

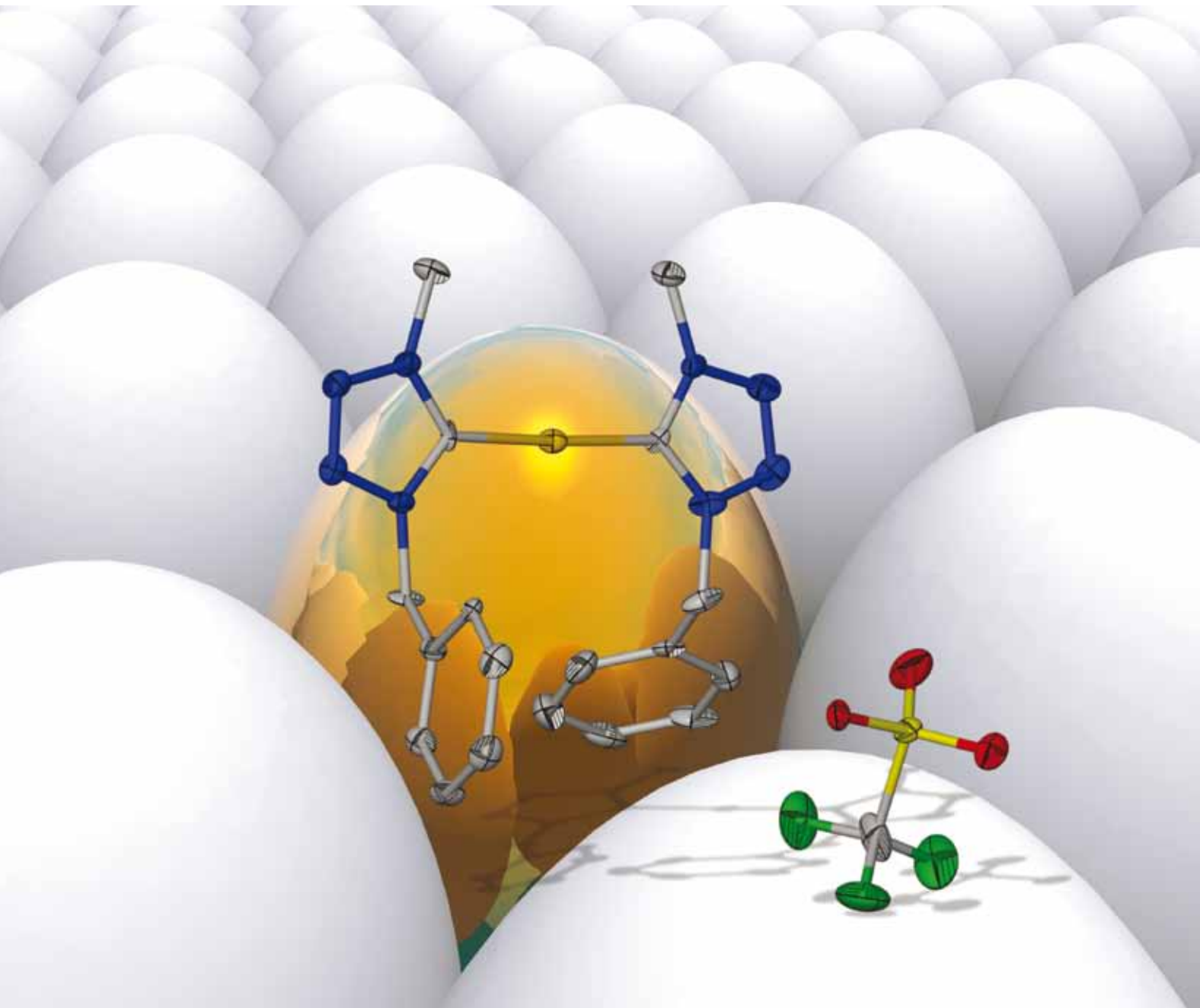
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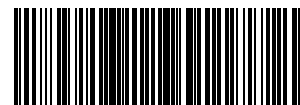


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**PAPER**  
Helgard G. Raubenheimer *et al.*  
Tetrazolyl and tetrazolylidene  
complexes of gold: a synthetic and  
structural study



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# Tetrazolyl and tetrazolylidene complexes of gold: a synthetic and structural study†

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Lithiation of 1-benzyl-1*H*-tetrazole followed by transmetallation with [AuCl(PPh<sub>3</sub>)], [Au(C<sub>6</sub>F<sub>5</sub>)(tht)] or [AuCl(tht)] (tht = tetrahydrothiophene) and subsequent alkylation afforded cationic 1-benzyl-4-methyl-4,5-dihydro-1*H*-1,2,3,4-tetrazol-5-ylidene(triphenylphosphine)gold(i), **1**, neutral 1-benzyl-4-methyl-4,5-dihydro-1*H*-1,2,3,4-tetrazol-5-ylidene(pentafluorophenyl)gold(i), **2**, and a cationic biscarbene complex, bis(1-benzyl-4-methyl-4,5-dihydro-1*H*-1,2,3,4-tetrazol-5-ylidene)gold(i), **3**. The first complex underwent a homoleptic rearrangement in solution to form **3**. Reaction of [Au(N<sub>3</sub>)PPh<sub>3</sub>] with the three isocyanides (CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, <sup>*t*</sup>BuNC and CyNC, respectively, yielded the corresponding neutral tetrazolyl(phosphine) complexes of gold, [1-(2,6-dimethylphenyl)-1*H*-tetrazol-5-yl](triphenylphosphine)gold(i), **4**, [1-(*tert*-butyl)-1*H*-tetrazol-5-yl](triphenylphosphine)gold(i), **6**, and [1-(cyclohexyl)-1*H*-tetrazol-5-yl](triphenylphosphine)gold(i), **7**. Alkylation of **4** with methyl triflate on N<sup>4</sup> allowed isolation of the crystalline carbene complex 1-(2,6-dimethylphenyl)-4-methyl-4,5-dihydro-1*H*-1,2,3,4-tetrazol-5-ylidene(triphenylphosphine)gold(i), **5**. Complex **7** was not isolable in pure form but converts by isocyanide substitution of triphenylphosphine into [1-cyclohexylisocyanide][1-(cyclohexyl)-1*H*-tetrazol-5-yl]gold(i), **8**. From a product mixture of **7** and **8** the transformed molecules [(cyclohexylamino)(ethoxy)carbene][1-(cyclohexyl)-1*H*-tetrazol-5-yl]gold(i), **9**, and [bis(cyclohexylamino)carbene][1-(cyclohexyl)-1*H*-tetrazol-5-yl]gold(i), **10**, co-crystallised spontaneously after a long time at –20 °C.

## Introduction

The study of N-heterocyclic carbene (NHC) complexes of various metals remains a topical field of research in inorganic chemistry. Since the first isolable NHC was characterised more than a decade ago, dedicated efforts have been made to develop transition metal derivatives of such compounds.<sup>1</sup> The emerging interest in NHCs as surrogates for phosphines in organometallic catalysis is testimony to the remarkable stability and versatility observed for such transition metal complexes.<sup>2</sup> NHCs have also replaced phosphines recently in chrysotherapy and in the pursuit of gold(i) compounds as anti-tumour agents.<sup>3a,b</sup> Several synthetic approaches now exist to prepare gold(i) NHC complexes.<sup>4</sup> These include (i) homolytic cleavage of electron rich olefins; (ii) transmetallation of carbene ligands from group 6 carbonyl complexes and (iii) transmetallation between Ag(i)–NHCs and Au(i) precursors.<sup>5</sup> A further preparative route *via* the sequential lithiation of an azole substrate, transmetallation to a gold(i) substrate,

followed by alkylation or protonation, has been developed in our laboratory and provides an access route to a variety of this class of gold(i) carbene.<sup>6</sup> Both mono and bis(carbene) complexes of gold(i) derived from lithiated pyridine have, for example, been prepared and structurally characterised.<sup>7</sup> Furthermore, numerous thiazolyl, imidazolyl and triazolyl gold(i) carbene complexes are obtainable from routes and methods described in the literature.<sup>8</sup> Glaring in their absence from the range of well-characterised C-bonded or carbene-bonded N-heterocyclic gold(i) complexes are those that contain tetrazole rings. To the best of our knowledge, the only reports of C-bonded tetrazolyl gold(i) complexes are of the type (RNC)(RN<sub>4</sub>C)Au(i) (R = methyl, cyclohexyl, phenyl) that have been prepared in the group of Beck and Fehlhhammer.<sup>9</sup> Although these complexes have been isolated as crystalline solids, their rapid decomposition in the X-ray beam impedes their structural characterisation. The preparation of a carbene complex by protonation of the corresponding tetrazolyl precursor is reported but the authors acknowledge that no unambiguous proof exists to confirm that such a reaction had indeed taken place. A search in the Cambridge Crystallographic Database shows a solitary entry of a tetrakis(tetrazol-5-yl)gold(III) complex prepared by the same research group.<sup>10</sup> The synthesis of tetrazole-derived NHC complexes of gold(i) poses, from a structural point of view, certain challenges. First, lithiated tetrazoles are innately unstable and readily lose molecular nitrogen to form cyanamide by-products<sup>11</sup>

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and, second, although alkylation should be favoured on the more nucleophilic adjacent  $\alpha$ -nitrogen in (tetrazolyl)aurates, electrophilic additions could also occur at one of two remote nitrogens,  $\beta$  placed with regard to the coordinated carbon owing to the delocalisation of electronic charge around the ring. Herrmann and co-workers have recently reported on the preparation of the first thermodynamically stable, *trans*-(dicarbene)tetracarbonylchromium complex derived from the corresponding tetrazolium salt.<sup>12</sup> They further exploit the weak  $\sigma$ -donating ability of the tetrazolylidene ligand to effect a single carbon monoxide substitution in preparing the *sym-mer* configured tricarbonyl-chromium complex.

The 1,3-dipolar cycloaddition of organic isocyanides to metal azides ('click chemistry'), in this regard, provides an elegant alternative for the preparation of various C-coordinated tetrazolyl gold(I) complexes. In contrast to the widely applied and related cycloaddition reaction of nitriles and coordinated azides which afford N-coordinated tetrazolate complexes, the former reaction, yielding carbon-metal bonded complexes, is limited to only a few reports.<sup>13–15</sup> Ironically, the structural motifs found in these complexes, *i.e.* metal-coordinated isocyanides, are representatives of the first known gold(I) carbene precursor functionalities. A well established methodology to functionalise these "masked carbenes", *i.e.* by the nucleophilic addition of alcohols and amines, to afford acyclic (diamino)- and (alkoxy)(amino)carbene gold(I) complexes, exists.<sup>16,17</sup> In recent times such gold(I) carbene types have often been found to display interesting photoluminescent properties both in the solid state and in solution.<sup>18</sup>

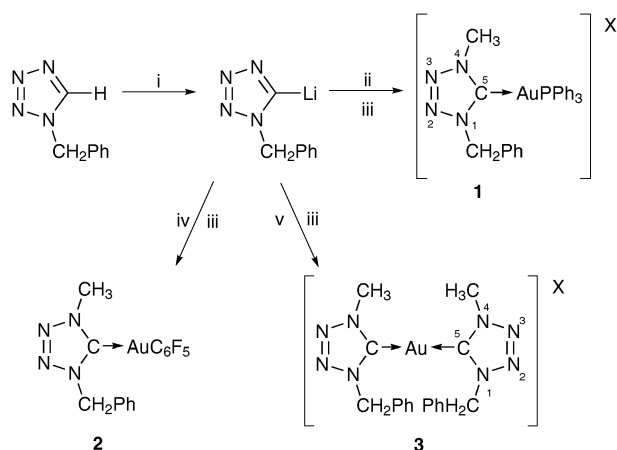
Herein, as a contribution to the rapidly expanding field of (NHC)gold(I) chemistry,<sup>4</sup> we report for the first time the crystal and molecular structures of *normal* gold(I) carbene complexes derived from tetrazoles. By adopting known classical preparative routes with small variations, these interesting nitrogen-rich heterocyclic azolylidenes could now be prepared and isolated. En-route, interesting behaviour in solution of these complexes was also observed and unexpected acyclic carbene complexes were espied.

## Results and discussion

### NHC complexes derived from lithiated precursors

Scheme 1 illustrates the protocol used in the preparation of various novel (tetrazolylidene)gold(I) complexes. The procedure involves sequential lithiation of the CH-acidic tetrazole, transmetallation involving a gold(I) substrate, and finally alkylation of the resultant azolyl complex which could be neutral or an aurate.

The cationic mono(carbene)gold(I) complex **1** was prepared by lithiation of 1-benzyltetrazole in thf with *n*-butyllithium at  $-98^\circ\text{C}$  (for related applications compare ref. 19*a–d*), followed by the addition of  $[\text{Au}(\text{Cl})(\text{PPh}_3)]$  at  $-68^\circ\text{C}$  and direct alkylation with  $\text{CF}_3\text{SO}_3\text{CH}_3$ . Although complex **1** could initially be isolated in microcrystalline form, it was unstable in solution and underwent a gradual homoleptic rearrangement. The rearrangement afforded the corresponding bis(carbene)-gold(I) and bis(triphenylphosphine)gold(I) triflate complexes, and their formation could be followed by  $^1\text{H}$  NMR measurements



**Scheme 1** The synthetic route towards mono- and bis(tetrazolylidene) gold(I) complexes;  $\text{X} = \text{CF}_3\text{SO}_3^-$ : (i) *n*-butyllithium in thf; (ii)  $[\text{AuCl}(\text{PPh}_3)]$ ; (iii)  $\text{CF}_3\text{SO}_3\text{CH}_3$ ; (iv)  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ ; (v)  $[\text{AuCl}(\text{tht})]$ .

(*vide infra*). A number of attempts to recrystallise **1** only yielded crystals of the homoleptic by-products. Furthermore, in the solid state complex **1** is highly hygroscopic which ruled out an accurate elemental analysis.

The neutral mono(carbene)gold(I) complex **2** was prepared by treatment of a thf solution containing lithiated 1-benzyltetrazole, with  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  (tht = tetrahydrothiophene). The aurate salt was not isolated but directly alkylated with  $\text{CF}_3\text{SO}_3\text{CH}_3$  at low temperature. The neutral complex was extracted from the residual product with a diethyl ether–*n*-pentane (1 : 1) mixture. The colourless microcrystalline material of complex **2** is thermodynamically stable in air at room temperature.

The cationic bis(carbene)gold(I) complex **3** was prepared in very much a similar fashion as described for **1** and **2**. The addition of half a molar amount of  $[\text{AuCl}(\text{tht})]$  to a solution of 1-benzyltetrazol-5-yl lithium in thf at  $-98^\circ\text{C}$  afforded the corresponding aurate complex, which was directly alkylated with  $\text{CF}_3\text{SO}_3\text{CH}_3$  at a slightly elevated temperature ( $-68^\circ\text{C}$ ) to give complex **3** in high yield. An analytically pure sample of **3** could be obtained by recrystallisation from a dichloromethane solution layered with *n*-pentane at  $-20^\circ\text{C}$ . The colourless needle-like crystals are thermodynamically stable in air and in solution at room temperature. The formation of trace amounts of an isomeric product to **3** was indicated by  $^{15}\text{N}$  NMR measurements (*vide infra*).

### Homoleptic rearrangement of complex 1

The spontaneous rearrangement of mixed carbene complexes of gold(I) has been described on a few occasions in the literature. Shaw and co-workers<sup>20</sup> also found that for neutral gold(I) complexes of the type  $[\text{Au}(\text{CN})\text{PR}_3]$ , a ligand scrambling reaction occurs to afford ionic mixtures of  $[\text{Au}(\text{CN})_2]^-$  and  $[\text{Au}(\text{PR}_3)_2]^+$ . Similar reactions occur with anionic gold(I) complexes of the type  $[\text{Au}(\text{CN})\text{SR}]^-$  to yield the dicyanate and dithiolate gold(I) complexes.<sup>21</sup> We have previously established that (pentafluorophenyl)(isothiazol-5-ylidene)gold(I) rearranges slowly and the process can be followed by  $^1\text{H}$  NMR spectroscopy.<sup>22</sup> This reaction occurs more rapidly for the precursor complex, (pentafluorophenyl)(isothiazol-5-yl)gold(I), which has

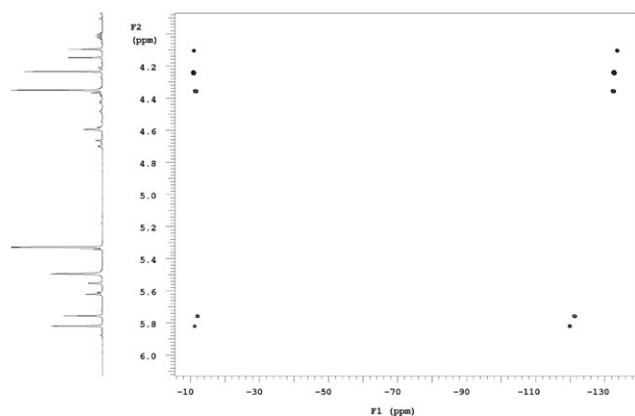
prompted an *in situ* carbene preparation by immediate alkylation to avoid complicating reactions. In contrast, (triphenylphosphine)(isothiazol-5-yl)gold(I) is very stable in solution and could be isolated in pure form. Using the same methodology as described above, *i.e.* circumvention of the isolation of the (tetrazol-5-yl)(phosphine)gold(I) complex by immediate alkylation of the reaction product at low temperature ( $-78\text{ }^{\circ}\text{C}$ ), a white microcrystalline solid was obtained, after the precipitation of the cationic product, **1**, with diethyl ether.

The  $^{31}\text{P}$  NMR spectrum of the crystalline material dissolved in  $\text{CD}_2\text{Cl}_2$  revealed a broadened singlet signal at  $\delta$  44.1, typical of an exchanging phosphorus atom. In addition, crystallisation from the NMR tube, by slow evaporation of the solvent, afforded colourless crystals of  $[\text{Au}(\text{PPh}_3)_2][\text{CF}_3\text{SO}_3]$ . The phosphorus resonance at  $\delta$  31.8 assigned to this bis(phosphine) complex is in close agreement with the signal for  $[\text{Au}(\text{PPh}_3)_2]\text{Cl}$  at  $\delta$  29.7.<sup>23</sup> The  $^{15}\text{N}$  chemical shifts of the nitrogen atoms in complex **1** were measured in a long range  $^1\text{H}$ -detected,  $^1\text{H}$ ,  $^{15}\text{N}$  gHMQC experiment in which a specified proton resonance could be used to locate coupling N atoms that are removed by two to three bonds. The resulting spectrum thus represents not only signals pertaining to complex **1** but also to the homoleptically rearranged product, **3**. Fig. 1 shows two sets of four closely related nitrogen resonances, separated as shielded (alkyl substituted) and deshielded (imine) nitrogen nuclei. The signals for compound **3** were also observed in the  $^{15}\text{N}$  NMR spectrum of **3** prepared according to the procedure mentioned above.

In each case the nitrogen atoms can be related to the proton two or three bonds removed. Two further resonances ( $\delta$   $-133.2$ ,  $\delta$   $-11.5$ ) are also noted, and they have been ascribed to the possible formation of a benzylmethylcyanamide compound as a product of ring fragmentation. In this instance the benzylic proton resonance ( $\text{CH}_2$ ) is correlated to the only two remaining nitrogen atoms, after the loss of dinitrogen in the cyanamide product.

### Carbene formation by remote alkylation

Members of our research group have shown that by using the lithiation–transmetallation–protonation route atypical



**Fig. 1**  $^1\text{H}$ ,  $^{15}\text{N}$  gHMQC experiment of **1**, collected over a 24 h period in  $\text{CD}_2\text{Cl}_2$  at ambient temperature; for **1** [ $\delta$   $-119.9$  ( $\text{N}^1$ ),  $\delta$   $-11.2$  ( $\text{N}^2$ ),  $\delta$   $-11.5$  ( $\text{N}^3$ ),  $\delta$   $-132.5$  ( $\text{N}^4$ )] and **3** [ $\delta$   $-121.3$  ( $\text{N}^1$ ),  $\delta$   $-12.0$  ( $\text{N}^2$ ),  $\delta$   $-10.9$  ( $\text{N}^3$ ),  $\delta$   $-132.8$  ( $\text{N}^4$ )].

Öfele–Wanzlick-type carbene complexes can be prepared from precursors in which the nucleophilic heteroatom is located  $\gamma$  to the co-coordinated carbon atom and not in the conventional  $\alpha$ -position.<sup>24</sup> The reaction of phenylpyrazol-5-ylolithium, and  $[\text{Fe}(\text{Cp})(\text{CO})_2\text{Cl}]$ , followed by protonation, yields the amino(organo)carbene complex, dicarbonyl( $\eta^5$ -cyclopentadienyl)-(1-phenylpyrazol-5-ylidene)iron(I) triflate, representing carbene complex formation mediated by a remote protonation on a nitrogen atom more than one bond removed from the metal-coordinated carbon atom. This procedure has later been extended to include complexes in which the nucleophilic heteroatom in the precursor substrate is located outside the coordinated ring and separated from the coordinated carbon by more than two bonds.<sup>25</sup>

During the preparation and structural characterisation of **3**, it was established that alkylation of the bis(1-benzyltetrazol-5-yl)gold(I) precursor complex on the N atom in the 4-position ( $\alpha$  to the coordinated carbon) is favoured above alkylation of the nitrogen atoms in the 2- and 3-positions. This result elucidates the findings by Wehlan and co-workers,<sup>10</sup> who reported that the protonation of sodium tetrakis(tetrazol-5-yl)aurate(III) affords a (supposedly *normal*) monocarbene complex by alkylation on one of the four tetrazole rings. Their finding has not been confirmed by either structural or spectroscopic analysis.  $^1\text{H}$  NMR analysis of the crude product mixture of **3** revealed that trace amounts of secondary products, which share common diagnostic resonances, *i.e.* benzylic and NMe protons, with complex **3**, were present. Such by-products could arise from the alkylation of the nitrogen atoms in the 2- or 3-positions,  $\beta$  to the coordinated carbon. Future studies should concentrate on such possibilities especially since 3-alkylation would afford an *abnormal* carbene ligand.

### NHC complexes derived from azide complex templates

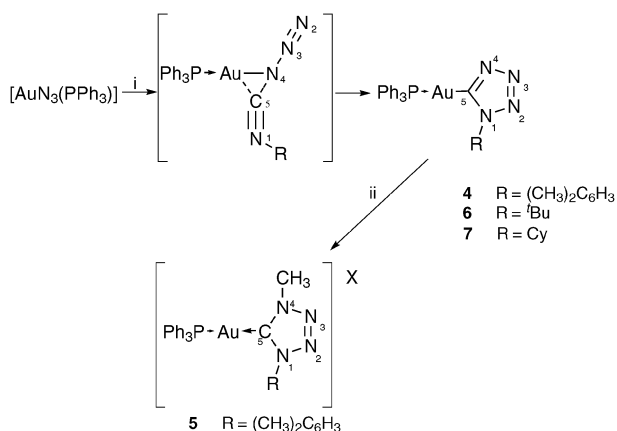
The reaction of metal azides with isocyanides, first reported by Beck and co-workers,<sup>9</sup> represents a straightforward and elegant route to a series of novel carbon-bonded metal tetrazolates. Under very mild conditions, the addition of a large excess (25 fold) of isocyanide (methylisocyanide, cyclohexylisocyanide and phenylisocyanide) to a dichloromethane solution of azido(triphenylphosphine)gold(I) affords, after precipitation by the addition of diethyl ether, the neutral but relatively unstable isocyanide(tetrazol-5-yl)gold(I) complexes.

Later Wehlan and co-workers<sup>10</sup> report that the reactivity of chosen isocyanides in such reactions increases with their assumed nucleophilicity, *i.e.* 1-*tert*-butylisocyanide > 1-cyclohexylisocyanide  $\sim$  2,6-dimethylphenylisocyanide.

After a further investigation of the 1,3-dipolar cycloaddition reactions of isocyanides to metal azides, we now report alternative phosphine-containing products that are obtained when  $[\text{Au}(\text{N}_3)(\text{PPh}_3)]$  is reacted with a smaller excess of related isocyanides (Scheme 2).

The reaction of 2,6-dimethylphenylisocyanide (10 fold excess) with  $[\text{Au}(\text{N}_3)(\text{PPh}_3)]$  at ambient temperature (while protected from light) affords after 17 h [1-(2,6-dimethylphenyl)-1H-tetrazol-5-yl](triphenylphosphine)gold(I), **4**, in good yield. The colourless crystalline solid is stable in air at room

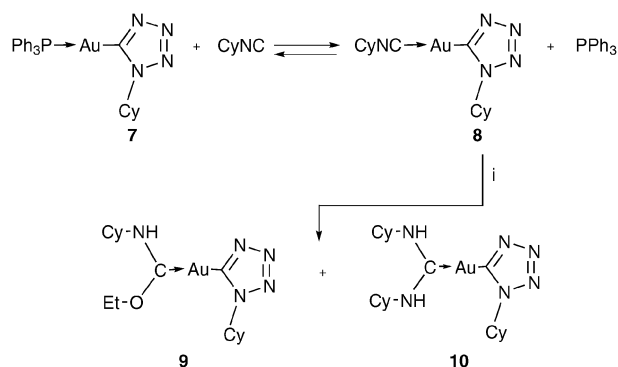




**Scheme 2** The synthesis of C-tetrazolyl gold(I) complexes; X = CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>: (i) RNC = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, <sup>t</sup>BuNC or CyNC; (ii) CF<sub>3</sub>SO<sub>3</sub>CH<sub>3</sub>.

temperature and is readily soluble in polar solvents, and insoluble in diethyl ether and pentane. Colourless prisms of complex **4** were obtained from a dichloromethane solution layered with diethyl ether overnight at −20 °C. Alkylation of the carbenate complex, **4**, at −70 °C afforded the mono(carbene)gold(I) complex, [1-(2,6-dimethylphenyl)-4-methyl-4,5-dihydro-1*H*-1,2,3,4-tetrazol-5-ylidene](triphenylphosphine)-gold(I) triflate, **5**, in almost quantitative yield. In striking contrast to both the observations made during the preparation of the tetrazolylidene complex **1**, carbene complex **5** appeared, according to this preparative procedure, as the exclusive product. In complex **5**, the steric bulk and/or an additional electronic effect of the N<sup>1</sup> substituent may play a role in selectively directing alkylation on the N<sup>4</sup> atom. The propensity of NHC(phosphine)gold(I) complexes to convert to the homoleptic bis(carbene)gold(I) complexes has been mentioned above and it could be a reason behind the limited number of structurally characterised mono(carbene) complexes described in the literature [1,3-bis(5*H*-dibenzo[*a,d*]cycloheptenyl)imidazol-2-ylidene](triphenylphosphine)gold(I) chloride and [1,3-di(*tert*-butyl)imidazol-2-ylidene](triphenylphosphine)-gold(I) hexafluorophosphate].<sup>3,26</sup> Pykkö and co-workers<sup>27</sup> have concluded that the structural, NMR and solution equilibrium data describing the homoleptic rearrangement of neutral gold(I) complexes of the type LAuX (L = donor ligand, X = anionic ligand) suggest that reactants and products energetically do not differ much. However, it remains tempting to ascribe the stability of **5** (towards homoleptic rearrangement), in part to the sterically bulky substituent on N<sup>1</sup>.

Using the same methodology as for the preparation of complex **5**, the related carbenate complex, [1-(*tert*-butyl)-1*H*-tetrazol-5-yl](triphenylphosphine)gold(I), **6**, could be obtained from the metal azide and *tert*-butylisocyanide (10 fold excess). However, whereas complex **4** was isolated by precipitation from a dichloromethane solution after the addition of diethyl ether, **6** formed overnight as an insoluble precipitate from the reaction mixture. The colourless microcrystalline solid is stable in air at room temperature. Subsequent alkylation of this compound to afford the corresponding mono(carbene)gold(I) complex was unsuccessful, probably



**Scheme 3** Postulated steps in the formation of complexes **9** and **10**: (i) CyNH<sub>2</sub> (as hydrolysis product), ethanol.

owing to its extremely low solubility in most common organic solvents. Numerous attempts to obtain suitable crystals for X-ray structure determination were fruitless. However this complex could be characterised by NMR spectroscopy (slight solubility in d<sub>6</sub>-DMSO), and FAB-MS spectrometry (in an *m*-nitrobenzylalcohol matrix).

The reaction of a larger (20 fold) excess of cyclohexylisocyanide with [Au(N<sub>3</sub>)(PPh<sub>3</sub>)] afforded, after work-up, the (1-cyclohexyl-1*H*-tetrazol-5-yl)(triphenylphosphine)gold(I) complex, **7**. However now a further substitution product, (cyclohexylisocyanide)(1-cyclohexyl-1*H*-tetrazol-5-yl)gold(I), **8**, appeared to be in equilibrium with the phosphine complex **7** (Scheme 3). In agreement with the findings of Beck and co-workers<sup>9</sup> the mixture of **7** and **8**, upon exposure to air, almost immediately exhibited a bright yellow luminescence. Further evidence for the presence of **8** in solution is infrared bands typical of the C≡N moiety, as well as the spontaneous formation of two acyclic carbene complexes derived from **8** (Scheme 3 and crystallography section). The presence of both complexes **7** and **8** could be clearly identified by NMR measurements in the resulting solution occurring in a 1 : 2 ratio but eventually a crystalline product was isolated that contained co-crystallised **9** and **10**. The formation of **10** required the formation of CyNH<sub>2</sub> in the alcohol solution.

In an attempt to crystallise the non-isocyanide-containing complex **7** from a mixture of **7** and **8** (the former the major component) a mixed co-crystallised product (**9**–**10**) that contained both of the two well documented Bonati–Minghetti-type<sup>16</sup> complexes **9** and **10** shown in Scheme 3 was isolated. Ethanol (solvent with pentane) and cyclohexylamine addition to the gold isocyanide has been invoked to explain the formation of the complexes. The amine is most likely a hydrolysis product of **7** or of free isocyanide. Schmidbaur and co-workers<sup>28</sup> have reported a similar example, where the formation of (isocyanide)(diaminocarbene)gold(I) chloride results from the addition of an alkylamine, present owing to the hydrolysis of the free isocyanide, to bis(isocyanide)gold chloride. Aliphatic and aromatic amines react readily in low concentrations and under mild conditions, whereas alcohols normally require prolonged reaction times at higher temperatures. Such variance in nucleophilicity is illustrated in this reaction (at −20 °C over 8 months) which only required a limited amount of amine to form **10** despite the overwhelming excess of alcohol present.

## NMR spectroscopy

Many of the NMR signals are found in their normal positions and are not discussed here in detail. In the  $^1\text{H}$  NMR spectra of **1** and **3** the singlet signals at  $\delta$  4.26 and 4.36, which are respectively assigned to the three and six NMe protons in the cationic complexes, confirm the formation of mono- and biscarbene complexes. The corresponding resonance in the neutral complex **2** appears slightly upfield at  $\delta$  3.85, in close agreement with that of (1,3-dimethylimidazol-5-ylidene)-(pentafluorophenyl)gold(i) ( $\delta$  3.82).<sup>29</sup> The  $^{13}\text{C}$  NMR spectra reveal characteristic NMe resonances for **1** ( $\delta$  38.7), **2** ( $\delta$  38.4) and **3** ( $\delta$  39.9). The carbene carbon in **1** resonates as a singlet at  $\delta$  180.6, and the phenyl carbons appear as uncharacteristically broad signals, devoid of distinguishing C–P coupling patterns. This observation could be due to phosphine group exchange during the homoleptic rearrangement of **1** in solution. Also in agreement, the  $^{31}\text{P}$  NMR spectrum of this complex in solution reveals a broad signal ( $\delta$  44.0) and then a sharp singlet ( $\delta$  31.1) for the homoleptic cationic gold(i) product, bis(triphenylphosphine)gold(i), indicative of an irreversible reaction. Well-defined  $^{13}\text{C}$  NMR signals at  $\delta$  186.6 and  $\delta$  182.6 are assigned to the carbene carbons in **2** and **3**, respectively. These resonances are again in close agreement with reported values for the two-N-heterocycles in (1,3-dimethylimidazol-5-ylidene)-(pentafluorophenyl)gold(i) ( $\delta$  189.5) and bis(1,3-dimethylimidazol-2-ylidene)gold(i) chloride ( $\delta$  185.7).<sup>29</sup> The complex coupling patterns for the  $\text{C}_6\text{F}_5$  ligand in **2** are well resolved, and the presence of the ligand is also confirmed by three sets of multiplets in the  $^{19}\text{F}$  NMR spectrum.

The  $^{15}\text{N}$  NMR signals of the nitrogen atoms of **1** and **3** could be determined in a long range  $^1\text{H}$  detected  $^1\text{H}$ ,  $^{15}\text{N}$  gHMQC experiment. The shielded nitrogens,  $\text{sp}^3$  hybridised  $\text{N}^1$  and  $\text{N}^4$ , appear at highest field for both complexes **1** and **3**. Large downfield changes in chemical shift are observed for  $\text{N}^1$  in **1** ( $\Delta\delta$  21.7) and **3** ( $\Delta\delta$  20.0) in relation to 1-benzyltetrazole. Notable is the simultaneous pronounced upfield change in chemical shift found for the  $\text{N}^4$  resonance in both **1** ( $\Delta\delta$  81.8) and **3** ( $\Delta\delta$  83.2) confirming that  $\text{N}^4$  obtains more p character in the process of carbene formation. In the  $^1\text{H}$  NMR spectra of **4** and **5** the signals at  $\delta$  1.94 and  $\delta$  2.05 are, respectively, assigned to the  $\text{CCH}_3$  groups. The only other proton resonance at high field is a sharp singlet resonance at  $\delta$  4.51, representing the three NMe protons in **5**.

The  $^{13}\text{C}$  NMR spectrum reveals a characteristic NMe resonance for complex **5** at  $\delta$  39.0, in addition to the single carbon resonance ( $\delta$  18.0) observed for the chemically equivalent methyl phenyl carbons. The latter observation suggests a free rotation of the 2,6-dimethylphenyl substituent about the  $\text{N}^1\text{--C}^6$  axis, a crucial impediment towards  $\text{N}^2$  alkylation. For both complexes **4** and **5**, the carbon signals of the phosphine ligands are well resolved, showing distinctive phosphorus coupling to all four chemically inequivalent carbon atoms. This result is in contrast to the broad singlet resonances, suggestive of a dynamic system, reported above for complex **1**. The diagnostic carbene resonance of **5** appears as a strong doublet resonance at  $\delta$  186.9 (d,  $^2J_{\text{C--P}} = 121.6$  Hz), similar to the chemical shift of the signal for the same atom in **4** ( $\delta$  186.6). This result is also in agreement with the carbene

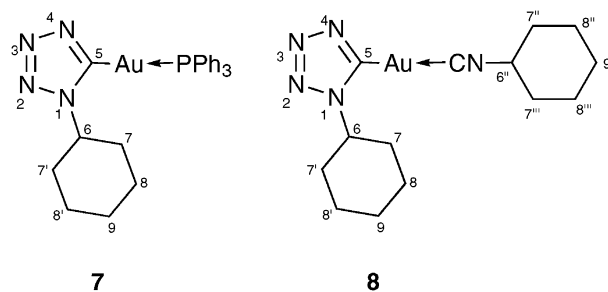


Fig. 2 Complexes **7** and **8** showing the numbering schemes.

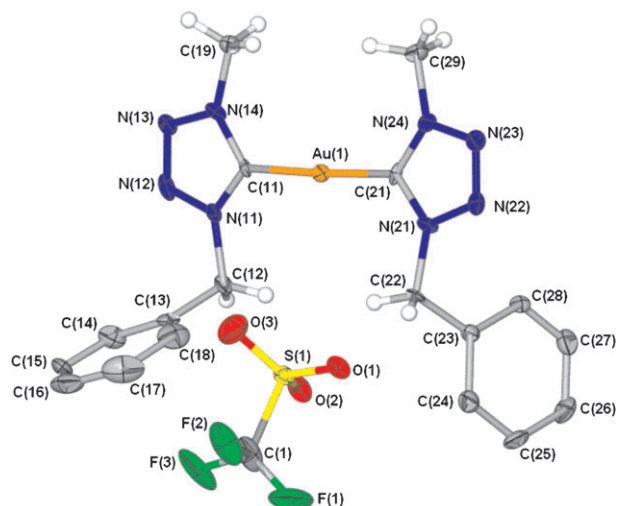
carbon–phosphorus coupling *via* a gold(i) centre, observed for (3,4-dimethylthiazol-2-ylidene)(triphenylphosphine)gold(i) triflate (209.8,  $^2J_{\text{C--P}} = 126$  Hz).<sup>30</sup> Because of the low solubility of complex **6** the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra could only be measured in  $d_6$ -DMSO where only broad signals were observed. The broad signal at  $\delta$  172.9 is assigned to the metal-bonded carbon atom. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows a single resonance at  $\delta$  26.7.

Owing to the fact that the attempted synthesis of **7** also afforded the related complex **8**, an unambiguous assignment of signals in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the product mixture was challenging (Fig. 2).

In their preparation of **8**, Beck and co-workers<sup>9</sup> reported the proton resonances, which could now be subtracted in the spectrum of the mixture of **7** and **8**. Furthermore, using a two-dimensional gHSQC experiment,  $^{13}\text{C}$  NMR resonances could be assigned to carbon nuclei in **7**. The combined  $^1\text{H}$  NMR spectra of **7** and **8** reveal two sets of proton resonances which integrate in an approximately 1 : 2 ratio, for the *ipso*-H signals of the Cy-groups. The well-resolved multiplet at  $\delta$  4.65 is assigned to the tetrazole  $\text{H}^6$  protons occurring in both **7** and **8**. The corresponding resonance  $\text{H}^{6''}$  in the Cy-group, attached to the coordinated isocyanide, appears as a broad signal at  $\delta$  3.71. The  $\text{H}^7$ ,  $\text{H}^{7'}$ ,  $\text{H}^8$  and  $\text{H}^{8'}$  resonances of the tetrazole-bonded Cy-group can be distinguished from the corresponding signals in the isocyanide Cy-group ( $\text{H}^{7''}$ ,  $\text{H}^{7'''}$ ,  $\text{H}^{8''}$  and  $\text{H}^{8'''}$ ). However, the three sets of  $\text{H}^4$  protons overlap and could not be assigned independently. In the  $^{13}\text{C}$  NMR spectrum a singlet at  $\delta$  59.4 is assigned to the *ipso*- $\text{C}^6$  which occurs in both **7** and **8**. The other carbon resonances of the two inequivalent Cy-rings can be assigned by correlation with the  $^1\text{H}$  NMR resonances. Four sets of doublet signals are assigned to the phenyl carbons exhibiting characteristic carbon–phosphorus coupling patterns. The coordinated isocyanide carbon atom in **8** is not resolved and a weak signal at  $\delta$  181.7 is assigned to the metal-bonded tetrazole carbon atoms. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows a single broadened signal at  $\delta$  38.3, assigned to the coordinated phosphine in **7**.

## Crystallography

The unprecedented molecular structure of a coordinated tetrazolylidene in **3** (Fig. 3) embodies a two-coordinated, cationic bis(carbene) complex with the angle about the Au(i) centre approximately linear [ $\text{C}(21)\text{--Au}(1)\text{--C}(11)$  177.3(3)°]. The tetrazole rings are only slightly twisted from planarity [torsion angles  $\text{N}(11)\text{--C}(11)\text{--C}(21)\text{--N}(21)$  and  $\text{N}(14)\text{--C}(11)\text{--C}(21)\text{--N}(21)$ , respectively,  $-6.6^\circ$  and  $174.4^\circ$ ] in agreement

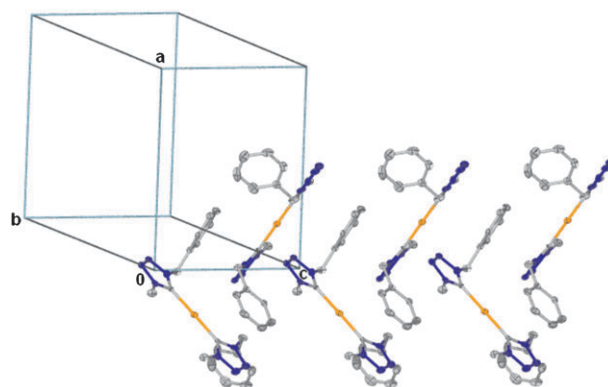


**Fig. 3** Molecular structure of **3** showing the numbering scheme; phenyl hydrogen atoms omitted for clarity (thermal ellipsoids drawn at 50% probability level). Selected bond lengths (Å) and bond angles (°): Au(1)–C(11) 2.035(7), Au(1)–C(21) 2.001(7), C(11)–N(11) 1.31(1), C(11)–N(14) 1.36(1), C(21)–N(21) 1.35(1), C(21)–N(24) 1.34(1); C(21)–Au(1)–C(11) 177.3(3), N(11)–C(11)–Au(1) 132.2(6), N(14)–C(11)–Au(1) 124.6(6), N(21)–C(21)–Au(1) 129.9(6), N(24)–C(21)–Au(1) 128.7(6).

with the perfectly co-planar classical NHC complex, bis(1,3-dimethylbenzimidazol-2-ylidene)gold(i) pentafluorophosphate<sup>8</sup> but in contrast to the larger interplanar angles of the dimeric bis(1-benzylimidazol-2-ylidene)gold(i) chloride [52.7° and 49.8°]<sup>31</sup> and bis(1,3-diethylbenzimidazol-2-ylidene)gold(i) pentafluorophosphate [52.96°].<sup>8</sup>

The Au(1)–C(11) and Au(1)–C(21) separations [2.035(7) Å and 2.001(7) Å] are similar within 4σ and correspond to Au(i)–NHC bonds in related compounds, bis(1-benzylimidazol-2-ylidene)gold(i) chloride [2.01(1) Å, 2.02(1) Å],<sup>31</sup> (1,3-dimethylimidazol-5-ylidene)(1-methylimidazol-5-ylidene) gold(i) triflate [1.99(1) Å, 2.00(2) Å],<sup>32</sup> bis(1,3-dimethylbenzimidazol-2-ylidene)gold(i) pentafluorophosphate [2.05(1) Å], bis(1,3-diethylbenzimidazol-2-ylidene)gold(i) pentafluorophosphate [2.02(1) Å] and bis(1-methylpyridin-2-ylidene)gold(i) chloride [2.03(2) Å, 2.02(2) Å].<sup>8</sup> It is worth noting that the N–N bond lengths within the tetrazole ring in **3** are consistent with those in 1-benzyltetrazole. The only notable difference occurs in the N(14)–C(11) and N(24)–C(21) separations [1.36(1) Å and 1.34(1) Å, respectively], which are similar to the N–C distances in other Au(i)–NHC but marginally longer than the related 1-benzyltetrazole [1.315(8) Å].<sup>8,33</sup> The organisation of the molecules in the crystal lattice, along the *c*-axis, is shown in Fig. 4, which illustrates the stacking of the phenyl and 5-membered rings of adjacent molecules (at 3.504 Å and 3.639 Å).

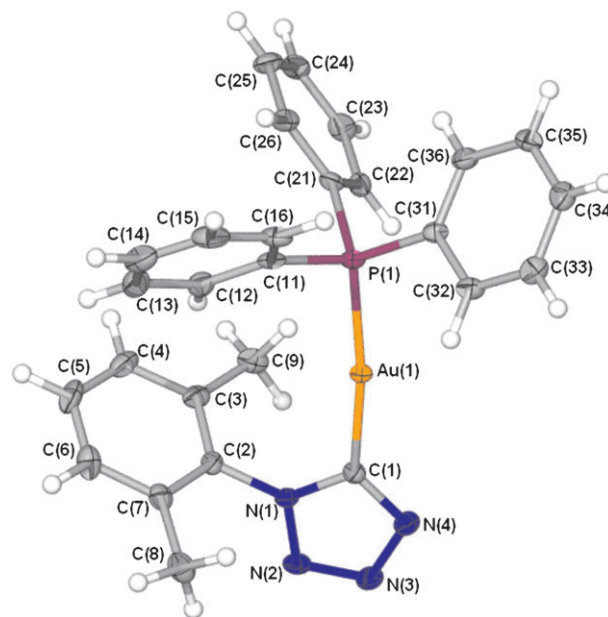
The lack of intermolecular Au···Au interactions can partly be ascribed to the steric bulk of the N<sup>1</sup>-benzyl substituents, which prevent a close approach of the metal centres. Bonati and co-workers<sup>31</sup> reported that bis(1-benzylimidazol-2-ylidene)gold(i) chloride aggregates as two independent molecules with Au···Au interactions [3.2630(5) Å]. In this instance, the benzyl moieties are in a *trans* disposition with regard to the



**Fig. 4** Unit cell and packing pattern along the *c*-axis in the crystal lattice of **3**, showing π–π interactions between the phenyl and tetrazole rings.

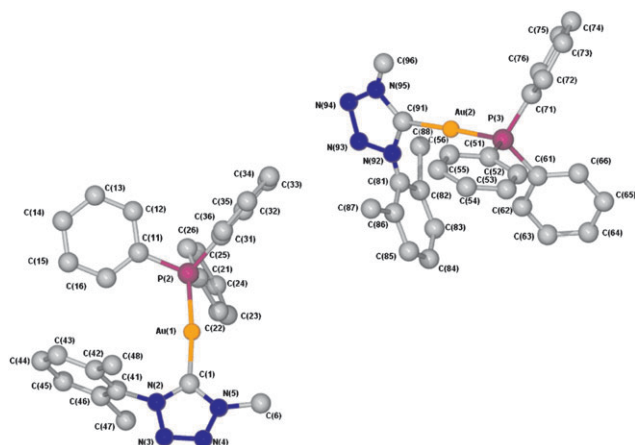
Au(carbene)<sub>2</sub> core allowing two chlorine ions to join the two complex cations through four hydrogen bond bridges. The organisation of the cations, however, is in agreement with the monomeric structure of (1,3-dimethylimidazol-5-ylidene)-(1-methylimidazol-5-ylidene)gold(i) triflate, which exhibits no aurophilic interactions.<sup>32</sup>

The gold centre in compound **4** (Fig. 5) is coordinated to a phosphorus atom of a PPh<sub>3</sub> moiety and to an azolyl carbon on the tetrazolyl ring. The coordination about the metal is significantly distorted from linearity, [C(1)–Au(1)–P(1) 172.60(3)°], in contrast to the essentially linear (isothiazol-5-yl)(triphenylphosphine)gold(i) [177.1(2)°],<sup>22</sup> and [1,3-di(*tert*-butyl)imidazol-2-ylidene](triphenylphosphine)gold(i) hexafluorophosphate [177.0(1)°],<sup>3a</sup> but comparable to



**Fig. 5** Molecular structure of **4** showing the numbering scheme; the included dichloromethane is omitted for clarity (thermal ellipsoids drawn at 50% probability level). Selected bond lengths (Å) and bond angles (°): Au(1)–C(1) 2.031(3), Au(1)–P(1) 2.2775(7), N(1)–C(1) 1.353(3), N(4)–C(1) 1.333(3); C(1)–Au(1)–P(1) 172.61(8), N(4)–C(1)–Au(1) 132.6(2), N(1)–C(1)–Au(1) 121.2(2).





**Fig. 6** The molecular structure of **5** showing two independent, two-coordinate molecules in the asymmetric unit. The hydrogen atoms and two triflate counter anions are omitted for clarity.

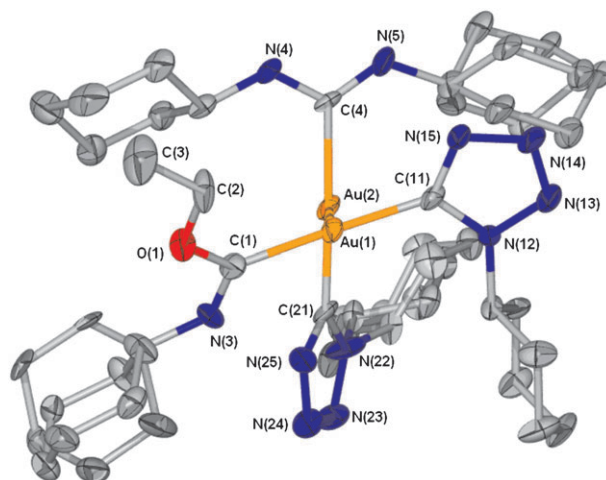
{1,3-bis(5*H*-dibenzo[*a,d*]cycloheptenyl)imidazol-2-ylidene}-(triphenylphosphine)gold(i) chloride (a bistropNHC gold carbene complex) [173.8(2)°].<sup>26</sup> The Au(1)–C(1) and Au(1)–P(1) bond separations [2.031(3) Å and 2.2777(7) Å, respectively] are normal. Unfortunately, due to the unsatisfactory refinement of the parent carbene complex, **5** (Fig. 6), a critical assessment cannot be made with regard to common structural parameters found in complexes **4** and **5**. However, compared to the structures of the two known mixed phosphine, NHC gold(i) complexes, the Au–P bonds appear not to change significantly upon subsequent carbene complex formation, *i.e.* {1,3-bis(5*H*-dibenzo[*a,d*]cycloheptenyl)imidazol-2-ylidene}-(triphenylphosphine)gold(i) chloride [2.299(2) Å]<sup>26</sup> and [1,3-di(*tert*-butyl)imidazol-2-ylidene](triphenylphosphine)gold(i) hexafluorophosphate [2.275(1) Å].<sup>3a</sup> The Au–C single bond in **4** [2.031(3) Å] differs somewhat from the corresponding bond length found for the carbene complex, {1,3-bis(5*H*-dibenzo[*a,d*]cycloheptenyl)imidazol-2-ylidene}(triphenylphosphine)-gold(i) chloride [2.111(7) Å],<sup>26</sup> but is essentially similar to the Au–C<sub>carbene</sub> bond in [1,3-di(*tert*-butyl)imidazol-2-ylidene](triphenylphosphine)gold(i) hexafluorophosphate [2.034(1) Å]. Molecules of **4** pack in regular rows along the *a*-axis as monomeric units and are interspersed with included dichloromethane. The latter molecule is disordered in two positions with equal occupancy. No intermolecular auriphilic interactions are present, presumably due to the overcrowding around the metal centre as a result of the presence of the triphenylphosphine and 2,6-dimethylphenyl moieties.

Despite repeated efforts under various conditions and from various solvent systems, only poor quality crystals of **5** were obtained by layering a dichloromethane solution of the complex with diethyl ether. Multiple attempts to collect a satisfactory crystallographic data set from these crystals were fruitless. We mention this structure since only two examples of NHC(phosphine)gold(i) complexes have been reported in the CCD. However, the data obtained allowed us to at least establish a basic connectivity of **5** which is corroborated by other analytical methods, such as elemental analysis, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy and mass spectrometry. Details of the data collection and structure determination of **5** are

summarised in the ESI† for completeness. Due to the low quality of the structure determination, only basic structural features of **5** will be discussed.

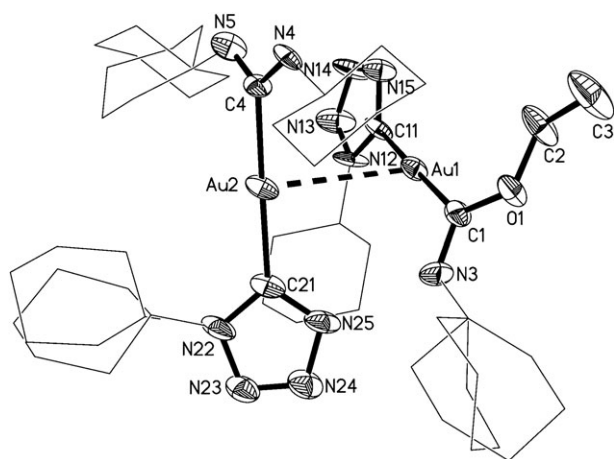
From dichloromethane–diethyl ether **5** crystallises in the monoclinic space group *P*2<sub>1</sub>/*c* with *Z* = 8 formula units in the unit cell. The asymmetric unit thus consists of 2 independent formula units. Fig. 6 depicts the best structural model obtained for the two independent cations of **5**. In both cases a PPh<sub>3</sub>Au<sup>+</sup>-fragment is bonded to the carbene carbon of a tetrazolylidene ligand, giving rise to a virtually linear P–Au–carbene carbon unit. The steric bulk of the 2,6-dimethylphenyl N<sup>1</sup> substituent is clearly visible and no intermolecular Au···Au contacts are discernible. A selective alkylation on the N<sup>4</sup> atom is confirmed, similar to complex **3**.

Colourless crystals that contain both carbene complexes, [alkoxy(amino)carbene][tetrazol-5-yl]gold(i), **9**, and (diamino-carbene)(tetrazol-5-yl)gold(i), **10**, were isolated. The bis(cyclohexylamine)- and ethoxy(cyclohexylamine)-substituents are coordinated to two (1-cyclohexyltetrazol-5-yl)gold(i) units (Fig. 7). Coordination around the metal center is essentially linear [C(4)–Au(2)–C(21) 178.1(4)° and C(1)–Au(1)–C(11) 176.7(4)°]. Notably all four trigonally planar metal-bonded carbon atoms have equal bond distances to gold: [C(1)–Au(1) 2.02(1) Å, C(11)–Au(1) 2.01(1) Å, C(4)–Au(2) 2.07(1) Å and C(21)–Au(2) 2.02(1) Å]. These bond lengths are in good agreement with related compounds, [{*cis,cis*-(*p*-MeC<sub>6</sub>H<sub>4</sub>NH)-(EtO)C<sub>2</sub>Au(i)] [ClO<sub>4</sub>] [2.03(3) Å and 1.93(3) Å],<sup>34</sup> [(ArNH)(EtO)-CAuCl] [2.04(4) Å and 1.98(3) Å],<sup>34</sup> [(MeNH)(Me<sub>2</sub>N)-C<sub>2</sub>Au(i)] [PF<sub>6</sub>] [2.050(3) Å]<sup>18</sup> and [(MeNH)<sub>2</sub>C<sub>2</sub>Au(i)] [Cl·H<sub>2</sub>O] [2.039(4) Å].<sup>35</sup>



**Fig. 7** Molecular structure of **9-10** showing the two independent molecules in the asymmetric unit and the numbering scheme (thermal ellipsoids drawn at 50% probability level). Selected bond lengths (Å) and bond angles (°): Au(1)–C(11) 2.01(1), Au(1)–C(1) 2.02(1), Au(2)–C(21) 2.02(1), Au(2)–C(4) 2.07(1), Au(1)–Au(2) 3.2880(9), C(11)–N(15) 1.33(1), C(11)–N(12) 1.37(1), C(21)–N(25) 1.33(1), C(21)–N(22) 1.37(1); C(11)–Au(1)–C(1) 176.8(4), C(11)–Au(1)–Au(2) 89.0(3), C(1)–Au(1)–Au(2) 93.9(3), C(21)–Au(2)–C(4) 178.1(4), C(21)–Au(2)–Au(1) 91.4(3), C(4)–Au(2)–Au(1) 88.2(3), N(15)–C(11)–Au(1) 129.1(8), N(4)–C(4)–Au(2) 119.0(8), N(25)–C(21)–Au(2) 126.4(8).





**Fig. 8** Molecular structure of **9-10** with the modelled disorder in the cyclohexyl rings.

Schmidbaur and co-workers<sup>28</sup> reported the complex  $[(\text{CyNC})\{(\text{CyNH})_2\text{C}\}\text{Au}(\text{I})][\text{Cl}]$  with an identical ligand to the one in complex **9**, but which contains a 1-cyclohexylisocyanide ligand instead of the 1-cyclohexyltetrazol-5-yl present in **9**. In  $[(\text{CyNC})\{(\text{CyNH})_2\text{C}\}\text{Au}(\text{I})][\text{Cl}]$  and **9** the metal–carbene bonds are similar [ $\text{Au}-\text{C}_{\text{carbene}}$  2.03(1) Å and  $\text{Au}(2)-\text{C}(4)$  2.07(1) Å]. The two molecules that co-crystallise (in **9-10**) illustrate that the relative *trans* influence of ethoxy(amino)carbene and di(amino)carbene substituents are very similar, based on the very consistent  $\text{Au}-\text{C}(\text{tetrazolyl})$  bond lengths [2.01(1) and 2.02(1) Å]. In both complexes **9** and **10**, the acyclic carbene ligands are rotated out of plane to the plane occupied by the heterocyclic rings. Within the crystalline lattice, the two carbene complex types aggregate by relatively weak  $\text{Au}(\text{I}) \cdots \text{Au}(\text{I})$  interactions [3.2880 (9) Å]. The two molecules approach each other at an almost perpendicular angle [torsion angles  $\text{C}(11)-\text{Au}(1)-\text{Au}(2)-\text{C}(21)$ ,  $\text{C}(1)-\text{Au}(1)-\text{Au}(2)-\text{C}(21)$ , at  $109.6(4)^\circ$  and  $-69.1(4)^\circ$ , respectively] (Fig. 8). Three of the four cyclohexyl rings [N(3), N(5) and N(22)] are disordered in two positions, the modelled disorder is shown in Fig. 8.

## Conclusions

In the present study we reconfirmed that stable tetrazolyl and tetrazolylidene complexes of gold(I), although rare, can be prepared according to two classic procedures. First, by following a lithiation–transmetallation–alkylation sequence, neutral and cationic mono(carbene)gold(I) complexes can be obtained. The first X-ray structure analysis performed on a C-bonded tetrazole-derived carbene gold(I) complex, bis(1-benzyltetrazol-5-ylidene)gold(I) triflate (**3**)—also obtained by homoleptic rearrangement of **1**—revealed that alkylation to afford carbene complex formation occurs selectively on the nucleophilic  $\text{N}^4$  heteroatom. Secondly, by using the elegant “click chemistry” of Beck and co-workers,<sup>9</sup> we could show that simultaneous 1,3-cycloaddition and ligand substitution reactions to afford various neutral isocyanide(tetrazol-5-yl)gold(I) complexes are strongly dependent on the reactivity and concentration of isocyanide employed.

A series of phosphine-containing (tetrazolyl)gold(I) complexes, some different from the Beck and Fehlhammer examples, were prepared. These isolable compounds are precursors to new NHC compounds of gold(I), as illustrated by the successful isolation of a mono(carbene) complex. Structural analysis of this compound revealed that electrophilic addition is again favoured on the  $\text{N}^4$  position. In our contribution to the Bonati–Minghetti approach towards carbene complex formation, a tetrazolyl(phosphine)gold(I) complex, **7**, is converted in a serendipitous finding to an amino(ethoxy)carbene complex of gold, **9**, and a di(amino)carbene complex, **10**, which co-crystallise.

## Experimental

### General procedures and instruments

Reactions were carried out under argon using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (thf), *n*-hexane, *n*-pentane and diethyl ether were distilled under  $\text{N}_2$  from sodium benzophenone, dichloromethane from  $\text{CaH}_2$ , ethanol and methanol from magnesium. 2,6-Dimethylphenyl-, *tert*-butyl-, 1-cyclohexyl- and benzotriazol-1-ylmethyl-isocyanide, 1,2,4-triazol-3-ylamine, butyllithium (1.6 M solution *n*-hexane) and  $\text{CF}_3\text{SO}_3\text{Me}$  were purchased from Aldrich. TMEDA was purchased from Merck. Literature methods were used to prepare 1-benzyltetrazole,<sup>36</sup>  $[\text{AuCl}(\text{tht})]$ ,<sup>37</sup>  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ ,<sup>38</sup>  $[\text{AuCl}(\text{PPh}_3)]$ ,<sup>39</sup>  $[\text{Au}(\text{NO}_3)(\text{PPh}_3)]$ <sup>40</sup> and  $[\text{Au}(\text{N}_3)(\text{PPh}_3)]$ .<sup>41</sup> Melting points were determined on a Stuart SMP3 apparatus and are uncorrected. Mass spectra were recorded on an AMD 604 (EI, 70 eV), VG Quattro (ESI, 70 eV methanol, acetonitrile) or VG 70 SEQ (FAB, 70 eV, (nitrophenyl)methanol matrices) instrument. In the instance of EI and FAB MS the isotopic distribution patterns were checked against the theoretical distribution. All NMR spectra were recorded on a Varian VXR 300 or Varian INOVA 400 or 600 MHz spectrometer ( $^1\text{H}$  NMR at 300/400/600 MHz,  $^{13}\text{C}\{^1\text{H}\}$  NMR at 75/100/150 MHz,  $^{31}\text{P}\{^1\text{H}\}$  NMR at 121/162/243 MHz,  $^{15}\text{N}$  NMR at 60.8 MHz,  $^{19}\text{F}$  NMR at 284/376/564 MHz). Chemical shifts ( $\delta$ ) are reported relative to solvent resonance or external reference of 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ),  $\text{NH}_3\text{NO}_2$  ( $^{15}\text{N}$ ) or  $\text{CFCl}_3$  ( $^{19}\text{F}$ ). Infrared spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR with a Smart OMNI ATR (attenuated total reflectance) sampler. Elemental analyses were carried out at the School of Chemistry, University of the Witwatersrand. For elemental analysis, products were evacuated under high vacuum for 10 h prior to analysis.

### Syntheses

**(1-Benzyl-4-methyl-4,5-dihydro-1H-1,2,3,4-tetrazol-5-ylidene)-(triphenylphosphine)gold(I) triflate, 1.** A solution of 1-benzyltetrazole (0.24 g, 1.5 mmol) in thf (15 ml) was treated with *n*-butyllithium in hexane (1.0 ml, 1.5 mmol) at  $-98^\circ\text{C}$ . After 30 min of stirring  $[\text{AuCl}(\text{PPh}_3)]$  (0.74 g, 1.5 mmol) in thf (10 ml) was added to the orange coloured solution. The reaction mixture was stirred for a further 1.5 h between  $-98^\circ\text{C}$  and  $-78^\circ\text{C}$ , during which time the solution became colourless. The product was treated with  $\text{CF}_3\text{SO}_3\text{CH}_3$  (0.18 ml, 1.6 mmol) at  $-78^\circ\text{C}$ , reacted for 1 h, and slowly allowed to reach room temperature. The solvent was removed *in vacuo* to

yield a colourless oily residue. The residue was extracted sequentially with a diethyl ether–*n*-pentane mixture (1 : 1, 30 ml), and dichloromethane (30 ml) and the extracts were filtered individually through MgSO<sub>4</sub>. The dichloromethane extract was concentrated *in vacuo* to afford a colourless microcrystalline solid, **1** (0.83 g, 71%); mp 61–63 °C.  $\delta_{\text{H}}$  [300 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 7.51–7.67 (15H, m, PPh<sub>3</sub>), 7.16–7.42 (5H, m, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 5.82 (2H, s, NCH<sub>2</sub>), 4.36 (3H, s, CH<sub>3</sub>).  $\delta_{\text{C}}$  [75 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 180.6 (s, AuC), 134.7 (br s, *o*-PC<sub>6</sub>H<sub>5</sub>), 130.3 (br s, *m*-PC<sub>6</sub>H<sub>5</sub>), 129.7 (s, *o*/*m*-C<sub>6</sub>H<sub>5</sub>), 129.4 (br s, *i*-PC<sub>6</sub>H<sub>5</sub>), 129.3 (br s, *p*-PC<sub>6</sub>H<sub>5</sub>), 129.3 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 129.2 (s, *m*/*o*-C<sub>6</sub>H<sub>5</sub>), 128.9 (s, *i*-C<sub>6</sub>H<sub>5</sub>), 55.4 (s, NCH<sub>2</sub>), 38.70 (s, CH<sub>3</sub>).  $\delta_{\text{N}}$  [61 MHz, CD<sub>2</sub>Cl<sub>2</sub>] –11.2 (s, N<sub>2</sub>), –11.5 (s, N<sub>3</sub>), –119.9 (s, N<sub>1</sub>), –132.5 (s, N<sub>4</sub>).  $\delta_{\text{P}}$  [121 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 44.0 (s). *m/z* (EI) 633 [2, (M – CF<sub>3</sub>SO<sub>3</sub>)<sup>+</sup>], 459 [15, (M – CF<sub>3</sub>SO<sub>3</sub> – C<sub>9</sub>H<sub>10</sub>N<sub>4</sub>)<sup>+</sup>], 371 [2, (M – CF<sub>3</sub>SO<sub>3</sub> – PPh<sub>3</sub>)<sup>+</sup>].

**(1-Benzyl-4-methyl-4,5-dihydro-1H-1,2,3,4-tetrazol-5-ylidene)-(pentafluorophenyl)gold(i), 2.** Complex **2** was prepared as described above using 1-benzyltetrazole (0.14 g, 0.87 mmol), *n*-butyllithium in hexane (0.56 ml, 0.87 mmol), [Au(C<sub>6</sub>F<sub>5</sub>)(tht)] (0.39 g, 0.87 mmol) and CF<sub>3</sub>SO<sub>3</sub>CH<sub>3</sub> (0.10 ml, 0.87 mmol) to afford a colourless microcrystalline solid, **2** (0.36 g, 77%); mp 136–139 °C. Found: C, 33.3; H, 2.0; N, 10.5%. C<sub>15</sub>H<sub>10</sub>AuF<sub>5</sub>N<sub>4</sub> requires C, 33.5; H, 1.9; N, 10.4%.  $\delta_{\text{H}}$  [300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO] 7.28–7.52 (5H, m, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 5.91 (2H, s, NCH<sub>2</sub>), 3.85 (3H, s, CH<sub>3</sub>).  $\delta_{\text{C}}$  [75 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 186.6 (s, AuC), 150.6 (dm, *J*<sub>CF</sub> 227.6, *o*-C<sub>6</sub>F<sub>5</sub>), 139.7 (dm, *J*<sub>CF</sub> 230.8, *p*-C<sub>6</sub>F<sub>5</sub>), 138.1 (dm, *J*<sub>CF</sub> 250.5, *m*-C<sub>6</sub>F<sub>5</sub>), 134.2 (tm, *J*<sub>CF</sub> 61.2, *m*-C<sub>6</sub>F<sub>5</sub>), 131.2 (s, *i*-C<sub>6</sub>H<sub>5</sub>), 131.2 (s, *o*/*m*-C<sub>6</sub>H<sub>5</sub>), 131.1 (s, *m*/*o*-C<sub>6</sub>H<sub>5</sub>), 129.9 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 123.0 (q, *J*<sub>C-F</sub> 320.9, CF<sub>3</sub>SO<sub>3</sub>), 55.6 (s, NCH<sub>2</sub>), 38.4 (s, CH<sub>3</sub>).  $\delta_{\text{F}}$  [376 MHz, CD<sub>2</sub>Cl<sub>2</sub>] –115.6 (m, *o*/*m*-C<sub>6</sub>F<sub>5</sub>), –160.3 (m, *p*-C<sub>6</sub>F<sub>5</sub>), –163.5 (m, *m*/*o*-C<sub>6</sub>F<sub>5</sub>). *m/z* (EI) 538 [12, (M)<sup>+</sup>], 510 [7, (M – CF<sub>3</sub>SO<sub>3</sub> – N<sub>2</sub>)<sup>+</sup>], 364 [2, (M – CF<sub>3</sub>SO<sub>3</sub> – C<sub>9</sub>H<sub>10</sub>N<sub>4</sub>)<sup>+</sup>], 334 [15, (C<sub>12</sub>F<sub>10</sub>)<sup>+</sup>].

**Bis(1-benzyl-4-methyl-4,5-dihydro-1H-1,2,3,4-tetrazol-5-ylidene)-gold(i) triflate, 3.** The same experimental procedure as described for **1** was used to prepare **3** from 1-benzyltetrazole (0.31 g, 1.9 mmol), *n*-butyllithium in hexane (1.3 ml, 1.9 mmol), [AuCl(tht)] (0.31 g, 0.98 mmol) and CF<sub>3</sub>SO<sub>3</sub>CH<sub>3</sub> (0.22 ml, 1.9 mmol) to obtain a colourless solid, which was recrystallised from a dichloromethane solution layered with diethyl ether at –20 °C to yield colourless needles, **3** (0.47 g, 69%). Mp 118–120 °C (decomp.). Found: C, 32.6; H, 2.8; N, 16.3%. C<sub>19</sub>H<sub>20</sub>AuF<sub>3</sub>N<sub>8</sub>O<sub>3</sub>S requires C, 32.7; H, 2.9; N, 16.1%.  $\delta_{\text{H}}$  [300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO] 7.41–7.56 (5H, m, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 5.96 (2H, s, NCH<sub>2</sub>), 4.36 (3H, s, CH<sub>3</sub>).  $\delta_{\text{C}}$  [75 MHz, (CD<sub>3</sub>)<sub>2</sub>CO] 182.6 (s, AuC), 131.4 (s, *o*/*m*-C<sub>6</sub>H<sub>5</sub>), 131.3 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 131.0 (s, *m*/*o*-C<sub>6</sub>H<sub>5</sub>), 130.8 (s, *i*-C<sub>6</sub>H<sub>5</sub>), 123.6 (q, *J*<sub>C-F</sub> 322.8, CF<sub>3</sub>SO<sub>3</sub>), 56.7 (s, NCH<sub>2</sub>), 39.9 (s, CH<sub>3</sub>).  $\delta_{\text{N}}$  [61 MHz, CD<sub>2</sub>Cl<sub>2</sub>] –12.7 (s, N<sub>3</sub>), –14.4 (s, N<sub>2</sub>), –123.0 (s, N<sub>1</sub>), –134.2 (s, N<sub>4</sub>). *m/z* (EI) 545 [7, (M – CF<sub>3</sub>SO<sub>3</sub>)<sup>+</sup>], 517 [13, (M – CF<sub>3</sub>SO<sub>3</sub> – N<sub>2</sub>)<sup>+</sup>], 489 [9, (M – CF<sub>3</sub>SO<sub>3</sub> – 2N<sub>2</sub>)<sup>+</sup>].

Crystals suitable for X-ray diffraction were grown from a dichloromethane solution layered with diethyl ether.

**[1-(2,6-Dimethylphenyl)-1H-tetrazol-5-yl](triphenylphosphine)-gold(i), 4.** A solution of [Au(N<sub>3</sub>)(PPh<sub>3</sub>)] (0.23 g, 0.46 mmol) in

dichloromethane (25 ml) was reacted with 2,6-dimethylphenylisocyanide (0.91 g, 6.9 mmol) in dichloromethane (10 ml). The reaction was protected from sunlight and left unstirred for 17 h, upon which the solution was concentrated to approximately 15 ml. The addition of diethyl ether to the solution produced a colourless precipitate, which upon recrystallisation from a dichloromethane solution layered with diethyl ether afforded colourless prisms of **4** (0.20 g, 69%). Mp 97–98 °C. Found: C, 51.8; H, 3.6; N, 9.0%. C<sub>27</sub>H<sub>24</sub>AuN<sub>4</sub>P requires C, 51.3; H, 3.8; N, 8.9%.  $\delta_{\text{H}}$  [300 MHz, (CD<sub>2</sub>Cl<sub>2</sub>)] 7.34–7.56 (15H, m, PPh), 7.23 (2H, d, <sup>3</sup>*J*<sub>HH</sub> 1.2, *m*-C<sub>6</sub>H<sub>5</sub>), 7.21 (1H, dd, <sup>3</sup>*J*<sub>HH</sub> 1.3, <sup>3</sup>*J*<sub>HH</sub> 1.4, *p*-C<sub>6</sub>H<sub>5</sub>), 1.94 (6H, br s, 2CH<sub>3</sub>).  $\delta_{\text{C}}$  [75 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 186.6 (s, AuC), 137.0 (s, *i*-C<sub>6</sub>H<sub>3</sub>[CH<sub>3</sub>]<sub>2</sub>), 136.7 (s, *o*-C<sub>6</sub>H<sub>3</sub>[CH<sub>3</sub>]<sub>2</sub>), 134.7 (d, *J*<sub>CP</sub> 13.9, *o*-PC<sub>6</sub>H<sub>5</sub>), 132.3 (d, *J*<sub>CP</sub> 2.2, *p*-PC<sub>6</sub>H<sub>5</sub>), 129.9 (s, *p*-C<sub>6</sub>H<sub>3</sub>[CH<sub>3</sub>]<sub>2</sub>), 129.8 (d, *J*<sub>CP</sub> 11.4, *m*-PC<sub>6</sub>H<sub>5</sub>), 129.8 (d, *J*<sub>CP</sub> 56.6, *i*-PC<sub>6</sub>H<sub>5</sub>), 128.7 (s, *m*-C<sub>6</sub>H<sub>3</sub>[CH<sub>3</sub>]<sub>2</sub>), 17.9 (s, 2CH<sub>3</sub>).  $\delta_{\text{P}}$  [121 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 41.3 (s). *m/z* (EI) 459 [9, AuPPh<sub>3</sub><sup>+</sup>], 262 [19, PPh<sub>3</sub><sup>+</sup>].

Crystals suitable for X-ray diffraction were grown from a dichloromethane solution layered with diethyl ether.

**[1-(2,6-Dimethylphenyl)-4-methyl-4,5-dihydro-1H-1,2,3,4-tetrazol-5-ylidene](triphenylphosphine)gold(i) triflate, 5.** A solution of **4** (0.14 g, 0.22 mmol) in dichloromethane (10 ml) was cooled to –70 °C, treated with CF<sub>3</sub>SO<sub>3</sub>Me (0.03 ml, 0.2 mmol) and stirred for 30 min, whereafter the mixture was allowed to reach room temperature. The solvent was removed *in vacuo* to yield a dark brown residue. The residue was extracted sequentially with diethyl ether (30 ml) and dichloromethane (30 ml) and the extracts were filtered individually through MgSO<sub>4</sub>. The ether extract was concentrated *in vacuo* to yield a colourless solid. Recrystallisation from a dichloromethane solution layered with diethyl ether afforded colourless needles of **5** (0.13 g, 91%). Mp 165–167 °C. Found: C, 43.5; H, 3.3; N, 7.6%. C<sub>29</sub>H<sub>27</sub>AuF<sub>3</sub>N<sub>4</sub>O<sub>3</sub>PS requires C, 43.7; H, 3.4; N, 7.0%.  $\delta_{\text{H}}$  [300 MHz, (CD<sub>2</sub>Cl<sub>2</sub>)] 7.46–7.63 (15H, m, PPh), 7.33 (2H, m, *m*-C<sub>6</sub>H<sub>5</sub>), 7.31 (1H, m, *p*-C<sub>6</sub>H<sub>5</sub>), 4.51 (3H, s, NCH<sub>3</sub>), 2.05 (6H, br s, 2CH<sub>3</sub>).  $\delta_{\text{C}}$  [75 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 186.9 (d, *J*<sub>CP</sub> 121.6, AuC), 136.3 (s, *o*-C<sub>6</sub>H<sub>3</sub>[CH<sub>3</sub>]<sub>2</sub>), 134.7 (d, *J*<sub>CP</sub> 13.8, *o*-PC<sub>6</sub>H<sub>5</sub>), 134.1 (s, *i*-C<sub>6</sub>H<sub>3</sub>[CH<sub>3</sub>]<sub>2</sub>), 133.1 (d, *J*<sub>CP</sub> 2.6, *p*-PC<sub>6</sub>H<sub>5</sub>), 132.4 (d, *p*-C<sub>6</sub>H<sub>3</sub>[CH<sub>3</sub>]<sub>2</sub>), 130.2 (d, *J*<sub>CP</sub> 11.9, *m*-PC<sub>6</sub>H<sub>5</sub>), 129.7 (s, *m*-C<sub>6</sub>H<sub>3</sub>[CH<sub>3</sub>]<sub>2</sub>), 127.8 (d, *J*<sub>CP</sub> 60.8, *i*-PC<sub>6</sub>H<sub>5</sub>), 121.7 (q, *J*<sub>CF</sub> 322.5, CF<sub>3</sub>SO<sub>3</sub>), 39.0 (s, NCH<sub>3</sub>), 18.0 (s, 2CH<sub>3</sub>).  $\delta_{\text{P}}$  [121 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 39.7 (s). *m/z* (ESI) 647 [49, (M – CF<sub>3</sub>SO<sub>3</sub>)<sup>+</sup>], 619 [91, (M – CF<sub>3</sub>SO<sub>3</sub> – N<sub>2</sub>)<sup>+</sup>], 459 [7, AuPPh<sub>3</sub><sup>+</sup>], 385 [2, (M – CF<sub>3</sub>SO<sub>3</sub> – PPh<sub>3</sub>)<sup>+</sup>].

Crystals more suitable for X-ray diffraction studies were grown from a dichloromethane solution layered with diethyl ether.

**[1-(*tert*-Butyl)-1H-tetrazol-5-yl](triphenylphosphine)gold (i), 6.** The same experimental procedure as for the preparation of **4** was used to prepare **6** from [Au(N<sub>3</sub>)(PPh<sub>3</sub>)] (0.30 g, 0.60 mmol) and *tert*-butylisocyanide (0.50 g, 6.0 mmol) to produce a colourless microcrystalline product, **6** (0.26 g, 74%); mp 146 °C (decomp.). Found: C, 47.0; H, 4.6; N, 9.3%. C<sub>23</sub>H<sub>24</sub>AuN<sub>4</sub>P requires C, 47.3; H, 4.1; N, 9.6%.  $\delta_{\text{H}}$  [300 MHz, (CD<sub>2</sub>Cl<sub>2</sub>)] 7.51–7.75 (15H, m, PPh), 1.75 (9H, br s,

C[CH<sub>3</sub>]<sub>3</sub>).  $\delta_{\text{C}}$  [75 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 172.9 (s, AuC), 134.1 (d,  $J_{\text{CP}}$  13.7, *o*-PC<sub>6</sub>H<sub>5</sub>), 132.3 (d,  $J_{\text{CP}}$  2.8, *p*-PC<sub>6</sub>H<sub>5</sub>), 129.8 (d,  $J_{\text{CP}}$  11.9, *m*-PC<sub>6</sub>H<sub>5</sub>), 129.3 (d,  $J_{\text{CP}}$  63.4, *i*-PC<sub>6</sub>H<sub>5</sub>), 31.1 (s, C[CH<sub>3</sub>]<sub>3</sub>), 28.7 (s, C[CH<sub>3</sub>]<sub>3</sub>).  $\delta_{\text{P}}$  [121 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 26.7 (s).  $m/z$  (FAB) 583 [13, M<sup>+</sup>], 555 [3, (M – N<sub>2</sub>)<sup>+</sup>], 501 [3, (M – C<sub>4</sub>H<sub>9</sub>N<sub>2</sub>)<sup>+</sup>], 486 [3, (AuPPh<sub>3</sub>CN)<sup>+</sup>].

**The formation of [1-(cyclohexyl)-1*H*-tetrazol-5-yl](triphenylphosphine)gold(i), 7, and [1-cyclohexylisocyanide][1-(cyclohexyl)-1*H*-tetrazol-5-yl]gold (i), 8.** The same experimental procedure as described for 4 was used to prepare the mixture of 7 and 8 from [Au(N<sub>3</sub>)(PPh<sub>3</sub>)] (0.50 g, 1.00 mmol) and 1-cyclohexylisocyanide (2.18 g, 20.0 mmol) to form a colourless microcrystalline product, a mixture of complexes 7 and 8 (0.37 g).

7  $\delta_{\text{H}}$  [300 MHz, (CD<sub>2</sub>Cl<sub>2</sub>)] 7.47–7.62 (15H, m, PPh), 4.65 (1H, m, C<sub>6</sub>H<sub>11</sub>), 2.08 (4H, m, C<sub>6</sub>H<sub>11</sub>), 1.38 (4H, m, C<sub>6</sub>H<sub>11</sub>), 1.24 (2H, m, C<sub>6</sub>H<sub>11</sub>).  $\delta_{\text{C}}$  [75 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 181.7 (s, AuC), 134.7 (d,  $J_{\text{CP}}$  13.9, *o*-PC<sub>6</sub>H<sub>5</sub>), 132.4 (d,  $J_{\text{CP}}$  2.5, *p*-PC<sub>6</sub>H<sub>5</sub>), 129.9 (d,  $J_{\text{CP}}$  58.1, *i*-PC<sub>6</sub>H<sub>5</sub>), 129.8 (d,  $J_{\text{CP}}$  11.6, *m*-PC<sub>6</sub>H<sub>5</sub>), 59.4 (s, C<sub>6</sub>H<sub>11</sub>), 34.6 (s, C<sub>6</sub>H<sub>11</sub>), 25.9 (s, C<sub>6</sub>H<sub>11</sub>), 25.0 (s, C<sub>6</sub>H<sub>11</sub>).  $\delta_{\text{P}}$  [121 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 38.3 (br s).  $m/z$  (ESI) 611 [10, M<sup>+</sup>], 459 [7, AuPPh<sub>3</sub><sup>+</sup>].

8  $\delta_{\text{H}}$  [300 MHz, (CD<sub>2</sub>Cl<sub>2</sub>)] 4.65 (1H, m, C<sub>6</sub>H<sub>11</sub>), 3.71 (1H, br s, C<sub>6</sub>H<sub>11</sub>), 2.08 (4H, m, C<sub>6</sub>H<sub>11</sub>), 1.89 (4H, m, C<sub>6</sub>H<sub>11</sub>), 1.70 (4H, m, C<sub>6</sub>H<sub>11</sub>), 1.38 (4H, m, C<sub>6</sub>H<sub>11</sub>), 1.24 (4H, m, C<sub>6</sub>H<sub>11</sub>).  $\delta_{\text{C}}$

[75 MHz, CD<sub>2</sub>Cl<sub>2</sub>] 181.7 (s, AuC), 59.4 (s, C<sub>6</sub>H<sub>11</sub>), 34.6 (s, C<sub>6</sub>H<sub>11</sub>), 32.5 (s, C<sub>6</sub>H<sub>11</sub>), 25.9 (s, C<sub>6</sub>H<sub>11</sub>), 25.5 (s, C<sub>6</sub>H<sub>11</sub>), 25.0 (s, C<sub>6</sub>H<sub>11</sub>), 23.0 (s, C<sub>6</sub>H<sub>11</sub>).  $m/z$  (ESI) 611 [10, M<sup>+</sup>], 459 [7, AuPPh<sub>3</sub><sup>+</sup>].  $\nu_{\text{max}}$ /cm<sup>–1</sup> 3050s, 2861vs, 2251vs.

**The formation of complexes, [1-(cyclohexyl)-1*H*-tetrazol-5-yl]-[cyclohexylamine(ethoxy)ylidenel]gold(i), 9, and [1-(cyclohexyl)-1*H*-tetrazol-5-yl]bis(cyclohexylamine)ylidenel]gold(i), 10.** The product mixture of 7 and 8 (containing some residual amounts of 1-cyclohexylisocyanide) was dissolved in freshly distilled ethanol layered with *n*-pentane and was stored in a narrow Schlenk tube at –20 °C for 8 months. Apart from an unidentified and insoluble bright yellow luminescent microcrystalline solid which formed towards the base of the gas-inlet tap and cap, colourless needle-like crystals, a co-crystallate of 9 and 10, formed from the solution.

### Crystal structure determination

Specimens of suitable quality and size of 3, 4, 5 and 9–10 were mounted on the ends of glass fibres in inert oil and used for intensity data collection on a Bruker SMART Apex CCD diffractometer,<sup>42</sup> employing graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data reduction was carried out using the SAINT<sup>43</sup> suite of programs and multi-scan absorption corrections were performed with SADABS.<sup>44,45</sup> The structures

**Table 1** Crystallographic and data collection parameters of 3, 4 and 9–10

Compound	3	4	9–10
Empirical formula	C <sub>19</sub> H <sub>20</sub> AuF <sub>3</sub> N <sub>8</sub> O <sub>3</sub> S	C <sub>28</sub> H <sub>26</sub> AuCl <sub>2</sub> N <sub>4</sub> P	C <sub>36</sub> H <sub>63</sub> Au <sub>2</sub> N <sub>11</sub> O
$M_r$	694.46	717.36	1059.91
$T/K$	100(2)	100(2)	173(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
$a/\text{\AA}$	11.812(2)	8.6440(8)	10.569(3)
$b/\text{\AA}$	22.452(3)	12.738(1)	12.484(3)
$c/\text{\AA}$	8.892(1)	24.885(2)	16.827(5)
$\alpha/^\circ$	90	90	95.641(4)
$\beta/^\circ$	90	94.429(2)	98.979(4)
$\gamma/^\circ$	90	90	110.714(4)
Volume/Å <sup>3</sup>	2358.1(5)	2731.8(4)	2022.8(9)
$Z$	4	4	2
$d_{\text{calcd}}/\text{g cm}^{-3}$	1.956	1.744	1.740
Absorption coefficient, $\mu/\text{mm}^{-1}$	6.390	5.664	7.287
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
$F(000)$	1344	1400	1044
Crystal size/mm	0.20 × 0.20 × 0.10	0.30 × 0.20 × 0.10	0.20 × 0.10 × 0.10
$\theta$ -Range for data collection/ $^\circ$	1.81 to 26.72	2.29 to 26.76	1.77 to 25.35
Index range	–10 ≤ $h$ ≤ 14, –25 ≤ $k$ ≤ 28, –11 ≤ $l$ ≤ 11	–10 ≤ $h$ ≤ 10 –16 ≤ $k$ ≤ 16 –29 ≤ $l$ ≤ 31	–12 ≤ $h$ ≤ 12 –15 ≤ $k$ ≤ 15 –20 ≤ $l$ ≤ 20
No. of reflections collected	12 896	20 718	19 845
No. independent reflections	4842 [ $R_{\text{int}}$ = 0.0356]	5797 [ $R_{\text{int}}$ = 0.0239]	7361 [ $R_{\text{int}}$ = 0.0635]
Max. and min. transmission	0.5280 and 0.3181	0.4182 and 0.6012	0.5294 and 0.3235
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	4842/1/318	5797/0/355	7361/258/599
Flack parameter	0.037(11)		
Goof on $F^2$	1.108	1.047	1.077
Final $R$ -indices [ $I > 2\sigma > (I)$ ] <sup>a</sup>	$R_1$ = 0.0407 $wR_2$ = 0.0854	$R_1$ = 0.0213 $wR_2$ = 0.0487	$R_1$ = 0.0589 $wR_2$ = 0.1180
$R$ indices (all data)	$R_1$ = 0.0517 $wR_2$ = 0.0890	$R_1$ = 0.0241 $wR_2$ = 0.0498	$R_1$ = 0.0874 $wR_2$ = 0.1283
Largest diff. peak and hole/e Å <sup>–3</sup>	2.900 and –1.222	1.176 and –0.698	2.108 and –2.521
Weighting scheme	$a$ = 0.0355, $b$ = 3.4720	$a$ = 0.0223, $b$ = 2.9786	$a$ = 0.0582, $b$ = 0.2758

<sup>a</sup>  $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ ;  $w = 1/[\sigma^2(F_o)^2 + ap^2 + bp]$  where  $p = (F_o^2 + 2F_c^2)/3$ .

were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on  $F^2$  (SHELXL-97)<sup>46</sup> within the X-Seed environment.<sup>47</sup> Thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated in ideal positions and refined using a riding model. The asymmetric unit of **3** contains one molecule of dichloromethane which is disordered over two sites. A split atom model was used to take this into account. Three cyclohexyl groups in the structure of **9-10** are disordered over two sites each. Similarity restraints were applied to obtain similar geometries for each pair of corresponding cyclohexyl positions. The nitrogen bound hydrogen atoms were placed on maxima on a difference fourier map. For subsequent refinements their coordinates had to be fixed to the positions of original placement. Fixed isotropic displacement parameters were used for the refinement of these three hydrogen atoms. Further details regarding the data collection and structure refinement for compounds **3**, **4** and **9-10** are listed in Table 1, details for compound **5** can be found in the ESI†.

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