A Dispensable Methoxy Group? Phenyl Fencholate as a Chiral Modifier of *n*-Butyllithium

B. Goldfuss,*[a] M. Steigelmann,[b] T. Löschmann,[c] G. Schilling,[d] and F. Rominger[d]

Dedicated to Professor Dr. Paul von Ragué Schleyer on the occasion of his 75th birthday

Abstract: Phenyl fenchol forms a 3:1 aggregate with *n*-butyllithium (**3**-BuLi), showing unique lithium–HC agostic interactions both in toluene solution (^{1}H,^{7}Li-HOESY) and in the solid state (X-ray analysis). Although methoxy–lithium coordination is characteristic for many mixed aggregates of anisyl fencholates with *n*-butyllithium, *endo*-methyl coordination to lithium ions compensates for the missing methoxy groups in **3**-BuLi. This gives rise to a different orientation of the fenchane moiety, encapsulating and chirally modifying the butylide unit.

Keywords: chiral aggregates · lithium · NMR spectroscopy · structure elucidation · X-ray diffraction

Introduction

Organolithiums are among the most versatile and widely used reagents in organic chemistry.[1] Their use in enantioselective alkylations[2] and lithiations[3] is of special interest. Structural elucidations of chiral *n*BuLi complexes in the solid state[4] and in solution[5] provide the basis for more rational developments of new and efficient, chirally modified organolithium compounds for asymmetric synthesis.[6] We have recently shown that modular fenchols[7] are efficiently accessible and applicable in both organozinc[8] and organopalladium[9] catalysts for the purpose of exploring the origins of enantioselectivities. Mixtures of anisyl fenchols (**1**) with *n*-butyllithium in hexanes generate enantiopure *n*BuLi aggregates. Such species are unique in terms of their variable

stoichiometries, binding modes and enantioselectivities in C−C couplings with benzaldehyde, because all of these properties can be tuned by modification of the anisyl *ortho*-substituents **X** (Scheme 1).[10]

The anisyl methoxy unit appears to be essential for the formation of such unusual mixed *n*BuLi aggregates: With the strong chelating side-arm in *N,N*-dimethylaminobenzyl fenchol (**2**), only a simple, organolithium-free, pure lithium fencholate (**2**-Li)$_2$ is created with *n*BuLi (Scheme 2).[11]
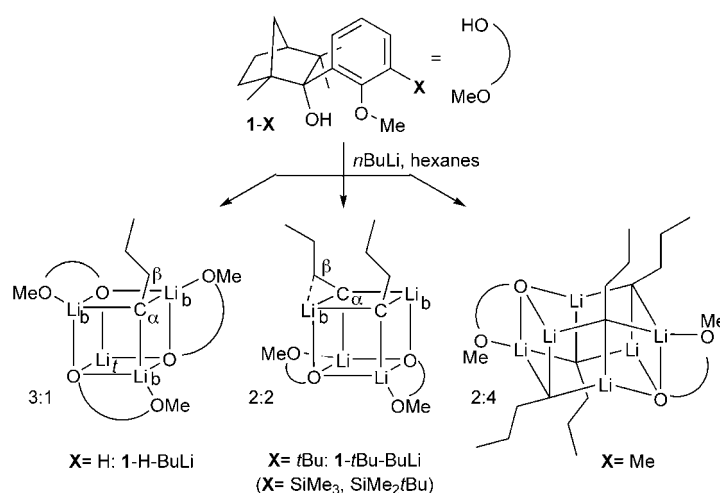
Scheme 1. Anisyl fenchols (**1-X**) form a variety of *n*BuLi aggregates (**1-X**-BuLi), depending on the *ortho*-substituent **X**, with 3:1, 2:2 or 2:4 compositions.[10]

[a] Prof. Dr. B. Goldfuss
    Institut für Organische Chemie, Universität zu Köln
    Greinstrasse 4, 50939 Köln (Germany)
    Fax: (+49) 221-470-5057
    E-mail: goldfuss@uni-koeln.de

[b] Dr. M. Steigelmann
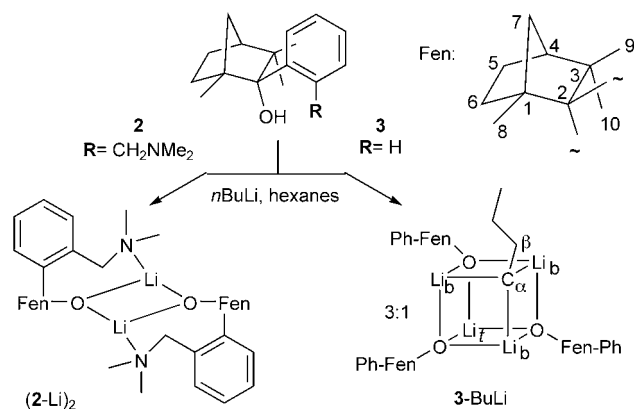   BASF AG, Ludwigshafen (Germany)

[c] Dr. T. Löschmann
    Dottikon Exclusive Synthesis AG, Dottikon (Switzerland)

[d] Dr. G. Schilling,$^+$ Dr. F. Rominger^{++}
    Organisch-Chemisches Institut der Universität Heidelberg
    Im Neuenheimer Feld 270, 69121 Heidelberg (Germany)

[$^+$] NMR analysis.

[$^{++}$] X-ray analysis.

Scheme 2. Instead of an *n*BuLi aggregate, a simple lithium fencholate (**2**-Li)$_2$ is formed with **2** and *n*BuLi.[11] However, the new 3:1 aggregate **3**-BuLi originates from methoxy-free phenyl fenchol (**3**). Butylide-binding and *trans*-lithium ions are denoted as Li$_b$ and Li$_t$, respectively.

Here, we report the formation and structural characterisation, both in solution and in the solid state, of the methoxy-free aggregate **3**-BuLi (Scheme 2), which demonstrates that methoxy groups are indeed dispensable for chiral modifications of *n*BuLi with aryl fencholates.
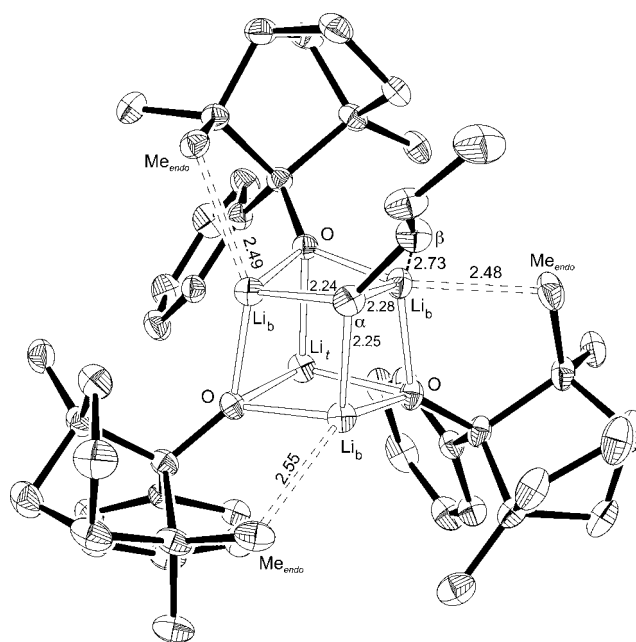

Figure 1. X-ray crystal structure of **3**-BuLi. *Endo*-methyl groups (C$_{10}$, Me$_{endo}$) exhibit close contacts to butylide-binding lithium ions (Li$_b$, distances in Å, for Li–H distances see Table 1) and compensate the missing lithium coordination of methoxy groups.

Results and Discussion

The aggregate **3**-BuLi crystallises with a 3:1 composition from mixtures of phenyl fenchol **3** and *n*-butyllithium in hexanes (Figure 1), and hence shows the same stoichiometry as the parent anisyl fencholate **1**-H-BuLi (Scheme 1).[10d] Both **3**-BuLi and **1**-H-BuLi[10d] exhibit a distorted cubic [Li$_4$O$_3$C] core in which three lithium ions bind to the butylide unit (Li$_b$, Figure 1). Although in **1**-H-BuLi, methoxy groups coordinate to these butylide-binding lithium ions (Li$_b$, Scheme 1),[10d] in methoxy-free **3**-BuLi, *endo*-methyl groups (C$_{10}$, Me$_{endo}$) of the bicyclic [2.2.1]heptane moieties develop close contacts to the Li$_b$ ions, and hence compensate for the missing methoxy coordination (Li–H: 2.1 Å, Table 1, Figure 1). Agostic Li–C$_{(\beta)}$ contacts with butylide units appear in some 2:2 aggregates with "naked" Li$_b$ cations, for example, in **1**-SiMe$_3$-BuLi (Scheme 1, Li$_b$–C$_{(\beta)}$: 2.38 Å).[10b,c,12] Apparently due to rather strong C$_{10}$–Me$_{endo}$ coordination, no close agostic Li$_b$–C$_\beta$ butylide contact is formed in **3**-BuLi (Figure 1, Li$_b$–C$_{(\beta)}$: 2.73 Å). In the case of **1**-H-BuLi, the lithium cation *trans* to the butylide unit (Li$_t$) tends to be contacted by C$_{(8)}$H$_3$

Table 1. Li–H distances [Å] in the X-ray crystal structure of phenyl fencholate **3**-BuLi (Scheme 2, Figure 1).[a]

	Ph–H$_m$	Ph–H$_o$	C$_{(8)}$H$_3$	C$_{(10)}$H$_3$	C$_{(6)}$H$_{endo}$	C$_{(\beta)}$H*H*	C$_{(\beta)}$H*H*	C$_{(\alpha)}$H*H*	C$_{(\alpha)}$H*H*
Li$_b$	–	2.9	2.9	2.2	2.4	3.6	4.0	2.1	2.8
Li$_b$	–	3.0	3.2	2.1	2.3	2.6	2.8	2.9	3.0
Li$_b$	–	2.9	2.9	2.1	2.3	3.4	4.0	2.1	2.9
Li$_t$	3.8[b]	2.1[b]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]

[a] Hydrogen atoms at butylide C(α) are refined, other hydrogen atoms are constructed with a C–H bond length of 0.990 Å. [b] Mean value. [c] Distances longer than 4.50 Å.

Table 2. Li–H distances [Å] in the parent anisyl fencholate **1**-H-BuLi due to X-ray structure analysis (Schemes 1 and 2)[a] and to cross-peaks (+) of ^{1}H,^{7}Li-HOESY experiments (in [D$_8$]toluene at −10 °C).[b]
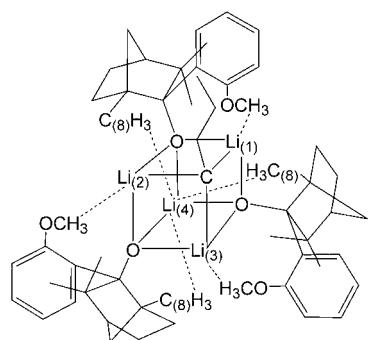
	OCH$_3$ (δ=3.76 ppm)	C$_{(8)}$H$_3$ (δ=0.98 ppm)	C$_{(\alpha)}$H*H* (δ=−0.39 ppm)	C$_{(\alpha)}$H*H* (δ=−0.63 ppm)
Li$_b$ (δ=1.06 ppm)	3.1, 3.3, 3.2 (+)[c]	4.3, 4.4, 4.2 (+)[c]	2.3, 2.6, 3.1 (+)[c]	2.6, 3.1, 2.2 (+)[c]
Li$_t$ (δ=0.73 ppm)	–(−)[e]	2.7[d] (+)[c]	–(−)[e]	–(−)[e]

[a] The X-ray crystal structure is reported in reference [10d]. [b] Hydrogen atoms at butylide C$_{(\alpha)}$ are derived from a Fourier-map, other hydrogen atoms are constructed with a C–H bond length of 0.990 Å. [c] (+)-NOE-effect indicating short ^{1}H–^{7}Li distances in solution. [d] Mean value. [e] Distances longer than 4.50 Å, no NOE-effects (−) were detected.

methyl groups (Li–H: 2.7 Å, Table 2).[10d] However, in **3**-BuLi, this Li$_t$ cation experiences significant *ortho*-hydrogen coordination by phenyl C–H$_{ortho}$ units (mean value: Li–H$_o$ 2.1 Å, Table 1). Hence, in contrast to anisyl fencholates (Scheme 1), **3**-BuLi encapsulates its butylide with the fenchane moiety rather than with the methoxy-free aryl units (Figure 1).

To complement the solid-state structural analyses of *n*BuLi fencholates and to gain additional information about

aggregation and coordination in solution, ^{1}H,^{7}Li-HOESY experiments were performed in [D$_8$]toluene at $-10\,°$C.[13] A toluene solution of the parent anisyl fencholate aggregate **1**-H-BuLi shows a ^{1}H NMR singlet at $\delta = 3.76$ ppm for the methoxy group (Table 2). Two triplets at $\delta = -0.39$ and -0.63 ppm can be assigned to the diastereotopic α-CH$_2$ protons of the butylide unit, which couple to β-CH$_2$ protons. This diastereotopy of the α-CH$_2$ butylide protons indicates a significant chiral butylide modification and rigidity induced by the anisyl fencholate. The 9:1:1 intensities of the methoxy proton and the two α-CH$_2$ protons agree with the 3:1 composition of **1**-H-BuLi found in the solid state (Scheme 1).[10d] Two ^{7}Li NMR signals at $\delta = 0.73$ and 1.06 ppm show intensities in the ratio of 1:3. The results of ^{1}H,^{7}Li-HOESY experiments reveal that short contacts due to NOE correlations are apparent in **1**-H-BuLi between the three lithium ions at $\delta = 1.06$ ppm and the methoxy groups at $\delta = 3.76$ ppm (Table 2). In contrast, no such methoxy contacts are found for the lithium ion at $\delta = 0.73$ ppm, which is rather close to the C$_{(8)}$-methyl groups ($\delta = 0.98$ ppm) of the bicyclic [2.2.1]heptane fragments (Table 2). This suggests a methoxy-coordination of three Li$_b$ cations and a non-coordinated Li$_t$ cation, in agreement with the X-ray crystal structure of **1**-H-

Figure 2. Two-dimensional ^{1}H,^{7}Li-HOESY contour plot of complex **1**-*t*Bu-BuLi ($-10\,°$C, [D$_8$]toluene, 500 MHz). Dashed lines indicate the selected correlations. Only one fencholate and one *n*-butylide unit are shown for clarity.

Scheme 3. ^{1}H,^{7}Li-HOESY experiments of the parent anisyl fencholate aggregate **1**-H-BuLi in toluene solution ($-10\,°$C) reveal a structure similar to that found from X-ray analysis (Scheme 1, Table 2).[10d]

BuLi (Scheme 3).[10d]

The *t*-butyl-substituted anisyl fencholate **1**-*t*Bu-BuLi (Scheme 1) shows a ^{1}H NMR singlet at $\delta = 3.71$ ppm, which again can be assigned to the methoxy group of the anisyl moiety (Figure 2). The butylide group in **1**-*t*Bu-BuLi gives rise to two triplets of doublets at $\delta = -0.74$ and -0.85 ppm ($^2J = 4.2$, $^3J = 12.8$ Hz), which originate from diastereotopic α-CH$_2$ protons by coupling with non-equivalent β-CH$_2$ protons (multiplets at $\delta = 0.70$ and 1.04 ppm). The 3:1:1 intensities of the methoxy and α-CH$_2$ signals, as well as the same intensities of two ^{7}Li signals at $\delta = 1.03$ and 2.15 ppm, reveal **1**-*t*Bu-BuLi to be a 1:1 aggregate in solution, as it was also found in the solid state (Scheme 1).[10b] From the ^{1}H,^{7}Li-HOESY cross-peaks between the methoxy group ($\delta = 3.71$ ppm) and the ^{7}Li signal at $\delta = 1.03$ ppm, but not the signal at $\delta = 2.15$ ppm (Figure 2), methoxy coordination corresponding to that exhibited by the X-ray structure of **1**-
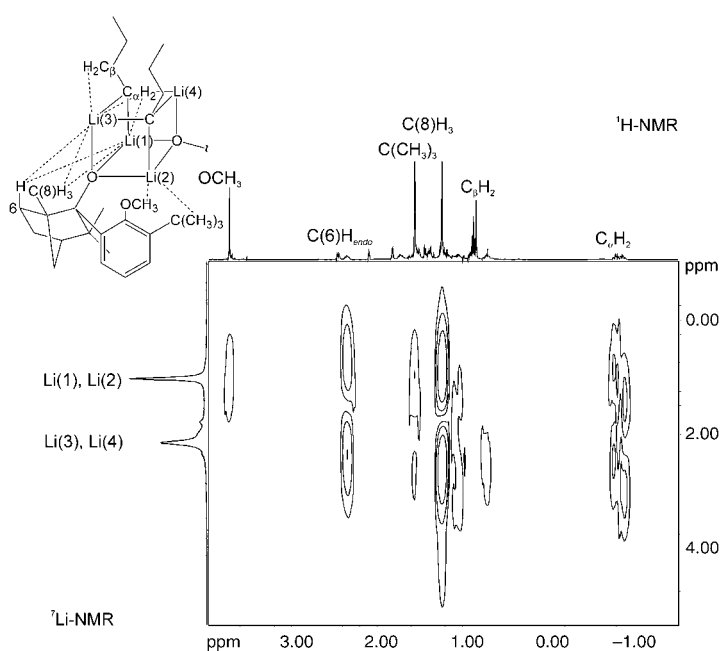
*t*Bu-BuLi can be derived.[10b] From this X-ray structure, short Li−H distances between non-methoxy-coordinated lithiums and C$_{(8)}$H$_3$ groups, as well as butylide β-CH$_2$ groups, are apparent (Table 3).[10b] ^{1}H,^{7}Li-HOESY cross-peaks indicate analogous short contacts in solution (Figure 2) and signify the close similarity between the solid-state and solution structures of **1**-*t*Bu-BuLi.

Table 3. Li−H distances [Å] in the X-ray crystal structure of the anisyl fencholate **1**-*t*Bu-BuLi (Scheme 1).[a]

	OCH$_3$	C$_{(6)}$H$_{endo}$	C(CH$_3$)$_3$	C$_{(8)}$H$_3$	C$_{(\beta)}$HH	C$_{(\beta)}$HH
Li(**1**)	3.2	2.3	3.1	3.8	—[b]	—[b]
Li(**2**)	3.1	3.2	3.4	3.3	—[b]	—[b]
Li(**3**)	—[b]	2.6	—[b]	2.1	2.6	2.5
Li(**4**)	—[b]	2.9	—[b]	2.0	2.8	2.5

[a] The X-ray crystal structure is reported in reference [10b]. Hydrogen atoms are constructed with a C−H bond length of 0.990 Å. [b] Distances longer than 4.50 Å.

The new phenyl fencholate **3**-BuLi exhibits ^{1}H-multiplets at $\delta = -0.21$ ppm for the butylide α-CH$_2$ group, with intensities of 2:15 relative to phenyl protons (Figure 3). This is in agreement with a 3:1 composition (Figure 1). In analogy to the solid-state structure of **3**-BuLi, ^{7}Li signals ($\delta = 0.48$ ppm, one lithium and $\delta = 2.15$ ppm, three lithium nuclei) indicate Li$_{b(1,2,3)}$ and Li$_{t(4)}$ differentiations (Figure 3). The unique agostic interactions of Li$_b$ ions with the *endo*-C$_{(10)}$H$_3$ methyl groups (^{1}H $\delta = 1.29$ ppm) are not only apparent from the X-ray crystal structure of **3**-BuLi (Figure 1, Table 1), but also from ^{1}H,^{7}Li-HOESY cross-peaks (Figure 3). In addition, Li$_b$ ions have close contacts to C$_{(6)}$H$_{endo}$ (^{1}H $\delta = 2.37$ ppm) of the
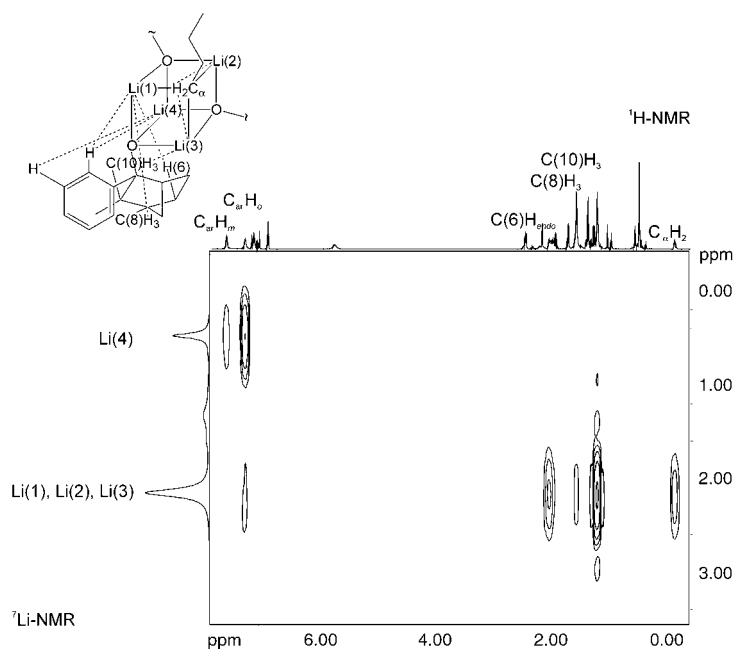
Figure 3. ^{1}H,^{7}Li-HOESY contour plot of **3**-BuLi (-10°C, [D$_8$]toluene, 500 MHz). Dashed lines indicate the selected correlations. Only one fencholate unit is shown for clarity.

bicyclic [2.2.1]heptane unit. In agreement with the solid state structure (Table 1, Figure 1), the Li$_t$ ion exhibits agostic interactions mainly with *ortho*-hydrogen atoms of phenyl groups (Figure 3).

Conclusion

The new *n*-butyllithium phenyl fencholate **3**-BuLi demonstrates that methoxy groups are indeed dispensable for the formation of mixed organolithium aggregates with fenchols, although the manifold of *n*BuLi anisyl fencholates was hitherto ascribed to methoxy coordination. In methoxy-free **3**-BuLi, agostic *endo*-methyl coordination to the lithium ions compensates for the lack of missing Li−OMe contacts. In contrast to "classical" *n*BuLi anisyl fencholates, the aryl group orients towards the lithium ion *trans* to butylide (Li$_t$), and the chiral fenchane unit encapsulates the *n*-butylide unit to a greater extent. This might give rise to altered enantioselectivities in C−C couplings or lithiations. In non-polar toluene solutions and in the solid state, basically the same structures are apparent, as revealed by the results of NMR spectroscopic analysis. Hence, with **3**-BuLi, an even broader range of aryl fencholates becomes available for the design of new chiral *n*-butyllithium modifiers.

Experimental Section

General: Reactions were conducted under argon atmosphere (by using Schlenk and needle-septum techniques) with dried and degassed solvents.

X-ray crystal analyses were performed by using a Bruker Smart CCD diffractometer with a Mo$_{K\alpha}$ radiation at 200 K. Data sets corresponding to a complete sphere of data were collected by using 0.3° ω-scans. The structure was solved by using direct methods, least-squares refinement and Fourier techniques. Most hydrogen atoms were taken into account at geometrically calculated positions, C(α) hydrogen atoms were refined isotropically. NMR spectra were recorded by using a Bruker Ac 300 and DRX 500 spectrometer (^{1}H chemical shifts refer to toluene, ^{7}Li to LiBr). CCDC 192453 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

^{1}H,^{7}Li-HOESY NMR spectroscopy experiments: All measurements were performed by using [D$_8$]toluene at -10°C and a Bruker DRX 500 spectrometer. All 2D spectra were acquired by using non-spinning 5 mm tube diameter samples with deuterium field-frequency locking. Spectra were processed in phase-sensitive mode with square sinebell weighting both in F_1 and F_2. The following parameters were used:[12e] spectral window of 1000 Hz ($F_1 = {}^7$Li) and 6000 Hz ($F_2 = {}^1$H); 128 increments and 16 scans per increment in t_1; sinebell weighting in F_1 and F_2 for the phase-sensitive spectra; 10.1 µs proton 90° decoupler pulse, in inverse mode with gradient selection.

Synthesis and characterisation of 3: *n*-Butyllithium (50.3 mL, 0.08 mol, 1.6 M solution in hexane) was added to a solution of 2-bromobenzene (12.6 g, 0.08 mol) in 20 mL THF at -78°C over 30 min. A white precipitate was formed after stirring for 20 min at -78°C. An amount of ($-$)-fenchone (12.9 mL, 0.08 mol) was added slowly to this suspension at -78°C, and the mixture was stirred for 12 h at room temperature. Hydrolytic workup, drying and concentration of the organic layer and distillation yielded colourless **3** (17.1 g, 93%). B.p. 106°C (1.0×10^{-2} mbar). $[\alpha]_{Na}^{20} = -31.5$ (*n*-hexane); ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.45$ (s, 3H; CH$_3$), 1.05 (s, 3H; CH$_3$), 1.14 (s, 3H; CH$_3$), 1.22 (m, 1H; CH$_2$), 1.41 (m, 1H; CH$_2$), 1.50 (m, 1H; CH$_2$), 1.61 (s, 1H; OH), 1.81 (m, 1H; CH$_2$), 2.21 (m, 1H; CH$_2$), 2.34 (m, 1H; CH$_2$), 7.17 (m, 1H; H$_{ar}$), 7.28 (m, 2H; H$_{ar}$), 7.56 ppm (m, 2H; H$_{ar}$); ^{13}C NMR (CDCl$_3$, 75.5 MHz): $\delta = 17.4$, 21.3, 24.1, 30.1, 33.7, 41.9, 45.7, 49.0, 52.8, 84.1, 126.0, 127.2, 127.6, 145.1 ppm; MS(EI): 230.0 [M^+], 213.0 [M^+-OH], 153.0 [$M^+-C_6H_5$]; IR (neat): $\tilde{\nu} = $ 3494 (s, OH), 3091 (w, aryl), 2990–2874 cm^{-1} (s, alkyl); elemental analysis calcd (%): C 83.43, H 9.63; found: C 83.16, H 9.60.

Synthesis and characterisation of 3-BuLi: A solution of *n*BuLi in hexanes (1.60 M, 0.42 mL, 0.66 mmol) was added to phenyl fenchol **3** (0.115 g, 0.5 mmol) at RT. Maintaining the reaction mixture at -60°C for some days yielded **3**-BuLi as colourless crystals. Yield 54%. M.p. 160°C bubbly, 165°C gelatinous; ^{1}H NMR (500 MHz, [D$_8$]toluene, -10°C): $\delta = -0.16$ (m, 2H; C$_\alpha$H$_2$, BuLi), 0.45 (s, 9H; 3CH$_3$), 0.96 (m, 2H; CH$_2$, BuLi), 1.18 (s, 9H; 3CH$_3$), 1.23 (m, 2H; CH$_2$, BuLi), 1.31 (m, 3H; CH$_3$, BuLi; m, 2H; CH$_2$), 1.53 (s, 9H; 3CH$_3$; m, 2H; CH$_2$), 1.67 (s, 3H; CH), 1.93 (m, 6H; CH$_2$; m, 2H; CH$_2$, BuLi), 2.41 (m, 3H; CH$_2$), 6.88 (t, $J = 7.3$ Hz, 3H; H$_{ar}$), 7.09 (m, 6H; H$_{ar}$), 7.28 (d, $J = 7.0$ Hz, 3H; H$_{ar}$), 7.59 ppm (d, $J = 7.7$ Hz, 3H; H$_{ar}$); ^{13}C NMR (125 MHz, [D$_8$]toluene, -10°C): $\delta = 10.1$ (C(α)H$_2$-BuLi), 14.0 (CH$_3$-BuLi), 19.2 (CH$_3$), 23.3 (CH$_3$), 26.0 (CH$_2$), 30.9 (CH$_3$), 33.5 (CH$_2$-BuLi), 34.7 (CH$_2$-BuLi), 35.2 (CH$_2$), 42.0 (CH$_2$), 46.5 (C$_q$), 49.5 (CH), 53.7 (C$_q$), 84.1 (C$_q$), 124.9 (C$_{ar}$), 125.0 (C$_{ar}$), 125.1 (C$_{ar}$), 127.0 (C$_{ar}$), 127.1 (C$_{ar}$), 152.0 ppm (C$_{ar}$); ^{7}Li NMR (194 MHz, [D$_8$]toluene, -10°C): $\delta = 0.48$, 2.15 ppm; X-ray crystal analysis of **3**-BuLi: C$_{52}$H$_{72}$Li$_4$O$_3$, $M_r = 772.86$, $T = 200(2)$ K, $\lambda = 0.71073$ Å, monoclinic crystal system, space group $P2_1$, $Z = 4$, $a = 12.6737(3)$, $b = 22.5085(5)$, $c = 16.1657(3)$ Å, $\beta = 94.045(1)$°, $V = 4600.04(17)$ Å^3, ρ_{calcd}: 1.116 g cm^{-3}, reflections collected: 34814, independent reflections: 14599, observed reflections: 10711 [$I > 2\sigma(I)$], absorption coefficient µ: 0.065 mm^{-1}, Flack parameter: 0.2(8), R-values [$I > 2\sigma(I)$]: $R1 = 0.046$, $wR2 = 0.093$, largest diff. peak and hole: 0.17, -0.18 e Å^{-3}; goodness-of-fit: 0.98.

Acknowledgements

[1] a) D. M. Hodgson, *Organolithiums in Enantioselective Synthesis, Topics in Organometallic Chemistry, Vol. 5*, Springer, Heidelberg, **2003**; b) J. Clayden, *Organolithiums: Selectivity for Synthesis, Tetrahedron Organic Chemistry Series, Vol. 23*, Pergamon, Amsterdam, **2002**; c) M. Hanack, *Houben-Weyl, Methoden der Organischen Chemie, Vol. E 19d*, Carbanionen, Thieme, Stuttgart, **1993**.

[2] a) T. F. Briggs, M. D. Winemiller, B. Xiang, D. B. Collum, *J. Org. Chem.* **2001**, *66*, 6291–6298; b) P. I. Arvidsson, O. Davidsson, G. Hilmersson, *Tetrahedron: Asymmetry* **1999**, *10*, 3, 527–534; c) N. Bremand, I. Marek, J. F. Normant, *Tetrahedron Lett.* **1999**, *40*, 3383–3386; d) A. Corruble, J.-Y. Valnot, J. Maddaluno, P. Duhamel, *Tetrahedron: Asymmetry* **1997**, *8*, 10, 1519–1523.

[3] a) A. Deiters, D. Hoppe, *J. Org. Chem.* **2001**, *66*, 2842–2849; b) E.-U. Würthwein, K. Behrens, D. Hoppe, *Chem. Eur. J.* **1999**, *5*, 3459–3463; c) D. Hoppe, T. Hense, *Angew. Chem.* **1997**, *109*, 2376–2410; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2282–2316; d) P. Beak, A. Basu, D. J. Gallagher, Y. S. Park, S. Thayumanavan, *Acc. Chem. Res.* **1996**, *29*, 552–560; e) D. Enders, U. Reinhold, *Tetrahedron: Asymmetry* **1997**, *8*, 1895–1946; f) S. E. Denmark, O. J.-C. Nicaise, *Chem. Commun.* **1996**, 999–1004; g) C. Fehr, *Angew. Chem.* **1996**, *108*, 2726–2748; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2566–2587; h) E. Juaristi, A. K. Beck, J. Hansen, T. Matt, T. Mukhopadhyay, M. Simson, D. Seebach, *Synthesis* **1993**, 1271–1290; i) D. Seebach, *Angew. Chem.* **1988**, *100*, 1685–1715; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1624–1654; j) D. Seebach, *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1984**, *27*, 93–145.

[4] a) J. G. Donkervoort, J. L. Vicario, E. Rijnberg, J. T. B. H. Jastrzebski, H. Kooijman, A. L. Spek, G. van Koten, *J. Organomet. Chem.* **1998**, *550*, 463–467; b) D. J. Pippel, G. A. Weisenburger, S. R. Wilson, P. Beak, *Angew. Chem.* **1998**, *110*, 2600–2602; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2522–2524; c) P. G. Williard, C. Sun, *J. Am. Chem. Soc.* **1997**, *119*, 11693–11694; d) I. Hoppe, M. Marsch, K. Harms, G. Boche, D. Hoppe, *Angew. Chem.* **1995**, *107*, 2328–2330; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2158–2160.

[5] a) G. Hilmersson, B. Malmros, *Chem. Eur. J.* **2001**, *7*, 337–341; b) X. Sun, M. D. Winemiller, B. Xiang, D. B. Collum, *J. Am. Chem. Soc.* **2001**, *123*, 8039–8046; c) F. Xu, R. A. Reamer, R. Tillyer, J. M. Cummins, E. J. J. Grabowski, P. J. Reider, D. B. Collum, J. C. Huffman, *J. Am. Chem. Soc.* **2000**, *122*, 11212–11218; d) A. Thompson, E. G. Corley, M. F. Huntington, E. J. J. Grabowski, J. F. Remenar, D. B. Collum, *J. Am. Chem. Soc.* **1998**, *120*, 2028–2038; e) D. Hoffmann, D. B. Collum, *J. Am. Chem. Soc.* **1998**, *120*, 5810–5811; For studies on *n*-butyllithium aggregates by means of diffusion-ordered NMR spectroscopy (DOSY) see: f) I. Keresztes, P. G. Williard, *J. Am. Chem. Soc.* **2000**, *122*, 10228–10229.

[6] P. I. Arvidsson, P. Ahlberg, G. Hilmersson, *Chem. Eur. J.* **1999**, *5*, 1348–1354.

[7] With biphenlybisfenchol (BIFOL), a chelating, C_2-symmetric fenchol-based diol is available: B. Goldfuss, F. Rominger, *Tetrahedron* **2000**, *56*, 881–884.

[8] a) M. Steigelmann, Y. Nisar, F. Rominger, B. Goldfuss, *Chem. Eur. J.* **2002**, *8*, 5211–5218; b) B. Goldfuss, M. Steigelmann, S. I. Khan, K. N. Houk, *J. Org. Chem.* **2000**, *65*, 77–82; c) B. Goldfuss, M. Steigelmann, *J. Mol. Model.* **2000**, *6*, 166–170; d) B. Goldfuss, M. Steigelmann, F. Rominger, *Eur. J. Org. Chem.* **2000**, 1785–1792.

[9] For fenchylphosphinites (FENOPs) in Pd-catalysed allylic substitutions see: a) B. Goldfuss, T. Löschmann, F. Rominger, *Chem. Eur. J.* **2004**, *10*, 5422–5431; For a fenchol-based phosphorane see: b) B. Goldfuss, T. Löschmann, F. Rominger, *Chem. Eur. J.* **2001**, *7*, 2028–2033; corrigendum *Chem. Eur. J.* **2001**, *7*, 2284.

[10] a) "Enantioselective Addition of Organolithiums to C=O and Ethers", B. Goldfuss, *Top. Organomet. Chem.* **2003**, *5*, 21–36; b) B. Goldfuss, M. Steigelmann, F. Rominger, H. Urtel, *Chem. Eur. J.* **2001**, *7*, 4456–4464; c) B. Goldfuss, M. Steigelmann, F. Rominger, *Angew. Chem.* **2000**, *112*, 4299–4302; *Angew. Chem. Int. Ed.* **2000**, *39*, 4133–4136; d) B. Goldfuss, S. I. Khan, K. N. Houk, *Organometallics* **1999**, *18*, 2927–2929.

[11] The X-ray crystal structure of (**2**-Li)$_2$ reveals a distorted, trigonal pyramidal environment of the lithium cations: B. Goldfuss, F. Eisenträger, *Aust. J. Chem.* **2000**, *53*, 209–212.

[12] For electrostatic interactions of "naked" lithium ions with neutral thienyl groups, acetylene units and cyclopropyl groups see, respectively: a) B. Goldfuss, P. von R. Schleyer, F. Hampel, *Organometallics* **1997**, *16*, 5032–5041; b) B. Goldfuss, P. von R. Schleyer, F. Hampel, *J. Am. Chem. Soc.* **1997**, *119*, 1072–1080; c) B. Goldfuss, P. von R. Schleyer, F. Hampel, *J. Am. Chem. Soc.* **1996**, *118*, 12183–12189.

[13] For ^{1}H,^{6}Li-HOESY NMR spectroscopy experiments see: a) B. Goldfuss, P. von R. Schleyer, S. Handschuh, Hampel, W. Bauer, *Organometallics* **1997**, *16*, 5999–6003; b) A. Fuerstner, G. Seidel, H.-E. Mons, R. Mynott, *Eur. J. Inorg. Chem.* **1998**, *11*, 1771–1774; c) D. Hoffmann, W. Bauer, P. von R. Schleyer, *J. Chem. Soc. Chem. Commun.* **1990**, *3*, 208–211; d) W. Bauer, P. von R. Schleyer, *Magn. Reson. Chem.* **1988**, *26*, 827–833; For ^{1}H,^{7}Li-HOESY NMR spectroscopy experiments see: e) W. Bauer, *Magn. Reson. Chem.* **1996**, *34*, 532–537.