Introduction

Interest in methods for refining the regioselective functionalization of aromatics by using more selective bases has grown significantly since the inception of what have become known as 'synergic bases'. These heterobimetallic systems – in their simplest form RₘM(NR')ₙAM (R = organyl; m = 0, 2, 3; M = less polarizing metal; NR' = amide; n = 1, 2, 3; AM = more polarizing (alkali) metal) – have afforded new levels of reactivity, regioselectivity and functional group tolerance not hitherto available through traditional main group organometallic bases. Recently, a fruitful area of synergic base chemistry that has developed has involved directed cupration using lithium cuprate reagents. The structural variability manifest in lithium cuprate chemistry, which derives in part from the potential to enhance reactivity by introducing an alkali metal salt, highlights the need to better understand structural variability in synergic systems. The corresponding elucidation of synergic bases was initially dominated by crystallographic determination. However, their heterobimetallic composition has led to the need for solution analysis to establish the nature of competition between structure retention of the heterobimetallic moiety versus the cooperative action of individually monometallic reagents and the permutations for dynamic deaggregation/recombination.

First developed 50 years ago, lithium cuprates have been subsequently modified in two main ways. First, lithium amidocuprates have been developed, offering often unique reactivities as well as the potential of the amido group as a non-transferable ligand and as a chiral auxiliary. Second, yield enhancements have been sought by combining so-called Gilman lithium cuprates (R₂CuLi) with lithium salts. For the deployment of LiCN as the latter, the resulting cuprates (R₂Cu(CN)Li₂) were coined Lipshutz cuprates and spectroscopic studies suggested the possibility that transfer of cyanide to Cu would give a higher order (tricoordinate) metal. However, the alternative of retention of lower order (dicoordinate) copper was suggested on theoretical, spectroscopic and, more recently, X-ray diffraction grounds. The isolation and characterization of lithium cyanocuprates 1a-c, which were prepared using amidolithium reagents with CuCN, revealed the bonding characteristics of Cu in systems that could demonstrate either higher or lower order structural properties. In line with...
theoretical expectations, lower order \( (\text{TMP})_2\text{Cu}(\text{CN})\text{Li}_2(L) \) \( L = \text{OEt}_2, \text{THF}, \text{THP} = \text{tetrahydropyran} \) \( ^{17,28} \) structures were observed crystallographically, with agglomeration giving essentially planar dimers based on lithium–nitrogen cores (Scheme 1). The observation that, whilst in other respects 1a–c pertained to Lipshutz cuprate characteristics, they lack a Cu–CN interaction led to investigation of the generality of this motif. To this end \( (\text{TMP})_2\text{Cu}(\text{X})\text{Li}_2(L) \) \( X = \text{Cl} 2, \text{Br} 3, \text{I} 4, L = \text{OEt}_2, 2\text{a}–\text{a}, \text{THF} \text{2b}–\text{b} \) were isolated (Scheme 1).\(^{19,20} \) As with the previously reported cyanide structures, these revealed lower order Cu in the solid state. The extension of monoatomic bridges to the field of triatomic inorganic anions was achieved by the development of thiocyanatocuprates. These utilize SCN\(^-\) in place of CN\(^-\) and formed \( (\text{TMP})_2\text{Cu}(\text{SCN})\text{Li}_2(L) \) \( L = \text{OEt}_2, 5\text{a}, \text{THF} 5\text{b}, \text{THP} 5\text{c} \), which demonstrated 8-membered metallacyclic \( \text{Li}_2(\text{SCN})_2 \) cores supported by 6-membered \( \text{N}_2\text{CuLi}_2 \) rings in the solid state (Scheme 2). In these structures, significant solvent effects were noted through the adoption of either planar, boat or chair conformers for the 8-membered core depending on whether the cuprate was additionally stabilized by OEt\(_2\), THF or THP, respectively.\(^{21} \)

The recent observation that cyanide-incorporating Lipshutz cuprates exhibit solvent-controlled conversion to their Gilman counterparts\(^7\) by the abstraction of LiCN\(^{22} \) has been superseded by the discovery that this process is likely to be responsible for the in situ creation of active species in solution.\(^{23} \) This has reinvigorated interest in the properties of lithium amido-cuprates and it has been noted that the ability of bimetallates of the type \( (\text{R}_2\text{N})_2\text{CuLi} \) to dimerize, coupled with the acknowledged issue of metal exchange between Li and Cu, as elucidated by van Koten and co-workers,\(^{16a,b,24} \) means that the field of Gilman cuprate chemistry is closely interwoven with that of copper–nitrogen metallacycles. These have been observed to constitute tetrameric ketimides,\(^{25} \) hydrazides,\(^{25} \) phosphinimides\(^{26} \) mixed amides/guanidinates\(^{27} \) and amides\(^{28} \) with the last of these ligand-types also supporting 3D clusters.\(^{28} \) Copper amides, first prepared a century ago\(^{29} \) and more recently the focus of intense study,\(^{11e,30} \) have proven to be synthetically important, with solid state tetramers shown to deaggregate and participate in modified Ullmann amination\(^{31} \) with amines in the presence of 1,10-phenanthroline.\(^{32} \) Meanwhile, Gilman lithium amidocuprates have been established to constitute the active species in directed aromatic cupration.\(^{33} \) However, synthetic studies having established that as-prepared Gilman cuprates are ineffectual, the need to convert Lipshutz(-type) cuprates to their Gilman counterparts in solution has been shown.\(^{23} \)

The current work sees further efforts to study the use of polyatomic inorganic salts in lithium amidocuprate chemistry, through the deployment of the rarely used cyanate ligand. This accesses a range of new lithium cyanatocuprates. Metal disorder in some examples of these new materials sheds important new light on the predilection of Cu for lower/higher order structure formation. Advances are also reported in our understanding of the solution behaviour of lithium cuprates.

## Results and discussion

### Synthesis and solid state analysis

\( \text{Cu(NO}_3)_2(\text{H}_2\text{O})_3 \) was reacted sequentially with \( \text{LiOAc(}\text{H}_2\text{O})_2, \) and \( \text{LiOCN} \) (see ESI†). The addition of \( \text{SO}_2 \) gave a green solution from which \( \text{CuOCN} \) 7 precipitated.\(^{22} \) The ability to prepare 7 offers the possibility of analyzing the cyanate analogue of recently reported \( (\text{TMP})_2\text{Cu(OCN)}\text{Li}_2(\text{THF}) \).\(^{21} \) A hexane solution of TMPLi was therefore reacted with CuOCN in a 2 : 1 ratio in the presence of THF (1 eq. wrt Cu). This gave a modest yield of crystalline blocks. IR spectroscopy showed a strong peak at 2208 cm\(^{-1} \) and X-ray diffraction pointed to the formulation \( (\text{TMP})_2\text{M(OCN)Li}_2(\text{THF}) \) but revealed disorder at the TMP-bridging metal site. The optimal crystallographic refinement suggests \( \text{M} = \text{Cu}_0.1\text{Li}_{0.9}, \) and therefore a 1 : 9 co-crystalline mixture of \( (\text{TMP})_2\text{Cu(OCN)}\text{Li}_2(\text{THF}) \) 8a and \( (\text{TMP})_2\text{Cu(OCN)Li}_2(\text{THF}) \) 8b (Scheme 3 and Fig. 1).

The X-ray diffraction structure of 8 reveals dimerization based on an 8-membered metallacyclic (LiOCN)\(_2\) core that incorporates a 3-coordinate Li centre (LiI2). This core is supported by two 6-membered \( \text{N}_2\text{MLi}_2 \) rings, within which the coordination sphere of LiI3 is completed by THF. However, in contrast to the previously noted THF-solvated thiocyanate 5b,\(^{21} \)

![Scheme 2](https://example.com/scheme2.png)
8 reveals not a boat conformation but an essentially planar arrangement, with only TMP and THF deviating significantly from a plane defined by the three conjoined metallacycles and the O(THF)–Li bonds (ESI, Fig. S1†). Of most interest is the observation that whereas the cores of 8a and 8b are essentially identical, the geometries of the 6-membered N3MLi2 rings vary significantly. In 8a (M = Cu) the obtuse angle of 167.3(4)° at Cu1 results in a non-bonding N3–Cu1 distance of 2.93(1) Å. Insofar as this distance is consistent with a dicoordinate (lower) order Cu centre this bonding pattern is consistent with the recent characterization of Lipshutz cuprates1a–c,17,18,21 halogenocuprates2–4 (ref. 19 and 20) and thiocyanatocuprates5a–c.21 In contrast, Li1 in the N3Li3 metallacycle of 8b is located significantly closer to N3 than is Cu1 in 8a, resulting in a reflex

Scheme 3 Solvent-dependent synthesis of 8a/b and 9.

N1–Li1–N2 angle of 186.6(5)°. The observation of a N3–Li1 2.597(11) Å distance suggests a weak interaction between these two centres and yields a motif reminiscent of intercepted ladder-type structures reported in the past for amidolithium aggregates.21

Reasoning that the depletion of copper in 8 may have been caused by the rapid sequestration of in situ formed LiOCN by TMPLi, we attempted to prepare 8a by a route in which these two components were not present simultaneously. A solution of donor-free TMP2CuLi (9a) was therefore prepared using hydrocarbon solvent. This was combined with LiOCN and THF was introduced, later being replaced with hexane. The resulting solution gave radiating fans of crystals (Scheme 4). X-ray crystallography reveals the expected centrosymmetric dimer of 8a (ESI, Fig. S3†). Though pure 8a and its counterpart component of 8 are not strictly isostructural, the differences in molecular structure are small. In particular, marginally reduced planarity in pure 8a when compared to its partner component of 8, results in a larger value of mean deviation from the plane of 0.205 Å (excluding THF and TMP-carbons, cf. 0.085 Å for 8a in 8). These observations suggest that although weak, the N3–Li1 transannular interaction in component 8b of 8 exerts an influence, via crystal packing, over minor component 8a in the same structure.

To attempt the synthesis of pure 8b, two different routes were pursued. The documented use of a secondary ammonium
salt to generate a mixed lithium halide–lithium amide aggregate in situ\(^a\) led us to synthesize cyanate salt (TMPH\(_2\)OCN) \(10\) (see ESI†). This was then reacted with TMPH and \(n\)BuLi in a 1 : 1 : 3 ratio. The deployment of bulk THF as reaction medium followed by its removal and replacement with hexane gave crystals. Alternatively, direct combination of LiOCN with TMPLi (1 : 2) in THF followed by recrystallization from hexane provided the same product.\(^1\)H NMR spectroscopy revealed these to comprise TMP and THF in a 1 : 1 ratio and IR spectroscopy gave a strong peak at 2207 \(\text{cm}^{-1}\)/C\(_1\). X-ray diffraction confirmed the formulation ((TMPH\(_2\)OCN)_3Li_2(THF)) \(11\) (Scheme 5), with dimerization occurring in the same way as with \(8\) (Fig. 1). The observation that this O–Li interaction is longer in \(11\) (O3A–Li2 1.968(3) \(\text{Å}\); Fig. 2) than in \(8\) is explained by additional THF rendering Li2 tetracoordinate. The result of this THF-inclusion on the wider structure is significant. With Li2 now pseudo-tetrahedral, \(11\) adopts a chair conformation in which only the core (LiOCN)_2 ring occupies a single plane. In contrast to the structure of \(8\) (ESI, Fig. S1†) the lithium–nitrogen heterocycles and the THF molecules now deviate significantly above or below this central plane. Peripheral to the structure core, the geometry of the (NLi)_3 arrangement in \(11\) imitates that in \(8\), though the expanded N1–Li1–N2 reflex angle of 196.61(16)\(^\circ\) allows a transannular interaction (N3–Li1 = 2.198(3) \(\text{Å}\)) shorter than that in \(8\) and similar to other N–Li bonds in the structure. A further point of contrast between \(8\) and \(11\) lies in the orientation of the amido groups. The ability of these to adopt different orientations for steric reasons has been noted previously in lithiocuprate systems.\(^{18}\) In the current work, the TMP ligands in \(8\) mimic the amido groups in lithiocuprate \(5\) whereby the 6-membered rings of the two TMP groups bonded to a Cu centre are each oriented away from one another and so lie flat or endo, endo with respect to the (LiOCN)_2 structure core (Fig. 1). However, the inclusion of additional THF appears instrumental in causing one TMP ligand to adopt an upright orientation in \(11\),\(^{35}\) giving an exo, endo ligand pattern instead (Fig. 2).

The ability to isolate \(8\) proved solvent dependent; an equivalent synthesis in bulk THF (Scheme 3) yielded a crystalline material, \(9\), which analyses in the solid state as an 8-membered metallacyclic copper-rich material TMPlvCu\(_n\)Li\(_m\) (in \(9\), \(m + n = 4\); Fig. 3). The contribution of different species to the overall

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**Scheme 5** Lithiation of 10 and TMPH in bulk THF to give 11.
composition of 9 could only be elucidated by solution studies (see below). The structure shown in Fig. 3 can be rationalized in conjunction with the observation of that of 8; the excess THF solvating NCOLi and abstracting it from Lipshutz-type 8 to give 9. This view explains the deficiency of Cu in 8.

We next investigated the use of stronger Lewis bases as solvents for lithiocuprates. TMEDA (N,N',N',N'-tetramethylthlenediamine) was introduced to 2 : 1 mixtures of amidolithium i.e. (DA)₂Cu(Br)Li₂(TMEDA)₂ to give pure isolable Lipshutz-type cuprate (DA)₂Cu(Br)Li₂(TMEDA)₂ X-ray diﬀraction revealed a monomer, with the bromide disordered at the amide-bridging metal site, with the N1–Cu1–N2 angle being 208.4(8). This view explains the deficiency of Cu in 8.

The structure of 12b bears comparison with the highly unusual lithium amide–lithium chloride adduct (DA)₂Li(Cl)Li₂(TMEDA)₂ (ref. 34) and, in the same way that the synthesis of amidolithium–cyanatolithium 8b could be systematized using the cyanate salt 10, it proved possible to achieve a synthesis of pure 12b by reacting (DAH₂)Br with nBuLi in the presence of TMEDA (Scheme 7 and ESI, Fig. S4†). The removal of metal disorder to target pure cuprate 12a was also attempted; DAH was treated with nBuLi and TMEDA and then with CuOCN in

![Scheme 6 Anion-dependent synthesis of 12a/b and 13.](Image)

![Scheme 7 Lithiation of (DAH₂)Br and DAH to give pure 12b.](Image)

**Fig. 4** Molecular structure of the monomers of 12a and 12b (30% probability and with H-atoms omitted). Selected bond lengths (Å) and angles (°): N1–Cu1 1.823(13), N2–Cu1 2.064(13), Br1–Cu1 3.073(10), N1–Li1 1.997(16), Br1–Li1 2.640(8), Br1–Li3 3.073(10), N1–Cu1–N2 176.0(7), N1–Li2–Br1 101.1(4), N2–Li3–Br1 102.5(4), Li2–Br1–Li3 125.5(3).
hexane. The resulting crystalline material yielded NMR spectroscopic data that pointed to the presence of DA and TMEDA in a 2 : 1 ratio, while IR spectroscopy revealed a cyanate peak at 2208 cm\(^{-1}\). These data were inconsistent with the structure type exhibited by \(^{12}\)a and, in due course, X-ray diffraction revealed 13 to be a 2 : 1 adduct between DALi and the cuprate (DA)\(_2\)-Cu(OCN)Li\(_2\)(TMEDA).\(_2\). Crystallography pointed to a complete lack of metal disorder at the DA-bridging position (Fig. 5a). It is immediately apparent that the behaviour of the cyanate ligand contrasts with that noted recently for the thiocyanate and facilitated dimerization. This variability in cyanate coordination is similar to that noted recently for the thiocyanate ligand\(^{12}\) and, in the current case, the cyanate ligand participates in the formation of an 8-membered N\(_2\)CuLi\(_2\)NCO ring. The capture of two molecules of DALi gives 4-membered N\(_2\)Li\(_2\) and NOLi\(_2\) rings. Whereas \(^{8}\)a incorporates an essentially flat N\(_2\)CuLi\(_2\)N ring, the 8-membered metallacycle in 13 deviates significantly from planarity, allowing the DALi molecules to project above and below the plane incorporating the N–Cu–N unit and the cyanate C-centre (Fig. 5b).

NMR spectroscopy

Interpretation of the convoluted solution behaviour for the systems described above has been attempted. It was anticipated that compound \(^{8}\) would yield two species in solution – \(^{8}\)a and \(^{8}\)b. In the event, NMR spectroscopy of the bulk material could not be reconciled with this simple model of metal disorder. \(^{7}\)Li NMR spectroscopy, for example, revealed multiple solution species (Fig. 6). With NMR spectra of \(^{9}\)a reported previously,\(^{19}\) its presence at \(\delta\) 0.90 ppm was easily established. To aid the assignment of other components, the spectroscopy of (TMP)\(_2\)(OCN)Li\(_2\)(THF)\(_2\) \(^{11}\) was examined. The reproducible \(\textit{in situ}\) reformation of a limited amount of TMPH in all TMP-based systems is attributed to the presence of trace moisture in the deuterated solvent in spite of its storage over molecular sieves (3 Å). This notwithstanding, \(^{13}\)C NMR spectroscopy revealed the existence of \(^{11}\) as the only species observable in solution (Fig. 7).

Returning to the \(^{7}\)Li NMR spectrum of bulk \(^{8}\), the broad features at \(\delta\) 2.18 and 1.41 ppm can now be accounted for by \(^{11}\) and, by comparison with an authentically prepared sample (see ESI†), \(^{9}\)b, respectively, leaving two signals to be identified at \(\delta\) 1.64 ppm and at \(\delta\) 0.48 ppm. To assign the first of these, \(^{1}H\) NMR spectroscopy was used. Firstly, THF notwithstanding, the \(^{1}H\) NMR spectrum of \(^{11}\) was dominated by three singlets, at \(\delta\) 1.76, 1.57 and 1.39 ppm in a 1 : 2 : 1 integral ratio. HSQC spectroscopy identified these as belonging to TMP-Me groups, which was examined. The reproducible \(\textit{in situ}\) reformation of a limited amount of TMPH in all TMP-based systems is attributed to the presence of trace moisture in the deuterated solvent in spite of its storage over molecular sieves (3 Å). This notwithstanding, \(^{13}\)C NMR spectroscopy revealed the existence of \(^{11}\) as the only species observable in solution (Fig. 7).

\[\text{Fig. 5 (a) Molecular structure of 13 (30\% probability and with minor disorder and H-atoms omitted). Selected bond lengths (Å) and angles (°): N2–Cu1 1.910(2), N3–Cu1 1.909(2), N2–Li2 2.058(5), N1–Li2 1.991(5), N1–Li1 2.044(5), N3–Li3 2.053(5), N4–Li3 1.985(5), N4–Li4 2.048(5), N9–Li3 2.159(6), N9–Li4 2.026(5), O1–Li2 2.137(6), O1–Li1 2.090(5), N9–C37 1.202(4), O1–C37 1.205(4), N2–Cu1–N3 179.09(11), N2–Li2–O1 117.7(2), N3–Li3–N9 117.4(2), Li2–O1–C37 126.3(2), Li2–O1–Li1 81.6(2), Li2–N1–Li1 84.4(2), N1–Li1–O1 98.0(2), Li3–N9–C37 121.9(2), Li3–N9–Li4 81.3(2), Li3–N4–Li4 85.1(2), N4–Li4–N9 97.9(2). (b) 13 viewed along the C37···Cu1 vector and with the N3–Cu1–N2 unit oriented horizontally.}\]
and comparison with the TMP-Me resonances in authentic samples of 9a-c (see ESI†) revealed that each of the aforementioned singlets falls within the expected chemical shift range for these compounds. Overall, these data suggest an isomeric variant of the previously reported dimer of Gilman cuprate 9a (Fig. 8a). We propose inverse-9a (i-9a); a tetranuclear metal-lacycle incorporating adjacent pairs of Li and Cu centres (Fig. 8b) best viewed as resulting from the agglomeration of dimers of TMPLi 9b and TMPCu 9c. The arrangement of i-9a yields three distinct TMP environments (Fig. 8). We hypothesise i-9a to be a kinetic product since it results formally from the catenation of dinuclear units of 9b and 9c without requiring the formation of Gilman cuprate 9a. This thesis suggests that under suitable conditions, i-9a will rearrange to 9a. To test this, a typical sample of bulk 8 was heated to reflux and allowed to stand at room temperature. Fine needles crystallized, which were shown to be (thermodynamically preferred) Gilman cuprate by NMR spectroscopy.

Lastly, the minor signal at $\delta$ 0.48 ppm in Fig. 6 most logically belonged to either 8a or 8b. The spectroscopic analysis of pure 8a was therefore carried out. This revealed a system whose behaviour paralleled that of previously reported 5a,21 with the deposition of a fine white powder occurring upon sample dissolution in C$_6$D$_6$ (presumed LiOCN in this case). Except for the presence of THF, the signals matched those of 9a ($^7$Li NMR $\delta$ 0.90 ppm). This suggests that the signal at $\delta$ 0.48 ppm in Fig. 6 is due to 8b not 8a.

Both the metal disorder in single crystal 8 and the presence of multiple products in the bulk reaction mixture are unusual features in amidocuprate systems. However, they can be explained by reactions (1)–(3) below. In (1), CuOCN reacts with 9b to expel LiOCN. This is rapidly sequestered in (2) at a rate competitive with (3). Remaining 9b reacts with in situ formed 9c (3) to then generate any compound in the series TMP$_m$Li$_n$Cu$_m$(THF)$_n$ (e.g. i-9a). The failure to isolate i-9a in previous lithium amidocuprate work is best explained by a combination of the kinetic properties of i-9a and the ability of 9a (but not i-9a) to also be generated by the dissociation of Lipshutz-type cuprates.

![Diagram](image)

**Fig. 8** (a) The dimer of 9a reveals one distinct TMP environment, whereas (b) dimers of 9b and 9c can aggregate to give i-9a, which reveals three.

**Formation of TMPCu 9c**

\[
\text{TMPLi + CuOCN} \rightarrow \text{TMPCu + LiOCN} \quad \text{(1)}
\]

**Formation of TMPLi$_2$OCN(THF)$_2$ 11**

\[
2\text{TMPLi + LiOCN + 2THF} \rightarrow \text{TMPLi$_2$OCN(THF)$_2$} \quad \text{(2)}
\]

**Formation of TMPCuLi 9a and i-9a**

\[
\text{TMPLi + TMPCu} \rightarrow \text{TMPCuLi} \quad \text{9a and i-9a} \quad \text{(3)}
\]

Moving to the behaviour of lithium amidocuprates in more polar reaction media, the 2 : 1 reaction of TMPLi and CuOCN in THF followed by recrystallization from hexane gave 9, which crystallographic refinement indicated to be rich in Cu (Fig. 3),
clearly, \(^7\)Li NMR spectroscopy reveals signals in the expected conjunction with that of pure solution (alongside minimal reformation of DAH, relatively straightforward. It suggests one species dominant in not be established by solid state analysis. In contrast, \(^7\)Li NMR spectroscopy in C\(_6\)D\(_6\) (see ESI†) identified three Li-containing species in solution: a minor signal at \(\delta 1.65\) ppm which matched \(i\)-9\(a\), a dominant resonance at \(\delta 0.91\) ppm corresponding to 9\(a\) and a shoulder at \(\delta 0.94\) ppm. Since 9\(a\) and \(i\)-9\(a\) contain equal amounts of Cu and Li, it was anticipated that the unidentified species should be rich in Cu to ensure that the sample was Cu-rich overall. Strong contenders include TMP\(_3\)-Cu\(_2\)Li and TMP\(_3\)Li\(_2\) – since literature precedents exist for trimeric and tetrameric variants of 9\(b\) and 9\(c\), \(^3\)H NMR spectroscopic data for pure 12\(b\) proves relatively straightforward. It suggests one species dominant in solution (alongside minimal reformation of DAH, Fig. 9). Most clearly, \(^3\)Li NMR spectroscopy reveals signals in the expected 1 : 2 ratio at \(\delta 2.28\) and 1.26 ppm (ESI, Fig. S11c†). Moving to co-crystalline 12, peaks corresponding to 12\(b\) are added to by signals for 12\(a\) (ESI, Fig. S12a–f†). \(^1\)H NMR spectroscopic data for multiple samples of 12 clearly show the levels of 12\(a\) and 12\(b\) to be variable (Fig. 9), pointing to the possibility of incorporating higher levels of Cu than evidenced by X-ray crystallography.

**Conclusions**

The recent development of thiocyanatocuprate reagents has been extended to yield cyanatocuprates. Copper–lithium exchange in this new field has been evidenced by the observation of co-crystalline products of the type (TMP)\(_2\)M(OCN)Li\(_2\) where M = Cu, Li. An analysis of the geometry at M reinforces the view, recently expressed for X = CN, halide, and SCN, that in (amido)\(_2\)M(X)Li\(_2\) systems (X = inorganic anion) Cu prefers a linear, dicoordinate geometry (viz. 8). This disinclination for higher order structure formation is emphasised when, for M = Li, a tendency for transannulation emerges and M becomes tricoordinate within the same structure-type (viz. 11). These data are reinforced by attempts to fabricate monomeric Lipshutz-type cuprates, with Cu linear in (DA)\(_2\)-Cu(Br)Li\(_2\)(TMEDA)\(_2\) 12\(a\) and amidolithium-lithiocuprate adduct 13 and Li trigonal in (DA)\(_2\)(Br)Li(TMEDA)\(_2\) 12\(b\).

Solution studies have helped elucidate the complex chemistry on offer. In particular, insights into the behaviour of bulk 8 and also of 11 establish the in situ formation of Gilman cuprate 9\(a\). We show that this can form directly or through the rearrangement of a newly observed species (\(i\)-9\(a\)) that we propose to form kinetically from the combination of amidolithium 9\(b\) and amidocopper 9\(c\). In the case of 12, results from crystallographic refinement could be combined with spectroscopic studies of 12\(b\) to distinguish copper-containing Lipshutz-type monomers from their lithium-only congeners. Work is being initiated to deconvolute the complex solution chemistry of 13 and to establish the synthetic portfolio of cyanocuprates. This is focusing on enhancing atom efficiency in directed ortho cupration\(^{23}\) and halopyridine\(^{44}\) derivatization by combining Gilman dimer 9a\(_2\) with substoichiometric LiOCN. The current work demonstrates, for the first time, the ability of an inorganic salt to combine with a dimeric Gilman cuprate to yield a Lipshutz-type dimer. Taking this together with previous work establishing Lipshutz-type dimers as a source of reactive Gilman monomers\(^{19}\) alongside reformed lithium salt, we are now testing the non-stoichiometric deployment of LiOCN with a view to furthering recent interest in transferring main group polar organometallic chemistry to the catalytic regime.

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**Fig. 9** \(^1\)H NMR spectra in C\(_6\)D\(_6\) of (a) 12\(b\) (b) 12\(c\) (c) 12\(b\). *DAH.
**Experimental section**

**General synthetic and analytical details**

Reactions were carried out under dry nitrogen, using double manifold and glove-box methods. Solvents were distilled off sodium (toluene) or sodium–potassium amalgam (THF, hexane) immediately before use. 2,2,6,6-Tetramethylpiperidinidine (TMPH) was purchased from Alfa Aesar and stored over molecular sieves (4 Å). Other chemicals were used as received. nBuLi (1.6 M in hexanes) was purchased from Acros and used as received. For details of the syntheses of Ba(OCN)₂, 6,32 CuOCN 7 (ref. 32) and (TMPH₂)OCN 10 see the ESL. The syntheses of reference materials TMPLi 9b and TMPCu 9e were based on the literature64 and details are provided in the ESL. IR spectra were collected on a Perkin Elmer Spectrum One FT IR spectrometer. The abbreviations used are: m = medium, s = strong.

**Crystallographic details**

For details of data collections see Table 1. Crystals were transferred from the mother liquor to a drop of perfluoropolyether oil mounted upon a microscope slide under cold nitrogen gas.44 Suitable crystals were attached to the goniometer head via a MicroLoop44, which was then centred on the diffractometer.

Data were collected on a Bruker Avance III HD 500 MHz Smart Probe FT NMR spectrometer (500.20 MHz for ¹H, 125.775 MHz for ¹³C, 194.397 MHz for ⁷Li). Spectra were obtained at 25 °C using deuterated solvent stored over molecular sieves (3 Å). For ¹H and ¹³C, chemical shifts are internally referenced to deuterated solvent and calculated relative to TMS. For ⁷Li, an external reference was used (1 M LiCl in D₂O). Chemical shifts are expressed in δ ppm. The following abbreviations are used: br = broad, m = multiplet, s = singlet, sh = shoulder.

**Synthesis and characterization of (TMP)₂Cu₂Li₂(OCN)Li₂(THF) 8a**

To a stirred solution of TMPH (0.34 mL, 2 mmol) and THF (0.08 mL, 1 mmol) in hexane (4 mL) was added nBuLi (1.25 mL, 1.6 M in hexanes, 2 mmol) at −78 °C. The mixture was returned to room temperature to give a yellow solution. This was added to a suspension of CuOCN (0.11 g, 1 mmol) in hexane (1 mL) at −78 °C. The mixture was returned to room temperature to give a pale yellow suspension. Filtration gave a yellow solution and storage at −27 °C gave crystalline material from which a well-faceted, block-like crystal of (TMP)₂Cu₀.₃Li₀.₃(OCN)Li₂(THF) was selected for X-ray diffraction. The following characterization refers to the bulk crystalline product. Yield 54 mg, melting point dec. from 125 °C. Selected IR spectroscopy (nujol) ν 2208 (s, CN), 1340 (m, CO), 1229 (m, CO) cm⁻¹. ¹H NMR spectroscopy (500 MHz, C₆D₆) δ 3.56 (m, 6H, THF), 2.17–1.77 (br, 8H, TMP-4), 1.75 (s, 6H, TMP-Me), 1.74–1.60 (br, m, 12H, TMP-3,5, TMP-Me), 1.57 (s, 12H, TMP-Me), 1.56–1.41 (br, m, 12H, TMP-3,5, TMP-Me), 1.39 (s, 6H, TMP-Me), 1.36 (m, 8H, THF), 1.34–1.13 (br, 12H, TMP-3,5), 1.12–1.07 (m, 4H, TMP-3,5), 1.06 (s, 2H, TMP-Me). ¹³C NMR (125 MHz, C₆D₆) δ 64.8 (THF), 56.9 (TMP-2, 6-í, 9a), 54.2 (TMP-2, 6-9a/TMP-2, 6-9a), 53.4 (TMP-2, 6-í, 9a), 51.6 (TMP-2, 6-11), 49.2 (TMP-2, 6-í, 9a), 42.6 (TMP-3, 5-í, 9a), 42.5 (TMP-3, 5-í, 9a), 42.4 (TMP-3, 5-í, 9a), 42.1 (TMP-3, 5-í, 9a), 41.9 (TMP-3, 5-11), 40.5 (TMP-Me 8), 40.2 (TMP-Me 9a), 39.7 (TMP-Me í, 9a), 38.1 (TMP-3, 5), 37.5 (br, [b, TMP-Me 11], 37.0 (TMP-Me í, 9a), 36.8 (TMP-Me í, 9a), 35.7 (TMP-Me 8), 34.5 (TMP-Me 9a), 32.8 (TMP-Me í, 9a), 32.5 (br, TMP-Me 11), 31.6 (TMP-Me-2, 6), 25.1 (THF), 20.1 (TMP-4 11), 19.6 (TMP-4 í, 9a), 19.2 (TMP-4 í, 9a/TMP-4 9a), 19.1 (TMP-4 í, 9a), 18.4 (TMP-4 í, 9a). ⁷Li NMR (194 MHz, C₆D₆) δ 2.17 (br, s, 1Li, 9b), 1.64 (s, 1.5Li, í), 1.39 (br, s, 2Li, 11), 0.90 (s, 0.5Li, 9a), 0.48 (s, 0.5Li, 8).

**Synthesis and characterization of (TMP)₂CuOCN)Li₂(THF) 8a**

To a stirred solution of TMPH (0.68 mL, 4 mmol) in hexane (2 mL) and toluene (2 mL) was added nBuLi (2.5 mL, 1.6 M in hexanes, 4 mmol) at −78 °C. The solution was warmed to room temperature and transferred to a suspension of CuSCN (0.243 g, 2 mmol) in hexane (2 mL) and toluene (2 mL). The suspension was warmed to room temperature then heated to reflux whereupon a grey discolouration was observed. To remove LiSCN, this mixture was filtered whilst hot onto LiOCN (0.10 g, 2 mmol) and the solvent was removed in vacuo. THF (6 mL) was added and the suspension was stirred at room temperature for 30 minutes, during which time partial dissolution of the LiOCN occurred. The THF was removed in vacuo to give a sticky solid, which dissolved when hexane (6 mL) was added. The solution was filtered and the filtrate stored at −27 °C for 1 week during which time 8a deposited as radiating fans of crystals. Yield 310 mg (33% wrt. CuSCN), melting point 192–194 °C. Elemental analysis C₂₄H₄₆Cu₂Li₂N₂O₂, requires (%) C, 58.52; H, 9.40; N, 8.90. Found (%) C, 58.06; H, 9.38; N, 9.01. Selected IR spectroscopy (nujol) ν 2241 (s, CN), 2208 (s, CN), 1340 (m, CO), 1228 (m, CO) cm⁻¹. ¹H NMR spectroscopy (500 MHz, C₆D₆) δ 3.57 (br, m, 4H, THF), 1.89–1.76 (br, m, 2H, TMP-4), 1.67–1.61 (m, 4H, TMP-3,5), 1.60 (s, 12H, TMP-Me), 1.59–1.57 (m, 2H, TMP-4), 1.56 (s, 12H, TMP-Me), 1.41 (br, m, 4H, THF), 1.09 (m, 4H, TMP-3,5), 1.06 (s, 1.3H, TMP-Me). ¹³C NMR spectroscopy (125 MHz, C₆D₆) δ 67.4 (br, THF), 54.2 (TMP-2,6, 42.1 (TMP-3,5, 40.1 (TMP-Me), 38.2 (TMP-3,5), 34.5 (TMP-Me), 31.6 (TMP-Me), 25.3 (br, THF), 19.2 (TMP-4, 18.4 (TMP-4). ⁷Li NMR spectroscopy (194 MHz, C₆D₆) δ 0.90.

**Synthesis and characterization of (TMP)₂Cu₁.₃₃Li₆.₆₅ 9**

To a stirred solution of TMPH (0.34 mL, 2 mmol) and THF (2 mL) was added nBuLi (1.25 mL, 1.6 M in hexanes, 2 mmol) at
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<th>82</th>
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<th>12</th>
<th>12b</th>
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<td>C₄₆H₄₆Cu₄Li₄N₆O₄</td>
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<td>C₅₄H₁₀₄Li₆N₆O₆</td>
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<td>P1/c</td>
<td>P2₁/c</td>
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<td>90.0000(10)</td>
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<td>95.808(2)</td>
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* Based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions.
Synthesis and characterization of (TMP)₃Cu₉₀₈L₄₀₉₁(Br)₆L₄(TMEDA)₁₁

Method (a). A suspension of (TMPh)OCN 10 (0.09 g, 0.5 mmol) in THF (2 mL) was treated with TMPh (0.08 mL, 0.5 mmol). nBuLi (0.95 mL, 1.5 mmol) was added dropwise at −78 °C and the resulting suspension was left to warm to room temperature, whereupon it dissolved. The solvent was removed in vacuo and replaced with hexane (3 mL). The colourless solution was filtered, with storage of the filtrate at −27 °C for 1 day giving colourless crystals. Yield 65 mg (27% wrt. NCO), melting point 90–92 °C. Selected IR spectroscopy (nujol) ν 2207 (s, CN), 1352 (s, CO), 1226 (s, CO) cm⁻¹. ¹H NMR spectroscopy (500 MHz, C₆D₆) δ 3.56 (m, 8H, THF), 2.27–1.37 (br, m, 30H, TMP-3,4,5,6Me), 1.35 (s, 6H, TMP-Me), 1.34 (m, 8H, THF), 1.06 (s, 3.2H, TMP-Me), 0.31 (br, s, 0.31H, TMP-NH). ¹³C NMR (126 MHz, C₆D₆) δ 67.8 (THF), 52.0 (TMPh-2,6), 51.7 (TMPh-2,6 11), 49.2 (TMPh-2,6), 42.4 (TMPh-3,5 9b), 41.9 (TMPh-3,5 11), 38.2 (TMPh-3,5), 37.5 (br, TMP-Me 11), 36.5 (TMPh-9b), 33.5 (br, TMP-Me 11), 31.6 (TMPh-Me), 25.0 (THF), 20.2 (TMPh-11), 18.4 (TMPh-4). ⁷Li NMR (194 MHz, C₆D₆) δ 2.21 (s, br, 1Li, 9b), 1.48 (s, br, 2Li, 11), −1.54 (s, 0.2Li, unidentified).

Method (b). TMPh (0.34 mL, 2 mmol) in THF (2 mL) was treated with nBuLi (1.25 mL, 1.6 M in hexane, 2 mmol) at −78 °C. The pale yellow solution was returned to room temperature whereupon it dissolved to a suspension of LiOCN (0.05 g, 1 mmol) in THF at −78 °C. The mixture warmed to room temperature and was stirred for ca. 15 minutes, during which time the LiOCN was observed to dissolve. The solvent was removed in vacuo, leaving a sticky white solid which dissolved upon the addition of hexane (6 mL) with gentle warming. The solution was filtered and the filtrate stored at −27 °C for 24 h hours to give colourless crystals. Yield 75 mg (15% wrt LiOCN). Elemental analysis, C₇₉H₉₈Li₄O₃ requires (%) C 66.52, H 10.75, N 8.62; found (%) C, 66.08; H, 10.76; N, 8.83. ¹H NMR (500 MHz, C₆D₆): δ 3.56 (m, 5H, THF), 2.31–1.38 (br, 30H, TMP-Me), 1.35 (m, 8H, THF), 1.32–1.12 (br, 6H, TMP-Me), 1.06 (s, 1H, TMP-Me). ¹³C NMR (125 MHz, C₆D₆): δ 67.9 (THF), 51.6 (TMPh-2,6), 49.2 (TMPh-3,5), 41.9 (TMPh-3,5), 38.2 (TMPh-3,5), 37.1 (br, TMP-Me), 33.5 (br, TMP-Me), 31.6 (TMPh-Me), 25.0 (THF), 20.1 (TMPh-4), 18.4 (TMPh-4). ⁷Li NMR (194 MHz, C₆D₆): δ 1.38 (s, br).

Synthesis and characterization of (DA)₂Cu₀₉₀₈L₄₀₉₁(Br)₆L₄(TMEDA)₁₁

nBuLi (2.5 mL, 1.6 M in hexanes, 4 mmol) was added to a stirred solution of DAH (0.56 mL, 4 mmol) and TMEDA (0.6 mL, 4 mmol) in hexane (4 mL) at −78 °C. The resulting solution was returned to room temperature to give a yellow solution that was transferred to a −78 °C suspension of CuBr (0.28 g, 2 mmol) in hexane (2 mL). The mixture was returned to room temperature to give a brown suspension. Filtration gave a pale yellow solution. Storage of this at −27 °C for 24 hours gave colourless blocks of cocrystalline Lipshutz-type (DA)₂Cu₉₀₈L₄₀₉₁(Br)₆L₄(TMEDA)₁₂ and (DA)₁ₙ(Br)L₄(TMEDA)₁₂. Yield 350 mg.

Representative sample (1). ¹H NMR spectroscopy (500 MHz, C₆D₆) δ 3.76 (sh, br, 0.36H, DA–CH, 12a), 3.67 (s, br, 3.15H, DA–CH, 12b), 3.25 (septet, JHH = 6 Hz, 0.02H, DA–CH, 12a), 3.16 (septet, JHH = 6 Hz, 0.08H, DA–CH, 12a), 3.10 (septet, JHH = 6 Hz, 0.28H, DA–CH, 12a), 2.78 (octet, JHH = 6 Hz, 0.4H, DAH–CH), 2.13 (s, 24H, TMEDA–Me), 1.99 (s, 8H, TMEDA–CH₂), 1.63–1.20 (br, m, 24H, DA–CH, 12a + 12b), 0.95 (d, JHH = 6 Hz, 2H, DAH–Me). ¹³C NMR (126 MHz, C₆D₆) δ 57.0 (TMEDA–CH₂), 50.1 (DA–CH, 12a), 48.8 (DA–CH, 12b), 46.5 (TMEDA–CH₂), 44.9 (DAH–CH), 28.2, 27.0 (DA–Me, 12a), 26.2 (br, DA–Me, 12b), 23.2 (DAH–Me), ⁷Li NMR (194 MHz, C₆D₆) δ 2.34 (s, 1Li, DA₂Li₁₂, 1.58 (s, 0.4Li, Li(TMEDA), 1.18 (s, 2Li, Li(TMEDA), 1.2b).

Representative sample (2). ¹H NMR spectroscopy (500 MHz, C₆D₆) δ 3.76 (sh, br, 0.11H, DA–CH, 12a), 3.67 (s, br, 1.90H, DA–CH, 12b), 3.25 (septet, JHH = 6 Hz, 0.02H, DA–CH, 12a), 3.16 (septet, JHH = 6 Hz, 0.64H, DA–CH, 12a), 3.11 (septet, JHH = 6 Hz, 1.00H, DA–CH, 12a), 2.78 (octet, JHH = 6 Hz, 0.16H, DAH–CH), 2.14 (s, 24H, TMEDA–Me), 2.02 (s, 8H, TMEDA–CH₂), 1.60–1.31 (br, m, 20H, DA–Me, 12a + 12b), 1.25 (d, JHH = 6 Hz, 2H, 12a), 1.22 (d, JHH = 6 Hz, 2H, 12a), 0.94 (d, JHH = 6 Hz, 1H, DAH–Me). ¹³C NMR (125 MHz, C₆D₆) δ 57.0 (TMEDA–CH₂), 50.9 (DA–CH, 12a), 50.4 (DA–CH, 12b), 50.1 (DA–CH, 12a), 48.8 (DA–CH, 12b), 46.3 (TMEDA–Me), 44.8 (DAH–CH), 28.4 (DA–Me, 12a), 28.2 (DA–Me, 12a), 27.6 (DA–Me, 12a), 27.5 (DA–Me, 12a), 27.0 (DA–Me, 12a), 26.9 (DA–Me, 12a), 26.1 (br, DA–Me, 12b), 23.4 (DAH–Me). ⁷Li NMR (194 MHz, C₆D₆) δ 2.37 (s, 1.0Li, 12b, 1.63 (s, 1.2Li, 12a, 1.59 (s, 1.0Li, 12a, 1.17 (s, 2Li, 12b).

Synthesis and characterization of (DA)₂₃Br₉₀₈L₄₀₉₁(Br)₄(TMEDA)₁₁

To a suspension of DAH–HBr (0.18 g, 1 mmol) in hexane (6 mL) was added DAH (0.14 mL, 1 mmol) and TMEDA (0.30 mL, 2 mmol). The mixture was cooled to −78 °C, treated with nBuLi (1.9 mL, 1.6 M in hexanes, 3 mmol) and returned to room temperature to give a pale yellow solution. The solution was filtered, concentrated (to ca. 4 mL) and stored at −27 °C for 1 day after which colourless block-like crystals of 12b were
deposited. Yield 320 mg (60% wrt. Br), melting point 76–78 °C. Elemental analysis, C_{24}H_{49}BrLi_{12}N_{6} requires (% C) 54.03, H 11.34, N 15.75; found (% C) 54.09, H 11.66, N 15.58. 1H NMR spectroscopy (500 MHz, C$_6$D$_6$) $\delta$ 3.66 (s, br, 2H, DA–CH), 2.79 (octet, $^1$J$_{HH}$ = 6 Hz, 0.06H, DAH–CH), 2.13 (s, 24H, TMEDA–Me), 1.96 (s, 8H, TMEDA–CH$_2$), 1.41 (s, br, 24H, DA–Me), 0.95 (d, $^3$J$_{HH}$ = 6 Hz, 1.35H, DA–Me). 13C NMR (126 MHz, C$_6$D$_6$) $\delta$ 56.9 (TMEDA–CH$_2$), 48.8 (DA–CH), 46.5 (TMEDA–CH$_3$), 44.9 (DAH–CH), 26.2 (DA–Me), 23.2 (DAH–Me). 7Li NMR (194 MHz, C$_6$D$_6$) $\delta$ 2.28 (s, br, 1Li, (DAH)$_2$Li) 1.26 (s, 2 Li, Li(TMEDA)).

**Synthesis and characterization of (DA)$_3$Cu(OCN)Li$_4$(TMEDA)$_2$**

nBuLi (1.25 mL, 1.6 M in hexanes, 2 mmol) was added to a stirred solution of DAH (0.28 mL, 2 mmol) and TMEDA (0.3 mL, 2 mmol) in hexane (4 mL) at 78 °C. The resulting solution was returned to room temperature to give a yellow solution that was transferred to a suspension of CuOCN (0.11 g, 1 mmol) in hexane (1 mL) at −78 °C. The mixture was returned to room temperature to give a grey suspension, which was filtered to give a pale yellow solution. Storage at +5 °C for 24 hours gave white needle-like crystals of 13. Yield 0.11 g (14% wrt. CuOCN), melting point 78 °C.

Acknowledgements

This work was supported by the U.K. EPSRC through grants EP/J500380/1 and EP/K039520/1. Thanks go also to Dr Andrew Bond (University of Cambridge) for help with crystallographic analysis. Detailed supporting data for this paper are available at the University of Cambridge data repository (see https://doi.org/10.17863/CAM.9469).

References