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INTRAMOLECULAR ACYLATION OF (η^5-C_5H_4COCl)$(CO)_2FeCH_2Ph$. CRYSTAL STRUCTURE OF $(CO)_2Fe(\eta^5$-$C_5H_4COC_6H_4CH_2)$

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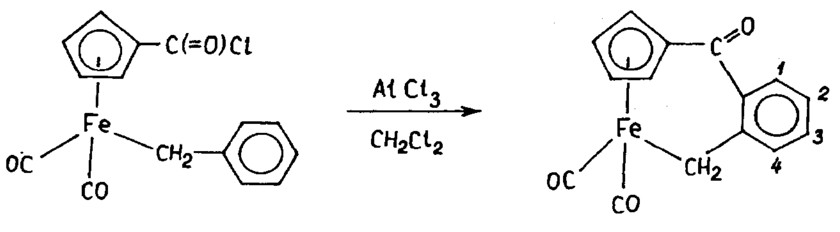
Summary

Treatment of $C_5H_4C(=O)Cl(CO)_2FeCH_2Ph$ with $AlCl_3$ in CH_2Cl_2 yields the cyclic complex $(CO)_2Fe(\eta^5$-$C_5H_4COC_6H_4CH_2)$ (II) as a result of intramolecular acylation of the phenyl ring of the σ-benzylic ligand. The structure of II was established by X-ray crystallography.

In the course of our previous investigation of the reactivity of the complexes $Cp(CO)_nMCH_2Ph$ where $n = 2$, M = Fe, $n = 3$, M = Mo or W by the hydrogen isotope exchange technique, we found the $Cp(CO)_nMCH_2$-substituent to have an extremely high activating ability with respect to hydrogen exchange in the phenyl ring under conditions favourable for electrophilic substitution [1,2]. On the basis of these results, and taking into account the work of A.N. Nesmeyanov et al. [3] in which the complex $Cp(CO)_2FeCH_2Ph$ was shown to undergo acylation into the phenyl ring under Friedel–Crafts conditions, one could expect intramolecular acylation of the phenyl ring by the C(=O)Cl substituent attached to the Cp ring.

In fact, it was found that the treatment of $C_5H_4C(=O)Cl(CO)_2FeCH_2Ph$ (I) with an equimolar amount of $AlCl_3$ in CH_2Cl_2 yields a metallocyclic complex in which the Cp ring and the phenyl ring are linked via a carbonyl group:



(I) (II)

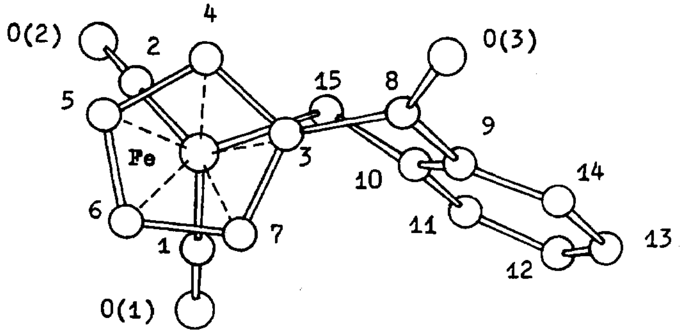
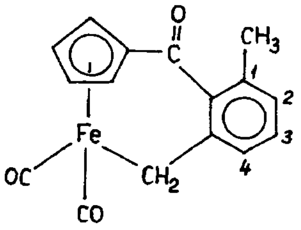
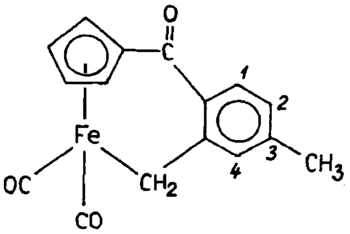


Fig. 1. Molecular structure of II (hydrogen atoms are omitted for clarity).

If the *meta*-methyl substituent is attached to the phenyl moiety of the σ-benzylic ligand, the acylation proceeds, with the formation of two isomeric metallocyclic ketones, III and IV:



(III)



(IV)

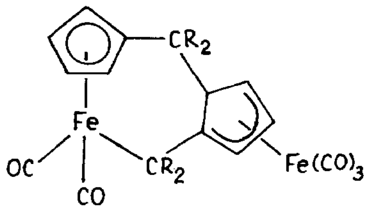
TABLE 1

GEOMETRY OF MOLECULE II

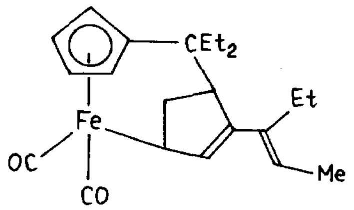
Bond distances (Å)					
Fe–C(1)	1.745(3)	O(2)–C(2)	1.144(3)	C(9)–C(10)	1.406(3)
Fe–C(2)	1.752(3)	O(3)–C(8)	1.218(3)	C(9)–C(14)	1.390(4)
Fe–C(3)	2.097(2)	C(3)–C(4)	1.407(4)	C(10)–C(11)	1.394(4)
Fe–C(4)	2.116(3)	C(3)–C(7)	1.419(4)	C(10)–C(15)	1.486(4)
Fe–C(5)	2.103(3)	C(3)–C(8)	1.494(3)	C(11)–C(12)	1.381(5)
Fe–C(6)	2.108(3)	C(4)–C(5)	1.421(4)	C(12)–C(13)	1.381(5)
Fe–C(7)	2.077(3)	C(5)–C(6)	1.390(5)	C(13)–C(14)	1.375(4)
Fe–C(15)	2.070(3)	C(6)–C(7)	1.426(4)		
O(1)–C(1)	1.134(3)	C(8)–C(9)	1.473(4)		
Bond angles (°)					
C(1)FeC(2)	93.0(1)	C(4)C(5)C(6)	109.0(3)	C(9)C(10)C(11)	117.1(3)
C(1)FeC(15)	87.5(1)	C(5)C(6)C(7)	107.8(3)	C(9)C(10)C(15)	121.4(2)
C(2)FeC(15)	87.8(1)	C(3)C(7)C(6)	107.6(3)	C(11)C(10)C(15)	121.1(3)
FeC(1)O(1)	178.6(3)	O(3)C(8)C(3)	119.8(2)	C(10)C(11)C(12)	121.6(3)
FeC(2)O(2)	178.5(3)	O(3)C(8)C(9)	123.5(2)	C(11)C(12)C(13)	120.5(3)
C(4)C(3)C(7)	108.1(2)	C(3)C(8)C(9)	116.7(2)	C(12)C(13)C(14)	119.4(3)
C(4)C(3)C(8)	127.8(3)	C(8)C(9)C(10)	118.8(2)	C(9)C(14)C(13)	120.5(3)
C(7)C(3)C(8)	124.1(2)	C(8)C(9)C(14)	120.3(2)	FeC(15)C(10)	113.9(2)
C(3)C(4)C(5)	107.5(3)	C(10)C(9)C(14)	120.9(3)		
Torsion angles (°)					
C(4)C(3)C(8)O(3)	53.9	0(3)C(8)C(9)C(14)	38.5		
C(7)C(3)C(8)C(9)	52.5	C(9)C(10)C(15)Fe	−62.5		
C(3)C(8)C(9)C(10)	41.8				

The structure of II, established by X-ray crystallography, is shown in Fig. 1 (geometric parameters are given in Table 1). The planar cyclopentadienyl (Cp) and the phenyl (B) rings form a dihedral angle of 76.6°, the keto group being non-coplanar with respect to both cycles (see Table 1). The Fe atom, located 1.72 Å away from the Cp plane, forms the common "piano stool" type arrangement with the Cp planes. Atoms C(8) and C(15) are tilted with reference to plane B by 0.05 and 0.21 Å (towards the Fe atom and in the opposite direction, respectively).

The length of the Fe–C(15) σ-bond, 2.070 Å, is close to the lower limit of Fe–C(sp^3) bond lengths (2.06–2.16 Å, mean value 2.11 Å [4]), and much shorter than that in complexes V (2.150 Å) [5], VI (2.096 Å), and VII (2.111 Å) [6] in which the Cp ring and σ-coordinated carbon are linked (as in II) by three-membered bridges.



(V, R = Me; VI, R = H)



(VII)

Experimental

The complexes $Cp(CO)_2FeCH_2Ph$ and $Cp(CO)_2FeCH_2C_6H_4Me$-*m* were obtained according to a known procedure [7]. Complex $C_5H_4C(=O)Cl(CO)_2FeCH_2Ph$ was prepared according to ref. 8. IR spectra were recorded on a Zeiss UR-20 spectrometer and ^1H NMR spectra on a Bruker WP-200-SY apparatus. The X-ray structural experiment was performed on a Enraf–Nonius CAD-4 automatic diffractometer (graphite monochromated Mo-K_α radiation) at room temperature. Calculations were done with a PDP-11/23 computer using programs as outlined in ref. 9.

Crystallographic data: $C_{15}H_{10}FeO_3$, monoclinic, space group $P2_1/c$, a 10.269(1), b 8.074(1), c 15.840(2) Å, β 102.25(1)°, V 1283.3 Å^3, $M = 294.4$ a.m.u., $Z = 4$, d_{calcd} 1.52 g cm^{-3}, μ(Mo-K_α) 11.7 cm^{-1}. Intensities of 2258 independent reflections with $\theta \leqslant 25°$ were measured by the θ/ω scan procedure (rate ratio 5/3) [10]. 1559 reflections with $I \geqslant 3\sigma$ were used in the calculations. The structure was solved by the direct method and refined by the full matrix least squares method (nonhydrogen atoms in anisotropic and all hydrogen atoms in isotropic approximations) up to $R = 0.025$, $R_w = 0.033$. Weighting scheme $w^{-1} = \sigma^2(F) + (0.02F_{meas})^2$. The final atomic parameters are given in Table 2.

Preparation of $(CO)_2Fe(\eta^5\text{-}C_5H_4COC_6H_4CH_2)$. $AlCl_3$ 0.17 g, (0.9 mmol) was added to $C_5H_4C(=O)Cl(CO)_2FeCH_2Ph$(I) 0.2 g, (0.9 mmol) in 30 ml CH_2Cl_2 on cooling with ice water (+5 to +10°C). The reaction mixture was stirred at this temperature for 4 h and then warmed to room temperature. The mixture was poured into water, extracted with ether, dried over Na_2SO_4, filtered, the ether was removed, and the residue was chromatographed on silica gel, eluting the product II with benzene. Yield 0.12 g (42%). After low-temperature crystallization from hexane the m.p. was 71–72°C. ^1H NMR (acetone-d_6, δ 2.05 ppm): 7.474 (dd, 1H, H_1, ^3J(HH)

TABLE 2

ATOMIC COORDINATES ($\times 10^4$, FOR Fe $\times 10^5$, FOR H $\times 10^3$) AND $B_{eq} = 1/3 \sum_{ij} B_{ij} a_i^* a_j^* (a_i a_j)$ (B_{iso} FOR H)

Atom	x	y	z	B (Å^2)
Fe	17099(3)	19558(4)	37938(2)	2.70(1)
O(1)	−291(2)	−578(3)	3686(2)	7.07(7)
O(2)	2106(2)	1223(3)	2076(1)	5.52(5)
O(3)	4617(2)	3488(3)	5976(1)	4.89(5)
C(1)	485(3)	435(4)	3727(2)	3.94(6)
C(2)	1955(3)	1534(3)	2753(2)	3.53(6)
C(3)	2676(3)	3285(3)	4885(2)	2.97(5)
C(4)	2860(3)	4121(3)	4140(2)	3.80(6)
C(5)	1578(3)	4544(4)	3649(2)	4.70(8)
C(6)	618(3)	4009(4)	4088(2)	4.63(7)
C(7)	1286(3)	3188(4)	4855(2)	3.64(6)
C(8)	3720(3)	2597(3)	5603(2)	3.14(5)
C(9)	3575(2)	850(3)	5833(2)	2.85(5)
C(10)	3185(2)	−313(3)	5166(2)	3.07(5)
C(11)	3027(3)	−1948(4)	5411(2)	4.61(7)
C(12)	3271(3)	−2413(4)	6269(2)	5.21(8)
C(13)	3698(3)	−1263(4)	6913(2)	4.54(7)
C(14)	3854(3)	362(4)	6694(2)	3.63(6)
C(15)	3101(3)	135(4)	4247(2)	3.60(6)
H(4)	369(2)	431(3)	399(2)	3.3(7)
H(5)	143(3)	511(4)	314(2)	5.3(7)
H(6)	−24(3)	406(4)	391(2)	5.9(7)
H(7)	93(2)	272(3)	527(2)	3.7(6)
H(11)	279(2)	−269(3)	501(2)	3.6(6)
H(12)	317(3)	−343(4)	645(2)	6.4(8)
H(13)	386(3)	−162(4)	751(2)	4.9(7)
H(14)	411(2)	123(4)	711(2)	4.2(6)
H(15)	390(2)	68(3)	413(2)	3.8(6)
H′(15)	293(3)	−81(4)	389(2)	5.3(7)

7.5 Hz, ^4J(HH) 1.5 Hz, Ph), 7.374 (td, 1H, H_2, ^3J(HH) 7.5 Hz, ^4J(HH) 1.6 Hz, Ph), 7.273 (dd, 1H, H_4, ^3J(HH) 7.5 Hz, ^4J(HH) 1.6 Hz, Ph), 7.151 (td, 1H, H_3, ^3J(HH) 7.5 Hz, ^4J(HH) 1.5 Hz, Ph), 5.285 (t, 2H, Cp-(H_α), $J(H_\alpha H_\beta)$ 2.2 Hz, Cp), 4.844 (t, 2H, Cp-H_β, $J(H_\alpha$-$H_\beta)$ 2.2 Hz, Cp), 2.567 (s, 2H, CH_2). IR (in hexane): ν 2030, 1980, 1685 cm^{-1}. Found: C, 62.07; H, 3.63; Fe, 18.77. $C_{15}H_{10}O_3Fe$ calcd.: C, 61.22; H, 3.40; Fe, 19.04%. MS: m/z 294 (M^+), 266 ($M^+ -$ CO), 238 ($M^+ -$ 2CO).

When, under the same conditions, $Cp(CO)_2FeCH_2C_6H_4Me$-*m* is used as starting material, a mixture of isomers III and IV is formed; in 45 and 55% ratio, according to ^{1}H NMR data. The isomers III and IV can be separated chromatographically on silufol in an ether/hexane mixture (1/1), the difference in R_f being 0.1. III: ^{1}H NMR (acetone-d_6): δ(ppm) 7.185 (t, 1H, H_3, ^3J(HH) 7.6 Hz), 7.052 (dd, 1H, H_4, ^3J(HH) 7.6, ^4J(HH) 1.2 Hz, Ph), 6.936 (dd, 1H, H_2, ^3J(HH) 7.6 Hz, ^4J(HH) 1.2 Hz, Ph), 5.286 (t, 2H, Cp-H_α, $J(H_\alpha H_\beta)$ 2.3 Hz, Cp), 4.796 (t, 2H, Cp-H_β, $J(H_\alpha H_\beta)$ 2.3 Hz, Cp), 2.478 (s, 2H, CH_2), 2.363 (s, 3H, CH_3). IV: ^{1}H NMR (acetone-d_6): δ(ppm) 7.382 (d, 1H, H_1, ^3J(HH) 7.7 Hz, Ph), 7.093 (s, 1H, H_4, Ph), 6.991 (dd, 1H, H_2, ^3J(HH) 7.7 Hz, Ph, ^4J(HH) 1.0 Hz, Ph), 5.264 (t, 2H, Cp-H_α, $J(H_\alpha H_\beta)$ 2.1 Hz, Cp), 4.826 (t, 2H, Cp-H_β, $J(H_\alpha H_\beta)$ 2.1 Hz, Cp), 2.535 (s, 2H, CH_2), 2.328 (s, 3H, CH_3). IR (in methylene chloride): ν 2020, 1965, 1670 cm^{-1}. MS: m/z 308 (M^+), 280 ($M^+ - CO$), 252 ($M^+ - 2CO$).

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