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CARBANION ADDITION TO A METALATED ACETALDEHYDE. A NEW REGIOSPECIFIC ALKENE SYNTHESIS *

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Summary

The reaction of 2-[(dicarbonyl)(η^5-cyclopentadienyl)iron]acetaldehyde with organolithium and Grignard reagents results in efficient addition to the aldehyde carbonyl. The intermediate alkoxides have been treated with tetrafluoroboric acid to give high yields of isolated η^2-alkene complexes of the dicarbonyl(η^5-cyclopentadienyl)iron cation. Using this procedure the following alkenes were produced as complexed ligands to iron in 50–90% yield: propene, 1-hexene, 3-methyl-1-pentene, 3,3-dimethyl-1-butene, 1,3-butadiene, and styrene.

A variety of different types of products have been observed when the (η^5-C_5H_5)$(CO)_2$FeL ≡ FpL (**1**) system and carbanions are reacted. These reactions have involved nucleophilic attack at the C_5H_5 ring [1], terminal CO [1], L [2] and iron [1,2] to give addition or substitution products plus electron transfer to give reduction products (Fp_2) [1–3]. The nature of L and the carbanion, plus the charge on iron has a dramatic effect on the type of reaction found in a particular system. In our studies of transition metal containing carbanions, we were interested in those cases of **1** where L has an organic carbonyl group. The examples that have already been reported by others include the attack of alkyllithiums at a terminal carbonyl for L = acyl to give β-diketonate structures [6] attack at the complexed alkene in the cationic η^2-acrolein complex with organocopper reagents [2] and electron transfer when L = CH_2O_2CR and alkyllithiums are reacted [3]. In none of these cases was the carbanion reported to react at the organic carbonyl carbon. We decided to examine the known $FpCH_2C(=O)H$ (**2**) [5] in carbanion reactions to further define the chemistry of this system (**1**). The reaction of **2** with strongly basic carbanions could follow any of the routes described above. In addition, **2** could undergo nucleophilic addition to the aldehyde carbonyl to yield an intermediate alkoxide, or

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TABLE 1

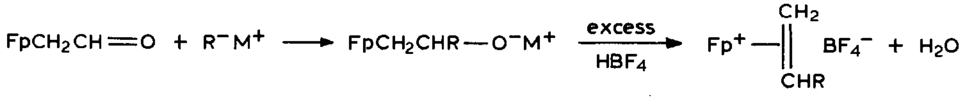
YIELDS OF CARBANION ADDITION TO 2 PRODUCING 4 FOLLOWING ACIDIFICATION

RM	4:R =	Yield (%)	RM	4:R =	Yield (%)
n-BuLi	n-Bu	90	MeLi	Me	90
n-BuMgCl	n-Bu	50	CH_2=CH-MgBr	CH=CH_2	65
s-BuLi	s-Bu	81	PhLi	Ph	61
t-BuLi	t-Bu	88	PhMgBr	Ph	76

undergo deprotonation to form an enolate [6]. We report here the results of the reaction of **2** with unstabilized alkyllithium and Grignard reagents.

Results and discussion

When butyllithium was added to **2** in tetrahydrofuran (THF) at −78°C the light yellow solution darkened slightly. Excess tetrafluoroboric acid in ether was added and a yellow solid precipitated. This solid was dissolved in methylene chloride, filtered, precipitated with ether and identified as Fp(η^2-1-hexene)$^+$ BF_4^- which must have arisen from the efficient addition to the aldehyde carbonyl in **2**; producing **3** as an intermediate. A similar result was obtained with butylmagnesium chloride where the 1-hexene complex was also produced. Other alkyllithiums plus



$$FpCH_2CH{=}O + R^-M^+ \longrightarrow FpCH_2CHR{-}O^-M^+ \xrightarrow[HBF_4]{excess} Fp^+{-}\left\| \begin{matrix} CH_2 \\ CHR \end{matrix} \right. BF_4^- + H_2O$$

(2) (3) (4)

Grignard reagents and **2** were reacted and the results are presented in Table 1. Even the very basic s-butyl- and t-butyllithium reagents cleanly reacted and excellent yields of the alkene complexes were obtained.

The wide range of carbanions that add to **2** demonstrates the selectivity for addition over any of the other possibilities described above. In addition, this procedure provides for a very efficient synthesis of η^2-1-alkene and diene complexes which have been shown to be versatile synthetic intermediates. The intermediate alkoxide **3** is the same as that produced in the reaction of a terminal epoxide with Fp anion [7]. It has been previously demonstrated that the free alkenes can be obtained either directly by thermal elimination in **3** or via the action of iodide ion on **4** [7]. The method described here complements the recently described Fp(η^2-vinyl ether) cation system [8] which works best with stabilized nucleophiles to give other examples of **4**. Further work on extending the procedure to the stereoselective synthesis of disubstituted alkenes is in progress.

Experimental

Infrared spectra were recorded on a Beckman 3750 or a Perkin–Elmer 298 spectrometer. NMR spectra were recorded on Varian T-60, EM-360, XL-100 or XL-300 spectrometers. Solvents were routinely dried and distilled prior to use. All reactions were carried out under a nitrogen atmosphere. Elemental analyses were performed by Galbraith Laboratories.

The organolithium reagents were purchased from Aldrich Chemical Co. while vinylmagnesium bromide was obtained from Alfa-Ventron. The other Grignard reagents were prepared from the corresponding alkyl halide and magnesium turnings in THF. The Fp(propene; 1,3-butadiene and styrene) cations have been previously reported [9].

General procedure

To a 100 ml round bottom flask with a side arm was added **2** (2.0 mmol) and 25 ml THF. The flask was cooled to −78°C and the Grignard or organolithium added. The yellow solution slowly darkened and after 10 min an ether solution of 1.25 g of 48% HBF_4 (6.8 mmol) was added. On warming, a yellow solid formed which was isolated by filtration. The product was dissolved in CH_2Cl_2, filtered and reprecipitated with ether. The yields reported in Table 1 are for this isolated product.

Fp(η^2-1-hexene)$^+$ BF_4^-

IR (KBr) 2038, 2080 cm^{-1}. ^1H NMR (CD_3NO_2) δ 0.92 (m, 3H), 1.2–1.8 (m, 5H), 2.50 (m, 1H), 3.44 (d, 1H, J 15 Hz), 3.92 (d, 1H, J 8 Hz), 5.4 (m, 1H). Anal. Found: C, 44.94; H, 4.86. $C_{13}H_{17}BF_4FeO_2$ calc: C, 44.87; H, 4.92%.

Fp(η^2-3-methyl-1-pentene)$^+$ BF_4^-

Two diastereomers in 60/40 ratio. IR (KBr) 2070, 2027 cm^{-1}. ^1H NMR (CH_3NO_2) 300 mHz; major isomer: δ 5.66 (s, 5H, Cp), 5.07 (ddd, 1H, J 15.0, 8.5, 8.5 Hz), 3.80 (d, 1H, J 8.5 Hz), 3.46 (d, 1H, J 15.0 Hz), 1.60 (m, 1H), 1.55 (m, 1H), 1.46 (d, 3H, J 6.2 Hz), 1.36 (m, 1H), 0.95 (t, 3H, J 7.4 Hz); minor isomer: δ 5.66 (s, 5H, Cp), 5.30 (ddd, 1H, J 15.0, 8.6, 6.1 Hz), 3.95 (d, 1H, J 8.6 Hz), 3.36 (d, 1H, J 15.0 Hz), 2.08 (m, 1H), 1.93 (m, 1H), 1.60 (m, 1H), 1.01 (t, 3H, J 7.4 Hz), 0.87 (d, 3H, J 5.6 Hz). Anal. Found: C, 45.25; H, 5.12. $C_{13}H_{17}BF_4FeO_2$ calc: C, 44.87; H, 4.92%.

Fp(η^2-3,3-dimethyl-1-butene)$^+$ BF_4^-

IR (KBr) 2070, 2030 cm^{-1}, ^1H NMR (CD_3NO_2) δ 5.7 (s, 5H, Cp), 5.46 (dd, 1H, J 15.0, 8.7 Hz), 4.05 (d, 1H, J 8.7 Hz), 3.22 (d, 1H, J 15.0 Hz), 1.20 (s, 9H). Anal. Found: C, 44.84; H, 4.86. $C_{13}H_{17}BF_4FeO_2$ calc: C, 44.87; H, 4.92%.

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