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The Difluorovinylidene Complex [(CO)$_8$Fe$_2$(μ-C=CF$_2$)]

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Fluorinated organometallic compounds have the potential to be synthons of fluorinated groups in organic and pharmaceutical chemistry. Well-characterized organometallic compounds containing fluorine bound either to the metal or to the ligand(s) are scarce in comparison to the total number of organometallic compounds. Methods of introducing fluorine or fluorinated ligands into organometallic complexes have not been extensively investigated. Some of the few exceptions are the preparation of σ-bonded perfluoroalkene complexes,[1] the recent synthesis of various complexes of octafluorocyclooctatetraene[2] and the synthesis of Fe$_3$(CO)$_9$(μ_3-CF)$_3$ and its reactions.[3,4]

Use of difluoromalonyl dichloride has resulted in the difluoromethane-bridged complexes [(CO)$_4$Mn(μ-CF$_2$)$_2$Mn(CO)$_4$] and [(CO)$_3$Co(μ-CO)(μ-CF$_2$)Co(CO)$_3$] in a straightforward manner.[5] In a more complicated reaction, the fluoromethylidyne complex [C$_5$H$_5$(CO)$_2$Mo]$_3$CF has been found, though only in moderate yields.[6] The products first formed in the reactions of difluoromalonyl dichloride with organometallic anions are the malonyl-bridged dimetal complexes such as [C$_5$H$_5$(CO)$_3$MoCOCF$_2$COMo(CO)$_3$C$_5$H$_5$], which have been isolated in the three examples given above.[5,6] Secondary reactions, among which are exchanges of bridging versus terminal carbonyls, give the final products. We wish to report now the formation of a difluorovinylidene complex with the same fluorine precursor.

Results and Discussion

The reaction of CF$_2$(COCl)$_2$ with [Fe$_3$(CO)$_{11}$]$^{2-}$ is more complicated than its reaction with [Mn(CO)$_5$]$^-$ or [Co(CO)$_4$]$^-$. We have not been able to identify any intermediates. A possible reaction pathway is given in Scheme I. We assume attack of the difluoromalonyl chloride at an oxygen atom of a bridging carbonyl and an iron atom. The intermediate cleaves off CO$_2$ and an iron carbonyl fragment, and so the difluorovinylidene complex is formed. The latter is identified by conventional physical measurements including a crystal structure analysis; see Figure 1, Table I, and the supplementary material.

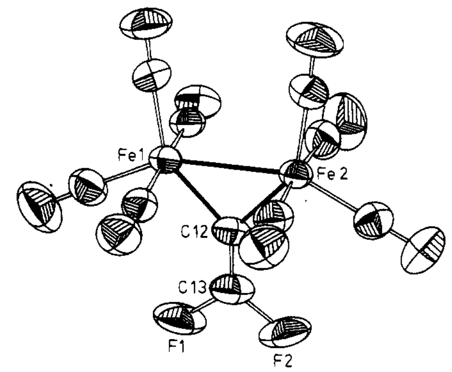

Figure 1. Molecular structure of [(CO)$_8$Fe$_2$(μ-C=CF$_2$)]. Ellipsoids represent 50% probability. Distances (pm): Fe(1)-Fe(2), 267.4 (1); Fe-C12, 195.4 (4), 195.6 (4); C12-C13, 128.8 (6); C-F, 135.3 (5); 134.4 (6). Angles (deg): Fe-C-Fe, 86.3 (2); F-C-F, 106.4 (3).

Scheme I

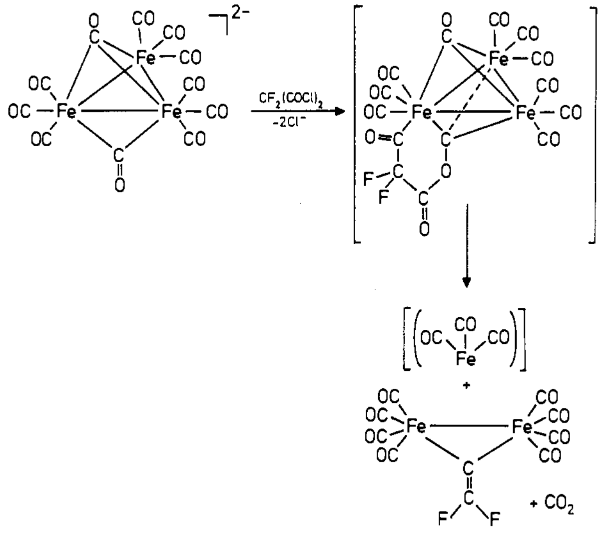

Table I. Final Positional Parameters for All Atoms of [(CO)$_8$Fe$_2$(μ-C=CF$_2$)] with Atoms Labeled As Shown in Figure 1

atoms	x	y	z
Fe1	1.00423 (7)	0.36519 (4)	0.72495 (3)
Fe2	1.03189 (7)	0.25950 (4)	0.57467 (3)
C1	0.9175 (6)	0.2513 (3)	0.7793 (3)
O1	0.8700 (5)	0.1837 (3)	0.8177 (2)
C2	1.1174 (7)	0.4771 (4)	0.6813 (3)
O2	1.1920 (6)	0.5489 (3)	0.6607 (3)
C3	1.0939 (7)	0.4113 (4)	0.8340 (3)
O3	1.1579 (7)	0.4385 (4)	0.9022 (3)
C4	0.7618 (7)	0.4168 (4)	0.6969 (3)
O4	0.6121 (5)	0.4463 (3)	0.6763 (3)
C12	1.2051 (5)	0.2789 (3)	0.6842 (3)
C13	1.3716 (6)	0.2462 (4)	0.7171 (3)
F1	1.4622 (4)	0.2691 (3)	0.7986 (2)
F2	1.4898 (4)	0.1839 (3)	0.6776 (3)
C21	1.1389 (7)	0.3692 (4)	0.5250 (3)
O21	1.2116 (6)	0.4333 (3)	0.4902 (3)
C22	0.9522 (8)	0.1418 (4)	0.6230 (3)
O22	0.9086 (8)	0.0644 (3)	0.6481 (3)
C23	1.1570 (7)	0.1811 (4)	0.5018 (3)
O23	1.2375 (7)	0.1312 (3)	0.4565 (3)
C24	0.7924 (7)	0.2855 (4)	0.5181 (3)
O24	0.6422 (6)	0.3018 (4)	0.4861 (3)

This difluorovinylidene complex is the first example of its kind, related to the diphenylvinylidene complex [(CO)$_8$Fe$_2$(μ-C=C(C$_6$H$_5$)$_2$]^7. The molecule has a planar Fe$_2$C=CF$_2$ backbone. One major difference in the difluorovinylidene complex is that here the carbonyl groups are eclipsed, resulting in a molecular C_2 symmetry. The Fe—Fe distance of 267.5 pm is quite long. The C=C bond length of 128.8 pm is very short if compared with those of C$_2$H$_4$ (133.7 pm),[8] [(CO)$_8$Fe$_2$-μ-C=C(C$_6$H$_5$)$_2$] (133.0 pm),[7] and *trans*-[(C$_5$H$_5$)$_2$(CO)$_3$Ru$_2$-μ-C=CH$_2$] (132.5 pm).[9] This must be caused by the fluorine atoms, since in C$_2$F$_4$ the carbon–carbon bond length is also shorter, but not by quite as much (131.1 pm).[10] Even more pronounced is the effect of fluorine substitution on the geminal bond angle. These angles are 117.8° in C$_2$H$_4$,[8] 116.0°

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in $[(CO)_8Fe_2\text{-}\mu\text{-}C{=}C(C_6H_5)_2]$,[7] and already 112.4° in C_2F_4.[10] In the difluorovinylidene complex the F–C–F angle is even smaller, 106.2°.

Experimental Section

Material. Difluoromalonyl dichloride[11] and triiron undecacarbonylate[12] were obtained by literature procedures.

Synthesis of $[(CO)_8Fe_2(\mu\text{-}C{=}CF_2)]$. Under anhydrous and oxygen-free conditions difluoromalonyl dichloride (0.84 g, 48 mmol), dissolved in a few milliliters of THF, is slowly added at −78 °C to a freshly prepared solution of 2.3 g (4.8 mmol) $[Fe_3(CO)_{11}]^{2-}$ in 50 mL of THF. Warming to −50 °C led to evolution of gas. At room temperature the solvent is pumped off to dryness. The solid residue is sublimed at 70 °C in vacuum onto a −30 °C finger, giving a yellow sublimate and a black residue. Chromatography of the yellow sublimate in CH_2Cl_2/pentane (1:3) on silica gel affords 0.47 g of pure $[(CO)_8Fe_2(\mu\text{-}C{=}CF_2)]$ in 25% yield.

IR (solid in KBr): ν_{CO} 2117, 2068, 2039, 2022 cm^{-1}; ν_{CC} 1698 cm^{-1}; mass spectrum: m/z 398 (M^+), and smaller fragments, mainly due to subsequent loss of CO. ^{19}F NMR (CH_2Cl_2): $\delta = -68.8$.

Crystal Structure Analysis. An orange crystal of about 0.2 mm size in all dimensions was obtained from recrystallization in pentane, and mounted on a Siemens diffractometer using Mo Kα radiation ($\lambda = 71.06$ pm) and a graphite monochromator at room temperature.

Crystal data: space group $P2_1/n$, $a = 700.9$ (3) pm, $b = 1307.4$ (7) pm, $c = 1504.3$ (6) pm, $\beta = 96.10$ (3)°, $Z = 4$, $\rho_{calcd} = 1.93$ g cm^{-3}, 2500 measured reflections up to $2\theta = 50°$ ($\pm h,k,l$), 2180 reflections with $I > 2\sigma(I)$, 200 parameters. The structure was solved with the program SHELX; the scattering factors were taken from the *International Tables for X-Ray Crystallography*. The function $\sum w(|F_o| - |F_c|)^2$ was minimized. Absorption correction: numerical, $\mu = 22.5$ cm^{-1}. Extinction correction: isotropic, $g = 5.5 \times 10^{-4}$. Weighing scheme: $w = 1.7291 - 0.822F + 0.0002F^2 - 0.0000066F^3$. $R = 0.037$, $R_w = 0.036$.

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Supplementary Material Available: Complete listings of anisotropic thermal parameters, bond lengths, and bond angles (3 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Facile Synthesis of New Classes of Free and Complexed Polyaza Phosphorus Macrocycles

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Binucleating macrocyclic ligands have been the subject of intensive studies.[1] In particular phosphorus macrocycles possessing P–C,[2] P–O, or P–S[3] bonds have been the focus of much attention since these derivatives can react as hard or soft chelating units depending of the hybridization of the phosphorus atoms. In contrast very few reports deal with the preparation of azaphospha macrocycles,[4] and to our knowledge no similar work has been devoted to the synthesis of bis(phosphodihydrazino) macrocycles derived from heterocyclic dicarbonyls. Here we describe the high-yield one-pot synthesis of the first 20- and 22-membered ring macrocycles possessing P–N–N linkages, as well as the preparation of related complexes.

Experimental Section

All experiments were performed under an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^1H NMR spectra were recorded on a Bruker WM 250 or a Bruker AC 80 spectrometer. ^1H chemical shifts are reported in ppm relative to Me_4Si as internal standard. ^{31}P and ^{11}B NMR spectra were obtained on a Bruker AC 80 instrument and are reported in ppm. Standards for the shifts are 85% H_3PO_4 and $BF_3O(C_2H_5)_2$ for phosphorus and boron, respectively. Infrared spectra were recorded on a Perkin-Elmer 225 instrument. Mass spectra were obtained on a Varian MAT 311A instrument.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and must be handled with great caution.[5]

Synthesis of Macrocycles 3a–h. A solution of phosphodihydrazides, **1**[6] (0.02 mol), in 50 mL of methanol and a solution of dialdehydes, **2** (0.02 mol), in 50 mL of methanol are added simultaneously and dropwise at room temperature over a period of 1 h. The mixture is stirred for 2 h, during which a yellow precipitate is formed. The solution is filtered and the precipitate washed with 2 × 20 mL of methanol and recrystallized from acetonitrile/chloroform 4:1. An additional amount of macrocycles **3** is obtained by evaporation of methanol and recrystallization of the residue from acetonitrile/chloroform 4:1.

3a: yellow powder; yield 85%; mp, dec >180 °C. ^{31}P NMR ($CDCl_3$): 23.90. ^1H NMR ($CDCl_3$): 3.0 (d, $^3J_{PH} = 7$ Hz, N—CH_3) 6.40 (s, C_4OH_2) 7.4 (m, C_6H_5) 7.9 (s, HC═N–). ^{13}C NMR ($CDCl_3$): 31.54 (d, $^2J_{PC} = 7.85$ Hz), 110.78 (s, *C*—C—O furfural), 132.59 (s, C—*C*—O furfural), 128.30 and 133.48 (m, C_6H_5), 151.92 (s, *C*═N). IR (KBr) 1660 (C═N), 1250 (P═O). MS: m/e 604. Anal. Calcd for $C_{28}H_{30}N_8O_4P_2$: C, 55.62; H, 4.96; N, 18.54. Found: C, 55.26; H, 4.98; N, 18.50.

3b: yellow powder; yield 95%; mp, dec >180 °C. ^{31}P NMR ($CDCl_3$): 78.73. ^1H NMR ($CDCl_3$): 3.08 (d, $^3J_{PH} = 9.1$ Hz, N—CH_3), 6.33 (s, C_4OH_2), 7.34 (m, C_6H_5) 8.08, (s, HC═N–). ^{13}C NMR ($CDCl_3$) 31.78 (d, $^2J_{PC} = 8.66$ Hz), 111.10 (s, C—*C*—O furfural), 132.23 (s, *C*—C—O furfural), 128 and 134.19 (m, C_6H_5), 151.67 (s, *C*═N–). IR (KBr): 1670 (C═N), 730 (P═S) cm^{-1}. MS: m/e 636. Anal. Calcd for $C_{28}H_{30}N_8O_2P_2S_2$: C, 52.84; H, 4.71; N, 17.61. Found: C, 52.43; H, 4.82; N, 17.28.

3c: yellow powder; yield 75%; mp, dec >150 °C. ^{31}P NMR ($CDCl_3$): 1.40. ^1H NMR ($CDCl_3$): 3.2 (d, $^3J_{PH} = 6.92$ Hz, N—CH_3), 6.50 (s, C_4OH_2), 7.2 (m, C_6H_5), 7,4 (s, *H*C═N). IR (KBr): 1670 (C═N), 1270 (P═O) cm^{-1}. MS: m/e 636. Anal. Calcd for $C_{28}H_{30}N_8O_6P_2$: C, 52.83; H, 4.71; N, 17.61. Found: C, 52.51; H, 4.61; N, 17.51.

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