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Syntheses and structures of thermally stable diketiminato complexes of gold and copper†

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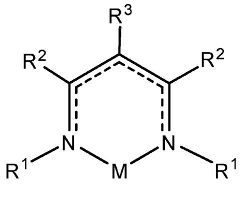
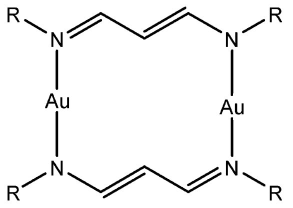
While most metallic elements across the Periodic Table form stable chelating β-diketiminato complexes, examples of Au(I) are conspicuous by their absence. We report here the reaction of $K[HC(F_3CC{=}NR)_2]$ with $AuCl(PPh_3)$ which provides a rare example of a thermally stable gold(I) diketiminato complex, $(Ph_3P)Au[RN{=}C(CF_3)CH(CF_3)C{=}NR]$ [$R = 3,5\text{-}C_6H_3(CF_3)_2$]. The complex is highly fluxional in solution but in the solid state adopts a U-conformation. By contrast, the analogous reaction of $K[HC(F_3CC{=}NR)_2]$ with $CuBr(PPh_3)_3$ gives the rigid 18-electron chelate complex $(Ph_3P)_2Cu[\kappa^2\text{-}HC\{(CF_3)C{=}NR\}_2]$.

Diketiminato anions are widely used as versatile ligands with easily tuneable steric and electronic properties. Derivatives with sterically hindered *N*-aryl substituents, notably mesityl and 2,6-diisopropylphenyl, have proved particularly useful. Most metallic elements across the Periodic Table are now known to form β-diketiminato complexes of the well-known *N,N*-bonded chelate type (structure **A**).[1] One element that is conspicuous by its absence in this important class of compounds is gold(I). Although AuCl mixed with the diketiminate $Li[HC(MeC{=}NC_6H_3Pr^i_2)_2]$ has been reported as an oxidation catalyst, the assumption being that under such conditions Au(I) diketiminato chelate complexes form *in situ* as catalytically active species,[2,3] evidence for its formation was scant. To our knowledge the only examples of isolated and fully characterised β-diketiminato gold(I) complexes are the binuclear species $[Au(RN{=}CHCH{=}CH\text{-}NR)]_2$ ($R = 2,6\text{-}Pr^i_2C_6H_3$ and $2,4,6\text{-}Br_3C_6H_2$), in which Au(I) is linearly coordinated to two ligands, each of which adopts a W conformation (structure **B**).[4] By contrast, β-diketiminato complexes of gold(III) show the expected chelate structure.[5] We report here the synthesis and structure of the first examples of monomeric gold(I) diketiminato complexes supported by phosphine ligands.



A



B

Preliminary screening reactions of AuCl or AuCl(tht) (tht = tetrahydrothiophene) with either $Li[HC(MeC{=}NC_6H_3Pr^i_2)_2]$ or $Na[HC(MeC{=}NC_6H_4Bu^t\text{-}4)_2]$ in THF or diethyl ether at 0 °C led in all cases to the rapid precipitation of metallic gold; evidently, these electron-rich ligands lead only to reduction. By contrast, the potassium salt of the less electron-donating trifluoromethyl-substituted ligand **1**[6] reacted cleanly with $AuCl(PPh_3)$ in diethyl ether at 0–20 °C to give the corresponding gold(I) diketiminato complex **2** as orange crystals in essentially quantitative yield (Scheme 1; for experimental details and the crystal structure of **1**-H see the ESI†). In the solid state and in solution this complex is remarkably temperature-stable.

The crystal structure of **2** (Fig. 1) shows that the diketiminato ligands adopts a U-conformation, a with linear N–Au–P moiety. There is no coordination to the second nitrogen atom. In the solid state both C–N bonds adopt *E*-conformations. The $C_6H_3(CF_3)_2$ rings are approximately parallel.

Complex **2** is fluxional. In toluene-d_8 at 22 °C, two separate but broadened ^{19}F signals are observed for the two CF_3 substituents in 2- and 4-positions of the diazapentadiene, at δ −71.2 and −65.5, respectively (Fig. 2). These signals coalesce at 67 °C and at 105 °C have merged into a singlet at δ −66.5. This behaviour is consistent with the exchange of the metal centre between the two nitrogen donors of the diketiminato ligand. However, as the chemical shift of the coalescence singlet differs from the arithmetic mean of the two low-temperature resonances, it is possible that a third component participates in the equilibrium under these conditions, conceivably a ligand rearrangement product of the type $[Au(PR_3)_2]^+[Au(N\text{–}N)_2]^-$ that is not observed at lower temperatures but that contributes to the time-averaged chemical shift (Scheme 2).

Another form of fluxionality is the inversion at the non-coordinating nitrogen atom.[6] At room temperature and above the ^{19}F chemical shift at −65.5 is apparently due to a mixture of *E* and *Z* isomers of the $C(CF_3){=}NAr$ moiety. Cooling to −94 °C shifts

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† Electronic supplementary information (ESI) available. CCDC reference numbers 800528–800530. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01422b

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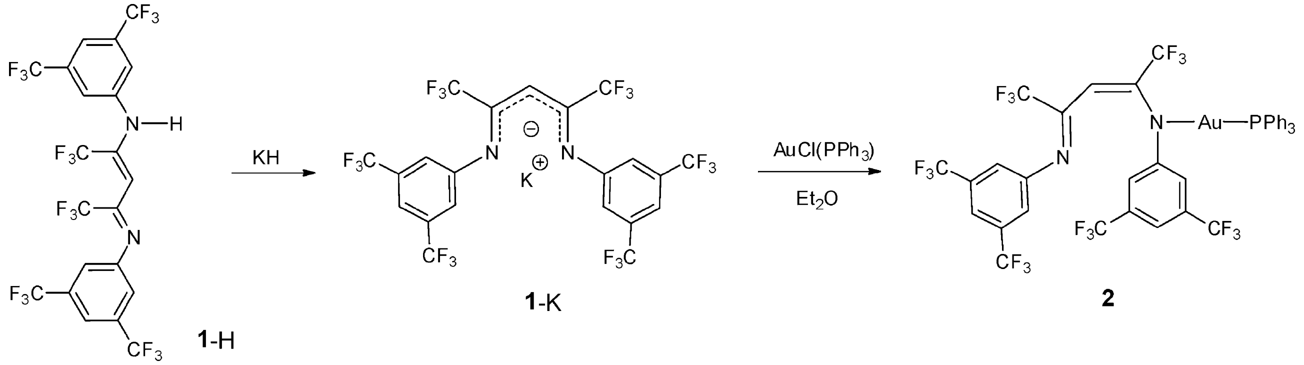

Scheme 1

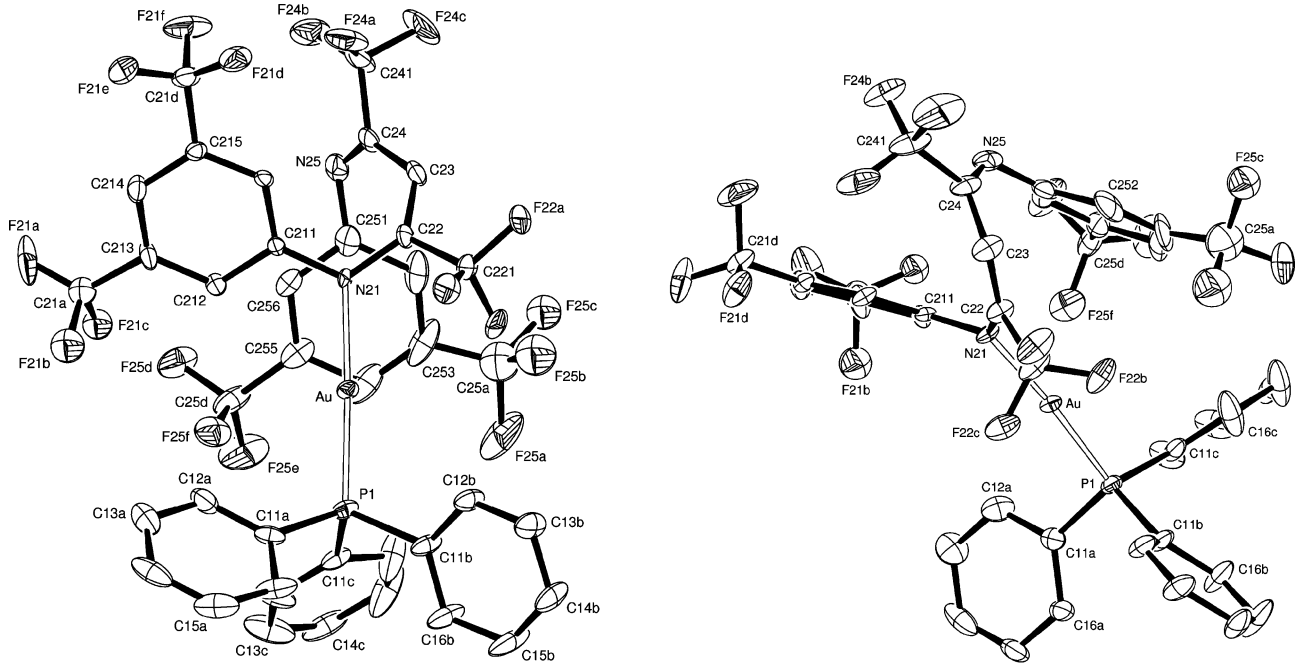

Fig. 1 Two views of the molecular structure of **2**, indicating the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Only the atoms of the major components of the disordered groups are shown. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Au–N(21) 2.075(4), Au–P(1) 2.2360(12), N(21)–C(22) 1.368(6), C(24)–N(25) 1.263(7); C(22)–C(23) 1.342(7), C(23)–C(24) 1.467(7); N(21)–Au–P(1) 175.59(11).

this equilibrium, most probably towards the *E* isomer present in the crystal structure (see ESI†).

An analogous copper(I) complex was prepared for comparison. Treating **1**-K with $CuBr(PPh_3)_3$ gives the bis(phosphine) complex **3** as red crystals (Scheme 3). Unlike **2**, the copper(I) diketiminate adopts the expected chelate structure (Fig. 3), analogous to a number of previously reported Cu(I) benzene and CO complexes with the $\mathbf{1}^-$ ligand.[7] Silver also forms a chelate with this diketiminate but gives a trigonal complex with only one PPh_3 ligand.[8] A number of related mono-phosphine copper complexes are known.[9–13] Tetrahedral copper diketiminato complexes with two phosphine ligands are comparatively rare but are favoured by sterically less hindered chelate ligands.[14] In the case of **3** the formation of an 18-electron bis(phosphine) complex is seen as a reflection of the electron withdrawing properties of the fluorinated ligand.

In summary, while there was no evidence for the formation of thermally stable diketiminato gold(I) complexes with the anions $[HC(MeC{=}NAr)_2]^-$ (Ar = 2,6-$C_6H_3Pr^i_2$ or $C_6H_4Bu^t$-4), the introduction of electron withdrawing CF_3 substituents leads to the first examples of mononuclear gold(I) diketiminato complexes with phosphine ligands which are stable in solution to >100 °C. In the ground state these compounds show 2-coordinate gold but also intricate fluxional behaviour. By contrast, copper(I) forms rigid tetrahedral 18-electron N–N chelates with this ligand.

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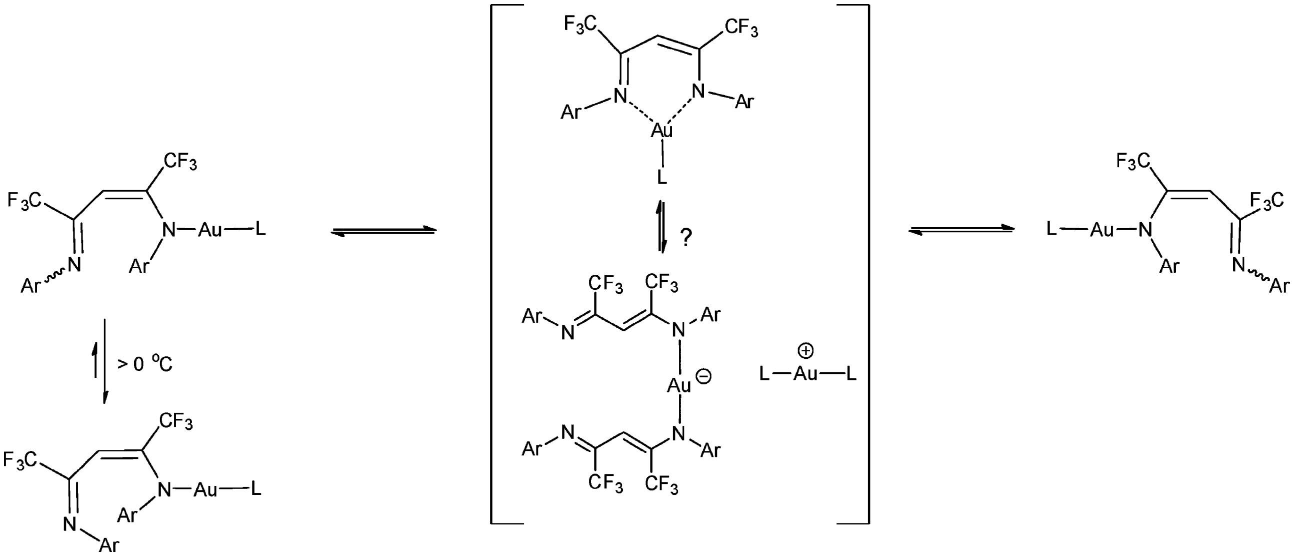
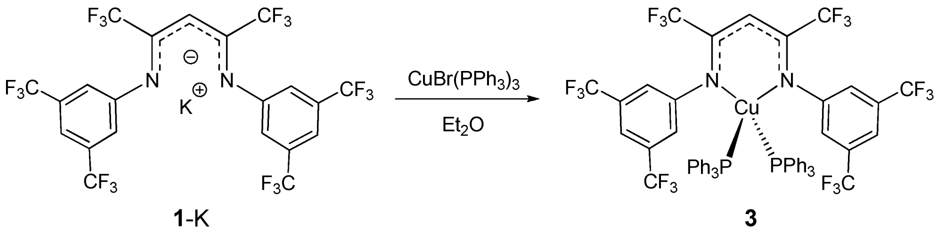


Scheme 2



Scheme 3

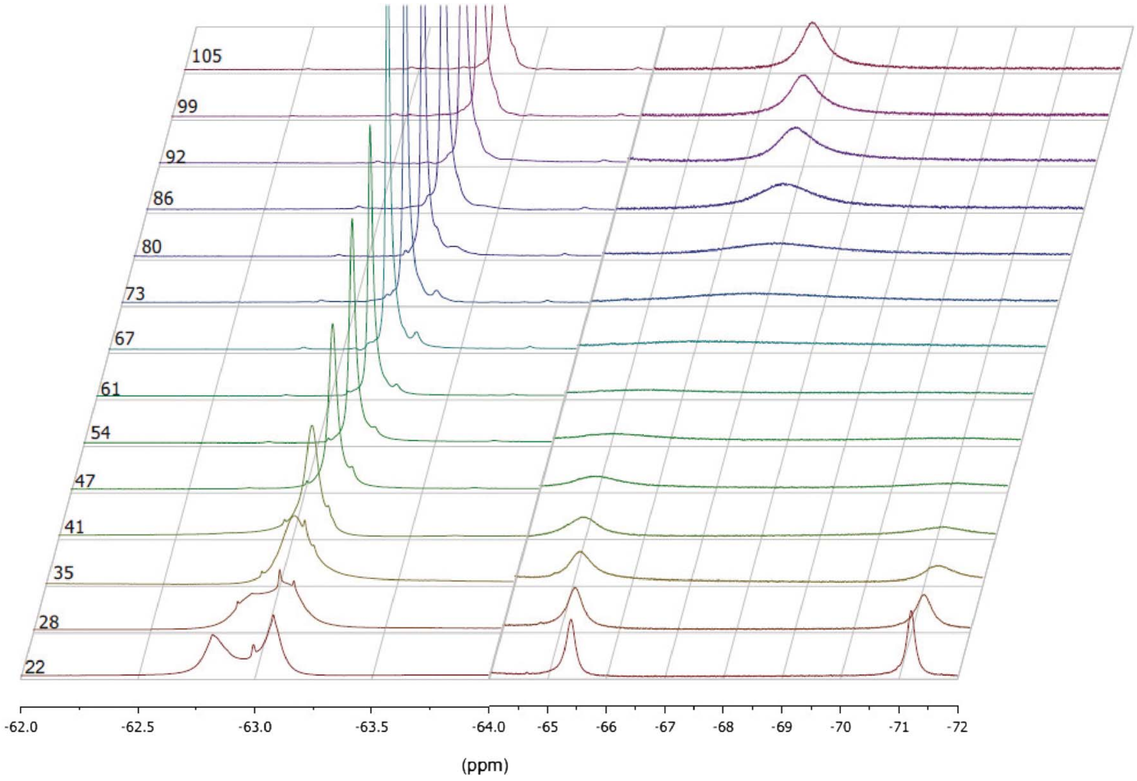


Fig. 2 ^{19}F NMR spectra of **2** at 22–105 °C (toluene-d_8). At 22 °C the CF_3 substituents in 2- and 4-positions of the diazapentadiene are found at δ −71.2 and −65.5, respectively, while peaks around δ −63 are due to aryl-CF_3.

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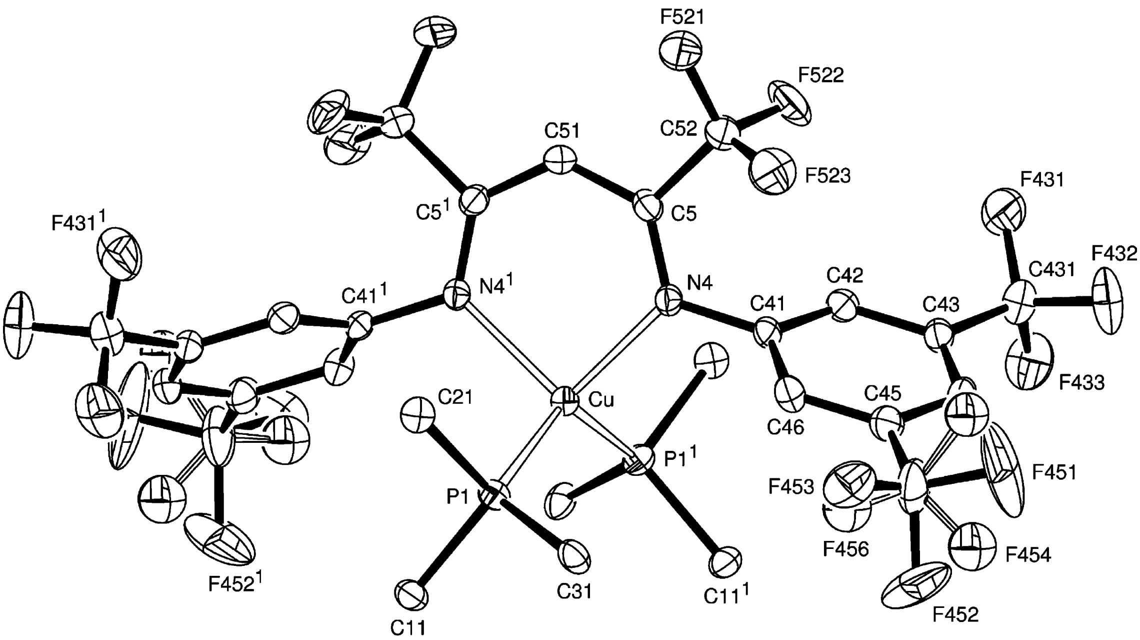

Fig. 3 Molecular structure of **3**, indicating the atom numbering scheme. Hydrogen atoms and the phenyl groups have been omitted for clarity. Two of the phenyl-CF$_3$ substituents are disordered. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Cu–N(4) 2.0929(15), Cu–P(1) 2.2953(5), N(4)–C(5) 1.316(2), C(5)–C(51) 1.398(2); N(4^{a})–Cu–N(4) 94.65(8), N(4)–Cu–P(1^{a}) 102.67(4), N(4)–Cu–P(1) 113.31(4), P(1^{a})–Cu–P(1) 126.03(3).

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