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Expanding the tools available for direct *ortho* cupration – targeting lithium phosphidocuprates

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Reaction of *in situ* generated lithium phosphides with 0.5 eq. Cu(I) is employed as a means of targeting lithium phosphidocuprates of either Gilman- or Lipshutz-type formulation – e.g.,
10 $(R_2P)_2CuLi \cdot n(LiX)$ ($n = 0, 1$). For R = Ph, X = CN in toluene followed by thf or R = Ph, X = I in thf/toluene an unexpected product results. $[(Ph_2P)_6Cu_4][Li \cdot 4thf]_2$ **1** reveals an ion separate structure in the solid state, with solvated lithium cations countering the charge on an adamantyl dianion $[(Ph_2P)_6Cu_4]^{2-}$. Deployment of R = Ph, X = CN in thf affords a novel network based on the dimer of $Ph_2PCu(CN)Li \cdot 2thf$ **2** with trianions based on 6-membered $(PCu)_3$ rings acting as
15 nodes in the supramolecular array and solvated alkali metal counter-ions completing the linkers. Cy_2PLi (Cy = cyclohexyl) has been reacted with CuCN in thf/toluene to yield Gilman-type lithium bis(phosphido)cuprate $(Cy_2P)_2CuLi \cdot 2thf$ **3** by the exclusion of *in situ* generated LiCN. A polymer is noted in the solid state.

Introduction

20 The deployment of bimetallic bases that combine enhanced deprotonative activity with superior ancillary group tolerance and in which the two metals interact such as to modulate the reactivity of one another has been documented.[1] This research, typically into new and more highly controllable methods for the
25 achievement of directed arene elaboration, has led to the development of highly effective heterometallic organyl (R) amido (e.g., tmp = 2,2,6,6-tetramethylpiperidido) bases. Specifically, it has proved possible to modulate the reactivities of bimetallic bases by manipulating the synergic relationship between the two
30 metals and the kinetic control offered by the active amide ligand. Such reagents include bases of the type $R_nM(\mu\text{-tmp})M'$ ($n = 2$, M = Zn,[2] Mn,[3] M´ = Li, Na; $n = 3$, M = Al,[4] M´ = Li). Most recently, these studies have been extended to the development of new lithium organocuprate compounds of the type that, since
35 their inception by Gilman[5] and more recent development by Power,[6] have been employed very successfully to enable new avenues in organic and organometallic chemistry.[7]

Two types of structure are pervasive in bis(organo)cuprate chemistry;[8] so-called Gilman-type and Lipshutz-type species.
40 The bis(organo)cuprate unit in each such system is based on an essentially linear $[R–Cu–R]^-$ ion. Gilman-type species are already known that exhibit homo-dimeric structures, with the corresponding bis(alkyl)-[9] and bis(aryl) systems[10] having been reported. However, heteroleptic Gilman-type cuprates have also
45 been seen for organo(amido) ligand combinations (Scheme 1).[11] Hence, recent advances in our understanding of the structural chemistry of lithium aryl(amido)cuprates has come from the work of Davies, with a monomer and head-to-tail dimer noted for $MesCu[\mu\text{-N(CH}_2Ph)Et]Li \cdot 3thf^{12}$ and $MesCu[\mu\text{-N(CH}_2Ph)_2]Li$
50 (Mes = mesityl),[13] respectively. The tris(thf) solvate of $PhCu(\mu\text{-tmp})Li$ has been shown to be an exact analogue of the first of these systems, while the same monomeric motif has also been reported recently for the tmeda solvated alkyl(amido)cuprate $MeCu(\mu\text{-tmp})Li \cdot tmeda$ (tmeda = N,N,N',N'-tetramethylethylene-
55 diamine).[14] In the context of bis(amido)cuprates, Fenske has reported that the solid-state structure of heteroleptic $MesNHCu(\mu\text{-NHPh})Li \cdot dme$ (dme = dimethoxyethane) dimerises by forming an octameric $(NCuNLi)_2$ ring.[15]

Whilst work on Gilman-type cuprates has been ongoing,
60 studies have also focused on developing a better
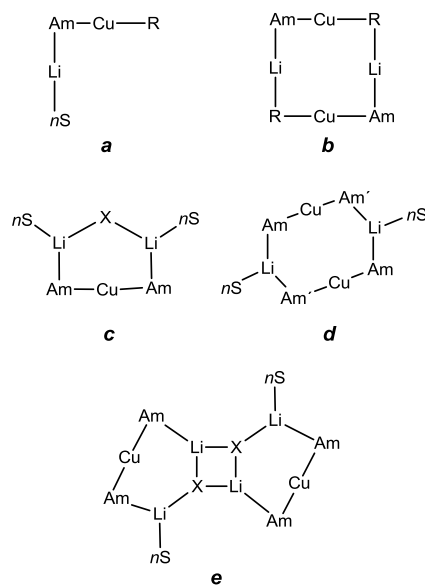
Scheme 1: Structure-types previously recorded for lithium organo(amido)- and bis(amido)cuprates; a) Am = N(CH$_2$Ph)Et, R =
65 Mes, $n = 3$, S = thf;[12] Am = tmp, R = Ph, $n = 3$, S = thf;[14] Am = tmp, R = Me, $n = 1$, S = tmeda;[14] b) Am = N(CH$_2$Ph)$_2$, R = Mes;[13] c) Am = X = NPh$_2$, $n = 1$, S = OEt$_2$;[15] d) Am = NHMes, Am´ = NHPh, $n = 1$, S = dme;[15] e) Am = tmp, X = CN, I, $n = 1$, S = thf.[18,19b]

understanding of the structural modification necessary to potentially enhance reactivity[16] by incorporating a lithium salt (LiX) and so form a Lipshutz-type structure (Scheme 1).[17] For X = [NPh$_2$]$^-$ a hexanuclear metallocyclic core is noted in the monomeric solid-state structure of (Ph$_2$N)$_3$Cu(Li·OEt$_2$)$_2$.[15] More recently, Lipshutz-type cuprates bearing sterically demanding amide ligands have been shown to exhibit high levels of reactivity in the selective directed *ortho* cupration (DoC) of aromatic rings.[18] The isolation and characterization of such bases has revealed dimeric aggregation based on the formulation (tmp)$_2$CuXLi$_2$·thf (X = CN, I)[18,19] with the structure i) revealing a core based on a (LiX)$_2$ metallocycle and, ii) reinforcing the view, first proposed by Bertz[20] and later backed up theoretically[21] and by solid-state structural evidence,[22] that there is no Cu–X interaction. Recently, mechanistic studies have shed light on the mechanisms available to Lipshutz-type amidocuprates for the derivatization of substituted arenes by DoC.[19b] DFT investigations of the potential reaction pathways for DoC suggest that the single-step formation of amine occurs in a fashion akin to that recently reported for alkali metal mediated alumination reactions,[4a,c] but that quenching of the amine, as has been seen in alkali metal mediated zincation chemistry,[2b,23] is unlikely.

Two issues have become apparent from our own recent studies into DoC using amidocuprates. First, the thermal stability of organo(amido)- and (to a lesser extent) bis(amido)cuprates represents a potential limiting factor insofar as the general applicability of these reagents is concerned. Secondly, whilst theory has been used in an attempt to understand the reactivity of lithiocuprates,[24] our mechanistic understanding of the activity of such systems in DoC would be enhanced if the base incorporated a spectroscopically active component. In the present study, we therefore present initial efforts aimed at fabricating both Gilman- and Lipshutz-type lithium phosphidocuprates that promise both enhanced thermal stability and the opportunity to deploy ^{31}P NMR spectroscopy as a means of monitoring deprotonative activity. Thus, treatment of the lithium bis(organyl)phosphides R$_2$PLi (R = Ph, Cy; Cy = cyclohexyl) with a Cu(I) salt has been found to yield both cyano(phosphido)- and bis(phosphido)cuprate moieties. In the latter case, the homoleptic Gilman-type cuprate (Cy$_2$P)$_2$CuLi is successfully obtained.

Experimental details

Reagents and materials

Reactions and manipulations were carried out under dry N$_2$, using standard double manifold and glove-box techniques. Solvents were distilled off sodium (toluene) or sodium-potassium amalgam (thf) immediately prior to use. Phosphine reagents were stored under an inert atmosphere at +5°C. The base Bu^{n}Li (1.6 M in hexanes) was purchased from Aldrich and used as received.

Synthesis

Synthesis and characterization of [(Ph$_2$P)$_6$Cu$_4$][Li·4thf]$_2$ **1**: a) Bu^{n}Li (1.25 ml, 1.6 M in hexanes, 2 mmol) was added dropwise to a solution of diphenylphosphine (0.36 ml, 2 mmol) in dry toluene (3 ml) under N$_2$ at –78°C. The resulting solution of lithium bis(phenyl)phosphide was allowed to reach room temperature whereupon it was added to a suspension of copper cyanide (0.089 g, 1 mmol) in dry toluene (3 ml) under N$_2$ at –78°C. The resulting orange slurry was allowed to reach room temperature whereupon it was filtered. The solvent was removed *in vacuo* and replaced with dry thf (10 ml) to yield a bright orange solution from which [(Ph$_2$P)$_6$Cu$_4$][Li·4thf]$_2$ **1** was deposited after 24 hr at room temperature, as confirmed by X-ray crystallographic analysis. b) Lithium bis(phenyl)phosphide solution, prepared as for method a), was added to a suspension of copper iodide (0.190 g, 1 mmol) in dry thf (3 ml) under N$_2$ at –78°C. The resulting orange slurry was allowed to reach room temperature whereupon dry thf (5 ml) was added and the mixture was gently warmed. From the resultant bright orange solution, **1** was deposited after 24 hr at room temperature. Yield 239 mg (49% wrt CuI); m.p. 122-124°C; elemental analysis calcd (%) for C$_{104}$H$_{124}$Cu$_4$Li$_2$O$_8$P$_6$: C 63.86, H 6.39, P 9.50; found: C 62.81, H 6.61, P 9.06; ^{1}H NMR spectroscopy (500 MHz, d_6-benzene, 300K): δ = 7.78 (m, 28H; Ph), 7.05 (m, 42H; Ph), 5.72 (d, trace; [1]J_{PH} = 290 Hz, PH), 3.51 (m, 32H; thf), 1.37 (m, 32H; thf); {^{1}H}^{13}C NMR spectroscopy (100 MHz, d_6-benzene, 300K): δ = 144.5 (d, [1]J_{CP} = 231 Hz, *ipso*-Ph), 135.2, 134.4, 124.3 (Ph-CH), 68.2 (thf), 25.6 (thf); {^{1}H}^{31}P NMR spectroscopy (202 MHz, d_6-benzene, 300K): δ = –22.1 (br s, Ph$_2$PCu), –32.6 (s, Ph$_2$PH); ^{31}P NMR spectroscopy (202 MHz, d_6-benzene, 300K): δ = –22.1 (br s, Ph$_2$PCu), –32.6 (d, [1]J_{PH} = 290 Hz, Ph$_2$PH); a crystallographic cell check verified the formation of **1**. Synthesis and characterization of Ph$_2$PCu(CN)Li·2thf **2**: Bu^{n}Li (1.25 ml, 1.6 M in hexanes, 2 mmol) was added dropwise to a solution of diphenylphosphine (0.36 ml, 2 mmol) in dry thf (3 ml) under N$_2$ at –78°C. The resulting solution of lithium bis(phenyl)phosphide was allowed to reach room temperature. It was then added to a suspension of copper cyanide (0.089 g, 1 mmol) in dry thf (2 ml) under N$_2$ at –78°C. The mixture was left to reach temperature whereupon a dark orange slurry was obtained. Gentle heating gave a bright orange solution from which **2** deposited after storage at room temperature for 12 hr. Yield 229 mg (54% wrt CuCN); m.p. decomp. from 210°C; elemental analysis calcd (%) for C$_{42}$H$_{52}$Cu$_2$Li$_2$N$_2$O$_4$P$_2$: C 59.22, H 6.15, N 3.29, P 7.27; found: C 58.93, H 6.03, N 3.25, P 7.59; ^{1}H NMR spectroscopy (500 MHz, d_6-benzene, 300K): δ = 7.79-6.57 (m, 5H; Ph), 5.49 (d, trace; [1]J_{PH} = 233 Hz, PH), 3.49 (m, 4H; thf), 1.70 (m, 4H; thf); {^{1}H}^{13}C NMR spectroscopy (100 MHz, d_6-benzene, 300K): δ = 144.5 (br d, [1]J_{CP} = 231 Hz, *ipso*-Ph), 135.2, 134.1, 124.1 (Ph-CH), 68.2 (thf), 26.4 (thf); {^{1}H}^{31}P NMR spectroscopy (202 MHz, d_6-benzene, 300K): δ = –14.9, –21.6, –28.1 (s, Ph$_2$PCu), –38.3 (s, Ph$_2$PH); ^{31}P NMR spectroscopy (202 MHz, d_6-benzene, 300K): δ = –14.9, –21.6, –28.1 (s, Ph$_2$PCu), –38.3 (d, [1]J_{PH} = 233 Hz, Ph$_2$PH). Synthesis and characterization of (Cy$_2$P)$_2$CuLi·2thf **3**: Bu^{n}Li (1.25 ml, 1.6 M in hexanes, 2 mmol) was added dropwise to a solution of dicyclohexylphosphine (0.4 ml, 2 mmol) in dry thf (3 ml) under N$_2$ at –78°C. The resulting solution of lithium bis(cyclohexyl)phosphide was allowed to

reach room temperature whereupon it was added to a suspension of copper cyanide (0.089 g, 1 mmol) in dry thf (2 ml) under N_2 at –78°C. The resulting mixture was left to reach temperature whereupon it was allowed to stir for 10 minutes. The solvent was removed *in vacuo* and replaced with dry toluene (6 ml) and dry thf (6 ml) to yield a pale yellow solution from which **3** deposited after storage at –30°C for 24 hr. Yield 88 mg (15% wrt CuCN); m.p. 151-153°C; elemental analysis calcd (%) for $C_{32}H_{60}CuLiO_2P_2$: C 63.08, H 9.93, N 10.17; found: C 62.89, H 9.85, N 9.92; ^{1}H NMR spectroscopy (500 MHz, d_6-benzene, 300K): δ = 3.63 (m, 8H; thf), 3.09 (dt, trace; $^1J_{PH}$ = 200 Hz, $^3J_{HH}$ = 6 Hz, PH), 2.21 (br m, 4H; Cy-CH$_2$), 1.94, 1.78 (br m, 10H; Cy-CH + Cy-CH$_2$), 1.47 (m, 8H; thf), 1.24, 1.06 (br m, 8H; Cy-CH$_2$); {^{1}H}^{13}C NMR spectroscopy (125 MHz, d_6-benzene, 300K): δ = 67.8 (thf), 35.2 (d, $^1J_{CP}$ = 255 Hz; Cy-CH), 26.7, 26.4 (Cy-CH$_2$), 25.8 (thf), 25.3 (Cy-CH$_2$); {^{1}H}^{31}P NMR spectroscopy (162 MHz, d_6-benzene, 300K): δ = –14.2, –16.4, –19.7 (s, Cy$_2$PCu), –26.6 (s, Cy$_2$PH); ^{31}P NMR spectroscopy (162 MHz, d_6-benzene, 300K): δ = –14.2, –16.4, –19.7 (s, Cy$_2$PCu), –26.6 (d, $^1J_{PH}$ = 200 Hz, Cy$_2$PH).

Single crystal X-ray diffraction

Crystallographic data (excluding structure factors) for **1-3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-859/209 (**1**), -210 (**2**), -211 (**3**). 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). Data were collected using either an Oxford Gemini diffractometer eqipped with a cryojet (**1**) or a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream low-temperature device (**2**, **3**). Structures were solved by direct methods[25] and refined against F^2 using SHELXL-97.[26] Crystal data for [(Ph$_2$P)$_6$Cu$_4$][Li·4thf]$_2$ **1**: $C_{106}H_{124}Cu_4Li_2O_8P_6$, M = 1955.89, trigonal, space group $P31c$, $a = b$ = 15.4214(3), c = 25.0344(5) Å, V = 5156.0(3) Å^3, Z = 2, ρ_{calcd}= 1.260 g cm^{-3}; Mo-K$_\alpha$ radiation, λ = 0.71070 Å, μ = 0.959 mm^{-1}, T = 180K. 26194 data (5271 unique, R_{int} = 0.0576, θ < 30.44°). Structure solved by direct methods and refined by full-matrix least-squares on F^2 values of all data. $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.1772, conventional R = 0. 0674 for F values of 5027 reflections with $F_o^2 > 2\sigma(F_o^2)$, GoF = 1.200 for 363 parameters. Residual electron density extrema 0.928 and –0.483 eÅ^{-3}. Crystal data for $C_{42}H_{52}Cu_2Li_2N_2O_4P_2$ **2**: M = 851.76, trigonal, space group $P3$, $a = b$ = 18.3517(3), c = 14.0350(4) Å, V = 4093.50(15) Å^3, Z = 3, ρ_{calcd}= 1.037 g cm^{-3}; Mo-K$_\alpha$ radiation, λ = 0.71073 Å, μ = 0.870 mm^{-1}, T = 180K. 17038 data (8002 unique, R_{int} = 0.0318, θ < 26.34°). Structure solved by direct methods and refined by full-matrix least-squares on F^2 values of all data. $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.1984, conventional R = 0. 0690 for F values of 5957 reflections with $F_o^2 > 2\sigma(F_o^2)$, GoF = 1.066 for 463 parameters. Residual electron density extrema 0.805 and –0.414 eÅ^{-3}. Crystal data for (Cy$_2$P)$_2$CuLi·2thf **3**: $C_{64}H_{120}$ Cu$_2$Li$_2$O$_4$P$_4$, M = 1218.44, triclinic, space group P-1, a = 11.03790(10), b = 16.0222(2), c = 20.8778(3) Å, α = 77.1870(10), β = 82.6640(10), γ = 75.7050(10)°, V = 3478.45(7) Å^3, Z = 2, ρ_{calcd}= 1.163 g cm^{-3}; Mo-K$_\alpha$ radiation, λ = 0.71073 Å, μ = 0.744 mm^{-1}, T = 180K. 53328 data (16555 unique, R_{int} = 0.0627, θ < 27.87°). Structure solved by direct methods and refined by full-matrix least-squares on F^2 values of all data. $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.1126, conventional R = 0. 0526 for F values of 10332 reflections with $F_o^2 > 2\sigma(F_o^2)$, GoF = 1.009 for 685 parameters. Residual electron density extrema 0.438 and –0.356 eÅ^{-3}.

Results and discussion

[(Ph$_2$P)$_6$Cu$_4$][Li·4thf]$_2$ 1

Initial attempts to fabricate lithium phosphidocuprates focused on the *in situ* generation of a lithium bis(organyl)phosphide *via* the 1:1 treatment of R$_2$PH with Bu^{n}Li, followed by the introduction of a Cu(I) salt (Scheme 2). Accordingly, for R = Ph, Ph$_2$PLi was generated in hydrocarbon solvent. The combination of this with 0.5 eq. CuCN was intended to yield a simple lithium bis(phosphido)cuprate of either Gilman- or Lipshutz-type formulation – (Ph$_2$P)$_2$CuLi·n(LiCN) (n = 0, 1). In the event, concentration of the reaction mixture followed by treatment with thf yielded a single isolable product in low yield. This was analyzed by single crystal X-ray diffraction and found to be [(Ph$_2$P)$_6$Cu$_4$][Li·4thf]$_2$ **1** (Figure 1 and Scheme 2, see also electronic supplementary information) Whereas this synthesis proved problematic to reproduce, recent work on the synthesis of (tmp)$_2$CuLi·LiX (X = CN, I)[18,19b] has established the abilty of multiple Cu(I) salts to act as precursor to Lipshutz-type cuprates. Modification of the reaction of Ph$_2$PLi with CuX was therefore attempted in order to replicate the synthesis of **1**. Gratifyingly, for X = I a single crystalline product was reproducibly obtained. Verification of the crystallographic cell parameters established the identity of this as **1**.

8 Ph$_2$PLi + 4 CuX

↓ i, ii

[(Ph$_2$P)$_6$Cu$_4$][Li·4thf]$_2$ + 4 LiX + 2 Ph$_2$PLi
1
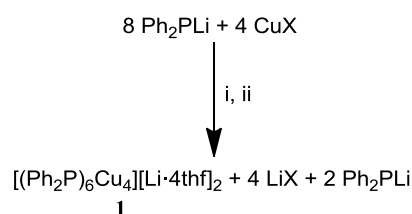
Scheme 2: i) tol., –78°C → rt; ii) thf (X = CN) or i) tol./thf, –78°C → rt; ii) add thf (X = I)

^{31}P NMR spectroscopy on redissolved crystals of **1** reveals a dominant singlet attributable to this species at δ –22.1 ppm, though very limited solution decomposition is suggested by the observation of a minor doublet (δ –32.6 ppm) owing to trace Ph$_2$PH (a view reinforced by ^{1}H NMR spectrocscopy). The crystal structure of **1** reveals a remarkable ion separate structure. Two tetra(thf)-solvated lithium ions balance the charge on [(Ph$_2$P)$_6$Cu$_4$]$^{2-}$. Copper clusters based on dianionic adamantane-type structures and incorporating a variety of inorganic ligands of groups 16[27] and 17[28] are well documented. However, analogous inorganic, adamantane-

type dianions with phosphorus donor ligands are less common. Recently, the mixed ligand system [Cl$_4$Phos$_2$Cu$_4$]$^{2-}$ (Phos = 1-phenyl-2,5-bis(2-pyridyl)phosphole) was reported to incorporate a distorted adamantyl core.[29] Closer to the structure of **1**, [(Ph$_2$P)$_{10}$Cd$_4$]$^{2-}$ has been characterized[30] and, in comparing the two inorganic dianions, it is noteworthy that the previously reported somewhat variable geometry at Cd ((μ-P)–Cd–(μ-P) 99.11(8)-109.43(9)°) is not replicated by Cu in the present system ((μ-P)–Cu–(μ-P) 117.32(9)-118.80(9)°). In **1**, both metal centres are near trigonal planar, with the angles at Cu1 and Cu2 summing to 355.77 and 354.86°, respectively. Moreover, the previously noted Cd–P–Cd angles (115.97(9)-121.62(9)°) prove to be significantly more massive than their Cu–P–Cu analogues in **1** (84.85(8) and 85.80(8)° at P1 and P2, respectively).
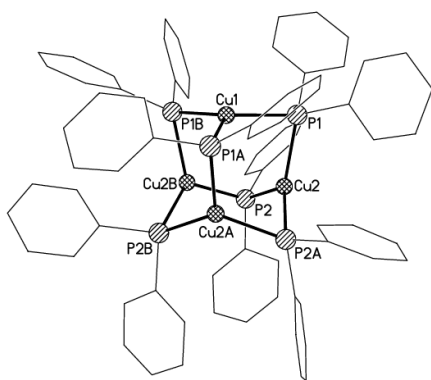

Fig. 1: Molecular structure of the dianionic component of **1**; thf-solvated Li$^+$ counterions and hydrogen atoms omitted for clarity. Selected bond lengths and angles (Å and °): P1–Cu1 2.289(2), P1–Cu2 2.289(2), P2–Cu2 2.280(2), P2A–Cu2 2.290(2), mean P–Cu–P 118.77, mean Cu–P–Cu 85.33.

Ph$_2$PCu(CN)Li·2thf 2

Whereas **1** was fabricated using Ph$_2$PLi with either CuI in a thf/toluene mixture or CuCN in toluene followed by replacement with thf, reaction of Ph$_2$PLi with CuCN in thf affords a single crystalline material that X-ray diffraction identifies as being Ph$_2$PCu(CN)Li·2thf **2** (Scheme 3). {^{1}H}^{31}P NMR spectroscopy on crystalline material redissolved in d_6-benzene reveals a major signal attributable to Ph$_2$PCu(CN)Li at δ −14.9 ppm, with minor signals also seen at δ −21.6 and −28.1. The observation of a signal at δ −38.3 ppm compares with that of a singlet at δ −39.9 ppm in a reference sample of Ph$_2$PH, and splitting of the highfield signal upon the removal of ^{1}H decoupling indicates that it is attributable to Ph$_2$PH, pointing to the solvent sensitivity of **2**. ^{1}H NMR spectroscopy reveals, however, that phosphine substrate has only reformed in trace amounts. Variable temperature ^{31}P NMR spectroscopic studies in d_8-toluene revealed only the two dominant signals noted above, with the low-field signal migrating from δ −13.3 ppm at 313K to δ −14.3 ppm at 253K but otherwise remaining essentially unchanged.

Whilst being empirically straightforward, X-ray diffraction

$$2\ \text{Ph}_2\text{PLi} + \text{CuCN} \xrightarrow{\text{thf}} \text{Ph}_2\text{PCu(CN)Li·2thf} + \text{Ph}_2\text{PLi}$$
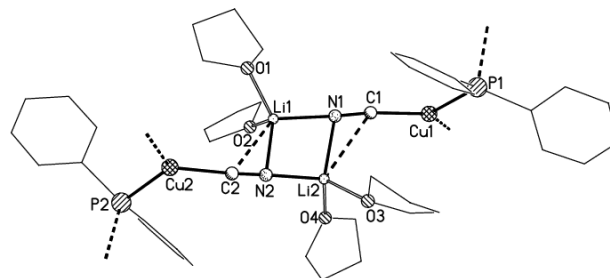
2
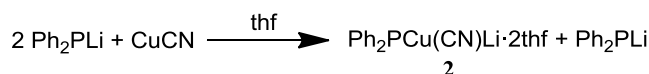
Scheme 3

Fig. 2: Structure of the dimeric building block that constitutes the linker unit in **2**; hydrogen atoms omitted for clarity. Selected bond lengths and angles (Å and °): N1–Li1 2.00(2), N2–Li2 1.96(2), N1–Li2 2.17(3), C1···Li2 2.74(3), N2–Li1 2.17(3), C2···Li1 2.69(3), C1–N1 1.157(11), C2–N2 1.131(10), Cu1–C1 1.919(9), Cu2–C2 1.945(9), Cu1–P1 2.260(2).
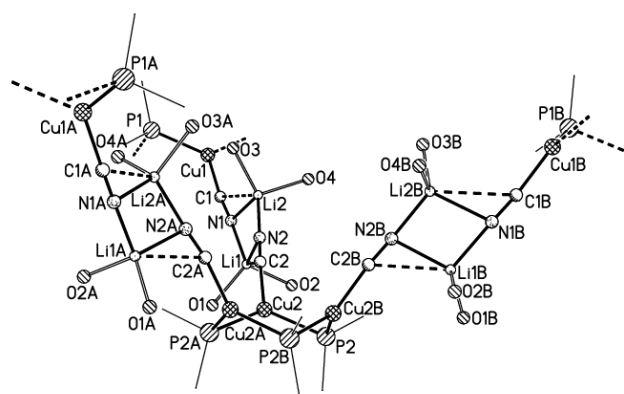

Fig. 3: Structure of the trigonal symmetry (PCu)$_6$ node (composed of Cu2, P2 and symmetry equivalents) in the extended network formed by **2** in the solid state; hydrogen and carbon atoms (except for CN and C-*ipso*) omitted for clarity. Selected bond lengths and angles (Å and °): P2–Cu2 2.264(2), P2A–Cu2 2.256(2), P2–Cu2–P2A 119.74(10), P2–Cu2–C2 119.4(2), P2A–Cu2–C2 119.8(2), Cu2–P2–Cu2B 95.40(8), Cu2–C2–N2 172.0(9), C2–N2–Li1 106.0(10), C2–N2–Li2 177.0(13), Li1–N1–Li2 75.2(11), Li1–N2–Li2 76.6(11).

reveals that the agglomeration of **2** in the solid state results in the formation of a highly unusual supramolecular array in which the 6-membered (PCu)$_3$ rings at the cores of [(Ph$_2$P)$_3$(CuCN)$_3$]$^{3-}$ anions act as trigonal-symmetry nodes. These are linked by 4-membered (NLi)$_2$ metallocycles which form from interaction of each cyanide ligand with a solvated alkali metal ion. The linker can therefore be viewed as being constituted by the dimerization of two crystallographically independent monomers of the cuprate Ph$_2$PCu(CN)Li·2thf (Figure 2), with a 4-membered (NLi)$_2$ ring forming based upon relatively long and short N–Li interactions (mean 2.17 and 1.98 Å, respectively). Consistent with recent structural observations of the dimer of Lipshutz-type cuprate (tmp)$_2$CuLi·LiCN,[18] the cyano groups in **2** are arranged approximately *trans* to the shorter of the N–Li bonds (mean C–N–Li 174.2°). The extended N–Li interactions can be viewed as being based on π-stabilization of the second alkali metal centre by the cyano group, as evidenced by the

concomitantly short distances between cyano carbon centres and alkali metal (mean C⋯Li 2.72 Å). The coordination sphere of each alkali metal centre is completed by bis(thf) solvation.

The cyano groups that constitute the core of the dimer are σ-bonded to Cu (mean C–Cu 1.932 Å) in near linear fashion (mean N–C–Cu 172.7°). While each Cu centre interacts formally with one diphenylphosphido unit (e.g. P1–Cu1 2.260(2) Å), three such PCu moieties are revealed crystallographically as interacting (e.g. P1A–Cu1 2.265(2) Å) to give a cyclohexane-type (PCu)$_3$ node (*viz.* (PCu)$_3$ ring formation in **1**) with threefold symmetry in the solid state. The three interactions between Cu centres and cyano C-centres associated with each node gives a basket motif (one such trigonal node is seen at the foot of Figure 3).

$$2\ Cy_2PLi + CuCN \xrightarrow{\text{i, ii}} (Cy_2P)_2CuLi \cdot 2thf + LiCN$$
3
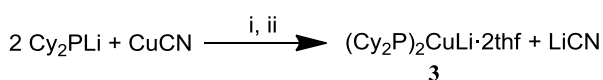
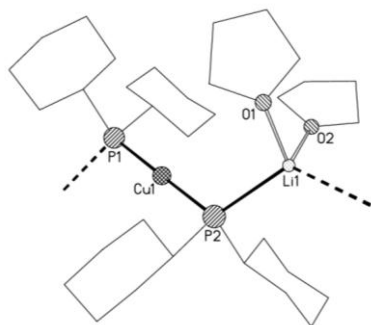Scheme 4: i) thf, –78°C → rt; ii) thf/tol.

Fig. 4: Structure of the monomeric component of Gilman-type lithiocuprate **3**. Selected bond lengths and angles (Å and °): P1–Cu1 2.2308(7), P2–Cu1 2.2327(7), P2–Li1 2.591(4), P3–Li1 2.581(4), P1–Cu1–P2 176.11(3), Cu1–P2–Li1 110.53(10).

(Cy$_2$P)$_2$CuLi·2thf 3

Based on our recent experience of the solvent dependent synthesis and isolation of Lipshutz- and Gilman-type lithiocuprates that incorporate the R(tmp)CuLi moiety (R = tmp, Me, Ph), coupled with DFT analysis of the tendency of excess Lewis base to favour the abstraction of LiCN from a Lipshutz-type formulation,[14] further experiments continued to focus on the deployment of bulk etherate solvent. Moving from Ph$_2$PH to Cy$_2$PH, treatment in thf solution with Bu^{n}Li led to the successful formation of the lithium bis(cyclohexyl)phosphide. The combination of this with a thf solution of CuCN (0.5 eq.), followed by the introduction of toluene to aid recrystallization, led to the reproducible isolation of pale yellow crystals (Scheme 4). ^{1}H NMR spectroscopy on this crystalline material redissolved in d_6-benzene revealed the presence of cyclohexyl groups and thf molecules in a 2:1 ratio as well as trace reformation of phosphine substrate. {^{1}H}^{31}P NMR spectroscopy pointed to the existence of one dominant, broad ^{31}P environment for **3** in solution at δ –14.2 ppm alongside very minor signals at δ –16.4 and –19.7 ppm. The observation of a weak signal at δ –26.6 ppm compares with a singlet at δ –27.4 ppm in a Cy$_2$PH

reference. Splitting of the highfield signal in the ^{31}P NMR spectrum indicated the reformation of starting material, though, as with **2**, ^{1}H NMR spectroscopy suggested only trace levels of reformed phosphine. Variable temperature NMR spectroscopic studies in d_8-toluene revealed only the two major ^{31}P signals discussed above, with the low-field signal migrating from δ –12.1 ppm at 333K to δ –15.8 ppm at 253K but otherwise remaining essentially unchanged. The issue of whether **3** is Lipshutz- or Gilman-type is not clearly elucidated by NMR analysis. Both structure types would be expected to yield multiple phosphide environments, suggesting dynamic solution behaviour. The amount of thf noted in the ^{1}H NMR spectrum of **3** (one thf molecule per phosphide ligand) is inconsistent with the formulations recently reported for known comparable Lipshutz-type bis(amido)cuprates (one thf molecule per two amide ligands).[18,19b] By analogy with MeCu(μ-tmp)Li·tmeda[14] and (MesNH)Cu(μ-NHPh)Li·dme[15] the monomeric Gilman-type (Cy$_2$P)$_2$CuLi·2thf might be proposed. Meanwhile, higher Gilman-type aggregates might also be possible, including a centrosymmetric dimer that would be analogous to the recently characterized cyclic dimer of (tmp)$_2$CuLi.[19b] In fact, crystallography establishes the formation of a bis(thf)-solvated Gilman-type lithium bis(bis(cyclohexyl)phosphido)-cuprate (Scheme 4).

X-ray diffraction reveals a polymeric structure in the solid-state, based on the aggregation of two crystallographically independent monomers (of which one representative monomer will be discussed in detail). In contrast to the ^{31}P NMR spectroscopic observation of just one phosphorus environment in **3**, each monomeric unit reveals two chemically different phosphorus centres (P1, P2 in Fig. 4). However, the crystal structure also demonstrates that, within standard deviations, both bonds between any given Li centre (or Cu centre) and its two adjacent P centres are equivalent, arguing against the possibility of inequivalent phosphorus environments in aggregated structures. As expected for a Gilman-type cuprate, Cu1 is, at 176.11(3)°, near linear. In contrast to recent work with bis(amido)cuprates, the relatively soft phosphide ligands do not retain the *in situ* generated LiCN moiety (Scheme 4). Instead, this is abstracted by solvent[14] and the resulting crystals demonstrate a Gilman-type formulation. This is something seen only in the heteroleptic chemistry of lithium amidocuprates in which one of the Cu-bonded ligands was unfunctionalized.[14] The bis(phosphide) formulation of **3** explains its ability to polymerize in the solid state. While Gilman-type homoleptic bis(organyl)-[9,10] and heteroleptic organyl(amido)cuprates[11] have been experimentally studied, theory has suggested a preference for head-to-tail dimerization in the heterocuprate case.[31] This has been experimentally confirmed in the dimer of MesCu[N(CH$_2$Ph)$_2$]Li,[13] though the presence of Lewis base has been shown to result in monomer formation.[12,14] In contrast to the study of homo- and heteroleptic cuprates bearing organyl and/or amido ligands, that of phosphidocuprate chemistry is at a significantly less advanced stage, with the structure of (Bu$^t_2$P)$_2$CuLi·2thf representing the only reported structure analogous to **3**.[32] However, the synthetic methodology used to achieve the bis(*tert*-butyl) complex is at variance with that employed here. Hence,

whereas it was formerly reported that Bu^t_2PLi could only be rendered active towards Cu(I) by the addition of $Bu^t_2PSiMe_3$, which was found to undergo efficient desilylation, the same is not true in the present case. Instead, in extending the recent synthesis of lithium amidocuprates the present work shows that the 1:2 treatment of CuCN with R_2PLi offers a potentially general route to lithium phosphidocuprates.

Conclusions

In summary, preliminary steps have been taken in the systematic syntheses of lithium phosphidocuprate substrates for DoC. Reaction of *in situ* generated Ph_2PLi with 0.5 eq. of either CuCN or CuI in the presence of toluene results in incomplete conversion of the lithium phosphide, reproducibly giving the unusual ion separate $[(Ph_2P)_6Cu_4][Li·4thf]_2$ **1**. The dianionic component of **1** takes the form of an adamantyl P_6Cu_4 network. In contrast, the reaction of Ph_2PLi with CuCN in thf, targeting Gilman-type $(Ph_2P)_2CuLi$ or its Lipshutz-type LiCN adduct, results in a different reaction pathway, affording $Ph_2PCu(CN)Li·2thf$ **2** as the only isolable product. The agglomeration of **2** yields a novel network based on the creation of cyclohexyl-type $[(Ph_2P)_3(CuCN)_3]^{3-}$ nodes. Each exocyclic CN ligand interacts with a bis(thf) solvated alkali metal cation to create the linkers that hold the resulting puckered 2D sheets together. Lastly, the treatment of Cy_2PLi with 0.5 eq. CuCN in thf establishes a new route to Gilman-type lithium phosphidocuprates. In contrast to the structure-types previously reported for lithium amidocuprates, the structure of $(Cy_2P)_2CuLi$ reveals a polymeric motif, with phosphide ligands acting not only to bridge between metals within the monomeric unit, but also to incur polymer formation to the exclusion of LiCN and Lipshutz-type cuprate formation.

Further work will seek to investigate the generality with which Gilman-type analogues of **3** can be prepared using a variety of phosphine substrates. The propensity for the inclusion of LiCN in both the solid- and solution states will also be investigated – as will the possibility of interaction of lithium phosphide with $Ph_2PCu(CN)Li$ (*cf.* **2**) in solution. This last field suggests the possibility of i) spectroscopically probing the reaction mixture that yields **2** for evidence of Lipshutz-type species in solution but also, ii) combining pre-isolated **2** with R_2PLi (R ≠ Ph) as a potentially convenient route to heteroleptic bis(phosphido)cuprates. Thereafter, selected DoC reactions will be attempted using **2** + R_2PLi and **3** (+ LiCN) and analogues thereof.

Notes and references

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Table of contents entry

2 R₂PLi + CuCN

O   -LiCN

Gilman-type bis(phosphido)cuprate