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SILICA SUPPORTED CATALYSIS: A PRACTICAL USE OF AN IRON LEWIS ACID

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Abstract

The silica-supported iron Lewis acid $[(\eta^5-C_5H_5)Fe(CO)_2(THF)]^+$ [BF₄]⁻ (1), was found to catalyze the formation of an enol ester, cyclopropane, or aziridine from a diazo compound and an aldehyde, olefin, or imine, respectively. Unlike the non silica-supported iron Lewis acid, the catalyst is recoverable and reusable.

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Previously, our group has reported that the iron Lewis acid $[(\eta^{5}-C_{3}H_{3})Fe(CO)_{2}(THF)]^{+}$ [BF₄]⁻ (1) is an effective catalyst for the formation of cyclopropanes,¹ enol esters,² epoxides,³ and aziridines.⁴ The iron Lewis acid is inexpensive, easily synthesized, and the reactions proceed in good to excellent yields with a minimum of necessary workup. Recently, there has been an increase in the development of polymer- and silica-supported transition metal-based Lewis acids.⁵ In light of this, we have developed a silica-bound analogue of 1 (SS-Fe) which is readily prepared, applicable to several synthetic reactions, and easily separated from the reaction mixture and reused. Even after repeated use for up to 52 days, the silica-bound catalyst remains active. Herein, we wish to report our results using this heterogeneous system in several reactions.



Figure 1: Iron Lewis Acid 1

The iron Lewis acid 1 was easily synthesized in high yield by protonation of the known methyl complex (η^5 -C₅H₅)Fe(CO)₂CH₃ by HBF₄·OEt₂.² A solution of 1 in CH₂Cl₂ becomes colorless upon addition of silica. The supernatant solution was decanted from the silica-supported iron Lewis acid, and the solid was dried under vacuum. An elemental analysis of SS-Fe indicated 1.36% iron by mass in the sample.⁶ The IR spectrum of SS-Fe showed stretches at 2059, 2012 and 1080 cm⁻¹ corresponding to the carbonyls and THF (C-O str.) ligands, respectively. Analysis of the supernatant solution by ¹H NMR shows neither "free" iron Lewis acid nor THF in solution. This shows that there is a strong adsorption of 1 on the silica support, but one that does not displace any of the ligands around the iron metal center.

Scheme 1: Formation of 3 Catalyzed by Silica-supported 1



A suspension of SS-Fe in dichloromethane was found to catalyze reactions between diazo compounds and olefins, imines, or aldehydes. When EDA was added to a suspension of SS-Fe and 2,4-dimethoxybenzaldehyde 2 at 0°C, 72% of the corresponding enol ester 3 resulted (Scheme 1).⁷ The supernatant solution was easily decanted from SS-Fe and the catalyst was dried under vacuum and reused. Results are shown in Table 1. Entries 1-5 were done over a period of 16 days. Even after 36 days from its previous use, the catalyst was able to effect the transformation in good yield (53%). Reaction of 1 without silica support produces 3 in 80% yield.²

Similarly, EDA reacts with styrene 4 in the presence of SS-Fe to produce the corresponding *cis* and *trans* cyclopropanes 5 in good yield (Scheme 2).⁷ The same catalyst was used five times over a period of 14 days. The products were

<u>Use</u>	Reaction time (h)	<u>% yield °</u>
1	12	72
2	18	78
3	36	68
4	36	65
5	36	54
6	48	53

Table 1. Isolated Yields of Enol Ester 3 a.b

^a All reactions were performed at 0°C. ^b 10 mol % of the catalyst used relative to the aldehyde. ^c Isolated yield based on aldehyde.

extracted by washing the reaction mixture with diethyl ether and decanting the liquid layer from the catalyst. Results of these reactions are summarized in Table 2. Without silica support, 1 produces 40% of cyclopropanes 5 with a *cis:trans* ratio of 84/16.^{1a} It is interesting to note that the overall yield of cyclopropanes under heterogeneous conditions is higher than the same reaction in the homogeneous phase. However, *cis* selectivity of SS-Fe in cyclopropanation reactions is decreased in comparison to the non silica-supported reactions. Perez et al. have also demonstrated a decrease in selectivity when their heterogeneous system is used compared to the same catalyst used without silica support.^{5a}

Scheme 2: Formation of 5 Catalyzed by Silica-supported 1



<u>Use</u>	<u>Reaction time (h)</u>	<u>% yield ^c</u>	<u>trans/cis ^d</u>
1	30	61	1. 2 : 1
2	30	53	1.5 : 1
3	48	54	2 : 1
4	48	48	2:1
5	48	45	2:1

Table 2. Isolated Yields of Cyclopropanes 5^{a,b}

^{*a*} All reactions were done at rt. ^{*b*} 10 mol % of the catalyst used relative to EDA; 5 equiv styrene used. ^{*c*} Isolated yield based on EDA. ^{*d*} cis/trans ratios determined by ¹H NMR.

SS-Fe can also be used in an aziridine-forming reaction (Scheme 3). When 1.5 equivalents of PDM was added dropwise to a suspension of SS-Fe and *N*-benzylideneaniline 6, the resulting *cis*-aziridine 7 was formed in 92% yield.⁷ The products were simply extracted from the catalyst with diethyl ether, and the catalyst was dried and reused. The catalyst was used 5 times over a period of nine days (Table 3). In all cases, the PDM was entirely consumed. However, consumption of the imine decreases with each successive cycle, and the formation of stilbene and azine by-products increases. In the last cycle, the aziridine forms

Scheme 3: Formation of 7 Catalyzed by Silica-supported 1



<u>Use</u>	Reaction time (h)	<u>% yield °</u>
1	17	92
2	24	90
3	25	60
4	37	38
5	35	25

Table 3. Isolated Yields of cis-Aziridines^{a,b}

^a All reactions were performed at rt. ^b 10 mol % of the catalyst used relative to imine; 1.5 equiv PDM used. ^c Isolated yield based on imine.

in only 25% yield. When non silica-supported 1 is used, the aziridine is produced in 95% yield.⁴

In conclusion, we have expanded the practical use of the iron Lewis acid 1 by developing a readily prepared, recoverable, silica-supported analogue of 1. This heterogeneous system has been demonstrated to effect the reaction between diazo compounds and an aldehyde, olefin, or imine. In all reactions, the products are easily separated from SS-Fe by decanting off the supernatant solution. Current research is directed toward the preparation of asymmetric variants of 1 which may have extended catalytic lifetimes when bound to solid support.

Experimental Section

General Considerations. Previously reported compounds were identified by proton NMR using a 250 MHz or 300 MHz spectrometer. IR spectra were obtained from solid samples in KBr disks. CH elemental analysis was performed on a CE Elantech EA 1110 elemental analyzer. All organometallic operations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. All of the glass flasks were flamed under vacuum and filled with nitrogen prior to use. Neutral silica gel (EM Science, 70-230 mesh) was used for the silica support and column chromatography. HPLC grade CH₂Cl₂ was distilled under nitrogen from P₂O₅. HPLC grade pentane was distilled under nitrogen from sodium immediately prior to use. Reagent grade THF and diethyl ether were freshly distilled under nitrogen from sodium benzophenone ketyl. Ethyl diazoacetate (EDA) 90% and styrene 99+% were obtained from Aldrich Chemical Co. 2,4-dimethoxybenzaldehyde 98% was obtained from Acros (Fisher). The iron Lewis acid was synthesized by protonation of the known methyl complex.² Phenyldiazomethane⁸ (PDM) and *N*-benzylideneaniline⁹ were prepared using literature procedures.

Preparation and Characterization of the Silica-supported Iron Lewis Acid (SS-Fe). The iron Lewis acid 1 (0.0418 g, 0.125 mmol) was dissolved in 8 mL CH₂Cl₂. Silica (0.4515 g) was added and the solution became colorless within 1 minute of the addition. The solution was allowed to stir for 5 minutes after which the solvent was decanted from the red silica and the solid was dried under vacuum. IR (KBr) 2059, 2012, 1080 cm⁻¹. Anal. Calcd for SS-Fe: Fe, 1.41; C, 3.34; H, 0.33. Found: Fe, 1.36; ⁶ C, 3.33; H, 0.18.¹⁰

Reaction of EDA with 2,4-Dimethoxybenzaldehyde. 2,4-Dimethoxybenzaldehyde (0.3156 g , 1.863 mmol) was added to a stirred suspension of SS-Fe (0.7352 g , 0.186 mmol) in 12 mL CH₂Cl₂. The mixture was cooled to 0°C. EDA (0.26 mL , 2.235 mmol) was diluted with 4 ml of CH₂Cl₂ and was added dropwise over a period of 6-7 h via a syringe pump. After stirring the mixture for the indicated time at 0°C, the solid was allowed to settle and the clear solution on top was decanted into a different flask. The catalyst was washed several times with CH₂Cl₂ and the washings were combined in the other flask. The solvent was removed by rotary evaporation, and an NMR spectrum was taken of the crude products. The catalyst was dried under vacuum and stored at 0°C until its next use. The products were purified by column chromatography (pentane / Et₂O), yielding 338 mg (72%) of the enol ester:² ¹H NMR (CDCl₃, 250 MHz) δ 11.89 (d, 1H), 7.12 (d, 1H), 7.00 (d, 1H), 6.47 (s, 1H), 6.45 (d, 1H), 4.22 (q, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 1.23 (t, 3H). Anal. Calcd for C₁₃H₁₆O₅: C, 61.90; H, 6.30. Found: C, 61.73; H, 6.18. After 54h from the previous reaction, SS-Fe was suspended in 12 mL CH₂Cl₂ and reused in an identical reaction, yielding 366 mg (78%) of the enol ester. The final four reactions were performed in a similar manner, after intervals of 12h, 156h, 12h, and 828h, respectively, from the preceding reaction.

Reaction of EDA with styrene. Styrene (0.650 mL, 5.67 mmol) was added to a stirred suspension of SS-Fe (0.4508 g, 0.114 mmol) in 10 mL CH₂Cl₂. In a separate flask, 0.130 mL (1.11 mmol) EDA was dissolved in 5 mL CH₂Cl₂. The EDA solution was added via syringe pump over 6-7 h. After allowing the solution to stir for the appropriate time, the reaction was quenched by addition of 3 mL THF. The solution was allowed to settle and the clear liquid was decanted from the solid. The silica was washed repeatedly with ether (4 x 30 mL) and the washings were combined with the reaction solution. The silica-bound catalyst was dried under vacuum and stored at 0°C until the next use. The solvent was

removed from the extracts by rotary evaporation and an NMR spectrum was taken of the crude product. Column chromatography (0-10% ethyl acetate / pentane) of the crude products vielded 0.129 g (61%) of ethvl 2phenylcyclopropanecarboxylate: bp 87-88 °C (0.15 mmHg) [lit.11 bp 80.5-82 °C (0.14 mmHg)]. ¹H NMR¹² (CDCl₃, 300MHz) δ cis, 0.96 (3H, t), 1.30 (1H, m), 1.70 (1H, m), 2.06 (1H, m), 2.58 (1H, m), 3.88 (2H, q); trans, 1.26 (3H, t), 1.30 (1H, m), 1.86 (1H, m), 2.52 (2H, m), 4.18 (2H, q). The catalyst was reused in an identical reaction after 18h, using identical amounts of reagents as listed above. Workup of the reaction yielded 0.112 g (53%) of the cyclopropanes. Three more reactions were performed similarly, after intervals of 18h, 48h, and 48h, respectively, from the preceding reaction.

Reaction of PDM with *N*-benzylideneaniline. *N*-benzylideneaniline (0.330g, 1.78 mmol) was added to a stirred suspension of SS-Fe (0.7199g, 0.178 mmol) in 10mL CH₂Cl₂. In a separate flask, a PDM solution was prepared by diluting 0.91 mL of PDM (3.11M solution in CH₂Cl₂, 2.67 mmol) to 5 mL with CH₂Cl₂. The PDM solution was then added dropwise to the reaction flask over 6h. After the reaction mixture had stirred for the indicated time, the reaction was quenched by the addition of 5mL THF. The solution was stirred for an additional 30 minutes, and the supernatant solution was decanted from the catalyst. The catalyst was extracted with diethyl ether (4 x 50mL), and the supernatant plus the combined extracts had the solvent removed by rotary evaporation. The catalyst was dried under vacuum and either used immediately in the next reaction or stored under N₂ at 0°C. Products were isolated by column chromatography (0-

10% ethyl acetate / pentane), providing 446mg (92%) of *cis*-1,2,3triphenylaziridine:⁴ ¹H NMR (CDCl₃) δ (ppm) 7.35-7.03 (m, 15H), 3.67 (s, 2H). Anal. Calcd for C₂₀H₁₇N: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.73; H, 6.29; N, 5.16. The SS-Fe was reused 3h later in an identical reaction to the one above, yielding 436mg (90%) of the aziridine after workup. The same catalyst was reused in three more identical reactions after intervals of 45h, 5h, and 4h, respectively, from its previous use.

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