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THE PREPARATION OF α-METHOXYALKYLIRON COMPLEXES: PRECURSORS OF SECONDARY CARBENEIRON COMPLEXES

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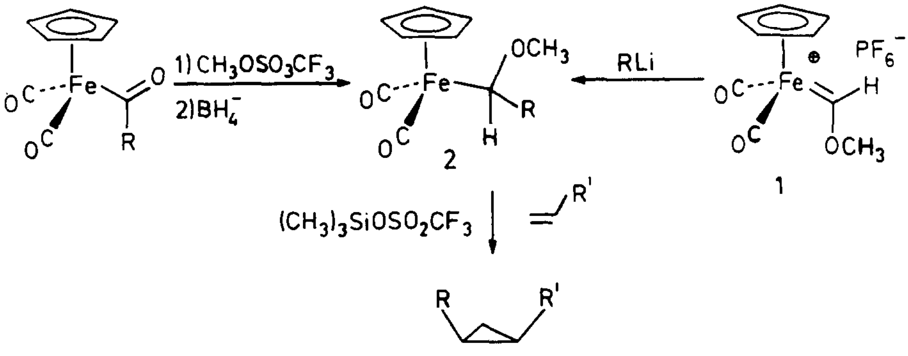
Summary

The addition of methyl-, n-butyl-, phenyl-, and *p*-tolyl-lithium reagents to $(C_5H_5)(CO)_2Fe{=}CHOCH_3{}^+$ $PF_6{}^-$ gives the respective α-methoxyalkyliron complexes in good yield. The addition of vinyllithium or vinylmagnesium bromide to $(C_5H_5)(CO)_2Fe{=}CHOCH_3{}^+$ $PF_6{}^-$ yields rearranged product *cis*-$(C_5H_5)(CO)_2$-$FeCH_2CH{=}CHOCH_3$.

There has been considerable recent interest in the use of carbenemetal complexes as cyclopropanating reagents [1–9]. Electrophilic carbenemetal complexes such as $(C_5H_5)(CO)_2Fe{=}CH_2{}^+$ [2,3], $(CO)_5W{=}CHC_6H_5$ [4], $(C_5H_5)(CO)_2Fe{=}CHC_6H_5{}^+$ [5], and $(C_5H_5)(CO)_2Fe{=}CHCH_3{}^+$ [6,7,8] have been shown to react with a wide range of alkenes to give cyclopropanes in good to excellent yields. Recently, we reported that $(C_5H_5)(CO)_2Fe{=}C(CH_3)_2{}^+$ reacts with styrene and isobutylene to give *gem*-dimethylcyclopropanes [9], although we have not yet found conditions to yield cyclopropanes from less reactive alkenes such as 1-octene [10]. Two efficient routes to electrophilic carbenemetal complexes have been developed: (1) the addition



of electrophiles to MCHRX (X = OR, SR, Cl) derivatives [2–7] and (2) the addition of strong acids to vinylmetal compounds [7–9].

Brookhart [6] and Cutler [8] have developed a general route to the α-methoxyalkyliron complexes $(C_5H_5)(CO)_2FeCH(OCH_3)(R)$ (**2**) by hydride reduction of the corresponding carbeneiron complexes $(C_5H_5)(CO)_2Fe{=}C(OCH_3)R^+$ and have demonstrated their utility as precursors of electrophilic carbene complexes. Here we describe an alternative method for the preparation of α-methoxyalkyliron complexes **2** by addition of organolithium reagents to $(C_5H_5)(CO)_2Fe{=}CHOCH_3^+ PF_6^-$ (**1**).

Experimental

General. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Methylene chloride and hexane were distilled from CaH_2. All reactions were carried out under an atmosphere of dry nitrogen in flame-dried glassware. NMR spectra were recorded on JEOL-MH-100, FX-60 or Bruker WH-270 spectrometers. Infrared spectra were recorded on a Beckman 4230 spectrometer.

$(C_5H_5)(CO)_2FeCH_2OCH_3$ was prepared from $Na[(C_5H_5)(CO)_2Fe]$ and $ClCH_2OCH_3$ [11]. Triphenylcarbenium hexafluorophosphate was prepared from $(C_6H_5)_3COH$ and aqueous HPF_6 in acetic anhydride or propionic anhydride [12].

$(C_5H_5)(CO)_2Fe{=}CHOCH_3^+ PF_6^-$ (1) [14]. $(C_5H_5)(CO)_2FeCH_2OCH_3$ (6.93 g, 31.2 mmol) was added to a stirred solution of $(C_6H_5)_3C^+ PF_6^-$ (12.13 g, 31.2 mmol) in 100 ml of CH_2Cl_2 at −78°C. When the red solution was warmed to room temperature a yellow precipitate formed. The precipitate was filtered, washed with CH_2Cl_2 (4 × 50 ml) and dried under vacuum to give **1** (10.03 g, 88%) as a yellow powder. ^1H NMR (CD_3NO_2, 270 MHz): δ 13.13 (s, 1H, FeCH), 5.63 (s, 5H, C_5H_5), 4.73 ppm (s, 3H, OCH_3); ^{13}C NMR (CD_3NO_2, 15.04 MHz): δ 321.9 (Fe=CH), 207.3 (CO), 91.3 (C_5H_5), 79.4 ppm (OCH_3); IR (CH_3NO_2): 2075, 2033 cm^{-1}.

$(C_5H_5)(CO)_2FeCH(OCH_3)(CH_3)$ (2a) [6,8]. CH_3Li (5.1 ml, 4.9 mmol, 0.97 *M* in ether) was added to a stirred yellow suspension of **1** (1.61 g, 4.40 mmol) in 10 ml of ether at −78°C. The resulting cloudy red solution was warmed to room temperature and ethanol (0.1 ml) was added to quench excess lithium reagent. The solvent was evaporated under vacuum and the residue was extracted with hexane (4 × 15 ml). The combined hexane extracts were evaporated and the crude product was sublimed (40°C, 10^{-3} mmHg) to yield yellow crystalline **2a** (0.73 g, 70%), m.p. 65–67°C. ^1H NMR (C_6D_6, 100 MHz): δ 4.90 (q, *J* 6 Hz, 1H, FeCH), 4.30 (s, 5H, C_5H_5), 3.18 (s, 3H, OCH_3), 1.74 ppm (d, *J* 6 Hz, 3H, CH_3); ^{13}C NMR (C_6D_6, 15.04 MHz): δ 218.6, 217.7 (diastereotopic CO's), 86.4 (C_5H_5), 79.7 (Fe–C), 57.5 (OCH_3), 32.4 ppm (CH_3); IR ($CHCl_3$): 1997, 1938 cm^{-1}.

$(C_5H_5)(CO)_2FeCH(OCH_3)(CH_2CH_2CH_2CH_3)$ (2b). n-Butyllithium (1.6 ml, 2.5 mmol, 1.55 *M* in hexane) was added to a stirred yellow suspension of **1** (0.81 g, 2.21 mmol) in 10 ml of ether at −78°C. Workup as described for **2a** gave a red suspension. A quick short path distillation (60°C, 10^{-3} mmHg) gave pure **2b** (0.38 g, 64%) as a red oil. ^1H NMR (C_6D_6, 270 MHz): δ 4.81 (dd, *J* 8, 2 Hz, 1H, FeCH); 4.21 (s, 5H, C_5H_5); 3.17 (s, 3H, OCH_3); 2.16 (m, 1H), 1.88 (m, 1H), 1.72 (m, 1H) and 1.35 (m, 3H), diastereotopic protons of $(CH_2)_3$ unit; 0.95 ppm (t, *J* 8 Hz, 3H, CH_3); ^{13}C NMR (C_6D_6, 15.04 MHz): δ 218.6, 217.2 (diastereotopic CO's), 86.5 (C_5H_5), 85.0 (Fe–C), 58.0 (OCH_3), 47.9, 32.6, 22.8 (CH_2's), 14.3 ppm (CH_3); IR

($CHCl_3$): 1997, 1938 cm^{-1}. **2b** was too unstable to obtain an elemental analysis.

*$(C_5H_5)(CO)_2FeCH(OCH_3)(C_6H_5)$ (**2c**) [5].* Phenyllithium (7.1 ml, 5.0 mmol, 0.70 *M* in ether) was added to a suspension of **1** (1.61 g, 4.40 mmol) in 10 ml of ether at −78°C. The workup was as described for **2a**, followed by a column chromotography (activity IV alumina, hexane) to give **2c** (1.13 g, 86%) as a red oil which solidified on standing, m.p. 39–41°C. ^{1}H NMR ($CDCl_3$, 100 MHz): δ 7.20 (m, 5H, C_6H_5), 5.76 (s, 1H, FeCH), 4.49 (s, 5H, C_5H_5), 3.11 ppm (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 15.04 MHz): δ 216.5, 216.4 (diastereotopic CO's), 153.0 (*ipso*), 127.8, 123.5 (*ortho, meta*), 124.1 (*para*), 86.4 (C_5H_5), 80.6 (Fe–CH), 58.9 ppm (OCH_3); IR ($CHCl_3$): 2001, 1954 cm^{-1}.

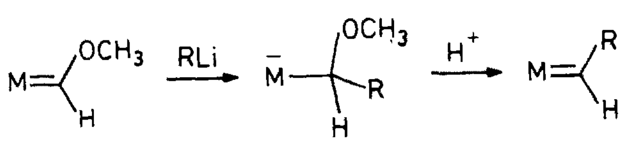
*$(C_5H_5)(CO)_2FeCH(OCH_3)(p\text{-}CH_3C_6H_4)$ (**2d**) [5].* *p*-Tolyllithium (2.6 ml, 2.5 mmol, 0.95 *M* in ether) was added to a stirred suspension of **1** (0.81 g, 2.21 mmol) in 10 ml of Et_2O at −78°C. The workup was as described for **2a**, followed by column chromatography (activity IV alumina, hexane) to give **2d** (0.49 g, 71%) as a yellow crystalline solid, m.p. 70–72°C. ^{1}H NMR ($CDCl_3$, 100 MHz): δ 7.37 (d, *J* 8 Hz, 2H, aromatic), 7.11 (d, *J* 8 Hz, 2H, aromatic), 5.89 (s, 1H, FeCH), 4.22 (s, 5H, C_5H_5), 3.18 (s, 3H, OCH_3), 2.28 ppm (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 15.04 MHz): δ 216.6, 216.4 (diastereotopic CO's), 149.9 (*ipso*), 133.4 (*para*), 128.5, 123.5 (*ortho, meta*), 86.5 (C_5H_5), 80.8 (FeC), 58.9 (OCH_3), 20.9 ppm (CH_3); IR ($CHCl_3$): 2003, 1955 cm^{-1}.

*cis-$(C_5H_5)(CO)_2FeCH_2CH{=}CHOCH_3$ (**3**) [15].* Vinylmagnesium bromide prepared from vinyl bromide (0.50 ml, 7.0 mmol) and magnesium (0.19 g, 8.0 mmol) in tetrahydrofuran was added to a suspension of **1** (1.83 g, 5.00 mmol) in tetrahydrofuran (20 ml) at −23°C. Workup as described for **2a** followed by preparative thin layer chromatography (silica gel; 75/25 hexane/ether) gave **3** as an oily red solid (0.45 g, 36%). Recrystallization from pentane gave pure **3**, m.p. 45–47°C. ^{1}H NMR (C_6D_6, 270 MHz): δ 5.61 (d, *J* 6 Hz, 1H, C*H*OCH$_3$), 4.75 (td, *J* 9, 6 Hz, 1H, CH$_2$C*H*=C), 4.20 (s, 5H, C_5H_5), 3.27 (s, 3H, OCH_3), 2.33 ppm (d, *J* 9 Hz, 2H, $FeCH_2$); ^{13}C NMR (C_6D_6, 15.04 MHz): δ 217.6 (CO), 141.7 (C=*C*HOCH$_3$), 118.3 (*C*=CHOCH$_3$), 85.6 (C_5H_5), 58.9 (OCH_3), −4.4 ppm ($FeCH_2$); IR ($CHCl_3$): 2001, 1947, 1640 cm^{-1}.

Vinyllithium (5.6 mmol), prepared by the addition of 7.5 ml of 1.5 *M* (11.2 mmol) t-butyllithium to vinyl bromide (0.75 g, 7.0 mmol) in ether (10 ml), was added to **1** (1.61 g, 4.40 mmoles) in ether at −78°C. Subsequent workup gave **3** (28%).

Results and discussion

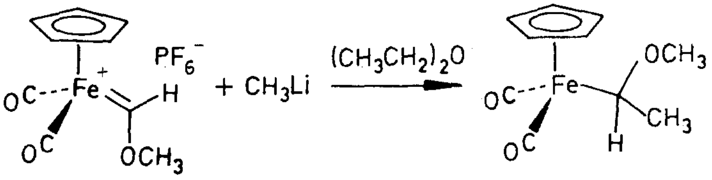
The addition of organolithium reagents to M=CH(OCH_3) complexes is an attractive route to α-alkoxymetal complexes, which are precursors to a wide variety of secondary carbenemetal complexes [1].



We had hoped to prepare secondary carbene complexes of tungsten from $(CO)_5W{=}CH(OCH_3)$ but we have been unable to prepare this compound [13]. When the anionic formyltungsten complex $(CO)_5WCHO^-$ was treated with

$(CH_3)_3O^+ BF_4^-$, only $W(CO)_6$ and methane were observed and none of the desired $(CO)_5W=CH(OCH_3)$ was detected. The availability of $(C_5H_5)(CO)_2Fe=CH(OCH_3)^+ PF_6^-$ (**1**), which Cutler [14] first prepared from $(C_5H_5)(CO)_2FeCH_2OCH_3$ and $(C_6H_5)_3C^+ PF_6^-$, allowed us to test its use as a general precursor to secondary carbeneiron complexes.

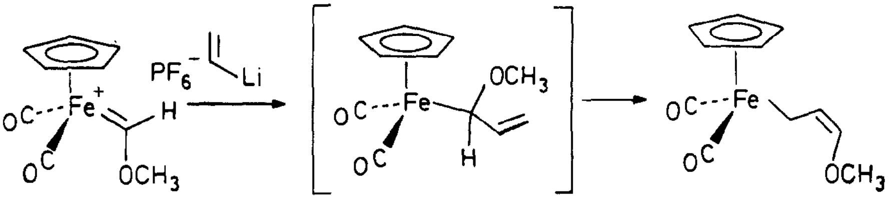
We have found that the addition of alkyl- and aryllithium reagents to **1** proceeds in good yield to give α-methoxyalkyliron complexes $(C_5H_5)(CO)_2FeCH(OCH_3)R$ (**2a**, $R = CH_3$, 70%; **2b**, $R = CH_3(CH_2)_3$, 64%; **2c**, $R = C_6H_5$, 86%; **2d**, $R = C_6H_4$-*p*-CH_3, 71%). Reproducible yields for the reaction of **1** with lithium reagents were obtained only when **1** was prepared from freshly prepared $(C_6H_5)_3C^+ PF_6^-$ which was thoroughly washed to remove acidic impurities. The presence of large amounts of hydroxide in the lithium reagent resulted in lower yields of **2**. Alkyl- and aryl-lithium reagents appear to be superior to Grignard reagents for the synthesis of **2a**–**2d**. The addition of methylmagnesium iodide to **1** resulted only in the formation of $C_5H_5(CO)_2FeI$. The yield of **2c** from phenylmagnesium bromide was much lower than from phenyllithium.



1 2a

The α-methoxyiron complexes have modest thermal stability. **2b** can be quickly distilled (60°C, 10^{-3} mmHg) but decomposes to $[(C_5H_5)(CO)_2Fe]_2$ on standing at room temperature over several days. Attempted distillation of complexes **2c** and **2d** even under high vacuum led to decomposition.

We had hoped that the addition of a vinyl organometallic reagents to **1** would lead to the ether precursors of vinylcarbene complexes. However, we found that the addition of vinylmagnesium bromide or vinyllithium to **1** did not give the desired product but rather the known complex **3** [15]. Complex **3** is the [1,3] rearrangement product of **2e**, the expected product of addition of vinyllithium to the carbene carbon of complex **1** [16]. Related [1,3] rearrangements of allyliron compounds have been observed by Rosenblum who demonstrated that the rearrangement proceeds by a radical chain process [17].



1 2e 3

The procedure outlined in this paper and the hydride reduction of alkoxycarbeneiron complexes reported by Brookhart [6] and Cutler [8] provide two convenient complementary synthetic routes to the α-alkoxyalkyliron compounds **2**.

Brookhart has shown that these α-alkoxyalkyliron compounds are useful cyclopropanating agents [5,6].

Acknowledgement

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