Ligand Transfer from a Tris(imino)stannate Anion; Syntheses and Structures of [{Cu[μ-N=C(Bu^t)Ph]}$_4$]·thf (thf = tetrahydrofuran) and [{Cu[μ-N=C(Bu^t)Ph]}$_4$(PPh$_3$)$_2$]·6thf

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The Group 11 metal imino complexes [{Cu[μ-N=C(Bu^t)Ph]}$_4$]·thf **2** (thf = tetrahydrofuran) and [{Cu[μ-N=C(Bu^t)Ph]}$_4$(PPh$_3$)$_2$]·6thf **3** have been prepared by the unusual ligand-transfer reactions of the tris(imino)stannate complex Sn[μ-N=C(Bu^t)Ph]$_3$Li·thf with CuCl; both complexes have been shown by crystallography to contain planar Cu$_4$ cores.

We showed recently that nucleophilic substitution of the cyclopentadienyl groups in E(cp)$_2$ (E = Sn or Pb; cp = C$_5$H$_5$) with imino ligands results in mixed-ligand[1] and tris(imino)-stannate and -plumbate complexes,[2] depending on the nucleophilicity and steric bulk of the nucleophiles employed. Nucleophilic substitution of E(cp$_2$) with [LiN=CPh(Bu^t)]$_n$ gives the trigonal-bipyramidal cage complexes E[μ-N=C(Bu^t)Ph]$_3$Li·thf in which substitution of both cp groups followed by addition of a third imino anion has occurred.[2] Apparently as a result of the weakness of Pb–N compared to Sn–N bonds, the reaction of Pb[μ-N=C(Bu^t)Ph]$_3$Li·thf with Sn(cp)$_2$ leads to complete imino-group transfer and formation of Sn[μ-N=C(Bu^t)Ph]$_3$Li·thf **1** together with Pb(cp)$_2$.[2b] We here report our preliminary investigations of the reactivity and ligand behaviour of **1** with metal salts and of the syntheses and structures of the first imino complexes of a Group 11 metal.

In an attempt to prepare a Cu complex in which the tris(imino)stannate anion [Sn{N=C(Bu^t)Ph}$_3$]$^-$ functions as a tripodal ligand to Cu, **1** was treated with CuCl (1 : 1 equivalent) in thf. However, this treatment resulted in ligand transfer of one imino group from **1** and the formation of [{Cu[N=C-(Bu^t)Ph]}$_4$]·thf **2**. The presence of PPh$_3$ (1 equivalent) fails to block this ligand-transfer reaction and [{Cu[N=C(Bu^t)Ph]}$_4$-(PPh$_3$)$_2$]·6thf **3**, rather than [Sn{μ-N=C(Bu^t)Ph}$_3$Cu(PPh$_3$)] is isolated (Scheme 1).†

Complexes **2** and **3** have been structurally characterised by low-temperature X-ray diffraction studies.‡ The structure of [{Cu[μ-N=C(Bu^t)Ph]}$_4$]·thf **2** contains two crystallographically independent, but structurally similar, molecules in the asymmetric unit (Fig. 1). In addition, one thf molecule is present in the lattice for each molecule of **2**. The structure contains a square-planar Cu$_4$ core [Cu···Cu (av.) 2.76 Å, Cu···Cu···Cu (av.) 89.9°] which is linked together by imino ligands in a saddle-shaped arrangement [Cu–N (av.) 1.857 Å, N–Cu–N (av.) 168.7°, Cu–N–Cu 95.8°]. This *cis,trans,cis,trans* arrangement presumably minimises steric crowding of the Bu^t and Ph groups at the periphery of the molecule.

In the crystal structure of [{Cu[μ-N=C(Bu^t)Ph]}$_4$(PPh$_3$)$_2$]·6thf **3**, the molecule sits on a crystallographic centre of symmetry. In addition, there are six lattice-bound thf molecules for each molecule of **3**. The two phosphine ligands of **3** are coordinated to only two opposite Cu centres of the Cu$_4$ core

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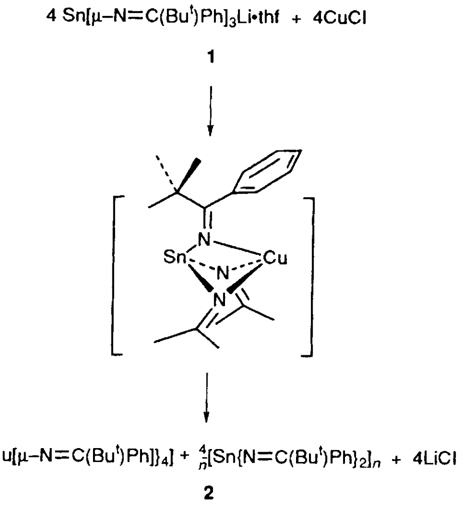
† *Syntheses.* **2**: A solution of **1** (1.68 g, 2.5 mmol) in thf (10 cm^3) was added to a suspension of freshly prepared CuCl (0.25 g, 2.5 mmol) in thf (10 cm^3). The mixture was stirred at 20 °C (30 min) before being filtered (Celite, P3). The orange solution was reduced to *ca.* 6 cm^3 and a yellow precipitate was formed, which was gently warmed into solution and storage at 20 °C (24 h) and gave yellow needles of **2**. Placing **2** under vacuum [*ca.* 10 min, 10^{-1} atm (≈10 133 Pa)] removed all the lattice-bound thf and produced a yellow powder, yield 0.20 g (36%); m.p. 236 °C [Found: C, 60.0; H, 6.2; N, 6.5. Calc. for (C$_{11}$H$_{14}$CuN)$_n$: C, 59.0; H, 6.3; N, 6.3%]. IR spectrum (Nujol, NaCl), 3040s (C–H, Ph), 1120s (C$\equiv$N, imino); ^{1}H NMR (CD$_3$)$_2$SO, 250 MHz, +25 °C), 1.15 (9 H, s, Bu^t), 7.1 7.4 (5 H, m, Ph).

3: A solution of **1** (1.68 g, 2.5 mmol) in thf (10 cm^3) was added to a stirred suspension of [CuCl(PPh$_3$)], prepared *in situ* from CuCl (0.25 g, 2.5 mmol) and PPh$_3$ (0.66 g, 2.5 mmol) in thf (10 cm^3), at 20 °C. The mixture was stirred (1 h) and heated briefly to reflux, giving an orange-brown solution, filtered (Celite, P3) to remove a small quantity fine precipitate and the filtrate was reduced to *ca.* 7 cm^3. A yellow precipitate formed, which was gently warmed into solution; storage at −10 °C (48 h) gave large yellow crystalline blocks of **3**. Placing **3** under vacuum (*ca.* 10 min, 10^{-1} atm) removes all the lattice-bound thf and produces a yellow powder, yield 0.56 g (63%); decomp. 150 °C, m.p. 171 °C [Found: C, 68.1; H, 6.4; N, 4.2; P, 5.0. Calc. for (C$_{40}$H$_{43}$Cu$_2$N$_2$P): C, 67.6; H, 6.1; N, 4.0; P, 4.4%].

‡ *Crystal data.* **2**: C$_{44}$H$_{56}$Cu$_4$N$_4$·C$_4$H$_8$O, M = 967.19, triclinic, space group $P\bar{1}$ (no. 2), a = 14.527(3), b = 17.544(4), c = 20.026(4) Å, α = 76.88(3), β = 73.18(3), γ = 75.45(3)°, U = 4663(2) Å^3, Z = 4, ρ_{calc} = 1.378 Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, T = −120 °C, μ(Mo-Kα) = 1.838 mm^{-1}. Data collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly-cooled crystal (0.4 × 0.4 × 0.3 mm)[3] by θ–ω method (7.02 ⩽ 2θ ⩽ 50.00°). Of 14 971 total collected reflections, 14 362 independent (R_{int} = 0.0512). Structure solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1$ [$F > 4\sigma(F)$] = 0.081 and $wR2$ = 0.208 and $R1$ = 0.127 and $wR2$ = 0.273 (all data) [$R1 = \Sigma|F_o - F_c|\Sigma F_o$ and $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{0.5}$];[4] largest peak and hole in final difference map 1.084 and −0.879 e A^{-3}. All non-hydrogen atoms refined anisotropically; hydrogen atoms fixed in geometrically idealised positions and allowed to ride on the relevant C atom. All eight Bu^t groups and one of the two independent thf molecules in asymmetric unit disordered and refined on two positions with distance and ADP-restraints.

3: C$_{80}$H$_{86}$Cu$_4$N$_4$P$_2$·6C$_4$H$_8$O, M = 1852.26, triclinic, space group $P\bar{1}$ (no. 2), a = 13.033(3), b = 13.688(3), c = 14.762(3) Å, α = 82.52(3), β = 66.29(3), γ = 87.86(3)°, U = 2390.3(9) Å^3, Z = 2, ρ_{calc} = 1.287 Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, T = −120 °C, μ(Mo-Kα) = 0.966 mm^{-1}. Data collected as for **2**[3] for crystal of dimensions 0.5 × 0.3 × 0.3 mm and 8.08 ⩽ 2θ ⩽ 45.00°. Of 7053 total collected reflections, 6190 independent (R_{int} = 0.0424). Structure solved and refined as above, with $R1$ [$F > 4\sigma(F)$] = 0.056 and $wR2$ = 0.142, $R1$ = 0.062 and $wR2$ = 0.156 (all data), largest peak hole in the final difference map 1.111 and −1.161 e Å^{-3}. All non-hydrogen atoms, with exception of the three crystallographically independent thf molecules, refined anisotropically. Hydrogen atoms fixed in geometrically idealised positions and allowed to ride on the relevant C atom. Two thf molecules disordered and refined on two positions. All three thf molecules in asymmetric unit treated with distance restraints and restraints for isotropic thermal parameters.



Scheme 1

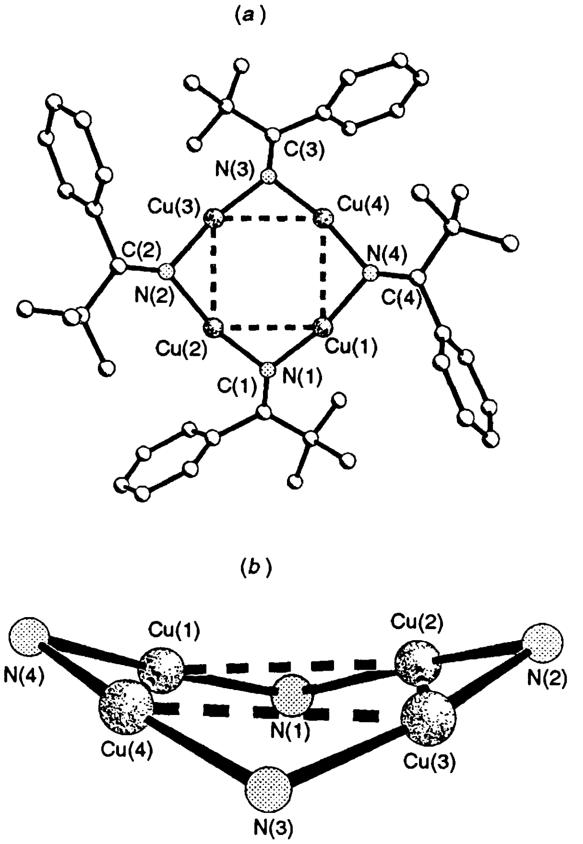


Fig. 1 (*a*) Molecular structure of **2**. Hydrogen atoms and the lattice-bound thf solvation omitted for clarity. Bond lengths (Å) and angles (°): molecule 1, Cu(1)–N(1) 1.847(8), Cu(1)–N(4) 1.871(8), Cu(2)–N(1) 1.863(8), Cu(2)–N(2) 1.872(8), Cu(3)–N(2) 1.871(8), Cu(3)–N(3) 1.863(8), Cu(4)–N(3) 1.845(9), Cu(4)–N(4) 1.858(8), imino C=N (av.) 1.27, Cu ··· Cu (av.) 2.770; Cu–N–Cu (av.) 96.2, N–Cu–N (av.) 169.0, Cu ··· Cu ··· Cu (av.) 89.9; molecule 2, Cu(5)–N(5) 1.865(8), Cu(5)–N(8) 1.867(8), Cu(6)–N(5) 1.832(9), Cu(6)–N(6) 1.848(8), Cu(7)–N(6) 1.857(8), Cu(7)–N(7) 1.842(8), Cu(8)–N(7) 1.860(8), Cu(8)–N(8) 1.850(8), imino C=N (av.) 1.27, Cu ··· Cu (av.) 2.740, Cu–N–Cu (av.) 95.4, N–Cu–N (av.) 168.4, Cu ··· Cu ··· Cu 89.9; (*b*) Cu_4 core of **2**

[Cu(1)–P(1) 2.221(1) Å], and this forces the surrounding imino-ligand framework into a chair-shaped (*cis,cis,trans,trans*) conformation (Fig. 2). Further phosphine complexation of the remaining Cu atoms of **3** [Cu(2) and Cu(2a)] is rendered

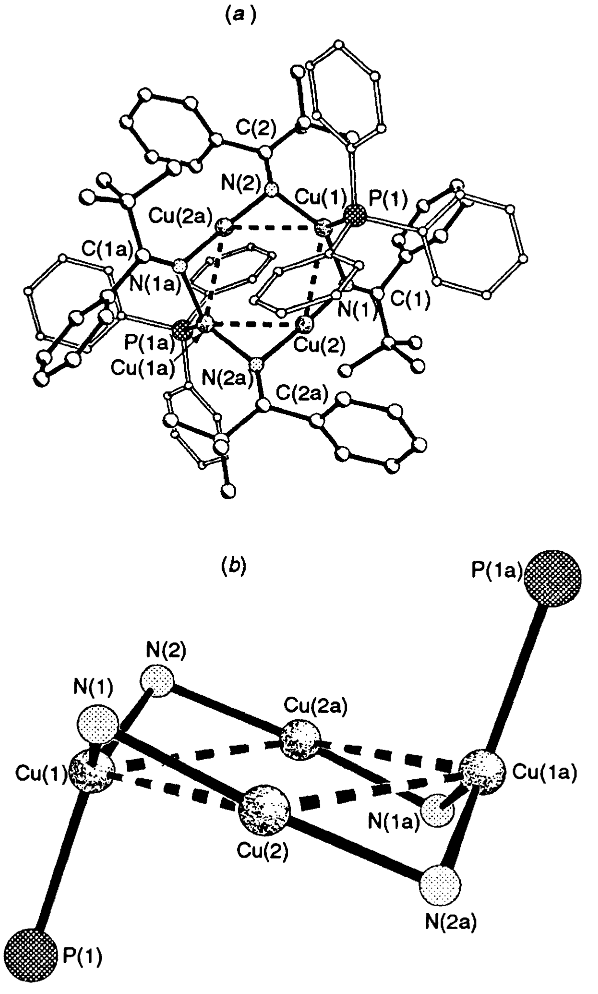


Fig. 2 (*a*) Molecular structure of **3**. Hydrogen atoms and the six lattice-bound thf ligands omitted for clarity. Bond lengths (Å) and angles (°): Cu(1)–N(1) 1.953(4), Cu(1)–N(2) 1.946(4), Cu(2)–N(1) 1.858(4), Cu(2)–N(2a) 1.866(4), imino C=N (av.) 1.272, Cu(1)–P(1) 2.221(1), Cu(1) ··· Cu(2a) 2.764(2), Cu(1) ··· Cu(2) 2.793(1), Cu(2) ··· Cu(2a) 3.540(2); Cu(1)–N(1)–Cu(2) 94.2(2), Cu(1)–N(2)–Cu(2a) 92.9(2), N(1)–Cu(1)–N(2) 122.6(1), N(1)–Cu(2)–N(2a) 174.4(2), Cu(2) ··· Cu(1) ··· Cu(2a) 79.16(3), Cu(1) ··· Cu(2) ··· Cu(1a) 100.84(3); (*b*) Cu_4 core of **3**

sterically unfavourable as a result of the *cis,trans* orientation of the imino ligands about these centres. Although the Cu ··· Cu [2.78 Å (av.) and Cu–N 1.91 Å (av.)] distances in **3** are very similar to those in **2**, there are large angular distortions both within the Cu_4 core and within the surrounding imino-ligand framework. Most obviously, the N–Cu–N angles at the phosphine-complexed Cu centres are compressed well below those at the uncomplexed centres [N(1)–Cu(1)–N(2) 122.6(1); *cf.* N(1)–Cu(2)–N(2a) 174.4(2)°]. As a result, the Cu_4 core of **3** is distorted into a diamond shape [Cu(2) ··· Cu(1) ··· Cu(2a) 79.16(3), Cu(1) ··· Cu(2) ··· Cu(1a) 100.84(3)°] in which the uncomplexed Cu centres of **3** are forced into closer contact [Cu(2) ··· Cu(2a) 3.540(2); *cf.* 3.89 Å (av.) for the Cu ··· Cu diagonals in **2**]. The restricted phosphine complexation of a Cu_4 core has also been observed in the butterfly-shaped $[\{CuL\}_4(PPh_3)_2]$ complex (L = 2-sulfanylthiazoline).[5] However, the structural characterisation of both the uncomplexed and phosphine-complexed species (**2** and **3**, respectively) provides, to our knowledge, a unique opportunity to examine the effects of phosphine complexation on the metal and ligand geometries in such a system.

Planar and butterfly-shaped M_4 (M = Ag or Au) arrangements are comparatively common for both organometallic[6] and co-ordination compounds of Group 11. However, there are only a handful of amido Cu^{I} complexes[7] and complexes **2** and **3** are the first structurally characterised imino Group 11 metal compounds. The ligand-transfer behaviour of $[Sn\{N{=}C(Bu^{t})Ph\}_3]^-$, observed in the syntheses of **2** and **3**, is unique with respect to the reactivities of related anions, which remain *intact* in their transmetalation reactions. Thus, triorgano-stannates and -plumbates function as Sn- and Pb-centred ligands[8] and tris(alkoxy)stannates[9] and tris(amido)stannates[10] interact as multidentate ligands with a range of metals. In view of the behaviour of the tris(imino)stannate anion noted here, and by relation to the applications of triorganostannates in organic synthesis,[11] it is conceivable that tris(imino)stannates may function as 'soft' imino-group transfer reagents with organic substrates (*e.g.*, affecting Michael addition of an imino anion to α,β-unsaturated ketones).

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