Alkali-metal complexes of a triazacyclononane-functionalized tetramethylcyclopentadienyl ligand†

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Reaction of (1,4-diisopropyl-1,4,7-triazacyclononane)Li with $C_5Me_4HSiMe_2Cl$ yields the new donor-functionalized ligand, $[C_5Me_4SiMe_2(tacn)]H$; the alkali-metal salts $[C_5Me_4SiMe_2(tacn)]M$ (M = Li, Na, K) are obtained upon reaction with BuLi, $NaN(SiMe_3)_2$ or $KN(SiMe_3)_2$.

In recent years, the design of new ligands has opened up new vistas in organometallic chemistry. Our group is interested in developing monoanionic ligands that are capable of stabilizing species of the general type LMX_n, where M = trivalent, or tetravalent metal, and we have recently shown that donor-functionalized amidines are effective in this role.[1,2] Here we describe a new ligand system that incorporates two particularly efficient stabilizing fragments: an anionic Cp and a neutral triazacyclononane.[3] Conceptually related ligands are well known;[4] for example, linked cyclopentadienyl–amido species have advanced to become one of the most versatile ligand sets for the polymerization of α-olefins[5–7] since their original introduction by Bercaw *et al.* over a decade ago.[8–10] While the neutral lanthanide complexes, $[C_5Me_4SiMe_2NCMe_3]LnR$ (Ln = Sc, Y, La, *etc.*; R = alkyl, hydride) have been extensively investigated,[8–12] analogous lanthanide dialkyl complexes incorporating a single anionic cyclopentadienyl group linked to a neutral nitrogen-based donor are virtually unknown.[13–15] Given the tendency of monocyclopentadienyl lanthanide dihalides to redistribute, we reasoned that the combination of a cyclopentadienyl group and a neutral, tridentate macrocycle may stabilize some unusually reactive lanthanide complexes. A second characteristic of our ligand design seeks to exploit the combination of a "hard" cyclopentadienyl ring and a "soft" azamacrocycle within the same ligand framework which may allow for the synthesis of hetero-bimetallic complexes where an early transition metal binds to the anionic arene group, while a late metal is coordinated by the pendant nitrogen-containing macrocycle.

Here we describe the synthesis of the first examples of ligands of this type, along with their alkali metal complexes. The latter are useful synthetic reagents for subsequent chemistry[16] and their structural characterization serves to demonstrate the chelating character of the ligand system.

In an analogous manner to the synthesis of $C_5Me_4HSiMe_2NHCMe_3$ from $C_5Me_4HSiMe_2Cl$ and $LiNHCMe_3$,[9] a suitable precursor for the synthesis of our target donor-functionalized tetramethylcyclopentadienyl ligand is the lithium salt of (1,4-diisopropyl-1,4,7-triazacyclononane) ((tacn)H). Reaction of (tacn)H with one equiv. of BuLi in diethyl ether leads to the formation of [(1,4-diisopropyl-1,4,7-triazacyclononane)Li]$_2$ ([(tacn)Li]$_2$ **1**) in quantitative yield (Scheme 1). Cooling a saturated pentane or diethyl ether solution to −30 °C resulted in large, colorless blocks. An X-ray diffraction study revealed a dimeric structure in which each lithium center

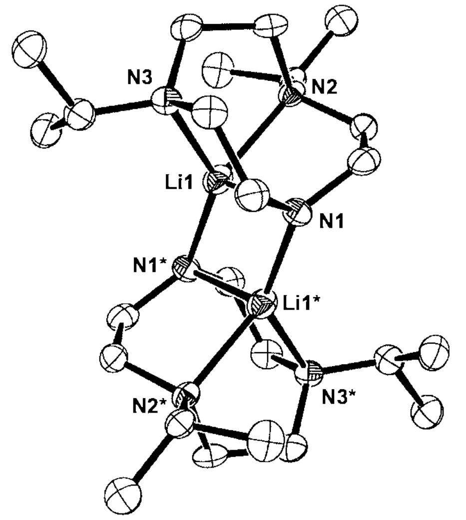
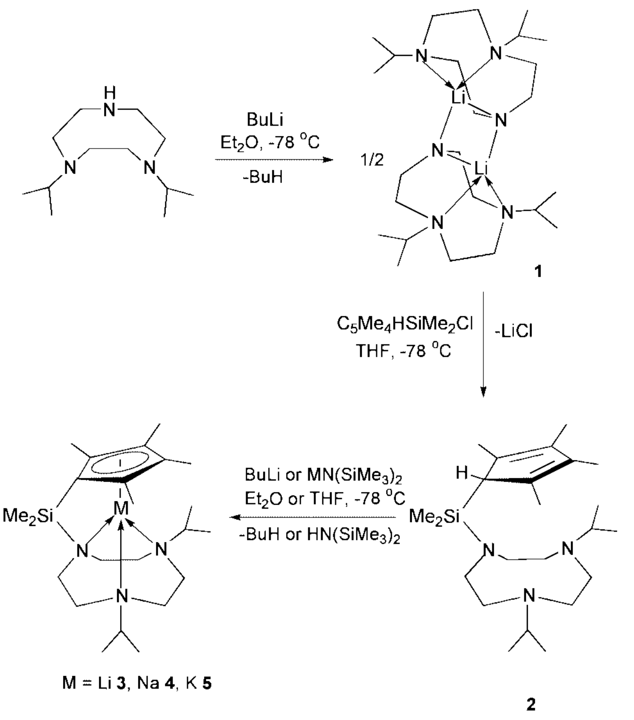


Fig. 1 ORTEP[21] view of [(tacn)Li]$_2$ **1** drawn with 50% probability ellipsoids. Selected bond distances (Å) and angles (°): Li1–N1 1.961(6), Li1–N2 2.097(6), Li1–N3 2.101(6), Li1–N1* 2.049(7); N1–Li1–N1* 106.2(3), N1–Li1–N2 90.1(3), N1–Li1–N3 89.9(3), N1*–Li1–N2 130.3(3), N1*–Li1–N3 136.2(3), N2–Li1–N3 89.0(2).



Scheme 1

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† Electronic supplementary information (ESI) available: experimental detail. See http://www.rsc.org/suppdata/dt/b0/b007075k/

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is pseudo-tetrahedral, ligated by three nitrogens of a single triazacyclononane ligand, and the amide nitrogen of a second tacn ring (N–Li–N = 89.0(2)–136.2(3)°) (Fig. 1).‡ The unit cell contains two independent molecules in which each dimer sits on a crystallographic inversion center; thus each dimer contains a symmetric Li_2N_2 core. The lithium centers exhibit two longer (2.097(6) and 2.101(6) Å) and two shorter (1.961(6) and 2.049(7) Å) Li–N bonds consistent with two metal–amine bonds and the two bridging metal–amide bonds of the Li_2N_2 unit. The structure and facile synthesis of **1** suggests that the triazacyclononane framework, in which two amines and an amide are linked together in a macrocyclic manner, may be used as a nitrogen analogue of the ubiquitous pentamethylcyclopentadienide ligand (Cp^*-) in the isolation of reactive transition metal compounds. The only other anionic triazamacrocycle to be structurally characterized is the mixed-metal species μ-(1,4-dimethyl-1,4,7-triazacyclononane)(methylamine)(1,4,7-trimethyl-1,4,7-triazacyclononane)dilithium nitride.[3,17] We have embarked upon a study of Group IV complexes supported by the tacn ligand system; our initial results will be reported shortly.[16]

Compound **1** reacts smoothly with $C_5Me_4HSiMe_2Cl$ in cold THF to yield $[C_5Me_4SiMe_2(tacn)]H$ **2** as a yellow oil following removal of the solvent, extraction with pentane and filtration to remove LiCl. In contrast to $[C_5Me_4SiMe_2NHR]H$ (R = ^{t}Bu, CH_2CH_2OMe, $CH_2CH_2NMe_2$, $CH_2CH{=}CH_2$, $CMe_2CH_2{}^tBu$, $CHMe_2$, $CH_2(C_5H_4N)$-2, CH_2Ph) which are purified by vacuum distillation,[9,18–20] **2** is sufficiently pure following normal work-up conditions to be employed in future reactions. The molecule has C_s symmetry in solution and exhibits a single doublet for the two diastereotopic isopropyl methyl groups in the ^{1}H NMR spectrum, in contrast to that found for **1**. In addition, we see no evidence for double bond isomerism in the cyclopentadienyl ring; only a well-defined cyclopentadienyl proton peak (δ 3.01) and two singlets for the cyclopentadienyl methyl groups are observed. Compound **2** may be used directly to generate transition metal complexes *via* alkylolysis or aminolysis reactions with homoleptic metal–alkyls and –amides.[16]

Compound **2** is deprotonated by bases such as BuLi, $NaN(SiMe_3)_2$ or $KN(SiMe_3)_2$ in either cold diethyl ether or THF to form the alkali-metal salts $[C_5Me_4SiMe_2(tacn)]M$ (M = Li **3**, Na **4**, K **5**) in good yields. The lithium and sodium salts of the ligand are soluble in THF, whereas the larger potassium cation requires the use of a more Lewis basic solvent such as pyridine or acetonitrile. Despite the strongly donating properties of these solvents, ^{1}H NMR spectra of **3**–**5** show no evidence of solvent incorporation; this is also supported by the elemental analyses and crystallographic studies of these complexes.

The ^{1}H NMR spectra of **3**–**5** are indicative of fluxional species in solution; for example, the spectra of **3** and **5** (d^8-THF or d^5-pyridine) consist of broad resonances consistent with a coalescence temperature near ambient conditions. The sodium salt **4** exhibits sharp resonances and a spectrum similar to that observed for the free-base **2**; however, on the basis of the solid state structure of **4** (see later), one would expect diastereotopic ligand resonances for the methylene groups of the triazacyclononane ring and the isopropyl methyl groups, as seen for the lithium salt **1**. This implies that **4** is highly fluxional in solution, with a coalescence temperature that is significantly lower than the lithium or potassium analogues.

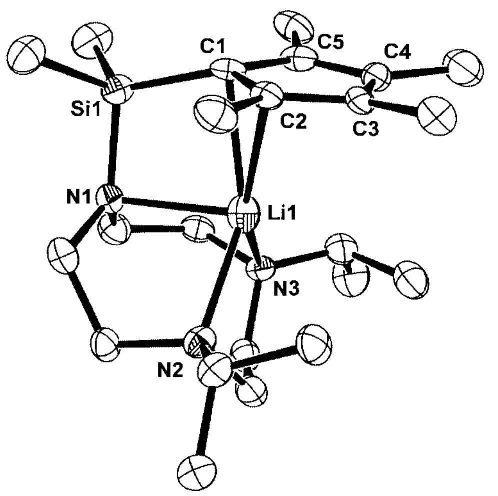

Fig. 2 ORTEP view of $[C_5Me_4SiMe_2(tacn)]Li$ **3** drawn with 50% probability ellipsoids. Selected bond distances (Å) and angles (°): Li1–N1 2.214(8), Li1–N2 2.202(8), Li1–N3 2.091(7), Li1–C1 2.293(8), Li1–C2 2.346(8); N1–Li1–N2 84.0(3), N1–Li1–N3 86.4(3), N1–Li1–C1 79.7(3), N1–Li1–C2 103.2(3), N2–Li1–N3 86.0(3), N2–Li1–C1 145.1(3), N2–Li1–C2 121.5(3), N3–Li1–C1 123.2(3), N3–Li1–C2 151.4(4), C1–Li1–C2 36.4(2).

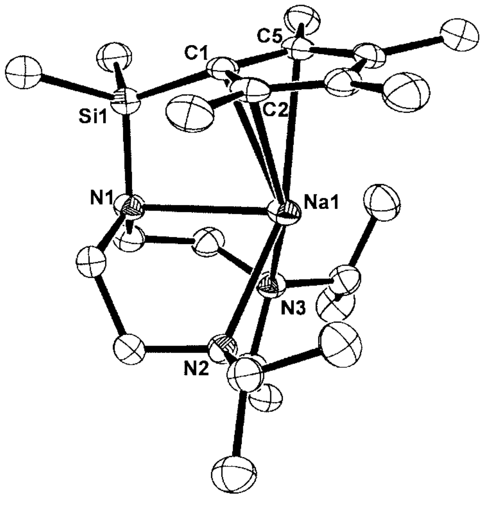

Fig. 3 ORTEP view of $[C_5Me_4SiMe_2(tacn)]Na$ **4** drawn with 50% probability ellipsoids. Selected bond distances (Å) and angles (°): Na1–N1 2.596(3), Na1–N2 2.471(2), Na1–N3 2.470(2), Na1–C1 2.544(3), Na1–C2 2.636(3), Na1–C5 2.703(3); N1–Na1–N2 73.2(8), N1–Na1–N3 73.29(7), N1–Na1–Cp*(centroid) 97.8, N2–Na1–N3 74.46(8), N2–Na1–Cp*(centroid) 139.2, N3–Na1–Cp*(centroid) 142.4.

Crystals of **3** suitable for X-ray diffraction were grown by cooling a saturated THF solution to 4 °C;‡ an ORTEP view along with selected bond lengths and angles is presented in Fig. 2. In contrast to the structure of $[(tacn)Li]_2$ **1**, **3** is monomeric in the solid state. The lithium center forms dative bonds with each of the three nitrogens of the triazacyclononane ring (Li–N = 2.091(7)–2.214(8) Å) which accounts for the lack of additional interaction with a coordinating solvent such as Et_2O or THF. The lithium atom shares close contacts with only two of the carbons of the tetramethylcyclopentadienyl unit (Li1–C1 = 2.293(8), Li1–C2 = 2.346(8) Å) which reflects the steric constraints of the linked ligand system in binding to a small metal center. Crystals of the sodium derivative were obtained by layering a saturated THF solution of **4** with toluene. The X-ray crystal structure of **4** along with selected bond lengths and angles are available in Fig. 3.‡ The structure is similar to that for the lithium derivative **3**, with the metal center ligated by all three nitrogens of the azamacrocycle. Because of the larger size of sodium *versus* lithium, the metal sits farther out of the cavity defined by the tetramethylcyclopentadienyl unit and the tacn ring, and in this case the sodium atom engages in bonding interactions with three of the five carbons of the arene moiety (Na–C = 2.544(3)–2.703(3) Å). In both examples, the N1–Si1–C1 bond angles are close to that expected for tetrahedral silicon (106.3(2) for **3**, 108.3(1)° for **4**), indicating that the ligand accommodates metal centers of differing sizes by changing the hapticity of the arene ring instead of varying the bite angle of the ligand.

In conclusion, a new mono-anionic, donor-functionalized tetramethylcyclopentadienyl ligand may be easily prepared in a two-step procedure in high yield. The structures of the lithium and sodium salts of this ligand system illustrate that metals of various sizes are readily introduced to and accommodated by the cavity defined by the cyclopentadienyl ring and the azamacrocycle. A study of early transition–metal and lanthanide complexes supported by this ligand system will be reported shortly.

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Notes and references

‡ Crystallographic data for **1**: $C_{24}H_{52}N_6Li_2$, $M = 438.60$, triclinic, $a = 10.556(1)$, $b = 10.717(1)$, $c = 13.677(2)$ Å, $\alpha = 87.669(2)$, $\beta = 87.928(2)$, $\gamma = 61.012(1)^\circ$, $V = 1352.0(4)$ Å^3, $T = 146$ K, space group $P\bar{1}$ (no. 2), $Z = 4$, μ(Mo-Kα) = 6.4 mm^{-1}, 7023 reflections measured, 4308 unique ($R_{int} = 0.055$), $D_{calc} = 1.08$ g cm^{-3}, $R = 0.046$, $R_w = 0.050$. **3**: $C_{23}H_{44}N_3SiLi$, $M = 397.65$, orthorhombic, $a = 16.7928(3)$, $b = 19.1555(6)$, $c = 14.9487(5)$ Å, $V = 4808.6(3)$ Å^3, $T = 125$ K, space group *Iba*2 (no. 45), $Z = 8$, μ(Mo-Kα) = 11.0 mm^{-1}, 9854 reflections measured, 3273 unique ($R_{int} = 0.055$), $D_{calc} = 1.10$ g cm^{-3}, $R = 0.035$, $R_w = 0.036$. **4**: $C_{23}H_{44}N_3SiNa$, $M = 413.70$, monoclinic, $a = 11.770(1)$, $b = 17.035(2)$, $c = 11.904(1)$ Å, $\beta = 92.254(2)^\circ$, $V = 2385.1(6)$ Å^3, $T = 174$ K, space group $P2_1/n$ (no. 14), $Z = 4$, μ(Mo-Kα) = 13.0 mm^{-1}, 12149 reflections measured, 4204 unique ($R_{int} = 0.030$), $D_{calc} = 1.15$ g cm^{-3}, $R = 0.036$, $R_w = 0.041$. CCDC reference number 186/2200.

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