FULL PAPER

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Structures and reactions of monomeric and dimeric lithium diazapentadienyl complexes with electrophiles: synthesis of α-*C,C′*-dialkyl-β-diimines, and dissolution-reversible synthesis of an α-alkoxylithium-β-diimine

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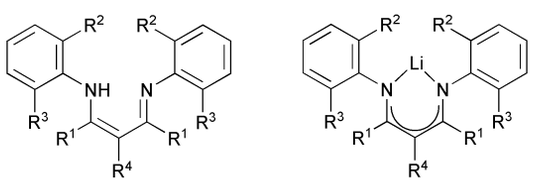
Received 6th December 2002, Accepted 31st January 2003
First published as an Advance Article on the web 20th February 2003

Direct acid-catalysed condensation of substituted anilines with acetylacetone was found to give convenient access to β-enamineimines [2-Pr^i-C_6H_4NCMeCHCMeNH-2-Pr^i-C_6H_4] and [2-MeO-C_6H_4NCMeCHCMeNH-2-MeO-C_6H_4], whereas $TiCl_4$-mediated condensation was required to produce [2,6-Pr$^i_2$-C_6H_3NHC(CF_3)CHC(CF_3)N-2,6-Pr$^i_2$-C_6H_3], which was crystallographically characterized. All are conveniently metallated using Bu^{n}Li. The structures of monomer [2-Pr^i-C_6H_4NCMeCHCMeN-2-Pr^i-C_6H_4·Li(thf)$_2$], and dimer [{ 2-MeO-C_6H_4NCMeCHCMeN-2-MeO-C_6H_4·Li}$_2$] are reported. The structure of the dimeric product of aldol addition of adamantan-2-one to [2-Pr^i-C_6H_4NCMeCHCMeN-2-Pr^i-C_6H_4·Li.], the lithium scorpionate [{($C_{10}H_{14}$OLi)CH(CMeN-2-Pr^i-C_6H_4)$_2$}$_2$], is also reported. It undergoes retro-aldol dissociation upon dissolution in non-co-ordinating solvents. The efficient synthesis of α-*C,C′* dialkylated 'true' β-diimines by repeat lithiation/alkylation of di- and mono-*ortho*-isopropylanilino diketiminates is also reported. The differing reactivity of the monomers and dimer with electrophiles, and its relation to the structures of the intermediates, are discussed.

Introduction

Since the first diketiminate complexes appeared in 1968,[1] there has been sporadic use of this ligand class, otherwise known as diazapentadienyl, vinamidine, β-iminatoaminate *etc*., in many different scenarios.[2] However, the introduction of diaryl diketiminates possessing extreme *ortho* bulk in 1997,[3] followed rapidly by the first demonstrations of their use as N–N bidentate, monoanionic ligands of remarkable steric control in 1998,[4] prompted a relative explosion of effort in the field: The ligand has enabled significant milestones to be reached across the Periodic Table.[5] Different chemistry can be effected with subtle changes of steric demand in the R^1, R^2 and R^3 positions,[6] but so far the ligands have been adopted overwhelmingly as inert manifolds on which to hang unusual chemistry.[2,5] Only recently has effort been directed at manipulations at position R^4. Chlorination of **2a** at R^4 has recently been demonstrated[7] to give **1d**, and a copper variant of the less bulky **2e** has also been reported, though its synthesis was somewhat different.[8] A photochemical rearrangement of a $Pt^{IV}Me_3^+$ complex of deprotonated **1a** led to methylation at R^4.[9] Continuing this theme of investigating the reactions of species **2**, rather than their employment as spectator ligands, we report here our studies of the reactions of **2** with electrophiles, and attempt to rationalise these on the basis of structural characterizations of further examples of **2** while varying steric, electronic and functional characteristics. This we have achieved by employing trifluoromethyl substitution at position R^1, thus introducing a fluorinated version (**1f**) of the most widely used variant **1a**, and by leaving R^2 unsubstituted while employing isopropyl and methoxy substituents in position R^3 to generate reactants **1c** and **1g** and their lithiated complexes **2c** and **2g**. We also extend discussion of some previously communicated results on use of adamantanone as the electrophile.[10] Finally, we report the efficient α-*C,C′*-dialkylation of **2a** and **2c** to yield 'true' β-diimines, devoid of α-C acidity or imino-azaenol tautomerism.



1 **2**

1,2a: R^1 = Me; R^2,R^3 = Pr^i; R^4 =H
1,2b: R^1 = Bu^t; R^2,R^3 = Pr^i; R^4 =H
1,2c: R^1 = Me; R^2 = H; R^3 = Pr^i; R^4 =H
1,2d: R^1 = Me; R^2 = Pr^i; R^3 = Pr^i; R^4 =Cl
1,2e: R^1, R^2, R^3 = H, R^4 = NO_2
1,2f: R^1 = CF_3; R^2, R^3 = Pr^i; R^4 =H
1,2g: R^1 = Me; R^2 = H; R^3 = OMe; R^4 =H

Experimental

All manipulations requiring dry conditions were carried out under a protective argon blanket, either in a double manifold argon/vacuum line or argon-filled recirculating glovebox. Argon was dried over phosphorus pentoxide supported on vermiculite. Toluene, n-hexane and thf were used freshly distilled under argon from sodium–benzophenone; acetonitrile and dichloromethane from calcium hydride. 2,6-Diisopropylaniline and 2-isopropylaniline were distilled from potassium hydroxide prior to use. $CDCl_3$ and hexamethylphosphoramide (CAUTION: suspected carcinogen) were stored over 4 Å molecular sieves. The hexane solution of Bu^{n}Li was used as received and standardised using *N*-benzylbenzamide.[11] For cryoscopy, spectrograde benzene was dried with freshly activated molecular sieves 3Å and standardised using benzil to an experimental cryoscopic constant of 5.04. Meaurements were made under argon in an air-jacketed Schlenk tube fitted with a Beckman thermometer and placed in a cooling bath held at 0 °C.

Enamine-imine **1a** was synthesised by a literature method.[4] All other reagents were obtained from standard commercial vendors and used as received.

Melting points were determined in sealed glass capillaries under argon. Elemental analyses were performed by the microanalytical group in the Chemistry Department at UMIST.

DOI: 10.1039/b212079h

^{1}H NMR solution spectra were recorded on Bruker DPX 200 MHz, 300 MHz and 400 MHz NMR spectrometers. ^{13}C{^{1}H} NMR solution spectra were recorded on a Bruker DPX 300 or 400 MHz spectrometer operating at 75 or 100 MHz respectively. Chemical shifts are given in ppm and referenced to residual H solvent shifts or ^{13}C-NMR solvent shifts. Assignments were made with the aid of DEPT and HMQC experiments. Solid-state NMR spectra were acquired on a Bruker AMX400WB spectrometer system operating at 100.6 MHz interfaced to Bruker temperature control and spinning units. All experiments were performed using Bruker double resonance MAS probes fitted with 4 mm spinning modules. Samples were contained in zirconia MAS rotors fitted with Kel-F caps and were spun at MAS frequencies of between 3 and 11 kHz at ambient temperature.

Infrared spectra were recorded on a Nicolet Nexus-FTIR/Raman spectrometer using NaCl plates and Nujol mulls. Raman spectra were recorded from powdered samples in Lindemann capillaries using the same instrument.

2-(2-Isopropyl)phenylamino-4-(2-isopropyl)phenyliminopent-2-ene (1c)

In a modification of a literature procedure,[12] a solution of 2,4-pentanedione (9.48 ml, 92.03 mmol), 2-isopropylaniline (25.50 ml, 184.07 mmol) and toluene (*ca*. 120 ml) was prepared. A catalytic amount of *para*-toluenesulfonic acid was added and the resultant mixture was heated under reflux for 7 h. The water (≈ 3.3 ml) produced in the reaction was collected in a Dean–Stark apparatus as a toluene azeotrope. The majority of the toluene (≈ 100 ml) was then removed from the reaction by distillation into the Dean–Stark arm and the remaining mixture was triturated with methanol and filtered to yield a cream crystalline solid, **1c**. Cooling the toluene/methanol filtrate to −25 °C yielded further cream crystals; mp: 105–108 °C. Combined yield: 17.65 g, 57%. ^{1}H NMR (200 MHz; $CDCl_3$): δ 1.22 (12H, d, $^{3}J_{HH}$ = 7.0 Hz, *Me*CH*Me*); 1.95 (6H, s, NC*Me*CHC*Me*N); 3.25 (2H, septet, $^{3}J_{HH}$ = 7.0 Hz, MeC*H*Me); 4.96 (1H, s, NCMeC*H*CMeN); 6.92–7.38 (8H, non-first-order m, aromatic protons); 12.53 (1H, br s, N*H*). ^{13}C NMR (75 MHz; $CDCl_3$): δ 21.2 (NC*Me*CHC*Me*N); 23.6 (*Me*CH*Me*); 28.5 (Me*C*HMe); 96.6 (NCMe*C*HCMeN); 124.3, 124.7, 125.9 and 126.2 (aromatic CH); 142.0 (*C*(CH(Me)$_2$), aromatic C); 143.7 (*C*–NH, aromatic C); 160.4 (*C*=N). Elemental analysis, Calcd. for $C_{23}H_{30}N_2$: C, 82.6; H, 9.0; N, 8.4. Found: C, 82.6; H, 9.1; N, 8.4%. IR: 1628 cm^{-1} (s, *v*(C=N)), 1557 cm^{-1} (s, *v*(C=C, aromatic)).

2-(2-Methoxy)phenylamino-4-(2-methoxy)phenylimino-pent-2-ene (1g)

A solution of 2,4-pentanedione (25 mL, 0.24 mol), 2-methoxyaniline (60 mL, 0.53 mol) and toluene (150 ml) was prepared. A catalytic amount of *para*-toluenesulfonic acid was added and the resultant mixture was heated under reflux for 4 h with a Dean–Stark trap, protected from the atmosphere by a drying tube. The water (8 ml) produced in the reaction was continuously removed as a toluene azeotrope. The majority of the toluene (≈ 130 ml) was then removed from the reaction by distillation into the Dean–Stark arm and the remaining brown oil crystallized on cooling to room temparature. The semi-solid mass was triturated with a small amount of methanol, filtered, washed with cold methanol, and recrystallized from methanol/hexane (4 : 1) to furnish 12.99 g (87.3%) of **1g** as pale yellow plates; mp: 129–130 °C. ^{1}H NMR (300 MHz; $CDCl_3$): δ 2.00 (6H, s, NC*Me*CHC*Me*N); 3.89 (6H, s, *Me*O); 4.94 (1H, s, NCMeC*H*CMeN); 6.88–7.28 (8H, non-first-order m, aromatic protons); 12.75 (1H, br s, N*H*). ^{13}C NMR (75 MHz; $CDCl_3$): δ 21.5 (NC*Me*CHC*Me*N); 56.1 (*Me*O); 98.3 (NCMe*C*HCMeN); 111.9, 120.9, 123.4 and 124.0 (aromatic CH); 135.8 (*C*OMe, aromatic C); 151.7 (*C*–NH, aromatic C); 160.4 (*C*=N). Elemental analysis, Calcd. for $C_{19}H_{22}N_2O_2$: C, 73.5; H, 7.1; N, 9.0. Found: C, 73.7; H, 7.2; N, 9.0%. IR: 1630 cm^{-1} (s, *v*(C=N)), 1555 cm^{-1} (s, *v*(C=C, aromatic)).

1,1,1,5,5,5-Hexafluoro-2-(2,6-diisopropyl)phenylamino-4-(2,6-diisopropyl)phenyliminopent-2-ene (1f)

A solution of 2,6-diisopropylaniline (28.3 ml, 150 mmol) in dry hexane (*ca*. 100 ml) was prepared under argon. Titanium tetrachloride diluted in dry hexane (16 ml, 3.42 M, 54.7 mmol) was added dropwise to the stirring solution of 2,6-diisopropylaniline at 0 °C. A dense yellow-brown precipitate formed immediately. The mixture was left to stir for 12 h under argon. 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (3.5 ml, 25 mmol) was then added dropwise to the mixture which turned orange-brown. After heating under reflux for 2 h, the mixture became yellow-brown. Titanium dioxide was removed by filtration and 2,6-diisopropylaniline hydrochloride was removed by carrying out a water/hexane extraction. The bright yellow-orange hexane phase was reduced in volume and triturated with methanol to yield a bright yellow crystalline solid, **1f**, that was filtered off and vacuum dried. Large yellow hexagonal-prism-shaped crystals were grown from the filtrate at −25 °C; mp: 154–156 °C. Yield: 3.42 g, 26%. ^{1}H NMR (200 MHz; $CDCl_3$): δ 1.15 (12H, d, $^{3}J_{HH}$ = 6.8 Hz, *Me*CH*Me*); 1.27 (12H, d, $^{3}J_{HH}$ = 6.8 Hz, *Me*CH*Me*); 2.99 (4H, septet, $^{3}J_{HH}$ = 7.0 Hz, MeC*H*Me); 5.84 (1H, s, NC(CF_3)C*H*C(CF_3)N); 7.13–7.31 (6H, non-first-order m, aromatic protons); 11.20 (1H, br s, N*H*). ^{13}C NMR (75 MHz; $CDCl_3$): δ 23.1 (*Me*CHMe); 25.4 (MeCH*Me*); 28.9 (Me*C*HMe); 87.6 (NC(CF_3)*C*HC(CF_3)N); 118.2 (q, $^{1}J_{CF}$ = 286 Hz, NC(*C*F_3)CHC(*C*F_3)N); 123.6 and 127.0 (aromatic carbons); 138.0 (*C*–N, aromatic C); 142.0 (*C*(CH(Me)$_2$)); 150.8 (q, $^{2}J_{CF}$ = 30.2 Hz, N*C*(CF_3)CH*C*(CF_3)N). ^{19}F NMR (188 MHz, $CDCl_3$): δ −65.9 (NC(C*F*$_3$)CHC(C*F*$_3$)N). Elemental analysis, Calcd. for $C_{29}H_{36}F_6N_2$: C, 66.1; H, 6.9; N, 5.3; F, 21.6. Found: C, 66.2; H, 6.6; N, 5.4; F, 21.3%. IR: 1642 cm^{-1} (s, *v*(C=N)).

Lithiation of 1c: 2c·2thf

To **1c** (1.46g, 4.4 mmol) in thf (4 mL) and n-hexane (5 mL) was added Bu^{n}Li in hexanes (1.75 ml of a 2.5 M solution, 4.4 mmol) with ice cooling. The solution was evacuated to *ca*. 4 ml volume and rediluted with hexane (2 ml). Overnight refrigeration yielded a crop of colourless rhomboids, which were isolated by vacuum filtration, upon which solvent was lost from the crystal lattice. Yield: 1.68 g. mp: 74–76 °C. ^{1}H NMR (300 MHz; C_6D_6): δ 1.35 (20H, overlapping m, *Me*CH*Me*, O(CH_2CH_2)$_2$); 2.09 (6H, s, NC*Me*CHC*Me*N); 3.36 (8H, t, O(*CH*$_2$CH$_2$)$_2$); 3.55 (2H, septet, $^{3}J_{HH}$ = 6.8 Hz, MeC*H*Me); 5.05 (1H, s, NCMeC*H*CMeN); 7.00 (2H, dd, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, aryl 2-H); 7.12 (2H, td, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, aryl 3-H); 7.21 (2H, td, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, aryl 4-H); 7.37 (2H, dd, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, aryl 4-H). ^{13}C NMR (75 MHz, C_6D_6): δ 23.6, Me*C*HMe); 24.1 (NC*Me*CHC*Me*N); 25.8 (O(CH_2CH$_2$)$_2$); 28.9 (*Me*CH*Me*); 68.2 (O(*C*H$_2$CH$_2$)$_2$); 94.0 (NCMe*C*HCMeN); 122.8, 124.7, 125.1, 126.0 (aromatic *C*H); 141.6 (*C*(CH(Me)$_2$), aromatic C); 153.4 (aromatic *C*–N); 163.3 (*C*=N). Elemental analyses were variable (solvent loss).

Lithiation of 1g: (2g)$_2$

To a suspension of **1g** (1.59 g, 5.12 mmol) in n-hexane (10 ml) at 0 °C was added Bu^{n}Li (2.1 ml of a 2.5M solution in toluene) with stirring. The mixture was heated to boiling, whereupon a slightly turbid orange solution formed. Stirring was ceased, and the solution deposited yellow crystals on slow cooling to room temperature. These were isolated by filtration to yield 0.984 g (60.7%) of **2g**; mp: 177–179 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 2.10 (6H, s, NC*Me*CHC*Me*N); 3.11 (6H, s, O*Me*); 5.00 (1H, s, NCMeC*H*CMeN); 6.06 (d), 6.85 (t), 6.95 (t), 7.05 (d), all 2H, $^{3}J_{HH}$ = 7.5 Hz, aromatic CH. ^{13}C NMR (75 MHz, C_6D_6): δ 24.0

(NC*Me*CHC*Me*N); 55.1 (O*Me*); 102.6 (NCMe*C*HCMeN); 110.6, 121.3, 121.7, 125.1 (aromatic CH); 143.4 (MeO*C*); 152.3 (aromatic *C*–N); 164.2 (*C*=N). Elemental analysis, Calcd. for $C_{19}H_{21}N_2O_2Li$: C, 72.1; H, 6.7; N, 8.8. Found: C, 76.2; H, 6.6; N, 5.4%.

Cryoscopy. Addition of **2g** (0.275 g) to 25 ml of benzene (0.0348 M solution, expressed as monomer) depressed its freezing point by 0.149 ± 0.002 °C, corresponding to an average molecular weight of 425.7 ± 10, association state of 1.3.

2,4-(2-Isopropylphenylimino)-3,3-dimethylpentane (3ca)

Bu^{n}Li (5.26 ml of a 1.42 M hexane solution, 7.49 mmol) was added dropwise to a stirring solution of **1c** (2.50 g, 7.47 mmol) in hexane (40 ml) at 22 °C. The solution turned bright yellow. Methyl iodide (0.49 ml, 7.47 mmol) diluted in hexane (6.71 ml) was then added at 0 °C and the resultant mixture was allowed to warm to 22 °C with stirring. After 1 h a dense white precipitate had formed and the yellow colouration had disappeared. The mixture was stirred for a further 4 h. A further 5.25 ml of 1.42 M Bu^{n}Li in hexane was then added which turned the mixture yellow. The mixture was again cooled to 0 °C and a further 7.20 ml of methyl iodide/hexane solution was added. The resultant mixture was allowed to return to 22 °C and stirred overnight under argon after which time the yellow colouration had disappeared and a large amount of white precipitate had formed. A water/hexane extraction was carried out to isolate **3ca** in the hexane fraction. The hexane fraction was dried using anhydrous $MgSO_4$ and the hexane was evaporated, yielding a pale brown oil. A hexane solution of the oil yielded large colourless crystals of **3ca** after *ca*. 7 days at −25 °C. However, the yield was poor due to the high solubility of the β-diimine in hexane. Recrystallisation from methanol gave a higher yield. Yield: 1.95 g, 72%; mp: 64–66 °C. ^{1}H NMR (200 MHz; $CDCl_3$): δ 1.21 (12H, d, $^3J_{HH}$ = 7.0 Hz, *Me*CH*Me*); 1.60 (6H, s, NCMeC(*Me*)$_2$CMeN); 1.85 (6H, s, NC*Me*C(Me)$_2$C*Me*N); 2.98 (2H, septet, $^3J_{HH}$ = 7.0 Hz, MeC*H*Me); 6.51–6.57 and 7.04–7.35 (8H, non-first-order m, aromatic protons). ^{13}C NMR (75 MHz; $CDCl_3$): δ 17.2 (NC*Me*C(Me)$_2$C*Me*N); 23.2 (*Me*CH*Me*); 24.3 (NCMeC(*Me*)$_2$CMeN); 28.4 (Me*C*HMe); 54.8 (NCMe*C*-(Me)$_2$CMeN); 118.6, 123.9, 126.0 and 126.5 (aromatic CH); 138.1 (*C*(CH(Me)$_2$), aromatic C); 149.2 (*C*–N, aromatic C); 173.6 (*C*=N). Elemental analysis, Calcd. for $C_{25}H_{34}N_2$: C, 82.8; H, 9.5; N, 7.7. Found: C, 82.9; H, 9.8; N, 7.9%. IR: 1645 cm^{-1} (s, ν(C=N)), 1593 cm^{-1} (s, ν(C=C, aromatic)).

Other β-diimines were prepared similarly.

2,4-(2,6-Diisopropylphenylimino)-3,3-dimethylpentane (3aa). Using **1a** and MeI, crystals from hexane solution at −25 °C; mp: 104–106 °C. Yield: 2.16 g, 81%. ^{1}H NMR (200 MHz; $CDCl_3$): δ 1.20 and 1.22 (12H + 12H, two d overlapped, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH'}$ = 6.8 Hz, *Me*CH*Me*); 1.66 (6H, s, NCMeC(*Me*)$_2$-CMeN); 1.79 (6H, s, NC*Me*C(Me)$_2$C*Me*N); 2.84 (4H, septet, $^3J_{HH}$ = 6.8 Hz, MeC*H*Me); 7.01–7.20 (6H, non-first-order m, aromatic protons). ^{13}C NMR (75 MHz; $CDCl_3$): δ 17.9 (NC*Me*C(Me)$_2$C*Me*N); 23.4 and 23.7 (*Me*CH*Me*); 24.8 (NCMeC(*Me*)$_2$CMeN); 28.3 (Me*C*HMe); 55.2 (NCMe*C*(Me)$_2$-CMeN); 123.3 and 123.7 (aromatic CH); 136.5 (*C*(CH(Me)$_2$); 146.2 (C–N, aromatic C); 174.4 (C=N). Elemental analysis, Calcd. for $C_{31}H_{46}N_2$: C, 83.3; H, 10.4; N, 6.3. Found: C, 83.2; H, 10.7; N, 6.5%. IR: 1647 cm^{-1} (s, ν(C=N)), 1590 cm^{-1} (s, ν(C=C, aromatic)).

2,4-(2-Isopropylphenylimino)-3,3-diethylpentane (3cb). Using **1c** and EtBr, crystals from hexane; mp: 87–89 °C. Yield: 2.30 g, 76%. ^{1}H NMR (200 MHz; $CDCl_3$): δ 1.21 (12H, d, $^3J_{HH}$ = 7.5 Hz, *Me*CH*Me*); 0.96 (6H, t, $^3J_{HH}$ = 7.0 Hz, NCMeC-(CH$_2$*Me*)$_2$CMeN); 1.82 (6H, s, NC*Me*C(Et)$_2$C*Me*N); 2.20 (4H, q, $^3J_{HH}$ = 7.5 Hz, NCMeC(C*H*$_2$Me)$_2$CMeN); 3.00 (2H, septet, $^3J_{HH}$ = 7.0 Hz, MeC*H*Me); 6.49–6.55 and 7.04–7.36 (8H, non-first-order m, aromatic protons). ^{13}C NMR (75 MHz; $CDCl_3$): δ 8.6 (NCMeC(CH$_2$*Me*)$_2$CMeN); 17.7 (NC*Me*C(Et)$_2$C*Me*N); 23.5 (*Me*CH*Me*); 23.8 (NCMeC(*C*H$_2$Me)$_2$CMeN); 28.3 (Me*C*HMe); 61.6 (NCMe*C*(Et)$_2$CMeN); 118.6, 123.9, 126.0 and 126.6 (aromatic CH); 138.0 (*C*(CH(Me)$_2$)); 149.4 (*C*–N); 172.7 (*C*=N). Elemental analysis, Calcd. for $C_{27}H_{38}N_2$: C, 83.0; H, 9.8; N, 7.2. Found: C, 83.3; H, 9.7; N, 7.2%. IR: 1645 cm^{-1} (s, ν(C=N)), 1595 cm^{-1} (s, ν(C=C, aromatic)).

2,4-(2,6-Diisopropylphenylimino)-3,3-diethylpentane (3ab). Using **1a** and EtBr. Crystals from hexane solution at −25 °C; mp: 142–144 °C. Yield: 1.68 g, 74%. ^{1}H NMR (200 MHz; $CDCl_3$): δ 1.2 (12H + 12H, two d overlapped, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH'}$ = 6.8 Hz, *Me*CH*Me*); 1.01 (6H, t, $^3J_{HH}$ = 7.5 Hz, NCMeC(CH$_2$*Me*)$_2$CMeN); 1.80 (6H, s, NC*Me*C(Et)$_2$C*Me*N); 2.32 (4H, q, $^3J_{HH}$ = 7.5 Hz, NCMeC(C*H*$_2$Me)$_2$CMeN); 2.81 (4H, septet, $^3J_{HH}$ = 6.8 Hz, MeC*H*Me); 7.04–7.21 (6H, non-first-order m, aromatic protons). ^{13}C NMR (75 MHz; $CDCl_3$): δ 9.0 (NCMeC(CH$_2$*Me*)$_2$CMeN); 18.1 (NC*Me*C(Et)$_2$C*Me*N); 23.5 and 23.9 (*Me*CH*Me*); 24.6 (NCMeC(*C*H$_2$Me)$_2$CMeN); 28.3 (Me*C*HMe); 62.3 (NCMe*C*(Et)$_2$CMeN); 123.4 and 123.6 (aromatic CH); 136.0 (*C*(CH(Me)$_2$), aromatic C); 147.0 (*C*–N, aromatic C); 173.1 (*C*=N). Elemental analysis, Calcd. for $C_{33}H_{50}N_2$: C, 83.5; H, 10.6; N, 5.9. Found: C, 83.6; H, 10.4; N, 6.0%. IR: 1640 cm^{-1} (s, ν(C=N)), 1590 cm^{-1} (s, ν(C=C, aromatic)).

2,4-(2-Isopropylphenylimino)-3,3-dibenzylpentane (3cc). Using **1c** and PhCH$_2$Br, crystals from hexane; mp: 91–93 °C. Yield: 2.96 g, 76%. ^{1}H NMR (200 MHz; $CDCl_3$): δ 1.14 (12H, d, $^3J_{HH}$ = 7.0 Hz, *Me*CH*Me*); 1.91 (6H, s, NC*Me*C(CH$_2$Ph)$_2$-C*Me*N); 2.65 (2H, septet, $^3J_{HH}$ = 7.0 Hz, MeC*H*Me); 3.70 (4H, s, NCMeC(C*H*$_2$Ph)$_2$CMeN); 6.20–6.30 and 7.01–7.49 (18H, non-first-order m, aromatic protons). ^{13}C NMR (75 MHz; $CDCl_3$): δ 18.9 (NC*Me*C(CH$_2$Ph)$_2$C*Me*N); 23.5 (*Me*CH*Me*); 28.1 (Me*C*HMe); 38.4 (NCMeC(*C*H$_2$Ph)$_2$CMeN); 63.0 (NCMe*C*(CH$_2$Ph)$_2$CMeN); 118.1, 124.1, 126.0, 126.6, 126.9, 128.6 and 130.8 (aromatic CH); 138.0 (*C*(CH(Me)$_2$), aromatic C); 138.9 (NCMeC(CH$_2$*Ph*)$_2$CMeN, substituted aromatic C); 148.8 (*C*–N, aromatic C); 171.4 (*C*=N). Elemental analysis, Calcd. for $C_{37}H_{42}N_2$: C, 86.3; H, 8.2; N, 5.4. Found: C, 86.4; H, 8.2; N, 5.5%. IR: 1636 cm^{-1} (s, ν(C=N)), 1595 cm^{-1} (s, ν(C=C, aromatic)).

2,4-(2,6-Diisopropylphenylimino)-3,3-dibenzylpentane (3ac). Using **1a** and PhCH$_2$Br, crystals from hexane; mp: 148–150 °C. Yield: 2.96 g, 69%. ^{1}H NMR (200 MHz; $CDCl_3$): δ 1.0 (12H + 12H, two d overlapped, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH'}$ = 7.0 Hz, *Me*CH*Me*); 1.86 (6H, s, NC*Me*C(CH$_2$Ph)$_2$C*Me*N); 2.22 (4H, septet, $^3J_{HH}$ = 7.0 Hz, MeC*H*Me); 3.94 (4H, s, NCMeC-(C*H*$_2$Ph)$_2$CMeN); 6.98–7.14, 7.31–7.43 and 7.54–7.63 (16H, non-first-order m, aromatic protons). ^{13}C NMR (75 MHz; $CDCl_3$): δ 19.2 (NC*Me*C(CH$_2$Ph)$_2$C*Me*N); 23.0 and 24.1 (*Me*CH*Me*); 28.1 (Me*C*HMe); 38.9 (NCMeC(*C*H$_2$Ph)$_2$-CMeN); 64.4 (NCMe*C*(CH$_2$Ph)$_2$CMeN); 123.3, 123.6, 127.2, 128.9 and 131.3 (aromatic CH); 135.7 (*C*(CH(Me)$_2$), aromatic C); 139.0 (NCMeC(CH$_2$*Ph*)$_2$CMeN, substituted aromatic C); 146.5 (*C*–N, aromatic C); 171.5 (*C*=N). Elemental analysis, Calcd. for $C_{43}H_{54}N_2$: C, 86.2; H, 9.1; N, 4.7. Found: C, 86.2; H, 9.4; N, 4.8%. IR: 1620 cm^{-1} (s, ν(C=N)), 1590 cm^{-1} (s, ν(C=C, aromatic)).

Attempted preparation of 2,4-(2-methoxyphenylimino)-3,3-dimethylpentane

To a suspension of **1g** (0.10 g, 0.32 mmol) in 10 ml n-hexane was added Bu^{n}Li (0.22 ml of a 1.45 M solution in hexanes), followed by hexamethylphosphoramide (0.12 ml, 0.64 mmol). To the resultant orange solution was added MeI (0.20 ml, 0.32 mmol) at rt. After 18 h stirring, further equimolar aliquots of Bu^{n}Li and MeI were added. A cloudy solution resulted. This

was taken up in hexane (5ml) and washed with water (3 × 5 ml), dried over $MgSO_4$ and filtered. Removal of solvent *in vacuo* yielded an oil which gave a very complex NMR spectrum. TLC on silica in 4 : 1 hexane/dichloromethane indicated components of R_f 0.77, 0.34 and streaking from 0 to 0.11. Flash chromatography on silica in the same solvent system gave two fractions, the first of which still contained numerous species. For example, there appeared to be seven methoxy proton resonances in the range 3.8–3.9 ppm. There was also a new peak at 2.8 ppm (*Me*N?). Other runs in thf or hexane produced even greater distributions of product. No further separation was attempted.

Lithium {2-[2-(2-isopropyl)phenylimino-1-(1-(2-isopropyl)-phenyliminoethyl)propyladamantan-2-olate} (4)

To a stirred suspension of **1c** (2.44 g, 7.3 mmol) in hexane (8 mL) in a Schlenk tube at 0 °C was added Bu^nLi (4.86 ml of a 1.51 M solution in hexanes, 7.3 mmol). Heat and butane were evolved. The resultant pale yellow solution was re-cooled to 0 °C with stirring, causing a pale cream, fine precipitate to form. To this was added adamantan-2-one (1.095 g, 7.3 mmol), which caused momentary dissolution of the precipitate, but solid re-precipitated upon stirring for 5 min. The suspension was evacuated to remove butanes and concentrated *in vacuo* to approximately 8 ml, then briefly heated to boiling to re-dissolve the precipitate. A crop of pale yellow blocks was deposited after standing overnight. These were isolated by filtration to yield 2.42 g (4.93 mmol, 68%) of **4**; mp: 76–78 °C. ^{1}H NMR (400 MHz; C_6D_6, 300K): δ 1.2–1.5 (24H, overlapping m, *Me*CH*Me* and adamantyl resonances); 1.85 (2H, apparent br s, adamantyl OC(C*H*)$_2$; 2.14 (6H, s, NC*Me*CH(Ad)C*Me*N); 3.68 (2H, sept, $^3J_{HH}$ = 7.0 Hz, MeC*H*Me); 5.20 (1H, s, NCMeC*H*(Ad)CMeN); 7.1–7.4 (8H, non-first-order m, aromatic protons). ^{1}H NMR in deuterohexane was also recorded. Though it was not possible to lock on the signal, and some field drift was present, the peaks were essentially the same. The alkenyl resonance (NCMeC*H*-(Ad)CMeN) shifted slightly upfield to 4.85 ppm. ^{13}C NMR (100 MHz; C_6D_6, 300 K): δ 23.8 (*Me*CH*Me*); 24.2 (NC*Me*CH-(Ad)C*Me*N); 27.5 (MeCHMe); 28.3 (adamantyl *C*H); 36.1, 39.5 (adamantyl CH_2) 47.3 (adamantyl OC(*C*H)$_2$), 94.7 (NCMe*C*H(Ad)CMeN); 122.8, 125.0, 126.0 and 126.4 (aromatic CH); 141.8 (*C*(CH(Me)$_2$), aromatic C); 153.3 (aromatic C–N); 163.7 (*C*=N); 227 (*C*O). Elemental analysis, Calcd. for $C_{33}H_{43}N_2OLi$: C, 80.8; H, 8.8; N, 5.7. Found: C, 79.6; H, 9.2; N, 5.4%. IR: 1650, 1626 cm^{-1} (s, ν(C=N), *syn* and *anti*), 1596 cm^{-1} (s, ν(C=C, aromatic)). Raman showed the same vibrations. On exposure of the IR plates to moist air, 3566 (sharp, LiOH), 1720 (C=O), 1628, 1556 (free **1c**) cm^{-1}. Attempts to collect data by dissolving **4** in freshly distilled hexane and injecting the solution into a pre-dried and flushed IR solution cell were thwarted by hydrolysis, as indicated by peaks in the 1720, 1628 and 1555 cm^{-1} regions.

Cryoscopy. Addition of 0.182 g of **4** to 25 ml of benzene (0.0148 M solution, expressed as monomer) depressed its freezing point by 0.092 ± 2 °C, corresponding to an average molecular weight of 456.3 ± 10, association state of 0.93; a 0.041 M solution gave an average molecular weight of 452.4 ± 10.

Solid state CP-MAS NMR. A powdered sample of **4** was packed into a rotor in a glovebox, and ^{13}C{^{1}H} spectra were recorded in portions over a time period of 12 h to check for decay. There was none, and so all data sets were combined to give a low-noise spectrum. Resolution was good, with symmetry inequivalent/chemically equivalent peaks often being resolved, though in some cases the two (or four) resonances overlapped with other groups of resonances, obscuring assignments: δ 20.5, 21.1 (*Me*CH*Me*); 24.5 (NC*Me*CH(Ad)C*Me*N); 25.1, 26.2, 26.6, 27.3, 28.8 (MeCHMe, adamantyl *C*H); 34.7, 36.3, 38.4, 41.1 (adamantyl CH_2, adamantyl OC(*C*H)$_2$), 62.5, 63.4 (NCMe*C*H(Ad)CMeN); 85.6, 91.4 (*C*O) 121.5, 122.0, 123.2, 124.3, 124.7, (aromatic CH); 136.1, 137.3, 138.2, 138.8 (*C*(CH(Me)$_2$), aromatic C); 148.6, 149.8 (aromatic C–N); 169.0, 170.6 (*C*=N); 180–230 ppm region totally silent.

Quenching experiments. *(a) Solution phase.* A crystalline lump of **4** (0.26 g) was removed from the glovebox, taken up in hexane (10 ml) and washed with distilled water (2 × 20 ml). The organic phase was separated, dried *in vacuo* and subjected to NMR analysis. Peaks corresponding to **1c** and adamantanone were observed. Using saturated aqueous NH_4Cl in place of pure water produced identical results.

(b) Solid phase. (i) In a glovebox, a sample of **4** (0.32 g) was ground in an agate mortar and pestle with solid anhydrous NH_4PF_6 (0.55 g, excess) for 15 minutes. The mixture was extracted into deuterobenzene and filtered through glass wool into an NMR tube. NMR analysis indicated resonances corresponding to **1c** and adamantanone.

(ii) In a glovebox, a sample of **4** (0.27 g) and Bu^tMe_2SiCl (0.35 g, excess) were ground as above for 15 minutes. The mixture fully dissolved in deuterobenzene, and exhibited NMR resonances corresponding to solutions of **4** plus Bu^tMe_2SiCl. No reaction had occurred.

X-Ray crystallography

The structures of **1f**, **2c**, **2g** and **4** were determined by X-ray crystallography. Crystals were selected from the mother-liquor and mounted using the oildrop method (Fomblin 1800 oil). Experimental parameters are summarized in Table 1.

CCDC reference numbers 199213 and 199312–199314.

See http://www.rsc.org/suppdata/dt/b2/b212079h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Enamineimine preparations

The direct acid-catalyzed condensation route from acetylacetone and the appropriate aniline by Dean–Stark azeotropic distillation which proceeded rapidly with modest though acceptable yields in the previously discussed[4] case of **1a** worked acceptably for **1c** and exceptionally well for the methoxy-substituted **1g**, resulting in an 87% yield after 4 hours of reaction. This provided a rapid and convenient route to the first *ortho*-functional, potentially tetradentate diiminate ligands. However, it did not proceed well for **1f**, the fluorinated variant of **1a**; at the temperature required to remove the water of condensation, the hexafluoroacetylacetone reactant was lost. An alternative means of encouraging condensation was required. Recently, it has been shown that a single CF_3 group could be introduced to diiminate ligands by a C–C coupling methodology[18] reminiscent of that used[6] to prepare the exceedingly bulky **1b**, which also is not accessible by means of direct condensation of 1,3-diketones with anilines. However, our preparation of the bulky, symmetrically fluorinated **1f** retained the condensation route, but facilitated reaction at lower temperature by reacting with a preformed titanium tetrachloride/diisopropylaniline mixture. Such mixtures are not well characterized in the case of diisopropylaniline, and resisted our attempts to remedy this situation, but in cases concerning other amines are known to contain amidotitanium and imidotitanium species.[19] These may be the true reacting species in the condensation used to prepare **1f**. The stoichiometry is explained in Scheme 1. A similar method has been used to prepare *N*,*N*′-cyclohexyl variants of **1**.[20]

Though the yield was not high, usable quantities of the fluorinated ligand are available by performing the reaction on a large scale.

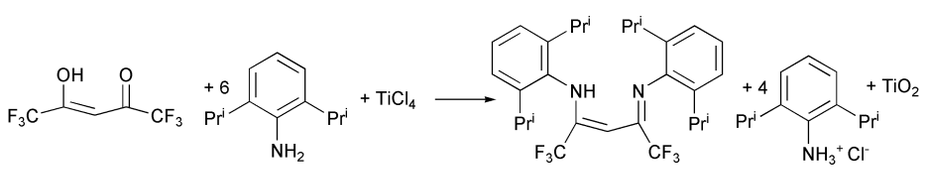
Table 1 X-Ray data collection and refinement details[a]

	1f	**2c**·2thf	**2g**	**4**
Formula	$C_{29}H_{36}F_6N_2$	$C_{35}H_{53}LiN_2O_3$	$C_{38}H_{42}Li_2N_4O_4$	$C_{66}H_{86}Li_2N_4O_2$
M	526.6	556.73	632.64	981.27
Crystal system	Monoclinic	Trigonal	Triclinic	Orthorhombic
a/Å	11.5857(10)	32.123(9)	10.6917(4)	10.6269(3)
b/Å	9.3714(10)	32.123(9)	11.8407(5)	22.2662(3)
c/Å	26.8363(10)	9.273(2)	15.3648(9)	23.8287(4)
α/°	(90)	(90)	77.010(2)	(90)
β/°	92.389(10)	(90)	85.387(2)	(90)
γ/°	(90)	(120)	66.242(2)	(90)
Space group (no.)	$P2_1/n$ (15)	$R\bar{3}m$ (160)	$P\bar{1}$ (2)	$P2_12_12_1$ (19)
Z	4	9	2	4
T/K	293	203	150	150
μ/mm^{-1}	0.097	0.062	0.078	0.068
Reflns. measd.	5173	5339	21314	37520
Reflns. obsd[b] (R_{int})	4916 (0.0139)	1817 (0.0682)	7179 (0.0748)	10524 (0.0603)
R_1(observed)	0.0571	0.0605	0.0592	0.0432
wR_2(all data)[c]	0.1482	0.1434	0.1619	0.0848

[a] Programs: Data collection: COLLECT,[13] DENZO-SMN,[14] SORTAV.[15] Solution and refinement: SHELXS-97[16] or SIR92,[17] SHELXL-97.[16] [b] $I = I > 2\sigma(I)$. [c] $wR_2 = \{\sigma[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]\}^{½}$.

Table 2 Selected bond lengths (Å) and angles (°) for **1f**

F(1/5)–C(1/5)	1.306–1.341(3–4)	C(1)–C(2)	1.500(4)
N(6)–C(2)	1.357(3)	C(2)–C(3)	1.363(4)
N(6)–C(7)	1.442(3)	C(3)–C(4)	1.429(3)
N(19)–C(4)	1.289(3)	C(4)–C(5)	1.531(4)
N(19)–C(20)	1.434(3)		
C(2)–N(6)–C(7)	129.6(2)	C(2)–C(3)–C(4)	124.8(2)
C(4)–N(19)–C(20)	125.9(2)	N(19)–C(4)–C(3)	121.3(2)
N(6)–C(2)–C(3)	124.2(2)	N(19)–C(4)–C(5)	125.3(2)
N(6)–C(2)–C(1)	117.6(2)	C(3)–C(4)–C(5)	113.3(2)
C(3)–C(2)–C(1)	118.1(2)		



Scheme 1

A structure of **1f** was obtained, and it is of interest to examine what effect, if any, the fluorination of the backbone has on the ligand. Examination of Fig. 1 (see also Table 2) reveals that the iminoenamine form exists in the crystal, and in this respect it is identical to its non-fluorinated analogue, **1a**.[21] Interestingly, the bulkier **1b** is known to adopt a true β-diimine form in the solid state.[22] The ligand core bond lengths show an alternating pattern consistent with the localized, though strongly hydrogen bonded, proton on N(1). There appears to be little significant structural effect caused by fluorination, the C–C and C–N distances of **1f** being closely comparable with those of **1a**, notably in the alternation of C–C and C–N lengths within the aminoenimine ring. The intramolecular hydrogen bond (freely refined) between the amine and imine nitrogens appears to be marginally weaker, the amino N–H distance being 0.88(4) and the imino N ··· H distance being 1.97(4) Å, *cf*. 0.97(4) and 1.86(4) Å respectively, for **1a**;[21] these differences are, however, within error. The most significant difference is to be found sterically: the fluorination of the backbone methyl groups causes increased repulsion of the aryl groups, squeezing the co-ordinating void of the ligand. This is manifested in C–N(H)–C angles of 130°, and C=N–C angles of 126°, which correspond to angles of 123° and 124° in the unfluorinated **1a**. In the yet bulkier **1b**,[22] the angles are more comparable with those in **1f**, but since the tautomer is different, the comparison is less revealing.

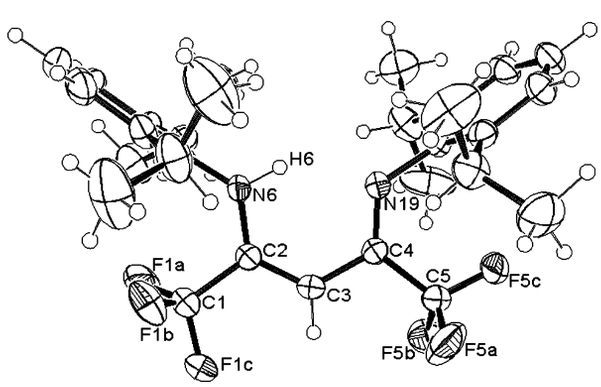


Fig. 1 ORTEP[46] diagram (40% probability) of **1f**.

While the structure of **1f** showed little change with respect to unfluorinated **1a**, its reactivity was considerably different. Successful alkylation experiments described below for **1a** and **1c** failed for **1f**. These, and further differences, were addressed by probing the structures of the lithiated intermediates.

Preparation and structures of lithium diazapentadienyl complexes

The preparation and structures of **2a** have already been recently reported by other workers.[21] It is known to exist in two unsolvated forms, one dimeric and one dodecameric, though it

Table 3 Selected bond lengths (Å) and angles (°) for **2c**

C(1)–N(1)	1.3121(17)	N(1)–Li(1)	1.955(2)
C(1)–C(2)	1.3979(13)	O(1)–Li(1)	1.994(3)
C(1)–C(3)	1.5110(16)	O(2)–Li(1)	1.947(3)
N(1)–C(1)–C(2)	123.88(10)	C(4)–N(1)–Li(1)	115.88(11)
N(1)–C(1)–C(3)	119.86(9)	O(2)–Li(1)–N(1)	122.61(10)
C(2)–C(1)–C(3)	116.26(12)	N(1)#1–Li(1)–N(1)	95.84(14)
C(1)–C(2)–C(1)#1	128.80(16)	O(2)–Li(1)–O(1)	102.98(15)
C(1)–N(1)–C(4)	121.93(9)	N(1)–Li(1)–O(1)	105.49(12)
C(1)–N(1)–Li(1)	121.42(9)		

Symmetry transformation used to generate equivalent atoms: #1 $-y+1, -x+1, z$.

is assumed that in solution monomers are present. From diethyl ether or thf, monomeric monosolvates with trigonal planar lithium environments are obtained,[21] as is the case with **2b**.[6] Complex **2c**, being less bulky, rapidly precipitates from hexane solution upon metallation with Bu^{n}Li, but crystals were obtained from a thf/hexane solution (Fig. 2, Table 3). The molecule crystallizes in the space group *R*3*m*; the trigonal packing arrangement generates channels which are occupied by disordered solvent. A further thf solvent is trapped along a crystallographic plane. These are predominantly lost upon isolation by vacuum filtration, but served to make elemental analysis figures irreproducible. It proved difficult to satisfactorily model all the solvent in the crystal, since the three-fold symmetry of the channel was difficult to reconcile with the five-membered ring of thf.[23] The NMR spectra confirm that both co-ordinated thf molecules survive the isolation procedure. The spectra indicate that, with regard to the isopropyl configurations, rapid equilibration of *syn* and *anti* conformers is occurring at room temperature. Low temperature studies were not attempted.

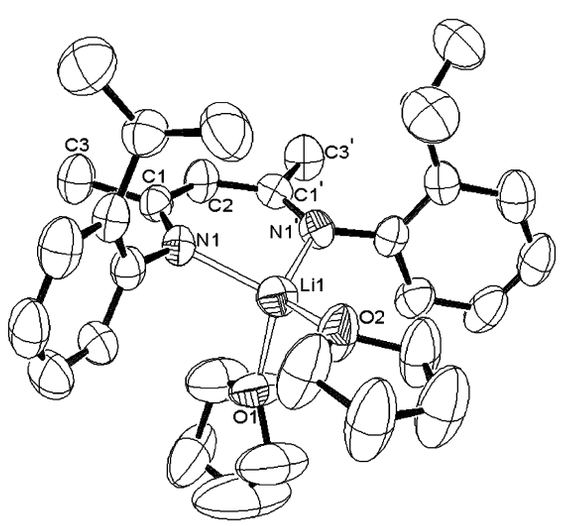


Fig. 2 ORTEP diagram (50% probability) of the monomer **2c**·2thf. Hydrogens, one contributor to thf disorder, and a further disordered non-co-ordinated solvent, are omitted for clarity. A crystallographic plane cuts through C(2), Li(1), O(1) and O(2).

A crystallographic plane bisects the molecule down the C(2)–Li(1)–O(2)–O(1) plane. It dictates the *syn* orientation of both isopropyl groups, and (indirectly) the perfect planarity of the diazapentadienyl ring and the thf containing O(2), to which it is perpendicular.

The structure of monomer **2c**·2thf appears to be similar in most respects to the previously published monomer **2a**·thf isolated from the same solvent,[21] save for the obvious difference that two molecules of thf are co-ordinated, rather than one, thus giving the lithium its favoured tetrahedral environment, though heavily distorted. This is in fact only the second lithium diazapentadienyl complex which has been established to be 4-co-ordinate, since high degrees of steric bulk tend to be employed. The first was a dimeric hexamethylphosphoramide-bridged structure, with unsubstituted phenyl groups.[24] In common with all structures derived from **1a** or **1b**, the aryls in **2c** lie almost perpendicular to the diazapentadienyl plane (the aryls are twisted only 7.9° from the perpendicular to the NCCCN plane). It is the *syn* arrangement of the isopropyl groups which generates the space for the second molecule of thf to bind. In fact, the lithium lies close (only 0.49 Å above) to the plane formed by O(2) and the two nitrogen atoms such that these atoms together almost form a basal plane, with the other thf occupying an 'axial' position. This plane is shared by the diazapentadienyl fragment and the equatorial thf in a manner which makes the mapping with the related diisopropylaryl structure **2a** very close. This is mirrored in the similarity of behaviour with respect to electrophiles, *vide infra*. While **1a** and **1b** have proved, by virtue of the shape of the ligating cavity of the anions, to be highly efficient in stabilizing unusual examples of trigonal planar co-ordination or bent di-co-ordination, the less bulky **1c** may be expected to offer frequent examples of heavily distorted tetrahedral co-ordination. Alternatively, the metal may distort out of the diazapentadienyl plane to give envelope conformations, which was the outcome in the homoleptic zinc complex which is the only other structurally characterized complex from **1c**.[12]

The reaction of **1f** with Bu^{n}Li in hexane produced a crop of small crystals of poor quality. A preliminary X-ray determination showed **2f** to be co-crystallized with **1f**, but the data are not of publishable standard. It did show that the lithium in **2f** was 2-co-ordinate monomeric, with none of the unusual oligomerization motifs of **2a**.

Lithiation of **1g** in hexane gave a good crop of crystalline **2g**, which has the dimeric solid-state structure depicted in Fig. 3. In this case, the single isopropyl substitution of **1c** has been replaced with the sterically similar though functionally different methoxy group, intended to act as an internal chelation site. As such, **2g** represents only the second structurally characterized tetradentate acyclic diketiminate ligand complex, the first being the recently reported $[\{N(CH_2CH_2NEt_2)C(Me)\}_2CH{\cdot}ScCl_2]$.[25]

There is a conflict between optimum co-ordination geometry at lithium and ideal bond lengths and angles within the ligand. This conflict is substantially resolved by dimerization (Fig. 3). One diazapentadienyl unit of the dimer (binding through N(1) and N(2)) has an *anti* configuration of 2-methoxy substituents,

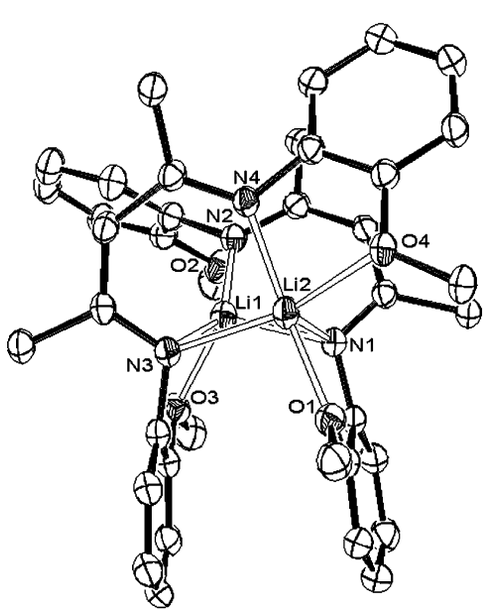


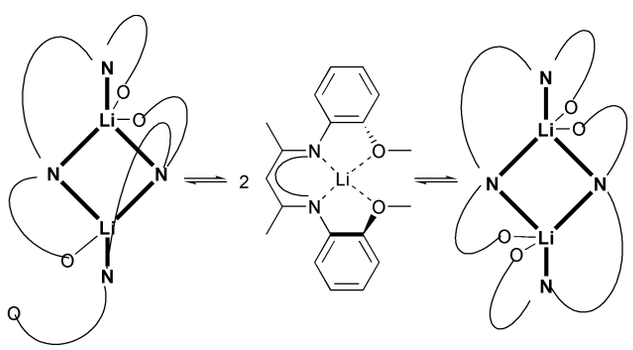
Fig. 3 ORTEP diagram (30% probability) of the cisoid dimer **2g**. Hydrogens are omitted for clarity.

Table 4 Selected bond lengths (Å) and angles (°) for **2g**

O(1)–Li(2)	2.000(4)	C(4)–C(5)	1.502(3)
N(1)–C(2)	1.356(3)	O(4)–Li(2)	2.168(3)
N(1)–Li(1)	2.009(4)	N(3)–C(21)	1.343(2)
N(1)–Li(2)	2.151(4)	N(3)–C(25)	1.430(3)
N(2)–C(4)	1.317(3)	N(3)–Li(2)	2.148(3)
N(2)–Li(1)	1.898(4)	N(4)–C(23)	1.325(2)
O(3)–Li(1)	1.997(4)	N(4)–Li(2)	1.995(4)
N(3)–Li(1)	2.085(4)	C(20)–C(21)	1.512(3)
Li(1)–Li(2)	2.432(5)	C(21)–C(22)	1.389(3)
C(1)–C(2)	1.520(3)	C(22)–C(23)	1.415(3)
C(2)–C(3)	1.376(3)	C(23)–C(24)	1.505(3)
C(3)–C(4)	1.423(3)		
N(2)–Li(1)–N(3)	143.2(2)	C(25)–N(3)–Li(1)	104.03(16)
O(3)–Li(1)–N(3)	82.01(15)	C(21)–N(3)–Li(2)	121.69(15)
N(1)–Li(1)–N(3)	104.36(18)	C(25)–N(3)–Li(2)	115.71(14)
N(1)–C(2)–C(3)	124.03(17)	Li(1)–N(3)–Li(2)	70.11(15)
N(1)–C(2)–C(1)	119.52(19)	C(23)–N(4)–C(32)	121.62(17)
C(3)–C(2)–C(1)	116.44(19)	C(23)–N(4)–Li(2)	127.90(17)
C(2)–C(3)–C(4)	130.49(19)	C(32)–N(4)–Li(2)	109.49(15)
N(2)–C(4)–C(3)	123.27(19)	N(4)–Li(2)–O(1)	165.0(2)
N(2)–C(4)–C(5)	120.75(19)	N(4)–Li(2)–N(3)	88.84(14)
C(3)–C(4)–C(5)	115.96(19)	O(1)–Li(2)–N(3)	96.35(15)
C(21)–N(3)–C(25)	118.56(16)	N(4)–Li(2)–N(1)	111.08(19)
C(21)–N(3)–Li(1)	113.99(17)	O(1)–Li(2)–N(1)	82.29(14)
C(2)–N(1)–C(6)	118.19(16)	N(3)–Li(2)–N(1)	97.56(15)
C(2)–N(1)–Li(1)	117.51(17)	N(4)–Li(2)–O(4)	77.99(13)
C(6)–N(1)–Li(1)	117.43(15)	O(1)–Li(2)–O(4)	92.27(14)
C(2)–N(1)–Li(2)	117.07(15)	N(3)–Li(2)–O(4)	157.0(2)
C(6)–N(1)–Li(2)	105.27(17)	N(1)–Li(2)–O(4)	104.72(15)
Li(1)–N(1)–Li(2)	71.45(15)	N(3)–C(21)–C(22)	123.52(17)
C(4)–N(2)–C(13)	120.20(18)	N(3)–C(21)–C(20)	120.04(19)
C(4)–N(2)–Li(1)	121.42(17)	C(22)–C(21)–C(20)	116.43(18)
C(13)–N(2)–Li(1)	118.36(17)	C(21)–C(22)–C(23)	130.27(18)
N(2)–Li(1)–O(3)	116.9(2)	N(4)–C(23)–C(22)	121.60(18)
N(2)–Li(1)–N(1)	99.98(17)	N(4)–C(23)–C(24)	123.16(18)
O(3)–Li(1)–N(1)	106.57(17)	C(22)–C(23)–C(24)	115.18(18)

in contrast with the 2-isopropyl variant **2c**. It shares with most other N–N′ diaryl diazapentadienyl complexes a near perpendicular relationship between the aryl planes and the diazapentadienyl NCCCN plane (deviations of +11.9 and −8.1°). However, the other anion, containing ligating sites N(3) and N(4), has one ring near perpendicular (+13.4°), but another ring much closer to coplanarity, at a rotation angle of 43.9° from perpendicular. It is this aryl which is the only one to engage in 'intramonomer' chelation, that is to say, O(4) of this aryl binds to the lithium which forms the six-membered ring through N(3) and N(4), part of the same anion. In contrast, two other methoxy arms serve to bind the dimer together by forming inter-monomer links. The final methoxy arm lies unbound. There are no significant intermolecular interactions. The 'intramonomer′ chelation through O(4) has the longest Li–O bond. (Table 4). The two monomeric units are also bound by bridging nitrogens, N(1) and N(3), in a manner reminiscent of the first structurally characterized lithium diketiminate, $[\{Me_3SiNC(Ph)CHC(Ph)CNSiMe_3Li\}_2]$.[26] The co-ordination of two lithium ions to each of N(3) and N(1) serves to localise more negative charge on those nitrogens, so that the alternation of bond lengths is almost as clear in both diazapentadienyl rings of **2g** as in the case of **1f**, in stark contrast to **2c**, where the completeness of delocalization is evidenced by the crystallographic symmetry plane bisecting the diazapentadienyl ring. This incomplete delocalization is also seen in $[\{Me_3SiNC(Ph)CHC(Ph)CNSiMe_3Li\}_2]$. In that case, each lithium was merely 3-co-ordinate,[26] whereas in **2g** there is one 4-co-ordinate (pseudo-tetrahedral) and one 5-co-ordinate (pseudo-square-based-pyramidal) environment. The other major difference between these two dimeric lithium diketiminates is that the 3-co-ordinate example was transoid, whereas **2g** has an unusual cisoid arrangement of diazapentadienyl planes.[27] There is a significant butterfly puckering of the central Li_2N_2 ring, the angle between the Li(1)N(1)Li(2) plane and the Li(1)N(3)Li(2) plane being 37.7°. It remains somewhat surprising that the diazapentadienyl nitrogens were pressed into service as bridging atoms when a plausible monomeric structure seemed able to furnish the lithium with its favoured 4-co-ordination, especially when the structure of **2g** is compared to the structure of $[\{PhN(CH)_3NPhLi{\cdot}OP(Me_2)_3\}_2]$, in which dimerization occurred *via* the bridging phosphoric amide oxygens in preference to the diazapentadienyl nitrogens.[24]

In solution in C_6D_6, the simplicity and sharpness of the NMR data are consistent only with rapidly equilibrating isomers. Scheme 2 is intended to represent just two of the many possible isomers showing exchange of cisoid and transoid forms through a putative dissociated monomeric intermediate. This hypothesis is supported by the fact that cryoscopy in benzene at a similar concentration to that used for the NMR measurements gives an average association state of 1.3. It is tempting to speculate that the isolation of the cisoid arrangement is due to some geometric or steric conflict in more symmetrically bound dimers. There is some intramolecular (intermonomer) offset π-stacking interaction between the aryls carrying O(1) and O(3), *e.g.* C(7)–C(25) = 3.26 Å. However, the reason may simply be because the higher dipole moment of a non-centrosymmetric molecule makes it less well-solvated by hexane; hence the cisoid isomer is deposited. Furthermore, the relatively high melting point suggests efficient intermolecular crystal packing in this conformation.



Scheme 2

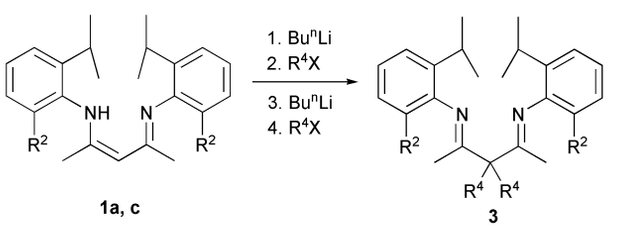
The fact that one 5- and one 4-co-ordinate lithium is found in **2g** suggests that there is a fine balance between the extra energy to be gained from the fifth co-ordination event and the increased steric and angle-strain necessary to make this happen.

Reactions of diazapentadienyllithiums with electrophiles

While compounds **1** are often referred to as β-diketimines, their observation in this form is rare; 'enamineimine' is a more accurate term for the normal tautomer in the solid state and in solution.[21] The very bulky **1b** adopts the β-diketimine tautomer,[22] and **1a** has been observed once in this neutral diimine form, co-ordinated to nickel.[3] This first report of the now omnipresent ligand **1a** also included a palladium complex, but it was one where the palladium atom was co-ordinated to the α-carbon. The complex **1a**·$NiBr_2$ was activated using methylaluminoxane to give an ethylene polymerization catalyst of very modest efficacy.[3] Almost certainly, the α-CH would have been deprotonated under these conditions.[28] Noting the recent interest in α-diimines,[29] we reasoned that it should be possible to access 'true' β-diketimines by a double alkylation protocol, removing the problematic C–H acidity by α,α′ dialkylation. Such rational double C-alkylation of eneamineimines has, to our knowledge, never been previously attempted, though in one of only two prior reports, concerning alkylation of a variant of **1** lacking *ortho* substitution, a dialkylated species was reported in low yield among the numerous products of an intended single alkylation.[30] The second, also with only a single alkylation, was more recent, and involved reaction with CH_2Br_2

in order to link two diketiminate ligands.[31] This report is the first of which we are aware specifically directed at synthesis of simple β-diimines lacking α-carbon reactivity. There have been some other more recent examples of mono-substitution at the α-carbon.[7–9]

By a cycle of deprotonation/alkylation (Scheme 3), it proved possible to dimethylate, diethylate, or dibenzylate **1a** and **1c** cleanly. Isolated yields were limited only by the high solubility of the products in most organic solvents. Most notable in these syntheses was the absence of *N*-alkylation, or any other identifiable side-reaction, by NMR analysis of crude product. The double alkylation provides convenient access to diaryl β-diimines with significant *ortho* bulk. The previous work on alkylation of diaryl diazapentadienyls lacked this feature, and was plagued by multiple by-products.[30] Other conceivable routes involving direct condensation of anilines with 3,3′-dimethylpentan-2,4-dione are likely to be difficult in cases of such bulk, and in any case would not give control of imine geometry, which was exclusively *E*/*E*, as appropriate for metal chelation, possibly as a result of freezing of the structure of the chelated lithium intermediate. While so-called β-diimines have been known since the early work of Holm,[1] these are the first which exist exclusively in the tautomeric form implied by that name, rather than the much more abundant eneamine-imine form,[21] save for **1b**. In the case of **1b**, two isomers were present in the solid state, one *E*/*Z* and one *E*/*E* with respect to imine conformation, both differerent from the *E*/*E* conformation of **3**. †



1a, c **3**

R^4 =	Me	Et	Bz
R^2 = Pr^i	**3aa**	**3ab**	**3ac**
R^2 = H	**3ca**	**3cb**	**3cc**

Scheme 3

The complexity experienced by the earlier workers, on diketiminates bearing no *ortho* substitution,[30] suggests that the structural features of the diazapentadienyllithium intermediates are critical in determining the efficacy of the alkylation. The structure of **2a** is found to be a weakly-bound hexamer or polymer depending on crystallization conditions, but in all cases a solution-state monomer, even in non-co-ordinating solution.[21] In thf a single solvent molecule is bound to the lithium in **2a**; in **2c**, two thf molecules can be incorporated. These are most likely the identity of the reacting species in thf. ‡ In both cases the nitrogen atoms are well shielded from attacking nucleophiles by the isopropyl and solvent molecules; the aryl rings lie close to perpendicular with the diazapentadienyl ring. The same is not true of diaryldiazapentadienyllithium complexes lacking *ortho* substitution; in this case, the aryls lie between coplanarity and orthogonality,[24] thereby allowing attack from the electrophile from above or below the diazapentadienyl plane on the nitrogen atoms. In all cases, such attack is not hindered for the α-carbon position. More puzzling is the case of **1g**. Repetition of the double lithiation/methylation procedure on **1g** in thf, where a single methoxy group took the place of the single isopropyl group of **1c**, produced a forest of products which resisted chromatographic separation. The mixture was so complex as to indicate that the route, which was clean for **1a** and **1c**, would not be preparatively useful for **1g**. However, there was evidence of *N*-alkylation, and in some of the fractions also there was evidence of addition of Bu^{n}Li across imine bonds; both modes of reactivity have been previously observed in the case where no *ortho* substituents were present.[30] Despite the fact that sterically the methoxy group of **1g** almost matches the isopropyl group of **1c**, functionally it differs. Since the cryosopic result implies significant amounts of monomer in benzene solution, we can assume a predominance of monomer in thf. In **2g**, *ortho*-chelation of the methoxy groups is likely to occur, giving rise to an aryl–diazapentadienyl angle more akin to the unsubstituted case (as shown in the structure of **2g** by the sole intramolecularly co-ordinated methoxyaryl) and therefore again failing to prevent approach of methyl iodide to the diazapentadienyl nitrogen atoms. The reaction was also attempted in hexane, with and without added hexamethylphosphoric triamide (hmpa). The least cluttered data, where *N*-alkylation was clearly contributing, were obtained from the hmpa run, where the strong donor was employed in order to free the methoxy group from its chelating role, but clean *C,C*-dialkyl product from **1g** was not accessible by any means attempted.

Notwithstanding these limitations, dialkylation appears to be an attractive method for provision of gram quantities of *bulky* diaryl β-diimines lacking acidic protons, the co-ordination chemistry of which will be compared with their α-diimine counterparts in a forthcoming paper.[32]

The fluorination in **1f** appears to calm the reactivity of the central carbon atom, perhaps by absorbing excess electron density. No alkylation was found; only unreacted **1f** was recovered.

In order to determine if mixed alkylations could be performed, a single methylation was attempted on **2a**, but only a reduced amount of **3aa**, and unreacted **1a**, were isolated. This implied that a fast equilibrium was set up as the rather slow alkylation proceeded. As the slow alkylation began, a neutral monoalkylated molecule which could exchange protons with unalkylated **2a** was produced (see Scheme 4).

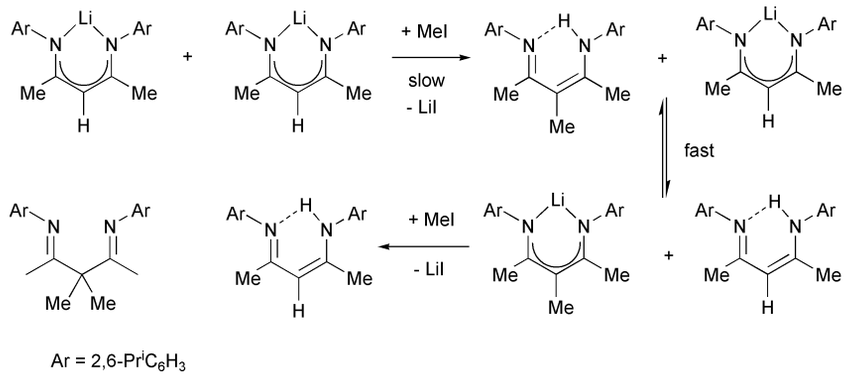
The greater electron-richness of the monomethylated **2a** α-carbon made it the preferred site of attack for the remainder of electrophile. Interestingly, the older paper on the matter, where monoalkylation was the target, also reported significant amounts of dialkylated product.[30] More recent, successful monofunctionalizations at position R_4 have utilised more reactive electrophiles (CF_3SO_2Cl), where the greater rate of reaction and the opposite inductive effect of the substituent eliminates the problem of equilibration.[7]

The most interesting results on electrophilic attack of **2** were obtained by use of adamantanone as the electrophile. These results have been previously communicated.[10] Addition of adamantanone to a hexane suspension of **2c** gave a solution from which the addition product **4** was isolated. A new C–C bond had formed by addition of the carbanion form of the diazapentadienyl unit across the C=O double bond. Where the diazapentadienyl anion is seen as a resonance-stabilized aza version of an enolate, this reaction is a type of aldol addition. The dimeric structure of the resultant lithium β-diimine-alkoxide is depicted in Fig. 4. The new ligand has a 'scorpionate' architecture, giving an *O,N,N* alternative[33] to the *N,N,N*, donor set of the tris(pyrazolyl)borates.[34]

The bulk identity of the crystallographically characterised **4** was confirmed by IR, Raman, elemental analysis and solid-state NMR, as well as a reproduction of the single-crystal structure determination from independently prepared batches.

† The differing substitution patterns change nomenclature priorities about the C=N bonds such that *Z*/*Z* **4** would be topologically equivalent to *E*/*E* 2,2,6,6-tetramethyl-3,5-bis(2,6diisopropylphenylimino)-heptane. The conformations were estabished by crystallography. The structures of the free ligands will be reported along with co-ordinated examples in a forthcoming paper.

‡ While the details in the Experimental section report our alkylations performed in hexane, we have found equally clean products and high yields using thf as solvent.



Scheme 4

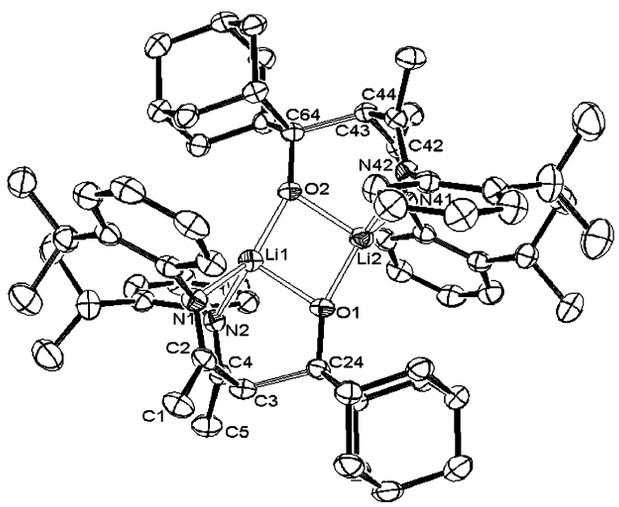


Fig. 4 An ORTEP diagram (50% probability) of **4** showing the pseudo-centrosymmetric dimerization *via* bridging oxygens. Hydrogens are omitted for clarity. Bonds linking the putative monomers are greyed.

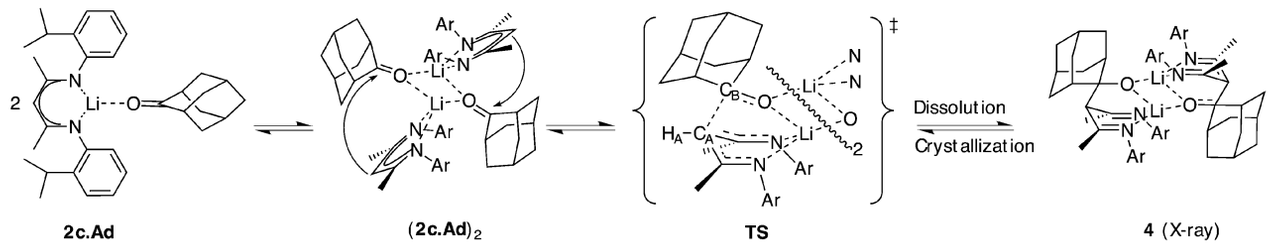
Table 5 Selected bond lengths (Å) and angles (°) for **4** (values for one crystallographically independent monomer only; the other is chemically comparable). Hydrogen atoms have been removed for clarity

C(1)–C(2)	1.507(3)	C(24)–C(25)	1.559(3)
C(2)–N(1)	1.284(3)	C(24)–C(29)	1.562(3)
C(2)–C(3)	1.520(3)	N(1)–Li(1)	2.090(4)
C(3)–C(4)	1.514(3)	N(2)–Li(1)	2.079(4)
C(3)–C(24)	1.642(3)	O(1)–Li(2)	1.812(4)
C(4)–N(2)	1.278(3)	O(1)–Li(1)	1.874(4)
C(4)–C(5)	1.502(3)	O(2)–Li(1)	1.795(4)
C(24)–O(1)	1.353(2)	O(2)–Li(2)	1.875(4)
N(2)–C(4)–C(5)	124.09(19)	C(29)–C(24)–C(3)	109.45(16)
N(2)–C(4)–C(3)	119.71(18)	C(2)–N(1)–C(6)	120.35(16)
C(5)–C(4)–C(3)	116.19(19)	C(2)–N(1)–Li(1)	110.02(17)
O(1)–C(24)–C(25)	111.58(17)	C(6)–N(1)–Li(1)	125.02(16)
O(1)–C(24)–C(29)	111.23(15)	C(4)–N(2)–C(15)	120.21(17)
C(25)–C(24)–C(29)	106.29(17)	C(4)–N(2)–Li(1)	111.09(16)
O(1)–C(24)–C(3)	108.48(16)	C(15)–N(2)–Li(1)	126.92(16)
C(25)–C(24)–C(3)	109.78(15)	C(24)–O(1)–Li(2)	154.79(17)
N(1)–C(2)–C(1)	124.4(2)	C(24)–O(1)–Li(1)	121.48(16)
N(1)–C(2)–C(3)	120.33(17)	Li(2)–O(1)–Li(1)	81.80(15)
C(1)–C(2)–C(3)	115.30(19)	O(2)–Li(1)–O(1)	98.24(17)
C(4)–C(3)–C(2)	115.02(17)	O(2)–Li(1)–N(2)	128.86(19)
C(4)–C(3)–C(24)	109.87(16)	O(1)–Li(1)–N(2)	94.91(16)
C(2)–C(3)–C(24)	109.25(16)	O(2)–Li(1)–N(1)	137.6(2)
O(1)–Li(2)–O(2)	97.61(17)	O(1)–Li(1)–N(1)	93.34(15)
O(1)–Li(2)–N(42)	129.36(19)	N(2)–Li(1)–N(1)	90.18(15)
O(2)–Li(2)–N(42)	93.92(16)	N(42)–Li(2)–N(41)	88.52(14)
O(1)–Li(2)–N(41)	139.3(2)	O(2)–Li(2)–N(41)	93.32(15)

This unusual care was deemed necessary because of the unexpected solution behaviour of **4**: in deuterobenzene the resonances were more in keeping with complex **2c** co-ordinated by adamantanone, which indicated that the aldol addition reaction responsible for the formation of **4** had reversed upon dissolution. Notable were the diagnostic solution chemical shifts of H{C(3)/C(43)}, C(3/43), C(2/4/42/44) C(24/64) which were almost identical to the corresponding shifts of **2c**·2thf. Most crucially, the C(24/64) resonance, which was, as expected for an alkoxide carbon, at 91/85 ppm in the ^{13}C CP MAS NMR spectrum, had in deuterobenzene solution shifted to 227 ppm, firmly in the carbonyl region. This represented a downfield co-ordinative shift from free adamantanone at 215 ppm. In hexane there was only a very slight upfield shift in H{C(3)/C(43)}, which at 4.8 ppm was still in the alkenyl range expected for **2c** in solution, indicating that even in the solvent from which **4** crystallized, it existed predominantly as an uncoupled diazapentadienyllithium–adamantanone complex.

It is known that lithium-mediated aldol additions are disfavoured by polar, co-ordinating solvents and high temperatures,[35] but these results indicate that it is possible to harvest aldol addition product *in the solid state* at room temperature, even where dissolution in the least polar of solvents totally reverses the process. To shed further light on the phenomenon, cryoscopy in benzene, the solvent used in most of the NMR studies, was carried out. This indicated that in the concentration range used for spectroscopic measurement, the species had dissociated to monomer **2c**·Ad (Scheme 5).

Inspection of the detailed structural parameters (Table 5) reveals why this may be occurring. Addition of the electrophile to the diazapentadienyl unit resulted in localization of the bonds to correspond to the true β-diimine tautomer, and most bond lengths and angles are within the expected ranges for such a situation. However, at the two carbons which have undergone the sp^2/sp^3 transition, C(3/43) and C(24/64), there are some deviations. The angle C(2/42)–C(3/43)–C(4/44) lies, at 115°, almost precisely between the sp^2 and the sp^3 angle. More significantly, the newly formed bond length C(3/43)–C(24/64) was 1.644(2) Å averaged over the two monomers. While this is significantly longer than the standard C–C distance of 1.52 Å, it is not among the longest of such bonds.[36] Furthermore, the C–O bond was short (1.35 and 1.36 Å) in comparison to those from the analogous 2-cumyl adamantanol and a tantalum-ligated adamantan-alkoxide (both 1.44 Å).[37] Given the long C–C and short C–O bonds, it is tempting to view the structure of **4** as a transition state analogue (TS, Scheme 5) for the aldol addition. However, computations on lithium aldols, and aza-versions[38] more similar to the situation in **4**, all indicate a very early transition state, with C–C distances of 2.2–2.5 Å. The only previously characterizaed lithium aldolate displayed normal C–C and C–O bond lengths in the tetrameric aggregated structure it assumed, such that it represented the terminus of the aldol addition reaction.[39] Clearly, **4** is not a transition state analogue, but a ground state, albeit one in which the steric bulk of each reagent and the electronic stability of the 6π-planar delocalized reagent 1,5-diazapentadienyllithium has compressed the reaction co-ordinate to the extent that the terminus of the reaction



Scheme 5

is separated from the reagents by an extraordinarily small barrier.

Aside from the only other crystallized lithium aldolate,[39] there also exists structural data for a sodium enolate complexed by unenolized ketone.[40] Complex **4** represents a data point some way along the reaction co-ordinate for carbanion-addition to ketone, between these two extremes. It clearly lies in a shallow potential well, since dissolution in non-co-ordinating, non-polar solvents reverses its formation, an event likely to be under entropic control. We postulate that the transfer from solution monomer to dimer upon crystallization is intimately connected to the aldol addition reaction in this case. The monomer species **2c**·Ad, with a 3-co-ordinate planar lithium, has ample precedent in the thf and diethyl ether complexes of **2a** and **2b**.[21,6] Inspection of Fig. 4 reveals that the shortest Li–O bonds lie almost in the Li–N–Li plane; the lithium atom Li(1) lies only 0.18 Å above the plane of N(41), N(42) and O(1) (0.20 Å in the other monomer) such that little more than re-hybridization of C(2/42) and C(24/64) to sp^2 and rupture of the longest/weakest Li–O and C–C bonds, would generate a plausible solution-phase monomer with regained delocalization-derived stability and increased entropy. In both directions of this equilibrium, the putative intermediate would be a dimer (**2c**·Ad)$_2$ with terminal diazapentadienyls and bridging carbonyls (see Scheme 5). A similar structure is known where hexamethylphosphoramide acts as the bridge.[24] Furthermore, a computational study confirmed the capacity of carbonyls to bridge in lithium dimers.[41] In fact, a primary motivation for this experiment was the isolation of just such a model for the precursor of ketone enolization by amidolithium bases, in support of the hypothesis that such reactions proceed *via* bridging ketones.[41] While the neutral bridging ketone motif has yet to be seen in lithium chemistry, it has precedent for sodium.[42] As to the reason why aldol addition occurs at all for this resonance-stabilized carbanion, upon co-ordination of *two* lithium ions to the carbonyl oxygens, the greater polarization of the carbonyl[41] facilitates carbanion attack. Dimerization would also push the two reactants together in the correct fashion, whereas in the monomer, close approach is unlikely. Given that the only other characterized lithium aldolate is a tetramer, with more normal C–C and C–O bond lengths and *three* lithiums attached to each alkoxide oxygen,[39] the aggregation phenomenon appears to play a major role in the positon of the aldol/retro-aldol equilibrium.[43]

Lithium alkoxides, and their close relatives, lithium enolates, are known to exist in the solid state and in solution frequently as tetramers and hexamers.[40] Dimers are also not unusual, but are normally accompanied by extreme bulk and/or ancillary co-ordinating solvent ligands.[44] Complex **4** is unusual in employing intramolecular imine nitrogen co-ordination in completing the lithium's co-ordination sphere, though a recent result almost duplicates this feature: The samarium-mediated (irreversible) reductive coupling of an α-diimine with benzophenone also gives a tridentate *N,N,O* ligand, though one of the imine nitrogens is reduced and carries an acidic proton.[45]

Aqueous quenches on solutions of **4** produced recovered, uncoupled starting materials **1** and adamantanone, a result entirely consistent with the solution-state spectroscopic results. However, our attempts at solid-state quench, by grinding with anhydrous ammonium salts under argon, also resulted in the identification only of uncoupled starting materials. This may be because protonation, even in the solid state, destabilizes a structure held together only by the co-ordinative demands of the lithium cations, or it may mean that the retro-aldol reaction on the alcohol occurred upon dissolution for NMR analysis. Silylation did not proceed in the solid state or in solution.

The main factor in the equilibrium is clearly the transition from the solid to the solution state: the solid state favours higher aggregation states, and dimerization favours C–C coupling in this case; the greater entropy in solution reverses the process.

It should be recognized that the analysis of the structure of intermediates in lithium-mediated syntheses is infrequent. Had this not been done, neither the solution spectroscopic evidence nor the quenched product analysis would have indicated that any reaction had occurred. This leaves open the question of whether such phenomena may be common in reactions deemed to have 'failed'. In cases of aldol reactions known to proceed, but with poor yields, carrying out quenches in the solid state may offer a means of improved product recovery. It has not escaped our attention that aldol additions are one of the most widely studied and employed methods of C–C bond formation,[35] and so this first demonstration of the importance of physical phase in the aldol addition merits further study.

Conclusion

Direct acid catalysed, or $TiCl_4$-mediated, condensation was employed to extend the range of diketiminate (diazapentadienyl) ligands available to co-ordination chemists with cases of variable bulk, electron donicity and functionality. Double electrophilic alkylation proceeded smoothly only for diaryldiketiminates with significant *ortho* bulk, which serves to protect the nitrogen atoms from side reactions. This was established by structural characterization of the lithiated intermediates. Simple bulky diaryl β-diimines protected from α-C reactivity result, the co-ordination chemistry of which will be discussed in comparison with otherwise identical α-diimines in a future paper. Where adamantanone was used as the electrophile on the lithium diazapentadienyl complex, the reaction proceeded in an aldol-like manner, but did not go to completion, resulting in long C–C and short C–O bonds to the adamantanone. The product undergoes retro-aldol dissociation upon dissolution in even the least polar of solvents.

Acknowledgements

Thanks are due to Dr D. A. Middleton for practical assistance in collection of solid state NMR data, and to Mr I. Crossley for collection of Raman scattering data. EPSRC (R. J. W., J. E. W.) and the European Social Fund (E. K. C.-E.) are thanked for studentship funding. Creators Ltd is thanked for Total Technology funding (J. E. W.). EPSRC are also thanked for equipment grants for NMR, crystallography and vibrational spectroscopy.

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