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Structural Diversity in Alkali Metal Complexes of Sterically Demanding Carbazol-9-yl Ligands

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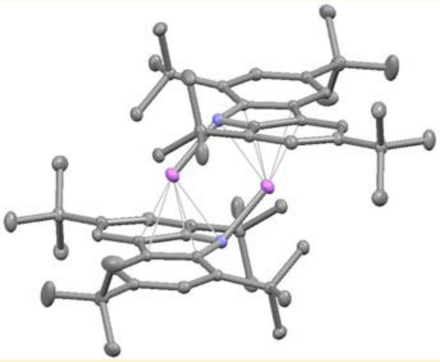
Supporting Information

ABSTRACT: The solid state structures of alkali metal complexes of the 1,3,6,8-tetra-*tert*-butylcarbazol-9-yl (^{t}Bu$_4$carb$^-$) ligand are compared. Lithium complex [^{t}Bu$_4$carbLi]$_2$ ([**1**]$_2$) is a dimer in the solid state featuring a planar LiNLiN rhomboid ring, with the differing Li−N distances within the ring due to the effects of σ- and π-interactions. Recrystallization of lithium, sodium, and potassium complexes of the 1,3,6,8-tetra-*tert*-butylcarbazol-9-yl ligand from THF leads to the formation of ^{t}Bu$_4$carbLi(THF)$_2$ (**1**·2THF), ^{t}Bu$_4$carbNa(THF)$_3$ (**2**·3THF), and ^{t}Bu$_4$carbK(THF)$_4$ (**3**·4THF), respectively, in the solid state. For these THF adducts, on proceeding from lithium to sodium to potassium there is an increase in hapticity of the binding of the carbazol-9-yl ligands to the metal cations, mirroring the increasing ionic bonding character in these compounds.



INTRODUCTION

Lithium complexes of amide ligands represent an important class of compounds in inorganic chemistry due to their applications in a wide range of areas.[1] The most important applications of these complexes are as the precursors of choice for the synthesis of related complexes *via* metathesis chemistry[2] and in organic chemistry, where reagents such as lithium diisopropylamide (LDA) have found widespread use as strong bases for the deprotonation of weakly acidic compounds.[3] To this end, the understanding of the stabilities and structures of such compounds, aggregation, and solvent effects is of paramount importance for the understanding of the organic chemistry of lithium amides.[4] In comparison to their lithum counterparts, analogous complexes featuring the heavier alkali metal congeners have been less studied.[2] Although monomers have been observed,[5−8] many alkali metal complexes of simple aromatic amides such as pyrrolyl, indolyl, and carbazol-9-yls featuring coordinating O or N ligands display dimeric aggregates in the solid state.[9−17] The unsolvated carbazol-9-yl complexes of potassium, rubidium, and cesium adopt polymeric arrangements in the solid state.[18]

As part of our investigations into the stabilization of low-coordinate transition metal complexes featuring sterically demanding amide ligands,[19−21] we have become interested in the use of carbazol-9-yl ligands with bulky substituents in the 1- and 8-positions.[19,21] These ligands can be conveniently varied to tune the steric demands they impart; the resulting steric loading of the d-block cations has been shown to heavily influence the propensity for σ- and π-bonding within these complexes. In this study we present the synthesis and characterization of carbazol-9-yl complexes of lithium, sodium, and potassium cations. It is envisaged that these complexes will serve as useful starting materials with which to access a range of compounds *via* metathetical reactions.

EXPERIMENTAL SECTION

General. All manipulations were carried out under an argon or nitrogen atmosphere using standard Schlenk line or glovebox techniques. Solvents were predried over Na wire prior to passing through a column of activated alumina, followed by storage over a potassium mirror (hexane, toluene) or distilled from Na/benzophenone ketyl, followed by storage over 4 Å molecular sieves (THF). 1,3,6,8-Tetra-*tert*-butylcarbazole was prepared by minor modification of literature methods.[22] NaH and KH (Aldrich) were purchased as suspensions in mineral oil; they were washed with hexane and dried *in vacuo* prior to use. ^{n}BuLi (2.5 M in hexanes, Aldrich) was used as received. Benzene-d_6 (Goss) was dried over potassium, while THF-d_8 (Goss) was dried over CaH$_2$; these NMR solvents were degassed with three freeze−pump−thaw cycles prior to use. ^{1}H, ^{13}C{^{1}H}, and ^{7}Li{^{1}H} NMR spectra for these complexes were collected on Bruker DPX 300 or DPX 400 spectrometers. Residual signals of solvent were used for reference for ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and chemical shifts are quoted in ppm relative to TMS (^{1}H and ^{13}C{^{1}H}) and LiCl/D$_2$O solution (^{7}Li{^{1}H}). Elemental analyses were performed by Mr. Stephen Boyer, Microanalysis Service, London Metropolitan University. Due to the extreme air and moisture sensitivity of **2**·3THF, and possible issues with loss of coordinated solvent, it was not possible to obtain a satisfactory elemental analysis of this complex, despite repeated attempts. This is a well-established issue for s-block organometallic complexes.[23]

Syntheses. *Synthesis of [^{t}Bu$_4$carbLi]$_2$ ([**1**]$_2$) and ^{t}Bu$_4$carbLi(THF)$_2$ (**1**·2THF).* To a solution of 1,3,6,8-tetra-*tert*-butylcarbazole (2.0 g, 5.0 mmol) in hexane (10 cm^3) at 0 °C was added a solution of ^{n}BuLi in

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hexane (2.0 cm^3, 2.5 mol dm^{-3}, 5.0 mmol). This mixture was allowed to warm slowly to room temperature and stirred for 12 h. During this time [**1**]$_2$ precipitated out of solution as a yellow powder (yield 1.41 g, 71%). Recrystallization from a saturated hexane solution afforded dimeric [**1**]$_2$ and recrystallization from a saturated hexane/THF mixture afforded the adduct **1**·2THF, as crystals suitable for X-ray diffraction, after storage at −30 °C for several weeks.

Data for [1]$_2$. Calcd for $C_{56}H_{80}Li_2N_2$: C 84.59, H 10.14, N 3.52. Found: C 84.66, H 10.23, N 3.40. ^{1}H NMR (400 MHz, benzene-d_6, 23 °C): δ/ppm = 1.45 (s, 36H, 1,8-^{t}Bu), 1.47 (s, 36H, 3,6-^{t}Bu), 7.35 (d, $^4J_{HH}$ = 1.6 Hz, 4H, carbazolyl 2,7-C*H*), 7.89 (d, $^4J_{HH}$ = 2 Hz, 4H, carbazolyl 4,5-C*H*). ^{13}C{^{1}H} NMR (101 MHz, benzene-d_6, 23 °C): δ/ppm = 30.7 (1,8-C(CH_3)$_3$), 32.3 (3,6-C(CH_3)$_3$), 34.9 (1,8-*C*(CH_3)$_3$), 36.1 (3,6-*C*(CH_3)$_3$), 113.7 (aromatic 4,5-CH), 119.0 (aromatic 2,7-CH), 123.6 (aromatic quaternary 4a,4b-C), 137.9 and 138.1 (aromatic quaternary 1,3,6,8-*C*), 147.9 (aromatic quaternary 8a,9a-*C*). ^{7}Li{^{1}H} NMR (156 MHz, benzene-d_6, 23 °C): δ/ppm = −5.9. Data for **1**·2THF follow. Calcd for $C_{36}H_{56}LiNO_2$: C 79.81, H 10.42, N 2.59. Found: C 79.86, H 10.31, N 2.65. ^{1}H NMR (300 MHz, benzene-d_6/THF-d_8, 25 °C): δ/ppm = 1.27 (m, THF, under residual solvent peak for THF-d_8), 1.65 (s, 18H, 3,6-^{t}Bu), 1.94 (s, 18H, 1,8-^{t}Bu), 3.16 (m, THF, under residual solvent peak for THF-d_8), 7.54 (d, $^4J_{HH}$ = 1.8 Hz, 2H, carbazolyl 2,7-C*H*), 8.18 (d, $^4J_{HH}$ = 1.4 Hz, 2H, carbazolyl 4,5-C*H*). ^{13}C{^{1}H} NMR (101 MHz, benzene-d_6/THF-d_8, 25 °C): δ/ppm = 25.9 (THF), 30.4 (1,8-C(CH_3)$_3$), 32.3 (3,6-C(CH_3)$_3$), 34.8 and 35.1 (1,8-*C*(CH_3)$_3$ and 3,6-*C*(CH_3)$_3$), 67.8 (THF), 114.6 (aromatic 4,5-CH), 120.3 (aromatic 2,7-CH), 124.8 (aromatic quaternary 4a,4b-*C*), 132.0 (aromatic quaternary 1,8-*C*), 135.9 (aromatic quaternary 3,6-*C*), 142.3 (aromatic quaternary 8a,9a-*C*). ^{7}Li{^{1}H} NMR (156 MHz, benzene-d_6/THF-d_8, 23 °C): δ/ppm = −1.3.

*Synthesis of ^{t}Bu$_4$carbNa(THF)$_3$ (**2**·3THF).* To a suspension of sodium hydride (0.04 g, 1.7 mmol) in THF (10 cm^3) was added a solution of 1,3,6,8-tetra-*tert*-butylcarbazole (0.50 g, 1.3 mmol) in THF (10 cm^3), and the resulting mixture was stirred at room temperature for 4 days. The orange solution was filtered, and solvent was removed *in vacuo*; the resulting solid was extracted into THF (5 cm^3) and dried *in vacuo* (yield = 0.58 g, 71%). Crystals of **2**·3THF suitable for single crystal X-ray diffraction were grown from cooling a saturated THF/hexane mixture to −30 °C. ^{1}H NMR (400 MHz, benzene-d_6/THF-d_8, 25 °C): δ/ppm = 1.46 (m, THF, under residual solvent peak for THF-d_8), 1.56 (s, 18H, 3,6-^{t}Bu), 1.97 (s, 18H, 1,8-^{t}Bu), 3.53 (m, THF, under residual solvent peak for THF-d_8), 7.42 (d, $^4J_{HH}$ = 2.0 Hz, 2H, carbazolyl 2,7-C*H*), 8.18 (d, 2H, $^4J_{HH}$ = 2.0 Hz, carbazolyl 4,5-C*H*). ^{13}C{^{1}H} NMR (101 MHz, benzene-d_6/THF-d_8, 25 °C): δ/ppm = 26.2 (THF), 31.2 (1,8-C(CH_3)$_3$), 33.3 (3,6-C(CH_3)$_3$), 35.3 (3,6-*C*(CH_3)$_3$), 36.7 (1,8-*C*(CH_3)$_3$), 68.1 (THF), 113.9 (aromatic 4,5-CH), 116.8 (aromatic 2,7-CH), 126.1 (aromatic quaternary 4a,4b-*C*), 135.0 (aromatic quaternary 3,6-*C*), 136.5 (aromatic quaternary 1,8-*C*), 149.6 (aromatic quaternary 8a,9a-*C*).

*Synthesis of ^{t}Bu$_4$carbK(THF)$_4$ (**3**·4THF).* To a suspension of potassium hydride (0.4 g, 11.0 mmol) in THF (10 cm^3) was added a solution of 1,3,6,8-tetra-*tert*-butylcarbazole (4.0 g, 10.2 mmol) in THF (20 cm^3) at −78 °C; the resulting mixture was warmed slowly to room temperature and stirred for 12 h. The orange-brown solution was filtered, solvent was removed *in vacuo*, and the resulting pale yellow solid was washed with hexane (2 × 30 cm^3) and dried *in vacuo*, affording **3** (yield = 3.5 g, 80%). Crystals of **3**·4THF suitable for single crystal X-ray diffraction were grown from cooling a saturated THF solution to −35 °C. Analytical data were measured on an unsolvated sample. Calcd for $C_{28}H_{40}KN$: C 78.26, H 9.38, N 3.26. Found: C 78.14, H 9.30, N 3.33. ^{1}H NMR (400 MHz, benzene-d_6/THF-d_8, 25 °C): δ/ppm = 1.60 (s, 18H, 3,6-^{t}Bu), 2.03 (s, 18H, 1,8-^{t}Bu), 7.51 (d, $^4J_{HH}$ = 2.0 Hz, 2H, carbazolyl 2,7-C*H*), 8.27 (d, $^4J_{HH}$ = 2.0 Hz, 2H, carbazolyl 4,5-C*H*). ^{13}C{^{1}H} NMR (101 MHz, benzene-d_6/THF-d_8, 25 °C): δ/ppm = 30.4 (3,6-C(CH_3)$_3$), 32.3 (1,8-C(CH_3)$_3$), 34.8 and 35.1 (1,8- and 3,6-*C*(CH_3)$_3$), 114.7 (aromatic 2,7-CH), 120.4 (aromatic 4,5-CH), 124.9 (aromatic quaternary 4a,4b-*C*), 132.0 (aromatic quaternary 1,8-*C*), 135.6 (aromatic quaternary 3,6-*C*), 142.3 (aromatic quaternary 8a,9a-*C*).

Crystallographic Methods. Crystals of [**1**]$_2$, **1**·2THF, **2**·3THF, and **3**·4THF were mounted on dual-stage glass fibers using YR-1800 perfluoropolyether oil (Lancaster) and cooled rapidly in a stream of cold nitrogen using an Oxford Cryosystems low-temperature device.[24] Diffraction data for [**1**]$_2$ (173 K) were collected on an Agilent SuperNova diffractometer equipped with a mirror-monochromated Cu Kα radiation source (λ = 1.541 84 Å), for **2**·3THF (90 K) on a Bruker SMART APEX diffractometer, and for **1**·2THF and **3**·4THF (150 K) on a Bruker SMART1000 diffractometer, the last two instruments equipped with graphite-monochromated Mo Kα radiation sources (λ = 0.710 73 Å). Absorption corrections were applied using an analytical method (for [**1**]$_2$) and a multiscan method (SADABS) (for **1**·2THF, **2**·3THF, and **3**·4THF).[25] All non-H atoms were located using direct methods[26] and difference Fourier syntheses. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained in calculated positions and refined with a riding model. In **1**·2THF, one THF ligand [O(1), C(29), C(30), C(31), C(32)] exhibited positional disorder. The disorder was successfully resolved using a two-part disorder model with major and minor occupancies of 0.528(8) and 0.472(8), respectively. Distance and displacement parameter restraints were applied, and the five atoms were refined isotropically. Atoms C(14), C(15), and C(16) of a *tert*-butyl moiety exhibited disorder over two positions. This was successfully modeled using a two-part disorder model with major and minor occupancies of 0.842(5) and 0.158(5), respectively, and both distance and anisotropic displacement parameter restraints were applied. In **3**·4THF, atoms C(27), C(28), and C(29) of a *tert*-butyl moiety exhibited disorder over two positions. This was successfully resolved using a two-part disorder model with major and minor occupancies of 0.847(4) and 0.153(4), respectively. CCDC 914545−914548 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cm.ac.uk/data_request/cif.

■ RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization. The reaction between 1,3,6,8-tetra-*tert*-butylcarbazole and a slight excess of ^{n}BuLi in hexane or MH (M = Na, K) in THF produces the corresponding carbazol-9-yl complexes in good yields. The crystallization of powder samples of *N*-lithio-1,3,6,8-tetra-*tert*-butylcarbazole from hexane or THF solutions affords the dimeric complex [^{t}Bu$_4$carbLi]$_2$ ([**1**]$_2$) or the solvated carbazolyl complex ^{t}Bu$_4$carbLi(THF)$_2$ (**1**·2THF), respectively. Both of these complexes have been characterized spectroscopically and by the results of single crystal X-ray diffraction measurements. Crystallization of *N*-sodio-1,3,6,8-tetra-*tert*-butylcarbazole and *N*-potassio-1,3,6,8-tetra-*tert*-butylcarbazole from THF solution affords the corresponding THF adducts ^{t}Bu$_4$carbNa(THF)$_3$ (**2**·3THF) and ^{t}Bu$_4$carbK(THF)$_4$ (**3**·4THF) as crystalline materials suitable for single crystal X-ray diffraction.

NMR measurements on all alkali metal complexes in this study indicate only one species in solution with one ligand environment in all spectra. Although sparingly soluble in hexane, dimeric [**1**]$_2$ is soluble in solvents such as benzene and toluene, presumably due to the greater covalent character of lithium amides compared to their sodium and potassium analogues. The NMR spectrum of this complex has therefore been recorded in benzene-d_6. The ^{7}Li{^{1}H} NMR chemical shift for [**1**]$_2$ displays a single peak at −5.9 ppm; upfield shifts in this region have been observed in other systems where the lithium cation is located directly above the plane of an aromatic carbanion in the shielding region of the diamagnetic ring current in the aromatic anion.[27] This chemical shift is a strong indicator that the η^5-interaction between the Li^+ and the central carbazolyl ring viewed in the solid state structure of [**1**]$_2$

remains intact in solution. Addition of THF-d_8 to a benzene-d_6-containing NMR sample of $[\mathbf{1}]_2$ leads to a change in the ^{7}Li{^{1}H} NMR chemical shift for this resonance downfield from −5.9 to −1.1 ppm, which is similar to that measured for a sample of **1**·2THF in a mixture of benzene-d_6 and THF-d_8 (δ_{7Li} for **1**·2THF = −1.3). Potassium complex **3**·4THF loses all coordinated THF *in vacuo*, as shown by elemental analysis on dried crystallographic samples. The sodium and potassium complexes of the 1,3,6,8-tetra-*tert*-butylcarbazol-9-yl ligand are found to be insoluble in hexane, benzene, and toluene, and as such they were dissolved in a mixture of benzene-d_6 and THF-d_8 for NMR spectroscopy; it is therefore likely that there is THF coordinated to the metal cations in these samples. Given the steric demands of the ^{t}Bu$_4$carb$^-$ ligand and the presence of coordinating THF-d_8 in the NMR samples, it is likely that these complexes are monomers in solution, although the formation of oligomers cannot be ruled out.

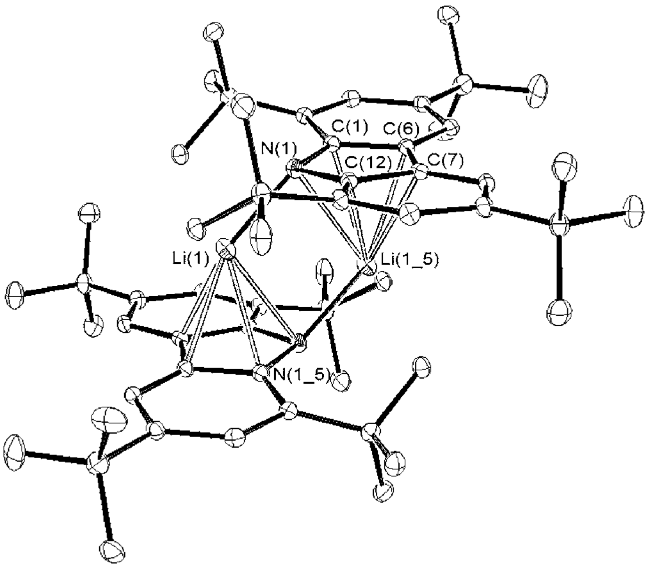

Figure 1. Molecular structure of $[\mathbf{1}]_2$, with displacement ellipsoids set at the 30% probability level. Hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (deg): Li(1)−N(1) 2.017(4), Li(1)−N(1_5) 2.434(4), Li(1)−C(1) 2.406(4), Li(1)−C(6) 2.363(4), Li(1)−C(7) 2.390(4), Li(1)−C(12) 2.449(4), Li(1)···Li(1_5) 2.715(7), Li(1)−N(1)−Li(1_5) 74.49(16), N(1)−Li(1)−N(1_5) 105.51(16), carb−N−Li(σ) 139.2(1), carb−N−Li(π) 33.7(1) (symmetry operation _5 = −*x*, 2 − *y*, −*z*).

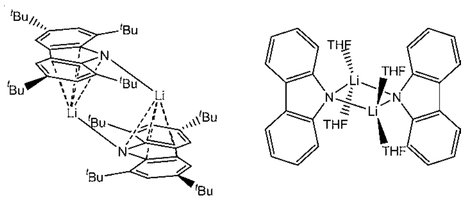

Figure 2. Illustration of the different bonding modes between $[\mathbf{1}]_2$ (left) and *N*-lithiocarbazole·2THF dimer (right).

Crystallographic Characterization. Crystals of lithium complex $[\mathbf{1}]_2$, which exists as an amide-bridged dimer in the solid state (Figure 1), can be crystallized from a saturated hexane solution of the compound at −30 °C. Complex $[\mathbf{1}]_2$ sits on a crystallographic inversion center, which requires the tetra-*tert*-butylcarbazol-9-yl ligands to be parallel. The individual ^{t}Bu$_4$carbLi units dimerize *via* the formation of carbazolyl bridges with the lithium atoms each σ-bonded in an η^1 manner to one carbazolyl nitrogen atom and simultaneously π-bonded to the central five-membered ring of the second carbazolyl ligand in an η^5 manner. This configuration is not observed for the lithium complex of the parent carbazolyl ligand, $[C_{12}H_8NLi(THF)_2]_2$, which features additional coordination of THF molecules per lithium (Figure 2),[9] but is seen in the solid state structure of *N*-cesiocarbazole·PMDTA (PMDTA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine).[10] This simultaneous σ-interaction between the lithium cation and the in-plane lone pair of nitrogen and the coordination of the other lithium atom to the π-system has been predicted by MNDO and *ab initio* calculations for *N*-lithiopyrrole.[9] During investigations of the tuning of main group redox chemistry through steric loading, Aldridge and co-workers have postulated that less bulky carbazolyl ligands function more like σ-donors;[8] it is therefore conceivable that the steric demands of the ^{t}Bu$_4$carb$^-$ ligand is a contributor to the simultaneous σ- and π-donation occurring in the solid state structure of $[\mathbf{1}]_2$.

The dimeric configuration for $[\mathbf{1}]_2$ gives rise to a planar Li−N−Li−N unit (Σ internal angles = 360° by symmetry), which has also been observed in other lithium amide dimers.[10,12,28] The two ^{t}Bu$_4$carb$^-$ ligands lie parallel, but are rotated 180° away from each other, with the Li−N σ-bond lying 139.2(1)° and the Li−N π-bond lying 33.7(1)° out of the plane of the carbazolyl ligand. The Li−N distance for the σ-bond in $[\mathbf{1}]_2$ is 2.017(4) Å, which is comparable to the shorter of the Li−N distances in $[C_{12}H_8NLi(THF)_2]_2$ [2.012(2) Å].[9] The π-bonded Li−N distance, at 2.434(4) Å, is somewhat longer than this, and along with the Li−C(ring) distances of Li(1)−C(1) = 2.406(4) Å, Li(1)−C(6) = 2.363(4) Å, Li(1)−C(7) = 2.390(4) Å, Li(1)−C(12) = 2.449(4) Å, indicates the presence of an η^5-bonding interaction; these distances are at the longer end of the range displayed in other η^5 Li−C interactions [e.g., 2.333(4)−2.356(4) Å in indacenediyldilithium·4THF].[29] The difference between the σ- and π-bond lengths in $[\mathbf{1}]_2$ is 0.42 Å, indicating that the Li−N π-interaction must be significantly weaker than the σ-bond. This difference between σ- and π-interactions is significantly larger than that in $[C_{12}H_8NLi(THF)_2]_2$ (0.14 Å),[9] *N*-lithioindole·TMEDA (0.23 Å; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine),[11] and *N*-cesiocarbazole·PMDTA, which is 0.24 Å.[10] The Li···Li distance in $[\mathbf{1}]_2$ is 2.714(7) Å, which is longer than that in dimeric $[C_{12}H_8NLi(THF)_2]_2$ [2.655(2), 2.660(2) Å][9] and the Li_2 molecule (2.672 Å).[30] The N(1)−Li(1)−N(1_5) angle of 105.51(16)° (symmetry operation _5 = −*x*, 2 − y, −z) is larger than that in the related *N*-cesiocarbazole·PMDTA dimer [88.1(2)°].[10]

For the alkali metals it has been proposed that multihapto bonding should become more important with the increasing size of the cation as is observed in the *N*-cesiocarbazole·PMDTA dimer.[10] Previously, in the case of the zinc complex (^{t}Bu$_4$carb)$_2$Zn we have observed significant puckering of the tetra-*tert*-butylcarbazol-9-yl ligand.[21] It is likely that the carbazol-9-yl ligand puckering in $[\mathbf{1}]_2$ (∠aryl plane-aryl plane = 7.7°) is necessary to avoid unacceptably short contacts between the ^{t}Bu$_4$carb$^-$ ligands in this complex.

Recrystallization of **1** from a saturated THF solution at −30 °C affords the solvated lithium carbazol-9-yl complex ^{t}Bu$_4$carbLi(THF)$_2$ (**1**·2THF, Figure 3), which is monomeric in the solid state (the closest Li···Li distance in the solid state is 9.46 Å), in contrast to the lithium complex of the parent carbazolyl anion, $[C_{12}H_8NLi(THF)_2]_2$, which crystallizes as an

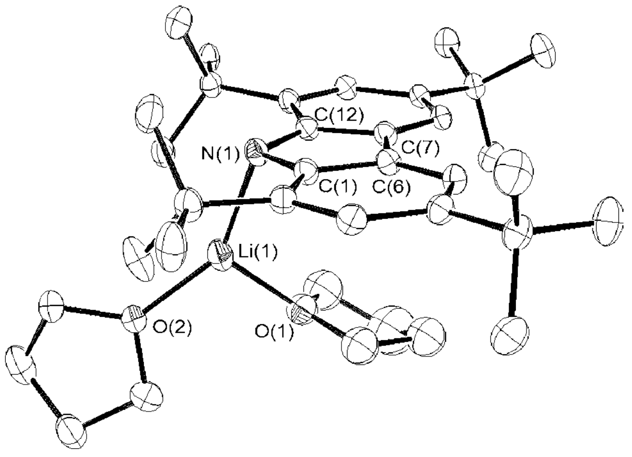

Figure 3. Molecular structure of **1**·2THF, with displacement ellipsoids set at the 30% probability level. Hydrogen atoms and the disorder component of THF molecule (O1′/C29′/C30′/C31′/C32′) are omitted for clarity. Relevant bond lengths (Å) and angles (deg): Li(1)−N(1) 2.028(6), Li(1)−C(1) 2.737(6), Li(1)−C(12) 2.701(6), Li(1)−O(1) 1.981(8), Li(1)−O(1′) 1.924(7), Li(1)−O(2) 1.942(6), Li(1)−N(1)−centroid (five membered ring) 111.56(2).

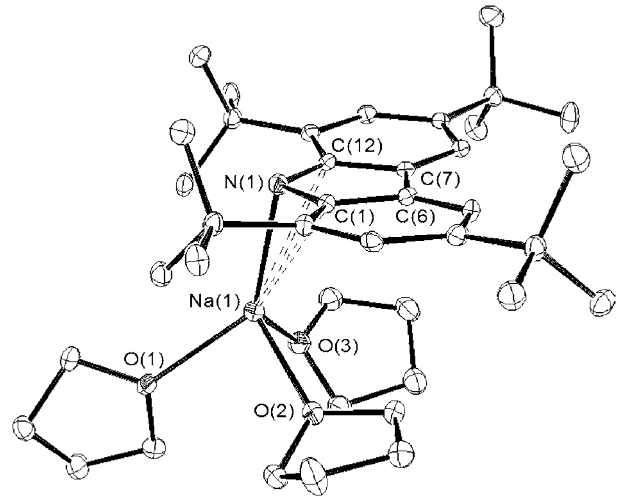

Figure 4. Molecular structure of **2**·3THF, with displacement ellipsoids set at the 30% probability level. Hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (deg): Na(1)−N(1) 2.464(3), Na(1)−C(1) 3.020(4), Na(1)−C(12) 2.977(4), Na(1)−O(1) 2.342(3), Na(1)−O(2) 2.334(3), Na(1)−O(3) 2.399(3), Na(1)−N(1)−centroid (five membered ring) 102.23(2).

amide bridged dimer,[9] presumably due to the greater steric demands of ^{t}Bu$_4$carb$^-$ compared to the parent carbazol-9-yl anion. Note that Aldridge and co-workers have recently reported the crystal structure of the solvent separated ion pair [Li(THF)$_4$][^{t}Bu$_4$carb];[8] presumably the differences between crystallization of these two forms of the lithium carbazol-9-yl complex from THF-containing solutions are relatively small. In the solid state structure of **1**·2THF the lithium cation is coordinated to the nitrogen atom of the 1,3,6,8-tetra-*tert*-butylcarbazol-9-yl ligand and two THF moieties in a trigonal planar arrangement (Σ angles around Li = 359.8°). The Li−N distance for **1**·2THF [2.030(6) Å], which is relatively long compared to other monomeric complexes of the formula R$_2$NLi(THF)$_2$,[6,28a,31] but is similar to those distances measured for the Li−N σ-bonds in [**1**]$_2$ and [C$_{12}$H$_8$NLi(THF)$_2$]$_2$.[9] The Li···C distances for the α-carbon atoms are 2.701(6) and 2.737(6) Å; such distances are shorter than in *N*-lithiopyrrole·TMEDA (2.76 Å), indicating the presence of an additional weak C···Li interaction.[11] The Li−O distances for **1**·2THF are 1.942(6) Å [Li(1)−O(2)] and 1.981(8) Å [Li(1)−O(1)],[32] which are in the range reported for [C$_{12}$H$_8$NLi(THF)$_2$]$_2$ [1.943(2)−1.973(2) Å].[9]

Single crystals of ^{t}Bu$_4$carbNa(THF)$_3$ (**2**·3THF; Figure 4) suitable for X-ray diffraction were obtained from the storage of a saturated THF solution at −30 °C. The monomeric formulation exhibited by **2**·3THF is very rare, and there is very little structural information regarding monomeric sodium amides in the literature.[2] The Na$^+$ cation is coordinated by the carbazolyl nitrogen atom and the two adjacent carbon atoms, and the coordination sphere is completed by three THF molecules, leading to a hexacoordinate metal center. The Na−N distance in **2**·3THF is 2.464(3) Å, which is in the range reported for the *N*-sodiocarbazole·ether complexes reported by Bock and co-workers (2.34−2.53 Å)[5] and is very similar to the shorter of the Na−N distances exhibited by dimeric *N*-sodioindole·TMEDA [2.478(5) Å] and *N*-sodioindole·PMDTA [2.474(4) Å].[11] Compared to lithium complex **1**·2THF, sodium compound **2**·3THF has the metal situated more centrally over the nitrogen atom, which satisfies the increased coordination requirements of Na$^+$ by allowing the interaction with the α-carbon atoms [Na−C distances are 2.977(4) and 3.020(4) Å]. These distances are similar to those found in *N*-sodioindole·TMEDA [2.967(7), 2.994(6) Å].[11] The Na−O distances in **2**·3THF are in the range 2.334(3)−2.399(3) Å, which are similar to those measured for other hexacoordinate Na complexes.[33,34]

Single crystals of ^{t}Bu$_4$carbK(THF)$_4$ (**3**·4THF; Figure 5) suitable for X-ray diffraction were obtained from the storage of

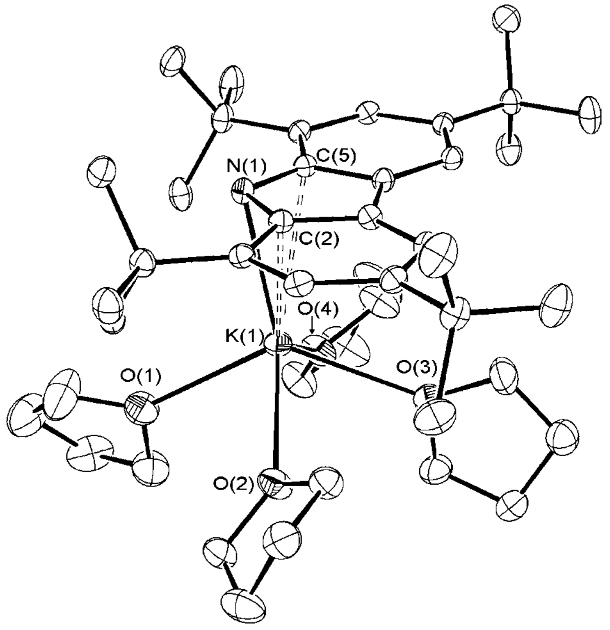

Figure 5. Molecular structure of **3**·4THF, with displacement ellipsoids set at the 30% probability level. Hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (deg): K(1)−N(1) 2.9053(19), K(1)−C(2) 3.128(2), K(1)−C(5) 3.071(2), K(1)−O(1) 2.728(2), K(1)−O(2) 2.6899(18), K(1)−O(3) 2.7071(18), K(1)−O(4) 2.744(2), K(1)−N(1)−centroid (five membered ring) 80.51(2).

a saturated THF solution at −30 °C. Reflecting the larger ionic radius of K^+ compared to Li^+ and Na^+, the solid state structure of **3**·4THF features the potassium cation bound to the nitrogen of the 1,3,6,8-tetra-*tert*-butylcarbazol-9-yl ligand, four THF molecules, and the five-membered ring of the carbazolyl ligand in an η^3 fashion. This additional interaction with the α-carbon atoms leads to a seven-coordinate metal center. The K−N distance [2.9053(19) Å] is significantly longer than that found in $[(1,8\text{-}Ph_2\text{-}3,6\text{-}Me_2C_{12}H_4N)K]_2$ [K−N = 2.745(2) Å],[17] but similar to the longer K−N distance in unsolvated carbazolyl potassium, which adopts a helical polymeric arrangement *via* the lone pair on the amido group [K−N distances = 2.870(5), 2.892(6) Å].[18] The K−O distances in **3**·4THF occur in the range 2.6899(18)−2.744(2) Å, and as such are similar to that found in $Ph_2P(Me_3SiN)_2K(THF)_4$ (av = 2.735 Å).[35] The additional coordination to the potassium is provided by the carbon atoms next to the nitrogen in the five-membered ring leading to K−C distances of 3.128(2) Å [K(1)−C(2)] and 3.071(2) Å [K(1)−C(5)], which are significantly shorter than the K−C π-interaction in *N*-potassiocarbazole·PMDTA (3.35 Å).[10]

The carbazolyl centroid−N−M angles for THF-coordinated carbazolyl complexes of the alkali metals decrease in order of increasing metal size, the values being 111.56(2)°, 102.23(2)°, and 80.51(2)° for **1**·2THF, **2**·3THF, and **3**·4THF, respectively. We have investigated the significant deviation from planarity of the central carbazolyl ring in the homoleptic zinc complex $({}^tBu_4carb)_2Zn$, leading to puckering of the 1,3,6,8-tetra-*tert*-butylcarbazol-9-yl ligands which appears to be necessary to avoid unacceptably short contacts between these moieties.[21] Comparison of this deviation from planarity of the central five-membered ring of the alkali metal carbazol-9-yl moiety in the THF adducts reveals that the puckering is greatest for the sodium complex **2**·3THF (angle between the best mean planes of the flanking phenyl rings = 8.7°); analogous measurements for **1**·2THF and **3**·4THF are 2.3° and 3.6°, respectively. These variations are presumably due to the complex interplay between ligand sterics, the metal···ligand distance, and the number of THF ligands coordinated to the metal.

■ CONCLUSIONS

In conclusion we have demonstrated the synthesis and characterization of lithium, sodium, and potassium complexes of the 1,3,6,8-tetra-*tert*-butylcarbazol-9-yl ligand. The number of coordinated THF molecules in the adducts in the solid state reflects the increasing size of the cation from Li^+ through Na^+ to K^+. For **1**·2THF, **2**·3THF, and **3**·4THF as group 1 is descended there is an increase in hapticity of the binding of the carbazol-9-yl ligands to the metal cations reflecting the increasing ionic bonding character in these compounds. Recrystallization of the lithium complex of the 1,3,6,8-tetra-*tert*-butylcarbazol-9-yl ligand from hexane solution yields structurally authenticated, which dimerizes *via* the formation of carbazolyl bridges where the lithium atoms are each σ-bonded in an η^1 manner to one carbazolyl nitrogen atom and simultaneously π-bonded to the central five-membered ring of the second carbazolyl ligand in an η^5 manner. Lithium 1,3,6,8-tetra-*tert*-butylcarbazolyl compounds are already proving to be versatile precursors in the synthesis of main group and d-block complexes;[8,21] the provision of a greater repertoire of alkali metal compounds of this ligand will serve to facilitate access to a larger range of complexes with varying structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format for complexes $[\mathbf{1}]_2$, **1**·2THF, **2**·3THF, and **3**·4THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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