Diverse Multinuclear Alkali Metallated (Li, Na, K, Rb, Cs) Family of the 1,3,5-tris-2-aminopyridyl-2,4,6-triethylbenzene Framework

Jennifer R. Lynch,[a] Marta Navarro,[b] Alan R. Kennedy,[a] Stuart D. Robertson,[a] Robert E. Mulvey,[a] and Alberto Hernán-Gómez*[b]

Literature on Group One organoelement chemistry is dominated by lithium, though sodium and potassium also feature prominently, whereas rubidium and caesium are rarely mentioned. With recent breakthroughs hinting that organoelement compounds of these two heavier metals can perform better than their lighter congeners in particular applications, important advantages could be missed unless complete sets of alkali metals are included in studies. Here, we report the synthesis and characterisation of a complete set of multi-alkali-metallated molecular compounds of the 1,3,5-tris[(4,6-dimethylpyridin-2-yl)aminomethyl]-2,4,6-triethylbenzene framework. Made by de-

protonating the framework N–H bonds by a suitable base, the set comprises six THF-solvated compounds, four of which are homometallic, either containing Li in a trinuclear structure or Na, K, and Rb in hexanuclear structures. Since deprotonation was incomplete with Cs, its homometallic compound is tetranuclear containing two un-metallated N–H bonds. A heterobimetallic trilithium-tricaesium hexanuclear compound was also obtained by using a bimetallic Li–Cs base for deprotonation. Such alkali-metallated frameworks are often precursors to other multimetallic frameworks with unique properties across different fields of science.

Introduction

The development of multimetallic compounds represents a burgeoning area of inorganic chemistry, driven by the potential of such compounds to manifest unique properties, offering promising applications across a diversity of fields, including catalysis, biological processes, and materials science.[1] Often inspired from biochemistry, metal metal cooperative effects within these compounds can promote enhanced or entirely new reactivities compared to those of their mononuclear counterparts.[2] Such cooperativity represents a major stimulus for the study of multimetallic compounds.

Mimicking that of monometallic compounds, multimetallic compounds are often synthesised in a stepwise procedure via initial formation of the corresponding alkali metal intermediate, followed by transmetallation to the desired new metal compound.[3] This approach enables integration of different metal centres into a single molecular framework, offering a

versatile pathway for the sometimes-challenging synthesis of complicated multimetallic structures. A huge diversity of single molecular frameworks has been studied for this purpose. To mention a selective few, this includes the triphenylene frame, that in addition to offering multiple bonding sites can facilitate communication between metal centres due to its π-conjugation, which has been extensively studied with transition metals. For example, by anchoring palladium or gold to a triphenylene-based tris(N-heterocyclic carbene) ligand (Figure 1a), Peris et al. have reported remarkable multimetallic catalysts showing enhanced efficiency in various reactions, as well as metallocages with applications in molecular recognition.[4]
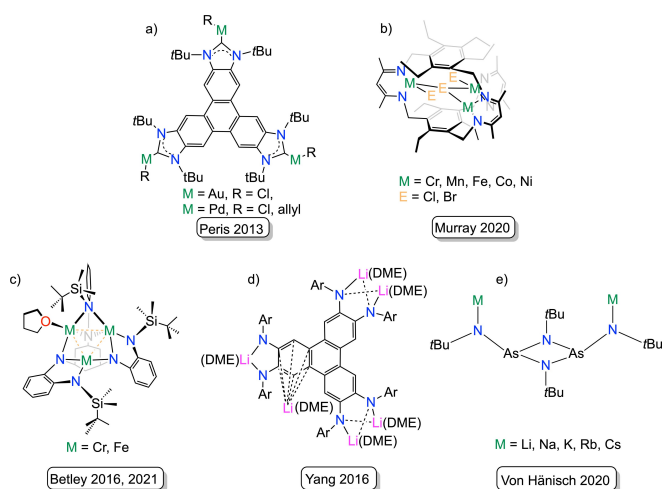
[a] J. R. Lynch, A. R. Kennedy, S. D. Robertson, R. E. Mulvey
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, (UK)

[b] M. Navarro, A. Hernán-Gómez
Departamento de Química Orgánica y Química Inorgánica, Instituto de Investigación Química "Andrés M. del Río" (IQAR), Universidad de Alcalá, Campus Universitario, Alcalá de Henares, Madrid E-28805, Spain
E-mail: alberto.hernan@uah.es

Figure 1. A selection of multimetallic frame complexes reported in the literature.

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202403544

Chemistry Europe
European Chemical
Societies Publishing

Another common preorganized ligand frame is based on 1,3,5-trisubstituted phenyl rings with different anchoring groups attached at specific sites. In this category, Murray *et al.* have reported a series of trinuclear transition metal compounds supported by *β*-diketiminate ligands held between two trisubstituted aromatic rings in a cyclophane (Figure 1b), with applications in small molecule activation,[5] including reductive silylation of N_2 catalysed by Cr, Mn, Fe, Co, and Ni compounds.[5a] Small molecule reduction of a series of nitrogen compounds has also been described by Betley *et al.* using iron and chromium compounds within a hexadentate *o*-phenyl-enediamine ligand frame (Figure 1c).[6]

Though alkali metal compounds are often the starting point for building these transition metal framework complexes, they have mostly been used as *in situ* transmetallation agents and not studied to any significant extent in their own right. Comparisons between the same frames but with different alkali metal centres are rarely made, a notable exception being the work of Yang *et al.*,[7] who characterised Li, Na, and K complexes built on a combined triphenylene and *ortho*-phenylenediamine hexamine frame (see Li example in Figure 1d) before using them to transmetallate to tris(N-heterocyclic tetrylenes) of Ge, Sn, and Pb.

Similarly, Von Hänisch *et al.*[8] reported a series of structurally diverse alkali metal (Li, Na, K, Rb and Cs) bis(amido)diazadiarsetidine compounds as transfer reagents towards tertbutyl substituted pnictogens. Herein, the primary aims of these studies were to synthesise and structurally characterise a complete alkali metal (Li–Cs) set of multimetallic framework compounds employing a frame not used previously for this purpose. These reports have been incentivised by the current growing interest in heavier alkali metal organoelement compounds[9] that includes our recent group one comparisons in alkene and imine transfer hydrogenation catalysis.[10] For the frame we selected the tris(2-aminopyridyl) precursor **LH₃** (Scheme 1) introduced by Mazik in 2004.[11] Part of the 2,4,6-trisubstituted benzene frame family but with tris 1,3,5-2-aminopyridine functionality, **LH₃** has been overlooked in this field but Mazik has utilised it and related compounds in host-guest chemistry probing their affinity to act as carbohydrate receptors.[12] Our interest was piqued since the 2-aminopyridine unit was found to make a significant impact in the binding affinities of these frames.

Results and Discussion

Synthesis and Solid State Characterisation of Alkali-metal Framework Complexes (1–4)

Full threefold deprotonation of **LH₃** was achieved with the metallation agents $LiCH_2SiMe_3$ or M(HMDS) [where M = Na, K, Rb; HMDS = 1,1,1,3,3,3-hexamethyldisilazide, $N(SiMe_3)_2$] in hexane at room temperature. Note that in the cases of Li, Na, and K the multinuclear products formed initially as suspensions in bulk hexane solvent but dissolved on addition of the more polar solvent tetrahydrofuran (THF). For Rb, the reaction was best carried out in neat THF solution. These products were all successfully synthesised (Scheme 1) in X-ray quality colourless crystalline form upon slow evaporation of a THF solution and identified as the desired new multinuclear alkali-metal complexes [$Li_3L \cdot (THF)_6$], (**1**) and [$M_6L_2 \cdot (THF)_n$] [M = Na (**2**), n = 4; K (**3**), n = 6; Rb (**4**), n = 6] in reasonable to high isolated yields (40%, 56%, 64%, and 89% respectively). Compounds **1–4** are air and moisture sensitive and readily decompose to generate the precursor **LH₃**, upon exposure. However, they can be stored under argon at room temperature without any sign of decomposition.

Single crystal X-ray diffraction studies (SCXRD) were carried out on compounds **1–4**. Full details including tables of crystal data, bond lengths and bond angles are provided in the Supporting Information (Tables S1–S4), with only the most interesting metric features highlighted here. These studies reveal a monomeric trinuclear lithium complex in **1**, whereas compounds **2–4** display dimeric hexanuclear arrangements. In general, these differences can be attributed to the larger coordination spheres of the heavier alkali metals which often lead to high coordination numbers, a need that in these specific cases is satisfied by a combination of THF solvation, the bidentate coordination of two amidopyridine units from two different ligands and a preponderance of heavier alkali metal-π-bonding interactions.[13]

The molecular structure of **1** shows each lithium centre in a distorted tetrahedral environment formed by two nitrogen atoms of the amidopyridine arms and two terminal THF molecules (Figure 2). According to the amido nature of the deprotonated ligand, the observed $Li-N_{amido}$ bond distances [range: 1.982(3)–1.987(3)Å; see Table S1] are in the same ballpark as those reported in the literature for similar multi-
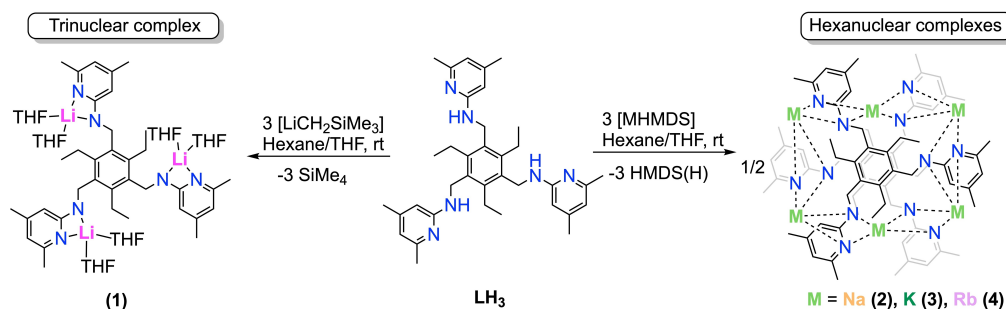
Scheme 1. Synthesis of trinuclear and hexanuclear alkali-metal complexes **1–4** with THF omitted from **2–4**.
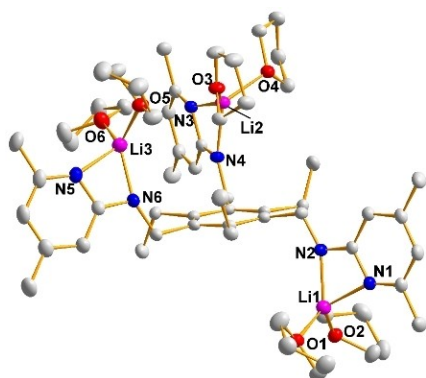
Figure 2. Molecular structure of one of the independent molecules of lithium complex **1**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level.

Figure 3. Molecular structure of sodium complex **2**. Hydrogen atoms and disordered THF molecule of solvation are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Symmetry operation to generate equivalent atoms labelled ': −2-x, −2-y, −1-z.

nuclear lithium amide complexes,[7,14] and the Li–N_{pyr} bonds are as expected longer [range: 2.050(3)–2.072(3) Å]. The lithium centres are distorted from tetrahedral (τ_4 values = 0.82/0.69/0.79 for Li1-Li3 respectively)[15] as a consequence of the acute N-Li-N angles (mean value 68.5°) imposed as part of a strained four-membered ring with an aromatic sp^2 hybridized backbone. Two of the lithiated amidopyridine arms lie to the same side of the central phenyl ring, though there are no intramolecular Li–N contacts between the two separate arms, while the third arm is turned to the opposite side to minimize clashing, mimicking the structure of the parent tris-amine.[11]

Moving to the heavier alkali metals Na, K, and Rb, the molecular structures of hexanuclear **2–4** are all centrosymmetric dimers with all three amidopyridine arms of the L^{3-} ligands lying on the same side of the phenyl ring plane. The phenyl rings are roughly coplanar to one another and the cations bridge the two ligands via bidentate coordination to an amidopyridine unit from each ligand. The coordination spheres around the metal centres expand relative to that for Li, with each heavier metal complex having two or three distinct metal coordinative environments (see Figures 3–5). In the case of Na complex **2**, whereas Na1(1′) is surrounded by four N atoms, two amido N1/N3′ and two pyr N2/N4′ (mean Na–N bond lengths, 2.402 Å and 2.430 Å, respectively) of two different **L** ligands, Na2(2′) and Na3(3′) occupy five-coordinate heteroatom environments comprising also two amido- and two pyr N-atoms but with an additional THF O-atom. This coordinative alteration is accompanied by more asymmetry at Na2(2′) and Na3(3′) with the two Na–N_{pyr} bonds of significantly different sizes to each other [Na2–N2/Na2–N6′, 2.925(3)Å/2.464(2)Å: Na3–N4/Na3–N6′, 2.967(3)Å/2.624(2)Å], in contrast to their two Na–N_{amido} bonds which differ little from each other [Na2–N1/Na2–N5′, 2.414(2)/2.539(2)Å; Na3–N3/Na3–N5′, 2.410(2)Å/2.474(2)Å]. The coordination of the THF molecule can be attributed to the reduced steric hindrance around Na2(2′) and Na3(3′) compared with Na1(1′), evident from the wider separation of the two amidopyridine rings (those containing N2/N6′ and N4/N6′ respectively) straddling the former pair of Na centres seen prominently in the aforementioned long Na2–N2 and Na3–N4 bonds compared to those much shorter bonds of Na1–N2 [2.408(2)Å] and Na1–N4′
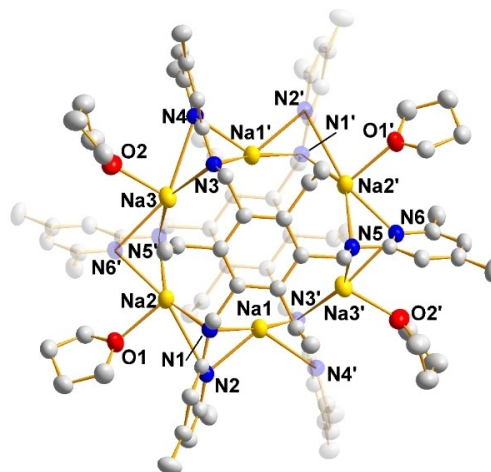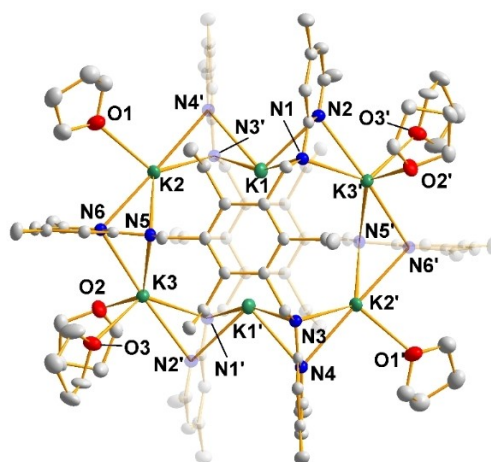

Figure 4. Molecular structure of potassium complex **3**. Hydrogen atoms and disordered component of one THF molecule are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Symmetry operation to generate equivalent atoms labelled ': 1-x, 1-y, 1-z.

[2.452(2)Å]. The propagation of **2** into a dimer arises from the Na centres bonding to a pair of amidopyridine N atoms from each of its two adjacent L^{3-} neighbours, which now act as bridging ligands, ultimately leading to a closed cycle in a departure from the open variant found for the lithium congener **1**, where L^{3-} acts terminally. In contrast to the geometry in complex **1**, all three amidopyridine groups are positioned on the same side of the central phenyl ring in **2** to allow the frame structure to close up. Furthermore, the unsolvated sodium atoms (Na1/Na1′) come into reasonably close proximity to a C–C unit of the central aromatic rings, raising the possibility of η^2-π-interactions and thus an increased coordination number of 6. These Na–C distances fall in the range 3.455(3)–3.900(3)Å, or 3.496(1)/3.809(1)Å when considered relative to the centre of the C–C bond.
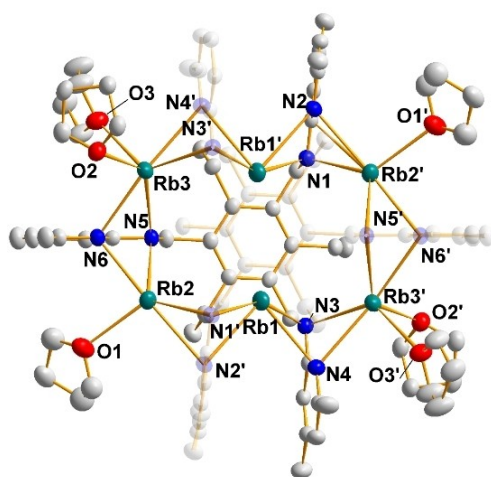
Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202403544

Chemistry Europe
European Chemical
Societies Publishing

Figure 5. Molecular structure of rubidium complex **4**. Hydrogen atoms and disordered component of THF molecule are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Symmetry operation to generate equivalent atoms labelled ′: 1-x, 1-y, 1-z.

The dimeric structure of the potassium congener **3** (Figure 4) bears a close resemblance to that of **2**. The most obvious change is the number of THF ligands at the periphery, six in total, with K1, K2 and K3 and their symmetry equivalents carrying none, one, and two respectively. With respect to heteroatoms, K3 is the most unique of the metal series so far since it is hexacoordinate surrounded by four N and two O atoms. Again, this higher coordination number due to extra THF solvation is enabled by eased steric restraints through longer metal-N bond lengths around the larger alkali metal. The mean

K–N_{amido} distances are 2.72 Å for K1 (having no THF ligand), 2.83 Å for K2 (having one THF ligand) and 2.95 Å for K3 (having two THF ligands) while their K–N_{pyr} distances show less variation with mean values of 2.866, 2.84 and 2.84 Å respectively. Similar to the bonding situation in complex **2**, the unsolvated alkali-metal K1 (and K1′) in **3** lies in reasonably close proximity to the C–C unit of the central aromatic ring, range 3.462(1)–3.675(1) Å from the C atoms themselves or 3.500(1)/3.555(1) Å from the C–C midpoints.

This increasing THF solvation discontinues at Rb in **4** (Figure 5), the structure of which is essentially identical to that of K complex **3** but with appropriately longer bond lengths as expected from the larger size of Rb versus K. That said, the mono-THF-solvated Rb2 atom lies 3.580(4)Å from the β-C atom (C42) of a solvating THF molecule of a neighbouring hexanuclear frame, with this agostic-type interaction increasing the coordination number of this larger alkali-metal to six.

Reactivity with Caesium Bases

Perhaps surprisingly, Cs deviates significantly from the rest of the aminopyridyl frame series, so is worthy of discussion on its own. A key synthetic distinction is that the three molar equivalents of the metallating agent used per ligand, CsHMDS in this case, appeared not to completely deprotonate/caesiate the **LH₃** substrate (Scheme 2) as a suspension obtained from a reaction performed in hexane and subsequently dissolved in THF produced isolable crystals which still contained two un-metallated amine NH bonds. This complex was therefore found to be tetranuclear with the molecular formula **[Cs₄(LH)₂·(THF)₆]**
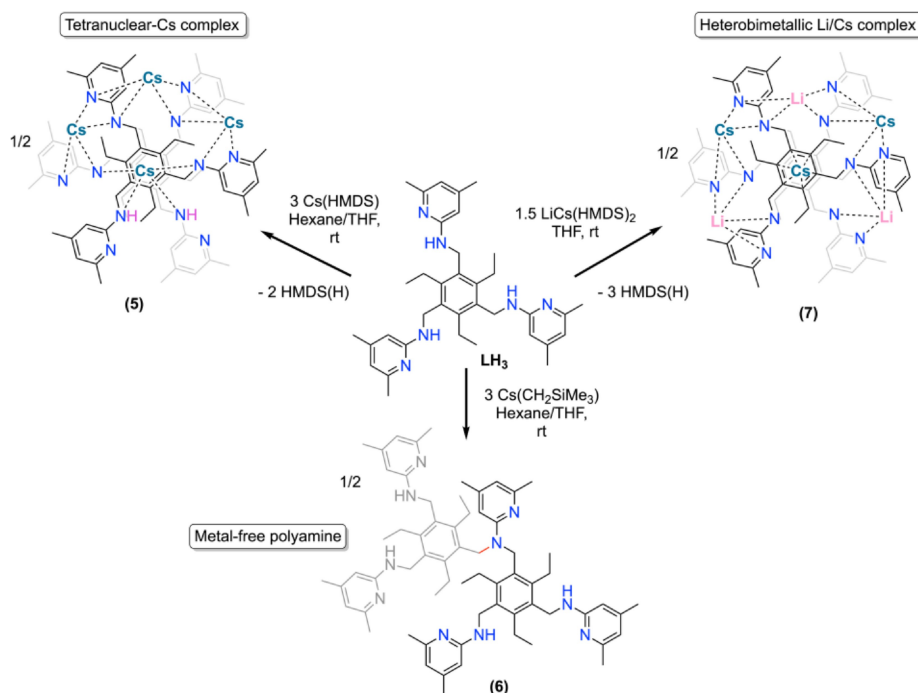
Scheme 2. Synthesis of Cs-homo and hetero-multimetallic complexes **5** and **7** with THF ligands omitted and the metal-free side product **6** with the connecting bond of two LH₃ derived rings denoted in red.

Chem. Eur. J. **2024**, e202403544 (4 of 9)

© 2024 The Author(s). Chemistry - A European Journal published by Wiley-VCH GmbH

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202403544

**Chemistry
Europe**
European Chemical
Societies Publishing

(**5**). The SCXRD data for **5** revealed its pseudo-dimeric structure (Figure 6), where three Cs atoms (Cs2-4) are each solvated by two THF ligands while Cs1 is THF-free. This unique Cs atom bonds to the two protonated amine N arms [3.485(6)/3.441(7)Å] as well as forming shorter bonds to two deprotonated amido N arms [3.232(5)/3.235(5)Å]. Furthermore, it appears to bind to the π-system of the phenyl rings in a η^3 fashion, with the closest carbon of each ring at 3.288(6)/3.285(7)Å and their adjacent carbon atoms in the range 3.425(6)–3.608(7)Å from Cs1, resulting in a C–Cs-C angle of 169.4(2)°. The other three Cs centres are six-coordinate bonding to pairs of N_{amido} and N_{pyr} atoms with little difference in their distances despite them being formally anionic and neutral [mean values 3.132 Å and 3.130 Å, respectively] as well as to a pair of THF ligands in a similar fashion to those bis-solvated alkali-metal atoms in **3** and **4**. Attempts to achieve full threefold deprotonation with the alternative base $Cs(CH_2SiMe_3)$ also failed.

Interestingly, however, this attempted metallation process did produce an isolable caesium-free product in compound **6**. Determined by SCXRD, its structure (Figure S6) suggests that formally C–N bond and N–H bond cleavages have occurred to eliminate one 2-amino-4,6-dimethylpyridine molecule, with a concomitant C–N bond formation process having occurred between two **LH₃** units (the new CN bond is highlighted in red in Scheme 2) with these two units fused by a N-C-N bridge exhibiting single N–C bond distances [1.471(2)Å, 1.477(2)Å], resulting in a tertiary amine centre. Since this was a metal-free side product of the intended reaction it was not investigated any further.

Inspired by the beautiful work on homometallic and heterobimetallic caesium HMDS complexes by O'Hara *et al.*,[16] we next studied an alternative approach to try and fully deprotonate **LH₃** via its reaction with an equimolar mixture of bimetallic $LiCs(HMDS)_2$ in THF solution. A SCXRD determination of the colourless crystals obtained from this reaction revealed

the formation of the heterobimetallic complex [**Li₃Cs₃L₂·(THF)₄**] (**7**) (see Scheme 2).

Its molecular structure (Figure 7) reveals an eye-catching hexanuclear arrangement confirming that the six amine groups of the two **L** ligands have been fully deprotonated to **L³⁻** and that the 1:1, Li:Cs stoichiometry of the $LiCs(HMDS)_2$ starting material has been maintained in this bimetallic product. Similar to the arrangements of the homometallic complexes of composition M_6L_2 already discussed, the amidopyridine ligands are all located on the same side of the triethylphenyl ring to maximize M–N interactions and provide a coordination layer for the metal cations to reside. While all three Li atoms are tetracoordinated by four nitrogen atoms of two deprotonated amidopyridine arms, the dimensions are highly distorted from an idealised tetrahedron since the N_{amido}-Li-N_{amido} bond angles lie in the range 153.9(3)–164.4(2)°, likely as a consequence of the acute angles enforced by the 4-membered N_{amido}-C-N_{pyr}-Li endocyclic ring angles which are in the range 67.5(2)–69.1(2)°. Contrasting with the similarity of these Li atoms, the larger Cs atoms separate into two distinct types. Whereas Cs2 and Cs3 lie in between two different amidopyridine planes bonding to four N atoms and each capped by two terminal THF ligands, Cs1 coordinates to four amido nitrogen anions [N1, N3, N9, N11, range 3.435(2)–3.727(2)Å] whilst it is simultaneously uniquely sandwiched in the middle of the two slightly offset aromatic rings stabilized by their π-clouds in a η^6 fashion to each (Figure 8). Note the two phenyl rings lie almost parallel to each other with the angle between planes being only 2.73(8)°. The Cs interactions to the phenyl rings lie in the range 3.292(2)–3.592(2)Å for one ring and 3.291(2)–3.605(2)Å for the other ring, and 3.162(1)/3.168(1)Å to the ring centroids, respectively. Such metal-π-arene interactions are common for caesium in a variety of different frameworks such as those containing anionic polyarenes,[17] or as part of mono-[9c,18] or bimetallic complexes,[19] often helping to hold together and stabilize low-valent Al(I) centres (or their post-reaction products)[20] or highly reactive Mg–H bonds.[21] To the best of our knowledge,
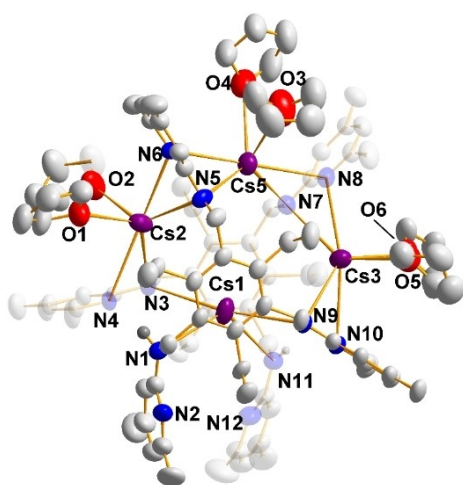

Figure 6. Molecular structure of tetranuclear caesium complex **5** with hydrogen atoms other than those on N1/N11 and minor disordered components of THF omitted for clarity and thermal ellipsoids drawn at the 50% probability level.
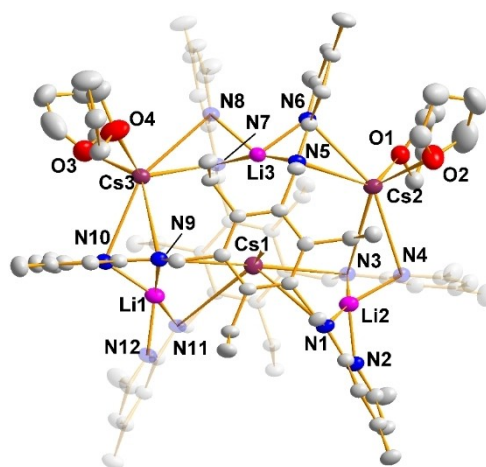

Figure 7. Molecular structure of the mixed lithium-caesium frame complex **7** with hydrogen atoms, THF molecules of crystallisation and minor disordered components of coordinated THF omitted for clarity and thermal ellipsoids drawn at the 50% probability level.
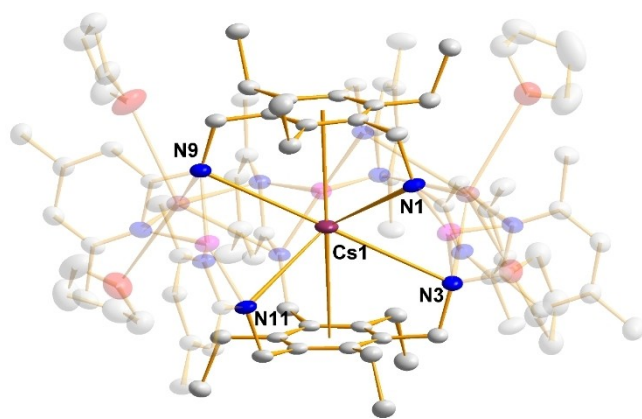
Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202403544

Chemistry Europe
European Chemical
Societies Publishing

Figure 8. Side on view of the structure of complex **7** displaying the unique coordination sphere of Cs1.

Table 1. Selected ^{1}H NMR spectroscopic data for parent ligand and soluble Li (**1**), K (**3**) and Rb (**4**) complexes.

	LH$_3$		**1**	**3**	**4**
	THF-D$_8$	C$_6$D$_6$	THF-D$_8$	C$_6$D$_6$	C$_6$D$_6$
CH$_2$ Et	1.20	1.16	1.17	1.57	1.61
CH$_3$ Et	2.82	2.83	2.83	2.72	2.74
CH$_2$-N	4.48	4.67	3.98	4.30	4.38
CH$_3$ py	2.27	2.41	2.00	2.20	2.24
CH$_3$ py	2.13	1.97	1.95	1.91	1.89
CH py	6.23	6.21	5.61	6.14	6.19
CH py	6.06	5.87	5.37	5.76	5.77
NH	5.04	4.23	–	–	–

heterobimetallic lithium-caesium complexes based on a single polyanionic organoelement ligand are structurally unknown. The closest lithium-caesium monoanionic organoelement structure for comparison is 2[Cs(15-crown-5)$_2$]$^+$ [Li(NHPy)$_3$]$^{2-}$, but this adopts a markedly different structure in a simple solvent-separated arrangement where the amidopyridine ligand bonds only to the lithium centre with the crown ethers sequestering the pair of Cs cations.[22] The structure of **7** showcases the different characters of the two extreme non-radioactive members of the alkali metal family with hard lithium favouring sigma interactions with heteroatoms, while soft caesium seeks out any available π-clouds.

Solution Study of Alkali-metal Framework Complexes

Despite the high reactivity typically associated with metal-nitrogen bonds for alkali metals, all compounds were stable in solution. In contrast, according to their air and moisture sensitivity in solid state, exposure of solutions containing compounds **1**–**4** to air result in the formation of ligand **LH$_3$**.

Lithium complex **1** displayed poor solubility in C$_6$D$_6$ so instead it was analysed by NMR spectroscopy in more polar THF-D$_8$ (Table 1). Loss of the NH resonance at 5.04 ppm in the ^{1}H NMR spectrum confirms deprotonation of the ligand, whilst the resonances around the site of metallation are all noticeably upfield shifted, consistent with the shielding effects induced by the enhanced anionic character following metallation. For example, the N-CH$_2$ resonance moves from 4.48 to 3.98 ppm, the pyridyl methyl groups move from 2.27/2.13 to 2.00/1.95 ppm and the pyridyl CH groups move from 6.23/6.06 to 5.61/5.37 ppm. The ethyl group resonances barely change on account of their remote nature with respect to Li. Unfortunately, sodium complex **2** was virtually insoluble in THF as well as in benzene so no solution state NMR spectroscopy data could be collected.

Interestingly, dimeric hexanuclear complexes **3** (potassium) and **4** (rubidium) were benzene soluble (Table 1). Mirroring complex **1**, the resonances of the hydrogen atoms in the

vicinity of the alkali-metal are again shielded, exemplified by the CH$_2$ group adjacent to the deprotonated N atom moving from 4.67 to 4.30/4.38 ppm for **3** and **4** respectively. Unlike complex **1**, the ethyl resonances are also noticeably moved, in particular the phenyl-bound methylene group which is downfield shifted from 1.16 ppm in the starting material to 1.57/1.61 ppm in the metallated complexes.

This perhaps suggests that the dimeric constitution is retained in solution, maintaining the positioning of all the ethyl groups on the same side of the aromatic ring rather than the favoured position of them as seen in the free ligand and monomeric complex **1**. Similar to compound **2**, caesium species **5** and heterobimetallic compound **7** are insoluble in THF-D$_8$ and C$_6$D$_6$ precluding further analysis in solution.

Conclusions

This work has compiled a rare complete set of multi-alkali-metallated molecular compounds of a single framework molecule, namely that of 1, 3, 5-tris-2-aminopyridyl-2, 4, 6-triethylbenzene, where the identity of the alkali metal is a major factor behind the conformational characteristics of the framework amido arms. The lighter congeners fall into two distinct sets, the lithium example uniquely adopts a trinuclear arrangement with the metallated amidopyridine arms split in a 2:1 ratio either side of the aromatic benzene plane. In contrast, the larger coordination spheres of sodium, potassium, and rubidium permit construction of hexameric arrangements, necessitating that all three amidopyridine arms within both trianionic ligands project outwards on the same side of the aromatic plane with metal atoms bridging between the two benzene frames. Adding to the diversity, incomplete metallation of the N—H bonds ligand was encountered with caesium that led to a tetranuclear arrangement, while a mixed lithium-caesium Li$_3$Cs$_3$ variant produced another but uniquely different hexanuclear arrangement where five metals occupy peripheral sites of a bis-benzene type sandwich with the remaining caesium atom located in the middle of the sandwich η^6-bonded to both aromatic benzene rings.

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202403544

Chemistry
Europe

European Chemical
Societies Publishing

Aside from potential application of these new compounds in transmetallation chemistry in specific future work, the diversity of their structures uncovered in this study has strengthened the case for greater development of rubidium and caesium organoelement chemistry and for more comparative consideration of the complete family of alkali metals in future studies. While the poor solubility of some of these new complexes may negate their usefulness in solution chemistry, they could impact mechanochemistry, which though gaining momentum in the search for eco-friendly developments in inorganic chemistry is not so well developed for alkali metal organoelement compounds.[23]

Experimental Section

General Considerations

Proligand 1,3,5-tris[[(4,6-dimethylpyridin-2-yl)aminomethyl]-2,4,6-triethylbenzene was synthesized as described in the literature.[10] Alkali deprotonative metallation of this proligand was then attempted using a suitable Brønsted base of the metal involved, namely the commercial reagents $LiCH_2SiMe_3$, LiHMDS, NaHMDS, and KHMDS purchased from Sigma-Aldrich and used as received, while RbHMDS and CsHMDS had to be synthesised using commercially available reagents via literature preparations.[24] All reactions were performed under a protective argon or nitrogen atmosphere using either standard Schlenk or glove box techniques.[25] Hexane and THF were dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. C_6D_6 and acetonitrile were degassed by freeze-pump-thaw methods and stored over activated 4 Å molecular sieves. All other reagents were purchased from commercial sources and were also used as received.

NMR spectra were recorded on a Bruker AV3 or AV400 MHz spectrometer operating at 400.13 MHz for ^1H, 155.47 MHz for ^7Li and 100.62 MHz for ^{13}C. All ^{13}C NMR spectra were proton decoupled. ^1H, $^{13}C\{^1H\}$ and ^7Li chemical shifts are expressed in parts per million (δ, ppm) and where appropriate referenced to residual solvent peaks or external references.

Single Crystal X-ray Crystallography

All crystallographic measurements were made with monochromatic Cu radiation ($\lambda = 1.54184$ Å) using a Rigaku Synergy-i diffractometer. Raw data processing utilised the program CrysalisPro.[26] The structures were solved using direct methods and were refined against F^2 to convergence using all unique reflections and the program Shelxl,[27] as implemented within WinGX.[28] Across the structures, many groups were found to be disordered, see deposited cif for details. Disordered groups were modelled across two sites and appropriate restraints and constraints were added to ensure that each approximated to normal geometry and displacement behaviour. Structure **5** was treated with the SQUEEZE routine available in the programme PLATON.[29] A total of 171 electron equivalents were removed from approximately 990 Å^3 of unit cell space. The disordered solvent so treated is believed to be hexane, with a ratio of just less than one hexane molecule per complex molecule. Selected crystallographic and refinement parameters are given in Table S8 and full information in cif format has been deposited with the CCDC as reference numbers 2378915 to 2378921. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Synthetic Details

$[Li_3L \cdot (THF)_6]$, (1).

Proligand LH_3 (0.057 g, 0.1 mmol) was suspended in hexane (2 ml) before $LiCH_2SiMe_3$ (0.029 g, 0.3 mmol) was introduced to give a yellow suspension. The suspension was stirred for 1 hour, after which THF (0.5 ml) was added, resulting in a pale-yellow solution. Upon cooling the solution to $-20\,°C$, a batch of colourless crystals of compound **1** was obtained (0.040 g, 0.04 mmol, 40%). Note this compound was poorly soluble in C_6D_6 so spectra were recorded in THF-D_8.

^1H NMR (400.1 MHz, C_6D_6/THF-D_8, 300 K): δ 5.61 (m, 3H, CH_{pyr}), 5.37 (m, 3H, CH_{pyr}), 3.98 (s, 6H, CH_2, $C-CH_2-N$), 3.58 (THF), 2.83 (m, 6H, CH_2, Et), 2.00 (s, 9H, $CH_{3\ pyr}$), 1.95 (s, 9H, $CH_{3\ pyr}$), 1.71 (THF), 1.17 (m, 9H, CH_3, Et) ppm.

$^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6/THF-D_8, 300 K): δ 170.1 (C_{Ar}), 154.7 (C_{Ar}), 147.1 (C_{Ar}), 140.5 (C_{Ar}), 139.4 (C_{Ar}), 128.5 (C_6D_6), 102.1 (CH_{pyr}), 99.6 (CH_{pyr}), 67.4 (THF), 46.6 (CH_2), 25.3 (THF), 24.7 (CH_2, Et), 23.3 (CH_3), 21.9 (CH_3), 17.5 (CH_3, Et) ppm.

^7Li NMR (155.5 MHz, THF-D_8, 298 K) δ 1.31 ppm.

$[Na_6L_2 \cdot (THF)_4]$ (2)

Solid Na(HMDS) (0.0549 g, 0.3 mmol) was added to a suspension of LH_3 (0.0565 g, 0.1 mmol) in hexane (2 mL), and the mixture was stirred for two days. THF (4 mL) was then introduced, and the suspension was stirred overnight before the solvent was removed in vacuo. The powdery residue was then treated with THF to generate a solution, which upon slow evaporation of THF afforded colourless crystals of **2** (0.047 g, 0.028 mmol, crude yield 56%). These crystals were of good enough quality for an X-ray crystallographic study. Hydrocarbon and donor solvents were used to try and dissolve these crystals without success, since weak NMR spectra were obtained that only showed a small quantity of the non-metallated LH_3.

$[K_6L_2 \cdot (THF)_6]$ (3)

LH_3 (0.057 g, 0.1 mmol) was suspended in hexane (2 mL) to which K(HMDS) (0.060 g, 0.3 mmol) was added, resulting in an off-white suspension. Next, the mixture was stirred for 48 hours. THF (0.5 mL) was subsequently added to form a solution, which was placed in a $-20\,°C$ freezer. Colourless crystals of the product, suitable for X-ray analysis, were obtained overnight (0.057 g, 0.032 mmol, yield 64%).

^1H NMR (400.1 MHz, C_6D_6, 300 K): δ 6.14 (s, 3H, CH_{pyr}), 5.76 (s, 3H, CH_{pyr}), 4.30 (s, 6H, CH_2), 3.56 (m, 8H, CH_2, THF), 2.72 (m, 6H, CH_2, Et), 2.20 (s, 9H, CH_{3pyr}), 1.91 (s, 9H, CH_{3pyr}), 1.57 (t, 9H, CH_3, Et), 1.42 (m, 8H, THF) ppm.

$^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 300 K): δ 167.6 (C_{Ar}), 156.9 (C_{Ar}), 148.0 (C_{Ar}), 140.8 (C_{Ar}), 137.3 (C_{Ar}), 104.3 (CH_{pyr}), 101.3 (CH_{pyr}), 67.7 (THF), 46.3 (CH_2), 25.8 (THF), 24.5 (CH_2, Et), 23.5 (CH_3), 21.7 (CH_3), 17.3 (CH_3, Et) ppm.

$[Rb_6L_2 \cdot (THF)_6]$ (4)

LH_3 (0.141 g, 0.25 mmol) was dissolved in THF (4 mL) and Rb(HMDS) (0.185 g, 0.75 mmol) was introduced, resulting in a yellow solution,

Chem. Eur. J. **2024**, e202403544 (7 of 9)

© 2024 The Author(s). Chemistry - A European Journal published by Wiley-VCH GmbH

which was stirred overnight. Colourless crystals of the product were obtained by slow evaporation of the solvent in vacuo (0.230 g, 0.11 mmol, yield 89%).

^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 6.19 (s, 3H, CH_{pyr}), 5.77 (s, 3H, CH_{pyr}), 4.38 (s, 6H, CH_2), 3.57 (m, 8H, CH_2, THF), 2.74 (m, 6H, CH_2, Et), 2.24 (s, 9H, CH_{3pyr}), 1.89 (s, 9H, CH_{3pyr}), 1.61 (t, 9H, CH_3, Et), 1.42 (m, 8H, THF) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 166.8 (C_{Ar}), 156.4 (C_{Ar}), 147.6 (C_{Ar}), 140.4 (C_{Ar}), 137.8 (C_{Ar}), 103.6 (CH_{pyr}), 101.3 (CH_{pyr}), 67.8 (CH_2, THF), 46.5 (CH_2), 25.8 (CH_2, THF), 24.4 (CH_2, Et), 23.5 (CH_3), 21.8 (CH_3), 17.3 (CH_3, Et) ppm.

$[Cs_4(LH)_2 \cdot (THF)_6]$ (5)

To a suspension of LH_3 (0.339 g, 0.6 mmol) in hexane (7 mL), Cs(HMDS) (0.530 g, 1.8 mmol) was added resulting in an off-white suspension. The reaction mixture was stirred overnight then the solvent was removed in vacuo. The residue was placed in a vial to which THF was added to give a solution that afforded a crop of colourless crystals (0.435 g, 0.21 mmol, crude yield 70%). These crystals were of suitable quality for an X-ray crystallographic study. Mimicking compound 2, this product was essentially insoluble in C_6D_6 or THF-D_8 solvents and so no diagnostic NMR data could be obtained, though again a small quantity of non-metallated LH_3 was detectable in ^{1}H NMR spectra.

Side Product (6)

LH_3 (0.058 g, 0.1 mmol) was suspended in hexane (5 mL), followed by the addition of $Cs(CH_2SiMe_3)$ (0.066 g, 0.3 mmol), resulting in a brown-coloured suspension. This mixture was stirred overnight then the solvent was removed in vacuo. Colourless crystals were obtained by slow evaporation of a solution of the residue in a mixture of acetonitrile and THF. X-ray crystallographic analysis revealed the crystals to be a mixture of compound (6), trimerized acetonitrile (2,4,6-trimethyl-1,3,5-triazine),[30] and compound (5). Due to this mixture of products, and its poor solubility, no useful NMR data could be obtained, and a pure sample of and yield for compound (6) could not be determined.

$[Li_3Cs_3L_2 \cdot (THF)_4]$ (7)

LH_3 (0.0570 g, 0.1 mmol) was dissolved in THF (2 mL), followed by the addition of the bimetallic compound $LiCs(HMDS)_2$ (0.0453 g, 0.1 mmol), resulting in a yellow solution. The mixture was stirred for one hour and then placed in a $-20\,°C$ freezer. After several weeks, colourless crystals of the product were obtained (0.0580 g, 0.03 mmol, crude yield 63%). Again, this product was essentially insoluble in C_6D_6 or THF-D_8 solvents and so no diagnostic NMR data could be obtained, though again a small quantity of non-metallated LH_3 was detectable in ^{1}H NMR spectra.

Deposition Numbers

2378915-2378921 for complexes 1–7 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in edatos.consorciomadrono.es at https://doi.org/10.21950/QOREAQ.

[1] a) R. Maity, B. S. Birenheide, F. Breher, B. Sarkar, *ChemCatChem* **2021**, *13*, 2337–2370; b) A. C. Ghosh, C. Duboc, M. Gennari, *Coord. Chem. Rev.* **2021**, *428*, 213606.

[2] I. Bratko, M. Gomez, *Dalton Trans.* **2013**, *42*, 10664–10681.

[3] a) Y. Su, Y. Zhao, J. Gao, Q. Dong, B. Wu, X.-J. Yang, *Inorg. Chem.* **2012**, *51*, 5889–5896; b) J. A. DeGayner, I.-R. Jeon, T. D. Harris, *Chem. Sci.* **2015**, *5*, 6639–6648; c) R. B. Ferreira, L. J. Murray, *Acc. Chem. Res.* **2019**, *52*, 447–455.

[4] a) S. Gonell, M. Poyatos, E. Peris, *Angew. Chem. Int. Ed.* **2013**, *52*, 7009–7013; b) S. Ibañez, E. Peris, *Angew. Chem. Int. Ed.* **2019**, *58*, 6693–6697.

[5] a) M. C. Eaton, B. J. Knight, V. J. Catalano, L. J. Murray, *Eur. J. Inorg. Chem.* **2020**, 1519–1524; b) D. M. Ermert, I. Ghiviriga, V. J. Catalano, J. Shearer, L. J. Murray, *Angew. Chem. Int. Ed.* **2015**, *54*, 7047–7050; c) B. J. Cook, G. N. Di Francesco, K. A. Abboud, L. J. Murray, *J. Am. Chem. Soc.* **2018**, *140*, 5696–5700.

[6] a) T. M. Powers, T. A. Betley, *J. Am. Chem. Soc.* **2013**, *135*, 12289–12296; b) A. K. Bartholomew, C. E. Juda, J. N. Nessralla, B. Lin, S. G. Wang, Y.-S. Chen, T. A. Betley, *Angew. Chem. Int. Ed.* **2019**, *58*, 5687–5691; c) A. K. Bartholomew, R. A. Musgrave, K. J. Anderton, C. E. Juda, Y. Dong, W. Bu, S.-Y. Wang, Y.-S. Chen, T. A. Betley, *Chem. Sci.* **2021**, *12*, 15739–15749; d) R. H. Sanchez, A. K. Bartholomew, T. M. Powers, G. Menard, T. A. Betley, *J. Am. Chem. Soc.* **2016**, *138*, 2235–2243.

[7] F. Zhong, X. Yang, L. Shen, Y. Zhao, H. Ma, B. Wu, X.-J. Yang, *Inorg. Chem.* **2016**, *55*, 9112–9120.

[8] a) C. Ritter, F. Weigend, C. von Hänisch, *Chem. Eur. J.* **2020**, *26*, 8536–8540; b) C. Ritter, J. Bergunde, F. Weigend, C. von Hänisch, *Z. Anorg. Allg. Chem.* **2021**, *647*, 1830–1839.

[9] a) L. Brieger, C. Unkelbach, C. Strohmann, *Chem. Eur. J.* **2021**, *27*, 17780–17784; b) K. G. Pearce, H.-Y. Liu, S. E. Neale, H. M. Goff, M. F. Mahon, C. L. McMullin, M. S. Hill, *Nat. Commun.* **2023**, *14*, 8147; c) C. Knüpfer, L. Klerner, J. Mai, J. Langer, S. Harder, *Chem. Sci.* **2024**, *15*, 4386–4395; d) D. E. Anderson, A. H. N. Truong, E. Hevia, *Chem. Eur. J.* **2024**, *30*, e202400492.

[10] a) T. X. Gentner, A. R. Kennedy, E. Hevia, R. E. Mulvey, *ChemCatChem* **2021**, *13*, 2371–2378; b) P. A. Macdonald, S. Banerjee, A. R. Kennedy, A. van Teijlingen, S. D. Robertson, T. Tuttle, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2023**, *62*, e202304966.

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202403544

Chemistry Europe
European Chemical
Societies Publishing

[11] M. Mazik, W. Radunz, R. Boese, *J. Org. Chem.* **2004**, *69*, 7448–7462.

[12] a) M. Mazik, H. Cavga, P. G. Jones, *J. Am. Chem. Soc.* **2005**, *127*, 9045–9052; b) J. Lippe, W. Seichter, M. Mazik, *Org. Biomol. Chem.* **2015**, *13*, 11622–11632; c) J. Lippe, M. Mazik, *J. Org. Chem.* **2015**, *80*, 1427–1439.

[13] a) S. Banerjee, P. A. Macdonald, S. A. Orr, A. R. Kennedy, A. van Teijlingen, S. D. Robertson, T. Tuttle, R. E. Mulvey, *Chem. Eur. J.* **2022**, *28*, e202201085; b) A. Rae, K. M. Byrne, S. A. Brown, A. R. Kennedy, T. Krämer, R. E. Mulvey, S. D. Robertson, *Chem. Eur. J.* **2022**, *28*, e202104260.

[14] T. Janes, J. M. Rawson, D. Song, *Dalton Trans.* **2013**, *42*, 10640–10648.

[15] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955–964.

[16] A. I. Ojeda-Amador, A. J. Martinez-Martinez, A. R. Kennedy, C. T. O'Hara, *Inorg. Chem.* **2016**, *55*, 5719–5728.

[17] S. N. Spisak, Z. Wei, A. Y. Rogachev, T. Amaya, T. Hirao, M. A. Petrukhina, *Angew. Chem. Int. Ed.* **2017**, *56*, 2582–2587.

[18] a) C. Eaborn, P. B. Hitchcock, K. Izod, J. D. Smith, *Angew. Chem. Int. Ed.* **1995**, *34*, 687–688; b) C. Eaborn, W. Clegg, P. B. Hitchcock, M. Hopman, K. Izod, P. N. O'Shaughnessy, J. D. Smith, *Organometallics* **1997**, *16*, 4728–4736; c) A. I. McKay, M. L. Cole, *Dalton Trans.* **2019**, *48*, 2948–2952.

[19] a) S. F. McWilliams, K. R. Rodgers, G. Lukat-Rodgers, B. Q. Mercado, K. Grubel, P. L. Holland, *Inorg. Chem.* **2016**, *55*, 2960–2968; b) G. M. Ballmann, T. X. Gentner, A. R. Kennedy, E. Hevia, R. E. Mulvey, *Chem. Eur. J.* **2022**, *28*, e202201716; c) J. J. C. Struijs, M. A. Ellwanger, A. E. Crumpton, V. Gouverneur, S. Aldridge, *Nat. Chem.* **2024**, *16*, 1473–1480.

[20] a) T. X. Gentner, M. J. Evans, A. R. Kennedy, S. E. Neale, C. L. McMullin, M. P. Coles, R. E. Mulvey, *Chem. Commun.* **2022**, *58*, 1390–1393; b) S. Grams, J. Mai, J. Langer, S. Harder, *Dalton Trans.* **2022**, *51*, 12476–12483;

c) G. M. Ballmann, M. J. Evans, T. X. Gentner, A. R. Kennedy, J. R. Fulton, M. P. Coles, R. E. Mulvey, *Inorg. Chem.* **2022**, *61*, 19838–19846; d) H.-Y. Liu, M. S. Hill, M. F. Mahon, C. L. McMullin, R. J. Schwamm, *Organometallics* **2023**, *42*, 2881–2892; e) S. Banerjee, G. M. Ballmann, M. J. Evans, A. O'Reilly, A. R. Kennedy, J. R. Fulton, M. P. Coles, R. E. Mulvey, *Chem. Eur. J.* **2023**, *29*, e202301849.

[21] a) M. J. Evans, C. Jones, *Inorg. Chem.* **2023**, *62*, 14393–14401; b) T. X. Gentner, G. M. Ballmann, S. Banerjee, A. R. Kennedy, S. D. Robertson, R. E. Mulvey, *Organometallics* **2024**, *43*, 1393–1401.

[22] S. T. Liddle, W. Clegg, *J. Chem. Soc. Dalton Trans.* **2001**, 3549–3550.

[23] J. F. Reynes, F. Leon, F. Garcia, *ACS Org. Inorg. Au* **2024**, *4*, 4c00001.

[24] S. Krieck, P. Schüler, H. Görls, M. Westerhausen, *Dalton Trans.* **2018**, *47*, 12562–12569.

[25] D. F. Shriver, M. A. Drezdzon, *The Manipulation of Air-Sensitive Compounds*, John Wiley & Sons Ltd., New York, **1986**.

[26] Rigaku OD (2016). *CrysAlis PRO.* Rigaku Oxford Diffraction Ltd., Yarnton, England **2016**.

[27] G. M. Sheldrick, *Acta Cryst. C* **2015**, *71*, 3–8.

[28] L. J. Farrugia, *J. Appl. Cryst.* **2012**, *45*, 849–854.

[29] A. L. Spek, *Acta Cryst. C* **2015**, *71*, 9–18.
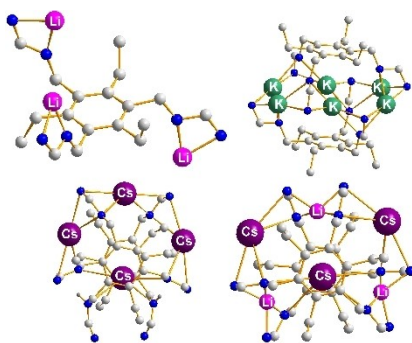
[30] B. H. Hoff, *Synthesis* **2018**, *50*, 2824–2852.

RESEARCH ARTICLE

This study demonstrates how the co-ordination conformation of a tris-amine molecule built on a central benzene frame changes when multi-metallated by a different set of alkali metals

J. R. Lynch, M. Navarro, A. R. Kennedy, S. D. Robertson, R. E. Mulvey, A. Hernán-Gómez*

1 – 10

Diverse Multinuclear Alkali Metallated (Li, Na, K, Rb, Cs) Family of the 1,3,5-tris-2-aminopyridyl-2,4,6-triethylbenzene Framework