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# Spectroscopic and electronic properties of 1-azaallylmetal(I) (M = Cu or Au) complexes; molecular structure of [{Au[μ-N(R)-C(Ph)CR$_2$]}$_2$] (R = SiMe$_3$)

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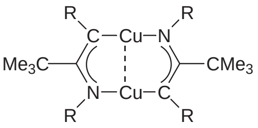
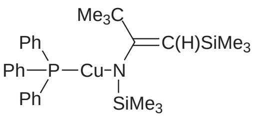
The reaction of [Li{N(R)C(Ph)CR$_2$}(thf)] (R = SiMe$_3$) with CuI or [AuCl(SMe$_2$)] gave the stable metal complexes [{M[μ-N(R)C(Ph)CR$_2$]}$_2$] (M = Cu or Au) which were fully characterised by multinuclear NMR spectroscopy, mass spectrometry, microanalysis and for M = Au X-ray diffraction. Their spectroscopic and electrochemical properties are compared with the related copper complexes [{Cu[μ-N(R)C(Bu$^t$)C(H)R]}$_2$], [Cu{N(R)C(Bu$^t$)=C(H)R}(PPh$_3$)] and [Li(dme)$_3$][Cu{N(R)C(Bu$^t$)=C(H)R}$_2$].

We recently reported the synthesis and molecular structures of the new 1-azaallyl copper(I) complexes [{Cu[μ-N(R)C(Bu$^t$)C(H)R]}$_2$] **1**, [Cu{N(R)C(Bu$^t$)=C(H)R}(PPh$_3$)] **2** and [Li(dme)$_3$][Cu{N(R)C(Bu$^t$)=C(H)R}$_2$] **3**,[1] which were readily accessible from CuI and [{Li[μ-N(R)C(Bu$^t$)C(H)R]}$_2$][2] (R = SiMe$_3$); particular features of interest were the low coordination number at the copper atom and in the case of **1** a clearly visible fluorescence.



**1**



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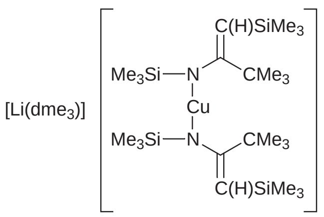
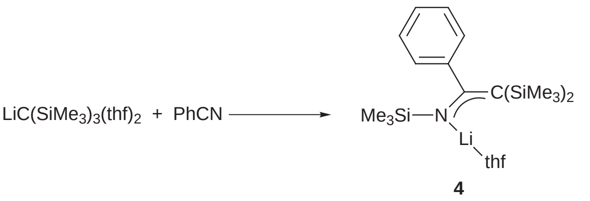


**3**

We have also drawn attention to the new lithium 1-azaallyl [Li{N(R)C(Ph)CR$_2$}(thf)] **4** which was obtained from LiCR$_3$(thf)$_2$[3] and one equivalent of PhCN [eqn. (1)].[4]



(1)

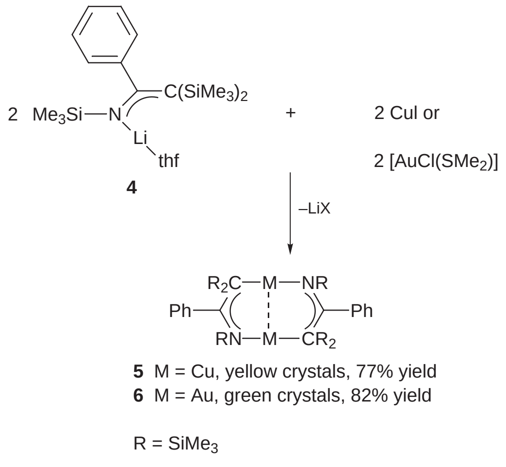
**4**

[Li{N(R)C(Ph)CR$_2$}(thf)] **4** ([N(R)C(Ph)CR$_2$]$^-$ ≡ [LL′]$^-$) was shown to be a useful precursor for a series of novel Group 14 element(II) 1-azaallyls M(Cl)[LL′] and M[LL′]$_2$ (M = Sn or Pb);[4,5] the latter were unusual in having one ligand coordinated in an η$^1$-enamido and the other in an η$^3$ 1-azaallyl fashion. The compounds Li[LL′](thf) **4** and a series of related *p*-phenyl-substituted lithium 1-azaallyls were also of interest as precursors for the synthesis of trimethylsilyl aryl acetylenes.[6]

This paper is concerned with (i) the use of the ligand [LL′]$^-$ in the context of Group 11 metal chemistry and (ii) an investigation of the spectroscopic and electronic properties of the new products as well as the copper(I) 1-azaallyls **1**–**3**.

## Results and discussion

The reaction of Li[LL′](thf) **4** with CuI or [AuCl(SMe$_2$)][7] led, after recrystallisation from pentane, in high yield to the yellow compound Cu[LL′] **5** or the dark green [{Au(μ-LL′)}$_2$] **6**, respectively, Scheme 1. The properties of **5** and **6** were similar to those of the related copper complex **1**, as demonstrated by their high thermal stability (stable up to *ca.* 163 °C for **5** or 146 °C for **6**), their fragmentation pattern in the MS (both compounds showed signals for the dimeric formula unit) and the molecular structure of **6** which was shown by single crystal X-ray diffraction to consist of individual bridged dimers, similar to those in crystalline **1**.



**Scheme 1** Preparation of **5** and **6**.

The characteristic $^{13}$C NMR spectroscopic shift values[4,5] for CSi$_2$ of $\delta = 57.9$ (**5**, M = Cu) and $\delta = 46.6$ (**6**, M = Au) and for CN of $\delta = 205.4$ (**5**) or $\delta = 205.6$ (**6**) indicated that both compounds adopted in solution a configuration similar to that

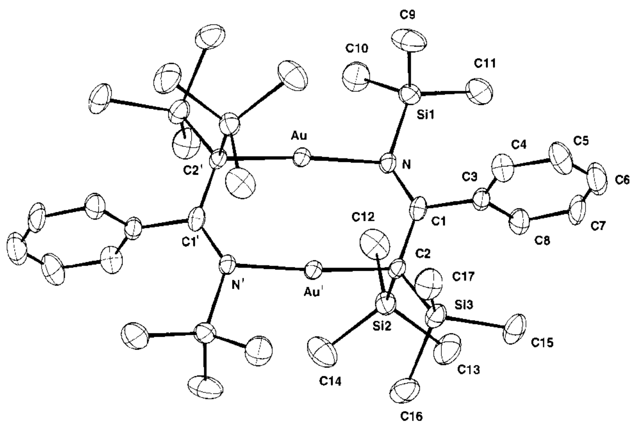


**Fig. 1** Molecular structure of complex **6**.

**Table 1** Selected bond distances (Å) and angles (°) of complex **6**

| | | | |
|---|---|---|---|
| Au–N | 2.099(5) | Au–C(2′) | 2.104(6) |
| Au···Au′ | 2.6887(8) | Si(1)–N | 1.799(5) |
| Si(2)–C(2) | 1.920(7) | Si(3)–C(2) | 1.895(6) |
| N–C(1) | 1.297(8) | C(1)–C(2) | 1.490(9) |
| C(1)–C(3) | 1.497(9) | | |
| N–Au–C(2′) | 173.0(2) | C(1)–N–Si(1) | 128.8(5) |
| C(1)–N–Au | 122.1(4) | Si(1)–N–Au | 109.2(3) |
| N–C(1)–C(2) | 126.7(6) | N–C(1)–C(3) | 116.1(6) |
| C(3)–C(1)–C(2) | 117.2(5) | C(1)–C(2)–Si(2) | 108.4(4) |
| Si(3)–C(2)–Si(2) | 115.0(2) | C(1)–C(2)–Si(3) | 117.7(5) |
| C(1)–C(2)–Au′ | 112.0(4) | Si(2)–C(2)–Au′ | 101.5(3) |

Primed atoms are related to unprimed ones by the symmetry transformations $-x + 1, -y, -z$.

found in the solid state for **6** (see below), the ligands being arranged in an η$^2$-bridging fashion. Similar NMR spectroscopic values were observed for [{Cu[μ-N(R)C(Bu$^t$)C(H)R]}$_2$] **1**, but while the latter was found to exist in solution as a mixture of two isomers (*cis* and *trans* with respect to the orientation of the trimethylsilyl groups in the two individual ligands of the dimer), **5** and **6** showed only signals for a single isomer.

Attempts to prepare the corresponding silver complex Ag[LL′] in a similar way from [AgI(PMe$_3$)] and Li[LL′] in thf failed, but we were able to obtain the related thallium compound Tl[LL′] **7** as yellow crystals from TlCl and the lithium starting material **4**. Compound **7** was extremely air- and light-sensitive and decomposed, probably auto-catalytically, during an attempt to recrystallise **7** to remove some traces of Tl metal.

## Molecular structure of [{Au[μ-LL′]}$_2$] 6

The molecular structure of **6** with the atomic numbering scheme is illustrated in Fig. 1. Selected bond distances and angles are listed in Table 1.

The crystalline complex [{Au[μ-LL′]}$_2$] **6** is a centrosymmetric dimer in which the [LL′]$^-$ ligand acts in a bridging mode and thereby forms a distorted six-membered ring (excluding Au atoms) in chair conformation. The plane of the aromatic ring forms an angle of 68.2° to the plane defined by the atoms N, C(1) and C(2). Each Au atom is symmetrically placed between two ligands, as is evident from the essentially identical Au–N and Au–C(2′) bond distances of 2.099(5) and 2.104(6) Å, respectively, and the approximately linear coordination of the Au atom, C(2′)–Au–N 173°. The short N–C(1) and long C(1)–C(2) bond distances of 1.297(8) and 1.490(9) Å, respectively, in the backbone of the ligand indicate that the complex is closer to being a metal iminoalkyl than an enamide. This is consistent with the solution NMR spectral shift values (see above) and similar to observations made for the related complexes **1** or [Au{μ-CR$_2$(C$_5$H$_4$N)}$_2$],[8] but contrasts with data on complexes such as M(Cl)[LL′] and M[LL′]$_2$ (M = Sn, Pb),[4] in which [LL′]$^-$ behaved as an η$^3$-azaallyl or η$^1$-enamido ligand.

Table 2 summarises some important structural parameters of **6** and compares them with those for the related complexes [{Au[μ-CR$_2$(C$_5$H$_4$N)]}$_2$],[8] and [{Au[μ-N(R)C(Ph)NR]}$_2$],[9] which have similar geometries to **6**. It is interesting that the related metal complex [{Au[μ-N(Ph)NN(Ph)]}$_4$] is tetrameric,[10] while its copper analogue is a dimer.[11]

Closed shell d$^{10}$–d$^{10}$ interactions between heavy metals have been of considerable interest for theoreticians and synthetic chemists for many years and the subject has recently been reviewed.[12] Gold is seen as one of the prototypes for such interactions and experimental support comes from compounds such as [{Au[μ-(CH$_2$)$_2$PPh$_2$]}$_2$],[13] [Au(Cl)P(C$_6$H$_2$Bu$^t_3$-2,4,6)H$_2$],[14] Me$_3$P=C[P(Ph$_2$)AuCl]$_2$[15] or Se[Au(PPh$_3$)]$_2$[16] (see also refs. 12 and 17).

The case of bridging ligands such as [LL′]$^-$ or [CR$_2$(C$_5$H$_4$N)]$^-$ is more difficult to evaluate as the bite of the ligand brings the metals in close contact to one another, independent of d$^{10}$–d$^{10}$ interactions. This is evident from the fact that the Au···Au contacts of 2.65–2.69 Å in the examples summarised in Table 2 are comparatively short (*cf.*, the distance in gold metal is 2.89 Å,[18] while Au···Au interactions are discussed for distances in the wider range of 2.5 to 3.2 Å[17]). Furthermore, in these examples the widening of the angle of the sp$^2$-hybridised central carbon atom in the backbone of the ligands from 120° to a maximum of nearly 127° in **6** indicates a slightly repulsive interaction between the metal atoms which is not observed in the case of the related copper complexes [{Cu[μ-N(R)C(Bu$^t$)C(H)R]}$_2$] **1** [119.6(5)°][1] and [{Cu[μ-CR$_2$(C$_5$H$_4$N)]}$_2$] [120.5(2)°].[8]

## Spectroscopic and electronic properties

Spectroscopic and electrochemical investigation on these compounds was motivated by the very obvious fluorescence of the present dinuclear copper complexes and reports on the luminescence properties of related d$^{10}$–d$^{10}$ binuclear metal (M) complexes (M = Cu$^+$, Ag$^+$, Au$^+$) with weak to medium M···M interactions.[15,19] Also relevant is the fact that in some multi-electron redox enzymes, such as nitrous oxide reductase[20] and cytochrome c oxidase[21] the electron transfer sites are considered to be pairs of copper ions with copper–copper separations of 2.5–2.6 Å.[22]

## Electrochemistry

The ability of the compounds **1**, **2**, **4**, **5** and **6** to take up or lose electrons was investigated using cyclic voltammetry, square-wave voltammetry and quantitative chronocoulometry and chronoamperometry. Compound **3** was not examined due to its sensitivity to traces of moisture in the solvent. At 298 K, each of the copper complexes **1** and **2** showed an irreversible reduction wave at *ca.* −3.2 V (Table 3). Compounds **4**–**6** exhibited two irreversible reduction waves at markedly lower potentials than for **1** or **2**. The potential of the first reduction increased in the series **4** < **5** < **6**. At 243 K, the dinuclear copper compound **1** exhibited re-oxidation waves for both the first and the second reduction reaction. The peak-to-peak separations ($\Delta E_{pp}$) were 96 mV for the first and 199 mV for the second. Hence at a lower temperature a rapid chemical reaction which follows the electron uptake is slowed down to such a degree as to make the first reduction partly reversible.

The electrochemical oxidation of the copper complexes **1** and **2** appeared to be irreversible with slightly lower potential for the dinuclear compound **1**. The copper compound **5** exhibited an irreversible oxidation wave at 0.47 V when measured in thf solution at 298 K followed by a second irreversible oxidation wave. At 243 K the first oxidation wave appeared to be much more reversible ($\Delta E_{pp}$ = 112 mV). When measured in CH$_2$Cl$_2$ solution, the first oxidation at +0.27 V ($\Delta E_{pp}$ = 84 mV) appeared to

**Table 2** Selected bond distances (Å) and angles (°) of complex **6** and two related compounds

| Compound | Au···Au | Au–N | Au–C(N) | C–N | C–C(N) | N–Au–C | N–C–C(N) |
|---|---|---|---|---|---|---|---|
| **6** | 2.6887(8) | 2.099(5) | 2.104(6) | 1.297(8) | 1.490(9) | 173.0(2) | 126.7(6) |
| [{Au[μ-N(R)C(Ph)NR]}$_2$] | 2.646(2) | 2.060(8) | 2.060(8) | 1.30(1) | 1.34(1) | 170.0(4) | 126.3(8) |
| [{Au[μ-CR$_2$(C$_5$H$_5$N)]}$_2$] | 2.672(1) | 2.08(1) | 2.09(1) | 1.39(2) | 1.49(2) | 176.3(5) | 124(1) |

**Table 3** Electrochemical data[a]

| Compound | $E_{pa}$oxII[b] | $E_{\frac{1}{2}}$oxI ($\Delta E_p$)[c] | $E_{\frac{1}{2}}$redI ($\Delta E_p$)[c] | $E_{\frac{1}{2}}$redII ($\Delta E_p$)[c] | $E_{pc}$[d] redIII | Solvent, temperature/K |
|---|---|---|---|---|---|---|
| **1** | — | 0.61[b] | −3.19[d] | — | — | thf, 298 |
| **2** | — | 0.81[b] | −3.20[d] | — | — | thf, 298 |
| **4** | 1.36 | 0.66[b] | −2.97[d] | −3.13[d] | — | thf, 298 |
| **5** | 0.81 | 0.47[b] | −2.92[d] | −3.09[d] | — | thf, 298 |
| **5** | 0.83 | 0.45 (112) | −2.91 (96) | −3.06 (199) | −3.55 | thf, 268 |
| **5** | 1.23 | 0.27 (84) | — | — | — | CH$_2$Cl$_2$, 298 |
| **6** | 1.13 | 0.46 (89) | −2.77[d] | −2.90[d] | −3.15 | thf, 298 |
| **6** | 1.15 | 0.28 (82) | — | — | — | CH$_2$Cl$_2$, 298 |

[a] From cyclic voltammetry in 0.1 M [NBu$_4$][PF$_6$] solutions at 100 mV s$^{-1}$ scan rate. Potentials in V *vs.* ferrocene–ferrocenium couple. [b] Anodic peak potentials $E_{pa}$ for irreversible oxidation. [c] Half-wave potentials $E_{\frac{1}{2}}$, peak potential differences $\Delta E_p = E_{pa} - E_{pc}$ in mV (in parentheses). [d] Cathodic peak potential $E_{pc}$ for irreversible reduction.

be reversible, whereas the second was still irreversible. The number of electrons for the first oxidation process was determined to be unity, using a square-wave voltammogram of combined weighed samples of the complex **5**, ferrocene and [Co(η-C$_5$H$_5$)$_2$][PF$_6$]. The $\Delta E_{pp}$ of the three samples, all being in the same range, leads to the conclusion that there is only one electron involved and thus that the reaction leads to a Cu(I)/Cu(II) mixed-valent species. This contrasts with the findings on the related complex [{Cu[μ-CR$_2$(C$_5$H$_4$N)]}$_2$] (R = SiMe$_3$),[8] where both Cu(I) centres were oxidised independently at the same potential yielding a Cu(II)/Cu(II) species. The behaviour of the copper complex **5** is similar to the reported examples of related dinuclear copper complexes formed by aza-macrocyclic ligands which favour the formal valencies Cu(I)/Cu(I), Cu(II)/Cu(II) and quite stable mixed-valent states Cu(I)/Cu(II).[23,24] The gold compound **6** showed a reversible wave at +0.28 V in CH$_2$Cl$_2$ solution; the number of electrons was close to unity, determined measuring a square-wave voltammogram of combined weighed samples of the complex and ferrocene. The quantitative method described by Baranski *et al.*,[25] using chronocoulometric and chronoamperometric experiments gave 0.98 electrons to be involved in the first oxidation process of **6**. Assuming a metal-centred oxidation reaction, this step thus leads to a Au(I)/Au(II) mixed-valent species. The second oxidation reaction for **6** occurred irreversibly at +1.15 V. Using the simple eqn. (2) and the difference between these two oxidation

$$K_C = 10^{\Delta E/59\ \mathrm{mV}} = [\mathrm{M}^{(n+1)}]^2/[\mathrm{M}][\mathrm{M}^{(n+2)}]$$

$$\mathrm{M} + \mathrm{M}^{(n+2)} = 2\,\mathrm{M}^{(n+1)} \qquad (2)$$

potentials (although the second is irreversible), the comproportionation constant of **6**$^{+\bullet}$ can be calculated as $K_C = 10^{14.8}$ (in CH$_2$Cl$_2$) or $10^{11.24}$ (in thf). For the copper complex (**5**$^{+\bullet}$), the calculation yields $K_C = 10^{16.3}$ (in CH$_2$Cl$_2$) or $10^{6.44}$ (in thf) for the mixed-valent species Cu(I)/Cu(II).

From the electrochemical experiments, we conclude that electron-uptake takes place in an orbital that is mainly centred on the azaallyl ligand. This is supported by the fact that the electron-withdrawing phenyl substituent facilitates the electron uptake leading to less negative potentials for analogous complexes. Thus, the change from **1** to **2** does not influence the reduction potential. The one-electron oxidation reactions take place at the metal centres, leading to mixed valent M$^+$/M$^{2+}$ species that seem to be more stable for the systems **5** and **6** bearing the phenyl substituent on the ligand than for the *tert*-butyl analogue **1**. Very striking is the role of the solvent. It seems that the donor capacity of tetrahydrofuran has a strong influence on the electronic properties of the dinuclear compounds.

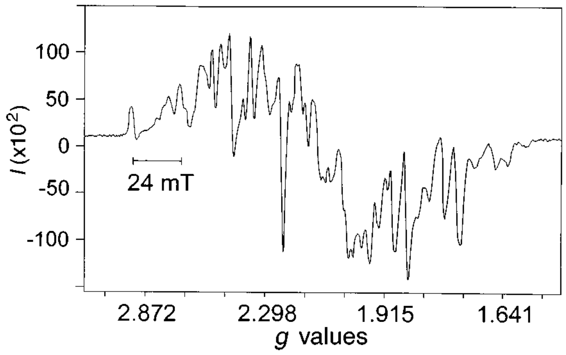


**Fig. 2** ESR spectrum of **6**$^{+\bullet}$ generated by *in situ* electrolysis in CH$_2$Cl$_2$–[NBu$_4$][PF$_6$] solution, measured at 3.3 K in a glassy frozen solution at X-band frequency.

## ESR Spectroscopy on 5$^{+\bullet}$ and 6$^{+\bullet}$

The copper compound **5** and the gold compound **6** were further investigated by ESR spectroelectrochemical experiments. *In situ* electrochemical oxidation and measurements at temperatures between 298 K (in fluid solution) and 110 K (in glassy frozen solution) gave no detectable signal for the generated paramagnetic compounds **5**$^{+\bullet}$ or **6**$^{+\bullet}$. On cooling to 3.3 K, we obtained unsymmetrical and complex spectra as shown for **6**$^{+\bullet}$ in Fig. 2. The large spectral width of about 2000 G clearly indicates the presence of an essentially metal-localised unpaired electron. Further studies in the high field regime (Q-band or W-band) may yield the Hamiltonian parameters (*g* and *A*).

## UV/Vis Absorptions, excitation and emission

The dinuclear compounds **1**, **5** and **6** exhibited not only quite similar absorption spectra but also showed emission at ambient temperature in fluid solution. The absorption spectra showed intense bands in the UV region and long-wavelength bands in the visible-to-near-UV region. By comparison with the spectrum of the free ligand **4** ($\lambda_{max}$ = 279 nm), the latter bands are assigned to intraligand π–π* transitions with in part an admixture of metal d orbitals.[19a] Two bands were discernible for the dinuclear copper complexes, one for the gold compound **6**; none showed marked sensitivity to the solvent polarity (solvatochromy). For the mononuclear copper compound **2**, no such

**Table 4** Absorption, excitation and emission maxima (nm) of azaallyl complexes[a]

| | Absorption | | | | |
|---|---|---|---|---|---|
| Compound | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | Excitation[b] | Emission[c] |
| **1** | 260 (38430) | 318 (31440) | 410 (24420) | 285sh, 390 | 489 [410] (20450) |
| **2** | 257 (38960) | 275sh (36460) | 335sh (29850) | — | — |
| **4** Li[LL′](thf) | 279 (35870) | | | — | — |
| **5** Cu[LL′] | 245 (40870) | 327 (30630) | 396 (25270) | 296sh, 340, 398 | 508 [400] (19690) |
| **6** [{Au[μ-LL′]}$_2$] | 249 (40200) | 294sh (33990) | 412 (24225) | 327sh, 347, 408 | 526 [420] (19010) |

[a] Absorption measured in heptane solution; the most intense bands are underlined; values in parentheses are given in cm$^{-1}$. [b] Excitation spectrum for the given emission band. [c] Excitation wavelength [in square brackets].

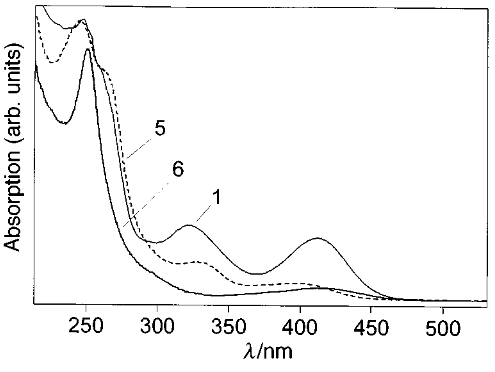


**Fig. 3** UV/Vis absorption spectra of **1**, **5** (dashed line), and **6** in heptane solution at 298 K.

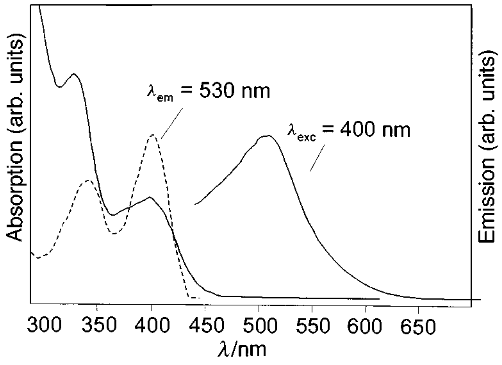


**Fig. 4** UV/Vis absorption, emission and excitation (dashed) spectra of **5** in heptane solution at 298 K.

long-wavelength bands were found. The data are summarised in Table 4 and illustrated in Figs. 3 and 4.

The dinuclear compounds **1**, **5** and **6** exhibited luminescence at ambient temperature in fluid solution. They each showed a single broad band when excited at wavelengths at the low-energy edge of the long wavelength absorption maximum. The maxima increased in the series **1** < **5** < **6**. The large Stokes shifts of 4000–5500 cm$^{-1}$ make an assignment of emission from an excited triplet state (phosphorescence) likely; measurements of the emission lifetimes may confirm this. The corresponding excitation spectra were also taken; the observed bands fit very well with the long-wavelength absorption bands. Neither for the mononuclear copper complex **2**, nor for the Li complex **4**, was emission observed. Hence this property, as well as the appearance of a long-wavelength transition in the visible region, must be attributed to the metal–metal contact in the dinuclear compounds. This is in accord with the few examples of copper[19a,c,23] and gold[19d] dimeric compounds where such long-wavelength absorptions and/or emissive behaviour were observed.

Further investigations should focus on the origin of these low-energy transitions by more sophisticated emission experiments or resonance Raman spectroscopy.[23] Spectroelectrochemical experiments are required to search for spectroscopic evidence for the mixed-valent species, *e.g.*, in order to locate inter-valence charge-transfer bands.[24]

## Experimental

All manipulations were carried out under argon using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. The NMR spectra were recorded in $C_6D_6$ or $C_7D_8$ at 298 K using the following Bruker instruments: DPX 300 ($^1$H, 300.1; $^{13}$C, 75.5 MHz) and AMX 500 ($^1$H, 500.1; $^{13}$C, 125.7 MHz) and referenced internally to residual solvent resonances (data in δ). Unless otherwise stated, all NMR spectra other than $^1$H were proton-decoupled. Electron impact mass spectra were from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected. Elemental analyses were determined by Medac Ltd., Brunel University, Uxbridge, UK.

UV/Vis/NIR absorption spectra were recorded on a Bruins Instruments Omega 10 instrument. A Perkin-Elmer fluorescence spectrometer LS-3B served to record emission spectra. Cyclic voltammetry and square-wave voltammetry measurements were carried out using a three-electrode configuration (glassy carbon working electrode, platinum counter electrode and Ag–AgCl reference electrode) and a PAR 273 potentiostat and function generator with PAR M270/250 software. The ferrocene–ferrocenium couple was used as internal standard. ESR spectra were recorded in the X-band mode on a Bruker ESP 300 system equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. Paramagnetic species were generated using a platinum two-electrode capillary for *in situ* electrolysis.

### Syntheses

**[{Cu[μ-N(R)C(Ph)CR$_2$]}$_2$] 5.** A solution of [Li{N(R)C(Ph)-CR$_2$}(thf)] (1.26 g, 3.0 mmol) in pentane (30 cm$^3$) was added dropwise at −30 °C to a suspension of CuI (0.58 g, 3.0 mmol) in $Et_2O$ (30 cm$^3$); the reaction mixture was stirred at room temperature for a further 2.5 h and all volatiles were removed *in vacuo*. Extraction of the residue with pentane (60 cm$^3$), filtering and concentration of the filtrate gave upon cooling yellow crystals of **5** (0.92 g, 76%). A second crop of crystals (0.27 g, 22%) was isolated from the mother liquor, mp 163 °C (decomp.) (Found C, 51.4; H, 8.36; N, 3.58. $C_{17}H_{32}CuNSi_3$ requires C, 51.0; H, 8.56; N, 3.50%); mass spectrum: *m*/*z* (%) 796 (25 [M]$^+$), 781 (10 [M − Me]$^+$), 719 (6 [M − Ph]$^+$), 382 (25 [M$_{1/2}$ − Me]$^+$); $^1$H NMR ($C_6D_6$): δ 0.06 [s, NSiMe$_3$], 0.41 [s, SiMe$_3$], 6.96–6.98 [Ph, 3H], 7.15–7.18 [Ph, 2H]; $^{13}$C NMR ($C_6D_6$): δ 3.5 [s, NSiMe$_3$], 6.5 [s, C(SiMe$_3$)$_2$], 57.9 [s, CSi$_2$], 127.6, 127.8 and 128.4 [s, Ph], 146.0 [s, *ipso*-C], 205.4 [s, CN].

**[{Au[μ-N(R)C(Ph)CR$_2$]}$_2$] 6.** Solid [AuCl(SMe$_2$)] (0.40 g, 1.36 mmol) was added to a solution of [Li{N(R)C(Ph)-CR$_2$}(thf)] (0.57 g, 1.36 mmol) in pentane (25 cm$^3$) at −60 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. All volatiles were removed *in vacuo* and the residue was extracted with pentane (40 cm$^3$) and filtered. The yellow filtrate was concentrated and cooled to −30 °C to give green crystals of **6** (0.44 g, 61%). A second crop of crystals (0.16 g, 22.2%) was isolated from the mother liquor, mp 146 °C (decomp.) (Found: C, 38.1; H, 5.99; N, 2.57. $C_{17}H_{32}AuNSi_3$ requires C, 38.4; H, 6.07; N, 2.63%); mass spectrum: *m*/*z* (%) 1062 (4 $[M]^+$), 1047 (1.6 $[M - Me]^+$); $^1$H NMR ($C_6D_6$): $\delta$ 0.11 [s, $NSiMe_3$], 0.45 [s, $SiMe_3$], 6.90–6.94 [Ph, 3H], 7.12–7.15 [Ph, 2H]; $^{13}$C NMR ($C_6D_6$): $\delta$ 3.1 [s, $NSiMe_3$], 6.2 [s, $C(SiMe_3)_2$], 46.6 [s, $CSi_2$], 126.9, 128.2 and 128.6 [s, Ph], 148.0 [s, *ipso*-C], 205.6 [s, CN].

**Tl[N(R)C(Ph)CR$_2$] 7.** To a suspension of TlCl (0.36 g, 1.5 mmol) in pentane (30 cm$^3$) was added solid [Li{N(R)C(Ph)CR$_2$}(thf)] at −50 °C. The mixture was allowed to warm to room temperature, thf (20 cm$^3$) was added and then stirred for 14 h to give a yellow solution with an off-white precipitate. The solvent was removed *in vacuo* to give a yellow light-sensitive residue. Extraction with pentane and filtration, followed by cooling of the filtrate gave **7** (0.45 g, 56%) as yellow, extremely air- and light-sensitive crystals, which prevented the obtaining of a mass spectrum or elemental analysis. $^1$H NMR ($C_6D_6$): $\delta$ 0.04 (s, $NSiMe_3$), 0.07 (s, $SiMe_3$), 7.00–7.12 (m, Ph). An attempt to recrystallise the sample from thf led to immediate deposition of Tl metal.

### Crystal data and refinement details

$C_{34}H_{64}Au_2N_2Si_6$, $M = 1063.35$, monoclinic, $a = 10.087(7)$, $b = 17.602(5)$, $c = 13.092(3)$ Å, $\beta = 108.78(3)°$, $U = 2201(2)$ Å$^3$, $T = 293$ K, space group $P2_1/c$ (no. 14), $Z = 2$, $D_c = 1.61$ Mg m$^{-3}$, $\mu$(Mo-K$\alpha$) = 6.85 mm$^{-1}$, $R1 = 0.034$ for 2932 reflections with $I > 2\sigma(I)$, $wR2 = 0.072$ for all 3855 unique reflections.

Data were collected on an Enraf-Nonius CAD4 diffractometer using monochromated Mo-K$\alpha$ radiation ($\lambda$ 0.71073 Å). Crystals of **6** were sealed in a Lindemann capillary under argon. Cell dimensions were calculated from the setting angles for 25 reflections with $7 < \theta < 10°$. Intensities were measured by an $\omega$–$2\theta$ scan. Corrections were made for Lorentz and polarisation effects and also for absorption by $\psi$-scans ($T_{max} = 1.00$, $T_{min} = 0.75$). There was no crystal decay as measured by two standard reflections. Positions of non-hydrogen atoms were derived by direct methods using SHELXS-86[26] and refined on $F^2$ with anisotropic thermal parameters for non-hydrogen atoms and H atoms in riding mode, by full-matrix least-squares using SHELXL-93.[27]

CCDC reference number 186/1375.

See http://www.rsc.org/suppdata/dt/1999/1455/ for crystallographic files in .cif format.

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