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## COMMUNICATION

## A multipurpose gold(I) precatalyst†

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**[Au(tmbn)<sub>2</sub>](SbF<sub>6</sub>) is the first gold(I) complex supported by two nitrile ligands that is indefinitely stable at room temperature. This is a highly versatile precatalyst that can be used for the preparation of active and robust solid-supported gold(I) catalysts.**

Screening different gold(I) catalysts for the development of new methods or in total synthesis requires the time-consuming preparation of a series of gold(I) complexes with different electrophilicities.<sup>1–7</sup> Therefore, it would be highly desirable to develop a gold(I) precatalyst that could play a role similar to that of Pd<sub>2</sub>(dba)<sub>3</sub> in palladium chemistry. For this purpose bis-nitrile complexes [Au(RCN)<sub>2</sub>]<sup>+</sup>X<sup>–</sup> appear as the best candidates.<sup>8</sup> Unfortunately, these complexes have been prepared in low yields and none are stable under ordinary conditions.<sup>9–11</sup> From a different perspective, [Au(RCN)<sub>2</sub>]<sup>+</sup>X<sup>–</sup> could play a fundamental role in supporting Au(I) complexes on properly functionalized resins. This much less explored area<sup>12,13</sup> holds great potential for the development of gold-catalyzed transformations with improved economic characteristics suitable for process intensification and medium scale production.

In a first attempt to fill the gap, we prepared [Au(NCPh)<sub>2</sub>](SbF<sub>6</sub>) in 59% yield by treatment of AuCl with AgSbF<sub>6</sub> (1 equivalent) and PhCN in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 43 h. However, this complex is unstable to air and moisture and readily decomposes to form 2,4,6-triphenyl-1,3,5-triazine when treated with moist MeNO<sub>2</sub> or PPh<sub>3</sub>. We reasoned that a robust Au(I) complex could be formed by using more electron-donating 2,4,6-trimethoxybenzonitrile (tmbn) as the ligand. Here we report that complex [Au(tmbn)<sub>2</sub>](SbF<sub>6</sub>) (**1**) (Fig. 1) is stable for months when stored under ambient conditions and can be used as a multipurpose precursor for the ready preparation of gold(I) complexes [AuL(tmbn)](SbF<sub>6</sub>). This complex has also been used to prepare solid-supported catalysts that show excellent reactivity and stability.

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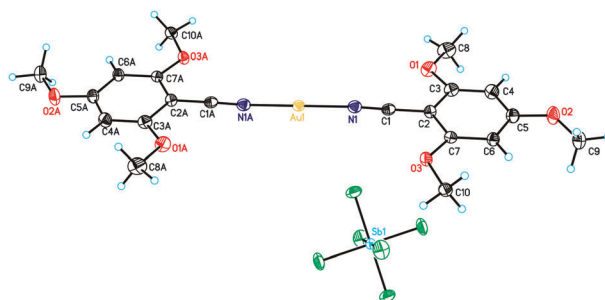
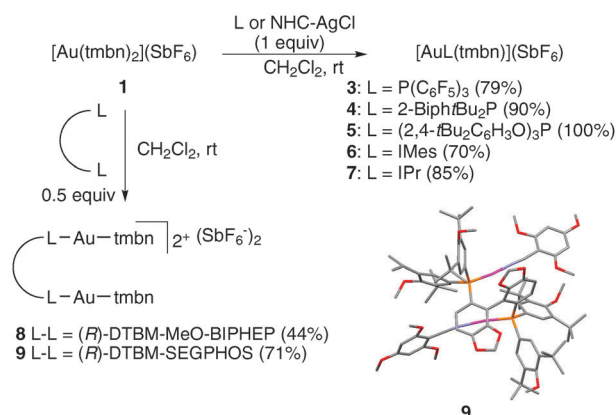


Fig. 1 Gold(I) complex [Au(tmbn)<sub>2</sub>](SbF<sub>6</sub>) (**1**).

Gold(I) complex **1** was prepared as a white crystalline solid by reaction of AuCl and tmbn (7 equivalents) with 1 equivalent of AgSbF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> in 75–83% yield (1–2 gram scale). The reaction was complete in only 20 min, whereas almost 2 days were required for the preparation of [Au(NCPh)<sub>2</sub>](SbF<sub>6</sub>). Complex **1** can easily be separated from more soluble [Ag(tmbn)<sub>2</sub>](SbF<sub>6</sub>) (**2a**) by crystallization.<sup>14</sup> Both linear complexes were characterized by X-ray diffraction.

Complex **1** reacts within time of mixing with 1 equivalent of the donor ligand. Thus, reaction of **1** with tris(pentafluorophenyl)phosphine, (2-biphenyl)di-*tert*-butylphosphine (JohnPhos),<sup>15</sup> and tris(2,4-di-*tert*-butylphenyl)phosphite gave cleanly **3–5** in good yields (Scheme 1). The straightforward synthesis of **4** illustrates the potential of this method for the ready preparation of a variety of cationic gold(I) complexes with bulky dialkylbiarylphosphane ligands.<sup>16,17</sup> Importantly, transmetalation



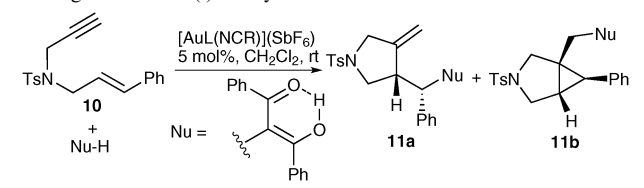
Scheme 1 Synthesis of cationic [AuL(tmbn)]SbF<sub>6</sub> and [Au<sub>2</sub>(L-L)(tmbn)<sub>2</sub>](SbF<sub>6</sub>)<sub>2</sub> complexes.

with NHC–AgCl complexes provided cationic NHC–gold(I) complexes **6** and **7** in good yields.<sup>2a,3</sup> Mixing complex **1** with 0.5 equivalents of bidentate ligands led to complexes [Au<sub>2</sub>(L–L)(tmbn)<sub>2</sub>](SbF<sub>6</sub>)<sub>2</sub> **8** and **9**, whose structure was confirmed by X-ray diffraction.<sup>18</sup>

Complexes [AuL(tmbn)]SbF<sub>6</sub> **4** and **5** formed *in situ* from **1** led to almost identical site-selectivities in the addition of dibenzoylmethane to enyne **10** to those obtained with the isolated complexes bearing different nitrile ligands as catalysts<sup>2a</sup> (Table 1, entries 1–4). Results with the preformed or prepared *in situ* catalyst **6** were almost identical (Table 1, entries 5 and 6). Importantly, enantioselectivities<sup>19</sup> obtained in [4 + 2]-cycloadditions of aryl-substituted enynes<sup>16</sup> and intermolecular cyclopropanation of alkenes with propargylic carboxylates<sup>20</sup> using preformed complexes **8** or **9** were the same as those obtained with catalysts formed *in situ* from **1** and (*R*)-DTBM–MeO–BIPHEP or (*R*)-DTBM–SEGPHOS.<sup>20,21</sup>

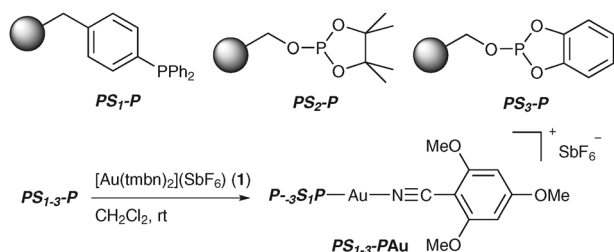
Supported cationic Au<sup>I</sup> complexes **PS**<sub>1–3</sub>–**PAu** were readily prepared by simple treatment of P-functionalized polystyrene resins **PS**<sub>1–3</sub>–**P** with [Au(tmbn)<sub>2</sub>](SbF<sub>6</sub>) (**1**) (Scheme 2). The catalytic performance of **PS**<sub>1–3</sub>–**PAu** was probed in the skeletal rearrangement of enyne **12a**, a reaction that can give rise to 1,3-dienes **13a** and **14a** (Table 2).<sup>22</sup> Although the three supported catalysts **PS**<sub>1–3</sub>–**PAu** were active, the most satisfactory results were obtained using **PS**<sub>2</sub>–**PAu** bearing a pinacolyl phosphite ligand. The same results were obtained with **PS**<sub>2</sub>–**PAu**

**Table 1** Addition of dibenzoylmethane to enyne **10** with isolated or *in situ* generated Au(I) catalysts<sup>a</sup>



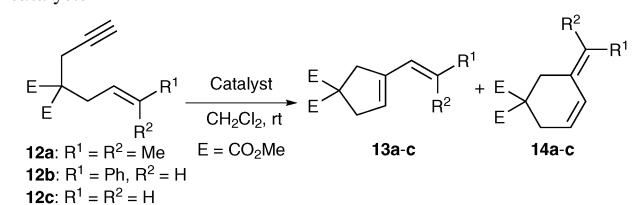
| Entry          | Catalyst (mol%)   | Time/min | Yield (%)<br>( <b>11a</b> / <b>11b</b> ratio) |
|----------------|---|----------|---|
| 1 <sup>b</sup> | <b>1</b> ( <b>6</b> ) + JohnPhos ( <b>7</b> )                                 | 30       | 53 (35 : 65)                                  |
| 2              | [Au(JohnPhos)(NCMe)](SbF <sub>6</sub> ) ( <b>5</b> )                          | 30       | 85 (33 : 67) <sup>2a</sup>                    |
| 3 <sup>c</sup> | <b>1</b> ( <b>6</b> ) + (ArO) <sub>3</sub> P <sup>d</sup> ( <b>7</b> )        | 15       | 69 (75 : 25)                                  |
| 4              | [Au((ArO) <sub>3</sub> P)(NCPh)](SbF <sub>6</sub> ) <sup>d</sup> ( <b>5</b> ) | 20       | 83 (77 : 23) <sup>2a</sup>                    |
| 5              | <b>1</b> ( <b>6</b> ) + ImesAgCl ( <b>7</b> )                                 | 20       | 84 <sup>e</sup> (2 : 98)                      |
| 6              | <b>6</b> ( <b>5</b> )   | 20       | 86 (< 1 : 99) <sup>2a</sup>                   |

<sup>a</sup> Reactions with 5 equiv. of NuH. Reactions in entries 2, 4, and 5 were carried out with a slight excess of L ligand to form 5 mol% of [AuL(tmbn)]SbF<sub>6</sub> + 1 mol% of inactive [AuL<sub>2</sub>](SbF<sub>6</sub>)<sub>2</sub>. <sup>b</sup> Reaction in the presence of **2b** (6 mol%). <sup>c</sup> Reaction with AgNTf<sub>2</sub> (12 mol%). <sup>d</sup> Ar = 2,4-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>. <sup>e</sup> Yield determined by <sup>1</sup>H NMR.



**Scheme 2** Synthesis of supported **PS**<sub>1–3</sub>–**PAu** catalysts.

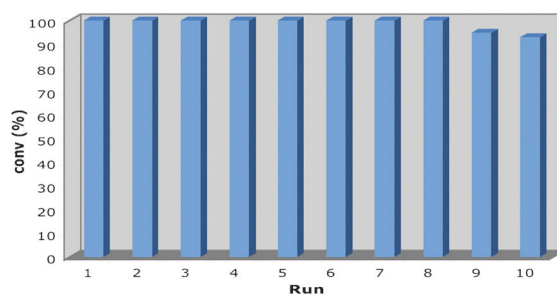
**Table 2** Skeletal rearrangement of **12a** with **PS**<sub>1–3</sub>–**PAu** and reference catalysts



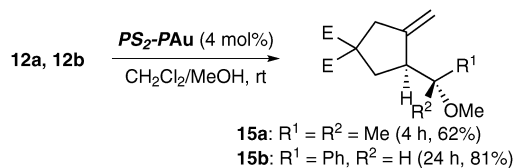
| Entry | <b>12</b>  | Catalyst (mol%)  | Time/min | Yield (%)<br>( <b>13</b> / <b>14</b> ratio) |
|-------|------------|--|----------|---|
| 1     | <b>12a</b> | [AuCl(PPh <sub>3</sub> )] ( <b>2</b> ) + AgSbF <sub>6</sub> ( <b>2</b> ) | 25       | 91 (100 : 0) <sup>22</sup>                  |
| 2     | <b>12a</b> | <b>PS</b> <sub>1</sub> – <b>PAu</b> ( <b>5</b> )                         | 30       | 100 (85 : 15)                               |
| 3     | <b>12a</b> | <b>PS</b> <sub>2</sub> – <b>PAu</b> ( <b>2</b> )                         | 5        | 85 (100 : 0)                                |
| 4     | <b>12a</b> | <b>PS</b> <sub>3</sub> – <b>PAu</b> ( <b>2</b> )                         | 60       | 53 (100 : 0)                                |
| 5     | <b>12b</b> | [AuCl(PPh <sub>3</sub> )] ( <b>2</b> ) + AgSbF <sub>6</sub> ( <b>2</b> ) | 5        | 91 (1 : 1.1) <sup>22</sup>                  |
| 6     | <b>12b</b> | <b>PS</b> <sub>2</sub> – <b>PAu</b> ( <b>2</b> )                         | 30       | 69 (1.6 : 1)                                |
| 7     | <b>12c</b> | [AuCl(PPh <sub>3</sub> )] ( <b>2</b> ) + AgSbF <sub>6</sub> ( <b>2</b> ) | 20       | 82 (1 : 2) <sup>22</sup>                    |
| 8     | <b>12c</b> | <b>PS</b> <sub>2</sub> – <b>PAu</b> ( <b>4</b> )                         | 480      | 81 (1 : 9.3)                                |

using non-dry, reagent grade CH<sub>2</sub>Cl<sub>2</sub>. Remarkably, the skeletal rearrangement of **12a** to **13a** could be repeatedly performed with the same sample of **PS**<sub>2</sub>–**PAu**. In this series of experiments, symptoms of partial catalyst deactivation only started to appear after the 8th recycling (Fig. 2), but full conversion can still be achieved by slightly extending the reaction time. It is interesting to note that the supported phosphite Au(I) catalyst **PS**<sub>2</sub>–**PAu** provided the *endo*-type rearranged product **14c** from 1,6-enyne **12c** with a better selectivity than that obtained with [AuCl(PPh<sub>3</sub>)] and AgSbF<sub>6</sub><sup>22</sup> (Table 2, entry 7). Excellent results were also obtained using **PS**<sub>2</sub>–**PAu** in the methoxycyclization of 1,6-enynes **12a** and **12d** (Scheme 3).<sup>22</sup>

In summary, a variety of catalytically active [AuL(tmbn)](SbF<sub>6</sub>) and [Au<sub>2</sub>(L–L)(tmbn)<sub>2</sub>](SbF<sub>6</sub>)<sub>2</sub> complexes can be readily prepared from air-stable [Au(tmbn)<sub>2</sub>](SbF<sub>6</sub>) (**1**). Catalysts prepared *in situ* from **1** show almost identical selectivities to those of isolated complexes, which could allow for the rapid screening



**Fig. 2** Recycling of the supported catalyst **PS**<sub>2</sub>–**PAu** in the skeletal rearrangement of **12a** to **13a**. All reactions were run with 5 mol% catalyst in CH<sub>2</sub>Cl<sub>2</sub> for 10 min. The catalyst was recovered by filtration, washed with CH<sub>2</sub>Cl<sub>2</sub> and used for the following run.



**Scheme 3** Methoxycyclization of **12a** and **12b** with **PS**<sub>2</sub>–**PAu** as the catalyst.

of the optimal catalyst to achieve the desired chemo- or enantioselectivity in new transformations. Complex **1** can also be used for the straightforward preparation of supported catalysts, as demonstrated in the case of **PS<sub>2</sub>-PAu**, which shows an excellent recyclability.

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