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# Gold(I) Complexes of the Geminal Phosphinoborane $t\text{Bu}_2\text{PCH}_2\text{BPh}_2$

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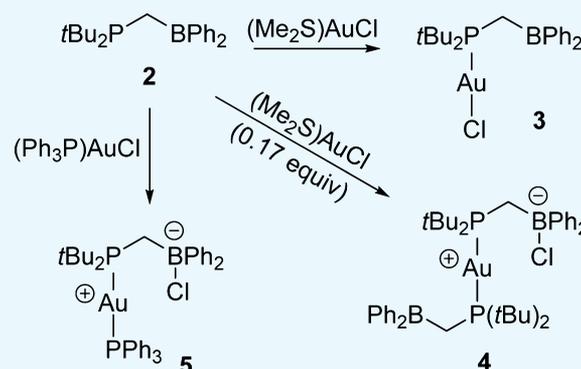
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## Supporting Information

**ABSTRACT:** In this work, we explored the coordination properties of the geminal phosphinoborane  $t\text{Bu}_2\text{PCH}_2\text{BPh}_2$  (**2**) toward different gold(I) precursors. The reaction of **2** with an equimolar amount of the sulfur-based complex  $(\text{Me}_2\text{S})\text{AuCl}$  resulted in displacement of the  $\text{SMe}_2$  ligand and formation of linear phosphine gold(I) chloride **3**. Using an excess of ligand **2**, bisligated complex **4** was formed and showed dynamic behavior at room temperature. Changing the gold(I) metal precursor to the phosphorus-based complex,  $(\text{Ph}_3\text{P})\text{AuCl}$  impacted the coordination behavior of ligand **2**. Namely, the reaction of ligand **2** with  $(\text{Ph}_3\text{P})\text{AuCl}$  led to the heterolytic cleavage of the gold–chloride bond, which is favored over  $\text{PPh}_3$  ligand displacement. To the best of our knowledge, **2** is the first example of a P/B-ambiphilic ligand capable of cleaving the gold–chloride bond. The coordination chemistry of **2** was further analyzed by density functional theory calculations.

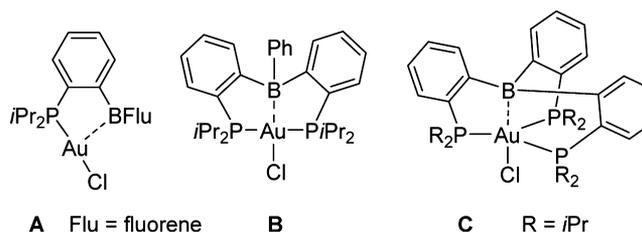


## INTRODUCTION

Ambiphilic ligands bearing a Lewis basic site for  $\sigma$ -donation and a Lewis acidic site for  $\sigma$ -acceptation have been recognized as ligands with unique coordination properties,<sup>1</sup> resulting in unusual bonding situations (Z-type interactions)<sup>2,3</sup> or halide abstraction from the metal precursor, which are both of interest for catalytic applications.<sup>4,5</sup> The coordination behavior of ambiphilic ligands has been extensively studied in combination with late transition metals, in particular, complexes with coinage metals. Among these coinage metals, gold(I) is the most explored and a plethora of gold complexes have been reported, which are mainly dominated by ligands bearing a Lewis basic phosphine, in combination with a variety of Lewis acidic sites based on boron,<sup>6,7</sup> aluminum,<sup>8</sup> gallium,<sup>9</sup> indium,<sup>10</sup> bismuth,<sup>11</sup> silicon,<sup>12</sup> tin,<sup>12a</sup> antimony,<sup>13</sup> zirconium,<sup>14</sup> and tellurium.<sup>15</sup>

In 2006, Bourissou and co-workers reported a bidentate phosphinoborane ligand that reacts with  $(\text{Me}_2\text{S})\text{AuCl}$  to form complex **A** (Chart 1).<sup>6a</sup> In this example, the ambiphilic ligand reacts with the metal precursor by the displacement of the dimethyl sulfide ligand, resulting in the coordination of the phosphine to the gold(I) center. Interestingly, the solid-state structure of **A** revealed a Au–B distance of 2.66 Å, which is well within the sum of the van der Waals radii ( $\sim 3.9$  Å), as well as slight pyramidalization of the boron center ( $\sum(\text{CBC}) = 355.8^\circ$ ), indicating a Z-type interaction between the gold(I)

## Chart 1. Ambiphilic Ligand Complexes of Gold(I) Chloride



center and the Lewis acid. A year later, Bourissou and co-workers reported a tridentate phosphinoborane ambiphilic ligand, which can react with the same metal precursor also by the displacement of dimethyl sulfide to form complex **B** (Chart 1).<sup>6b</sup> The slightly distorted square planar coordination geometry forces the boron center in a closer proximity to the gold center (2.31 Å) compared to **A**, resulting in a stronger pyramidalization ( $\sum(\text{CBC}) = 341.2^\circ$ ), which suggests a stronger boron–gold interaction. To complete this family of phosphinoborane ligands with unique Z-type interactions,

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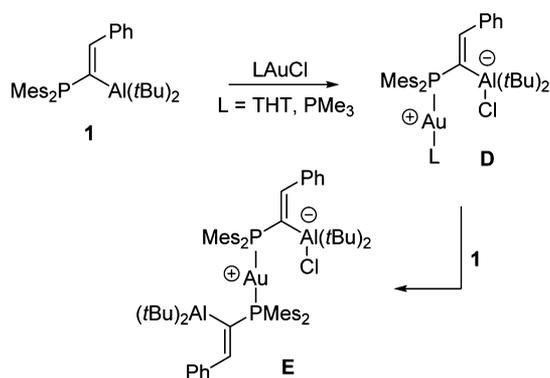
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Bourissou and co-workers reported a tetradentate phosphinoborane (TPB) ligand that forms complex **C** (Chart 1) upon coordination to  $(\text{Me}_2\text{S})\text{AuCl}$ .<sup>6c</sup> Dissociation of the gold–chloride bond was easily achieved by the addition of an external Lewis acid to **C**, giving rise to cationic  $(\text{TPB})\text{Au}^+$  species.<sup>6d</sup>

Interestingly, tri- and tetradentate phosphine-based ambiphilic ligands with heavier main-group Lewis acidic sites based on aluminum,<sup>8c,d</sup> gallium,<sup>9</sup> indium,<sup>10</sup> and silicon<sup>12c</sup> are reported to facilitate heterolytic Au–Cl bond cleavage without an additional halide abstracting agent. To date, phosphorus–aluminum ligand **1** is the only main-group-based bidentate ligand<sup>14</sup> that has been reported to perform this bond activation when reacted with tetrahydrothiophene gold(I) chloride ( $(\text{THT})\text{AuCl}$ ) forming zwitterionic complex **D** (Scheme 1),<sup>8a,b</sup> which proved to be an active catalyst for the cyclization

### Scheme 1. Reactivity of **1** Toward Au(I) Precursors



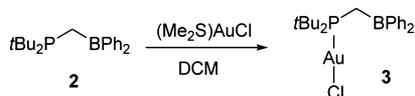
of propargylamides in the absence of any additives. This demonstrates the potential of ambiphilic ligands as an alternative to silver salts for the activation of gold(I) precatalysts.<sup>16</sup>

Recently, we developed ambiphilic phosphinoborane **2** which exhibits frustrated Lewis pair reactivity<sup>17–19</sup> when reacted with, for example,  $\text{H}_2$ ,  $\text{CO}_2$ , isocyanates, alkynes, nitriles, and nitrilium triflates,<sup>20</sup> but can also act as an ambiphilic ligand forming a luminescent complex upon coordination to  $\text{Cu(I)-Cl}$ .<sup>21</sup> The related geminal P/Al-based FLP **1** and its capability to activate a gold–chloride bond inspired us to explore the coordination behavior of **2** toward gold(I) chloride complexes and also to study the underlying factors experimentally and computationally.

## RESULTS AND DISCUSSION

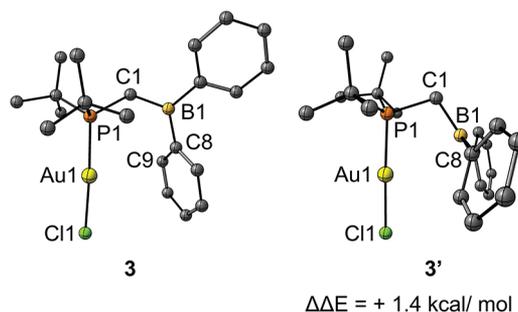
Reacting a solution of  $(\text{Me}_2\text{S})\text{AuCl}$  in dichloromethane (DCM) with 1 equiv of  $t\text{Bu}_2\text{PCH}_2\text{BPh}_2$  (**2**) resulted in the formation of two new species in solution, observed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy at  $\delta = 75.3$  (major, 75%) and 80.5 (minor, 25%) and the formation of small amounts of insoluble purple solids (Scheme 2).<sup>a</sup> The X-ray diffraction analysis of colorless crystals obtained by vapor diffusion of *n*-pentane into a DCM solution confirmed the molecular structure of the major product **3**, in which ligand **2** has displaced the  $\text{SMe}_2$  moiety,

### Scheme 2. Ligand Displacement by Phosphinoborane **2**



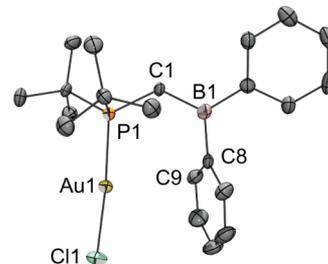
and in contrast to **1** (Scheme 1), did not cleave the gold–chloride bond.<sup>b</sup> In the solid state, the  $\text{P1–Au1–Cl1}$  bond angle is slightly bent ( $174.35(4)^\circ$ )<sup>22</sup> and the  $\text{P1–C1–B1}$  bond angle ( $119.8(3)^\circ$ ) is comparable to that of the optimized geometry<sup>20a</sup> of the free ligand ( $2.1^\circ$  increase). The  $\text{B1–Au1}$  distance of  $3.798(5)$  Å is just within the sum of the van der Waals radii ( $\sim 3.9$  Å), however, the planar geometry of the boron center ( $\sum(\text{CB1C}) = 359.8^\circ$ ) is rotated away from the gold center (torsion angle  $\text{P1–C1–B1–C8} = 46.4(5)^\circ$ ), making any Z-type interaction unlikely. Interestingly, one of the phenyl groups of the ligand is oriented in an almost parallel fashion to the metal chloride bond,<sup>23</sup> and the  $\text{Au1–C8}$  and  $\text{Au1–C9}$  bond distances of  $3.326$  Å indicate a possible weak  $\pi$ -interaction, comparable to those previously reported for Au(I) complexes bearing biarylphosphine ligands.<sup>24,25</sup> The  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum showed one signal at  $70.2$  ppm, which is comparable to that of the free ligand ( $72.3$  ppm)<sup>20</sup> and is indicative for a planar diarylalkylborane, supporting the absence of any Z-type interaction.

Analysis of compound **3** by density functional theory (DFT) calculations at the  $\omega\text{B97X-D/6-31G}^*$  (Def2-QZVP for Au) level of theory<sup>26</sup> revealed two possible conformers which are close in energy (**3** and **3'**, Figure 1). Conformer **3** was found to



**Figure 1.** Two optimized geometries for compound **3** (hydrogens are omitted for clarity). Selected bond lengths (Å) and angles ( $^\circ$ ): **3**:  $\text{P1–Au1}$  2.28,  $\text{B1–Au1}$  3.94,  $\text{C8–Au1}$  3.50,  $\text{C9–Au1}$  3.28,  $\text{P1–Au1–Cl1}$  176.9,  $\text{P1–C1–B1}$  119.0,  $\text{P1–C1–B1–C8}$  53.8. **3'**:  $\text{P1–Au1}$  2.28,  $\text{B1–Au1}$  3.18,  $\text{P1–Au1–Cl1}$  177.1,  $\text{P1–C1–B1}$  106.4,  $\text{P1–C1–B1–C8}$  92.7.

be the global minimum and closely resembles the geometry of **3** in the solid state as determined by single-crystal X-ray crystallography (Figure 2). Interestingly, also a local minimum was found, albeit higher in energy (**3'**,  $\Delta\Delta E = 1.4$  kcal/mol). **3'**

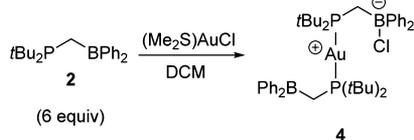


**Figure 2.** Molecular structure of compound **3** (ellipsoids are set at 50% probability; hydrogens are omitted for clarity). Selected bond lengths (Å) and angles ( $^\circ$ ):  $\text{P1–Au1}$  2.2466(11),  $\text{Au1–Cl1}$  2.2035(11),  $\text{P1–C1–B1}$  119.8(3),  $\text{B1–Au1}$  3.798(5),  $\text{C8–Au1}$  3.262(4),  $\text{C9–Au1}$  3.263(3),  $\text{P1–Au1–Cl1}$ ,  $174.35(4)$   $\sum(\text{CB1C})$  359.8.

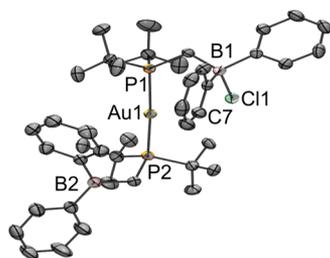
revealed a significantly more bent P1–C1–B1 backbone ( $106^\circ$ ) compared to **3** ( $119^\circ$ ), and the empty p orbital on boron is oriented toward the gold center (torsion angle =  $92.7^\circ$ ), analogous to the reported complex **A** (Chart 1).<sup>6a</sup> The different backbone of 3' ( $C_1$  linker) compared to the  $C_2$  bridge in **A** results in a larger B1–Au1 distance ( $3.18 \text{ \AA}$  vs **A**:  $2.663(8) \text{ \AA}$ ), which would lead to a much weaker Z-type interaction.

The minor product of the reaction was identified as a result of double addition of phosphinoborane **2** to  $(\text{Me}_2\text{S})\text{AuCl}$  and concomitant cleavage of the gold–chloride bond forming bisligated zwitterionic complex **4** (Scheme 3), which compares

### Scheme 3. Formation of Bisligated Complex **4**



well with complex **E** that is obtained with P/Al analogue **1** (Scheme 1).<sup>8a</sup> Colorless crystals suitable for X-ray diffraction were obtained by slow vapor diffusion of *n*-hexane into a solution of **4** in tetrahydrofuran (THF). The molecular structure of gold complex **4** (Figure 3) revealed a slightly

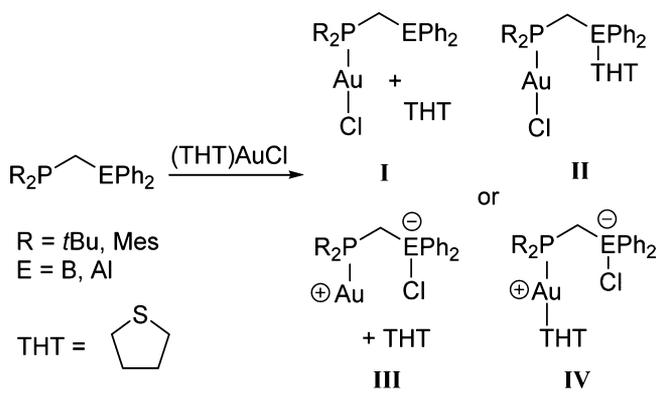


**Figure 3.** Molecular structure of compound **4** (ellipsoids are set at 50% probability; hydrogens are omitted for clarity). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): P1–Au1  $2.3387(8)$ , P2–Au1  $2.3217(8)$ , Cl1–Au1  $3.2522(8)$ , C7–Au1  $3.798(3)$ , B1–Au1  $3.863(4)$ , B2–Au1  $4.175(4)$ , B1–Cl1  $1.961(3)$ , P1–Au1–P2  $169.11(3)$ , P1–C1–B1  $121.0(2)$ , P2–C22–B2  $120.9(2)$ ,  $\sum(\text{CB1C})$   $337.1$ ,  $\sum(\text{CB2C})$   $359.5$ .

bent P1–Au1–P2 bond angle ( $169.11(3)^\circ$ ) and remarkably similar P–C–B bond angles ( $121.0(2)^\circ$  and  $120.9(2)^\circ$ ). The closest aryl–gold distance is Au1–C7 ( $3.798(3) \text{ \AA}$ ), suggesting the absence of any  $\pi$ -interaction, and the B2–Au1 distance of  $4.175(4) \text{ \AA}$  reveals no Z-type interaction. The side product **4** can be synthesized and isolated in 82% yield by the reaction of an excess (6 equiv) of ambiphilic ligand **2** with  $(\text{Me}_2\text{S})\text{AuCl}$  in DCM. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** revealed only one signal as a singlet at 80.5 ppm at room temperature, which splits at  $-50^\circ\text{C}$  into two broad singlets at 79.6 and 78.6 ppm. At  $-50^\circ\text{C}$ , still no signal was observed in the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum, indicating a fast exchange of the chloride atom between the Lewis acidic boron sites.

Interestingly, the ambiphilic P/B- and P/Al-based ligands **1** and **2** react differently with sulfur-based gold(I) chlorides; therefore, we systematically evaluated all possible coordination modes (I–IV; Scheme 4). In the first case, the sulfur-based ligand is displaced by the ambiphilic ligand (I), which was found for phosphinoborane **2** (Scheme 2), with the possibility of additional interaction of the boron moiety of the ligand with the liberated sulfur ligand (II). Another possibility is that the

### Scheme 4. Computational Analysis of the Various Coordination Modes of $C_1$ -Bridged Ligands



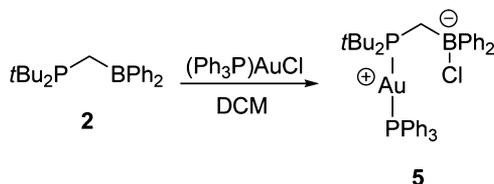
ambiphilic ligand facilitates cleavage of the gold–chloride bond to afford compound **III**, which is unstable and can be stabilized at the cationic gold(I) center by the sulfur-based ligand (IV), which was reported for phosphinoalane **1** (Scheme 1).

To gain more insights into the distinct reactivity of ambiphilic ligands **1** and **2**, we resorted to DFT calculations at the  $\omega\text{B97X-D/6-31G}^*$  (Def2-QZVP for Au) level of theory<sup>26</sup> and investigated the influence of P substituents ( $R = t\text{Bu}, \text{Mes}$ ) and Lewis acids (B, Al) on the reaction, using a methylene linker as a common  $C_1$  bridge between the Lewis acid and the base.<sup>c</sup> In accordance with our experimental data, phosphinoborane **2** ( $R = t\text{Bu}, E = \text{B}$ , Scheme 2) favors coordination mode I ( $\Delta E = -32.1 \text{ kcal/mol}$ ). Additional interaction of the complex with THT (mode II) is weak ( $\Delta\Delta E_{\text{I-II}} = -12.9 \text{ kcal/mol}$ ) and entropically disfavored ( $\Delta\Delta G_{\text{I-II}} = 4.6 \text{ kcal/mol}$ ). Exchange of the relatively strong Au–Cl bond for the weaker B–Cl bond (mode III) is highly disfavored ( $\Delta\Delta E_{\text{I-III}} = 37.6 \text{ kcal/mol}$ ), which could be compensated by Au–THT bond formation (mode IV,  $\Delta\Delta E_{\text{III-IV}} = -45.8 \text{ kcal/mol}$ ), albeit this stabilization is insufficient to account for the entropy effect ( $\Delta\Delta G_{\text{I-IV}} = 7.7 \text{ kcal/mol}$ ) and prevents the formation of complex IV. Interestingly, changing the Lewis acid from boron to aluminum had a large impact on the relative stabilities ( $R = t\text{Bu}, E = \text{Al}$ , Scheme 4). Cleavage of the Au–Cl bond becomes less endothermic ( $\Delta\Delta E_{\text{I-III}} = 17.3 \text{ kcal/mol}$ ) because of the formation of a stronger Al–Cl bond compared to the B–Cl bond (approx.  $21 \text{ kcal/mol}$  stronger). Additional stabilization by THT makes coordination mode IV now the most favorable complex ( $\Delta E = -68.1 \text{ kcal/mol}$ ;  $\Delta G = -51.3 \text{ kcal/mol}$ ),<sup>d</sup> which explains the distinct difference in reactivity between a P/B and P/Al ambiphilic ligand and is fully consistent with the formation of complex **3** (Scheme 2) and **D** (Scheme 1). The influence of the P substituents is in both cases very limited, resulting in the same trend for the mesityl-substituted phosphinoborane ( $R = \text{Mes}, E = \text{B}$ ) with a preference for coordination mode I and phosphinoalane ( $R = \text{Mes}, E = \text{Al}$ ) that prefers heterolytic cleavage of the gold–chloride bond (IV).<sup>e</sup> These findings illustrate that for these geminal Lewis acid/base pairs, the P substituent has a modest influence on the preferred coordination mode, whereas the nature of the Lewis acid is decisive and thus is an important design element for the development of ambiphilic ligands for the coordination chemistry and catalysis.

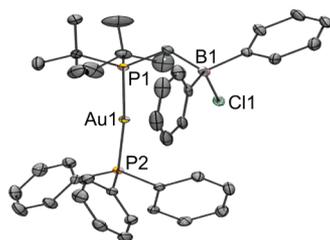
To further explore the reactivity of phosphinoborane **2** toward gold(I) complexes, we also used  $(\text{Ph}_3\text{P})\text{AuCl}$  that bears

the stronger donating triphenylphosphine ligand. Slow addition of a solution of **2** in DCM to a solution of  $(\text{Ph}_3\text{P})\text{AuCl}$  in DCM at  $0^\circ\text{C}$  resulted in a clean conversion to a new product **5** (Scheme 5).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy revealed two doublets

**Scheme 5.** Gold–Chloride Cleavage by Phosphinoborane **2**



(AB system, 79.6 and 43.9 ppm,  $J_{\text{P,P}} = 305$  Hz), indicating that both ligand **2** and triphenylphosphine are coordinated to the gold(I) metal center in a linear fashion. The  $^{11}\text{B}\{^1\text{H}\}$  NMR chemical shift of 3.1 ppm is the characteristic for a quaternary boron center. Colorless crystals suitable for the X-ray diffraction analysis were obtained by layering a saturated solution of **5** in toluene with pentane at room temperature (Figure 4). The

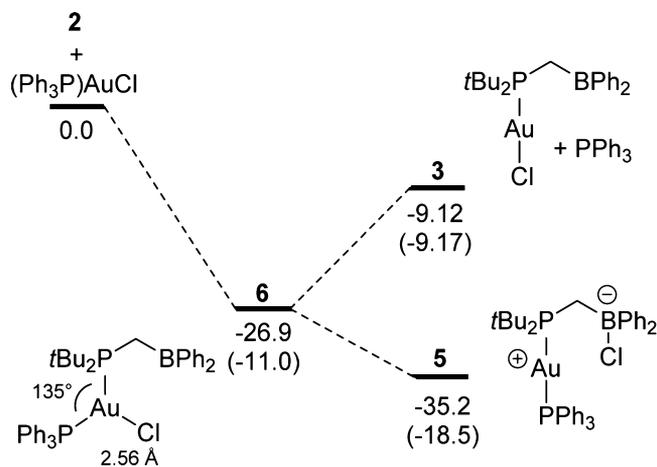


**Figure 4.** Molecular structure of compound **5** (ellipsoids are set at 50% probability; hydrogens and a pentane molecule are omitted for clarity). Selected bond lengths (Å) and angles ( $^\circ$ ): P1–Au 2.3251(7), P2–Au 2.2974(7), P1–Au–P2 173.71(3), Au–Cl 3.2386(8), B–Cl 1.971(3),  $\sum(\text{CB1C})$  335.8.

molecular structure of **5** displays that both triphenylphosphine and phosphinoborane **2** are coordinated to gold in an almost linear fashion ( $\text{P–Au–P}$  173.71(3) $^\circ$ ). Remarkably, the chloride atom is transferred to the borane moiety of the ligand and, with a Au–Cl distance of 3.2386(8) Å, any Au–Cl interaction is excluded. Pyramidalization around the boron center ( $\sum(\text{CBC}) = 336^\circ$ ) because of the formation of a chloroborate is in accordance with the strong upfield  $^{11}\text{B}$  NMR chemical shift. To the best of our knowledge, **2** is the first example of a bidentate phosphinoborane ambiphilic ligand to cleave a gold–chloride bond.

To verify the role of the Lewis acid in the gold–chloride bond cleavage, we resorted to DFT calculations at the  $\omega\text{B97X-D}/6\text{-31G}^*$  (Def2-QZVP for Au) level of theory.<sup>26</sup> These calculations showed that ligation of phosphinoborane **2** to  $(\text{Ph}_3\text{P})\text{AuCl}$  initially affords the neutral Y-shaped complex **6** (Figure 5), a geometry which could not be located on the potential energy surface when using  $(\text{THT})\text{AuCl}$ .<sup>27,28</sup> Subsequently, the pendent borane of intermediate **6** is able to abstract the chloride from the gold center to form product **5** ( $\Delta E = -35.2$  kcal/mol,  $\Delta G = -18.5$  kcal/mol), which is favored over the formation of the linear Au(I)Cl complex **3** ( $\Delta E = -9.12$  kcal/mol,  $\Delta G = -9.17$  kcal/mol) by dissociation of  $\text{PPh}_3$  from intermediate **6**.

The distinct difference in reactivity of **2** with  $(\text{Me}_2\text{S})\text{AuCl}$  and  $(\text{Ph}_3\text{P})\text{AuCl}$ , forming **3** and **5**, respectively, can be directly



**Figure 5.** Energy and (Gibbs free energy) profile calculated for the gold–chloride bond cleavage by phosphinoborane **2**. The relative energies are given in kcal/mol.

related to the difference in bond strength of the Au–Cl and B–Cl bond and to the stabilization by the coligand ( $\text{SMe}_2$  or  $\text{PPh}_3$ ) of the different coordination modes (Scheme 4). When ligand **2** is reacted with  $(\text{Me}_2\text{S})\text{AuCl}$ , the  $\text{SMe}_2$  coligand does not bind strongly enough to gold to compensate the formation of the weak B–Cl bond and to facilitate the Au–Cl bond cleavage, and therefore **2** only displaces the weakly bound sulfur ligand. In contrast, when **2** is reacted with  $(\text{Ph}_3\text{P})\text{AuCl}$ , the triphenylphosphine coligand is more strongly bound to gold (approximately 18 kcal/mol stronger compared to THT) and is thereby able to compensate for the formation of the weaker B–Cl, leading to the cleavage of the Au–Cl bond, which emphasizes the diverse reactivity of **2** as ambiphilic ligand.

## CONCLUSIONS

Linear phosphine gold(I) chloride complex **3** can be obtained by the reaction of ambiphilic ligand **2** with  $(\text{Me}_2\text{S})\text{AuCl}$ . The side product of this reaction was identified as bisligated complex **4** and can be isolated by reacting an excess of ligand **2** with  $(\text{Me}_2\text{S})\text{AuCl}$ . The distinct difference in reactivity between the geminal P/Al-based ligand **1** and its P/B-analogue **2** toward sulfur-based gold(I) precursors was studied by DFT calculations, which revealed that the nature of the Lewis acid determines the preference for ligand displacement versus gold–chloride abstraction. Changing  $(\text{Me}_2\text{S})\text{AuCl}$  for triphenylphosphine gold chloride drastically changed the outcome of the reaction with ambiphilic ligand **2**, which forms complex **5** by the cleavage of the gold–chloride bond, instead of the displacement of  $\text{PPh}_3$ . To the best of our knowledge, the geminal phosphinoborane **2** is the first example of a P/B-ambiphilic ligand that is capable of cleaving a gold–chloride bond.

## EXPERIMENTAL SECTION

**General Procedures and Starting Materials.** All manipulations were carried out under an atmosphere of dry nitrogen, using standard Schlenk and drybox techniques, and were performed in the dark as a precaution to prevent decomposition. Solvents were purified, dried, and degassed according to standard procedures.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker Avance 400 spectrometer and internally referenced to the residual solvent resonances

(CD<sub>2</sub>Cl<sub>2</sub>: <sup>1</sup>H δ 5.32, <sup>13</sup>C{<sup>1</sup>H} δ 53.8). <sup>31</sup>P{<sup>1</sup>H} and <sup>11</sup>B{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance 400 spectrometer and externally referenced (85% H<sub>3</sub>PO<sub>4</sub>, BF<sub>3</sub>·OEt<sub>2</sub>, respectively). Mass spectra were collected on an AccuTOF GCv 4g, JMS-T100GCV mass spectrometer (JEOL, Japan). FD emitter, Carbotec or Linden (Germany), FD 10 μm. Current rate 51.2 mA/min over 1.2 min. Typical measurement conditions are counter electrode −10 kV and ion source 37 V. *t*Bu<sub>2</sub>PCH<sub>2</sub>BPh<sub>2</sub> (**2**) was prepared following a literature procedure;<sup>20a</sup> (Me<sub>2</sub>S)AuCl and (Ph<sub>3</sub>P)AuCl were purchased from Sigma-Aldrich and used without any further purification.

**Preparation of Compound 3.** A solution of *t*Bu<sub>2</sub>PCH<sub>2</sub>BPh<sub>2</sub> (**2**; 0.100 g, 0.31 mmol, 1.00 equiv) in DCM (5 mL) was added dropwise to a solution of (Me<sub>2</sub>S)AuCl (0.091 g, 0.31 mmol, 1.00 equiv) in DCM (5 mL) at 0 °C. Next, the reaction mixture was warmed to room temperature and a colorless solution with a purple precipitate was obtained. The reaction mixture was filtered and dried in vacuo. The obtained white solids were washed with *n*-pentane (3 × 4 mL) and dried in vacuo to yield a pale purple solid (0.130 g, 75% purity based on <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy). Colorless X-ray quality crystals were grown at room temperature by vapor diffusion of *n*-pentane into a solution of **3** in DCM. <sup>1</sup>H NMR (400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 7.77 (d, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 4H, *o*-PhH), 7.58 (t, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 2H, *p*-PhH), 7.49 (t, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 4H, *m*-PhH), 2.58 (d, <sup>2</sup>J<sub>H,P</sub> = 15.5 Hz, 2H, PCH<sub>2</sub>B), 1.36 (d, <sup>3</sup>J<sub>H,P</sub> = 15.2 Hz, 18H, PC(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 141.2 (only observed in the HMBC spectrum, <sup>2</sup>J<sub>C,H</sub> coupling with *o*-PhH, <sup>3</sup>J<sub>C,H</sub> coupling with *m*-PhH and PCH<sub>2</sub>B; *ipso*-PhC), 136.4 (s, *o*-PhC), 132.5 (s, *p*-PhC), 128.6 (s, *m*-PhC), 36.5 (d, <sup>1</sup>J<sub>C,P</sub> = 27.1 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 29.9 (d, <sup>2</sup>J<sub>C,P</sub> = 5.7 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 17.0 (only observed in the HSQC spectrum, <sup>1</sup>J<sub>C,H</sub> coupling with PCH<sub>2</sub>B; PCH<sub>2</sub>B). <sup>31</sup>P{<sup>1</sup>H} NMR (162.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 75.3 (s). <sup>11</sup>B{<sup>1</sup>H} NMR (128.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 70.2 (br s).

**Preparation of Compound 4.** A solution of (Me<sub>2</sub>S)AuCl (0.040 g, 0.115 mmol, 1.00 equiv) in DCM (5 mL) was quickly added to a solution of *t*Bu<sub>2</sub>PCH<sub>2</sub>BPh<sub>2</sub> (**2**; 0.224 g, 0.69 mmol, 6.00 equiv) in DCM (6 mL). Subsequently, the reaction mixture was stirred for 10 min after which the solvent was removed in vacuo. The obtained pale white solids were washed with *n*-pentane (3 × 5 mL) and dried in vacuo to yield a pale white solid (0.83 g, 82%). Colorless X-ray quality crystals were obtained by vapor diffusion of *n*-hexane into a solution of **4** in THF. <sup>1</sup>H NMR (400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 7.70 (d, <sup>3</sup>J<sub>H,H</sub> = 7.6 Hz, 8H, *o*-PhH), 7.28–7.21 (m, 12H, *m,p*-PhH), 2.24 (br t, 4H, PCH<sub>2</sub>B), 1.22 (t, <sup>3</sup>J<sub>H,P</sub> = 7.2 Hz, 18H, PC(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 135.0 (s, *o*-PhC), 127.7 (s, *m*-PhC), 36.8 (t, <sup>1</sup>J<sub>C,P</sub> = 11.5 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 30.3 (t, <sup>2</sup>J<sub>C,P</sub> = 3.2 Hz, PC(CH<sub>3</sub>)<sub>3</sub>) 18.1 (only observed in the HSQC spectrum, <sup>1</sup>J<sub>C,H</sub> coupling with PCH<sub>2</sub>B; PCH<sub>2</sub>B), the signals for *p*-PhC and *ipso*-PhC are unresolved. <sup>31</sup>P{<sup>1</sup>H} NMR (162.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 80.5 (s). <sup>11</sup>B{<sup>1</sup>H} NMR (128.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): not observed due to fast chloride exchange between the boron atoms. HR-MS (FD): 845.40609 [M – Cl]<sup>+</sup>, calcd for C<sub>42</sub>H<sub>60</sub>Au<sub>1</sub>B<sub>2</sub>P<sub>2</sub> 845.40219. Melting point (nitrogen, sealed capillary): 129 °C (decomp.).

**Preparation of Compound 5.** A solution of *t*Bu<sub>2</sub>PCH<sub>2</sub>BPh<sub>2</sub> (**2**; 0.055 g, 0.17 mmol, 1.00 equiv) in DCM (4 mL) was added dropwise to a solution of (PPh<sub>3</sub>)AuCl (0.084 g, 0.17 mmol, 1.00 equiv) in DCM (5 mL) at 0 °C. Subsequently, the reaction mixture was warmed to room temperature and stirred for 30

min after which the solvent was removed in vacuo. The obtained white solids were washed with *n*-pentane (3 × 4 mL) and dried in vacuo to yield **5** as a white solid (0.121 g, 87%). Colorless X-ray quality crystals were grown by layering a saturated solution of **5** in toluene with *n*-pentane at room temperature. <sup>1</sup>H NMR (400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 7.64–7.51 (m, 15H, PPhH), 7.47 (m, 4H, *Bm*-PhH), 6.93 (m, 6H, *Bo*-PhH, *Bp*-PhH), 1.77 (d, <sup>2</sup>J<sub>H,P</sub> = 13.6 Hz, 2H, PCH<sub>2</sub>B), 1.21 (d, <sup>3</sup>J<sub>H,P</sub> = 14.0 Hz, 18H, PC(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 299 K): δ 156.8 (only observed in the HMBC spectrum, <sup>2</sup>J<sub>C,H</sub> coupling with *o*-PhH and PCH<sub>2</sub>B; *ipso*-PhC), 134.7 (d, <sup>1</sup>J<sub>C,P</sub> = 13.9 Hz, *o*- or *m*-PPhC), 133.5 (s, *m*-PhC), 132.1 (d, <sup>4</sup>J<sub>C,P</sub> = 2.3 Hz, *p*-PPhC), 130.2 (d, <sup>1</sup>J<sub>C,P</sub> = 52.5 Hz, *ipso*-PPhC), 129.7 (d, <sup>1</sup>J<sub>C,P</sub> = 11.2 Hz, *o*- or *m*-PPhC), 126.7 (s, *o*-PhC), 124.4 (s, *p*-PhC), 36.0 (d, <sup>1</sup>J<sub>C,P</sub> = 22.5 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 30.6 (d, <sup>2</sup>J<sub>C,P</sub> = 5.5 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 19.3 (only observed in the HSQC spectrum, <sup>1</sup>J<sub>C,H</sub> coupling with PCH<sub>2</sub>B; PCH<sub>2</sub>B). <sup>31</sup>P{<sup>1</sup>H} NMR (162.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 79.6 (d, <sup>2</sup>J<sub>P,P</sub> = 304.5 Hz), 43.9 (d, <sup>2</sup>J<sub>P,P</sub> = 304.5 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (128.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 3.1 (br s). HR-MS (FD): 783.27866 [M – Cl]<sup>+</sup>, calcd for C<sub>39</sub>H<sub>45</sub>Au<sub>1</sub>B<sub>1</sub>P<sub>2</sub> 783.27550. Melting point (nitrogen, sealed capillary): 143 °C (decomp.).

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsoomega.8b00143.

NMR spectral data; Cartesian coordinates for all computed species; computational details; crystal structure data of compound **3**, **4**, and **5**; high-resolution mass measurement data; and the crystallographic data CCDC 1572409 (**3**), 1572410 (**4**), and 1572411 (**5**) (PDF) Crystallographic data for compounds **3**, **4**, and **5** (CIF) Optimized geometry (Cartesian coordinates) and uncorrected energy (in a.u.) for compounds **2**, **3**, **3'**, **4**, **5** (XYZ)

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### Notes

The authors declare no competing financial interest.

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## ■ ADDITIONAL NOTES

“Same reactivity was observed when (THT)AuCl was used as gold(I) metal precursor. However, the selectivity was lower compared to (Me<sub>2</sub>S)AuCl and the formation of several unidentified products was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, therefore (Me<sub>2</sub>S)AuCl was solely used as sulfur-based metal precursor.

<sup>b</sup>Compound 3 is unstable in solution over time. A solution of 3 in DCM slowly degrades at room temperature into unidentifiable products observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, as well as insoluble purple solids.

<sup>c</sup>We used (THT)AuCl as a metal precursor for our computational study because the reactivity of phosphinoalane 1 with (THT)AuCl was already well-described, and ligand 2 reacts with (THT)AuCl and (Me<sub>2</sub>S)AuCl in a similar fashion.

<sup>d</sup>This observation compares well with the findings of Bourissou and co-workers for tridentate ambiphilic ligands, see ref 8c.

<sup>e</sup>For a comprehensive overview of the computational analysis including the effect of the phosphorus substituents, see the Supporting Information.

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