[Supporting Information]

Imidazolinium Salts as Catalysts for the Ring-Opening Alkylation of *meso* Epoxides by Alkylaluminum Complexes

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Supporting information available: Synthetic procedures and characterization data for **2** and **6**, experimental and analytical procedures (including a typical GC trace) (3 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

General information and materials. Toluene and C_6D_6 was distilled over sodium/benzophenone. Cyclohexene oxide, cyclopentene oxide, 2,3-butene oxide, and 2,3-epoxy-2,3-dimethylbutane were dried over CaH_2. All solvents were distilled under nitrogen and saturated with nitrogen prior to use. 2,3-epoxy-2,3-dimethylbutane was a gift from Dr. Chunbang Li and was synthesized according to literature procedure.[1] All other reagents were purchased from the Aldrich Chemical Company and used without further purification, unless otherwise noted.

^1H NMR spectra were recorded on a Varian Mercury 400 FT-NMR (400.75 MHz for ^1H and 75.432 MHz for ^{13}C). ^1H and ^{13}C chemical shifts are in ppm downfield from tetramethylsilane (TMS, δ scale) with the residual solvent resonances as internal standards. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

GC analyses of reaction mixtures were carried out on a Hewlett Packard 5890A equipped with an FID detector and an HP3396A integrator. The column used was a 30-m HP-5 capillary column with 0.32-mm inner diameter and 0.25-μm film thickness. Flow rate = 1.8 mL/min for He carrier gas. GC yields were determined through integration of the product peak against 1,2,4,5-tetramethylbenzene (internal standard) using pre-established response factors. Retention times for various components of the reaction mixture were assigned by the injection of a pure sample of each component in the reaction.

General reaction procedure for catalyst synthesis: Imidazolinium salts[2,3] **1**, **3**, and **4** and olefin **7**[4] were synthesized according to literature procedures. Compound **2** was synthesized by adapting the literature procedure for the known imidazolinium salts. The free carbene **5** can be generated by the deprotonation of the imidazolinium salt **1** with potassium hydride.[3]

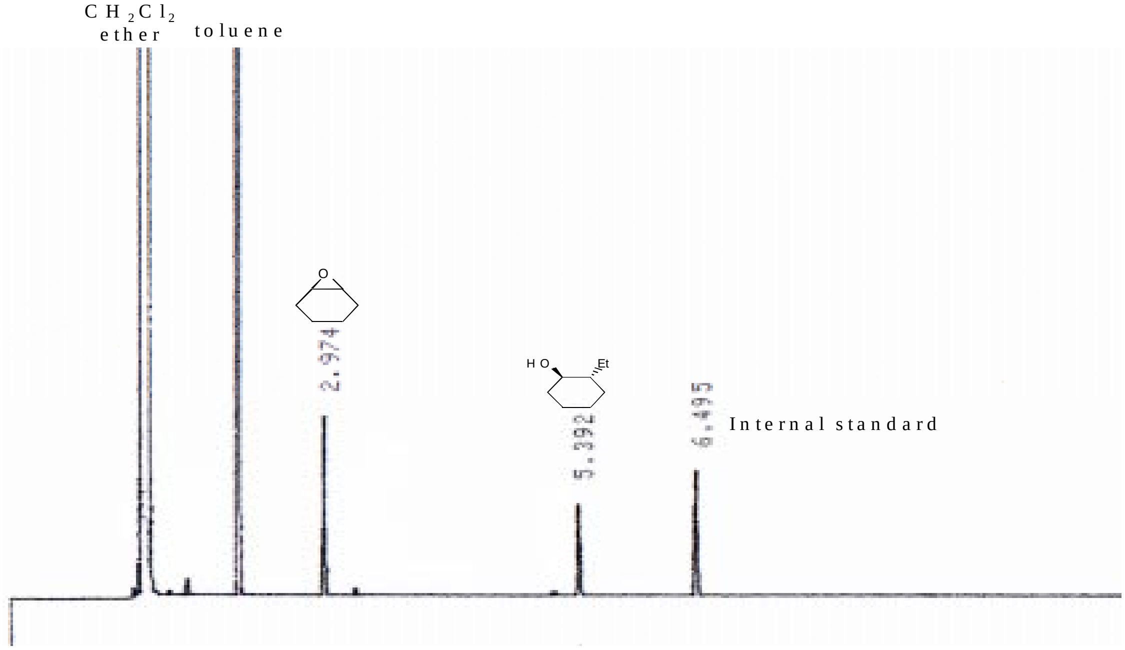
Synthesis of *N,N'*-bis-(2,6-di*iso*propylphenyl)-4,5-dimethylimidazolinium tetrafluoroborate (2): Into a 10-mL round bottom flask was added triethyl orthoformate (1.52 g, 8.63 mmol), ammonium tetrafluoroborate (0.91 g, 8.63 mmol) and *N*, *N'*-*bis*-(2,6-di*iso*propylphenylamino)-1,2-dimethylethane (3.52 g, 8.63 mmol). The mixture was heated at 120 °C for 12 h. The ethanol formed during the reaction was removed under reduced pressure. The crude product was crystallized from absolute ethanol and the solid was dried *in vacuo* to give white needles. Yield = 1.48 g (33%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.91 (s, 1H, ArN-C$^+$*H*-ArN), 7.54 (m, 2H, Ar*H*), 7.36 (d, 4H, *J* = 8 Hz, Ar*H*), 5.03 (d, 2H, *J* = 1.6 Hz, -N(Ar)-C*H*-CH_3), 2.97(m, 4H, C*H*$(CH_3)_2$), 1.39 (d, 18H, *J* = 6.8 Hz, CH$(CH_3)_2$), 1.22 (m, 12H, CH$(CH_3)_2$, CH_3). ^{13}C NMR (400MHz, CD_2Cl_2): δ 157.1 (ArN-*C*$^+$*H*-ArN), 147.0, 146.9, 131.9, 127.7, 125.7, 125.4, 65.2, 29.9, 29.7, 26.2, 25.2, 24.1, 23.6, 19.2, 12.8. APCIMS: *m/z* 419.4 (M$^+$, 100). Anal. Calcd. for $C_{29}H_{39}BF_4N_2$: C, 68.77; H, 8.56; N, 5.53; Found: C, 68.97; H, 8.76; N, 5.59.

Synthesis of 1,3-bis-(2,6-di*iso*propylphenyl)imidazol-2-ylidene triethylaluminum (6). This compound was synthesized using a modified literature procedure.[5] Triethylaluminum (95 mg, 0.83 mmol) in toluene (10 mL) was added into a 50-mL Schlenk flask equipped with a stir bar and stirred rapidly. A solution of the freshly prepared 1,3-*bis*-(2,6-di*iso*propylphenyl)imidazol-2-ylidene (320 mg, 0.82 mmol) in toluene (25 mL) was added dropwise via a syringe. After complete addition, the reaction was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to afford the product in quantitative yield. ^{1}H NMR (400 MHz, C_6D_6): δ 7.40 (m, 2H), 7.05 (d, 4H, *J* = 6.0 Hz), 3.36 (s, 4H), 3.19 (m, 4H), 1.44 (d, 12H, *J* = 6.0 Hz), 1.26 (t, 9H, *J* = 13.2 Hz), 1.02 (d, 12H, *J* = 6.0 Hz). ^{13}C NMR (C_6D_6): δ 205.98, 147.06, 136.16, 130.29, 128.68, 125.11, 54.59, 29.27, 26.65, 23.85, 11.91, 1.19. EIMS: *m/z* 389.3 ($[M-AlEt_3]^+$, 100).

General reaction procedure for the alkylation of *meso* epoxides. All reactions were carried out under a dry nitrogen atmosphere using either standard Schlenk techniques or in an inert-atmosphere glovebox unless otherwise noted. Into a 25-mL round bottom flask equipped with a magnetic stir bar was added the epoxide (1.0 mmol), internal standard (30 mg, 0.22 mmol) and toluene (3 mL). The catalyst (5 mol%) and the triethylaluminum reagent (280 µL, 2.0 mmol) was added to the flask and the reaction was stirred at room temperature for 12-24 h.

The reaction was quenched with HCl (4 mL of a 1M solution in H_2O) and extracted with ether (3 x 5 mL). The combined organic extracts was washed successively with brine (10 mL) and H_2O (10 mL) and dried over $MgSO_4$. The solution was filtered and an aliquot was analyzed on GC to determine yield.

GC trace for the alkylation of cyclohexene oxide by $AlEt_3$ catalyzed by catalyst 2



Temp. Program: intial temp. = 50 ºC, initial time = 0 min, ramp = 10 ºC/min, final temp. = 250 ºC, final time = 10 min.

References

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