Metal Bis((perfluoroalkyl)sulfonyl)amides as Novel Lewis Acid Catalysts in Diels-Alder Reaction

Hiroshi Kobayashi,* Jin Nie, and Takaaki Sonoda*
Institute of Advanced Material Study, Kyushu University, Kasuga, Fukuoka 816

(Received January 20, 1995)

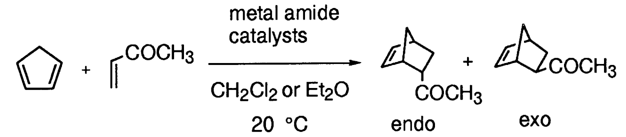
Some stable and lipophilic metal bis((perfluoroalkyl)-sulfonyl)amides are prepared and employed as remarkable Lewis acid catalysts in the Diels-Alder reaction of cyclopentadiene with methyl vinyl ketone.

Trifluoromethylsulfonyl(trifyl) group is one of the strongest neutral electron-withdrawing groups and the versatility of trifluoromethanesulfonic acid(TfOH) and its derivatives is widely known in organic chemistry.[1] On the other hand, in a recent report about the relative gas-phase acidities of very strong carbon(CH)-, nitrogen(NH)-, and oxygen(OH)-Brønsted acids,[2] bis((trifluoromethyl)sulfonyl)amine $HNTf_2$ is a stronger acid than TfOH. Since metal triflates have been employed as versatile Lewis acid catalysts,[3] we are interested in preparing some metal bis((perfluoroalkyl)sulfonyl)amides to investigate their utility as Lewis acid catalysts, for example, in Diels-Alder reaction.

The metal bis((perfluoroalkyl)sulfonyl)amides were easily prepared from the reactions of the corresponding acids such as $HNTf_2$,[4] $HNTfSO_2C_4F_9$,[5] and $HNTfSO_2C_8F_{17}$,[5] with metal acetates, oxides, carbonates, or hydroxides in water.[6] The metal amides we prepared here were very stable and non-oxidative. Most of them were hygroscopic and more soluble under the reaction conditions in dichloromethane than the corresponding triflates. These amides could be easily recovered as the acids by sublimation from conc. sulfuric acid solution of the metal amides.

Some metal amides were employed as Lewis acid catalysts in the Diels-Alder reaction of cyclopentadiene with methyl vinyl ketone in dichloromethane and diethyl ether at 20 °C(Scheme 1). GC analysis of the reaction mixtures showed that most of the reactions with active catalysts such as $Mg(NTf_2)_2$, $Zn(NTf_2)_2$, and $La(NTf_2)_3$ 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 dichloromethane and diethy ether were shown in Tables 1 and 2, respectively.[7]

Scheme 1.



In Table 1 the order of the catalytic reactivity of alkali and alkali earth metal ions($Mg^{2+} > Ca^{2+} > Ba^{2+} \approx Li^+$) in dichloromethane 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 metal amides were more effective compared with the corresponding chloride and triflate; especially $La(NTf_2)_3$ was very active in dichloromethane and even in coordinating diethyl ether solvent in comparison with $La(OTf)_3$. This higher activity of the metal amides may be due to the presence of the non-coordinating NTf_2^- anion whose anionic center is highly delocalized by two Tf groups to increase the solubility and the Lewis acidity of the metal amides. In dichloromethane, the decreased solubility of magnesium and lanthanum amides with a longer perfluoroalkylsulfonyl group caused the decreased catalytic activities of the amides in the reactions with both of 1 and 9 mol % catalysts (relative k_{obs}; $Mg(NTf_2)_2 > Mg(NTfSO_2C_4F_9)_2 > Mg(NTfSO_2C_8F_{17})_2$; $La(NTf_2)_3 > La(NTfSO_2C_4F_9)_3 > La(NTfSO_2C_8F_{17})_3$). On the other hand, in Table 2 in diethyl ether under the homogeneous reaction conditions with 1 mol % of the lanthanum amides, the order of the catalytic activity was reversed; $La(NTfSO_2C_8F_{17})_3 > La(NTfSO_2C_4F_9)_3 > La(NTf_2)_3$, which is in accord with the order of the intrinsic stability of the amide anions in gas phase.[2] However, in the reactions with 9 mol % catalysts in diethyl ether, the lower solubility of $La(NTfSO_2C_8F_{17})_3$ caused again the decreased catalytic activity in comparison with $La(NTfSO_2C_4F_9)_3$.

Interestingly, in the reactions with the lanthanum amides, the reaction rates were accelerated in both of dichloromethane and diethyl ether, while the stereoselectivity (endo/exo product ratio) was increased in dichloromethane but slightly decreased in diethyl ether compared with the results of the uncatalyzed reactions.

Table 1. Metal Ions-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
$Ba(NTf_2)_2$	1	2	7 / 1
$Ca(NTf_2)_2$	1	5	7 / 1
$Mg(NTf_2)_2$	1	18	12 / 1
$Mg(NTfSO_2C_4F_9)_2$	1	6	10 / 1
$Mg(NTfSO_2C_8F_{17})_2$	1	2	7 / 1
$Mg(NTf_2)_2$	9	380	12 / 1
$ZnCl_2$	1	23	19 / 1
$Zn(NTf_2)_2$	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
$La(NTfSO_2C_4F_9)_3 \cdot 2H_2O$	1	248	8 / 1
$La(NTfSO_2C_8F_{17})_3 \cdot 1.5H_2O$	1	114	9 / 1

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

Table 2. Metal Ions-Catalyzed Diels-Alder Reactions of Cyclopentadiene with Methyl Vinyl Ketone in Diethyl Ether

catalyst	mol%	rel. k_{obs}	endo / exo[a]
none	0	1[b]	4 / 1
$La(OTf)_3\cdot H_2O$	1	2	4.7 / 1
$La(NTf_2)_3\cdot H_2O$	1	17	3.8 / 1
$La(NTfSO_2C_4F_9)_3\cdot 2H_2O$	1	35	3.7 / 1
$La(NTfSO_2C_8F_{17})_3\cdot 1.5H_2O$	1	59	3.7 / 1
$La(OTf)_3\cdot H_2O$	9	4	6 / 1
$La(NTf_2)_3\cdot H_2O$	9	347	3.6 / 1
$La(NTfSO_2C_4F_9)_3\cdot 2H_2O$	9	872	3.5 / 1
$La(NTfSO_2C_8F_{17})_3\cdot 1.5H_2O$	9	705	3.5 / 1

[a]Determined by GC. [b]k_{obs}(no. cat) = 2.1×10^{-3} $l\cdot mol^{-1}\cdot min^{-1}$.

In summary we have demostrated the novel Lewis acidity of some metal bis((perfluoroalkyl)sulfonyl)amides in Diels-Alder reaction. Further applications of these metal amides and the comparison with metal salts of other weakly coordinating anions are under progress.

This work was partially suported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

References and Notes

1 A. Senning, *Chem. Rev.*, **65**, 385(1965); R. D. Howells, J. D. McCown, *Chem. Rev.*, **65**, 385(1965); P. J. Stang, M. Hanack, and L. R. Subramanian, *Synthesis*, **1982**, 85; P. J. Stang and M. R. White, *Aldrichimica Acta*, **16**, 15(1983).

2 I. A. Koppel, R. W. Taft, F. Anvia, S-Z. Zhu, L.-Q. Hu, K.-S. Sung, D. D. DesMarteau, L. M. Yagupolskii, Y. L. Yagupolskii, N. V. Ignat'ev, N. V. Kondratenko, A. Y. Volkonskii, V. M. Vlasov, R. Notario, and P.-C. Maria, *J. Am. Chem. Soc.*, **116**, 3047(1994).

3 Recent reports have demonstrated remarkable Lewis acidity of some lanthanide and scandium trifrates in Diels-Alder reactions: S. Kobayashi, I. Hachiya, and T. Takahori, M. Araki, and H. Ishitani, *Tetrahedron Lett.*, **33**, 6815(1992); S. Kobayashi, I. Hachiya, H. Ishitani, and M. Araki, *Tetrahedron Lett.*, **34**, 4535(1993); S. Kobayashi, I. Hachiya, M. Arakiand, and H. Ishitani, *Tetrahedron Lett.*, **34**, 3755(1993); S. Kobayashi and H. Ishitani, *J. Am. Chem. Soc.*, **116**, 4083(1994).

4 J. Foropoulos and Jr; D. D. DesMarteau, *Inorg. Chem.*, **23**, 3720(1984). We thank Mr. Hiroaki Sakaguchi of Ube Research Center of Central Glass Co. for generous samples of H_2NTf and $HNTf_2$.

5 J. N. Meußdoerffer and H. Niedeprüm, *Chem. Ztg.* **96**, 582(1972); S. Singh and D. D. DesMarteau, *Inorg. Chem.*, **32**, 5007(1990).

6 The preparation of $ZnNTfSO_2C_4F_9$: Zinc acetate dihydrate(1.31 mmol, 288 mg) was added to an aqueous solution(50 v/v %) of $HNTfSO_2C_4F_9$(2.62 mmol, 1.148 g), and the mixture was stirred at room temperature for 1 h. Remained solid was filtered off and evaporation in vacuo gave hydrous zinc amide. Overnight dehydration under 10^{-5} mmHg at 110°C gave anhydrous $Zn(NTfSO_2C_4F_9)_2$ (1.25 mmol, 95 % yield). ^1H NMR showed the complete exchange of acetate ions with $NTfSO_2C_4F_9^-$ ions. ^{19}F NMR and IR spectra and the elemental analysis gave satisfactory results. The above dehydration operation gave anhydrous amides of lithium, barium, calcium, magnesium, and zinc, while lanthanum triflate and amides were obtained as hydrates; $La(OTf)_3\cdot H_2O$, $La(NTf_2)_3\cdot H_2O$, $La(NTfSO_2C_4F_9)_3\cdot 2H_2O$, $La(NTfSO_2C_8F_{17})_3\cdot 1.5H_2O$.

7 A typical kinetic experiment for the reaction with $La(NTfSO_2C_4F_9)_3$ in dichloromethane: a dichloromethane(25 ml) solution of methyl vinyl ketone(5.44 mmol) containing internal standard decane(2.68 mmol) was mixed with a dichloromethane (25 ml) solution of cyclopentadine(8.38 mmol) and 17.5 ml of this mixed solution was dropped into a two-neck flask containing $La(NTfSO_2C_4F_9)_3\cdot 2H_2O$ (31.8 mg, 1 mol%). The Diels-Alder reaction was carried out at 20 °C under argon atmosphere with magnetic stirring. The concentration of water(9 ppm) in the dichloromethane solution was measured by a Karl-Fischer moisture titrator. In given time a 0. 1 ml solution was sampled, diluted four times, passed through a micro silica-gel column, and monitored by gas chromatography to determine the rate constant and the endo/exo product ratio.

8 A. Casaschi, G. Desimoni, G. Faita, A. G. Invernizzi, S. Lanati, and P. P. Righetti, *J. Am. Chem. Soc.*, **115**, 8002(1993).