

[Supporting Information]**Imidazolinium Salts as Catalysts for the Ring-Opening Alkylation of *meso* Epoxides by Alkylaluminum Complexes****Hongying Zhou, E. Joseph Campbell, and SonBinh T. Nguyen***

*Department of Chemistry
Northwestern University
2145 Sheridan Rd.
Evanston IL 60208-3113*

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 C₆D₆ was distilled over sodium/benzophenone. Cyclohexene oxide, cyclopentene oxide, 2,3-butene oxide, and 2,3-epoxy-2,3-dimethylbutane were dried over CaH₂. 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 ¹³C). ¹H and ¹³C 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- μ m 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-diisopropylphenyl)-4,5-dimethylimidazolinium tetrafluoroborate (2**):**

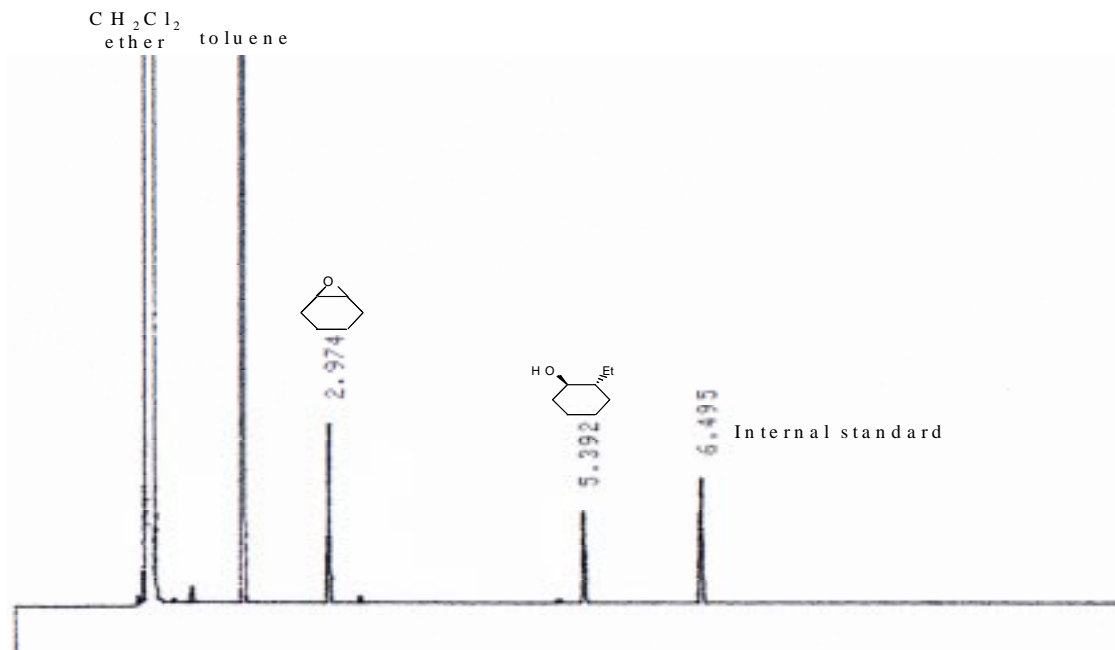
Into a 10-mL round bottom flask was added triethyl orthoformate (1.52 g, 8.63 mmol), ammonium

tetrafluoroborate (0.91 g, 8.63 mmol) and *N, N'*-bis-(2,6-diisopropylphenylamino)-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%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.91 (s, 1H, ArN-C⁺H-ArN), 7.54 (m, 2H, ArH), 7.36 (d, 4H, *J* = 8 Hz, ArH), 5.03 (d, 2H, *J* = 1.6 Hz, -N(Ar)-CH-CH₃), 2.97 (m, 4H, CH(CH₃)₂), 1.39 (d, 18H, *J* = 6.8 Hz, CH(CH₃)₂), 1.22 (m, 12H, CH(CH₃)₂, CH₃). ¹³C NMR (400 MHz, CD₂Cl₂): 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 C₂₉H₃₉BF₄N₂: 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-diisopropylphenyl)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-diisopropylphenyl)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. ¹H NMR (400 MHz, C₆D₆): 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). ¹³C NMR (C₆D₆): 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-AlEt₃]⁺, 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 H₂O) and extracted with ether (3 x 5 mL). The combined organic extracts was washed successively with brine (10 mL) and H₂O (10 mL) and dried over MgSO₄. The solution was filtered and an aliquot was analyzed on GC to determine yield.

GC trace for the alkylation of cyclohexene oxide by AlEt₃ catalyzed by catalyst 2

**Temp. Program: initial temp. = 50 °C, initial time = 0 min, ramp = 10 °C/min,
final temp. = 250 °C, final time = 10 min.**

References

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