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THE INTERACTION OF 1,1,3,3-TETRAKIS(TRIFLUOROMETHYL)ALLENE WITH SODIUM DERIVATIVES OF IRON AND RHENIUM CARBONYL COMPOUNDS. SYNTHESIS AND STRUCTURE OF THE σ- AND π-COMPLEXES

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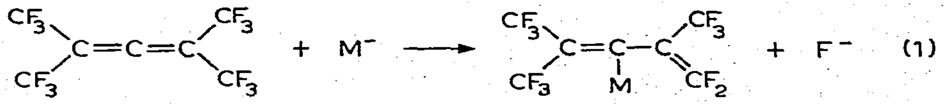
Summary

1,1,3,3-Tetrakis(trifluoromethyl)allene reacts with π-$C_5H_5Fe(CO)_2^-$ and $Re(CO)_5^-$ to give σ-complexes. The iron σ-complex, when refluxed in decalin or exposed to UV radiation, is transformed to the π-allylidene analogue. Structures of the σ-complexes are determined from IR, Raman, ^{19}F NMR and X-ray spectral data.

In a short communication [1], we reported that 1,1,3,3-tetrakis(trifluoromethyl)-allene (I) looses a fluorine atom under the action of π-$C_5H_5Fe(CO)_2^-$ or $Re(CO)_5^-$ in THF.

The most electron-deficient site in I is known [2—4] to be the central carbon atom, consequently, it is assumed that this is the site of attack of the carbonylate anion. One of the double bonds migrates; the fluorine in the allyl position β to the site attacked is eliminated, and the diene σ-complex is formed (eq. 1). The



(1)

(I)

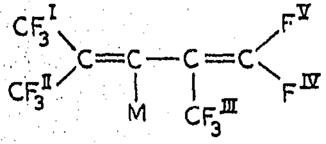
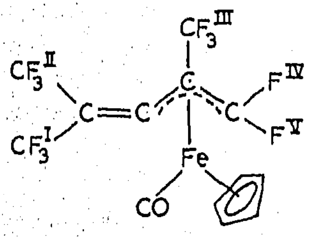
(II, M = π-$C_5H_5Fe(CO)_2$
III, M = $Re(CO)_5$)

compounds II and III are stable crystalline solids, highly soluble in common organic solvents. The solutions are stable in air for several hours, the solutions of III are, however, more stable than those of II.

IR and Raman spectra of II and III contain no allene bands at 760 or 2020 cm^{-1} but they do contain C=C stretching vibration bands at 1558 and 1728 cm^{-1}

TABLE 1

CHEMICAL SHIFTS AND SPIN—SPIN COUPLINGS IN ^{19}F NMR SPECTRA OF COMPOUNDS II, III AND IV

Formula		Chemical shift [a] (δ, ppm)					Spin—spin coupling (Hz)					
		CF_3(I) (or CF_3(II))	CF_3(II) (or CF_3(I))	CF_3(III)	F(IV)	F(V)	CF_3(I)—CF_3(II)	CF_3(III)—F(IV)	CF_3(III)—F(V)	F(IV)—F(V)	CF_3(II)—CF_3(III)	CF_3(II)—F(V)
	(II)	53.3	≈55.1 [b]	≈55.1 [b]	88.8	80.5	10	14	9.5	26	—	4.8
	(III)	53.2	56.8	56.05	87.4	79.6	10	14	9.5	28	4	4
	(IV)	59.4	61.9	56.35	84.8 [c]	69.3 [c]	7.5	22	15	109.6	7.5	<0.7

[a] Relative to $CFCl_3$. [b] The CF_3(II) and CF_3(III) signals are overlapped. [c] The inverse assignment is probable.

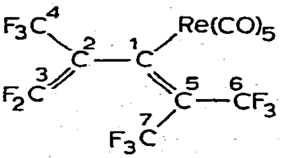
(II) or 1570 and 1730 cm^{-1} (III). The C—F IR patterns of II and III are, though complicated, practically identical, indicating that the ligands in the complexes have identical structure. The $Fe(CO)_2$ group in II gives two strong ν(CO) bands (1995 and 2050 cm^{-1}); the $Re(CO)_5$ group in III displays bands at 2000, 2030, 2090, and 2150 cm^{-1}. The cyclopentadienyl ring in II gives IR bands at 1000, 1100, 1420 and 3120 cm^{-1}, and a singlet at 5.02 ppm (THF) in the PMR spectrum.

^{19}F NMR parameters for II (in THF) and III (in ether) are listed in Table 1. Both spectra are similar in their number of signals, multiplicity, and relative intensities. The assignments are based on the spin-decoupling experiments and comparisons of the data with literature values. An example is discussed below for compound III.

The spectrum consists of five signals lying at δ 53.2, 56.0, 56.8, 79.6 and 87.4 ppm (upfield from $CFCl_3$), the intensity ratios being 3/3/3/1/1 respectively. The signal at 53.2 ppm is a quartet with a spin—spin coupling constant of 10 Hz. When irradiating with the second frequency corresponding to this chemical shift, the multiplicity of just one of the signals (at 56.8 ppm) is affected, therefore these signals may be assigned to the geminal CF_3 groups [CF_3 (I) and CF_3 (II)] at the double bond, at which there are no other fluorine-containing substituents. The third multiplet (at 56.0 ppm, rel. int. 3) belongs, evidently, to CF_3 (III). At higher field there are two complex multiplets each of which have a relative intensity of 1. When irradiating with the second frequency field, the frequency of which coincides with the CF_3 (III) resonance frequency, the signal at 87.4 ppm is transformed to a doublet (the geminal coupling constant J(F(IV)—F(V)) is 28 Hz) and the signal at 79.6 ppm is transformed to a doublet of quartets, with one coupling constant of 28, and the other of 4 Hz. The double resonance experiments have shown that the CF_3 (III) coupling constant is 14 Hz with the more shielded fluorine, 9.5 Hz with the less shielded atom. It is known [5] that the *cis* CF_3—F coupling constants in olefines are higher than those of the *trans* configurations, consequently, the assignment may be made unambiguously: at lower fields lies the F(V) signal positioned *trans* vis-à-vis the CF_3 (III) group. Long range coupling across six bonds have been found between one of the geminal CF_3 groups and F(V) and between the former group and CF_3 (III). Both coupling constants are 4 Hz. However, whether the group involved in coupling is CF_3 (I) or CF_3 (II) remains so far unclear, owing to distortions in the geometry of the site.

Thus, IR, Raman, and ^{19}F NMR spectral data confirm the theoretical structures proposed.

X-Ray analysis of compound III has shown that the pentadienyl ligand is not

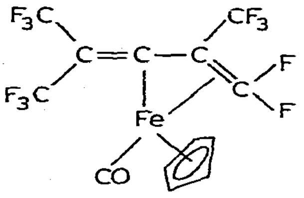


(III)

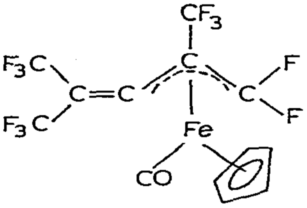
flat; the torsional angle at the C(1)—C(2) bond (the angle between the planes C(5)—C(1)—C(2) and C(1)—C(2)—C(3)) is 82.5°. The bond lengths have the usual values (C(1)=C(5), 1.37(3); C(2)=C(3), 1.29(4); C(1)—C(2), 1.52(3); C(2)—C(4), 1.47(4); C(5)—C(6), 1.51(6); C(5)—C(7), 1.55(5) Å). The rhenium atom lies in a distorted octahedron comprising five carbon atoms, five CO groups, and the σ-bonded central carbon of the unsaturated ligand (Re—C(1), 2.25(3) Å).

Mass spectra of II and III are typical for carbonyl complexes containing a fluorinated ligand and verify the compositions of the complexes. The heaviest ion resulting from III, acted upon by electron impact at 30 eV, is at *m/e* 442, corresponding to the elimination of one CO group.

When compound II is refluxed in decalin or irradiated by UV light in pentane a carbon monoxide molecule is lost. After three hours irradiation (PRK-4 lamp, 220 W) the starting complex is transformed completely to a yellow compound (m.p. 46—47°C (IV)) which is stable in the solid state. The IR spectrum of IV contains only one ν(CO) band at 2050 cm^{-1} and one ν(C=C) band at 1725 cm^{-1}. The C—F stretching pattern is much simpler than that of compound II (the number of bands is halved). IR spectra of IV are practically identical, whether recorded in cyclohexane or in the solid state. The comparative spectral pattern indicates formation of a π-complex by bonding to one of the double bonds of the diene ligand, followed by CO elimination. Two structures of IV, σ—π (A), or π-allylidene (B), are possible.



(A)



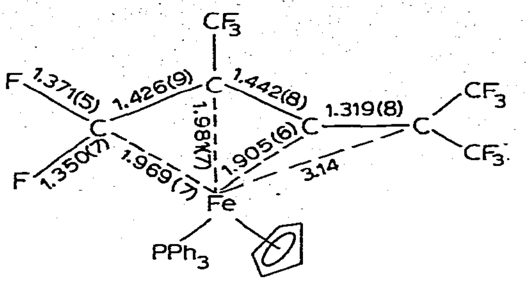
(B)

π-Allylidene complexes or, in particular, their fluorinated analogues have never been described in the literature, so neither the detailed assignment of the vibrational spectrum of IV nor the choice between the alternative structures A and B, are possible at the present stage.

^{19}F NMR parameters for IV (in benzene) are listed in Table 1. The spin—spin couplings of IV are different from those of compound II, the largest difference is observed for the geminal F(IV)—F(V) coupling constant which increases to 109.6 Hz, and is thus witness to coordination of the double bond with the metal atom. Similar behaviour of this constant has been observed in a number of metal-coordinated fluorinated ethylenes [6—8]. NMR data, however, do not allow us to discern between the structures A and B unambiguously.

X-ray data obtained for V synthesised by replacing CO with PPh_3 in IV, show the complex to have structure B.

Unlike II, complex III does not loose carbon monoxide when irradiated by UV light in hexane (3 h, PRK-7 lamp, 1,000 W). Irradiating III whilst refluxing in hexane decomposes the complex gradually, and just 6% of the starting material can be recovered in 22 hours. The fact that III is stable, under the conditions in which II gives a π-complex, may be assigned to a greater stability of the Re—CO bond when compared to the Fe—CO bond.



(V)

σ-Complexes of fluorinated hydrocarbons with transition metals are usually stable toward reagents that can split a metal—ligand σ-bond [9]. Bromine, hydrogen chloride and mercuric chloride, at room temperature in inert solvents, do not break the ligand—metal σ-bond in II and III. The compound II when refluxed with bromine in CCl_4 is recovered in a 50% yield. Under the same conditions, III is destroyed completely in three hours and gives $Re(CO)_5Br$. Sodium amalgam in tetrahydrofuran transforms II to an unidentified fluorinated compound which contains no CO bands in its IR spectrum. Under the same conditions, III gradually decomposes to give inorganic rhenium compounds.

Experimental

IR spectra were recorded on a Zeiss UR-20 instrument, as KBr pellets or in cyclohexane solutions, in the region 4000 to 400 cm^{-1}. Raman spectra of solid samples were obtained on a Coderg PHO spectrometer with He/Ne laser (6328 Å) excitation.

^{19}F NMR spectra were taken on a Varian XL-100 machine. The chemical shifts were measured relative to a C_6F_6 or C_6H_5F internal standard. Thin-layer chromatographs were run on neutral alumina (2nd degree of activity).

Synthesis of II

1,1,3,3-Tetrakis(trifluoromethyl)allene (4 ml) and 50 ml of absolute tetrahydrofuran were placed into a four-necked flask fitted with a stirrer, a condenser (acetone plus Dry Ice), a dropping funnel and an inlet for argon. A solution of $Na[\pi\text{-}C_5H_5Fe(CO)_2]$ in 100 ml of tetrahydrofuran, prepared preliminarily from 20 ml of 0.5% sodium amalgam and 3.5 g of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, was added over 1.5 h at —70°C under stirring. The mixture was stirred for 1 h more at room temperature and for 3 h at 50—60°C. Tetrahydrofuran was removed, the residue was placed on an alumina column, and a yellow oil was eluated by light petroleum. A pentane extract of the oil gave yellow crystals, 2.11 g (22%), m.p. 55—56°C, $R_f(Al_2O_3)$ 0.77 (light petroleum). (Found: C, 35.52, 35.66; H, 0.97, 1.12; F, 43.81, 44.31; Fe, 11.77, 11.62, $C_{14}H_5F_{11}FeO_2$ calcd.: C, 35.74; H, 1.06; F, 44.47; Fe, 11.92%. Mol. wt. 470.)

Synthesis of III

A solution of $NaRe(CO)_5$ in 100 ml of tetrahydrofuran was added to 5 ml of 1,1,3,3-tetrakis(trifluoromethyl)allene in 50 ml of tetrahydrofuran, placed in a flask (described in the synthesis of II) and stirred at —70° C for 1 h. The $NaRe(CO)_5$

solution was prepared from 25 ml of 0.5% sodium amalgam and 5 g of $Re_2(CO)_{10}$. The mixture was stirred for an additional hour at room temperature, 3 h at 50—60°C, and the solvent removed. The residue, when applied to an alumina thin-layer chromatograph, in light petroleum, gave a colourless oil and an insignificant amount of the unreacted rhenium carbonyl. A pentane extract of the oil gave a white crystalline compound, 3.75 g (40%), m.p. 56—57°C, $R_f(Al_2O_3)$ 0.84 (light petroleum). (Found C, 23.48, 23.32; F, 34.06, 34.06. $C_{12}F_{11}O_3Re$ calcd.: C, 23.26; F, 33.76%. Mol. wt. 619.)

Synthesis of IV

(a). The compound I (0.3 g) in 30 ml of decalin was refluxed in an argon atmosphere for 10 h. The solution was filtered, the filtrate evaporated and placed on an alumina column. A yellow oil was eluated by a 4/1 ether/benzene mixture. A pentane extract of the oil gave yellow crystals, 0.15 g (53%), m.p. 46—47°C, $R_f(Al_2O_3)$ 0.28 (light petroleum). (Found: C, 35.59, 35.51; H, 1.25, 1.28; F, 46.39, 46.08. $C_{13}H_5F_{11}FeO$ calcd.: C, 35.29; H, 1.13; F, 47.28%. Mol. wt. 442.)

(b). The compound I (0.3 g) in 30 ml pentane was irradiated (PRK-4, 220 W) in an argon atmosphere for 3 h. The solution was filtered and worked up as in *a*. The compound isolated had the same melting point and R_f value as the compound obtained in *a*. The yield was 0.23 g (80%).

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