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TRICARBONYL-IRON(0) COMPLEXES OF 3a-AZONIAAZULENES

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Summary

The synthesis and spectroscopic data of tricarbonyl-3a-azonia-azulene-iron(0) complexes are described.

Because of their theoretical interest, 3a-azoniaazulene derivatives [1] have been investigated in the past decade as has their application in the synthesis of nitrogen bridged annulenes (cyclazines) [2]. Because of their instability associated with their aromatic character, parent cycl[4.3.2]azine [1c,3a] or cycl-[4.4.2]azinium salts [4], which would add significantly to knowledge of this class of compounds, cannot be made via azoniaazulenes. High temperatures and/or long reaction times are required, leading to decomposition. A recent paper described the stabilization of cycl[4.3.2]azines by conversion into the corresponding tricarbonyl-iron(0) complexes [1c].

We now describe the synthesis of the first tricarbonyl-3a-azoniaazulene-iron(0) complexes (Ia—Ie and II) [5] which may be valuable precursors for the above-mentioned unknown cyclazines, since the synthesis of sensitive organic molecules can often be facilitated by prior complexation to transition metal moieties [6]. The orange-red complexes were obtained in fairly high yield from the free ligands on treatment with iron enneacarbonyl (N_2, ether, $t = 10$ h, $T = 20^\circ$C) in absence of sunlight. Table 1 shows the effect of the transition metal on the proton shift and vicinal coupling constants of the seven-membered ring. Complexation leads to an up-field shift of 3.06—3.58 ppm in the ^{1}H NMR spectrum of tricarbon-3a-azaazulen-4-one-iron(0) derivatives Ia—Id and 2.34—2.98 ppm in the 8-one compound II, compared to the corresponding free ligand spectra. The $^3J_{cis}$ decrease of about 3—4 Hz is in accord with the literature [7].

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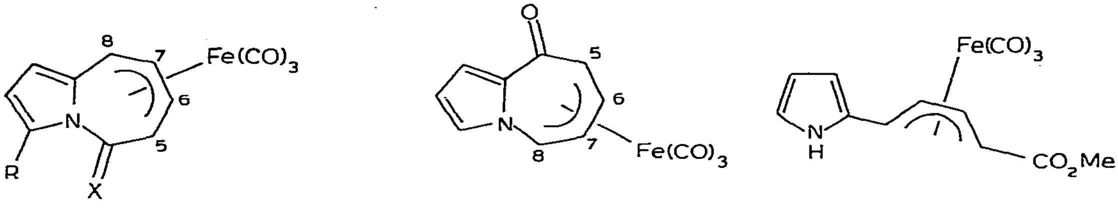
TABLE 1

^{1}H NMR DATA FOR COMPLEXES I AND II IN ACETONE-d_6 [a]

	H(5)	H(6)	H(7)	H(8)	J_{56}	J_{67}	J_{78}	m.p. (°C)	Yield (%)
Ia	3.17(6.48)	6.40	6.15	4.05(7.48)	7.65(12.32)	4.95(8.33)	7.78(11.32)	104	64
Ib	3.24(6.62)	6.54	6.36	3.97(7.55)	7.02(12.60)	4.68(8.55)	7.38(10.89)	189	86
Ic	3.20(6.46)	6.76	6.21	4.13(7.38)	7.53(12.69)	4.35(7.65)	7.49(10.89)	128	48
Id	3.24(6.43)	6.84	6.17	4.00(7.57)	7.29(12.60)	4.78(7.92)	7.02(11.43)	168	51
Ie	3.99(—) [b]	6.23	— [b]	4.03(7.05)	7.65(—) [b]	— [b] (7.28)	7.02(10.89)	158	28
II	3.51(6.49)	6.49	5.99	5.47(7.81)	8.19(12.33)	5.31(8.55)	6.48(9.36)	134	73

[a] Chemical shifts δ in ppm from TMS, coupling constants in Hz; the proton shifts of the free ligands are given in parenthesis. [b] Unassigned owing to the complexity of the spectrum.

SCHEME 1



(Ia, R = H, X = O;
Ib, R = CHO, X = O;
Ic, R = CH=CH—COCH$_3$, X = O;
Id, R = CH=C(COCH$_3$)$_2$, X = O;
Ie, R = H, X = CH—CN)

(II)[a]

(III)

[a] For a better comparison the indices are not in accordance with the IUPAC rules.

Finally, we wish to mention the synthesis of the tricarbonyl-5-(2-pyrrolyl)-2,4-pentadiene methylester-iron(0) complex (III). The large shift of 4.4 ppm to high field in the ^{1}H NMR spectrum of the complexed diene compared to the free ligand is typical of non-cyclic iron-complexed 1,3-dienes [8].

The use of these transition metal complexes as precursors in the synthesis of cyclazines is under investigation.

Experimental

General

Melting point were determined on an original Kofler-Mikroheiztisch (Reichert) apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker WH 90 NMR spectrometer. Spectra were obtained by using acetone-d_6 as solvent. Chemical shifts are reported to tetramethylsilane as an internal standard. IR spectra were obtained with the Perkin-Elmer Models 257 and 177 using polystyrene film for calibration and are reported as $\tilde{\nu}_{max}$ values (cm^{-1}). Mass spectra were taken on the Varian-MAT spectrometers SM 1 and CH 7 at 70 eV. The elemental analyses for C, H, N were provided by the Microanalytical Laboratory of Organisch-chemisches Institut of the University in Münster. Electronic spectra were recorded with a Leitz-UNICAM SP 8000 A spectrometer; ethanol was used as solvent.

All experiments were performed under purified nitrogen. Organic solvents were purified by conventional methods. They were freed from oxygen before use, by repeated degassing and saturating with nitrogen.

Tricarbonyl(4H-3a-azoniaazulen-4-one)iron(0) (Ia)

To an ether solution (50 ml) of 4H-3a-azoniaazulen-4-one (50 mg, 0.34 mmol) [Ia] were added 200 mg (0.55 mmol) iron enneacarbonyl. After 12 h stirring at room temperature the mixture was filtered and the solvent removed under reduced pressure. The residue was chromatographed on silica gel (light petroleum/benzene/ethyl acetate = 1/1/1) to yield pure Ia (63 mg, 0.22 mmol. 64%), which was recrystallised from acetone/petroleum ether to yield orange-yellow needles: m.p. 104°C; IR (KBr): 2065, 1995, 1980, 1665 cm^{-1}; mass spectrum *m/e* (% rel. intensity): 285(M^+, 9), 257(22), 229(43), 201(18), 173(69), 146(32), 117(85), 56(28), 32(55), 28(100); UV (ethanol): λ_{max} (log ϵ) = 231(3.77), 272(3.69), 332 nm (3.19). Anal. Found: C, 50.23; H, 2.49; N, 4.92. Calcd. for $C_{12}H_7NO_4Fe$: C, 50.56; H, 2.48; N, 4.91%.

Tricarbonyl(3-formyl-4H-3a-azoniaazulen-4-one)iron(0) (Ib)

Same procedure as above: 50 mg (0.29 mmol) 3-formyl-4H-3a-azoniaazulen-4-one [Ia], 200 mg (0.55 mmol) iron enneacarbonyl, 20 ml ether. Ib: 78 mg (0.25 mmol, 86%), m.p. 189°C (red needles from acetone/ether); IR (KBr): 2065, 1995, 1982, 1650 cm^{-1}; mass spectrum *m/e* (% rel. intensity): 313(M^+, 29), 285(17), 257(96), 229(63), 201(75), 173(50), 145(29), 144(25), 117(100), 91(29), 90(25), 32(17); UV (ethanol): λ_{max} (log ϵ) = 233(4.53), 325(4.08), 420 nm (3.48). Anal. Found: C, 49.86; H, 2.22; N, 4.46. Calcd. for $C_{13}H_7NO_5Fe$: C, 49.88; H, 2.25; N, 4.47%.

Tricarbonyl(3-[4-(2-butenon)yl]-4H-3a-azoniaazulen-1.4-one)iron(0) (Ic)

Same procedure as above. 50 mg (0.16 mmol) 3-[4-(2-butenon)yl]-4H-3a-azoniaazulen-4-one [4], 200 mg (0.55 mmol) iron enneacarbonyl, 20 ml ether; t = 24 h. Ic: 40 mg (0.11 mmol, 48%); m.p. 128°C (orange-red needles from acetone/petroleum ether). IR (KBr): 2065, 2990, 2980, 1665—1660 cm^{-1}; mass spectrum *m/e* (rel. intensity): 353(M^+, 18), 325(12), 297(48), 269(27), 241(39), 213(56), 198(4), 116(58), 32(64), 28 (100). Anal. Found: C, 54.63; H, 3.16; N, 3.95. Calcd. for $C_{16}H_{11}NO_5Fe$: C, 54.42; H, 3.14; N, 3.97.

Tricarbonyl(3-[(2,4-pentanedion)yl-3-methyliden]-4H-3a-azoniaazulen-4-one)-iron(0) (Id)

Same procedure as above. 50 mg (0.20 mmol) 3-[(2.4-pentanedion)yl-3-methylidene)-4H-3a-azoniaazulen-4-one [4], 200 mg (0.55 mmol) iron enneacarbonyl, 20 ml ether, t = 2 d. Id: 39 mg (0.10 mmol, 51%); m.p. 168°C (orange-yellow needles from methanol; IR (KBr): 2062, 1995, 1985, 1700, 1650 cm^{-1}; mass spectrum *m/e* (rel. intensity): 395(M^+, 15), 367(8), 339(44), 311(36), 293(7), 255(14), 251(10), 217(100), 170(33), 141(47), 43(17), 28(78); UV (ethanol): λ_{max} (log ϵ) = 232(4.36), 276(4.16), 373(4.20), 440 nm (3.82). Anal. Found: C, 54.31; H, 3.28; N, 3.50. Calcd. for $C_{18}H_{13}NO_6Fe$: C, 54.71; H, 3.32; N, 3.55%.

Tricarbonyl(4-cyanomethylene-4H-3a-azoniaazulen-iron(0) Ie)

50 mg (0.30 mmol) of 4-cyanomethylene-4H-3a-azoniaazulen [Ia] and 200 mg (0.55 mmol) iron enneacarbonyl were refluxed in 15 ml benzene. The solution was filtered, the solvent removed under reduced pressure, and the crude product recrystallized from petroleum ether to yield ochre-yellow needles (25.8 mg, 60.08 mmol, 28%); m.p. 158°C; IR (KBr): 2061, 1996, 1955, 2210 cm^{-1}; mass spectrum *m/e* (rel. intensity), 308(M^+, 8), 280(28), 254(65), 224(100), 197(36), 168(70), 192(24), 141(28), 115(23), 56(27), 32(12), 28(37); UV (ethanol) λ_{max} (log ϵ) = 244(4.55), 276(4.52), 303(4.41), 415 nm (3.98). Anal. Found: C, 54.21; H, 2.67; N, 9.25. Calcd. for $C_{14}H_8N_2O_3Fe$: C, 54.58; H, 2.62; N, 9.09%.

Tricarbonyl(8H-3a-azoniaazulen-8-one)iron(0) (II)

Same procedure as above. 60 mg (0.34 mmol) 8H-3a-azoniaazulen-8-one [Ib], 200 mg (0.55 mmol) iron enneacarbonyl, 20 ml ether, t = 12 h at room temperature. II: 72 mg (0.25 mmol, 73%); m.p. 134°C (citrine needles from acetone/petroleum ether); IR (KBr): 2070, 1981, 1972, 1609 cm^{-1}; mass spectrum *m/e* (% rel. intensity): 285(M^+, 3), 257(28), 229(45), 201(8), 174(2), 145(30), 117(76), 91(6), 90(4), 56(8), 40(7), 32(57), 28(100); UV (ethanol): λ_{max} (log ϵ) = 227(4.02), 258(3.94), 20 nm (3.66). Anal. Found: C, 50.60; H, 2.44; N, 4.82. Calcd. for $C_{12}H_7NO_4Fe$: C, 50.56; H, 2.48; N, 4.91%.

Tricarbonyl[ethyl-5-(2-pyrrolyl)-2,4-trans,trans-1,5-pentadiene carboxylate]-iron(0) (III)

50 mg (0.28 mmol) ethyl 5-(2-pyrrolyl)-2,4-*trans,trans*-pentadiene-carboxylate [Ia] and 200 mg (0.55 mmol) iron enneacarbonyl in 50 ml benzene were refluxed for 4 h. Cooling to room temperature was followed by filtration. The solvent was removed under reduced pressure and the residue recrystallized from acetone/petroleum ether to yield copper-coloured needles (88 mg, 0.28 mmol, quant.); m.p. 161°C; IR (KBr): 2050, 1975, 1960, 1684 cm^{-1}; mass spectrum *m/e* (rel. intensity): 317(M^+, 8), 289(8), 261(18), 233(24), 218(8), 201(22), 173(28), 146(13), 118(18), 117(251), 78(82), 32(40), 28(100); UV (methanol): λ_{max} (log ϵ) = 256(4.16), 3.48 nm (4.17); ^{1}H NMR: δ = 10.19(s), 6.76(dd), 6.21(dd), 6.04(dd), 6.01(dd), 5.90(dd), 3.61(s), 3.10(d), 1.35 ppm (d). Anal. Found: C, 48.85; H, 3.46; N, 4.43. Calcd. for $C_{13}H_{11}NO_5Fe$: C, 49.24; H, 3.50; N, 4.42%.

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