Journal of Organometallic Chemistry, 267 (1984) 309–312
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION OF η^5-$C_5H_5COOH(CO)_2Fe$-η^1-R CARBOXYLIC ACIDS

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(Received January 6th, 1984)

Summary

η^5-$C_5H_4(COOH)(CO)_2FeR$ (R = Ph, $C_5H_4Mn(CO)_3$ or CH_2Ph) carboxylic acids were obtained in high yields via metallation with BuLi followed by treatment with CO_2.

In our earlier studies of the reactivity of cyclopentadienylcarbonyliron complexes with σ-bonded ligands by the isotopic hydrogen exchange (IHE) technique, we discovered that in η^5-$C_5H_4(CO)_2Fe$-η^1-Ph (I) the H atoms of the cyclopentadienyl ligand undergo exchange under conditions favouring protophilic substitution (EtOD, EtONa) [1].

Continuing the investigation, we found that in complexes of similar structure, η^5-$C_5H_5(CO)_2Fe$-η^1-$C_5H_4Mn(CO)_3$ (II) and η^5-$C_5H_5(CO)_2Fe$-η^1-CH_2Ph (III), under the same conditions only those H atoms which were π-bonded to iron were exchangable. Apparently, the lack of hydrogen exchange in $C_5H_4Mn(CO)_3$ (complex II) is due to the passivating effect of the strong electron donor $C_5H_5(CO)_2Fe$ on protophilic hydrogen exchange.

Kinetic measurements have enabled us to evaluate the C–H acidity of the cyclopentadienyl ligands as a function of the nature of the σ-bonded ligand R. The IHE rate constants in a mixture of 10% EtONa, EtOD and benzene at 100°C are 1.0×10^{-5}, 2.1×10^{-6} and 4.0×10^{-7} s^{-1} for complexes I, II and III, respectively. The relative rate constants are 25/5/1.

From the above data it follows that the C–H acidity of the cyclopentadienyl ligands in I–III is rather high: it is close to that of the methyl hydrogen atom in Ph_3CH ($pK_a = 29$) for I (R = Ph) and to the C–H acidity of the methyl hydrogen atoms in Ph_2CH_2 ($pK_a = 30$) for II (R = $C_5H_4Mn(CO)_3$) and for III (R = CH_2Ph) [2].

On the basis of the results of the investigation, we carried out metallation of complexes I and II at the cyclopentadienyl ring and demonstrated the possibility of using this reaction for the synthesis of complexes substituted in the Cp-ring of $XC_5H_4(CO)_2FeR$ [3].

TABLE 1

ELEMENTAL ANALYSIS, IR AND ^{1}H NMR SPECTRAL DATA AND OTHER CHARACTERISTICS OF η^5-$C_5H_4COOH(CO)_2Fe$-η^1-R

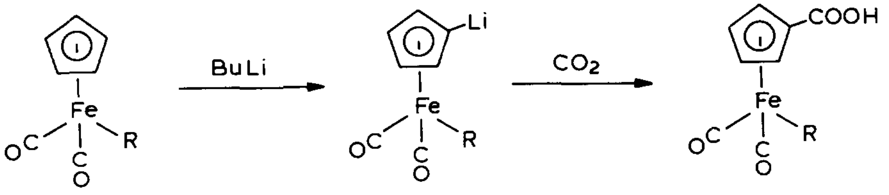
R	M.p. (°C)	Analyses (Found (calcd.) (%))			IR (CCl_4; $\nu(CO)$ cm^{-1})	^{1}H NMR ($(CD_3)_2CO$ rel. to TMS, σ ppm)	Yield (%)
		C	H	Fe			
Ph	112–113	56.23 (56.38)	3.17 (3.35)	18.26 (18.76)	ν(C=O) 1695 ν(C≡O) 1985 2033	5.24(t,2H,Cp) 5.55(t,2H,Cp) 6.81–7.00(m,3H,Ph) 7.36–7.45(m,2H,Ph)	63
$C_5H_4Mn(CO)_3$	146.5–147.5	45.22 (45.28)	2.34 (2.17)	13.10 (13.20)	ν(C=O) 1695 ν(C≡O) 1932 2000 2011 2035 2049	4.65–4.66(t,2H,CpFe) 4.89–4.91(t,2H,CpFe) 5.32–5.34(t,2H,Cp) 5.63–5.65(t,2H,Cp)	53
CH_2Ph	122–123	57.70 (57.69)	3.89 (3.85)	18.33 (17.94)	ν(C=O) 1693 ν(C≡O) 1972 2021	2.90(s,2H,CH_2) 5.10(t,2H,Cp) 5.44(t,2H,Cp) 5.86–7.21(m,5H,Ph)	67

TABLE 2

pK_a AND K_a VALUES FOR η^5-$C_5H_4COOH(CO)_2Fe$-η^1-R

R	pK_a	$K_a \times 10^{-6}$
Ph	5.07	8.5
$C_5H_4Mn(CO)_3$	5.09	8.1
CH_2Ph	5.29	5.1

In the present work, novel carboxylic acids, η^5-$C_5H_4COOH(CO)_2Fe$-η^1-R (IV, R = Ph; V, R = $C_5H_4Mn(CO)_3$ and VI, R = CH_2Ph), have been obtained in high yields by metallation of I–III followed by treatment with CO_2:



(I–III)

(IV–VI)

(I , R = Ph ,
II , R = $C_5H_4Mn(CO)_3$;
III , R = CH_2Ph)

(IV , R = Ph ;
V , R = $C_5H_4Mn(CO)_3$;
VI , R = CH_2Ph)

The fact that a carboxylic group is attached to the ligand π-bonded to the iron atom has been shown by the ^{1}H NMR spectra of IV–VI. The resulting acids IV–VI are yellow powders with the characteristics (m.p., elemental analysis, IR and ^{1}H NMR spectral data, etc.) presented in Table 1.

By potentiometric titration we estimated the strength of carboxylic acids IV–VI. The pK_a and K_a values for these acids in 50 vol.% aqueous ethanol are given in Table 2.

Under the same conditions, the pK_a of benzoic acid is 5.70 [4] and that of ferrocenecarboxylic acid 6.09 [4].

Thus the carboxylic acids obtained in this work proved to be 2–4 times stronger than benzoic acid and 6–10 times stronger than ferrocenecarboxylic acid.

Experimental

The complexes η^5-$C_5H_5(CO)_2Fe$-η^1Ph (I), η^5-$C_5H_4(CO)_2Fe$-η^1-$C_5H_4Mn(CO)_3$ (II) and η^5-$C_5H_5(CO)_2Fe$-η^1-CH_2Ph (III) were prepared as described earlier [5–7].

Hydrogen exchange in I–III was effected in sealed tubes in argon at 100°C. The molar ratio of the reactants was: complex/EtOD/EtONa/C_6H_6 = 1/80/8/45.

The results of the kinetic measurement are given in Table 3.

The content of D was determined by a drop technique according to the excessive density of combustion water or by a mass spectral technique.

The absence of hydrogen exchange in $C_5H_4Mn(CO)_3$ of complex II was demonstrated by cleaving the deuterated complex II with iodine at the Fe–C σ-bond and analysing the concentration of D in the resulting $C_5H_5(CO)_2FeI$.

TABLE 3

ISOTOPIC HYDROGEN EXCHANGE IN COMPLEXES I–III

Complex	Time (s)	% of equilibrium	$k \times 10^6$ (s^{-1})	$k_{aver} \times 10^6$ (s^{-1})	k_{rel}
I	4620	5.5	12		
	5700	5.0	9	10.5	25
	9000	15	7		
	11880	13	12		
II	8100	1.8	2.2		
	14520	3.7	2.6	2.1	5
	25500	4	1.5		
III	8760	0.3	0.4		
	27060	1.5	0.4	0.4	1
	32460	1.3	0.4		

Preparation of η^5-$C_5H_4COOH(CO)_2FeR$ *(R = Ph,* $C_5H_4Mn(CO)_3$ *and* CH_2Ph*).*

To 0.25 g (1 mmol) of η^5-$C_5H_5(CO)_2Fe$-η^1-Ph in dry THF was added at −78°C 3.5 ml (3–4 mmol) of 0.8–0.9 *N* n-BuLi solution in hexane. The reaction mixture was stirred for 15–20 min, poured onto solid CO_2 and the reaction continued for another 1–1.5 h while the temperature was gradually raised to room temperature. The solvent was removed in vacuo, the residue was dissolved in a small quantity of water, and the solution was filtered, followed by dropwise addition of concentrated HCl. The light-yellow precipitate was separated, precipitated again several times from the alkali solution with an acid and recrystallized from toluene. The product was η^5-$C_5H_4COOH(CO)_2$-Fe-η^1-Ph (0.18 g, 0.6 mmol); the characteristics of acid IV are given in Table 1.

Acids V and VI were prepared in the same way as IV.

IR spectra were taken with a Zeiss-UR 20 spectrometer and NMR spectra with a Bruker WP-200-SY instrument.

The pH-values of the solutions were measured by means of a pH-673 pH-meter. A 1×10^{-4} mol sample of the acid was dissolved in 50 ml of 50 vol.% aqueous ethanol and titrated with an alcohol solution of NaOH in nitrogen atmosphere. The pK_a values were calculated by the conventional formula. [8]. Table 2 reports the results averaged over three measurements. The r.m.s. error was ± 0.1.

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