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Revealing the Activity of π -Acid Catalysts Using a 7-Alkynyl Cycloheptatriene

Marie Vayer,^[a] Regis Guillot,^[a] Christophe Bour,*^[a] and Vincent Gandon*^{[a],[b]}

Abstract: A compound that isomerizes into distinct products depending on the Lewis or Brønsted acid catalyst used is disclosed. One product can only be obtained with the softest π -acids such as Au, Pt, Ga or In complexes. Another is formed only with harder π -acids such as Ag or Cu salts. The formation of the third one requires even harder π -acids or protons. This simple benchmark reaction allows to predict the category of transformations that can be catalyzed by a new complex. It also informs whether protons have been accidentally generated in the reaction mixture.

The addition of nucleophiles to alkynes, alkenes and allenes is a well-established synthetic strategy. It has been made possible under mild conditions by using carbophilic catalysts able to deprive C-C multiple bonds from part of their electron density, turning them electrophilic. These catalysts are referred to as π acids.^[1] Even though C-C π bonds are considered as soft according to the HSAB principle,^[2] the π -acid denomination is actually not reserved to the softest Lewis acids. Depending on the ability of the substrate to give rise to a stabilized carbocationic intermediate, even Brønsted acids can sometimes activate C-C π -bonds. In the case of simple substrates, such as unconjugated alkynes, the softest π -acids are usually the most efficient ones. Among them, complexes of the relativistic elements Pt, Au, and Hg have shown a great versatility.^[1,3,4] These species do not simply act as "large soft protons".[4a,5] They are also able to stabilize incipient positive charges in the nucleophilic addition transition state (e.g. kinetic alkynophilicity), as well as the carbocation resulting from it.[1,3,6] In particular, in 1,n-enyne systems, the nucleophilic addition of the alkene to the alkyne can lead to vinylcyclopentenes through a metal-stabilized carbenelike nonclassical carbocation (Scheme 1, eq 1).^[7] Although such a mechanism is typical for soft π -acids, there is no well-defined border between soft and hard ones since the ancillary ligands, the oxidation state, the charge and the counterions of the metal ions can tune their activity.^[8] For instance, whereas phosphine ligated (R₃P)Au⁺ ions readily follow eq 1,^[7,9] they are sometimes unable to trigger hydroarylations of alkenes^[10] or allenes^[11] as in eq 2. The latter reaction, on the other hand, can be catalyzed by

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Brønsted acids such as HOTf or HNTf₂, as well as hard Lewis acids.^[12] Changing the phosphine of (R₃P)Au⁺ for a more π -accepting phosphite or related ligands makes the gold ion more electrophilic and requalifies the complex (i.e. ((RO)₃P)Au⁺) as an activator for simple alkenes and allenes.^[13,14]



Scheme 1. Prototypical Examples of Reactions Catalyzed by π -Acids.

These guidelines suffer from many exceptions and there is no simple reaction that would allow to predict the "carbene-like" or the "large proton-like" behavior of a new π -acid. In addition, the use of some Lewis acids can be the source of protons that can outcompete the π -acid as the true catalyst.^[15] We report herein a substrate which sheds light on these issues. It combines the chemistry of enynes and that of hydroarylations shown in Scheme 1

Instead of a simple enyne fragment, we have used a 7-alkynyl cycloheptatriene framework as in 1 (Scheme 2). Echavarren et al described the Au-catalyzed cycloisomerization of such compounds into indenes.^[16] Fluxional nonclassical Au-stabilized 9-barbaralyl cations^[17] are likely intermediates in this reaction. In the case of our model substrate 1, they would correspond to 4, 4', and other isomers. Depending on the catalyst, 1 can give rise to either indenes 7 or 9, or to the hydroarylation products 14 and 16. Their transformation could take place through the σ -complex 5, followed by 6 after a 1,2-H shift, and then indene 7 after a second 1,2-H shift. Alternatively, the σ -complex 8 could be formed, leading directly to indene 9 after a 1,2-alkyl shift. These pathways are supported by M06//QZVP/6-311+G(2d,p) computations (see the Supporting Information). Besides, 7-alkynyl cycloheptatrienes can undergo valence tautomerism to the norcaradiene form,^[18] which would be 2 in our case. Computations support its transformation into the allyl cation 10, and its isomerization into indene 9 though intermediates 11 and 12. Since 10 is less delocalized than the barbaralyl cations, one can anticipate that this pathway will be less favorable with the softest π -acids, which is indeed corroborated by computations. Finally, under hard acidic conditions, norcaradienes are known to isomerize into phenylallenes.^[19] In our case, compound 3 would lead to 14 after

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allene hydroarylation through the allyl cation **13**, and possibly **16** after alkene hydroarylation through **15**. These steps should be favored by π -acids even harder than those leading to **14**, or even by protons. Thus, the chemoselectivity of the isomerization of **1** should reveal the category to which a π -acid belongs.



Scheme 2. Isomerization Pathways of Compound 1 (R = CH_2XCH_2Ph) Supported by DFT Computations.

Compound **1a** (Table 1) was easily synthesized in 2 steps from dimethyl propargyl malonate. At 80 °C in 1,2-dichloroethane (DCE) or toluene, no reaction took place with the hard oxophilic acids HCl, AlCl₃, TiCl₄, or SnCl₄ (5 mol%). The reaction of **1a** was then carried out in the presence of various Au(I) complexes. In contrast with the alkyl- and aryl-substituted 7-alkynyl cycloheptatrienes studied by Echavarren,^[16] no reaction took place with AuCl or AuCl₃ (entries 1 and 2). With 3 mol% of cationic phosphine-Au(I) complexes, indenes **7a** and **9a** were obtained, the former being the major one (entries 3-5). When gold(I) chloride complexes activated with silver salts were used (entries 6-12), only indenes were obtained as well. The **7a/9a** ratio depended on the ligand/counterion combination.





1	AuCl	-/-	0
2	AuCl ₃	-/-	0
3	[(Ph ₃ P)Au][NTf ₂]	100/0	68
4	[(Me ₄ - <i>t</i> Bu-XPhos)Au][NTf ₂]	90/10	78
5	[(JohnPhos)Au(MeCN)][SbF ₆]	80/20	76
6	(Ph₃P)AuCl/AgOTf ^[a]	90/10	64
7	(Ph ₃ P)AuCl/AgNTf ₂ ^[a]	75/25	59
8	(Ph ₃ P)AuCl/AgBF ₄ ^[a]	85/15	59
9	(Ph₃P)AuCl/AgSbF ₆ ^[a]	60/40	69
10	(phosphite)AuCl/AgSbF ₆ ^[a]	85/15	42
11	(JohnPhos)AuCl/AgSbF6 ^[a]	100/0	48
12	IPr-AuCI/AgSbF ₆ ^[a]	58/42	72

[a] Same charge for each component. [b] Isolated.



Of note, indenes **7a** and **9a** are easily identifiable by ¹H NMR of the crude (Figure 1).



Figure 1. Diagnostic ¹H NMR Peaks of 1a, 7a and 9a.

Importantly, the selectivity for indenes with gold(I) complexes generated in situ using silver salts was the same, no matter if the anion metathesis had been performed prior to adding **1a** or directly in its presence. This suggests that the cyclization is faster than the anion metathesis since the silver salts alone led to different products (Table 2). With AgSbF₆, no reaction took place in toluene (**B**, entries 1-3). In DCE (**A**), a mixture of **14a** and **16a** was obtained at a catalytic charge of 3 or 5 mol% (entries 1 and 2), but only **16a** was isolated at 7 mol% (entry 3).^[20] This transformation was monitored by ¹H NMR in CD₂Cl₂,^[21] which clearly revealed the subsequent formation of **3a**, **14a** (*E* and *Z* isomers), and finally **16a** (Figure 2). The selective formation of

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16a was also observed with SbF_5 (entry 4). With AgNTf₂ and AgOTf, only **14a** was obtained in both solvents (entries 5 and 6).

Table 2. Other Acid-Catalyzed Rearrangements of 1a.



Entry	cat.	x ^[a]	Cond ^[b]	Product ^[c,d]	Yield [%] ^[e]
1	AgSbF ₆	3	A/B	14a ^[f] : 16a (90:10)/-	36/0
2	AgSbF ₆	5	A/B	14a:16a (90:10)/-	57/0
3	AgSbF ₆	7	A/B	16a/-	71/0
4	SbF₅	5	Α	16a	41
5	AgNTf ₂	5	A/B	14a/14a	81/70
6	AgOTf	5	A/B	14a/14a	52/77
7	(JohnPhos)AuCl/ Cu(OTf)2	5	A	7a:14a (20:80)	82
8	(Ph ₃ P)AuCl/ Cu(OTf) ₂	5	Α	7a:14a (20:80)	87
9	Cu(OTf) ₂	5	A/B	14a/14a	96/98
10	[(MeCN)₅Cu][SbF ₆]₂	5	Α	14a ^[g]	74
11	Bi(OTf) ₃	5	A/B	14a/14a	91/72
12	In(NTf ₂) ₃	5	A/B	14a/14a	73/81
13	Ca(NTf ₂) ₂ / <i>n</i> Bu ₄ NPF ₆	5	Α	14a	70
14	HOTf	5	Α	14a	69
15	HNTf ₂	5	A/B	14a:16a (60:40)/ 14a	54/80
16	PtCl ₂	5	A/B	-/ 7a:9a (55:45)	0/54
17	[{(o-tolyl) ₂ -C,P} Pt(MeCN) ₂][SbF ₆]	5	в	7a:9a (60:40)	99
18	GaCl ₃	5	A/B	7a/7a	42/63
19	Hg(OTf) ₂	5	Α	7a	21
20	InCl ₃	5	A/B	7a/7a	63/85
21	IPr⋅GaCl₃/AgSbF ₆	5	Α	14a ^[f] : 16a (80:20)	96

[a] Same charge for each component. [b] A = DCE; B = toluene. [c] Ratio based on the NMR spectra of the crude. [d] **14a** has *E* configuration unless otherwise noted. [e] Isolated. [f] *E*/*Z*-**14a**: 55/35. [g] *E*/*Z*-**14a**: 50/50.



Figure 2. ¹H NMR Monitoring of the AgSbFe-Catalyzed Skeletal Rearrangement of 1a.

It has been shown that active cationic mono-coordinated gold(I) complexes can be generated from the corresponding chloride and Cu(OTf)₂ instead of a silver salt.^[22] However, the anion metathesis is slow, which means that the activator can compete with the gold catalyst. With LAuCI/Cu(OTf)₂ catalytic mixtures (entries 7 and 8), 7a was obtained as minor product and 14a as the major one. Clearly the former results from the activity of the gold ion (see Table 1) and the latter from the copper salt. Indeed, when used alone, Cu(OTf)₂ provided 14a only (entry 9). A similar result was obtained with [(MeCN)5Cu][SbF6]2 (entry 10). Compound 14a was In(NTf₂)₃,^[23] also obtained selectively with Bi(OTf)₃, Ca(NTf₂)₂/nBu₄NPF₆^[24] and HOTf (entries 11-14). With HNTf₂ in DCE, a 37:63 mixture of 14a and 16a was isolated, but only 14a formed in toluene (entry 15).

This first set of results validated the above hypotheses about the peculiarities of type 1 compounds and encouraged us to test other Lewis acids. At this point of the study, the reactivity of 1a had identified only Au(I) complexes as truly soft π -acids. If the test is relevant, other species known to isomerize enyne systems through nonclassical carbocations should also lead to 7a/9a. This was indeed the case with PtCl2,[1] a cationic Pt(II) complex,[25] GaCl₃,^[26] Hg(OTf)₂^[9a] and InCl₃ (entries 16-20),^[27] which also led selectively to indenes. The use of gallium complexes of type IPr·GaX₂⁺ as π -acids has been described, and it was shown that these species are harder than $\mbox{GaCl}_3.^{\mbox{\tiny [28]}}$ In a logical manner, the Ga⁺ complex gave no indene (entry 21). Cationic gallium π -acids are usually less reactive when stabilized by a nitrile.^[28a] By using such a complex, we could selectively obtain allene 3a, which is the putative intermediate to 14a and 16a (Scheme 3). No reaction took place when **3a** was treated with Ph₃PAuCl/AgSbF₆ (5 mol%). Only the most electrophilic gold complex, i.e. the phosphitederived one, sluggishly transformed 3a into 14a (33% yield), but not into indene 7a or 9a. With AgOTf, 14a was isolated in 78% vield.

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Scheme 5. In(I)- and Ga(I)-Catalyzed Cyclization of 1a into Indene 7a.

Scheme 3. Synthesis and Reactivity of Allene **3a** (TFBN = 2,4,6-trifluorobenzonitrile).

Compound **16a** was mostly observed with acids of the SbF₆⁻ series in DCE. This result supports the hypothesis that **16a** is encouraged by the presence of highly dissociated protons. Pertaining to this idea, no reaction took place when **1a** was treated with AgSbF₆ (7 mol%) and the proton scavenger 2,6-di-*t*Bu-pyridine (7 mol%). On the other hand, the Au-catalyzed isomerization of **1a** into **7a** was not affected by the presence of 2,6-di-*t*Bu-pyridine (see the Supporting Information). Compound **16a** was also observed with HNTf₂ in DCE, but not with metal triflimides, which seems to rule out an exclusive proton-catalyzed sequence between **1a** and **16a**.

We have applied the benchmark reaction to a new catalytic system composed of IPr·InBr₃ and AgSbF₆ (Scheme 4).^[29] It gave rise to indene **7a** and the hydroarylation products **14a** and **16a**. The presence of both **7a** and **14a** tell-tales the continuum between soft and hard acids. The test also reveals that protons are likely to be formed, which is fully consistent with our finding that HSbF₆ is released under such conditions.^[29b]

$$1a \xrightarrow{\text{AgSbF}_{6} (5 \text{ mol}\%)}{\text{DCE, 80 °C, 20 h}} 7a : 14a : 16a (30 : 55 : 45) (68\%)$$

Scheme 4. Reaction of 1a in the Presence of a New $\ln(III)/Ag(I)$ Catalytic System.

Encouraged by the above results in the cationic In(III) series, we speculated that a cationic indium complex with a lower oxidation state would be softer and less prone to generate protons. We tested the In(I) complex [In(PhF)₂][Al(pftb)₄],^[30] which, just like some of the cationic gold(I) complexes shown in Table 1, converted **1a** into **7a** selectively in DCE or toluene (Scheme 5). Other In(I) species such as InCl or InOTf left the substrate unchanged. We also found that Ga₂Cl₄, which is actually a cationic Ga(I) species of formula [Ga][GaCl₄],^[31] is able to act as a soft π -acid. Thus, the reaction of **1a** has allowed to reveal the π -acidic property of Lewis acids that had never been exploited as such.

In conclusion, compound 1a allows the selective formation of distinct products arising from the activation of an alkyne (1 or 2), an allene (3), or an alkene (14), each of them deriving from the preceding one. The softest π -acids of the Au, Pt, Hg, Ga, and In series treat 1a as an envne and transform it into indenes through nonclassical "soft carbocations". The preference for this pathway is supported by M06 computations with (Me₃P)Au⁺, GaCl₃ and InCl₃. Harder π -acids transform it into **14a** through "harder" allyl cations derived from an allene (13). Computations confirmed that the indene pathway is disfavored with AgOTf. With even harder π -acids, **1a** is transformed into **16a**. Our results in different solvents and with a broad range of catalysts displaying various weakly coordinating anions strongly suggest that 16a is obtained via the participation of protons.^[15] Thus, if a new complex converts 1a into 7a (or 9a), it will be probably a good catalyst for skeletal rearrangement of 1, n-enyne systems as a general rule. If it gives 14a, it will probably be a good hydroarylation catalyst. If it leads to **16a**, it will also be a good hydroarylation catalyst but it is likely that the activity is explained by hydrolysis of the metal salt.^[31] In particular, this simple reaction could allow to identify surrogates of noble metal complexes within the main group metal series. Two of them have been identified thanks to this simple test.

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Keywords: alkynes • allenes • carbenes • noble metals • rearrangement

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The reaction takes longer in CD_2Cl_2 than in DCE (30 h vs 20 h). This can [21] be attributed to the change of solvent and also to a lack of stirring in the NMR tube.

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A simple benchmark reaction allows to predict the category of transformations that can be catalyzed by a new complex. Soft π -acids follow a carbenoid pathway leading to indenes from a 7-alkynyl cycloheptatriene. Harder π -acids follow a "large proton" pathway, yielding a hydroarylation product. If these hard species liberate protons in the reaction mixture, the latter further cyclizes into a tricyclic product.

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