Convenient Large Scale *in situ* Synthesis of 3-(*N,N*-dialkylamino)-1,1-bis(trimethylsilyl)-propyllithium: Source of a New Sterically Demanding γ-Donor functionalized Alkyl Ligand

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The addition of $Li[CH_2NR_2]$ to the olefin $[Me_3Si]_2C{=}CH_2$ yields almost quantitatively the new γ-donor functionalized organolithium compounds $(Me_3Si)_2C(Li)CH_2CH_2NR_2$ which are used to synthesize the intramolecularly adduct stabilized organo-gallium and -zinc complexes $R_2GaC(SiMe_3)_2CH_2CH_2NR_2$, $\{ClZnC(SiMe_3)_2CH_2CH_2NR_2\}_2$.

The effects of steric shielding, *e.g.* by the tris(trimethylsilyl)-methyl[1] moiety, on the reactivity and structural properties especially of organometallic alkyl compounds is well documented in the literature and a matter of continuing interest.[2] In metal alkoxide and amide chemistry the combination of steric crowding with Lewis donor functionalization in the same ligand has been a powerful concept to obtain intramolecularly adduct stabilized systems of unique properties.[3] Attempts to transfer this idea to the chemistry of metal alkyl systems have been rather rare so far.[4,5]. The entry into the chemistry of metal compounds with ω-donor-functionalized alkyl groups usually requires the respective organolithium compounds, which synthesis may sometimes be non-trivial. This is especially true for systems of the type $Li\{C[(SiMe_3)_2(CH_2)_nDo]\}$ ($n \geqslant 2$; Do = OR', NR'$_2$ and PR'$_2$).

The treatment of $Li[CH_2NR_2]$ (R = Me, Et)[6] with the olefin $(Me_3Si)_2C{=}CH_2$[7] in THF solution yielded almost quantitatively the C–C coupling product **1a**–, **b**–Li. Subsequent hydrolysis gave the alkylamine **1**§ (Scheme 1). This result shows that nucleophilic additions to the olefin $(Me_3Si)_2C{=}CH_2$, which were previously known only for some alkyllithium compounds (*e.g.* Bu^{t}Li) and lithium amides,[6] are also extendable to heteroatom functionalized methyllithium compounds and occurs selectively in anti-Markownikoff orientation. Interestingly, the alkylamine **1** itself cannot be converted back into its lithium derivative with a reasonable yield. Various reagents and conditions failed to achieve deprotonation of **1**. The purification of the compounds $Li[CH_2NR_2]$ from the byproduct Bu_4Sn (step i in Scheme 1) may be a problem in certain cases, *e.g.* for R = Et. Pure **1a**–Sn‡ can be derived from **1a**–Li and transmetallation of **1a**–Sn with methyllithium readily yields pure **1a**–Li. Attempts to crystallize **1a**–, **b**–Li have failed so far.

Addition of $Li[CH_2PMe_2]$[8] to the olefin does also give the C–C coupling product similar to **1**, however the selectivity of this reaction is lower. NMR and GC–MS data of the hydrolysed products suggest reaction of the primary addition product with another molecule of the olefin.

The organogallium compounds **2a**, **b** were obtained by treatment of R_2GaCl with *in situ* synthesized **1a**–Li and **1b**–Li. In case of $GaCl_3$ (R = Cl) a yield of only 40% was reached. Without intramolecular adduct stabilization it may be difficult to obtain monomeric solvent- and alkyl halide-free alkylgallium halides with bulky substituents. This is shown for example by the reaction of $GaCl_3$ with $Li[C(SiMe_3)_3]$ giving $Li(THF)_3GaCl_3[C(SiMe_3)_3]$ from which $Cl_2Ga[C(SiMe_3)_3]$ could not be obtained preparatively.[9] The spectroscopic data of **2a**, **b** are very similar to those of the known compounds $R_2Ga[(CH_2)_3NR_2]$[10] and agree with the structure shown in Scheme 1,§ *e.g.* the ^1H NMR spectrum of **2a** shows the diasterotopic splitting of the methylene protons of the ethyl moieties at the nitrogen. When zincdichloride was treated with **1b**–Li in THF solutions under various conditions only the mono-substituted product **3**¶ was obtained. The steric shielding by the silyl groups at the α-carbon atom also alters the reactivity of **2a** towards transition metal nucleophiles compared with the unsubstituted congener. While the 'parent' organogallium halide $Cl_2Ga[(CH_2)_3NR_2]$ yields an tetranuclear complex[11] when treated with $K_2[Fe(CO)_4]$ (1 equiv.), the corresponding reaction of **2a** stopped as expected at the intermediate $\{(CO)_4Fe\text{-}Ga(Cl)[C(SiMe_3)_2CH_2CH_2NR_2]^-\}$.

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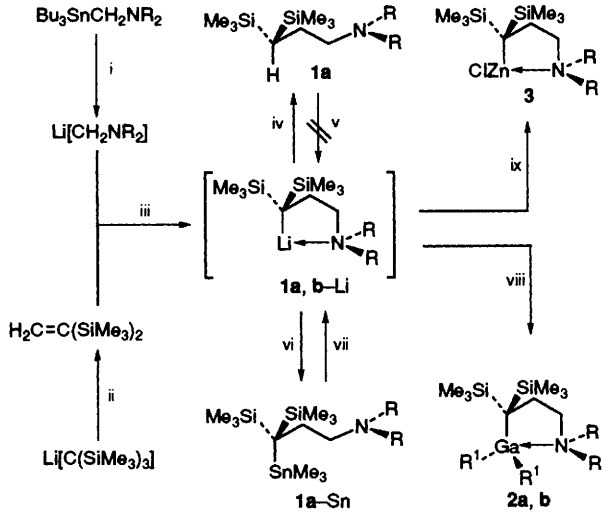

Scheme 1 (**1a**–Li: R = Et, **1b**–Li: R = Me, **2a**: R' = Me, **2b**: R' = Cl, **3**: R = Me)

Reagents and conditions: i, BuLi, THF, −78 °C to room temp., 1 h; ii, *p*-CH_2O, THF, 0 °C, 0.5 h, H_2O; iii, −78 °C to room temp., THF, 16 h; iv, H_2O; v, BuLi, Bu^{t}Li, MeLi, Bu^{t}Li/KOBu^t, heptane, THF, reflux, 1 h up to 1 week; vi, Me_3SnCl, THF, −78 °C to room temp., 0.5 h; vii, MeLi, THF, −78 °C to room temp., 3 h; viii, $ClGaR'_2$, −78 °C to room temp., 10 h; ix, $ZnCl_2$, THF, −78 °C to room temp., 3 h

Footnotes

† 3-(*N,N*-Diethylamino)-1,1-bis(trimethylsilyl)propane **1a**.—To a solution of 2.33 g (25 mmol) *N,N*-diethylaminomethyllithium in 50 ml THF, 4.3 g (25 mmol) of 1,1-bis(trimethylsilyl)ethene dissolved in 20 ml of precooled THF was added dropwise at −78 °C with stirring. The reaction solution was stirred at this temperature for 2 h and was then allowed to warm up to room temp. After additional 15 h the mixture was hydrolysed with diluted hydrochloric acid at 0 °C. The product was then extracted from the acid phase after addition of an excess of sodium alkoxide with pentane. After drying the combined organic extracts ($MgSO_4$) and removal of the solvent at reduced pressure, the product was purified by short path distillation *in vacuo*, yielding 5 g (78%) of a colourless liquid, bp 43–44 °C (10^{-3} Torr). ^1H NMR (399.78 MHz, $CDCl_3$, 25 °C): δ −0.52 (1H, t, $CHCH_2CH_2N$), −0.01 (18H, s, $Si(CH_3)_3$, $^1J_{CH}$ 120.8 Hz, $^2J_{SiH}$ 32.4 Hz), 0.98 (6H, t, NCH_2CH_3), 1.54 (2H, m, $CHCH_2CH_2N$), 2.29 (2H, m,

$CHCH_2CH_2N$), 2.47 (4H, q, NCH_2CH_3); $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 25 °C) δ 0.0 ($SiCH_3$), 11.3 ($CHCH_2CH_2N$), 11.8 (NCH_2CH_3), 23.3 ($CHCH_2CH_2N$), 46.9 (NCH_2CH_3), 56.2 ($CHCH_2CH_2N$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C) δ 0.0 (q, $SiCH_3$), 11.3 (d, $CHCH_2CH_2N$), 11.8 (q, NCH_2CH_3), 23.3 (t, $CHCH_2CH_2N$), 46.9 (t, NCH_2CH_3), 56.2 (t, $CHCH_2CH_2N$); EI-MS (70 eV) *m/z* 259 (n. obs., $[M^+]$), 244 (5%, $[M - CH_3]^+$), 86 (100, $[CH_2NEt_2]^+$), 73 (15, $[Si(CH_3)_3]^+$).

‡ 3-(*N,N*-Diethylamino)-1,1-bis(trimethylsilyl)-1-trimethyl-stannane (**1a**-Sn).—According to the above procedure 25 mmol of **1a**–Li was prepared *in situ* and was treated with trimethyltinchloride (1 equiv.) at 0 °C. The solvent was removed using vacuum distillation and the residue was extracted twice with 20 ml of pentane. The product was obtained by fractional vacuum distillation. Yield 10.3 g (98%) as a colourless liquid, bp 118–123 °C (10^{-3} Torr); ^1H NMR (399.78 MHz, $CDCl_3$, 25 °C): δ 0.06 (18H, s, $SiCH_3$), 0.13 (9H, s, $SnCH_3$), 0.98 (6H, s, NCH_2CH_3), 1.94 (2H, m, CH_2CH_2N), 2.26 (2H, m, CH_2CH_2N), 2.50 (4H, q, NCH_2CH_3); $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 25 °C) δ −4.5 ($SnCH_3$, $^1J_{119SnC}$ 154.4 Hz, $^1J_{117SnC}$ 148.0 Hz), 0.1 ($SnCSi$), 2.4 ($SiCH_3$), 11.8 (NCH_2CH_3), 29.8 (CH_2CH_2N), 47.1 (NCH_2CH_3), 54.9 (CH_2CH_2N); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C) δ −4.5 (q, $SnCH_3$), 2.4 (q, $SiCH_3$), 11.8 (q, NCH_2CH_3), 29.8 (t, CH_2CH_2N), 47.1 (t, NCH_2CH_3), 54.9 (t, CH_2CH_2N); $^{119}Sn\{^1H\}$ NMR (149.08 MHz, $CDCl_3$, 25 °C): δ 12.3. ^{119}Sn NMR (149.08 MHz, $CDCl_3$, 25 °C): δ 12.3 (ttdc, $^2J_{119SnH}$ 49.6 Hz, $^3J_{119SnH}$ 65.3 Hz, $^4J_{119SnH}$ 4.6 Hz).

§ [3-(*N,N*-Diethylamino)-1,1-bis(trimethylsilyl)propyl]-dimethyl-gallium **2a**.—3.34 g (25 mmol) of dimethylgalliumchloride dissolved in 20 ml of precooled THF were added dropwise to a solution of 25 mmol **1a**–Li in 50 ml THF at −78 °C. The mixture was allowed to warm up to room temp. within 1 h. The solvent was removed under reduced pressure and the crude product was extracted from the obtained residue with pentane. The gallium compound **2a** was separated from the byproduct $SnBu_4$ by careful short path distillation, and was washed with cold pentane. Yield 8 g (97%) of pale crystals, mp 37 °C; ^1H NMR (399.78 MHz, C_6D_6, 25 °C): δ −0.10 (6H, s, $GaCH_3$), 0.22 (18H, s, $SiCH_3$), 0.51 (6H, t, NCH_2CH_3), 1.69 (2H, t, CH_2CH_2N), 2.15 (2H, t, CH_2CH_2N), 2.24 (2H, dq, NCH_2CH_3, $^2J_{HH}$ 13.7, $^3J_{HH}$ 6.7 Hz), 2.33 (2H, dq, NCH_2CH_3, $^2J_{HH}$ 13.7, $^3J_{HH}$ 6.7 Hz); $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C) δ −0.9 ($GaCH_3$), 2.9 ($SiCH_3$), 7.6 (NCH_2CH_3), 27.4 (CH_2CH_2N), 43.7 (NCH_2CH_3), 56.3 (CH_2CH_2N), $SiCGa$ not observed, which was probably due to extensive line broadening. EI-MS (70 eV) *m/z* 357 (not obs., $[M^+]$), 342 (100%, $[M-CH_3]^+$), 258 (2, $[M-CH_3-CH_2NEt_2]^+$), 228 (3, $[M-2CH_3-Ga(CH_3)_2]^+$), 86 (72, $[CH_2NEt_2]^+$), 73 (22, $[Si(CH_3)_3)]^+$), correct isotope patterns observed.

¶ [3-(*N,N*-Dimethylamino)-1,1-bis(trimethylsilyl)propyl]zincchloride **3**.—According to the above procedures 1.36 g (10 mmol) zincdichloride were added as THF solution to 10 mmol of *in situ* synthesized **1b**–Li. After 3 h the solvent was removed and the product was extracted from the residue with diethyl ether. Colourless crystals of **3** (3.1 g, 93%) were grown from pentane, subl. 160 °C (10^{-4} Torr); ^1H NMR (399.78 MHz, C_6D_6, 25 °C) δ 0.31 (18H, s, $SiCH_3$), 1.78 (2H, t, CH_2CH_2N), 1.98 (2H, t, CH_2CH_2N), 2.01 (6H, s, NCH_3); $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C) δ 2.9 ($SiCH_3$), 7.3 ($SiCZn$), 27.5 (CH_2CH_2N), 45.7 (NCH_3), 63.1 (CH_2CH_2N). EI-MS (70 eV) *m/z* 329 (0.5%, $[M^+]$), 314 (0.5, $[M-CH_3]^+$), 200 (12.6, $[M-Zn-Cl-2CH_3]^+$), 73 (19.2, $[SiMe_3]^+$), 58 (100, $[CH_2NMe_2]^+$), correct isotope patterns observed; CI-MS (isobutene) *m/z* 627 (12.7%, $[M_2-Cl]^+$), 329 (13.3, $[M^+]$), 314 (6.3, $[M-CH_3]^+$), 294 (100, $[M-Cl]^+$), 200 (55.8, $[M-Zn-Cl-2CH_3]^+$), correct isotope patterns observed.

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