

## $\pi$ Complexes of P<sup>^</sup>P and P<sup>^</sup>N Chelated Gold(I)

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**Abstract:** Tricoordinate gold(I)  $\pi$ -complexes featuring P-based chelating ligands (P<sup>^</sup>P and P<sup>^</sup>N) were prepared. The structure of the gold(I) styrene complexes have been analysed in detail based on NMR and XRD data. The P<sup>^</sup>N complex is a competent catalyst for indole alkylation. The reaction proceeds with complete C3 and Markovnikov selectivity.

Polyfunctional ligands are gathering growing interest in gold chemistry. The ability of chelating and cyclometalated ligands to stabilize gold in high oxidation states, gold(III) in particular, was recognized early on and is widely used.<sup>1</sup> The tendency of gold(I) complexes to be linear dicoordinate<sup>2</sup> makes the use and interest of bidentate ligands less straightforward at first glance. Nevertheless, gold(I) complexes featuring bifunctional ligands have also attracted increasing attention over the past 5 years, and new avenues have started to emerge. The second moiety of the ligand, a coordination site or a functional group, may interact with the first or second coordination sphere of gold and thereby modifies its properties, emulates and controls its reactivity.<sup>3</sup>

In this respect, our group has been recently interested in *o*-carboranyl-bridged diphosphines (*o*-CBD) and *o*-phenylene-bridged P<sup>^</sup>N ligands (Fig. 1). With *o*-CBD, chelation enforces unusual bent geometry at gold(I) while the P<sup>^</sup>N ligand displays hemilabile character and the combination of soft and hard coordination sites is ideally suited to cycle between Au(I) and Au(III) oxidation states. Accordingly, both the P<sup>^</sup>P and P<sup>^</sup>N ligands were found to enable oxidative addition of C–X (X = I, Br)<sup>4</sup> and strained C–C bonds to gold under mild conditions.<sup>5</sup> Ultimately, the P<sup>^</sup>N ligand was shown to promote Au(I)/Au(III) catalysis and it was successfully applied to the C3 arylation of indoles.<sup>6</sup> In addition, the chelating P<sup>^</sup>P ligand proved to efficiently stabilize CO and carbene gold(I) complexes thanks to enhanced back-donation from Au.<sup>7</sup> Lately, the basic N atom of the P<sup>^</sup>N ligand was used to form and fully characterize gold(I) complexes featuring genuine X–H...Au hydrogen bonding.<sup>8</sup>

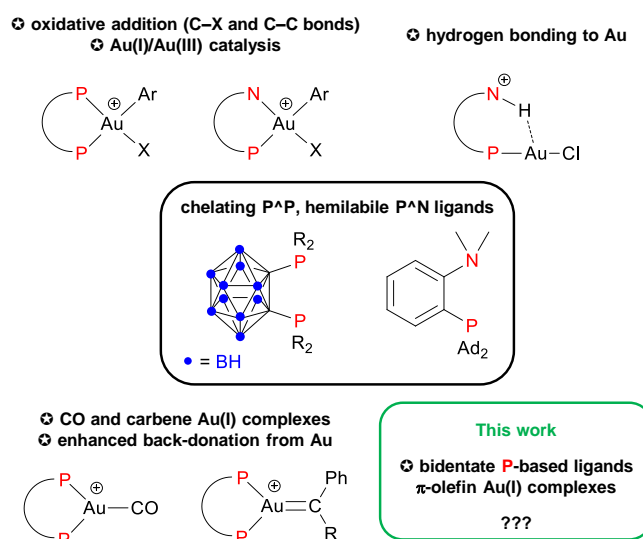
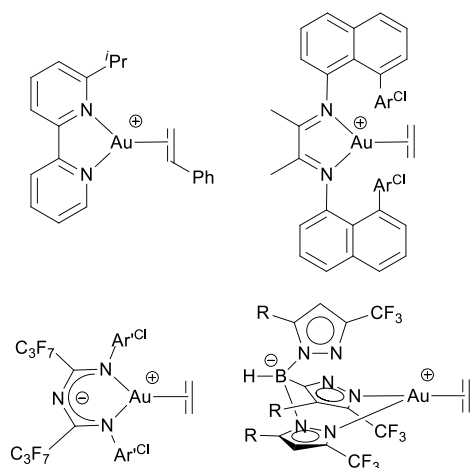


Fig. 1 Gold complexes deriving from bidentate P-based ligands.

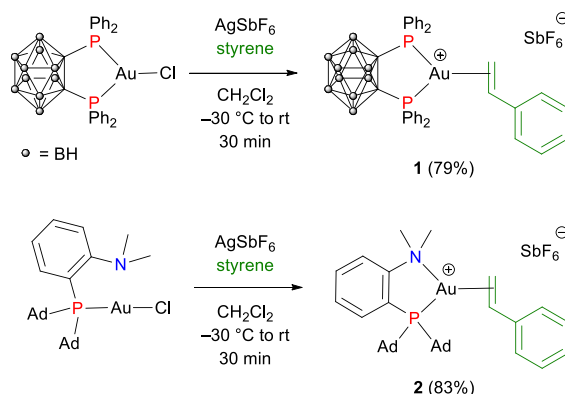
The unique ability of gold(I) to activate  $\pi$ -systems and promote thereby a variety of catalytic transformations prompted us to investigate the coordination of alkenes to P<sup>^</sup>P and P<sup>^</sup>N chelated Au(I) centres. Over the last 15 years, gold(I)  $\pi$ -complexes have been characterized with alkenes, alkynes, conjugated dienes, allenes, enamines and enol ethers.<sup>9,10</sup> Mainly dicoordinate gold(I)  $\pi$ -complexes have been reported, with *N*-heterocyclic carbenes (NHCs) or phosphines as ancillary ligands. A few tricoordinate species have also been authenticated with a bipyridine, phenanthroline,  $\alpha$ -diimine triazapentadienyl or tris(pyrazolyl)borate behaving as N<sup>^</sup>N chelating ligand (Fig. 2).<sup>11</sup> Herein we report gold(I)  $\pi$ -complexes featuring *o*-CBD and MeDalphos ligands. The coordination mode of styrene is

analysed in detail based on NMR spectroscopy and X-ray crystallography. The influence of the chelating P-based ligand is discussed.



**Fig. 2** Representative examples of known tricoordinate Au(I)  $\pi$ -complexes (Ar = 3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Ar<sup>Cl</sup> = 2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R = CF<sub>3</sub> or Ph).

The target complexes were prepared by reacting the *o*-carboranyl diphosphine<sup>4a,12,13</sup> and MeDalphos gold(I) chlorides with AgSbF<sub>6</sub> in the presence of an excess of styrene (5 equiv.) in dichloromethane (Scheme 1). Monitoring the reactions by <sup>31</sup>P NMR spectroscopy revealed instantaneous formation of new species (**1** and **2**, respectively). In parallel, the <sup>1</sup>H NMR spectra display a new set of well-defined vinylic signals (distinct from those of free styrene), indicating the coordination of styrene to gold (Figure S12). Also noteworthy is the presence of two distinct <sup>1</sup>H NMR singlets at 3.09 and 2.82 ppm for the N(CH<sub>3</sub>)<sub>2</sub> group of complex **2**, while the (MeDalphos)AuCl complex displays only one singlet at 2.57 ppm. The splitting and downfield shift of the N(CH<sub>3</sub>)<sub>2</sub> signal suggest that the nitrogen atom coordinates to the Au(I) centre in **2**, and thus that the MeDalphos ligand becomes chelating.



**Scheme 1** Synthesis of the gold(I) styrene complexes **1** and **2**.

Filtration of the reaction mixtures through short pads of Celite followed by washes with Et<sub>2</sub>O afforded the pure gold(I)  $\pi$ -complexes **1** and **2** in good yields (75 and 83%, respectively). Both complexes are air stable solids. The alkene is tightly bonded to the gold(I) centre. Two distinct sets of NMR signals are observed in solution at 25 and even 100°C, indicating the absence of chemical exchange between coordinated and free styrene within the NMR time-scale (Figure S11).<sup>13</sup> No sign of styrene decoordination was observed either under vacuum.

For complexes **1** and **2**, the coordination of styrene to gold induced noticeable upfield shifts of the <sup>1</sup>H and <sup>13</sup>C NMR vinylic signals with respect to free styrene (Table S1). For the P<sup>A</sup>P complex **1**, <sup>1</sup>H NMR shift differences of 0.46, 0.63 and 0.95 ppm were observed for the three vinylic protons. Even larger shift differences of 0.69, 1.07 and 1.42 ppm were encountered for the P<sup>A</sup>N complex **2**. The same trend was witnessed by <sup>13</sup>C NMR spectroscopy. The signals for the vinylic carbons are shifted upfield by 37–48 ppm in complexes **1** and **2** compared to free styrene. At this point, comparison with known Au(I) styrene complexes proved informative. Relevant NMR data are collected in Table S1. Accordingly, complexes **1** and **2** much more resemble the bipyridine complex reported by Cinellu *et al.*,<sup>11a,b</sup> with equally large upfield shifts of the <sup>1</sup>H and <sup>13</sup>C vinylic signals. The chelating N and P-based ligands induce some metallacyclic character as a result of significant Au→alkene back-donation. In marked contrast, only minor changes were observed upon coordination of styrene to gold(I) centres ligated by phosphines or NHCs.<sup>14</sup> This comparison

emphasizes the impact of the ancillary ligand at gold, in particular its mono *versus* bidentate character, on the coordination of styrene.

As mentioned above, complex **2** displays two inequivalent NCH<sub>3</sub> groups in <sup>1</sup>H NMR spectroscopy at room temperature (25°C). Interestingly, raising the temperature of the solution revealed some fluxional behavior. The two <sup>1</sup>H NMR signals coalesce at T > 50°C (Fig. 3b) and a detailed variable temperature (VT) study enabled to estimate the energy barrier for this process to *ca* 15.1±0.2 kcal/mol (Fig. S15 and S16).<sup>13</sup> Further NMR analysis of complex **1** unveiled a similar phenomenon. A single peak is observed by <sup>31</sup>P NMR spectroscopy at room temperature, indicating symmetric coordination of the diphosphine and fast rotation of the π-coordinated styrene in solution within the NMR time scale, but at low temperature (T < 0°C), the <sup>31</sup>P NMR spectrum displays two separate signals in the typical zone for P-coordinated atoms (Fig. 3a). This indicates chelating coordination of the P<sup>∧</sup>P ligand, but frozen geometry of the styrene coordinated to gold. The energy barrier associated with this fluxional behavior (14.1±0.1 kcal/mol, as estimated by VT NMR) is very similar to that found for the P<sup>∧</sup>N complex **2** (Fig. S13 and S14).<sup>13</sup>

Single crystals of complexes **1**<sup>13,15</sup> and **2** suitable for X-ray diffraction analysis were obtained by layering or slowly diffusing pentane on saturated dichloromethane solutions. The two complexes adopt similar structures in the solid state. The counter anion is completely dissociated, the P-based ligand chelates gold and a styrene molecule is η<sup>2</sup>-coordinated (Fig. 4). In complex **1**, the *o*-CBD ligand is symmetrically coordinated to Au (within margin of error, the P–Au distances are equal at 2.38 Å) and the P1–Au–P2 bite angle [89.13(3)°] is similar to those previously observed in the *o*-CBD gold(I) complexes [(P<sup>∧</sup>P)Au(CO)]<sup>+</sup> [93.95(5)°] and [(P<sup>∧</sup>P)Au=C(Ph)R]<sup>+</sup> [90.26(4) and 90.57(2)°].<sup>7</sup> The MeDalphos ligand is chelating in complex **2**. The P–Au–N bite angle is small at 82.2(1)°, the P–Au and Au–N bond lengths are almost identical at 2.3365(11) and 2.381(4) Å, respectively. Taking into account the smaller size of nitrogen compared to phosphorus (covalent radii of 0.71 and 1.07 Å, respectively),<sup>16</sup> the coordination of the P<sup>∧</sup>N ligand is in fact electronically dissymmetric. The soft P atom is more strongly bonded to gold(I) than the hard N centre (in line with HSAB theory). In both complexes, the gold centre is in planar environment, the styrene molecule coordinates in the same plane as the P<sup>∧</sup>P/P<sup>∧</sup>N ligand. This arrangement induces steric shielding between the alkene and the substituent of the ancillary ligand,<sup>13,17</sup> but maximises the overlap between the HOMO of the [(P<sup>∧</sup>P/P<sup>∧</sup>N)Au<sup>+</sup>] fragment (in-plane d<sub>xy</sub>-type orbital) and the π\* orbital of styrene. It is a sign for substantial Au→styrene back-donation in **1** and **2**, as for the related bipyridine complex.<sup>11a,b</sup>

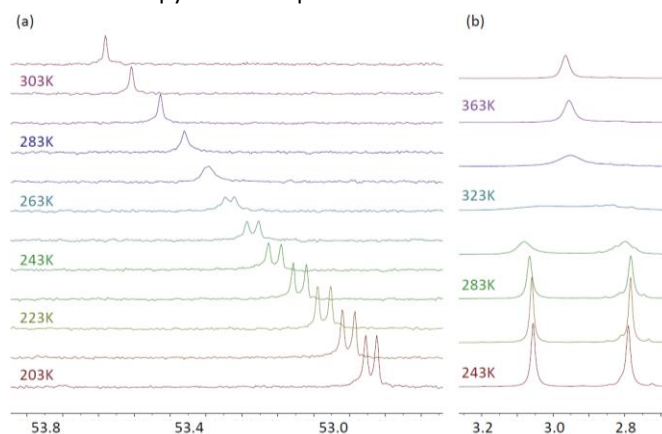
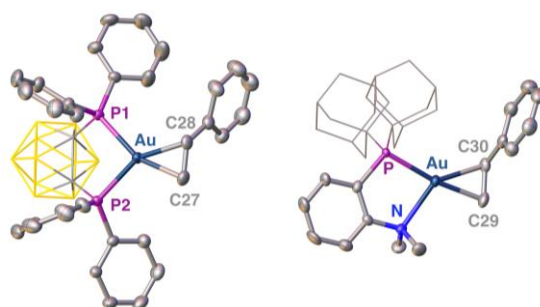


Fig. 3 (a) VT <sup>31</sup>P NMR spectroscopy of complex **1** in CD<sub>2</sub>Cl<sub>2</sub> and (b) VT <sup>1</sup>H NMR spectroscopy of complex **2** in C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> (NCH<sub>3</sub> region).

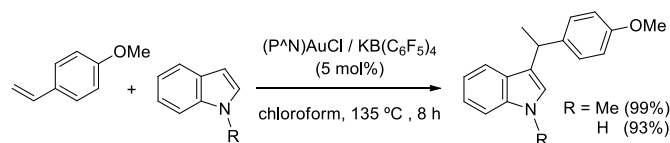
The metrical parameters for the styrene molecule coordinated to gold are very similar in complexes **1** and **2**. The C=C bond (1.39 Å) is noticeably elongated compared to that of free styrene (1.35 Å), in agreement with significant Au→styrene back-donation. A similar feature was observed in the bipyridine complex (1.38 Å)<sup>11a,b</sup> whereas gold(I) complexes featuring monodentate ligands display shorter C=C bonds (1.31–1.33 Å).<sup>14</sup> In complexes **1** and **2**, the η<sup>2</sup>-coordination of styrene is quasi-symmetric (the Au–CHPh bond is only 0.05–0.06 Å longer than the Au–CH<sub>2</sub> bond). However, the position of the C=C double bond with respect to the PAuP/PAuN metal fragment differs. The axis defined by the middle of the C=C bond (referred to as C<sub>i</sub>) and the gold centre nearly perfectly bisects the P–Au–P skeleton in complex **1** (the P–Au–C<sub>i</sub> bond angles amount to 138.1 and 132.7°), in line with the geometrical and electronic symmetry of the P<sup>∧</sup>P ligand. In contrast, the C=C double bond is shifted to the position *trans* to phosphorus in complex **2** (the P–Au–C<sub>i</sub> and N–Au–C<sub>i</sub> bond angles are quite different at 152.4 and 125.4°, respectively), resulting in a geometry at half-way between Y and T-shape. The structure of **2** reflects the electronic and steric dissymmetry of the MeDalphos ligand. To complete the picture, the steric demands of the different chelating ligands were estimated using steric maps and calculating percent buried volumes (%V<sub>Bur</sub>) with the SambVca application.<sup>18</sup> Accordingly, quite similar values were obtained for the P<sup>∧</sup>P and P<sup>∧</sup>N ligands (53.7 and 49.1,

respectively), albeit with higher dissymmetry among the different quadrants for MeDalpos. Of note, Cinellu's bipyridine ligand is comparatively much less hindering with a %VBur of 36.8.<sup>13</sup>



**Fig. 4** Molecular structures of complexes **1-GaCl<sub>4</sub>** and **2**. Hydrogen atoms, counter anion and solvate molecules are omitted; the carboranyl and adamantyl groups are simplified for clarity. Selected bond lengths (Å) and angles (°) for complex **1-GaCl<sub>4</sub>**: Au–P1 2.3818(6), Au–P2 2.3790(6), Au–C28 2.219(2), Au–C27 2.164(3), C27–C28 1.395(4), P1–Au–P2 89.12(2); for complex **2**: Au–P 2.3365(11), Au–N 2.381(4), Au–C29 2.143(5), Au–C30 2.208(5), C29–C30 1.387(8), P–Au–N 82.19(10).

A few recent studies have pointed out the catalytic relevance of P-based chelating ligands including MeDalpos in gold catalysis.<sup>6,19</sup> This prompted us to study the reactivity of the (P<sup>^</sup>N)AuCl complex towards indole alkylation.<sup>20</sup> Such intermolecular hydroarylation reaction is a very attractive way to functionalize (hetero)arenes by formal addition of C–H bonds towards alkenes. Gratifyingly, the (P<sup>^</sup>N)AuCl complex was found to efficiently catalyse the addition of *N*-methyl indole to 4-vinylanisole in the presence of KB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> as chloride abstractor. The reaction is complete in 8 h at 135 °C with 5 mol% catalyst and quantitatively affords the corresponding alkylated indole with complete C3 and Markovnikov selectivity (Scheme 2).<sup>13,21</sup> The reaction also works well with indole itself (93% yield). To support the catalytic relevance of the tricoordinate π-complex **3** (the 4-vinylanisole analogue of **2** which was independently synthesized and fully characterized).<sup>13</sup> The key role of the gold(I) π-complex **3** in the indole alkylation was further corroborated by performing the catalytic reaction with a preformed complex, which led to similar results than the *in situ* experiment.<sup>13</sup>



**Scheme 2** Hydroarylation of 4-vinylanisole with indoles catalysed by the (P<sup>^</sup>N) gold(I) complex.

In summary, the gold(I) styrene complexes **1–3** were prepared. NMR spectroscopy and X-ray crystallography provided comprehensive structural information. The P<sup>^</sup>P/P<sup>^</sup>N ligands are chelating, the gold centre is tricoordinate, styrene is η<sup>2</sup> and in-plane coordinated. In addition, the MeDalpos gold(I) chloride was proved to be an efficient catalyst for the hydroarylation of 4-vinylanisole by indoles, and the gold(I) π-complex **3** was identified as a key intermediate. These results demonstrate the ability of gold(I) to form tricoordinate π-complexes with P-based chelating ligands and open a new facet for the o-CBD and MeDalpos ligands in gold chemistry.

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