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Homogeneous Catalysis

Metal Triflimidates: Better than Metal Triflates as Catalysts in Organic Synthesis—The Effect of a Highly Delocalized Counteranion

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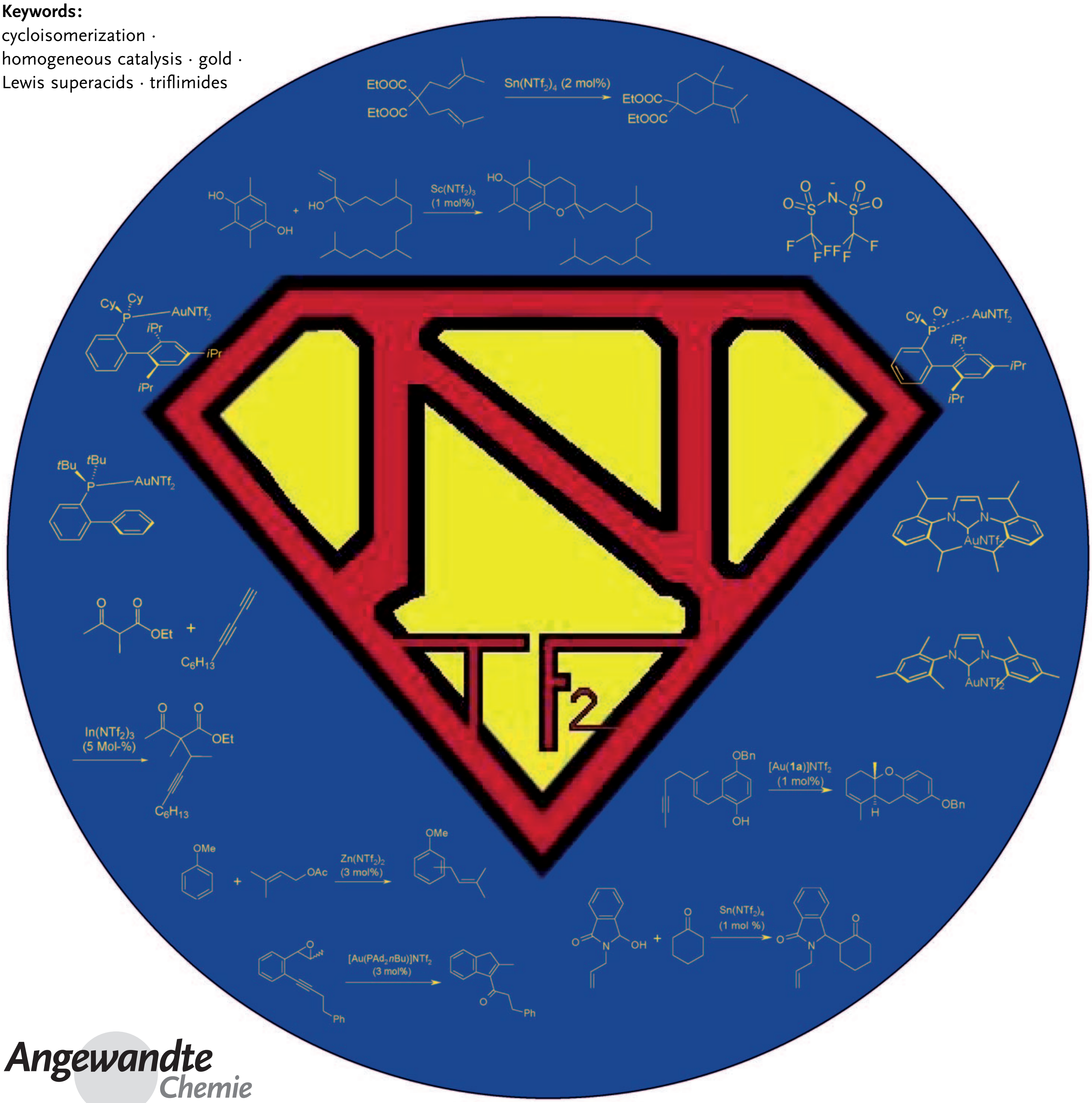

The continuously increasing need for novel and selective methods in organic synthesis to aid drug discovery and to address environmental concerns is a constant source of stimulation to develop novel and more efficient reaction systems. This has often resulted in a focus on transition metals, ligands, and additives, with much less attention paid to the counterion(s) of the metal cation. Recently, metal salts with one or more triflimidate counterion(s) have appeared as a unique class of catalysts that display outstanding σ- and π-Lewis acid character. The highly delocalized nature of the triflimidate counterion, combined with its high steric hindrance results in virtually no nucleophilic behavior and an extremely high positive charge density on the metal cation, thus enhancing its Lewis acid character. Consequently, these metal triflimidates often outperform their metal halide or triflate analogues. This Review describes general methods for the preparation of metal triflimidate salts and their use as catalysts.

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1. Introduction

The electrophilic activation of organic substrates through acid catalysis with either protons or by Lewis acids constitutes an important method for the synthesis of fine and bulk chemicals. While Lewis acids have been widely used for carbon–carbon bond-forming reactions, the use of Brønsted acids has mostly been employed in acid-catalyzed isomerization, alkylation, acylation, or protection/deprotection reactions.[1–4]

An increasing interest in the catalytic activity of superacids has risen over the last 30 years, in particular in the field of homogeneous catalysis. Protic and Lewis superacids offer several unique advantages, such as high catalytic activity, which results in low catalyst loadings and low energy demand. Their recent development as catalysts in organic reactions has broadened their field of applications, thereby allowing for novel and highly efficient processes under mild conditions.[5,6]

Superacids are defined as protic compounds that have a greater acidity than pure sulfuric acid[7,8] and they typically possess a Hammett acidity function H_0 below -12.[9,10] Besides SbF_5 and other strong Lewis acids, a metallic salt formed from a metal cation with the conjugated base of a superacid could also be termed Lewis superacids.

Among the protic superacids, trifluoromethane sulfonic acid (commonly called triflic acid; $HOSO_2CF_3$, HOTf) and fluorosulfonic acid ($HOSO_2F$) are among the main representative compounds. The electronegativity of the $CF_3SO_2^-$ (triflyl) group has been well documented, and the trifluoromethanesulfonyl moiety is one of the strongest known neutral electron-withdrawing groups.[11] These unique properties have led to the development and general use of metal triflate salts, which are now widely used as Lewis acid catalysts in many reactions. Several of these triflate salts are now commercially available, which has resulted in their widespread use in organic synthesis on a laboratory scale.[12–15] Other trifluoromethanesulfonyl derivatives have also been prepared, such as perfluorinated sulfonic acids supported on organic resins, which have also been used to catalyze reactions in organic synthesis.[16]

Particularly interesting is triflimide ($HNTf_2$; $HN(SO_2CF_3)_2$) also called triflimidic acid or bis(trifluoromethanesulfonyl)imide, and sometimes abbreviated as TFSIH. The presence of two highly electron-withdrawing trifluoromethanesulfonyl groups on a nitrogen atom strongly increases the acidity of the N-bound hydrogen atom.[17,18] However, the relative acidities of HOTf and $HNTf_2$ are the subject of debate, with their out-of-range acidities only being estimated or measured indirectly. The gas-phase acidity of $HNTf_2$ ($\Delta G_{acid} = 291.8\ \mathrm{kcal\,mol^{-1}}$) has been measured to be greater than that of HOTf ($\Delta G_{acid} = 299.5\ \mathrm{kcal\,mol^{-1}}$).[19] Gas-phase acidities below $300\ \mathrm{kcal\,mol^{-1}}$ where recently revised, with the ΔG_{acid} value of $HNTf_2$ dropping to 286.5; the value for HOTf was not provided.[20] Conversely, the pK_a values of $HNTf_2$ is 1.7 in H_2O,[17] while that for HOTf is -5.9.[21] The pK value of $HNTf_2$ and HOTf have been estimated to be negative (up to -14) by the H_0 method;[22] however, those values are strongly dependent on the solvation and concentration.[23] pK_a values of 7.8 and 4.2 were measured in for $HNTf_2$ and HOTf, respectively, in acetic acid.[17] These data suggest that $HNTf_2$ is a poorer Brønsted acid than HOTf, which seems to be confirmed by the better ability of HOTf over $HNTf_2$ to protonate poor Lewis bases such as carbonyl groups.[24] The nucleophilicity of the $(CF_3SO_2)_2N^-$ ion is, however, significantly lower than that of $CF_3SO_3^-$, as evidenced by their donor numbers[25] of 5.4 and 16.7, respectively.[24] Another

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striking observation in regard to triflimide derivatives is that trialkylsilylbis(trifluoromethanesulfonyl)imide derivatives of general formula R_3SiNTf_2 exhibit stronger Lewis acidity than the corresponding silyltriflates.[24] The comparative Lewis acidities do not follow the order of Brønsted acidities, and this dichotomy could result from the difference in the sizes of the two anions: the bis(trifluoromethanesulfonyl)imidate anion is much larger than the triflate one, and the higher hindrance in R_3SiNTf_2, which does not exist in a protic acid, would thermodynamically favor the formation of a complex with a smaller ligand such as a carbonyl group. These considerations combined with the unique and exceptional reactivity often displayed by catalysts based on metallic triflimides resulted in us considering Tf_2N^- derivatives as superior Lewis superacids than TfO^- derivatives. As the Brønsted acidity seems to decrease and the Lewis acidity to increase with the number of electron-withdrawing groups attached to the atom bound to the labile hydrogen atom (Bronsted acid, $\mathrm{OH} > \mathrm{NH} > \mathrm{CH}$) or the metal center (Lewis acid, $\mathrm{OM} < \mathrm{NM} < \mathrm{CM}$), the metallic salt of tris(triflyl)methane ($HC(SO_2CF_3)_3$) is expected to be even more active than the triflimidate derivative; this proposal is confirmed by the limited data available.[26,27] However, although a higher activity is generally observed for metallic triflimidate salts than triflate analogues, it is necessary to ensure that both Lewis acids were prepared by the same method and that their hydration/solvation are of the same order of magnitude. A discussion is ongoing as to the role of ligands, and particularly of water, on the activity of Lewis superacids. It is known that metal triflates could occasionally suffer from several undesirable events, such as partial hydrolysis to release TfOH[28] or formation of a hydrate such as $(TfO)_nMOH_2$—a kind of Lewis acid assisted Brønsted acid (LBA).[29] Higher reaction rates could, therefore, possibly stem from a synergistic effect between Brønsted and Lewis acid catalysis.

Likewise, the presence of a coordinating molecule in the metal environment can modify the reaction kinetics and change the mechanistic outcome, as recently shown in related $PtCl_2$-catalyzed cationic processes.[30,31] As stated above, metal triflates and triflimidates may undergo partial hydrolysis in the presence of water to form metal–OH bonds, with HOTf or $HNTf_2$ released, respectively. The protons have been suspected to be the true catalysts in some processes and their role in reactions catalyzed by metal triflates or triflimidates, therefore, has to be considered, especially when the reactions have been reported to occur with similar rates and selectivities as those with strong protic or Lewis acid catalysts.[27,32] Conversely, other processes are not catalyzed by protons, and these may thus be considered as strictly Lewis acid catalyzed. Protons can also act as co-catalysts, as inferred from other examples.[33] Recent calculations have indicated that the coordination of DMSO or water molecules to a metal triflate is an exothermic process, whereby these ligands may replace a triflate moiety and this species then plays a role in the metal catalysis and prototropy.[34]

Triflimidate derivatives have a high degree of ionic character, because of the high electronegativity of the Tf_2N^- ion, which results in high solvation energies. This is a major factor that leads to the high solubilities of most triflimidates in a variety of polar organic solvents. The high electronegativity of the triflimidate anion, together with its relatively large volume and low charge density, results in poor complexing ability, which allows their metal salts to act as strong σ- or π-Lewis acids, depending on the metal center. Pronounced delocalization of the negative charge of the Tf_2N^- ion on the nitrogen, sulfur, oxygen, and fluorine atoms and a marked double bond character of both N–S bonds were evidenced by spectroscopic and theoretical studies.[35] It is noteworthy that triflimidates are almost insensitive to oxidation or reduction.

Data on the structural analysis of the triflimidate anion are scarce, they only consider X-ray crystal structures or DFT gas-phase studies, while ignoring the dynamic behavior of this labile ligand in the solvant phase and in the presence of competing ligands and/or substrate molecules. The Tf_2N^- ion is generally described as highly delocalized,[36,37] with partial negative charges on the oxygen atoms of both sulfonyl moieties (0.9–1.0 from Natural Bond Orbital analysis[38]) and four possible modes of coordination: η^1-N, η^1-O, η^2-N,O, and η^2-O,O.[37] The η^2-O,O mode seems to be the most frequent mode of coordination, with the anion adopting a cisoid conformation (the CF_3 groups lying on the same side of the S-N-S plane) which leads to a delocalized six-membered ring when coordinated to a metal center; the Tf_2N^- ion behaves more like a ligand.[39] By comparing data from metallic triflate and triflimidate salts, it appears that the bond lengths between the coordinating oxygen atom and the metal center are usually of the same order of magnitude[37–42] (typically between 2.1 and 2.5 Å); the longest Yb^{II}–O bond of 2.41–

Sylvain Antoniotti was born in Nice, France, in 1975, and gained his PhD in 2003 in the group of E. Duñach. After post-doctoral research at the Rensselaer Polytechnic Institute (Troy, NY) in the group of J. S. Dordick, he became assistant professor (ATER) at the Ecole Nationale Supérieure de Chimie de Paris (France), where he worked with J.-P. Genêt and V. Michelet on gold-catalyzed cycloisomerization. Since 2005, he has been a CNRS researcher in a joint laboratory with the University of Nice-Sophia Antipolis, where he works on the development of environmentally friendly methods for organic synthesis, catalysis, and biocatalysis, and completed his habilitation in 2008.

Vincent Dalla was born in Châlons en Champagne, France, in 1967. He obtained his PhD in 1994 under the supervision of P. Pale. In 1995 he was appointed Maître de Conférences at the Ecole Nationale Supérieure de Chimie de Lille, and then in 1999 he moved to the University of Le Havre, where he became professor in 2008. His research interests include the development of catalytic, stereoselective, and tandem reactions in N-acyliminium ion chemistry and their synthetic applications towards alkaloids, by using the super Brønsted acid $HNTf_2$ and its metallic salts $M(NTf_2)_n$.

2.52 Å was reported for [mppyr][Yb(NTf_2)$_4$] (mppyr = 1-methyl-1-propylpyrrolidinium).[38] Interestingly, when coordinated, the triflimidate anion has the capacity to undergo structural changes, compared to the free anion, depending on the environment.[37] It has been shown in the reactions of silicon-based Lewis acids that although the Bronsted acidity of HOTf is superior to that of $HNTf_2$, R_3SiNTf_2 is a superior Lewis acid than R_3SiOTf because of the greater steric repulsion between the R_3Si and NTf_2 groups.[24] When explaining the superiority of the triflimide derivatives over the triflate analogues presented in this Review, one also has to consider the effect of the protic acid released from these compounds: in the latter case the superacid HOTf is released, whose acidity could be responsible for deleterious side reactions, while $HNTf_2$, although strong, remains less active towards organic compounds.

The activity of metal triflimidates can be tuned and a number of elegant solutions have been devised. The high electropositivity of aluminum makes $Al(NTf_2)_3$ a prototypic superactive triflimidate reagent. Its reactivity can be controlled by tuning the number of triflimidate ligands in $[Al(L)_m](NTf_2)_n$ where $m+n=3$ (Lewis acidity control), and/or by introducing a very bulky ligand L (steric control) by derivatizing Me_3Al through a stepwise sequence.[43–46] These strategies should find a more general application with other organometallic compounds of type $M(R)_n$ (R = alkyl, aryl). Solvent effects have also been observed, with the activity of a given triflimidate reagent significantly lowered in the presence of a coordinating solvent.[47] The solubility of the catalyst is also an important parameter that may affect the activity of triflimidate-based salts.[48] Several examples illustrating the regulation of the catalytic activity of gold(I) triflimidates—an important subclass of metallic triflimidates—by proper choice of the steric and electronic features of the stabilizing ligand (either a phosphine or a N-heterocyclic carbene) have been reported.[49–53]

Of the metallic triflimidate salts, only lithium triflimidate ($LiNTf_2$), a safe substitute for lithium perchlorate, has been used in industrial applications, in particular as an electrolyte in batteries for electric vehicles.[54–56]

This Review will focus on the preparation and use of metallic triflimidate salts in catalytic reactions, with their main applications in the field of organic transformations up until March 2010 highlighted. Except for the lithium and silver salts, metallic bis(trifluoromethanesulfonyl)imide salts are, to our knowledge, not commercially available.[57] The use of $LiNTf_2$ as an electrolyte in lithium batteries[54–56] and its electrochemical behavior[58] as well as the applications of organic triflimidate salts as ionic liquids are excluded from this Review.[59–61]

Other reviews focusing on certain types of transformations (enyne cycloisomerization,[62,63] heterocyclization,[64,65] carbocyclization,[65] or other C–C bond-forming reactions[66]) or certain types of catalysts ($HNTf_2$,[67] oxazaborolidinium triflimidates,[68] gold catalysts[69,70]) also mention triflimidate derivatives as catalysts.

Elisabet Duñach was born in Barcelona, Spain. She obtained her PhD at the University of Barcelona in 1981 in the group of J. Castells. After postdoctoral research at the University California, Berkeley (K. Vollhardt; 1981–1983) and then at the University Paris XIII, Orsay (H. Kagan; 1983–1985) she became CNRS researcher in 1985 at LECSO, Thiais (France) in the group of J. Périchon. In 1991 she headed (with J. Riess) the Laboratoire de Chimie Moléculaire at the University of Nice, where she is now Director of Research, as well as Director of the "Institut de Chimie de Nice". Her interests involve the development of novel methods in organic synthesis.

2. Preparation of $M(NTf_2)_n$

A fair number of different methods exist for the preparation of metal triflimidate salts, and the choice of a given method is mainly driven by the availability and cost of the starting materials, as well as safety concerns and practical aspects.

A common, general, and high-yielding strategy for preparing metallic triflimidates involves the reaction of metal oxides, carbonates, hydroxides, or halides with triflimidic acid in aqueous media or directly in water.[71–74] The pronounced hygroscopic nature of these salts means they are obtained as hydrates of general formula $M(NTf_2)_n{\cdot}x\,H_2O$-($1 \leq x \leq 9$). Displacement strategies have been used, for example, to prepare $Mg(NTf_2)_2$ from the corresponding hydroxide,[75] or $AgNTf_2$ from the corresponding carbonate (Scheme 1).[76] Several lanthanide and rare earth triflimidates have also been prepared from the corresponding carbonates and excess $HNTf_2$ in water.[73,77,78] The preparation of $Al(NTf_2)_3$, $Yb(NTf_2)_3$, and $Ti(NTf_2)_4$ has been reported from the corresponding chlorides and $HNTf_2$ in water.[79] However, the exact formula of the salts, including the number of solvating water molecules, is rarely provided.

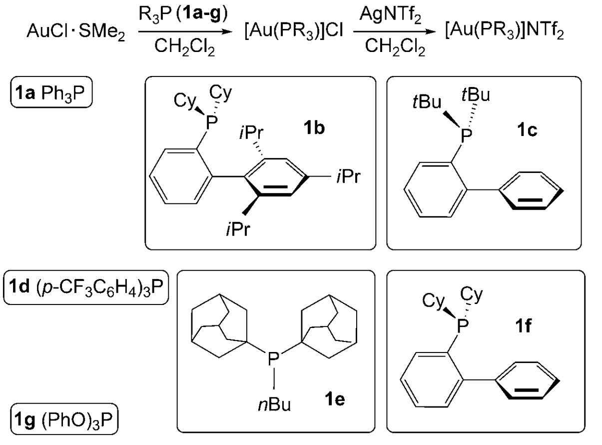
$$2\ HN(SO_2CF_3)_2 \;+\; Ag_2CO_3 \xrightarrow[H_2O,\ 65\ ^\circ C]{} \underset{79\%}{2\ AgN(SO_2CF_3)_2{\cdot}nH_2O}$$

Scheme 1.

Alkali metal triflimidate salts have also been prepared from alkali metal carbonates in the presence of $HNTf_2$ in a methanolic medium.[39] $CsNTf_2$ has been prepared from CsF and $HNTf_2$ at low temperature, with slow evolution of HF.[11,56]

Another method for the preparation of metal triflimidates involves the use of a metathesis reaction between a metal complex and a metallic triflimidate, which results in exchange of the counterion and precipitation of a mineral substance, most generally a chloride salt. For example, a metathesis reaction involving two equivalents of $NaNTf_2$ and $MgSO_4{\cdot}6H_2O$ in Et_2O has been used to prepare $Mg(NTf_2)_2{\cdot}8H_2O$.[36] The exchange reaction between $AgNTf_2$ and trialkyltin chlorides allowed access to $R_3Sn(NTf_2)$ derivatives (R = Me, Bu, and Ph).

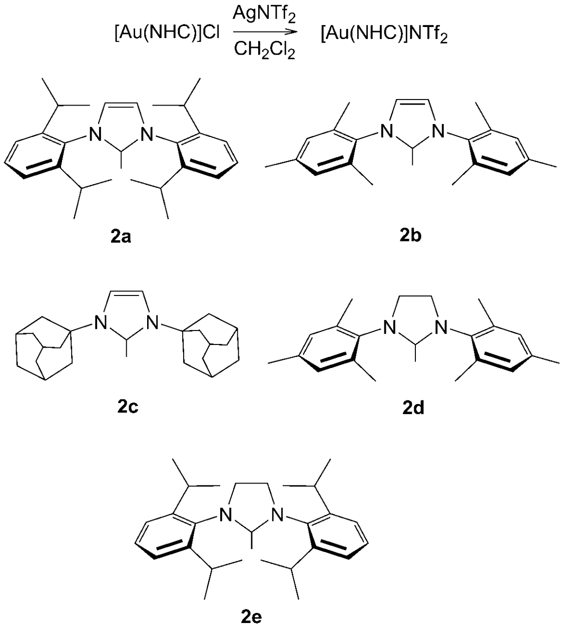
A useful application of such metathesis-based transformations is the preparation of cationic gold triflimidates. There is a great demand in the field of gold catalysis[80–83] to prepare novel active gold complexes, such as cationic gold species with the poorly coordinating triflimidate anion. Gold triflimidates stabilized by a phosphine ligand were the first generation of these catalysts, which have been prepared by metathesis between $[Au(PR_3)]Cl$ and $AgNTf_2$ in dichloromethane. The procedure appeared amenable to various phosphine ligands and allowed the preparation of a small library of catalysts (Scheme 2).[84]



Scheme 2. Some phosphine gold(I) triflimidate complexes. Cy = cyclohexyl.

In sharp contrast to similar cationic phosphine gold species bearing a non-nucleophilic counteranion such as BF_4^-, PF_6^-, or SbF_6^-, these $[Au(PR_3)]NTf_2$ salts are crystalline air-stable compounds, and thus offer significant advantages in terms of preparation, storage, and handling.

A second category of Au^I catalysts is obtained from the reaction between N-heterocyclic carbene[85] complexes of gold(I) chloride[86] and $AgNTf_2$ under similar conditions (Scheme 3). The resulting N-heterocyclic carbene gold(I) triflimidates were, again, mostly isolated as crystalline and air-stable materials,[87] and showed a unique reactivity profile in a number of reactions.



Scheme 3. Some carbene gold(I) triflimidate complexes.

Although some Lewis acids are stable in water and may remain active in an aqueous environment,[88–92] some reactions do not tolerate water, and thus the preparation of anhydrous metal salts is desirable. An alternative strategy for preparing metal triflimidates relies on ligand exchange between an organometallic compound of type R_nM and $HNTf_2$ through protodemetalation, which results in the replacement of the organic substituent at the metal center by Tf_2N^-, with the concomitant liberation of RH (gas evolution).[43,44] For example, $Bi(NTf_2)_3$ has been obtained from triphenylbismuth and stoichiometric amounts of $HNTf_2$ in dichloromethane, with formation of benzene.[93] One of these water-free strategies was applied to alkoxy metal complexes of type $M(OR)_n$, and it has been used for the preparation of $Ti(OiPr)_2(NTf_2)_2$.[79] An alternative water-free, mild, and simple electrochemical procedure for the preparation of anhydrous metallic triflates and triflimidates has been developed.[94,95] It is based on the anodic oxidation of the desired metal in the presence of triflic or triflimidic acid, with evolution of dihydrogen as the only by-product (Scheme 4).

Cathodic reaction: $Tf_2NH + e^- \longrightarrow Tf_2N^- + \tfrac{1}{2} H_2$

Anodic reaction: $M \longrightarrow M^{n+} + n\,e^-$

In solution: $n\,Tf_2NH + M \longrightarrow M(NTf_2)_n + \tfrac{n}{2} H_2$

Scheme 4.

$Ni(NTf_2)_2$, $Zn(NTf_2)_2$, $Mg(NTf_2)_2$, $V(NTf_2)_2$, $Sm(NTf_2)_3$, $Al(NTf_2)_3$, and $Sn(NTf_2)_4$[95] were prepared in almost quantitative yields in DMF or nitromethane at room temperature by this procedure. This method illustrates the advantage of obtaining the metallic salts as solvates with organic solvent molecules (DMF or $MeNO_2$) instead of water, since it provides access to anhydrous salts. The anodic dissolution of aluminum in the presence of $LiNTf_2$ and other perfluoroalkylsulfonylimides has been investigated for electrochemical access to several Al^{III} salts.[96]

More recently, a straightforward method based on the oxidative dissolution of metal powders in the presence of triflimidic acid in DMSO under molecular oxygen has been described for the preparation of metallic triflimidates.[97] Anhydrous $Cu(NTf_2)_2$, $Sn(NTf_2)_4$, $Bi(NTf_2)_3$, and $Mg(NTf_2)_2$ were prepared quantitatively and were obtained as solvates with DMSO molecules.

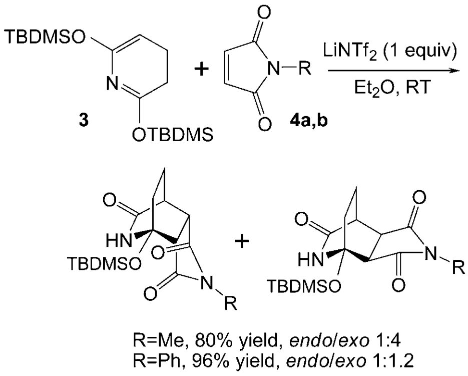
Various triflimidate salts were prepared by treatment of *N*-benzyltriflimide with ethanol to form an oxonium intermediate, which was then neutralized by metallic hydroxides to provide the corresponding metallic salts. In addition to alkali and alkaline earth metals triflimidates, the preparation of Ag^I, Zn^{II}, and Sc^{III} triflimidates has also been described.[98]

3. C–C Bond-Forming Processes Catalyzed by Metallic Triflimidates

3.1. Cycloaddition Reactions

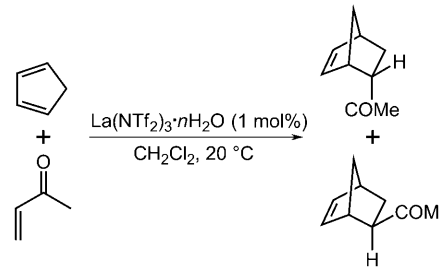
3.1.1. [4+2] Cycloadditions

The first example of using metallic triflimidates in organic synthesis was reported in 1995. In this case, lithium trifluoromethanesulfonimide ($LiNTf_2$) was used for the acceleration of a range of Diels–Alder cycloadditions involving heterodienes and electron-deficient dienophiles.[99,100] The use of stoichiometric amounts of $LiNTf_2$ in concentrated acetone or diethyl ether solutions (2.5–4.0 M) was shown to be an efficient and safe alternative to the previously used 5 M solution of $LiClO_4$ in diethyl ether.[101] Interestingly, $LiNTf_2$ was found to reverse the reaction diastereoselectivity in favor of the *exo* adducts, as illustrated in the example of the cycloaddition of azadiene **3** with cyclic dienophiles **4a**,**b** (Scheme 5). Besides the safety concerns regarding the use of perchlorates compared to $LiNTf_2$, these results highlighted the stereocomplementarity of these two systems.



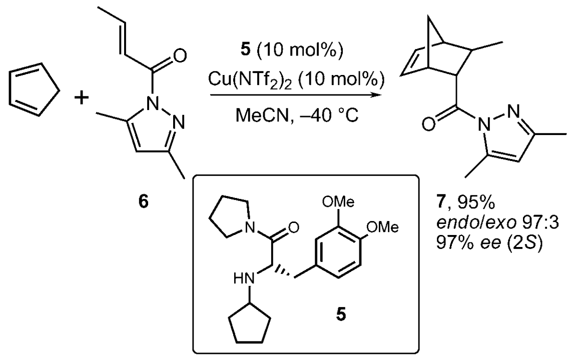
Scheme 5. TBDMS = *tert*-butyldimethylsilyl.

The first catalytic example of the use of metal triflimidates in organic synthesis was demonstrated by the Diels–Alder cycloaddition of cyclopentadiene with methyl vinyl ketone (Scheme 6). A much lower catalyst loading of 1 mol% $La(NTf_2)_3{\cdot}n\,H_2O$ was sufficient compared to lithium, barium, calcium, magnesium, and zinc triflimidates.[48] Kinetic analysis indicated that the $La(NTf_2)_3{\cdot}H_2O$-catalyzed reaction was 1440 times faster than the uncatalyzed process, while the triflate analogue $La(OTf)_3{\cdot}H_2O$ showed no acceleration effect. Furthermore, the triflimidate salts were also shown to display an interesting solubility effect. Thus, $La(NTf_2)_3{\cdot}H_2O$ had higher catalytic activity in CH_2Cl_2 than related and more Lewis acidic perfluoroalkyl triflimidate salts $La(NTfC_nF_{2n+1})_3{\cdot}H_2O$, because the latter salts were less soluble in this solvent. Catalyst solubility thus appeared to be a tunable parameter to regulate the reactivity of Lewis superacids.[48,102]



Scheme 6.

An artificial Diels–Alderase prepared in situ from $Cu(OTf)_2$ or $Cu(NTf_2)_2$ and a L-DOPA-derived ligand was designed.[103,104] These chiral complexes were effective at 2—10 mol% in a highly *endo*-(2*S*)-selective Diels–Alder reaction with α,β-unsaturated 1-acyl-3,5-dimethylpyrazoles.[104] The use of the more active $Cu(NTf_2)_2$-derived complex obtained with chiral ligand **5** instead of the $Cu(OTf)_2$-derived complex allowed cycloadditions of various conjugated amides with different dienes to be perfomed efficiently at lower temperature. These reactions afforded the Diels–Alder adducts with generally improved *endo* selectivity and enantioselectivity. The reaction between the *trans*-crotyl dienophile **6** and cyclopentadiene to afford **7** is shown as an example (Scheme 7).

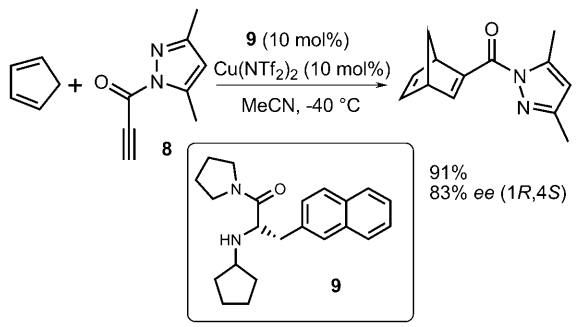


Scheme 7.

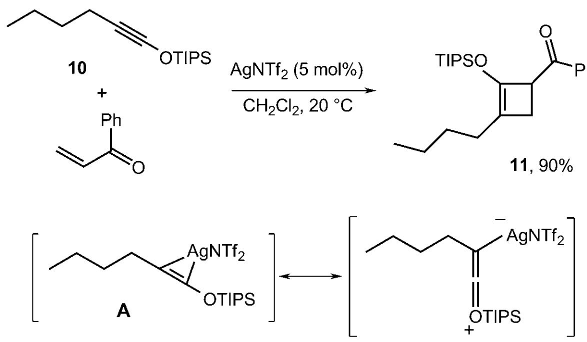
This method was further extended to the [4+2] and [2+2] cycloadditions of propynamide derivatives such as **8** with dienes and enol ethers to generate the corresponding adducts.[105] Only the use of $Cu(NTf_2)_2$ in combination with a modified naphthyl ligand **9** allowed the lower reactivity of alkynes versus alkenes as dienophiles to be overcome (Scheme 8).[105]

3.1.2. [2+2] Cycloadditions

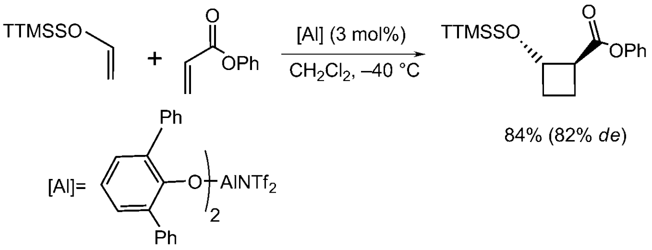
A mechanistically novel [2+2] cycloaddition catalyzed by silver triflimidate and involving siloxy alkynes and unsaturated ketones, esters, and nitriles was recently reported.[106] Of the various reagents evaluated in a model reaction between 1-triisopropylsiloxy-1-hexyne (**10**) and phenyl vinyl ketone, $AgNTf_2$ (5 mol%) was shown to be superior to $AgSbF_6$ and



Scheme 8.



Scheme 9. TIPS = triisopropylsilyl.



Scheme 10. TTMSS = tris(trimethylsilyl)silyl.

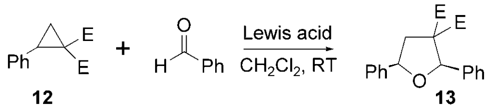
AgOTf, with the siloxy cyclobutene **11** obtained in 90 % yield within a few minutes (Scheme 9). The reaction was extended to the synthesis of several siloxy cyclobutenes in 68–83 % yield. The same 2,4-disubstituted siloxycyclobutene regioisomer was obtained from the reaction between **10** with either (*E*)- or (*Z*)-methyl crotonates. This observation seems consistent with an unprecedented mechanism, in which the formation of a silver-siloxyalkyne intermediate (π-complex **A**) through activation of the triple bond is preferred to the conventional σ-Lewis acid activation of the enone.

Another interesting feature of the triflimidate salts is the possibility to tune their reactivity and stereocontrol by controlling their stoichiometry, coordination, and steric hindrance. This was illustrated with a novel, highly stereoselective [2+2] cycloaddition of aldehyde-derived tris-trimethylsilyl enol ethers and acrylates. The use of 3 mol % $EtAlCl_2$ or Et_2AlNTf_2 afforded good catalytic efficiency but moderate stereocontrol, while low yields were recorded with $EtAl(NTf_2)_2$ and $Al(NTf_2)_3$ because their Lewis acidities were too high. The catalytic efficiency and stereocontrol issues of this challenging coupling between sensitive reaction partners were solved by using the bulky bis(2,6-diphenylphenoxide)aluminum triflimidate at 3 mol % (Scheme 10). The cyclobutane derivative was obtained in 84 % yield and 82 % diastereomeric excess in favor of the *trans* isomer.[43,44]

The reaction was efficient when bulky vinyl-1-tris(trimethylsilyl)silyloxy was used, but did not proceed when the acid-sensitive TMS or TIPS groups were present (they decomposed under the reaction conditions). The subtle interplay between the mild Lewis acidity and steric hindrance of the catalyst and the silylated nucleophile was the key to the reaction, which was achieved by fine tuning of the stoichiometry of the Tf_2N^- counterion.

3.1.3. [3+2] Cycloadditions

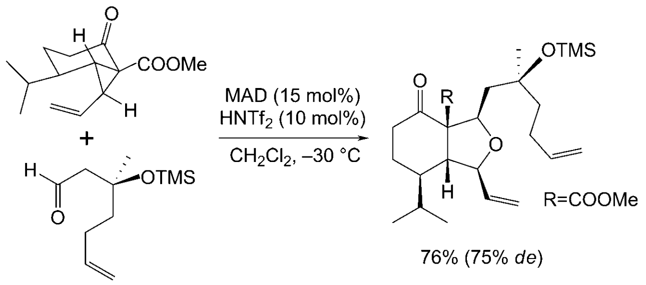
$AgNTf_2$ was shown to promote the highly diastereoselective [3+2] cycloaddition of benzaldehyde and donor/acceptor-substituted cyclopropane **12**, which functions as a three-carbon 1,3-dipole, to give the highly functionalized *cis*-2,5-disubstituted tetrahydrofuran **13** in 73 % yield.[107] $AgNTf_2$ was the only triflimide salt tested in this reaction, and although it performed better than AgOTf, several metallic triflates, and in particular $Sn(OTf)_2$, also gave good results (Scheme 11).



Lewis acid	Yield [%]	d.r.
AgOTf (0.5 equiv)	5	n.d
$AgNTf_2$ (0.5 equiv)	73	>100:1
$Sn(OTf)_2$ (0.5 equiv)	97	>100:1
$Sn(OTf)_2$ (5 mol%)	98	>100:1

Scheme 11.

The propensity of the bulky aluminum triflimidate reagents to prevent decomposition of sensitive materials[43,44] was again illustrated by the [3+2] cycloadditions and the formal [4+2] cycloadditions of aliphatic aldehydes with donor/acceptor cyclopropanes and cyclobutanes, respectively.[45,46] Protonolysis of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide[108] (MAD) by $HNTf_2$ afforded $MADNTf_2$, which appeared to be the best catalyst to control these reactions when used in situ (the aliphatic aldehydes decomposed with many other Lewis acids). This triflimidate reagent was successfully implemented in an asymmetric total synthesis of (+)-polyanthellin A to construct a key tetrahydrofuran intermediate (Scheme 12).

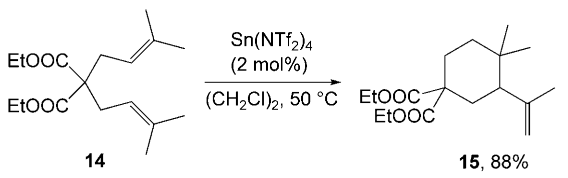


Scheme 12. TMS = trimethylsilyl.

3.2. Rearrangement Reactions

3.2.1. Cycloisomerization of 1,6-Dienes and Eneallenes

The first Lewis acid catalyzed cycloisomerization of 1,6-dienes to give functionalised cyclohexanes was reported to be catalyzed by $Sn(NTf_2)_4$,[109] while conventional 1,6-diene cycloisomerization mainly leads to five-membered ring derivatives.[110] A model reaction with the hindered bisprenyl malonate derivative **14** revealed that $Sn(NTf_2)_4$ was a more active catalyst than other tin salts or other metal triflates or triflimidates. The substituted cyclohexane derivative **15** was produced in 88 % yield by using 2 mol % of $Sn(NTf_2)_4$ (Scheme 13).

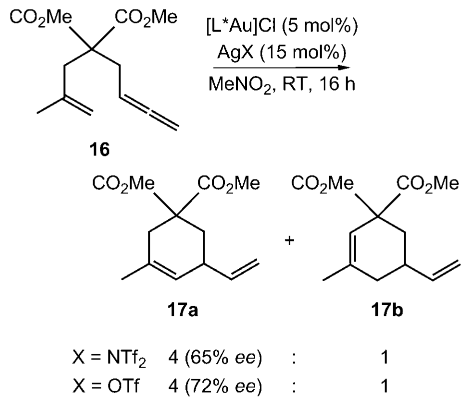


Scheme 13.

The procedure was extended to a series of 1,6-dienes with differently substituted double bonds, and cyclization yields of 46–92 % were obtained. The rearrangement involved a Markovnikov-type addition of one double bond to the other double bond, presumably activated by Sn^{IV}, thus supporting a carbocationic-type mechanism in which the ring size could be controlled by the olefin substitution. Replacing one ester function by a cyano, keto, sulfono, or phosphono group allowed differently functionalized cyclohexane derivatives to be obtained.

An enantioselective, structurally and mechanistically related cycloisomerization of 1,6-eneallenes into vinylcyclohexenes catalyzed by in situ generated cationic gold(I) species has been developed.[111] Two isomeric vinylcyclohexenes **17a** and **17b** were formed from **16**, with (*R*)-3,5-xylylbinap found to be the best ligand in terms of enantioselectivity. [Au(3,5-xylylbinap)]NTf_2 resulted in 65 % *ee* for the major isomer **17a** whereas the corresponding triflate gave 72 % *ee* (Scheme 14).

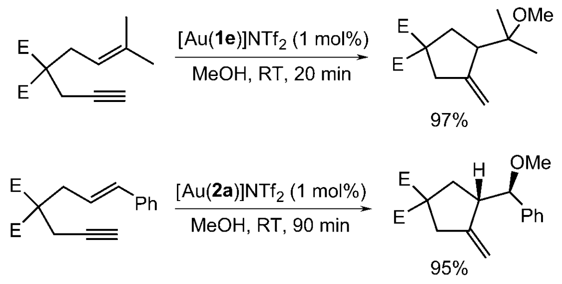
A number of mechanistic experiments suggested a possible role of Ag^+ in the process. The possible involvement of competitive Ag^+- and H^+-catalyzed side reactions could partially account for the moderate *ee* values obtained in these reactions.



Scheme 14. L* = (*R*)-3,5-xylylbinap.

3.2.2. Cyclization of 1,n-Enynes and 1,n-Diynes

The gold-catalyzed cycloisomerization of enynes in processes terminated by proton elimination or by the intra- or intermolecular addition of heteronucleophiles or arenes has been studied extensively in recent years.[62,80,82,112] Various catalysts of type [Au(PR_3)]NTf_2 with exotic phosphine or N-heterocyclic carbene (NHC) ligands (Schemes 2 and 3) have been used successfully as catalysts for the cycloisomerization of various 1,6-enynes and 1,5-enynes as well as for the disfavored 1,6-enyne methoxycyclization to methoxymethylidenecyclopentane derivatives (Scheme 15).[84,87]

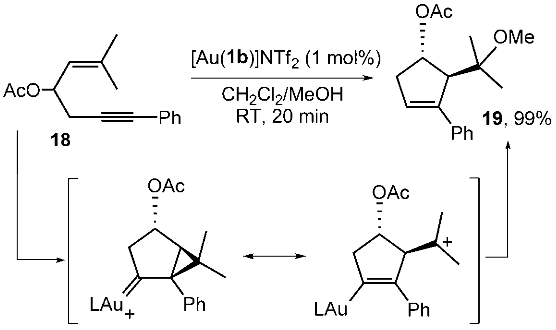


Scheme 15. E = COOMe.

These novel cationic gold triflimidates were also shown to exhibit excellent activities in several other transformations, including the Conia-ene reaction, the Rautenstrauch reaction,[113] the propargyl Claisen rearrangements,[49] the intramolecular hydroarylation of alkynes,[84] and the alkoxylation (carbene-transfer reaction) of ethyl diazoacetate.[87] These reactions were generally achieved with lower catalyst loadings (typically 0.01–1 mol %) and shorter reaction times with respect to earlier related examples involving metallic triflates or hexafluoroantimonates.[84]

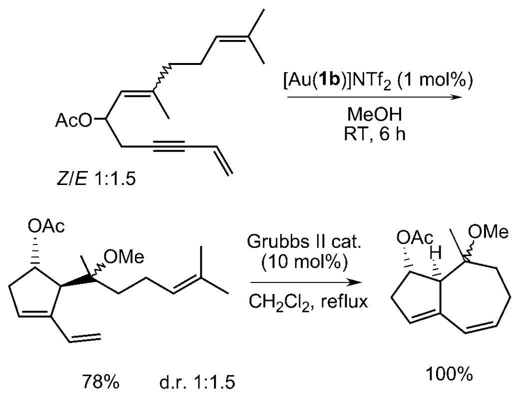
The cyclization of 1,5-enynes such as **18** to cyclopentene derivatives was also reported by using bulky biphenylphosphine-based gold species as the catalyst (1 mol %).[50] Although the triphenylphosphine gold triflimidate gave the cyclopentene derivative **19** in 58 % yield, the use of a bulkier catalyst with ligand **1b** considerably enhanced both the reactivity and the selectivity to reach 99 % yield

(Scheme 16); this finding demonstrates additional aspects of fine tuning the triflimidate catalysts. The transformation afforded the *anti* product stereoselectively through a 5-*endo*-type cyclization.



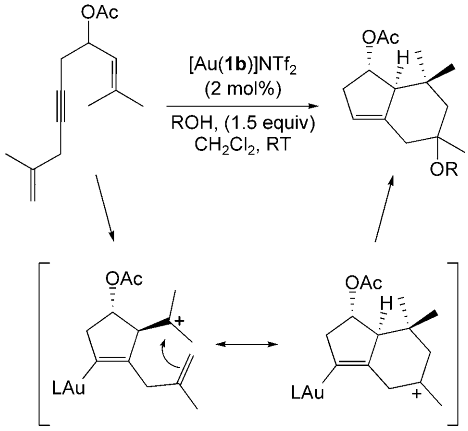
Scheme 16.

Variations in the substitution pattern of the substrate were tolerated, as well as the choice of the incoming hydroxy nucleophiles—including primary, secondary, or phenolic hydroxy groups and even acetic acid. In a further application, this gold-catalyzed alkoxycyclization process was followed by a ring-closing metathesis reaction for the synthesis of functionalized bicyclo[5.3.0]decanes and bicyclo[6.3.0]undecanes, which correspond to the core structure of terpenoids isolated from the root bark of *Dictamnus dasycarpus* (Scheme 17).[50]



Scheme 17.

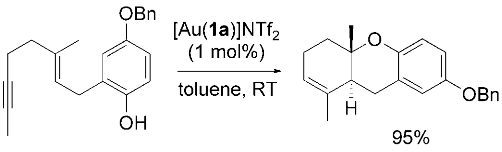
The enyne cyclization was also combined with a further cation-olefin annulation step when 1,8-dien-4-ynes were used, thereby providing a new and straightforward access to bicyclo[4.3.0]nonenes (Scheme 18).[51] Although the monocyclic alkoxy cyclopentene product still competes to an important extent when MeOH is used as a scavenger (1.5 equiv), its formation is significantly limited by the use of weaker nucleophiles, such as phenols, carboxylic acids, or carbamates.



Scheme 18.

Recently, the same bulky catalyst [Au(**1b**)]NTf$_2$ was reported to catalyze the unusual cycloisomerization of 1,9- and 1,10-diynes into medium-sized cycloalkynes. The process was proposed to proceed through nucleophilic attack of a gold acetylide on a gold-activated alkyne.[52] [Au(PPh$_3$)]NTf$_2$ also catalyzed the cycloisomerization of enynes to form axially chiral racemic[114] and nonracemic[115] biaryls.

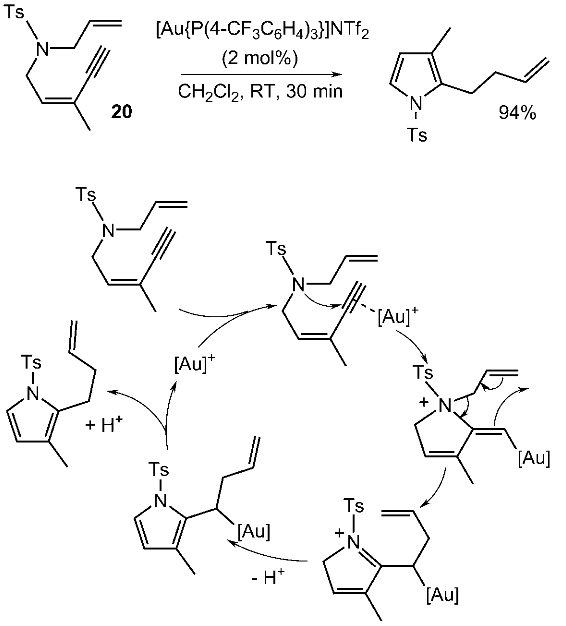
Mimicking enzyme-catalyzed carbocyclization reactions of polyenes is a fascinating area to both chemists and biochemists. The development of routes for the catalytic, stereoselective cyclization of polyunsaturated substrates is a major recent advance in the field. In this context, a tandem gold-catalyzed 6-*endo*-dig intramolecular phenoxycyclization of 1,5-enynes was recently reported by using phosphine gold triflimidate [Au(**1a**)]NTf$_2$ as the catalyst (Scheme 19).[116] In this biomimetic cascade process to produce a tricyclic derivative present in natural hydroquinone sesquiterpene derivatives, [Au(**1a**)]NTf$_2$ outperfomed other electrophilic alkyne initiators, including the in situ generated [Au(PPh$_3$)]SbF$_6$ and AuCl$_3$. The scope of the reaction was large and the process was both rapid and high-yielding when only 1 mol% catalyst was used. An extension of the reaction was presented with the cyclization of phenoxy-1,5,9-dienyne, which successfully afforded the corresponding tetracyclic derivative.



Scheme 19. Bn = benzyl.

3.2.3. Rearrangements of N- and Si-Containing Unsaturated Substrates

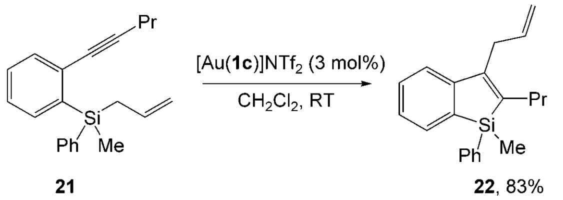
An example of an aza-Claisen type rearrangement catalyzed by gold(I) triflimidate has been reported to afford a variety of pyrrole derivatives in high yields, short reaction times, and mild conditions.[49] The reaction involves a 5-*exo* cyclization of substrates such as 1-(*N*-allyl-*N*-tosylamino)-pent-2-en-4-yne (**20**) substituted at the 3-position by methyl or phenyl groups. This transformation clearly benefited from the use of the highly electrophilic [Au{P(p-CF$_3$C$_6$H$_4$)$_3$}]NTf$_2$ catalyst, which significantly enhanced the reaction rate compared to other Au^I triflimidates or $AuBr_3$. From a mechanistic viewpoint, the possibility of an allylic cation intermediate was considered on the basis of previous results,[117,118] but various experiments instead supported a mechanism involving a concerted aza-Claisen-type process (Scheme 20).



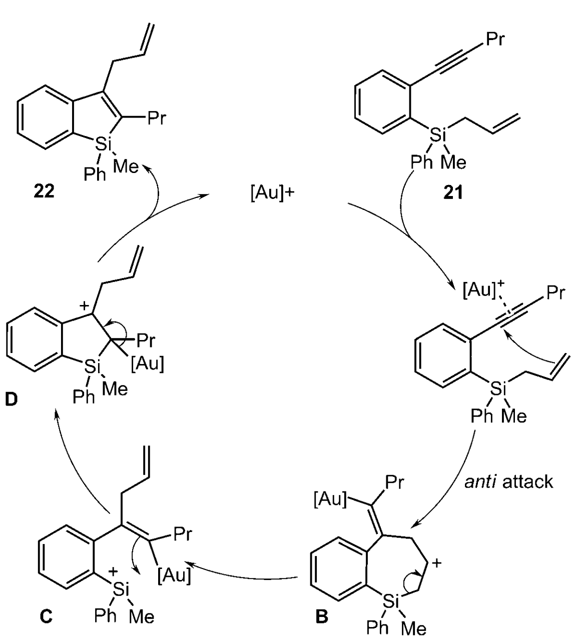
Scheme 20. Ts = tosyl.

A structurally similar, although mechanistically different, unusual rearrangement of allylsilanes bearing alkyne moieties, such as **21**, has been reported. A hindered $[Au(PR_3)]NTf_2$ complex with ligand **1c** (3–12 mol%) catalyzed the isomerization of **21** to 3-allyl-1-silaindenes **22**.[53] As for other examples, the use of a hindered catalyst $[Au\{P(o\text{-}PhC_6H_4)tBu_2\}]NTf_2$ (3–12 mol%) improved the yields of the isomerization of **21** to afford **22**. The reaction was tolerant to a large array of substituents at the alkynyl terminus and different allylsilane residues, and the isomerization could be extended to allylgermane derivatives (Scheme 21).

The formation of **22** was proposed to start with π activation of the alkyne moiety by $[Au]^+$, followed by the intramolecular addition of the pendant allyl group to form seven-membered ring intermediate **B**. Subsequent ring-opening to alkenyl gold silylium species **C** is followed by the silylium electrophilic ring closure to the cationic alkylgold **D**, which after deauration furnishes silacycle **22** with regeneration of the catalyst (Scheme 22).



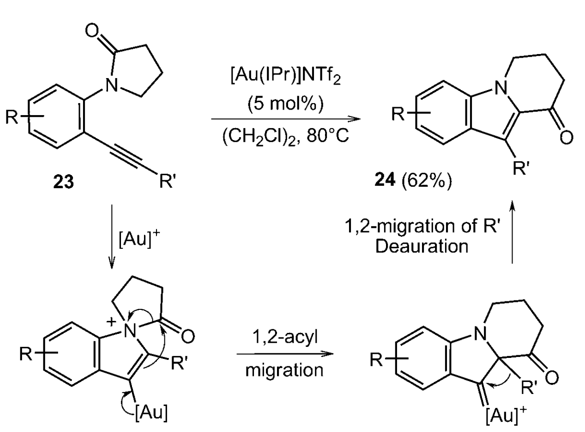
Scheme 21.



Scheme 22.

ortho-Heterosubstituted aryl alkynes are excellent substrates for gold- and platinum-catalyzed cycloisomerizations, particularly when the heteroatom bears a group that has the ability to undergo migration (allyl, benzyl, alkoxyalkyl, acyl, sulfonyl, trimethylsilyl). A common feature of these reactions is that the labile group on the heteroatom undergoes selective 1,3-migration via an alkenyl metal intermediate in a process similar to that depicted in Scheme 20.[118–120] An alternative strategy based on the more difficult 1,2-migration has recently been developed. Cyclic ketone-fused indoles **24** could be obtained by a sequential metal-catalyzed cyclization, 1,2-acyl migration, and final 1,2-migration of the R′ group by using γ-lactams **23** derived from *ortho*-alkynylaniline, (Scheme 23).[121] When $[Au(IPr)]NTf_2$ was used as the catalyst, **24** (R = H, R′ = *n*Bu) was formed in 62% yield (Scheme 23).

The process was further extended to the cyclization of *N*-(pent-2-en-4-ynyl)-β-lactams to afford a new straightforward



Scheme 23.

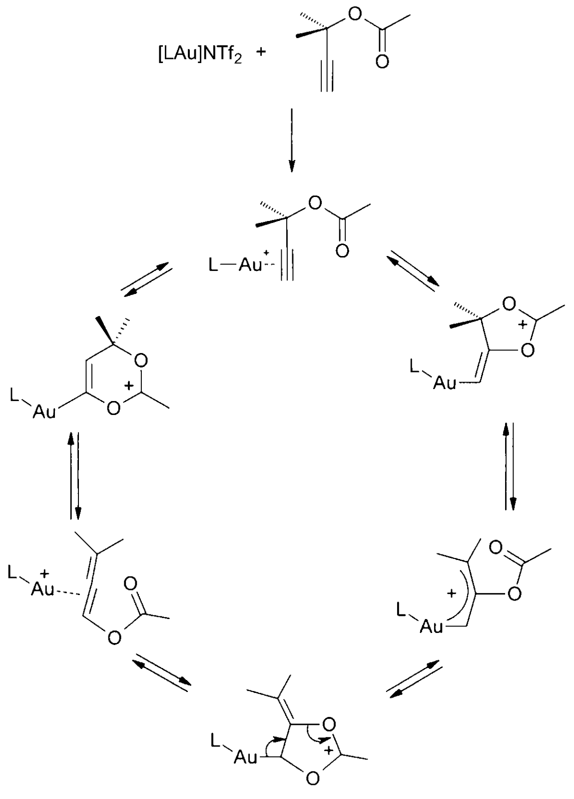
entry to 5,6-dihydro-8*H*-indolizidin-7-ones. $[Au(IPr)]NTf_2$ was a more efficient catalyst than $[Au(PPh_3)]NTf_2$ and $PtCl_4$ in the reaction, and afforded yields of up to 90%. Several substitution patterns were tolerated in both the β-lactam and enyne moieties, while internal alkynes and pyrrolidinones did not undergo cyclization. A concise application to the formal synthesis of reduced indolizidine illustrates the interest in this method.[122]

3.2.4. *Reactivity of Propargylic and Allenic Carboxylates*

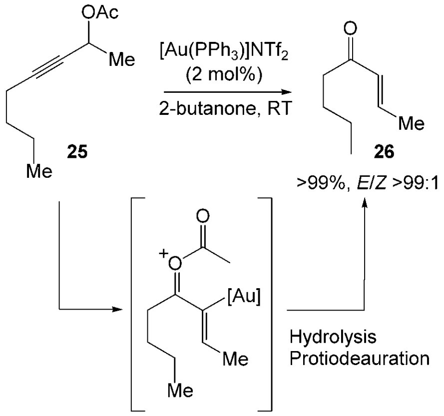
The rearrangement of propargylic carboxylates and derivatives is one of the cornerstones of gold catalysis.[123–125] Depending on the reaction parameters (substrate, ligand, gold oxidation state, solvent, ...), a large variety of rearranged products can be formed through 1,2-[113,126–128] or 1,3-acyloxy shift (also termed 3,3-rearrangement).[129–134] As recently proposed, all the key species involved in these processes are in rapid equilibrium, thereby resulting in a "golden carousel"[123] that accounts for the diverse, and sometimes unpredictable, formation of products from gold-catalyzed reactions of propargylic esters (Scheme 24).

Propargylic esters with a terminal alkyne or with an alkyne substituted by an electron-withdrawing group generally follow the 1,2-shift pathway, while the 3,3-rearrangement is often preferred in reactions of sterically and electronically unbiased internal C–C triple bonds.

The reaction of a propargylic acetate such as **25** in the presence of a phosphine-gold triflimidate catalyst resulted in the high-yielding 3,3-rearrangement to form the corresponding α,β-unsaturated ketone **26** (Scheme 25).[47] The reaction of propargylic acetates derived from aldehydes in wet butanone required only 2 mol% of $[Au(PPh_3)]NTf_2$ to afford β-monosubstituted enones with complete *E* stereocontrol. Similar transformations of the ketone-derived propargylic acetates were initially difficult to realise. They were finally achieved by adding 5 mol% of a dilute solution of $[Au(PPh_3)]NTf_2$ in acetone to the reactant mixture in CH_3CN/water (80:1). This result illustrates that proper adjustment of the polarity of the reaction medium provides a useful means of controlling the reactivity of a metal triflimidate catalyst.

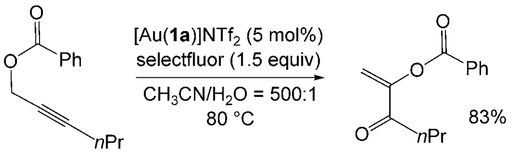


Scheme 24.



Scheme 25.

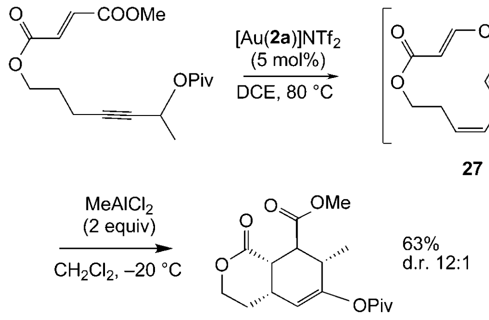
A highly efficient production of α-haloenones took place when the rearrangement of these propargylic acetates was carried out in the presence of an *N*-halosuccinimide of type NXS (X = I, Br).[135] The use of other catalysts, including the bulky $[Au(PR_3)]NTf_2$, dichloro(2-picolidinato)gold(III), or $PtCl_2$ resulted in a less-efficient process. The quantity of water present in the medium was found to strongly influence the outcome of the reaction in terms of both the efficiency and stereocontrol. A high yield and complete stereoselectivity was observed when an acetone/water ratio of 800:1 (1.4 equiv H_2O relative to substrate) was used. The use of selectfluor in place of NXS reagents did not provide α-fluoroenones, but instead led to α-benzoyloxyenones (Scheme 26). This unanticipated reaction was explained by electrophilic fluorination at the Au center in the oxocarbenium intermediate (Scheme 25). The resulting oxidized Au^{III} intermediate then undergoes a cyclization with benzoate displacement assisted by the addition of one molecule of water, followed by reductive elimination of an $[Au\text{-}F]^+$ entity.[136] A careful optimization of the reaction conditions showed that $[Au(PPh_3)]NTf_2$ was a better catalyst than bulkier triflimidate



Scheme 26.

counterparts, dichloro(2-picolidinato)gold(III), and $PtCl_2$, while Tf_2NH did not catalyze the reaction.

A significant step in improving the otherwise disfavored 1,2-acyloxy migration for substrates such as **25** to afford 2-acyloxy-1,3-dienes was the use of the NHC complex [Au(IPr)]NTf_2 (5 mol%) instead of its phosphine counterpart, combined with the replacement of the acetate function by the larger pivalate.[137] A large variety of propargyl carboxylates substituted by an alkyl group at the alkyne terminus gave the desired 2-pivaloxy-1,3-dienes such as **27** in generally good yields and high diastereoselectivities (Scheme 27).

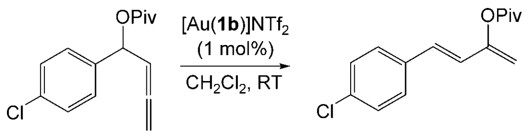


Scheme 27. DCE = dichloroethane, Piv = pivaloyl.

[Au(IPr)]NTf_2 proved to be a unique catalyst for this reaction, thus highlighting the high synthetic utility of [Au(NHC)]NTf_2 complexes. This method constitutes an atom economical approach to such substituted dienyl esters, which were previously prepared by the gold-catalyzed 3,3-rearrangement of trimethylsilyl-substituted propargyl esters.[134] The use of either [Au(IPr)]NTf_2 or [Au(PPh_3)]NTf_2 at 5 and 2 mol% respectively, yielded 2,3-bis(acetoxy)-1,3-dienes in good yields from symmetrical and unsymmetrical propargyl 1,4-bis(acetates).[138]

Allenyl carbinol esters can also follow the 3,3-rearrangement mechanism, and this is illustrated by the ability of the hindered complex [Au(**1b**)]NTf_2 to catalyze this isomerization to afford 1,3-butadienyl-2-ol esters.[139] While transformation of a model substrate in the presence of $AuBr_3$ and $AgNTf_2$ was inefficient, the use of a Au^I catalyst with **1b** (1 mol%) catalyzed this rearrangement in quantitative yield. Besides acetate, other ester groups such as benzoate and pivalate also underwent this 1,3-acyloxy shift quantitatively, with shorter reaction times, as illustrated by the transformation of **28** into **29** (Scheme 28).

A broad range of allenic substrates derived from aromatic and aliphatic aldehydes or ketones could be isomerized with high stereoselectivities to afford *E*/*Z* ratios of > 8:1 and up to 19:1.

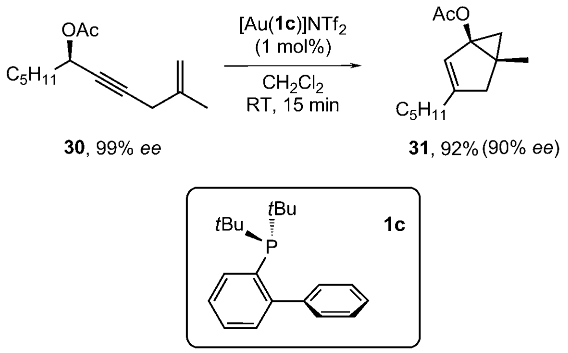


28 **29** (100%, *Z*/*E* 1:18)

Scheme 28.

A novel straightforward access to cyclopent-2-enimines was achieved by an overall [4+1] annulation between propargyl tosylates bearing a tertiary or quaternary homopropargylic carbon atom and *N*-tosylimines in the presence of the catalyst [Au(**1a**)]NTf_2.[140] From a mechanistic viewpoint, this reaction starts with 1,2-shift of the tosyloxy group, with a specific role played by the S–O bonds.

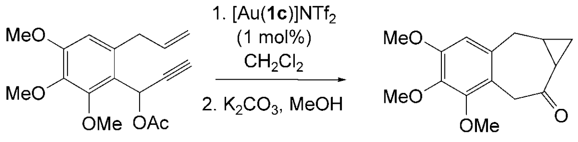
The biphenylphosphine-based ligand **1c** and related bulky Au^I complexes turned out to be efficient catalysts for the selective tandem cycloisomerization of functionalized enyne acetates such as **30**. Thus, the cycloisomerization of 5-en-2-yn-1-yl acetates led to acetoxybicyclo[3.1.0]hexenes in good yields (72–99%) under mild reaction conditions, through the proposed formation of 1,4-enallene intermediates.[141] Interestingly, the enantiomerically enriched substrate **30** (99% *ee*) was transformed into bicyclic **31** with 90% *ee*, which illustrates there is a good transfer of chirality (Scheme 29).



30, 99% *ee* **31**, 92% (90% *ee*)

Scheme 29.

Catalyst [Au(**1c**)]NTf_2 was also able to mediate the cycloisomerization of 1,7- and 1,8-enynes with a propargyl acetate moiety to afford cyclopropyl derivatives fused with seven- and eight-membered rings, as illustrated by the transformation of **32** into **33** in 80% yield (Scheme 30).[142] Lower yields were obtained when gold triflimidate [Au(**1b**)]NTf_2 or $PtCl_2$ were employed.



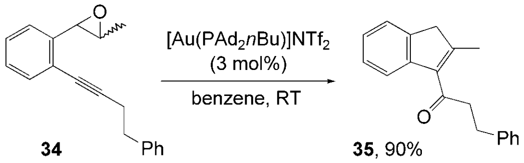
32 **33**, 80%

Scheme 30.

Cyclopropyl adduct **33** was further used as an intermediate in the total synthesis of a new allocolchicinoid derivative.[142]

3.2.5. Rearrangement of Epoxyalkynes

In addition to carboxylates and tosylates, oxiranes are also latent internal nucleophiles that are able to attack gold-alkyne complexes and thus induce C–C bond-forming processes.[143–145] Gold(I) triflimidates appeared to be a privileged class of catalysts for the cycloisomerization of 2-alkynylaryl epoxides into 3-acylindenes.[146] Indeed, when a diastereomeric mixture of 2-alkynylaryl epoxides **34** was exposed to 3 mol% of $[Au(PAd_2nBu)]NTf_2$ in benzene at room temperature, both isomers were converted into acylindene **35** in 90% yield (Scheme 31). Typical gold catalysts such as $AuCl_3$, $[AuCl_2(picolinate)]$, or $[(AuMes_3P)_2Cl]BF_4$ gave unselective reactions and low conversions. Substrates with terminal alkynes or with alkynes substituted by bulky groups (*t*Bu, $SiMe_3$) as well as those with an epoxy ester moiety did not react.



Scheme 31.

A mechanism for the epoxyalkyne isomerization to form acylindenes was proposed in which a ring opening of an oxepin intermediate was followed by a recyclization/deauration. This mechanism has some similarity to that proposed for the preparation of silaindenes discussed previously (Scheme 22),[53] and accounted for the overall intramolecular oxygen transfer, which was evidenced by ^{18}O-labeling experiments.

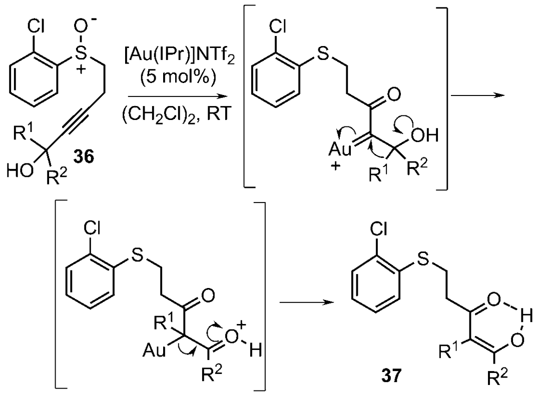
Indoles can also act as internal nucleophiles towards gold-alkyne complexes because of the nucleophilicity of their π bond. Accordingly, a novel transformation of C3-propargylated indoles into 2-indenylindole derivatives initiated by 1,2-indole migration has recently been reported.[147] Cationic gold triflimidate $[Au(\mathbf{1a})]NTf_2$ afforded yields of 50–82%. Similar results were obtained with the analogous in situ formed SbF_6^- complex.

3.2.6. *Rearrangements of Sulfinylalkynes*

Recently, a gold-catalyzed intramolecular redox reaction involving sulfinyl alkynes was developed.[148,149] This strategy used a sulfoxide tethered to an alkyne that acted as an internal oxidant through an addition/elimination process. This approach thus extended the scope of nucleophiles used in gold-catalyzed additions to alkynes.

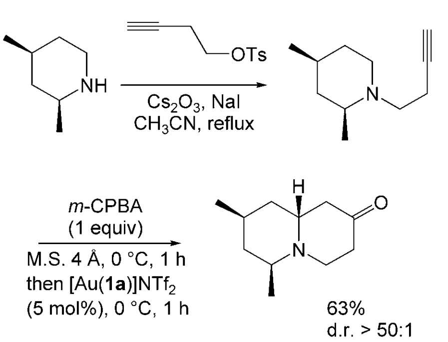
When the alkyne was connected to a carbinol moiety (either secondary or tertiary) as in substrate **36**, the preferred pathway involved a tandem oxygen atom transfer/pinacol rearrangement to give the β-diketone **37** in moderate to good yields (Scheme 32).[149] The substrate scope of this transformation was interesting, and the NHC complex $[Au(IPr)]NTf_2$ was much more efficient than $[Au(PPh_3)]NTf_2$ and dichloro(2-picolidinato)gold(III).

Homopropargylic tertiary aniline derivatives were similarly converted into tetrahydrobenz[*b*]azepin-4-ones in the presence of 5 mol% $[Au(\mathbf{1a})]NTf_2$. The reaction occurred by in situ oxidation of the nitrogen atom by *m*-CPBA and subsequent intramolecular transfer of an oxygen atom from the aniline *N*-oxide to the gold-activated C–C triple bond.[150] $[Au(\mathbf{1a})]NTf_2$ gave slightly better results than bulky $[Au(\mathbf{1c})]NTf_2$, electrophilic $[Au\{P(p\text{-}CF_3C_6H_4)_3\}]NTf_2$ or dichloro(2-picolidinato)gold(III). In contrast, $[Au(PPh_3)]SbF_6$ and $AgBF_4$ were poor catalysts, and $PtCl_2$ and Tf_2NH did not catalyze the reaction. Interestingly, when the triple bond was substituted with electron-withdrawing groups (COOMe, COMe, COPh, and SO_2Me) the reaction could be carried out efficiently without a gold catalyst.



Scheme 32.

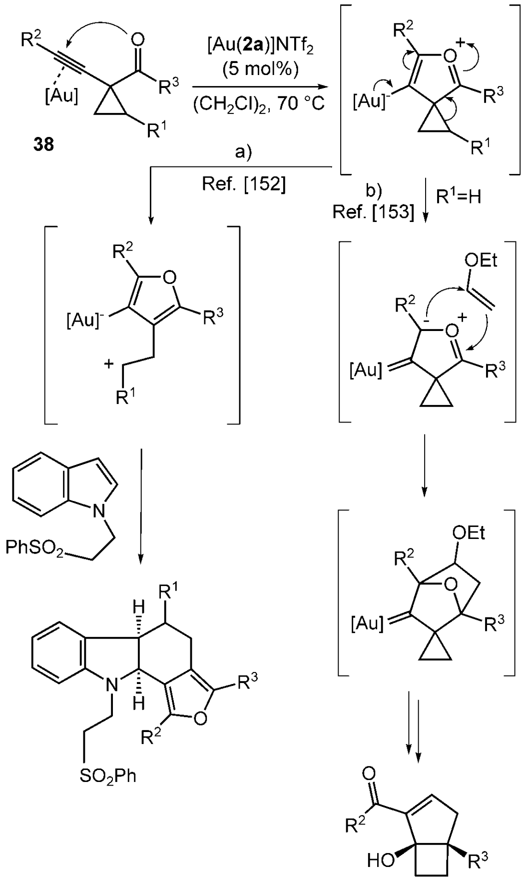
This ability of *N*-oxides to relay the oxidation of tethered terminal alkynes was extended with the preparation of piperidin-4-ones. These could be formed from the reaction of but-3-ynyl tertiary amines with *m*-CPBA followed by the addition of $[Au(PPh_3)]NTf_2$.[151] Initial oxidation of the tertiary amine to *N*-oxide allowed an intramolecular redox reaction similar to that observed with sulfinylalkynes (Scheme 32). This was followed by intramolecular hydride migration to give a key intermediate containing both an electrophilic iminium and a nucleophilic gold enolate. An intramolecular Mannich ring closure ended the sequence of this general reaction. The reaction proceeded with good to excellent regio- and stereocontrol, as illustrated by the synthesis of the indolizidinone shown in Scheme 33, which is an advanced intermediate in the synthesis of (±)-cermizine C.



Scheme 33. *m*-CPBA = *meta*-chloroperbenzoic acid. M.S. = molecular sieves.

3.2.7. Rearrangements of Homo- and Bis(homo)propargylic Oxygenated Derivatives

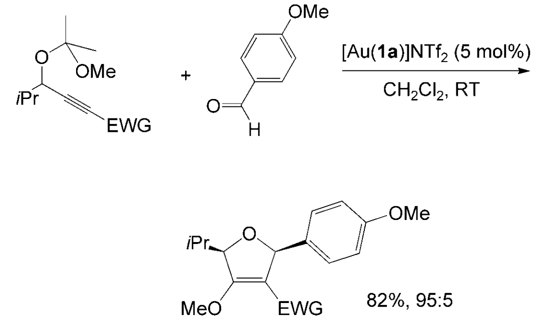
The gold triflimidate with the NHC ligand **2a** (5 mol%) was used to generate gold-containing 1,4-dipoles from cyclopropyl propargyl ketones such as **38**. These transient species readily underwent stepwise [4+2] annulation in situ with dipolarophilic indoles, silyl enol ethers, aldehydes, ketones, and imines to provide the corresponding six-membered carbocycles and oxygen/nitrogen-containing heterocycles in good to excellent yields.[152] This reaction showed broad applicability and high functional group tolerance. [Au(**2a**)]NTf$_2$ was much more efficient than other catalysts ([Au(PPh$_3$)]NTf$_2$, PtCl$_2$, and AuCl) in these annulations (Scheme 34).



Scheme 34.

The reaction of the same substrate in the presence of the catalyst [Au(**2a**)]NTf$_2$ but with ethyl vinyl ether used as the dipolarophile led to the formation of hydroxybicyclo[3.2.0]heptane,[153] the core structure of various natural products, such as repraesentin F and kelsoene. This quite different reaction outcome on switching from silyl enol ethers or indoles to ethyl vinyl ether was attributed to the greater reactivity of the latter species, which allowed direct cycloaddition on the initially formed oxycarbenium intermediate (Scheme 34, right) instead of the opening of the cyclopropane ring and aromatization (left). In this modified reaction, [Au(IPr)]NTf$_2$ again turned out to be a more efficient catalyst than PtCl$_2$ or AuCl$_3$.

The scope of this gold-catalyzed annulation/cycloaddition methodology was further extended to the generation of gold-containing all-carbon 1,3-dipoles and their application in [3+2] cycloadditions. [Au(PPh$_3$)]NTf$_2$ catalyzed the reaction of electron-deficient propargylic ketals bearing an electron-withdrawing group connected to the triple bond with various enals/enones, *p*-methoxybenzaldehyde, furan, 5-methylthiophene, 2-carboxaldehydes, and *N*-benzylindole.[154] The reaction afforded highly substituted 2,5-dihydrofurans and cyclopentene derivatives efficiently in 60–84% yields and 95:5 to complete *cis* stereoselectivities through an original migration/fragmentation of the ketal unit to give the key 1,3-dipolar intermediate (Scheme 35).

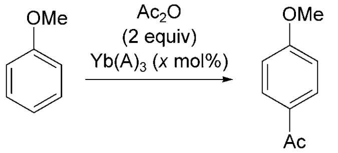


Scheme 35. EWG = electron-withdrawing group.

3.3. Acylation and Alkylations Reactions

3.3.1. Arenes as Nucleophiles

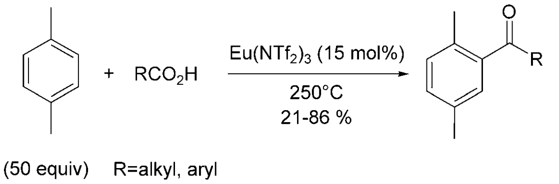
The Friedel–Crafts acylation of anisole was examined with Al(NTf$_2$)$_3$, (*i*PrO)$_2$Ti(NTf$_2$)$_2$ and Yb(NTf$_2$)$_3$ at loadings of 5—20 mol%.[79] These metal triflimidates appeared to be more efficient than the corresponding triflates under the same conditions. The acylation reactions yielded the corresponding acetophenones quantitatively and with selectively at the *para* position (Scheme 36). High catalytic activities were also found for scandium triflimidate, bis(perfluorobutylsulfonyl)amides [M{(C$_4$F$_9$SO$_2$)$_2$N}$_3$] (M = Sc^{III} or Yb^{III}),[102] and lanthanum(III) tris(perfluorobutylsulfonyl)methines [La{(C$_4$F$_9$SO$_2$)$_3$C}$_3$].[155]



A	*x*	Conditions	Yield [%]
OTf	20	MeNO$_2$, 50 °C, 18 h	99
NTf$_2$	20	MeNO$_2$, RT, 4 h	99
N(SO$_2$C$_4$F$_9$)$_2$	5	benzotrifluoride, 50 °C, 3 h	87
C(SO$_2$C$_4$F$_9$)$_3$	5	benzotrifluoride, 50 °C, 3 h	91

Scheme 36.

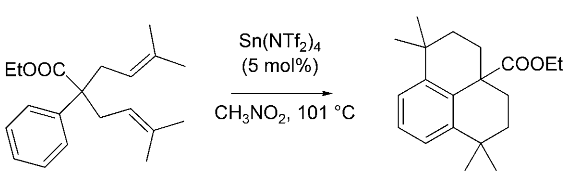
Interestingly, it was also shown that simple acylating agents (carboxylic acids) could be used in similar reactions catalyzed by metallic triflimidates, which resulted in the development of a reaction that liberated water as the only by-product.[156] Eu(NTf_2)$_3$ (15–20 mol %) turned out to be a better catalyst than Sc(NTf_2)$_3$, Yb(NTf_2)$_3$, Bi(NTf_2)$_3$, or a large array of metallic triflates for the acylation of *p*-xylene (50 equivalents) with heptanoic acid at 250 °C. At this temperature, the higher Lewis acidity associated with Sc(NTf_2)$_3$ and Yb(NTf_2)$_3$ caused considerable side reactions of the ketone products (Scheme 37). Mono- and dialkylbenzenes, anisole, and naphthols were selectively acylated with a set of carboxylic acids in yields of 21–86 %.



Scheme 37.

Bi(NTf_2)$_3$ was by far the most efficient catalyst at 220 °C and allowed the acylated adducts to be obtained in synthetically useful yields at a remarkable loading of 1 mol %. This good catalytic activity was studied in detail, and it was shown that the amount of water continuously released into the medium during the acylation process caused rapid hydrolysis of Bi(NTf_2)$_3$, thus generating $HNTf_2$, which significantly contributed to the catalysis.[156]

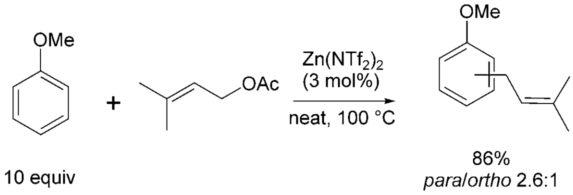
A catalytic double Friedel–Crafts allylation of the aryl diene derivative **39** has been reported.[109] This substrate afforded the tricyclic compound **40** in 78 % yield with 5 mol % of tin(IV) triflimidate (Scheme 38). It is noteworthy that analogous substrates such as **14** (see Scheme 13) led to a 1,6-diene cycloisomerization with the same catalyst under similar conditions.



39 **40**, 78%

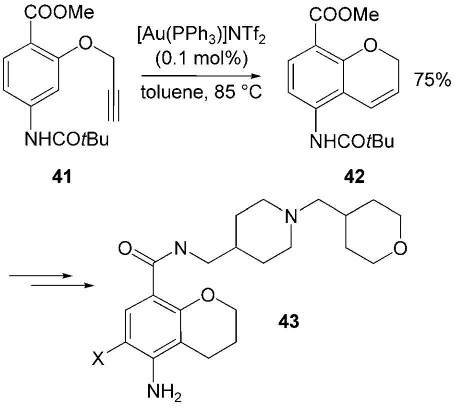
Scheme 38.

A catalytic Friedel–Crafts allylation reaction was developed by using allylic acetates in the presence of 3 mol % Zn(NTf_2)$_2$ without added solvent. This reaction afforded the allylbenzene derivatives in yields of 16–93 % and with good *para* selectivity (*para*/*ortho* 2.6:1–6.9:1). The coupling of anisole and prenyl acetate led to the allylated product in 86 % yield and a *para*/*ortho* selectivity of 2.6:1 (Scheme 39). Similar results were obtained with Ni(NTf_2)$_2$.[157]



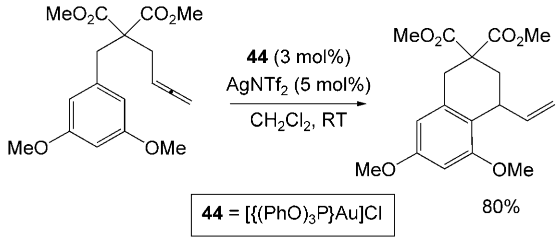
Scheme 39.

The gold-catalyzed cyclization of arenes tethered to an alkyne generally proceeds by an n-*endo*-dig cyclization process, and represents a powerful tool for the synthesis of fused (hetero)bicyclic unsaturated compounds such as chromenes, 1,2-dihydroquinolines, and related compounds.[158] The mechanism of these reactions seems well established and, in contrast to the above Friedel–Crafts reactions, competitive Brønsted acid catalysis[156] is unlikely since the proton source is mainly involved in the key protodeauration step that regenerates the gold catalyst and also because Brønsted superacids (AH) are less efficient alkyne activators than their gold(I) salts [LAu]•A.[159] It was shown that [Au(PPh_3)]NTf_2 is an excellent catalyst for such cyclizations. Thus, the ring closure of the deactivated aryl compound **41** bearing an alkyne group led to benzopyran derivative **42** in 75 % yield; **42** is an intermediate in the synthesis of 5-HT4 agonist **43** and related compounds of therapeutic relevance.[160] The use of the gold triflimide complex at only 0.1 mol % proved to be a better catalyst in terms of reaction rate and yield than its in situ preformed triflate analogue [Au(PPh_3)]OTf (Scheme 40).



Scheme 40.

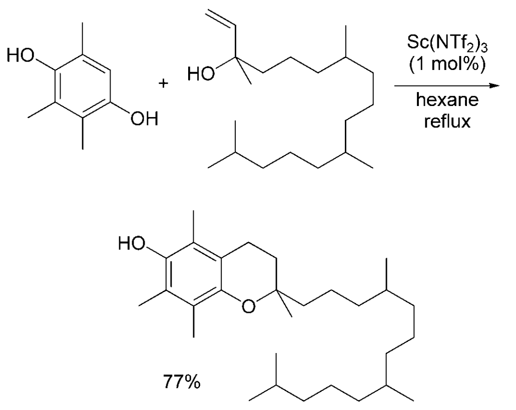
As for C–C triple bonds, gold salts are excellent activators of allenes, and the resulting allenyl-gold complexes are readily captured by nucleophiles in both intra- and intermolecular modes. Accordingly, an intramolecular hydroarylation of 4-allenylarenes that proceeds in an *exo* fashion was developed by using in situ formed cationic phosphite gold(I) catalysts including [Au(**1g**)]NTf_2 (**44**; Scheme 41).[161] The highly electrophilic triphenylphosphite gold(I) salts appeared to be superior than other conventional gold catalysts in terms of catalytic activity.



Scheme 41.

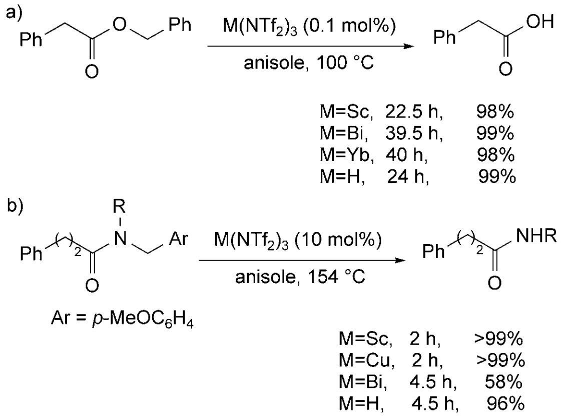
The catalyst [Au(**1a**)]NTf_2 appeared to be very useful in elucidating the mechanism of this reaction, which appeared to be more complex than usually proposed. ^1H and ^{31}P NMR spectroscopic experiments clearly showed that the initially proposed vinylgold species coexists with a much more stable three-center diaurated vinylgold entity;[162] this was the first experimental evidence of computationally predicted diaurated reaction intermediates.[163] The nature of the organogold intermediates in gold catalysis is a fascinating topic of current research.[164,165] The same catalysts were used in the development of an intermolecular variant of this reaction.[166]

A catalytic tandem allylation/cyclization process has been reported for the functionalization of trimethylhydroquinone with isophytol to afford (±)-α-tocopherol (vitamin E). The reaction was catalyzed efficiently by 1 mol% $Sc(NTf_2)_3$ in hexane at reflux. The target compound was obtained in 77% yield, thus surpassing previous results using $Sc(OTf)_3$ and making these improved conditions amenable to an industrial process (Scheme 42).[167,168]



Scheme 42.

Several other strong acid catalysts have also been examined for this tandem Friedel–Crafts alkylation/cyclodehydration; of these, $HNTf_2$ had an even greater catalytic activity than $Sc(NTf_2)_3$, an observation which seems in line with that discussed previously.[156] Although triflic acid also showed good catalytic activity, (±)-α-tocopherol was not produced in adequate purity, thus illustrating the deleterious effects that the stronger acidity of TfOH over Tf_2NH can cause.

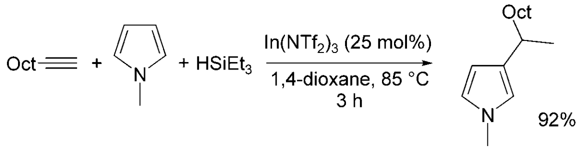


Scheme 43.

The catalytic alkylative debenzylation of benzyl esters, ethers, and amides has been examined with a series of metal triflimidates, including $Sc(NTf_2)_3$, $Yb(NTf_2)_3$, $Bi(NTf_2)_3$, and $Cu(NTf_2)_2$ salts (Scheme 43a).[27] Sc^{III}, Bi^{III}, and Yb^{III} trifluoromethanesulfonimidates were efficient catalysts (0.1 mol%) for the debenzylation of benzyl phenylacetate, which proceeds through the concomitant Friedel–Crafts benzylation of the anisole used as the solvent. In contrast, $Sc(OTf)_3$ was ineffective under the same conditions. It is noteworthy that tris(triflyl)methane ($HCTf_3$) and its scandium salt $Sc(CTf_3)_3$[26] were the most active catalysts for this reaction, and afforded phenylacetic acid quantitatively in 1.5 h and 0.5 h, respectively. The remarkable chemoselectivity of this process is also noteworthy, since the competitive acylation process never occurred with either ester substrates or the formed carboxylic acids[156] under the reaction conditions used. Debenzylation of ethers of secondary alcohols initially proved challenging, but the difficulties were overcome by using the *p*-methoxybenzyl group and $HNTf_2$, $Sc(NTf_2)_3$, or $Bi(NTf_2)_3$ (1 mol%) catalysts. The quantitative debenzylation of the less-reactive tertiary *p*-methoxybenzylamides to afford the expected secondary amides also proved possible by using $Cu(NTf_2)_3$, $Sc(NTf_2)_3$, or $HNTf_2$ (10 mol%) as catalysts (Scheme 43b).[27]

Pyrrole derivatives are excellent π nucleophiles in catalytic electrophilic aromatic substitutions. However, the preferential α-nucleophilicity of pyrroles actually makes their β-functionalization considerably challenging. Electrophilic indium derivatives have proven to be excellent catalysts for the highly β-selective alkylation of pyrroles.[169] In this context, $In(NTf_2)_3$ has been particularly efficient in promoting the first indium-catalyzed reductive β-alkylation of *N*-methylpyrroles with terminal alkynes in the presence of triethylsilane. $In(NTf_2)_3$ was found to be superior to $In(OTf)_3$, $In(ONf)_3$,[170] $InCl_3$, or HNTf in terms of both conversion and yield for the synthesis of β-alkylpyrroles (Scheme 44).[171]

A number of experimental observations and control experiments strongly supported an original mechanism that begins with the production of an isomeric mixture of α,β′- and β,β′-dipyrrolylalcane through an indium-catalyzed double alkylation of the alkyne.[169] The two regioisomers then



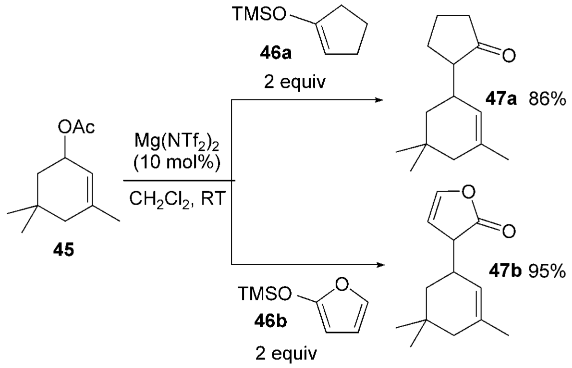
Scheme 44.

undergo an indium-catalyzed retroaddition to release α- and β-indenylpyrrole, respectively. An identical stabilized pyrrolium cation is formed, which is ultimately trapped by H^-.

3.3.2. *Electron-Rich Alkenes and Enolates as Nucleophiles*

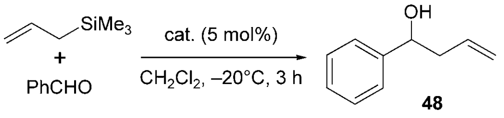
In the area of catalytic alkylation of ketone and ester enolates by allylic or benzylic electrophiles,[172–176] the $Mg(NTf_2)_2$-catalyzed (10 mol%) alkylation of benzylic and allylic acetates by silyl ketene acetals has been described.[75] High yields of the corresponding esters were obtained, in particular with secondary acetates. $Mg(NTf_2)_2$ gave comparable results to the hazardous magnesium(II) perchlorate, while $LiNTf_2$ was ineffective.

$Mg(NTf_2)_2$ was also an efficient catalyst for the reactions of isophorol acetate (**45**) with nucleophiles **46a** and **46b** to give **47a** and **47b** in good yields (Scheme 45). Other silyl enolates and silyl-based nucleophiles, including $TMSN_3$ and allyltrimethylsilane, could also be used.



Scheme 45.

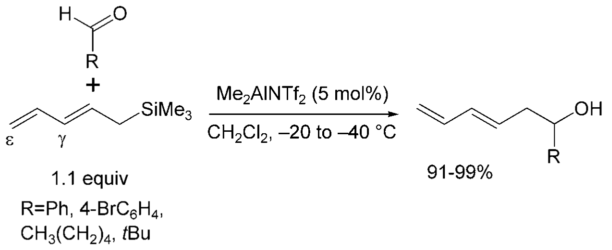
Since the discovery of the Hosomi–Sakurai reaction in the 1970s, the search for strong Lewis acid catalysts that enable the rapid and clean production of homoallylic alcohol derivatives has remained a long-standing issue. The reaction of benzaldehyde and allyltrimethylsilane at low temperature has been studied with a series of triflimide-based catalysts.[43] The strongly acidic catalysts $HNTf_2$, Me_3SiNTf_2, $[Ti(iPrO)_2](NTf_2)_2$, and $Al(NTf_2)_3$ gave the homoallyl alcohol **48** in only moderate yields together with substantial amounts of the bisallylated product. With only one triflimidate ligand, Me_2AlNTf_2 appeared to be a tailor-made catalyst that exhibits sufficient Lewis acidity to trigger the reaction without generating side products. Me_2AlNTf_2 (5 mol%) indeed catalyzed the reaction with excellent control to give the homoallylic alcohol **48** in 93% yield (Scheme 46). Both aromatic and aliphatic aldehydes could also be allylated in excellent yields. It should be noted that the absence of over-alkylation proved that Me_2AlNTf_2 is the true catalyst in this reaction—the in situ production of Me_3SiNTf_2 or $HNTf_2$ would have led to diallylated side products. This report established the possibility of controlling the reactivity of metal triflimidate reagents by finely adjusting the number of triflimidate ligands.



$HNTf_2$	52%
$TMSNTf_2$	53%
$(iPrO)_2Ti(NTf_2)_2$ (–78°C)	45%
$Al(NTf_2)_3$	35%
Me_2AlNTf_2	93%

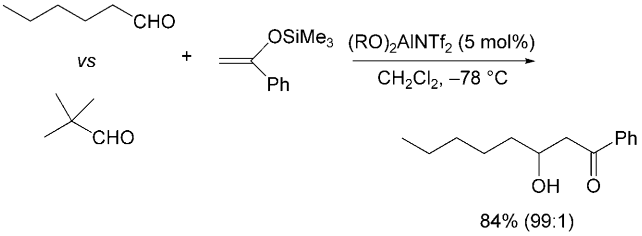
Scheme 46.

Me_2AlNTf_2 (5 mol%) was also reported to be an efficient Lewis acid catalyst for the pentadienylation of aldehydes through a vinylogous Sakurai addition. Several aldehydes were converted into the corresponding hydroxydienes with 1-trimethylsilyl-2,4-pentadiene in excellent yields and complete ε selectivities (Scheme 47).[43]



Scheme 47.

The ability of Me_2AlNTf_2 to catalyze Mukaiyama aldol reactions with excellent yields was further shown in the cross-aldol reaction of ketone acceptors and in the Mukaiyama Michael addition to enones. The analogous hindered bis(2,6-diphenylphenoxide)aluminum triflimidate complex was used successfully for the chemoselective activation of less-hindered aldehydes (Scheme 48). Apart from its synthetic efficiency, this reaction indicates that the bulky reagent is the true



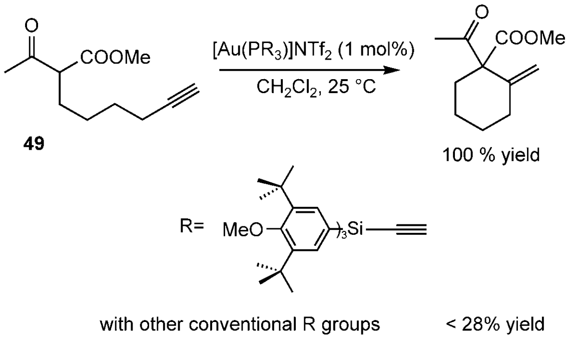
Scheme 48. $R = 2,6\text{-}Ph_2C_6H_3$.

catalyst for the whole process. The generation of active silyl species, as typically encountered with $HNTf_2$, would indeed have led to a less chemoselective process. This seems to be an important feature of these aluminum-based triflimidate reagents and could be the starting point for the design of chiral versions of this catalyst.

The alkylation of 1,3-dicarbonyl compounds is a common method for the formation of carbon–carbon bonds; the alkylation step generally requires the use of a stoichiometric amount of base and an organic halide as an electrophile. Several atom-economic approaches based on the metal-catalyzed addition of 1,3-dicarbonyl compounds to unactivated alkenes,[177,178] alkynes,[179–183] and 1,6-enynes[184] have recently been developed.

The cationic Au^I complex $[Au(PPh_3)]OTf$ has been reported to be an efficient catalyst for the carbocyclization of β-ketoesters with tethered alkynes (Conia-ene reaction) to form functionalized five-membered rings under mild and neutral conditions (1 mol% catalyst at room temperature).[84,179,182] A rate acceleration was observed with the analogous gold triflimidate complex $[Au(PPh_3)]NTf_2$, with the reaction proceeding efficiently with only 0.1 mol% catalyst.[84]

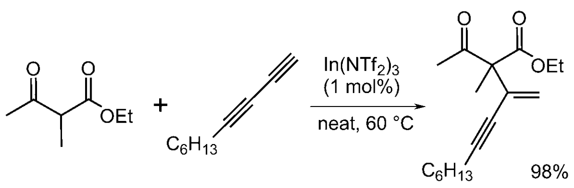
Since $[Au(PPh_3)]^+$ displayed limited activity in the 6- and 7-*exo*-dig cyclization of acetylenic keto esters such as **49**, a triethynylphosphine-gold triflimidate complex bearing bulky end caps at the alkyne termini was developed. This complex allowed significant rate accelerations (Scheme 49).[185] The high reactivity observed with this very bulky phosphine-gold complex was attributed to its holey shape creating a catalytic cavity which forces the nucleophilic (enolic) center close to the gold-bound alkyne.



Scheme 49.

The same catalyst efficiently catalyzed the otherwise difficult cyclization of β-ketoesters with internal alkynes. A mixture of 5-*exo*-dig and 6-*endo*-dig products were obtained in high combined yields at a remarkable catalyst loading of 1 mol%.[186]

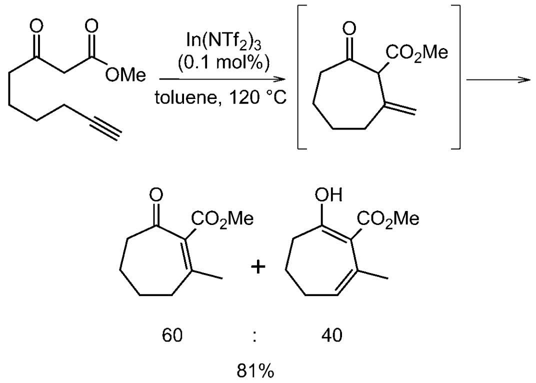
In regard to the intermolecular Conia-ene reaction of β-keto esters with terminal alkynes catalyzed by $In(OTf)_3$,[183,187,188] 1,3-diynes could also be used as partners in this process.[189] The 1,3-diynes were, however, less-reactive than terminal alkynes, and $In(OTf)_3$ displayed insufficient reactivity under standard conditions (60 °C, neat, 2 equiv of diyne). In contrast, $In(NTf_2)_3$ appeared to be an excellent catalyst, and could be used at 1 mol% loading (Scheme 50).[189]



Scheme 50.

Similar reactions with 1-iodoalkynes were developed and allowed the formation of a vinyl iodide product, which is a useful synthon for further functionalization of the molecule.[190] Here again, $In(NTf_2)_3$ outperformed $In(OTf)_3$.

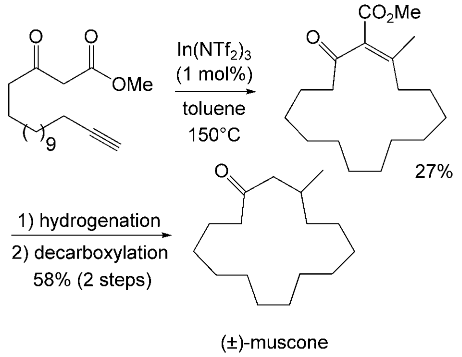
The synthetic value of the transition-metal-catalyzed Conia-ene reaction has mainly been seen in the formation of five-,[84,179,182] six-, and seven-membered rings.[185] $In(NTf_2)_3$ (1 mol%) turned out to be a better catalyst than $In(OTf)_3$ for the formation of 6 to 15-membered rings from alkynyl β-keto esters.[191] The structure of the final products appeared to be considerably dependent on the substrate. γ-Alkynyl-β-keto esters gave furan derivatives, because of the oxygen-centered mode of cyclization, while substrates with a longer tether gave the C-cyclized products as *endo/exo* alkene mixtures and keto-enol tautomers. β-Keto esters with a linear (unbranched) tether gave six- and seven-membered rings in high yields, with the unusual feature that the seven-membered rings formed faster than six-membered rings. Even 0.1 mol% $In(NTf_2)_3$ catalyzed the reaction efficiently to afford the seven-membered ring products in good yields (Scheme 51).



Scheme 51.

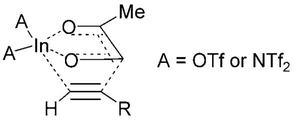
The cyclization efficiency of substrates with longer tethers decreased gradually, with 9- to 11- membered rings being formed only in very poor yields. In contrast, cyclization to form a 15-membered ring could be achieved in 27% yield;[191] the macrocycle obtained was further transformed in two steps into the benchmark musk odorant (±)-muscone[192] (Scheme 52).

In good agreement with a computational transition-state model established for the intermolecular addition,[188] this efficient cyclization to form medium-sized rings at low catalyst loading and at rather high concentrations was



Scheme 52.

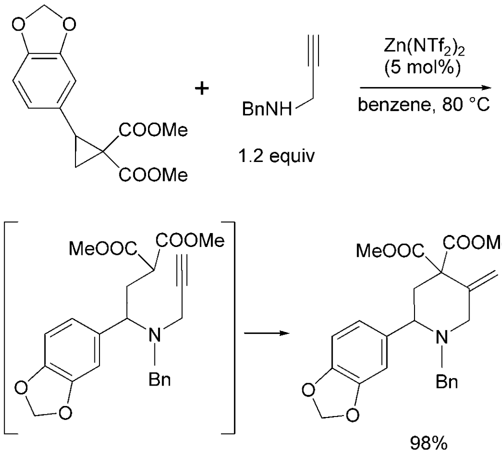
attributed to a dual activation of both the enolate and acetylenic moieties: the indium enolate of the 1,3-dicarbonyl and the acetylene group form a well-ordered bicyclo-[2.2.2]octane type structure, which forces the substituents and the reactants to point toward unencumbered directions, thus facilitating the selective carbometalation step (Scheme 53).



Scheme 53.

An intermolecular variant has further been developed with β-ketoesters and α,ω-diynes in the presence of In(NTf$_2$)$_3$. This led to the generation of 1,3-dimethylenecycloalkane derivatives in good yields after a [1+*n*] annulation process.[193]

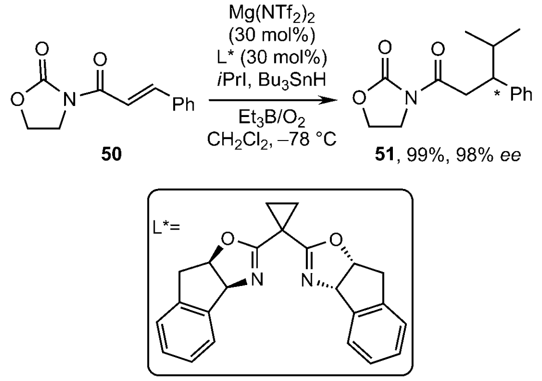
A tandem ring-opening of 1,1′-cyclopropane diesters by a propargylamine/Conia-ene reaction was reported to proceed in the presence of Zn(NTf$_2$)$_2$ to give piperidines in good yields (Scheme 54).[194] To better demonstrate the superiority of triflimidate derivatives in this reaction, it was shown that the use of Zn(OTf)$_2$ resulted in lower yields, whereas no reaction could be observed with In(OTf)$_3$.



Scheme 54.

3.3.3. *Addition of Free Radicals*

The first application of enantioselective catalysis involving metal triflimidate salts in association with chiral bisoxazoline ligands was reported for the conjugate radical additions of an isopropyl radical to the cinnamate derivative **50** (Scheme 55).[195] Chiral complexes derived from divalent metals (Mg, Zn, and Fe) showed superior catalytic activity than the monovalent (Li, Ag) and trivalent (Sc, Y, and Yb) analogues. The chiral complexes derived from Mg(NTf$_2$)$_2$ and Fe(NTf$_2$)$_2$ gave adduct **51** with high enantioselectivities.

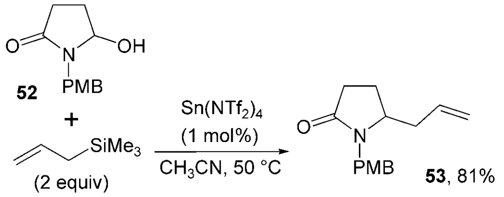


Scheme 55.

Similar chiral complexes [Mg(L*)](NTf$_2$)$_2$ were shown to catalyze the enantio- and diastereoselective addition of various free radicals to α,β-unsaturated conjugated imides.[196,197] In a similar approach, novel chiral complexes of Mg(NTf$_2$)$_2$ with dibenzofuranbisoxazoline (dbfox) ligands were used to catalyze the enantioselective free-radical 1,4-addition to α,β-unsaturated nitroamides to afford β-substituted α-amino acid derivatives in good enantioselectivity, but poor diastereoselectivity.[198]

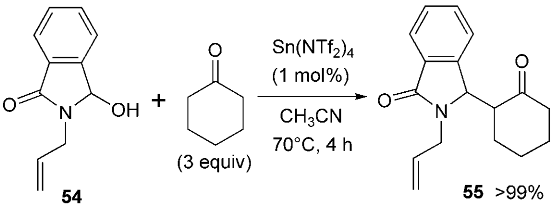
3.3.4. *N-Acyliminium Ions as Electrophiles*

The ability of triflimide-based catalysts to generate *N*-acyliminium ions was applied to the catalytic alkylation of unmodified (*N-OH*)-aminals, which are known to be less reactive than the corresponding (*N-OAc*)- or (*N-OMe*)-aminals.[199–201] Sn(NTf$_2$)$_4$ (1 mol %) catalyzed the allylation of hydroxylactam **52** to **53** in 81 % yield (Scheme 56).[202] Of the metal triflimidate salts tested, Sn(NTf$_2$)$_4$ displayed the best catalytic activity.



Scheme 56. PMB = *para*-methoxybenzyl.

$Sn(NTf_2)_4$ showed broad applicability in the reaction of a variety of hemi-*N*,*O*-acetals with silicon-based nucleophiles, as well as with β-dicarbonyl derivatives and electron-rich arenes. The activity of $Sn(NTf_2)_4$ in *N*-acyliminium ion reactions was emphasized with the quantitative transformation of **54** into **55**; this reaction represents the first direct catalytic α-amidoalkylation of a simple ketone (Scheme 57).[202]

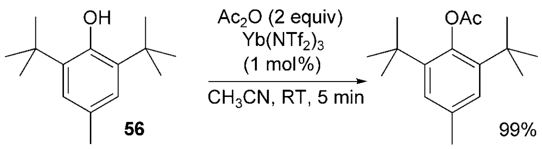


Scheme 57.

4. Carbon–Heteroatom Bond Formation Catalyzed by $M(NTf_2)_n$

4.1. Carbon–Oxygen Bond-Forming Reactions

Ytterbium triflimidate (1 mol %) has been reported to be an efficient catalyst for the acylation of hindered alcohols such as **56** with acetic anhydride to give high yields of the corresponding acetylated compounds within short reaction times (Scheme 58).[79]

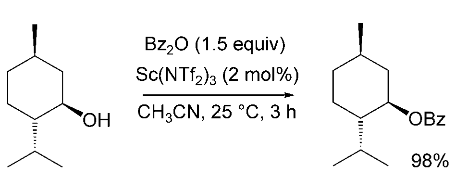


Scheme 58.

$Sc(NTf_2)_3$ (1 mol %) has also been demonstrated to be an extremely active catalyst for the acetylation and the more difficult benzoylation of secondary and tertiary alcohols such as menthol or 2-methyl-2-undecanol under mild conditions (Scheme 59).[203] $Sc(NTf_2)_3$ displayed a much higher catalytic activity than $Sc(OTf)_3$ in these reactions.

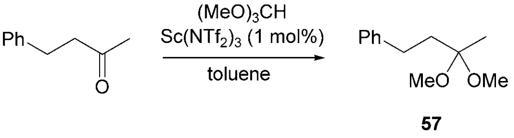
$Mg(NTf_2)_2$ was also used as the catalyst for the acylation of alcohols.[204] Thus, the acylation of 2-naphthol, 4-nitrophenol, and 1-phenylethanol could be easily carried out in the presence of 1.2 equivalents of Ac_2O and 1 mol % $Mg(NTf_2)_2$ without solvent.

$Mg(NTf_2)_2$ displayed a higher catalytic activity than $LiNTf_2$ or Mg^{II} halides, in particular for the acylation of secondary alcohols. Phenols bearing either electron-donating or -withdrawing groups, as well as thiol derivatives, could be acylated quantitatively without elimination side reactions. Even if $Mg(NTf_2)_2$ was less efficient than $Sc(NTf_2)_3$ in these acylation reactions, the much lower Lewis acidity of the former might be advantageous in the acylation of alcohols bearing acid-sensitive functional groups.[203]



Scheme 59. Bz = benzoyl.

A comparative study between the activity of metal triflates and triflimidates in the acetalization of ketones and aldehydes indicated that $Sc(NTf_2)_3$ (1 mol %) in toluene was superior to $Sc(OTf)_3$ in acetonitrile. This was illustrated, for example, by the preparation of dimethoxyketal **57** from 4-phenyl-2-butanone by using trimethyl orthoformate (Scheme 60).[205]

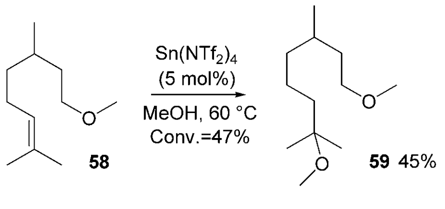


Scheme 60.

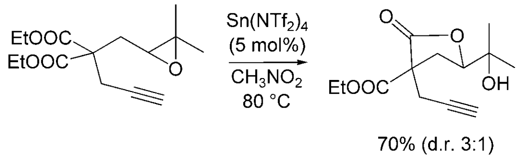
The $Sc(NTf_2)_3$-catalyzed (0.1 mol %) acetalization reactions were extended to the diastereoselective formation, with moderate to high selectivities, of chiral 1,3-dioxolanones and 1,3-dioxanones through condensation between carbonyl substrates and α- and β-hydroxycarboxylic acids. Interestingly, Tf_2NH could also be used as the catalyst to provide dioxolanones with similar stereoselectivities, albeit in lower yields.[205]

The intermolecular hydroalkoxylation of non-activated olefins in the presence of alcohols has recently been reported to be catalyzed by $Sn(NTf_2)_4$ as well as by $Sn(OTf)_4$.[206] An efficient intramolecular version of this type of reaction had previously been described in the presence of $Sn(OTf)_4$,[207] $Al(OTf)_3$,[208] and TfOH catalysts.[209] Natural terpene derivatives were mainly used in alcoholic solvents for the intermolecular addition. The hydroalkoxylations occurred with high Markovnikov-type regioselectivities and, for example, citronellyl methyl ether (**58**) afforded the diether **59** in 45 % yield and 91 % regioselectivity with 47 % conversion (Scheme 61).

$Sn(NTf_2)_4$ was also used as the catalyst in the dealkylative cyclization of epoxyesters derived from diethyl malonate. In these reactions, 5 mol % catalyst resulted in the formation of δ-hydroxy-γ-lactones in yields of 48–98 %, sometimes together with rearranged compounds after oxirane isomerization (Scheme 62).[210]

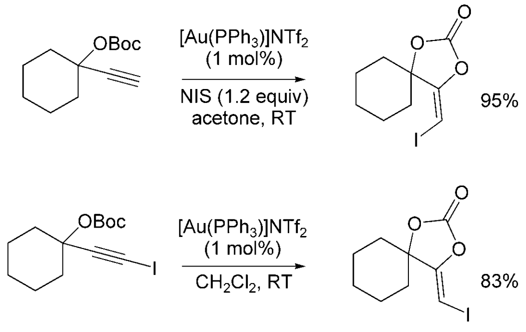


Scheme 61.



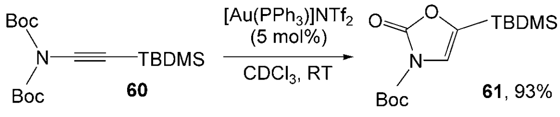
Scheme 62.

The transition-metal-catalyzed addition of heteronucleophiles to activated alkynes is a straightforward route to create carbon–heteroatom bonds.[65,211] Carbonates have been used as internal oxygen nucleophiles in cyclizations of propargylic[212] and homopropargylic carbonates[213] to give dioxolanones and dioxanones, respectively (Scheme 63). These reactions were catalyzed by the cationic gold complex [Au(PPh$_3$)]NTf$_2$, which appeared particularly efficient in the case of terminal alkynes. Less-reactive internal alkynes were also converted when the more electrophilic [Au{P(p-CF$_3$C$_6$H$_4$)$_3$}]NTf$_2$ catalyst was used. The reaction was applied to the formation of iodo-enolcarbonate derivatives through a combined gold-catalyzed cyclization and trapping of the vinylgold intermediates by electrophilic iodine. Since the gold-activated triple bonds typically induce *anti* addition of the incoming nucleophile, (E)-vinyl iodides were obtained selectively; the isomeric (Z)-vinyl iodide could be obtained by using an iodopropargyl carbonate as the starting material. A similar reactivity involving propargylic *tert*-butyl carbamates was reported to afford 5-methylene-1,3-oxazolidin-2-ones in high yields.[214]



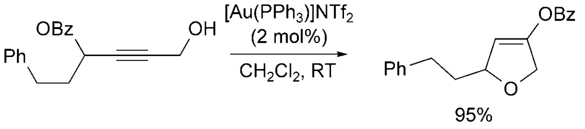
Scheme 63. Boc = *tert*-butoxycarbonyl.

The two-step preparation of oxazolones, such as **61**, starting with carbamatation of alkynyl iodonium salts by *tert*-butyloxycarbamates and followed by gold-catalyzed 5-*endo*-dig ring closure of the resulting N-alkynyl carbamates, such as **60**, by using 5 mol% [Au(PPh$_3$)]NTf$_2$ has been reported (Scheme 64).[215] AgNTf$_2$ has also been shown to be able to catalyze a similar cyclization, albeit with a limited substrate scope.[216]



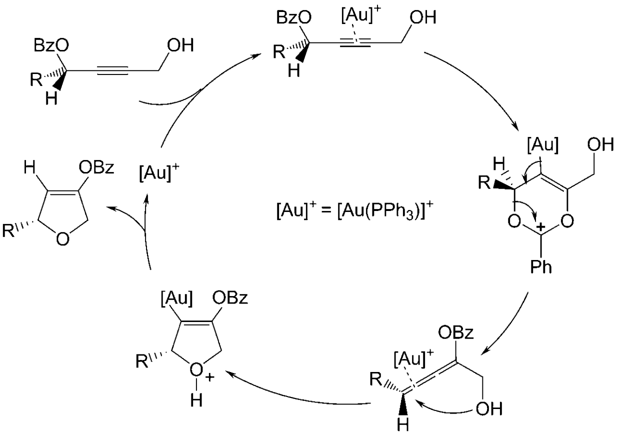
Scheme 64.

[Au(PPh$_3$)]NTf$_2$ has been reported to catalyze the isomerization/cyclization of butynediol monobenzoates into functionalized 2,5-dihydrofuran derivatives in high yields (Scheme 65).[217] This transformation provides an additional example of a gold-catalyzed cascade reaction of propargylic carboxylates by a pathway involving a 1,3-acyloxy shift.



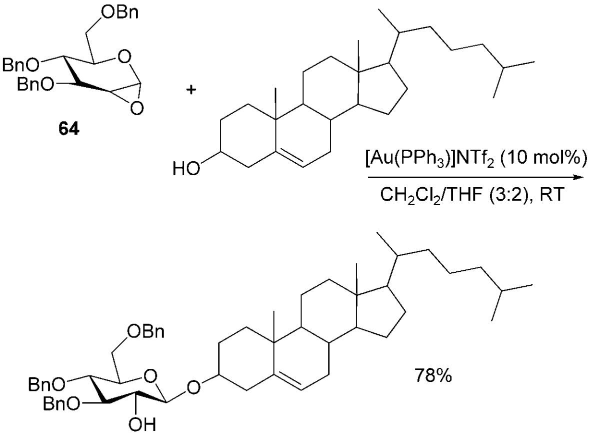
Scheme 65.

The cyclization of a series of optically enriched substrates showed that the stereochemical integrity was usually preserved. Although secondary and tertiary alcohols reacted with complete conservation of the optical activity, substrates with a primary hydroxy group were prone to partial epimerization, most likely because of a gold-catalyzed isomerization of the allenic intermediate prior to the key oxa-cyclization step (Scheme 66). The racemization could be limited to a large extent by modification of the substituents on the phosphorus ligand and by the use of a less electrophilic catalyst such as [Au(PAd$_2n$Bu)]NTf$_2$ (Ad = adamantyl).



Scheme 66.

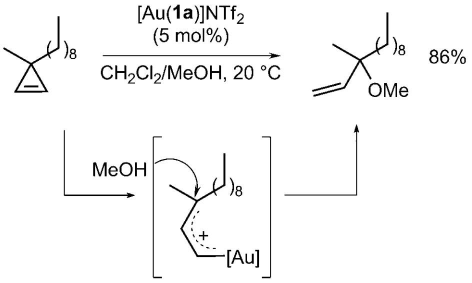
In the chemistry of carbohydrates, glycals are recognized as unique donors for glycosidations that give coupling products containing a free hydroxy group with high stereoselectivity.[218] Unfortunately, most glycosidations of 1,2-anhydro sugars are promoted by excess ZnCl$_2$, which often gives products in moderate yields. Soft oxophilic gold(I) catalysts such as [Au(PPh$_3$)]NTf$_2$ result in weak but sufficient activation of the oxirane ring for the stereoselective glycosidation of the 1,2-anhydrosugar **64** with primary and nonhindered secondary alcohols to give the coupling products in yields of 78–89% (Scheme 67).[219] The yields obtained in these gold-catalyzed glycosidations are considerably superior to those previously obtained using ZnCl$_2$ as the promoter,



Scheme 67.

thus expanding the scope of gold catalysis to carbohydrate chemistry.[220]

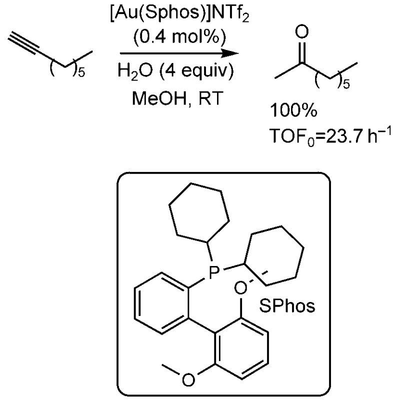
The gold(I)-catalyzed opening of a 3,3-dialkyl cyclopropene via a putative transient highly stabilized gold vinyl carbenoid has recently been disclosed.[221] When the reaction is carried out in the presence of either primary or secondary alcohols, tertiary allylic ethers are formed as the result of the highly regioselective intermolecular trapping of the intermediate arising by attack at C3 (Scheme 68). The complex $[Au(PPh_3)]NTf_2$ displayed greater efficiency than the in situ formed $[Au(PPh_3)]OTf$ in these reactions, which have proven to be gold(I)-catalyzed processes.



Scheme 68.

The Markovnikov hydration of terminal alkynes in the presence of a $[Au(PR_3)]NTf_2$ catalyst was reported, without an acidic co-catalyst and at room temperature (Scheme 69).[222] A significant positive effect of triflimidate over triflate was shown. In addition, the use of bulkier and better donor phosphine ligands than Ph_3P strongly accelerated the reaction: $[Au(SPhos)]NTf_2$ gave the highest turnover frequency and a quantitative yield in the hydration of 1-octyne compared to other cationic gold catalysts.

The extremely mild reaction conditions of this method appeared to be particularly useful for the hydration of propargyl alcohols and alkynols bearing acid-sensitive protecting groups. Optically pure (*S*)- and (*R*)-but-3-yn-1-ol were quantitatively hydrated to the corresponding (*S*)- and (*R*)-acetoins with complete conservation of the optical purity. A systematic comparative study with a previously reported gold-catalyzed process[223] ($[AuMe(PPh_3)]$ 0.02–1 mol% + H_2SO_4 1–50 mol%) probed the superiority of the triflimidate method, and found it to rank as one of the most attractive protocols so far reported for this transformation.



Scheme 69.

Although alkynes have so far been the prefered substrates for the π activation of triple bonds by gold triflimidate catalysts, the catalytic hydration of nitriles to amides by $[Au(\mathbf{2a})]NTf_2$ was recently reported.[224]

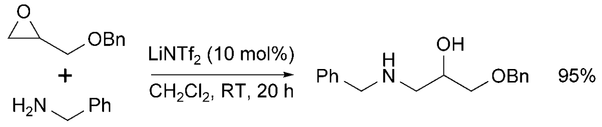
4.2. Carbon–Nitrogen Bond-Forming Reactions

The effect of the counterion in a range of aromatic electrophilic substitution processes catalyzed by indium salts has been studied. While both $In(OTf)_3$ and $In(NTf_2)_3$ efficiently catalyzed the nitration of electron-rich aromatic compounds in an aqueous environment, the triflimidate salt displayed much higher efficiency in the reaction of deactivated substrates.[225] $In(NTf_2)_3$ appeared to be quite effective for the nitration of a range of deactivated aromatic compounds including chloro- and bromobenzene as well as aryl carboxylic acids to give the desired products with yields above 84% at 10 mol% catalyst loading. The difference in reactivity was explained by the higher Lewis acidity of $In(NTf_2)_3$ combined with a better transport of the transient nitronium triflimidate into the organic phase.

In a more recent study, lanthanide bis[(trifluoromethyl)-sulfonyl]imides were shown to accelerate these nitration reactions in triflimidate-based ionic liquids (HNO_3/arene ratio between 1:1 and 1.3:1, room temperature). Importantly, the triflimidate catalysts were used at low loadings (2–5 mol%) and they could be recovered and successfully reused up to five times with almost no loss of efficiency.[226]

$LiNTf_2$ (0.1–0.5 equiv) was found to catalyze the ring opening of a broad range of epoxides with primary and secondary amines efficiently to give the corresponding amino alcohols (Scheme 70).[227] The reactions were found to proceed efficiently and regioselectively, with the nucleophile attacking the terminal position of the epoxides. Weak nucleophiles such as *N*,*N*-dimethylhydrazine or thiophenol could also be used under solvent-free conditions.

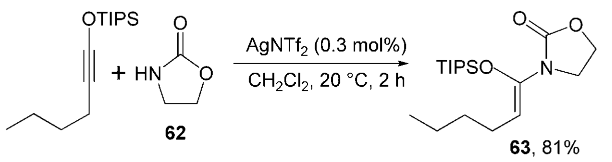
$LiNTf_2$ (20 mol%) was also shown to be a useful catalyst for the ring opening of aziridines by various amines.[228] For



Scheme 70.

example, cyclohexene *N*-benzylaziridine afforded several diamines in good yields. As for the case of epoxides, $LiNTf_2$ was demonstrated to strongly accelerate the reaction rate and to enhance the regioselectivity of the aziridine ring opening. The regioselectivity was the reverse of that observed in reactions catalyzed by $Yb(OTf)_3$.[229] $LiNTf_2$ exhibited similar activating properties in the aminolysis of lactones. Thus, a range of lactones were readily transformed into the corresponding hydroxyamides in the presence of 0.5 equivalents of catalyst.[230]

A highly efficient $AgNTf_2$-catalyzed *syn*-hydroamination of siloxy alkynes by secondary carbamates and amides has recently been developed to generate the corresponding silyl ketene aminals in high yields and with exclusive *Z* geometry.[231] $AgNTf_2$ proved to be a better catalyst than AuCl, $AuCl_3$, $PdCl_2$, $PtCl_2$, and $HNTf_2$ (5 mol %), which gave almost no conversion. For example, the $AgNTf_2$-catalyzed (0.3 mol %) hydroamination of 1-siloxy-1-hexyne by oxazolidinone **62** led to compound **63** in 81 % yield with complete *syn* selectivity (Scheme 71).

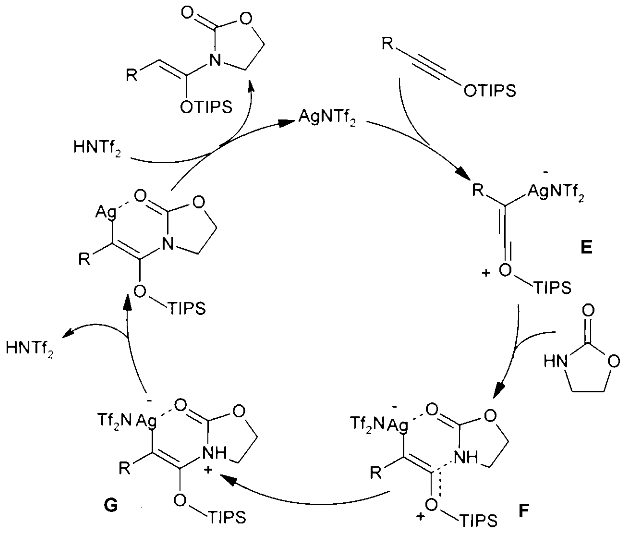


Scheme 71.

In line with previous studies on the [2+2] cycloaddition of siloxy alkynes,[106] the proposed mechanism involves an initial electrophilic activation of an alkyne by $AgNTf_2$ to account for the exclusive formation of the *syn* products. The silver complex **E** would then facilitate the key *syn* addition (with respect to silver) of the amide, via a six-membered chelated transition state **F** to give **G**. Further protodemetalation would then liberate the final product and recycle the catalyst (Scheme 72). As a consequence of its catalytic character and mildness, this silver-catalyzed method seems more efficient than the traditional approaches using strong bases and/or super silylated reagents (R_3SiOTf), and therefore offers a useful alternative entry to these compounds.

These *N,O*-ketene acetals tethered to an alkyne function have found great utility as substrates in gold-catalyzed cycloisomerizations to afford carbocyclic imides with good efficiency. A one-pot $AgNTf_2$-catalyzed *syn*-hydroamidation/gold-catalyzed carbocyclization has been reported.[232]

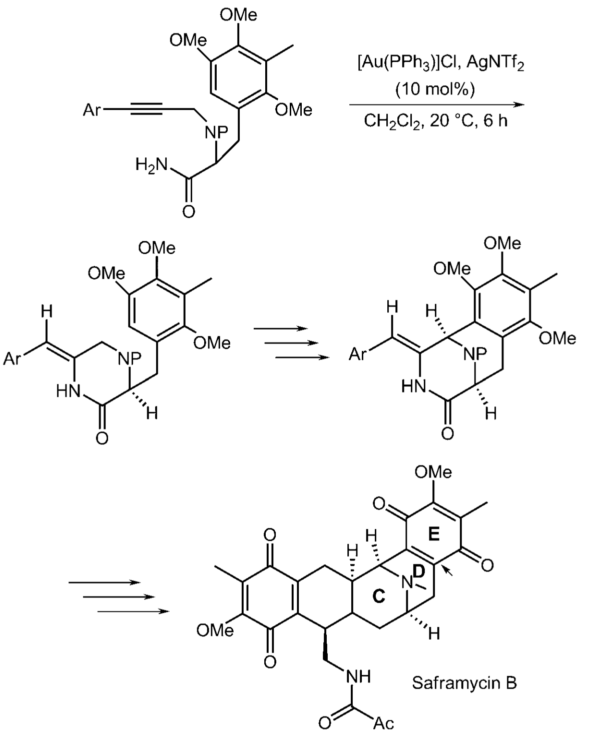
A stereospecific intramolecular 6-*exo-dig-trans*-hydroamidation of alkynes catalyzed by in situ formed $[Au(PPh_3)]NTf_2$ has been developed and applied to the preparation of the CDE ring system of tetrahydroisoquinoline antitumor alkaloids such as saframycins, renieramycins, and ecteinascidins (Scheme 73).[233]



Scheme 72.

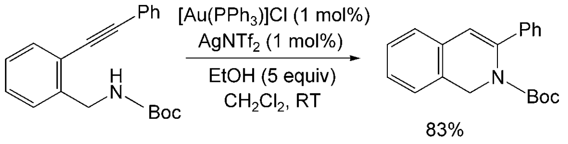
Isoquinoline-*N*-oxides have been prepared in a very straightforward manner from 2-alkynylbenzaldoxime derivatives. This regio- (6-*endo*-dig) and chemospecific (*N* versus *O*) cyclization was efficiently catalyzed by various cationic Au^I complexes and Ag^I metal salts including $AgNTf_2$.[234]

A related strategy in which *ortho*-arylalkynylaminomethyl compounds as well as *ortho*-aryl- and alkylalkynyl aminoethyl derivatives are transformed into 1,2-dihydroisoquinolines (6-*endo-dig* cyclization) and 1-alkylidenyl-1,2,3,4-



Scheme 73.

tetrahydroisoquinolines (6-*exo-dig* cyclization) has been developed.[235] The transformation tolerates various nitrogen protecting groups (Boc, Cbz, Ms, PMP). In situ generated catalysts appeared to be the most efficient in forming the desired heterocycles at room temperature in high yields at low catalyst loading (1–3 mol%; Scheme 74).



Scheme 74.

Metal triflimidates of Ni^{II}, Cu^{II}, and Yb^{III} have been used as catalysts for the three-component Biginelli-type reaction involving ethyl acetoacetate, urea, and several aldehydes, both aromatic and aliphatic, in water to provide an environmentally friendly access to pyrimidinone derivatives.[236]

5. Conclusion and Outlook

Metal triflimidate salts may offer an improved and often unique reactivity in reactions, mainly because of the increased σ- or π-Lewis acidity of the metal center in the corresponding complexes. Novel Lewis superacid metal salts can be prepared by many different methods from Brønsted superacids. The development of protic superacids with novel structures originating either from derivatization of the sulfonyl groups or bearing a different linkage at the NTf_2 moiety is still continuing. Tris(triflyl)methane ($HCTf_3$), for example, has a gas-phase acidity (ΔG_{acid}) of 289.0 kcal mol^{-1}, while the values for H_2SO_4, HOTf, and $HNTf_2$ are 302.2, 299.5, and 291.8 kcal mol^{-1}, respectively.[19] The Brønsted superacid bis-trifluoromethylsulfonylimino)trifluoromethanesulfonic acid ($(CF_3)(NTf)_2SOH$) was recently shown to have a greater acidity than triflic acid as well as a remarkable performance in catalytic Friedel–Crafts acylations.[237] It is likely that the conjugated base of these novel superacids will soon be used as the counteranions of highly electrophilic metal catalysts. Besides perfluorosulfonyl and perfluorosulfonylimine groups, novel highly delocalized boron-derived moieties such as sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$),[238] or diprotic boron acid $H_2(B_{12}X_{12})$[239] derivatives will probably be of future interest to the field.

The combination of protic and Lewis superacid catalysis also constitutes an interesting perspective, in light of the significant results obtained with Lewis acid assisted Brønsted acid (LBA) catalysis.[29,240–245]

The development of chiral NTf_2-derived structures offers exciting prospects in both asymmetric Brønsted superacid organocatalysis and related cationic metal-catalyzed reactions where the metal cation is bound to the chiral counteranion.[246] The synthesis and use of a pseudo-C_2-symmetric chiral binol-derived *N*-triflylphosphoramide Brønsted acid[247,248] and its metal complexes[249] in enantioselective transformations has been reported, as well as a chiral *N*-triflylthiophosphoramide Brønsted acid.[250] An even more acidic and totally C_2-symmetric bis(sulfonylimino) analogue has recently been described[251] and has shown high efficiency in the enantioselective Mukaiyama-aldol reaction.[252] The corresponding metal and ammonium salts of these or other chiral Brønsted superacids should be useful for diverse applications such as in asymmetric counteranion-directed catalysis.[253,254]

The possibility to recycle the metal triflimidate complexes is of high interest for more environmentally efficient processes. Thus, the preparation of triflimide supported catalysts should be of wide applicability, in particular for high-scale synthetic applications, although studies on supported Lewis superacids have mainly been devoted to metallic triflates to date.[255–258]

From a mechanistic viewpoint, the catalytic role of the metal ion versus the activity of residual H^+ is an active debate in Lewis superacid catalysis. Most of the commercially available metal triflates and triflimidates are hydrates. Despite the fact that some salts are stable in an aqueous media, the possibility that the metal catalyst undergoes hydrolysis or hydration to form free acid or hybrid species with both Lewis and Brønsted acid sites cannot be excluded.[259] Moreover, H_2O molecules simply coordinated to the metal triflimidates could exhibit an increased acidity, and also liberate protons. Preliminary information on the role of the protons in the catalytic cycle can be gained from reactions carried out in the presence of a base, generally a hindered, noncoordinating amine such as 1,6-di-*tert*-butylpyridine.[260] Whereas some Lewis superacid processes have been shown to proceed even in the presence of such an amine functioning as a proton scavenger, some other reactions are found to be inhibited. However, the mechanism of most of these reactions remains unclear, and even if it involves a proton shift that is inhibited by the base, most of the process remains catalyzed by the Lewis acid. For example, the final step of protonolysis (frequently encountered in metal-catalyzed transformations), which cleaves carbon–metal bonds and allows for recycling of the catalyst, might be excluded in the presence of a base. Mechanistic aspects, therefore, need to be thoroughly examined in a case-by-case approach.

The out-of-range acidity of these entities constitutes a limit of our current knowledge for both the measurement of their physical properties and a comparison of their activity as catalysts, and still needs a general Lewis superacidity scale.

Addendum

Several reports on metal triflimidate-catalyzed reactions have appeared since the submission of this manuscript, most of them describing novel applications of $[Au(PPh_3)]NTf_2$. For example, a $[Au(PPh_3)]NTf_2/[MoO_2(acac)_2]$ bimetallic catalytic system (1 mol% each) allowed formation of α-bromo- and iodoenals/enones from propargyl alcohols in the presence of *N*-halosuccinimide.[261] The construction of indole-fused carbocycles from (*Z*)-enynols through an intermolecular Friedel–Crafts alkylation/intramolecular *7-endo-dig* hydroarylation cascade sequence was also described.[262] A similar approach in which furans were used instead of indoles was developed, through the intramolecular addition of furan across the alkyne followed by ring opening to give β-arylated (*Z*)-enones/enals with high stereoselectivity.[263] The gold(I)-catalyzed rearrangement of 3-alkyne-1,2-diols to produce furan derivatives through a heterocyclization/dehydratation one-pot sequence has been reported by using 0.05–0.5 mol% $[Au(PPh_3)]NTf_2$ as the catalyst.[264] In situ formed $[Au(PPh_3)]NTf_2$ (3 mol%) was shown to catalyze an oxidative cleavage of benzyl propargyl ethers to provide a mixture of two esters resulting from the simultaneous cleavage of C–H, C–C, and C≡C bonds.[265] A $[Au(PPh_3)]NTf_2$-catalyzed regiospecific intermolecular hydroamination of internal ynamides and propiolic acid derivatives with anilines has been developed, which furnished in all cases the Markovnikov product.[266] The complex $[Au(PMes_3)]NTf_2$ was found to catalyze a novel rearrangement of furan-ynol ethers wherein the alkene and alkyne functions are tethered by three-atom linkers. This rearrangement leads to a new class of tetracyclic systems with two stereocenters that are produced through an 6-*endo-dig* cyclization followed by a sequence of two consecutive electrophilic additions.[267] Evidence supporting the coexistence of bimetallic Au-C-Ag 3-center-2-electron bond species with already known vinylgold and digold vinyl (Au-C-Au 3-center) intermediates,[268] in reactions wherein $[Au(PPh_3)]NTf_2$ is generated in situ from $[Au(PPh_3)]Cl$ and $AgNTf_2$, have been established. The propensity of a yet unreactive Ag^+ salt to intercept putative organogold intermediates and subsequently effect catalyst speciation and reaction kinetics is thus demonstrated.[269] An asymmetric Diels–Alder catalyst consisting of a bis(oxazoline)-$Cu(NTf_2)_2$ complex bearing 4,4′-sulfonamidomethyl groups was rationally designed.[270] This system showed uniformly high efficiency (1–5 mol% loadings), high stereocontrol (*endo* selectivity, high enantioselectivity), and demonstrated a wide scope in the cycloaddition of oxazolidinone-derived α,β-unsaturated imides with various dienes. This catalyst design was based on intramolecular secondary *n*–cation interactions by coordination of the sulfonyl oxygen atoms to the Cu^{II} ion, combined with hydrogen bonding between the counteranions Tf_2N^- and the proton of the $NHSO_2R$ group (rather than coordination to the Cu^{II} ion, which would have resulted in a lowering of the Lewis acidity of Cu^{2+}).

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