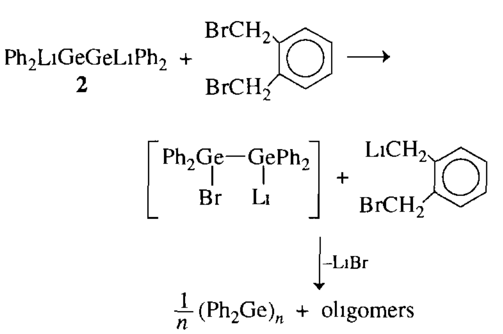
Compound	^{13}C NMR (THF-d_8)			
	C_1	C_2	C_3	C_4
$Ph_2LiGeGeLiPh_2$	156.98	137.67	127.01	124.51
$Ph_2HGeGeHPh_2$	136.35	136.15	129.64	126.16



(7)

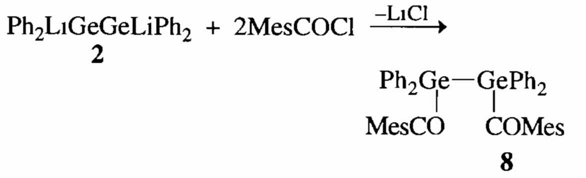
However, the secondary formation of polygermylenes $(Ph_2Ge)_n$, due probably to an exchange reaction halogen/lithium, was also observed. The same digermacyclopentane could otherwise be synthesized by the dehydrogenation reaction, using dibutylmercury, of the corresponding digermane.

In the presence of α,α'-dibromoorthoxylene this secondary exchange reaction becomes dominant and polygermylenes were obtained almost exclusively.



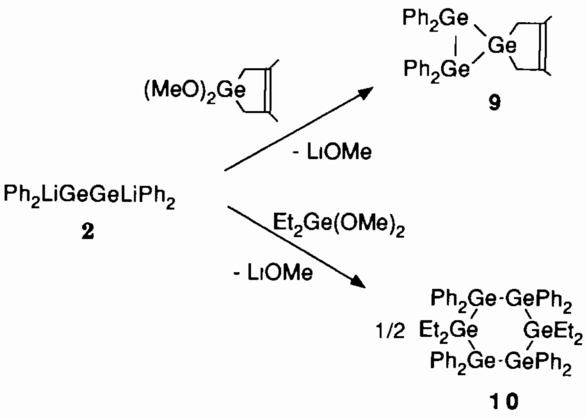
(8)

The same reaction using 2,4,6-trimethylbenzoyl chloride gave the novel digermyldiketone, a previously unknown species. It is stable at ambient temperature and was isolated as a yellow powder. Its IR spectrum shows an intense band at 1639 cm^{-1} due to $\nu(C{=}O)$ and characteristic of germylketones [13]. In its ^{13}C NMR spectrum, we observed a strong deshielding of the carbonyl carbon atom (δ CO = 242 ppm), similar to that reported for silylketones and silylthioketones [14, 15].



$$\underset{\mathbf{2}}{Ph_2LiGeGeLiPh_2} + 2MesCOCl \xrightarrow{-LiCl} \underset{\mathbf{8}}{\underset{MesCO\qquad COMes}{Ph_2Ge{-}GePh_2}} \qquad (9)$$

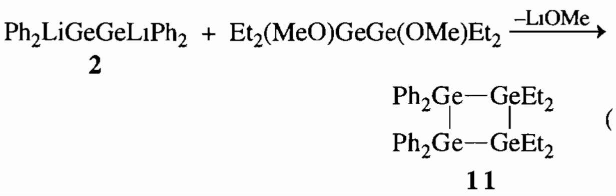
Transmetallation reactions beginning with germanium halides are more difficult. They are less selective and often produce polygermanes as secondary products, probably because of Cl/Li exchange. Success was achieved by using alkyldimethoxygermane, the methoxy group being well known for giving minor exchange reactions.



(10)

The new cyclogermane **9** could be perfectly characterized by physicochemical methods, but it was always contaminated by trace amounts of $(Ph_2Ge)_n$ which were difficult to extract from the reaction mixture. By contrast, when the substituent bound to germanium is an ethyl group, dimerization of the cyclotrigermane is observed and compound **10** is obtained almost exclusively.

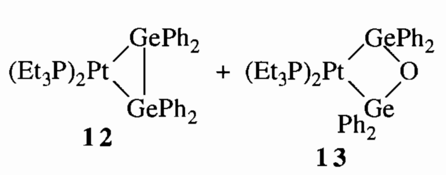
Similarly, the tetragermane **11** was obtained starting with tetraalkyldimethoxydigermane.



$$\underset{\mathbf{2}}{Ph_2LiGeGeLiPh_2} + Et_2(MeO)GeGe(OMe)Et_2 \xrightarrow{-LiOMe} \underset{\mathbf{11}}{\begin{array}{c}Ph_2Ge{-}GeEt_2\\ |\qquad\quad |\\ Ph_2Ge{-}GeEt_2\end{array}} \qquad (11)$$

Digermyldilithium **2** reacts with *trans*-dichlorobis(triethylphosphine)platinum(II) to form a mixture of the expected cyclic complex **12** and its corresponding oxide **13**:

$$Ph_2LiGeGeLiPh_2 + trans(Et_3P)_2PtCl_2 \xrightarrow[-40\ °C]{-LiCl}$$



(12)

In this case, there was no evidence of dimerization of the cyclic complex **12**. The two complexes **12** and **13** were always obtained regardless of the experimental conditions including solvents rigorously dried and manipulations under argon, and they could not be separated. However, they were unambiguously characterized by ^1H and ^{31}P NMR and mass spectrometry.

This work shows that organodigermyldilithiums are interesting reagents in organometallic chemistry, especially for the synthesis of bifunctional digermanes like **8** and small heterocycles **6**, **9**, **11**, **12** and **13**.

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