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Synthesis of ferrocenyl derivatives of anthracene

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Abstract

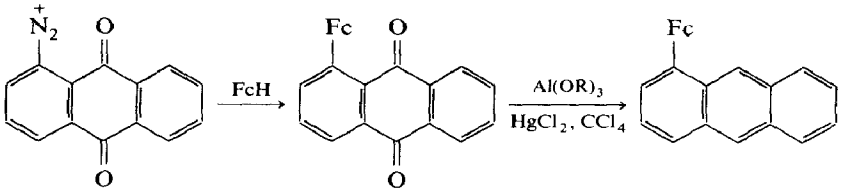
1-Ferrocenylanthraquinone has been synthesised from the cheap and commercially available 1-diazoniumanthraquinone (Aldrich Fast Red Al salt). Reduction of this anthraquinone with aluminium alkoxide has given good yields of 1-ferrocenylanthracene, the first preparation of such polycyclic ferrocenes. The TCNE adduct of the anthracene was prepared in good yield, in marked contrast to the outcome of the redox reaction of ferrocene itself with TCNE. No oxidation was observed with TCNQ. Diels–Alder addition of benzyne resulted in a very low yield (~ 1%) of 1-ferrocenyltriptycene. The ^{1}H and ^{13}C NMR spectra are reported, and discussed in detail together with ^{57}Fe Mössbauer data.

Introduction

The synthesis of ferrocenyl derivatives of polycyclic aromatic hydrocarbons has received little attention. Charge transfer complexes of 1-ferrocenylnaphthalene with CBr_4 have been reported [1], and studies of the structure and properties of 1,8-diferrocenylnaphthalene have recently been described [2–4]. The corresponding anthracenes have been entirely neglected. This paper describes the first synthesis of these potentially interesting polycyclic derivatives, together with the results of a study of their structure and reactivity.

Results and discussion

1-Ferrocenylanthraquinone (1-FcAnQ) was prepared in 45% yield from the commercially available 1-diazoniumanthraquinone salt, Fast Red Al salt (Aldrich ~ 20% diazonium salt content). This dark blue derivative was converted into the corresponding anthracene (1-FcAnH) in 62% yield by the method of Gaylord and Stepan [5] (eq. 1).

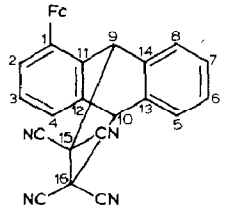


(1)

1-FcAnH underwent a facile Diels–Alder addition with ethenetetracarbonitrile (tetracyanoethylene, TCNE) to form 1-ferrocenyl-9,10-dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarbonitrile (1-FcAnH-TCNE) in 69% yield. This is in direct contrast to the outcome of the reaction of ferrocene with TCNE, in which a redox reaction occurs, to give a ferricinium-TCNE salt [6]. This suggests that the anthracenyl substituent increases the Fc/Fc^+ redox potential. Supporting this is the observation that no oxidation was obtained with 2,5-cyclohexadiene-Δ-1α-4α'-dimalononitrile(7,7,8,8-tetracyanoquinodimethane, TCNQ), which again functions as an oxidant for ferrocenes [7]. In this case no Diels–Alder addition was observed. This lack of oxidation may also be due to the difficulty of approach of the oxidant to the iron centre. Benzyne addition to 1-FcAnH by the modified [8] Friedman and Logullo method resulted in a very low yield ($\sim$ 1%) of 1-ferrocenyl triptycene.

^1H and ^{13}C NMR spectroscopies

The numbering of the derivatives of based on that of anthracene itself, viz. for 1-FcAnH-TCNE:



Primes are used to denote the ferrocenyl carbon atoms. The assignments of ^{13}C shifts of 1-FcAnQ can be made by reference to other 1-substituted anthraquinones. Berger et al. [9] have made a detailed study of substituent effects in these derivatives and found reasonably good correlations between the C(1), C(2), and C(4) shifts of the anthraquinones and those of the corresponding carbons in monosubstituted benzenes. There was, however, an error in the signs used in their equations, which should read:

$$\delta(C1) = 1.039\delta(C_6H_5X) - 5.941$$

$$\delta(C(2)) = 1.118\delta(C_6H_5X) - 6.815$$

$$\delta(C(4)) = 1.215\delta(C_6H_5X) - 27.629$$

By use of these correlations and the chemical shift data for phenylferrocene [10], values for C(1), C(2) and C(4) of 138.9, 134.4 and 126.2 ppm were calculated. However, examination of the ^{13}C spectrum of 1-FcAnQ revealed major discrepancies. C(1) was found to be at 142.1 ppm and C(2) at 139.4 ppm. This clearly indicates that the ferrocenyl substituent is not exerting its normal shielding effects on the aromatic ring. Examination of molecular models leads to the conclusion that

there are strong steric interactions between the α-hydrogens of the substituted cyclopentadienyl (Cp) ring and the carbonyl oxygen at C(9). The most stable conformation appears to be one in which the substituted Cp plane lies at a dihedral angle of between 50 and 60° to the plane of the benzene ring to which it is attached, the unsubstituted Cp ring being directed away from the central carbonyl group. Such a rotation would bring C(2) within the deshielding zone of the ferrocene nucleus (for a description of the anisotropy of ferrocene see the paper by McGuire et al. [11], and references therein). This would account for the observed downfield shift of the the C(2) resonance. It is noteworthy that the two carbonyl carbons are magnetically non-equivalent.

The geometry of 1-FcAnH is likely to be similar to that of 1-FcAnQ, with a comparable twist of the ferrocenyl substituent out of the plane of anthracene. The chief feature of interest of the ^{1}H spectrum is the large difference ($\Delta\delta$) in the shifts of the H(9) and H(10) signals (0.84 ppm) compared with the corresponding shifts for 1-MeAnH [12] and 1-PhAnH [13] (0.12 and 0.06 ppm, respectively). If it is assumed that the above geometry obtains, H(9) should be in the shielding zone of the neighbouring Fc group. The observed deshielding (δ 9.24 ppm) is, I suggest due to a direct field effect of the Cp rings. Some evidence supporting this type of interaction comes from an examination of the ^{1}H and ^{13}C NMR spectra of 1-MeAnH [12]. Here the H(9) proton is deshielded relative to H(10), whereas the reverse is true of the C(9) and C(10) resonances, indicating a polarisation of the C–H bond electrons towards the carbon. As with 1-FcAnQ, C(2) should now be deshielded by the ferrocenyl anisotropy. The downfield resonance at 131.4 ppm is assigned to this carbon since it is difficult to make a logical case for assigning it to any of the other carbons (possessing a hydrogen) in the anthracene framework. Complete assignment of the ^{13}C spectrum is not easy, since many of the resonances lie in a very narrow spectral range. The assignments quoted in the experimental section should therefore be treated with caution. They are based mainly on a comparison with data for other 1-substituted anthracenes [12].

Both the ^{1}H and ^{13}C NMR spectra of 1-FcAnH-TCNE reveal some interesting features. The proton shifts of H(9) and H(10) are markedly different (5.64 and 5.12 ppm, respectively). The assignment was made by reference to the TCNE adduct of anthracene itself where $\delta(H(9)) = \delta(H(10))$ has a value of 5.21 ppm. Models indicate that there are somewhat lower steric compressions between the Fc group and the bridgehead hydrogen at C(9), resulting in a smaller dihedral angle. However, H(9) should again be shielded by the neighbouring Cp ring anisotropy, but it is not. A steric/direct field effect is again the most likely explanation. Support comes from the ^{13}C spectrum where the chemical shifts of C(9) and C(10) are markedly different (49.6 and 53.2 ppm, cf. 53.1 ppm for AnH-TCNE). This provides further evidence for the polarisation of the CH bond electrons towards C(9). By similar arguments to those used for 1-FcAnQ and 1-FcAnH, the peak at 132.2 ppm is assigned to C(2), and represents deshielding due to the anisotropy of the neighbouring ferrocene group. Assignments of the remaining tertiary carbons are relatively straightforward in this case. The bridge carbons are non-equivalent, though no difference was found for the nitrile carbons. The effect of the twisted conformation is also manifest in the magnetic non-equivalence of the α-hydrogens (H(2′,5′)) of the substituted Cp ring. This is probably due to the approach of one of these hydrogens to the deshielding zone of one of the CN groups (on C(15)) in the bridge.

The ^{1}H spectrum of 1-ferrocenyltriptycene showed similar non-equivalence of H(9) and H(10), the observed shifts being 6.35 and 5.86 ppm respectively.

Mössbauer spectroscopy

Isomer shifts (*IS*) for 1-FcAnQ, I-FcAnH and 1-FcAnH-TCNE were identical within experimental error. The quadrupole splittings (*QS*) were also identical, being somewhat lower than that for ferrocene (2.38 mm s^{-1}) [10] but higher than that for phenylferrocene [10]. This is the expected result for arene substituents with appreciable dihedral angles between the arene and Cp planes, since conjugate electron withdrawal is markedly reduced.

Experimental

^{1}H NMR spectra were recorded on a Jeol PMX 60SI NMR spectrometer: (s, singlet; t, triplet;, m, multiple and ^{13}C NMR spectra on a Bruker WP80 FT instrument, q, quaternary carbon). Mössbauer data were obtained and fitted as previously described [14].

Anthracene-TCNE adduct

A solution of a mixture of anthracene (0.9 g 5.0 mmol) and TCNE (0.7 g 5.5 mmol) in CH_2Cl_2) (100 ml) was kept overnight. The initial blue colour gradually faded to give a nearly colourless final solution. This was evaporated, and the residue washed with a little CH_2Cl_2 to give an almost quantitative yield of the adduct. ^{1}H NMR ($CDCl_3$ δ ppm) 5.21s (2H), 6.8–7.3m (8H), ^{13}C NMR (acetone-d_6, ppm rel TMS) 47.6 (C(15,16)), 53.1 (C(9,10)), 112.6 (CN), 127.8 (C(2,3,6,7)), 130.2 (C(1,4,5,8)).

1-Ferrocenylanthraquinone

A stirred solution of ferrocene (3.7 g, 19.8 mmol) in dry CH_2Cl_2 was treated in portions with Aldrich Fast Al Red Salt (10 g, 7.4 mmol 1-diazoniumanthraquinone). Almost immediately N_2 was evolved. The mixture was kept overnight, then filtered and evaporated, to give a blue-black solid. Chromatography on neutral alumina, with hexane as eluent, gave first unchanged ferrocene then a dark blue band which yielded 1.3 g (45% based on 1-diazoniumanthraquinone) of 1-ferrocenylanthraquinone as dark blue solid MP 188–190 °C (uncorr.). UV (Et_2O): λ_{max} 544 nm, ϵ 1190. Analysis: Found: C, 73.8; H,4.1. $C_{24}H_{16}FeO_2$ calc.: C, 73.5; H, 4.1%.

^{1}H NMR (60 MHz, $CDCl_3$, ext TMS δ(ppm): 4.23s, (5H); 4.57m, (4H); 7.84m, (3H); 8.30m, (4H). ^{13}C-{H^1} NMR (80 MHz, $CDCl_3$, ext TMS). 68.3 (C(2′,5′)), 69.8 (Cp), 70.8 (C(3′,4′)), 87.3 q (C(1′)), 126.2 (C(4)), 126.6 (C(8)), 127.1 (C(5)), 131.6 (C(3)), 133.2 (C(7)), 134.7 (C(6)), 139.4 (C(2)), 132.7, 135.3 both q, 142.1 q (C(1)), 183.1, 183.5 (CO) both q. The signals of the remaining quaternary cabons are masked by other resonances. Mössbauer data: IS 0.52(1), QS 2.33(1), Γ (width at half height) 0.16(1) all in mms^{-1}.

1-Ferrocenylanthracene

1-FcAnQ was reduced to 1-ferrocenylanthracene by the method of Gaylord and Stepan [5]. A mixture of $HgCl_2$ (48 mg, 0.17 mmol), CCl_4 (1 ml), Al turnings (2.0 g,

0.074 g. atoms) and cyclohexanol (40 ml) was heated cautiously until a vigorous reaction set in. When the initial reaction had subsided, the mixture was refluxed until all the Al had reacted (2 h). 1-FcAnQ (2 g, 5.1 mmol) was added in portions and the mixture refluxed for a further $2\frac{1}{2}$ h, then cooled and added to ice-cold 2*N* aqueous HCl. The mixture was extracted with CH_2Cl_2 to yield an orange-red oil. Chromatography on neutral alumina (elution with Et_2O) followed by evaporation, gave a red oil, which on trituration with MeOH gave 1.1 g (62%) of 1-ferrocenylanthracene, m.p 125–127°C, as a red-orange solid. Analysis. Found: C, 79.4; H, 5.1. $C_{24}H_{18}Fe$ calcd.: C, 79.6; H, 5.0%. ^1H NMR ($CDCl_3$): δ 4.24s (5H), 4.46t (2H), 4.76t (2H), 7.1–8.1m, (7H), 8.40s (1H), 9.24s (1H); ^{13}C-({H^1} NMR ($CDCl_3$); 68.3 (C(2′,5′)) 69.7 (Cp), 70.4 (C(3′,4′)), 87.4 q (C(1′)), 124.9 (C(9)), 125.3 (C(6,7)), 125.6 (C(3)), 126.7 (C(4)), 127.1 (C(10)), 127.3 (C(5)), 127.9 (C(8)), 131.4 (C(2)), 126.3, 128.8, 130.5, 132.3 all q (C(11–14)), 136.1 q (C(1)). Mössbauer data: IS 0.50(1), QS 2.35(1), *Γ* 0.13(1) all in mms^{-1}.

1-Ferrocenylanthracene-TCNE adduct

1-FcAnH (0.35 g, 0.97 mmol) and TCNE (0.16 g, 1.25 mmol) were dissolved in dry CH_2Cl_2 (10 ml). The original deep-red colour became progressively lighter. After 5 h standing at room temperature the solution was evaporated to give a sticky solid. Trituration with a small quantity of MeOH gave an orange-brown product, which when washed with a little cold methanol gave 0.33 g (69%) of a yellow solid, m.p. 219–220°C (dec). Analysis. Found: C, 72.8; H, 3.8; N, 10.9. $C_{30}H_{18}FeN_4$ calcd.: C, 73.5; H, 3.7; N, 11.4%.

^1H NMR ($CDCl_3$): δ 4.28s (5H), 4.41t (1H), 4.57t (2H), 4.77t (1H), 5.12s (1H), 5.64s (1H), 7.5–8.0m (7H). ^{13}C ($CDCl_3$): 45.9 (C(15)), 46.4 (C(16)), 49.6 (C(9)), 53.2 (C(10)), 69.3 (C(2′,5′)), 69.9 (Cp), 70.2 (C(3′,4′)), 84.1 (C(1′)), 110.8 (CN), 124.8 (C(4)), 126.8 (C(6,7)), 128.9 (C(3)), 129.8 (C(5,8)), 132.2 (C(2)), 133.9, 134.4, 134.8, 135.0 all q (C(11–14), 138.3 (C(1)). Mössbauer data: IS 0.52(1), QS 2.33(1), *Γ* 0.12(1) all in mms^{-1}.

1-Ferrocenyltriptycene

1-FcAnH (0.5 g, 1.38 mmol) was treated with benzenediazonium 2-carboxylate-hydrochloride (0.5 g 2.72 mmol) in 1,1-diethoxy-ethyl ether by the procedure described by Streitwieser et al. [8]. The product mixture was then extracted with CH_2Cl_2 and the extract evaporated at 50°C under 1 mmHg to remove the 1,1-diethoxyethyl ether. Repeated chromatography on neutral alumina with benzene as eluent yielded 5 mg (1%) of a pale yellow solid, m.p. 116–120°. ^1H NMR ($CDCl_3$): δ 4.47s (5H), 4.61m 4.80 m (4H), 5.86s (1H0, 6.36s (1H), 7.5m (11H).

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References

1 G.A. Shvekhgeimer, L.V. Balabanova, G.S. Stankevich and N.I. Kunavin, Dokl. Akad. Nauk SSSR, 292 (1987) 931.

2 M.T. Lee, B.M. Foxman and M. Rosenblum, Organometallics, 4 (1985) 539.
3 R. Arnold, B.M. Foxman, M. Rosenblum and W.B. Euler, Organometallics, 7 (1988) 1253.
4 R. Arnold, S.A. Matchett and M. Rosenblum, Organometallics, 7 (1988) 2261.
5 N.H. Gaylord and V. Stepan, Coll. Czech. Chem. Comm., 39 (1974) 1700.
6 B.W. Sullivan and B.M. Foxman, Organometallics, 2 (1983) 187.
7 J.S. Miller, J.C. Calabrese, H. Rommelmann, S.R. Chittipeddi, J.H. Zhang, W.M. Reiff and A.J. Epstein, J. Am. Chem. Soc., 109 (1987) 769.
8 A. Streitwieser and G.R. Ziegler, J. Am. Chem. Soc., 91 (1969) 5081.
9 Y. Berger, M. Berger-Deguée and A. Castonguay, Org. Mag. Res., 15 (1981) 303.
10 R.M.G. Roberts, J. Silver and B. Yamin, J. Organomet. Chem., 270 (1984) 221.
11 R.R. McGuire, R.E. Cochoy and J.A. Winstead, J. Organomet. Chem., 84 (1975) 269.
12 M.L. Caspar, J.B. Stothers and N.K. Wilson, Can. J. Chem., 53 (1975) 1958.
13 H.O. House, D.G. Koepsell and W.J. Campbell, J. Org. Chem., 37 (1972) 1003.
14 M.Y. Hamed, R.C. Hider and J. Silver, Inorg. Chim. Acta, 66 (1982) 13.