J. Am. Chem. Soc. **1998,** *120,* 7637−7638

Synthesis and Application of the First Chiral and Highly Lewis Acidic Silyl Cationic Catalyst

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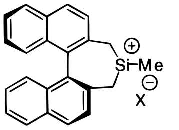
Received March 26, 1998

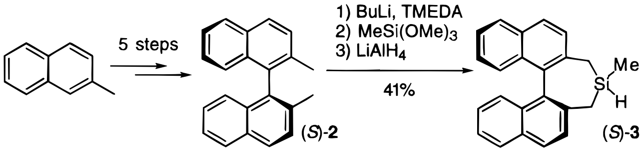
Recently, great progress has been made in the field of silylium chemistry and it seems possible to prepare the long-desired silicon cation in condensed phase.[1−15] Although there is a widespread use of silicon-based Lewis acids in organic chemistry, only very little attention has been paid to the utilization of the more reactive cationic species.[16] To our knowledge, no attempts have ever been made to synthesize chiral silicon-based Lewis acids, nor has the expected high reactivity of these chiral cationic species as catalysts ever been investigated. The chemistry of chiral silicon catalysts can be of great importance to the synthetic chemist, as silicon complexes are some of the few metal complexes which catalyzes important reactions, such as addition to imines and Friedel−Crafts reactions.[17−21] Another important aspect is the application of these catalysts as chiral cationic polymerization initiators.[22] On the basis of the recent developments in silyl cation chemistry, it is now reasonable to assume that a very reactive Lewis acid catalyst can be obtained by a careful choice of anion and solvent.[3−5,14,16]

This paper presents the first preparation, partial characterization, and catalytic reactions using a silylium-based chiral Lewis acid ((*S*)-**1a**,**b**). It appears from (*S*)-**1a**,**b** that the chirality is anchored in a C_2-symmetric 2,2′-dimethyl-1,1′-binaphthyl backbone, related to the BINOL ligand.



(*S*)-**1**
a: X = TPFPB
b: X = TFPB

Scheme 1



The synthesis of the chiral binaphthylic skeleton (*S*)-**2** starts from 2-methylnaphthalene and involves a resolution step of the binaphthyl ligand.[23−25] The silylation of (*S*)-**2** was carried out by a nucleophilic addition of the dilithiated ligand to methyltrimethoxysilane giving the methoxy substituted silane,[26] which could be converted to (*S*)-**3** by reduction (Scheme 1).

The chiral silane (*S*)-**3** is an air and moisture stable solid which can be handled without any special precautions. Several attempts have been performed to convert (*S*)-**3** into the corresponding silyl cationic complex. Protonolysis with various Brønsted acids were too harsh, cleaving both the Si−H and Si−C bonds. Attempts were also performed to convert the silane to the silyl chloride by heating with $CuCl_2$.[27] The chiral silyl chloride was more moisture sensitive than the parent silane, and treatment with silver triflate gave the silyl triflate. According to NMR spectroscopy, this approach was more successful, although the catalyst was still more than 50% impure. The key method for the preparation of the silyl cationic species was a Corey hydride transfer[28,29] between the silyl hydride (*S*)-**3** and trityl tetrakis(pentafluorophenyl)borate (TrTPFPB) (**4**)[30,31] or trityl tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate (TrTFPB) (**5**).[32] After 5 min of reaction time, the yellow color of the trityl reagent had vanished and (*S*)-**1a**,**b** was formed as the only product according to NMR spectroscopy [Figure 1].

The choice of anion and solvent is crucial for the preparation and catalytical properties of (*S*)-**1**. The almost chemically inert and noncoordinating TPFPB and TFPB were chosen as they are more attractive than the triflate anions from a synthetic point of view. Not only are they more stable and easy to handle than trityl triflate but the complex formed is presumably also significantly more active than the triflate counterpart.[31,33−35] The solvent is also important, and even the relatively nonnucleophilic solvent CH_2Cl_2 is fatal as the silyl cation immediately abstracts a chloride anion from the solvent and the catalyst is destroyed.[14] The optimal solvent is a perfectly nonnucleophilic solvent. Benzene and toluene have emerged as good candidates, although toluene has been shown to coordinate to the TMS cation in the solid.[7] The stability of the TMS cation in toluene is good; however, only trace amounts of the silyl cationic species (*S*)-**1** were obtained in benzene and toluene. The focus were therefore turned to CH_3CN as the solvent. Compared to benzene, the ^{29}Si NMR shift of the TMS cation in CD_3CN is at a higher field (see Table 1, entries

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S0002-7863(98)01021-X CCC: $15.00

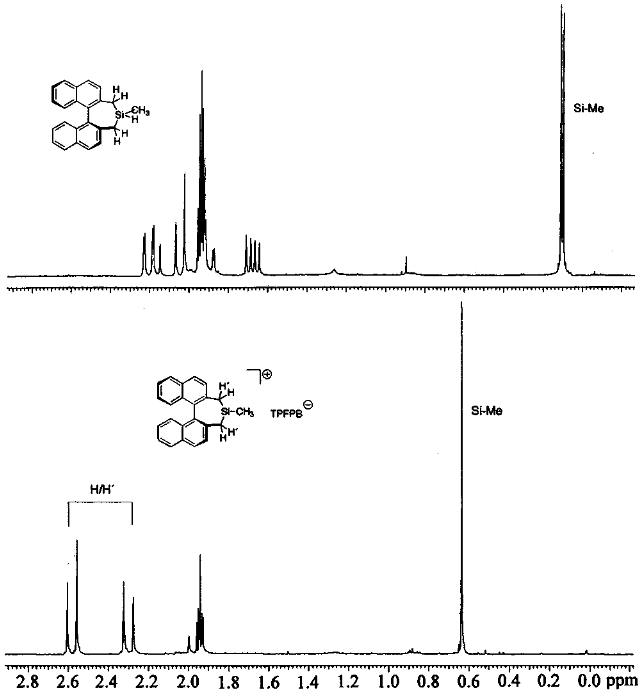


Figure 1. ^{1}H NMR spectrum of silyl hydride (*S*)-**3** and the crude reaction mixture between TrTPFPB and (*S*)-**3** in CD_3CN recorded after 5 min reaction time.

Table 1. ^{29}Si, ^{13}C and ^{1}H NMR Chemical Shifts for Me_3SiX, (*S*)-3 and (*S*)-**1a**,**b**

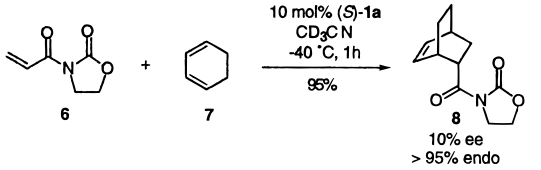
			chemical shifts/ppm		
entry	compound	solvent	^{29}Si	^{13}C (CH_3)	^{1}H (CH_3)
1	Me_3Si TPFPB	benzene-d_6	83.6[4]		
2	Me_3Si TFPB	CD_3CN	36.7[36]		
3	Me_3SiH	CD_2Cl_2	−15.5[14]	−3.4[36]	0.04[36]
4	(*S*)-**3**	$CDCl_3$	0.2[a]	−6.1	0.0
5	(*S*)-**1a**	CD_3CN	34.0	−4.2	0.64
6	(*S*)-**1b**	CD_3CN	34.0	−4.2	0.64

[a] Measured in the solid by cross polarization (CP) magic-angle spinning (MAS) NMR.

1 and 2). If the NMR shift can be considered as a measure of the Lewis acidity/electrophilicity of the silyl cation, the activity of the complex in this solvent should decrease. At the same time, however, the stability of the Lewis acid will probably increase due to a coordination of the solvent to the cation. For comparison, the ^{29}Si, ^{13}C, and ^{1}H NMR shifts for Me_3SiH and (*S*)-**3** are also given in Table 1 (entries 3 and 4).

It appears from Table 1 that the ^{29}Si NMR shifts of the two chiral silyl borate complexes (*S*)-**1a**,**b** (entries 5 and 6) are very close to the one obtained for TMS−TFPB in CD_3CN (entry 2). Moreover, both the ^{29}Si, the ^{13}C and the ^{1}H NMR shifts of the catalysts (*S*)-**1a**,**b** resonate at the same frequency, respectively. This indicates a weak, if any, interaction between the chiral cation and the anions in CD_3CN and that the solvent acts as a neutral ligand, stabilizing the active catalyst. Silyl−CD_3CN adducts have previously been proposed to consist of either a tetracoordinate species with one CD_3CN coordinating to the silicon atom or a pentacoordinated trigonal bipyramidial silicon adduct with two CD_3CN ligands.[36] In Figure 1 the ^{1}H NMR spectrum of (*S*)-**3** and the crude reaction spectrum of the reaction of (*S*)-**3** with TrTPFPB **4** after 5 min of reaction time are presented. It appears that the reaction of (*S*)-**3** with TrTPFPB **4** is very clean, giving only resonances corresponding to stabilized silyl cation and tritan (lower field). The spectrum of (*S*)-**1a** shows a singlet at 0.64 ppm corresponding to the methyl group and two doublets at 2.30 and 2.59, respectively, for the homotopic pairs of hydrogens at the methylene bridges. This shows that (*S*)-**1a** exhibits C_2-symmetric behavior which either can be due to a trigonal bipyramidial structure or a tetracoordinated species where the CD_3CN ligand is exchanged faster than the NMR time scale. It is evident from Figure 1 that the ^{1}H NMR spectrum of (*S*)-**3** is more complex, as the methylene hydrogens all are diastereotopic, while in (*S*)-**1a** they become homotopic due to the C_2-symmetry.

The chiral silyl cationic species (*S*)-**1a** has been tested as Lewis acid catalyst for various reactions. For catalytic reactions the solvent can play a crucial role, and in some cases the use of a polar solvent in combination with cationic catalysts have led to an improvement of the catalytic system.[37,38] The possibility that a polar solvent such as CH_3CN coordinates too strongly to the silyl cation to allow any reaction to be catalyzed is however also present. Fortunately, (*S*)-**1a** acts as a highly active Lewis acid catalyst for both Diels−Alder and hetero-Diels−Alder reactions. Some initial experiments show that the Diels−Alder reaction between acryloyl oxazolidione (**6**) and 1,3-cyclohexadiene (**7**) were completed within 1 h even at −40 °C by application of 10 mol % of (*S*)-**1a** as the catalyst [eq 1].[39] Although only the *endo*-diastereomer **8** could be detected by ^{1}H NMR spectroscopy the enantioselectivity was moderate being around 10% ee.[40] The hetero-Diels−Alder reaction between benzylidene-2-methoxyaniline **9** and Danishefsky's diene **10** was also catalyzed by (*S*)-**1a** giving adduct **11** in 74% isolated yield [eq 2]. Generally, (*S*)-**1a** proved to be a highly active catalyst for hetero-Diels−Alder reactions of imines giving the aza-Diels−Alder adducts in high yield; however, all products turned out to be racemic.



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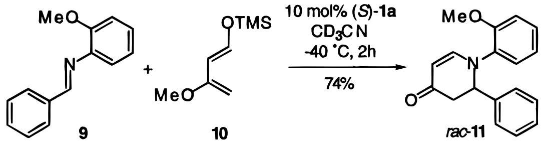

(2)

In summary, the first chiral silyl cationic species has been prepared, characterized, and shown to be a highly Lewis acidic catalyst for Diels−Alder reactions. The selectivity observed using this catalyst is still modest, but the activity is very promising.

Acknowledgment. The Danish National Science Foundation is gratefully acknowledged for financial support. We are indebted to Professor M. E. Jung for help concerning the synthesis of (*S*)-**3**. Thanks are also expressed to Dr. G. Schilling for recording the ^{29}Si NMR in solution and to Professor Hans Jørgen Jacobsen and Rigmor S. Johansen for the solid state ^{29}Si NMR measurements.

Supporting Information Available: Experimental procedures for the preparation of (*S*)-**3** and (*S*)-**1a**,**b**, the application of (*S*)-**3** in catalytic reactions and ^{29}Si, ^{13}C, and ^{1}H NMR spectra for the catalyst (*S*)-**1a** and (*S*)-**3** are available (15 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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