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Reaction between benzyllithium and 2-ethylpyridine: chiral crystals of a 1-(2-pyridyl)ethyllithium complex versus formation of lithium 4-benzyl-2-ethyl-1,4-dihydropyridinide

Tove Wiklund · Susanne Olsson · Anders Lennartson

Abstract The reaction between benzyllithium and prochiral 2-ethylpyridine in tetrahydrofuran has been studied. In the presence of N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDTA), it was found that 1-(2-pyridyl)ethyllithium was formed as a PMDTA complex. This complex is mononuclear, with lithium coordinated to the pyridyl nitrogen atom only; there are no short lithium–carbon distances and the structure approaches that of an enamide rather than a carbanion. The complex undergoes spontaneous resolution and forms chiral crystals with two molecules in the asymmetric unit; the two molecules have different configurations at the chirogenic pyridyl nitrogen atoms but share the same chiral conformation of the chelate ring systems. Reaction between benzyllithium and 2-ethylpyridine in tetrahydrofuran in the absence of PMDTA was found to give a high proportion of lithium 4-benzyl-2-ethyl-1,4-dihydropyridinide, and crystals of a dinuclear complex displaying tetrahydrofuran ligands and co-crystallised n-hexane molecules were isolated.
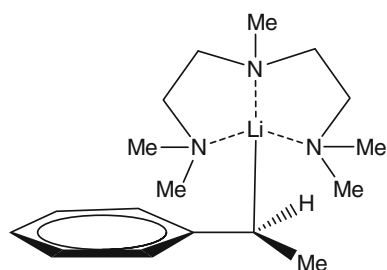
Keywords Chirality · Chiral resolution · X-ray structure determination · Dihydropyridine · Spontaneous resolution · Organolithium chemistry

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Introduction

Chiral organometallic reagents are useful in enantioselective organic synthesis, and this paper is a part of a study of complexes displaying chirogenic α-carbon atoms [1–3]. Such reagents may give a variety of chiral products upon reaction with different electrophiles without the need to form new chirogenic centres by asymmetric induction. Depending on the choice of metal, these compounds may be either configurationally labile or inert. Lithium reagents are frequently labile at ambient or slightly elevated temperature [4–7], whereas for instance secondary alkylzinc reagents are more inert [3, 8]. Stereochemical lability is a severe problem if the reagent is prepared from an optically active alkyl halide in solution, but may on the other hand enable total spontaneous resolution [9]. Spontaneous resolution occurs when a substance crystallises in one of the Sohncke [10] (or chirodescriptive [11]) space groups; the two enantiomers will appear in separate crystals and each crystal will thus be enantiomerically pure. Equal amounts of the two enantiomorphs are obtained upon complete crystallisation, a so-called conglomerate, and the bulk product is racemic. Spontaneous resolution is a rare phenomenon [12, 13], and there is currently no way to predict its occurrence. Total spontaneous resolution requires one additional criterion to be fulfilled; the solute must be stereochemically labile. A stereochemically labile solute will rapidly enantiomerise in solution; any enantiomeric excess built up in solution by preferential crystallisation of one enantiomer is eliminated. An overall enantiomeric excess may be observed in the crystallised product if crystallisation is initiated by a single nucleation event. This is a possible means of performing absolute asymmetric synthesis [14, 15], i.e. synthesis of optically active products from achiral or racemic precursors, not using chiral

Scheme 1

reagents, catalysts, or auxiliaries. One of the reagents in our study was 1-phenylethyllithium, a simple organometallic molecule displaying a potentially chirogenic α-carbon atom. The complex [Li(phet)(pmdta)] [2], where phet is 1-phenylethyl and pmdta is the tridentate ligand N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDTA, Scheme 1), was prepared first, but was unfortunately found to form racemic crystals. Replacing PMDTA with N,N,N',N'-tetramethyl-1,3-propanediamine (TMPDA) gave the analogous complex [Li(phet)(tmpda)] which forms chiral crystals. The successful synthesis and spontaneous resolution of a simple organolithium reagent inspired us to investigate functionalised organolithium reagents, including lithiated sulfides and silanes [2]. The next logical step was to extend this series of chiral organolithium reagents to include lithiated heterocyclic compounds that may be of more interest e.g. in the pharmaceutical chemistry. The presence of heteroatoms may lead to aggregation and a larger degree of structural diversity in both solid state and solution. In this paper we describe the results from our study of the metallation of prochiral 2-ethylpyridine with benzyllithium.

Results and discussion

The choice to metallate 2-ethylpyridine is logical, because 2-ethylpyridine is isoelectronic with ethylbenzene, and the lithiated product is thus closely related to 1-phenylethyllithium. Although deprotonative metallation of benzylic hydrocarbons, like ethylbenzene, by strong alkyllithium bases often suffers from competing side reactions e.g. deprotonation at the aromatic ring [16], deprotonation of 2-ethylpyridine with benzyllithium in the presence of PMDTA in tetrahydrofuran (THF) only gave crystals of the α-deprotonated product **1** on cooling. The molecular structures of **1** (Fig. 1; Table 1) and the isoelectronic complex [Li(phet)(pmdta)] are very different, as expected. In **1**, lithium coordinates to the pyridyl nitrogen atoms only, leaving the benzylic carbon atoms non-coordinating. The benzylic carbon atoms are not chirogenic centres, but the molecules of **1** are still chiral; upon coordination to lithium, the pyridyl nitrogen atoms become chirogenic centres, with trigonal pyramidal geometry. Atom N1 is displaced by 0.270(4) Å from the least-squares plane formed by Li1, C3, and C7, while atom N5 is displaced by 0.296(4) Å from the least-squares plane formed by atoms Li2, C19, and C23. The bonding situation in picolyllithium derivatives has been a matter of discussion [17], and 2-picolyllithium was recently subjected to a charge density study [17]. It was found that the bulk negative charge is located at the nitrogen atom rather than at the benzylic carbon atom and 2-picolyllithium can therefore be described as an enamide rather than a carbanion-based structure. This description also fits with the crystal structure of **1**, which also approaches an enamide structure (Scheme 2, right hand). The C2–C3 and C18–C19 bonds are 1.380(5) and 1.378(6) Å, respectively, and are thus approaching the 1.33 Å expected for a $C(sp^2)=C(sp^2)$ double

Fig. 1 Molecular structures of the two molecules in the asymmetric unit of **1**, displaying the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and all hydrogen atoms have been omitted for clarity. As can be clearly seen, the two molecules display different configurations at N1 and N5, while the chelate ring systems display the same sense of chirality
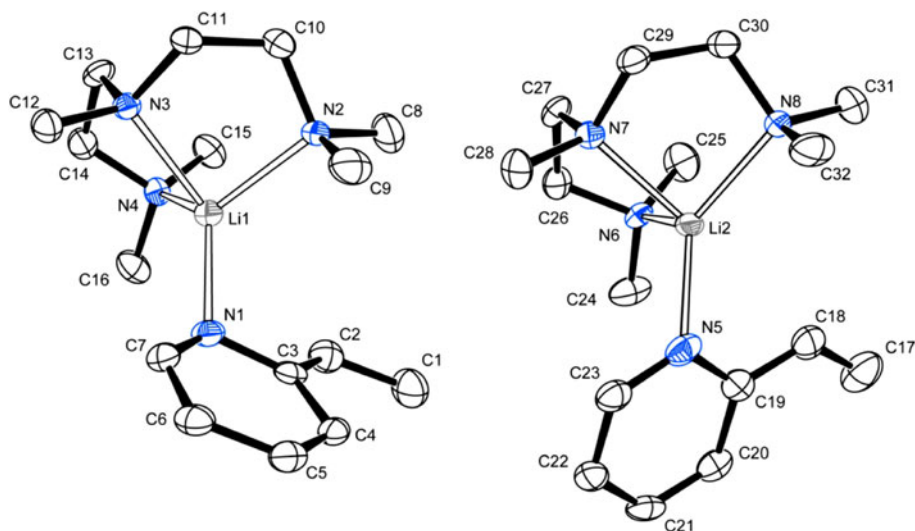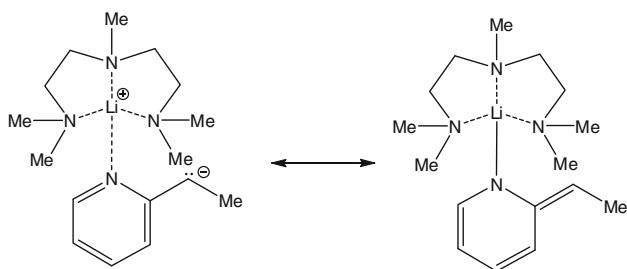
Table 1 Selected bond distances for **1**

Selected bond distances (Å)			
(Molecule 1)		(Molecule 2)	
Li(1)–N(1)	2.014(7)	Li(2)–N(5)	2.017(7)
Li(1)–N(2)	2.143(7)	Li(2)–N(6)	2.121(7)
Li(1)–N(3)	2.166(7)	Li(2)–N(7)	2.160(7)
Li(1)–N(4)	2.119(7)	Li(2)–N(8)	2.162(7)
Li(1)–C(2)	2.989(7)	Li(2)–C(18)	2.789(7)
Li(1)–C(3)	2.807(7)	Li(2)–C(19)	2.683(7)

Scheme 2

bond. In the three phenylethyllithium complexes prepared by us, the corresponding distances ranged between 1.403(3) and 1.410(4) Å [2]. There are no previous structures of lithiated 2-ethylpyridines in the Cambridge Structural Database [18] and only a few structures of other picolyllithium derivatives. Among these structures, there are examples of dimers, where Li^+ coordinates the nitrogen atom of one ligand and the benzylic carbon atom of another ligand [17, 19]. In most structures lithium coordinates to both the nitrogen atom and the benzylic carbon atom of the same ligand [20–22]. Compared with these structures, **1** displays considerably longer lithium–carbon distances (Table 1) with no indications of bonding interactions. The molecular structure of **1** thus brings further support for the enamide interpretation of 2-picolyllithium derivatives.

Compound **1** crystallises in Sohncke space group $P2_12_12_1$, meaning that it forms chiral crystals. The situation is different from [Li(phet)(tmpda)], where spontaneous resolution results in separation of molecules having (R)- and (S)-configuration at the α-carbon atom into different crystals. The crystal structure of **1** reveals two molecules in the asymmetric unit with different configurations at the pyridyl nitrogen atoms N1 and N5. Co-crystallisation of two enantiomers in a chiral crystal structure is extremely rare [10], two examples being iron(III) acetylacetonate [23] and (2-hydroxyphenyl)alanine [24]. On closer examination, the chelate rings give rise to a sense of conformational chirality and all of the four chelate rings have λ-conformation. In a broad sense, the two molecules in the crystal structure of **1** could be described as a form of diastereomers rather than

enantiomers. The fast interconversion between the two chiral conformations of **1** makes total spontaneous resolution possible, but proving this is difficult. Because no atoms heavier than nitrogen are present, no significant anomalous dispersion will be observed using standard X-ray diffraction, and determination of the absolute structure was not possible. Circular dichroism (CD) spectroscopy can be performed in the solid state [25, 26], and we have previously shown that this can be done quantitatively [27], but so far only for air-stable compounds. Crystals of **1** are highly air-sensitive, and when bulk samples were exposed to air, the red crystals instantaneously turned into a red oil with evolution of heat and smoke. The oil finally turned into a colourless gel. Previous investigations from this laboratory [1, 2, 27–34] have shown that total spontaneous resolution often indeed is spontaneous, not requiring special conditions such as stirring [35, 36] or grinding [37]. Thus, it may be quite likely that the samples of **1** prepared were actually optically active and absolute asymmetric synthesis may have been achieved. Similar problems were encountered while working with the spontaneously resolving [Li(phet)(tmpda)] complex. No absolute structure could be obtained, and in addition, there was a racemic polymorph crystallising under certain conditions. Carbonation of bulk samples of [Li(phet)(tmpda)] invariably gave racemic 2-phenylpropionic acid. This may have been due to failure to obtain optically active bulk samples, or due to the fact that the reaction mixture turned more or less liquid during the course of the reaction, with the possibility of racemisation. The validity of the concept was eventually proved by total spontaneous resolution of a more rigid diindenylzinc complex, $[Zn(ind)_2(pic)_2]$, where ind is 1-indenyl and pic is 3-picoline [1]. 1-Chloroindene with up to 89% enantiomeric excess (ee) was obtained upon reaction of $[Zn(ind)_2(pic)_2]$ crystals with N-chlorosuccinimide in the presence of benzoquinone and methanol.

On close examination of the crystal structure, there is no obvious explanation for its preference for a chiral crystal packing over the more common formation of racemic crystals. Viewed along the crystallographic a-axis, the structure of **1** is composed of homochiral stacks of molecules (Fig. 2), while stacks of heterochiral molecules (with respect to the configuration at nitrogen) are formed along the b-axis. There is only one possible set of intermolecular interactions in **1**, a set of CH/π interactions [38, 39] between the two molecules in the asymmetric unit; the distance between H29B and the centroid (C_g) of the N1–C3–C4–C–5–C6 phenyl ring is 2.74 Å and the C29–H29B-C_g angle is 147.9°.

Attempts to isolate analogous crystalline 1-(2-pyridyl)ethyllithium complexes by replacement of PMDTA with other nitrogen donor ligands failed. The reason for this is unknown, and may have been due to a less pronounced tendency for these complexes to crystallise under the
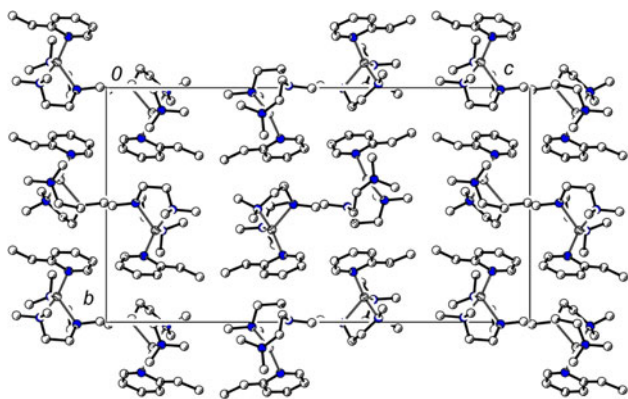
Fig. 2 Molecules displaying (*R*)- and (*S*)-configuration at the pyridyl nitrogen atoms form separate stacks parallel to the crystallographic *a*-axis. The crystal structure is still chiral because all molecules display the same chiral conformation of the chelate ring systems

conditions employed, or due to the formation of by-products which frequently inhibit crystallisation. Therefore, the deprotonation was investigated both in the presence and absence of PMDTA (Scheme 3).

The reaction of 2-ethylpyridine and benzyllithium in THF solution in the presence of one equivalent of PMDTA is rapid and gives a blood-red solution. Solutions kept at ambient temperature under nitrogen atmosphere for 1 month show no constituents by ^{1}H NMR other than 2-ethylpyridine, PMDTA, toluene, and THF after quenching with water. In the absence of PMDTA, however, the reaction proceeds with competing side reactions, in particular 1,4-addition of benzyllithium to 2-ethylpyridine. Quenching solutions of equivalent amounts of benzyllithium and 2-ethylpyridine in THF with water revealed significant amounts of 4-benzyl-2-ethyl-1,4-dihydropyridine. Solutions were stored at temperatures ranging between ambient temperature and −80 °C for time periods ranging between 2 h and 27 days. Even after 2 h at 0 °C nearly 30% of the 2-ethylpyridine had been transformed to 4-benzyl-2-ethyl-1,4-dihydropyridine, and no further reaction appeared to occur on longer standing. Similar reactions between benzyllithium and pyridine derivatives have been observed previously [40, 41]. Long storage of a solution of 2-ethyl-pyridine and benzyllithium in THF/*n*-hexane even deposited red crystals of a dihydropyridinide complex **2** as a hexane
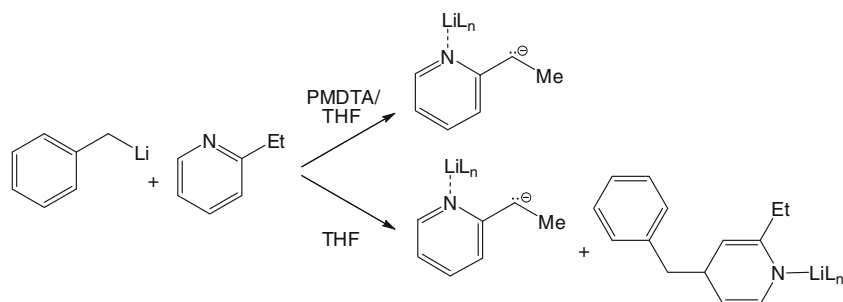
solvate. Crystal quality was poor, but single-crystal X-ray diffraction revealed a dinuclear structure (Scheme 4; Fig. 3; Table 2) where two 4-benzyl-1,4-dihydropyridinide ligands bridge between two Li$^+$ cations. The two lithium ions have distorted tetrahedral coordination geometries with two tetrahydrofuran ligands completing each coordination sphere. The complex crystallises in the centrosymmetric space group *P*-1 with the molecule located at an inversion centre. This is possible because **2** crystallises in a *meso*-form rather than as a racemate of chiral molecules. The more polar motifs in **2** are well shielded inside the molecules, which display a non-polar surface (Fig. 4). CH/π or π–π interactions would still be possible, but there are no indications of any such directed interactions in the crystal structure of **2**. The structure is built up by stacks of complex molecules and hexane molecules, respectively, along the crystallographic *a*-axis (Fig. 5).
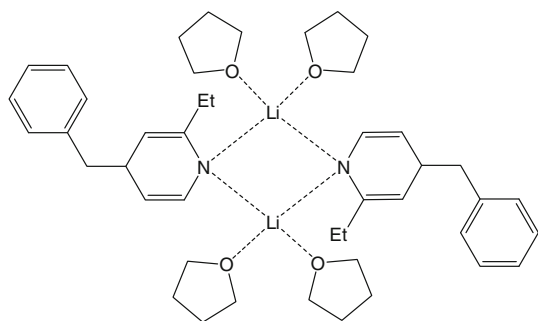
Only four crystal structures of lithiated dihydropyridines are to be found in the Cambridge Structural Database; the structures are all dinuclear and similar to the structure of **2**. Three of the structures display substituted ethylidene substituents in the *para* position [42], whereas one structure displays the unsubstituted 1,4-dihydropyridyl ligand [43, 44] and was obtained by the reaction of pyridine and butyllithium. It is noteworthy that the addition of benzyllithium to 2-ethylpyridine generates a chirogenic centre. Benzyllithium forms chiral crystals both as its THF [45] and 1,4-diazabicyclo[2.2.2]octane [46] complex, and it will perhaps be found possible to react these complexes with 2-ethylpyridine in the solid state to obtain 4-benzyl-2-ethyl-1,4-dihydropyridine in an optically active form through absolute asymmetric synthesis.

Experimental

All experiments were performed under nitrogen atmosphere using Schlenk techniques. All glassware was dried at 130 °C overnight. Toluene and THF were distilled from sodium/benzophenone, hexane was distilled from sodium/benzophenone/tetraglyme, 2-ethylpyridine and PMDTA were distilled from calcium hydride shortly prior to use.

Scheme 3

Scheme 4

Fig. 4 Molecules of **2** are non-polar, with potential oxygen, nitrogen, and lithium atoms hidden inside an envelope of hydrocarbon groups
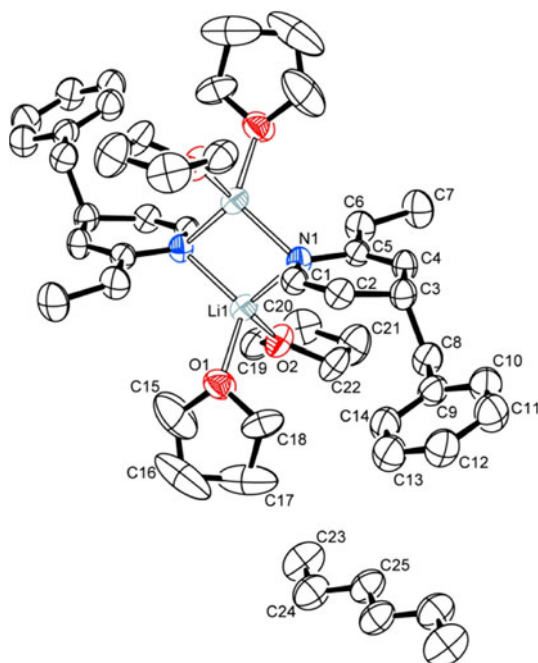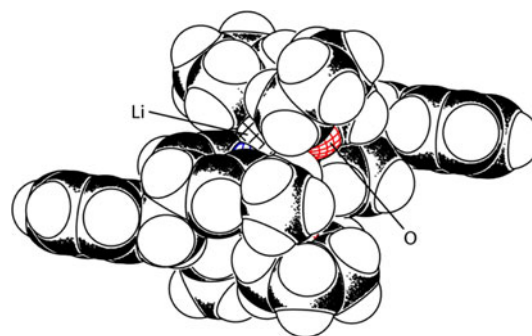

Fig. 3 Molecular structure of **2** displaying the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and all hydrogen atoms have been omitted for clarity. The molecule is an achiral *meso*-form situated at a crystallographic inversion centre
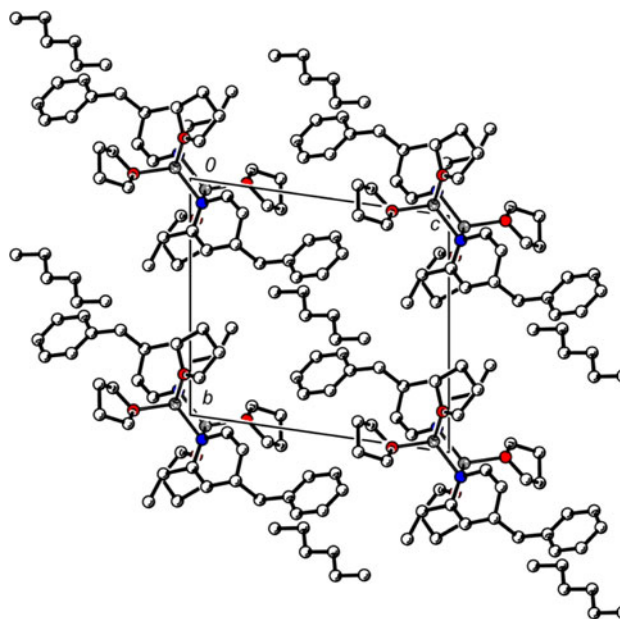

Fig. 5 Molecules of **2** form stacks parallel to the crystallographic *a*-axis, with the co-crystallised hexane molecules located in channels

n-BuLi solution in hexane (2.5 M, Acros Organics) was used as received.

Benzyllithium solution

Benzyllithium in THF was prepared using published procedures [45] with minor modifications. *n*-BuLi in hexane (2.5 M, 20 cm^3, 50 mmol) was evaporated and cooled on an ice bath. Toluene (6.4 cm^3, 60 mmol) was added followed by 40 cm^3 THF. The solution was kept 24 h at 0 °C, and for 2 h at ambient temperature.

Reaction of benzyllithium and 2-ethylpyridine in the presence of PMDTA: typical procedure

PMDTA (0.42 cm^3, 2 mmol) was added to 1.6 cm^3 benzyllithium in THF (2 mmol) at −80 to 22 °C.

Table 2 Selected bond distances for **2**

Selected bond distances (Å)		Selected bond angles (°)	
Li(1)–N(1)	2.077(6)	N(1)–Li(1)–N(1)[b]	100.8(2)
Li(1)–N(1)[a]	2.075(6)	N(1)–Li(1)–O(1)	112.7(3)
Li(1)–O(1)	2.024(6)	N(1)–Li(1)–O(2)	115.8(3)
Li(1)–O(2)	2.006(6)	N(1)[b]–Li(1)–O(1)	117.6(3)
		N(1)[b]–Li(1)–O(2)	115.1(3)
		O(1)–Li(1)–O(2)	95.7(3)

Superscript letters indicate symmetry operations used to generate equivalent atoms

[a] −x + 1, −y + 1, −z + 1

[b] −x, −y, −z

2-Ethylpyridine (0.23 cm^3) was added, and the solution was kept at −80 to 22 °C for 2 h to 27 days. The solution was quenched by addition of 1 cm^3 brine; the organic phase was evaporated and analysed by NMR. No differences were observed between experiments performed at different temperatures or reaction times. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 8.48 (m, Ar), 7.56 (m, Ar), 7.04–7.26 (m, Ar), 2.79 (q, CH$_2$), 2.44 (m, CH$_2$ in PMDTA), 2.37 (m, CH$_2$ in PMDTA), 2.19–2.24 (m, CH$_3$ in PMDTA), 1.27 (t, CH$_3$) ppm. Single-crystals of **1** suitable for X-ray diffraction were grown in 70% yield by concentrating a THF solution, prepared at 0 °C as described above, in vacuo and keeping it at −80 °C overnight.

Reaction of benzyllithium and 2-ethylpyridine: typical procedure

2-Ethylpyridine (0.23 cm^3, 2 mmol) was added to 1.6 cm^3 benzyllithium in THF (2 mmol) at −80 to 22 °C, and the solution was kept at −80 to 22 °C for 2 h to 27 days. The solution was quenched by addition of 1 cm^3 brine; the organic phase was evaporated and analysed by NMR. No trends in reactivity were observed between experiments performed at different temperatures or reaction times. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 8.50 (m, Ar), 7.56 (m, Ar), 7.07–7.29 (m, Ar), 6.00 (m, =CH–N), 4.47 (bs, NH), 4.33 (m, =CH–C), 4.14 (=CH–C), 3.73 (m, CH), 2.82 (q, CH$_2$ in ethylpyridine), 2.64 (d, CH$_2$ in Bn), 2.34 (s, toluene), 1.95 (q, CH$_2$), 1.30 (t, CH$_3$ in ethylpyridine), 1.04 (t, CH$_3$). Single-crystals of **2** suitable for X-ray diffraction were grown in 30% yield by concentrating a THF solution, prepared at ambient temperature as described above, in vacuo, diluting the solution to approximately half the concentration with hexane and keeping the solution at −80 °C for approximately 3 months.

X-ray crystallography

The crystals of **1** and **2** were carefully selected using a microscope at low temperature [47]. Data were recorded at 100 K using a Rigaku R-AXIS IIc area detector with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) from a Rigaku RU-H3R rotating anode, operating at 50 kV and 90 mA. A number of 90 oscillation photos with a rotation angle of 2° were collected. Data were processed using the CrystalClear software package [48], and an empirical absorption correction was applied using the REQAB program included in CrystalClear. The structures were solved using the program SIR-92 [49] and refined using full-matrix least squares calculations on F^2 using the SHELXL-97 program [50]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions and refined using a riding model.

Table 3 Crystal and refinement data for compounds **1** and **2**

Parameter	**1**	**2**
Empirical formula	LiC$_{16}$H$_{31}$N$_4$	Li$_2$C$_{50}$H$_{78}$N$_2$O$_4$
M	286.39	785.02
T (K)	100(2)	100(2)
Crystal system	Orthorhombic	Triclinic
Space group	P2$_1$2$_1$2$_1$	P-1
a (Å)	9.2133(12)	8.9262(6)
b (Å)	14.769(2)	11.5634(10)
c (Å)	26.662(3)	12.8399(10)
α (°)	90	76.613(19)
β (°)	90	70.657(18)
γ (°)	90	71.870(19)
V (Å^3)	3,627.9(8)	1,176.15(16)
Z	8	1
D$_c$ (g cm^{-3})	1.049	1.108
μ (Mo Kα) (mm^{-1})	0.063	0.068
Crystal size (mm)	0.4 × 0.3 × 0.2	0.2 × 0.2 × 0.2
θ range (°)	1.58–25.00	1.70–25.00
Reflections collected	22,495	7,438

^{a} $R_1(F) = \sum (||F_o| - |F_c||) / \sum |F_o|$

^{b} $wR_2(F^2) = \left\{ \sum [w(F_o^2 - F_c^2)^2] \Big/ \sum [w(F_o^2)^2] \right\}^{1/2}$

Structures were drawn using ORTEP3 [51] for Windows and Pluton [52, 53]. SIR-92, SHELXL-97, Pluton, and ORTEP3 were enclosed in the WinGX-software package [54]. Crystal and refinement data are given in Table 3.

CCDC 802212 (**1**) and 802213 (**2**) contain 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.

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