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A New One-Pot Arylacetylene Synthesis: 4-$RC_6H_4C{\equiv}C(TMS)$ from 4-RC_6H_4CN and $LiC(TMS)_3(THF)_2$ via $\overline{Li[N(TMS)C(C_6H_4R\text{-}4)C(TMS)_2]}(THF)$ (TMS = $SiMe_3$, R = H, F, Br, OMe or Bu^t)

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Abstract:

Treatment of $LiC(TMS)_3(THF)_2$ with the nitrile 4-RC_6H_4CN in Et_2O at ambient temperature yields the new lithium 1-aza-allyl $\overline{Li[N(TMS)C(C_6H_4R\text{-}4)C(TMS)_2]}(THF)$ which readily eliminates $LiN(TMS)_2$ upon heating in refluxing benzene yielding the acetylene 4-$RC_6H_4C{\equiv}C(TMS)$ in quantitative (TMS = $SiMe_3$; R = H, Br, OMe or Bu^t) or low (R = F) yield.

Recent publications from this laboratory have demonstrated that, irrespective of stoichiometry, the reaction between bis(trimethylsilyl)methyllithium $LiCH(TMS)_2$ (TMS = $SiMe_3$) and cyanobenzene or 2-cyano-2-methylpropane at ambient temperature in diethyl ether gave the 1 : 2 or 1 : 1 adduct, the lithium β-diketiminate **1** [1] or 1-aza-allyl **2** [2]. By contrast 1-aza-allyllithium compounds **3** [3] or **4a** were obtained from benzonitrile and either $LiCH(TMS)_2$ in presence of the strong neutral donor TMEDA or $LiC(TMS)_3(THF)_2$ {≡ 1/2 $[Li(THF)_4][Li\{C(TMS)_3\}_2]$ [4]}, respectively [3]. Compounds **1** - **4** have been used as (i) ligand transfer agents (yielding 1-aza-allyls of Mg [5], K [2], Fe(II) [6], Co(II) [7], Ni(II) [6], Cu(I) [8], Zr(IV) [2], Sn(IV) [2], Sn(II) [3; 9], Ce(III) [10], Nd(III), Sm(II), Sm(III), Yb(II), Yb(II), Pb(II) [3], and Th(IV) [11]), (ii) sources of imines such as $(TMS)N{=}C(Bu^t)CH_2(TMS)$ or $[(TMS)N{=}C(Bu^t)C(H)(TMS)]_2$ [10], or (iii) precursors of cyclic PN

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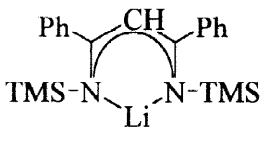
compounds such as ClPN(R)P(Cl)NR [R = C(Bu^t)CH(TMS)] or [Bu^{t}CN(TMS)P(Cl)P(Ph$_2$)CH]Cl] [8].



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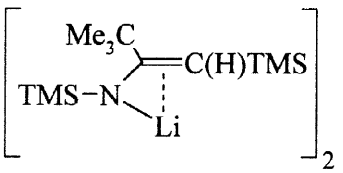

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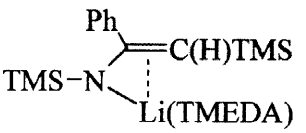

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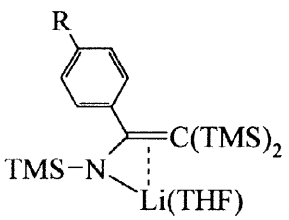
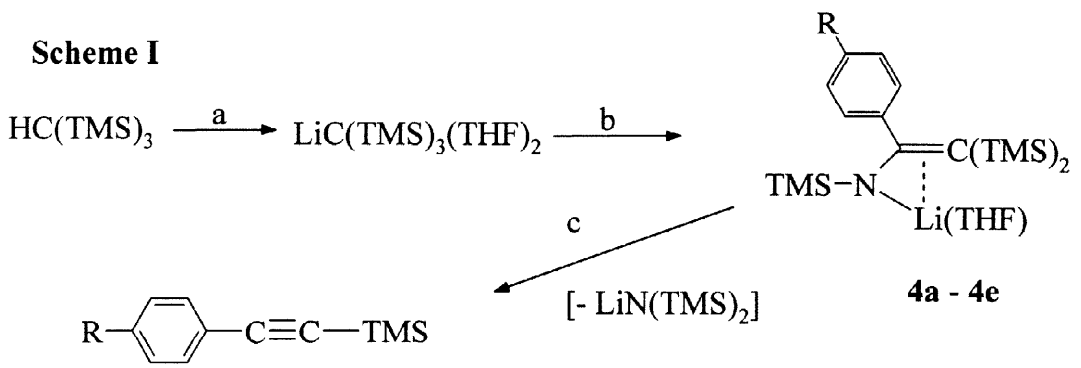


4a R = H, **4b** R = F, **4c** R = Br, **4d** R = OMe, **4e** R = Bu^t

We now draw attention to a further use of members of one class (**4**) of the above 1-aza-allyllithium compounds, namely their ready thermal fragmentation (step c of Scheme I) to yield quantitatively (NMR, except **5b**) the arylacetylene 4-RC$_6$H$_4$C≡C(TMS) **5** and lithium bis(trimethylsilyl)amide. The procedure may be modified into a one-pot synthesis of **5**, employing HC(TMS)$_3$, LiMe and 4-RC$_6$H$_4$CN as reagents and the successive steps a -c of Scheme I. In the case of [Li{N(TMS)C(C$_6$H$_4$R-4)C(TMS)$_2$}(THF)] **4b**, unidentified

Scheme I



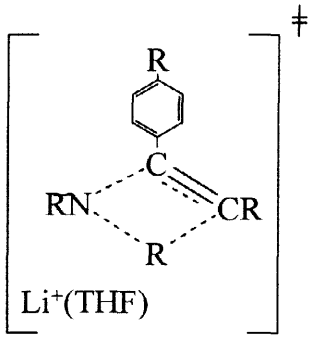
5a R = H, **5b** R = F, **5c** R = Br
5d R = OMe, **5e** R = Bu^t

a) LiMe, THF, 65 °C, 3.5 h [3]. b) 4-RC$_6$H$_4$CN, Et$_2$O, *ca.* 20 °C. c) C$_6$H$_6$, 80 °C, 60 h; then quenching with MeOH and subsequent distillation or sublimation of the acetylene.

by-products as well as the acetylene **5b** were observed, possibly due to the ease of nucleophilic displacement of F$^-$ from 4-FC$_6$H$_4$C≡C(TMS) **5b** or **4b** by $\overline{N}$(TMS)$_2$ or [N(TMS)(4-

$FC_6H_4)C(TMS)_2]^-$. Similarly, whereas the isolated yields of recrystallized (from n-C_5H_{12}) **4a** and **4c** - **4e** were satisfactory (**4a**, 89 %; **4c**, 88 %; **4d**, 70 %; **4e**, 81 %), that of **4b** was only 12 %. A further limitation of the sequence of Scheme I as a general route to arylacetylenes resides in step b , and specifically on the nature of R in 4-RC_6H_4CN, which must be less responsive to nucleophilic attack (by $\bar{C}(TMS)_3$) than its cyano group. Thus, not only for R = F, but also for R = NO_2 or Me (or another potentially protic substituent, $HC(TMS)_3$ being produced), step b afforded little or no lithium 1-aza-allyl. Compound **3** did not yield PhC≡C(TMS), even upon prolonged heating.

Each of the compounds **4** and **5** gave satisfactory analysis and NMR spectra. For crystalline complex **4c** a single crystal X-ray diffraction study was also carried out (Fig. 1); earlier structural studies [1 -3, 5 - 11] had revealed a diversity of bonding modes for 1-aza-allylmetal complexes: the ligand being either terminal and mono-(enamidometal) or bidentate (iminoalkylmetal), or bridging. Crystalline **4c** is a monomer, with the 1-aza-allyl ligand chelating the three-coordinate lithium. The short Li-N and Li-O and rather long Li-C distances, as well as the wide N-Li-O angle [12], indicate that N and O are the principal electron donors towards the lithium cation. We suggest, therefore, that the step c of Scheme I involves a *syn*-addition of R to the CC bond, implicating the cyclic transition state **6**.



6

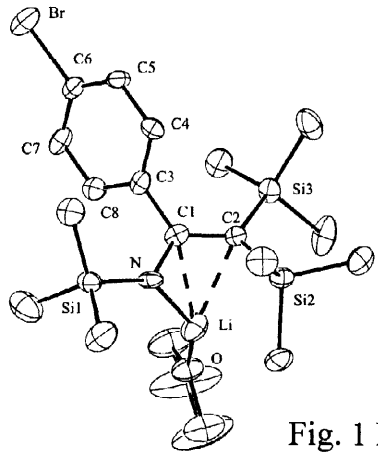


Fig. 1 Molecular structure of **4c**

A typical one-pot synthesis is outlined in a footnote [13].

The new arylacetylene synthesis of Scheme I is somewhat analogous to the Peterson olefination (*e.g.*, $Ph_2CO + LiCH_2SiMe_3 \rightarrow Ph_2C{=}CH_2$ [14]). The use herein of a 4-substituted benzonitrile is deemed to be illustrative; it is likely that many other benzonitriles will behave similarly to 4-RC_6H_4CN. The TMS group of compound **5** or a related arylacetylene is readily convertible into an alternative substituent. Hence the present procedure offers a route to a wide range of arylacetylenes.

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References and Footnotes

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[12] Selected bond lengths and an angle; Li-N, 1.93(2); Li-C(α), 2.23(2); Li-C(β), 2.32(2); Li-O, 1.84(2) Å; N-Li-O, 141.7(11)°.

[13] Methyllithium (7 ml of a 1.4 M solution, 1.3 mmol) was placed in a 100 ml flask and the solvent removed *in vacuo*. THF (15 ml) and $HC(TMS)_3$ (2.5 g, 1.1 mmol) were added and the mixture refluxed for 3.5 h. The solvent was removed *in vacuo*, the residue dissolved in Et_2O (30 ml) and 4-BrC_6H_4CN (1.97 g, 1.1 mmol) was added at -30 °C. The reaction mixture was allowed to warm to room temperature, stirred for another 18 h, a dark brown solution being obtained. The solvent was the removed *in vacuo* and the residue extracted into benzene (10 ml) and the extract heated for 60 h at 80 °C. The reaction mixture was cooled to room temperature, treated with MeOH (1 ml, 2.5 mmol) and stirred for 1 h. Removal of the solvent *in vacuo* and sublimation of the residue gave the colourless 4-$BrC_6H_4C{\equiv}C(TMS)$ **5c** (0.80 g, 29 % overall yield; ^{1}H-NMR authentic [15]). Although the reaction sequence above is described as a one-pot synthesis, it was easier to obtain a clean product, if the intermediates $LiC(TMS)_3(THF)_2$ [4] and $Li[N(TMS)C(C_6H_4R\text{-}4)C(TMS)_2](THF)$ **4** were isolated and purified by recrystallisation. This is described for **4c**: In a typical procedure the aryl nitrile (3.63 ml, 3.55 mmol) was added at room temperature to a solution of tris(trimethylsilyl)methyllithium (13.59 g, 3.55 mmol) in ether (100 ml). The colour of the reaction mixture changed immediately from colourless to yellow. The mixture was stirred for 15 h at room temperature, the solvent was removed and the colourless solid dried for 4 h *in vacuo* at 60 °C. The colourless residue was extracted with pentane (200 ml), the extract filtered and the filtrate cooled to -30 °C to give colourless crystals of $Li[N(TMS)C(C_6H_4Br\text{-}4)C(TMS)_2](THF)$ **4c** (9.85 g, 67%). The insoluble residue was extracted a second time with pentane (100 ml), and combined with the mother liquor of the first extraction yielding a second crop of crystals (3.05 g, 21%); total yield: 88%; m.p.(dec): 107-122 °C, Anal. found: C 48.7; H 7.69; N 2.84; $C_{22}H_{39}BrLiNOSi_3$ calc.: C 51.2; H 7.98; N 2.84 %; ^{1}H NMR (C_6D_6): δ 0.05 [s, $NSiMe_3$], δ 0.19 [s, $SiMe_3$], δ 1.12 [t, THF], δ 3.26 [t, THF], δ 7.09 [d, Ph, $^3J(^1H\text{-}^1H)$ 7.2 Hz], δ 7.37 [d, Ph, $^3J(^1H\text{-}^1H)$ 7.2 Hz]; ^{7}Li NMR (C_6D_6): δ 0.24; ^{13}C NMR (C_6D_6): δ 3.1 [s, $NSiMe_3$], δ 3.5 [s, $SiMe_3$], δ 25.2 [s, CH_2, THF], δ 68.9 [s, OCH_2, THF], δ 77.8 [s, CSi_2], δ 121.9 [s, C(Br)], δ 130.7 and 130.8 [s, *o/m*-C], δ 149.0 [s, *ipso*-C], δ 187.9 [s, CN].

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