Solvent-Free Access to Lappert’s Heavier Tetrylenes
E{N(SiMe$_3$)$_2$}$_2$ (E = Ge, Sn, Pb)

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Abstract: Mechanochemistry is a rapidly emerging synthetic approach that gained momentum in the organic synthesis, catalysis, and materials chemistry. Its growing popularity stems from its ability to provide fast and efficient chemical transformations with a reduced environmental footprint as well as enabling products not accessible in solution. However, and despite its demonstrated advantages, the number of examples in the realm of main group chemistry are still rare and far between. Herein, iconic Lappert’s heavier tetrylenes E{N(SiMe$_3$)$_2$}$_2$ (E = Ge(1), Sn(2), Pb(3)) have been successfully prepared from GeCl$_2$·(1,4-dioxane), SnCl$_2$ or PbCl$_2$ and Li{N(SiMe$_3$)$_2$} via completely solvent-free mechanochemical route and subsequent sublimation. This high-yielding and scalable approach represents a significantly greener improvement over all previously reported procedures.

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General experimental data

All reactions were performed with Retsch MM400, MM500 Vario and PM100 ball mills using stainless steel (440B type) grinding jars with stainless steel (440B type) ball bearings. All reagent and product manipulations were carried out under argon in an MBraun UNIlab Pro glovebox, sealing the grinding jars with Teflon tape. SnCl2, GeCl4-(dioxane) and Li[N(SiMe2)3]2 were purchased from commercial suppliers and stored in the glove box. NMR spectra were run on Bruker NAV-400, AV-400 and DPX-300 instruments, using as standards the residual prolic solvent resonance for 1H [δ(C6D6) 7.16 ppm], the solvent resonance for 13C [δ(C6D6) 128.1 ppm], external SnMe6 in CDCl3 for 119Sn (δ 0.0 ppm) and calculated on a 9.4 T instrument for 207Pb [δ(PbMe4) 0 ppm, Σ 20.920599%]. The liquid-assisted grinding (LAG) parameter (η) is defined as the ratio of liquid (in μL) to the combined weights of solid reactants (in mg).

Synthetic procedures and characterization data

Ge[N(SiMe2)3]2 (1): A mixture of GeCl4-(1,4-dioxane) (1.16 g, 5 mmol, η = 0.2) and Li[N(SiMe2)3]2 (1.67 g, 10 mmol) was ball-milled for 15 min at 30 Hz in a 25 mL jar having one ball bearing (9/16 in, i.e., 15 mm), 13.62 g). A pale orange slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by 1H NMR (Figure S1), showing the almost quantitative formation of compound 1. After cooling at −20 °C to facilitate manipulation, the reaction crude was transferred to a cold finger sublimation apparatus, allowing the isolation of 1 as yellow crystals (1.80 g, 92% yield). The sublimation was performed at 75 ºC (7.1×10−2 mbar). 1H NMR (CD6, 300.1 MHz, 298 K, Figure S2): δ 0.33 (s) ppm. 13C(1H) (CD6, 75.5 MHz, 298 K; Figure S3): δ 5.3 (s) ppm.

Test to prepare Sn[N(SiMe2)3]2 (2) using no 1,4-dioxane: A mixture of SnCl2 (0.95 g, 5 mmol) and Li[N(SiMe2)3]2 (1.67 g, 10 mmol) was ball-milled for 16 h at 30 Hz rpm in a 25 mL jar having one ball bearing (9/16 in, i.e., 15 mm), 13.62 g). A bright orange slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by 1H NMR at different reaction times (see Figures S4 and S6).

Test to prepare Sn[N(SiMe2)3]2 (2) using 1 μL of 1,4-dioxane: A mixture of SnCl2 (0.95 g, 5 mmol), Li[N(SiMe2)3]2 (1.67 g, 10 mmol) and 1,4-dioxane (1 μL, η = 4×10−4) was ball-milled for 5 h at 30 Hz in a 25 mL jar having one ball bearing (9/16 in, i.e., 15 mm), 13.62 g). A bright orange slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by 1H NMR at different reaction times (see Figures S7 and S8).

Sn[N(SiMe2)3]2 (2): A mixture of SnCl2 (0.95 g, 5 mmol), Li[N(SiMe2)3]2 (1.67 g, 10 mmol) and 1,4-dioxane (500 μL, ηsolv = 1, which corresponds to η = 0.19) was ball-milled for 15 min at 30 Hz in 25 mL jar having one ball bearing (9/16 in, i.e., 15 mm), 13.62 g). A bright orange slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by 1H NMR (Figure S9), showing the almost quantitative formation of compound 2. After cooling at −20 °C to facilitate manipulation, the reaction crude was transferred to a cold finger sublimation apparatus, allowing the isolation of 2 as orange crystals (1.84 g, 84% yield). The sublimation was performed at 75 ºC in vacuo (3.1×10−2 mbar). 1H NMR (CD6, 300.1 MHz, 298 K; Figure S10): δ 0.29 (s) ppm. 13C(1H) (CD6, 100.6 MHz, 298 K; Figure S11): δ 5.8 (s) ppm. 119Sn(1H) (CD6, 149.5 MHz, 298 K; Figure S12): δ 768.5 (m) ppm.

Pb[N(SiMe2)3]2 (3): A mixture of PbCl2 (1.39 g, 5 mmol), Li[N(SiMe2)3]2 (1.67 g, 10 mmol) and 1,4-dioxane (500 μL, ηsolv = 1, which corresponds to η = 0.16) was ball-milled for 2 h at 30 Hz in a 25 mL jar (the reaction progress was monitored by 1H NMR at 15 min and 45 min; see Figures 13 and 14) having one ball bearing (9/16 in, i.e., 15 mm), 13.62 g). A bright yellow slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by 1H NMR (Figure S15), showing the formation of compound 3 as major species. After cooling at −20 °C to facilitate manipulation, the reaction crude was formed inside the jar, allowing the isolation of 3 as orange crystals (1.74 g, 67% yield). The sublimation was performed in the dark at 75 ºC in vacuo (3.5×10−2 mbar). 1H NMR (CD6, 400.1 MHz, 298 K; Figure S16): δ 0.24 (s) ppm. 13C(1H) (CD6, 100.6 MHz, 298 K; Figure S17): δ 5.6 (s) ppm. 207Pb(1H) (CD6, 84.1 MHz, 298 K; Figure S18): δ 4900 (br s) ppm.

Test to prepare Sn[N(SiMe2)3]2 (2) at larger scale: A 250 mL jar was charged with 450 g of ball bearings (8/16 in, i.e., 12 mm and 9/16 in, i.e., 15 mm), SnCl2 (18.96 g, 100 mmol), Li[N(SiMe2)3]2 (33.46 g, 200 mmol) and 1,4-dioxane (10 mL, ηsolv = 1, which corresponds to η = 0.19). The jar was sealed with a safety closure device and put in a planetary mill. A bright orange-brown slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by 1H NMR (Figure S19), showing the almost quantitative formation of compound 2.
**Figure S1.** $^1$H NMR spectrum (C$_6$D$_6$, 300.1 MHz, 298 K) of the crude outcome of the reaction of GeCl$_2$·(1,4-dioxane) with two equivalents of Li(N(SiMe$_3$)$_2$) after 15 min of reaction.

**Figure S2.** $^1$H NMR spectrum (C$_6$D$_6$, 300.1 MHz, 298 K) of Ge(N(SiMe$_3$)$_2$)$_2$ (1).
Figure S3. $^{13}$C($^1$H) NMR spectrum (C$_6$D$_6$, 75.5 MHz, 298 K) of Ge[Li(N(SiMe$_3$)$_2$)$_2$]$_2$ (1).

Figure S4. $^1$H NMR spectrum (C$_6$D$_6$, 300.1 MHz, 298 K) of the crude outcome of the reaction of SnCl$_2$ with two equivalents of Li[Li(N(SiMe$_3$)$_2$)$_2$] after 15 min of reaction.
Figure S5. $^1$H NMR spectrum ($^{13}$C$_6$D$_6$, 300.1 MHz, 298 K) of Li[N(SiMe$_3$)$_2$].

Figure S6. $^1$H NMR spectrum ($^{13}$C$_6$D$_6$, 300.1 MHz, 298 K) of the crude outcome of the reaction of SnCl$_2$ with two equivalents of Li[N(SiMe$_3$)$_2$] after 16 h of reaction.
Figure S7. $^1$H NMR spectrum ($C_6D_6$, 300.1 MHz, 298 K) of the crude outcome of the reaction of SnCl$_2$ with two equivalents of Li[N(SiMe$_3$)$_2$] and 1μL of 1,4-dioxane after 15 min of reaction.

Figure S8. $^1$H NMR spectrum ($C_6D_6$, 300.1 MHz, 298 K) of the crude outcome of the reaction of SnCl$_2$ with two equivalents of Li[N(SiMe$_3$)$_2$] and 1μL of 1,4-dioxane after 5 h of reaction.
Figure S9. $^1$H NMR spectrum ($CD_6$, 300.1 MHz, 298 K) of the crude outcome of the reaction of SnCl$_2$ with two equivalents of Li[N(SiMe$_3$)$_2$] and one equivalent of 1,4-dioxane after 15 min of reaction.

Figure S10. $^1$H NMR spectrum ($CD_6$, 300.1 MHz, 298 K) of Sn[N(SiMe$_3$)$_2$]$_2$ (2).
Figure S11. $^{13}\text{C}^{[1\text{H}]}$ NMR spectrum ($\text{C}_6\text{D}_6$, 100.6 MHz, 298 K) of Sn[N(SiMe$_3$)$_2$]$_2$ (2).

Figure S12. $^{119}\text{Sn}[^{1\text{H}}]$ NMR spectrum ($\text{C}_6\text{D}_6$, 149.5 MHz, 298 K) of Sn[N(SiMe$_3$)$_2$]$_2$ (2).
Figure S13. $^1$H NMR spectrum ($^6$D$_6$, 300.1 MHz, 298 K) of the crude outcome of the reaction of PbCl$_2$ with two equivalents of Li[N(SiMe$_3$)$_2$] and one equivalent of 1,4-dioxane after 15 min of reaction.

Figure S14. $^1$H NMR spectrum ($^6$D$_6$, 300.1 MHz, 298 K) of the crude outcome of the reaction of PbCl$_2$ with two equivalents of Li[N(SiMe$_3$)$_2$] and one equivalent of 1,4-dioxane after 45 min of reaction.
Figure S15. $^1$H NMR spectrum (C$_6$D$_6$, 300.1 MHz, 298 K) of the crude outcome of the reaction of PbCl$_2$ with two equivalents of Li[N(SiMe$_3$)$_2$] and one equivalent of 1,4-dioxane after 2 h of reaction.

Figure S16. $^1$H NMR spectrum (C$_6$D$_6$, 400.1 MHz, 298 K) of Pb[N(SiMe$_3$)$_2$]$_2$ (3).
Figure S17. $^{13}$C($^1$H) NMR spectrum (C$_6$D$_6$, 75.5 MHz, 298 K) of Pb(N(SiMe$_3$)$_2$)$_2$ (3).

Figure S18. $^{207}$Pb($^1$H) NMR spectrum (C$_6$D$_6$, 84.1 MHz, 298 K) of Pb(N(SiMe$_3$)$_2$)$_2$ (3).
Figure S19. $^1$H NMR spectrum (C$_6$D$_6$, 300.1 MHz, 298 K) of the crude outcome of the reaction of SnCl$_2$ with two equivalents of Li[N(SiMe$_3$)$_2$] and one equivalent of 1,4-dioxane after 30 min of reaction (larger scale test).
**Table S1.** Relevant methodological information for representative synthetic routes found for the preparation of 1-3

<table>
<thead>
<tr>
<th>Year</th>
<th>Ref.</th>
<th>Compound</th>
<th>Yield (%)</th>
<th>Li{N(SiMe₃)₂} synthesis</th>
<th>Transmetalation with ECl₂ (E = Ge, Sn, Pb)*</th>
<th>Solvent removal</th>
<th>Compound extraction</th>
<th>LiCl filtration</th>
<th>Solvent removal</th>
<th>Additional purification step</th>
</tr>
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<tr>
<td>1974</td>
<td>1</td>
<td>1</td>
<td>67</td>
<td>not detailed</td>
<td>In Et₂O at 0 °C</td>
<td>not detailed</td>
<td>not detailed</td>
<td>not detailed</td>
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<td>not detailed</td>
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<tr>
<td></td>
<td>2</td>
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<td>79</td>
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<td>3</td>
<td>69</td>
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<td></td>
</tr>
<tr>
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<td>50</td>
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<td>not detailed</td>
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</tr>
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<td>3</td>
<td>69</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1990</td>
<td>4</td>
<td>2</td>
<td>75</td>
<td>HN(SiMe₃)₂ + nBuLi (solution in hexanes) at 0 °C</td>
<td>SnCl₃ in THF transferred slowly to Li(N(SiMe₃)₂) in THF at 0 °C and stirred for 3-4.5 h at room temperature.</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
<td>Distillation</td>
</tr>
<tr>
<td>1977</td>
<td>3</td>
<td>1</td>
<td>67</td>
<td>HN(SiMe₃)₂ + nBuLi in Et₂O</td>
<td>Li(N(SiMe₃)₂) in Et₂O transferred slowly to a suspension of ECl₂ in Et₂O and stirred for 2 h</td>
<td>YES</td>
<td></td>
<td>YES</td>
<td>YES</td>
<td>Distillation</td>
</tr>
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<td></td>
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</tr>
<tr>
<td>2014</td>
<td>5</td>
<td>1</td>
<td>57</td>
<td>HN(SiMe₃)₂ + nBuLi (solution in heptane) at -196 °C stirred 30 min while thawing</td>
<td>Solution of ECl₂ in Et₂O (E = Ge) or THF (E = Sn) added slowly to Li(N(SiMe₃)₂) solution and stirred for 2h</td>
<td>YES</td>
<td>NO</td>
<td>NO</td>
<td>NA</td>
<td>Distillation</td>
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<td>81</td>
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<td></td>
</tr>
<tr>
<td>2018</td>
<td>6</td>
<td>1</td>
<td>75</td>
<td>Solid Li{N(SiMe₃)₂} commercially obtained</td>
<td>Li(N(SiMe₃)₂) in Et₂O transferred slowly (40-45 min) to ECl₂ in Et₂O (E = Ge, Pb) or Et₂O/THF (E = Sn) and stirred for 3-4.5 h. LiCl allowed to settle for 30 min</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
<td>Distillation</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>73</td>
<td>Solid Li{N(SiMe₃)₂} commercially obtained</td>
<td>Li(N(SiMe₃)₂) and SnCl₃ cooled to -78 °C followed by addition of THF. Slow warming to RT.</td>
<td>YES</td>
<td>In toluene</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>69</td>
<td>not detailed</td>
<td></td>
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</tr>
<tr>
<td>2022</td>
<td>7</td>
<td>2</td>
<td>84</td>
<td>Solid Li{N(SiMe₃)₂} commercially obtained</td>
<td>Li(N(SiMe₃)₂) and SnCl₃ cooled to -78 °C followed by addition of THF. Slow warming to RT.</td>
<td>YES</td>
<td>In toluene</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
</tr>
</tbody>
</table>

*For E = Ge, ECl₂ is ECl₂-dioxane
Green metrics calculations

Green chemistry metrics (GCM)

<table>
<thead>
<tr>
<th>Metric</th>
<th>Abbreviation</th>
<th>Formula</th>
<th>Optimal value</th>
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<tbody>
<tr>
<td>Atom Economy</td>
<td>AE</td>
<td>( \frac{\text{Formula weight product (g/mol)}}{\text{Formula weight of all reactants used in reaction (g/mol)}} \times 100 )</td>
<td>100%</td>
</tr>
<tr>
<td>Reaction Mass Efficiency</td>
<td>RME</td>
<td>( \frac{\text{Formula weight product (g/mol)}}{\text{Formula weight of all reactants used in reaction (g/mol)}} \times \text{Yield} )</td>
<td>100%</td>
</tr>
<tr>
<td>Environmental Factor</td>
<td>E-factor</td>
<td>( \frac{\text{Mass of wastes (g)}}{\text{Mass of the product of interest (g)}} )</td>
<td>0</td>
</tr>
<tr>
<td>Process Mass Intensity</td>
<td>PMI</td>
<td>( \frac{\text{Total mass used in the process (g)}}{\text{Mass of product (g)}} )</td>
<td>1</td>
</tr>
</tbody>
</table>

FW: Formula weight in g.mol\(^{-1}\)
E-factor calculations

Ge\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}:

- General formula used for mechanochemical synthesis*:
  \[
  E \text{- factor} = \frac{GeCl\textsubscript{2} \cdot dioxane + Li[N(SiMe\textsubscript{3})\textsubscript{2}] - Ge[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}}{Ge[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}}
  \]
  * All quantities are expressed in grams

  \[E = \frac{1.16 + 1.67 - 1.80}{1.80} = 0.57\]

- General formula used for Inorganic Syntheses 2018*:
  \[
  E \text{- factor} = \frac{GeCl\textsubscript{2} \cdot dioxane + Li[N(SiMe\textsubscript{3})\textsubscript{2}] + Et\textsubscript{2}O(10\%) - Ge[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}}{Ge[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}}
  \]
  * All quantities are expressed in grams

  \[E = \frac{5.002 + 7.224 + 10.344 - 6.402}{6.402} = 2.53\]

 Density of ether: 0.7134 g/cm\textsuperscript{3}  145 mL = 103.443 g => 10% = 10.344 g

Sn\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}:

- General formula used for mechanochemical synthesis*:
  \[
  E = \frac{SnCl\textsubscript{2} + Li[N(SiMe\textsubscript{3})\textsubscript{2}] + dioxane - Sn[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}}{Sn[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}}
  \]
  * All quantities are expressed in grams

  \[E = \frac{0.95 + 1.67 + 0.51685 - 1.84}{1.84} = 0.70\]

 Density of dioxane: 1.0337 g/cm\textsuperscript{3}  500µL = 0.51685 g

- Considering dioxane as "solvent"*
  \[
  E = \frac{SnCl\textsubscript{2} + Li[N(SiMe\textsubscript{3})\textsubscript{2}] + dioxane (10\%) - Sn[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}}{Sn[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}}
  \]
  * All quantities are expressed in grams

  \[E = \frac{0.95 + 1.67 + 0.051685 - 1.84}{1.84} = 0.45\]

 Density of dioxane: 1.0337 g/cm\textsuperscript{3}  500µL = 0.51685 g => 10% = 0.051685 g

- General formula used for Inorganic Syntheses 2018*:
  \[
  E = \frac{SnCl\textsubscript{2} + Li[N(SiMe\textsubscript{3})\textsubscript{2}] + Et\textsubscript{2}O(10\%) + THF(10\%) - Sn[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}}{Sn[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}}
  \]
  * All quantities are expressed in grams

  \[E = \frac{10.00 + 17.65 + 20.886 + 17.752 - 20.31}{20.31} = 1.48\]

 Density of ether: 0.7134 g/cm\textsuperscript{3}  290 mL = 206.886 => 10% = 20.886

 Density of THF: 0.8876 g/cm\textsuperscript{3}  20 mL = 17.752 => 10% = 1.7752
**Pb(N(SiMe₃)₂)₂**

- General formula used for mechanochemical synthesis*:

\[
E = \frac{PbCl₂ + Li[N(SiMe₃)₂] + \text{dioxane} - Pb[N(SiMe₃)₂]₂}{Pb[N(SiMe₃)₂]₂}
\]

* All quantities are expressed in grams

\[
E = \frac{1.39 + 1.67 + 0.51685 - 1.74}{1.74}
\]

E = 1.06

Density of dioxane: 1.0337 g/cm³

500 µL = 0.51685 g

- Considering dioxane as "solvent"*

\[
E = \frac{PbCl₂ + Li[N(SiMe₃)₂] + \text{dioxane (10%)} - Pb[N(SiMe₃)₂]₂}{Pb[N(SiMe₃)₂]₂}
\]

* All quantities are expressed in grams

\[
E = \frac{1.39 + 1.67 + 0.051685 - 1.74}{1.74}
\]

E = 0.79

Density of dioxane: 1.0337 g/cm³

500 µL = 0.51685 g => 10% = 0.051685 g

- General formula used for Inorganic Syntheses 2018*:

\[
E = \frac{PbCl₂ + Li[N(SiMe₃)₂] + Et₂O (10%) - Pb[N(SiMe₃)₂]₂}{Pb[N(SiMe₃)₂]₂}
\]

* All quantities are expressed in grams

\[
E = \frac{10.00 + 12.03 + 17.216 - 15.31}{15.31}
\]

E = 1.56

Density of ether: 0.7134 g/cm³

240 mL = 171.216 => 10% = 17.216
Process mass intensity (PMI) calculations

**Ge{N(SiMe3)2}2**

General Formula used for mechanochemical synthesis*:

\[
PMI = \frac{GeCl_2 \cdot \text{dioxane} + \text{Li}[N(SiMe3)2]}{Ge[N(SiMe3)2]2}
\]

* All quantities are expressed in grams

PMI = 1.57

General formula used for Inorganic Syntheses 2018*:

\[
PMI = \frac{(GeCl_2 \cdot \text{dioxane} + \text{Li}[N(SiMe3)2] + Et2O)}{Ge[N(SiMe3)2]2}
\]

* All quantities are expressed in grams

PMI = 18.07

Density ether: 0.7134 g/cm³ 145 mL = 103.443g

**Sn{N(SiMe3)2}2**

General Formula used for mechanochemical synthesis*:

\[
MI = \frac{(SnCl2 + \text{dioxane} + \text{Li}[N(SiMe3)2])}{Sn[N(SiMe3)2]2}
\]

* All quantities are expressed in grams

PMI = 1.70

Density dioxane: 1.0337 g/cm³ 500µL = 0.51685 g

**Pb{N(SiMe3)2}2**

General Formula used for mechanochemical synthesis*:

\[
MI = \frac{(PbCl2 + \text{dioxane} + \text{Li}[N(SiMe3)2])}{Pb[N(SiMe3)2]2}
\]

* All quantities are expressed in grams

PMI = 2.06

Density of dioxane: 1.0337 g/cm³ 500µL = 0.51685 g

---

*All quantities are expressed in grams*
Generalized Reaction Mass Efficiency (RME)

**Ge[N(SiMe3)2]2**

General Formula used for mechanochemical synthesis and for Inorganic Synthesis 2018*

\[ RME = \left( \frac{\text{Mw GeCl2}}{\text{Mw GeCl2} \cdot \text{dioxane} + 2 \times \text{Mw Li[N(SiMe3)2]}} \right) \times \text{Yield} \]

* All quantities are expressed in grams/mol

\[ RME = \frac{393.38}{231.65 + 2 \times 167.33} \times 92 \]

RME = 63.91 (mechanochemical)

\[ RME = \frac{393.38}{231.65 + 2 \times 167.33} \times 75 \]

RME = 52.10 (Inorganic Syntheses 2018)

Mw GeCl2 dioxane = 231.65
Mw Ge[N(SiMe3)2]2 = 393.38
Mw Li[N(SiMe3)2] = 167.33

**Sn[N(SiMe3)2]2**

General Formula used for mechanochemical synthesis and for Inorganic Synthesis 2018*

\[ RME = \left( \frac{\text{Fw SnCl2}}{\text{Fw SnCl2} + 2 \times \text{Li[N(SiMe3)2]}} \right) \times \text{Yield} \]

* All quantities are expressed in grams

\[ RME = \frac{439.48}{189.62 + 2 \times 167.33} \times 84 \]

RME = 70.41 (mechanochemical)

\[ RME = \frac{439.48}{189.62 + 2 \times 167.33} \times 73 \]

RME = 61.19 (Inorganic Syntheses 2018)

Mw SnCl2 = 189.62
Mw Sn[N(SiMe3)2]2 = 439.48
Mw Li[N(SiMe3)2] = 167.33

**Pb[N(SiMe3)2]2**

General Formula used for mechanochemical synthesis

\[ RME = \left( \frac{\text{Fw PbCl2}}{\text{Fw PbCl2} + 2 \times \text{Li[N(SiMe3)2]}} \right) \times \text{Yield} \]

* All quantities are expressed in grams

\[ RME = \frac{527.97}{278.11 + 2 \times 167.33} \times 67 \]

RME = 57.72

General formula used for Inorganic Syntheses 2018*:

\[ RME = \left( \frac{\text{Sn[N(SiMe3)2]2}}{\text{SnCl2} + 2 \times \text{Li[N(SiMe3)2]}} \right) \times \text{Yield} \]

* All quantities are expressed in grams

\[ RME = \frac{527.97}{278.11 + 2 \times 167.33} \times 69 \]

RME = 59.45

Mw PbCl2 = 278.11
Mw Pb[N(SiMe3)2]2 = 527.97
Mw Li[N(SiMe3)2] = 167.33
**Generalized Atom Economy (AE)**

Ge{N(SiMe3)2}2

*General Formula used for mechanochemical synthesis and for Inorganic Syntheses 2018*

\[
RME = \frac{Mw Ge[N(SiMe3)2]2}{(Mw GeCl2 · dioxane + 2 x Mw Li[N(SiMe3)2])} \times 100
\]

* All quantities are expressed in grams

\[
RME = \frac{393.38}{231.65 + 2 \times 167.33} \times 100
\]

\[RME = 69.46\]

Mw GeCl2-dioxane = 231.65
Mw Ge{N(SiMe3)2}2 = 393.38
Mw Li{N(SiMe3)2}2 = 167.33

Sn{N(SiMe3)2}2

*General Formula used for mechanochemical synthesis and for Inorganic Syntheses 2018*

\[
RME = \frac{Fw Sn[N(SiMe3)2]2}{(Fw SnCl2 + 2 x Li[N(SiMe3)2])} \times 100
\]

* All quantities are expressed in grams

\[
RME = \frac{439.48}{189.62 + 2 \times 167.33} \times 100
\]

\[RME = 83.83\]

Mw SnCl2 = 189.62
Mw Sn{N(SiMe3)2}2 = 439.48
Mw Li{N(SiMe3)2}2 = 167.33

Pb{N(SiMe3)2}2

*General Formula used for mechanochemical synthesis and for Inorganic Syntheses 2018*

\[
RME = \frac{Fw Pb[N(SiMe3)2]2}{(Fw PbCl2 + 2 x Li[N(SiMe3)2])} \times 100
\]

* All quantities are expressed in grams

\[
RME = \frac{527.97}{278.11 + 2 \times 167.33} \times 100
\]

\[RME = 86.16\]

Mw PbCl2 = 278.11
Mw Pb{N(SiMe3)2}2 = 527.97
Mw Li{N(SiMe3)2}2 = 167.33
References