Table II. Product Ratios of Reactions of Bis(2,4,6-triisopropylphenyl)silylene and 2-Butene[a]

		product ratios (%)	
starting materials	irradtn time[b]	**3b** (cis)	**4b** (trans)
1b + 	10 min	41	59
	3 h	34	66
	9 h	32	68
	10 min[c]	79	21
	1 h[d]	84	16
1b + 	10 min	93	7
	3 h	96	4
	9 h	86	14
	10 min[c]	97	3
	1 h[d]	99	1

[a] The product ratios were determined by ^{13}C NMR and HLPC (solvent $MeOH:H_2O$ = 9:1). [b] The reaction was carried out at −5 °C. [c] The reaction was carried out at −95 °C. [d] The photolysis in 3MP matrix at 77 K, the addition reaction of the silylene occurred during the annealing.

The siliranes **3** and **4** are extremely stable at room temperature, and **3b**[8] and **4b**[9] were recrystallized from ethanol. Stereochemistry of siliranes **3** and **4** could be clearly distinguished by ^1H and ^{13}C NMR; cis isomer **3** has nonequivalent aryl groups. The key product **3b** was also confirmed by X-ray crystal analysis (Figure 1).

Appropriate control experiments show that cis–trans isomerization of olefins is inefficient and that silirane **4b** does not isomerize to the cis isomer **3b** under the reaction conditions.[10]

The reaction was monitored by HPLC as functions of reaction time and temperature. The ratios of *cis*- and *trans*-siliranes were nearly constant with reaction time (Tables I and II). The most marked change was observed in the addition of silylenes to *trans*-2-butene at −95 °C; unexpectedly, nonstereospecific adduct **3b** became a major product.

On the analogy of the reactivity of triplet carbene,[11] triplet silylenes may add to the olefin to produce a diradical in which rotation about a carbon–carbon single bond competes with spin inversion and closure. On the other hand, if rotation prevailed sufficiently over closure, one would expect that the stepwise addition of singlet silylene might occur.

It is possible that nonstereospecificity is a result peculiar to an electronically excited silylene. To examine this, we investigated the reaction in a glass matrix.

When **1b** was photolyzed in 3-methylpentane (3MP) at 77 K, the resulting matrix turned to intense blue, and the absorption spectrum assigned to silylene **2b** was observed at 584 nm.[12] On melting the matrix, **2b** dimerized to give tetrakis(2,4,6-triisopropylphenyl)disilene (λ_{max} = 433 nm, ^{29}Si NMR in C_6D_6 52.9 ppm).[13] Similarly, in the irradiation of **1b** in 3-MP matrices containing *cis*- or *trans*-2-butenes, initially only bands due to the silylene were observed. After the light was interrupted for 1 h, the intensity of the absorption bands did not change at all, but upon annealing these bands disappeared. Warming the matrix, no disilene could be found although two products were **3b** and **4b**, respectively (Table II). The ratios obtained are independent of secondary reaction of siliranes. These results show that the electronically excited silylenes do not participate in these addition reactions.[14]

Since the most important factor is the spin state of silylene, we tried to measure an ESR spectrum of silylene at 77 K. Although the ESR sample showed the silylene to be an intense color, no signal could be observed in 0.02–1.2 T.

Apparently the reaction of silylene **2** gives a nonstereospecific adduct, which largely depends on the bulkiness of the silylene. These results suggest especially difficult and interesting problems as other divalent singlet species of the IVb group might also be expected to add to olefin nonstereospecifically.

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Supplementary Material Available: Spectroscopic data for **1b** and listings of final atomic coordinates and temperature factors and bond lengths and angles (9 pages); listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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[8] Compound **3b**: mp 134–135 °C; ^1H NMR ($CDCl_3$, 500 MHz) 0.9–1.5 (br, 12 H), 1.15 (br d, 12 H), 1.22–1.24 (deformed d, 6 H), 1.26 (d, 6 H; J = 6.9 Hz), 1.27 (d, 6 H, J = 7.0 Hz), 1.39–1.43 (deformed q, 2 H), 2.87 (sep, 1 H, J = 7.0 Hz), 2.89 (sep, 1 H, J = 6.9 Hz), 3.57 (sep, 2 H, J = 6.7 Hz), 3.79 (sep, 2 H, J = 6.7 Hz), 6.96 (s, 2 H), 7.01 (s, 2 H); ^{13}C NMR at 58 ($CDCl_3$, 25 MHz) 11.2, 15.6, 23.8, 24.5, 25.1, 34.2, 34.6, 35.4, 121.0, 121.2, 128.0, 130.9, 150.0, 150.3, 155.3, 156.2; ^{29}Si NMR ($CDCl_3$, 18 MHz) −85.2; mass m/e 490 (M^+). Anal. Calcd for $C_{34}H_{54}Si$: C, 83.19; H 11.08. Found: C, 82.98; H, 11.17.

[9] Compound **4b**: mp 151–152 °C; ^1H NMR ($CDCl_3$, 500 MHz) 0.6–0.9 (br, 6 H), 0.97–1.03 (deformed q, 2 H), 1.09–1.13 (deformed d, 6 H), 1.2–1.4 (br, 18 H), 1.269 (d, 6 H, J = 6.9 Hz), 1.270 (d, 6 H, J = 6.9 Hz), 2.89 (sep, 2 H, J = 6.9 Hz), 3.4–3.7 (br, 2 H), 4.1–4.3 (br, 2 H), 6.8–7.2 (br, 4 H); ^{13}C NMR at 58 ($CDCl_3$, 25 MHz) 16.5, 19.8, 23.8, 25.4, 34.2, 34.8, 121.1, 127.0, 150.3, 156.3; ^{29}Si NMR ($CDCl_3$, 18 MHz) −81.4; mass m/e 490 (M^+). Anal. Calcd for $C_{34}H_{54}Si$: C, 83.19; H, 11.08. Found: C, 82.90; H, 11.21.

[10] Photolysis of **4b** gave silylene and only *trans*-2-butene. Photolysis of **3b**, however, gave silylene and a mixture of *cis*- and *trans*-2-butenes in the molar ratio ca. 2.5:1. The silylene was trapped by triethylsilane.

[11] Bethell, D. *Organic Reactive Intermediates*; McManus, S. P.; Ed.; Academic Press: New York, 1973; pp 61–126.

[12] Dimesitylsilylene have absorption bands at 577 nm. West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. West, R. *Science (Washington, D.C.)* **1984**, *225*, 1109.

[13] Watanabe, H.; Takeuchi, K.; Fukawa, N.; Kato, M.; Goto, M.; Nagai, Y. *Chem. Lett.* **1987**, 1341.

[14] Nearly the same product ratio was obtained in a methylcyclohexane matrix, which is ca. 10^4 times as hard as the 3MP matrix: Ling, A. C.; Willard, J. E. *J. Phys. Chem.* **1968**, *72*, 1918.

Preparation and Catalytic Activity of a New Solid Acid Catalyst

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The preparation and use of strong solid acid catalysts and superacids are active areas of research for isomerization, cracking, hydrocracking, dehydration, alkylation, acylation, methanol to gasoline, etc.[1] Because of the reported advantages of solid catalysts,[2] recent research has focused on the preparation and characterization[2-4] of stronger solid acids. In view of the higher activity associated with tetrahedral compared to octahedral aluminum Lewis acids, we are interested in preparing solids containing stable tetrahedral aluminum sites. In this paper we report the synthesis, characterization, and catalytic activity for these new solid acid catalyst systems.[5]

Our catalyst is prepared by reacting an inorganic oxide with aluminum chloride (Al_2Cl_6) in refluxing carbon tetrachloride (CCl_4), Scheme I. The reaction of aluminum chloride with silicon

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[1] Tanabe, K. In *Heterogeneous Catalysis*; *Catalysis by Novel Solid Strong Acids and Superacids*; Shapiro, B. L., Ed.; Texas A & M University Press: College Station, TX, 1984; pp 71–94.

[2] Vedrine, J. C.; Auroux, A.; Bolis, V.; Dejaifve, P.; Naccache, C.; Wierzchowski, P.; Derovane, E. G.; Nagy, J. B.; Gilson, J.; Van Hooff, J. H. C.; Van Den Berg, J. P.; Wolthoizen, J. *J. Catal.* **1979**, *59*, 248–262.

[3] Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversion*; Academic Press: New York/London, 1981; pp 100–122.

[4] Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Superacids*; Wiley: *new* York, 1985; p 53.

[5] Drago, R. S.; Getty, E. E.; US Patent 4719190, January 12, 1988.

0002-7863/88/1510-3311$01.50/0

Scheme I

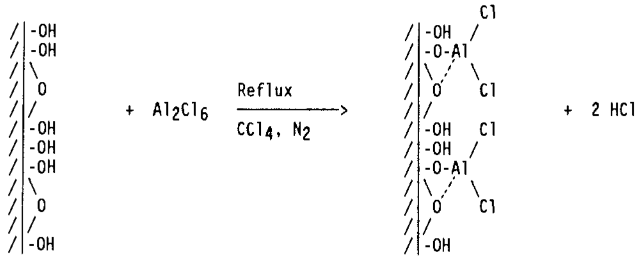

Table I. Infrared Shift Data for Pyridine Adsorbed onto $AlCl_2$–X Catalysts

X	solvent[a]	shift of Lewis band[b]
SiO_2	CCl_4	18.0
Al_2O_3	CCl_4	15.2
silicalite[c]	CCl_4	18.1
B_2O_3	CCl_4	18.1
TiO_2	CCl_4	14.1
MgO	CCl_4	7.8
SiO_2	$CHCl_3$	9.3
SiO_2	CH_2Cl_2	8.6
SiO_2	C_6H_{14}	8.9
SiO_2	C_6H_6	8.3

[a] This solvent was used to prepare the catalyst. [b] This shift is measured after pumping at 150 °C on the sample exposed to pyridine. The free pyridine band occurs at 1438.5 cm^{-1}. [c] A high silica zeolite.

Table II. Activities for Different $AlCl_2$-Functionalized Supports[a]

X	propane[b,14]	isobutane[b,14]	*n*-butane[b,14]
SiO_2	4.2 E-3	7.1 E-2	5.4 E-6
Al_2O_3	6.2 E-3	5.3 E-2	3.0 E-6
silicate[c]	1.8 E-2	1.1 E-1	3.3 E-3
B_2O_3	1.1 E-2	5.0 E-2	1.5 E-5
TiO_2	5.0 E-8	5.0 E-4	none
MgO	2.4 E-9	7.8 E-5	none
Al_2Cl_6	1.9 E-2	8.9 E-2	1.5 E-4

[a] Made in CCl_4. [b] Units: mol product/mol Al per 18 h. [c] A high silica zeolite.

Table III. Activities for $AlCl_2$–SiO_2 Catalysts Prepared in Different Solvents[a]

solvent prepared	propane[b,14]	isobutane[b,14]	*n*-butane[b,14]
CCl_4	4.2 E-03	7.1 E-02	5.4 E-06
$CHCl_3$	6.0 E-09	4.1 E-05	4.1 E-05
CH_2Cl_2	1.8 E-08	7.1 E-07	3.3 E-07
$ClCH_2CH_2Cl$	2.4 E-08	none	none
C_6H_6	1.0 E-08	none	none

[a] All reactions run in 50 mL of 1.195 M *n*-hexadecane in CCl_4 at 100 °C and 25 psig H_2. [b] Units: mol product/mol Al per 18 h.

dioxide resulted in the evolution of 1.1 mol of hydrogen chloride (HCl) for every mol of $AlCl_3$ used suggesting that over 90% of the chloroaluminum species on the surface of this support has the composition $(-O-)AlCl_2$. Since the average composition is two chlorides per aluminum and Al_2Cl_6 would sublime off on heating (which does not occur), there is little $(-O-)_2AlCl$ present. Past attempts[6] of this reaction have employed solvents other than CCl_4. We find chloroform, methylene chloride, ethylene dichloride, and saturated hydrocarbons (to name a few) do not produce a solid acid catalyst with the properties described for CCl_4. Several patents have been issued for treatment of inorganic oxides with aluminum chloride to form strong acid catalysts.[6-8] In all cases aluminum chloride is evolved from the surface with time, and only short term activity results.

The infrared spectrum of adsorbed pyridine on various aluminum chloride treated inorganic oxides ($AlCl_2$-X; where X = inorganic support) indicates the presence of both Lewis and Bronsted acid sites.[9-11] Large shifts (18 cm^{-1}) were observed for coordinated pyridine when X = SiO_2 or a high silica zeolite (Table I).

Since the frequency shifts for the Lewis acid band is comparable to those exhibited by conventional cracking catalysts[9,12] we decided to investigate the catalytic activity. One of the largest uses of solid acid catalysts is in the area of catalytic cracking. A typical probe reaction is the cracking of *n*-hexadecane shown by GC to be free of olefin impurities.[12] The cracking reactions were conducted in a 250-mL batch reactor with 50 mL of a 1.195 M *n*-hexadecane in carbon tetrachloride solution, 1–1.5 g catalyst, and 25 psig H_2 for 18 h at 100 °C. The results are described in Table II. The batch reactor is a closed system, and previous work[13] has shown cracking approaches an equilibrium, hindering the progress of the desired reaction. The extent of conversion to light hydrocarbon products is a measure of catalyst activity in this closed system. We find by GC and GC/FTIR that product selectivity for C_5 was less than that for C_3–C_4 with no C_6 or higher hydrocarbons detected. Blank supports prepared by refluxing the support in carbon tetrachloride without addition of Al_2Cl_6 were also investigated under identical conditions. For all untreated supports 1×10^{-9} mol of *n*-butane, 1×10^{-10} mol of isobutane, and 1×10^{-12} mol of propane or less was detected.

The three major products from the cracking of *n*-hexadecane are propane, isobutane, and *n*-butane. As shown in Table II the most active catalysts are those prepared on SiO_2, Al_2O_3, high silica zeolite, and B_2O_3. In all cases the catalysts are much more active than the untreated support. A blank reaction using Al_2Cl_6 led to comparable activity for the three major products but was very unselective leading to large amounts of C_5–C_{15} products and a high molecular weight tar. The aluminum chloride reaction also liberates large quantities of hydrogen chloride gas and is very corrosive to the reactor. Our solid acids are much more selective, do not form the high molecular weight tar, and are not corrosive to the reactor, and no dissolved aluminum chloride is found in the product solution. A typical fluid cracking catalyst run under these conditions produces no observable cracking products.

Further evidence for the strong acidity of our catalyst is obtained from the cracking of hexadecane in a gas phase flow reactor at 175 °C. By using an addition rate of 4.3×10^{-5} mol/min of hexadecane and CCl_4 in a flow of H_2 at 3 cc/min, a 22% conversion of hexadecane resulted with selectivity comparable to that of the batch process. Under these conditions untreated silica gel and alumina and zeolite cracking catalysts (LZY-82) are unreactive.

The results for the catalytic cracking of *n*-hexadecane in carbon tetrachloride using catalysts prepared in different solvents with SiO_2 as the support are shown in Table III. The catalyst prepared in CCl_4 is the most active, and when the catalyst is prepared in other solvents the activity is decreased substantially though still more active than the untreated support.

We are currently studying our catalyst by ^{27}Al and ^{29}Si solid-state NMR, and results show that the aluminum chloride retains its tetrahedral conformation upon reaction with the inorganic oxide support as $-O-AlCl_2$ and $(-O-)_2AlCl$ groups. A strong supported Lewis acid with discrete acid sites has potential for the acid catalysis of many reactions, and the scope of the reactions that can be catalyzed by these solid acids will be investigated and reported in full in a future publication.

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(6) Kelly, J. T.; Schoen, W.; Sechrist, C. N.; US Patent 3 248 343, April 26, 1966.

(7) Antos, G. J.; Hayes, J. C.; Pollitzer, E. L.; US Patent 3 960 711, June 1, 1976.

(8) Olah, G. A.; Messina, G.; US Patent 3 993 587, November 23, 1976.

(9) Parry, E. P. *J. Catal.* **1963**, *2*, 371.

(10) Jacobs, P. A. *Chemical Industries*; Delannay, F., Ed.; Marcel Dekker, Inc.: New York, 1984; Vol. 15, p 367.

(11) Primet, M.; Ben Taarit, Y. *J. Phys. Chem.* **1977**, *81*, 1317.

(12) Corma, A.; Wojciechowski, B. W. *Catal. Rev.-Sci. Eng.* **1985**, *27*, 29.

(13) Hightower, J. W.; Emmett, P. H. *J. Am. Chem. Soc.* **1965**, *87*, 939.

(14) The mol aluminum refers to mol Al_2Cl_6 used to prepare the catalyst. For X = Al_2Cl_6, pure aluminum chloride was used in the reaction. All reaction was conducted at 100 °C.