

Terminal vs. Bridging NHCs

Lithium Complexes with Bridging and Terminal NHC Ligands:
The Decisive Influence of an Anionic TetherKieren J. Evans,^[a] Cameron L. Campbell,^[a] Mairi F. Haddow,^[a] Christian Luz,^[a]
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Abstract: Deprotonation of the fluorenyl-tethered imidazolium salt [9-(C₁₃H₉)C₂H₄N(CH)₂H₄N(2,4,6-Me₃C₆H₂)] [BF₄]⁻ gave a spirocyclic compound that reacted with a synergic mixture of LiPh/LiN(SiMe₃)₂ or LinBu/LiN(SiMe₃)₂ to give a dilithium complex incorporating a bridging N(SiMe₃)₂ ligand. In contrast, deprotonation of the imidazolium salt [9-(C₁₃H₉)C₂H₄N(CH)-C₂H₂N(Me)] [Br]⁻ instead yielded the free NHC, which reacted with *n*BuLi to form a dimeric, NHC-bridged dilithium complex. Addition of LiN(SiMe₃)₂ led to coordination and the formation

of a dilithium complex with a bridging N(SiMe₃)₂ ligand, which was characterised in the solid state as a 1D coordination polymer. The reaction of 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene (SIPr) with lithium indenide and lithium fluorenyl gave soluble species with terminal binding of the NHC to the lithium cation and η⁵ coordination of indenyl or fluorenyl. A symmetrical bridging mode for an NHC donor was therefore observed only if a tethered fluorenyl anion was present with no additional amide ligand.

Introduction

N-heterocyclic carbenes (NHCs) are well established as strong σ-donor ligands in coordination chemistry and homogeneous catalysis.^[1] The N-substituents can be changed to predominantly alter the steric profile of the ligand,^[2] and the carbon backbone can be unsaturated, benzannulated or saturated to change the influence of aromaticity on the NHC's properties.^[3] It has been established that saturated NHCs, whilst giving Rh carbonyl or Ni carbonyl complexes with very similar CO stretching frequencies to unsaturated NHCs,^[1a,4] can have substantially different donor properties to unsaturated NHCs^[1a,5] including: i) increased activity in catalytic reactions,^[6] ii) the potential for enhanced π-backdonation^[4c,6c,7] and iii) enhanced stability against reactions of the backbone.^[8] NHCs, and other stabilised carbenes, have also been utilised extensively for supporting unusual bonding and oxidation states in the p-block, with the strong σ-donor properties of these ligands proving essential in stabilising many molecules of fundamental interest.^[9] These include the first examples of a molecule with a boron-boron triple bond and a disilicon(0) compound with a Si-Si double bond, both achieved using the stabilisation provided by the coordination of two NHCs.^[10] For the s-block,^[11] coordination chemistry has mainly focused on unsaturated NHCs,^[8c,12] with

far fewer complexes of saturated NHCs^[13] and CAACs (cyclic alkyl amino carbenes)^[14] described.

Tethered NHC ligands feature an NHC attached to another donor group, such as neutral P, S or N donors,^[15] or anionic donors^[16] such as amide,^[17] alkoxide/aryloxide^[15g,18] and Cp, including benzannulated analogues such as indenyl (Ind) or fluorenyl (Flu).^[19] With the anionic donors, a hybrid ligand is realised^[20] that features very different bonding from the two donors, with the "soft" NHC donor featuring a large component of covalency in bonding to metals, whereas the anionic donors, particular with "hard" O atoms, feature a substantial ionic component to the bonding. This can lead to interesting hemilability effects of the NHC in early transition metal and lanthanide complexes,^[21] or the potential for lability/reactivity of the O donor in late transition metal complexes.^[22] With Cp, Ind and Flu donors, the situation is more nuanced with strong donation expected from both donors to late transition metals. This will lead to enhanced overall stability of the complex through the chelate effect, whilst constraining the bite angle between the two donors. This has a knock-on effect on the energies of the various metal orbitals involved in ligand bonding, as well as the frontier molecular orbitals, as seen in small bite-angle ligand systems.^[23]

Although NHCs are predominantly observed as terminal ligands, there are situations where bridging behaviour is seen,^[24] a situation more widely encountered in the tin analogues of saturated NHCs, N-heterocyclic stannylenes (NHSns).^[25] Bridging behaviour is most often observed with tethered NHCs when coordinated to Cu and Ag.^[26] Here, the geometric constraints of the tether lead to many complexes that feature bridging NHCs, however, there are few investigations into the factors that produce terminal and bridging complexes with alkali metals.^[11] In this work, we explore how the coordination to lithium cations

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is affected by tethering the NHC to a fluorenyl anion, how modifying the NHC can produce structural differences and what effect a bridging amide ligand has. This is contrasted with terminal 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene (SIPr) coordination to lithium indenide or fluorenyl.

Results and Discussion

Dilithium Complexes of Fluorenyl-Tethered NHCs

The mesityl-substituted imidazolium salt **1** was synthesised in an analogous fashion to the Dipp (2,6-diisopropylphenyl) analogue^[27] (see the Supporting Information). Although the methyl imidazolium salt **4** is known,^[28] we report a detailed synthetic route and spectral properties. The imidazolium salt **1** was found to undergo cyclisation to the spirocycle **2** upon addition of one equivalent of base in modest isolated yield (Scheme 1). **2** was characterised by its distinctive ¹H and ¹³C NMR spectral properties, including the imidazolidine H resonance at 5.47 ppm, and ¹³C{¹H} resonance at 95.8 ppm, and by high resolution mass spectrometry. As with the Dipp analogue,^[27] synergic mixtures of LiPh or Li^{*n*}Bu and LiN(SiMe₃)₂ were required to deprotonate and ring open this species, which yielded **3** in 47% – 59% yield as a red powder. With LiPh, loss of PhH was observed and, presumably, the initially formed anion is unstable leading to cleavage of the C–C bond and formation of a stabilised fluorenyl anion. An alkoxide-tethered saturated NHC was formed in a similar fashion from a spirocyclic precursor.^[29] Recrystallisation from benzene gave analytically pure red crystals that were analysed by single-crystal X-ray diffraction. This

revealed the molecular structure to consist of a fluorenyl-tethered NHC ligand bound to two Li atoms bridged by a hexamethyldisilazide ligand (Figure 1). The Li–NHC distance is 2.109(6) Å, identical to the Dipp analogue [2.109(3) Å].^[27] The Li–N bond lengths [N3–Li1 = 1.936(6), N3–Li2 = 2.002(6) Å] are also comparable [1.949(3) and 1.967(3) Å respectively], but the NHC–Li–N angle is less obtuse [N3–Li2–C16 = 149.5(3)°] com-

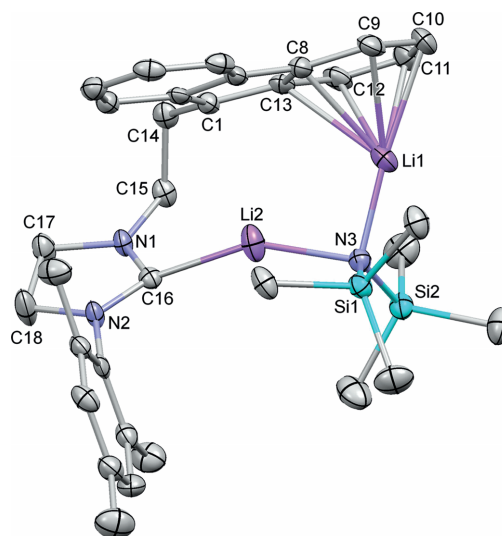
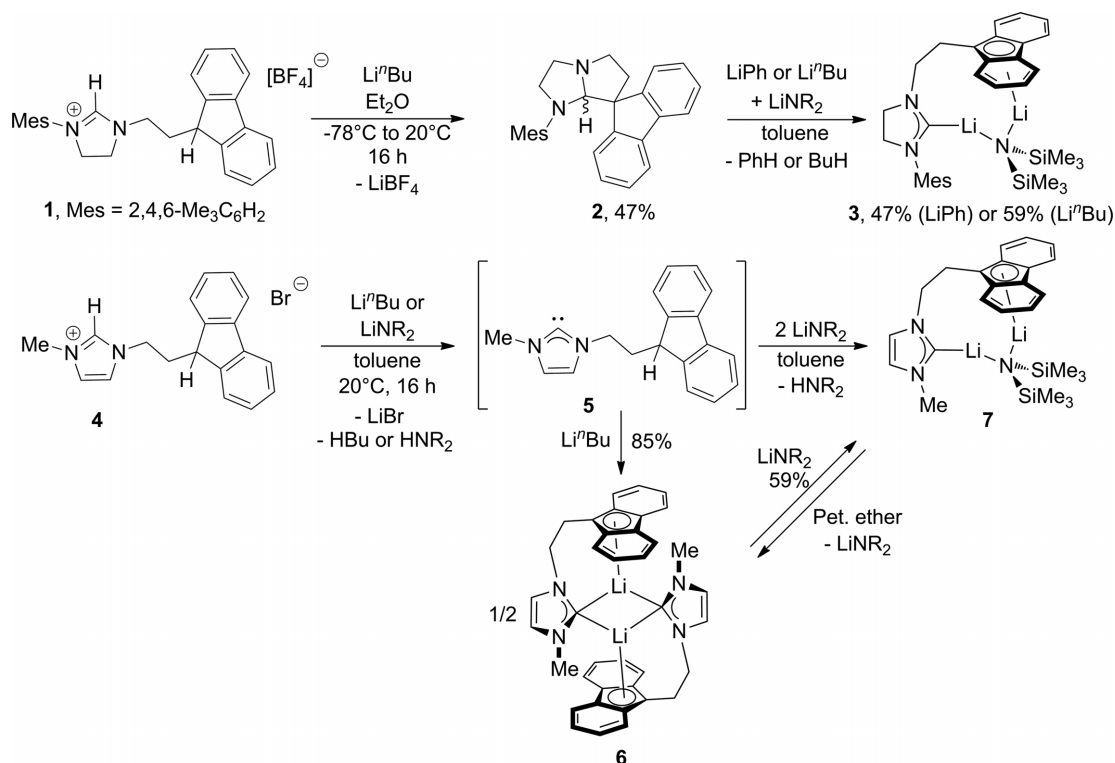


Figure 1. Molecular structure of **3** (thermal ellipsoids at 50% probability) with all H-atoms removed for clarity. Selected distances [Å] and angles [°]: C16–Li2 2.109(6), N3–Li1 1.936(6), N3–Li2 2.002(6), C8–Li1 2.394(6), C9–Li1 2.348(6), C10–Li1 2.298(6), C11–Li1 2.314(6), C12–Li1 2.389(6), C13–Li1 2.438(6), Li1–N3 Li2–93.8(3), N3–Li2–C16 149.5(3).



Scheme 1. Synthesis of dilithium complexes of fluorenyl-tethered saturated- and unsaturated-NHCs. R = SiMe₃.

pared to the Dipp analogue [162.0(2)°].^[27] This demonstrates that altering the N-substituent does not affect coordination of Li amide and formation of this favourable homo-bimetallic structure.

We were interested in reducing the steric demands of the N-substituent by replacing mesityl (Mes) with methyl in order to suppress any potential cyclometallation of this substituent when coordinated to very reactive metal centres, because a strained 4-membered ring would need to be formed compared to a 6-membered ring for an N-Mes substituent. An unsaturated

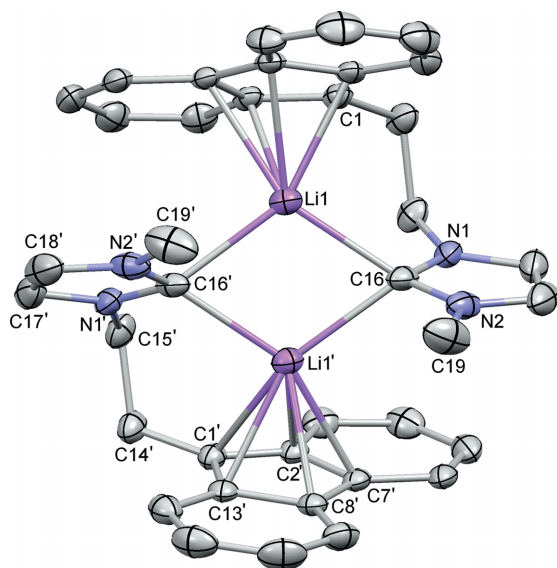


Figure 2. Molecular structure of **6** (thermal ellipsoids at 50% probability) with all H-atoms and benzene solvate molecule removed for clarity. Selected distances [Å] and angles [°]: C1–Li1 2.269(4), C2–Li1 2.300(4), C7–Li1 2.343(4), C8–Li1 2.330(4), C13–Li1 2.290(4), C16–Li1 2.226(4), C16–Li1' 2.246(4), Li1–C16' 2.246(4), Li1–Li1' 2.541(7). Symmetry operator for symmetry-generated atoms ('): 1 – x, 1 – y, +z.

ligand system was readily synthesised starting from the imidazolium salt **4**. Mono deprotonation produced the neutral NHC **5**,^[28] which was identified by ¹H NMR spectroscopy. A key point here is that, in contrast to reactions of spirocycle **2**, we were now able to use single-component bases instead of a synergic mixture of bases, which allowed us to probe what would happen with and without lithium amide present. After filtration to remove LiBr, this species was treated with either *n*BuLi to precipitate the dilithium species **6**, or reacted with LiN(SiMe₃)₂ to produce the lithium-amide incorporated **7**, no matter what stoichiometry of LiN(SiMe₃)₂ was used (Scheme 1). These two species were interconvertible by addition of LiN(SiMe₃)₂ (**6** → **7**), the cleanest route to compound **7**, or from washing with petroleum ether to remove LiN(SiMe₃)₂ (**7** → **6**). Single crystals of **6** suitable for X-ray diffraction studies were grown from a slowly cooled benzene solution of **6/7** that had been previously washed with petroleum ether (Figure 2); single crystals of **7** were grown from a saturated benzene solution (Figure 3).

The molecular structure of **6** shows two Li atoms complexed to two NHC-tethered fluorenyl ligands bridged through the NHC C atoms with the whole molecule positioned on a two-fold rotation axis. The Li cations are η⁵-coordinated to the fluorenyl anions [Li–C distances from 2.269(4) to 2.343(4) Å], and the Li–NHC distances are very similar [2.226(4) and 2.246(4) Å], although slightly longer than the terminal interaction in **3** [2.109(6) Å]. The solid-state structure of **7** shows an extended 1D coordination polymer of tethered NHC ligands, with Li atoms η⁵-coordinated to the central fluorenyl rings and connected to a μ²-N(SiMe₃)₂ ligand. Connections between molecules are formed with the other 3-coordinate Li atoms that are bound to the NHC, μ²-N(SiMe₃)₂ and a neighbouring fluorenyl ring. These intermolecular interactions could be considered to be η¹ or η², as the closest Li–C distance is between 2.431(3) to 2.514(3) Å, whilst the interaction to the neighbouring C atom ranges between 2.542(3) and 2.728(3) Å. The angles between

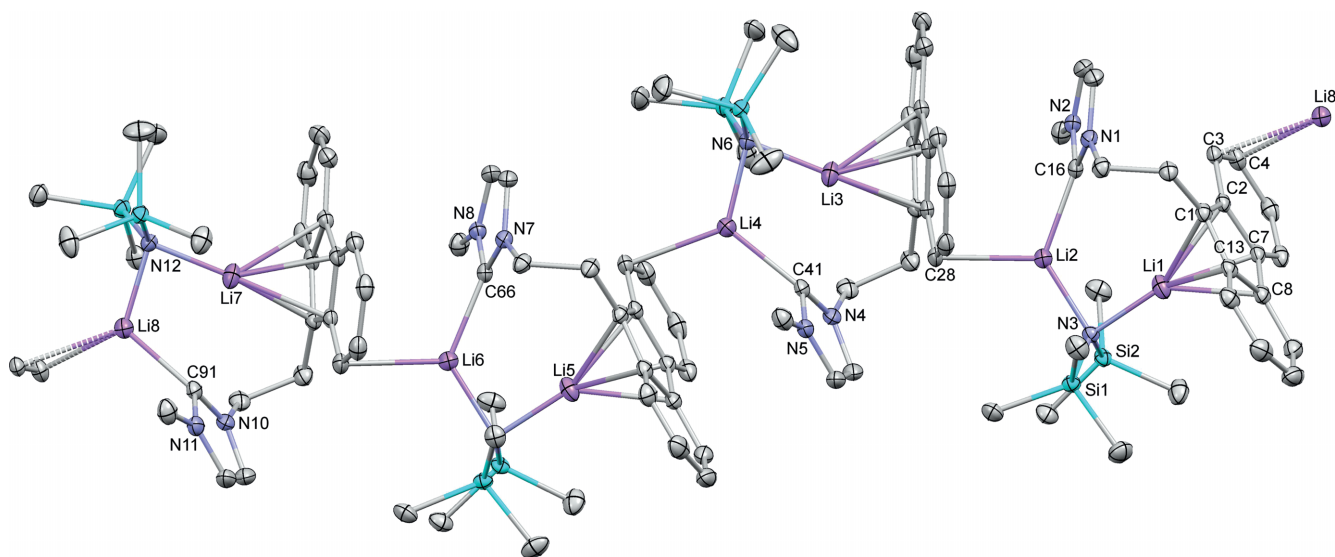


Figure 3. Solid-state structure of all four crystallographically-independent molecules of **7** (thermal ellipsoids at 50% probability) with all H-atoms and benzene solvate molecules removed for clarity. Selected distances [Å] and angles [°]: Li1–N3 1.977(3), Li2–N3 2.006(3), Li3–N6 2.004(3), Li4–N6 1.987(3), Li5–N9 1.983(3), Li6–N9 2.003(3), Li7–N12 1.992(3), Li8–N12 1.991(3), C16–Li2 2.134(3), C41–Li4 2.175(3), C66–Li6 2.141(3), C91–Li8 2.145(3).

the centroids of the η^5 -fluorenyl interactions, Li atoms and bridging N atoms are 174.9, 151.4, 171.8 and 153.4° for Li1, Li3, Li5, and Li7, respectively, indicating an alternating structure between two slightly different motifs (the analogous angle in **3** is 148.9°). This is also seen in the semi-bridging nature of C41 and C91 [C41...Li3 = 2.637(3), C41–Li4 = 2.175(3) Å; C91...Li7 = 2.706(3), C91–Li8 = 2.145(3) Å], whereas C16 and C66 have only one short C–Li distance [2.134(3) and 2.141(3) Å respectively], with the other Li atom much further away [3.32 and 3.27 Å, respectively].

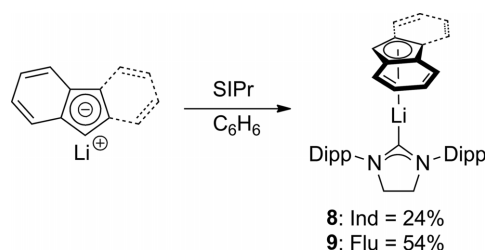
Comparing **3**, **6** and **7**, both **6** and **7** feature η^5 interactions to the central fluorenyl rings, whereas **3**, and the Dipp analogue,^[27] both feature η^6 interactions to flanking 6-membered rings of the fluorenyl system. A variety of coordination geometries for lithium fluorenyl species have been noted before.^[25d] It is likely that the smaller Me substituent in **7** leads to additional intermolecular interactions forming a coordination polymer, whereas the larger Mes and Dipp substituents sterically protect the 2-coordinate Li atom. Asymmetric bridging has been seen in other Li structures with bridging NHC ligands [C–Li = 2.169(5) and 2.339(5) Å; C–Li = 2.181(3) and 2.335(3) Å].^[24c,30]

In non-coordinating solvents, ^7Li NMR spectroscopy was useful in providing information about the coordination environment around the Li atoms in solution. For **3**, two ^7Li resonances were observed at –1.45 ppm and –5.62 ppm, in accordance with the solid-state structure that has a two-coordinate Li atom and a Li atom bound η^6 - to an aromatic benzene ring in the fluorenyl ligand observed at very low chemical shift. **6** could not be dissolved in non-coordinating solvents, while the use of $[\text{D}_8]\text{thf}$ resulted in the complete loss of the bridging structure as ^7Li NMR spectroscopy revealed 4-coordinate tetrahedral $[\text{Li}(\text{thf})_4]^+$ ions ($\delta = 0.0$ ppm). **7** showed ^7Li resonances that are very similar to **3** (–1.58 and –5.52 ppm). $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy showed a broad resonance for **7** at 195.8 ppm for the carbenic carbon due to coupling to the quadrupolar ^7Li nucleus. Very broad and weak resonances were observed for **3** and the Dipp analogue as well (see the Supporting Information), whereas **6** in thf showed a free, unbound carbene (sharp resonance at 197.5 ppm). Thus, it has been demonstrated that fluorenyl-tethered NHC systems bind $\text{LiN}(\text{SiMe}_3)_2$ to form homobimetallic structures with ease for a variety of N-substituents. The NMR spectroscopic properties and structures of these species are distinctive, and they are stable, soluble species in non-coordinating solvents. Without $\text{LiN}(\text{SiMe}_3)_2$, an NHC-bridged dimer is formed that is very poorly soluble (**6**), with the bridging structure lost in thf solution.

Lithium Complexes with SIPr

The coordination chemistry of NHCs with lithium cations is underexplored in general,^[11,31] so we sought to characterise simple monodentate NHC complexes of Li–Ind and Li–Flu to allow comparisons to be made to the tethered species above and to Cp analogues.^[12h] Adding SIPr to insoluble LiInd and LiFlu in benzene and heating to 80 °C caused the dissolution of these species forming either a pale-yellow (**8**) or orange solution (**9**,

Scheme 2). ^7Li NMR spectroscopic studies showed a single resonance for each species at very low chemical shift; –9.75 ppm for **8** and –8.95 ppm for **9**. Symmetrical η^5 binding of lithium cations to fluorenyl and indenide has previously been shown to give ^7Li chemical shifts between –7 and –8 ppm,^[32] and asymmetrical binding induced by a diamino-tethered fluorenyl was shown to increase the chemical shift to –5.7 ppm.^[25d] For unsaturated-NHC adducts of the Cp derivative $\text{C}_5\text{H}_2(\text{SiMe}_3)_3$, ^7Li NMR chemical shifts of $\delta = -7.78, -7.63$ and -9.01 ppm (NHC substituents = *tert*-butyl, 1-adamantyl and Mes, respectively) were observed^[12h] at lower chemical shift than LiCp (–6.9 ppm).^[32] Clearly, the additional NHC donor has led to substantially lower chemical shifts for the ^7Li atoms for a variety of NHCs and Cp, Ind and Flu. The ^{13}C NMR spectroscopic resonances for the carbene C atoms of both **8** and **9** were extremely broad and weak, presumably due to coupling to the quadrupolar ^7Li nucleus (see the Supporting Information). Upon standing at room temperature, colourless crystals of **8** (24 %) and yellow crystals of **9** (54 %) were formed that were suitable for X-ray diffraction experiments. Solving and refining this data demonstrated that the NHC ligands were bound in a terminal fashion to the lithium cations [Li–C_{carbene} = 2.103(2) Å for **8**, 2.102(3) Å for **9**] with identical bond lengths within error to that seen in **3** [2.109(6) Å]. The Li cation is bound η^5 to either Ind (Figure 4) or Flu (see the Supporting Information), although disorder in



Scheme 2. Coordination of SIPr [1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene] to lithium indenide (Ind) and fluorenyl (Flu).

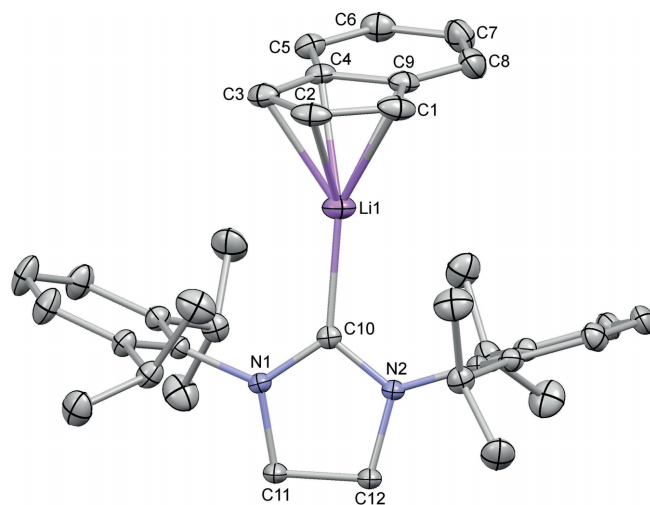


Figure 4. Molecular structure of **8** (thermal ellipsoids at 50 % probability) with all H-atoms and benzene solvate molecule removed for clarity. Selected distances [Å] and angles [°]: C1–Li1 2.218(2), C2–Li1 2.181(2), C3–Li1 2.204(2), C4–Li1 2.265(2), C9–Li1 2.272(2), C10–Li1 2.103(2), Flu_{centroid}–Li1–C10 169.0°.

the fluorenyl ligand in **9** prevents further discussion of the bond lengths and angles. The η^5 binding in **8** is symmetrical [Li–C_{Ind}: 2.181(2) – 2.272(2) Å], but the Ind_{centroid}–Li–C_{carbene} angle is not linear (169.0°). In comparison, the Li–C_{carbene} bond length in [Li{C₅H₂(SiMe₃)₃}{1,3-di(*tert*-butyl)-imidazol-2-ylidene}] was longer at 2.155(4) Å,^[12h] the Li cation was also symmetrically bound η^5 to the Cp derivative [average Li–C_{Cp} = 2.254(7) Å] and the Cp_{centroid}–Li–C_{carbene} angle was 167.4°.^[12h] Complexes **8** and **9** demonstrate the solubilising properties of the SIPr ligand through conventional terminal binding to the Li cation.

Conclusions

This study has revealed a variety of coordination modes for NHCs with lithium cations. The tethered NHC systems, whether they have a large substituent (Mes) or small substituent (Me), are all primed to coordinate one equivalent of lithium hexamethyldisilylazide, incorporating it into the ligand pocket with a bridging amide between the two lithium atoms. Without the bridging amide, which could only be achieved synthetically for the unsaturated NHC ligand because the saturated analogue required a synergic mixture of LiPh/Li amide, a dilithium species was produced with symmetrically-bridging NHC donors. The monodentate NHC SIPr ligand was found to coordinate in a conventional terminal fashion to lithium fluorenyl and lithium indenyl, greatly increasing the solubility of these organometallic reagents.

Experimental Section

General Details: All reactions requiring inert conditions were performed under an oxygen-free nitrogen atmosphere by using standard Schlenk-line techniques or by using an MBRUAN UNILab Plus glovebox, unless otherwise noted. Dry toluene, thf, MeCN and CH₂Cl₂ were obtained from a solvent purification system (MBraun SPS-800) and stored over 4 Å molecular sieves prior to use. Petroleum ether (40–60 °C) was dried with sodium wire, distilled and stored over 4 Å molecular sieves prior to use. Diethyl ether was dried with sodium/benzophenone, distilled and stored over 4 Å molecular sieves prior to use. *n*-Pentane was dried with activated 4 Å molecular sieves and degassed before use. C₆D₆ was dried with molten potassium, distilled and stored in the glovebox prior to use. Non-dry solvents were used as received from Fisher Scientific. Lithium bis(trimethylsilyl)amide (LiHMDS) was purchased from Sigma Aldrich and stored in the glovebox as received. Phenyllithium,^[33] MesN(H)C₂H₄NH₂,^[34] 1-bromo-2-(9-fluorenyl)ethane^[35] and 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene (SIPr)^[36] were synthesised according to literature procedures. NMR spectra were obtained on either a Bruker AVIII 300, AVIII 400 or AVIHD 400 MHz spectrometer. ¹H NMR spectra were recorded at either 300 MHz or 400 MHz and spectra referenced to their residual solvent peak (δ = 7.24 for CDCl₃, 1.94 for CD₃CN and 7.16 for C₆D₆). ¹³C{¹H} NMR spectra were recorded at 101 MHz and the spectra referenced to their residual solvent peak (δ = 1.32 for CD₃CN, 77.16 for CDCl₃ and 128.06 for C₆D₆). ⁷Li NMR spectra were recorded at 155 MHz and referenced to an external standard of LiCl in D₂O. ¹⁹F NMR spectra were recorded at 282 MHz. ²⁹Si{¹H} NMR spectra were recorded at 75.9 MHz using an INEPT pulse sequence and referenced to an external standard of Me₄Si. FTIR was performed on a Thermo Scientific Nicolet iS5/iD5 ATR spectrometer. Mass spectrometry was con-

ducted at the UK ESPRC Mass Spectrometry Facility at Swansea University using the techniques stated. Elemental analysis was performed by Dr Brian Hutton (Heriot-Watt University, stable samples) and Mr Stephen Boyer (London Metropolitan University, air sensitive). Meaningful elemental analysis data was found to be very difficult to obtain for several of these very air sensitive samples.

[9-(C₁₃H₉)C₂H₄N(CH)C₂H₄N(2,4,6-Me₃C₆H₂)](BF₄) (1): NH₄BF₄ (2.422 g, 23.1 mmol, 2 equiv.) and MesN(H)C₂H₄N(H)C₂H₄(C₁₃H₉) (4.227 g, 11.5 mmol, 1 equiv.) were combined in a Schlenk tube and dried under high vacuum. Triethyl orthoformate (15.4 cm³, 92.3 mmol, 8 equiv.), formic acid (cat., 2 drops) and toluene (15 cm³) were added. The apparatus was equipped with a condenser and the mixture was heated at 100 °C for 16 hours. All solvent and residual triethyl orthoformate were removed under reduced pressure. The crude product was extracted with dichloromethane and filtered. The filtrate was concentrated under reduced pressure and diethyl ether was added to precipitate the crude product. The crude product was then purified with column chromatography (SiO₂, CH₃CN/Et₂O, 3:20→3:10). Recrystallisation from MeCN/diethyl ether afforded the product as a colourless solid (4.153 g, 8.87 mmol, 77 %). ¹H NMR (CD₃CN, 400 MHz, 298 K): δ = 7.86 (d, 2H, ArH), 7.84–7.83 (m, 1H, ArH), 7.66 (m, 2H, ArH), 7.64 (m, 1H, NCHN), 7.42 (m, 4H, ArH), 6.98 (m, 2H, ArH), 4.21 (t, *J* = 5.58, 1H, FluH), 3.96 (m, 4H, NCH₂CH₂N), 3.26 (m, 2H, CH₂), 2.54 (m, 2H, CH₂), 2.27 (s, 3H, CH₃), 2.16 (s, 6H, CH₃). ¹³C{¹H} NMR (CD₃CN, 101 MHz, 298K): δ = 157.7 (Imid CH), 145.4 (Ar C), 140.7 (Ar C), 140.0 (Ar C), 135.5 (Ar C), 130.6 (Ar C), 129.3 (Ar CH), 127.4 (Ar CH), 127.2 (Ar CH), 124.3 (Ar CH), 120.0 (Ar CH), 50.5 (NCH₂CH₂N), 48.7(NCH₂CH₂N), 44.9 (Flu-H), 44.5 (NCH₂CH₂), 29.2 (CH₂CH₂Flu), 19.8 (CH₃), 16.5 (CH₃). ¹⁹F (CD₃CN, 282 MHz, 298 K) δ = –151.8 (s); HRMS (ESI⁺) 381.2320 [M – BF₄]⁺, C₂₇H₂₉N₂ requires 381.2325; C₂₇H₂₉N₂BF₄: calcd. C 69.24, H 6.24, N 5.98; found C 69.10, H 6.20, N 5.69.

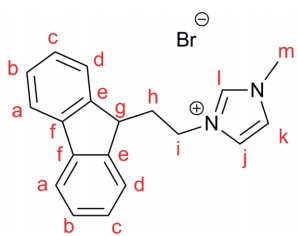
spiro([C₁₃H₉)C₂H₄N(CH)N(C₂H₄)(2,4,6-Me₃C₆H₂)] (2): To a suspension of **1** (3.794 g, 8.10 mmol, 1.1 equiv.) in diethyl ether (40 cm³), *n*BuLi (5 cm³ of a 1.473 M solution in hexanes, 7.37 mmol, 1 equiv.) was added at –78 °C. The reaction was warmed up to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue was extracted with petroleum ether (3 × 10 cm³) then filtered to remove LiBF₄. Upon analysis by ¹H NMR spectroscopy, it was often observed that an intermediate of unknown composition was formed, which could be transformed into the desired product by heating a toluene solution of the crude product at 75 °C for 2.5 hours to complete the reaction. The product was obtained as a colourless powder upon removing all volatiles under reduced pressure (1.260 g, 3.31 mmol, 47 %). ¹H NMR (C₆D₆, 400 MHz, 298 K): δ = 7.61–7.59 (m, 1H, ArH), 7.44–7.38 (m, 2H, ArH), 7.29–7.24 (m, 2H, ArH), 7.20 (m, 1H, ArH), 7.00–6.92 (m, 2H, ArH), 6.50 (br s, 1H, ArH), 6.39 (br s, 1H, ArH), 5.47 (s, 1H, imidazolidine CH), 3.50–3.39 (m, 3H, CH₂), 3.13–2.92 (m, 3H, CH₂), 2.44–2.36 (m, 2H, CH₂), 2.16 (br s, 3H, CH₃), 2.11–2.02 (m, 1H, CH₂), 1.86 (s, 3H, CH₃) 1.46 (Br s, 3H, CH₃). ¹³C{¹H} NMR (C₆D₆, 101 MHz, 298K): δ = 150.3 (Ar C), 149.7 (Ar C), 143.6 (Ar C), 141.7 (Ar C), 140.5 (Ar C), 138.4 (Br s, o-C) 134.5 (Br s, o-C) 134.2 (Ar C), 130.5 (Br s, *m*-CH), 128.9 (Br s, *m*-CH), 127.5 (Flu CH), 127.0 (Flu CH), 126.9 (Flu CH), 126.8 (Flu CH), 125.8 (Flu CH), 122.3 (Flu CH), 119.8 (Flu CH), 119.5 (Flu CH), 95.8 (imidazolidine CH), 61.9 (NCH₂CH₂N), 54.9 (NCH₂CH₂N), 54.4 (Flu), 53.6 (NCH₂CH₂), 39.6 (CH₂CH₂Flu), 20.4 (*p*-CH₃), 18.5 (Br s, o-CH₃) 17.7 (Br s, o-CH₃). HRMS (EI) 380.2244 [M]⁺, C₂₇H₂₈N₂ requires 380.2247; C₂₇H₂₈N₂: calcd. C 85.22, H 7.42, N 7.36; found C 84.19, H 7.39, N 7.30.

[Li₂{ μ -N(SiMe₃)₂}{ μ -(η^6 -C₁₃H₉)C₂H₄N(κ -C)N(C₂H₄)(2,4,6-Me₃C₆H₂)] (3): **Method A:** In a glovebox, **2** (295 mg, 0.776 mmol), LiN(SiMe₃)₂

(145 mg, 0.867 mmol, 1.1 equiv.) and LiPh (73 mg, 0.867 mmol, 1.1 equiv.) were combined in a flask equipped with a J. Young's tap. Toluene (5 cm³) was then added and the mixture was heated at 80 °C for 16 hours with stirring. After cooling to room temperature, the volatiles were removed under reduced pressure. Toluene (1 cm³) and pet. ether (20 cm³) was added and the mixture was stirred vigorously at room temperature for 5 h. After standing for 30 min, the resulting red precipitate was isolated by filtration and washed with petroleum ether (5 cm³), and dried under reduced pressure, affording the product as a red powder (202 mg, 0.365 mmol, 47 %). The product can be recrystallised from benzene to yield red, analytically pure crystals.

Method B: Compound **2** (292 mg, 0.762 mmol) and LiN(SiMe₂)₂ (128 mg, 0.762 mmol) were dissolved in toluene (2 cm³), *n*BuLi (0.5 mL, 0.762 mmol, 1.523 M in hexanes) was added and the solution stirred at room temperature for 48 hours. The volatiles were removed under reduced pressure, pentane (10 cm³) was added and the mixture was stirred for 30 min. After standing for 10 min, the resulting red precipitate was isolated by filtration and washed with pentane (2 × 5 cm³). The resulting solid was dried under reduced pressure affording the product as a red powder (250 mg, 0.420 mmol, 59 %). Using the Dipp analogue,^[27] a yield of 56 % was achieved. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ = 8.28 (dt, *J* = 7.88, 0.85 Hz, 2H, FluH), 7.54 (d, 8.19 Hz, 2H, FluH), 7.32–7.29 (m, 2H, FluH), 6.90–6.86 (m, 2H, FluH), 6.60 (s, 2H, MesH), 3.61–3.58 (m, 2H, NCH₂CH₂N), 3.19–3.17 (m, 2H, NCH₂CH₂N), 3.13–3.07 (m, 2H, CH₂CH₂), 3.02–2.98 (m, 2H, CH₂CH₂Flu), 1.99 (s, 6H, CH₃), 1.98 (s, 2H, CH₃), –0.35 (s, 15H, SiCH₃). ¹³C{¹H} NMR (C₆D₆, 101 MHz, 298K): δ = 220 (v. br, carbene), 137.0 (Ar C), 137.0 (Ar C), 135.8 (Ar C), 135.3 (Ar C), 128.9 (Ar CH), 121.0 (Ar C), 120.9 (Ar CH), 120.3 (Ar CH), 115.3 (Ar CH), 109.0 (Ar CH), 89.8 (Flu C) 51.6 (NCH₂CH₂N), 40.1 (NCH₂CH₂N), 49.8 (NCH₂CH₂), 25.8 (CH₂CH₂Flu), 20.4 (CH₃), 18.2 (CH₃), 4.5 (SiCH₃). ⁷Li NMR (C₆D₆, 155.5 MHz, 298K) δ = –1.45, –5.62. ²⁹Si NMR (C₆D₆, 79.5 MHz, 298 K): δ = –10.39. C₃₃H₄₅Li₂N₃Si₂: calcd. C 71.57, H 8.19, N 7.59; found C 71.26, H 8.24, N 7.21.

[9-(C₁₃H₉)C₂H₄N(CH)C₂H₂N(Me)][Br] (4): To a Schlenk flask containing 1-bromo-2-(9-fluorenyl)ethane (3.911 g, 14.23 mmol, 1 equiv.), dry toluene (10 cm³) and *N*-methylimidazole (2.0 mL, 25.1 mmol) was added and the mixture was stirred at 70 °C for 24 hours. The resulting precipitate was isolated by filtration, washed with Et₂O (3 × 10 cm³) and dried under reduced pressure. Further drying was achieved by heating at 70 °C under reduced pressure, and the resulting pale yellow, hygroscopic powder was stored in the glovebox (4.178 g, 11.8 mmol, 82 %).

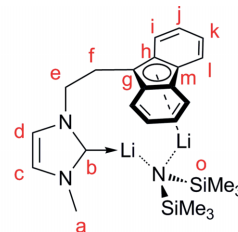


¹H NMR (300 MHz, CDCl₃): δ = 9.67 (s, 1H, H_i), 7.70 (d, *J* = 7.4 Hz, 2H, H_D), 7.51 (dd, *J* = 7.4, 0.7 Hz, 2H, H_A), 7.39–7.30 (m, 2H, H_B), 7.30–7.22 (m, 2H, H_C), 7.05 (t, *J* = 1.7 Hz, 1H, H_J), 6.68 (t, *J* = 1.8 Hz, 1H, H_K), 4.19 (t, *J* = 4.7 Hz, 1H, H_C), 3.87–3.80 (overlapping m, 5H, H_M and H_i), 2.94 (td, *J* = 6.8, 4.8 Hz, 2H, H_H), ¹³C NMR (101 MHz, CDCl₃): δ = 144.44 (s, Ar C, C_e), 141.09 (s, Ar C, C_f), 137.69 (s, Ar CH, C_i), 127.77 (s, Ar CH, C_g), 127.50 (s, Ar CH, C_d), 124.49 (s, Ar CH, C_b), 122.12 (s, Ar CH, C_j), 121.92 (s, Ar H, C_k), 120.14 (s, Ar CH, C_a), 46.52 (s, CH₂, C_i), 44.85 (s, Flu CH, C_g), 36.50 (s, CH₃, C_m), 31.70 (s, CH₂,

C_h); HRMS (ESI⁺) *m/z*: [M – Br]⁺ Calcd. for C₁₉H₁₉N₂: 275.1543, found 275.1538.

[Li₂{(η⁵-C₁₃H₉)C₂H₄N(μ-C)N(C₂H₂)(Me)}₂] (6): To a Schlenk flask containing **4** (1.353 g, 3.80 mmol), toluene (25 cm³) was added. The suspension was cooled to –78 °C followed by addition of 1 equiv. *n*BuLi (2.5 cm³, 3.80 mmol) during which time the starting material dissolved and the solution darkened. The reaction was left to warm to room temperature and was stirred for 16 h. The resulting dark orange solution was filtered and the precipitate was washed with toluene (3 × 5 cm³). The filtrates (containing intermediate **5**) were combined, cooled to –78 °C and 1 equiv. of *n*BuLi (2.5 cm³, 3.80 mmol) was added. The reaction mixture was then warmed to room temperature and was stirred for 16 h. The solution became yellow and precipitate was formed. The solution was filtered, the precipitate was washed with toluene (3 × 10 cm³) and dried under reduced pressure to afford **6** as a yellow air sensitive powder (0.904 g, 0.161 mmol, 85 %). ¹H NMR (400 MHz, [D₈]THF): δ = 7.89 (2H, d, *J* = 7.6 Hz), 7.07 (3H, d, *J* = 8.8 Hz), 6.85 (1H, s), 6.77 (2H, t, *J* = 7.3 Hz, NCHCHN), 6.38 (2H, t, *J* = 7.1 Hz, NCHCHN), 4.23 (2H, t, *J* = 6.7 Hz, NCH₂CH₂Flu), 3.46–3.42 (m, overlap of Me, CH₂); ¹³C NMR (101 MHz, [D₈]THF) δ = 197.5 (carbene), 135.9 (Ar C), 122.7 (Ar CH), 121.1 (Ar C), 120.5 (Ar CH), 119.2 (Ar CH), 119.0 (Ar CH), 113.3 (Ar CH), 108.1 (Ar CH), 88.1 (Flu C), 53.1 (FluCHCHN), 36.9 (FluCHCHN), 30.2 (Me); ⁷Li NMR (155 MHz, [D₈]THF) δ = 0.00 (s, [Li(THF)₄]).

[Li₂{μ-N(SiMe₃)₂}{μ-(η⁵-C₁₃H₉)C₂H₄N(κ-C)N(C₂H₂)(Me)}] (7): To a Schlenk flask containing a suspension of **6** (200 mg, 0.36 mmol) in toluene (5 cm³) was added a solution of lithium bis(trimethylsilyl)amide (238 mg, 1.43 mmol, 4 equiv.) in toluene (5 cm³). The red solution was allowed to stir for 16 hours. The supernatant solution was filtered away from the precipitate, concentrated in volume and stored at –25 °C for 7 days. The orange crystals produced were separated by cannula filtration and dried under high vacuum yielding **7** (188 mg, 0.42 mmol, 59 %).



¹H-NMR (400 MHz, C₆D₆, 298 K): δ = 8.29 (d, 2H, *J* = 7.8 Hz, ArH), 7.20–7.14 (m, 2H, ArH), 7.06 (d, 2H, ³J_{HH} = 8.3 Hz, ArH), 6.85 (ddd, 2H, *J*_{HH} = 7.8, 6.6, 1.1 Hz, ArH), 6.21 (d, 1H, ³J_{HH} = 1.5 Hz, NCHCHN), 6.02 (d, 1H, ³J_{HH} = 1.5 Hz, NCHCHN), 3.97–3.89 (m, 2H, NCH₂CH₂Flu), 3.17–3.13 (m, 2H, NCH₂CH₂Flu), 2.85 (s, 3H, Me), –0.09 (s, 18H, Si(Me)₃)₂ ppm; ¹³C{¹H}-NMR (101 MHz, C₆D₆, 298 K): δ = 195.8 (br, C_b), 135.2 (s, C_h), 121.0 (s, C_m), 120.82 (s, C_{k/l}), 120.81 (s, C_{k/l}), 120.29 (s, C_{c/d}), 120.19 (s, C_{c/d}), 115.5 (s, C_i), 109.9 (s, C_j), 89.5 (s, C_g), 53.4 (s, C_e), 37.1 (s, C_f), 29.10 (s, C_a), 5.5 (s, C_o) ppm; ⁷Li-NMR (155 MHz, C₆D₆, 298 K): δ = –1.58 (s, NHC-Li-N), –5.52 (s, N-Li-Flu) ppm; ²⁹Si NMR (79 MHz, C₆D₆, 298 K): δ = –9.98 (s, SiMe₃) ppm.

[Li(lnd)(SiPr)] (8): In a glovebox, LiI_{nd} (24.4 mg, 0.2 mmol) and SiPr (78.1 mg, 0.2 mmol) were combined in C₆H₆ (3 cm³). The reaction mixture was heated at 80 °C for 30 min to dissolve all of the starting materials and then left to crystallise for 3 days at room temperature. The product was isolated by filtration and dried yielding an off-white solid (25 mg, 24 %). ¹H NMR (400 MHz, C₆D₆, 298 K): δ = 7.46 (dd, 2H, *J* = 6.2, 3.1 Hz, ArH), 7.23 (t, 2H, *J* = 7.7 Hz, ArH), 7.07 (d, 4H, *J* = 7.7 Hz, ArH), 6.82 (dd, 2H, *J* = 6.3, 3.1 Hz, ArH), 6.36 (t, 1H, *J* =

3.4 Hz, Ind-H), 6.02 (d, 2H, $J = 3.3$ Hz, Ind-H), 3.05 (br s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.69 (br s, 4H, $\text{CH}(\text{CH}_3)_2$), 1.23 (d, 12H, $J = 6.8$ Hz, CH_3), 1.11 (br d, 12H, $J = 6.5$ Hz, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K): $\delta = 223$ (v. br., carbene), 146.8 (ArH), 129.4 (Ar), 128.7 (Ar), 125.9 (Ar), 124.4 (ArH), 120.9 (ArH), 116.6 (ArH), 114.1 (ArH), 92.3 (Ind-H), 53.4 ($\text{NCH}_2\text{CH}_2\text{N}$), 28.8 (CHMe_2), 24.8 (CH_3), 24.3 (CH_3); ^7Li NMR (155 MHz, C_6D_6 , 298 K): $\delta = -9.75$; $\text{C}_{42}\text{H}_{51}\text{N}_2\text{Li}$: calcd. C 84.34, H 8.85, N 5.46; found C 84.21, H 8.86, N 5.20.

[Li(Flu)(SiPr)] (9): In a glovebox, LiFlu (34.4 mg, 0.2 mmol) and SiPr (78.1 mg, 0.2 mmol) were combined in C_6H_6 (3 cm^3). The reaction mixture was heated at 80 °C for 30 min to dissolve all of the starting materials forming an orange solution. The reaction was then left to crystallise for 3 days at room temperature. The product was isolated by filtration and dried yielding a yellow microcrystalline solid (61 mg, 54 %). ^1H NMR (400 MHz, C_6D_6 , 298 K): $\delta = 8.03$ (d, 2H, $J = 8.0$ Hz), 7.38 (d, 2H, $J = 8.3$ Hz), 7.29–7.19 (m, 4H), 7.00 (t, 6H, $J = 7.1$ Hz), 6.83 (t, 2H, $J = 7.1$ Hz), 6.12 (br s, 1H), 2.93 (br s, 4H), 2.50 (br s, 4H), 1.19 (br s, 12H), 1.06 (br s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K): $\delta = 220$ (v. br., carbene), 146.5, 143.6, 142.3, 131.8, 129.5, 128.6, 127.1, 127.0, 125.3, 124.4, 122.2, 120.7, 120.2, 118.9, 117.4, 113.8, 79.6 (Ar and Flu C), 53.3 ($\text{NCH}_2\text{CH}_2\text{N}$), 37.0, 28.8 (CHMe_2), 24.8 (CH_3), 24.3 (CH_3); ^7Li NMR (155 MHz, C_6D_6 , 298 K): $\delta = -8.95$.

Crystallographic Details: Single crystals suitable for X-ray diffraction were covered in inert oil and placed under the cold stream of a Bruker D8 Venture at 100 K (7–9) or an Oxford Diffraction four-circle Supernova diffractometer (University of Edinburgh) at 120 K (3 and 6). Exposures were collected using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$). Indexing, data collection and absorption corrections were performed. The structures were then solved using SHELXT^[37] and refined by full-matrix least-squares refinement (SHELXL)^[38] interfaced with the programme OLEX2^[39] (Table S1). The fluorenyl ligand in **9** was found to be disordered over several positions and the C atoms could only be satisfactorily modelled isotropically.

CCDC 1946066 (for **3**), 1946067 (for **6**), 1946068 (for **7**), 1946069 (for **8**), and 1946070 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Lithium · Carbene ligands · Indenyl tethers · Fluorenyl tethers · Bridging coordination

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