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COMPLEXATION OF [2.2]PARACYCLOPHANE WITH AN (η^5-CYCLOPENTADIENYL)IRON$^+$ MOIETY: MONO- AND DI-CATIONS

ALI R. KORAY

Max-Planck-Institut für medizinische Forschung, Abteilung Organische Chemie, Jahnstr. 29, D 6900 Heidelberg 1 (B.R.D.)

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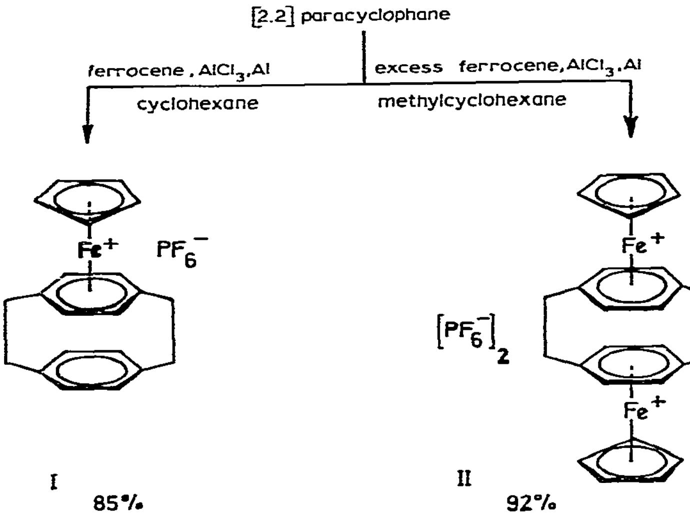
Summary

The reaction of [2.2]paracyclophane with ferrocene in the presence of $AlCl_3$ and Al/powder gives the new compounds [1-6-η-[2.2]paracyclophane-(η^5-cyclopentadienyl)iron]$^+$[PF_6] and [1-6-η; 9-14-η-[2.2]paracyclophane-[(η^5-cyclopentadienyl)iron]$_2$]$^{2+}$[PF_6]$_2$ in high yields. The species have been characterized by elemental analysis, and by ^1H and ^{13}C NMR spectroscopy.

After the discovery by Nesmeyanov and coworkers [1], that one of the cyclopentadienyl rings of ferrocene can be replaced by an arene ring in the presence of $AlCl_3$ and Al, a wide range of complexes of the type [(η^6-arene)-(η^5-cyclopentadienyl)iron]$^+X^-$ has been prepared, where X is usually PF_6 or BF_4 [2]; in certain polycyclic systems both mono- and di-substitution could be effected [3]. During the past few years cyclophanes have come to be seen by organometallic chemists as an interesting new class of π-ligands. Most of the work done on this aspect of their chemistry involves $Cr(CO)_3$ complexes [4], but recently the introduction of a chromium atom into the cavity of a paracyclophane molecule by the "metal atom technique" has offered new possibilities. This led to the synthesis of [η^{12}-[2.2]paracyclophane]chromium [5] and [η^{12}-[3.3]paracyclophane]chromium [6]. The latter was characterized by, among other methods, an X-ray structure analysis of its I_3^- and PF_6^- salts [7]. It was thus of interest to know what would happen when Nesmeyanov's procedure was applied to the [2.2]paracyclophane system. Some difficulty could arise due to the $AlCl_3$-catalyzed isomerisation of this compound to the [2.2]-metaparacyclophane [8]. The actual result was that both the mono- and di-cation I and II were obtained in very high yields.

Both compounds are air-stable, crystalline solids, which are very soluble in acetone, acetonitrile and nitromethane. The solutions on exposure to air for some hours undergo some decomposition. The elemental analyses for I and II



are in excellent agreement with the calculated values (see Experimental section). Conclusive proof of their structures was obtained from the ^1H and ^{13}C NMR spectra, which are presented in Table 1 and 2. X-ray structural studies are in progress.

It can be clearly seen from the NMR data that no isomerization of [2.2]paracyclophane occurred, only a sharp singlet for both the protons of the complexed and the uncomplexed ring is found in the ^1H NMR spectrum of each of I and II. The ^{13}C resonances are also consistent with a paracyclophane structure. Another characteristic feature of the NMR spectra is the upfield shift for the protons of the complexed rings compared with those for free paracyclophane and the downfield shift for the cyclopentadienylresonance compared with that for ferrocene. The ^1H resonances for the uncomplexed aromatic ring and the adjacent methylene groups of I show a slight upfield shift (0.21 and 0.04 ppm). The ^{13}C resonances for the same part of this molecule (aromatic, quarternary and methylene carbons), however, are all shifted slightly to higher field.

II can also be regarded as a "pseudo four-decker sandwich", with the second and third "slices" held together by two ethylene bridges instead of one metal atom.

TABLE 1

^1H NMR DATA [a] (δ, ppm rel. int. TMS)

Compound	Cp	Complexed ring	Uncomplexed ring	$-CH_2-$
I	4.84 (s; 5 H)	5.78 (s; 4 H)	6.71 (s; 4 H)	3.14 (m; 8 H)
II	4.93 (s; 5 H)	5.98 (s; 8 H)	—	3.26 (s; 8 H)
PC [b]	—	—	6.50 (s; 8 H)	3.10 (s; 8 H)

[a] Recorded in acetone-d_6. [b] PC = [2.2]paracyclophane.

TABLE 2

^{13}C NMR DATA (δ, ppm rel. int. TMS)

Compound	Cp	Complexed ring	Uncomplexed ring	—CH_2—
I [a]	69.67	79.12; 114.48 *	129.48; 135.28 *	28.07; 29.72
II [a]	70.63	79.63; 114.74 *	—	25.31
PC [b]	—	—	133.07; 139.62 *	35.67

[a] Recorded in acetone-d_6. [b] Recorded in $CDCl_3$. Absorptions marked with asterisk are due to quaternary carbons.

The complexation of some other para- and meta-cyclophanes with the (η^5-cyclopentadienyl)iron$^+$ unit as well as the organic chemistry of the complexed aromatic rings in these compounds is under active investigation.

Experimental

a) Preparation of I

A mixture of ferrocene (750 mg; 4 mmol), [2.2]paracyclophane (850 mg; 4 mmol), powdered anhydrous $AlCl_3$ (1 g; 7.6 mmol), Al powder (108 mg; 4 mmol), and 60 ml of cyclohexane was refluxed for 11—12 h under N_2 with rapid stirring. The mixture was cooled and (still under N_2) carefully hydrolyzed with ~60 ml of ice water. Solids were filtered off and the aqueous layer was separated, washed with cyclohexane (5 × 40 ml), and filtered into a concentrated aqueous solution of NH_4PF_6 (~2 g in a few ml). I separated immediately as an orange-brown powder. It was filtered off, sucked dry, and purified by preparative TLC with 1/3 acetone/dichloromethane as eluant: 1.65 g (85%) were obtained. Recrystallisation from acetone/light petroleum gave orange needles, dec. 187°C. (Found: C, 53.32; H, 4.28; P, 6.37; Fe, 11.65. $C_{21}H_{21}F_6FeP$ calcd.: C, 53.32; H, 4.46; P, 6.53; Fe, 11.78%).

b) Preparation of II

A mixture of ferrocene (5.58 g; 30 mmol), [2.2]paracyclophane (312 mg, 15 mmol), $AlCl_3$ (20.0 g; 150 mmol) and Al powder (1.35 g; 50 mmol) in 60 ml of methylcyclohexane was refluxed for 18—20 h under N_2 with rapid stirring. The work up was as described above for I, but purification by preparative TLC was unnecessary. Reprecipitation from acetone/pentane gave analytically pure II, which has a pale orange-yellow colour. A yield of 1.1 g (92%) was obtained. dec. 197°C. (Found: C, 42.35; H, 3.65; P, 8.12; Fe, 15.20. $C_{26}H_{26}F_{12}Fe_2P_2$ calcd.: C, 42.19; H, 3.54; P, 8.37; Fe, 15.09%).

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