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New options in directed cupration: Studies in heteroleptic bis(amido) cuprate formation

Andrew J. Peel, Jonathan Slaughter, Andrew E.H. Wheatley*

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

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Dedicated to the memory of Jack Lewis.

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ABSTRACT

The 2:1 combination of MPLi (MP = 2-methylpiperidide) with CuBr gives the novel complex [(MP)₂CuLi(THF)₂]₂LiBr **12** and introduces the chiral ligand MP to the evolving field of Directed *ortho* Cupration reagents. Subsequent syntheses have focused on developing heteroleptic bis(amido) arrangements at Cu, with 1:1 mixtures of two out of MPLi, DMPLi and TMPLi (DMP = 2,6-*cis*-dimethylpiperidide; TMP = 2,2,6,6-tetramethylpiperidide) being reacted with Cu^I salts in the presence of THF. Resulting lithiocuprates reveal solid state dimers based on the heteroleptic bis(amido) formulations R₂N(TMP)Cu(Br)Li₂(THF)₂ (R₂N = MP **13**; R₂N = DMP **14**). The heteroleptic Gilman lithiocuprate PIP(TMP)CuLi (PIP = piperidide) **15** has also been prepared. In each of **12–15**, significant variations in the orientations of the amide ligands can be rationalized in terms of steric effects and, in the case of **15**, stabilization of the alkali metal by Me...Li interaction is evidenced.

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1. Introduction

Improved methods for regioselectively functionalizing aromatics, which avoid the complications of selectivity [1] and product stability [2] that arise from the use of highly polar organometallic bases are of major importance to synthetic chemists. In this context, the advent of so-called 'synergic bases' of the type R_mM^{IP}(NR'₂)_nAM (R = alkyl; m = 2, 3; M^{IP} = less polarizing metal; NR'₂ = amide; n = 1, 2; AM = alkali metal) has furnished reagents capable of unprecedented behaviour [3]. The first such base to be reported was the putative lithium zincate (*t*-Bu)₂Zn(TMP)Li (TMP = 2,2,6,6-tetramethylpiperidide) and was effective in the *ortho* metalation of alkyl benzoates and the α -deprotonation of π -deficient azaromatics [4].

More recently, alkali metal complexes featuring Zn [5], Al [6], Mn [7] and Mg [8] as the less polarizing metal (Fig. 1) have demonstrated anionic activation [9], reduced aggregation [10], and scope in templated polymetalation [8c], and as a part of the growth of this field, organocuprates have also been explored [11]. First reported to result from the treatment of CuI with MeLi to give 'lower-order' or 'Gilman' cuprate Me₂CuLi **1** [12], recent focus has been on lithium

amidocuprates in general (including heteroleptic structures) [13] and lithium (TMP)cuprates specifically. In relation to the former, dimers of MesNHCu(PhNH)Li·DME **2** (Mes = mesityl, DME = 1,2-dimethoxyethane) [14] and MesCu(NBz)₂Li **3** (Bz = benzyl) [15] have been reported. In relation to the latter, the cyclic dimer of (TMP)₂CuLi **4** [16], and the amido(organyl) monomers PhCu(TMP)Li·3THF **5** and MeCu(TMP)Li·TMEDA **6** (TMEDA = *N,N,N',N'*-tetramethylethylenediamine; Scheme 1) [17] have been isolated.

Attempts to enhance cuprate reactivity [11] have focused on treating lower-order cuprates with LiX (X = halide, cyanide) [18,19]. This led to discussion over whether the resulting cuprates were lower-order [20] or whether sequestering of the inorganic anion by Cu would render a 'higher-order' structure based on 3-coordinate Cu [21], with calculations [22,23], solution [24] and solid state [25–27] analysis suggesting the former. The issue of the Cu-sequestering of cyanide in lithiocuprates was most recently visited on account of the emergence of the field of Directed *ortho* Cupration (DoC) [28], with reaction of TMPLi and CuCN giving reactive complexes, which were found by X-ray diffraction to be dimers based on (TMP)₂Cu(CN)Li₂(L) (L = THF **7a**, Et₂O **8a**) monomers that lacked CuCN components (Scheme 2). The ability to subsequently generate analogous cuprates using halide salts of Cu^I in either THF [16,29] or Et₂O [30], combined with the similarity between these structures and that of (Ph₂N)₂Cu(NPh₂)Li₂·2(OEt₂)₂ **9** [14], has allowed LiX-incorporating species to generally be

* Corresponding author.

E-mail address: aehw2@cam.ac.uk (A.E.H. Wheatley).

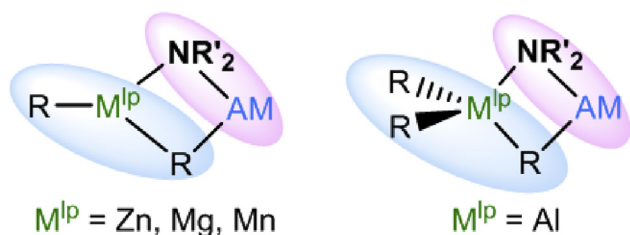
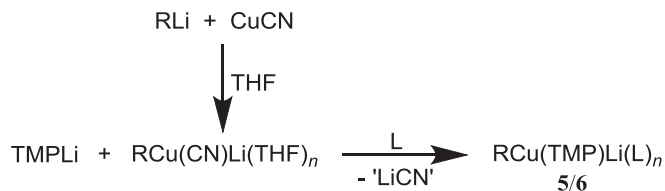
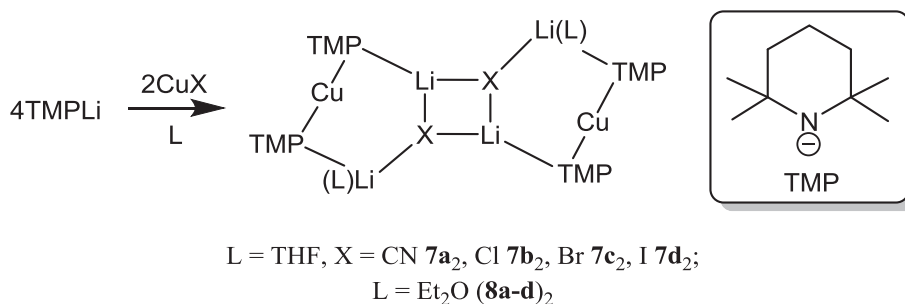


Fig. 1. AM = alkali metal, M^{IP} = less polarizing metal.



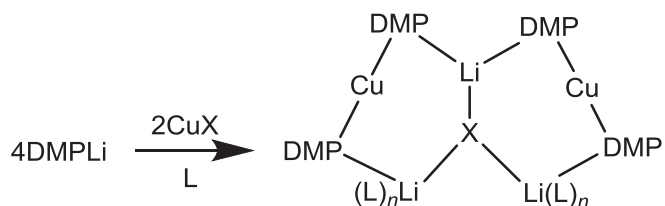
Scheme 1. Formation of **5** ($R = \text{Ph}$, $n = 3$, $L = \text{THF}$) and **6** ($R = \text{Me}$, $n = 1$, $L = \text{TMEDA}$).



Scheme 2. Formation of the dimers of cuprates **7** and **8**.

classified as ‘Lipshutz-type’ [31]. Understanding of the structural principles at work in these systems has proved important in fully appreciating differences in the outcomes of their reactions; explaining these in terms either of variations in reagent structure and type or factors such as organocopper abstraction by cuprates [32].

Very recently, amidocuprate preparation has utilized DMPH (= 2,6-*cis*-dimethylpiperidine) as the amido ligand source, with the aim of significant cost reduction [33,34]. However, the differing sterics significantly effected ligand orientation and led to the isolation of a new class of lithocuprate adduct. While the combination of DMPLi with CuCl in the presence of etherate solvents produced disorder at the metal sites [35], exactly controlling the amount of ether wrt metal obviated this and yielded both $[(\text{DMP})_2\text{CuLi}(\text{OEt}_2)]_2\text{LiX}$ **10** and $[(\text{DMP})_2\text{CuLi}(\text{THF})_2]_2\text{LiBr}$ **11** (Scheme 3) [30], which were interpreted as adducts between



Scheme 3. Synthesis of lithocuprate adducts ($L = \text{Et}_2\text{O}$, $n = 1$, $X = \text{Cl}$ **10a**, Br **10b**, **110c**; $L = \text{THF}$, $n = 2$, $X = \text{Br}$ **11**).

Gilman $(\text{DMP})_2\text{CuLi}(\text{L})_n$ and Lipshutz-type $(\text{DMP})_2\text{Cu}(\text{X})\text{Li}_2(\text{L})_n$ ($L = \text{Et}_2\text{O}$, $n = 1$, $X = \text{Cl}$, Br , I ; $L = \text{THF}$, $n = 2$, $X = \text{Br}$) species.

The transition in structure-type from Lipshutz-type dimers to adducts has been argued to be of mechanistic importance, with **10b** successfully used in DoC chemistry [30]. That said, ambiguity over the structural options available to different amido ligands, combined with a general paucity of data on heteroleptic bis(amido) cuprates, led to the present work; the Lipshutz(-type) and adduct structures outlined above being homoleptic with respect to the choice of amido ligand. Herein we utilize the amines MPH (= 2-methylpiperidine), DMPH and TMPH to fabricate heteroleptic bis(amido)cuprates of the type $\text{NR}_2(\text{NR}'_2)\text{Cu}(\text{X})\text{Li}_2(\text{L})_n$ and $\text{NR}_2(\text{NR}'_2)\text{CuLi}$ (NR_2 , NR'_2 = different amido ligands). The choice of ligands is designed to explore the scope for reducing the costs of DoC [34] (100 mL MPH = £19, 100 g DMPH = £23 and 100 g TMPH = £274 at time of writing), whilst also probing the steric effects of Me-group inclusion. These are already suggested to be structure-defining [30], and investigating the effects of sterically-based ligand reorientation in heteroamido cuprates promises not only new modes of reactivity but also insights into the transition from a preference for Lipshutz-type structures to one for Gilman-

(Lipshutz-type) adducts [30,31]. Moreover, ligand variation will allow the ability of Me-groups to stabilize the alkali metal in Gilman cuprates to be investigated; the relevance of this lies in the recent establishment that Gilman reagents promote effective DoC [16].

2. Results and discussion

In seeking to utilize chiral amides in lithium cuprate chemistry, the racemic substrate MPH was used in the attempted synthesis of an analogue of the recently reported pentametal adducts of the type $[(\text{NR}_2)_2\text{CuLi}(\text{L})_n]_2\text{LiX}$. To do this, a preformed hexane solution of MPLi containing also THF (1 eq. wrt Li) was added to CuBr (0.5 eq. wrt Li) in hexane. Upon prolonged chilling, the resultant orange solution yielded crystalline material that was shown to incorporate MP and THF in a 1:1 ratio by ^1H NMR spectroscopy and so to be consistent with a formulation analogous to that of previously reported adduct **11**. Corroboration of this view came from ^7Li NMR spectroscopy, which revealed two Li environments in a 1:2 ratio (Fig. 2) – this behaviour having been previously interpreted in terms of the retention of solid-state structural characteristics by adducts (e.g. **10** and **11**) in hydrocarbon solution [30].

The ^{13}C NMR spectrum is noteworthy; sharp resonances were located for THF but all other carbon resonances appeared as clusters of peaks. APT NMR spectroscopy identified the cluster at δ 59.3–57.4 ppm as being due to the chiral tertiary carbon atom at the 2-position of the ligand. The 3-, 5- and 6-position carbon atoms

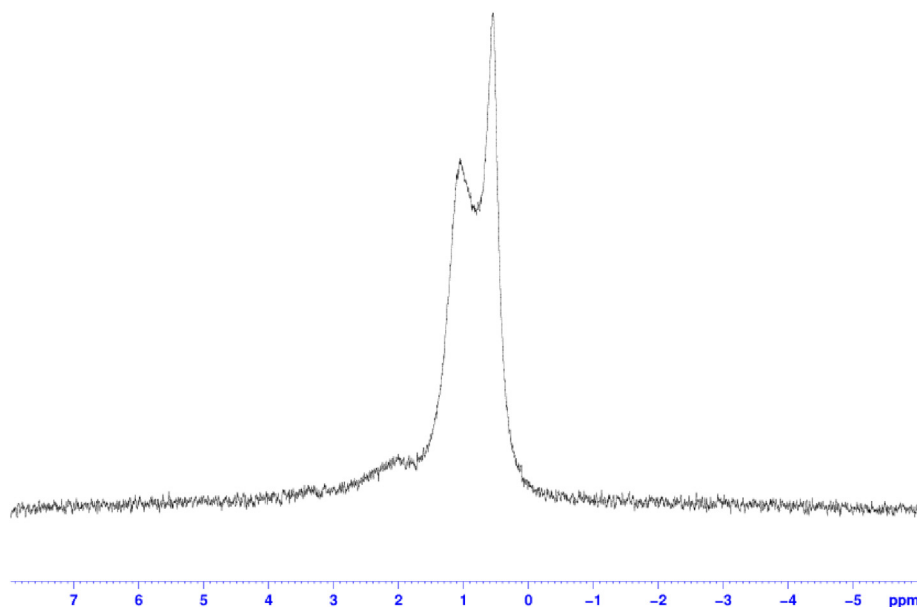


Fig. 2. ^7Li NMR spectra of **12** in C_6D_6 reflecting the 2:1 ratio of Li environments in the solid state structure. The signal at δ 2.03 ppm is attributable to low-level MPLi formation in solution.

were similarly prominent, whilst HSQC NMR spectroscopy revealed that the methyl group and 4-position carbon resonances were nearly superimposed, at δ 27.1 and 27.3 ppm respectively. Consistent with these solution data, X-ray diffraction established the product of reaction to be $[(\text{MP})_2\text{CuLi}(\text{THF})_2]_2\text{LiBr}$ **12** (Fig. 3 and Scheme 4). The essential features of this adduct are unambiguous, and it is clearly analogous to recently reported examples of pentametallc lithiocuprate adducts incorporating piperidide ligands [30]. In the present case, however, detailed analysis of the structure is complicated by the fact that the complex appears to exhibit considerable positional disorder intrinsic to the MP ligands by virtue of their racemic nature. The result of this, as implied by ^{13}C NMR spectroscopy, is that the use of racemic MPH ensures that individual complexes of **12** incorporate random combinations of

four chiral MP ligands. Each of these ligands can adopt two different *exo* orientations with respect to the structure core, rendering individual crystals of **12** multi-component; each molecular adduct in the lattice has a specific stereochemistry, but only the average can be seen in the crystal structure. One unique permutation is shown in Fig. 3.

Similar reactivity to that which furnished homoleptic bis(amido) adduct **12** has enabled the inclusion of the chiral amide 2-methylpiperidide into not just adduct-type lithiocuprate products but also into heteroleptic bis(amido) species. Hence, a hexane solution of preformed, equimolar MPLi and TMPLi was treated with THF (1 eq. wrt Li) before being added to CuBr (0.5 eq. wrt Li) to give an orange solution from which crystalline material deposited. ^1H and ^{13}C NMR spectroscopy suggested a small amount of decomposition (most clearly through the observation of methyl resonances attributable to TMPH) and this was attributed to the extreme sensitivity of the product in spite of the fact that NMR solvents were stored under N_2 over Na wire. Nevertheless, the presence of MP, TMP and THF were evidenced in the proportions 1:1:2, pointing to the successful fabrication of a heteroleptic bis(amido)-formulation cuprate that could conceivably take one of four forms (an adduct-type structure analogous to that of **12** being unlikely on the basis that TMP ligands appear unsuitable for such structures) [30]. Hence, spectroscopic data suggested either a heteroleptic bis(amido)cuprate or else a 1:1 mixture of homoleptic bis(amido)cuprates. Either model could exist in Gilman or Lipshutz-type formats depending upon the inclusion or not of LiBr. To elucidate which was the relevant motif, X-ray diffraction was deployed. It revealed the creation and isolation of the dimer of Lipshutz-type MP(TMP)Cu(Br)Li $_2$ (THF) $_2$ **13** (Scheme 5 and Fig. 4) in which each Cu centre was heteroleptically bound by MP and TMP amido ligands, revealing for the first time potential heterostructured bis(amido) DoC reagents. As was the case for adduct **12**, the structure of **13** formed a multi-component crystal by virtue of the racemic nature of MP and the fact that there appears to be little steric influence on the projection of the MP methyl group on one side or the other of the 6-membered $\text{N}_2\text{CuLi}_2\text{Br}$ ring that describes the monomeric Lipshutz-type building block in **13**. In each such ring, the amides act as Cu–N–Li inter-metal linkers (Cu–N^{TMPLi}–Li

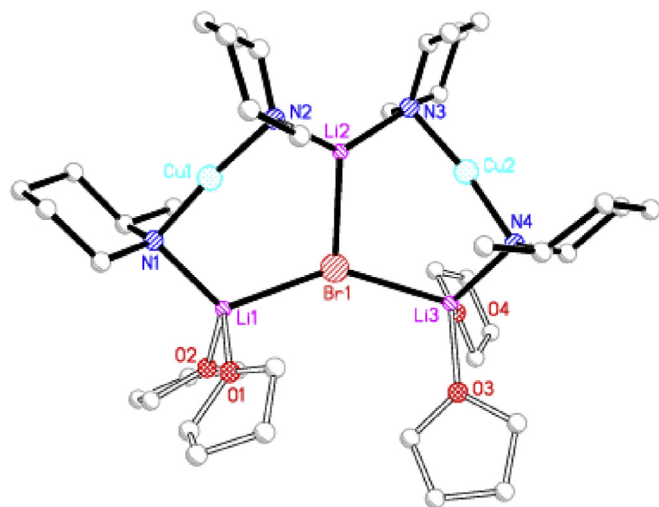
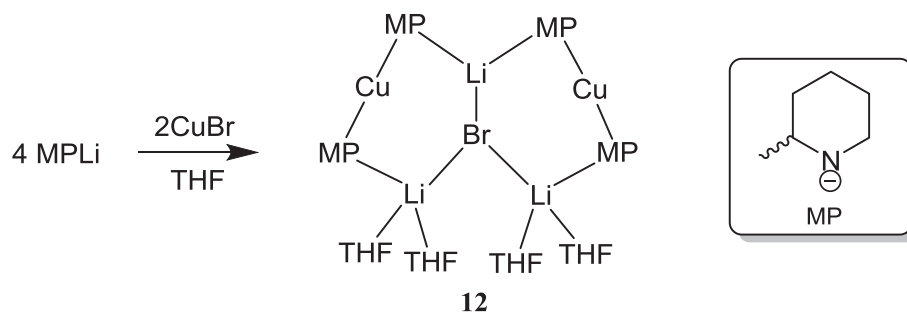
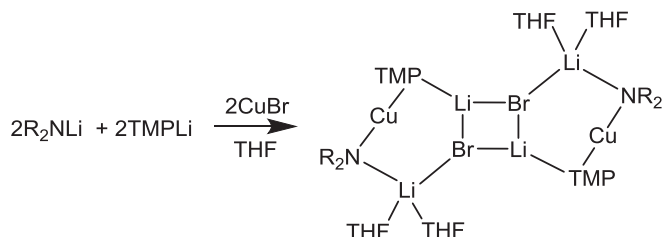


Fig. 3. Molecular structure of adduct **12**. H-atoms and ligand disorder omitted. Selected bond lengths (Å) and angles ($^\circ$): N1–Cu1 1.885(5), N2–Cu1 1.876(5), N3–Cu2 1.886(4), N4–Cu2 1.880(5), N1–Li1 2.050(10), N2–Li2 1.991(9), N3–Li2 2.018(9), N4–Li3 2.005(10), Br1–Li1 2.568(9), Br1–Li2 2.555(8), Br1–Li3 2.601(10), Cu1–N1–Li1 93.5(3), Cu1–N2–Li2 94.7(3), Cu2–N3–Li2 89.3(3), Cu2–N4–Li3 93.9(3).

Scheme 4. Synthesis of **12**.Scheme 5. Formation of the dimers of Lipshutz-type cuprates **13** ($\text{NR}_2 = \text{MP}$) and **14** ($\text{NR}_2 = \text{DMP}$).

available about heteroleptic bis(amido)cuprates we reverted to the use of DMPH in place of MPH in an attempt to fabricate $\text{DMP}(\text{TMP})\text{Cu}(\text{Br})\text{Li}_2(\text{THF})_2$. To this end, a hexane solution of DMPLi , TMPLi (1:1) and THF (1 eq. wrt Li) was added to CuBr (0.5 eq. wrt Li) to give an orange solution from which crystalline material could be obtained. As for **13**, ^1H and 2D NMR spectroscopy on the product revealed limited reformation of TMPH . That notwithstanding, it was clear that the bulk product exhibited a 1:1:2 $\text{DMP}:\text{TMP}:\text{THF}$ ratio, and this was reflected by X-ray crystallographic analysis. This indicated the successful formation of heteroleptic bis(amido)cuprate components of Lipshutz-type formulation and with linearly coordinated Cu participating in the centrosymmetric dimer of $\text{DMP}(\text{TMP})\text{Cu}(\text{Br})\text{Li}_2(\text{THF})_2$ **14** (Scheme 5 and Fig. 5).

As with **13**, the monomeric Lipshutz-type building blocks in **14** are based on 6-membered $\text{N}_2\text{CuLi}_2\text{Br}$ rings ($\text{Cu}-\text{N}^{\text{TMP}}-\text{Li}$ $91.3(3)^\circ$, $\text{Cu}-\text{N}^{\text{DMP}}-\text{Li}$ $94.1(3)^\circ$). The replacement of MP by DMP still allows the two different amides (DMP and TMP) to orientate themselves in markedly distinct ways – *endo*- TMP and *exo*- DMP – with the behaviour of the latter amide being crucial to allowing bis(THF) solvation of the adjoined Li_2 by ensuring significant space around that ion. This view is reinforced by the observation that the dimer of **14** (like that of **13**, see above) adopts a chair conformation, with the projection of Li_2 above (and symmetry related Li_2A below) the plane of the $(\text{LiBr})_2$ metalocyclic core. This allows the two THF molecules on each of Li_2 and Li_2A to adopt distinctly different positions; axial (O_2) and equatorial (O_1) wrt to the 6-membered $\text{N}_2\text{CuLi}_2\text{Br}$ metalocyclic monomer in which they participate (Fig. 6,

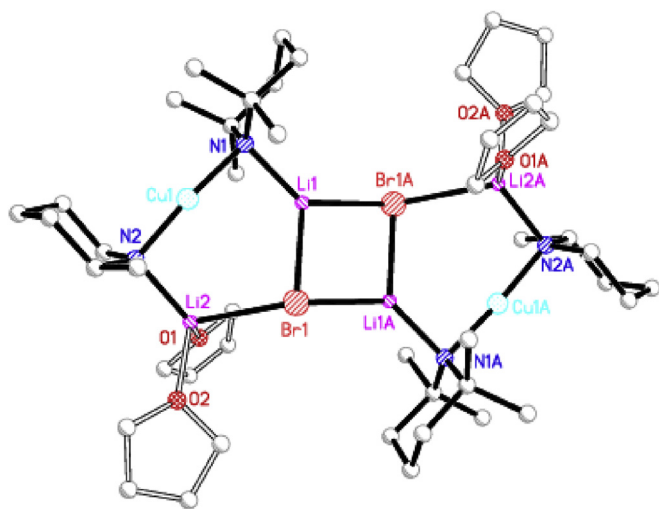


Fig. 4. Molecular structure of the dimer of cuprate **13**. H-atoms and THF and ligand disorder omitted. Selected bond lengths (\AA) and angles ($^\circ$): $\text{N}_1-\text{Cu}1$ 1.900(7), $\text{N}_2-\text{Cu}1$ 1.878(7), $\text{N}_1-\text{Li}1$ 1.969(13), $\text{N}_2-\text{Li}2$ 2.013(13), $\text{Br}1-\text{Li}1$ 2.498(13), $\text{Br}1\text{A}-\text{Li}1$ 2.478(12), $\text{Br}1-\text{Li}2$ 2.625(13), $\text{Cu}1-\text{N}1-\text{Li}1$ $90.9(5)$, $\text{Cu}1-\text{N}2-\text{Li}2$ $98.0(5)$.

$90.9(5)^\circ$, $\text{Cu}-\text{N}^{\text{MP}}-\text{Li}$ $98.0(5)^\circ$). Notably, the two different amides orientate themselves in markedly different ways. The TMP ligands adopt the *endo* orientation (lying flat wrt the structure core) seen previously in dimers of **7** and **8** [28,30]. In contrast, the MP ligands reside in the perpendicular *exo* orientation akin to the behaviour of DMP observed in adducts such as **11** [30], where bis(THF) solvation of the adjoined Li^+ was also noted. A comparison of the structures of **7**, **8**, **10** and **11** suggests the *exo* disposition of the DMP ligands to be crucial to enabling variability in the extent of Li^+ solvation and of allowing the presence of more than one solvent molecule on the alkali metal centre by ensuring significant space around the ion (see also **14** below).

In order to improve the quality of the structural information

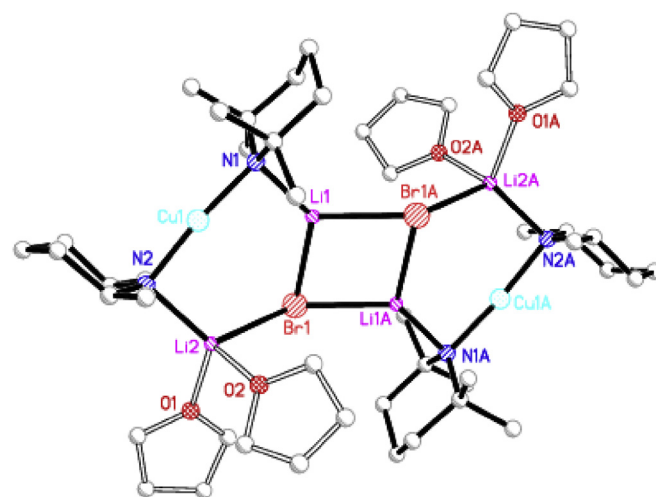


Fig. 5. Molecular structure of the dimer of cuprate **14**. H-atoms omitted. Selected bond lengths (\AA) and angles ($^\circ$): $\text{N}_1-\text{Cu}1$ 1.921(4), $\text{N}_2-\text{Cu}1$ 1.920(4), $\text{N}_1-\text{Li}1$ 1.987(11), $\text{N}_2-\text{Li}2$ 2.075(12), $\text{Br}1-\text{Li}1$ 2.461(10), $\text{Br}1-\text{Li}2$ 2.660(11), $\text{Br}1-\text{Li}1\text{A}$ 2.493(10), $\text{Cu}1-\text{N}1-\text{Li}1$ $91.3(3)$, $\text{Cu}1-\text{N}2-\text{Li}2$ $94.1(3)$.

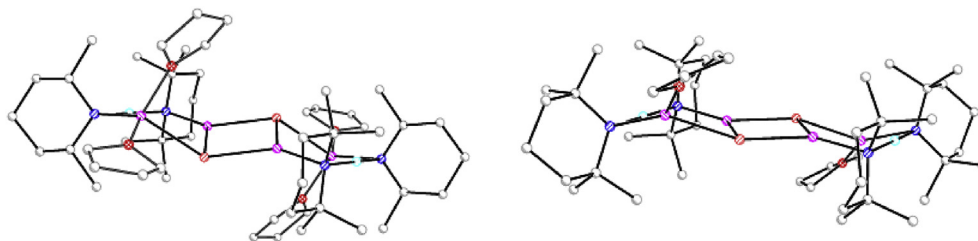


Fig. 6. Side-on views of the dimers of Lipshutz-type (DMP)(TMP)Cu(Br)Li₂(THF)₂ **14** (left) and (TMP)₂Cu(Br)Li₂(THF) **7c** (right) [29b], highlighting the chair conformation of the former complex and the axial/equatorial THF positions.

left) – a motif at subtle variance with the much more planar arrangement originally seen in the less extensively solvated (LiBr)₂-centred dimer of **7c** (Fig. 6, right) [29b]. Hence, the equatorial THF molecules reside in pockets that are derived from the presence of two (rather than four) Me-groups in DMP (or, in **13**, the presence of a single Me-group in MP) combined with the ability of this ligand to adopt an *exo* orientation – as summarized in Fig. 7. Lastly, the higher level of solvation in **14**₂ is reflected in the coordination spheres of Li1 and Li2, with the former showing shorter bonds to both N and Br (N1–Li1 1.987(11), Br1–Li1 2.461(10), N2–Li2 2.075(12), Br1–Li2 2.660(11) Å).

With the benefit of the crystal structures of **13** and **14** available it also becomes possible to interpret the convoluted spectroscopic data for these systems. In both cases, some decomposition was seen (for example TMPH formation could be identified). However, in spite of this and previous reports suggesting the importance of *in situ* Gilman cuprate formation [16], in the present cases divergent behaviour emerges, with **13** showing substantially more conversion to the Gilman form. This system gave a convoluted ¹³C NMR spectrum, which we attribute to the presence of chiral MP ligands, each of which can adopt two different *exo* orientations with respect to the structure core. The ⁷Li NMR spectrum was clearer, revealing resonances at δ 1.54 and 1.21 ppm in a 1:1 ratio next to a dominant signal at δ 1.05 ppm; the first two are attributed to Lipshutz-type structure retention in solution, with the highfield shift suggesting the development of a Gilman cuprate. In contrast, the interconversion of Lipshutz-type and Gilman species occurred to a lower level for **14**, with the behaviour of this system more closely following the recently observed solution characteristics of (TMP)₂Cu(Br)Li₂(THF)₂ **7c** [29b]. Although the ¹³C NMR spectrum of that complex revealed a low level of Gilman cuprate [29b] while a single species dominated in the ¹³C NMR spectrum of **14**, ⁷Li NMR spectroscopic data of the two complexes agreed well. The spectrum of **14** suggests a small amount of Gilman cuprate (presumably undetectable by ¹³C NMR spectroscopy) in solution by revealing a minor shoulder at δ 0.92 ppm alongside two dominant resonances at δ 1.38 and 1.12 ppm. The 1:1 ratio of these last two peaks is consistent with the presence of two alkali metal environments in the Lipshutz-type structure. These signals compare with a ⁷Li NMR

spectrum of **7c** that reveals a dominant singlet at δ 1.13 ppm alongside a much smaller highfield peak (see Electronic Supplementary Information, ESI, Fig. S1), suggesting that the dominant lowfield signal in the spectrum of **14** could be attributed to the DMPLi moiety in that complex whilst its highfield counterpart originated from the TMPLi moiety. The spectra of both **13** and **14** revealed also a minor broad feature at *ca.* δ 1.8 ppm of a type previously interpreted as being consistent with the presence of trace lithium amide [30].

The interconvertibility of Lipshutz-type and Gilman cuprates has been probed extensively by DFT analysis and is the subject of ongoing spectroscopic work [36]. Initial calculations led to the conclusion that higher-order structures were less stable than their lower-order analogues [37] and focused on the nature of the bonding in cyanocuprates, concluding [38,39] that a preference existed for the ‘lower order’ structural motif proposed based on spectroscopic data [40] and eventually directly observed in 2007 [28]. Subsequently, the spectroscopic analysis of Lipshutz-type **7b** and **7c** established partial conversion to Gilman cuprates in solution [29], though in contrast it has been reported that Gilman-(Lipshutz-type) adducts retain their structural integrity in solution [30]. It has been noted that the active species in DoC was a Gilman monomer [16] and this necessitated an understanding of the abstraction of LiX from a Lipshutz-type formulation. Though the full characterization of heteroleptic amido(organyl) monomers **5** and **6** [17] was consistent with this thesis and the more recent documentation of adducts **10–12** hinted at abstraction pathways [30], only one example of a Gilman bis(amido)cuprate directly relevant to DoC has so far been isolated; the dimer of (TMP)₂CuLi **4** [16]. This was prepared by the straightforward 2:1 combination of TMPLi with CuI and demonstrated a simple dimer structure based on an 8-membered ring. To extend the work in a heteroamido context, a hexane solution of preformed, equimolar PIPLi and TMPLi was added to CuBr (0.5 eq. wrt Li). This gave a straw-coloured solution from which crystals were obtained. ¹H and ¹³C NMR spectroscopy revealed some decomposition in solution but nevertheless suggested a product that incorporated one type of PIP ligand and one type of TMP ligand in a 1:1 ratio. This pointed to the formation of a heteroamido analogue of **4**; PIP(TMP)CuLi **15**. Based on the

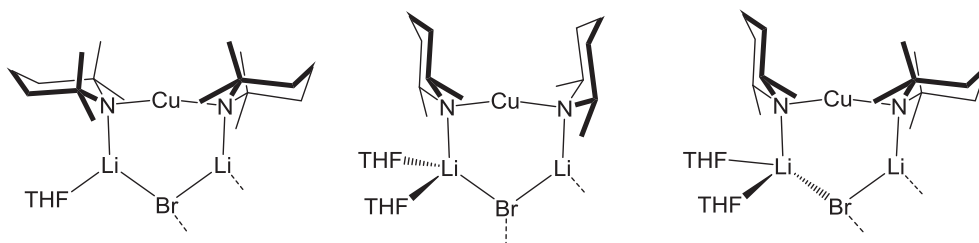


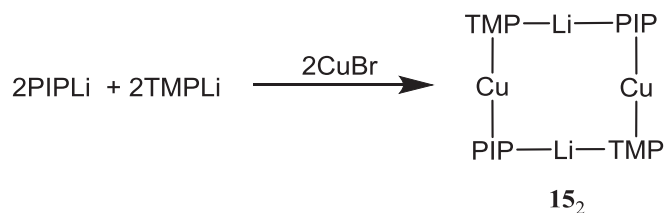
Fig. 7. Summary of amide ligand orientations in the monomeric components of Lipshutz-type (TMP)₂Cu(Br)Li₂(THF)₂ **7c** (left) [29b], adduct [(DMP)₂CuLi(THF)₂]₂LiBr **11** (middle) [30] and Lipshutz-type (DMP)(TMP)Cu(Br)Li₂(THF)₂ **14** (right).

previously reported homo(amido) structure it was postulated that **15** would likely form a dimer in the solid state with aggregation occurring in head-to-tail fashion – as previously demonstrated by the dimer of MesNHCu(PhNH)Li·DME [41]. This view was borne out by crystallography (Fig. 8 and Scheme 6).

As for previously reported dimer **4**₂ [16], the metal sites in **15**₂ are well defined (see Experimental section) [42], meaning that ligand orientations can be understood in terms of both inter-ligand sterics and also proximity to one or other metal centre. This is of use because the superficial similarity of **4**₂ and **15**₂ belies distinctly different ligand behaviour in each. In the case of **4**₂, the TMP ligands lie flat wrt Cu [16] in a fashion akin to that also noted in Lipshutz-type structures (e.g. **7**₂). Meanwhile, in **15**₂ the orientation displayed by each PIP ligand is akin to that of MP and DMP in, for example, adducts **11** and **12**. The result of this variance in ligand orientation, combined with head-to-tail dimerization [15], is a paddlewheel (Fig. 8, left). A further consequence of this arrangement is the close approach of two of the four methyl groups on each TMP ligand to a Li⁺ ion; the observed C···Li distances (C7...Li1A 2.866(4), C9...Li1A 2.844(4) Å, Fig. 8, right) residing in the range that has been attributed to support of alkali metal ions by methyl groups (in X–Me...Li; X = Al [43,44], B [45], Si [46,47]) where the coordinative behaviour of the methyl H-atoms has been thoroughly evidenced by neutron diffraction. Calculated hydrogen atom positions in **15** are also consistent with this view. Moreover, ⁷Li NMR spectroscopy revealed a singlet at δ 1.33 ppm that correlated with one of the two TMP methyl resonances in the ¹H NMR spectrum. Hence, ¹H,⁷Li-HOESY NMR spectroscopy revealed a cross-peak between the ⁷Li signal and the ¹H NMR signal at δ 1.28 ppm but not that at δ 1.50 ppm (see ESI, Fig. S2). Such behaviour is consistent with retention of the TMP ligand orientation displayed in the solid state.

3. Conclusions

The chiral amine MPH has been deployed for the first time to fabricate the adduct [(MP)₂CuLi(THF)₂]₂LiBr **12**. Subsequently, MP ligands have been included into the Lipshutz-type cuprate **13**, which incorporates an (LiBr)₂ core upon dimerization. In contrast to previous examples of this structure-type [16,28–30], these complexes reveal individually heteroleptic bis(amido)cuprate monomers. Previously, differences between TMP and DMP orientation in, for example, **8** and **10** have been speculatively attributed to steric effects borne of the interaction of Me groups on adjacent ligands. This is now more clearly demonstrable in the structures of **13** and



Scheme 6. Formation of the dimer of Gilman cuprate **15**.

14, where the tetramethylated TMP adopts an *endo* orientation whilst less sterically congesting MP and DMP both reside *exo*. In a similar vein, the dimer of Gilman cuprate **15** adopts a paddlewheel configuration, thereby minimizing steric interactions between TMP and PIP ligands. The orientation of TMP in this dimer also points to significant CH···Li stabilization, and neutron diffraction studies into this phenomenon have been initiated.

4. Experimental section

4.1. General synthetic and analytical details

Reactions and manipulations were carried out under an inert atmosphere of dry nitrogen, using standard double manifold and glove-box techniques. The solvents THF and hexane were distilled off sodium-potassium amalgam immediately prior to use. Copper(I) bromide and the amines piperidine (PIPH), 2-methylpiperidine (MPH), 2,6-*cis*-dimethylpiperidine (DMPH), 2,2,6,6-tetramethylpiperidine (TMPPH) were purchased from Aldrich. The amines were distilled and stored over molecular sieve (4 Å). *n*-BuLi (1.6 M in hexanes) was purchased from Acros and used as received. NMR data were collected on a Bruker Avance III HD 500 MHz Smart Probe spectrometer (500.200 MHz for ¹H, 125.775 MHz for ¹³C, 194.397 MHz for ⁷Li). Spectra were obtained at 25 °C and chemical shifts are internally referenced to C₆D₆ and calculated relative to TMS except for ⁷Li, for which an external reference was used (1 M LiCl in D₂O). Chemical shifts are expressed in δ ppm. The following abbreviations are used: br = broad, s = singlet, m = multiplet, sh = shoulder.

4.2. General crystallographic details

For details of data collections see Table 1. Crystals were transferred directly from the mother liquor to a drop of perfluoropolyether oil mounted upon a microscope slide under a

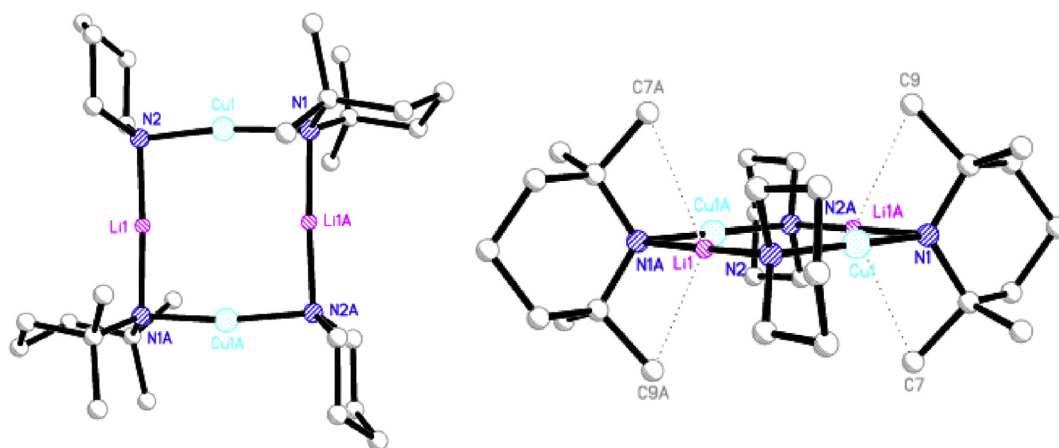


Fig. 8. Molecular structure of **15** (left) with close C...Li contacts highlighted (right). H-atoms omitted. Selected bond lengths (Å) and angles (°): N1–Cu1 1.8909(16), N2–Cu1 1.8757(16), N1–Li1A 1.952(3), N2–Li1 1.910(3), Cu1–N1–Li1A 92.16(10), Cu1–N2–Li1 92.16(11).

Table 1
X-ray crystal data for **12–15**.

| | 12 | 13 | 14 | 15 |
|--|---|---|---|--|
| Formula | C ₄₀ H ₈₀ BrCu ₂ Li ₃ N ₄ O ₄ | C ₄₆ H ₉₂ Br ₂ Cu ₂ Li ₄ N ₄ O ₄ | C ₄₈ H ₉₆ Br ₂ Cu ₂ Li ₄ N ₄ O ₄ | C ₂₈ H ₅₆ Cu ₂ Li ₂ N ₄ |
| <i>M</i> | 908.89 | 1079.89 | 1107.94 | 589.72 |
| Crystal system | Triclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ | $C2/c$ |
| <i>a</i> (Å) | 12.0150(2) | 10.9357(3) | 14.4774(5) | 20.1573(11) |
| <i>b</i> (Å) | 13.1207(3) | 11.0752(3) | 10.7720(3) | 9.0358(5) |
| <i>c</i> (Å) | 17.7475(4) | 12.4262(4) | 18.7374(7) | 17.5390(9) |
| α (°) | 83.9875(7) | 75.6840(10) | 90 | 90 |
| β (°) | 70.3373(7) | 85.0560(10) | 99.797(2) | 91.936(2) |
| γ (°) | 67.6336(14) | 75.4070(10) | 90 | 90 |
| <i>V</i> (Å ³) | 2435.59(9) | 1410.76(7) | 2879.49(17) | 3192.7(3) |
| <i>Z</i> | 2 | 1 | 2 | 4 |
| ρ_{calcd} (mg/m ³) | 1.239 | 1.271 | 1.278 | 1.227 |
| λ (Å) | 0.71073 | 0.71073 | 1.54184 | 1.54184 |
| μ (mm ⁻¹) | 1.731 | 2.209 | 2.837 | 1.779 |
| Data | 23822 | 17855 | 14155 | 13395 |
| Unique | 10967 | 5529 | 4915 | 2797 |
| <i>R</i> _{int} | 0.0442 | 0.0357 | 0.0474 | 0.0272 |
| θ (°) | 3.620–27.470 | 3.685–26.037 | 3.578–66.705 | 4.389–66.704 |
| <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)] | 0.0718 | 0.0909 | 0.0624 | 0.0303 |
| <i>wR</i> 2 | 0.2012 | 0.2740 | 0.1883 | 0.0927 |
| GoF | 1.033 | 1.043 | 1.041 | 1.037 |
| Parameters | 428 | 222 | 295 | 167 |
| Peak/hole (eÅ ⁻³) | 1.051/–0.776 | 1.591/–0.963 | 0.795/–0.864 | 0.511/–0.308 |

stream of cold nitrogen gas [48]. Suitable crystals were selected and attached to the goniometer head via a MicroLoop™, which was then centred on the diffractometer. Data were collected at 180 K on either a Bruker D8 Quest CCD or a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems low-temperature device. Structures were solved using direct methods [49], with refinement, based on *F*², by full-matrix least squares [50]. Except when disordered, non-hydrogen atoms were refined anisotropically and a riding model with idealised geometry was employed for the refinement of H-atoms. For severe disorder, occupancies were refined using a common isotropic atomic displacement parameter. 1,2- and 1,3- distance restraints, similarity restraints and positional constraints were applied as necessary. For **15** Li/Cu disorder was refined with occupancies of 97:3 and the 3% of substitutional disorder in the metals was not considered important [16]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1406319–1406322. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

4.3. Synthesis and characterization of [(MP)₂CuLi(THF)₂]₂LiBr **12**

A stirred solution of MPH (0.47 mL, 4 mmol) and THF (0.32 mL, 4 mmol) in hexane (4 mL) was treated with *n*-butyllithium (2.5 mL, 1.6 M in hexanes, 4 mmol) at –78 °C. The solution was warmed to room temperature whereupon a yellow suspension formed, which dissolved upon gentle warming. The solution was added dropwise to a stirred suspension of copper(I) bromide (0.286 g, 2 mmol) in hexane (2 mL) at –78 °C. The mixture was warmed to room temperature to give a black suspension. The suspension was filtered to give a bright orange solution that yielded colourless blocks after 7 days at –27 °C. Yield = 342 mg (38%, wrt. CuBr). ¹H NMR (500 MHz, C₆D₆): δ 4.25–3.64 (br, m, 4H, MP-6), 3.57 (m, THF, 16H), 3.37–2.86 (br, m, 4H, MP-6), 2.80–2.29 (br, m, 4H, MP-2), 2.26–2.00 (br, m, 4H, MP-4), 2.00–1.78 (br, m, 10H, MP-3,4,5), 1.78–1.56 (br, m, 10H, MP-3,4,5,Me), 1.56–1.42 (br, m, 12H, MP-3,4,5,Me), 1.36 (m, 16H, THF). ¹³C NMR (125 MHz, C₆D₆): δ 67.8 (THF), 59.3–57.4 (MP-2), 55.1–54.0 (MP-6), 40.6–38.9 (MP-5), 32.4–30.5 (MP-3), 27.3 (MP-

4), 27.1 (MP–Me). ⁷Li NMR (194 MHz, C₆D₆): δ 2.03 (br, s, 0.2Li), 1.05 (br, s, 1Li), 0.55 (s, 2Li) Mp: 73–75 °C. Anal. Calcd for C₄₀H₈₀BrCu₂Li₃N₄O₄: C, 52.86; H, 8.87; N, 6.16. found: C, 51.09; H, 8.74; N, 6.14.

4.4. Synthesis and characterization of MP(TMP)Cu(Br)Li₂(THF)₂ **13**

n-Butyllithium (2.5 mL, 1.6 M in hexanes, 4 mmol) was introduced to a stirred solution of MPH (0.24 mL, 2 mmol), TMPH (0.34 mL, 2 mmol) and THF (0.32 mL, 4 mmol) in hexane (4 mL) at –78 °C. The solution was warmed to room temperature to give a yellow solution that was then added dropwise to a stirred suspension of copper(I) bromide (0.286 g, 2 mmol) in hexane (2 mL) at –78 °C. The mixture was warmed to room temperature to yield a black suspension that could be filtered to give an orange coloured solution. This yielded crystals after storage –27 °C for 5 days. Yield = 430 mg (40%, wrt. CuBr). ¹H NMR (500 MHz, C₆D₆): δ 3.92–3.63 (br, m, 1H, MP-6), 3.58 (m, 16H, THF), 3.46–2.91 (br, m, 3H, MP-6), 2.91–2.57 (br, m, 2H, MP-2), 2.18–1.88 (m, 4H, TMP-4/MP-4), 1.88–1.59 (m, 18H, TMP-3,4,5/MP-3,4,5), 1.53–1.38 (m, 22H, TMP-3,4,5,Me/MP-3,4,5,Me), 1.38–1.26 (m, 20H, TMP-Me/MP-Me/THF), 1.26–1.14 (m, 4H, TMP-3,5), 1.04 (s, 1.8H, TMPH-Me) 0.94–0.78 (m, 2H, TMP-3,5). ¹³C NMR (125 MHz, C₆D₆): δ 68.1 (THF), 59.0–57.5 (MP-2), 55.2–53.1 (MP-6), 52.0 (TMP-2,6), 49.6 (TMPH-2,6), 43.0–41.2 (TMP-3,5), 40.8–38.6 (MP-5/TMP-Me), 38.5 (TMPH-3,5), 36.2–33.6 (TMP-Me), 31.9 (TMPH-Me), 31.7–29.7 (MP-3), 28.6–25.7 (MP-4,Me), 25.4 (THF), 20.9–19.2 (TMP-4), 18.7 (TMPH-4). ⁷Li NMR (194 MHz, C₆D₆): δ 1.80 (br, s, 0.8Li), 1.54 (s, 0.7Li), 1.21 (s, 0.7Li), 1.05 (s, 1.8Li). Mp: dec. > 80 °C. Anal. Calcd for C₄₆H₉₂Br₂Cu₂Li₄N₄O₄: C, 51.16; H, 8.59; N, 5.19. found: C, 49.84; H, 8.57; N, 5.39.

4.5. Synthesis and characterization of DMP(TMP)Cu(Br)Li₂(THF)₂ **14**

To a stirred solution of DMPH (0.27 mL, 2 mmol), TMPH (0.34 mL, 2 mmol) and THF (0.32 mL, 4 mmol) in hexane (4 mL) was added *n*-butyllithium (2.5 mL, 1.6 M in hexanes, 4 mmol) at –78 °C. The mixture was warmed to room temperature to give a yellow solution. To this, a stirred suspension of copper(I) bromide (0.286 g,

2 mmol) in hexane (2 mL) was added dropwise at $-78\text{ }^{\circ}\text{C}$. The mixture was warmed to room temperature to give a black suspension. This was filtered to give an orange solution, which yielded the crystalline product after storage $-27\text{ }^{\circ}\text{C}$ for 5 days. Yield = 410 mg (38%, wrt. CuBr). ^1H NMR (500 MHz, C_6D_6): δ 3.60 (m, 16H, THF), 2.96–2.68 (br, s, 4H, DMP-2,6), 2.13 (br, m, 2H, DMP-4), 2.0 (br, m, 2H, TMP-4), 1.93–1.68 (br, m, 20H, DMP-3,4,5,Me/TMP-3,5,Me), 1.68–1.37 (br, m, 32H, DMP-Me/TMP-Me), 1.36–1.26 (br, m, 18H, THF, TMP-3,5/DMP-Me), 1.24 (m, 2H, TMP-3,5/DMP-3,5), 1.07 (s, 1.6H, TMPH-Me). ^{13}C NMR (125 MHz, C_6D_6): δ 68.0 (THF), 59.0 (DMP-2,6), 53.7 (TMP-2,6), 49.2 (TMPH-2,6), 40.7 (TMP-3,5), 40.6 (DMP-3,5), 38.9 (DMP-3,5), 38.5 (TMP-Me), 38.2 (TMPH-3,5), 34.6 (TMP-Me), 31.6 (TMPH-Me), 27.3 (DMP-4), 26.3 (DMP-Me), 25.0 (THF), 19.4 (TMP-4), 18.3 (TMPH-4). ^7Li NMR (194 MHz, C_6D_6): δ 1.82 (br, s, 0.2Li), 1.38 (s, 1Li), 1.12 (s, 1Li), 0.92 (s, sh, 0.1Li). Mp: $78-80\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{48}\text{H}_{96}\text{Br}_2\text{Cu}_2\text{Li}_4\text{N}_4\text{O}_4$: C, 52.03; H, 8.73; N, 5.06. found: C, 52.20; H, 8.90; N, 5.38.

4.6. Synthesis and characterization of PIP(TMP)CuLi 15

To a stirred solution of TMPH (0.34 mL, 2 mmol) and PIPH (0.20 mL, 2 mmol) in hexane (4 mL), was added *n*-butyllithium (2.5 mL, 1.6 M in hexanes, 4 mmol) at $-78\text{ }^{\circ}\text{C}$. The solution was allowed to warm to room temperature, whereupon the resulting cream-coloured suspension was added to a suspension of copper(I) bromide (0.286 g, 2 mmol) in hexane (2 mL) at $-78\text{ }^{\circ}\text{C}$. The mixture was left to warm to room temperature, giving a black suspension which was filtered to give a pale straw-coloured solution. Storage at $+5\text{ }^{\circ}\text{C}$ for 1 day yielded the crystalline product. Yield = 103 mg (17% wrt. CuBr). ^1H NMR (500 MHz, C_6D_6): δ 3.36–2.99 (br, m, 8H, PIP-2,6), 1.84–1.74 (m, 2H, TMP-4), 1.74–1.59 (m, 14H, PIP-3,4,5/TMP-3,5), 1.59–1.51 (m, 4H, PIP-3,5/TMP-4), 1.50 (s, 12H, TMP-Me), 1.42–1.32 (br, m, 1.2H, TMPH), 1.28 (s, 12H, TMP-Me), 1.25–1.14 (m, 0.46H, TMPH), 1.07 (s, 3.16H, TMPH), 1.00–0.19 (m, 4H, TMP-3,5), 0.35 (br, s, 0.2H, TMPH {NH}). ^{13}C NMR (125 MHz, C_6D_6): δ 53.8 (TMP-2,6), 52.9 (PIP-2,6), 49.2 (TMPH-2,6), 41.3 (TMP-3,5), 38.7 (TMP-Me), 38.1 (TMPH-3,5), 34.3 (TMP-Me), 31.9 (PIP-3,5), 31.6 (TMPH-Me) 26.6 (PIP-4), 19.2 (TMP-4), 18.3 (TMPH-4). ^7Li NMR (194 MHz, C_6D_6): δ 1.33 (s). Mp: $115-117\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{28}\text{H}_{56}\text{Cu}_2\text{Li}_2\text{N}_4$: C, 57.02; H, 9.57; N, 9.50. found: C, 56.52; H, 9.37; N, 9.40.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2015.09.038>.

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