OL Organic Letters

pubs.acs.org/OrgLett

Letter

Benzotriazolium Salts: Emergent Readily Accessible Bench-Stable Lewis Acid Catalysts

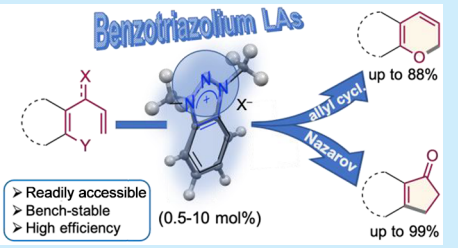
Tobias Danelzik, Sumi Joseph, Christian Mück-Lichtenfeld, Constantin G. Daniliuc, and Olga García Mancheño*

Cite This: *Org. Lett.* 2022, 24, 6105−6110

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

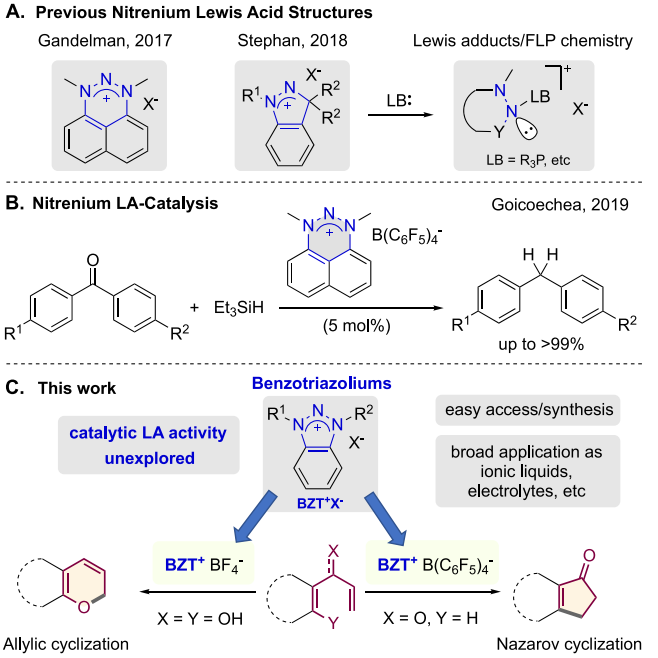
ABSTRACT: In this work, benzotriazolium salts have been introduced as efficient, readily accessible, bench-stable Lewis acid catalysts. Though these sorts of N-heterocyclic compounds have found wide applications as ionic liquids or electrolytes, their Lewis acid catalytic activity remained unexplored. Herein, their potential as Lewis acid catalysts was demonstrated in two prototypical allylic and Nazarov cyclization reactions, showing a matching reactivity and allowing low catalytic loadings (down to 0.5 mol %).



The ability of Lewis acids (LAs) to form acid−base adducts and activate small molecules has been widely used in synthesis and catalysis,[1] hence being established as a powerful tool in a large variety of chemical processes. Although classical main-group Lewis acids containing elements with low-lying free orbitals like boron, aluminum, silicon, or phosphorus have been studied intensively,[1,2] nitrogen-centered Lewis acids have just recently evoked a rising interest. This field was most probably long neglected since the common compounds showing an N-centered electrophilic behavior, such as nitrenes, azides, or diazo derivatives, led to rather unstable Lewis acid−Lewis base adducts or presented strong oxidizing properties like nitronium salts, hampering their application as Lewis acids.[3] Alternatively, the carbene-isoelectronic cationic nitrenium ions have proved more suitable for the design of novel nitrogen Lewis acid structures. Hence, although previously prepared, since the study on the electronic features of stable triazolium ions by the group of Boche in 1996,[4] this type of nitrenium salt became an important building block for the synthesis of organocatalysts, serving as precatalysts,[5] dual catalysts,[6] or ligands.[7] Nevertheless, stable adduct formation between triazinium ions and several Lewis bases was reported by Gandelman et al. in 2017 (Scheme 1A, left),[8] which resembled the Lewis acidic behavior that was already known for its heavier phosphonium[9,10] and arsenium[11] analogues. This Lewis acid reactivity was then further demonstrated by the group of Stephan using indazolium salts (Scheme 1A, middle)[12] and extended to frustrated Lewis pair (FLP)[13] driven chemistry (Scheme 1A, right).[14]

Furthermore, only very recently has the unprecedented use of nitrenium-based Lewis acids in catalysis been described. Thus, in 2020 Goicoechea et al. employed catalytic amounts of a triazinium cation to promote several organic reactions, including hydrogenations, reductions, and a Friedel−Crafts

Scheme 1. (A) Nitrenium-Based LA Structures Employed in Acid−Base Adduct Formation and FLP Chemistry, (B) First Nitrenium LA Catalysis, and (C) Benzotriazolium Salts (BZTs) as Novel LA Catalysts



Received: May 19, 2022
Published: August 16, 2022

https://doi.org/10.1021/acs.orglett.2c01697
Org. Lett. 2022, 24, 6105−6110

reaction (Scheme 1B).[15] However, in this pioneering report, only six-membered triaziniums have been proven as efficient N-based Lewis acids, and a few limited types of reactions involving mainly carbonyl and silane activation could be accomplished to date. Therefore, the development of further nitrenium-based catalysts with enhanced and/or adjusted Lewis acid properties to allow for a broader synthetic application is still highly desirable.

Inspired by state-of-the-art and encouraged to solve some of the current reactivity limitations, we envisioned benzotriazolium salts, which are widely used as ionic liquids (ILs), electrolytes, or fluids,[16] as suitable new platforms to provide alternative potent N-based Lewis acid catalyst structures. Despite their ready accessibility and easy modulability that make them excellent candidates for this purpose, their catalytic activity as Lewis acids remained rather unexplored.[17] We herein present the first example of benzotriazolium-based Lewis acids as efficient, bench-stable catalysts for two benchmark reactions implying a carbonyl and hydroxyl group activation, such as allylic and Nazarov cyclizations toward synthetically valuable chromenes and cyclopentenones, respectively (Scheme 1C).

We started our investigation by preparing a series of 1-methyl-3-methyl (**1a–d**), 3-(2,2,2-trifluoroethyl) (**1e–f**), and 3-aryl (**1g–i**) triazolium salts with different counteranions upon methylation of the corresponding benzotriazole with MeOTf or Me_3OBF_4, followed, when needed, by a subsequent counteranion exchange (Figure 1A, see SI for details).

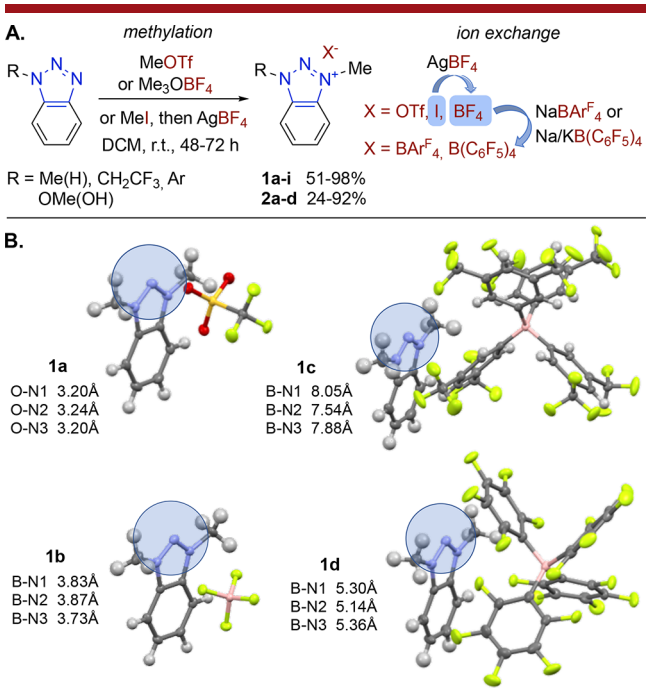
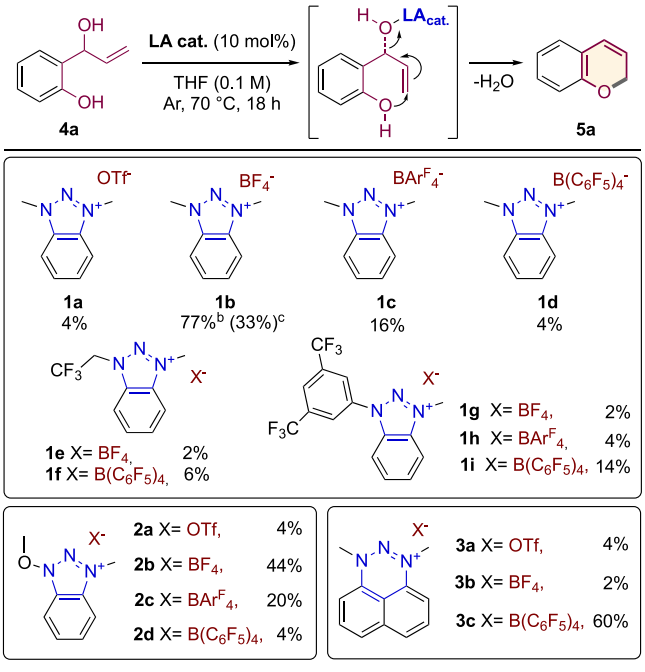


Figure 1. (A) Synthesis of benzotriazolium salts **1–2**. (B) X-ray structures of representative derivatives **1a–d** (ellipsoid contours given at the 50% probability level).

Alternatively, the iodide salt was also prepared by reaction with MeI, and the anion was later exchanged to BF_4^- and a BAr^F-type anion with $AgBF_4$ and $NaBAr^F_4$ or $Na/KB(C_6F_5)_4$, respectively. Similarly, various methoxytriazoliums **2a–d** and previously reported triaziniums **3a–c**[8,15] were also synthesized. To evaluate the relative Lewis acidity of the triazolium salts, the Gutmann–Beckett test (GBT)[18] was then performed in acetone-d_6, and the acceptor number (AN) was calculated (see Table S1 in the SI), revealing an apparent moderate Lewis acidity (≤20 AN).[19] Additionally, the global electrophilicity index (GEI) and fluoride ion affinity were calculated for a series of 1,3-dimethyl benzotriazoles (**1a**, **1b**, and **1d**) with their corresponding counteranion at the DFT level of theory, supporting the postulation of a negligible influence of the anion on the Lewis acidity (see SI for details). Hence, the exchange of BF_4^- with Na or $K[B(C_6F_5)_4]$ and $NaBAr^F_4$ to bulkier counteranions resulted in a counter-intuitively slight decrease of Lewis acidity. Moreover, the analysis of the X-ray structures of the benzotriazolium series **1a–d**[20] revealed the expected increasing benzotriazole–anion distance trend upon an increase of the bulkiness of the anion from OTf^- to the less coordinative barfates (Figure 1B, see SI for details).

Next, we focused on the evaluation of their reactivity toward cyclization reactions. We chose the allylic cyclization upon the activation of the alcohol **4a** to form 2*H*-chromene (**5a**)[21] in THF as a benchmark reaction to test the ability of benzotriazolium salts to act as Lewis acid catalysts (Scheme 2). This cyclization did not proceed in the absence of a Lewis acid, even at elevated temperatures (70 °C).

Scheme 2. Catalyst Screening for the Allyl Cyclization Reaction of 4a[a]



[a]Conditions: **4a** (0.2 mmol) and LA catalyst (10 mol %) in THF (0.1 M) for 18 h at 70 °C under Ar. Yield determined by ^1H NMR using CH_2Br_2 as an internal standard. (See SI for full optimization.) [b]Same yield for LA catalyst obtained from methylation with Me_3OBF_4 and exchange from I^- with $AgBF_4$, respectively. [c]Reaction performed under air.

The nitrenium series were then tested using 10 mol % of catalytic loading under an argon atmosphere. Dismissed yields or decompositions were generally observed for most of the Lewis acid catalysts **1–3**, as well as for the strong Lewis acid $BF_3{\cdot}Et_2O$. Gratifyingly, the LA catalysts **1b**, **2b**, and **3c** performed well in this benchmark reaction, showing up to 77% yield with catalyst **1b**. This result could not be improved by

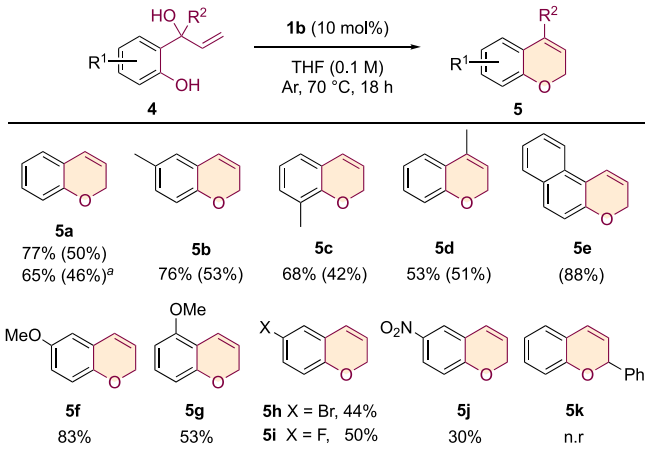
https://doi.org/10.1021/acs.orglett.2c01697
Org. Lett. 2022, 24, 6105–6110

changing the temperature or solvent, which both caused a decrease in yield (see SI). Moreover, the presence of oxygen led to a detriment of the yield, providing the product **5a** in only 33% yield when the reaction was run under air with **1b**, most probably due to partial oxidation/aromatization of the product.

To confirm that the catalytic activation is induced by our triazolium species, we carried out some control experiments. Since this kind of reaction can also be promoted by strong Brønsted acids that might be formed in the media, we tested our system in the presence of 1 mol % of triflic acid or Brookhart's-type acid $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$[22] as catalysts at both 70 °C and rt, but only decomposition could be detected (see SI, Table S6 for more details). This is in line with the observed beneficial moderate Lewis acidity to avoid decomposition while allowing for an efficient promotion of this cyclization reaction. Moreover, we were able to reproduce the good results with **1b** obtained through a different synthetic approach by I^- anion exchange using $AgBF_4$ instead of direct dimethylation with an excess of Me_3OBF_4 to rule out any traces of HBF_4 or Me_3OBF_4. Furthermore, we used $NaBF_4$ in catalytic amounts to exclude any influence of the counteranion on the activation process of this reaction. As expected, the ring closure did not proceed, proving that the triazolium cation is indeed inducing the ring closure.

With the optimized conditions in hand, the scope of the allylic cyclization was explored next (Scheme 3). First of all, it

Scheme 3. Scope of the Allylic Cyclization to 2*H*-Chromenes 5[b]

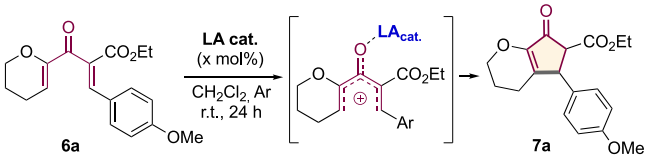


[a]1.0 mmol scale. [b]Yield determined by ^1H NMR using CH_2Br_2 as an internal standard. Isolated yield given in brackets.

is worthy to note that the reaction could be scaled up to 1 mmol without any significant detriment on the yield (65% vs 77%). Moreover, the formation of the products bearing different substitution patterns was pleasantly observed in every case. The methyl substitution at both the aryl and allylic moiety of the substrate gave the desired products **5b–d** in moderate to good yields (53–76%), while the π-extended compound **5e** showed a high stability, leading to a good 88% isolated yield. Moreover, strong electron-donating groups such as methoxy were well tolerated, providing 6- and 5-substituted chromenes **5f** and **5g** in 83% and 53% yield, respectively. Finally, less reactive substrates bearing electron-withdrawing groups such as halogen or nitro substituents could also be enrolled in the reaction, providing chromenes **5h–j** in moderate yields (30–50%),[23] while substrates with internal olefins were unreactive.

Due to the already known nitrenium activation of carbonyl groups for deoxygenation reactions (see Scheme 1B), we decided to further investigate the nitrenium series **1–3** in the Nazarov cyclization. This reaction is known to be activated by either LA metal-based catalysts[24] or phosphonium cations[10] and represents one of the most versatile methods for the synthesis of natural products and bioactive molecules containing cyclopentenone moieties.[25] In particular, we chose dienone **6a** as the model substrate[26] to determine the activity and requirements of the Lewis acid nitrenium salts (Table 1).

Table 1. Catalyst Screening in the Model Nazarov Cyclization of 6[a]



entry	LA catalyst (mol %)	yield **7a** (%)[b]
1	**1b** (1)	47
2	**1c** (1)	30
3	**1d** (1)	99(86)[c]
4	**2d** (1)	15
5	**3a** (1)	7
6	**1d** (1)	(77)[d,e]
7	**1d** (5)	>99
8	**1d** (0.5)	69[f]

[a]Conditions: **6** (0.2 mmol) and LA catalyst in CH_2Cl_2 (0.1 M) at rt for 24 h under Ar. [b]Yield determined by ^1H NMR using CH_2Br_2 as an internal standard. [c]>20:1 dr determined by ^1H NMR for all catalytic reactions. [d]Isolated yield in brackets. [e]Reaction performed under air. [f]0.4 mmol scale reaction.

Aiming at identifying highly efficient catalyst structures, 1 mol % of the salts **1–3** was initially employed at room temperature in CH_2Cl_2 as standard conditions. To our delight, LA catalysts **1b–d**, **2d**, and **3a** were able to promote the cyclization ranking from 7 to 99% conversion (entries 1–5), whereas the other nitrenium salts, including the already established triazinium catalyst **3c**, showed no catalytic activity in this reaction (see SI for full screening). However, there was not a perfect correlation between the LA strength and yield of the cyclopentanone **7**. Thus, catalyst **1d** with a slightly lower LA strength than the other catalysts led to full conversion and an excellent 86% isolated yield (entry 3). Moreover, performing this reaction under air instead of an inert atmosphere resulted in an insignificant drop of yield, which also shows the excellent bench, moisture, and air stability of this catalyst (entry 6). Additionally, while increasing the amount of catalyst to 5 mol % resulted in a similar nearly quantitative yield (entry 7). The remarkable performance of triazolium **1d** allowed the activation of the dienone system **6a** even at a 0.5 mol % loading to provide **7a** in a good 69% yield (entry 8).

These results encouraged us to further investigate the relative kinetics and potency of our catalytic system by monitoring the reaction with selected nitrenium LAs by ^1H NMR (Figure 2; shown 3 h, see SI for 15 h monitoring). For this purpose, we chose 5 mol % of catalyst loading due to the low conversion for most of the studied nitrenium salts during

https://doi.org/10.1021/acs.orglett.2c01697
Org. Lett. 2022, 24, 6105–6110

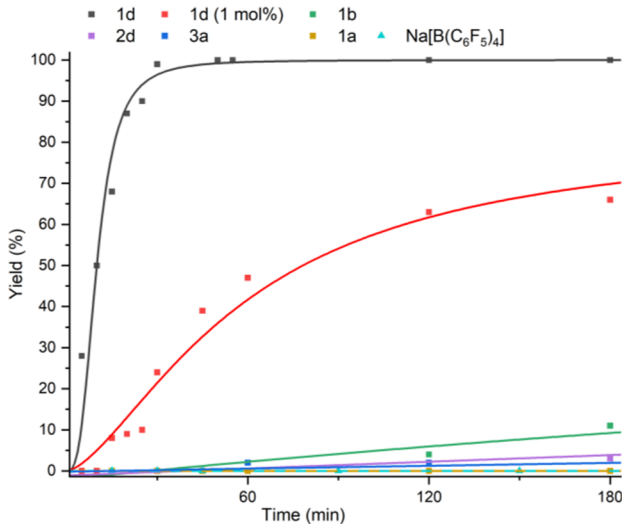
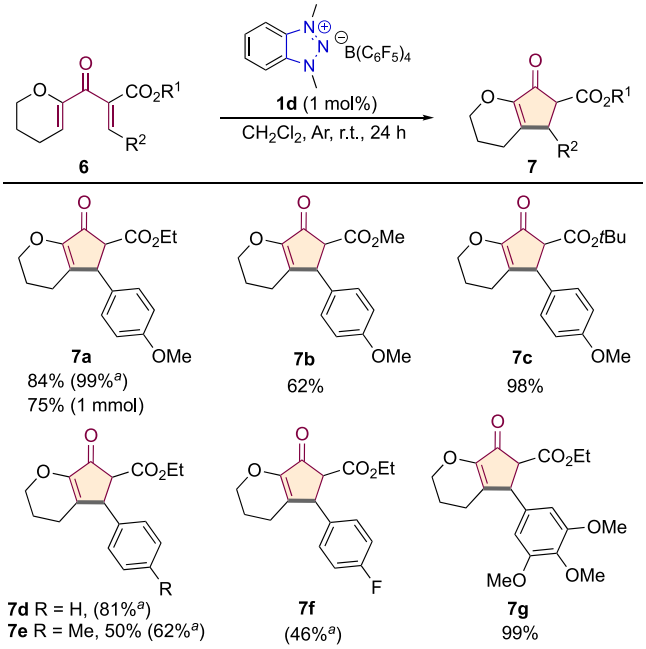


Figure 2. Kinetic experiment with an exemplary choice of catalysts **1**–**3** (5 mol %) in the Nazarov cyclization (see SI for full study).

the catalyst screening with 1 mol %. The highly activating triazolium **1d** showed full conversion after only 1 h. Due to this rapid evolution, the reaction with 1 mol % of **1d** was also investigated, in which a good 70% yield could still be observed after 3 h. As expected, for the less activating triazinium **3a** or catalysts **1b** and **2d**, a low linear conversion with less than 20% or 10% yield after 3 h was observed. Moreover, the control experiments with $Na[B(C_6F_5)_4]$ and **1a** showed no catalytic activity at all.

Lastly, the scope and limitations of the Nazarov cyclization were explored (Scheme 4). The upscaling of the standard reaction to 1 mmol using 1 mol % of the Lewis acid catalyst **1d** was first performed, showing the robustness of the method by providing a similar 75% yield. A different substitution on the ester moiety was well-tolerated (Me, **7b** and *t*Bu, **7c**), in which *tert*-butyl led to the best result with a 98% yield on the product **7c**. Furthermore, the different substitution on the R^2 group was also investigated. While the less reactive dienones bearing neutral Ph or weak activating *p*-tolyl rests (products: **7d**, 81%; **7e**, 62%) or electron-deficient aryl groups (product **7f**, 46%) required 5 mol % of the catalyst to provide synthetically useful conversions, electron-rich systems such as 3,4,5-triMeOPh provided the corresponding product **7g** in almost quantitative yield.

Scheme 4. Scope of the Nazarov Cyclization[b]



[a]Results with 5 mol % of **1d** in brackets. [b]Yields of the isolated products are given.

In summary, we have introduced benzotriazolium salts as a new class of bench-stable and efficient N-centered Lewis-acid catalysts. The new structures were benchmarked with already known nitrenium Lewis acids such as triazinium cations, showing a remarkably higher activity in the studied allylic cyclization and Nazarov reactions, implying a hydroxyl and carbonyl activation, respectively. Moreover, kinetic reaction monitoring of the Nazarov cyclization demonstrated the high reactivity of these N-based Lewis acid structures, which was confirmed by the low 1 mol % catalyst loading required and already shows their potential for a wide-ranging field of applications in Lewis acid catalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.2c01697.

Complete reaction screening, experimental procedures, characterization data, additional experiments, X-ray structure analysis of catalysts **1a**–**d**, **1f**, **1i**, and **2a**–**d**, and NMR spectra of isolated compounds (PDF)

Accession Codes

CCDC 2087003–2087011 and 2117634 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Olga García Mancheño − *Organic Chemistry Institute, Westfälische Wilhelms University Münster, 48149 Münster, Germany;* orcid.org/0000-0002-7578-5418; Email: olga.garcia@uni-muenster.de

Authors

Tobias Danelzik − *Organic Chemistry Institute, Westfälische Wilhelms University Münster, 48149 Münster, Germany*

Sumi Joseph − *Organic Chemistry Institute, Westfälische Wilhelms University Münster, 48149 Münster, Germany*

Christian Mück-Lichtenfeld − *Organic Chemistry Institute, Westfälische Wilhelms University Münster, 48149 Münster, Germany;* orcid.org/0000-0002-9742-7400

Constantin G. Daniliuc − *Organic Chemistry Institute, Westfälische Wilhelms University Münster, 48149 Münster, Germany*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.2c01697

https://doi.org/10.1021/acs.orglett.2c01697
Org. Lett. 2022, 24, 6105−6110

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The European Research Council (ERC-CG 724695) and the Deutsche Forschungsgemeinschaft (DFG) within the IRTG2027 are gratefully acknowledged for generous support. S.J. also thanks the German Academic Exchange Service (DAAD) for a Ph.D. fellowship.

■ REFERENCES

(1) Yamamoto, H., Ed. *Lewis Acids in Organic Synthesis*; Wiley-VCH: Weinheim, 2000.

(2) (a) Caputo, C. B.; Hounjet, L. J.; Dobrovetsky, R.; Stephan, D. W. Lewis acidity of organofluorophosphonium salts: hydrodefluorination by a saturated acceptor. *Science* **2013**, *341*, 1374−1377. (b) Gabbaï, F. P. Lewis acids with a difference. *Science* **2013**, *341*, 1348−1349.

(3) (a) Patai, S., Ed. *The Chemistry of Diazonium and Diazo Groups*, part 2; Wiley: New York, 1978. (b) Falvey, D. E.; Gudmundsdottir, A. D., Eds. *Nitrenes and Nitrenium Ions*; Wiley: New York, 2013.

(4) Boche, G.; Andrews, P.; Harms, K.; Marsch, M.; Rangappa, K. S.; Schimeczek, M.; Willeke, C. Crystal and Electronic Structure of Stable Nitrenium Ions. A Comparison with Structurally Related Carbenes. *J. Am. Chem. Soc.* **1996**, *118*, 4925−4930.

(5) (a) Enders, D.; Balensiefer, T. Nucleophilic Carbenes in Asymmetric Organocatalysis. *Acc. Chem. Res.* **2004**, *37*, 534−541. (b) Berry, M. T.; Castrejon, D.; Hein, J. E. Oxidative Esterification of Aldehydes Using Mesoionic 1,2,3-Triazolyl Carbene Organocatalysts. *Org. Lett.* **2014**, *16*, 3676−3679.

(6) (a) Shah, J.; Khan, S.; Blumenthal, H.; Liebscher, J. 1,2,3-Triazolium-Tagged Prolines and Their Application in Asymmetric Aldol and Michael Reactions. *Synthesis* **2009**, 3975−3982. (b) Yacob, Z.; Shah, J.; Leistner, J.; Liebscher, J. (*S*)-Pyrrolidin-2-ylmethyl-1,2,3-triazolium Salts - Ionic Liquid Supported Organocatalysts for Enantioselective Michael Additions to *β*-Nitrostyrenes. *Synlett* **2008**, 2342−2344. (c) Khan, S. S.; Shah, J.; Liebscher, J. Ionic-liquid tagged prolines as recyclable organocatalysts for enantioselective *α*-aminoxylations of carbonyl compounds. *Tetrahedron* **2011**, *67*, 1812−1820.

(7) Tulchinsky, Y.; Iron, M. A.; Botoshansky, M.; Gandelman, M. Nitrenium ions as ligands for transition metals. *Nat. Chem.* **2011**, *3*, 525−531.

(8) Pogoreltsev, A.; Tulchinsky, Y.; Fridman, N.; Gandelman, M. Nitrogen Lewis Acids. *J. Am. Chem. Soc.* **2017**, *139*, 4062−4067.

(9) (a) Burck, S.; Gudat, D.; Nieger, M. Diphosphanes with Polarized and Highly Reactive P−P Bonds. *Angew. Chem., Int. Ed.* **2004**, *43*, 4801−4804. (b) Bayne, J. M.; Stephan, D. W. Phosphorus Lewis acids: emerging reactivity and applications in catalysis. *Chem. Soc. Rev.* **2016**, *45*, 765−774. (c) Chitnis, S. S.; LaFortune, J. H. W.; Cummings, H.; Liu, L. L.; Andrews, R.; Stephan, D. W. Phosphorus Coordination Chemistry in Catalysis: Air Stable P(III)-Dications as Lewis Acid Catalysts for the Allylation of C−F Bonds. *Organometallics* **2018**, *37*, 4540−4544. (d) Augurusa, A.; Mehta, M.; Perez, M.; Zhu, J.; Stephan, D. W. Catalytic reduction of amides to amines by electrophilic phosphonium cations via FLP hydrosilylation. *Chem. Commun.* **2016**, *52*, 12195−12198. (e) Holthausen, M. H.; Mehta, M.; Stephan, D. W. The Highly Lewis Acidic Dicationic Phosphonium Salt: $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$. *Angew. Chem., Int. Ed.* **2014**, *53*, 6538−6541. (f) Mehta, M.; La Garcia de Arada, I.; Pérez, M.; Porwal, D.; Oestreich, M.; Stephan, D. W. Metal-Free Phosphine Oxide Reductions Catalyzed by $B(C_6F_5)_3$ and Electrophilic Fluorophosphonium Cations. *Organometallics* **2016**, *35*, 1030−1035. (g) Mehta, M.; Holthausen, M. H.; Mallov, I.; Pérez, M.; Qu, Z.-W.; Grimme, S.; Stephan, D. W. Catalytic Ketone Hydrodeoxygenation Mediated by Highly Electrophilic Phosphonium Cations. *Angew. Chem., Int. Ed.* **2015**, *54*, 8250−8254.

(10) Vogler, M.; Süsse, L.; LaFortune, J. H. W.; Stephan, D. W.; Oestreich, M. Electrophilic Phosphonium Cations as Lewis Acid Catalysts in Diels−Alder Reactions and Nazarov Cyclizations. *Organometallics* **2018**, *37*, 3303−3313.

(11) (a) Payrastre, C.; Madaule, Y.; Wolf, J. G.; Kim, T. C.; Mazières, M.-R.; Wolf, R.; Sanchez, M. Lewis acid properties of phosphenium and arsenium cations: Study of their adducts with pyridine. *Heteroat. Chem.* **1992**, *3*, 157−162. (b) Ould, D. M. C.; Melen, R. L. Arsenic Catalysis: Hydroboration of Aldehydes Using a Benzo-Fused Diaza-benzyloxy-arsole. *Chem. Eur. J.* **2018**, *24*, 15201−15204.

(12) (a) Zhou, J.; Liu, L. L.; Cao, L. L.; Stephan, D. W. Nitrogen-based Lewis acids: Synthesis and reactivity of a cyclic (alkyl)(amino) nitrenium cation. *Angew. Chem., Int. Ed.* **2018**, *57*, 3322−3326. (b) Zhou, J.; Liu, L. L.; Cao, L. L.; Stephan, D. W. An umpolung of Lewis acidity/basicity at nitrogen by deprotonation of a cyclic (amino) (aryl) nitrenium cation. *Chem. Commun.* **2018**, *54*, 4390−4393.

(13) Stephan, D. W.; Erker, G. Frustrated Lewis Pair Chemistry: Development and Perspectives. *Angew. Chem., Int. Ed.* **2015**, *54*, 6400−6441.

(14) Avigdori, I.; Pogoreltsev, A.; Kaushanski, A.; Fridman, N.; Gandelman, M. Frustrated Lewis Pairs Comprising Nitrogen Lewis Acids for Si−H Bond Activation. *Angew. Chem., Int. Ed.* **2020**, *59*, 23476−23479.

(15) Mehta, M.; Goicoechea, J. M. Nitrenium Salts in Lewis Acid Catalysis. *Angew. Chem., Int. Ed.* **2020**, *59*, 2715−2719.

(16) See for example: (a) Forsyth, S. A.; MacFarlane, D. R. 1-Alkyl-3-methylbenzotriazolium salts: ionic solvents and electrolytes. *J. Mater. Chem.* **2003**, *13*, 2451−2456. (b) Zhang, S. J.; Lu, X. M. *Ionic liquids: from fundamental research to industrial applications*; Science Press: Beijing, 2006. (c) Mudzakir, A. A New class of ionic solvents, electrolytes and engineering fluids based on 1,3-alkylmethyl-1,2,3-benzotrizoilium salts. *Indo. J. Chem.* **2006**, *6*, 111−116. (d) Buttrus, N. H.; Mohamed, H. A.; Saeed, F. T. Preparation and characterization of ionic complex salts based on benzotriazolium cations. *J. Educ. Sci.* **2012**, *25*, 19−26.

(17) A use of triazoliums as Lewis acid catalysts appeared during the revision of this work: (a) Ranolia, D.; Avigdori, I.; Singh, K.; Koronatov, A.; Fridman, N.; Gandelman, M. *Org. Lett.* **2022**, *24*, 3915−3919. (b) See also ref 8 for a Lewis adduct formation of BZT salts.

(18) Mayer, U.; Gutmann, V.; Gerger, W. The acceptor number — A quantitative empirical parameter for the electrophilic properties of solvents. *Monatsh. Chem.* **1975**, *106*, 1235−1257.

(19) Erdmann, P.; Greb, L. What Distinguishes the Strength and the Effect of a Lewis Acid: Analysis of the Gutmann−Beckett Method. *Angew. Chem., Int. Ed.* **2022**, DOI: 10.1002/anie.202114550.

(20) The structure of **1a** was previously reported: Rangappa, K. S.; Mallesha, H.; Anil Kumar, N. V.; Lokanath, N. K.; Sridhar, M. A.; Shashidhara Prasad, J. Synthesis and Crystal Structure of 1,3-Dimethyl Benzotriazolium Trifluoromethane Sulfonate. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **2001**, *357*, 291−298.

(21) For a recent review on biologically active chromenes, see: Raj, V.; Lee, J. 2H/4H-Chromenes—A Versatile Biologically Attractive Scaffold. *Front. Chem.* **2020**, *8*, 623−645.

(22) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920−3922.

(23) Due to the oxidation lability and/or volatile nature of product **5**, in some cases low isolated yields were obtained. See the SI.

(24) (a) Subramanium, S. S.; Handa, S.; Miranda, A. J.; Slaughter, L. M. Simple Silver Salts and Palladium Bis(*N*-heterocyclic carbene) Complexes As Complementary Catalysts for the Nazarov Cyclization. *ACS Catal.* **2011**, *1*, 1371−1374. (b) He, W.; Herrick, I. R.; Atesin, T. A.; Caruana, P. A.; Kellenberger, C. A.; Frontier, A. J. Polarizing the Nazarov Cyclization: The Impact of Dienone Substitution Pattern on Reactivity and Selectivity. *J. Am. Chem. Soc.* **2008**, *130*, 1003−1011.

https://doi.org/10.1021/acs.orglett.2c01697
Org. Lett. 2022, 24, 6105−6110

(c) Janka, M.; He, W.; Frontier, A. J.; Eisenberg, R. Efficient Catalysis of Nazarov Cyclization Using a Cationic Iridium Complex Possessing Adjacent Labile Coordination Sites. *J. Am. Chem. Soc.* **2004**, *126*, 6864−6865. (d) Liang, G.; Gradl, S. N.; Trauner, D. Efficient Nazarov Cyclizations of 2-Alkoxy-1,4-pentadien-3-ones. *Org. Lett.* **2003**, *5*, 4931−4934.

(25) (a) Cao, S.; Ross, L.; Tamayo, G.; Clardy, J. Asterogynins: Secondary Metabolites from a Costa Rican Endophytic Fungus. *Org. Lett.* **2010**, *12*, 4661−4663. (b) Musiek, E. S.; Breeding, R. S.; Milne, G. L.; Zanoni, G.; Morrow, J. D.; McLaughlin, B. Cyclopentenone isoprostanes are novel bioactive products of lipid oxidation which enhance neurodegeneration. *J. Neurochem.* **2006**, *97*, 1301−1313. (c) Bitar, A. Y.; Frontier, A. J. Formal Synthesis of (±)-Roseophilin. *Org. Lett.* **2009**, *11*, 49−52. (d) Malona, J. A.; Cariou, K.; Frontier, A. J. Nazarov Cyclization Initiated by Peracid Oxidation: The Total Synthesis of (±)-Rocaglamide. *J. Am. Chem. Soc.* **2009**, *131*, 7560−7561.

(26) He, W.; Sun, X.; Frontier, A. J. Polarizing the Nazarov Cyclization: Efficient Catalysis under Mild Conditions. *J. Am. Chem. Soc.* **2003**, *125*, 14278−14279.

https://doi.org/10.1021/acs.orglett.2c01697
Org. Lett. 2022, 24, 6105−6110