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Structural Effects in Lithiocuprate Chemistry: the Elucidation of Reactive Pentametallic Complexes

Philip J. Harford,^[a] Andrew J. Peel,^[a] Joseph P. Taylor,^[a] Shinsuke Komagawa,^[b] Paul R. Raithby,^[c] Thomas P. Robinson,^[c] Masanobu Uchiyama,^{*[b]} and Andrew E. H. Wheatley^{*[a]}

Abstract: TMPLi (TMP = 2,2,6,6-tetramethylpiperidide) reacts with Cu(I) salts in the presence of Et₂O to give the dimers [(TMP)₂Cu(X)Li₂·OEt₂]₂ (X = CN, halide). In contrast, the use of DMPLi (DMP = 2,6-*cis*-dimethylpiperidide) gives an unprecedented structural motif; [(DMP)₂CuLi·OEt₂]₂LiX (X = halide). This formulation suggests a hitherto unexplored route to the *in situ* formation of Gilman-type bases that are of proven reactivity in directed *ortho* cupration.

Organocuprate(I) complexes in general,^[1] and amidocuprates in particular, have proved to be tremendously important in effecting stereoselective organic transformations,^[2] with recent work yielding lithiocuprates of the type RR'CuXLi₂ (R, R' = organyl, TMP; TMP = 2,2,6,6-tetramethylpiperidide; X = CN, halide) and the new field of Directed *ortho* Cupration (DoC). It has been noted that the TMP group could react to achieve chemoselective DoC transformations and the subsequent trapping of electrophiles or oxidative ligand coupling showed the significant potential of these reagents in C–C and C–O bond formation.^[3,4]

Structural organocuprate(I) chemistry was recently the subject of review.^[5] Recent advances have revealed so-called Gilman-type monomers and dimers^[6] and (in line with theory)^[7] heteroleptic monomers^[8,9] and dimers (Fig. 1a,b,d).^[10] Conversely, cyanide-containing Lipshutz cuprates^[11] with hetero-aggregate structures have now been elucidated (Fig. 1e),^[3] with very recent work proving that the replacement of X = CN by X = halide

affords structurally analogous complexes,^[4c-d,6] and suggesting use of the term 'Lipshutz-type' to describe this wider group of comparable cuprates. Interestingly, while the reactivity of Lipshutz-type cuprates has been considered to often exceed that of their Gilman-type counterparts,^[4b,8,13] it was recently suggested that a Lipshutz-type reagent could be used to generate a *more reactive* Gilman-type intermediate *in situ*.^[6]

Presently we report the investigation of ligand effects through varying the amido component of new lithiocuprate bases. Data reveal a hitherto unrecognized class of cuprate heteroaggregate.

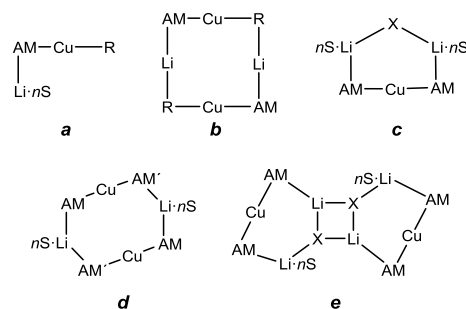


Figure 1. Established lithium amidocuprate structure-types; a) AM = N(CH₂Ph)Et, R = Mes, n = 3, S = THF;^[9] AM = TMP, R = Ph, n = 3, S = THF;^[8] AM = TMP, R = Me, n = 1, S = TMEDA;^[8] b) AM = N(CH₂Ph)₂, R = Mes;^[10] c) AM = X = NPh₂, n = 1, S = OEt₂;^[12] d) AM = NHMes, AM' = NPh, n = 1, S = DME;^[12] e) AM = TMP, X = CN, Cl, Br, I, n = 1, S = THF.^[3,4b-d,6]

We have recently sought to develop our understanding of ligand and solvent influences on lithiocuprate structures by modifying our previous syntheses of [(TMP)₂Cu(X)Li₂·THF]₂ (X = CN,^[3] halide^[6]). To this end, TMPLi was added to CuCN before introducing Et₂O. Storage of the resulting solution afforded crystalline **1**, which X-ray diffraction showed to be Lipshutz-type [(TMP)₂Cu(CN)Li₂·OEt₂]₂. Though the quality of the data was poor (*R*_{int} > 10%), the connectivity was unambiguous and the dimer was plainly analogous to that seen with THF.^[3] Comparable reactions (Scheme 1) using CuHal gave [(TMP)₂Cu(Hal)Li₂·OEt₂]₂ (Hal = Cl **2**, Br **3**, I **4**), establishing the general isolation of the structure-type seen for **1**. In each case superior crystal data were obtained (e.g. Fig. 2), with structural parameters found to be closely related to those seen in [(TMP)₂Cu(Hal)Li₂·THF]₂.^[4c-d,6] The monomeric Lipshutz-type building blocks revealed symmetrical 6-membered rings with

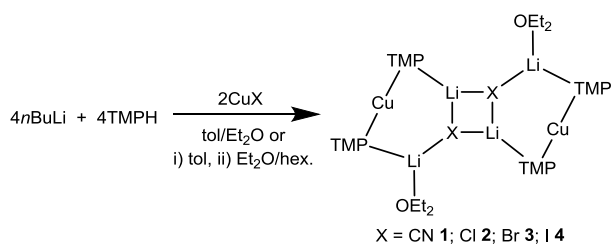
[a] P. J. Harford, A. J. Peel, J. P. Taylor, Dr. A. E. H. Wheatley
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge, CB2 1EW (UK)
Fax: (+) 1223 336362
E-mail: aehw2@cam.ac.uk

[b] Dr. S. Komagawa, Prof. Dr. M. Uchiyama
Elements Chemistry Laboratory, RIKEN
2-1 Hirosawa, Wako-shi, Saitama 351-0198, (Japan)
Graduate School of Pharmaceutical Sciences, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
E-mail: uchiyama@mol.f.u-tokyo.ac.jp

[c] Prof. P. R. Raithby, T. P. Robinson
Department of Chemistry, University of Bath
Claverton Down, Bath, BA2 7AY (UK)

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each amide acting as an inter-metal linker through the construction of uniform Cu–N–Li bridges (Cu–N–Li 90.4(2)–92.26(12)°, Cu–N–Li·OEt₂ 89.1(3)–91.8(2)°).



Scheme 1. Synthesis of 1-4.

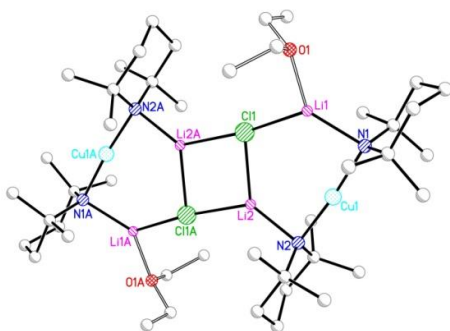


Figure 2. [(TMP)₂Cu(Cl)Li₂·OEt₂]₂ **2**. H atoms omitted. Selected bond lengths (Å) and angles (°): Li1–Cl1 2.344(6), Li2–Cl1 2.332(7), Li1–N1 2.024(6), Li2–N2 1.953(7), Li1–N1–Cu1 90.4(2), Li2–N2–Cu1 91.8(2), Cl1–Li1–N1 125.2(3), Cl1–Li2–N2 132.1(3).

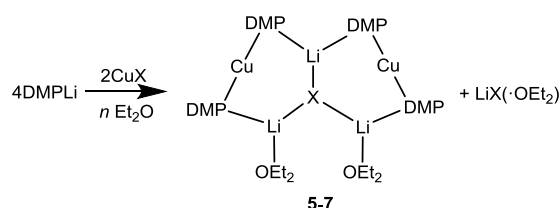
Recent studies have suggested the importance of steric effects in controlling amidocuprate reactivity.^[3] To further probe this issue we have investigated the effect of replacing TMP with less bulky DMP (= *cis*-2,6-dimethylpiperidine). Notably, DMPH also retails at a fraction of the cost of TMPH.^[14] In the present case, DMPLi was added to CuX in the presence of Lewis base (bulk or 1 or 2 eq. Et₂O wrt Cu). Attempts to isolate a product when X = CN are yet to bear fruit. However, for X = Hal a remarkable series of structurally analogous complexes was obtained (Scheme 2 and illustrated for X = Cl in Fig. 3).

For the use of X = Cl, the presence of bulk Et₂O (Scheme 2) allowed the isolation of crystals that ¹H NMR spectroscopy suggested contained Et₂O and DMP in a 1:2 ratio. However, the observable presence of an NH resonance (at δ 0.85 ppm) was inconsistent with the spectral data obtained for **1-4**. Crystallographic analysis revealed a unique triangulated structure based on a lithium halide core and having the formulation [(DMP)₂CuLi·OEt₂]₂LiCl **5**. This identification suggests that the (reproducible) observation of DMPH in solution is attributable to extreme moisture sensitivity in spite of the storage of deuterated solvents over a fresh Na mirror. The solid-state structure of **5** can be viewed as representing the first full characterization of an adduct between a Lipshutz- and a Gilman-type cuprate.

The formation of this new class of cuprate adduct was next replicated using CuBr in the presence of Et₂O in order to prepare [(DMP)₂CuLi·OEt₂]₂LiBr **6**. Initial attempts used *n*BuLi (1 eq. wrt amine) in the preparation of DMPLi. In the case of bulk Et₂O this led to **6** (Scheme 2).^[15] In contrast, the use of 2 eq. Et₂O afforded [(DMP)₂CuLi·OEt₂]_{1.45}[(DMP)₂CuLi·HDMP]_{0.55}LiBr **6'**.

This problem could be overcome, and the reproducible formation of **6** obtained, by using 1.1 eq. *n*BuLi.^[15]

Whereas the preparations of **5** and **6** used solvent conditions of bulk Et₂O (for Cl) or of either bulk or limited Et₂O (for Br), attempts to prepare the iodide analogue required that strictly limited quantities of Et₂O be present. The use of bulk donor failed to afford isolable material, whereas the presence of 2 eq. Et₂O wrt Cu afforded only LiI·OEt₂.^[16] However, the documented solubility of lithium iodide in Et₂O led us to suspect that this was causing the salt to largely remain in solution during filtration of the reaction mixture and to be subsequently crystallizing. The amount of donor solvent was therefore further restricted to promote lithium iodide precipitation and removal. Storage of the resulting filtrate at –27 °C yielded crystalline blocks that X-ray crystallography confirmed to be [(DMP)₂CuLi·OEt₂]₂LiI **7** (Scheme 2).^[15] As with **5** and **6**, the spectroscopic observation of NH was interpreted in terms of extreme moisture sensitivity.



Scheme 2. Synthesis of **5** (M = Cu, X = Cl, *n* = bulk), **6** (M = Cu, X = Br; *n* = bulk or 2 eq. wrt Cu) and **7** (M = Cu, X = I; *n* = 1 eq. wrt Cu).

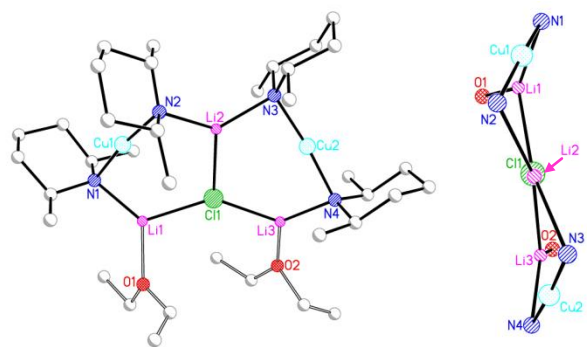


Figure 3. Adduct [(DMP)₂CuLi·OEt₂]₂LiCl **5** (H atoms and minor Et₂O disorder omitted) and the adduct core viewed along the Li2–Cl1 axis. Selected bond lengths (Å) and angles (°): Li1–Cl1 2.354(6), Li2–Cl1 2.412(6), Li3–Cl1 2.301(7), Li1–N1 1.986(8), Li2–N2 2.035(7), Li2–N3 2.054(6), Li3–N4 1.970(9), Li1–N1–Cu1 87.6(2), Li2–N2–Cu1 94.1(2), Li2–N3–Cu2 94.2(2), Li3–N4–Cu2 90.1(2), N2–Li2–N3 129.2(4), Li1–Cl1–Li3 139.5(2).

The structures of **6** and **7** are highly analogous to that of **5** and all exhibit approximate C₂ symmetry about a central lithium halide axis, as shown representatively in Fig. 3. In each case the halide shows triangulated coordination and two types of bond to Li⁺, with Li2–X being relatively extended (Li2–X 2.412(7), 2.592(7) and 2.971(16) Å in **5**, **6** and **7**, respectively). The Li1/3–X bonds are somewhat inequivalent: 2.354(6)/2.301(7), 2.474(8)/2.515(8) and 2.720(13)/2.667(14) Å in **5**, **6** and **7**, respectively. As would be expected, the metal-halide bonds extend as Group VII is descended. However, this extension is not consistent and the ratio between Li2–X and the mean of Li1/3–X is greater for iodide (1.10) than for chloride or bromide (1.04 in either case). This suggests that, rather than simply attributing this

bond extension to the ionic radius of the halide, competition between metal stabilization by hard and soft donors must also be considered. Thus, in the presence of soft iodide, Li2 is more inclined to be stabilized by the N2/3-based DMP ligands. This is reflected also in the Li2–N–Cu angles, which increase in response to the higher halide: Li2–N2/3–Cu1/2 94.1(2)/94.2(2) ° (5), 97.3(2)/97.5(3) ° (6), 100.1(5)/101.2(5) ° (7). A similar trend is seen for the remaining two (N1/4-based) ligands, though, consistent with the shorter Li1/3–X bonds, the angles are smaller: Li1/3–N1/4–Cu1/2 87.6(2)/90.1(2) ° (5), 92.5(3)/89.0(3) ° (6), 96.1(5)/96.8(5) ° (7). The asymmetry in these angles at nitrogen contrasts with the more symmetrical rings in 2-4, where the difference between Cu–N–Li and Cu–N–Li·OEt₂ was never more than 3 °.

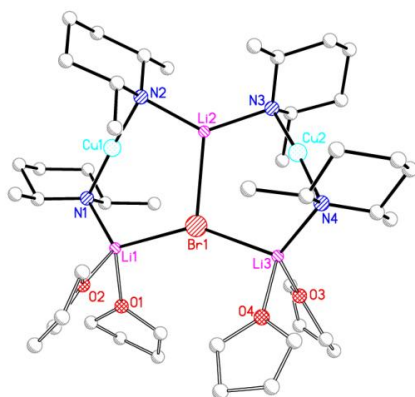


Figure 4. Adduct [(DMP)₂CuLi·2THF]₂LiBr **8**. H atoms omitted. Selected bond lengths (Å) and angles (°): Li1–Br1 2.609(11), Li2–Br1 2.677(11), Li3–Br1 2.602(12), Li1–N1 2.067(13), Li2–N2 2.045(11), Li2–N3 2.029(11), Li3–N4 2.094(15), Li1–N1–Cu1 94.3(4), Li2–N2–Cu1 93.9(4), Li2–N3–Cu2 94.2(4), Li3–N4–Cu2 92.0(4), N2–Li2–N3 132.2(6), Li1–Br1–Li3 147.3(4).

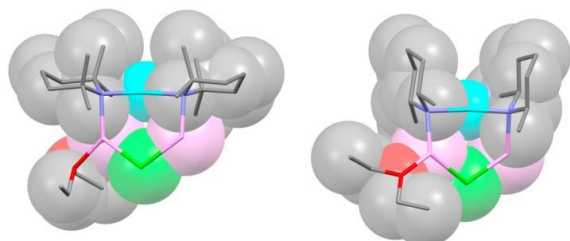


Figure 5. Structures of the Lipshutz-type monomers incorporated in TMP-based **2** (left) and DMP-based **5** (right) highlighting the *endo,endo* and *exo,exo* amide orientations in either.

Lastly, reaction of DMPLi with CuBr in dry toluene followed by recrystallization in the presence of THF at –27 °C yielded [(DMP)₂CuLi·2THF]₂LiBr **8** (Fig. 4) and established that adduct formation is not limited to the deployment of Et₂O. The two THF-solvated Li⁺ ions are now pseudotetrahedral. While the crystal structure of **8** is largely analogous to that of **6**, the effect of using a stronger Lewis base can be noted. Whereas Li2–N2/3 bonds are essentially unaffected, both Li1–N1 and Li3–N4 are extended in **8**. Similarly, Li1/3–Br1 increases significantly from 2.474(8)/2.515(8) Å in **6** to 2.609(11)/2.602(12) Å in **8**. The asymmetry in the Li–N–Cu bond angles noted in **6** is also now absent; the four angles in **8** being essentially identical. Lastly, evidence for additional stability conferred by the four THF molecules in **8** comes from the observation of a substantially smaller NH resonance in the ¹H NMR spectrum (*cf.* **5-7**).^[15]

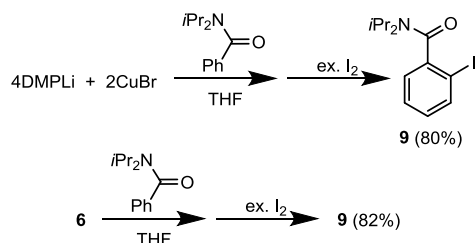
Although ¹H NMR spectroscopy on adducts **5-7** suggests some sensitivity towards trace moisture, ⁷Li NMR spectroscopic analysis is consistent with a significant level of retention of the solid-state structures. In all cases a low-field signal (at δ 2.16–2.18 ppm) matches the dominant signal (at δ 2.20 ppm) in a DMPLi reference spectrum. For each of **5**, **6** and **7** in C₆D₆ the dominant signals are seen at δ 1.83–1.84 and 1.41–1.50 ppm in a 1:2 ratio, consistent with the crystallographic data. In the case of **6'**, the spectrum is more complicated yet still consistent with crystallography. The presence of Li·DMP now introduces a signal at δ 1.66 ppm. However, the proximity of this to the δ 1.48 ppm signal attributable to Li·OEt₂ prevents their separate integration. Lastly, for **8** in C₆D₆ a single environment is observed by ⁷Li NMR methods, and we attribute this to the four THF molecules present in **8**, which create a more polar medium than the two Et₂O/DMPH molecules in **5-7**.

Subsequent investigation focused on the reasons for the transition in structure-type from dimers **1-4** to adducts **5-8**. The possibility that solvent identity or quantity was a determining factor having been removed, competition was presumed to be dictated by the amide. This can be seen from the chloride species shown in Figs. 2 and 3. In Fig. 2, the two TMP ligands associated with any given Cu atom (*viz.* N3, N4 in Fig. 2) project away from one another so as to lie *endo,endo* with respect to the structure core (Fig. 5, left). In contrast, the presence of DMP much reduces steric interaction between the methyl groups in the pair of amide ligands, allowing the piperidine rings to reside face-on to each other in a way that would be sterically precluded for TMP. The consequence of the face-on motif adopted by the DMP ligands is that they project away from the aggregate core in *exo,exo* fashion (Fig. 5, right). This configuration of the DMP ligands in **5-8** also avoids steric congestion between the two amides that are bonded to the single unsolvated Li⁺ centre in the structure.

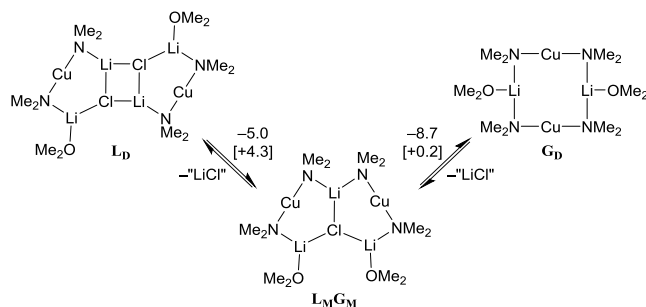
We already know that Gilman-type cuprates show inferior DoC activity when compared to their Lipshutz-type analogues.^[3] However, we have also established that DoC reactivity actually requires monomeric Gilman-type reagents *accessed from a Lipshutz-type precursor*,^[6] and we here reinforce the importance of LiHal inclusion in amidocuprate chemistry (Scheme 3). In THF, *N,N*-diisopropylbenzamide reacted to give 2-iodo-*N,N*-diisopropylbenzamide **9** in 80% yield using DMPLi, CuBr and the benzamide in a 4:2:1 ratio (*i.e.* 2 eq. Lipshutz-type Cu per arene) prior to I₂ work-up. Meanwhile, dissolution of pre-isolated **6** and *N,N*-diisopropylbenzamide in a 1:1 ratio (*i.e.* 2 eq. Cu per arene) gave **9** in an essentially identical yield of 82%. These data show that an adduct such as **6** can, like a Lipshutz-type dimer,^[6] be viewed as an efficient source of reactive Gilman-type monomers.

We sought to probe the relationship between Lipshutz- and Gilman-type dimers using DFT methods (Scheme 4).^[17] Results obtained with the simplified (Me₂N)₂CuLi·OMe₂ + LiCl system^[3,6,8] suggest that Lipshutz-type dimer **L_D** exhibits an enthalpic preference (Δ*E* = –13.7 kcal mol^{–1}) for eliminating a lithium halide solvate and forming a Gilman-type dimer, **G_D**.^[15] Meanwhile, a small entropy decrease, consistent with solvation of the eliminated halide, explains a slight increase (+4.5 kcal mol^{–1}) in Δ*G*. Though the adduct between a Lipshutz- and a Gilman-type monomer (**L_MG_M**) is not the preferred cuprate of the three, the energetic balance between species is a fine one. Lastly, the ability of **L_MG_M** to associate with a reagent such as *N,N*-

dimethylbenzamide prior to effecting a DoC reaction has been investigated.^[15,17] Results indicate that the conversion of $L_M G_M$ to a complex between G_M ($(Me_2N)_2CuLi-OMe_2$) and N,N -dimethylbenzamide along with $0.5L_D$ is accompanied by a change in ΔG of only $+6.1$ kcal mol⁻¹.^[15] This energy profile suggests a route to a N,N -dimethylbenzamide- G_M adduct that compares favourably with that recently calculated using a Lipshutz monomer as the starting point,^[6] and reinforces the view that $L_M G_M$ adducts such as **6** represent viable DoC reagents.



Scheme 3. Directed *ortho* iodination using DMPLi, CuBr and N,N -diisopropylbenzamide in a 4:2:1 ratio (top) or **6** and N,N -diisopropylbenzamide in a 1:1 ratio (bottom).



Scheme 4. The interconversion of Lipshutz- and Gilman-type dimers via adduct $[(Me_2N)_2CuLi-OMe_2]_2LiCl$ ($L_D-L_M G_M-G_D$) at B3LYP/SVP level.^[15,17] ΔE [ΔG] are in kcal/mol⁻¹. “LiCl” is $1/4[LiCl-OMe_2]_4 - OMe_2$.

To conclude, a previously unexplored class of triangulated lithium amidocuprate best viewed as a 1:1 adduct between Gilman- and Lipshutz-type monomers is reported. The formation of **5-8** can be viewed as resulting from the abstraction of lithium halide from a Lipshutz-type dimer and the relative orientations of the amide ligands in both dimers **2-4** and adducts **5-8** can be rationalized sterically. Derivatizations of an aromatic tertiary amide undertaken with i) 2:1 DMPLi:CuBr, and ii) **6** reinforce the importance of LiX-containing systems in amidocuprate reactivity.^[6] In both cases, high conversion is achieved using bases made with DMPH, suggesting major cost benefits.^[14] To improve our mechanistic understanding, we have now initiated a detailed study of the solution behaviour of these adducts.^[18] We are also seeking to use various amines to probe the relationship between ligand bulk and structure-type.

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Keywords: copper • directed metalation • lithium • solid-state structures • DFT calculations

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- [17] DFT calculations used Gaussian 09, revision C.01; Gaussian Inc., Wallingford, CT, 2010. See Supporting Information.
- [18] H. J. Reich, *J. Org. Chem.*, **2012**, *77*, 5471-5491.

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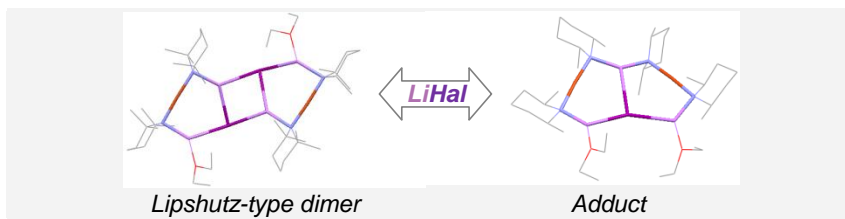
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Entry for the Table of Contents

Lithiocuprate structures

Philip J. Harford, Andrew J. Peel,
Joseph P. Taylor, Shinsuke
Komagawa, Paul R. Raithby,
Thomas P. Robinson, Masanobu
Uchiyama,* and Andrew E. H.
Wheatley* Page – Page

Structural Effects in Lithiocuprate Chemistry: the Elucidation of Reactive Pentametallic Complexes



A series of new amidocuprates have been studied. X-ray crystallographic analysis of amidocuprates prepared using copper(I) halides and 2,2,6,6-tetramethylpiperidine revealed Lipshutz-type dimers. The use of 2,6-*cis*-dimethylpiperidine gave a

remarkable new adduct motif; triangulated, pentametallic amidocuprates based on a lithium halide core. These adducts suggest a new mechanism for forming reactive monomeric Gilman-type cuprate bases.

