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COMPLEXATION OF CYCLOPHANES WITH THE (η^5-CYCLOPENTADIENYL)IRON$^+$ MOIETY

II *. SYNTHESIS AND CHARACTERIZATION OF [3—8-η-5,13-DIMETHYL[2.2]METACYCLOPHANE-(η^5-CYCLOPENTADIENYL)IRON]$^+$[PF_6^-] AND [3—8-η-;11—16-η-5,13-DIMETHYL[2.2]METACYCLOPHANE-[(η^5-CYCLOPENTADIENYL)IRON]$_2$]$^{2+}$[PF_6^-]$_2$ **

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Summary

The syntheses of the title compounds by the $AlCl_3$-catalyzed ligand exchange reaction between ferrocene and 5,13-dimethyl[2.2]metacyclophane are reported. The species have been characterized by elemental analysis and ^{1}H- and ^{13}C-NMR spectroscopy.

A previous paper [1] dealt with some aspects of a study of the complexation of [2.2]paracyclophane with the (η^5-cyclopentadienyl)iron$^+$ fragment [2]. In that study the $AlCl_3$-catalyzed ligand exchange reaction between ferrocene and a metacyclophane, namely 5,13-dimethyl[2.2]metacyclophane, was investigated. The resulting mono- and dications were characterized as PF_6 salts. Both compounds are air-stable, crystalline solids. They are very soluble in polar organic solvents such as acetone, acetonitrile and nitromethane and I is also soluble in dichloromethane. ^{1}H and ^{13}C NMR spectra were used to establish the molecular structure of the two compounds [3], and the data are presented in Tables 1 and 2. Recently Langer and Lehner investigated the ring current contribution to the ^{1}H NMR chemical shifts of the $Cr(CO)_3$ complexes of cyclophanes [4],

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* For part I see ref. 1.

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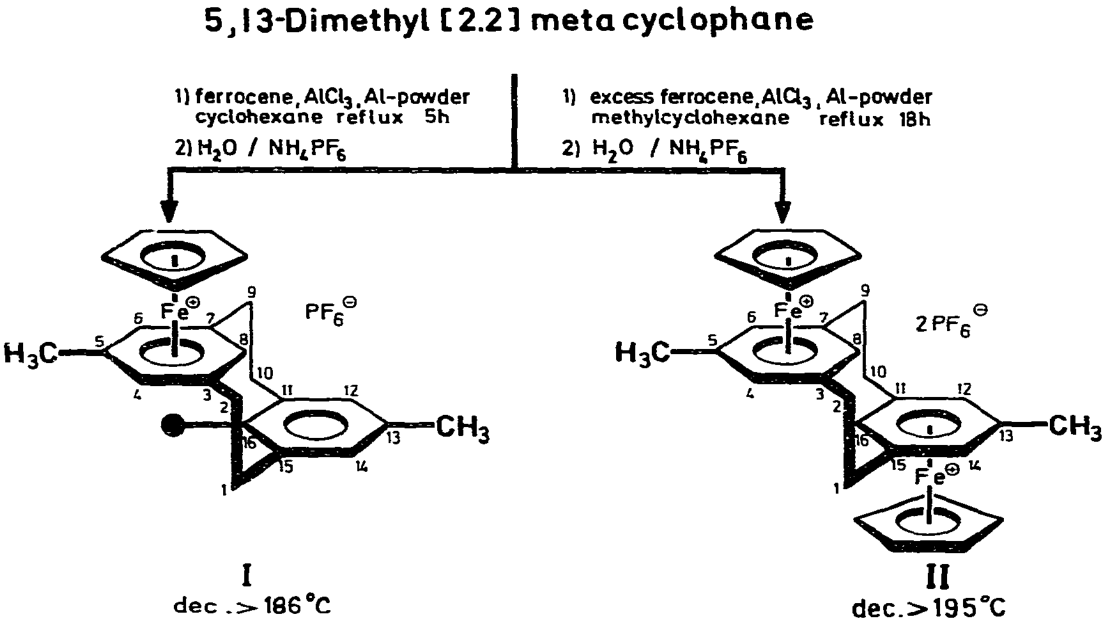

I
dec. > 186 °C

II
dec. > 195 °C

Fig. 1.

and chose, along with others, the complex of 5,13-dimethyl[2.2]metacyclophane as a model compound in which the "monitor proton" (H16)) is not directly bound to an arene moiety but is in close proximity to it. Moreover the compound incorporates a proton which can be used for monitoring the preser-

TABLE 1

^{1}H NMR DATA (360 MHz; δ, ppm rel. int. TMS)

Compound	Cp	Complexed ring	Uncomplexed ring	CH_3	$—CH_2—$[a]	Assignment
I[b]	4.88 (s; 5H)	5.78(s; H(4), H(6)) 2.78(s; H(8))	6.99(s; H(12), H(14)) 4.52(s; H(16))	2.58	3.26	2 eq. H adjacent to the complexed ring
				(s; 3H)	3.02	2 eq. H adjacent to the uncomplexed ring
				2.41 (s; 3H)	2.12	4 ax. H
II[c]	4.74 (s, 10H)	5.93(s; H(4), H(6), H(12), H(14)) 3.59(s; H(8), H(16))	—	2.59	3.15	4 eq. H
				(s; 6H)	2.14	4 ax. H
DMMC[d]	—	—	6.89(s; 4H) 4.10(s; 2H)	2.34	3.01	4 eq. H
				(s; 6H)	2.08	4 ax. H

[a] Centre of the multipletts. [b] Recorded in CD_2Cl_2. [c] Recorded in acetonitrile-d_3. [d] DMMC = 5,13-dimethyl-[2.2]metacyclophane.

TABLE 2

^{13}C NMR DATA [a] (80 MHz; δ, ppm rel. int. TMS)

Compound	Cp	Complexed ring	Uncomplexed ring	CH_3	$—CH_2—$
I	76.17	84.02(C(8)) 86.86(C(6); C(4)) 100.05(C(5)) 108.92(C(7); C(3))	128.25(C(16)) 137.57(C(12), C(14)) 139.11(C(13)) 142.00(C(11), C(15))	20.68 (at C(5)) 21.59 (at C(13))	38.59 C(2), C(9)) 39.68 (C(1), C(10))
II	76.83	84.97(C(8), C(16)) 87.15(C(6), C(4), C(11), C(15)) 101.64(C(5), C(13)) 108.408(C(3), C(7)) C(11), C(15))	—	20.66	36.48
DMMC	—	—	127.02(C(4), C(6)) 135.04(C(8)) 139.25(C(5)) 140.16(C(3), C(7))	21.45	41.60

[a] Recorded in acetonitrile-d_3.

vation of geometry on complexation (H8)). Thus shielding or deshielding contributions were reliably assessed experimentally, and in this way the ring current disrupture hypothesis, which has been discussed by several authors [5] was verified. This approach can also be used for the monocation I, which possesses the same general geometric features as its $Cr(CO)_3$ analogue. The "monitor proton" (H(16)) is significantly shifted to lower field when compared with the free ligand ($\Delta\delta = 0.42$) whereas H(8), still under the influence of the ring current shielding of the uncomplexed ring, is shifted to even higher field due to the complexation of the adjacent ring. This is clearly reflected in a chemical shift difference for H(8) compared to the other protons of the same ring ($\Delta\delta_{4,8} = 3.0$). The shift difference $\Delta\delta_{12,16} = 2.47$ shows the shielding influence of the (η^5-cyclopentadienyl)(η^6-arene)Fe^+ moiety on the protons of an uncomplexed arene. The decrease of this value compared with that for the free ligand indicates that there is a small attenuation of the ring current shielding for a proton located above the plane of an aromatic ring, which is complexed with a (η^5-C_5H_5)Fe^+ unit. Thus the ring current disrupture hypothesis is again verified.

Other features of the ^{1}H NMR spectra are consistent with the spectra of analogous complexes. A significant upfield shift for the protons of the complexed arene ring is observed while the adjacent methyl and methylene protons show a downfield shift compared with the free ligand. I is also of interest from another point of view; in that it offers the possibility of the relative assignment of the two different methyl groups and the adjacent aromatic *ortho* protons by a nuclear Overhauser experiment. Thus if one methyl signal is irradiated an intensity increase for the corresponding aromatic signal should be observed. As can be seen from Fig. 2 the methyl signal at lower field comes from the methyl group of the complexed arene ring whereas the signal at higher field comes from the methyl group on the uncomplexed ring [6].

In the ^{13}C NMR spectra the C_5H_5 resonances were readily assigned to the most intense signals. The quaternary carbon atoms were recognizable by the lack of

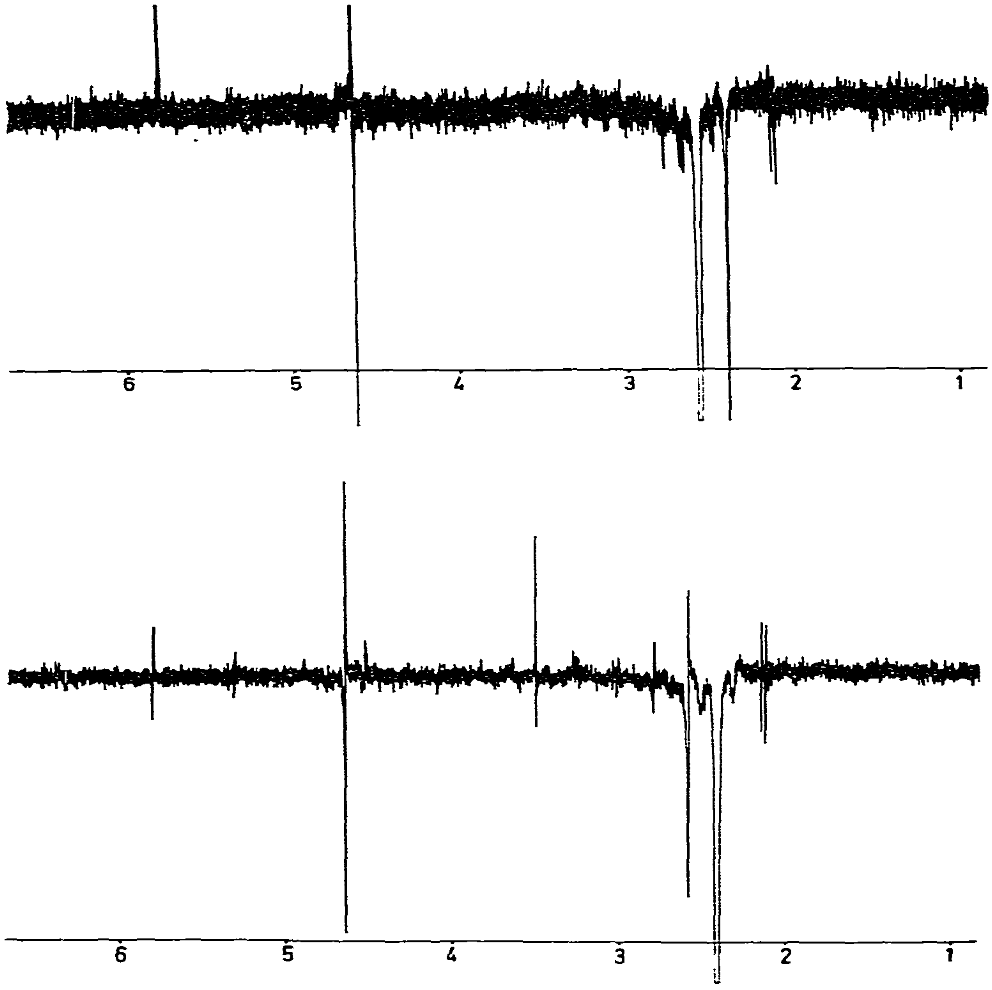

Fig. 2.

nuclear Overhauser enhancement. C(8) and C(16) were assigned by intensity considerations, their resonances being almost half as intense as those of C(4) and C(6) (or C(12) and C(14)). Other assignments were made on the basis of the literature data for analogous complexes [7].

Experimental

(a) Preparation of I by thermal reaction

A mixture of ferrocene (750 mg; 4 mmol), 5,13-dimethyl[2.2]metacyclophane (940 mg; 4 mmol), powdered anhydrous $AlCl_3$ (1 g; 7.6 mmol), Al powder (108 mg; 4 mmol) and cyclohexane (60 ml) was refluxed for 11—12 h under N_2 with rapid stirring. The mixture was cooled and (still under N_2) carefully hydrolyzed with 80 ml of ice water. Solids were filtered off and the aqueous layer was separated, washed with cyclohexane (5 × 50 ml), and filtered into a concentrated aqueous solution of NH_4PF_6 ($\approx$2.5 g in a few ml). The product separated immediately as a yellow-orange powder. It was filtered off, sucked dry, and purified by preparative TLC with 3/7 acetone/dichloromethane as eluant: 1.43 g (72%) were obtained. Recrystallisation from ethanol gave well-shaped, yellow crystals, dec. 186°C. (Found: C, 54.89; H, 5.28; P, 6.38; Fe, 10.87. $C_{23}H_{25}F_6FeP$ calcd.: C, 55.0; H, 5.0; P, 6.2; Fe, 11.1%).

(b) Preparation of I by the photochemical exchange reaction

A degassed solution of (η^6-*p*-xylene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate (372 mg; 1 mmol) and 5,13-dimethyl[2.2]metacyclophane (1.19 g; 5 mmol) in dry dichloromethane (100 ml) was irradiated with visible light (Osram reflector flood lamp, 150 W) for about 4 h. The mixture was filtered and the solvent was removed under reduced pressure. The resulting solid was washed repeatedly with hot cyclohexane to remove the unreacted cyclophane. 1.61 g (81%) of I was obtained, and was recrystallisized from ethanol.

(c) Preparation of II

A mixture of ferrocene (5.58 g; 30 mmol), 5,13-dimethyl[2.2]metacyclophane (354 mg; 1.5 mmol), $AlCl_3$ (20.0 g; 150 mmol) and Al powder (1.35 g; 50 mmol) in methylcyclohexane (75 ml) was refluxed for 18—20 h under N_2 with rapid stirring. The work up was as described above for I (a)) but purification by TLC was unnecessary. Reprecipitation from acetone/ether gave analytically pure II, which has a curry-yellow colour. A yield of 990 mg (86%) was obtained, dec. 195°C. (Found: C, 43.78; H, 3.96; P, 8.34; Fe, 14.47. $C_{28}H_{30}F_{12}Fe_2P_2$ calcd.: C, 43.78; H, 3.94; P, 8.06; Fe, 14.54%).

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References

1 Part I, see: A.R. Koray, J. Organometal. Chem., 212 (1981) 233.
2 Boekelheide et al. independently described the same mono- and dicationic complexes of [2.2]paracyclophane. Their synthesis of the monocation involved the photochemical exchange between the cyclophane and (η^6-*p*-xylene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate in dichloromethane using visible light: E.D. Laganis, R.G. Finke and V. Boekelheide, Proc. Natl. Acad. Sci. USA 78 (1981) 2657. When this method was used with 5,13-dimethyl[2.2]metacyclophane, the corresponding monocation was isolated in a slightly better yield than from the $AlCl_3$-catalyzed thermal ligand exchange reaction.
3 An X-ray structural analysis of I is in progress.
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6 This is exactly the opposite of the observations by Langer and Lehner. Therefore it seems advisable to carry out a NOE study of the $Cr(CO)_3$ complex of 5,13-dimethyl[2.2]metacyclophane, in order to assign the methyl groups correctly.

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