# Copper Diamidocarbene Complexes: Characterization of Monomeric to Tetrameric Species

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Ⓢ *Supporting Information*

ABSTRACT: Treatment of CuCl with 1 equiv of the in situ prepared *N*-mesityl-substituted diamidocarbene 6-MesDAC produced a mixture of the dimeric and trimeric copper complexes [(6-MesDAC)CuCl]$_2$ (**1**) and [(6-Mes-DAC)$_2$(CuCl)$_3$] (**2**). Combining CuCl with isolated, free 6-MesDAC in 1:1 and 3:2 ratios gave just **1** and **2**, respectively, while increasing the ratio to >5:1 allowed the isolation of small amounts of the tetrameric copper complex [(6-MesDAC)$_2$(CuCl)$_4$] (**3**). Efforts to bring about metathesis reactions of **1** with MO^{t}Bu (M = Li, Na, K) proved successful only for M = Li to afford the spectroscopically characterized ate product [(6-MesDAC)CuCl·LiO^{t}Bu·2THF] (**5**). Attempts to crystallize this species instead gave a 1:1 mixture of **1** and the monomer [(6-MesDAC)CuCl] (**6**). The X-ray structures of **1**−**3** and **1** + **6**, along with the cation [Cu(6-MesDAC)$_2$]$^+$ (**4**), have been determined.
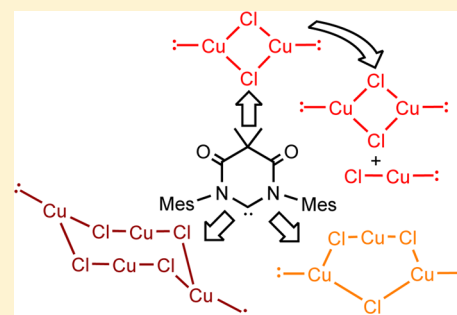
INTRODUCTION

A series of recent reviews have provided testimony to the remarkable advances made in the N-heterocyclic carbene (NHC) chemistry of the coinage metals over the past decade or so.[1−3] Interest in copper and, more recently, gold[4] NHC complexes has arisen predominantly out of their ability to catalyze a wide range of transformations which, in the case of copper, include hydrosilylation,[5] carbonylation/carboxylation,[6] conjugate additions,[7] and azide−alkyne click reactions.[8]

Due to the overwhelming attention that has been paid to the use of strongly σ donating, Arduengo-type imidazol-2-ylidene and imidazolidin-2-ylidene ligands, there have been very few reports dealing with other types of carbene ligands, particularly those with enhanced π-acceptor abilities. Amidocarbenes (e.g., the diamidocarbene (or DAC) **I** in Chart 1) constitute one such

Chart 1
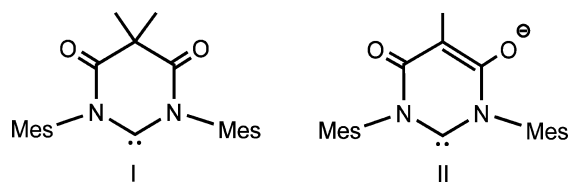
class of ligand, which in comparison to their diamino counterparts display a combination of reduced σ-donor capabilities, as well as greater π-acceptor properties. As a consequence, amidocarbenes display an intriguing mixture of nucleophilic and electrophilic character in terms of their ability to both coordinate to transition-metal centers and react with small molecules.[9,10]

In terms of synthetic usage, ligands such as **I** (abbreviated onward as 6-MesDAC) based on a six-membered ring tend to be

far more stable, and therefore easier to handle, than their five-membered-ring counterparts.[11] Given our recent interest in the chemistry of six-/seven-membered-ring carbenes in general,[12] and the fact that only a single amidocarbene Cu complex (derived from the anionic *N*-mesityl-substituted carbene **II**; Chart 1) has been described in the literature,[13] we have started to probe the coordination chemistry of **I** with simple Cu(I) precursors in an effort to prepare new Cu−DAC complexes with potential catalytic applications. In this paper, we describe our first studies of 6-MesDAC copper halide complexes and illustrate issues associated with the use of in situ methods in (i) providing control and selectivity for the synthesis of desired 6-MesDAC copper complexes and (ii) bringing about the conversion of (6-MesDAC)Cu−Cl precursors to (6-MesDAC)Cu−O^{t}Bu species, which are more important for catalysis.[14]

EXPERIMENTAL SECTION

All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques using dried and degassed solvents, unless otherwise stated. NMR spectra were recorded at 298 K (unless otherwise stated) on Bruker Avance 500 and 400 MHz NMR spectrometers and referenced to residual solvent signals for ^{1}H and ^{13}C spectra of C$_6$D$_6$ (δ 7.16, 128.0), THF-d_8 (δ 3.58), and CD$_2$Cl$_2$ (δ 5.32, 54.0). ^{7}Li spectra were referenced to LiCl (9.7 mol kg^{-1} in D$_2$O). ^{1}H DOSY experiments for **1** and **2** were carried out using a double-stimulated echo pulse sequence, using values of Δ = 75 ms and δ = 1.5 ms. DOSY experiments for **5** were carried out using stimulated echo sequences at 294 K (with the probe heater turned off to reduce convection effects), with Δ/δ = 50/3 ms for ^{1}H and 10/5 ms for ^{7}Li. For all DOSY experiments, the gradient strengths (previously calibrated using a sample of H$_2$O) were incremented in eight equal steps from 1.74

Table 1. Data Collection and Refinement Details for the Crystal Structures of 1−4 and 1 + 6

	1	2	3	4	1 + 6
chem formula	$C_{110}H_{128}Cl_4Cu_4N_8O_8$	$C_{24}H_{28}Cl_{1.50}Cu_{1.50}N_2O_2$	$C_{26}H_{32}Cl_2Cu_2N_2O_{2.50}$	$C_{50.55}H_{61.10}Cl_{5.10}CuF_6N_4O_4P$	$C_{76}H_{94}Cl_3Cu_3N_6O_7$
formula mass/amu	2086.16	524.97	610.52	1178.04	1500.54
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	28.5280(4)	30.4360(5)	8.1540(2)	12.2430(1)	13.3220(2)
b/Å	11.9880(2)	9.2330(2)	12.4010(4)	19.7610(2)	17.0760(2)
c/Å	31.5040(6)	22.1180(6)	14.8940(5)	23.8460(3)	18.5540(3)
α/deg	90.00	90.00	68.995(1)	90.00	113.943(1)
β/deg	99.347(1)	127.270(1)	88.842(2)	104.570(1)	104.890(1)
γ/deg	90.00	90.00	84.932(2)	90.00	91.572(1)
U/Å^3	10631.1(3)	4946.24(19)	1400.37(7)	5583.63(10)	3686.36(9)
Z	4	8	2	4	2
no. of rflns measd	151053	34944	22154	77176	66809
no. of indep rflns	18724	5611	6413	12724	16762
R_{int}	0.1761	0.0485	0.0547	0.0515	0.0547
final $R1$ value ($I > 2\sigma(I)$)	0.0625	0.0310	0.0378	0.0446	0.0421
final $wR2(F^2)$ value ($I > 2\sigma(I)$)	0.1140	0.0758	0.1004	0.1058	0.0846
final $R1$ value (all data)	0.1587	0.0430	0.0500	0.0599	0.0761
final $wR2(F^2)$ value (all data)	0.1467	0.0828	0.1051	0.1133	0.0971
goodness of fit on F^2	1.028	1.028	1.054	1.069	1.025

to 33.14 G cm^{-1}, and diffusion coefficients were calculated using Bruker's T_1/T_2 software. IR spectra were recorded as KBr disks on a Nicolet Nexus spectrometer. Elemental analyses were performed at London Metropolitan University, London, U.K. (6-MesDAC)HCl and 6-MesDAC were prepared according to literature methods.[10]

[(6-MesDAC)CuCl]$_2$ (1). A suspension of isolated, free 6-MesDAC (1.160 g, 3.080 mmol) and CuCl (0.271 g, 2.741 mmol) in THF (40 mL) was stirred at room temperature for 30 min. All volatiles were removed from the red suspension under reduced pressure, and the sticky, red residue was dissolved in toluene (20 mL). Addition of hexane (30 mL) with vigorous stirring afforded a red precipitate of **1**, which was washed with hexane (2 × 30 mL) and isolated by filtration. Yield: 1.167 g (90%). Single crystals suitable for X-ray diffraction studies were grown from toluene/hexane. ^{1}H NMR (C_6D_6, 500 MHz): δ 6.81 (8H, s, $C_6Me_3H_2$), 2.22 (s, 12H, p-$MeC_6Me_2H_2$), 2.05 (s, 24H, o-$Me_2C_6MeH_2$), 1.34 (s, 12H, CMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz): δ 212.7 (s, NCN), 172.3 (s, CO), 139.2 (s, p-$C_6Me_3H_2$), 136.4 (s, i-$C_6Me_3H_2$), 135.1 (s, o-$C_6Me_3H_2$), 130.4 (s, m-$C_6Me_3H_2$), 51.5 (s, CMe_2), 24.7 (s, CMe_2), 21.7 (s, p-$MeC_6Me_2H_2$), 18.4 (s, o-$Me_2C_6MeH_2$). IR (cm^{-1}): 1740 (s, ν_{CO}), 1717 (s, ν_{CO}). Anal. Found (calcd) for $C_{48}H_{56}N_4O_4Cl_2Cu_2$ (950.95): C, 60.73 (60.62); H, 5.90 (5.94); N, 5.79 (5.89).

[(6-MesDAC)$_2$(CuCl)$_3$] (2). A mixture of isolated, free 6-MesDAC (0.193 g, 0.512 mmol) and CuCl (0.082 g, 0.823 mmol) was stirred in THF (15 mL) at room temperature for 22 h. Removal of the volatiles gave a sticky, orange residue; redissolution in toluene (10 mL) and addition of hexane (30 mL) with vigorous stirring gave an orange powder of **2**, which was isolated by filtration and washed with hexane (5 mL). Yield: 0.226 g (84%). Single crystals of **2** suitable for X-ray diffraction were grown from toluene/hexane. ^{1}H NMR (C_6D_6, 500 MHz): δ 6.77 (s, 8H, $C_6Me_3H_2$), 2.15 (s, 12H, p-$MeC_6Me_2H_2$), 2.11 (s, 24H, o-$Me_2C_6MeH_2$), 1.38 (s, 12H, CMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz): δ 214.9 (s, NCN), 172.2 (s, CO), 139.9 (s, p-$C_6Me_3H_2$), 136.4 (s, i-$C_6Me_3H_2$), 135.2 (s, o-$C_6Me_3H_2$), 130.6 (s, m-$C_6Me_3H_2$), 51.6 (s, CMe_2), 24.7 (s, CMe_2), 21.6 (s, p-$MeC_6Me_2H_2$), 18.5 (s, o-$Me_2C_6MeH_2$). IR (cm^{-1}): 1740 (s, ν_{CO}), 1717 (s, ν_{CO}). Anal. Found (calcd) for $C_{48}H_{56}N_4O_4Cl_3Cu_3$ (1049.95): C, 55.02 (54.91); H, 5.49 (5.38); N, 5.25 (5.33).

[(6-MesDAC)$_2$(CuCl)$_4$] (3). Addition of THF (25 mL) to a mixture of isolated, free 6-MesDAC (0.081 g, 0.215 mmol) and CuCl (0.435 g, 4.391 mmol) quickly generated a gray-green suspension in an orange solution. After the mixture was stirred at room temperature for 43 h, the precipitate was removed by filtration and washed with THF (2 × 20 mL) and the THF washings were combined with the initial orange filtrate. When the filtrate was pumped down to dryness, an orange powder was produced. This was purified by dissolution in toluene (10 mL) and reprecipitation with hexane (30 mL). Layering a toluene solution of the powder with hexane gave a mixture of orange crystals of **2** (yield: 0.031 g, 27%) and beige crystals of **3** (yield: 0.004 g, 3%). In solution, **3** rapidly deposited a precipitate believed to be CuCl; this precluded any NMR characterization. IR (cm^{-1}): 1743 (s, ν_{CO}), 1719 (s, ν_{CO}). Anal. Found (calcd) for $C_{48}H_{56}N_4O_4Cl_4Cu_4$ (1148.95): C, 49.96 (50.18); H, 4.83 (4.91); N, 4.92 (4.88).

[Cu(6-MesDAC)$_2$]PF$_6$ (4). A mixture of isolated, free 6-MesDAC (1.153 g, 3.062 mmol) and [Cu(MeCN)$_4$]PF$_6$ (0.559 g, 1.499 mmol) was dissolved in CH_2Cl_2 (15 mL) and stirred at room temperature for 15 min. Removal of the volatiles gave a yellow powder, which was dried in vacuo and then washed with THF (2 × 20 mL) to afford a pale green powder. This was purified by dissolution in CH_2Cl_2 (10 mL) and reprecipitation with hexane (30 mL). Yield: 1.192 g (97%). X-ray-quality crystals were grown from CH_2Cl_2/hexane. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.10 (s, 8H, $C_6Me_3H_2$), 2.43 (s, 12H, p-$MeC_6Me_2H_2$), 1.71 (s, 24H, o-$Me_2C_6MeH_2$), 1.61 (s, 12H, CMe_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): δ 213.0 (s, NCN), 171.0 (s, CO), 142.0 (s, p-$C_6Me_3H_2$), 135.3 (s, o-$C_6Me_3H_2$), 134.7 (s, i-$C_6Me_3H_2$), 131.0 (s, m-$C_6Me_3H_2$), 52.5 (s, CMe_2), 25.0 (CMe_2), 21.5 (s, p-$MeC_6Me_2H_2$), 18.8 (s, o-$Me_2C_6MeH_2$). IR (cm^{-1}): 1768 (s, ν_{CO}), 1738 (s, ν_{CO}). Anal. Found (calcd) for $C_{48}H_{56}N_4O_4CuPF_6$ (961.47): C, 59.73 (59.96); H, 5.98 (5.87); N, 5.76 (5.83).

[(6-MesDAC)CuCl·LiO^{t}Bu·2THF] (5). A crystalline sample of complex **1** (0.020 g, 0.021 mmol) was dissolved in THF-d_8 (0.5 mL) and added to LiO^{t}Bu (0.003 g, 0.041 mmol). The red solution immediately turned dark purple; ^{1}H NMR spectroscopy revealed that the starting material was consumed within 5 min. ^{1}H NMR (THF-d_8, 400 MHz): δ 6.91 (s, 4H, $C_6Me_3H_2$), 2.27 (s, 6H, p-$MeC_6Me_2H_2$), 2.26 (s, 12H, o-$Me_2C_6MeH_2$), 1.67 (s, 6H, CMe_2), 0.66 (s, 8H, $OCMe_3$). ^{7}Li NMR (THF-d_8, 155 MHz): δ −0.74 (s). ^{1}H NMR (THF-d_8, 400 MHz, 200 K): δ 6.95 (s, 4H, $C_6Me_3H_2$), 2.35 (s, 6H, $MeC_6Me_2H_2$), 2.28 (s, 6H, $MeC_6Me_2H_2$), 2.20 (s, 6H, $MeC_6Me_2H_2$), 1.71 (s, 3H, CMe_2), 1.66 (s, 3H, CMe_2), 0.64 (s, 9H, $OCMe_3$).

Cocrystallization of [(6-MesDAC)CuCl]$_2$ (1) and [(6-MesDAC)-CuCl] (6). A crystalline sample of **1** (0.050 g, 0.053 mmol) in Et$_2$O (10 mL) was stirred at room temperature for 10 min, and the orange solution was then filtered. Slow evaporation at −30 °C gave red crystals,
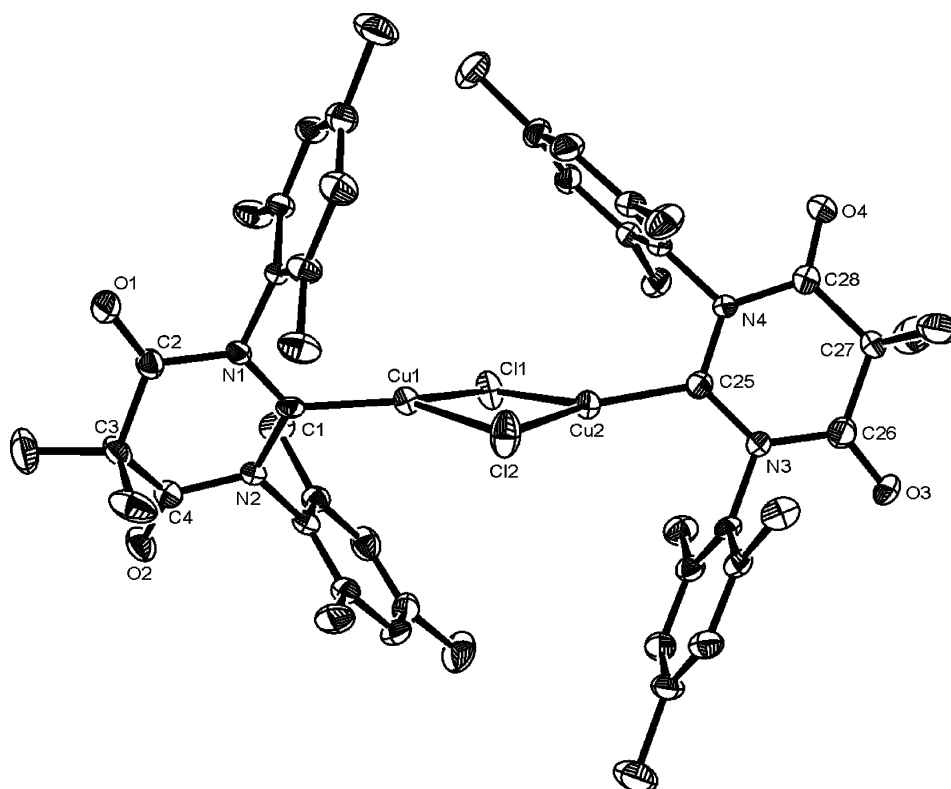
Figure 1. Molecular structure of one of the two molecules in the asymmetric unit of **1**. Ellipsoids are shown at the 30% level. Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−C(1) 1.871(5), Cu(2)−C(25) 1.867(5), Cu(1)−Cl(1) 2.2650(17), Cu(1)−Cl(2) 2.3001(1), Cu(2)−Cl(1) 2.2936(16), Cu(2)−Cl(2) 2.2548(17); Cl(1)−Cu(2)−Cl(2) 99.80(6), Cl(1)−Cu(1)−Cl(2) 99.80(6).
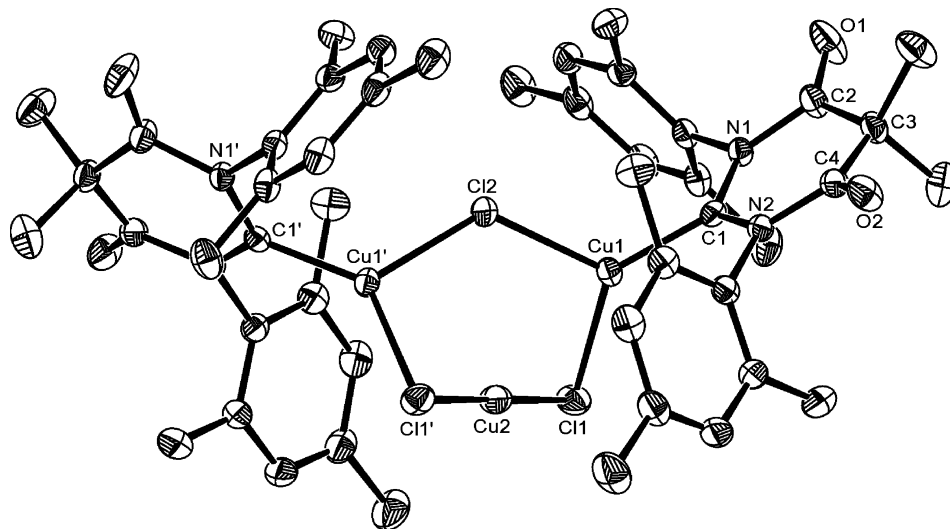
Figure 2. Molecular structure of **2**. Ellipsoids are shown at the 30% level. Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−C(1) 1.8860(18), Cu(1)−Cl(1) 2.2729(6), Cu(1)−Cl(2) 2.2948(4), Cu(2)−Cl(1) 2.1372(5); Cl(1)−Cu(1)−Cl(2) 99.80(6), Cl(1)−Cu(2)−Cl(1′) 179.75(3). Primed labeled atoms are related to those in the asymmetric unit by the $1 - x, y, {}^{3}/_{2} - z$ symmetry operation.

which were shown by X-ray diffraction to consist of a 1:1 mixture of **1** and the monomer [(6-MesDAC)CuCl] (**6**). Yield: 0.036 g (68%). ^{1}H NMR (C_6D_6, 500 MHz): δ 6.81 (s, 12H, $C_6Me_3H_2$), 2.22 (s, 18H, p-$MeC_6Me_2H_2$), 2.06 (s, 36H, o-$Me_2C_6MeH_2$), 1.35 (s, 18H, CMe_2). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz): δ 212.9 (NCN), 172.3 (CO), 139.3 (s, p-$C_6Me_3H_2$), 136.4 (s, i-$C_6Me_3H_2$), 135.2 (s, o-$C_6Me_3H_2$), 130.4 (s, m-$C_6Me_3H_2$), 51.5 (s, CMe_2), 24.7 (s, CMe_2), 21.7 (s, p-$MeC_6Me_2H_2$), 18.4 (s, o-$Me_2C_6MeH_2$). IR (cm^{-1}): 1739 (s, ν_{CO}), 1716 (s, ν_{CO}). Anal. Found (calcd) for $C_{72}H_{84}N_6O_6Cl_3Cu_3$ (1426.43): C, 60.50 (60.62); H, 6.03 (5.94); N, 5.64 (5.89).

Crystallography. Single crystals of compounds **1**−**4** and **1** + **6** were analyzed using a Nonius Kappa CCD diffractometer. Data were collected using Mo Kα radiation throughout. Details of the data collections, solutions, and refinements are given in Table 1. The structures were solved using SHELXS-97[15] and refined using full-matrix least squares in SHELXL-97.[15]

The asymmetric unit in **1** was seen to comprise two dimers and two molecules of toluene. Although the crystal was single, it displayed very poor diffracting power. Data were thus truncated to a Bragg angle of 25°. The higher than desirable R_{int} value reflects a rapid falloff in diffracted

Scheme 1

Conditions:
(i) 6-MesDAC (1 equiv)
(ii) 6-MesDAC (2/3 equiv)
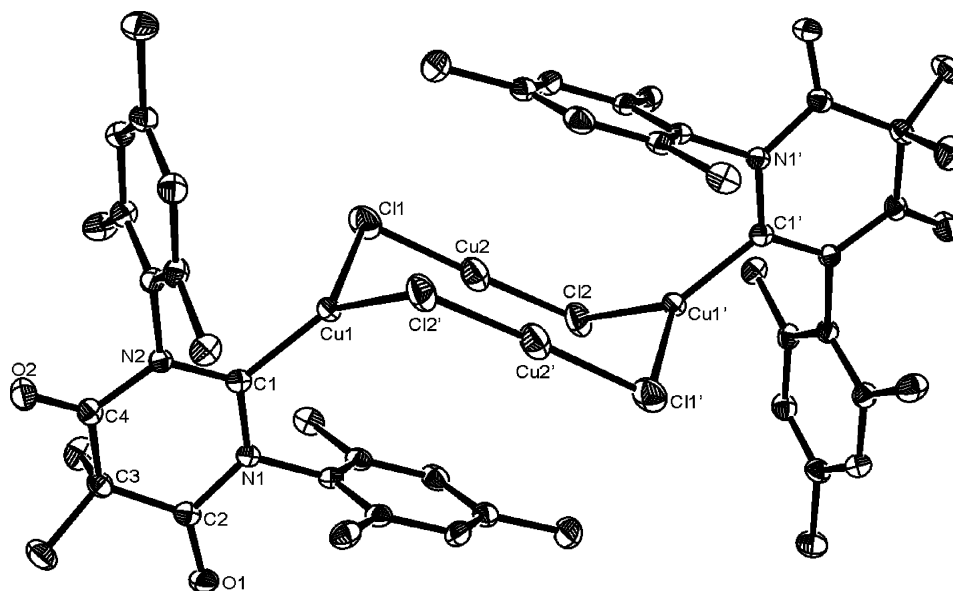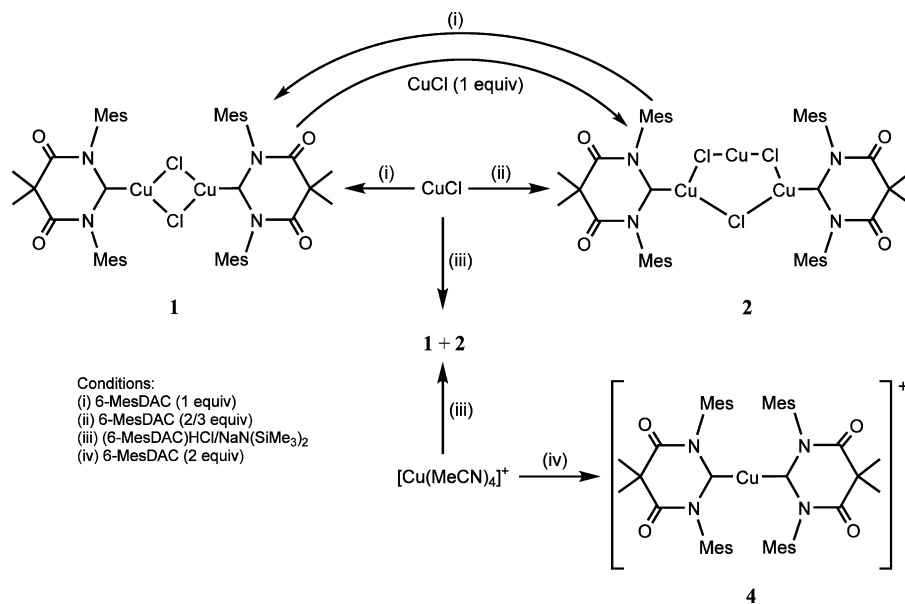(iii) (6-MesDAC)HCl/NaN(SiMe₃)₂
(iv) 6-MesDAC (2 equiv)

Figure 3. Molecular structure of **3**. Ellipsoids are shown at the 30% level. Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−C(1) 1.886(2), Cu(1)−Cl(1) 2.2735(7), Cu(2)−Cl(1) 2.1187(8), Cu(2)−Cl(2) 2.1145(8); Cl(1)−Cu(1)−Cl(2′) 107.15(3), Cl(1)−Cu(2)−Cl(2) 171.38(3). Primed labeled atoms are related to those in the asymmetric unit by the 1 − x, −y, 2 − z symmetry operation.

intensities above θ values of 20°. In **2**, the asymmetric unit consisted of half of a molecule in which atoms Cu(2) and Cl(2) are coincident with a crystallographic 2-fold rotation axis. In a similar fashion, half of a molecule was seen to constitute the asymmetric unit in **3**. In this case, however, proximity to a crystallographic inversion center serves to generate the remainder of the tetramer. There was also evidence for a small amount of solvent in the motif. This was highly disordered, but on the basis of the synthetic process, and employment of the Platon SQUEEZE algorithm, this has been included in the formula as one total THF moiety per unit cell.

The asymmetric unit of **4** was made up of one cation, one anion, and three dichloromethane solvent regions. With reference to the last regions, the molecule based on C(50) represents one full occupancy solvent entity. The fragments based on C(52)/C(52A) and C(49)/C(49A) each represent two localized disordered moieties with occupancy ratios of 20:45 and 70:20, respectively. C−Cl distance restraints and some ADP restraints were included in the disordered

regions to assist convergence. In the cocrystal of **1** and **6**, the asymmetric unit was seen to consist of one copper-containing monomer, one dimer, and one molecule of Et₂O.

Crystallographic data for compounds **1−4** and **1 + 6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 970405−970409. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (+44) 1223 336033, e-mail deposit@ccdc.cam.ac.uk).

■ RESULTS AND DISCUSSION

Formation of Dimeric and Trimeric 6-MesDAC Copper Chloride Complexes. Initial efforts to investigate the copper coordination chemistry of **I** involved the in situ generation of the carbene by treatment of (6-MesDAC)HCl with NaN(SiMe₃)₂ in THF, in the same reaction flask as 1 equiv of CuCl (the relevance
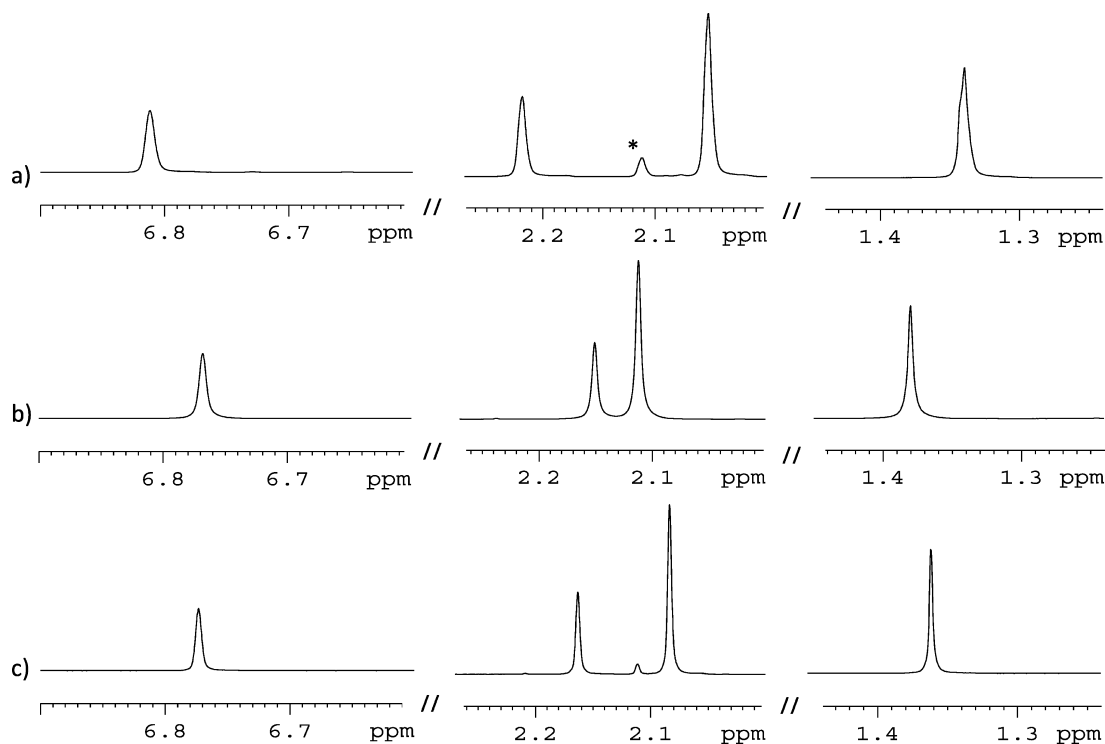
Figure 4. ^{1}H NMR spectra (500 MHz, C_6D_6, 298 K) of (a) **1**, (b) **2**, and (c) a 1:1 mixture of **1** and **2**. The asterisk denotes residual toluene from the crystalline samples.

Table 2. DOSY^a Data for Copper 6-MesDAC Complexes 1, 2, and 5

compd	D	r_H	$r_{X\text{-ray}}{}^d$
1^b		5.3	5.9
2^b		6.1	6.0
5^c	7.3 (^{1}H)		
	7.5 (^{7}Li)		

^{a}Units: D values, 10^{-10} m^2 s^{-1}; r_H values, Å. η(THF) = 0.47 × 10^{-3} kg s^{-1} m^{-1} at 294 K. η(toluene) = 0.55 × 10^{-3} kg s^{-1} m^{-1} at 298 K. ^{b}Conditions: 400 MHz, 2 mM, toluene-d_8. ^{c}Conditions: 400 MHz, 30 mM, THF-d_8. ^{d}See ref 22 for method of determination.

of the copper also being present is discussed later). Workup afforded a mixture of red and orange crystals which, upon separation and structural analysis by X-ray crystallography, were found to be the copper dimer and trimer [(6-MesDAC)CuCl]$_2$ (**1**) and [(6-MesDAC)$_2$(CuCl)$_3$] (**2**), respectively. A mixture of the two species was also formed upon reaction of in situ generated **1** with [Cu(MeCN)$_4$]PF$_6$ (N.B.: both species were again present in the same flask) in THF.

The structures are shown in Figures 1 and 2. The structure of the dimeric species **1** consisted of two molecules in the asymmetric unit. A slight deviation from planarity of the Cu$_2$Cl$_2$ molecular core was observed in both cases, with Cu(1)−Cl(1)−Cu(2)−Cl(2) torsion angles of 7.4 and 1.4°. The Cu−Cl bond lengths ranged from 2.2548(17) to 2.3001(10) Å; these values are similar to those found in the few other reported examples of dimeric (NHC)CuCl complexes.[16,17] The Cu−carbene distances (1.871(5), 1.867(5), 1.870(5), 1.866(5) Å) are at the short end of those found in diaminocarbene copper halide species in the literature,[13a,14,18] which presumably is a reflection of the DAC's ability to act as a π acceptor. There is no evidence for any stabilizing Cu···Cu interaction, given that the separation of the two copper centers (2.929 Å) is larger than the

sum of the van der Waals radii (2.80 Å). It is notable that the angles between the planes containing the DAC carbene carbon and nitrogens in each of the two molecules in the asymmetric unit are relatively close at 36 and 38°. In addition, the distances from the DAC nitrogen atoms to the mean planes containing their three adjacent carbons have a range of values, the maximum of which is 0.036 Å. These deviations are suggestive of distortions from idealized sp^2 hybridization in the case of some of the carbene nitrogen atoms.

The trimer **2** can be considered as arising from the insertion of a CuCl unit into one of the bridging Cu−Cl bonds of **1**. As shown in Figure 2, the structure comprises a planar Cu$_3$Cl core with bridging chloride ligands above and below the plane. The Cu−Cl distances from the two trigonal-planar DAC-bound Cu(1) atoms are identical with those in **1** (2.2729(6), 2.2948(4) Å) but significantly longer than those from the formally two-coordinate Cu(2) center (2.1372(5), 2.1373(5) Å). The long Cu(1)···Cu(2) distance of 2.8136(3) Å points to a lack of any significant metal−metal interactions.[19]

The structural relationship between **1** and **2** allowed us to rationalize separate routes for the preparation of the individual compounds. Thus, combining CuCl and a sample of isolated, free 6-MesDAC in a 1:1 ratio generated only **1**, which was isolated as a red, air-stable solid in 90% yield. Increasing the Cu:6-MesDAC ratio to 3:2 produced just **2**. Subsequent treatment of **1** with CuCl gave full conversion to **2**, while addition of free 6-MesDAC to **2** gave **1**.

A summary of the preparative chemistry of **1** and **2** (and **4**; vide infra) is provided in Scheme 1.

Structural Characterization of [(6-MesDAC)$_2$(CuCl)$_4$] (3). Perhaps unsurprisingly, a further increase in the ratio Cu:6-MesDAC to >5:1 afforded trimer **2** as the major product, although a small amount of the novel beige tetrameric copper complex [(6-MesDAC)$_2$(CuCl)$_4$] (**3**) was also isolated from the
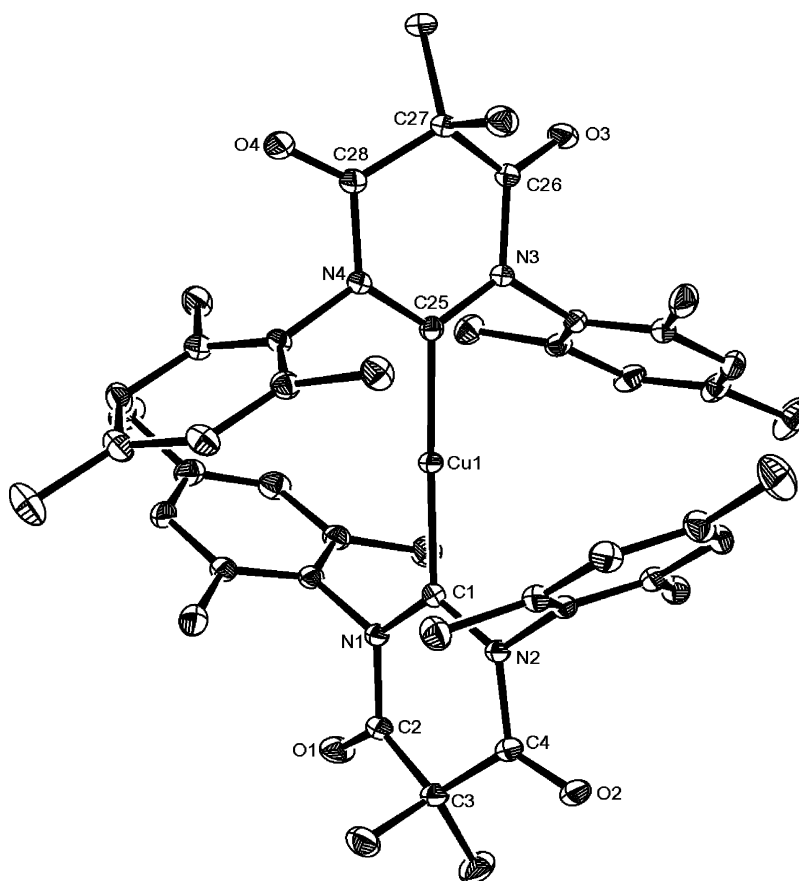
Figure 5. Molecular structure of the cation in **4**. Ellipsoids are shown at the 30% level. Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−C(1) 1.927(2), Cu(1)−C(25) 1.926(2); C(1)−Cu(1)−C(25) 178.39(9).

Scheme 2
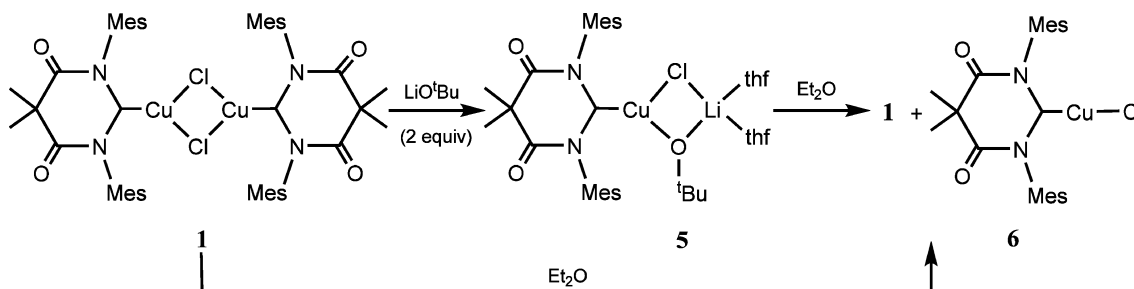
reaction. The X-ray crystal structure of **3** is shown in Figure 3 and reveals an unusual $(CuCl)_4$ motif in a chairlike conformation with terminal 6-MesDAC ligands.[20,21] The three-coordinate, carbene-bound Cu(1) atoms exhibit Cu−C and Cu−Cl distances comparable to those in **1** and **2**, while the two-coordinate, trans-linear Cu(2) centers (Cl(1)−Cu(2)−Cl(2) 171.38(3)°) display Cu−Cl bond lengths shortened further from those in **2** (Cu(2)−Cl(1) 2.1187(8) Å, Cu(2)−Cl(2) 2.1145(8) Å). Crystallographic symmetry necessarily means that the plane containing Cu(1), Cl(1), and Cl(2) and its symmetry-related counterpart within the molecule are parallel.

Efforts to characterize **3** by NMR spectroscopy were unsuccessful, due to the instability of the complex in solution. Dissolving **3** in C_6D_6 resulted in the rapid precipitation of a pale green-gray precipitate (presumed to be CuCl) at room temperature; the spectrum of the remaining solution showed a mixture of **1** and **2**.

Solution Characterization of 1 and 2. The ^1H NMR spectra of **1** and **2** in C_6D_6 are shown in parts a and b of Figure 4, respectively. Each displayed a single set of carbene resonances, but with chemical shifts that differed by ca. 0.07 ppm. A chemical shift difference was also seen in the corresponding $^{13}C\{^1H\}$ spectra with the carbenic signals appearing at δ 212.7 and 214.9, respectively.

As shown in Figure 4c, the spectrum of an equimolar mixture of the two compounds also revealed a single set of 6-MesDAC signals, but with chemical shifts intermediate between those of the individual components. This suggests that exchange may be taking place between **1** and **2** or that the dimer and trimer dissociate in solution to form species of different nuclearity. DOSY experiments afforded values of 5.3 and 6.1 Å for the hydrodynamic radii (r_H) of **1** and **2**, respectively (Table 2; see the Supporting Information for plots). The latter is in good agreement with the value of 6.0 Å calculated for the radius of **2**
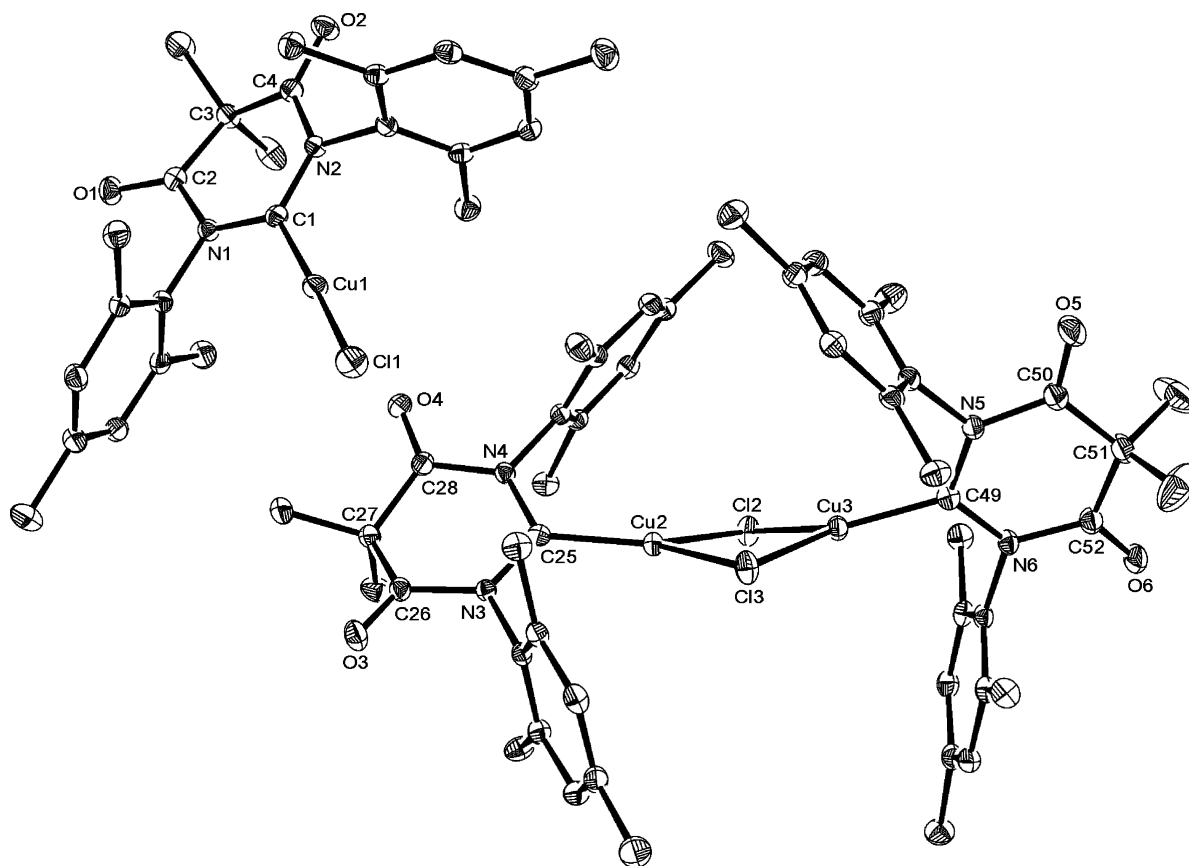
Figure 6. Molecular structure of a 1:1 mixture of **1** and [(6-MesDAC)CuCl] (**6**). Ellipsoids are shown at the 30% level. Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−C(1) 1.886(2), Cu(2)−C(25) 1.885(2), Cu(3)−C(49) 1.875(2), Cu(1)−Cl(1) 2.1150(7), Cu(2)−Cl(2) 2.3139(7), Cu(2)−Cl(3) 2.2974(7), Cu(3)−Cl(2) 2.2745(7), Cu(3)−Cl(3) 2.2906(7); C(1)−Cu(1)−Cl(1) 173.46(8), Cl(2)−Cu(2)−Cl(3) 95.79(2).

from the solid-state structure ($r_{X\text{-ray}}$),[22] suggesting that the trimer remains intact in solution. The value of 5.3 Å measured for **1** is midway between 5.9 Å (calculated from the structure of **1**) and 4.7 Å (calculated from the monomer **6**; see below), making it less clear as to how **1** behaves. It is worth noting that there was no change in the 1:1 spectrum shown in Figure 4c upon cooling to 180 K (toluene-d_8), implying that any fluxional process that is operating is still too rapid to freeze out even at this low temperature.

Isolation of [Cu(6-MesDAC)₂]PF₆ (4). Efforts to generate **1** and **2** through the addition of in situ generated 6-MesDAC to a THF solution of [Cu(MeCN)₄]PF₆ (N.B.: in a separate flask) produced only very small quantities of the products, yielding instead the cationic bis-carbene complex [Cu(6-MesDAC)₂]PF₆ (**4**) in 70% yield. Alternatively, **4** could be formed as the only copper-containing species when [Cu(MeCN)₄]PF₆ was treated with 2 equiv of isolated, free 6-MesDAC in CH₂Cl₂ (Scheme 1). The structure of **4** (Figure 5) revealed Cu−C distances of 1.926(2) and 1.927(2) Å, identical with that in [Cu(6-Mes)₂]⁺ (1.934(2) Å).[23] The torsion angle of 70.6° between the planes containing the carbene carbon and nitrogens in the two pyrimidine rings is comparable to those of other [Cu(NHC)₂]⁺ species bearing bulky N-aryl-substituted carbenes.[23,24]

Reaction of 1 with MO^{t}Bu (M = Li, Na, K) and Characterization of Monomeric [(6-MesDAC)CuCl]. In many catalytic applications, treatment of (NHC)CuCl precatalysts with KO^{t}Bu is used to bring about salt metathesis and formation of more reactive (NHC)Cu(O^{t}Bu) species.[3] In

processes such as hydrosilylation, these undergo conversion to transient (NHC)CuH intermediates.[2] Interrogation by ¹H NMR spectroscopy of THF-d_8 solutions of **1** following addition of 2 equiv of either KO^{t}Bu or NaO^{t}Bu indicated the rapid disappearance of all the starting material signals in the resulting orange-red solutions but formation of a forest of product resonances. In contrast, LiO^{t}Bu reacted under the same conditions to give a purple solution; ¹H and ⁷Li NMR spectroscopy suggested formation of the ate complex [(6-MesDAC)CuCl·LiO^{t}Bu·2THF] (**5**) as a result of a partial metathesis reaction (Scheme 2). The low-temperature (200 K) ¹H NMR spectrum displayed seven singlet resonances at δ 6.95, 2.35, 2.28, 2.20, 1.71, 1.66, and 0.64 in a ratio of 4:6:6:6:3:3:9 consistent with the presence of a (6-MesDAC)CuO^{t}Bu moiety.[25] A singlet was observed in the ⁷Li NMR spectrum at δ −0.74. ¹H and ⁷Li DOSY measurements (see the Supporting Information for plots) gave very similar diffusion coefficients for the carbene signals and the Li resonance, consistent with them being in the same molecule (Table 2).

Upon removal of the solvent, the purple solution transformed into a green solid, which upon redissolution in THF-d_8 regenerated a purple solution. When treatment of **1** with LiO^{t}Bu was repeated in protio THF and the green residue subjected to high vacuum for 1 h before redissolving in either THF-d_8 or C₆D₆, 2 equiv of protio THF per carbene was apparent in the ¹H NMR spectrum (signals at δ 3.62/1.77 in THF-d_8 and δ 3.59/1.41 in C₆D₆). The corresponding ⁷Li spectrum now exhibited a further peak at 0 ppm.

Efforts to induce LiCl loss from **5** by addition of 12-crown-4 were unsuccessful, as were all attempts to isolate crystals of the product by slow evaporation of THF solutions. Indeed, further characterization of **5** was thwarted by the instability of the product away from THF; an X-ray determination on a single (red) crystal formed from slow evaporation of a red toluene solution of the green residue gave cell parameters matching those of the dimer **1**. More surprisingly, we found that attempted crystallization of **5** by slow evaporation of an Et$_2$O solution of the green residue gave red, block-shaped crystals of a new compound, which upon structural analysis (Figure 6) consisted of a 1:1 cocrystal of **1** and the monomer [(6-MesDAC)CuCl] (**6**). As expected, the metrics of the dimer changed only slightly from those of **1** alone reported in Figure 1. The Cu−C distance (1.886(2) Å) in **6** was the same as that in the dimer, although the Cu−Cl distance was significantly shorter (2.1150(7) Å). Interestingly, both distances were the same as those reported in the diaminocarbene analogue [(6-Mes)CuCl],[26] despite the clear differences between 6-MesDAC and 6-Mes noted earlier.

The formation of **1** + **6** must reflect the relative stabilities/solubilities of the (6-MesDAC)Cu, Li, Cl, and O^{t}Bu components in **5**, as the product was also found to form upon simply recrystallizing **1** from Et$_2$O (Scheme 2).

CONCLUSIONS

Efforts to prepare the first examples of copper diamidocarbene complexes have led to the isolation of an array of products ranging from monomeric to tetrameric copper systems. Interconversion of some of these species occurs easily upon addition of either 6-MesDAC or CuCl or upon alteration of the solvent. Moreover, product formation is also influenced by the use of either the isolated, free diamidocarbene or in situ generated carbene; in the latter case, generation of the DAC in the presence or absence of the copper precursor is also significant.

The potential of 6-MesDAC as a ligand for copper catalysis remains to be established, as our attempts to prepare (6-MesDAC)CuO^{t}Bu by metathesis of **1** with alkali-metal alkoxides were unsuccessful. This substantiates Nolan's warnings about judging catalyst efficiency on the basis of in situ generated systems.[14]

ASSOCIATED CONTENT

ⓢ Supporting Information

Figures giving NMR and DOSY data for **1**, **2**, and **5** and CIF files giving crystallographic data for **1**−**4** and **1** + **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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ACKNOWLEDGMENTS

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