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Synthesis and characterisation of sterically bulky lithium amidinate and bis-amidinate complexes

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Abstract

The synthesis and characterisation of the amidines, (tript)C(NR)(NHR), R = Pr^i or cyclohexyl (Cy), tript = triptycenyl, and lithium amidinate complexes, [Li(THF)$_2${(tript)C(NR)$_2$}] bearing the bulky triptycenyl substituent on the amidine or amidinate backbone carbon is described. NMR spectroscopic studies have shown these to exist solely as their *Z-syn* isomeric forms in solution due to the steric effect of the triptycenyl moiety. The X-ray crystal structures of two examples confirm this is also the case in the solid state. A new bis-amidine ligand, 1,4-{(Pr^iHN)(Pr^iN)C}$_2${2,3,5,6-C$_6$(*p*-C$_6$H$_4$Bu^t)$_4$}, and the corresponding lithium bis-amidinate complex, [1,4-{Li(THF)$_2$(Pr^iN)$_2$C}$_2${2,3,5,6-C$_6$(*p*-C$_6$H$_4$Bu^t)$_4$}], which incorporate a sterically bulky tetraarylphenylene spacer unit have also been prepared. In solution, the amidine undergoes facile inter-conversion between its *E-syn*:*E-syn* and *Z-syn*:*E-syn* isomers. The bis-amidinate complex has been structurally characterised and shown to chelate both of its lithium centres.
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Keywords: Amidine; Amidinate; Organometallic reagent; Steric bulk; X-ray crystal structure

1. Introduction

Amidinate anions, [RNC(R′)NR]$^-$, have been extensively utilised as ligands for the coordination of s-, p-, d- and f-block metals [1,2]. These ligands have displayed an impressive array of coordination modes which reflect the nature of the coordinated metal and the N- and C-substituents of the amidinate. In the past, main group amidinate complexes have perhaps been overshadowed by their transition metal counterparts, though this situation is rapidly changing as they are finding applications as, for example, olefin [3] or lactide [4] polymerisation catalysts and materials precursors [5]. Such applications are generally restricted to p-block complexes, but s-block amidinates are equally important to the synthetic chemist as ligand transfer reagents. Because of this, much work has gone into understanding the solid state architectures that s-block amidinate [1,2] and formamidinate [6] complexes can adopt.

It is clear that the ability to tailor the steric bulk of amidinate anions is an important requirement in the design of main group metal catalysts derived from these ligands. It has been suggested that including bulky substituents at the N-centres of the amidinate ligand imparts steric protection mainly in the plane of the amidinate ligand [7], whereas large substituents, e.g., *m*-terphenyls, at the C-centre provide protection above and below the ligand plane and favour *N*,*N*-chelation of metal centres [8]. Both strategies have been successfully utilised in the formation of main group metal catalysts. In addition, they have been employed for the stabilisation of amidinate complexes of thermally labile p-block fragments, e.g., indium hydrides [9], and low oxidation state metal centres, e.g., In(I) [10]. A recent and important innovation in amidinate design has been the development of bifunctional ligands with two amidinate moieties bridged by a linker unit. Examples here include the phenylene or biphenylene bridged ligands, [1,4-C$_6$H$_4${C(NR)$_2$}$_2$]$^{2-}$, R = cyclohexyl (Cy), Pr^i [11] or SiMe$_3$ [12], and [{(Pr^iN)$_2$C}-

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C_6H_4-$C_6H_2Ph_2\{C(NPr^i)_2\}]^{2-}$ [13], the cyclohexyl bridged systems, $[1,2\text{-}C_6H_8\{NC(R)N(R')\}_2]^{2-}$, R = R′ = *p*-tolyl or R = Ph, R′ = $SiMe_3$ [14], and the oxalic amidinate, $[\{(Ph)NCN(Bu^t)\}_2]^{2-}$ [15].

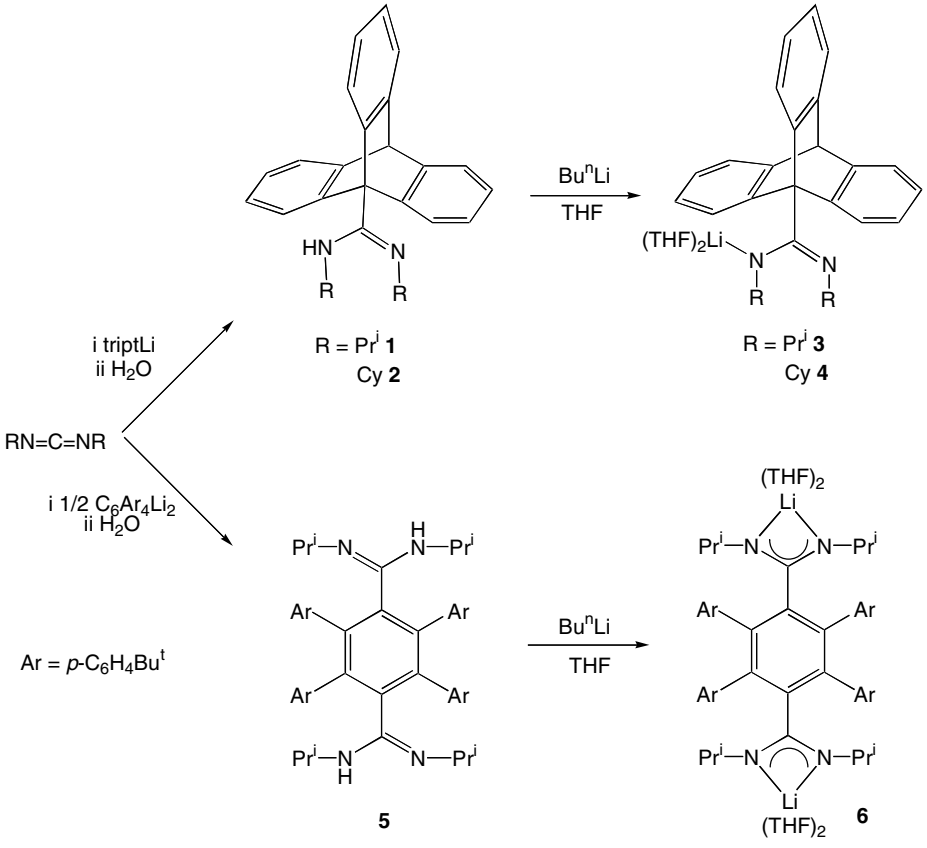
We have recently begun exploiting bulky formamidinate and amidinate ligands for the stabilisation of group 13 hydride and low oxidation state group 13 metal complexes [9,10]. To aid an extension of this work, we believed the development of new lithium amidinate and bis-amidinate ligand transfer reagents having very bulky C-substituents would be worthwhile. For this study we chose the triptycenyl moiety which we have previously shown to impart remarkable stability to primary pnictanes, (tript)EH_2, tript = triptycenyl, E = As or Sb [16], and the first diphosphaalkyne, P≡C(tript)C≡P [17]. In addition, the bulky tetraarylphenylene linker, –{2,3,5,6-C_6(*p*-$C_6H_4Bu^t)_4$}–, which has previously been used to stabilise diphosphaalkenes [18], was seen as an excellent candidate for the preparation of lithium bis-amidinate complexes. The results of our efforts in this direction are reported herein.

2. Results and discussion

2.1. Triptycenyl substituted amidines and lithium amidinate complexes

One of the most useful synthetic methods for preparing amidine ligands is the insertion of alkyl lithium reagents into the carbodiimide function. Accordingly, the triptycenyl substituted amidines, **1** and **2**, were prepared in good yields from the reaction of 9-lithiotriptycene with the appropriate *N*,*N*′-dialkylcarbodiimides, followed by aqueous work-up (Scheme 1). In contrast, no reaction occurred between ArN=C=NAr (Ar = 2,6-diisopropylphenyl) and 9-lithiotriptycene, presumably because of the steric bulk of both reactants. The infrared spectra of **1** and **2** are in accord with their proposed formulations and each exhibit N–H (**1** $\nu = 3388\ cm^{-1}$, **2** $\nu = 3395\ cm^{-1}$) and C=N (**1** $\nu = 1651\ cm^{-1}$, **2** $\nu = 1662\ cm^{-1}$) stretching absorptions in the normal region for amidines [19]. In addition, their NMR spectra indicate that only one isomer of each compound exists in solution. This was be assigned to the *Z-syn* isomer, as this minimises interactions between the N-substituents and the bulky triptycenyl substituent. In line with this hypothesis are the results of a previous study which have shown that, in solution, amidines which are not sterically demanding are involved in rapid equilibria between the *E-syn* and *Z-syn* isomers, whilst increasing the steric bulk of the amidine substituents shifts this equilibrium to a point where the *Z-syn* isomer dominates [20].

Compounds **1** and **2** can be smoothly converted to the lithium amidinate complexes, **3** and **4**, respectively, by treatment with Bu^nLi (Scheme 1). As expected, the infrared spectra of the complexes are devoid of N–H stretching absorptions, but C=N stretches (**3** $\nu = 1657\ cm^{-1}$; **4** $\nu = 1663\ cm^{-1}$) similar to those of the free amidines were



Scheme 1.

observed. This suggests that the amidinate ligands in both complexes have largely localised NC=N backbones. Moreover,the ^{1}H NMR spectra of **3** and **4** are indicative of the complexes containing chemically inequivalent Pr^i and Cy groups, respectively, thus implying that the amidinate ligands do not chelate the lithium centres, or act as bridging ligands in dimeric complexes. It is of note that examples of lithium amidinate complexes in which the amidinate acts as a monodentate, non-bridging ligand can be confined to two examples, [Li(tmeda){κ^1-N-(Pr^{i}N)$_2$C[C$_6$H$_3$(C$_6$H$_2$R$_3$-2,4,6)$_2$-2,6]}] R = Me or Pr^i [8,20], which are substituted with bulky *m*-terphenyl groups at the backbone C-centre.

The molecular structures of both the amidine, **1**, and the amidinate complex, **3**, are depicted in Figs. 1 and 2, respectively. These confirm that **1** exists as its *Z-syn* isomeric form and that the amidinate of **3** is acting as a monodentate ligand. The metrical parameters suggest a degree of NCN delocalisation in both compounds, though this is more pronounced in **1**. Another notable difference between the structures of **1** and **3** comes from their N–C–N angles, which in the case of the former is significantly more acute [129.91(18)°] than the latter [134.96(18)°]. The most interesting structural feature of **3** is the coordination geometry of the lithium centre. This is distorted trigonal planar (Σ angles = 357.5°), the metal being ligated by one N-centre of the amidinate ligand and two THF molecules. This can be compared to the situation in the closely related

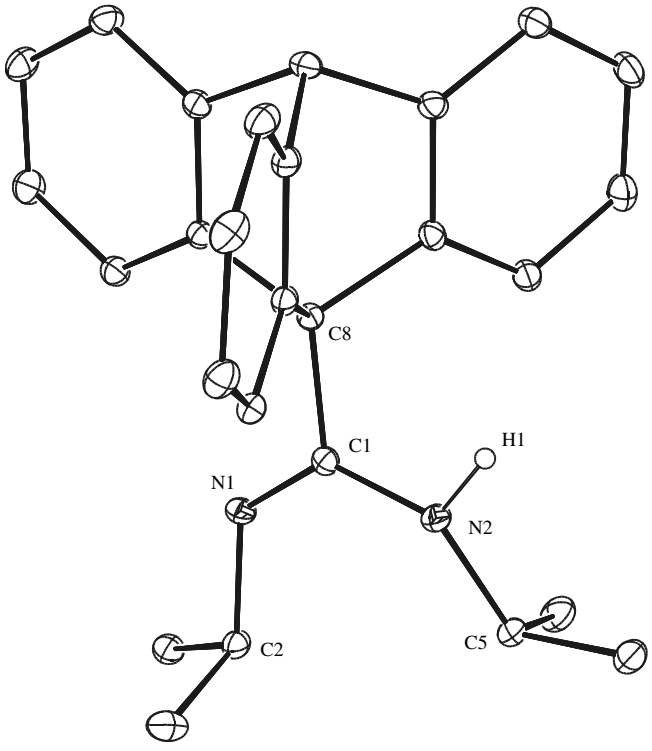


Fig. 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.276(2), N(1)–C(2) 1.467(2), N(2)–C(1) 1.391(2), N(2)–C(5) 1.467(2), C(1)–C(8) 1.537(3), C(1)–N(1)–C(2) 124.49(16), C(1)–N(2)–C(5) 130.19(16), N(1)–C(1)–N(2) 129.91(18), N(1)–C(1)–C(8) 119.13(17), N(2)–C(1)–C(8) 110.84(15).

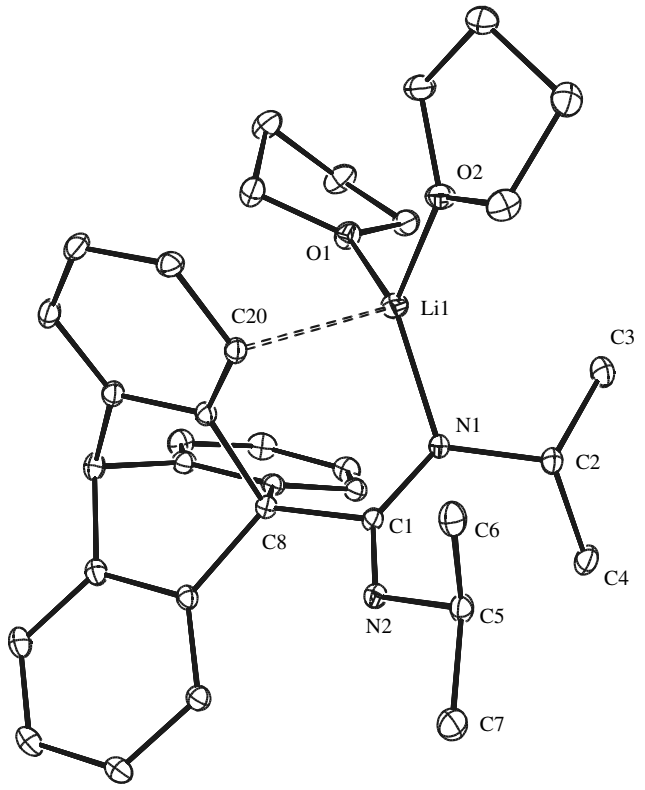


Fig. 2. Molecular structure of **3**. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.346(2), N(1)–C(2) 1.472(2), N(2)–C(1) 1.306(2), N(2)–C(5) 1.465(2), C(1)–C(8) 1.563(3), N(1)–Li(1) 1.946(4), Li(1)–O(1) 1.905(4), Li(1)–O(2) 1.917(4), Li(1)···C(20) 2.690(6), C(1)–N(1)–Li(1) 121.11(16), C(2)–N(1)–Li(1) 115.31(16), C(1)–N(2)–C(5) 123.16(16), N(1)–C(1)–N(2) 134.96(18), N(2)–C(1)–C(8) 113.71(16), N(1)–C(1)–C(8) 111.18(16).

complexes [Li(tmeda){κ^1-N-(Pr^{i}N)$_2$C[C$_6$H$_3$(C$_6$H$_2$R$_3$-2,4,6)$_2$-2,6]}] R = Me or Pr^i [8,20]. The metal centre in **3**, however, also appears to have an interaction with one aromatic C-centre of the triptycene substituent [Li(1)–C(20) 2.690(6) Å], which although weak, is within the known range for Li-arene π-interactions [mean 2.446 Å] [21]. As was the case with the aforementioned terphenyl substituted lithium amidinate complexes, the low coordination number for the lithium centre in **3** is most likely due to the considerable steric bulk of its backbone C-substituent. This leads to a very short amidinate–Li bond [1.946(4) Å] which is effectively identical to the shortest previously reported example of such an interaction, i.e., 1.942(6) Å in [Li(tmeda){κ^1-N-(Pr^{i}N)$_2$C[C$_6$H$_3$(C$_6$H$_2$Me$_3$-2,4,6)$_2$-2,6]}] [20].

2.2. A tetraarylphenylene bridged bis-amidine and a lithium bis-amidinate

Bis-amidines and bis-amidinate ligands incorporating sterically bulky linking groups are rare. We believed the tetraarylphenylene, –{2,3,5,6-C$_6$(*p*-C$_6$H$_4$Bu^t)$_4$}–, would make an excellent linking group in the preparation of such compounds. As already mentioned, this linker has been used to good effect in the synthesis of low-coordinate phosphorus compounds, where steric bulk is critical in the stabilisation

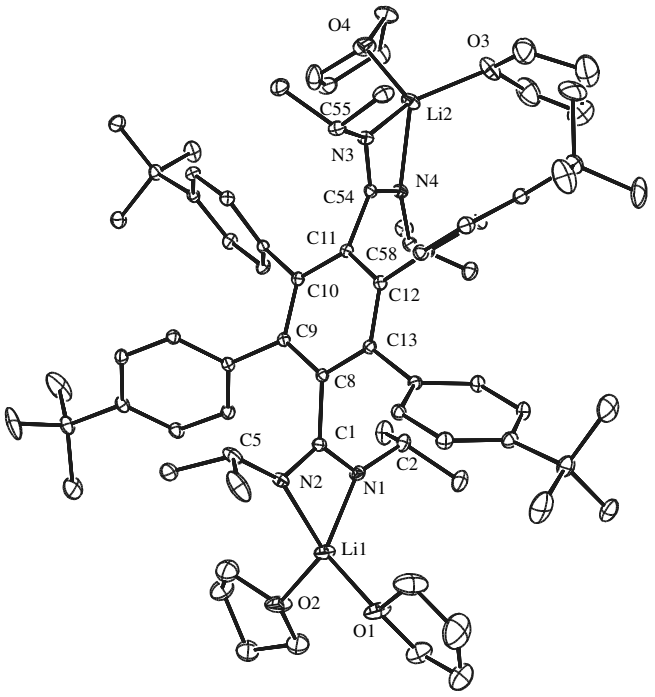


Fig. 3. Molecular structure of **6**. Selected bond lengths (Å) and angles (°): C(1)–N(1) 1.333(3), C(1)–N(2) 1.329(3), N(1)–Li(1) 2.003(5), N(2)–Li(1) 2.018(5), Li(1)–O(1) 1.973(5), Li(1)–O(2) 1.966(5), C(1)–C(8) 1.522(3), C(11)–C(54) 1.524(3), C(54)–N(3) 1.325(3), C(54)–N(4) 1.334(3), N(3)–Li(2) 1.983(5), N(4)–Li(2) 2.052(5), Li(2)–O(3) 1.943(5), Li(2)–O(4) 1.952(5), N(1)–C(1)–N(2) 116.1(2), C(1)–N(1)–Li(1) 87.90(19), C(1)–N(2)–Li(1) 87.4(2), N(1)–Li(1)–N(2) 68.36(15), N(1)–Li(1)–O(1) 120.9(3), O(1)–Li(1)–O(2) 103.8, N(3)–C(54)–N(4) 116.50(19), C(54)–N(3)–Li(2) 89.24(19), C(54)–N(4)–Li(2) 86.09(18), N(3)–Li(2)–N(4) 68.16(15), O(3)–Li(2)–O(4) 103.2(2).

of reactive phosphorus centres [18]. The reaction of the dilithium salt of the tetraarylphenylene ligand with two equivalents of *N*,*N*′-diisopropylcarbodiimide, followed by quenching with water, afforded the bis-amidine, **5**, in good yield (Scheme 1). Subsequent treatment of **5** with two equivalents of Bu^{n}Li in THF yielded the bis-amidinate complex, **6**, again in good yield after recrystallisation from THF.

The infrared spectrum of **5** displays N–H ($\nu = 3436\ cm^{-1}$) and C=N ($\nu = 1640\ cm^{-1}$) stretching absorptions in the expected region [19]. In solution, at 25 °C, the ^{1}H NMR spectrum of the compound exhibits only one very broad resonance at $\delta = 0.48$ ppm for the isopropyl methyl groups and two broad methine resonances at $\delta = 3.22$ and 3.65 ppm. This is presumably due to a fluxional interconversion between the *E-syn*:*E-syn* and *Z-syn*:*E-syn* isomers, as has been previously suggested for closely related systems, e.g., 1,4-$C_6H_4\{C(NHCy)(NCy)\}_2$ [11]. On cooling the NMR sample to −60 °C, three poorly resolved doublets are evident at $\delta = 0.30$, 0.49 and 0.57 ppm in an approximately 1:2:1 ratio, whilst the isopropyl methine resonances are still broad. This implies that the proposed fluxional process slows at this temperature, but not sufficiently to fully resolve the spectrum. Moreover, heating the NMR sample to 55 °C did not significantly sharpen the resonances observed at 25 °C. The ^{1}H NMR spectrum of **6** displays broad doublet and septet signals for the isopropyl methyl and methine protons, respectively. The broadness of these signals probably indicates a restricted rotation of the amidinate functions and/or their isopropyl substituents; a result of the bulky *p-tert*-butylphenyl groups on the aromatic linker unit.

Crystals of **5** were obtained from an ether solution but an X-ray crystal structure analysis of this compound gave poor data. Therefore, comment on metric parameters of this compound would not be valid. It is, however, clear from the low quality structure obtained that the compound exists as its *E-syn*:*E-syn* isomer in the solid state. Crystals of **6** suitable for X-ray diffraction were obtained from a THF solution and its molecular structure is depicted in Fig. 3. This shows the bis-amidinate to chelate two lithium centres which are additionally coordinated by two THF molecules to give them distorted tetrahedral geometries. The amidinate backbone C–N bond lengths are identical within experimental error at 1.33 Å (avge.), whilst the N–Li bond lengths are 2.014 Å (avge.). The average N–C–N and N–Li–N angles are 116.3° and 68.26°, respectively, and are typical for this type of complex. (cf. C–N = 1.328 Å avge.; Li–N = 1.996 Å avge.; N–C–N = 116.3(4)° and N–Li–N = 68.8(3)° in [Li(tmeda){(Pr^iN)$_2$C[C_6H_3(*p*-$C_6H_4Bu^t$)$_2$-2,6]}] [20].

3. Conclusion

In summary, we have reported the synthesis of a series of amidines and lithium amidinate complexes with the bulky triptycenyl moiety incorporated at the backbone carbon of the compounds. The steric influence of the triptycenyl group forces the *Z-syn* form of these compounds to be the only observed isomer in solution. A bis-amidine and its corresponding lithium bis-amidinate complex which include a sterically demanding tetraarylphenyl spacer have also been synthesised. In solution the amidine displays fluxional behaviour over a range of temperatures. The further coordination chemistry of these compounds will be reported in future publications.

4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. Toluene, THF and hexane were distilled over potassium, whilst diethyl ether was distilled over Na/K then freeze/thaw degassed prior to use. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DXP400 spectrometer operating at 400.13 and 100 MHz, respectively, or a Jeol Eclipse 300 spectrometer operating at 300.52 and 75.57 MHz, respectively, and were referenced to the residual ^{1}H or ^{13}C resonances of the solvent used. Mass spectra were obtained from the EPSRC National Mass Spectrometry Service at Swansea University (ESI). IR spectra were recorded using a Nicolet 510 FT-IR spec-

trometer as a Nujol mulls between NaCl plates. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. The complexes triptLi [22] and [1,4-Li_2\{2,3,5,6-C_6(p-$C_6H_4Bu^t$)$_4$\}] [18] were synthesized by literature methods. All other chemicals were purchased commercially and used as received.

4.1. [(tript)C(NPr^i)($NHPr^i$)] (1)

To a solution of triptLi (1.00 g, 3.84 mmol) in toluene (10 cm^3) was added a solution of $Pr^iN{=}C{=}NPr^i$ (0.66 g, 4.22 mmol) in diethyl ether (5 cm^3) at −78 °C over 5 min. The resulting solution was allowed to warm to room temperature and stirred for 12 h. Water (5 cm^3) was added and the mixture stirred for 2 h before volatiles were removed in vacuo. The residue was extracted with CH_2Cl_2 (50 cm^3), dried with $MgSO_4$ and filtered. The solvent was then removed under vacuum to yield a colourless solid which was recrystallised from hot hexane to give colourless crystals of **1** (1.14 g, 78%). M.p. 158–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 1.16 (d, $^3J_{HH} = 6.3$ Hz, 6H, CH_3), 1.36 (d, $^3J_{HH} = 6.1$ Hz, 6H, CH_3), 3.73 (sept, 1H, $^3J_{HH} = 6.3$ Hz, CH), 4.16 (sept, 1H, $^3J_{HH} = 6.1$ Hz, CH), 5.20 (s, 1H, C_3CH), 6.98 (m, 6H, Ar-H), 7.25 (m, 3H, Ar-H), 8.14 (m, 3H, Ar-H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 300 K): δ 25.2 (CH_3), 25.4 (CH_3), 46.2 (CH), 47.1 (CH) 55.0 (HCC_3), 123.2, 124.6, 125.1, 125.9, 145.5, 146.6 (Ar-C), 148.3 (NCN); MS/ES: m/z (%) 381 [MH^+, 100%]; IR (Nujol, cm^{-1}): ν 3388 (sh), 1651 (s), 1503 (s), 1454 (s), 1210 (m), 1182 (m), 1155 (m), 748 (s); accurate mass MS (ES) Calc. for MH^+: $C_{27}H_{29}N_2$: 381.2325; found: 381.2325.

4.2. [(tript)C(NCy)(NHCy)] (2)

A similar procedure to that used to synthesise **1** was used to prepare **2** (63%). M.p. 178–181 °C; ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 0.90–2.2 (m, 20H, Cy-CH_2) 3.45 (m, 1H, Cy-CH), 3.81 (m, 1H, Cy-CH), 4.26 (br., 1H, NH), 5.20 (m, 1 H, C_3CH), 6.91 (m, 6H, Ar-H), 7.24 (m, 3H, Ar-H), 8.14 (m, 3H, Ar-H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 300 K): δ 25.3, 25.4, 25.6, 26.1, 34.6, 35.9, 54.0, 55.1 (Cy), 56.2 (C_3CH), 60.4 (C_3CC), 123.2, 124.6, 125.0, 125.9, 145.7, 146.8 (Ar-C), 147.3 (NCN); MS ES: m/z (%) 461 [MH^+, 100%]; IR (Nujol, cm^{-1}): ν 3395 (sh), 1662 (s), 1507 (s), 1450 (s), 1376 (s), 1175 (m), 1152 (m), 1029 (m), 977 (w), 914 (w), 750 (s); accurate mass MS (ES) Calc. for MH^+: $C_{33}H_{37}N_2$: 461.2943; found: 461.2951.

4.3. [Li(THF)$_2$\{(tript)C(NPr^i)$_2$\}] (3)

To a solution of **1** (1.00 g, 2.62 mmol) in THF (20 cm^3) at −78 °C was added Bu^nLi (1.65 cm^3 of a 1.6 M solution in hexane) over 5 min. The resulting solution was allowed to warm to room temperature and stirred for 2 h. The mixture was concentrated to ca. 2 cm^3 and hexane added to precipitate **3** as a colourless powder. This was recrystallised from a THF solution (ca. 4 cm^3) placed at −35 °C overnight. (1.33 g, 93%). M.p. 112–120 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 0.88 (d, $^3J_{HH} = 6.3$ Hz, 6H, CH_3), 1.51 (m, 8H, THF), 1.60 (d, $^3J_{HH} = 6.1$ Hz, 6H, CH_3), 3.75 (m, 8H, THF), 4.03 (sept, 1H, $^3J_{HH} = 6.1$ Hz, CH), 4.26 (sept, 1H, $^3J_{HH} = 6.3$ Hz, CH), 5.26 (s, 1H, C_3CH), 7.01 (m, 3H, Ar-H), 7.12 (m, 3H, Ar-H), 7.33 (m, 3H, Ar-H), 8.60 (m, 3H, Ar-H); MS ES: m/z (%) 381 [(tript)C($NHPr^i$)$_2$]$^+$, 100%]; IR (Nujol, cm^{-1}): ν 1657 (m), 1544 (s), 1505 (m), 1454 (s), 1375 (m), 1347 (m), 1302 (m), 1288 (m), 1269 (m), 1209 (m), 1181 (m), 1151 (m), 1106 (m), 747 (s).

4.4. [Li(THF)$_2$\{(tript)C(NCy)$_2$\}] (4)

A similar procedure to that used to synthesise **3** was used to prepare **4** (84%). M.p. 260–264 °C (dec); ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 0.50–1.84 (m, 20H, Cy-CH_2), 1.24 (m, 8H, THF), 3.03 (m, 8H, THF), 3.74 (m, 1H, Cy-CH), 3.96 (m, 1H, Cy-CH), 4.97 (s, 1H, C_3CH), 6.62 (m, 3H, Ar-H), 6.73 (m, 3H, Ar-H), 6.96 (m, 3H, Ar-H), 8.65 (m, 3H, Ar-H); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 300 K): δ 24.6, 25.2, 26.7, 27.2, 35.2, 35.9, 55.3, 55.5 (Cy), 25.5 (THF), 56.1 (C_3CH), 60.6 (C_3CC), 67.5 (THF), 123.4, 124.5, 125.4, 126.4, 146.2, 147.1 (Ar-C), 147.8 (NCN); MS ES: m/z (%) 461 [(tript)C($NHCy)_2^+$, 100%]; IR (Nujol, cm^{-1}:ν 1663 (m), 1538 (s), 1452 (s), 1377 (m), 1303 (m), 1267 (m), 1152 (w), 1072 (s), 1043 (s), 888 (m), 749 (s).

4.5. [1,4-\{(Pr^iHN)(Pr^iN)C\}$_2$\{2,3,5,6-C_6(p-$C_6H_4Bu^t$)$_4$\}] (5)

To a solution of 1,4-Li_2\{2,3,5,6-C_6(p-$C_6H_4Bu^t$)$_4$\} (made in situ from 1,4-I_2\{2,3,5,6-C_6(p-$C_6H_4Bu^t$)$_4$ (1.00 g, 1.16 mmol) and Bu^nLi (3.0 cm^3 of a 1.6 M solution in hexane)) at −78 °C was added a solution of $Pr^iN{=}C{=}NPr^i$ (0.40 cm^3, 2.55 mmol) in THF (30 cm^3) over 5 min. The resulting solution was allowed to warm to room temperature and stirred for 12 h. Water (5 cm^3) was then added and the mixture stirred for 2 h. Volatiles were removed in vacuo and the residue extracted with CH_2Cl_2 (50 cm^3), filtered and volatiles removed in vacuo to give a colourless solid. This was recrystallised from hexane to yield **5** as colourless crystals (0.74 g, 75%). M.p. 265–268 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 0.58 (br, 24H, CH_3), 1.17 (s, 36H, Bu^t), 3.22 (br, CH), 3.65 (br, CH), 7.00–7.51 (br. m, 16H, ArH); MS/ES: m/z (%) 859 [MH^+, 100%]; IR (Nujol, cm^{-1}): ν 3436 (m), 1640 (s), 1510 (m), 1460 (m), 1377 (s), 1362 (s), 1323 (m), 1268 (m), 1222 (m), 1201 (w), 1176 (m), 1102 (m),702 (m); accurate mass MS (ES) Calc. for MH^+: $C_{60}H_{83}N_4$: 859.6612; found: 859.6625.

4.6. [1,4-\{Li(THF)$_2$(Pr^iN)$_2$C\}$_2$\{2,3,5,6-C_6-(p-$C_6H_4Bu^t$)$_4$\}] (6)

To a solution of **5** (1.00 g, 1.16 mmol) in THF (20 cm^3) at −78 °C was added Bu^nLi (1.50 cm^3 of a 1.6 M solution

Table 1
Crystal data for compounds **1**, **3** and **6** · THF

	1	**3**	**6** · THF
Chemical formula	$C_{27}H_{28}N_2$	$C_{35}H_{43}N_2LiO_2$	$C_{80}H_{120}Li_2N_4O_5$
Formula weight	380.51	530.65	1231.68
T (K)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2(1)/n$	$P2(1)/c$	$P\bar{1}$
a (Å)	13.448 (3)	11.492(2)	13.881(3)
b (Å)	11.908(2)	14.828(3)	14.374(3)
c (Å)	13.767(3)	18.034(4)	22.602(5)
α (°)	90	90	95.42(3)
β (°)	108.03(3)	93.43(3)	103.23(3)
γ (°)	90	90	110.48(3)
V (Å^3)	2096.4(7)	3067.5(11)	4036.5(14)
Z	4	4	2
μ(Mo Kα) (mm^{-1})	0.070	0.070	0.061
Reflections collected (R_{int})	16931 (0.0921)	15514 (0.0717)	66564 (0.0782)
Unique reflections $R_1(I > 2\sigma(I))$	4257 0.0549	5550 0.0571	15800 0.0797
wR_2 (all data)	0.1325	0.1268	0.2319

in hexane) over 5 min. The resulting solution was allowed to warm to room temperature and stirred for 2 h. The mixture was concentrated to ca. 2 cm^3 and hexane added to precipitate **6** as a colourless powder. This was recrystallised from THF (ca. 5 cm^3) after placement at −35 °C overnight (1.16 g, 84%). M.p. 260–264 °C (dec);^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 0.75 (br, d, $^3J_{HH}$ = ca. 6 Hz, 24H, CH_3), 1.15 (s, 36H, Bu^t), 1.24 (m, 16H, THF), 3.56 (m, 16H, THF), 4.02 (br., sept, $^3J_{HH}$ = ca. 6 Hz, 4H, CH), 7.08–7.52 (m, 16H, Ar-H); ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 25.2 (CH_3), 25.3 (THF), 31.1 (Bu^t), 34.1 (Bu^t), 41.8 (CH), 49.7 (THF), 123.9, 124.2, 130.8, 131.4, 137.1, 140.1 (Ar-C), 149.3 (NCN); MS/ES: *m/z* (%) 859 [(Pr^{i}HN)(Pr^{i}N)C}$_2${2,3,5,6-C$_6$(p- $C_6H_4Bu^t)_4H^+$, 100%]; IR (Nujol, cm^{-1}: *v* 1642 (s), 1510 (m), 1459 (m), 1362 (m), 1331 (m), 1269 (m), 1177 (m), 1133 (w), 1111 (w), 668 (m).

4.7. Crystallographic studies

Crystals of **1**, **3** and **6** suitable for X-ray crystal structure determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97) [23] using all unique data. Crystal data, details of data collections and refinement are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **1**, **3** and **6** have been deposited with the Cambridge Crystallographic Data Centre **1**: CCDC No. 279261; **3**: CCDC No. 279262; **6**: CCDC No. 279263. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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