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Additional Information

Iron(III) triflimide as a catalytic surrogate of Gold(I) for Hydroaddition Reactions to unsaturated Carbon-Carbon Bonds.

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Abstract: The substitution of expensive and toxic heavy-late transition metals by cheap and non-toxic surrogates is one of the main tasks in modern catalysis. Here we show that iron(III) catalyses as efficiently as gold(I) the hydroaddition of a wide array of nucleophiles including water, alcohols, thiols, amines, alkynes and alkenes to multiple C-C bonds. The study of the catalytic activity and

selectivity of iron(III), gold(I), and Brønsted triflimides has unveiled that iron(III) triflimide [Fe(NTf₂)₃] is a robust catalyst under heating conditions while gold(I) triflimide, even stabilized by PPh₃, readily decomposes at 80 °C and releases triflimidic acid [HNTf₂] that can catalyze the corresponding reaction, as shown by in-situ ¹⁹F-, ¹⁵N-, and ³¹P-NMR spectroscopy. The results presented here demonstrates that

iron(III) substitutes to gold(I) as a catalyst for hydroaddition reactions to unsaturated carbon-carbon bonds.

Keywords: Lewis and Brønsted catalysis • iron(III) triflimide • gold(I) triflimide complex • unsaturated carbon-carbon bonds • hydroaddition reactions

Introduction

Modern organic synthesis based on catalysis by transition metals has increased its possibilities with the introduction of gold for making new carbon-carbon and carbon-heteroatom bonds.^[1-13] Nonetheless, it is much incentive to substitute expensive and toxic heavy-late transition metals by cheaper, widely available and environmentally-friendly first-row transition metals such as iron.^[14-28] The aim or the work here is to study iron, gold, and triflimidic acid, representative examples of first-row and late-heavy transition metals and Brønsted acids, respectively, as catalysts for hydroaddition reactions to π -carbophilic unsaturated C-C bonds (alkenes and alkynes) of carbon, oxygen, nitrogen and sulfur nucleophiles, a set of complete atom-economical reactions with growing potential in organic synthesis.^[3, 8, 29, 30] The study includes reactivity tests, isotopic labeling, in-situ Nuclear and Electronic Paramagnetic Resonance (NMR, EPR) experiments, and cyclic voltammetry, which have helped to shed light on the exact nature of the catalytic process and active sites involved.

Results and discussion

Stability of triflimide salts.

The traditional division into Brønsted and Lewis catalysis is difficult to be separated when in-situ generated protons can contribute to the catalytic activity of some metals.^[31] Triflimide metal salts [Mⁿ⁺(NTf₂)_n], particularly those with gold, have gained much attention in the last years^[15, 16, 21, 32-35] due to its high Lewis acidity and easy handling compared to the corresponding triflimidic acid [HNTf₂]. Despite the fact that these salts are readily hydrolyzable, the possible role of acid protons on the final catalytic activity is not always tested.^[36-42] This is not surprising since unveiling the role of protons for metal-catalyzed reactions (and particularly for gold) is not trivial, because the claimed water-tolerance of gold catalysts has lead to a “wet” chemistry, early recognized by Hashmi as a possible source of catalytic protons.^[31] Blank experiments with the corresponding acid and addition of the non-coordinating base *di**tert*butyl pyridine are the two ways commonly employed to detect a possible Brønsted catalysis.^[15, 43] However, recent studies have shown that these methods sometimes fail when other factors come into play as we will discuss below. ^[36-42] For instance, it has been shown that the hydroamination^[42] of non-activated alkenes proceeds with catalytic amounts of triflic acid [HOTf] below 5 mol%, since higher amounts (20 mol%) only trigger the decomposition of the substrate.^[37, 39, 40] Related hydroalkoxylation reactions only proceed at temperatures below 50 °C when they are catalyzed by triflic acid since higher temperatures decompose the substrate. In contrast, the

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corresponding gold(I) triflate AuPPh_3OTf works nicely at 85 °C.^[39] In the other hand, the addition of *di*tertbutyl pyridine can generate rather than neutralize catalytic protons under specific reaction conditions, which is an opposite effect to the one expected. All these examples illustrate that Brønsted catalysis can be hidden by different factors that are only assessed through specifically designed experiments. In our case, we will show how the potential generation of protons from the triflimide salts can be systematically monitored by in-situ ^{19}F -, ^{15}N -, and ^{31}P -NMR experiments to determine the exact nature of the catalysis.

Prior to that, the stability of these Fe(III) and Au(I) triflimide species versus different nucleophiles was examined by ^{19}F -NMR spectroscopy. Figure 1 shows that the addition of H_2O , PhNH_2 , PhOH , and PhSH shifts the ^{19}F -NMR signal of $[\text{Fe}(\text{NTf}_2)_3]$. However, the broad singlet found in most cases suggests that no hydrolysis occurs but only the formation of the corresponding Fe- nucleophile adducts.

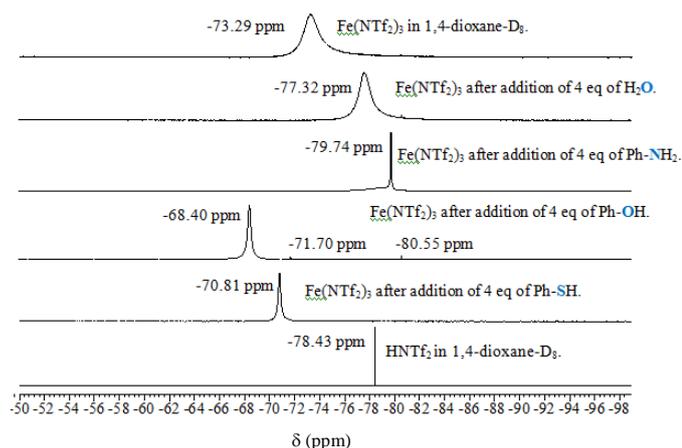


Figure 1. ^{19}F -NMR spectra in 1,4-dioxane- D_8 of the iron(III) salt $[\text{Fe}(\text{NTf}_2)_3]$ after the addition of different nucleophiles at room temperature.

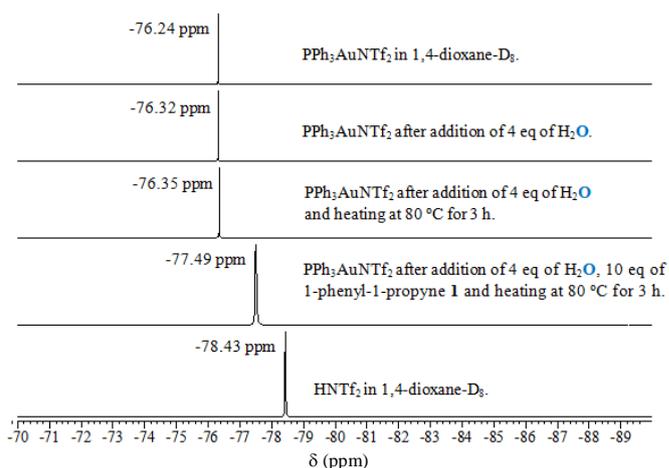


Figure 2. ^{19}F -NMR spectra in 1,4-dioxane- D_8 of the gold(I) complex $[\text{PPh}_3\text{AuNTf}_2]$ after the addition of an excess of water at two different temperatures or an excess of alkyne at 80 °C.

In the case of $[\text{PPh}_3\text{AuNTf}_2]$, Figure 2 shows that the addition of an excess of water does not produce any change on the catalyst signal after heating at 80 °C during 3 h but that the stability of gold towards hydrolysis readily disappears when a better ligand such as an alkyne, alkene or thiol is added.

Hydroaddition reactions to alkynes.

The results for the iron(III), gold(I), or Brønsted triflimide-catalyzed hydroaddition of: oxygen (reaction A), sulfur (reactions B and C), and carbon (reaction D) nucleophiles to alkynes are shown in Figure 3. Additional reactions and catalysts together with a complete set of numerical data can be seen in the Supporting Information (Tables S1-S7). The conversion (X) and the regioisomer distribution are indicated for each reaction and catalyst.

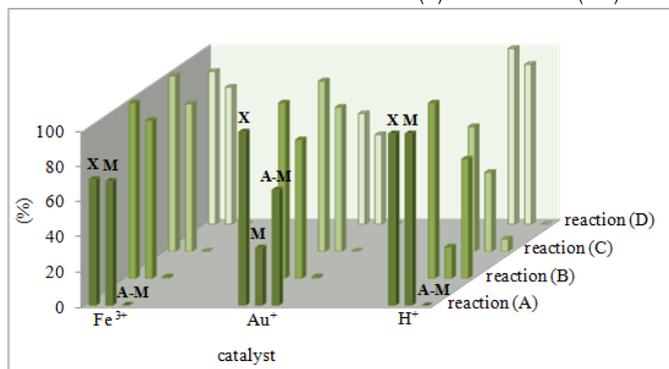
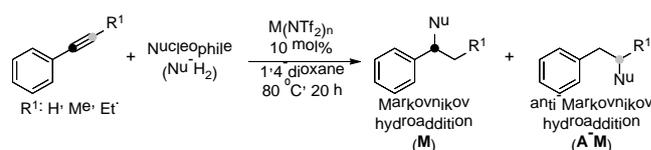


Figure 3. Catalytic study of iron(III), gold(I), and Brønsted triflimides for various hydroaddition reactions to phenylacetylenes. Gold(I) triflimide was used as $\text{PPh}_3\text{AuNTf}_2$ complex. Reaction (A): $\text{R}^1 = \text{Me}$ **1**, $\text{Nu-H}_2 = \text{H}_2\text{O}$ (3 eq), 20 mol% of $\text{Fe}(\text{NTf}_2)_3$ and 60 mol% of HNTf_2 were used. Reaction (B): $\text{R}^1 = \text{H}$ **9** (2 eq), $\text{Nu-H}_2 =$ benzene-1,2-dithiol **10**. Reaction (C): $\text{R}^1 = \text{Et}$ **4** (2 eq), $\text{Nu-H}_2 =$ benzene-1,2-dithiol **10**. Reaction (D): $\text{R}^1 = \text{H}$ **9**, $\text{Nu-H}_2 =$ mesitylene **20** (5 eq), dichloromethane as solvent and 30 mol% of HNTf_2 . GC conversions and yields were calculated using dodecane as an external standard.

The results show that the hydration^[16] of 1-phenyl-1-propyne **1** (reaction A) under heating conditions proceeds cleanly to the Markovnikov product (**M**) **2** with Fe(NTf₂)₃ and HNTf₂ as catalysts, while PPh₃AuNTf₂ gives a mixture of Markovnikov (**M**) **2** and anti-Markovnikov (**A-M**) **3** products. In-situ ¹⁹F-NMR spectroscopy reveals that the iron(III) triflimide does not hydrolyze to the Brønsted acid while the gold(I) triflimides readily does, as it can be seen in Figures 4 and 5 after comparing the original values of the catalysts at -73 and -76 ppms with the value of triflimidic acid at -79 ppms under the same reaction conditions. Differences in selectivity can be explained by considering that, while iron smoothly forms the intermediate adduct which catalyzes the regioselective reaction, gold catalyzes the unselective hydration and then decomposes.^[9, 16, 44] In-situ ³¹P-NMR spectroscopy^[45] (Figure S1) confirmed the decomposition of gold with formation of a black precipitate at the end of reaction. This precipitate was isolated, weighted and analyzed by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) to establish the gold mass balance.

To further confirm these observations, isotopically-labeled ¹⁵N-silver triflimide **8** was synthesized^[46] using ¹⁵N-benzylamine **7b** as starting material, as depicted in Scheme 1, and employed for the synthesis of ¹⁵N-labeled iron(III), gold(I), and Brønsted triflimides, which were used as catalysts while following the reaction by in-situ ¹⁵N-NMR. The results in Figures 6 and 7 confirmed that the active species for iron(III) triflimide is not triflimidic acid (compare the value of the catalyst during the reaction at 148 ppms with that observed for H¹⁵NTf₂ at 139 ppms, see also Figures S2-S5), while the gold(I) triflimide complex is readily hydrolyzed under the reaction conditions.

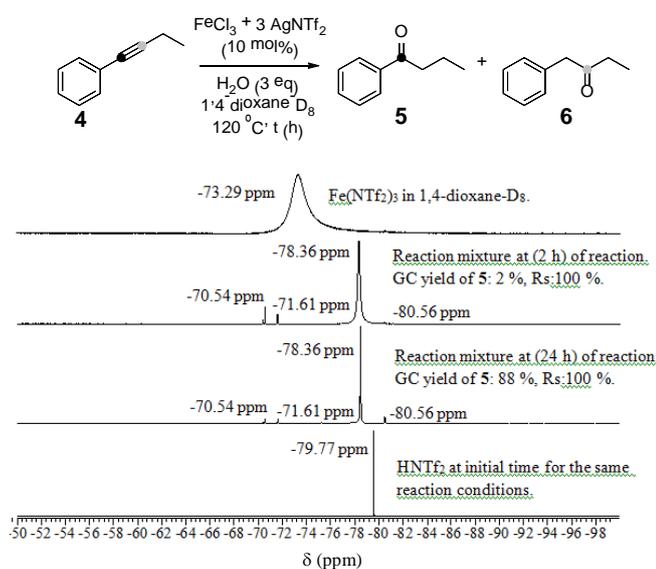


Figure 4. In-situ ¹⁹F-NMR spectra for the hydration of 1-phenyl-1-butyne **4** with H₂O (3 eq) using Fe(NTf₂)₃ as a catalyst.

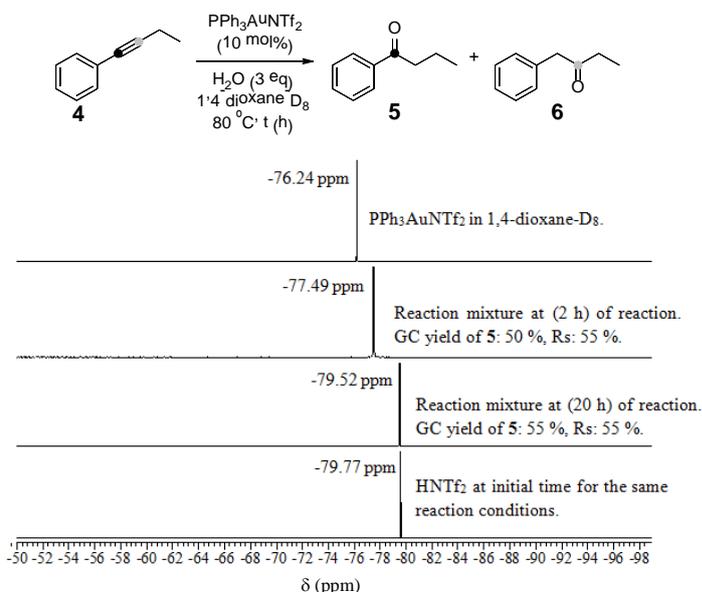
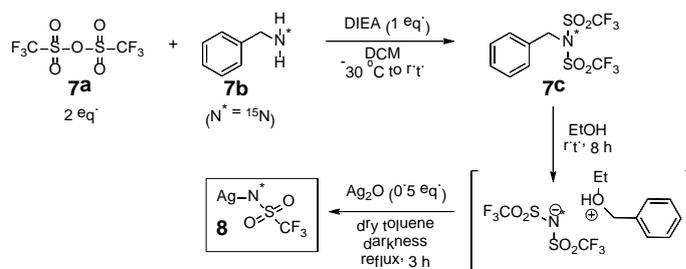


Figure 5. In-situ ¹⁹F-NMR spectra for the hydration of 1-phenyl-1-butyne **4** with H₂O (3 eq) using PPh₃AuNTf₂ as a catalyst.



Scheme 1. Synthesis of isotopically labeled Ag¹⁵NTf₂ **8** using ¹⁵N-benzylamine **7b** as starting material.

It is striking that the stable AuPPh₃NTf₂ gold(I) complex reduces so easily to gold(0) in the presence of a sterically demanding alkyne such as 1-phenyl-1-butyne **4** and a weak-bounded nucleophile such as water, even under heating conditions. Thus, it is reasonable to expect that many unsaturated C-C bonds and nucleophiles will promote the decomposition of the gold(I) complex. In the case of the dihydrothiolation^[47] of a simple terminal alkyne such as phenylacetylene **9** with benzene-1,2-dithiol **10** as nucleophile (reaction B, Figure 3), the three catalysts showed excellent conversion (>99 %) but only iron(III) triflimide gave excellent yields to the Markovnikov product (90 % of **11**), while gold(I) gave a lower selectivity (79 % of **11**) and the Brønsted triflimide gave the anti-Markovnikov product (68 % of **12**).

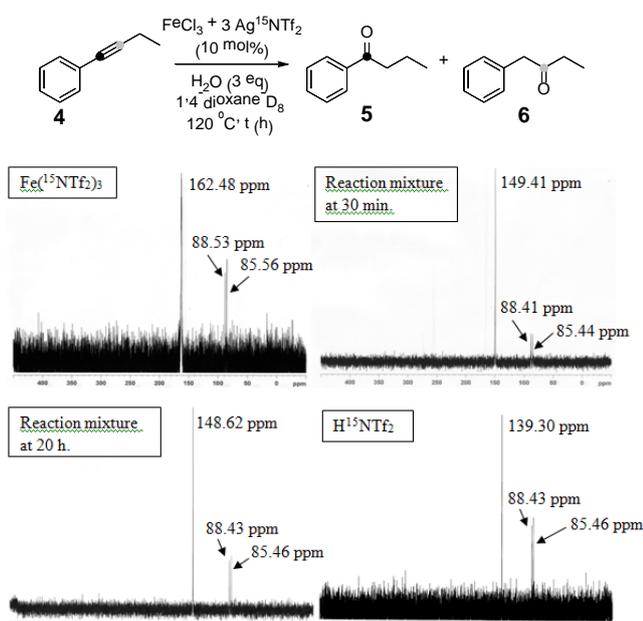


Figure 6. In-situ ^{15}N -NMR spectra for the hydration of 1-phenyl-1-butyne **4** with H_2O (3 eq) using $\text{Fe}(^{15}\text{NTf}_2)_3$ as a catalyst.

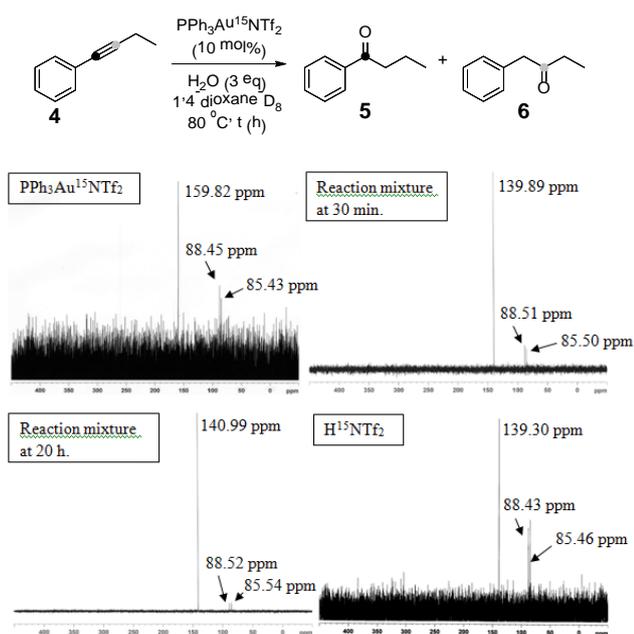


Figure 7. In-situ ^{15}N -NMR spectra for the hydration of 1-phenyl-1-butyne **4** with H_2O (3 eq) using $\text{PPh}_3\text{Au}^{15}\text{NTf}_2$ as a catalyst.

In-situ ^{19}F -NMR shows that the iron(III) triflimide does not decompose or hydrolyze under the reaction conditions (Figure S6) while the gold(I) triflimide does (Figure S7), since a new signal at -79 ppm appears after 15 min of reaction and is very similar to that observed for the Brønsted acid under the same reaction conditions. Working with another alkyne such as 1-phenyl-1-butyne **4** (reaction C, Figure 3) it was found again that iron(III) triflimide is a better catalyst (86 % of Markovnikov product **13**) than gold(I) (79 % of **13**) or the Brønsted triflimide (45 % of **14**).

Run ^[a]	Alkyne	Main product	Yield (%) ^[b]
1			71[65]
2			98[76]
3			88[74]
4			92[83]

Table 1. [a] Reaction conditions: alkyne (0.50 mmol), benzene-1,2-dithiol **10** (46.0 μL , 0.25 mmol), FeCl_3 (4.0 mg, 0.025 mmol), AgNTf_2 (30.0 mg, 0.075 mmol), anhydrous 1,4-dioxane (0.5 mL) at 80 °C for 24 h. [b] GC yield using dodecane as an external standard. Between brackets isolated yields calculated after isolation by preparative TLC.

With these catalytic results in hand, we expanded the iron(III)-catalyzed dihydrothiolation to other alkynes using benzene-1,2-dithiol **10** as nucleophile and the results in Table 1 show that aromatic (entries 1-3) and aliphatic alkynes (entry 4) are converted to dithioacetals with 10 mol% of $\text{Fe}(\text{NTf}_2)_3$ in good isolated yields and Markovnikov selectivity.

When a carbon-nucleophile such as mesitylene **20** was used for the hydroarylation^[48] of phenylacetylene **9** (reaction D, Figure 3) the results showed that the Brønsted triflimide gave the best results (> 99 % conversion and 91 % yield of **21**) and in-situ ^{19}F -NMR spectroscopy reveals that both iron and gold triflimide hydrolyze under reaction conditions (Figure S8 and S9), which explains the similar catalytic performance for the three triflimides. ^{31}P -NMR spectroscopy confirmed the decomposition of the gold(I) complex (Figure S10). The better result obtained with iron(III) triflimide respect to gold comes from the higher amount of HNTf_2 generated.

All these results point to a general decomposition of the $\text{AuPPh}_3\text{NTf}_2$ complex in the presence of C-C multiple bonds under heating conditions. However, it must be noted that gold(I) is also active at room temperature for intermolecular hydroadditions^[45, 49] to alkynes while iron(III) triflimide is inactive (Tables S5 and S6). As it could be expected, in-situ NMR studies revealed that $\text{AuPPh}_3\text{NTf}_2$ is more stable at lower temperatures^[45] but a significant degree of decomposition with time can be expected. In addition, iron(III) triflimide is also active for intramolecular hydroadditions such as, for instance, the hydroalkoxylation of internal alkynes, which is the most used gold-catalyzed transformation in total synthesis to date (Table S7).^[1, 3, 4, 50]

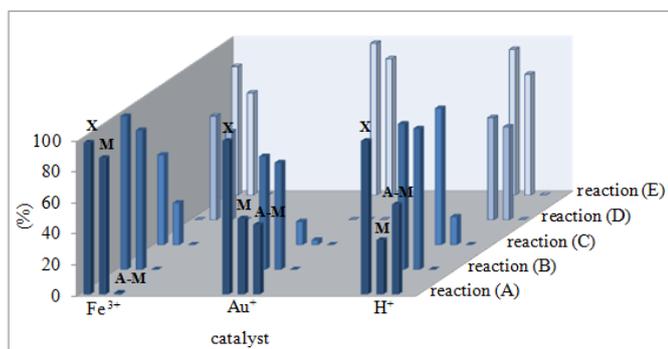
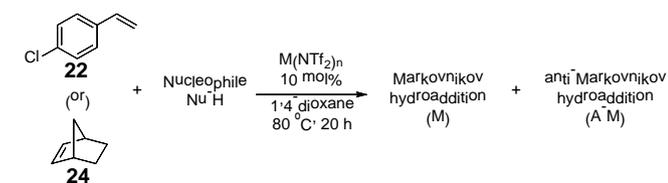


Figure 8. Catalytic study of iron(III), gold(I), and Brønsted triflimides for various hydroaddition reactions to alkenes. Gold(I) triflimide was used as $\text{PPh}_3\text{AuNTf}_2$ complex. Reaction (A): alkene = 4-chlorostyrene **22**, Nu-H = thiophenol **23** (1 eq). Reaction (B): alkene = 4-chlorostyrene **22**, Nu-H = 4-chlorostyrene **22**. Reaction (C): alkene = norbornene, Nu-H = phenylacetylene **9** (4 eq), 1,2-dichloroethane as solvent and 160 h reaction time. Reaction (D): alkene = norbornene **24**, Nu-H = tosylamine **25** (1 eq), 1,2-dichloroethane as solvent and 6 h reaction time. Reaction (E): alkene = norbornene **24**, Nu-H = *p*-methoxybenzoic acid **26** (1 eq). GC conversions and yields were calculated using dodecane as an external standard.

Hydroaddition reactions to alkenes.

Complementarily to the study of alkynes, the results for the hydroaddition of: sulfur (reaction A), carbon (reactions B and C), nitrogen (reaction D), and oxygen (reaction E) nucleophiles to alkenes using catalytic amounts of the three triflimide species are shown in Figure 8. For complete numerical information for these and more catalyst and additional reactions tested, see Tables S8-S17 in Supporting Information.

The results for the hydrothiolation^[15] of 4-chlorostyrene **22** with thiophenol **23** (reaction A, Figure 8) indicate that the iron(III) triflimide is the best catalyst, and in-situ ¹⁹F- and ¹⁵N-NMR spectroscopies (Figure S11 and S12) confirmed that it does not hydrolyze under the reaction conditions. Gold(I) gave poorer results since it hydrolyzes under reaction conditions as confirmed by ¹⁹F-, ³¹P, and ¹⁵N-NMR studies (Figures S13-15). The poorer activity of gold(I) in comparison with iron(III) can be ascribed to sulfur poisoning and the higher affinity of Au for S (Au-S = 418 KJ/mol) compared to Fe (Fe-S = 322 KJ/mol) would explain the catalytic differences observed with alkynes (see dihydrothiolation) and alkenes. In other words, besides gold(I) reduction there is a second way of gold(I) deactivation by sulfur poisoning, as evidenced by the small number of efficient gold-catalyzed transformations involving sulfur nucleophiles.^[3, 5, 8] Interestingly, we have shown that iron(III)

is able to by-pass this poisoning and transfer thiols to alkynes and alkenes.^[15]

If no additional nucleophiles are added to the reaction mixture, the alkene itself can act as a nucleophile and the head-to-tail dimerisation^[21] (or hydrovinylation) of 4-chlorostyrene **22** (reaction B, Figure 4) proceeds very well in the presence of either $\text{Fe}(\text{NTf}_2)_3$ or HNTf_2 , while $\text{PPh}_3\text{AuNTf}_2$ gave significantly poorer results. ¹⁹F-NMR spectroscopy (Figures S16 and S17) indicates that iron does not hydrolyze to HNTf_2 under reaction conditions, so the dimerisation of alkenes can also be classified as a hard Lewis-catalyzed reaction, since Fe^{3+} and H^+ perform better than Au^+ . It is not surprising that harder acidic centers are needed to activate alkenes since they are considered harder electrophiles than alkynes. This trend was confirmed after studying the hydroethinylation^[23] of the bicyclic alkene norbornene **24** (reaction C, Figure 4) since iron(III) and Brønsted triflimide gave again the best results, while gold(I) was significantly less active. The in-situ ¹⁹F-NMR experiments (Figure S18) with iron(III) triflimide confirms that this species does not hydrolyze during the reaction. Hydroadditions^[40] of nitrogen (tosylamine **25**, reaction D, Figure 8) and oxygen (*p*-methoxybenzoic acid **26**, reaction E) nucleophiles to norbornene **24** were also studied and Brønsted acids were the best catalysts (86 and 82 % yield for HOTf , and 70 and 78 % yield for HNTf_2 , respectively). These observations are in good agreement with the results reported by other authors.^[40]

Some conclusions about the stability and catalytic activity of the iron(III), gold(I) and acid triflimides can be taken from the results presented above. $\text{PPh}_3\text{AuNTf}_2$ readily decomposes in the presence of alkynes and alkenes under heating conditions, what contrasts with the stability towards water showed in Figure 2. We can say that decomposition of $\text{PPh}_3\text{AuNTf}_2$ occurs mainly by gold reduction (although sequestration by high-affinity ligands such as thiols can also occur) and, in consequence, gold is significantly less active than Fe^{3+} and H^+ as a catalyst under these reaction conditions. This behavior also occurs with alkenes, that interact better with harder Lewis acids such as Fe(III). The enhanced Lewis acidity of $\text{Fe}(\text{NTf}_2)_3$ towards alkynes and alkenes comes from the combination of a hard Lewis center with a soft low-coordinating anion.^[15, 16, 21, 34] According to Pearson's (hardness-softness) rules, hard cations bounded to soft anions become softer and it is not surprising that iron triflimides show an improved ability to activate (C-C) unsaturated double bonds.^[34] Incidentally, ferric triflimide [$\text{Fe}(\text{NTf}_2)_3$] presents a stabilized $3d^5$ high-spin (*hs*) semi-filled configuration as confirmed^[16] by UV spectroscopy and EPR

(Figures S19-20), that resembles in some way to the $5d^{10}$ stabilization of Au^+ and Hg^{2+} [51] and produces the softening of the Fe^{3+} cation (ionic radius: 64.5 pm for *hs* vs. 55.0 pm for *ls*). We expect that the increase in the ionic radius of iron would be reflected in the stabilization of the LUMO, which ultimately dictates the catalytic activity of Lewis acids in hydroaddition reactions to unsaturated C-C bonds.[34] Cyclic voltammetry experiments were performed for iron(III) triflimide, triflate, and chloride (Figure S21) and the reduction potential values for $[\text{Fe}^{3+}/\text{Fe}^{2+}]$ in Table 2 show a progressive decrease from chloride to triflimide, confirming the LUMO stabilization[52] of iron(III) triflimide respect to iron(III) triflate or iron(III) chloride.

Iron(III) salt	$E^0[\text{Fe}^{3+}/\text{Fe}^{2+}]$
FeCl_3	0.52 V
$\text{Fe}(\text{OTf})_3$	0.50 V
$\text{Fe}(\text{NTf}_2)_3$	0.42 V

Table 2. $[\text{Fe}^{3+}/\text{Fe}^{2+}]$ reduction potential values for three iron(III) salts.

Conclusions

Iron(III) triflimide is an active catalyst for the intermolecular hydroaddition to C-C multiple bonds of carbon, oxygen, sulfur, and nitrogen nucleophiles. $\text{PPh}_3\text{AuNTf}_2$ readily decomposes in the presence of alkynes and alkenes under heating conditions and the decomposition occurs mainly by gold reduction or sequestration by high-affinity ligands such as thiols. As a consequence, iron is a more active catalyst than gold for these reactions at temperatures $\sim 80^\circ\text{C}$ and the use of iron(III) triflimide, until now anecdotic in organic catalysis, could be a good alternative to the use of late-heavy transition metals for hydroaddition reactions.

Experimental Section

General. Reagents and solvents were obtained from commercial sources and were used without further purification otherwise indicated. All the products obtained were characterised by GC-MS, ^1H - and ^{13}C -NMR, and DEPT. When available, the characterisation given in the literature was used for comparison. Gas chromatographic analyses were performed in an instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone. GC/MS analyses were performed on a spectrometer equipped with the same column as the GC and operated under the same conditions. ^1H -, ^{13}C -, DEPT, ^{19}F -, ^{31}P -, and ^{15}N -NMR measurements were recorded in a 300 MHz instrument using CDCl_3 as solvent containing TMS as internal standard. For the ^{19}F -NMR experiments, fluorobenzene was used as internal standard. Absorption spectra were recorded on an UV/Vis spectrophotometer (UV0811M209, Varian) and EPR experiments were carried out with Bruker EMX/X equipment. IR spectra of the compounds were recorded on a Jasco 460 plus spectrophotometer by impregnating the windows with a dichloromethane solution of the compound and leaving to evaporate before analysis. IR peaks are defined as: very intense (vi), intense (i), medium (m), low (l), broad (br). Cyclic voltammetry measurements were carried out using the

conventional three electrode setup connected to an Amel potentiostat (model 7050) that was controlled by software allowing data storage and management. Platinum wire, gold wire and Ag/AgCl electrode (0.1 M KCl standard solution) were used as counter, working and reference electrodes, respectively. The electrodes were immersed into a N_2 purged 0.1 M tetrabutylammonium perchlorate electrolyte solution in acetonitrile. Measurements were carried out at a scan rate of 20 mV s⁻¹ in the range $-2.0/+2.0$ V.

Typical procedure for in-situ ^{19}F -NMR (Figure 1). FeCl_3 (97 %, Aldrich, 8.0 mg, 0.05 mmol) and AgNTf_2 (97 %, Aldrich, 60.0 mg, 0.15 mmol) were placed in a 2 mL vial. A rubber septum was fitted and dry 1,4-dioxane- D_8 (1.0 mL) was added. The mixture was magnetically stirred at room temperature for 30 min observing the precipitation of AgCl. Then, the liquid was passed through a microfilter syringe, and the filtrates were placed in a 2 mL vial. Then, 0.2 mmol of nucleophile (water, aniline, phenol, and thiophenol) was added in each case. The resultant mixture was magnetically stirred at room temperature during 5 min and analyzed by ^{19}F -NMR using fluorobenzene as internal standard.

Typical reaction procedure for hydration of 1-phenyl-1-propyne (1) (Table S1).

The corresponding catalyst was placed in a 2 mL vial and a rubber septum was fitted. 1,4-dioxane (0.5 mL), 1-phenyl-1-propyne **1** (31.3 μL , 0.25 mmol) and water (14 μL , 0.75 mmol) were added and the mixture was placed in a pre-heated oil bath at the corresponding temperature and magnetically stirred for 20 h. After cooling, *n*-hexane (1 mL) was added, the liquid was passed through a microfilter syringe, and the filtrates were analyzed by GC after addition of dodecane (11.0 μL , 0.048 mmol) as external standard.

Typical reaction procedure for dihydrothiolation of phenylacetylenes (Tables S2-S3).

The corresponding catalyst was placed in a 2 mL vial and a rubber septum was fitted. Dry 1,4-dioxane (0.5 mL), phenylacetylene (0.5 mmol) and benzene-1,2-dithiol **10** (46 μL , 0.25 mmol) were added and the mixture was placed in a pre-heated oil bath at room temperature and magnetically stirred for 24 h. After cooling, *n*-hexane (1 mL) was added, the liquid was passed through a microfilter syringe, and the filtrates were analyzed by GC after addition of dodecane (11.0 μL , 0.048 mmol) as external standard.

Synthesis of ^{15}N -benzyl sulfonamide (7c) (Scheme 1).

DIPEA (2.46 mL, 14.18 mmol) was added to a magnetically stirred solution of ^{15}N -benzylamine **7b** (776.5 μL , 7.1 mmol) in dry DCM (70 mL) under nitrogen atmosphere. The reaction mixture was cooled down -78°C , and then triflic anhydride **7a** (5.0 g, 17.73 mmol) was added dropwise. The reaction mixture was slowly warmed up to room temperature during 1 h and stirred for 1 h. Then, aqueous HCl (3 %) was added. The aqueous phase was extracted with DCM and the combined organic layers were dried over MgSO_4 . Filtration and evaporation of the solvent left a crude mixture, which was refluxed in pentane. Before cooling down to room temperature, the pentane phases were collected repeating this operation several times. Evaporation of the pentane fractions left *N*-benzyl sulfonamide **7c** as a pale brown solid (2.17 g, 83 %). ^1H NMR (300 MHz, CDCl_3): 7.52-7.46 (2H, m), 7.43-7.37 (3H, m), 5.09 (2H, s). ^{13}C NMR (300 MHz, CDCl_3): 131.7 (C), 129.9 (CH), 129.8 (2xCH), 128.9 (2xCH), 118.8 (CF₃, q, $J_{\text{C-F}} = 324.9$), 56.6 (CH₂).

Synthesis of ^{15}N -silver(I) triflimide (8) (Scheme 1).

N-benzyl sulfonamide **7c** (1.19 g, 3.20 mmol) was dissolved in ethanol (16 mL) and stirred during 8 h at room temperature. The volatiles were evaporated from the reaction mixture under reduced pressure at 60°C . The oil residue was dissolved in dry toluene (25 mL). Then, silver oxide (0.371 g, 1.6 mmol) was added and the light-protected reaction mixture was heated under reflux for 3 h, after which complete dissolution of the solid was observed. The reaction mixture was cooled down, filtered over Celite[®] and concentrated to 1:3 of the volume. Finally, the product $\text{Ag}^{15}\text{NTf}_2$ **8** was precipitated with pentane as a yellow hygroscopic solid (0.87 g, 70 %). ^{19}F NMR (300 MHz, 1,4-dioxane- D_8): -77.2 (s, CF₃). ^{15}N NMR (300 MHz, 1,4-dioxane- D_8): 141.7 (s, $^{-15}\text{NTf}_2$).

Typical reaction procedure for in situ ^{15}N -NMR experiments for the hydration of 1-phenyl-1-butyne (4) catalyzed by $\text{Fe}(^{15}\text{NTf}_2)_3$ (Figure 6). FeCl_3 (97 %, Aldrich, 8.0 mg, 0.05 mmol) and $\text{Ag}^{15}\text{NTf}_2$ (60.0 mg, 0.15 mmol) were placed in a 2 mL vial. A rubber septum was fitted and dry 1,4-dioxane- D_8 (1.0 mL) was added. The mixture was magnetically stirred at room temperature for 30 min. Then, 1-phenyl-1-butyne **4** (72.0 μL , 0.5 mmol) and water (28 μL , 1.5 mmol) were added and the mixture was placed in pre-heated oil bath at 120 $^\circ\text{C}$ and magnetically stirred for 20 h. The reaction mixture was periodically analyzed by ^{15}N -NMR at several times of reaction. One aliquot of (10 μL) was diluted in n-hexane (1 mL) and passed through a microfilter syringe. Then, dodecane (11 μL , 0.048 mmol) was added as external standard and the filtrates were analyzed by GC.

Typical reaction procedure for dihydrothiolation reactions (Table 1). FeCl_3 (97 %, Aldrich, 8.0 mg, 10 mol %) and AgNTf_2 (97 %, Aldrich, 60.0 mg, 30 mol%) were placed in a 10 mL round-bottomed flask. Then, dry 1,4-dioxane (1.5 mL) was added and the mixture was magnetically stirred at room temperature for 30 min. Then, alkyne (1.0 mmol) and benzene-1,2-dithiol **10** (92 μL , 0.5 mmol) were added and the mixture was placed in a pre-heated oil bath at 80 $^\circ\text{C}$ and magnetically stirred for 24 h. After cooling, n-hexane (10 mL) was added, observing the precipitation of the catalyst. The liquid was passed through a microfilter syringe and one aliquot of the filtrates were analyzed by GC after addition of dodecane (11.0 μL , 0.048 mmol) as external standard. Finally, the liquid was purified by preparative TLC using the corresponding eluent.

Typical procedure for cyclic voltammetry (Table 2 and Figure S21). 0.5 mM MeCN solutions of FeCl_3 were prepared as follows: FeCl_3 (> 99.99%, Aldrich, 4.0 mg, 0.025 mmol) was diluted in 5 mL of MeCN. Then, 500 μL of this solution were diluted in 5 mL of MeCN and purged with N_2 during 15 min. Cyclic voltammetry measurements were carried out using the equipment described in general procedures.

Typical procedure for cyclic voltammetry experiments for $\text{Fe}(\text{NTf}_2)_3$ (Table 2 and Figure S21). 0.1 mM MeCN solutions of $\text{Fe}(\text{NTf}_2)_3$ were prepared as follows: FeCl_3 (> 99.99%, Aldrich, 4.0 mg, 0.025 mmol) and AgNTf_2 (97 %, Aldrich, 30.0 mg, 0.075 mmol) were placed in a 2 mL vial. A rubber septum was fitted and MeCN (1.0 mL) was added. The mixture was magnetically stirred at room temperature for 30 min observing the precipitation of AgCl . Then, the liquid was passed through a microfilter syringe, and the filtrates were diluted to 5 mL of 1,4-dioxane and then 500 μL of this solution were diluted in 5 mL of MeCN and purged with N_2 during 15 min. Cyclic voltammetry measurements were carried out using the equipment described in general procedures.

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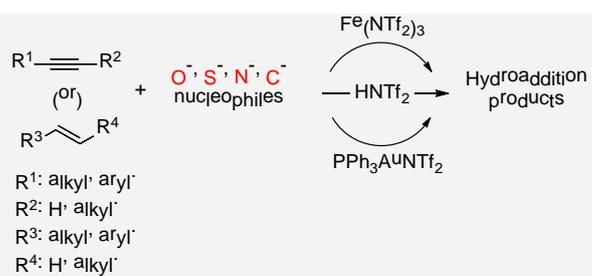
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Lewis and Brønsted catalysis

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Iron(III) triflimide as a catalytic surrogate of Gold(I) for Hydroaddition Reactions to unsaturated Carbon-Carbon Bonds.



Iron(III) catalyses as efficiently as gold(I) the hydroaddition of a wide array of nucleophiles including water, alcohols, thiols, amines, alkynes and alkenes to multiple C-C bonds.