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# Do Gold(III) Complexes Form Hydrogen Bonds? An Exploration of Au(III) Dicarboranyl Chemistry

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**Abstract:** The reaction of 1,1'-Li<sub>2</sub>[(2,2'-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)<sub>2</sub>] with the cyclometallated gold(III) complex (C<sup>^</sup>N)AuCl<sub>2</sub> affords the first examples of gold(III) dicarboranyl complexes. The reactivity of these complexes is subject to the *trans*-influence exerted by the dicarboranyl ligand, which is substantially weaker than that of non-carboranyl anionic C-ligands. In line with this, displacement of coordinated pyridine by chloride is only possible under forcing conditions. While treatment of (C<sup>^</sup>N)Au[(2,2'-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)<sub>2</sub>] (**2**) with triflic acid leads to Au-C rather than Au-N bond protonolysis, aqueous HBr cleaves the Au-N bond to give the pyridinium bromo complex **7**. The *trans*-influence of a series of ligands including dicarboranyl and bis(dicarboranyl) was assessed by means of DFT calculations. The analysis demonstrated that it was not sufficient to rely exclusively on geometric descriptors (calculated or experimental) when attempting to rank ligands for their *trans* influence. Complex (C<sup>^</sup>N)Au(C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)<sub>2</sub> containing two non-chelating dicarboranyl ligands was prepared similar to **2**. Its reaction with trifluoroacetic acid also leads to Au-N cleavage to give *trans*-(Hpy<sup>^</sup>C)Au(OAc<sup>F</sup>)(C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)<sub>2</sub> (**8**). In crystals of **8** the pyridinium N-H bond points towards the metal centre, while in **7** it is bent away. The possible contribution of gold(III) ...H-N hydrogen bonding in these complexes was investigated by DFT calculations. The results show that, unlike the situation for platinum(II), there is no evidence for an energetically significant contribution by hydrogen bonding in the case of gold(III).

## Introduction

Hydrogen bonding interactions consist of three components: an electronegative main group element that acts as donor D, a positively polarized hydrogen atom bound to D, and an acceptor atom A. This leads to a 4-electron-3-centre (4e-3c) interaction. While in general cases of hydrogen bonding the acceptor A is typically an electronegative heteroatom carrying one or more lone electron pairs, in certain cases a metal centre can play this acceptor role.<sup>[1]</sup> The ability of electron-rich transition metals to form hydrogen bonds has been much investigated.<sup>[2,3]</sup> More recently, the interactions of gold complexes with hydrogen

ligands have become a focus of discussion, and in particular the ability (or otherwise) of gold complexes to undergo hydrogen-bonding has been a matter of debate.<sup>[4-7]</sup> For gold(I), with its completely filled d-shell, a series of experimental and theoretical studies have demonstrated the presence of Au...HC interactions.<sup>[8-10]</sup> The nature of bonding in cases of close Au...HN contacts between Au(I) and protonated N-bases in the crystal remained uncertain, since such contacts could simply be the consequence of crystal packing effects. However, recent evidence has supported the concept of relatively weak (ca. 7-10 kcal/mol) but significant Au...HN-type hydrogen bonding interactions in gold chemistry<sup>[11-13]</sup> even in the gas phase where packing effects are excluded.<sup>[13]</sup>

Hydrogen bonding to d<sup>8</sup> systems is rather better established, in particular in the case of platinum(II). Both *intra*-<sup>[14-16]</sup> and *inter*-molecular<sup>[17]</sup> Pt...HX hydrogen bonding modes are well documented. These bonding interactions influence the <sup>195</sup>Pt NMR chemical shift and are significant in the context of the interaction of the well-known Pt(II) anti-cancer agents with intracellular targets.<sup>[18]</sup> Apart from hydrogen bonding to the ligands, M...HX bonding in these systems is predominantly between the proton and the occupied metal-d<sub>22</sub> orbital of the d<sup>8</sup> ion.<sup>[17]</sup>

Like Pt(II), complexes of the isoelectronic Au(III) ion show interesting cytotoxic properties and here, too, the mode of interaction of the metal centre with biological targets, notably proteins and DNA structures, is important.<sup>[19,20]</sup> It is therefore an intriguing question whether for Au(III) systems energetically significant H-bonding interactions can be identified that might contribute to the biological activity of gold compounds.

In the course of our exploration of gold(III) chemistry<sup>[20,21]</sup> we found that the nature of cyclometallated ligands had a profound effect on the thermal stability of potentially labile complexes. For example, whereas the Au(III) alkene complex [Me<sub>2</sub>Au(COD)]<sup>+</sup> could only be isolated and crystallized at low temperatures,<sup>[22]</sup> analogous complexes [(C<sup>^</sup>C)Au(COD)]<sup>+</sup> supported by chelating bis-carbanionic biphenyl instead of methyl ligands proved to be thermally stable (COD = 1,5-cyclooctadiene; C<sup>^</sup>C = 4,4'-di-*t*-butylbiphenyl-2,2'-diyl). This increased stability appeared to be related not least to the greater electron-accepting capacity of C<sup>^</sup>C compared to methyl.<sup>[23]</sup> 1,2-Dicarboranyl ligands and the potentially chelating 2,2'-bis(dicarboranyl) dianion are more electron-withdrawing than aryl ligands.<sup>[24]</sup> However, in contrast to the large number of dicarboranyl derivatives of Au(I),<sup>[25-31]</sup> to the best of our knowledge there are no reports of dicarboranyl complexes of gold(III).<sup>[32]</sup> We therefore explored synthetic routes to Au(III) complexes with [C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>]<sup>-</sup> and [2,2'-(C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)<sub>2</sub>]<sup>2-</sup> ligands and report here the synthesis and structures of the first examples of well-characterised gold(III) dicarboranyl derivatives. As part of these studies, we isolated zwitterionic compounds with close NH...Au contacts, which served as a convenient

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platform to search for evidence for a gold(III)-hydrogen bond.

## Results and Discussion

The reaction of  $\text{Li}_2[(2,2'\text{-C}_2\text{B}_{10}\text{H}_{10})_2]$  with the cyclometallated gold(III) 2-phenylpyridine complex  $(\text{C}^{\wedge}\text{N})\text{AuCl}_2$  (**1**) in diethyl ether affords the bis(dicarboranyl) complex **2** in good yield (Scheme 1).<sup>[33]</sup> The colourless crystalline product is soluble in dichloromethane and stable to air and moisture. By contrast, the reaction of  $\text{Li}_2[(2,2'\text{-C}_2\text{B}_{10}\text{H}_{10})_2]$  with  $\text{NaAuCl}_4$  led only to reduction and gave black gold nanoparticles.

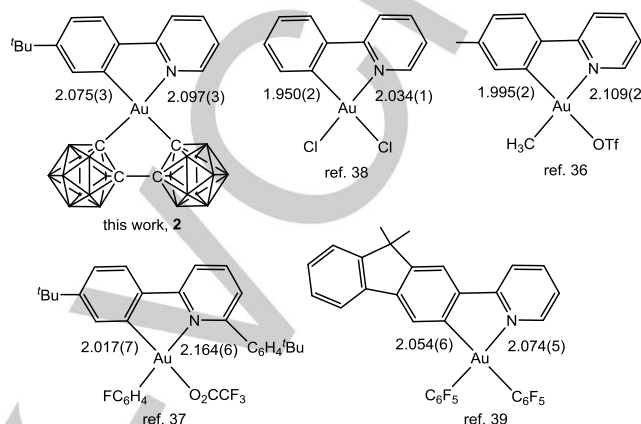
Treatment of **2** with triflic acid at  $-15^\circ\text{C}$  in an effort to remove the  $\text{C}^{\wedge}\text{N}$  scaffold by protonolysis led to cleavage of the Au-phenyl bond but left the pyridine ligand coordinated. Even the addition of an excess of  $\text{N}^t\text{Bu}_4\text{Cl}$  in dichloromethane at room temperature displaced only the triflate to give the chloro complex **3**, while the 2-phenylpyridine ligand was retained. Like **2**, complex **3** is stable to water and air. The reaction illustrates the electron-withdrawing properties of the dicarboranyl ligand, which increases the Lewis acidity of the gold(III) centre. Whereas aryl-type carbanions, e.g. in the 2-phenylpyridine  $\text{C}^{\wedge}\text{N}$  chelate, exert a strong *trans* influence and facilitate ligand substitution,<sup>[34–36]</sup> this effect is evidently much weaker for C-bound dicarboranyl ligands.

Complete removal of the  $\text{C}^{\wedge}\text{N}$  ligand by substituting the pyridine ligand in **3** with chloride was eventually achieved using more forcing conditions and required refluxing **3** in dichloromethane with an excess of  $\text{N}^t\text{Bu}_4\text{Cl}$  for 6 h. The resulting dichloro complex **4** was isolated as a white powder in quantitative yield. On the other hand, substitution of the coordinated pyridine was fast and quantitative with more basic ligands such as isocyanides; for example, the addition of xylol isocyanide at room temperature readily afforded the adduct **5**.

The structures of **2**, **3** and **5** were confirmed by single-crystal X-ray diffraction (Scheme 1). Complex **2** crystallizes with 0.7  $\text{CH}_2\text{Cl}_2$  and about 0.3 molecules of a disordered  $\text{C}_4$  hydrocarbon. All three compounds display the expected square-planar geometry. The Au-C and Au-N distances of the cyclometallated 2-aryl pyridine are a measure of the *trans*-influence exerted by the 2,2'-bis(dicarboranyl) ligand in gold(III) compounds. The Au-N distance is particularly sensitive to such effects (Figure 1), and comparison of these distances with those of other examples of the type  $(\text{C}^{\wedge}\text{N})\text{Au}(\text{X})(\text{Y})$ , where X and Y are ligands from different positions in the spectrochemical series such as  $\text{Me} > \text{aryl} > \text{trifluoroacetate} > \text{Cl}^- > \text{triflate}$ ,<sup>[37–40]</sup> allows an evaluation of the electronic effect of the bis(dicarboranyl) ligand.

However, using the experimental Au-N distances as a measure of the *trans* influence is problematic for several reasons. Firstly, the comparison is imperfect because several real complexes differ somewhat in their substitution pattern. Secondly, the high sensitivity of the Au-N bond length also implies sensitivity to packing effects, which can be expected to be non-systematic. Finally, the changes we are looking for are relatively modest compared to the error margins of some of the X-ray structure determinations. We therefore turned to density functional theory geometry optimization of pyridylphenyl complexes, where errors

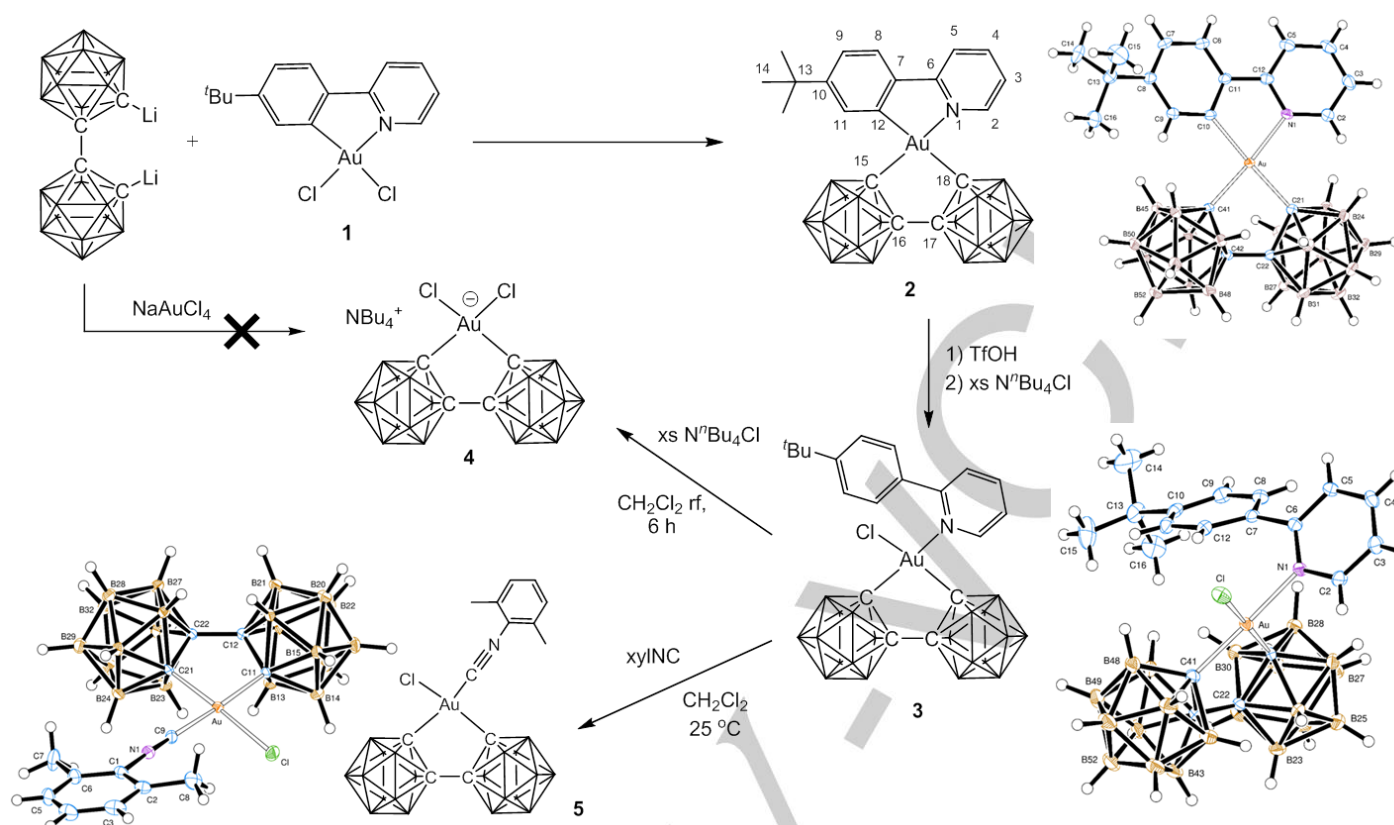
are expected to be systematic rather than random. Two series were examined:  $(\text{C}^{\wedge}\text{N})\text{Au}(\text{Z})(\text{OTf})$  (with Z *trans* to N) and  $(\text{C}^{\wedge}\text{N})\text{AuZ}_2$ , with Z = Me, aryl, halogen (Table 1). We considered three descriptors of the *trans*-influence: (a) the Au-N bond length mentioned above; (b) the Au-N Wiberg Bond Index (WBI);<sup>[41]</sup> and (c) the NPA charge on the nitrogen atom (NPA = natural population analysis).<sup>[42]</sup>



**Figure 1.** Comparison of Au-C and Au-N distances in cyclometallated gold(III) complexes as a function of *trans*-influence..

These descriptors show fairly consistent trends; on going from Me to F, (a) the Au-N bond length decreases from 2.17 to 2.04 Å, (b) the Au-N WBI increases from 0.29 to 0.45, and (c) the N atom becomes less negative, from -0.46 to -0.42 e.

The position of the 1,2-dicarboranyl ligand within the  $\text{Au}(\text{Z})(\text{OTf})$  series is seen to be very similar to that of a  $\text{C}_6\text{F}_5$  group for all three descriptors. In the  $\text{AuZ}_2$  compounds on the other hand, the bis(dicarboranyl) ligand behaves more like two separate *p*- $\text{C}_6\text{H}_4\text{F}$  groups, i.e. in this environment the two carboranyl groups appear to be more strongly donating. To check on this apparent chelate effect we also included monodentate *m*- $\text{C}_6\text{H}_4\text{tBu}$  in the  $\text{Au}(\text{Z})(\text{OTf})$  series, and its bidentate analogue  $\text{C}^{\wedge}\text{C}$  in the  $\text{AuZ}_2$  series. In terms of electronic descriptors (WBI,  $q(\text{N})$ ) both fit fairly well within their series, and do not indicate a specific chelate effect. However, the bidentate  $\text{C}^{\wedge}\text{C}$  complex shows an unexpectedly large Au-N distance that is not seen for the monodentate *m*- $\text{C}_6\text{H}_4\text{tBu}$  analogue. Inspection of the calculated structure of  $\text{Au}(\text{C}^{\wedge}\text{C})(\text{C}^{\wedge}\text{N})$  shows a close approach of the ligand  $\alpha$ - and *ortho*-Au hydrogens that is relieved by saddle deformation of both the  $\text{C}^{\wedge}\text{C}$  and  $\text{C}^{\wedge}\text{N}$  ligands, but apparently also by some elongation of the soft Au-N bond; the X-ray structure of the analogous Au complex lacking the  $\text{C}^{\wedge}\text{C}$  substituents shows instead a twist of  $\text{C}^{\wedge}\text{N}$  relative to  $\text{C}^{\wedge}\text{C}$ .<sup>[43]</sup> This type of steric clash is avoided in monodentate aryl complexes by simple rotation around the Au-Ar bonds. Such specific steric effects complicate the analysis, and we therefore recommend not to rely exclusively on geometric descriptors (calculated or experimental) when attempting to rank ligands for their *trans* influence.



**Scheme 1.** Synthesis of gold(III) bis(dicarboranyl) complexes. The structure of **2** shows the atomic numbering scheme used for NMR assignments. Ellipsoids of molecular structures are drawn at 50%. H-Atoms are depicted in idealized positions. Selected bond distances [Å] and angles [°]: **2**: Au-C(10) 2.075(3), Au-N(1) 2.097(2), Au-C(21) 2.157(3), Au-C(41) 2.059(3); C(41)-Au-C(10) 96.71(10), C(41)-Au-N(1) 174.87(9), C(10)-Au-N(1) 79.45(10), C(41)-Au-C(21) 87.21(10), C(10)-Au-C(21) 173.85(10), N(1)-Au-C(21) 96.34(9). **3**: Au-C(41) 2.039(2), Au-C(21) 2.065(2), Au-N(1) 2.0914(17), Au-Cl 2.3184(6); C(41)-Au-C(21) 88.59(9), C(41)-Au-N(1) 177.20(8), C(21)-Au-N(1) 94.20(8), C(41)-Au-Cl 90.61(7), C(21)-Au-Cl 175.59(6), N(1)-Au-Cl 86.60(6). **5**: Au-C(9) 2.0201(18), Au-C(11) 2.0524(17), Au-C(21) 2.0602(18), Au-Cl 2.3268(4); C(9)-Au-C(11) 173.97(7), C(9)-Au-C(21) 93.16(7), C(11)-Au-C(21) 87.93(7), C(9)-Au-Cl 86.95(5), C(11)-Au-Cl 92.36(5), C(21)-Au-Cl 176.18(5).

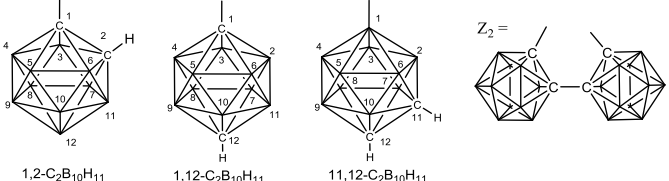
For the Au(Z)(OTf) series we also briefly examined isomeric 1,12- and 11,12-dicarboranys (Table 1). Compared to the 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> ligand studied experimentally, the 1,12 isomer appears to be a slightly stronger donor, as judged from the Au-N distance and WBI. These electronic characteristics contrast strongly with the B-bound 11,12-dicarboranyl ligand, which has a *much* stronger *trans*-influence than any other ligands considered including methyl, indicating considerable potential for ligand tuning using dicarboranys.<sup>[44]</sup>

Efforts to replace the chloride ligands by treating either **4** or **5** with AgSbF<sub>6</sub> in the presence of alkenes or alkynes to generate the corresponding  $\pi$ -complexes were unsuccessful. The reaction of the dichloride **4** with AgSbF<sub>6</sub> and 1,5-cyclooctadiene (COD) led to the formation of [Ag(COD)<sub>2</sub>]SbF<sub>6</sub> as the only identifiable product. Unlike the behaviour of the structurally similar C<sup>^</sup>C complex [(C<sup>^</sup>C)AuCl<sub>2</sub>], which reacts with AgSbF<sub>6</sub> even in weakly basic solvents like diethyl ether to give [(C<sup>^</sup>C)Au(OEt<sub>2</sub>)<sub>2</sub>]<sup>+</sup> and also readily forms the COD complex [(C<sup>^</sup>C)Au(COD)]<sup>+</sup>,<sup>[23]</sup> chloride abstraction in the case of carboranyl complexes is evidently much more difficult. Eventually the isocyanide complex **5** does react with silver trifluoroacetate in dichloromethane (2 days), to give the

corresponding OAc<sup>F</sup> complex **6** (Scheme 2). However, whereas in other cases of gold(III)-OAc<sup>F</sup> complexes the removal of trifluoroacetate with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> proved to be a mild and quantitative way to generate vacant coordination sites en-route to synthesizing gold(III) alkene and alkyne complexes,<sup>[23,45,46]</sup> this procedure failed in this case; for example, monitoring mixtures of **6** and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and 1,2-bis(adamantyl)acetylene in CD<sub>2</sub>Cl<sub>2</sub> by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy provided no evidence for OAc<sup>F</sup> displacement or alkyne binding. These results underline that the electronic characteristics of the dicarboranyl ligands differ significantly from those of more conventional carbon-based chelate ligands, and that the chemistry of C<sup>^</sup>C and C<sup>^</sup>N<sup>^</sup>C ligands cannot easily be transferred to the bis(dicarboranyl) system.

Whereas, as described above, the protonolysis of **2** with triflic acid led to Au-C bond scission to give **3**, a very different course of reaction was observed in the reaction of **2** with HBr. In this case, heating **2** with concentrated aqueous HBr at 65 °C for 2-3h in CHCl<sub>3</sub>/DMSO (1:1) led to cleavage of the Au-N instead of the



**Table 1.** Calculated Au-N bond lengths, WBI and natural charges on N for Au(Z)(OTf) and AuZ<sub>2</sub> complexes<sup>a,b</sup>


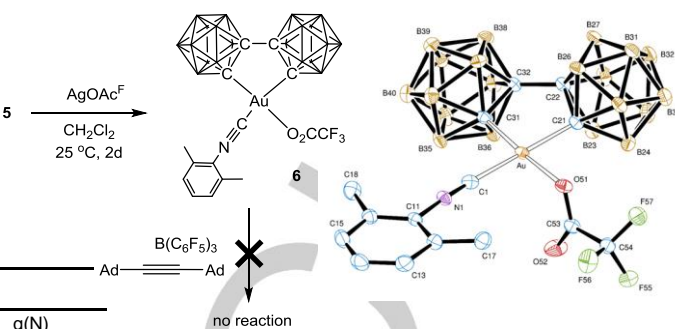
Z	Au-N Å	WBI (Au-N)	q(N) e	Au-N Å	WBI (Au-N)	q(N) e
H	2.158	0.312	-0.476	2.158	0.341	-0.480
Me	2.170	0.287	-0.469	2.179	0.312	-0.450
<i>m</i> -C <sub>6</sub> H <sub>4</sub> tBu <sup>d</sup>	2.172	0.285	-0.471	2.195	0.315	-0.458
Ph	2.168	0.289	-0.471	2.172	0.310	-0.453
<i>p</i> -C <sub>6</sub> H <sub>4</sub> F	2.164	0.294	-0.470	2.167	0.315	-0.455
1,2-dicarbonyl <sub>b,c</sub>	2.127	0.330	-0.456	2.141	0.314	-0.452
1,12-C <sub>2</sub> B <sub>10</sub> H <sub>11</sub>	2.141	0.317	-0.454			
11,12-C <sub>2</sub> B <sub>10</sub> H <sub>11</sub> <sub>c</sub>	2.228	0.234	-0.480			
C <sub>6</sub> F <sub>5</sub>	2.121	0.338	-0.460	2.129	0.359	-0.448
I	2.112	0.370	-0.441	2.137	0.379	-0.434
Br	2.090	0.394	-0.437	2.104	0.406	-0.429
Cl	2.076	0.409	-0.434	2.080	0.423	-0.426
F	2.044	0.448	-0.428	2.018	0.468	-0.422
OTf	2.036	0.459	-0.421	2.036	0.459	-0.421

<sup>a</sup> Optimized at TPSSH/Def2SVP; WBI and NPA at TPSSH/cc-pVTZ. <sup>b</sup> Z = 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>; Z<sub>2</sub> = bis(dicarbonyl) (C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)<sub>2</sub>. <sup>c</sup> Several rotamers were located for the 1,2 and 11,12 carboranyl series; values shown are for the lowest-energy conformer of each series. <sup>d</sup> Z<sub>2</sub> = 4,4'-di-*t*-butylbiphenyl-2,2'-diyl (C<sup>4</sup>C). <sup>e</sup> The dicarbonyl numbering is deliberately unconventional to maintain consistency with the Au atom always bonded to vertex 1 of the cage.

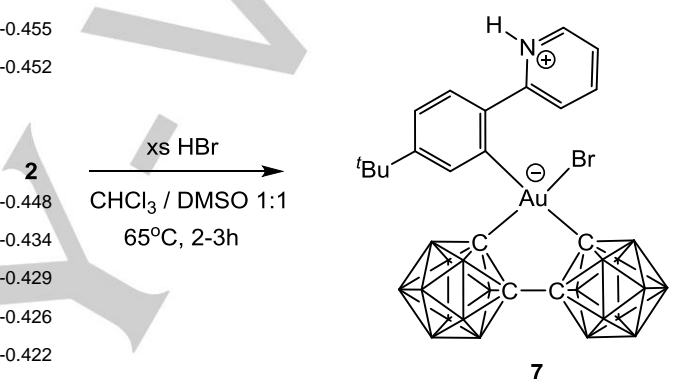
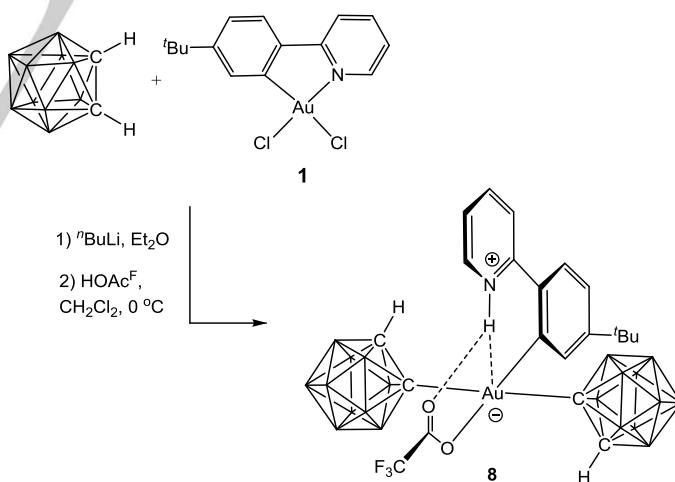
Au-C bond, with formation of the zwitterionic pyridinium complex **7** (Scheme 3).

Another zwitterionic pyridinium salt was obtained during attempts to cleave **2** with trifluoroacetic acid. A small amount of crystals of the single-cage dicarbonyl complex **8** were obtained, obviously the result of impurities of *ortho*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> in the 2,2'-(C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)<sub>2</sub> starting material. Complex **8** can be made in good yield from Li[C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] and **1**, followed by treatment with CF<sub>3</sub>CO<sub>2</sub>H in dichloromethane at 0 °C (Scheme 4).

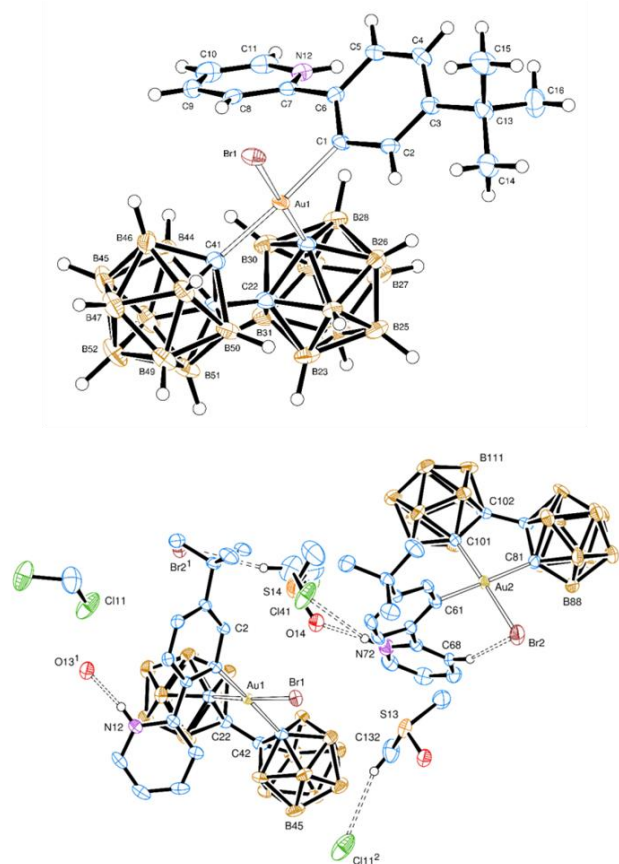
Both **7** and **8** contain a pyridinium cation and a negatively charged aurate(III) anion. However, as the crystal structures show, these compounds adopt very different conformations. In crystals of **7**, there are two independent gold complex molecules in the crystal, together with a discrete molecule of each of the solvents CH<sub>2</sub>Cl<sub>2</sub> and DMSO and a disordered, overlapping pair of these molecules in the ratio of ca 0.36:0.64. The solvents were modelled as 1.363(CH<sub>2</sub>Cl<sub>2</sub>), 1.637(OSMe<sub>2</sub>). The complex adopts a conformation in which the pyridinium-NH<sup>(+)</sup> bond, in both molecules, points away from the gold centre and is engaged in

**Scheme 2.** Synthesis and crystal structure of the trifluoroacetate complex **6**.

Ellipsoids are drawn at 50%. H-Atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Au-C(1) 2.031(2), Au-C(31) 2.0424(19), Au-C(21) 2.0494(18), Au-O(51) 2.0528(14); C(1)-Au-C(31) 94.17(8), C(1)-Au-C(21) 175.48(8), C(31)-Au-C(21) 88.58(7), C(1)-Au-O(51) 89.35(7), C(31)-Au-O(51) 175.36(6), C(21)-Au-O(51) 87.85(7).

**Scheme 3.** Formation of **7** by Au-N bond protonolysis with HBr.**Scheme 4.** Formation of the *trans*-dicarbonyl trifluoroacetate complex **8**.

hydrogen bonding with the O atom of a DMSO molecule (Figure 2). There is also a close C(68)-H...Br contact. The crystal packing diagram shows no evidence for any significant interactions with the square-planar Au(III) centre.

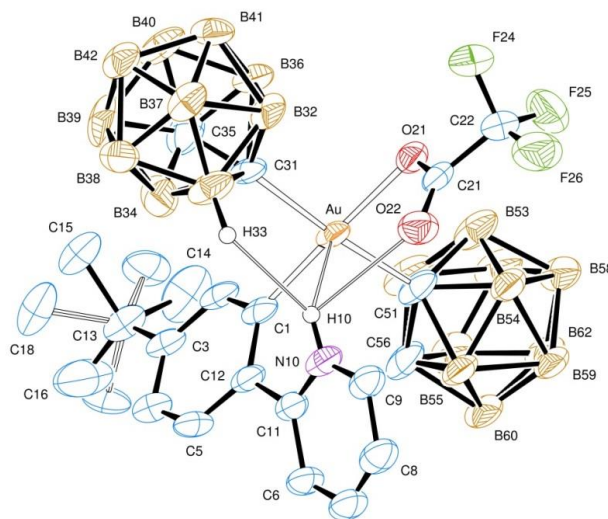


**Figure 2.** Molecular structure (top) and intermolecular interactions (bottom) of  $7 \cdot 1.363(\text{CH}_2\text{Cl}_2) \cdot 1.637(\text{OSMe}_2)$ . Ellipsoids are drawn at 50%. H-Atoms are depicted in idealized positions. There are two independent molecules in the unit cell; the parameters of molecule 1 are listed here. Selected bond distances [Å] and angles [°]: Au(1)-C(1) 2.046(3), Au(1)-C(21) 2.050(3), Au(1)-C(41) 2.107(3), Au(1)-Br(1) 2.444(4); C(1)-Au(1)-C(21) 93.49(12), C(1)-Au(1)-C(41) 176.61(11), C(21)-Au(1)-C(41) 88.17(13), C(1)-Au(1)-Br(1) 86.74(9), C(21)-Au(1)-Br(1) 176.60(8), C(41)-Au(1)-Br(1) 91.77(9). H-bonding distances: N(12)-H(12)···O(13') 0.86 and 1.78, N(72)-H(72)···O(14) 0.86 and 1.83, C(68)-H(68)···Br(2) 0.93 and 2.64.

The trifluoroacetate **8** crystallizes without solvent molecules (Figure 3). In this complex the pyridinium-NH<sup>(+)</sup> bond points towards the gold centre. The pyridinium-NH hydrogen atom was freely refined. The gold centre is four-coordinate in a square planar pattern, with the two dicarboranyl ligands perpendicular to the general Au-(phenyl-pyridinium)-TFA plane. The two dicarboranyl ligands, each linked to the Au atom through a carbon atom, are well-defined except that the second carbon atom in each ligand is disordered amongst four of the five  $\alpha$ -BH groups; the sites with the highest CH occupations are shown in Figure 3. The phenyl and pyridinium rings are twisted 30.87(14)° about the C(11)–C(12) bond, thus taking H(10) 2.51(5) Å from the gold centre, and towards the uncoordinated O atom of the  $\text{OCOCF}_3$  ligand at 2.54(6) Å.

There are several close contacts between the ligands: firstly, the 'hydrogen bond' between the pyridinium group and O(22) of the

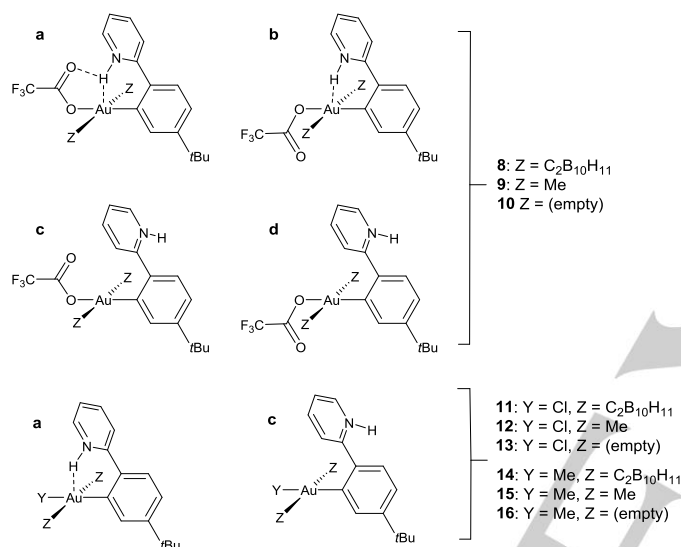
TFA ligand with an N-H···O angle of 128(5)°, and then the interactions of the bulky dicarboranyl ligands against their neighbours, in particular H(10)···H(33) 2.34 Å, H(2)···H(35) 2.30 Å, H(34)···C(1) 2.70 Å and H(56)···C(1) 2.63 Å, H(32)···C(21) 2.56 Å and H(54)···C(21) 2.64 Å. Intermolecular contacts are at normal van der Waals' distances.



**Figure 3.** Structure of **8**. Ellipsoids are drawn at 50%. H-Atoms are depicted in idealized positions. Selected bond distances [Å] and angles [°]: Au-C(1) 2.007(5), Au-C(31) 2.123(4), Au-C(51) 2.103(5), Au-O(21) 2.107(3); C(1)-Au-C(51) 91.1(2), C(1)-Au-O(21) 177.75(16), C(51)-Au-O(21) 88.30(18), C(1)-Au-C(31) 91.27(19), C(51)-Au-C(31) 172.97(16), O(21)-Au-C(31) 89.63(17). Distances within H-bonding range: N(10)-H(10)···O(22) 0.88(6)···2.54(6) Å; N(10)-H(10)···Au 0.88(6)···2.51(3) Å; angles N-H···O 112(4)°, NH···Au 128(3)°.

**DFT calculations.** The structure of **8** was used as the starting point to probe for the possible existence of energetically significant gold(III)-hydrogen bonding interactions. The crystallographically determined Au-H distance in complex **8** (2.51 Å) is shorter than the sum of the van der Waals radii (2.84 Å<sup>[47]</sup>), and the true Au-H distance is likely to be shorter still (~2.46 Å; see below). This raises the question whether there is any significant Au(III)···H interaction in this species. As discussed in the Introduction, even shorter Au-H contacts have been observed<sup>[12]</sup> and calculated<sup>[12,13]</sup> in Au(I) complexes, and have been interpreted in terms of Au···H hydrogen bonding based on both experimental and computational data. Interpretation of the structure of **8** is complicated by (a) the presence of the trifluoroacetate group which can also participate in H-bonding, and (b) the large, spherical dicarboranyl substituents which likely promote a vertical orientation of the protonated pyridinium fragment (C<sup>+</sup>NH) regardless of any Au···H interaction. In order to disentangle these factors, the structures of **8**<sup>[48]</sup> and a number of related model compounds (**9–16**) were calculated (see Figure 4): on the one hand, the bulky dicarboranyl groups were replaced by methyls (Au(III) complexes **9/12/15**) or deleted altogether (Au(I) complexes **10/13/16**) to eliminate the steric pressure effect, and on the other hand the  $\text{Ac}^{\text{F}}\text{O}$  group was replaced by Cl (**11/12/13**) or Me (**14/15/16**) to remove its hydrogen-bonding contribution. To

avoid rotamer issues in the dicarboranyl complexes, the 1,2- $C_2B_{10}H_{11}$  groups were modelled as 1,12-carboranyles; as mentioned earlier, the two are very similar both electronically and sterically. In addition, alternative conformations of the C<sup>^</sup>NH group (and for **8-10** also the Ac<sup>F</sup>O group) were considered as shown in Figure 4. All calculations were done using Gaussian09.<sup>[49]</sup> Geometries were optimized at the TPSSH<sup>[50]</sup>/def2-SVP<sup>[51]</sup> level, and vibrational analyses confirmed the nature of all stationary points as local minima. Improved electronic energies were calculated using M06<sup>[52]</sup>/cc-pVTZ<sup>[53]</sup> single-point calculations, and these were combined with thermal corrections from the TPSSH/def2-SVP vibrational analyses to obtain final calculated enthalpies. The results are summarized in Table 2.



**Figure 4.** Structures and conformations of complexes used in computational modelling.

Looking first at the geometries, it is clear that uniformly the Au...H distance decreases in the order Carb<sub>2</sub>Au(III)X > Me<sub>2</sub>Au(III)X > Au(I)X (i.e. **8a** > **9a** > **10a**; **11a** > **12a** > **13a**; **14a** > **15a** > **16a**). The corresponding N-H distance *increases* in the same order. We find that the potential energy surface for changing the Au-H distance is rather flat, and hence the optimized Au-H distances are method-sensitive but the overall trends are consistent (for further discussion of the Au-H distance in **8a** see the SI).

The Wiberg bond indexes (WBI) paint a similar but perhaps more quantitative picture. Au(I) complexes **13a** and **16a** show a modest WBI of ~0.15, corresponding to about 1/5 of a single Au-H bond (c.f. the terminal Au-H bond in Au<sub>2</sub>H<sub>6</sub>, WBI 0.70 at the same level); Bourissou cites a value of 0.12 for his Au(I)...H interaction.<sup>[12]</sup> For the Au(I) trifluoroacetate complex **10a** we calculate a lower value of 0.10, but this is restored to the "normal" value of 0.15 when the Ac<sup>F</sup>O group is rotated away to eliminate its H-bonding interaction (**9c**); this can be interpreted as evidence for competing Au...H and O...H interactions. Moving from these Au(I) species to the Me<sub>2</sub>Au(III) complexes (**9/12/15**), we see a lowering of the WBI by a factor of 3, demonstrating clearly that

Au(III) is less effective in hydrogen bonding than Au(I). Finally, for the dicarboranyl complexes **8/11/14** we find a further lowering to ~0.02, presumably due to the fact that the dicarboranyl groups are less electron-donating than methyl groups. From these numbers, it is clear that hydrogen bonding to Au(III) is considerably weaker than to Au(I), and is unlikely to be an important structure-determining factor.

**Table 2.** Calculated geometric and electronic descriptors of **8 - 16**.

	distances (Å)			angle (°)	dihedral angle (°)	WBI	
	Au-H	O-H	N-H	NHAu	CCCN	Au-H	O-H
<b>8a</b>	2.268	2.024	1.040	136.0	20.3	0.037	0.031
<b>8b</b>	2.554	5.415	1.030	118.8	34.5	0.015	0.000
<b>8c</b>	4.917	5.888	1.021		-136.6	0.000	0.000
<b>8d</b>	4.948	7.956	1.021		-136.2	0.000	0.000
<b>9a</b>	2.180	2.086	1.045	138.2	18.1	0.054	0.024
<b>9b</b>	2.226	4.916	1.055	131.5	25.7	0.044	0.000
<b>9c</b>	4.984	6.067	1.020		-143.1	0.000	0.000
<b>9d</b>	5.000	7.957	1.020		-143.9	0.000	0.000
<b>10a</b>	2.092	2.280	1.054	145.5	15.6	0.098	0.016
<b>10b</b>	1.998	4.938	1.069	159.3	1.5	0.148	0.002
<b>10c</b>	4.924	6.091	1.020		-140.2	0.000	0.000
<b>10d</b>	4.960	7.950	1.020		-142.1	0.000	0.000
<b>11a</b>	2.430		1.031	120.9	32.8	0.021	
<b>11c</b>	4.967		1.021		-137.5	0.000	
<b>12a</b>	2.193		1.057	132.8	24.7	0.049	
<b>12c</b>	4.991		1.020		-143.8	0.000	
<b>13a</b>	1.987		1.068	159.7	0.3	0.144	
<b>13c</b>	4.950		1.020		-142.6	0.000	
<b>14a</b>	2.462		1.031	126.5	29.3	0.021	
<b>14c</b>	5.105		1.021		-139.2	0.000	
<b>15a</b>	2.183		1.056	140.1	19.8	0.055	
<b>15c</b>	5.146		1.020		-147.9	0.000	
<b>16a</b>	1.981		1.076	163.6	0.1	0.158	
<b>16c</b>	5.080		1.020		-146.3	0.000	

One might be tempted to interpret energy differences between conformations **a/b/c/d** in terms of the strength of Au...H interactions, but inspection of Table 2 shows that this is not justified. For complex **7**, rotation of the C<sup>^</sup>NH group (**8c**) turns off both Au...H and O...H interactions, yet this costs less energy than just rotating the Ac<sup>F</sup>O group (**8b**) which only turns off the O...H interaction. Instead, the calculated conformational energy differences are better interpreted in terms of minimization of dipole moments. The differences are very similar for complexes **8 - 16** despite the very different Au...H interactions, and indeed both Bourissou *et al.*<sup>[12]</sup> and Rulišek and co-workers<sup>[13]</sup> report comparable differences for their Au(I) complexes.



The N-H stretching frequencies in Au...H bonded complexes are lowered relative to "free" stretching frequencies. We find this also for the calculated structures of **8** - **16**. Again, the largest changes are observed for Au(I)...H interactions (from 3540 cm<sup>-1</sup> for **16c** to 2575 cm<sup>-1</sup> for **16a**), but also for Me<sub>2</sub>Au(III) complexes the changes are significant (3540 cm<sup>-1</sup> for **15c** to 2896 cm<sup>-1</sup> for **15a**). Interpreting these frequency changes is, however, nontrivial because of the nonlinear Au...H-N arrangement in the real and model complexes studied.

In short, calculations indicate that, firstly, Au(III)...H hydrogen-bonding interactions are significantly weaker than the analogous Au(I)...H variations and are unlikely to be important determinants of molecular structure. Secondly, interpreting conformational energy differences in terms of the strength of hydrogen bonding interactions is not justified.

## Conclusions

The 2,2'-bis(dicarboranyl) dianion acts as C<sup>+</sup>C<sup>-</sup> chelate ligand towards gold(III) and gives thermally stable complexes which promise to be useful starting materials for organometallic gold compounds. While the direct synthesis from Li<sub>2</sub>(C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)<sub>2</sub> and [AuCl<sub>4</sub>]<sup>-</sup> did not prove possible, reduction could be circumvented by using cyclometallated (C<sup>+</sup>N)AuCl<sub>2</sub> as starting material, followed by removal of the C<sup>+</sup>N scaffold by protonolysis. Depending on the reaction conditions and the acid used, preferential Au-C or Au-N cleavage of the 2-arylpyridine ligand was observed. Cleavage of the Au-N bond afforded zwitterionic pyridinium aurate(III) complexes, including a case where the N-H bond is directed towards the gold centre. Computational modelling revealed however that in spite of a gold...H contact shorter than the sum of van der Waals radii, there is no energetically significant Au...H interaction akin to hydrogen-bonding, irrespective of the presence or absence of dicarboranyl ligands. The situation concerning Au(III)...HN<sup>+</sup> hydrogen bonding is therefore reminiscent of that reported by Schmidbaur *et al.* for an Au(III)...H-C system, where agostic interactions could be ruled out in spite of close Au...H-C distances.<sup>[54]</sup> In the present case no evidence for N-H hydrogen bonding to Au(III) was detected. This is further confirmed by the conformation of (Hpy-C<sub>6</sub>H<sub>3</sub><sup>t</sup>Bu)AuBr{(C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)<sub>2</sub>} (**6**), where the pyridinium moiety points away from the metal centre in the crystal. It is evident therefore that, unlike the isoelectronic platinum(II) ion, gold(III) does not engage in significant 4e-3c N-H...M hydrogen interactions.

## Experimental Section

CCDC numbers 1959410 (compound **8**), 1959411 (**2**), 1959412 (**3**), 1959413 (**5**), 1959414 (**6**) and 1959415 (**7**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. See the Supporting Information for experimental details.

## Acknowledgments

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**Keywords:** gold • carborane • hydrogen bonding • trans influence • organometallic

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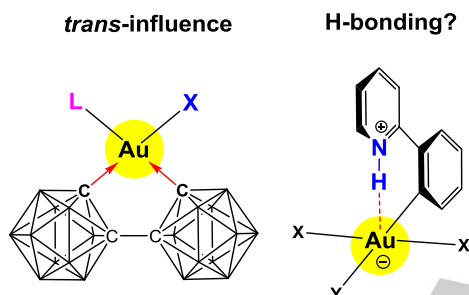
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## Entry for the Table of Contents (Please choose one layout)

Layout 1:

## FULL PAPER

First examples of gold(III) dicarboranyl and bis(dicarboranyl) complexes are reported, included an assessment of carboranyl *trans*-influence and of H-bonding to gold(III).



## Gold chemistry\*

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Page No. – Page No.

**Do Gold(III) Complexes Form Hydrogen Bonds? An Exploration of Au(III) Dicarboranyl Chemistry**