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# Synthesis of Pinacol Silylethers from Aromatic Aldehydes via α-Siloxybenzyliron Complexes

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*Abstract:* Quantitative synthesis of pinacol ethers **4**, $[p\text{-}C_6H_4X(OSiMe_3)CH\text{-}]_2$ (X = H, Me, OMe or Cl) from the α-siloxybenzyliron complexes, **3** is reported. The iron dimer, **5** was the only other product which was reused for the reaction.

The reductive coupling of carbonyl compounds to afford pinacols has been a widely used method in preparing organic molecules containing the 1,2-diol functionality.[1] The preparation of alkenes and unusual aldehydes and ketones from the corresponding pinacols or their trimethylsilyl ethers has also attracted much interest in their synthesis.[2] Our recent interest[3] in developing new methods in making carbon-carbon bonds mediated by organometallic complexes led us to investigate the synthesis of pinacol silylether from the α–siloxybenzyliron complexes. Herein we wish to report that the α-siloxybenzyliron complexes cleanly undergo thermal decomposition to provide pinacol silylether and Fp $[Cp(CO)_2Fe]$ dimer in excellent yields.[4]

The α-siloxybenzyliron complexes **3** were prepared[5] by the reaction of the Fp anion[6] **1** with substituted benzaldehydes **2**, followed by trapping the resulting alkoxide with trimethylsilylchloride. The pinacol silylethers **4** were prepared in almost quantitative yields by the thermodecomposition of the respective α–siloxybenzyliron complexes **3** *(Scheme I)*. Fp dimer **5** was isolated in high yield as the only by-product from the reaction, allowing the metal moiety to be reused for the synthesis of the precursors **3**.[6] In a typical reaction, the iron complex **1** was dissolved in dried benzene and placed in a Schlenk tube. The solution was degassed several times, kept under vacuum and immersed in a 60 °C oil bath overnight. The crude product was concentrated under vacuum and chromatographed on a silica gel column with pentane, providing the corresponding pure pinacolethers **4** as white crystals.[7] The Fp dimer **5** was eluted with a pentane/ether mixture. These results are summarized in Table I.

A new route to the synthesis of pinacol silylethers is reported from aromatic aldehydes mediated by Fp anion. More importantly, Fp dimer is isolated in high yields, allowing the recycling of this metal moiety to regenerate the Fp anion. Work is underway to determine the versatility of this method by utilizing α-siloxyalkyliron complexes and to prepare unusual aldehydes from the pinacol silylether by the method of Harada and Mukaiyama.[2b]

**Scheme I**

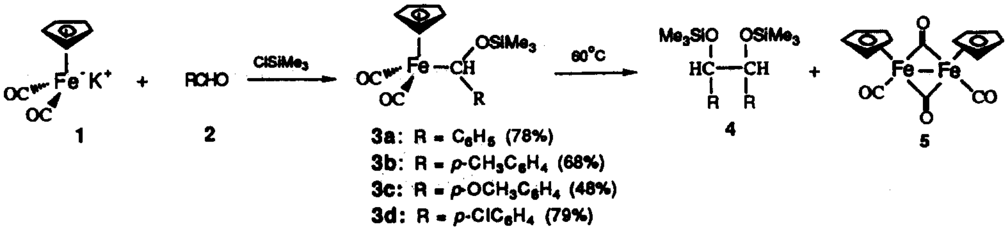

**Table 1.** Isolated Yields of Products from the Thermodecomposition of α-Siloxybenzyliron Complexes, 3

| Compound | Temperature | Time | 4, % yield (ds)[a,b] | 5, %yield[a] |
|---|---|---|---|---|
| **3a** | 60°C | 12 h | 100 (1:1) | 80 |
| **3b** | 60°C | 12 h | 96 (1:1) | 88 |
| **3c** | 60°C | 12 h | 100 (1:1) | 85 |
| **3d** | 60°C | 12 h | 94 (1:1) | 88 |

[a]Isolated yield. [b]Ratio of diastereomers were determined by $^1$H NMR spectroscopy.

## Reference and notes

1. a)Annunziata, R.; Cinquini, M.; Cozzi, F.; Giaroni, P.; Benaglia, M. *Tetrahedron* **1991**, *47*, 30, 5737. b) Pons, J. M.; Santelli, M. *Tetrahedron* **1988**, *44*, 4295.
2. a) McMurry, J. E. *Chem Rev.* **1989**, *89*, 1513. b) Harada, T.; Mukaiyama, T. *Chem. Lett.* **1992**, *1*, 81 and references cited therein.
3. Vargas, R. M.; Theys, R. D.; Hossain, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 777.
4. The α-siloxybenzylmanganese complexes, $(CO)_5Mn[CH(OSiMe_3)Ar]$ are also thermally decomposed to pinacol silylether: Gladysz, J. A.; Johnson, D. L. *Inorg. Chem.* **1981**, *20*, 2508.
5. **3b**: IR($CH_2Cl_2$): 2003, 1946 cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$) δ 0.00 (s, 9H), 2.25 (s, 3H), 4.50 (s, 5H), 6.57 (s, 1H), 7.01 (m, 4H). Anal. Calculated for $FeC_{18}H_{22}O_3Si$: C, 58.38; H, 5.99. Found: C, 58.77; H, 6.08. **3d**: IR($CH_2Cl_2$): 2006, 1948 cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$) δ 0.00 (s, 9H), 4.51 (s, 5H), 6.50 (s, 1H), 7.13 (s, 4H). Anal. Calculated for $FeC_{17}H_{19}O_3SiCl$: C, 52.26; H, 4.90. Found: C, 52.57; H, 4.84. For compounds **3a** and **3c** see reference 3.
6. Fp anion is prepared from iron dimer **5** by reacting with K in THF: Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284.
7. **4b**: $^1$H NMR (250 MHz, $CDCl_3$), δ -0.07/-0.26 (s, 18H), 2.32/2.27 (s, 6H), 4.59/4.42 (s, 2H), 6.94 (s, 8H), 7.19/7.07 (d, 8H). **4d**: $^1$H NMR (250 MHz, $CDCl_3$), δ -0.05/-0.25 (s, 18H), 4.58/4.36 (s, 2H), 7.13/6.95 (d, 8H), 7.24 (s, 8H). For compounds **4a** and **4c** see reference 4.

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