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Lewis acid-assisted C(sp³)-C(sp³) reductive elimination at gold

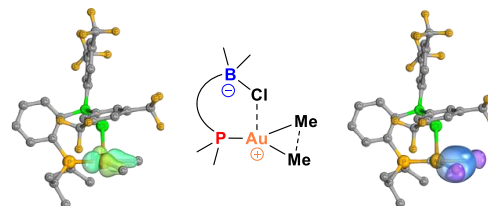
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KEYWORDS: boron, C–C coupling, gold, Lewis acid, reductive elimination.

ABSTRACT: The phosphine-borane *i*Pr₂P(*o*-C₆H₄)BF_{xyl}₂ (F_{xyl} = 3,5-(F₃C)₂C₆H₃) **1-Fxyl** was found to promote the reductive elimination of ethane from [AuMe₂(μ-Cl)]₂. NMR monitoring revealed the intermediate formation of the (**1-Fxyl**)AuMe₂Cl complex. DFT calculations identified a zwitterionic path as the lowest energy profile, with an overall activation barrier more than 10 kcal/mol lower than without borane assistance. The Lewis acid moiety first abstracts the chloride to generate a zwitterionic Au(III) complex, which then readily undergoes C(sp³)-C(sp³) coupling. The chloride is finally transferred back from boron to gold. The electronic features of this Lewis assisted reductive elimination at gold have been deciphered by IBO analyses. Sufficient Lewis acidity of boron is required for the ambiphilic ligand to trigger the C(sp³)-C(sp³) coupling, as shown by complementary studies with two other phosphine-boranes, and the addition of chlorides slows down the reductive elimination of ethane.



Introduction

Gold complexes were long considered quite inert and their synthetic use was mostly confined to Lewis acid behavior for the activation of CC multiple bonds towards nucleophilic addition.¹ However, this is no longer the case and intensive research efforts over the past 10-15 years have shown that versatile chemistry is in fact possible at gold. Recent studies have provided evidence for its ability to undergo several key elementary steps besides π -coordination: oxidative addition, migratory insertion and β -H elimination in particular.² Rational ligand design enables gold to display typical transition metal (TM) behaviour, but its reactivity profile is often very different from that of the other TMs, which makes it very complementary and useful.^{3,4}

Reductive elimination is a pivotal step in many TM-catalyzed transformations. It is the product-releasing step and often the driving force of the reaction. Pioneering studies on C–C coupling from Au(III) complexes date back

to the 1970-1990's with a series of seminal contributions by Tobias, Kochi, Komiya and Vicente.⁵⁻⁷ The field then remained dormant for about 2 decades, until Toste *et al.* reported that C(sp²)-C(sp²) reductive elimination is exceptionally fast at gold, much faster than with any other TM in fact.⁸ Comparatively, C-C coupling involving C(sp³) centers is much less favored and actually highly challenging with very scant examples reported so far. In 1976, Kochi *et al.* noticed a significant impact of the X co-ligand in the reductive elimination of the (Ph₃P)AuMe₂X complexes. The less coordinating was the X co-ligand, the faster was the C(sp³)-C(sp³) coupling.^{6b} More recently, Toste *et al.* achieved challenging Ar-CF₃ couplings within less than 1 minute at -10°C by reacting (phosphine)Au(Ar)(CF₃)I complexes with Ag salts.⁹ In addition, Bergman, Raymond and Toste devised and successfully applied a supramolecular catalytic approach to the H₃C-CH₃ coupling at gold. Polyanionic cages were used to entrap and activate LAuMe₂I complexes (L = PMe₃, PEt₃) through iodide dissociation.^{10,11}

These recent studies and the peculiar behaviour of gold stimulated renewed interest for C-C and C-X reductive elimination from Au(III) complexes.¹²⁻¹⁵ Besides experimental investigations, thorough DFT studies have shed light into the factors influencing C-C coupling at gold.^{10c-g,16} In general, two different scenarios can be distinguished depending on the hybridization of the carbon centers to couple. While C(sp²)-C(sp²) reductive eliminations proceed readily from 4-coordinated Au(III) complexes, C-C(sp³) reductive eliminations are more difficult to achieve and typically involve 3-coordinate Au(III) species (Figure 1a).

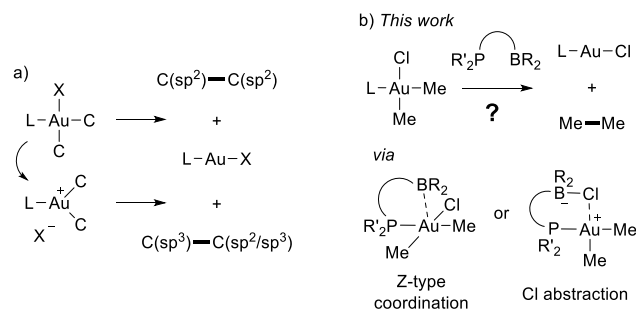


Figure 1. C-C Reductive elimination at gold. a) 4-Coordinate vs 3-coordinate pathways for the reductive elimination of C(sp²)-C(sp²) vs C(sp³)-C(sp²/sp³) bonds at Au(III). b) Possible scenarios for the H₃C-CH₃ reductive elimination at Au(III) assisted by phosphine-boranes, as investigated in this work.

Our interest in gold reactivity and ambiphilic ligands prompted us to consider the possibility to take advantage of a Lewis acid (LA) moiety to promote reductive elimination and C-C coupling at gold. Recent studies have pinpointed the positive impacts that external LAs (BR₃, ZnR₂, AgX, MgX₂...) may have on challenging C-C reductive eliminations.^{17,18} The LA may either coordinate to a remote basic site of the group to couple, behave as a Z-type ligand and withdraw electron-density from the metal, or abstract a co-ligand at the metal to generate a coordinatively unsaturated complex.

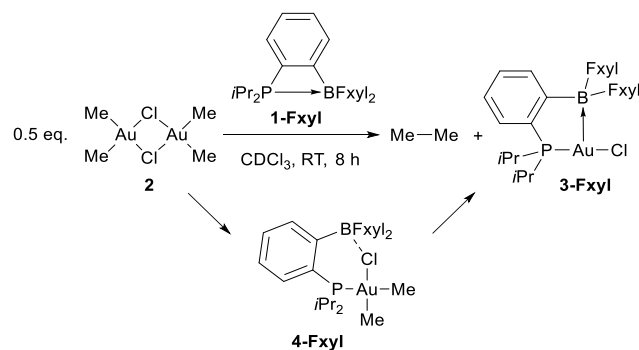
Phosphine-boranes and related ambiphilic ligands readily engage in $M \rightarrow B$ interactions and bridge $M-Cl$ bonds via $P \rightarrow M-Cl \rightarrow B$ interactions.¹⁹ Ultimately, chloride abstraction may be observed leading to zwitterionic complexes.²⁰ As for gold, we have shown that ambiphilic ligands offer an alternative to silver salts to activate Au(I) precatalysts.^{20d}

In this work, we questioned the ability of phosphine-boranes to trigger difficult reductive elimination at gold, in particular $C(sp^3)-C(sp^3)$ coupling. The Lewis acid may assist the reductive elimination by either coordination to gold as a Z-type ligand or by abstracting a chloride at gold to give a 3-coordinate zwitterionic complex (Figure 1b). As reported hereafter, phosphine-boranes were indeed found to efficiently promote H_3C-CH_3 elimination from $[AuMe_2(\mu-Cl)]_2$. The influence and the role of the borane moiety were thoroughly investigated by experimental and computational means.

Results and Discussion

For this study, $iPr_2P(o-C_6H_4)BFxyl_2$ ($Fxyl = 3,5-(F_3C)_2C_6H_3$) **1-Fxyl**²¹ was chosen as phosphine-borane since we recently found it readily reacts with organo (vinyl, alkynyl, aryl) Au(I) complexes to give zwitterionic species.²² The possibility for **1-Fxyl** to trigger reductive elimination was assessed with the $\mu-Cl$ bridged dimer $(AuMe_2Cl)_2$ **2**, which is reluctant to undergo $C(sp^3)-C(sp^3)$ coupling (Scheme 1). The phosphine-borane was mixed with 0.5 equiv. of **2** in chloroform at room temperature. NMR monitoring revealed complete conversion within 8 hours, with formation of ethane (as apparent from its diagnostic singlet at δ 0.88 ppm in the 1H NMR spectrum) along with the phosphine-borane Au(I) chloro complex **3-Fxyl** (identified by its ^{31}P NMR signal at δ 65.0 ppm).^{22b} Control analyses showed that the Au(III) dimer **2** is stable in the solid state (only traces of decomposition are detected after weeks) while some degradation occurs in solution, but it is very slow (94% within 8 days). Thus, the phosphine-borane **1-Fxyl** significantly speeds up $C(sp^3)-C(sp^3)$ coupling from **2** and somehow promotes reductive elimination at gold.

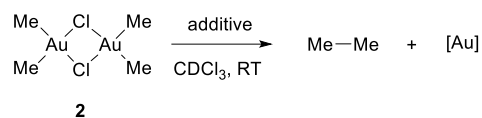
Scheme 1. Reductive elimination of ethane upon treatment of 2 with the phosphine-borane 1-Fxyl.



To gain more insight into the influence of the Lewis base and Lewis acid, the Au(III) dimer **2** was then treated separately with phosphines and boranes under similar conditions (Table 1). With the phosphine iPr_2PPh alone, the

μ -Cl bridge was immediately split to give *cis*-(*i*Pr₂PPh)AuMe₂Cl, whose structure was unambiguously ascertained by ³¹P, ¹H and ¹³C NMR spectroscopy.²³ This complex proved extremely stable over time, with only 8% conversion after 12 days. On their side, triaryl boranes were found to only marginally influence the stability of **2**. With BPh₃, only 50% conversion is achieved after 6 days and even with the very Lewis acidic borane B(C₆F₅)₃, 6 days are needed to reach 90% conversion. Thus, the presence of both the phosphine and borane seems crucial for the reductive elimination to proceed rapidly. Nonetheless, our first attempt by combining *i*Pr₂PPh and B(C₆F₅)₃ resulted in very slow conversion of (AuMe₂Cl)₂. In fact, the phosphine and borane react with each other (*via* nucleophilic aromatic substitution)²⁴ faster than with (AuMe₂Cl)₂ and the resulting phosphonium-borate (*i*Pr)₂PhP(*p*-C₆F₄)BF(C₆F₅)₂ is completely inert towards C(sp³)-C(sp³) coupling at gold. To prevent this irreversible quenching, the phosphine *i*Pr₂PPh was first reacted with (AuMe₂Cl)₂ and the ensuing complex was then treated with B(C₆F₅)₃. Under these conditions, reductive elimination proceeds quickly and is essentially complete within 10 minutes. All together, these experiments suggest that the phosphine and borane moieties of **1** act synergistically. The phosphine is presumed to coordinate to gold and split the μ -Cl bridge, while the borane is expected to coordinate to gold or to pull on the chloride at gold (and eventually abstract it).²⁰

Table 1. Conversion of the Au(III) dimer **2 at RT in CDCl₃ (determined by ¹H NMR spectroscopy, by relative integration with tetrachloroethane as internal standard).**



additive	Conversion / Time
none	94 % / 8 days
<i>i</i> Pr ₂ PPh	8 % / 12 days
B(C ₆ F ₅) ₃	90 % / 6 days
BPh ₃	50 % / 6 days
<i>i</i> Pr ₂ PPh + B(C ₆ F ₅) ₃	96 % / 7 days
<i>i</i> Pr ₂ PPh then B(C ₆ F ₅) ₃	90 % / <10 min.

With the aim to get more information about the way the phosphine-borane **1-FxyI** reacts with (AuMe₂Cl)₂ **2**, we tried to characterize some intermediate complex. Right after mixing the two components, 3 different compounds were detected by ³¹P NMR spectroscopy (Figure 2): the free phosphine-borane **1-FxyI** (δ 30.5 ppm), its Au(I) chloro complex **3-FxyI**, and a new species **4-FxyI** (δ 34.7 ppm). The amount of **4-FxyI** increases relatively quickly at the beginning of the reaction. It reaches a plateau after about 1 hour and then decreases in favour of the Au(I) chloro complex **3-FxyI**. To further characterize the intermediate complex **4-FxyI**, the phosphine-borane **1-FxyI** and Au(III) dimer (AuMe₂Cl)₂ **2** were let to react for 1 h 25 min at room temperature and the solution was then cooled to -15°C. At this point, **4-FxyI** is the major species (representing 47% of the P-containing compounds) and it remains so for several hours. Despite the presence of **1-FxyI** and **3-FxyI**, all the ¹H and ¹³C NMR signals for **4-FxyI** could be identified and attributed unequivocally.²³ It is the Au(III) complex *cis*-(**1-FxyI**)AuMe₂Cl. Most diagnostic are the two ¹³C NMR signals for the Me groups in *trans* and *cis* to P resonating as doublets at δ 21.4 and 10.3 ppm with

$^2J_{PC}$ coupling constants of 100.5 and 4.5 Hz, respectively. The slow generation of **4-Fxyl** contrasts with the immediate formation of its boron-free analog *cis*-(*i*Pr₂PPh)AuMe₂Cl. It is probably due to the closed form of **1-Fxyl** (with intramolecular P→B interaction),^{21a} which slows down the coordination to gold and the splitting of the μ-Cl bridge.

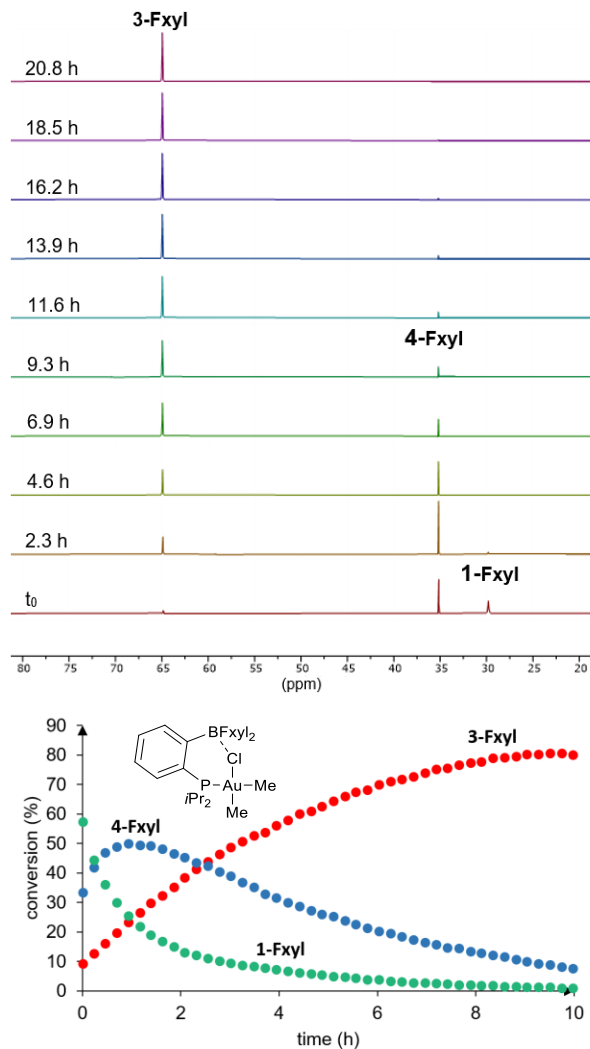


Figure 2. Reaction between the phosphine-borane **1-Fxyl** and (AuMe₂Cl)₂ **2** in CDCl₃ at room temperature. Top: Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Bottom: Variation of the relative percentage of P-containing species, as determined by ^1H NMR spectroscopy.

Given the lower activation barriers predicted for C(sp³)-C(sp³) reductive elimination at tricoordinate *versus* tetracoordinate Au(III) centers,^{16a} the borane moiety of **1-Fxyl** is expected to activate the Au-Cl bond in **4-Fxyl** via bridging coordination or even complete abstraction. Unfortunately, the exact bonding situation within **4-Fxyl** could not be authenticated experimentally. No ^{11}B NMR signal was observable for **4-Fxyl** (neither for the Au(I) complex **3-Fxyl**^{22b}). To nonetheless support the interaction between B and Cl, the influence of adding an external chloride

source (as a competitive inhibitor for boron) was investigated. The reaction between **1-Fxyl** and **2** was let to go to about 50% conversion to form complex **4-Fxyl** in maximum quantity. An excess of tetraphenylphosphonium chloride TPPCl (3 equiv. per gold and phosphine-borane, related to the initial amounts) was then added quickly at -80°C . From this time, the consumption of complex **4-Fxyl** was monitored at room temperature by $^1\text{H}\{^{31}\text{P}\}$ NMR spectroscopy.²³ Comparing the parallel experiments performed with and without added TPPCl (Figure 3) clearly shows a noticeable slowdown of the reductive elimination with extra chlorides. Indeed, more than two thirds of complex **4-Fxyl** are still observed after 24 hours in the presence of TPPCl while it is completely consumed within 8 hours without TPPCl.

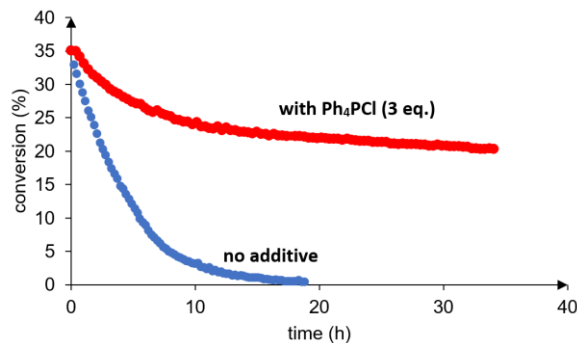


Figure 3. Evolution of complex **4-Fxyl** against time in CDCl_3 at room temperature with and without added tetraphenylphosphonium chloride (3 eq.) ($t = 0$ corresponds to the first NMR control after addition of chloride).

To gain further insight into the impact and mode of action of the borane moiety, the mechanism of $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ reductive elimination at gold was studied using Density Functional Theory (DFT). Calculations were performed on the actual $(\mathbf{1-Fxyl})\text{AuMe}_2\text{Cl}$ complex **4-Fxyl** at the PCM(chloroform)-B3PW91-D3(BJ)/SDD+f(Au),6-31G**//B3PW91/SDD+f(Au),6-31G** level of theory.²³

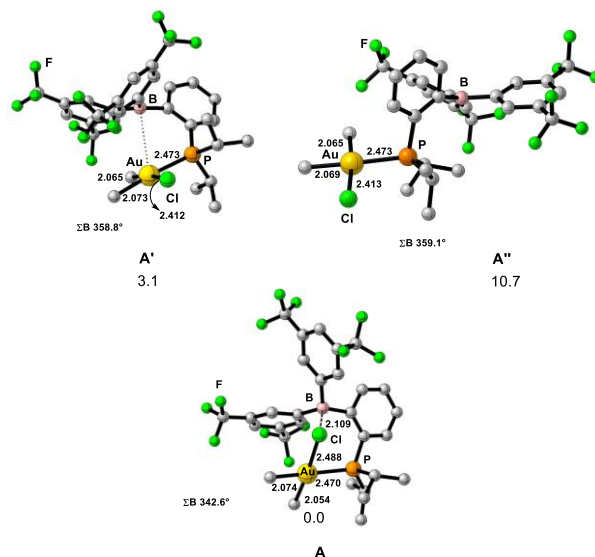


Figure 4. Optimized structures of the (1-FxyI)AuMe₂Cl complex: P→Au–Cl→B bridged ground state **A**, B-pendant forms **A'** (apical) and **A''** (rotated) at the B3PW91/SDD+f(Au),6-31G** level of theory. See Figure 5 for the zwitterionic form **A'''**. Corrected Gibbs free energies ΔG (in kcal/mol) related to **A** computed at the PCM(chloroform)-B3PW91-D3(BJ)/SDD+f(Au),6-31G** //B3PW91/SDD+f(Au),6-31G** level. Key structural data (distances in Å, angles in °).

The most stable form **A** involves P→Au–Cl→B bridging coordination (Figure 4). Strong Cl–B interaction is apparent from the short distance (2.109 Å), the noticeable pyramidalization of boron (ΣB_{α} 342.6°) and the elongation of the Au–Cl bond (2.488 Å). The Cl→B interaction is found as a polarized covalent bond upon Natural Bond Orbital analysis (NBO: 21.4% B, 78.6% Cl). Two B-pendant forms without interaction between the borane moiety and the AuMe₂Cl fragment were located on the potential energy surface. In **A'** (+ 3.1 kcal/mol), the boron center sits in an apical position, but remains far from gold (Au⋯B > 3.6 Å) and trigonal planar (ΣB_{α} 358.8°). In **A''** (+10.7 kcal/mol), the P–C(sp²) bond of the phosphine-borane ligand is rotated and the borane moiety points away from the metal center.

From **A**, reductive elimination to give ethane and the phosphine-borane Au(I) complex **B** is very downhill in energy (ΔG –46.7 kcal/mol). The lowest energy path is a stepwise process (Figure 6) involving (i) chloride transfer from Au to B to give the zwitterionic Au(III) complex **A'''**,²⁵ (ii) C(sp³)–C(sp³) coupling to give the zwitterionic Au(I) complex **INT-A'''** and release ethane, and finally (iii) back-transfer of the chloride from B to Au to give the neutral Au(I)→B complex **B**^{22b}. The zwitterionic complexes **A'''** and **INT-A'''** (Figure 5) are stabilized by π -coordination of a Fxyl moiety at B to the coordinatively unsaturated Au(III/I) center (short C_{ipso} –Au/ C_{ortho} –Au distances of 2.640/2.618 Å in **A'''** and 2.401/2.339 Å in **INT-A'''** are found).^{23,26} Relatively strong donor-acceptor interactions are found upon NBO analysis (with delocalization energies $\Delta E(2)$ of 33.3 and 41.3 kcal/mol, respectively). The respective Intrinsic Bond Orbitals (IBOs) are depicted in Figure 6. The zwitterionic Au(III) complex **A'''** lies 8.3 kcal/mol above **A** and the activation barrier for its formation is fairly accessible at 15.9 kcal/mol.

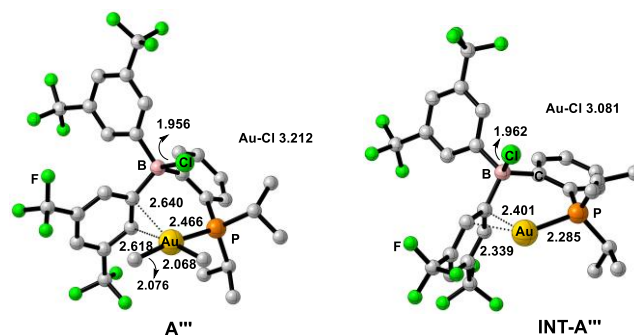


Figure 5. Optimized structures of the zwitterionic complexes **A'''** and **INT-A'''** at the B3PW91/SDD+f(Au),6-31G** level of theory. Key structural data (distances in Å).

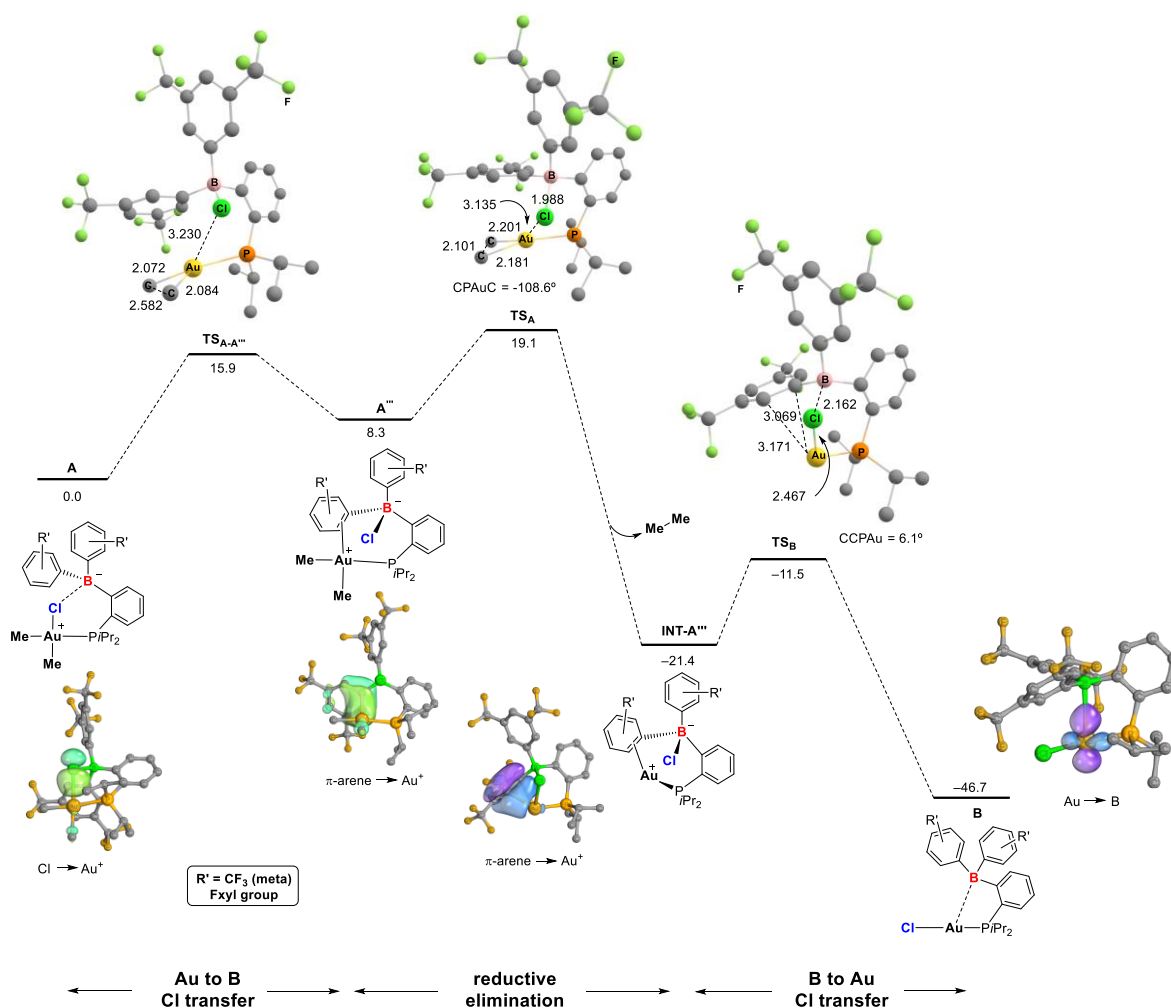


Figure 6. Energy profile computed for the transformation of the (1-Fxyl)AuMe₂Cl complex **A** into ethane and the (1-Fxyl)AuCl complex **B** at the PCM(CHCl₃)-B3PW91-D3(BJ)/SDD+f(Au),6-31G**//B3PW91/SDD+f(Au),6-31G** level of theory. Corrected Gibbs Free energies (ΔG) in kcal/mol, main distances in Å and bond angles in degrees (°). IBO orbitals accounting for the Cl→Au⁺, arene→Au⁺ and Au→B interactions.

The C(sp³)-C(sp³) coupling proceeds readily from **A'''**. The corresponding transition state **TS_A** sits only 10.8 kcal/mol above **A'''**, corresponding to an activation barrier of 19.1 kcal/mol from **A**. In **TS_A**, the BFxyl₂ group is

pendant and no longer engaged in π -arene coordination. The gold center is 3-coordinate and the $C(sp^3)-C(sp^3)$ coupling is rather advanced: the C–Au–C bond angle is shrunk (from 82.3° in **A'''** to 57.3°), the Au–C(sp^3) bonds are elongated (from 2.068/2.076 Å in **A'''** to 2.181/2.201 Å) and the $C(sp^3)\cdots C(sp^3)$ distance is shortened (from 2.728 Å in **A'''** to 2.101 Å). IBO analyses along the intrinsic reaction coordinate (Figure 7) confirm this view. The two $\sigma(\text{Au}-\text{C})$ orbitals accounting for the Au–C(sp^3) bonds progressively evolve into a $\sigma(\text{C}-\text{C})$ orbital (for $\text{H}_3\text{C}-\text{CH}_3$) and a $d(\text{Au})$ orbital (in line with the reduction of the d^8 Au(III) center into a d^{10} Au(I) center). This orbital redistribution is essentially done when the $C(sp^3)\cdots C(sp^3)$ distance reaches 2.54 Å, well before **TS_A**.

Finally, from the zwitterionic Au(I) complex **INT-A'''**, back-transfer of the chloride from B to Au to give **B** is very exergonic ($\Delta G -25.3$ kcal/mol) and its energy barrier is low ($\Delta G^\ddagger 9.9$ kcal/mol).

Overall, the activation barrier computed for this boron-assisted $C(sp^3)-C(sp^3)$ reductive elimination at gold is 19.1 kcal/mol, consistent with a reaction occurring over hours at 25°C . A similar barrier (17.2 kcal/mol) was also found for the coupling of ethyl groups from the analogous complex (**1-FxyI**)AuEt₂Cl.²³ These values are significantly lower than those reported previously for $(\text{R}_3\text{P})\text{AuMe}_2\text{X}$ complexes (R = Ph, Me; X = Cl, I) ($\Delta G^\ddagger > 30$ kcal/mol).^{10c,d,f,16a} With the aim to further assess the impact of the Lewis acid on the activation barrier, alternative pathways have been looked for on the potential energy surface of complex (**1-FxyI**)AuMe₂Cl. Two other transition states for $C(sp^3)-C(sp^3)$ coupling not involving Cl→B interaction were found (from **A'** and **A''**, with the borane moiety sitting above gold or opposite to gold).²³ The corresponding barriers are significantly larger (29.6 and 43.4 kcal/mol), making the boron-assisted route much more favored. The boron-free analog (*i*Pr₂PPh)AuMe₂Cl was also considered. The barrier for ethane formation was herealso estimated to be much higher (30.0 kcal/mol).²³

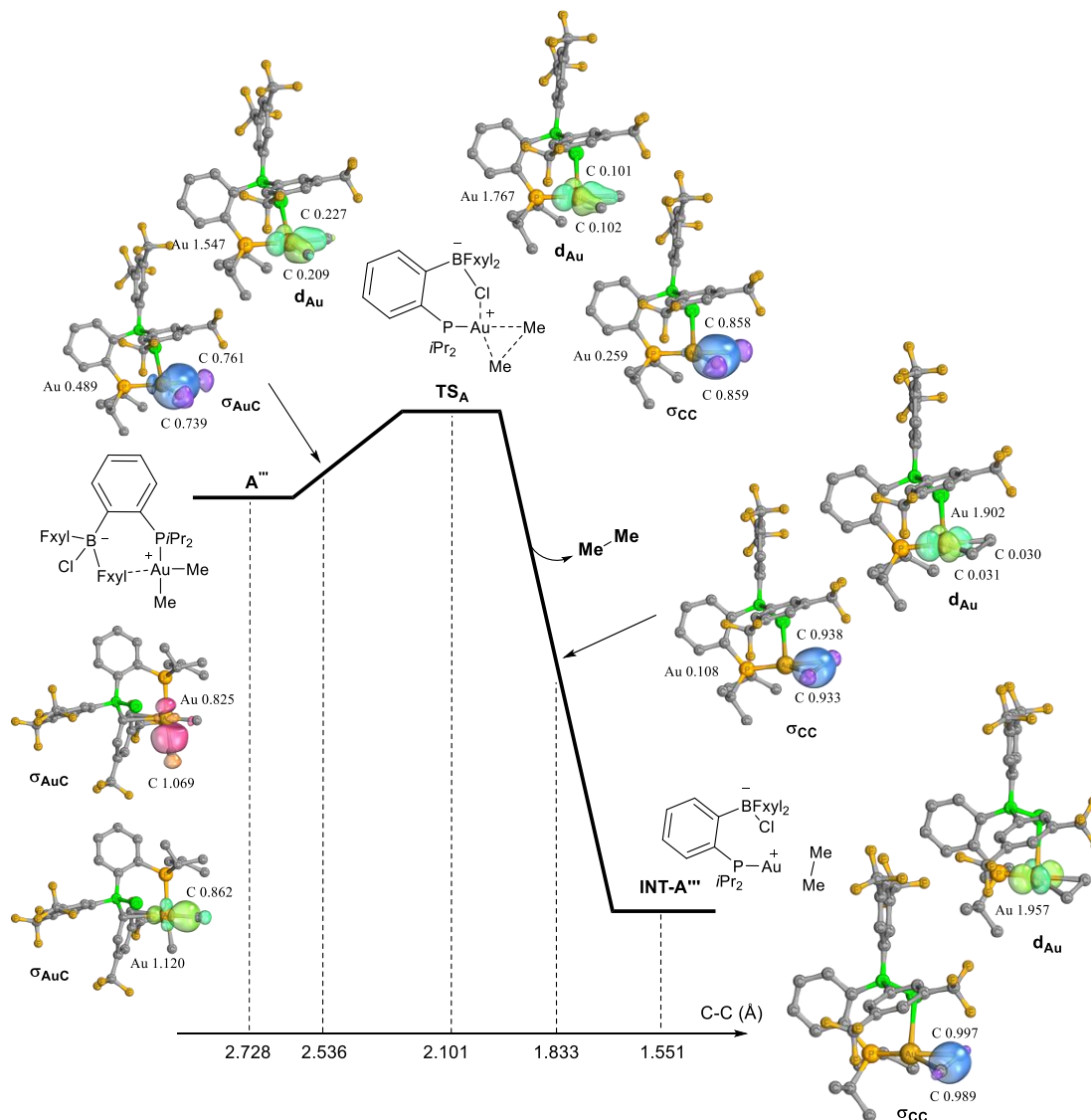
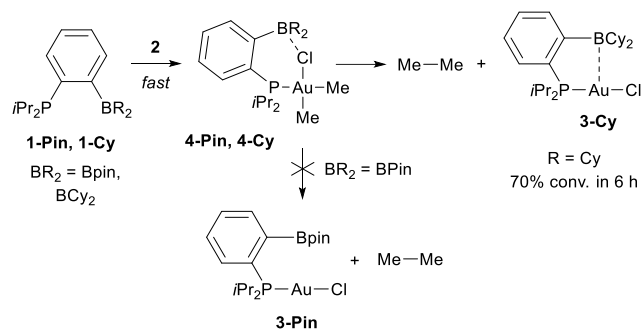


Figure 7. IRC path of the reductive elimination step accounting for the $C(sp^3)-C(sp^3)$ coupling at Au(III) with the most relevant IBO orbitals (d_{Au} , σ_{AuC} , σ_{CC}). Numbers relate the fraction of electrons of the doubly occupied orbitals assigned to each atom.

Finally, to assess how general are the observations made with **1-Fxyl**, the Au(III) dimer $(AuMe_2Cl)_2$ **2** was reacted with two other phosphine-boranes, **1-Pin** and **1-Cy** (Scheme 2). When replacing the $BFxyl_2$ group for a Bpin moiety,²⁷ the μ -Cl bridge was instantaneously split but the reaction stopped at **4-Pin**. No $C(sp^3)-C(sp^3)$ coupling was detected even after 8 days, indicating that a boron center of sufficient Lewis acidity is needed to assist the reductive elimination at gold.²³ Conversely, the phosphine-borane **1-Cy**²⁸ promotes reductive elimination, with 70% conversion in 6 hours. Upon reaction monitoring, the corresponding $(\mathbf{1-Cy})AuMe_2Cl$ complex **4-Cy** was identified as intermediate, with spectroscopic features very similar to those of **4-Fxyl**.²³ The borane moiety likely acts as chloride abstractor herealso, as supported by the strong inhibition observed upon addition of chlorides.²³ Thus, phosphine-boranes seem quite general in assisting $C(sp^3)-C(sp^3)$ reductive elimination at gold and the presence of a highly Lewis acidic borane is not required.

Scheme 2 Reaction of (AuMe₂Cl)₂ **2** with the phosphine-boranes **1-Pin** and **1-Cy**.



Conclusion

In conclusion, phosphine-boranes were found to trigger the reductive elimination of ethane at gold. Thanks to reversible chloride abstraction, the Lewis acid moiety opens a low-energy path for C(sp³)-C(sp³) coupling. It involves a 3-coordinate zwitterionic Au(III) complex as key intermediate.

Ambiphilic ligands are attracting growing interest in TM chemistry. Due to the Lewis acid moiety, they exhibit non-innocent behavior which inherently differs from that operating with classical donor ligands.²⁹ Over the past few years, Lewis acid assisted oxidative additions and transmetalations have been documented with ambiphilic ligands.³⁰ The results reported here demonstrate that ambiphilic ligands may also assist reductive elimination.³¹ Future studies will aim to generalize this concept to other challenging reductive eliminations at gold and to extend it beyond gold.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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