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LETTER

Photochemical reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2R$ (R = Me, Ph) with ArCHO (Ar = C_6H_5, $p\text{-}OCH_3C_6H_4$)

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Our interest in a new method for the preparation of iron carbene precursors, α-siloxyalkyliron complexes [1], has led us to investigate the reaction of iron silanes with aldehydes. Previously, aromatic aldehydes were reacted with manganese silane, $(CO)_5MnSiMe_3$, to provide α-siloxybenzylmanganese complexes [2]. The α-siloxyalkylcobalt complex was found to be the key intermediate in the catalytic hydrosilation of aldehydes by $Co(CO)_4SiR_3$ [3]. Here, we report the formation of α-siloxybenzyliron complexes **3** by the photochemical reaction of iron silyl complexes $FpSiMe_2R$ (**1**) with aromatic aldehydes.

Experimental

*Reaction of **1a** with benzaldehyde*

A sample of 0.11 g (0.43 mmol) of $FpSiMe_3$ (**1a**) [4] and 1.3 mmol of benzaldehyde was dissolved in 10 ml of 80:20 pentane:benzene at room temperature. A reflux condenser was affixed to the reaction flask under a nitrogen atmosphere. The reaction mixture was irradiated (a GE Sunlamp (275W) was used for the reaction) for 21 h and the solvent removed under reduced pressure. The residue was dissolved in a small amount of ether and transferred to a silica gel column. Elution with a 5% ether/pentane mixture gave 0.08 g (50%) of complex **3a** [1] contaminated with a small amount of the decomposition products, erythro and threo pinacol ethers $[\text{-}CH(C_6H_5)OSi(CH_3)_3]_2$ [2b] in a 1:1 ratio.

*Reaction of **1a** with p-anisaldehyde*

A solution of 0.23 g (0.94 mmol) of $FpSiMe_3$ (**1a**) and 0.38 g (2.80 mmol) *p*-anisaldehyde was irradiated for 13.5 h. Isolation of the reaction mixture on deactivated alumina column (Brockman Activity III) yielded 34% of complex **3b** [1]. Complex **3b** also contained a small amount of the decomposition products, erythro and threo pinacol ethers $[\text{-}CH(p\text{-}OCH_3C_6H_4)\text{-}OSi(CH_3)_3]_2$ [2b] in a 1:1 ratio.

*Reaction of **1b** with benzaldehyde*

A solution of 0.09 g (0.29 mmol) of $FpSiMe_2Ph$ (**1b**) [5] and 0.09 g (0.86 mmol) of benzaldehyde was irradiated for 16 h. Isolation on a silica column yielded 38% of the siloxy complex **3c** having the following spectral properties: IR (pentane) 1954, 2015 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 0.19 (s, 3H), 0.26 (s, 3H), 4.48 (s, 5H), 6.59 (s, 1H), 7.18 (m, 5H), 7.34–7.54 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.5 Mhz) δ −1.5, 71.0, 86.8, 123.3, 127.0, 127.2, 127.6, 127.8, 129.2, 133.5, 216.6. Isolation also provided 7% of the 1:1 ratio of pinacol ethers (erythro:threo) $[\text{-}CH(C_6H_5)OSi(CH_3)_2C_6H_5]_2$ with the following ^1H NMR characteristics ($CDCl_3$, 250 MHz): δ 0.11/−0.10 (s, 6H), 0.16/−0.03 (s, 6H), 4.51/4.68 (s, 2H), 6.98–7.40 (m, 20H).

*Reaction of **1b** with p-anisaldehyde*

A solution of 0.17 g (0.54 mmol) of $FpSiMe_2Ph$ (**1b**) and 0.22 g (1.63 mmol) of *p*-anisaldehyde was irradiated for 13.5 h. After the usual work-up, 45% of the siloxyiron complex **3b** was isolated having the following spectral properties: IR (pentane) 1952, 2014 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 0.18 (s, 3H), 0.25 (s, 3H), 3.73 (s, 3H), 4.49 (s, 5H), 6.60 (s, 1H), 6.65–6.88 (m, 5H), 7.11–7.54 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ −1.4, 55.3, 71.0, 86.8, 113.1, 113.2, 124.5, 127.5, 127.6, 128.8, 129.3, 133.6, 216.5. Isolation also provided 2% of the 1:1 ratio of pinacol ethers (erythro:threo) $[\text{-}CH(p\text{-}OCH_3C_6H_4)OSi(CH_3)_2C_6H_5]_2$ with the following ^1H NMR characteristics: ($CDCl_3$, 250 MHz) δ 0.13/−0.06 (s, 6H), 0.18/0.02 (s, 6H), 3.73/3.87 (s, 6H), 4.45/4.61 (s, 2H), 6.64–7.50 (m, 18H).

Results and discussion

The photochemical reactions of **1** were carried out at room temperature with benzaldehyde and *p*-anisaldehyde to provide α-siloxybenzyliron complexes **3** in moderate yields (Scheme 1).

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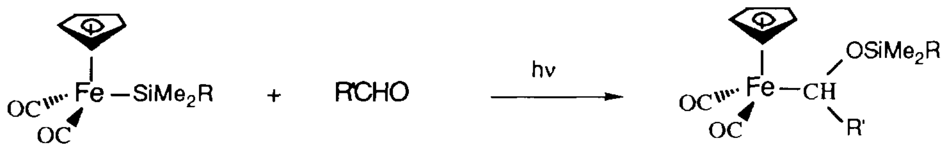

1a: R = CH_3
1b: R = C_6H_5

2a: R' = C_6H_5
2b: R' = p-$OCH_3C_6H_5$

3a: R = CH_3, R' = C_6H_5
3b: R = CH_3, R' = p-$OCH_3C_6H_5$
3c: R = C_6H_5, R' = C_6H_5
3d: R = C_6H_5, R' = p-$OCH_3C_6H_5$

Scheme 1.

The presence of 10 mol% of $AgBF_4$, Ph_3PO or Fp_2 had no effect on the rate of addition of **1a** to benzaldehyde. The photochemical reaction of **1a** with benzaldehyde was performed under an atmosphere of CO. However, the presence of CO did not improve the yield of this product. Use of a coordinating solvent, such as THF, did not speed up the reaction of **1a** with benzaldehyde, nor did it improve the yield of the product. Photolyzing pure benzaldehyde with iron silane **1a** did not result in an α-siloxyiron complex formation.

Several interesting points concerning the above reactions deserve attention. First, the reaction could be an alternative route in the preparation of α-siloxyiron complexes using air and thermally stable $FpSiR_3$*. Second, it is believed that the α-siloxyiron complex is the key intermediate in the catalytic photochemical hydrosilation of aldehyde by $FpCH_3$ or by $FpCOCH_3$ [6]. Our reactions firmly establish the viability of such a species in the catalytic process.

Work is underway to improve the yield of these reactions to make this method a viable route for the synthesis of iron carbenes. Mechanistic studies of this reaction are currently being pursued.

References

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*At present we prepare the α-siloxyalkyl iron complexes by reacting the Fp anion with aldehydes in the presence of trimethylsilylchloride [1].