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1,1-Phosphaboration of C≡C and C=C bonds at gold

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Abstract : The phosphine-borane *i*Pr₂P(*o*-C₆H₄)BFXyl₂ (F_xyl = 3,5-(F₃C)₂C₆H₃) was found to react with gold(I) alkynyl and vinyl complexes *via* an original 1,1-phosphaboration process. Zwitterionic complexes resulting from Au to B transmetallation have been authenticated as key intermediates. X-ray diffraction analyses show that the alkynyl-borate moiety remains pendant while the vinyl-borate is side-on coordinated to gold. According to DFT calculations, the phosphaboration then proceeds in a *trans* stepwise manner *via* decoordination of the phosphine, followed by *anti* nucleophilic attack to the π-CC bond activated by gold. The boron center acts as a relay and tether for the organic group.

Due to their accessibility and rich reactivity, CC multiple bonds are among the most widely used building blocks in synthesis. This stimulates the search for new ways to activate and transform C≡C and C=C bonds. Spectacular progress has been achieved in the area over the past few decades. In particular, gold complexes have proved to possess unique carbophilic properties making them extremely powerful catalysts for a range of C–C and C–X bond-forming transformations based on π-activation (Chart 1a).¹ On the other hand, Frustrated Lewis Pairs have been shown to readily react with a variety of CC multiply-bonded molecules.² Most typical are the *trans* 1,2- additions of phosphine-boranes and phosphino-boranes to alkynes, alkenes... (Chart 1b).^{3,4} Our interest in ambiphilic ligands⁵ and gold chemistry⁶ prompted us to explore the reactivity of phosphine-boranes towards gold(I) complexes featuring alkynyl/vinyl groups (Chart 1c). Doing so, we discovered an original 1,1-phosphaboration transformation. These results are reported hereafter. Mechanistic insights are discussed based on the reaction intermediates authenticated experimentally and on the reaction profiles computed by DFT.

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† Electronic Supplementary Information (ESI) available: Experimental procedures and characterization of complexes **2-7** (PDF). Crystallographic data for **2-7** (CIF), CCDC 2036098,2035740–2035744.

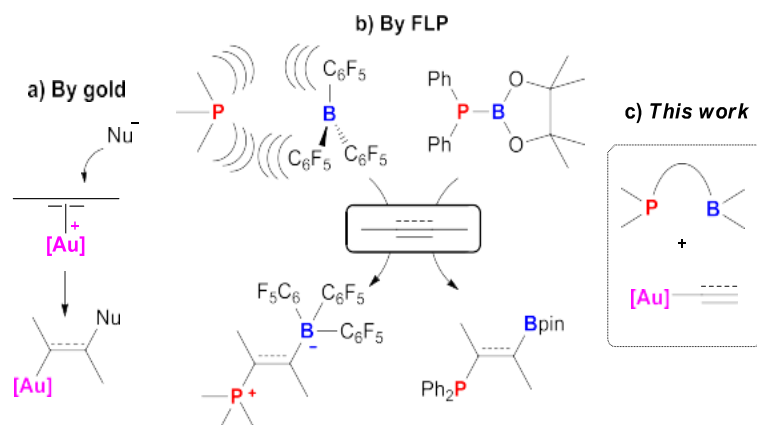
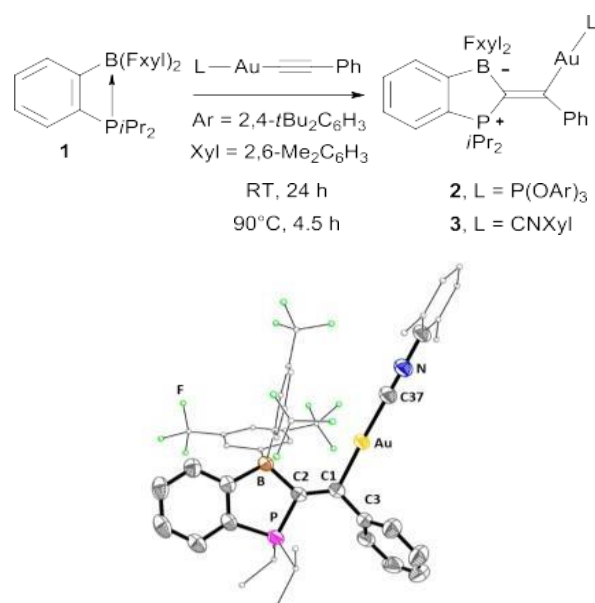


Chart 1 Schematic representation of the activation of CC π -bonds by gold complexes and Frustrated Lewis Pairs; reaction of phosphine-boranes with alkynyl/vinyl gold(I) complexes as studied in this work.

For this study, we employed the phosphine-borane *iPr*₂P(*o*-C₆H₄)BFXyl₂ (Fxy_l = 3,5-(F₃C)₂C₆H₃) **1** that we recently found to be an highly-active metal-free catalyst for the dehydrogenation of amine-boranes,⁷ as well as a versatile ambiphilic ligand to stabilize low-valent Rh complexes.⁸ The reaction of **1** with the gold(I) alkynyl complexes (L)AuC≡CPh (L = (2,4-*t*Bu₂-C₆H₃-O)₃P or 2,6-Me₂C₆H₃NC) led to the zwitterionic vinyl complexes **2** and **3** (Scheme 1). The phosphite complex **2** was obtained within 1 day at room temperature, whereas the formation of the related isonitrile complex **3** required 4.5 h of heating at 90°C. Both species were isolated by crystallization and fully characterized (isolated yields are moderate, 22 and 28%, respectively, due to high solubility).⁹ The two complexes display similar NMR data. The most diagnostic features are the sharp high-field ¹¹B NMR signal typical for a borate moiety ($\delta \sim -5$ ppm), the significant *J*_{PB} coupling (~ 22 Hz) and the very deshielded ¹³C NMR signal for the carbon atom bonded to gold ($\delta \sim 205$ -210 ppm).¹⁰ X-Ray diffraction studies were also performed on both complexes.⁹ Most noticeable are: (i) the transformation of the alkynyl moiety at gold into a vinyl group, with a tetrasubstituted short and planar C=C bond (1.340(4) and 1.357(4) Å for **2** and **3**, respectively) and (ii) the quaternarisation of the phosphorus and boron atoms, their geminal addition to the C≡C triple bond leading to a 5-membered ring.

Complexes **2** and **3** result from phosphaboration of the C≡C triple bond at gold. The reaction is regio and stereo-selective. Only the 1,1-addition products with the phosphorus atoms sitting in *trans* position to the Au(L) fragment are observed.¹¹ As mentioned in the introduction, the addition of phosphorus and boron to alkynes has some precedent, in particular 1,2-*trans* additions.^{3,4} Analogous 1,1-additions are comparatively scarce. The only example we are aware of was reported recently by Doherty and Wescott upon reacting the phosphino-borane Ph₂PBpin with phenylacetylene under Rh catalysis (Chart 1b).^{4a}

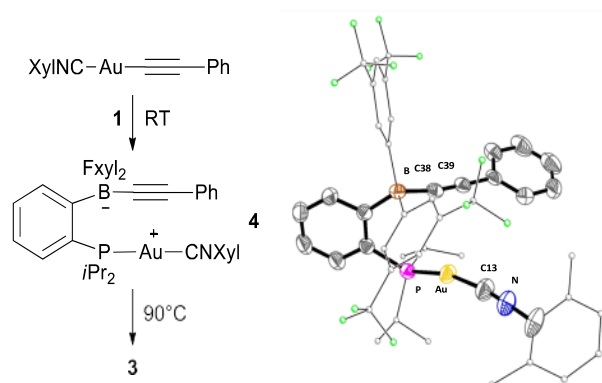


Scheme 1 Formation of the zwitterionic vinyl gold(I) complexes **2** and **3** by addition of the phosphine-borane **1** to alkynyl gold(I) precursors. Molecular structure of **3** as determined by X-Ray diffraction analysis. Ellipsoids are shown at 50% probability; hydrogen atoms are omitted; *i*Pr, Fxyl and Xyl are simplified for clarity. Selected bond distances (Å) and angles (°): P1–C2 1.814(3), B1–C2 1.648(5), C2–C1 1.357(4), C1–Au 2.043(3), B1–C2–P1 107.6(2), P–C2–C1 122.9(2), C1–C2–B1 129.0(3), C2–C1–Au 122.2(2), Au–C1–C3 113.6(2), C3–C1–C2 124.1(3).

Interestingly, the phosphine-borane **1** first reacts with the isonitrile gold(I) precursor to give complex **4** which could be isolated in 42% yield after 1 day at room temperature (Scheme 2). This zwitterionic species results from the coordination of the phosphine moiety of **1** to gold, with concomitant transfer of the alkynyl group from gold to boron (transmetalation). The gold centre is 2-coordinate and about linear in **4**, with a P–Au–C^{CNXyl} bond angle of 167.3(1)°. No sign of noticeable interaction between the alkynyl group and gold is detected: the B–C≡C fragment is only marginally bent (170.8(3)°) and the carbon atoms remain distant from gold (2.954(3) and 3.319(3) Å). This bonding situation contrasts with the strong π -coordination observed in alkynyl-borate gold(I) complexes prepared recently by treating alkynyl precursors with B(C₆F₅)₃.¹² Note that the formation of zwitterionic complexes by ionisation of M–X bonds with ambiphilic ligands is known, but not very common.⁵ We reported some examples in gold chemistry, using strong Lewis acid moieties (P,Al and P,Ga ligands) to abstract chloride from gold.¹³ As far as organic groups are concerned, the transfer of Me groups from Ni and Rh to boron were previously described.¹⁴

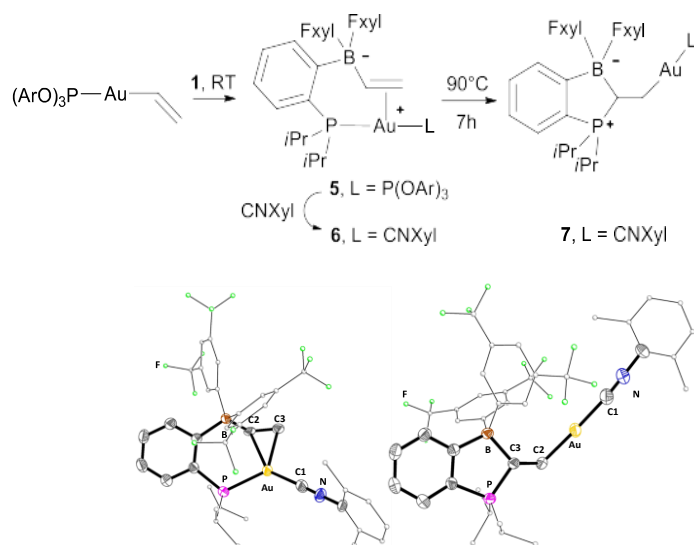
Upon heating to 90°C, complex **4** converts into **3**. In this transformation, the C≡C triple bond inserts into the P–Au bond of **4** with complete regio and stereo-selectivity. Such a process, which can also be seen as the 1,2-*trans* addition of P and Au across the C≡C triple bond (see below for further mechanistic discussions) is unusual. So far, it has only been observed with alkynyl-functionalized phosphines (intramolecular)¹⁵ or a very activated alkyne, dimethylacetylene carboxylate (intermolecular).^{10b,c} The characterization of **4** shows that the 1,1-phosphaboration of the C≡C bond at gold leading to complexes **2** and **3** is a 2-step process assisted by Au/B cooperation. Transmetalation of the alkynyl group from Au to B is followed by an intramolecular rearrangement. Some analogy can be drawn with the metal-

induced metallate rearrangement of boron “ate” complexes, as discovered and developed recently by Morken *et al.*¹⁶



Scheme 2 Phosphine gold(I) complex **4** with a pendant alkynyl-borate moiety, en route to the 1,1-phosphaboration complex **3**. Molecular structure of **4**, as determined by X-Ray diffraction analysis. Ellipsoids are shown at 50% probability; hydrogen atoms are omitted; *iPr*, *Fxyl* and *Xyl* are simplified for clarity. Selected bond distances (Å) and angles (°): B1–C38 1.605(5), C38–C39 1.201(5), P–Au 2.294(1), Au–C13 1.990(4), B–C38–C39 170.8(4), C38–C39–C40 177.0(4), P–Au–C13 167.3(1).

To assess the generality of this unusual phosphaboration transformation, the reaction of the phosphine-borane **1** with gold(I) vinyl precursors was then investigated. The zwitterionic complexes **5** and **6** obtained as shown in Scheme 3 were characterized by multi-nuclear NMR spectroscopy and X-ray diffraction analyses.⁹ The vinyl group has been transferred from gold to boron, which is now tetracoordinate (sharp ¹¹B NMR signals are observed at $\delta \sim -9$ ppm). The bonding situation of the vinyl group deserves further comments. The corresponding ¹H and ¹³C NMR signals are noticeably down-field shifted. For example, the =CH₂ resonance signal appears at $\delta \sim 88$ ppm in complexes **5** and **6**, whereas free vinyl borates display signals at $\delta > 120$ ppm.¹⁷ Furthermore, short Au–CH₂ and Au–CH distances are observed in the solid state (2.276(4) and 2.275(4) Å in **6**), while the C=C bond is elongated at 1.383(6) Å¹⁸ and the P–Au–L skeleton is strongly bent (126.6(2)° in **6**).¹⁹ These data as a whole indicate that the vinyl group transferred to boron is π -bonded to gold. Since 3-coordinate gold(I) π -complexes are rare, in particular with phosphorus-based ligands,²⁰ the bonding situation in **6** was analyzed computationally.⁹ Geometry optimization at the B3PW91/6-31G(d,p),SDD+f(Au) level of theory resulted in a structure very much resembling that determined crystallographically. According to NBO analyses, the vinyl-gold interaction is dominated by $\pi_{C=C} \rightarrow Au$ donation (91.6 kcal/mol), but $Au \rightarrow \pi^*_{C=C}$ back-donation is substantial (20.7 kcal/mol). Overall, the C=C bond is weakened, as apparent from the corresponding Wiberg bond index (1.598). Note that another structure **6_L** was localized on the potential energy surface.⁹ It is very close in energy (+0.9 kcal/mol) but very different in geometry and bonding. Here, the P–Au–L fragment much less deviates from linearity (166.1°) and the vinyl group is nearly perpendicular with long Au \cdots C distances (> 2.76 Å). The vinyl group only weakly interacts with gold in this case, as confirmed by NBO (weak $\pi_{C=C} \rightarrow Au$ donation of 8.6 kcal/mol and insignificant $Au \rightarrow \pi^*_{C=C}$ back-donation of 0.1 kcal/mol). The Wiberg bond index for the C=C bond is 1.893.



Scheme 3 Phosphine gold(I) complexes **5** and **6** with a pendant vinyl-borate moiety, en route to the 1,1-phosphaboration complex **7**. Molecular structures of complexes **6** (left) and **7** (right), as determined by X-Ray diffraction analysis. Ellipsoids are shown at 50% probability; hydrogen atoms are omitted; *i*Pr, Fxyl and Xyl are simplified for clarity. Selected bond distances (Å) and angles (°). **6**: C2–C3 1.383(6), Au–C1 2.014(5), Au–C2 2.275(4), Au–C3 2.276(4), P–Au–C1 126.6(2). **7**: P–C3 1.810(3), B1–C3 1.688(5), C3–C2 1.544(4), C2–Au 2.049(3), Au–C1 1.979(4), C2–Au–C1 175.2(1).

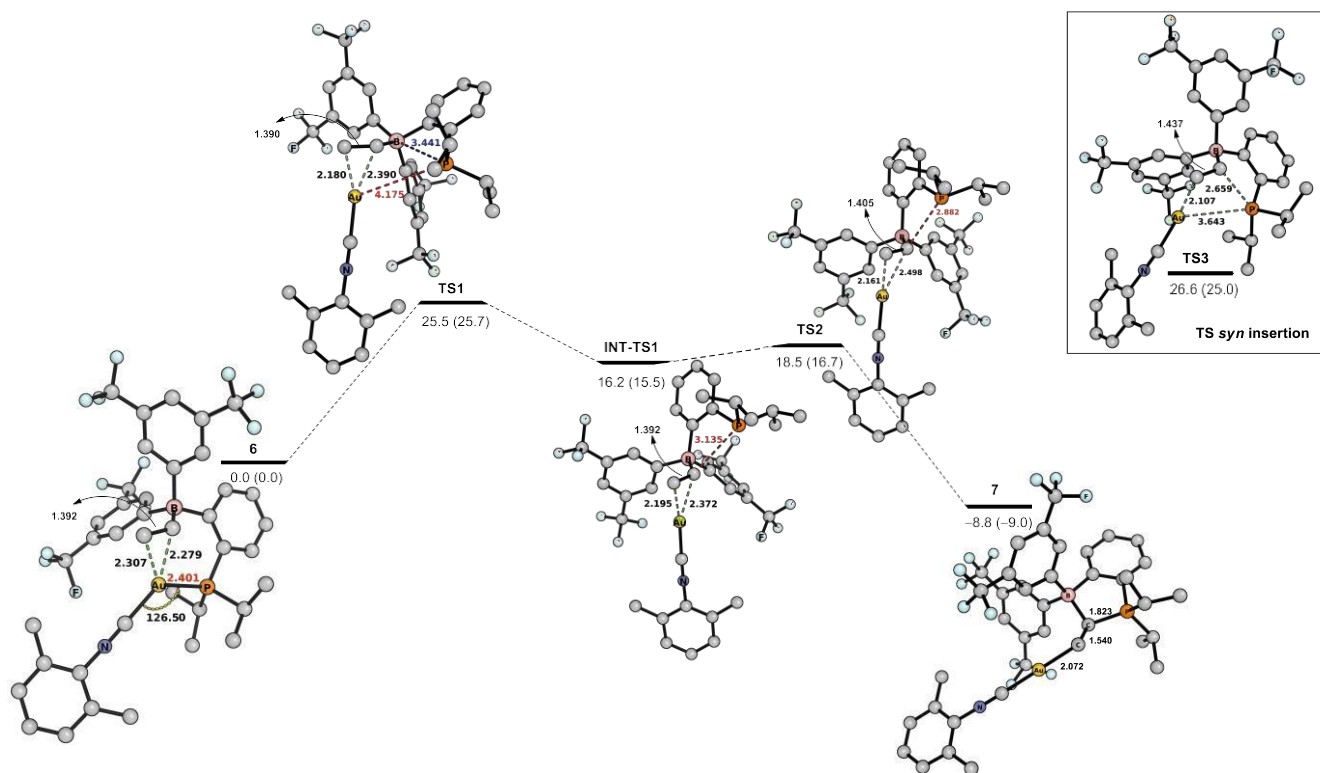


Fig. 1. Two-step mechanism accounting for the *trans*-phosphaboration of the C=C double bond at gold from **6** to **7**. Insert: transition state for concerted *syn* insertion of the C=C bond into the P–Au bond of **6**. Corrected Gibbs free energies computed at SMD(benzene)-B3PW91/6-311G(2df,2pd), SDD+2fg(Au)//B3PW91/6-31G(d,p),SDD+f(Au) level and Gibbs free (in parentheses) at B3PW91/6-31G(d,p),SDD+f(Au) level. Energy values, ΔG , in kcal/mol.

With the aim to induce phosphaboration of the C=C bond, complexes **5** and **6** were then heated. Only degradation was observed for the phosphite complex, but the isonitrile species was found to slowly and cleanly evolve into a new complex **7** at 90°C. The spectroscopic data clearly establish the insertion of the vinyl group between P and Au. In particular, the B–CH=CH₂ vinylic ¹³C NMR signals are replaced by high-

field resonances at δ 28.8 and 15.8 ppm. The structure of **7** was unambiguously confirmed by X-ray diffraction analysis (Scheme 3).⁹ In addition, kinetic studies were performed using mesitylene as solvent and 4,4'-difluorobiphenyl as internal standard.⁹ The rearrangement of **6** into **7** was found to follow first-order kinetics, and a Gibbs free energy of activation ΔG^\ddagger of 28.2 ± 3.3 kcal/mol was estimated from an Eyring plot in the 70-110°C temperature range.

To gain further insight into these phosphaboration processes and better understand the interplay between Au and B, the reaction profiles for the formation of complexes **3*** (with C \equiv CH instead of C \equiv CPh) and **7** were studied by DFT at SMD(benzene)-B3PW91/6-311G(2df,2pd),SDD+2fg(Au)//B3PW91/6-31G(d,p),SDD+f(Au) level of theory.⁹ As shown in Figure 1 and Figures S186-188,⁹ *trans* phosphaboration of the alkynyl and vinyl gold complexes **4*** and **6** was found to result from a stepwise process involving decoordination of P from Au (this is the rate-determining step). The ensuing linear π -complexes are 16.2-17.2 kcal/mol higher in energy than the starting zwitterionic complexes. They undergo *anti* nucleophilic attack of the phosphine, with the boron moiety acting as a tether. This step is almost barrierless (0.4-2.3 kcal/mol) but very exergonic (by 25-37 kcal/mol). Of note, the activation barrier computed for the rearrangement of **6** into **7** (25.5 kcal/mol) fits well with that measured experimentally. For sake of comprehensiveness, we looked for possible alternative pathways on the potential energy surface. Migratory insertion has little precedent in gold chemistry and usually hardly competes with *trans* addition. Recently, we have shown it is sometimes viable and actually quite easy.²¹ Concerted *syn* insertion of the C \equiv C/C=C bonds into the P–Au bonds of **4*** and **6** was indeed found to be conceivable (*via* a 4-membered transition state) and potentially competing (the difference in activation barrier is only 1 kcal/mol).⁹

In conclusion, an original 1,1-phosphaboration process was discovered upon reacting the ambiphilic ligand **1** with gold(I) alkynyl and vinyl complexes. This transformation represents a rare example of phosphine-borane \rightarrow phosphonium-borate rearrangement, for which a few precedents involving distinct mechanisms have been reported.^{3b,22} Mechanistic studies revealed that boron acts in concert to gold, abstracting and tethering the organic group. Zwitterionic complexes are first formed by Au to B transmetalation. Decoordination of the phosphine, followed by *anti* nucleophilic attack to the π -CC bonds activated at gold then affords the phosphaboration products. Bifunctional ligands are currently gathering more and more interest in gold chemistry. In particular, they have been shown to trigger unprecedented reactivity paths.²³ The results reported here suggest that ambiphilic ligands may open new avenues in this context and are certainly worthwhile to be studied further.

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