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Copper(II) bis((trifluoromethyl) sulfonyl) amide. A novel Lewis acid catalyst in Diels–Alder reactions of cyclopentadiene with methyl vinyl ketone

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Abstract

Copper(II) salt of weakly coordinating bis((trifluoromethyl)sulfonyl)amide anion was newly prepared. A remarkable catalytic effect of the copper salt $Cu(NTf_2)_2$ was demonstrated in the Diels–Alder reactions of cyclopentadiene with methyl vinyl ketone in CH_2Cl_2 in comparison with other metal salts.

Keywords: Diels–Alder reaction; Lewis acid; Catalytic effect; Metal salts

1. Introduction

Investigation of ''non-coordinating'' or ''weakly coordinating'' anions has attracted special attention of chemists in recent years [1–3] since cation–anion interaction plays an important role in the catalytic activity of metal complexes. The superacid property of bis((perfluoroalkyl)sulfonyl)amines ($HN(SO_2Rf)_2$) in gas-phase [4] and in solution [5] is due mainly to the weakly coordinating ability of the amide anions ($N(SO_2Rf)_2^-$) as conjugated base. The metal ions paired with these anions in weakly coordinating solvents such as CH_2Cl_2 and toluene are therefore to be highly activated to show their increased Lewis acidity. Recently we have reported the new syntheses of alkali, alkaline earth, and lanthanum salts of bis((perfluoroalkyl)sulfonyl)amides and demonstrated the utility of these metal amides as Lewis acid catalysts in Diels–Alder reactions [6].

In this work we further report the new synthesis and novel effect of copper(II)bis((trifluoromethyl)sulfonyl)amide $Cu(NTf_2)_2$ ($Tf = SO_2CF_3$) as a Lewis acid catalyst in the Diels–Alder reaction of cyclopentadiene with methyl vinyl ketone in comparison with other metal salts.

2. Experimental

2.1. Syntheses of metalbis((trifluoromethyl)sulfonyl)amides

Lithium, calcium, magnesium, zinc, and lanthanum salts of bis((trifluoromethyl)sulfonyl)amides ($LiNTf_2$, $Ca(NTf_2)_2$, $Mg(NTf_2)_2$, $Zn(NTf_2)_2$, $La(NTf_2)_3$) were prepared almost quantitatively by the reactions of $HNTf_2$ with stoichiometric amounts of the corresponding

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metal acetates, oxides, carbonates, or hydroxides in water [6]. Colourless solid of the metal amides obtained by filtration and evaporation of the reaction mixture were dried under ca. 10^{-3} mmHg at 50–100°C for 15 h. ^{19}F NMR and IR spectra and the elemental analyses gave satisfactory results [7]. The numbers of hydrated water molecules were determined by the ^{1}H NMR spectroscopy with $CHCl_3$ as an external standard. Overnight dehydration under 10^{-5} mmHg at 110°C gave anhydrous $LiNTf_2$, $Ca(NTf_2)_2$, $Mg(NTf_2)_2$, and $Zn(NTf_2)_2$, while the lanthanum salt was obtained as hydrate $La(NTf_2)_3 \cdot H_2O$. These metal salts were very stable and non-oxidative. Silver salt $AgNTf_2 \cdot 0.5H_2O$ was obtained by the reaction of $HNTf_2$ with stoichiometric Ag_2O in water, which was unstable under light. The copper salt $Cu(NTf_2)_2 \cdot H_2O$ was prepared by the reaction of $CuCl_2 \cdot 2H_2O$ with stoichiometric $AgNTf_2$ in water. After filtration of precipitated AgCl the reaction mixture was dried under 0.4 mmHg at 50°C to give a pale blue solid of $Cu(NTf_2)_2 \cdot H_2O$, which was decomposed at 145°C. The copper salt was very oxidative to change the colour of KBr plate to brown in measuring the IR spectrum of the solid salt. All of the metal amides were very hygroscopic and much more soluble in CH_2Cl_2 than the corresponding metal trifluoromethanesulfonates (triflates) and chlorides. Lanthanum triflate $La(OTf)_3$ was prepared similarly by the reaction of La_2O_3 with a stoichiometric amount of TfOH in water. After filtration and evaporation a colourless solid remained was dried for 12 h under 10^{-3} mmHg at 100°C to give $La(OTf)_3 \cdot H_2O$, which was non-hygroscopic and almost insoluble in most organic solvents even in CH_3CN but soluble in water and alcohol.

2.2. *Metal ion-catalyzed Diels–Alder reactions of cyclopentadiene with methyl vinyl ketone in CH_2Cl_2*

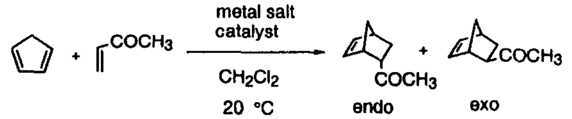
In kinetic experiments all of catalysts were handled in a dry box since most of the metal salts were very hygroscopic. The ''hydrated'' catalysts (catalyst $\cdot\, n H_2O$) are the catalysts which were dried under ca. 0.05 mmHg at 100°C for 3h before using in the Diels–Alder reactions. The numbers of the coordinated water molecules were determined by ^{1}H NMR by using $CHCl_3$ as an external standard as shown above. The ''dried'' catalysts are the catalysts which were dried under $1\text{–}3 \times 10^{-5}$ mmHg at 100°C for 15h and the numbers of the coordinated water molecules were normally less than one. The solvents were freshly distilled before the reaction and the concentration of water was determined by a Karl–Fisher moisture titrator to be in the range of 8–13 ppm. Cyclopentadiene and methyl vinyl ketone were also distilled just before use and their purity was checked by gas chromatography (GC).

The general kinetic experimental procedure was as follows: Given amounts of cyclopentadiene, decane (internal standard for GC analysis), and 50 ml dry CH_2Cl_2 were placed in a 100 ml two-necked flask provided with a condenser and a ball full of argon gas. Given amounts of methyl vinyl ketone was then added into this solution under fast stirring at 20°C to prepare the reaction mixture in which the concentration of cyclopentadiene was ca. 0.10 mol l^{-1} and methyl vinyl ketone ca. 0.17 mol l^{-1}. From the reaction mixture 17.5 ml was taken twice and one part was added into a 30 ml two-necked flask containing the ''hydrated'' catalyst provided with a condenser and a ball filled with argon gas, and the other part was added into a flask containing the ''dried'' catalyst to start the catalytic reaction under stirring at 20°C. The remained part of the reaction mixture was used for uncatalyzed standard reaction. Three operations were done within 1 or 2 min. At regular intervals 100 μl of the reaction mixture was sampled and filtered through a micro silica-gel column (Silicon-300) to remove the catalyst, and the reaction mixture was diluted four times with CH_2Cl_2. The conversion of the reaction was analyzed by GC with internal standard decane.

Typical experimental procedures were shown below in the cases of $Mg(NTf_2)_2$ and $Cu(NTf_2)_2$: Methyl vinyl ketone 392 mg (5.59 mmol, 0.1 mol l^{-1}), cyclopentadiene 594 mg (9.0 mmol, 0.18 mol l^{-1}), and decane 392 mg (2.76 mmol, 0.055 mol l^{-1}) as internal standard were mixed into a CH_2Cl_2 solution (50 ml) according to the procedure mentioned above. The one part of hydrated catalyst $Mg(NTf_2)_2 \cdot 3H_2O$ 9.64 mg (0.017 mmol, 1 mol%) was used for reaction with the "hydrated" catalysts and the other part of the same hydrated catalyst (0.017 mmol, 1 mol%) was dehydrated under high vacuum at 100°C for 15 h to be used as the "dried" catalyst. The "hydrated" catalysts of $Cu(NTf_2)_2 \cdot nH_2O$ 13.9 mg ($n = 4$, 0.018 mmol, 1 mol%) was dehydrated under 1.2×10^{-4} mmHg at 60°C for 15.5h to be used as the "dried" catalyst. During dehydration the pale blue solid of $Cu(NTf_2)_2$ became white and then deep purple coloured. For an experiment with the "hydrated" catalyst $Cu(NTf_2)_2 \cdot nH_2O$ 12.5 mg ($n = 4$, 0.017 mmol) was used without dehydration treatment. The concentration and the endo/exo ratio of the product were calculated by GC analysis.

3. Results and discussion

Some metal amides were employed as Lewis acid catalysts in the Diels–Alder reaction of cyclopentadiene with methyl vinyl ketone in CH_2Cl_2 at 20°C (Scheme 1). GC analysis of the reaction mixtures showed that most of the reactions with active catalysts gave the Diels–Alder reaction products in more than 95% yields. The relative second order rate constants (k_{obs}) and the endo/exo product ratio in CH_2Cl_2 are shown in Table 1.



Scheme 1.

Table 1
Metal ion-catalyzed Diels–Alder reactions of cyclopentadiene with methyl vinyl ketone in dichloromethane

Catalyst	mol%	rel. k_{obs}	endo/exo [a]
None	0	1 [b]	6/1
$LiNTf_2$	1	2	7/1
$Ca(NTf_2)_2 \cdot 1.5H_2O$	1	5	7/1
$Ca(NTf_2)_2$ (dried)	1	5	7/1
$Mg(NTf_2)_2 \cdot 3H_2O$	1	5	12/1
$Mg(NTf_2)_2$ (dried)	1	18	12/1
$Mg(NTf_2)_2 \cdot 3H_2O$	9	150	12/1
$Mg(NTf_2)_2$ (dried)	10	380	12/1
$ZnCl_2$	1	23	19/1
$Zn(NTf_2)_2 \cdot 7H_2O$	1	125	16/1
$Zn(NTf_2)_2$ (dried)	1	125	16/1
$La(OTf)_3 \cdot H_2O$	1	1	6/1
$La(OTf)_3 \cdot H_2O$	9	1	6/1
$La(NTf_2)_3 \cdot H_2O$	1	1440	12/1
$CuCl_2 \cdot 2H_2O$	1	1	7/1
$Cu(NTf_2)_2 \cdot nH_2O$	1	> 1770	13/1
$Cu(NTf_2)_2$ (dried)	1	> 1370	16/1

[a] Determined by GC.

[b] k_{obs} (no. cat) = 7.1×10^{-3} $l \cdot mol^{-1} \cdot min^{-1}$.

In Table 1 the order of the catalytic activity of alkali and alkaline earth metal ions ($Mg^{2+} > Ca^{2+} > Li^{+}$) in CH_2Cl_2 paralleled the order of effective cation charge (ion charge/radius) as observed in the similar Diels–Alder reactions catalyzed by metal perchlorates in acetone [8]. The effect of dehydration of magnesium salt to increase the reaction rate was obvious. Hydration of water molecules on the metal ion decreases the Lewis acidity of the metal ion. The Diels–Alder reaction in more coordinating ether solvent was not accelerated at all in the presence of 1 mol% of the metal amides and the rate acceleration was only 14 times in the presence of 10 mol% of $Mg(NTf_2)_2$ in ether. Recently the acceleration of Diels–Alder reactions in the presence of $LiNTf_2$ in acetone and ether was reported but only with excess amounts (4–5 M) of $LiNTf_2$ [9].

The transition metal and lanthanide amides such as $Zn(NTf_2)_2$, $La(NTf_2)_3$, and $Cu(NTf_2)_2$

were very effective Lewis acid catalysts compared with the corresponding chlorides and triflate such as $ZnCl_2$, $La(OTf)_3$, and $CuCl_2$, respectively. Although recent reports have demonstrated remarkable Lewis acidity of some lanthanide and scandium triflates in various carbon–carbon bond formation reactions, $La(OTf)_3$ has been reported less effective compared with other lanthanide salts as Lewis acid catalysts [10]. Thus, the higher reactivity of $La(NTf_2)_3$ compared with that of $La(OTf)_3$ is a good example of the effectiveness of the metal amides as Lewis acid catalysts. These higher activities of the metal amides are mainly due to the weakly coordinating property of NTf_2^- anion whose anionic center is highly delocalized and stabilized by electron-withdrawing SO_2CF_3(Tf) groups to increase the solubility and the Lewis acidity of the metal amides in CH_2Cl_2. In contrast to $CuCl_2 \cdot 2H_2O$ the catalytic effect of $Cu(NTf_2)_2$ was so remarkable that the catalytic reaction with 1 mol% of dried $Cu(NTf_2)_2$ was completed in several minutes at 20°C. Interestingly the color of the reaction solution changed from colourless to dark violet. The electronic spectrum of the reaction mixture indicated that the color change was due to an uncertain reaction of cyclopentadiene with $Cu(NTf_2)_2$ salt in CH_2Cl_2. On the other hand the reaction mixture of cyclopentadiene with trans-β-methylstyrene with the "dried" $Cu(NTf_2)_2$ (1 mol%) in CH_2Cl_2 was blue-coloured due to the $Cu(NTf_2)_2$ but no Diels–Alder reaction of cyclopentadiene with trans-β-methylstyrene was observed. The investigation of the mechanism of the remarkable catalytic reactions with $Cu(NTf_2)_2$ is now under progress.

4. Summary

The syntheses and remarkable catalytic effects of several metal bis((trifluoromethyl)sulfonyl)amides, especially $Cu(NTf_2)_2$, in Diels–Alder reaction were demonstrated. Further applications of these metal amides and the comparison with metal salts of other weakly coordinating anions are under progress.

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