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Lanthanide Perfluoroalkylsulfonylamide Catalysts for Fluorous Phase Organic Synthesis

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Abstract: Lanthanide perfluoroalkylsulfonylamide complexes catalyze the Friedel-Crafts acylation and Diels-Alder reaction more efficiently than $AlCl_3$ and $Yb(OTf)_3$ in benzotrifluoride and hexafluoro-*p*-xylene.

The fluorous phase organic synthesis was first introduced by Zhu, who used fluorous solvents in organic synthesis.¹ Horvath and Rabai then proposed the concept of fluorous biphasic catalysis.² The most effective fluorous moieties in catalysts are branched or linear perfluoroalkyl chains with a high carbon number (fluorous ponytails).³ In the course of our research project⁴ on lanthanide complexes as efficient catalysts in organic synthesis, we report the development of lanthanide bisperfluoroalkylsulfonylamide catalysts for fluorous phase organic synthesis.



The bis-sulfonylimides, HN(SO₂Rf)₂ (Rf: CF₃, C₂F₅, and C₄F₉) possess remarkably high Bronstead acidity and bis-perfluorobutylsulfonylimide, HN(SO₂C₄F₉)₂, in particular, is the strongest acid so far known in the gas phase.⁵ Therefore, the conjugate bases of these acids bind very weakly with metals, leading to the high Lewis acidity of the metal complexes. Thus, we prepared the ytterbium bisperfluorobutylsulfonylamide complexes, $Yb(N(SO_2C_4F_9)_2)_3$, according to the reported procedure for Yb(N(SO₂CF₃)₂)₃.^{6b} The catalytic activity of Yb(N(SO₂C₄F₉)₂)₃ (7 mol%) was examined in a haloalkane alternative, benzotrifluoride (BTF),⁷ at room temperature as compared with those of typical Lewis acid complexes, such as AlCl₃ or Yb(OTf)₃ in the Friedel-Crafts acylation with acetic anhydride of anisol. AlCl₃ and Yb(OTf)₃ were insoluble in BTF, however, and no acylation product was formed within 1 h. In contrast, $Yb(N(SO_2C_nF_{2n+1})_2)_3$ produced the acylation product, the yield increasing with elongating perfluoroalkyl chains. When the reaction temperature was increased (40°C), an almost quantitative yield of the acylation product of anisol was obtained by using Yb(N(SO₂C₄F₉)₂)₃ (10 mol%) after 2 h (eq. 1). A similar reaction of anisol with acetic anhydride in $\alpha, \alpha, \alpha, \alpha', \alpha', \alpha', \alpha'$ hexafluoro-p-xylene also produced a high yield (94%) of the acylation product. It should be noted that a one-phase system could be obtained under the reaction conditions. Higher catalytic activity of Yb(N(SO₂C₄F₉)₂)₃ than Yb(OTf)₃ was also observed with respect to the same acylation reaction in a homogeneous reaction system in CH₃CN (5 mol% of Yb catalyst, 70 °C, 1 h) (Yb(N(SO₂C₄F₉)₂)₃: 75% yield; Yb(N(SO₂CF₃)₂)₃: 61% yield; Yb(OTf)₃: 25% yield). Similar reactions, such as acylation of alcohol (eq. 2) or the Diels-Alder reaction of 2,3-dimethylbutadiene with methylvinylketone (eq. 3), were examined by the catalytic use of Ln(N(SO₂C₄F₉)₂)₃ as compared with the results obtained with Yb(OTf)3. These results clearly indicate the higher catalytic activity of Yb(N(SO₂C₄F₉)₂)₃ than the corresponding Yb(OTf)₃⁸.



Yb(N(SO2C4F9)2)3 95% (0.5 h)

cf. Yb(OTf)3 6% (1 h)

In summary, we report the development of lanthanide perfluoroalkylsulfonylamide catalysts in fluorous phase organic synthesis. Because fluorous synthesis combines the favorable purification features of solid-phase synthesis with the favorable reaction and analysis features of liquid-phase organic synthesis, it could prove valuable in the automated synthesis of libraries of organic compounds. Further work along this line, using fluorousyl catalysts directed towards asymmetric catalysis, are now under way in our laboratory.

References and Notes

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