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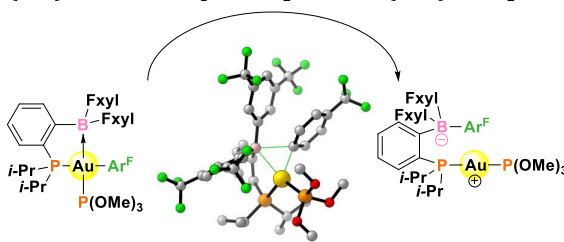
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# Gold to Boron Aryl Transfer From a T-Shape Phosphine-Borane Gold(I) Complex

Cyril A. Theulier, Yago García-Rodeja, Sonia Mallet-Ladeira, Karinne Miqueu, Ghenwa Bouhadir, Didier Bourissou\*

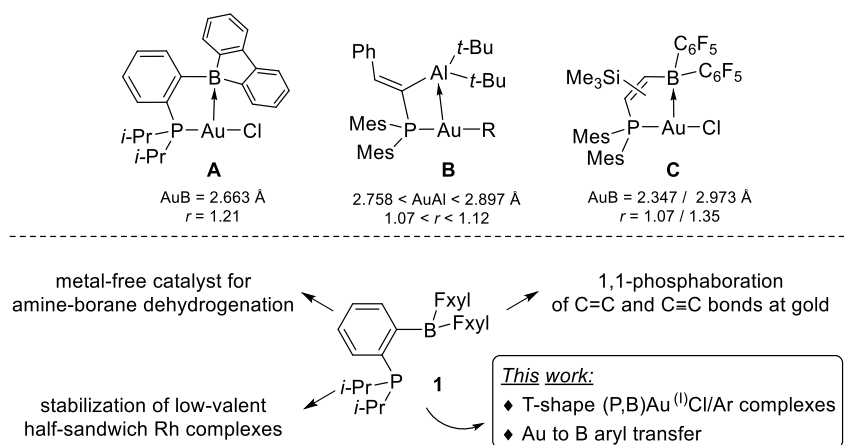
**ABSTRACT:** T-Shape gold(I) complexes with significant Au→B interactions were prepared from the phosphine-borane  $i\text{Pr}_2\text{P}(o\text{-C}_6\text{H}_4)\text{BFXyl}_2$  [FxyI = 3,5-(F<sub>3</sub>C)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]. The (P,B)AuAr<sup>F</sup> complex **4** [Ar<sup>F</sup> = 4-(F<sub>3</sub>C)C<sub>6</sub>H<sub>4</sub>] was obtained by an indirect route involving ligand exchange from (ArO)<sub>3</sub>PAuAr<sup>F</sup> **3a** [Ar = 2,4-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]. A different outcome was observed with the analogous precursor (MeO)<sub>3</sub>PAuAr<sup>F</sup> **3b**. Here, the phosphite remains bonded to gold and the borane moiety abstracts the Ar<sup>F</sup> group from gold to give the zwitterionic dicoordinate gold(I) complex **5**. DFT calculations support a 2-step associative pathway for this gold to boron aryl transfer. It involves a square-planar gold(I) complex with enhanced Au→B interaction as key intermediate, it proceeds *via* a 3-center transition.



Phosphine-boranes (P,B) and related ambiphilic ligands open interesting avenues in gold chemistry. The formation of Au→LA (LA = Lewis Acid) interactions has been thoroughly studied in the frame of  $\sigma$ -acceptor Z-type ligands<sup>1</sup> and the resulting electron-deprived complexes have been applied in  $\pi$ -activation-based gold catalysis.<sup>2</sup> Au→LA interactions supported by two or three donor buttresses are now quite common and actually known with various Lewis acid moieties based on B, Ga, In, Sn, Sb, Te...<sup>3,4</sup> Comparatively, T-shape gold(I) complexes deriving from bidentate ambiphilic ligands are much rarer (Figure 1). We reported in 2006 the first such complex **A**.<sup>5</sup> The highly Lewis acidic borafuorenyl moiety imparts significant Au→B interaction, but the corresponding phosphine-borane  $i\text{-Pr}_2\text{P}(o\text{-C}_6\text{H}_4)\text{BFlu}$  is stable only at very low temperature. In collaboration with the group of W. Uhl, we then prepared complexes **B** from the geminal phosphine-alane  $\text{Mes}_2\text{PC}(=\text{CHPh})\text{Alt-Bu}_2$ .<sup>6</sup> Here, the presence of an organic group at Au (R = Me, C<sub>6</sub>F<sub>5</sub>, C≡CPh) is needed to observe Au→Al interaction. In the case of chloride, the high Al/Cl affinity favors internal ionization and zwitterionic complexes are obtained.<sup>7</sup> In addition, Erker *et al* studied in 2019 gold(I) complexes **C** deriving from vicinal phosphine-boranes.<sup>8</sup> Of note, the strength of the Au→B interaction was found to markedly depend on the position of the SiMe<sub>3</sub> substituent on the ligand backbone.

We recently introduced the phosphine-borane (P,B) **1** featuring a highly Lewis acidic and moderately hindered boron center.<sup>9</sup> It proved an efficient and general catalyst for the dehydrogenation of amine-boranes under metal-free conditions.<sup>10</sup> Its ability to engage in strong M→B interactions was also substantiated and exploited to stabilize low-valent half sandwich Rh complexes,<sup>11</sup> while an original 1,1-phosphaboration process was observed with gold(I) alkynyl and vinyl complexes.<sup>12</sup>

In this work, the preparation of T-shape gold(I) complexes was investigated from **1**. The BFxyl<sub>2</sub> moiety was found to engage in strong Au→B interactions, but to remain reactive, as substantiated by internal abstraction of the aryl group from gold. The mechanism of this gold to boron aryl transfer has been investigated computationally.

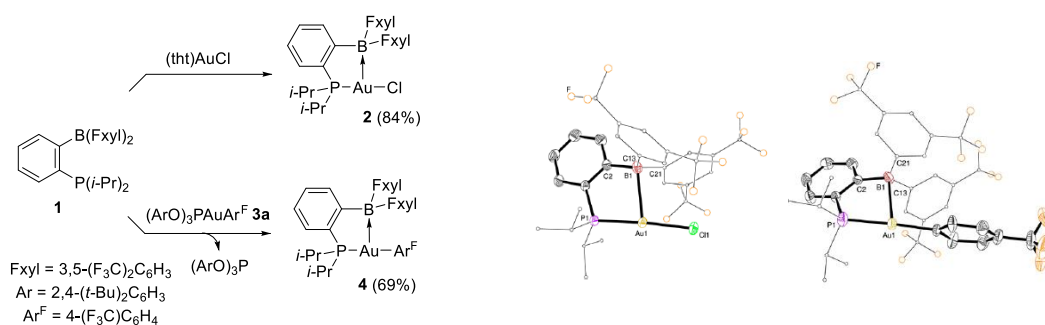


**Figure 1. Au→LA interactions in T-shape gold(I) complexes deriving from bidentate ambiphilic ligands (F<sub>xyl</sub> = 3,5-(F<sub>3</sub>C)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>;  $r$  refers to the ratio between the Au...LA distance and the sum of covalent radii).**

Access to the targeted (P,B)AuAr complex was first attempted by coordination of the phosphine-borane to gold(I) chloride followed by transmetalation (Scheme 1). Treatment of **1** with (tht)AuCl (tht = tetrahydrothiophene) cleanly and rapidly afforded the corresponding (P,B)AuCl complex **2** which was isolated in 84% yield as a white solid (mp 103.7 °C). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a saturated dichloromethane solution of **2** at -20°C.<sup>13</sup> Accordingly, the phosphine-borane ligand chelates the metal. As a result, gold is 3-coordinate and sits in T-shape geometry with P–Au–Cl and P–Au–B bond angles of 174.25(2) and 81.25(5)°, respectively. Rare precedents for T-shape Au(I) complexes derive from ambiphilic (Figure 1)<sup>5,6,8</sup> or pincer LXL ligands.<sup>14</sup> The Au–B distance in **2** is short at 2.555(2) Å. It is significantly shorter than that observed in the related complex **A** featuring a borafuorenyl moiety (2.663(8) Å)<sup>5</sup> and actually exceeds the sum of the covalent radii<sup>15</sup> by only 16%. The highly Lewis acidic BFxyl<sub>2</sub> moiety thus engages in relatively strong Au→B interaction, which is favored over chloride abstraction, in contrast to what was observed with the geminal (P,Al) ligand.<sup>7</sup> Substitution of the chloride at gold for an aryl group was then attempted but disappointingly, no suitable conditions could be found to obtain (P,B)AuAr complexes by transmetalation from **2**. We thus turned to an indirect route involving a gold(I) aryl precursor with a labile ligand that could be displaced by the phosphine-borane **1**. As for the gold(I) vinyl species we previously studied,<sup>12</sup> the sterically demanding triaryl phosphite P(OAr)<sub>3</sub> (Ar = 2,4-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) showed a suitable balance between the stability of the organogold precursor and the ligand exchange with the phosphine-borane. Hence, **1** was found to react slowly and cleanly with **3a** [prepared from (ArO)<sub>3</sub>PAuCl and Ar<sup>F</sup>ZnCl, Ar<sup>F</sup> = 4-(F<sub>3</sub>C)C<sub>6</sub>H<sub>4</sub>] in dichloromethane at room temperature. <sup>31</sup>P NMR monitoring shows the release

of free phosphite (ArO)<sub>3</sub>P ( $\delta$ 130 ppm) and concomitant formation of the (P,B)AuAr<sup>F</sup> complex **4** ( $\delta$ 71.4 ppm). The <sup>19</sup>F NMR spectrum displays two different CF<sub>3</sub> signals at  $\delta$ -63.1 and -62.8 ppm (integrating in 4:1 ratio) for the Fxyl and Ar<sup>F</sup> groups, respectively. Multiple precipitations in acetonitrile at -20°C enabled to remove the phosphite side-product and isolate complex **4** (69 % yield). Crystals were grown from a pentane solution at -20°C. The X-ray diffraction study revealed a T-shape structure similar to that of **2**, with P-Au-C and P-Au-B bond angles of 176.8(3) and 79.2(3)° in **4**. The Au-B distance (2.72(1) Å,  $r = 1.24$ ) is slightly higher than in the chloro complex **2** (2.555(2) Å) but remains well within the sum of van der Waals radii (3.90 Å).<sup>16</sup>

**Scheme 1. Synthesis and solid-state structures of the T-shape gold(I) complexes **2** and **4** deriving from phosphine-borane **1**.**

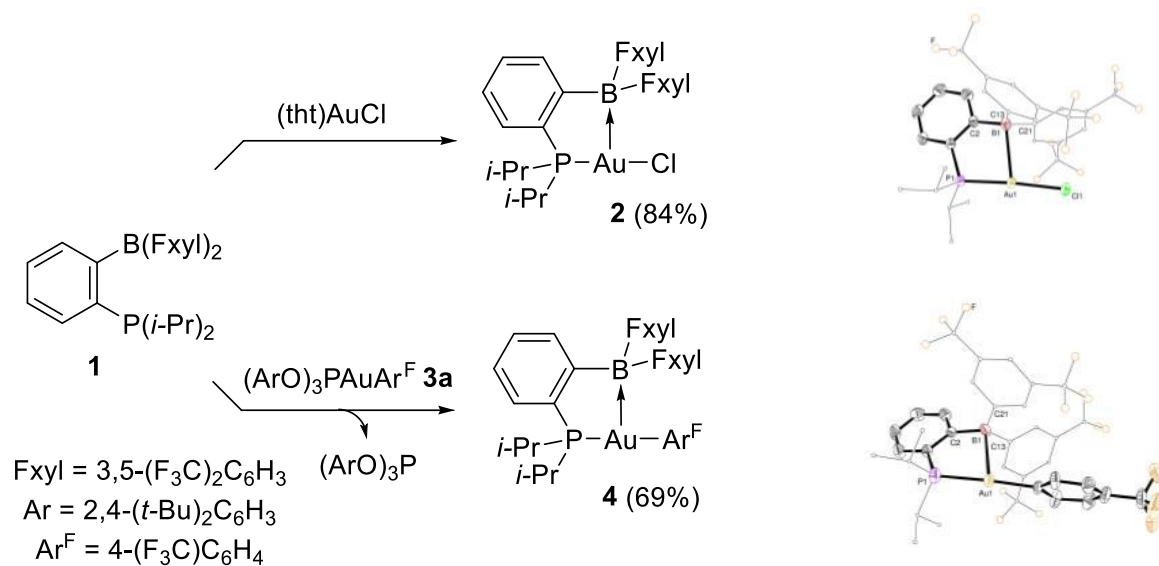


Ellipsoids are shown at 50% probability; hydrogen atoms are omitted; *i*-Pr, Fxyl and Ar<sup>F</sup> are simplified for clarity. Selected bond distances (Å) and angles (°). **2**: P1-Au1 2.2390(6), Au1-Cl1 2.3306(6), Au1-B1 2.555(2), P1-Au1-Cl1 174.25(2), P1-Au1-B1 81.25(5), B1-Au1-Cl1 102.64(5), C2-B1-C13 116.6(1), C13-B1-C21 119.4(1), C21-B1-C2 118.5(1). **4**: P1-Au1 2.303(3), Au1-C29 2.07(1), Au1-B1 2.72(1), P1-Au1-C29 176.8(3), P1-Au1-B1 79.2(3), B1-Au1-C29 103.9(4), C2-B1-C21 120(1), C21-B1-C13 120(1), C13-B1-C2 117(1).

The reaction of **1** with **3a** thus provides access to the targeted (P,B)AuAr complex **4**, but the removal of the (ArO)<sub>3</sub>P phosphite is laborious. With the aim to facilitate the work-up and improve the efficiency of the preparation, we envisioned to use a more easily removable phosphite such as (MeO)<sub>3</sub>P (bp = 110°C). The corresponding aryl gold precursor (MeO)<sub>3</sub>PAu(4-(CF<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>) **3b** was prepared from (MeO)<sub>3</sub>PAuCl and Ar<sup>F</sup>ZnCl and reacted with the phosphine-borane **1** in THF at room temperature (Scheme 2). <sup>31</sup>P NMR spectroscopy showed the disappearance of the signals for **1** and **3b** to give two doublets at  $\delta$  142.6 et 54.0 ppm with a large  $J_{\text{PP}}$  coupling constant of 425.6 Hz. This is indicative of the presence and *trans* coordination of the two phosphines at gold. Concomitantly, a sharp signal appears at  $\delta$ -6.3 ppm in the <sup>11</sup>B NMR spectrum, signaling the presence of a tetracoordinate boron center. After work-up, the resulting complex **5** was isolated in 82% yield as a white solid. The crystals obtained by addition of diethyl ether to a pentane solution of **5** at -20°C were analysed by X-ray diffraction. The gold center is dicoordinate and its geometry slightly deviates from linearity with a P1-Au-P2 bond angle of 167.8(1)°. The Ar<sup>F</sup> group has been transferred from gold to boron, which is

tetracoordinate. The shortest C...Au distances with the aryl groups at boron amount to 2.962 and 3.011 Å (with the C<sub>ipso</sub> and one C<sub>ortho</sub> atoms of Ar<sup>F</sup>), indicating the existence of only weak, if any, arene-gold interaction.<sup>17</sup> The more electron-donating and less sterically demanding phosphite P(OMe)<sub>3</sub> thus remains bonded to gold, in contrast to (ArO)<sub>3</sub>P.<sup>18</sup> The formation of **5** from **1** and **3b** can be understood as the insertion of the phosphine-borane into the Au–Ar<sup>F</sup> bond. A two-step associative process is more likely, with coordination of **1** to gold, followed by the transfer of the Ar<sup>F</sup> group from gold to boron (instead of phosphite release, as observed for the formation of complex **4**). This mechanistic scenario is supported by the reaction of P(OMe)<sub>3</sub> with the (P,B)AuAr<sup>F</sup> complex **4**, which also led to the zwitterionic complex **5**.

## Scheme 2. Formation and solid-state structure of the zwitterionic complex **5**.

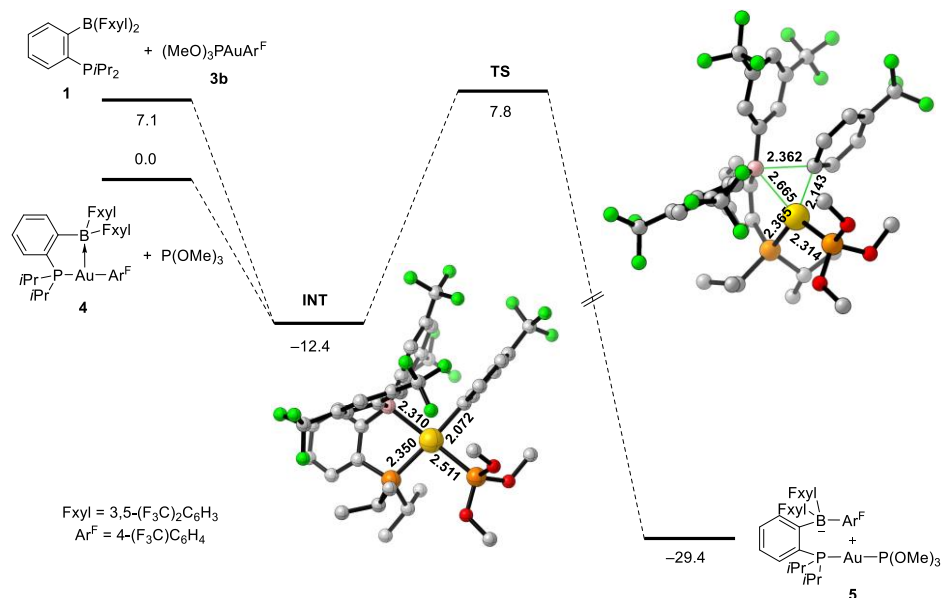


Ellipsoids are shown at 50% probability; hydrogen atoms are omitted; *i*-Pr, Fxyl and Ar<sup>F</sup> are simplified for clarity. Selected bond distances (Å) and angles (°): P1–Au1 2.316(3), P2–Au1 2.282(4), P1–Au1–P2 167.8(1), C2–B1–C20 110.2(7), C20–B1–C28 107.1(7), C28–B1–C2 109.1(7).

Abstractions of an organic fragment from a transition metal by the Lewis acid moiety of an ambiphilic ligand, as observed upon formation of the zwitterionic complex **5**, are rare,<sup>12,19</sup> and very little is known about the mechanism of such processes. This prompted us to investigate the formation of **5** computationally. Calculations were performed at the B3PW91-D3(BJ)/SDD+f(Au),6-31G\*\* (other atoms) level of theory on the actual species. The two synthetic routes leading to **5** experimentally, *ie* **4** + P(OMe)<sub>3</sub> and **1** + **3b**, were considered. In both cases, the formation of the zwitterionic complex was predicted to result from an associative, 2-step pathway. The 4-coordinate gold(I) complex **INT** (with the phosphine-borane, the phosphite P(OMe)<sub>3</sub> and the Ar<sup>F</sup> group bonded to Au) is found as key common intermediate (Figure 2).<sup>13</sup> No transition state could

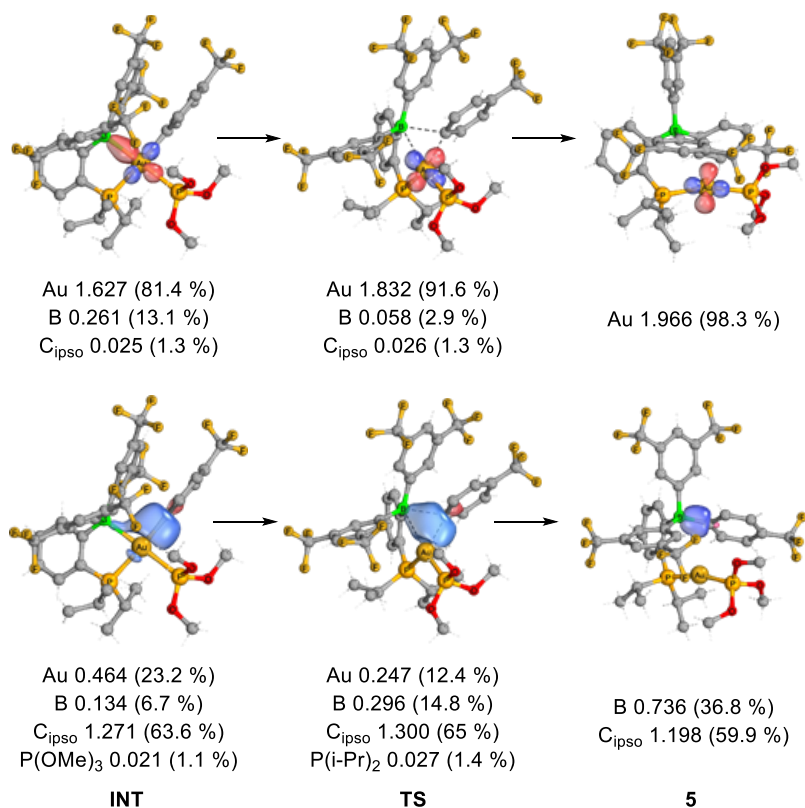
be located for an alternative pathway involving direct insertion of the phosphine-borane **1** into the Au–Ar<sup>F</sup> bond of the (MeO)<sub>3</sub>PAuAr<sup>F</sup> precursor **3b**. The formation of the zwitterionic complex **5** is very exergonic ( $\Delta G \leq -30$  kcal/mol), slightly more from **1** + **3b** due to the higher stability of **4** + P(OMe)<sub>3</sub> (by about 7 kcal/mol). The absence of significant arene-gold interaction in **5** is supported by NBO analysis, where only weak donor-acceptor interactions are found at the second-order perturbation level ( $\Delta E_{\text{NBO}} < 5$  kcal/mol for  $\pi_{\text{C=C}} \rightarrow \sigma_{\text{AuP(OMe)}_3}^*$  and  $< 1$  kcal/mol for  $d_{z^2(\text{Au})} \rightarrow \pi_{\text{C=C}}^*$ ).<sup>13</sup> The structure and bonding situation of **INT** deserve comments. The borane moiety acts as a  $\sigma$ -acceptor ligand. The ensuing Au→B interaction is stronger than in the 3-coordinate (P,B)AuAr<sup>F</sup> complex **4**. This is apparent from the Au⋯B distance which is substantially shortened (from 2.584 Å in **4** to 2.310 Å in **INT**), while the environment around boron is more pyramidalized ( $\Sigma(\text{CBC})$  from 356.1° in **4** to 344.0° in **INT**) and further corroborated by NBO analyses ( $\Delta E_{\text{NBO}}$ : 25.4 kcal/mol for **4** and 53.4 kcal/mol for **INT**). Of note, the geometry at Au is close to square-planar ( $\tau_8 = 0.16$ ),<sup>20</sup> with P–Au–P, *i*-Pr<sub>2</sub>P–Au–B and B–Au–P(OMe)<sub>3</sub> bond angles of 98.06°, 82.09° and 170.34°, respectively. This is a peculiar feature of tetra-coordinate Au(I) complexes featuring Z-type ligands, so far authenticated (and thoroughly studied) with tridentate diphosphine-boranes and related ambiphilic ligands.<sup>3a,g,4a,e,f,h-j</sup> The transition state **TS** with 3-center Au/B/C<sub>ipso</sub>(Ar<sup>F</sup>) interaction connects **INT** to the zwitterionic complex **5**. The Au→B interaction vanishes and simultaneously the Ar<sup>F</sup> group shifts from gold to boron. While 2-electron redox transformations at gold (oxidative addition/reductive elimination) have recently garnered huge interest,<sup>21</sup> the B–aryl coupling from **INT** to **5** proceeds at gold(I) (without change in the oxidation state of gold) and stands as a non-reductive elimination.<sup>22</sup>

The activation barrier computed for the conversion of **INT** into **5** (*ca* 20 kcal/mol) is consistent with the experimental observations (few hours of reaction at room temperature). In **TS**, the Ar<sup>F</sup> group bridges gold and boron (the C<sub>ipso</sub>–Au and C<sub>ipso</sub>–B bonds deviate from the Ar<sup>F</sup> plane by 26° and 47°, respectively). The Au–Ar<sup>F</sup> breaking bond (2.143 Å) is slightly elongated (by *ca* 3.4 %) with respect to the square-planar complex **INT** while the B–Ar<sup>F</sup> forming bond (2.362 Å) is elongated by > 40% with respect to the zwitterionic product **5**, indicating a relatively early transition state. The Ar<sup>F</sup> transfer from gold to boron induces significant elongation of the Au⋯B distance (from 2.310 Å in **INT**, to 2.665 Å in **TS**) and noticeable widening of the P–Au–P skeleton (from 98.06° in **INT** to 119.29° in **TS**).



**Figure 2.** Energy profiles computed for the migration of the  $\text{Ar}^{\text{F}}$  group from Au to B in the reactions  $1 + 3b$  and  $4 + \text{P}(\text{OMe})_3$  at the B3PW91-D3(BJ)/SDD+f(Au),6-31G\*\* (other atoms) level of theory.  $\Delta\text{G}$  values in kcal/mol, bond lengths in  $\text{\AA}$ .

Intrinsic Bond Orbital calculations (IBOs)<sup>23</sup> have recently emerged as a powerful mean to analyse reaction mechanisms and associated electron flows.<sup>24</sup> Here, the IBOs of **INT**, **TS** and **5** were inspected to gain more insight into the intricacies of the aryl migration from gold to boron (Figure 3).<sup>25</sup> Accordingly, the metal was found to disengage from  $\text{Au} \rightarrow \text{B}$  interaction. The associated IBO is more strongly localized on gold in **TS** (91.6 %) than in **INT** (81.4 %). The B contribution to the  $\text{Au}-\text{B}$  orbital decreases significantly from **INT** (13.1 %) to **TS** (2.9 %). In the meantime, the  $\text{Au}-\text{Ar}^{\text{F}}$  bond evolves to a 3-center  $\text{Au}/\text{B}/\text{C}_{\text{ipso}}(\text{Ar}^{\text{F}})$  interaction. The corresponding IBO is centered on  $\text{C}_{\text{ipso}}(\text{Ar}^{\text{F}})$  (64-65 %). The contribution of gold decreases from 23.2 % in **INT** to 12.4 % in **TS**, while that of boron increases from 6.7 % in **INT** to 14.8 % in **TS**.



**Figure 3.** Intrinsic Bond Orbital (IBOs) of the intermediate square-planar gold(I) complex INT, 3-centered transition state TS associated to the migration of the Ar<sup>F</sup> group from Au to B and zwitterionic product 5. Numbers relate the fraction of electrons of the doubly occupied IBO assigned to each atom. Percentages into brackets correspond to participation of the main atoms in the associated IBO.

In conclusion, the phosphine-borane **1** was found to readily chelate gold(I) and form T-Shape complexes. The borane moiety is engaged in significant Au→B interaction, but it remains active and may act as an internal acceptor, as substantiated by the formation of the zwitterionic complex **5** upon gold to boron aryl transfer. From a mechanistic viewpoint, the formation of **5** involves a square-planar gold(I) complex with enhanced Au→B interaction as key intermediate. The B–aryl coupling proceeds *via* a 3-center transition state. The metal disengages from the Au→B interaction while the Ar<sup>F</sup> group shifts from gold to boron. The gold to boron aryl transfer leading to **5** stands as a rare example of redox neutral elimination, and it is actually the first occurring at gold(I). Future work will seek to explore the generality of such a process, varying the ambiphilic ligand, the metal and the co-ligand. On long-term, it is our aim to study how ambiphilic ligands influence the reactivity of transition metals, to identify new paths assisted by the Lewis acid moiety, and to exploit them in catalytic transformations of synthetic interest.



## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/>.

Experimental and computational details, analytical data and NMR spectra (PDF)

Optimized cartesian coordinates (XYZ)

CCDC CCDC 2058919 (2), 2059569 (4) and 2059570 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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