

Synthesis and structures of 3-sila- β -diketiminato complexes of the coinage metals

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Abstract

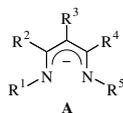
The dimeric copper(I) 3-sila- β -diketiminato $[\text{Cu}\{(\text{N}(\text{R})\text{C}(\text{Ar})_2\text{SiR})\}_2(\text{thf})]_2$ (**1**) was obtained from CuI and $[\text{Li}\{(\text{N}(\text{R})\text{C}(\text{Ar})_2\text{SiR})\}(\text{thf})_2]$ (**B**) in toluene ($\text{R} = \text{SiMe}_3$, $\text{Ar} = \text{C}_6\text{H}_3\text{Me}_{2-2,6}$). When $[\text{CuI}(\text{PPh}_3)_3]$ was used as a starting material, the LiI-containing compound $[\text{Cu}\{\text{Si}(\text{R})(\text{C}(\text{Ar})\text{N}(\text{R}))_2\text{Li}(\mu\text{-I})\}(\text{PPh}_3)]$ (**2**) was isolated. The reaction of $[\text{M}(\text{PPh}_3)_n]$ ($\text{M} = \text{Ag}$, $n = 3$; $\text{M} = \text{Au}$, $n = 2$) with two equivalents of **B** in toluene gave the isomorphous silver and gold 3-sila- β -diketiminates $[\text{M}\{\text{Si}(\text{R})(\text{C}(\text{Ar})\text{N}(\text{R}))_2\text{Li}\}_2(\mu\text{-I})]$ [$\text{M} = \text{Ag}$ (**3**), Au (**4**)]. Each of **1–4** was characterised by the multinuclear NMR spectroscopy and single-crystal X-ray diffraction crystallography.

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Keywords: Copper; Silver; Gold; β -Diketiminates; Silyl complexes

1. Introduction

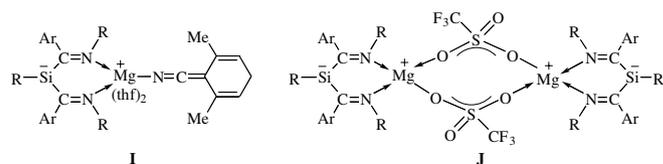
β -Diketiminato ligands, shown in **A** in π -delocalised monoanionic form, feature extensively in the coordination chemistry of nearly all the elements and in catalysis [1]. Most are β -diketiminates (R^2 and R^4 are alkyl, aryl or silyl); only a few are β -dialdiminates ($\text{R}^2 = \text{H} = \text{R}^4$) [2]. The ligands **A** generally function as N, N' -centred nucleophiles in their coordination chemistry, either as chelates or as bridges between two metal centres; but other ligating modes (rarely C -centred [3]) have also been observed.



A 3-sila- β -diketiminato ligand was first obtained as the lithium salt **B** ($\text{R} = \text{SiMe}_3$, $\text{Ar} = \text{C}_6\text{H}_3\text{Me}_{2-2,6}$) (Scheme 1) [4], prepared from $[\text{Li}(\text{SiR}_3)(\text{thf})_3]$ [5] and 2ArCN . Compound **B** has been the source of the derivatives **C1** [6], **C2** [7], **D** [6], **E1** to **E5** [7], **G** [7] and **H** [8], as shown in

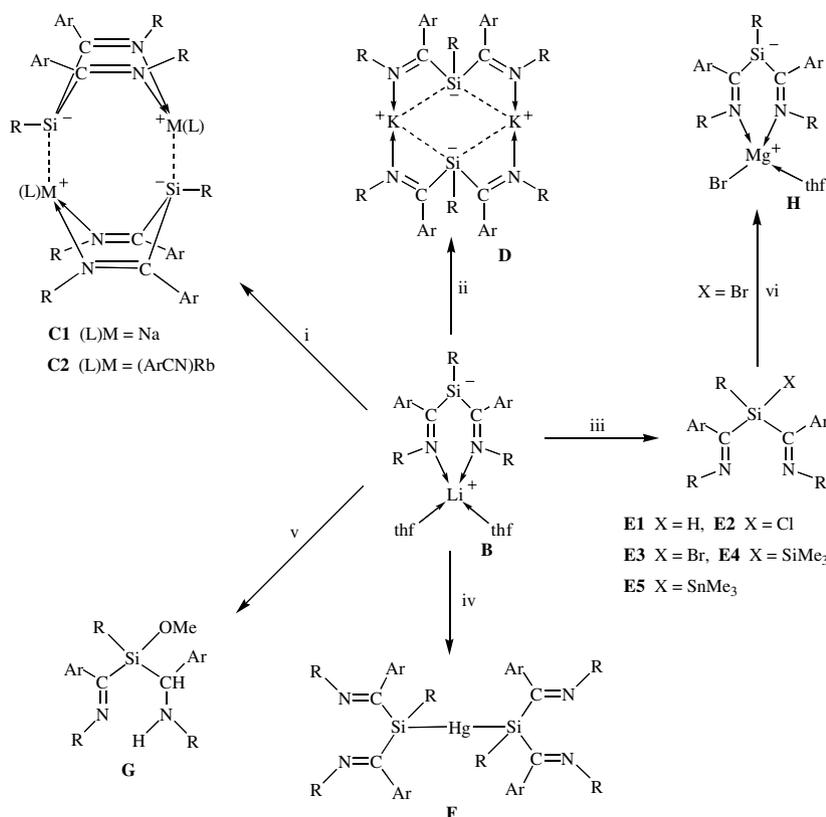
Scheme 1. X-ray structural data are available for $[\text{Li}\{(\text{N}(\text{R})=\text{C}(\text{Ar})_2\text{SiR})\}(\text{NCAR})_2]$ [4], $[\text{Li}\{(\text{N}(\text{R})=\text{C}(\text{Ar})_2\text{SiR})\}(\text{NCAR})]$ [7], **C1** [6], **C2** [7], **D** [6], **E2** [7], **E3** [7], **E5** [7], **F** [7] and **H** [8]. Two further crystalline magnesium 3-sila- β -diketiminates have been reported: **I** from $[\text{Mg}(\text{SiR}_3)_2(\text{thf})_2]$ [9] and 2ArCN , and **J** from **I** and Me_3SiOTf [8].

From these data, it will be evident that the 3-sila- β -diketiminato ligand operates as an Si -centred nucleophile in **E1** to **E5**, **F** and **G**. By contrast, the alkali metal (**B**, **C**, **D**) and Mg (**H**, **I**, **J**) complexes are zwitterionic, with the ligand behaving in an N, N' -chelating (**B**, **H**, **I**, **J**), N, N' -chelating and Si -bridging (**C1**, **C2**), or N, N' -bridging (**D**) fashion.



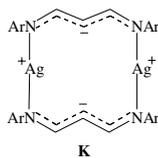
In this paper, we report extensions of our earlier studies on metal β -diketiminates to the coinage metals (M) in the +1 oxidation state. For comparison reference in made to the literature data on M^1 diiminates. Until recently such

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Scheme 1. Reactions of the 3-sila- β -diketiminato **B** ($R = \text{SiMe}_3$, $\text{Ar} = \text{C}_6\text{H}_3\text{Me}_{2-2,6}$) [6–8]; i, MOBu^+ ($M = \text{Na}, \text{Rb}$); ii, KOBu^+ ; iii, CpH (for **E1**), $[\text{TiCp}_2\text{Cl}_2]$ (for **E2**), HgBr_2 or $(\text{CH}_2\text{Br})_2$ (for **E3**), Me_3SiCl (for **E4**), Me_3SnCl (for **E5**); iv, Hg_2Cl_2 ; v, 2MeOH ; and vi, Mg , $\text{Et}_2\text{O}/\text{thf}$.

Group 11 metal complexes were restricted to those of Cu^{II} [1a] but since 2001 a few Cu^{I} compounds, including the dialdiminates $[\text{Cu}\{(\text{N}(\text{C}_6\text{H}_2\text{Me}_3-2,4,6)\text{C}(\text{H}))_2\text{CNO}_2\}(\text{L})]$ [10a], $[\text{Cu}\{(\text{N}(\text{Ar})\text{C}(\text{H}))_2\text{CPh}\}(\text{L})]$ ($\text{L} = \text{NCMe}$ [2a], PPh_3 [2e]), and several diketiminates such as $[\text{Cu}\{(\text{N}(\text{Ar})\text{C}(\text{Me}))_2\text{CH}\}(\text{L})]$ ($\text{L} = \text{C}_2\text{H}_4$ [10b], $\text{Ge}(\text{NR}_2)_2$ [10c]) and $[\text{Cu}\{(\text{N}(\text{Ar})\text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{Me})\text{N}(\text{C}_6\text{H}_3\text{Pr}^i-2-\text{CH}_2\text{SMe-6}))\}_4]$ [10d] have been described. Data on the first Ag^{I} β -diiminates appeared in 2005; these included the crystalline complex **K**, obtained from $\text{H}\{[\text{N}(\text{Ar})\text{C}(\text{H}))_2\text{CH}]\}$ and AgPF_6 and NEt_3 in MeOH , while from $\text{H}\{[\text{N}(\text{Ar})\text{C}(\text{Me}))_2\text{CH}]\}$ and the same reagents the product was the Ag -free C–C-coupled compound $[-\text{C}\{(\text{C}(\text{Me})\text{N}(\text{Ar}))\}\{(\text{C}(\text{Me})\text{N}(\text{Ar})\text{H})\}]_2$ [11]. Three further Ag^{I} β -diketiminates, having N,N' -chelating (and bridging) ligands, including $[\text{Ag}\{(\text{N}(\text{C}_6\text{H}_3(\text{CF}_3)_2-3,5)\text{C}(\text{CF}_3)_2\text{CH})\}(\eta^2-\text{C}_2\text{H}_4)]$ have been obtained from successively the parent diketimine and Ag_2O in MeCN and then C_2H_4 in benzene [12]. At the time we submitted this paper, a gold β -diketiminato, as far as we were aware, had not been described, but the product derived from AuCl and $\text{Li}\{[\text{N}(\text{Ar})\text{C}(\text{Me}))_2\text{CH}]\}$ was employed as a catalyst in the aerobic oxidation of PhCH_2OH to PhCHO [13].

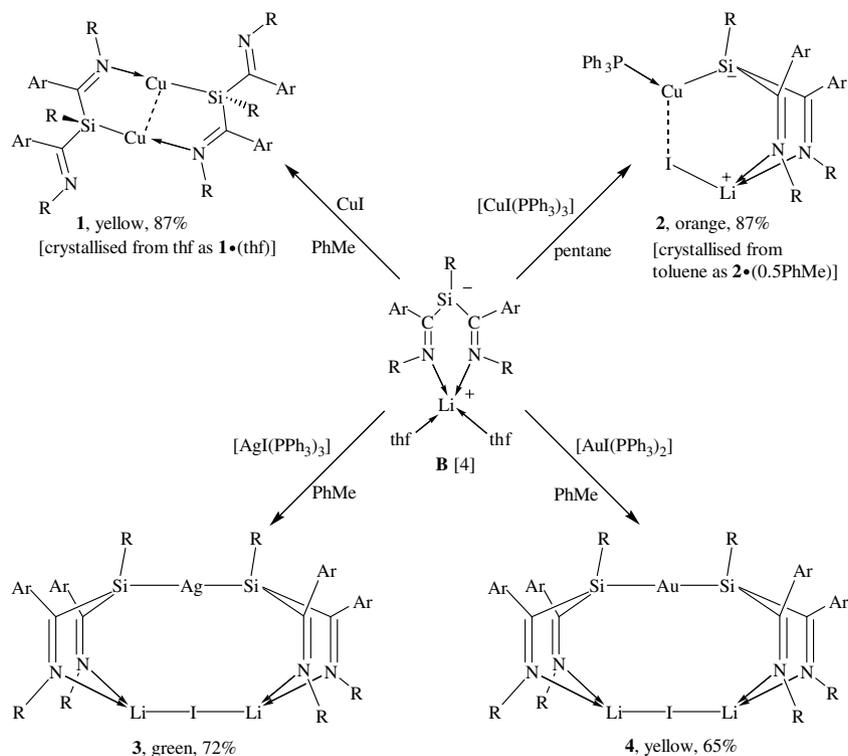


2. Results and discussion

2.1. The 3-sila- β -diketiminato-copper(I) complex **1**

Treatment of copper(I) iodide with the lithium 3-sila- β -diketiminato **B** in toluene, removal of volatiles and extraction of the residue with thf afforded (Scheme 2) the yellow crystalline dimeric Cu^{I} 3-sila- β -diketiminato- thf solvate **1**. The ^1H NMR spectrum of **1** in C_6D_6 showed the appropriate integrated signals for **1**, but even at -80°C in $\text{toluene-}d_8$ only a single SiMe_3 resonance was observed, indicative of a fast fluxional process, possibly due to weak $\text{N} \rightarrow \text{Cu}$ bonding and rapid $\text{Cu}-\text{Si}$ rotation. Compound **1** (like **2–4**) was labile in solution, slowly depositing metal; nevertheless the EI mass spectrum revealed the parent molecular ion.

The X-ray molecular structure of crystalline **1** is shown in Fig. 1. The core centrosymmetric molecule **1** is an eight-membered CuNCSiCuNCSi puckered ring, with each ligand bridging two copper atoms in an N,Si -bridging fashion. The two puckered CuNCSiCu moieties are arranged in a *transoid* fashion about the $\text{Cu}-\text{Cu}'$ vector. Similar eight-membered CuNXCuNCX rings, with short $\text{Cu}\cdots\text{Cu}'$ contacts have been reported in three dimeric Cu^{I} amidinates ($\text{X} = \text{N}$) and an 1-azaallyl ($\text{X} = \text{C}$); selected endocyclic geometric parameters for these and **1** are listed in Table 1. Selected exocyclic ligand parameters for **1** are closely similar to those for the mercury(II) 3-sila- β -diketiminato



Scheme 2. Synthesis of the crystalline Group 11 metal 3-sila- β -diketiminates **1–4** ($R = \text{SiMe}_3$, $\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$).

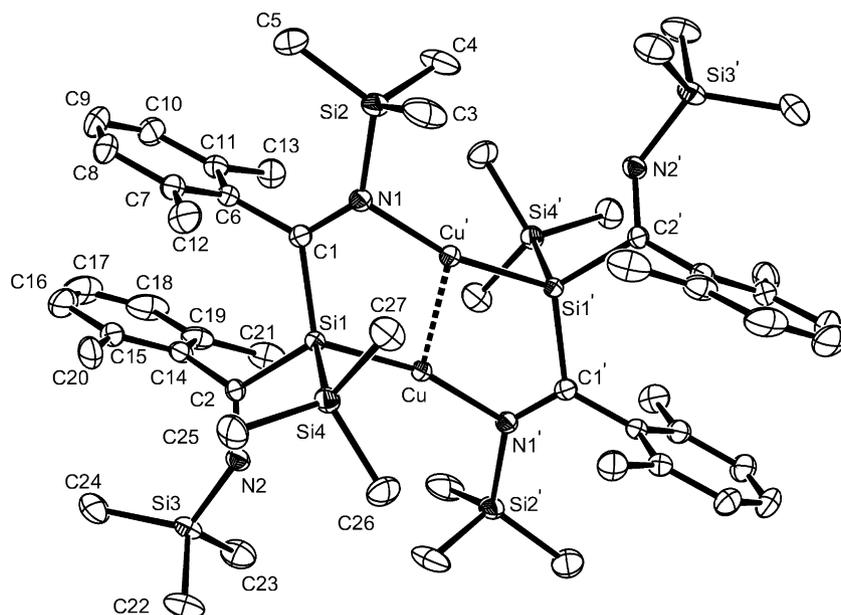


Fig. 1. ORTEP diagram of the molecular structure of **1** with thermal ellipsoids drawn at 20% probability level.

F [7], as illustrated in Table 2. The data of Tables 1 and 2 support the view that there is little, if any, π -delocalisation in the ligands of **1**, consistent with its valence bond representation in Scheme 2. The Cu–Si distance in **1** of 2.2728(8) Å is closely similar to that in $[\text{Cu}(\text{SiR}_3)\{\text{Sn}(\text{SiR}_3)(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})\}]$ which like **1** has the Cu and Si atoms in two- and four-coordination, respectively [18].

2.2. The 3-sila- β -diketiminatotris(triphenylphosphine)-copper(I)–LiI adduct **2**

Addition of the lithium 3-sila- β -diketimate **B** in pentane to $[\text{CuI}(\text{PPh}_3)_3]$ yielded (Scheme 2) complex **2** as a light orange crystalline material from toluene at -5°C . A freshly prepared sample of **2** in C_6D_6 gave ^1H NMR spectral signals

Table 1
Selected *endocyclic* geometric parameters for **1**, four Cu^I amidinates and a Cu^I 1-azaallyl (R = SiMe₃)

Compound	Cu··Cu' (Å)	Cu–N (Å)	C–N (Å)	Endocyclic angle at Cu (°)	Reference
1	2.4626(2)	1.964(2)	1.304(3)	162.15(9)	This work
[Cu{N(Pr ⁱ)C(Me)N(Pr ⁱ)} ₂]	2.414(1)	1.869(1)	1.329(2)	176.4(1)	[14a]
[Cu{N(Bu ^t)C(Me)N(Bu ^t)} ₂]	2.4031(6)	1.877(2)	1.326(3)	176.62(1)	[14b]
[Cu{N(C ₆ H ₃ Me ₂ -2,6)C(Ph)N(C ₆ H ₃ Me ₂ -2,6)} ₂]	2.4571(2)	1.880(2)	1.336(2)	175.37(2)	[15]
[Cu{N(R)C(Ph)N(R)} ₂]	2.425	1.890	1.330	175.9	[16]
[Cu{N(R)C(Bu ^t)C(H)R}] ₂	2.499(2)	1.921(5)	1.309(8)	166.2(2)	[17]

Table 2
Selected *exocyclic* geometric parameters for **1** and Hg[Si(R){C(Ar)N(R)}₂]₂ (**F**) (R = SiMe₃, Ar = C₆H₃Me₂-2,6)

Compound	Si–Si (Å)	Si–C (Å)	C–N (Å)	N–Si (Å)	Me ₃ Si–Si–C(Ar) (°)	Si–C(Ar)–N (°)	C(Ar)–N–SiMe ₃ (°)	Reference
1	2.3741(11)	1.926(3)	1.280(3)	1.745(2)	105.86(8)	113.2(2)	133.3(2)	This work
F	2.353(2)	1.920(6), 1.923(6)	1.275(7), 1.288(7)	1.740(5), 1.753(5)	106.3(2), 110.9(2)	111.5(4), 114.4(5)	132.1(4), 133.9(4)	[7]

of appropriate relative intensities. However, as for **1**, slow decomposition with deposition of copper was observed accompanied by formation of a benzene-soluble compound having ¹H NMR spectral characteristics of the ligand. Nevertheless, the solid sample was adequately robust to furnish satisfactory microanalytical data.

The X-ray molecular structure of crystalline **2** may be regarded as a composite of its two precursors with loss of 2(PPh₃ + thf). It is illustrated in Fig. 2 with selected geometrical parameters. The six atoms Li, N(1), C(13), Si(1), C(4) and N(2) of the Li[{N(R)C(Ar)}₂SiR] moiety adopt the boat conformation, as previously found for **B** [4], **C1**

[7], **C2** [7], **H** [8] and [Li({N(R)C(Ar)}₂SiR)(NCAr)] (**L**) [7]. Its Si(1) and Li atoms act as a bridge to the Cu and I atoms, respectively. The endocyclic parameters of the boat are somewhat similar to those in **L** as shown by the following data for **L**: Li–N(1) 1.954(5), Li–N(2) 1.950(5), N(1)–C(13) 1.311(3), N(2)–C(4) 1.303(3), C(13)–Si(1) 1.881(2), C(4)–Si(1) 1.881(2) Å; N(1)–Li–N(2) 111.4(2)°, Li–N(1)–C(13) 105.3(2)°, Li–N(2)–C(4) 107.0(2)°, N(1)–C(13)–Si(1) 124.4(2)°, N(2)–C(4)–Si(1) 123.9(2)°, C(4)–Si(1)–C(13) 108.8(1)°; and the dihedral angles between the N(1)C(13)–C(4)N(2) plane and the N(1)LiN(2) and C(13)Si(1)C(4) planes are 53.7(1)° and 28.4(1)°, respectively [7], which

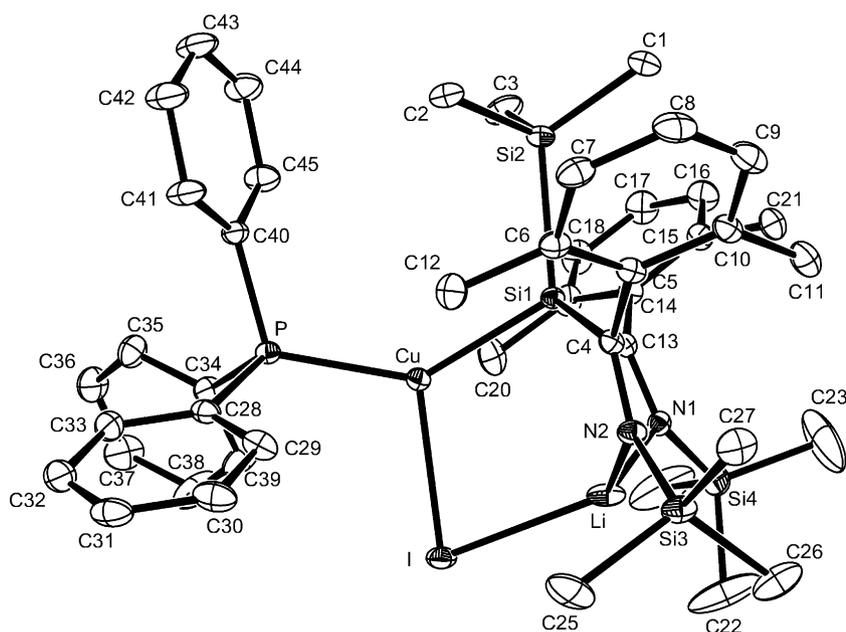


Fig. 2. ORTEP diagram of the molecular structure of **2** with thermal ellipsoids drawn at 20% probability level. Selected bond lengths (Å) and angles (°): Li–N(1) 1.953(9), Li–N(2) 1.958(8), N(1)–C(13) 1.293(6), N(2)–C(4) 1.295(5), C(13)–Si(1) 1.931(4), C(4)–Si(1) 1.932(4), Si(2)–Si(1) 2.3666(17), Li–I 2.640(10), Cu–Si(1) 2.3298(12), Cu–I 2.6572(6), Cu–P 2.2523(12); N(1)–Li–N(2) 108.3(4), Li–N(1)–C(13) 109.8(4), Li–N(2)–C(4) 110.7(4), N(1)–C(13)–Si(1) 120.9(3), N(2)–C(4)–Si(1) 120.4(3), C(4)–Si(1)–C(13) 105.13(18), N(1)–Li–I 116.9(4), N(2)–Li–I 118.3(4), Li–I–Cu 75.65(18); the dihedral angle between the P–I–Si(1) and N(1)–N(2)–I is 82.6(1)°; the Cu atom is 0.122(1) Å out of the P–I–Si(1) plane.

compares with $49.0(5)^\circ$ and $37.3(2)^\circ$ in **2**. The Si(1) atom of **2** is in an approximately tetrahedral environment with angles at Si(1) ranging from the Cu–Si(1)–C(13) at $102.60(13)$ to the Cu–Si(1)–Si(2) at $116.55(6)^\circ$. The three-coordinate Cu atom of **2** is in a distorted trigonal planar environment. The Cu–I and Li–I bond lengths of **2** are significantly longer and somewhat shorter, respectively, compared with those found in $[(Et_2O)_2Li\{\mu-I\}CuAr']$ [$Ar' = C_6H_3(C_6H_2^iPr_3-2',4',6')_2-2,6$] of 2.4512(8) and 2.690(11) Å, respectively [19]. The Cu–P distance in **2**, like its planar environment, are unexceptional, being similar to those found in crystalline $[Cu\{N(Ar)C(H)_2CPh\}(PPh_3)]$ in which $d(Cu-P) = 2.1645(8)$ Å [2e,20]. The Cu–Si bond length in **2** is similar to the 2.345 Å found in $[Cu(SiR_3)(PPh_3)_2]$ [21] which like **2** has the Cu and Si atoms in a 3- and 4-coordination environment, respectively.

2.3. The noble metal(I) iodide-bridged bis(lithium 3-sila-β-diketimate) $[M\{Si(R)(C(Ar)N(R))_2Li\}_2(\mu-I)]$ [$M = Ag$ (3**), Au (**4**)]**

The green (**3**) and the yellow (**4**) crystalline title compounds were obtained (Scheme 2) from the appropriate $[MI(PPh_3)_n]$ ($M = Ag$, $n = 3$; $M = Au$, $n = 2$) and two equivalent portions of the lithium compound **B** in toluene. When the silver reaction was carried out using an equimolar portion of the two reagents, approximately one half of the unreacted $[AgI(PPh_3)_3]$ was recovered. A freshly prepared sample of **3** or **4** in C_6D_6 gave 1H NMR spectra showing the appropriate relative intensities for signals corresponding to the ligand; and the ^{29}Si spectra of **3** revealed coupling of the ^{29}Si nucleus to both ^{107}Ag and ^{109}Ag , as

expected from the molecular structure shown for crystalline **3**.

The crystalline complexes **3** and **4** are isomorphous. Their molecular structure is illustrated for the gold complex **4** in Fig. 3. The framework tricyclic structure is shown in Fig. 4. It is composed of a ten-membered C(1)–N(1)–Li(2)–I–Li(1)–N(3)–C(28)–Si(5)–M–Si(1) (M = Ag, Au) ring having [C(13)–N(2)] and [C(40)–N(4)] bridges to the atom pairs [Si(1), Li(2)] and [Si(5), Li(1)], respectively. It may be regarded as being an adduct of M–I and two $[Li\{N(R)C(Ar)_2SiR\}]$ moieties in which the Li(1) and Li(2) atoms are bridged by an I atom, while the noble metal atom M bridges the atoms Si(1) and Si(5). Average geometrical parameters for these two moieties are listed in Table 3 together with corresponding data for $[Li\{N(R)C(Ar)_2-$

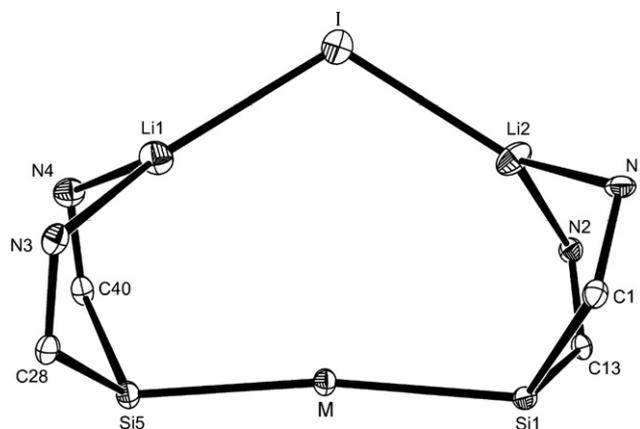


Fig. 4. The core structure of complexes **3** and **4** (M = Ag, Au).

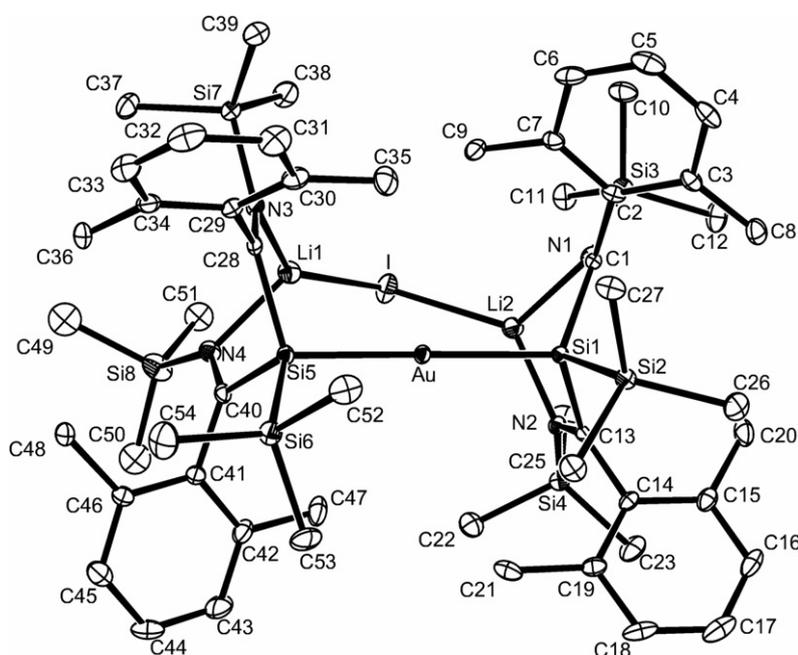


Fig. 3. ORTEP diagram of the molecular structure of **4** with thermal ellipsoids drawn at 20% probability level.

Table 3
Selected geometric parameters for the $[\text{Li}\{(\text{N}(\text{R})\text{C}(\text{Ar})_2\text{SiR})\}]$ moiety of **3**, **4** and $[\text{Li}\{(\text{N}(\text{R})\text{C}(\text{Ar})_2\text{SiR})\}(\text{NCAr})]$ (**L**)

Compound	Average (Li–N) (Å)	Average (N–C) (Å)	Average (C–Si) (Å)	Average (Si–Si) (Å)	Average (Li–N–C) (°)	Average (N–C–Si) (°)	Average (C–Si–Si) (°)	Reference
3	1.996	1.295	1.939	2.380	111.4, 106.2	118.7, 122.1	112.6	This work
4	2.009	1.286	1.966	2.362	110.7, 105.5	118.6, 121.3	113.1	This work
L	1.952	1.307	1.881	2.336	106.2	124.2	115.1	[7]

Table 4
Geometric parameters at the atoms I and M in **3** (M = Ag) and **4** (M = Au)

Compound	Li(1)–I	Li(2)–I	M–Si(1)	M–Si(5)	M···I					
<i>(a) Bond distances (Å)</i>										
3	2.620(9)	2.555(10)	2.4827(13)	2.4883(13)	3.703(1)					
4	2.626(12)	2.549(12)	2.4044(17)	2.4072(17)	4.083(1)					
	I–Li(1)–N(3)	I–Li(1)–N(4)	I–Li(2)–N(1)	I–Li(2)–N(2)	M–Si(1)–C(1)	M–Si(1)–C(13)	M–Si(1)–Si(2)	M–Si(5)–C(28)	M–Si(5)–C(40)	M–Si(5)–Si(6)
<i>(b) Bond angles (°)</i>										
3	139.4(4)	116.0(4)	122.3(4)	126.4(5)	111.71(14)	106.22(14)	109.44(6)	104.61(15)	112.29(15)	108.89(6)
4	144.8(6)	115.7(5)	122.4(6)	132.7(6)	121.01(19)	108.76(19)	106.90(8)	105.84(19)	112.61(19)	106.77(8)

SiR}(NCAr)] (**L**) [7], while parameters associated with the atoms I and Ag (**3**) or Au (**4**) are to be found in Table 4. The Au–Si distance in **4** may be compared with the 2.356(2) Å in $[\text{Au}(\text{SiR}_3)(\text{PMePh}_2)]$ [22]; Ag–Si-containing compounds were not found in the Cambridge Crystallographic Data Base [23]. The Li–I distances (see Table 4) in **3** and **4** are very short with the Li(2)–I distance being close to the value (2.54 Å) reported for the gaseous molecule $[\text{Li}(\mu\text{-I})_2]$ [24] and are much shorter than Li–I (bridging or terminal) distances found in solvated lithium iodide (e.g., 2.822(6) and 2.840(6) Å in $[\text{LiI}(\text{NEt}_3)_4]$ [25], 2.75(3) and 2.67(3) Å in $[\text{LiI}(\text{pmdeta})]$ [26]). Slightly longer (apparently due to the higher Li coordination number) Li–I distances [2.635(10) and 2.721(10) Å] have been found in the copper imidosulfite cluster $[\text{Cu}_3\{(\text{NBu}^t)_3\text{S}\}_2\{\text{Li}(\text{thf})_2(\mu\text{-I})\}]$ [27]. The Ag···I and Au···I distances in **3** and **4**, respectively, are clearly non-bonding, as evident from Table 4 and comparison with the M–I bond lengths in the starting compounds $[\text{AgI}(\text{PPh}_3)_3]$ [2.855(1) and 2.864(1) Å] [28] and $[\text{AuI}(\text{PPh}_3)_2]$ [2.754(1) Å] [29].

In conclusion, the synthesis and structures of the four crystalline Cu^{I} (**1**, **2**), Ag^{I} (**3**) and Au^{I} (**4**) 3-sila- β -diketiminato complexes are described. Whereas in Group 11 metal- β -diketiminato the negative charge of the ligand is π -delocalised, in the $[\{\text{N}(\text{SiMe}_3)\text{C}(\text{C}_6\text{H}_3\text{Me}_2, 2, 6)\}_2\text{Si}(\text{SiMe}_3)]^-$ ligand of **1–4** (as in Li, Na, K, Rb, Mg and Hg^{II} analogues) the 3-silicon atom carries the negative charge.

3. Experimental

3.1. General details

All manipulations were carried out under an inert atmosphere using Schlenk techniques. Solvents were distilled from appropriate drying agents and then degassed. The NMR spectra were recorded at 298 K using a Bruker DPX 300 (300.1 MHz for ^1H , 75.5 MHz for ^{13}C ,

116.2 MHz for ^7Li and 121.5 MHz for ^{31}P) or AMX 500 (99.4 MHz for ^{29}Si , 194.3 MHz for ^7Li) and referenced internally to residual solvent resonances in the case of ^1H and ^{13}C spectra. The ^7Li , ^{29}Si and ^{31}P spectra were referenced externally to LiNO_3 with D_2O lock, SiMe_4 and H_3PO_4 (85% aqueous solution), respectively. Compounds $[\text{MI}(\text{PPh}_3)_3]$ (M = Cu, Ag) were prepared using stoichiometric quantities of the appropriate MI and 3PPh_3 in CH_2Cl_2 [28], while $[\text{AuI}(\text{PPh}_3)_2]$ was obtained from $\text{H}[\text{AuCl}_4]$, KI and 2PPh_3 [30]; the synthesis of $[\text{Li}\{(\text{N}(\text{R})\text{C}(\text{Ar})_2\text{SiR})\}(\text{thf})_2]$ (**B**) was described previously [4,7]. Each of the compounds **1–4** in benzene slowly decomposed yielding a metallic precipitate; **1** and **2** were sufficiently robust to be sent away for microanalysis (Medac Ltd., Brunel University).

3.2. Preparation of $[\text{Cu}\{(\text{N}(\text{R})\text{C}(\text{Ar})_2\text{SiR})\}_2 \cdot (\text{thf})]$ (**1**)

CuI (0.23 g, 1.21 mmol) was added to a stirred solution of $[\text{Li}\{(\text{N}(\text{R})\text{C}(\text{Ar})_2\text{SiR})\}(\text{thf})_2]$ (**B**) (0.81 g, 1.22 mmol) in toluene (30 cm^3). The red mixture was stirred for 1 day, resulting in a brown suspension. Solvent was removed in vacuo. The solid was washed with pentane (ca. 5 cm^3) to leave a green residue, which was extracted into thf (40 cm^3). The orange extract was concentrated (to ca. 5 cm^3) and stored at 5 °C for 1 week to produce yellow crystals of compound **1** (0.64 g, 87%). Anal. Calc. for $\text{C}_{58}\text{H}_{98}\text{Cu}_2\text{N}_4\text{OSi}_8$: C, 57.1; H, 8.10; N, 4.60. Found: C, 57.3; H, 8.19; N, 4.53%.

^1H NMR (C_6D_6): δ 0.04 (s, 18H, NSiMe₃), 0.56 (s, 9H, SiSiMe₃), 1.40 (4H, m, thf), 2.06 (s, 6H, C₆H₃Me₂), 2.28 (s, 6H, C₆H₃Me₂), 3.57 (m, 4H, thf), 6.55 (d, 2H, $J = 7.6$ Hz, $m\text{-H}$), 6.60 (d, 2H, $J = 7.6$ Hz, $m\text{-H}$), 6.82 (t, 2H, $J = 7.6$ Hz, $m\text{-H}$). ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6): δ 1.75 (s, NSiMe₃), 3.95 (s, SiSiMe₃), 21.43 (s, 6H, C₆H₃Me₂), 21.48 (s, 6H, C₆H₃Me₂), 25.96 (s, thf), 67.98 (s, thf), 127.0 (s, $p\text{-C}$), 132.71 (s, $o\text{-C}$), 133.12 (s, $o\text{-C}$), 147.05 (s, $ipso\text{-C}$);

$^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6): δ -28.0 (s, SiSiMe_3), -10.3 (s, SiSiMe_3), 0.82 (s, NSiMe_3); EI-MS (70 eV): m/z (%) 1146 (M^+ , 4), 1073 ($\text{M}^+ - \text{SiMe}_3$, 5).

3.3. Preparation of $[\text{Cu}\{\text{Si}(\text{R})(\text{C}(\text{Ar})\text{N}(\text{R}))_2\text{Li}(\mu\text{-I})\}_2(\text{PPh}_3)]$ (**2**)

The lithium 3-sila- β -diketiminato **B** (0.25 g, 0.38 mmol) in pentane (20 cm^3) was added to a stirred suspension of $[\text{CuI}(\text{PPh}_3)_3]$ (0.37 g, 0.38 mmol) in pentane (30 cm^3). The red mixture was stirred for 1 day. The reaction mixture had turned yellow and a yellow precipitate had formed. Volatiles were removed in vacuo. The residue was dissolved in toluene (100 cm^3); the solution was concentrated (to ca. 50 cm^3) and stored at -5°C for 3 days, yielding light orange crystals of compound **2** ($0.5\text{C}_7\text{H}_8$) (0.35 g, 96%). Anal. Calc. for $\text{C}_{48.5}\text{H}_{64}\text{CuLiN}_2\text{PSi}_4$: C, 57.4; H, 6.35; N, 2.76. Found: C, 57.6; H, 6.65; N, 2.83%. ^1H NMR (C_6D_6): δ -0.29 (s, 9H, SiSiMe_3), 0.09 (s, 18H, NSiMe_3), 2.28 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 2.39 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 6.60 – 6.90 (m, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 6.90 – 7.10 (m, 15H, PPh_3); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6): δ 32.6 [d, $J(\text{SiP}) = 59.8$ Hz, SiSiMe_3], -17.3 (s, SiSiMe_3) -0.42 (s, NSiMe_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ -0.43 .

3.4. Preparation of $[\text{Ag}\{\text{Si}(\text{R})(\text{C}(\text{Ar})\text{N}(\text{R}))_2\text{Li}\}_2(\mu\text{-I})]$ (**3**)

$[\text{AgI}(\text{PPh}_3)_3]$ (1.53 g, 1.50 mmol) was added to a stirred solution of the lithium salt **B** (1.98 g, 2.99 mmol) in toluene

(60 cm^3). The mixture was stirred for 15 h. Volatiles were removed in vacuo. The residue was washed with pentane (ca. 5 cm^3), then dissolved in toluene (ca. 10 cm^3). The green solution was concentrated (to ca. 3 cm^3) and stored at -30°C for 2 days. Grass-green crystals of compound **3** (1.37 g, 72%) were isolated; ^1H NMR (C_6D_6): δ -0.25 (s, 9H, SiSiMe_3), 0.13 (s, 18H, NSiMe_3), 2.30 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 2.42 (6H, s, $\text{C}_6\text{H}_3\text{Me}_2$), 6.71 (d, 2H), 6.79 (d, 2H), 6.89 (t, 2H); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6): δ 23.8 [q, $J(^{29}\text{Si}^{107}\text{Ag}) = 149.29$, $J(^{29}\text{Si}^{109}\text{Ag}) = 172.24$ Hz, SiSiMe_3], 0.80 (s, NSiMe_3), -15.9 (d, $J(\text{SiAg}) = 3.31$ Hz, SiSiMe_3).

3.5. Preparation of $[\text{Au}\{\text{Si}(\text{R})(\text{C}(\text{Ar})\text{N}(\text{R}))_2\text{Li}\}_2(\mu\text{-I})]$ (**4**)

$[\text{AuI}(\text{PPh}_3)_2]$ (0.78 g, 0.92 mmol) was added to a stirred solution of the lithium salt **B** (1.21 g, 1.83 mmol) in toluene (60 cm^3). The mixture was stirred for 15 h. Volatiles were removed in vacuo. The residue was washed with pentane (ca. 5 cm^3), then dissolved in toluene (ca. 10 cm^3). The yellow solution was concentrated (to ca. 3 cm^3) and stored at -30°C for 2 days. Yellow crystals of compound **4** (0.81 g, 65%) were isolated. ^1H NMR (C_6D_6): δ -0.17 (s, 9H, SiSiMe_3), 0.21 (s, 18H, NSiMe_3), 2.13 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 2.67 (6H, s, $\text{C}_6\text{H}_3\text{Me}_2$), 6.76 (d, 2H, $J = 7.3$ Hz, $m\text{-H}$), 6.86 (d, 2H, $J = 7.3$ Hz, $m\text{-H}$), 6.95 (t, 2H, $J = 7.5$ Hz, $p\text{-H}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 1.32 (s, SiSiMe_3), 1.46 (s, NSiMe_3), 21.7 (s, $\text{C}_6\text{H}_3\text{Me}_2$), 23.6 (s, $\text{C}_6\text{H}_3\text{Me}_2$), 127.6 (s, $p\text{-C}$), 127.8 (s, $m\text{-C}$), 128.2 (s, $m\text{-C}$), 131.0 (s, $o\text{-C}$), 133.4 (s, $o\text{-C}$), 148.0 (s, $ipso\text{-C}$), 221.4 ($\text{N}=\text{C}\text{-Ar}$); $^7\text{Li}\{^1\text{H}\}$

Table 5
Crystallographic data and refinement parameters for complexes **1–4**

Compound	1	2	3	4
Empirical formula	$\text{C}_{54}\text{H}_{90}\text{Cu}_2\text{N}_4\text{Si}_8 \cdot (\text{C}_4\text{H}_8\text{O})$	$\text{C}_{45}\text{H}_{60}\text{CuLiN}_2\text{PSi}_4 \cdot 0.5(\text{C}_7\text{H}_8)$	$\text{C}_{54}\text{H}_{90}\text{AgI}_2\text{N}_4\text{Si}_8$	$\text{C}_{54}\text{H}_{90}\text{AuLi}_2\text{N}_4\text{Si}_8$
Formula weight	1219.20	1015.73	1268.67	1357.77
Crystal size (mm)	$0.25 \times 0.25 \times 0.10$	$0.4 \times 0.4 \times 0.3$	$0.4 \times 0.2 \times 0.2$	$0.4 \times 0.3 \times 0.3$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
<i>Unit cell dimensions</i>				
a (Å)	25.5037(11)	17.7212(3)	21.7677(9)	21.6689(10)
b (Å)	14.2252(4)	11.8240(2)	16.2573(7)	16.2254(8)
c (Å)	20.1496(9)	25.1970(4)	20.5227(6)	20.6837(7)
β (°)	111.005(2)	90.374(1)	110.619(2)	110.760(2)
V (Å ³)	6824.4(5)	5279.55(15)	6797.4(5)	6800.0(5)
Z	4	4	4	4
D_{calc} (Mg m^{-3})	1.109	1.28	1.24	1.33
Absorption coefficient (mm^{-1})	0.80	1.15	0.93	2.79
Reflections collected	18780	42833	27486	24591
Independent reflections (R_{int})	5993 (0.059)	15207 (0.046)	11877 (0.082)	14685 (0.057)
Reflections with $[I > 2\sigma(I)]$	4964	12482	9044	10496
Data/restraints/parameter	5993/0/349	15207/0/523	11877/30/562	14685/30/652
Goodness-of-fit on F^2	1.033	1.140	1.029	1.028
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.043$, $wR_2 = 0.106$	$R_1 = 0.067$, $wR_2 = 0.154$	$R_1 = 0.060$, $wR_2 = 0.149$	$R_1 = 0.053$, $wR_2 = 0.112$
R indices (all data)	$R_1 = 0.056$, $wR_2 = 0.114$	$R_1 = 0.082$, $wR_2 = 0.160$	$R_1 = 0.082$, $wR_2 = 0.165$	$R_1 = 0.090$, $wR_2 = 0.130$
Largest difference in peak and hole ($\text{e} \text{ \AA}^{-3}$)	0.55 and -0.46	1.27 and -1.06	1.32 and -1.41 (near Ag)	1.08 and -2.21 (near Au)

NMR (C_6D_6): δ 2.54; $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 7.31 (s, $SiSiMe_3$), 2.18 (s, $NSiMe_3$) –14.79 (s, $SiSiMe_3$).

3.6. X-ray crystallographic studies

Diffraction data for compounds **1–4** were collected on an Enraf-Nonius Kappa CCD diffractometer using monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ at 173(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. For **1** the $Si(2)Me_3$ group is disordered and the thf molecule is disordered across a twofold axis and was included as isotropic C atoms without H atoms. For **2** there is a molecule of toluene solvate disordered across an inversion centre which was included with isotropic C atoms, distance restraints, and H atoms omitted. For **4** the disordered $Si(8)Me_3$ group was refined with isotropic C atoms and distance constraints. The crystal **3** is isomorphous with **4**. Absorption corrections were applied using MULTISCAN and refinement using SHELXL-97 [31]. Further details are given in Table 5.

4. Note added in proof

Two Au(I) β -dialdiminates, analogues of **K**, have recently been reported by Dias and Flores [32].

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Appendix A. Supplementary material

CCDC 648094, 648095, 648096 and 648097 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article (which also contains characterisation of $[Cu\{(N(Ar)C(H))_2CPh\}(PPh_3)]$). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.07.012](https://doi.org/10.1016/j.jorganchem.2007.07.012).

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