Tuning Activity and Selectivity during Alkyne Activation by Gold(I)/Platinum(0) Frustrated Lewis Pairs

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ABSTRACT: Introducing transition metals into frustrated Lewis pair systems has attracted considerable attention in recent years. Here we report a selection of three metal-only frustrated systems based on Au(I)/Pt(0) combinations and their reactivity toward alkenes. We have inspected the activation of acetylene and phenylacetylene. The gold(I) fragments are stabilized by three bulky phosphines bearing terphenyl groups. We have observed that subtle modifications on the substituents of these ligands proved critical in controlling the regioselectivity of acetylene activation and the product distribution resulting from C(sp)−H cleavage of phenylacetylene. A mechanistic picture based on experimental observations and computational analysis is provided. As a result of the cooperative action of the two metals of the frustrated pairs, several uncommon heterobimetallic structures have been characterized.

INTRODUCTION

Frustrated Lewis pairs (FLPs) emerged more than a decade ago as a paradigmatic example of chemical cooperativity, permitting bond activation and catalysis in the absence of transition metals.1 However, the incorporation of the latter as core components of FLP systems has also attracted considerable attention in the last few years.2,3 In fact, the concept of frustration may be applied to a wide variety of transition-metal-mediated transformations that were described considerably earlier than the emergence of FLP chemistry and have so far been associated with the broader concept of chemical cooperativity. From an awareness of this sometimes diffuse frontier between “traditional” transition-metal cooperative chemistry and metallic frustration, the introduction of the latter concept remains useful as a driving force for the discovery of novel transformations. That being said, introducing transition metals into frustrated designs largely increases the amount and structural diversity of Lewis acid/base combinations available. In addition, it provides an array of elementary reactions accessible for transition metals that is foreseen to extend the catalytic usefulness of main-group FLPs beyond their current status. However, a fundamental knowledge on transition-metal FLPs regarding mechanistic aspects, solution dynamics, acid−base interactions, and selectivity effects is rather underexplored in comparison to main-group FLPs, despite the fact that this information is vital for expeditious catalyst development.

In this regard, the Wass group demonstrated that subtle ligand modifications have a strong effect on the ability of zirconocene-based FLPs toward dihydrogen splitting.4 This type of system was also examined to clarify the nature of Lewis acid−base interactions by DOSY NMR spectroscopy.5 Going beyond monometallic systems, our group focused on gaining a fundamental knowledge of FLPs in which the two Lewis components are based on transition metals. Thus, we recently reported the first example of its kind by combining Au(I) and Pt(0) species as the acidic and basic sites, respectively.6 To achieve frustration, we targeted sterically hindered phosphine ligands for both gold and platinum monometallic complexes. Our experimental/computational investigations regarding the heterolytic splitting of dihydrogen mediated by these pairs led us to propose a genuine bimetallic FLP-type pathway7 analogous to the models assumed for main-group counterparts.8 Moreover, we could analyze the strong influence that Au···Pt interactions have on the activation capacity of the bimetallic pairs, as well as the solution dynamic equilibria between the metal-only Lewis pairs and the individual monometallic fragments. This is a particularly important aspect in the field of FLPs that has been widely investigated for metal-free systems, where the term “thermally induced FLPs”9 was coined to refer those pairs in which the Lewis adduct is the resting state. Despite this fact, many of these pairs exhibit a rich FLP reactivity10 and in some
cases catalytic performance superior to that of their fully frustrated counterparts.\textsuperscript{11}

In this study, we extend our fundamental knowledge on transition-metal-only FLPs (TMOFLPs) by exploring regioselectivity effects derived from ligand modification during the activation of alkynes, also model substrates widely investigated in the field of frustrated systems.\textsuperscript{1,12} We have focused on the effects derived from varying the degree of frustration, for which we have used terphenylphosphine ligands PMe\textsubscript{2}ArXyl\textsubscript{2} (a), PMe\textsubscript{2}ArDipp\textsubscript{2} (b), and PCyp\textsubscript{2}ArXyl\textsubscript{2} (c) (Cyp = cyclopentyl), with different steric profiles, to stabilize electrophilic gold fragments 1 (Figure 1). These acidic complexes combined with the basic potential of using transition-metal Lewis acids (i.e., [PR\textsubscript{3}AuI]+ (Scheme 1)). These metallic species are highly reminiscent of the organic products derived from the reactivity of traditional phosphine/borane FLPs with alkynes, where the prevalence of one or the other isomer typically depends on the basicity of the phosphine.\textsuperscript{14}

We now tested the analogous reactivity using the gold precursors \([\text{[(PMe}_2\text{ArXyl}_2)\text{Au(NTf}_2\text{)]}} (1\text{a})\) and \([\text{[(PCyp}_2\text{ArXyl}_2)\text{Au(NTf}_2\text{)]}} (1\text{c})\) in our search for regioselectivity effects, while the basicity of the metallic base was kept unaltered (2). Moreover, the acidities of the gold precursors 1a–c barely differ from one another;\textsuperscript{15} thus, any anticipated outcomes mostly build on steric grounds. In fact, we found a drastic change in product distribution from the less hindered system (1a, PMe\textsubscript{2}ArXyl\textsubscript{2}) to the more congested one (1c, PCyp\textsubscript{2}ArXyl\textsubscript{2}), as determined by NMR spectroscopy. While the former yields around 95% of the bridging Au/Pt acetylide 3a and only a residual amount of the vinylene (4a, \(<5\%\)), the more hindered pair comprising the \([\text{[(PCyp}_2\text{ArXyl}_2)\text{Au]}^+\) fragment (1c) fully reversed the selectivity toward the exclusive formation of the corresponding vinylene 4c (Scheme 1). Attempts to isolate 3c by the reaction of independently prepared compounds \([\text{[(PCyp}_2\text{ArXyl}_2)\text{Au(C}_3\text{H}_4\text{)}]} (3\text{c})\) and \([\text{Pt(PBu}_3\text{)_2H]}[\text{NTf}_2]\text{)} (6)\) proved unsuccessful and resulted in intractable mixtures.

As mentioned above, this dramatic shift in regioselectivity seems to be dominated by steric effects, which contrast with prior strategies to modulate alkyne activation by FLPs that mostly rely on phosphine basicity. More importantly, it evinces the potential of FLP systems that incorporate transition-metal Lewis acids to easily tune the selectivity during bond activation processes and, as such, in subsequent catalytic applications that incorporate those activation events. As was pointed out earlier, this could be seen as a key advantage in comparison to traditional FLP designs that usually involve fluorinated boranes, since accessing these moieties already entails substantial synthetic challenges and limitations, not to mention their limited stability toward moisture and air.\textsuperscript{13} In stark contrast, the preparation of terphenylphosphines PR\textsubscript{2}Ar\textsuperscript{*} is straightforward and highly versatile,\textsuperscript{17} while the resulting gold precursors 1 are readily obtained in high yields and exhibit stability toward water or under moderate oxidizing conditions.\textsuperscript{18}

The nature of the new heterobimetallic compounds 3a and 4c was ascertained by a comparison of their \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\}\) NMR signals with those derived from their analogous species based on PMe\textsubscript{2}ArDipp\textsubscript{2}; that is, 3b and 4b, respectively.\textsuperscript{6a} The heterobimetallic nature of compounds 4 is evinced by the \(^{195}\text{Pt}\) satellites that flank the \(^{31}\text{P}\{^1\text{H}\}\) resonances associated with terphenylphosphines, which appear at 2.1 \(\text{ppm}\) \(J_{\text{PPt}} = 282 \text{ Hz}\) and 51.7 \(\text{ppm}\) \(J_{\text{PPt}} = 277 \text{ Hz}\) ppm. The bridging vinylene (\(\text{−CH═CH−}\)) moiety displays a distinctive pair of \(^1\text{H}\) NMR

![Figure 1. Au(1)/Pt(0) transition-metal-only frustrated Lewis pair (TMOFLP) combinations used in this work (Cyp = cyclopentyl; NTf\textsuperscript{−} = N(SO\textsubscript{2}CF\textsubscript{3})\textsuperscript{−} = trilimide).](https://dx.doi.org/10.1021/acs.organomet.0c00330)

**Scheme 1.** Regioselectivity in the Activation of Acetylene by TMOFLPs 1:2

Pt(0) compound \([\text{Pt(PBu}_3\text{)_2H]}\) (2) promote the cooperative activation of terminal alkynes. Our studies demonstrate the potential of using transition-metal Lewis acids (i.e., [PR\textsubscript{3}AuI]+ fragments) to control the selectivity in the activation of small molecules by tuning the steric properties of the ancillary ligands. This is particularly appealing in view of the challenging available protocols to synthesize the typically used acidic borides and their scant stability toward moisture.\textsuperscript{13}

### RESULTS AND DISCUSSION

To investigate regioselectivity effects during alkyne activation, we first examined the reactivity of the three Au/Pt bimetallic pairs depicted in Figure 1 toward acetylene, a reaction that we had previously reported with the 1b–2 combination.\textsuperscript{6a} When a dichloromethane or benzene solution of the latter pair is exposed to acetylene (0.5 bar, 25 °C), a rapid color change from bright yellow to intense orange takes place. Multinuclear NMR spectroscopic analysis revealed the formation of a clean mixture of two structurally different isomers, namely a bridging σ,π-acetylide (3b) and a rather unusual heterobimetallic vinylene (\(\text{−CH═CH−}\)) (4b), which are produced in a 4:1 ratio (Scheme 1). These metallic species are highly reminiscent of the organic products derived from the reactivity of traditional phosphine/borane FLPs with alkynes, where the prevalence of one or the other isomer typically depends on the basicity of the phosphine.\textsuperscript{14}

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signals in the region between 4.0 and 4.5 ppm that reveal scalar coupling to the $^{195}$Pt center in the range 120−200 Hz (see the Experimental Section for details). By analogy, we attribute a $^{31}$P{$_1^H$} NMR resonance at 3.67 ppm to the minor species (ca. 5%) in the PMe$_2$Ar$^{Xyli}$ system (4a), with an identical $^1$H NMR pattern comprised of signals at 4.54 and 4.37 ppm, though their corresponding $^{195}$Pt satellites could not be observed due to the low concentration of isomer 4a. Corresponding $^{13}$C NMR resonances for compounds 4b,c emerge at ca. 155 ($^1J_{CH} \approx 175$ Hz) and 115 ($^1J_{CH} \approx 190$ Hz) ppm, respectively, supporting the proposed formulation and the sp$^2$ hybridization of the carbon atoms.

The molecular structure of compounds 3a and 4c was further corroborated by X-ray diffraction studies (Figure 2).

![Figure 2](https://dx.doi.org/10.1021/acs.organomet.0c00330)

Figure 2. ORTEP diagrams of compounds 3a and 4c. For the sake of clarity most hydrogen atoms and triﬂimide anions are excluded and some substituents have been represented in wireframe format, while thermal ellipsoids are set at 50% probability.

presence of the $\sigma_{\pi}$-acetylide or vinylene linker distorts the linearity around the platinum center: P−Pt−P angles of around 165°, shifted from the ideal 180° due to the steric pressure exerted by the bulky gold fragments. The Pt1−C1 (2.016(6) Å) and Au1−C1 (2.311(5) Å) bond distances in 3a appear slightly shortened in comparison to 3b ($d_{\text{Pt1−C1}} = 2.044(7)$ Å; $d_{\text{Au1−C1}} = 2.360(7)$ Å). The average C−C bond distance of the vinylene linkers in the two crystallographically independent molecules of 4c accounts for 1.278(13) Å, comparable to those of 4b (1.287(11) Å). These and other geometric features are similar to those of previously reported related species.19

We had previously observed that the three investigated terphenylphosphines permit control of the equilibrium between complete frustration and bimetallic adduct formation.7 Thus, while a dative Pt→Au bond is immediately formed between [(PMe$_2$Ar$^{Xyli}$)Au(NTf$_2$)] (1a) and [Pt(P$^3$Bu$_3$)$_2$] (2), the formation of an identical adduct based on PCyp$_2$Ar$^{Xyli}$ is endergonic and could not be experimentally detected. An intermediate situation is reached for the medium-sized phosphine PMe$_2$Ar$^{Dipp}$, where the prevalence of the monometallic fragments or the bimetallic adduct depends upon experimental conditions. In this context, we have observed that TMOLFLPs (1:2) based on the gold precursors [(PMe$_2$Ar$^{Dipp}$)-Au(NTf$_2$)] (1b) and [(PCyp$_2$Ar$^{Xyli}$)Au(NTf$_2$)] (1c) are considerably more active toward alkyne activation in comparison to that one built on [(PMe$_2$Ar$^{Xyli}$)Au(NTf$_2$)] (1a). While full conversion toward compounds 3 and 4 was recorded by the time of placing the sample in the NMR probe (<5 min) in the case of using 1b:2 or 1c:2, the analogously transforming essayed with 1a required up to 24 h to reach completion under otherwise identical conditions (C$_2$H$_2$, 0.5 bar, 25 °C, toluene or C$_6$D$_6$). This fact speaks in favor of a genuine FLP mechanism that imposes an energetic demand to overcome the Pt→Au bond cleavage prior to acetylene activation, a requirement that only applies to the less hindered gold precursor 1a. Similar effects have been observed in the gold-catalyzed addition of P-nucleophiles to alkynes.20

In addition, it is key to highlight that the cooperative reactivity depicted in Scheme 1 contrasts with that of the individual Au(I) or Pt(0) fragments (Scheme 2). For instance, [Pt(P$^3$Bu$_3$)$_2$] (2) readily catalyzes acetylene polymerization, evinced by the rapid formation of a purple-black solid accompanied by the disappearance of a $^1$H NMR resonance at 1.34 ppm due to C$_2$H$_2$, while signals due to 2 remained unchanged. At variance, no indication of polyacetylene formation is apparent when gold...
is also present in solution. In the case of the individual gold compounds 1 there is no sign of chemical transformation in the short term (ca. 30 min), while at longer reaction times the gold trifluoride precursors evolve to bridging $\sigma_\pi$-acetylide complexes 7 (Scheme 2A), albeit only in moderate yields accompanied by other unidentified gold-containing species.

Having the previous experimental findings on hand, we were interested in further understanding the cooperative action of TMFOFLPs 1.2 to gain a fundamental knowledge of significance for future catalytic applications. As such, we initially wondered about the possible role of acetylide-bridged digold compounds such as 7 as precursors toward complexes 3 and 4. In fact, the reaction between 7b and $[\text{Pt}(\text{P}^\text{Bu}_3)_2\text{H}]\lbrack\text{NTf}_2 \rbrack$ (6) immediately yielded the corresponding heterobimetallic $\sigma_\pi$-acetylide compound 3b, where the unsaturated linker is now $\sigma$-bonded to the platinum center instead of the gold nucleus. Nevertheless, the complete absence of the vinylene isomer 4b during the latter reaction would require an additional competing route to provide access to this unusual bimetallic motif, which actually is the exclusive isolated isomer for the bulkier P(5-cyano-1-pyridyl)Ar$_2$-based system (Scheme 1). Moreover, the formation of compounds 7 requires several hours to proceed to appreciable conversions, while the activation of acetylene by 1:2 pairs is immediate (<5 min), except for the gold precursor 1a bearing P(5-C$_3$H$_7$-2-tolyl)$_2$ (5a), which as noted earlier takes around 24 h to convert into 3a in the presence of $[\text{Pt}(\text{P}^\text{Bu}_3)_2\text{H}]_2$ (2).

To further investigate the mechanism and the reasons for the drastically different regioselectivity observed, we carried out computational studies (DFT, $\omega$B97XD/6-31G(d,p)+SDD). Focusing on the system based on P(5-C$_3$H$_7$-2-tolyl)$_2$, we began searching for initial acetylene activation steps by approaching the acetylene molecule to the individual Au(I) (1b) and Pt(0) (2) fragments, assuming that Au–Pt dissociation is a prerequisite for alkynide activation, as deduced from the reduced reactivity of the pair 1a:2 in comparison to 1b:2 and 1c:2 and previous computational results. Interestingly, the formation of 3 and 4 seems to share a common intermediate, namely a Au(I) acetylene adduct of formula $[(\text{PR}_3\text{Ar})\text{Au}(\text{C}_2\text{H}_2)]^+$ (9). The formation of this type of $\pi$ complex has been previously proposed in the context of alkynes 12,14a and alkene $\pi$ activation by P/B pairs, but no experimental proofs of their existence have been reported. In an attempt to spectroscopically identify such an intermediate, we recorded the formation of a new gold-containing species by low-temperature NMR (−80 °C) as the major species (ca. 80%) upon exposing a CD$_2$Cl$_2$ solution of 1b to an acetylene atmosphere. This species exhibits a distinctive $^1\text{H}$ NMR signal at 3.43 ppm that correlates with a $^3\text{P}$ NMR resonance at −0.3 ppm (in comparison to $\delta_\text{P}$ = 9.9 ppm for 1b) and presents dynamic exchange with free acetylene ($\delta_\text{P}$ = 2.11 ppm) as seen by EXSY NMR experiments, while other $^1\text{H}$ NMR resonances are comparable to those of 1b. This finding constitutes an additional benefit of TMFOFLPs for mechanistic investigations in frustrated systems, since they provide additional modes of stabilizing otherwise fleeting intermediates.

With the acetylene adduct 9b as the starting point, our calculations indicate that the attack of the platinum compound 2 over 9b leads to either of the two bimetallic isomers 3b and 4b depending on the trajectory followed by 2 while it approaches 9b (Figure 3). Thus, if 2 approaches the acetylene adduct along the Au–C$_2$H$_2$ direction, the corresponding vinylene 4b forms ($\Delta^T = 23.4$ kcal mol$^{-1}$ from the 1b:2 Lewis pair + acetylene), in a process somehow reminiscent of the gold-mediated nucleophilic attack over activated alkynes (e.g., gold-catalyzed hydroamination). In contrast, the alignment of the basic 2 in an orthogonal disposition with respect to the Au–C$_2$H$_2$ bond results in deprotonation of the activated acetylene (15.6 kcal mol$^{-1}$ for the pair 1b:2) to yield the corresponding Au(I) terminal acetylide $[(\text{PM}^\text{Bu}_3\text{Ar}^{\text{p}2})\text{Au}(\text{C}≡\text{CH})]_2$ (5b) and $[\text{Pt}(\text{P}^\text{Bu}_3)_2\text{H}]\lbrack\text{NTf}_2 \rbrack$ (6). These two fragments readily rearrange to intermediates $[(\text{PR}_3\text{Ar})\text{Au}(\mu-\eta^1\eta^2\text{C}≡\text{C}≡\text{CH})\text{Pt}(\text{H})(\text{P}^\text{Bu}_3)_2]\}$ (A) that subsequently evolve to compounds 3 by rapid $\sigma_\pi$ isomerization of the bridging $\mu$-C≡CR unit. In experimental agreement, the reaction of independently synthesized $[(\text{PM}^\text{Bu}_3\text{Ar}^{\text{p}2})\text{Au}(\text{C}≡\text{CH})]_2$ (5b) and $[\text{Pt}(\text{P}^\text{Bu}_3)_2\text{H}]\lbrack\text{NTf}_2 \rbrack$ (6) rapidly yields complex 3b. As mentioned above, this does not apply to compound 5c, whose reaction with 6 resulted in a complex mixture of products that include decomposition into elemental gold. Nevertheless, the corresponding $[(\text{PCyp}_2\text{Ar}^{\text{XL}})\text{Au}(\mu-\eta^2\eta^2\text{C}≡\text{C}≡\text{CH})\text{Pt}(\text{H})(\text{P}^\text{Bu}_3)_2]\}$ (3c) has not been detected during the bimetallic activation of acetylene. An alternative orthogonal mechanism involving the initial oxidative addition of acetylene over 2, followed by cis–trans isomerization and coupling with 1, was ruled out on the basis of significantly higher overall activation barriers (see Figure S2).

Information on the activation of the simplest alkyn (C$_2$H$_2$) by FLPs is rather scarce. For the sake of completeness and to better compare our results with prior studies on main-group FLPs, we decided to test other more commonly employed triply bonded hydrocarbons. With regard to internal alkynes, all our attempts to access bimetalllic vinylenes were unsuccessful. Reactions of 1:2 pairs with diphenylacetylene, 2-butyne, and 1,4-diphenylbutadiyne did not result in the formation of any new species even under more forcing experimental conditions. At variance, addition of phenylacetylene to an equimolar mixture of 1 and 2 provided phosphine-dependent divergent outcomes derived from C(sp)$^\pi$–H bond cleavage (Scheme 3). In parallel with acetylene activation with the more congested pairs based on 1b,c, the reaction of these systems with PhC≡CH was also immediate. In contrast, while acetylene activation took up to 24 h for the nonfrustrated 1a:2 pair, the reaction was complete after around 15 min in the case of phenylacetylene.

The appearance of a distinctive low-frequency $^1\text{H}$ NMR resonance at around −10 ppm flanked by $^{195}$Pt satellites ($J_{\text{P}^\text{Bu}_3} = 608$ Hz, 1a:2; $J_{\text{P}^\text{Bu}_3} = 533$ Hz, 1b:2 and 1c:2) prompted us to

**Figure 3.** Energy profiles for the formation of the acetylide and vinylene complexes 3b and 4b from the common intermediate 9b and platinum(0) compound 2. The origin of energies is set to the 1b:2 Lewis pair + acetylene.
Scheme 3. Product Distribution from the Activation of Phenylacetylene by TMOFLP Pairs 1:2

believe that corresponding heterobimetallic $\sigma,\pi$-acetylide complexes were formed in all cases. However, a more careful analysis revealed unexpected differences in product distribution for the less bulky terphenylphosphine PMe$_2$Ar$^{XYl}_2$ in comparison to the more hindered systems (Scheme 3). Extracting the crude reaction mixtures with pentane permitted isolation of the same platinum-containing compound 10 for the pairs 1b:2 and 1c:2, while the less hindered gold fragment 1a did not lead to any metallic species soluble in nonpolar hydrocarbon solvents. An infrared band at 2090 cm$^{-1}$ was recorded for a Pt-hydride ligand in 10, while characteristic $^{13}$C($^1$H) NMR resonances at 118.8 and 117.6 ppm accounted for a $\sigma$-bonded acetylide ligand. On the basis of these spectroscopic features and the high solubility, we proposed a molecular formulation for 10 as $[\text{Pt(P} \text{Bu$_3$)$_2$(H)}]-(\text{C}═\text{CPh})$; that is, the formal oxidative addition of phenylacetylene over Pt(0) compound 2. This assumption was further corroborated by X-ray diffraction analysis (see Figure S3). Nevertheless, it is important to remark that compound 2 does not react with phenylacetylene even after longer reaction times (48 h) or at elevated temperatures (80 °C), which suggests a cooperative action between platinum and gold to account for alkyn C–H activation.

The only detectable gold-containing species in these reactions were assigned to the corresponding bridging $\sigma,\pi$-acetylide digold complexes 11. Those where characterized by $^{31}$P($^1$H) NMR signals at 0.4 (11b) and 53.9 (11c), shifted to higher frequencies with respect to their precursors 1 (cf. −11.9 for 1b and 48.8 ppm for 1c), in agreement with other related examples. Also similar to those results, the presence of a single $^{31}$P resonance for each compound suggests rapid exchange of the $\sigma,\pi$ coordination in solution. However, the process is frozen in the solid state. An ORTEP representation of the molecular structure of 11b is shown in Figure 4a. The $\sigma,\pi$ coordination of the acetylide is reflected by a nonsymmetric arrangement characterized by bond distances of 2.021(10) and 2.209(9) Å for the Au2–C1 and Au1–C1 bond distances, respectively. The Au1 center is also connected to C2 by a slightly longer bond length of 2.310(9) Å. The presence of an aurophile interaction can be inferred from a Au1–Au2 distance of 3.366(1) Å, which is faintly elongated in comparison to its related acetylide analogue $[\text{Au$_2$(μ-C═CH)}]$ ($d_{\text{Au1–Au2}} = 3.31$ Å), likely as a result of the higher steric pressure exerted by phenylacetylene. Digold complexes 11b,c were accompanied by equimolar amounts of $[\text{Pt(P} \text{Bu$_3$)$_2$(H)}]$ (6) that could not be washed out with pentane, as evinced by a broad low-frequency $^1$H NMR resonance at 1.16 ppm ($J_{\text{HP}} = 6.5$ Hz).

As noted earlier, the reaction of the less hindered 1a:2 pair with phenylacetylene yielded a divergent result. C(sp)$^3$–H activation became evident by the presence of a distinctive hydridic $^1$H NMR resonance at $−10.4$ ppm ($J_{\text{HP}} = 14$ Hz, $J_{\text{HP1}} = 608$ Hz). However, a single platinum complex was formed in this case, which resonates at 82.2 ppm ($J_{\text{PP1}} = 2810$ Hz) in its $^{31}$P($^1$H) NMR spectrum and could not be washed out using nonpolar hydrocarbon solvents. The corresponding C–C$\equiv$C stretching frequency rendered an infrared band shifted to lower wavenumbers ($\nu_{\text{C}═\text{C}} = 1982$ cm$^{-1}$; cf. 2048 cm$^{-1}$ for 11b, 2029 cm$^{-1}$ for 11c, and 2090 cm$^{-1}$ for 10), while sp-hybridized carbon atoms render $^{13}$C($^1$H) NMR resonances at lower frequencies (91.1 and 85.9 ppm) in comparison to compounds 11b,c and 10 (116–125 ppm). These observations expose the divergent product distribution derived from using phosphines with different steric profiles. Since the recorded parameters equate with heterobimetallic $\sigma,\pi$-acetylide compounds 3, we assumed an analogous structure for this complex (12a), a premise that we could substantiate by X-ray diffraction analysis (Figure 4b). The bulkier nature of the phenylacetylide moiety with respect to the unsubstituted acetylide in 3a is likely the cause of a more intense distortion of the T-shaped platinum fragment, where a P–Pt–P angle of 156.71(8)° is recorded (cf. 162.76(5)° for 3a). The close proximity between the acetylide phenyl fragment and the ortho substituents of one of the flanking
aryl rings of the terphenyl moiety may be responsible for the dissimilar product distributions found between PMe$_2$ArDipp$_2$ vs PMe$_2$ArDipp$_2$/PCyp$_2$ArXyl$_2$.

On the basis of our experimental and computational studies on acetylene activation, initial formation of a gold−alkyne adduct like 9 seems most plausible. The slightly higher acidity of phenylacetylene, as well as its higher size, may account for the prevalence of the deprotonation pathway in detriment of the 1,2-addition route toward vinylene structures, which were not detected. In turn, the dissimilar reaction products depicted in Scheme 3 might be understood on steric grounds. Thus, selective formation of compounds 11 for the bulkier PMe$_2$ArDipp$_2$/PCyp$_2$ArXyl$_2$-based systems could be the result of a higher sterically clash between the tert-butyl substituents on the platinum fragment and the phenyl moiety of the gold-bound phosphine. In contrast, the reduced steric pressure introduced by PMe$_2$ArXyl$_2$ may permit easier access to the heterobimetallic compound 12a, analogous to its unsubstituted acetylide version (3a).

We thought of interest to carry out several further experiments to shed some light into the operating cooperative mechanism. In the same manner as we observed for acetylene activation, the reactivity of the individual metallic fragments starkly contrasts with that of the bimetallic pairs. Accordingly, platinum compound 2 does not exhibit any reactivity toward phenylacetylene even after heating at 80 °C for 48 h (Scheme 4a). In reaction of 1 and phenylacetylene toward 11. Catalytic amounts of compound 6 may also derive from the cooperative Au/Pt C(sp)−H activation of phenylacetylene by a deprotonation mechanism. As anticipated, immediate conversion of 2 into 10 was observed at room temperature using either 1 or 6 in catalytic amounts as low as 2 mol % (Scheme 4b). The reaction of the independently prepared 10 with 1a leads to 3a as the major species by NMR analysis, though other unidentified side products are also formed. The reaction of the independently synthesized neutral σ-acetylide complex [(PMe$_2$ArDipp$_2$)Au-(C≡CPh)]$^+$ (13b; ORTEP diagram in Figure S4) with 1b yielded the expected digold σ,π-acetylide 11b under mild conditions (Scheme 4c). This result parallels the reactivity previously described for NHC-based gold complexes, where the latter transformation proceeds smoothly, as also occurs with the parent unsubstituted acetylide (C≡CH) fragment. Thus, terminal acetylides of type 13 may be regarded as key intermediates toward compounds 11 during the activation of PhCCH.

On consideration of all the information discussed above, Scheme 5 contains an overall mechanistic picture to account for the phosphine-dependent product distribution during the activation of alkynes. The common gold acetylene adduct 9 is proposed to be a key intermediate. While both deprotonation and 1,2-addition mechanisms (blue and red in Scheme 5, respectively) are viable for acetylene, only the deprotonation pathway seems to be operative in the case of the more acidic phenyl-substituted alkene. Once the latter is deprotonated to form an equimolar mixture of 13 and 6, steric factors appear to dominate the final product distribution. The combination of the more hindered terphenylphosphines with the bulkier phenylacetylene prevents formation of the corresponding Au/Pt heterobimetallic adducts likely due to a steric clash, while the latter is the only observed complex in the PMe$_2$ArXyl$_2$ system. In turn, terminal gold acetylides 13, although unable to react with [Pt(PCy$_3$)$_3$$_2$H]$^+$ (6), rapidly yield the corresponding digold σ,π-acetylide complexes 11 upon combination with still unreacted triflimide complexes 1. We can also infer from our experimental observations that several of the transformations depicted in Scheme 5 constitute dynamic equilibria that are dependent on reaction conditions.

**CONCLUSIONS**

In summary, we provide evidence for the potential of a cooperative Au(1)/Pt(0) bimetallic system that behaves as a metal-only frustrated Lewis pair for the activation of small molecules. We have demonstrated that subtle modifications of the phosphine ligands bound to gold have a strong effect on the regioselectivity of acetylene activation. Thus, simply by adjusting the steric hindrance of those phosphines, we have been able to select the operating mechanism (deprotonation vs 1,2-addition) during acetylene activation with full specificity. This is possible without the need to alter the basicity of the platinum(0) moiety, thus contrasting with main-group FLP systems. Moreover, ligand modification also permitted us to diverge from the product distribution that results from C−H bond cleavage in phenylacetylene. While the less congested system based on PMe$_2$ArXyl$_2$ yields a heterobimetallic σ,π-acetylide compound, the more hindered pairs constructed around PMe$_2$ArDipp$_2$ and PCyp$_2$ArXyl$_2$ resulted in the formation of equimolar mixtures of digold σ,π-acetylide compounds, [Pt(PCy$_3$)$_3$$_2$H)]$^+$, and [Pt(PCy$_3$)$_3$$_2$(C≡CPh)]. These results highlight one of the advantages of incorporating
transformation metals into frustrated designs, namely the ability to easily tune the stereoelectronic properties of the acidic site, in turn a challenging task in traditional FLPs that rely on the electrophilicity of fluorinated boranes. The straightforward control of these properties in TMFLPs may be exploited for the development of more selective catalytic transformations drawn on the concept of frustration.

### EXPERIMENTAL SECTION

**General Considerations.** All preparations and manipulations were carried out using standard Schlenk and glovebox techniques, under an atmosphere of argon and of high-purity nitrogen, respectively. All solvents were dried, stored over 4 Å molecular sieves, and degassed prior to use. Toluene (C7H8) and 2-pentane (10 mL) and stored at −40 °C overnight to yield compound 3a. Elemental analyses were performed by standard Schlenk and glovebox techniques. Under an atmosphere of argon and of high-purity nitrogen, respectively. All chemicals were commercially available and were used as received. Spectra were referenced to external SiMe4 (δ, ppm) using the residual proton solvent peaks as internal standards (1H NMR experiments) or the characteristic resonances of the solvent nuclei (13C NMR experiments), while 31P was referenced to H3PO4. Spectral assignments were made by routine one- and two-dimensional NMR experiments, while 31P was referenced to H3PO4. Spectral assignments were made by routine one- and two-dimensional NMR experiments. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

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**Scheme 5. Overall Representation of the Proposed Pathways to Account for Product Distribution during Alkyne Activation**

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**Figure 5. General labeling scheme used for 1H and 13C{1H} NMR assignments.**

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**Table 1.** Data for the Crystal Structure of Compound 2a.

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**References:**

1. C52H83AuF6NO4P3PtS2: C, 43.1; H, 5.8; N, 1.0; S, 4.4.
2. Found: C, 43.1; H, 5.8; N, 1.1; S, 4.4.
3. 1H NMR (400 MHz, CD2D2O, 25 °C): δ 7.26 (t, 2 H, JHH = 7.6 Hz, Hα), 7.18 (m, 1 H, Hβ), 7.15 (d, 4 H, JHH = 7.6 Hz, Hβ).
4. 13C{1H} NMR (100 MHz, CD2D2O, 25 °C): δ 159.4 (4 C), 113 (3 C), 198 Hz, CH3).

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Organometallics 2020, 39, 2534–2544
at room temperature for 18 h. The volatiles were removed in vacuo, and a toluene solution containing a small excess (1.2 equiv) of Mg(Cp)2 was added dropwise. The mixture was stirred for an additional 2 h at 40 °C. The volatiles were removed in vacuo, and the residue was extracted with pentane. Evaporation of the solvent led to compound 5c as a white powder (35 mg, 18%). Gold acetylides are potentially explosive and should be handled with caution. Anal. Calcd for C10H16AuCl3P: C, 60.4; H, 6.0. Found: C, 60.4; H, 5.8. 1H NMR (400 MHz, C6D6, 25 °C): δ 7.29 (t, 2 H, JCH = 7.6 Hz, H2), 7.09 (d, 4 H, JCH = 7.6 Hz, H2), 6.94 (td, 1 H, JCH = 7.6 Hz, JHH = 1.6 Hz, H4), 6.64 (dd, 2 H, JHH = 7.6 Hz, JHP = 2.17 Hz, H5), 2.17–2.05 (m, 2 H, CH2), 1.97 (s, 12 H, Me3G), 1.78 (d, 18 H, JCH = 5.5 Hz, Au=CH2), 1.7–1.1 (m, 16 H, CH2). 31P{1H} NMR (100 MHz, C6D6, 25 °C): δ 148.8 (d, 1H, JCP = 7 Hz, CH2), 141.9 (d, 1H, JCP = 5 Hz, CH2), 136.3 (C3), 132.0 (d, 1H, JCP = 7 Hz, CH2), 130.8 (d, 1H, JCP = 5 Hz, CH2), 128.5 (CH), 83.3 (JCP = 10 Hz, C3), 82.2 (JCP = 10 Hz, C5), 78.5 (JCP = 10 Hz, C7), 46.5 (JCP = 10 Hz, C9). IR (Nujol): ν(C=H) = 3144 cm⁻¹. For comparison studies was grown by slow crystallization from solution of compound 1b as a white powder (70 mg, 38%). Anal. Calcd for C10H16AuCl3P: C, 60.4; H, 6.0. Found: C, 60.4; H, 5.8. 1H NMR (400 MHz, C6D6, 25 °C): δ 7.32 (t, 2 H, JCH = 7.6 Hz, H2), 7.09 (d, 4 H, JCH = 7.6 Hz, H2), 6.94 (td, 1 H, JCH = 7.6 Hz, JHH = 1.6 Hz, H4), 6.64 (dd, 2 H, JHH = 7.6 Hz, JHP = 2.17 Hz, H5), 2.17–2.05 (m, 2 H, CH2), 1.97 (s, 12 H, Me3G), 1.78 (d, 18 H, JCH = 5.5 Hz, Au=CH2), 1.7–1.1 (m, 16 H, CH2). 31P{1H} NMR (100 MHz, C6D6, 25 °C): δ 148.8 (d, 1H, JCP = 7 Hz, CH2), 141.9 (d, 1H, JCP = 5 Hz, CH2), 136.3 (C3), 132.0 (d, 1H, JCP = 7 Hz, CH2), 130.8 (d, 1H, JCP = 5 Hz, CH2), 128.5 (CH), 83.3 (JCP = 10 Hz, C3), 82.2 (JCP = 10 Hz, C5), 78.5 (JCP = 10 Hz, C7), 46.5 (JCP = 10 Hz, C9). IR (Nujol): ν(C=H) = 3144 cm⁻¹. For comparison studies was grown by slow crystallization from solution of compound 1b as a white powder (70 mg, 38%). Anal. Calcd for C10H16AuCl3P: C, 60.4; H, 6.0. Found: C, 60.4; H, 5.8. 1H NMR (400 MHz, C6D6, 25 °C): δ 7.32 (t, 2 H, JCH = 7.6 Hz, H2), 7.09 (d, 4 H, JCH = 7.6 Hz, H2), 6.94 (td, 1 H, JCH = 7.6 Hz, JHH = 1.6 Hz, H4), 6.64 (dd, 2 H, JHH = 7.6 Hz, JHP = 2.17 Hz, H5), 2.17–2.05 (m, 2 H, CH2), 1.97 (s, 12 H, Me3G), 1.78 (d, 18 H, JCH = 5.5 Hz, Au=CH2), 1.7–1.1 (m, 16 H, CH2). 31P{1H} NMR (100 MHz, C6D6, 25 °C): δ 148.8 (d, 1H, JCP = 7 Hz, CH2), 141.9 (d, 1H, JCP = 5 Hz, CH2), 136.3 (C3), 132.0 (d, 1H, JCP = 7 Hz, CH2), 130.8 (d, 1H, JCP = 5 Hz, CH2), 128.5 (CH), 83.3 (JCP = 10 Hz, C3), 82.2 (JCP = 10 Hz, C5), 78.5 (JCP = 10 Hz, C7), 46.5 (JCP = 10 Hz, C9). IR (Nujol): ν(C=H) = 3144 cm⁻¹. For comparison studies was grown by slow crystallization from solution of compound 1b as a white powder (70 mg, 38%). Anal. Calcd for C10H16AuCl3P: C, 60.4; H, 6.0. Found: C, 60.4; H, 5.8. 1H NMR (400 MHz, C6D6, 25 °C): δ 7.32 (t, 2 H, JCH = 7.6 Hz, H2), 7.09 (d, 4 H, JCH = 7.6 Hz, H2), 6.94 (td, 1 H, JCH = 7.6 Hz, JHH = 1.6 Hz, H4), 6.64 (dd, 2 H, JHH = 7.6 Hz, JHP = 2.17 Hz, H5), 2.17–2.05 (m, 2 H, CH2), 1.97 (s, 12 H, Me3G), 1.78 (d, 18 H, JCH = 5.5 Hz, Au=CH2), 1.7–1.1 (m, 16 H, CH2). 31P{1H} NMR (100 MHz, C6D6, 25 °C): δ 148.8 (d, 1H, JCP = 7 Hz, CH2), 141.9 (d, 1H, JCP = 5 Hz, CH2), 136.3 (C3), 132.0 (d, 1H, JCP = 7 Hz, CH2), 130.8 (d, 1H, JCP = 5 Hz, CH2), 128.5 (CH), 83.3 (JCP = 10 Hz, C3), 82.2 (JCP = 10 Hz, C5), 78.5 (JCP = 10 Hz, C7), 46.5 (JCP = 10 Hz, C9). IR (Nujol): ν(C=H) = 3144 cm⁻¹.
Correction for Anharmonic Vibrations

The zero-point corrections, and thermal corrections were made to the entropy contribution was not overestimated.34 These anharmonic corrections were calculated with the Goodvibes code.35 The CYLview visualization software has been used to create some of the figures.36

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00330. Additional computational details, X-ray structural data, and NMR spectra of new compounds (PDF)

Cartesian coordinates of the calculated structures (XYZ)

Accession Codes

CCDC 1965525, 1965526 and 1986501–1986504 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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