

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

Devin H. A. Boom,[†] Andreas W. Ehlers,^{†,‡} Martin Nieger,[§] Marc Devillard,^{||} Ghenwa Bouhadir,^{||} Didier Bourissou,^{||} and J. Chris Slootweg^{*,†}

[†]Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, P.O. Box 94157, 1090 GD Amsterdam, The Netherlands

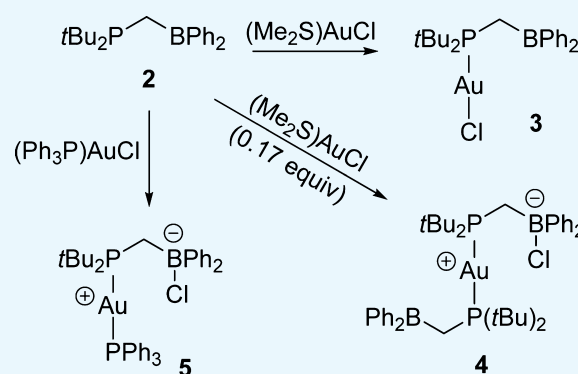
[‡]Department of Chemistry, University of Johannesburg, Auckland Park, Johannesburg 2006, South Africa

[§]Department of Chemistry, University of Helsinki, P.O. Box 55, 00014 Helsinki, Finland

^{||}CNRS, Université Paul Sabatier, Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA, UMR 5069), 118 Route de Narbonne, 31062 Toulouse Cedex 09, France

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 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 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.

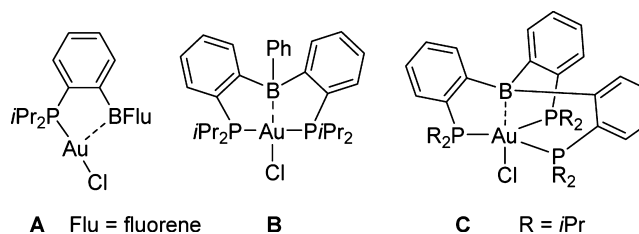


INTRODUCTION

Ambiphilic ligands bearing a Lewis basic site for σ -donation and a Lewis acidic site for σ -acceptation have been recognized as ligands with unique coordination properties,¹ resulting in unusual bonding situations (Z-type interactions)^{2,3} or halide abstraction from the metal precursor, which are both of interest for catalytic applications.^{4,5} 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,^{6,7} aluminum,⁸ gallium,⁹ indium,¹⁰ bismuth,¹¹ silicon,¹² tin,^{12a} antimony,¹³ zirconium,¹⁴ and tellurium.¹⁵

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).^{6a} 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 (~ 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).^{6b} 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,

Received: January 23, 2018

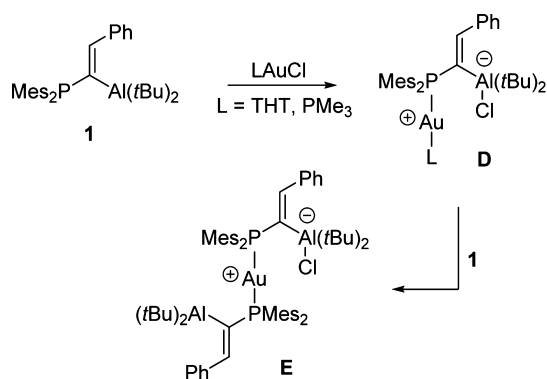
Accepted: February 21, 2018

Published: April 9, 2018

Bourissou and co-workers reported a tetradentate phosphino-borane (TPB) ligand that forms complex **C** (Chart 1) upon coordination to $(\text{Me}_2\text{S})\text{AuCl}$.^{6c} 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.^{6d}

Interestingly, tri- and tetradentate phosphine-based ambiphilic ligands with heavier main-group Lewis acidic sites based on aluminum,^{8c,d} gallium,⁹ indium,¹⁰ and silicon^{12c} 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 ligand¹⁴ 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),^{8a,b} which proved to be an active catalyst for the cyclization

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



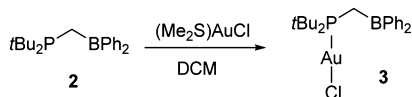
of propargylamides in the absence of any additives. This demonstrates the potential of ambiphilic ligands as an alternative to silver salts for the activation of gold(I) precatalysts.¹⁶

Recently, we developed ambiphilic phosphinoborane **2** which exhibits frustrated Lewis pair reactivity^{17–19} when reacted with, for example, H_2 , CO_2 , isocyanates, alkynes, nitriles, and nitrilium triflates,²⁰ but can also act as an ambiphilic ligand forming a luminescent complex upon coordination to Cu(I)-Cl .²¹ 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).^a 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 SMe_2 moiety,

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



and in contrast to **1** (Scheme 1), did not cleave the gold–chloride bond.^b In the solid state, the P1–Au1–Cl1 bond angle is slightly bent ($174.35(4)^\circ$)²² and the P1–C1–B1 bond angle ($119.8(3)^\circ$) is comparable to that of the optimized geometry^{20a} of the free ligand (2.1° increase). The B1–Au1 distance of $3.798(5)$ Å is just within the sum of the van der Waals radii (~ 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,²³ and the Au1–C8 and Au1–C9 bond distances of 3.326 Å indicate a possible weak π -interaction, comparable to those previously reported for Au(I) complexes bearing biarylphosphine ligands.^{24,25} 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)²⁰ 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 theory²⁶ revealed two possible conformers which are close in energy (**3** and **3'**, Figure 1). Conformer **3** was found to

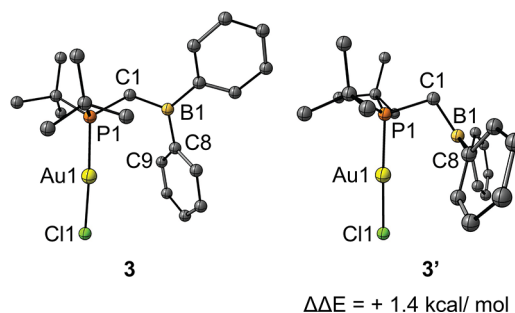


Figure 1. Two optimized geometries for compound **3** (hydrogens are omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): **3**: P1–Au1 2.28, B1–Au1 3.94, C8–Au1 3.50, C9–Au1 3.28, P1–Au1–Cl1 176.9 , P1–C1–B1 119.0 , P1–C1–B1–C8 53.8 . **3'**: P1–Au1 2.28, B1–Au1 3.18, P1–Au1–Cl1 177.1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

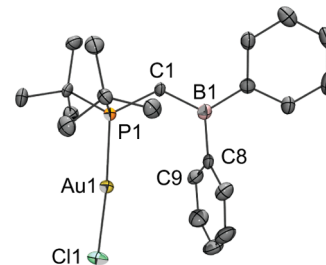
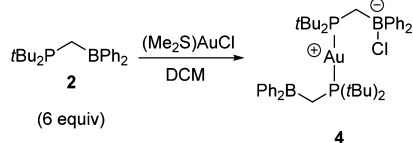


Figure 2. Molecular structure of compound **3** (ellipsoids are set at 50% probability; hydrogens are omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): P1–Au1 2.2466(11), Au1–Cl1 2.2035(11), P1–C1–B1 $119.8(3)$, B1–Au1 $3.798(5)$, C8–Au1 $3.262(4)$, C9–Au1 $3.263(3)$, P1–Au1–Cl1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

revealed a significantly more bent P1–C1–B1 backbone (106°) compared to **3** (119°), and the empty p orbital on boron is oriented toward the gold center (torsion angle = 92.7°), analogous to the reported complex **A** (Chart 1).^{6a} 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 \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).^{8a} 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

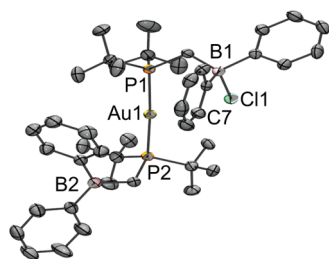
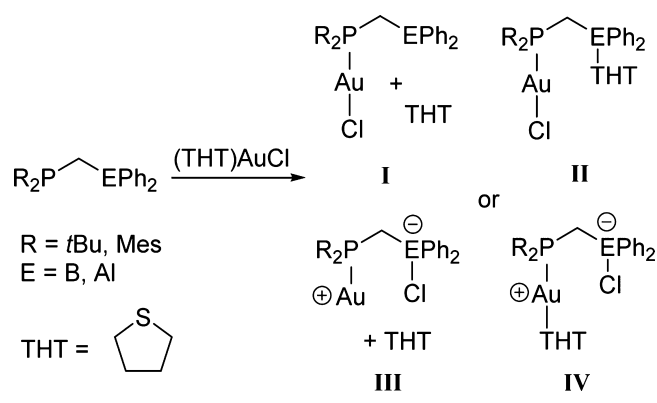


Figure 3. Molecular structure of compound **4** (ellipsoids are set at 50% probability; hydrogens are omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): P1–Au1 2.3387(8), P2–Au1 2.3217(8), Cl1–Au1 3.2522(8), C7–Au1 3.798(3), B1–Au1 3.863(4), B2–Au1 4.175(4), B1–Cl1 1.961(3), P1–Au1–P2 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 π -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°C into two broad singlets at 79.6 and 78.6 ppm. At -50°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



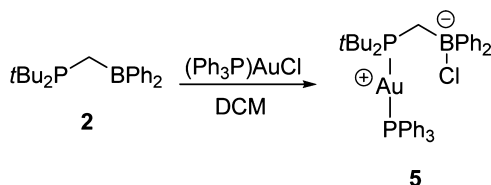
ambiphilic ligand facilitates cleavage of the gold–chloride bond to afford compound **III**, which is unstable and can be stabilized at the cationic gold(I) center by the sulfur-based ligand (IV), which was reported for phosphinoalane **1** (Scheme 1).

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 theory²⁶ and investigated the influence of P substituents ($\text{R} = \text{tBu, Mes}$) 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.^c In accordance with our experimental data, phosphinoborane **2** ($\text{R} = \text{tBu, E} = \text{B}$, 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 ($\text{R} = \text{tBu, E} = \text{Al}$, 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 kcal/mol stronger). Additional stabilization by THT makes coordination mode IV now the most favorable complex ($\Delta E = -68.1 \text{ kcal/mol}$; $\Delta G = -51.3 \text{ kcal/mol}$),^d 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 ($\text{R} = \text{Mes, E} = \text{B}$) with a preference for coordination mode I and phosphinoalane ($\text{R} = \text{Mes, E} = \text{Al}$) that prefers heterolytic cleavage of the gold–chloride bond (IV).^e 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°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

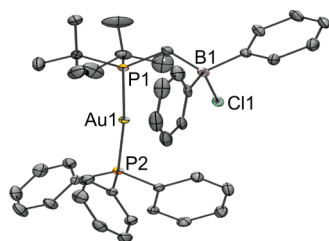


Figure 4. Molecular structure of compound **5** (ellipsoids are set at 50% probability; hydrogens and a pentane molecule are omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): P1–Au 2.3251(7), P2–Au 2.2974(7), P1–Au–P2 173.71(3), Au–Cl 3.2386(8), B–Cl 1.971(3), $\sum(\text{CB1C})$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

molecular structure of **5** displays that both triphenylphosphine and phosphinoborane **2** are coordinated to gold in an almost linear fashion (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}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.²⁶ 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 $(\text{THT})\text{AuCl}$.^{27,28} 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 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

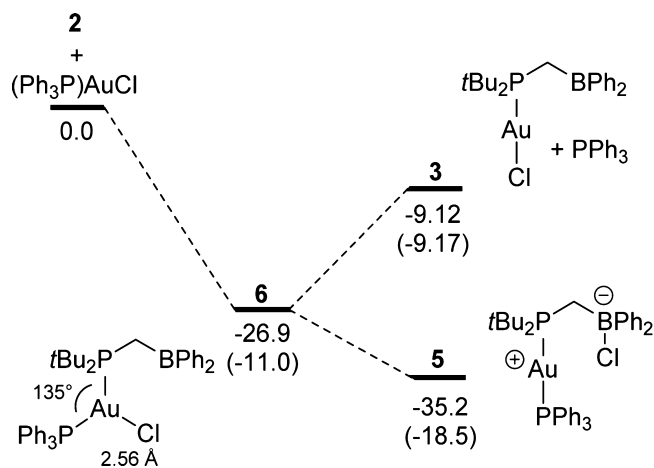


Figure 5. Energy and (Gibbs free energy) profile calculated for the gold–chloride bond cleavage by phosphinoborane **2**. The relative energies are given in kcal/mol.

related to the difference in bond strength of the Au–Cl and B–Cl bond and to the stabilization by the coligand (SMe_2 or PPh_3) of the different coordination modes (Scheme 4). When ligand **2** is reacted with $(\text{Me}_2\text{S})\text{AuCl}$, the 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 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. ^1H 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

(CD₂Cl₂: ¹H δ 5.32, ¹³C{¹H} δ 53.8). ³¹P{¹H} and ¹¹B{¹H} NMR spectra were recorded on a Bruker Avance 400 spectrometer and externally referenced (85% H₃PO₄, BF₃·OEt₂, 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*Bu₂PCH₂BPh₂ (**2**) was prepared following a literature procedure;^{20a} (Me₂S)AuCl and (Ph₃P)AuCl were purchased from Sigma-Aldrich and used without any further purification.

Preparation of Compound 3. A solution of *t*Bu₂PCH₂BPh₂ (**2**; 0.100 g, 0.31 mmol, 1.00 equiv) in DCM (5 mL) was added dropwise to a solution of (Me₂S)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 ³¹P{¹H} 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. ¹H NMR (400.13 MHz, CD₂Cl₂, 297 K): δ 7.77 (d, ³J_{H,H} = 7.4 Hz, 4H, *o*-PhH), 7.58 (t, ³J_{H,H} = 7.4 Hz, 2H, *p*-PhH), 7.49 (t, ³J_{H,H} = 7.4 Hz, 4H, *m*-PhH), 2.58 (d, ²J_{H,P} = 15.5 Hz, 2H, PCH₂B), 1.36 (d, ³J_{H,P} = 15.2 Hz, 18H, PC(CH₃)₃). ¹³C{¹H} NMR (100.62 MHz, CD₂Cl₂, 298 K): δ 141.2 (only observed in the HMBC spectrum, ²J_{C,H} coupling with *o*-PhH, ³J_{C,H} coupling with *m*-PhH and PCH₂B; *ipso*-PhC), 136.4 (s, *o*-PhC), 132.5 (s, *p*-PhC), 128.6 (s, *m*-PhC), 36.5 (d, ¹J_{C,P} = 27.1 Hz, PC(CH₃)₃), 29.9 (d, ²J_{C,P} = 5.7 Hz, PC(CH₃)₃), 17.0 (only observed in the HSQC spectrum, ¹J_{C,H} coupling with PCH₂B; PCH₂B). ³¹P{¹H} NMR (162.0 MHz, CD₂Cl₂, 297 K): δ 75.3 (s). ¹¹B{¹H} NMR (128.4 MHz, CD₂Cl₂, 297 K): δ 70.2 (br s).

Preparation of Compound 4. A solution of (Me₂S)AuCl (0.040 g, 0.115 mmol, 1.00 equiv) in DCM (5 mL) was quickly added to a solution of *t*Bu₂PCH₂BPh₂ (**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. ¹H NMR (400.13 MHz, CD₂Cl₂, 297 K): δ 7.70 (d, ³J_{H,H} = 7.6 Hz, 8H, *o*-PhH), 7.28–7.21 (m, 12H, *m,p*-PhH), 2.24 (br t, 4H, PCH₂B), 1.22 (t, ³J_{H,P} = 7.2 Hz, 18H, PC(CH₃)₃). ¹³C{¹H} NMR (100.62 MHz, CD₂Cl₂, 298 K): δ 135.0 (s, *o*-PhC), 127.7 (s, *m*-PhC), 36.8 (t, ¹J_{C,P} = 11.5 Hz, PC(CH₃)₃), 30.3 (t, ²J_{C,P} = 3.2 Hz, PC(CH₃)₃) 18.1 (only observed in the HSQC spectrum, ¹J_{C,H} coupling with PCH₂B; PCH₂B), the signals for *p*-PhC and *ipso*-PhC are unresolved. ³¹P{¹H} NMR (162.0 MHz, CD₂Cl₂, 297 K): δ 80.5 (s). ¹¹B{¹H} NMR (128.4 MHz, CD₂Cl₂, 297 K): not observed due to fast chloride exchange between the boron atoms. HR-MS (FD): 845.40609 [M – Cl]⁺, calcd for C₄₂H₆₀Au₁B₂P₂ 845.40219. Melting point (nitrogen, sealed capillary): 129 °C (decomp.).

Preparation of Compound 5. A solution of *t*Bu₂PCH₂BPh₂ (**2**; 0.055 g, 0.17 mmol, 1.00 equiv) in DCM (4 mL) was added dropwise to a solution of (PPh₃)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. ¹H NMR (400.13 MHz, CD₂Cl₂, 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, ²J_{H,P} = 13.6 Hz, 2H, PCH₂B), 1.21 (d, ³J_{H,P} = 14.0 Hz, 18H, PC(CH₃)₃). ¹³C{¹H} NMR (100.62 MHz, CD₂Cl₂, 299 K): δ 156.8 (only observed in the HMBC spectrum, ²J_{C,H} coupling with *o*-PhH and PCH₂B; *ipso*-PhC), 134.7 (d, ¹J_{C,P} = 13.9 Hz, *o*- or *m*-PPhC), 133.5 (s, *m*-PhC), 132.1 (d, ⁴J_{C,P} = 2.3 Hz, *p*-PPhC), 130.2 (d, ¹J_{C,P} = 52.5 Hz, *ipso*-PPhC), 129.7 (d, ¹J_{C,P} = 11.2 Hz, *o*- or *m*-PPhC), 126.7 (s, *o*-PhC), 124.4 (s, *p*-PhC), 36.0 (d, ¹J_{C,P} = 22.5 Hz, PC(CH₃)₃), 30.6 (d, ²J_{C,P} = 5.5 Hz, PC(CH₃)₃), 19.3 (only observed in the HSQC spectrum, ¹J_{C,H} coupling with PCH₂B; PCH₂B). ³¹P{¹H} NMR (162.0 MHz, CD₂Cl₂, 297 K): δ 79.6 (d, ²J_{P,P} = 304.5 Hz), 43.9 (d, ²J_{P,P} = 304.5 Hz). ¹¹B{¹H} NMR (128.4 MHz, CD₂Cl₂, 297 K): δ 3.1 (br s). HR-MS (FD): 783.27866 [M – Cl]⁺, calcd for C₃₉H₄₅Au₁B₁P₂ 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)

■ AUTHOR INFORMATION

✉ Corresponding Author

*E-mail: j.c.slootweg@uva.nl (J.C.S.).

ORCID

Didier Bourissou: 0000-0002-0249-1769

J. Chris Slootweg: 0000-0001-7818-7766

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (NWO/CW) by a VIDI grant (J.C.S.) and benefitted from interactions within the COST Action CM1205 CARISMA (Catalytic Routines for Small Molecule Activation).

■ ADDITIONAL NOTES

“Same reactivity was observed when (THT)AuCl was used as gold(I) metal precursor. However, the selectivity was lower compared to (Me₂S)AuCl and the formation of several unidentified products was observed by ³¹P{¹H} NMR spectroscopy, therefore (Me₂S)AuCl was solely used as sulfur-based metal precursor.

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

^cWe 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 (Me₂S)AuCl in a similar fashion.

^dThis observation compares well with the findings of Bourissou and co-workers for tridentate ambiphilic ligands, see ref 8c.

^eFor a comprehensive overview of the computational analysis including the effect of the phosphorus substituents, see the Supporting Information.

REFERENCES

- (1) Bouhadir, G.; Amgoune, A.; Bourissou, D. Phosphine-boranes and related ambiphilic compounds: synthesis, structure, and coordination to transition metals. *Adv. Organomet. Chem.* **2010**, *58*, 1–107.
- (2) Fontaine, F.-G.; Boudreau, J.; Thibault, M.-H. Coordination chemistry of neutral (L_n)-Z amphoteric and ambiphilic ligands. *Eur. J. Inorg. Chem.* **2008**, *2008*, 5439–5454.
- (3) Bouhadir, G.; Bourissou, D. Coordination of Lewis acids to transition metals: Z-type ligands. *The Chemical Bond III*; Springer International Publishing, 2016; pp 141–201.
- (4) Bouhadir, G.; Bourissou, D. Complexes of ambiphilic ligands: reactivity and catalytic applications. *Chem. Soc. Rev.* **2016**, *45*, 1065–1079.
- (5) Devillard, M.; Bouhadir, G.; Bourissou, D. Cooperation between transition metals and Lewis acids: a way to activate H₂ and H–E bonds. *Angew. Chem., Int. Ed.* **2015**, *54*, 730–732.
- (6) For bidentate ligands, see: (a) Bontemps, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D. On the versatile and unusual coordination behavior of ambiphilic ligands *o*-R₂P(Ph)BR₂. *J. Am. Chem. Soc.* **2006**, *128*, 12056–12057. For tridentate ligands see: (b) Sircoglou, M.; Bontemps, S.; Mercy, M.; Saffon, N.; Takahashi, M.; Bouhadir, G.; Maron, L.; Bourissou, D. Transition-metal complexes featuring Z-type ligands: agreement or discrepancy between geometry and dⁿ configuration? *Angew. Chem., Int. Ed.* **2007**, *46*, 8583–8586. For tetradentate ligands, see: (c) Bontemps, S.; Bouhadir, G.; Gu, W.; Mercy, M.; Chen, C.-H.; Foxman, B. M.; Maron, L.; Ozerov, O. V.; Bourissou, D. Metallaboratranes derived from a triphosphanylborane: intrinsic C₃ symmetry supported by a Z-type ligand. *Angew. Chem., Int. Ed.* **2008**, *47*, 1481–1484. (d) Sircoglou, M.; Bontemps, S.; Bouhadir, G.; Saffon, N.; Miqueu, K.; Gu, W.; Mercy, M.; Chen, C.-H.; Foxman, B. M.; Maron, L.; Ozerov, O. V.; Bourissou, D. Group 10 and 11 metal boratranes (Ni, Pd, Pt, CuCl, AgCl, AuCl, and Au⁺) derived from a triphosphine–borane. *J. Am. Chem. Soc.* **2008**, *130*, 16729–16738. (e) Taylor, J. W.; McSkimming, A.; Moret, M.-E.; Harman, W. H. A molecular boroauride: a donor-acceptor complex of anionic gold. *Angew. Chem., Int. Ed.* **2017**, *56*, 10413–10417.
- (7) For a carbon–boron based bidentate ambiphilic ligand, see: Toure, M.; Chuzel, O.; Parrain, J.-L. Synthesis and structure of Ag(I), Pd(II), Rh(I), Ru(II) and Au(I) NHC-complexes with a pendant Lewis acidic boronic ester moiety. *Dalton Trans.* **2015**, *44*, 7139–7143.
- (8) For bidentate ligands, see: (a) Devillard, M.; Nicolas, E.; Appelt, C.; Backs, J.; Mallet-Ladeira, S.; Bouhadir, G.; Slootweg, J. C.; Uhl, W.; Bourissou, D. Novel zwitterionic complexes arising from the coordination of an ambiphilic phosphorus–aluminum ligand to gold. *Chem. Commun.* **2014**, *50*, 14805–14808. (b) Devillard, M.; Nicolas, E.; Ehlers, A. W.; Backs, J.; Mallet-Ladeira, S.; Bouhadir, G.; Slootweg, J. C.; Uhl, W.; Bourissou, D. Dative Au→Al interactions: crystallographic characterization and computational analysis. *Chem.—Eur. J.* **2015**, *21*, 74–79. For tridentate ligands, see: (c) Sircoglou, M.; Bouhadir, G.; Saffon, N.; Miqueu, K.; Bourissou, D. A zwitterionic gold(I) complex from an ambiphilic diphosphino–alane ligand. *Organometallics* **2008**, *27*, 1675–1678. For tetradentate ligands see: (d) Sircoglou, M.; Saffon, N.; Miqueu, K.; Bouhadir, G.; Bourissou, D. Activation of M–Cl bonds with phosphine–alanes: preparation and characterization of zwitterionic gold and copper complexes. *Organometallics* **2013**, *32*, 6780–6784.
- (9) Sircoglou, M.; Mercy, M.; Saffon, N.; Coppel, Y.; Bouhadir, G.; Maron, L.; Bourissou, D. Gold(I) complexes of phosphanyl gallanes: from interconverting to separable coordination isomers. *Angew. Chem., Int. Ed.* **2009**, *48*, 3454–3457.
- (10) For tridentate ligands see: (a) Backs, J.; Lange, M.; Possart, J.; Wollschläger, A.; Mück-Lichtenfeld, C.; Uhl, W. Facile modulation of FLP properties: a phosphinylvinyl grignard reagent and Ga/P- and In/P₂-based frustrated Lewis pairs. *Angew. Chem., Int. Ed.* **2017**, *56*, 3094–3097. For tetradentate ligands, see: (b) Derrah, E. J.; Sircoglou, M.; Mercy, M.; Ladeira, S.; Bouhadir, G.; Miqueu, K.; Maron, L.; Bourissou, D. Original transition metal→indium interactions upon coordination of a triphosphine–indane. *Organometallics* **2011**, *30*, 657–660.
- (11) Tschersich, C.; Limberg, C.; Roggan, S.; Herwig, C.; Ernsting, N.; Kovalenko, S.; Mebs, S. Gold- and platinum–bismuth donor–acceptor interactions supported by an ambiphilic PBiP pincer ligand. *Angew. Chem., Int. Ed.* **2012**, *51*, 4989–4992.
- (12) For tridentate ligands, see: (a) Gualco, P.; Lin, T.-P.; Sircoglou, M.; Mercy, M.; Ladeira, S.; Bouhadir, G.; Pérez, L. M.; Amgoune, A.; Maron, L.; Gabbai, F. P.; Bourissou, D. Gold–silane and gold–stannane complexes: saturated molecules as σ-acceptor ligands. *Angew. Chem., Int. Ed.* **2009**, *48*, 9892–9895. (b) Gualco, P.; Mercy, M.; Ladeira, S.; Coppel, Y.; Maron, L.; Amgoune, A.; Bourissou, D. Hypervalent silicon compounds by coordination of diphosphine–silanes to gold. *Chem.—Eur. J.* **2010**, *16*, 10808–10817. For tetradentate ligands, see: (c) Gualco, P.; Mallet-Ladeira, S.; Kameo, H.; Nakazawa, H.; Mercy, M.; Maron, L.; Amgoune, A.; Bourissou, D. Coordination of a triphosphine–silane to gold: formation of a trigonal pyramidal complex featuring Au⁺→Si interaction. *Organometallics* **2015**, *34*, 1449–1453.
- (13) For bidentate ligands, see: (a) Jones, J. S.; Gabbai, F. P. Activation of an Au–Cl bond by a pendent Sb^{III} Lewis acid: impact on structure and catalytic activity. *Chem.—Eur. J.* **2017**, *23*, 1136–1144. For tridentate ligands, see: (b) Yang, H.; Gabbai, F. P. Activation of a hydroamination gold catalyst by oxidation of a redox-noninnocent chlorostibine Z-ligand. *J. Am. Chem. Soc.* **2015**, *137*, 13425–13432. For a review on ambiphilic ligands containing antimony, see: (c) Jones, J. S.; Gabbai, F. P. Coordination- and redox-noninnocent behavior of ambiphilic ligands containing antimony. *Acc. Chem. Res.* **2016**, *49*, 857–867.
- (14) For a zirconium/phosphorus based ambiphilic ligand that can cleave a gold–chloride bond see: Büschel, S.; Daniliuc, C.; Jones, P. G.; Tamm, M. Ambiphilic reactivity of a phosphane-functionalized cycloheptatrienyl–cyclopentadienyl zirconium sandwich complex. *Organometallics* **2010**, *29*, 671–675.
- (15) (a) Yang, H.; Lin, T.-P.; Gabbai, F. P. Telluroether to telluroxide conversion in the coordination sphere of a metal: oxidation-induced umpolung of a Te–Au bond. *Organometallics* **2014**, *33*, 4368–4373. For a review on ambiphilic ligands containing tellurium, see: (b) Jones, J. S.; Gabbai, F. P. Coordination and redox non-innocent behavior of hybrid ligands containing tellurium. *Chem. Lett.* **2016**, *45*, 376–384.
- (16) One phosphinoborane ambiphilic ligand is reported to cleave a methyl–nickel bond, resulting in the formation of a cationic metal center. Fischbach, A.; Bazinet, P. R.; Waterman, R.; Tilley, T. D. β-Phosphinoethylboranes as ambiphilic ligands in nickel–methyl complexes. *Organometallics* **2008**, *27*, 1135–1139.
- (17) Stephan, D. W. The broadening reach of frustrated Lewis pair chemistry. *Science* **2016**, *354*, 1248.
- (18) Stephan, D. W. Frustrated Lewis pairs: from concept to catalysis. *Acc. Chem. Res.* **2015**, *48*, 306–316.
- (19) Stephan, D. W.; Erker, G. Frustrated Lewis pairs: metal-free hydrogen activation and more. *Angew. Chem., Int. Ed.* **2010**, *49*, 46–76.
- (20) (a) Bertini, F.; Lyaskovskyy, V.; Timmer, B. J. J.; de Kanter, F. J. J.; Lutz, M.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K. Preorganized Frustrated Lewis pairs. *J. Am. Chem. Soc.* **2012**, *134*,

201–204. (b) Habraken, E. R. M.; Mens, L. C.; Nieger, M.; Lutz, M.; Ehlers, A. W.; Slootweg, J. C. Reactivity of the geminal phosphinoborane $t\text{Bu}_2\text{PCH}_2\text{BPh}_2$ towards alkynes, nitriles, and nitrilium triflates. *Dalton Trans.* **2017**, *46*, 12284–12292.

(21) Boom, D. H. A.; Ehlers, A. W.; Nieger, N.; Slootweg, J. C. Coordination of the ambiphilic phosphinoborane $t\text{Bu}_2\text{PCH}_2\text{BPh}_2$ to $\text{Cu}(\text{I})\text{Cl}$. *Z. Naturforsch., B: Chem. Sci.* **2017**, *72*, 781–784.

(22) For geometry around d^{10} Au(I) metal centers see: Carvajal, M. A.; Novoa, J. J.; Alvarez, S. Choice of coordination number in d^{10} complexes of group 11 metals. *J. Am. Chem. Soc.* **2004**, *126*, 1465–1477.

(23) Comparable parallel alignment of a mesityl group was found in a $(i\text{Pr}_2\text{P}-o\text{C}_6\text{H}_4\text{-BMes}_2)\text{PdCl}(\text{allyl})$ complex, see: Bontemps, S.; Bouhadir, G.; Apperley, D. C.; Dyer, P. W.; Miqueu, K.; Bourissou, D. Bridging M–Cl Bonds with ambiphilic phosphine–borane ligands. *Chem.—Asian J.* **2009**, *4*, 428–435.

(24) Partyka, D. V.; Robilotto, T. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. Dialkylbiarylphosphine complexes of gold(I) halides. Gold–aryl π -interactions in the solid state. *Organometallics* **2008**, *27*, 28–32.

(25) Partyka, D. V.; Washington, M. P.; Updegraff, J. B., III; Woloszynek, R. A.; Protasiewicz, J. D. Synergistic binding of both Lewis acids and bases to phosphinidenes. *Angew. Chem., Int. Ed.* **2008**, *47*, 7489–7492.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, R. J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.

(27) Gimeno, M. C.; Laguna, A. Three- and four-coordinate gold(I) complexes. *Chem. Rev.* **1997**, *97*, 511–522.

(28) For X-ray structures of neutral Y-shaped gold(I) chloride complexes, see: (a) Khan, M.; Oldham, C.; Tuck, G. T. The direct electrochemical synthesis of triphenylphosphine adducts of Group IB monohalides. *Can. J. Chem.* **1981**, *59*, 2714–2718. (b) Khin, C.; Hashmi, A. S. A.; Rominger, F. Gold(I) complexes of P,N ligands and their catalytic activity. *Eur. J. Inorg. Chem.* **2010**, *2010*, 1063–1069. (c) Mohapatra, S. K.; Büschel, S.; Daniliuc, C.; Jones, P. G.; Tamm, M. Selective lithiation and phosphane-functionalization of $[(\eta^7\text{-C}_7\text{H}_7)\text{Ti}(\eta^5\text{-C}_5\text{H}_5)]$ (Troticene) and its use for the preparation of early-late heterobimetallic complexes. *J. Am. Chem. Soc.* **2009**, *131*, 17014–17023.