

Alumina-mediated π -Activation of Alkynes

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ABSTRACT: The ability to induce powerful atom-economic transformation of alkynes is the key feature of carbophilic π -Lewis acids such as gold- and platinum-based catalysts. The unique catalytic activity of these compounds in electrophilic activations of alkynes is explained through relativistic effects enabling efficient orbital overlapping with π -system. For this reason, it is believed that noble metals are indispensable components in the catalysis of such reactions. In this study we report that thermally activated γ -Al₂O₃ activates enynes, diynes, and arene-ynes in a manner enabling reactions that were typically assigned to the softest π -Lewis acids, while some were known to be triggered exclusively by gold catalysts. We demonstrate the scope of these transformations and suggest a qualitative explanation of this phenomenon based on Dewar-Chatt-Duncanson model confirmed by DFT calculations.

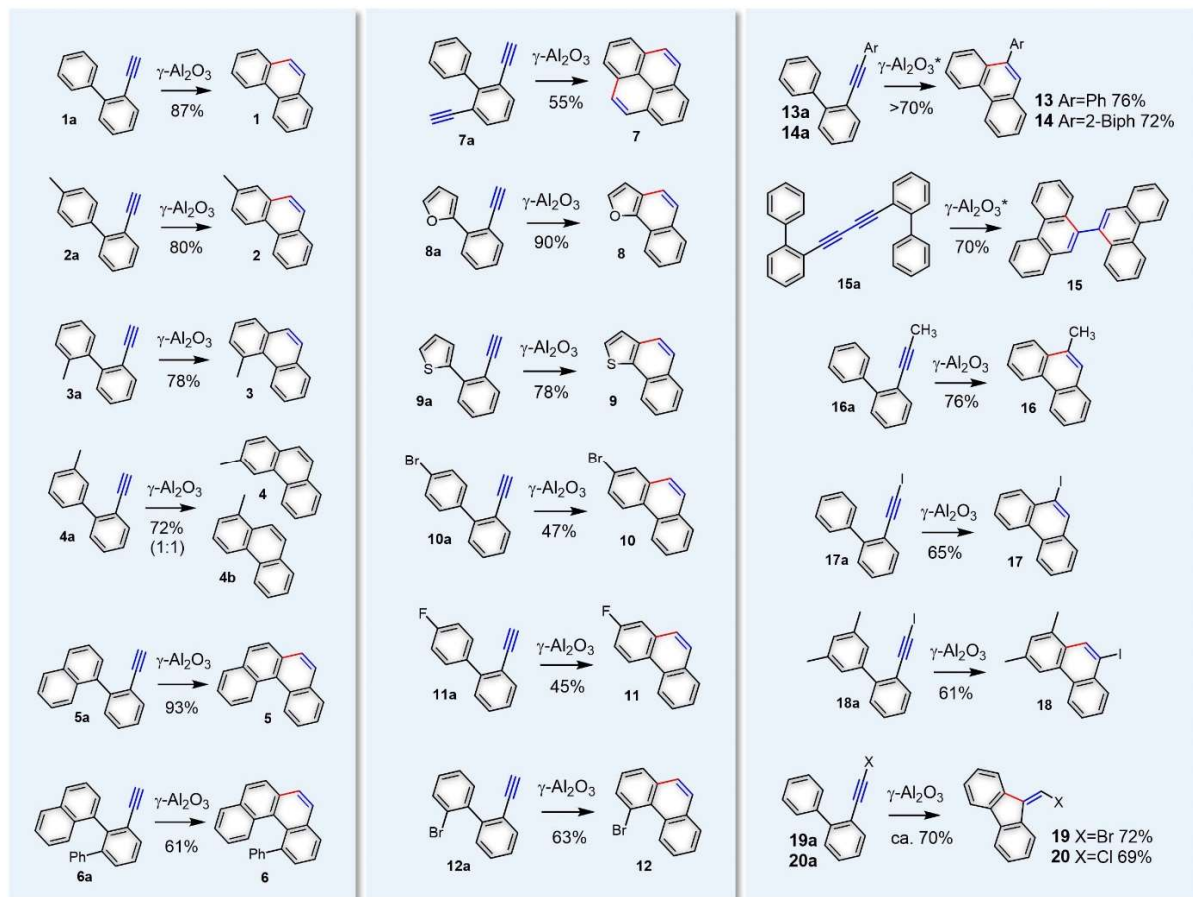
INTRODUCTION

Electrophilic activation of alkynes is a powerful synthetic tool enabling access to a broad range of organic scaffolds of a various complexity. Carbophilic π -Lewis acids such as complexes of Au(I),^{1,2} Pt(II),³ Ru(II),⁴ etc. constitute the group of the most efficient catalysts in this realm. The bonding of transition metals (TMs) with alkynes is usually described within the Dewar-Chatt-Duncanson (DCD) model,⁵ where the major interactions include two components: (a) σ -donation arising from the overlap of an empty metal orbital and the π -system of the ligand, (b) π -back-donation originating from a π -interaction of a filled metal d-orbital with an antibonding π^* -orbital of the alkyne. The unique catalytic properties of these metals are therefore inherently dependent on the presence of the filled d-orbitals, which enable the reactivity beyond the reach of Brønsted acids. Moreover, selective activation of alkynes by gold, platinum, and mercury catalysts is attributed to the relativistic effects,⁶ which reach a maximum in the periodic table with these metals and particularly with gold.⁷

In this study we provide the first evidence that elements bearing no filled d-orbitals are capable of a similar catalytic activity. Thus, we have found that activated γ -alumina enables atom-economic transformations of alkynes that have been previously assigned exclusively to the softest π -Lewis acids. We compare the outcomes of these transformations upon catalysis with γ -Al₂O₃ and noble metal-counterpart and suggest a possible explanation for the observed similarities and differences within the DCD model frameworks.

During our studies on alumina-mediated C-F bond activation⁸⁻¹⁰, we have serendipitously come across the cycloisomerization of **1a** into **1** on thermally activated Al₂O₃ (Scheme 1).¹¹ Interestingly, such 6-*endo* annulation of 2-ethynylbiaryls is a landmark transformation that was found by Fürstner et al. to be selectively induced with soft π -Lewis acids, primarily PtCl₂, AuCl₃, GaCl₃, and InCl₃.^{12,13} Surprised by this observation, we have decided to study the transformation in more details. Thus, full conversion of **1a** on Al₂O₃ can be achieved in solid-state already at 40°C; however, heating up to 90°C allows reducing the time of the reaction to a few hours with an excellent yield and without loss of the selectivity. Based on the previous report,¹⁴ we presume that Al₂O₃ plays a role of catalyst since the quantity of the converted substrate outnumbers the roughly estimated amount of the active defects by two orders of magnitude (Table S1). Moreover, the exploited alumina can be recycled and reactivated at least five times without loss of efficiency (Table S2). Aimed to investigate the scope of the transformation, we have exposed a series of ortho-ethynyl biaryls **2a-20a** to activated alumina (Scheme 1).

SCHEME 1. Scope of 6-endo cycloisomerization of *ortho*-ethynylbiaryls promoted by activated γ -alumina. The reactions were run in the solid-state for 6 hours at 90 °C (terminal alkynes) or 190 °C (internal alkynes marked with *) using 50 mg of the substrates and 10 g of γ -Al₂O₃ under vacuum. Isolated yields are given. In the case of **6**, the yield is based on ¹H-NMR quantification, as the compound was isolated as a mixture with impurities (<10%).



RESULTS AND DISCUSSION

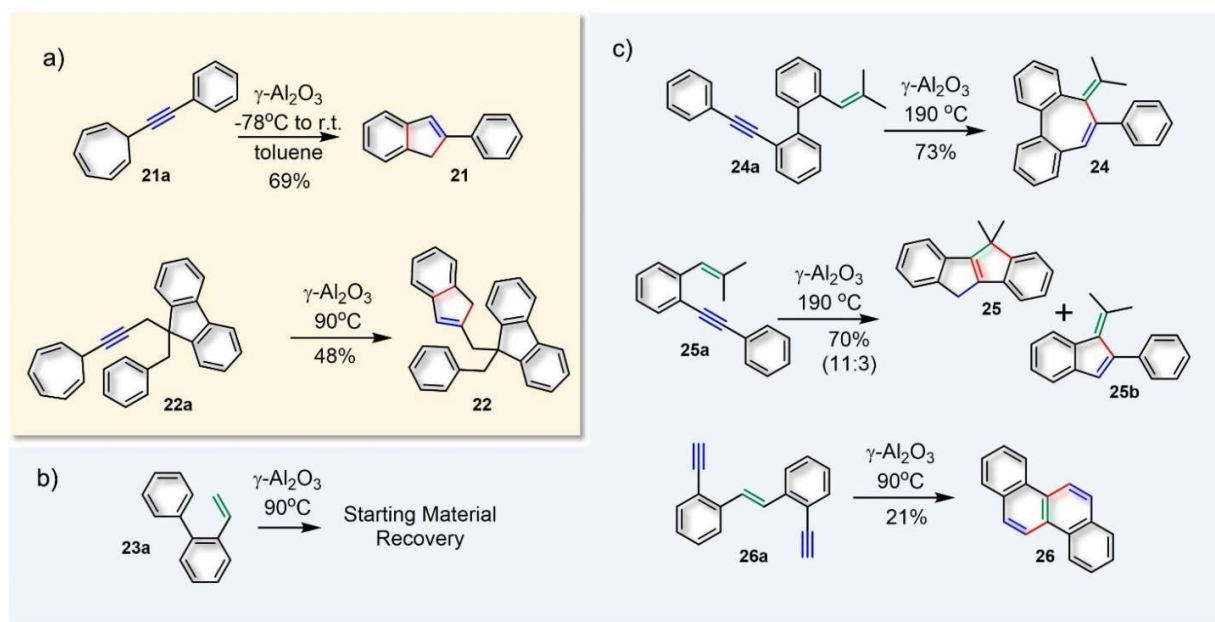
The weak donating groups decorating arene, such as methyl-substituents, do not significantly influence the outcome of the reaction, while the increase of the aromatic moiety (from benzene to naphthalene) leads to nearly quantitative conversion e.g. **5a** into [4]helicene. Noteworthy, the reaction proceeds even in the case of sterically hindered substrates such as **6a**, whereas TM catalysis requires introduction of cationic ligands to achieve such a challenging transformation.¹⁵ Two-fold hydroarylation of **7a** is another remarkable transformation that has been reported to occur in the presence of the gold catalyst.¹⁶ In contrast to this report, alumina-mediated annulation does not suffer the competing 5-exo cyclization and produces pyrene in substantially higher yields. Furan and thiophene derivatives **8a** and **9a** react readily, giving heterocyclic compounds **8** and **9** in good yields and thus expanding the scope to the synthesis of heteroarenes. Further investigation has revealed that alumina enables cycloisomerization even in the case of electron-poor substrates such as **10a-12a**. Thus, the developed technique overcomes unfavorable electronic factors, although they hinder full conversion.

We have found that 6-endo cyclization can be expanded also to internal arylalkynes. Unlike terminal acetylenes, readily isomerized under ambient conditions, internal triple bond requires higher temperatures. Arylalkynes **13a-15a** remain intact below 120°C, whereas 190°C is a sufficient temperature to achieve the full conversion within several hours. The need for higher temperatures is presumably linked to the steric hindrance caused by the substitution of hydrogen with bulky groups. At the same time, **16a-20a** can be easily converted already at 90°C. This fact supports the assumption that elevated temperatures are required due to steric hindrance rather than absence of acidic hydrogen. Interestingly, *o*-iodoalkynebiaryl **18a** reacts with alumina to give the phenanthrene **18** in which iodine has suffered a 1,2-shift. The same phenomenon occurs upon reaction of *o*-haloalkynebiaryls with AuCl,¹² whereas other π -acids do not induce such a shift of halogens. Meanwhile, the introduction of bromine or chlorine substituent on alkyne inverts the regioselectivity of the alumina-mediated transformation towards 5-exo pathway yielding **19** and **20**, respectively.

π -Acid catalysis is a powerful technique to transform alkenes or alkynes into valuable organic scaffolds or building

blocks, however, not all π -activators act in the same manner. Thus, cycloisomerizations of enynes via non-classical cation intermediates is a distinct feature of the soft π -Lewis acids.^{3,17-19} As described by Echavarren et al., gold(I) complexes treat 7-alkynylcycloheptatrienes as an 1,6-enyne that undergoes skeletal reorganization into the regioisomeric indenenes via formation of fluxional barbaralyl cations.²⁰ In contrast, other common π -acids such as PtCl₂ and GaCl₃ were found to be catalytically inactive. Similarly to gold catalysts, activated γ -alumina induces regioselective isomerization of **21a** into indene derivative **21** (Scheme 2a). Moreover, **21a** was found to undergo the transformation extremely fast i.e. within several minutes at ambient temperatures, whereas the cooling of the reaction mixture enabled the highest yield of 69%.

SCHEME 2. Alumina-mediated cycloisomerization of enynes. (a) Isomerization of 7-alkynylcycloheptatrienes. (b) Inertness of alkenes. (c) Transformations of 1,5- and 1,7- enynes. In the case of **25**, the yield is based on ¹H-NMR quantification, as the compound was isolated as a mixture with impurities (<10%).



We have found that the alkene **23a** remains intact upon exposure to γ -Al₂O₃ at 90°C, which indicates that cycloisomerizations of enynes are likely triggered by the activation of the triple C-C bonds. The alumina-mediated activation of alkynes also triggers cycloisomerization of 1,7- and 1,5-enynes (Scheme 2c). For example, **24a** undergoes 7-endo annulation, while **25a** follows 5-exo pathway leading to the mixture of **25** and **25b**, both of which are formed from the same intermediate via different proton shifts²⁴. Interestingly, 7-endo regioselectivity in the case of **24a** could not be efficiently achieved with gold-catalysts²⁵, which primarily induce 6-exo pathway. Interestingly, **25a** does not undergo the observed cycloisomerizations upon exposure to some common Brønsted acids. Thus, the corresponding enyne does not react or decomposes to give complex mixtures (Table S4). Meanwhile, in analogy with Ru(II)-catalysts, alumina converts diyne-ene species **26a** via tandem cyclization into chrysene **26**.²⁶

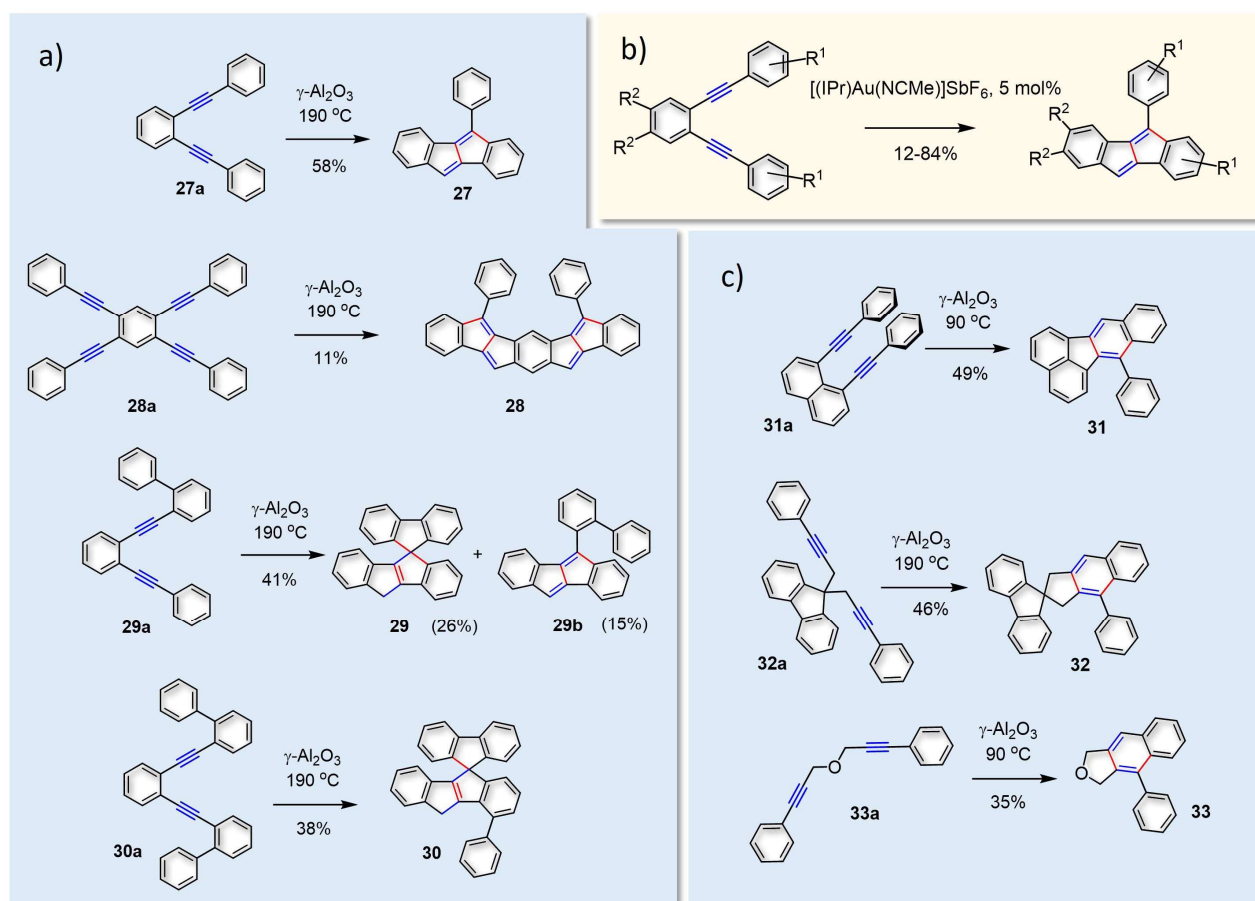
Based on the cycloisomerization of 7-alkynylcycloheptatrienes, Gandon et al. developed a test exploiting a chemical indicator, which allows assigning a π -acid as soft or hard in accordance with the obtained products.²¹ Thus, soft Lewis acids are supposed to transform **22a** into an indene's derivative, while harder acids lead to alternative bicyclic products.²² According to the test, alumina can be counter-intuitively classified as a soft π -acid since the major product was found to be the indene's derivative **22**.²³ Noteworthy, our method could not induce some other common cycloisomerizations of 1,6-enynes (Table S3).

Besides aromatic or alkene moieties, triple bond may also serve as nucleophile reacting with activated C=C bond. For instance, Hashmi et al. have reported gold-catalyzed isomerization of 1,5-diyne to give derivatives of dibenzopentalenes,²⁷ which show promising electronic properties (Scheme 3b).²⁸ Our experiments demonstrate that γ -alumina is also capable of inducing the mentioned cascade reaction. Upon exposure to γ -Al₂O₃, substrates **27a** and **28a** undergo the annulation into **27** and **28**, respectively (Scheme 3a). We have then turned our attention to the diyne that inherently have several possible transformation pathways upon activation of the triple bond. The precursors **29a** and **30a** were designed to enable competition between 6-endo cyclization giving phenanthrene's fragment and cycloisomerization leading to dibenzopentalenes. In both cases, the interactions of the activated triple bond with the aromatic π -system seem to be a minor

process, whereas the second mode of the reactivity accounts for the formation of the major products **29**, **29b**, and **30**. Unlike **27a** and **28a**, the reaction cascades initiated in diynes **29a** and **30a** may be terminated differently. This variation in the last step leads to a mixture of **29** and **29b**. The formation of the spiro compound **29** instead of the pentalene's derivative can be also explained in this manner

(Scheme S2-S3). Additionally, we have explored the reactivity of 1,6-diynes **31a-33a**, which turned out to selectively undergo [4+2] cycloaddition (Scheme 3c).^{29,30}

SCHEME 3. Alumina-mediated cycloisomerization of 1,5- and 1,6-diynes. (a) Gold-like isomerization of 1,5-diynes into dibenzopentalenes derivatives. (b) Gold-catalyzed annulation of 1,5-diynes. (c) [4+2] Cycloaddition of aryl-substituted 1,6-diynes.



Considering broad and compelling similarities between gold-catalyzed and alumina-mediated cycloisomerization of the arene-yne, enynes, and diynes, we have turned our attention to the mechanistic aspects of the discovered phenomenon. It is a serious challenge to determine the structure of the active centers by physical methods due to complex nature of γ -alumina's surface.³¹⁻³³ We have, therefore, attempted to suggest a possible mechanism and a structure of reactive centers based on the concept of DCD and support of DFT studies. Lewis acidic three-coordinated aluminium (Al_{III}) sites *per se* were excluded from the consideration due to its hardness and the absence of the filled *d*-orbitals or their equivalent suitable for the back-donation. Since oxygen atoms are the only reasonable sources of electron density, we have considered a dyad consisted of $\text{Al}_{\text{III}}\text{-O}_{\text{II}}$, which could act similarly to frustrated Lewis pairs

(FLPs) enabling concerted push-pull activation of substrates.³⁴⁻³⁶ However, such centers also do not seem to fit the observed reactivity. The typical interactions of FLPs with terminal alkynes include deprotonation or addition.³⁷ Moreover, the exposure of **1a** to FLPs have proved these modes of reactivity to be the only occurring transformations (Scheme S1).

Searching for an isolobal analog to TM center, we have assumed that the reaction might proceed on a frustrated Lewis triad (FLT) consisted of $\text{O}_{\text{II}}\text{-Al}_{\text{III}}\text{-O}_{\text{II}}$, which could hypothetically reproduce TM-like coordination of alkynes in accordance with DCD model (Fig. 1a). In general, gamma alumina is known to induce a wide range of transformations. For example, Sautet and co-workers showed that tri-coordinate aluminium Al_{III} "defect" sites are capable of heterolytic dissociation of H_2 ,¹⁴ and CH_4 ,³⁸ coordination of N_2 ,³⁹ and C-F activation⁴⁰. However, all these interactions

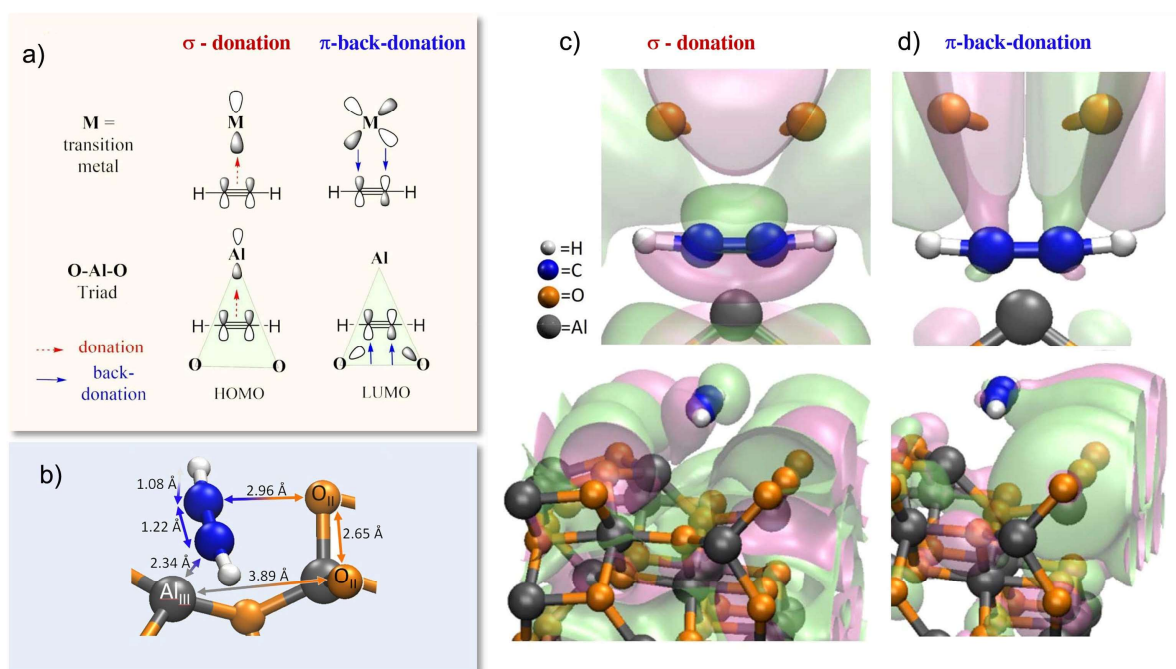
are assigned to Al_{III} centers *per se*, which are unlikely to trigger alkynes' cycloisomerizations.

According to the computational⁴¹ and physical data^{42,43}, (110) facet is believed to be the predominant termination of γ -Al₂O₃. Based on the comparison of different models,^{44,45} we have investigated (110) termination using Digne's^{41,46,47} and Pinto's⁴⁸ models. Regardless of the model chosen, (110) facet contains suitable "defect" sites that could account for the observed reactivity (Fig. S173).

To check our assumption and to investigate the modes of acetylene's coordination by FLT we have performed periodic-DFT-calculations using Digne's model of the alumina

surface and the Vienna Ab Initio Simulation Package (VASP).^{50,51} Noteworthy, the donation from acetylene's HOMO to the empty orbital of aluminum is an ordinary phenomenon (Fig. 1c), while mimicking the transition metal back-donation by two oxygen sites is far from trivial (Fig. 1d). Such an interaction would require intricate hybridization enabling two lone pairs located at different O_{II} sites to implement electron density transfer to the alkyne's LUMO.

FIGURE 1. (a) DCD model describing bonding of acetylene with TM and the O_{II}-Al_{III}-O_{II} triad (b) DFT-calculated interatomic distances in the acetylene-FLT η^2 -like-complex. (c) VB-16 wavefunction demonstrating electron transfer from the acetylene to the Al_{III}, top (underlying oxygen and aluminum atoms are omitted for clarity) and side views. (d) VB-2 wavefunction demonstrating back-donation to the acetylene from the O_{II} sites, top and side views. Contour levels are given for the value of 0.0045 e Bohr³.



Analysis of the wavefunctions obtained by integration of the valence bands (VB) over the gamma-point (performed independently in WAVECARPlot⁵²⁻⁵⁴ and LOBSTER⁵⁵) shows that the second uppermost VB i.e. VB-2 corresponds to the suitably shaped wavefunction (Fig.1d). The observed shape indicates that the wavefunction has the opposite signs in the regions located at O_{II} sites. Therefore, it symmetrically matches a double dumbbell of d-orbital and can interact with the acetylene's LUMO. It is also worth noting that the employed frontier orbitals of the alkyne are spatially orthogonal to each other (Fig. 1b and Fig. S175), which nicely explains the inertness of the alkene **23a** that does not have LUMO orthogonal to HOMO (Scheme 2b). Moreover, in agreement with complexes of transition metals, "back-donation orbital" has significantly higher energy in comparison to the "donation"-one. Our DFT study indicates that the adsorption energy of acetylene on FLT equals 29

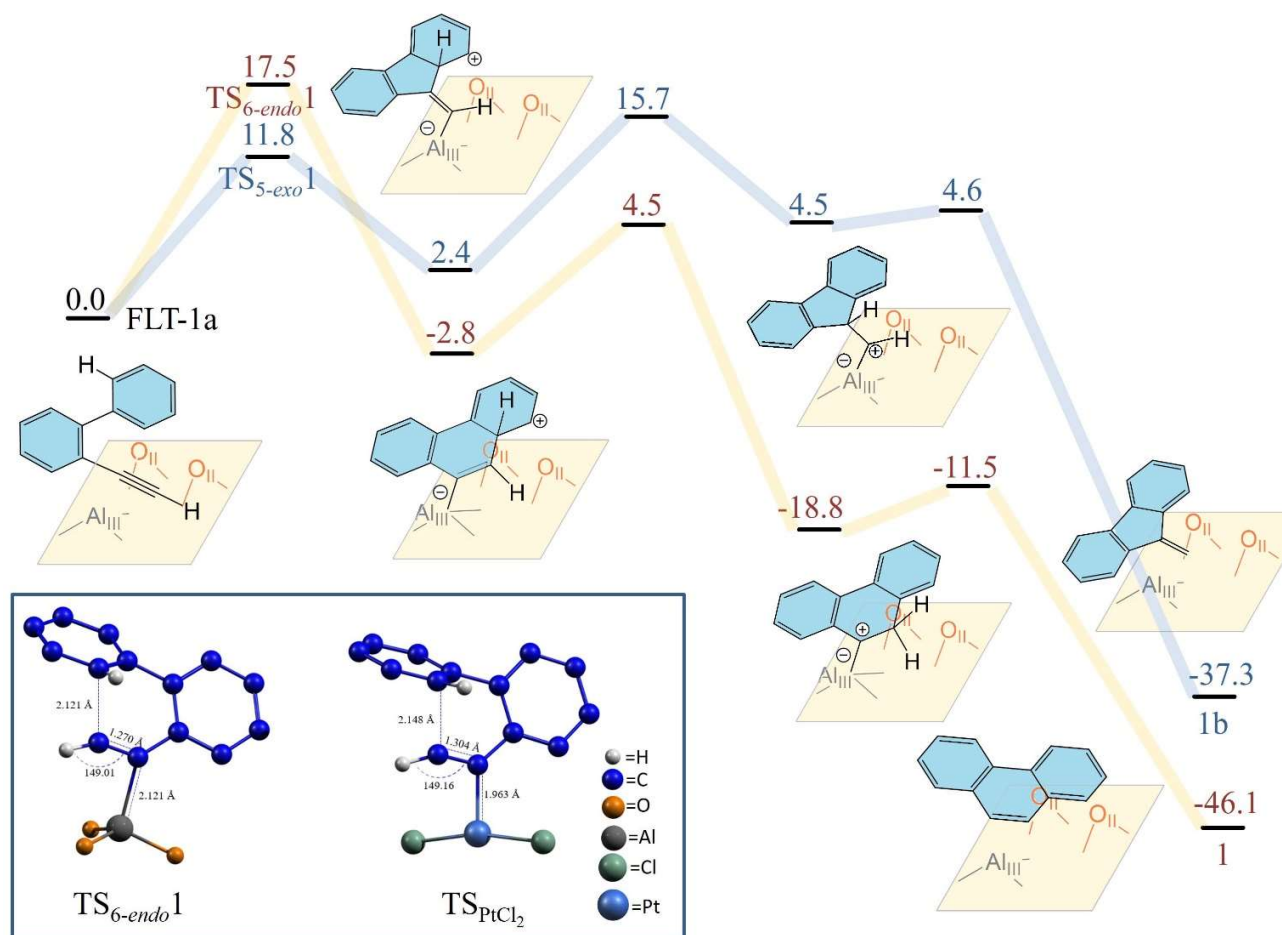
kcal/mol, which nicely correspond to the complexation energy of acetylene with AuCl₃ (Table S5). These results enable us to claim that back-donation to the antibonding π^* -orbital of the alkyne may indeed occur and resembles the η^2 -coordination with transition metals.

We have additionally analyzed two possible cycloisomerizations of **1a** into **1** and **1b** (Fig 2), which correspond to 6-*endo* and 5-*exo* pathways, respectively. These profiles are very close to those reported for PtCl₂-catalyzed transformation⁵⁶, moreover, head-to-head comparison of **TS**_{6-*endo*1 with noble metal-induced TSs also point out mechanistic similarities of the triple bond activation (Fig. 2 and Fig. S176). These factors also point out the analogy of the FLT- and transition-metal-complexes.}

The starting FLT-**1a** complex displays slipped η^1 -coordination, which is necessary for the subsequent nucleophilic attack to either external or internal alkyne carbon leading to Wheland-type intermediates **IM**_{6-endo1} and **IM**_{5-exo1}, respectively. Similarly to transition-metal-catalyzed transformation, the first step is followed by two consecutive [1,2]-H shift steps yielding the final products (Fig. 2). The analysis of the energy profiles shows that unlike **IM**₅

exo1 the formation of **IM**_{6-endo1} is exothermic, whereas the following hydrogen shift occurs with substantially lower energetic barriers in comparison to the 5-*exo* pathways.

FIGURE 2. Computed DFT-energy profiles of the reactions (kcal/mol). Geometries and energies of the corresponding minima and transition states can be found in SI. Bottom-left: Head-to-head comparison of **TS**_{6-endo1} and PtCl₂-induced **TS**_{PtCl₂} (non-participating hydrogen atoms omitted for clarity).



CONCLUSION

The diversity of the possible alumina's terminations, of course, complicates the unambiguous determination of the active centers and the assignment of their reactivity. Nevertheless, the results presented here demonstrate that FLT O_{II}-Al_{III}-O_{II} may act as carbophilic π -Lewis acid. Considering the mechanistic similarities to the activation by transition metals, this mode of reactivity for alumina represents a step forward in mimicking transition-metal-like behavior by elements outside the d-block.

ASSOCIATED CONTENT

The Supporting Information is available free of charge at <https://pubs.acs.org/>. Details of the synthetic procedures, DFT calculations, copies of NMR (PDF)

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