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SYNTHESIS OF CYCLOPENTADIENYLDICARBONYL-σ-BENZYLIRON DERIVATIVES WITH OXYGEN-CONTAINING FUNCTIONAL GROUPS IN THE CYCLOPENTADIENYL RING

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Summary

The carbinols $C_5H_4C(OH)RR'$ $(CO)_2FeCH_2Ph$ ($R = R' = Ph$; $R = H$, $R' = Ph$) and the aldehyde $C_5H_4CHO(CO)_2FeCH_2Ph$ were synthesized by metalation of $Cp(CO)_2FeCH_2Ph$ with BuLi in THF at −78°C and the subsequent addition of $RR'C(=O)$ or $Me_2NC(=O)H$. Treatment of $C_5H_4COOH(CO)_2FeCH_2Ph$ with PCl_5 in benzene, upon cooling with ice water, gave the chloroanhydride $C_5H_4COCl(CO)_2CH_2Ph$.

The reactivity of the Cp ring in complexes of the type, $Cp(CO)_nMR$ ($n = 2$, $M = Fe$; $n = 3$, $M = Mo$ or W; R is σ-bonded alkyl or aryl) has not been studied. We have recently found that hydrogen atoms of the Cp ring in these complexes undergo isotopic hydrogen exchange under the conditions of the protophilic substitution reaction (EtOD, EtONa). On this basis, these systems were metalated at the Cp ring [1,2,3]. The metalation reaction proved to be a convenient method for the synthesis of different derivatives substituted in the Cp ring, $R'C_5H_4(CO)_2FeR$, where $R' = Me$, $SiMe_3$, COOH, etc.; $R = Ph$, Me, CH_2Ph, etc. [1,2].

In the present work we describe the synthesis of the new derivatives, $Cp(CO)_2FeCH_2Ph$, with oxygen-containing functional groups on the Cp ring, $XC_5H_4(CO)_2FeCH_2Ph$, where $X = C(OH)RR'$, $C(=O)H$ or $C(=O)Cl$ *.

The carbinols $RR'(OH)C_5H_4(CO)_2FeCH_2Ph$ were prepared by the reaction of

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* Recently Macomber and Rausch have synthesized the complexes $RC_5H_4(CO)_3MMe$ ($R = CHO$, COOH, etc., $M = Cr$, Mo or W), from the substituted derivatives of sodium cyclopentadienyl(RC_5H_4Na) and $M(CO)_6$ with subsequent treatment of the anions $RC_5H_4(CO)_3M^-$ with methyl iodide [4].

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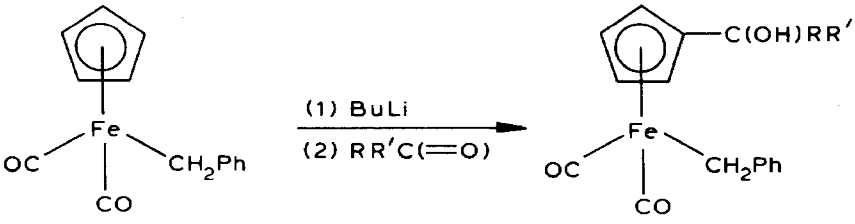
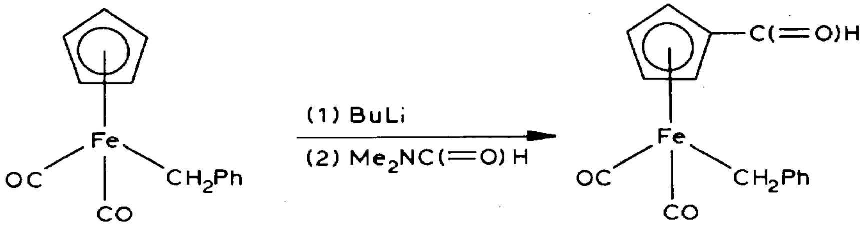
$Ph_2C(=O)$ and $LiC_5H_4(CO)_2FeCH_2Ph$. The reaction does not place with $PhMeC(=O)$.

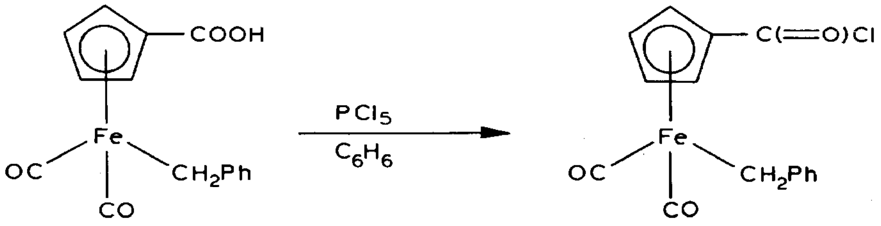


(Ia: $R = R' = Ph$;
Ib: $R = H, R' = Ph$)

The reaction of $LiC_5H_4(CO)_2FeCH_2Ph$ with $Me_2NC(=O)H$ results in the formation of the aldehyde $C_5H_4CHO(CO)_2FeCH_2Ph$.



The chloro anhydride $C_5H_4COCl(CO)_2FeCH_2Ph$ was obtained by the action of PCl_5 on the acid $C_5H_4COOH(CO)_2FeCH_2Ph$.



Experimental

The complexes $Cp(CO)_2FeCH_2Ph$ and $C_5H_4COOH(CO)_2FeCH_2Ph$ were prepared according to refs. 5,2. IR spectra were recorded on a UR-20 spectrometer and ^1H NMR spectra on a Bruker WP-200-SY spectrometer (200.13 MHz).

$C_5H_4C(OH)Ph_2(CO)_2FeCH_2Ph$ *(Ia)*

BuLi (2.5 ml (2 mmol) in hexane was added to $Cp(CO)_2FeCH_2Ph$ (0.56 g, 2 mmol) at −78°C. The mixture was stirred for 2 h at −78°C, after which 1 ml (5 mmol) of $Ph_2C(=O)$ in 20 ml of THF was added, with subsequent stirring at −78°C for 1.5 h. The mixture, still being stirred, was then warmed to room temperature. The solvent was removed in vacuo, and the residue chromatographed on Al_2O_3; the product Ia (0.29 g, 30%) was eluted with a hexane/ether mixture (1/1). Ia was crystallized from hexane at low temperature, m.p. 101–102°C.

^{1}H NMR (acetone-d_6); δ(ppm): 7.46–6.76 (m,15H,Ph), 5.47 (s,1H,OH), 4.81 (t,2H,Cp), 4.67 (t,2H,Cp), 2.8 (s,2H,CH_2). IR(hexane): ν 3620, 2014, 1961 cm^{-1}. Found: C, 72.33; H, 5.38; Fe, 12.34. $C_{27}H_{22}O_3$ Fe calcd.: C, 72.00; H, 4.8; Fe, 12.44%.

$C_5H_4C(OH)HPh(CO)_2FeCH_2Ph$ (Ib)

This compound was obtained in the same way as Ia. ^{1}H NMR spectrum (acetone-d_6) δ (ppm): 7.14–6.07 (m, 10H, Ph), 5.17 (t, 2H, Cp), 4.77 (t, 2H, Cp), 2.8 (s, 2H, CH_2), IR spectrum (hexane), ν 3629, 2010, 1960 cm^{-1}.

$C_5H_4CHO(CO)_2FeCH_2Ph$ (II)

BuLi (8 ml, (4 mmol) in hexane was added to of $Cp(CO)_2FeCH_2Ph$ (0.47 g, 2 mmol) in 40 ml of absolute THF at −78°C. The mixture was stirred at −78°C for 1.5 h, then 1 ml (20 mmol) of $Me_2NC(=O)H$ was added. Stirring was continued for 1 h at −78°C and then the mixture was allowed to warm to room temperature with stirring (1 h). The mixture was then poured into water and extracted with ether. After evaporation, the residue was chromatographed on alumina eluting II with a mixture; F hexane/ether (1/1) to obtain 0.1 g (20%) of the product, which had m.p. 75–76°C after low-temperature crystallization from hexane.

^{1}H NMR (benzene-d_6): δ (ppm) 9.57 (s, 1H, CHO), 7.23–6.87 (m, 5H, Ph), 5.60, (t, 2H, Cp), 5.17 (t, 2H, Cp), 2.8 (s, 2H, CH_2). IR spectrum (hexane) ν 2020, 1965, 1710 cm^{-1}. Found: C, 60.08; H, 4.20; Fe, 17.60. $C_{15}H_{12}O_3Fe$ calcd.: C, 60.84; H, 4.05; Fe, 18.92%.

$C_5H_4COCl(CO)_2FeCH_2Ph$ (III)

PCl_5 (0.4 g, 2 mmol) was added to $C_5H_4COOH(CO)_2FeCH_2Ph$ (0.67 g, 2 mmol) in 50 ml of absolute benzene upon cooling with ice water (+5 to +10°C). At this temperature the mixture was stirred for 5 h then the benzene was removed in vacuo and the residue chromatographed on silica gel by eluting product III with a mixture of hexane/benzene (1/1). Yield was 0.2 g (60% as calcd. for the acid that had reacted). Low-temperature crystallization from hexane gave the product with m.p. 51–52°C.

^{1}H NMR spectrum (benzene-d_6): δ (ppm) 7.17 (m, 5H, Ph), 4.67 (t, 2H, Cp), 3.7 (t, 2H, Cp), 2.75 (s, 2H, CH_2). IR spectrum (hexane); ν 2033, 1985, 1780 cm^{-1}. Mass spectrum (m/e): 302 ($M^+ - CO$), 274 ($M^+ - 2CO$), 183 ($M^+ - 2CO - CH_2Ph$). Found: C, 55.36; H, 3.58; Cl, 10.56; Fe, 16.48. $C_{15}H_{11}ClFeO_3$ calcd.: C, 54.49; H, 3.32; Cl, 10.73; Fe, 16.94%.

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