Journal of Organometallic Chemistry, 424 (1992) 57–63
Elsevier Sequoia S.A., Lausanne
JOM 22300

Synthesis and crystal structures of the isoelectronic monocyclopentadienyliron complexes $[\eta^5\text{-}C_5H_5)Fe(P\{OMe\}_3)(CO)(I)]$ and $[(\eta^5\text{-}C_5H_5)Fe(P\{OMe\}_3)(NO)(I)]BF_4$

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(Received August 12, 1991)

Abstract

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(P\{OMe\}_3)(CO)(I)]$ (**2**) with nitrosonium tetrafluorobate gave the isoelectronic nitrosyl cation $[(\eta^5\text{-}C_5H_5)Fe(P\{OMe\}_3)(NO)(I)BF_4$ (**3**). Both compounds have been characterised crystallographically in order to compare the steric and electronic demands of carbonyl and nitrosonium groups in a common ligand environment.

Introduction

Compounds of the general formula $[(\eta^5\text{-}C_5H_5)M(PR_3)(NO)(X)]^+$ where M = Fe, Ru are rare in the literature while the isoelectronic compounds $[(\eta^5\text{-}C_5H_5)M(PR_3)(CO)(X)]$ and $[(\eta^5\text{-}C_5H_5)M(PR_3)(CO)(L)]^+$ are very common. The study of related pairs of these compounds should provide a useful demonstration of the relative π-acceptor properties of carbonyl and nitrosonium groups in a common ligand environment. Both $[(\eta^5\text{-}C_5H_5)Fe(P\{OPh\}_3)(NO)(I)]PF_6$ and $[(\eta^5\text{-}C_5H_5)Fe(P\{OPh\}_3(NO)(I)]$ have been reported with very little spectroscopic data [1,2]. We recently reported the synthesis and solid state structure of the nitrosyl compound $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(NO)(Cl)]PF_6$ [3], whose isoelectronic carbonyl analogue $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CO)(Cl)]$ had been structurally characterised earlier earlier [4]. The carbonyl compound $[(\eta^5\text{-}C_5H_5)Fe(P\{OMe\}_3)(CO)(I)$ (**2**) has been reported by two groups [5,6] and the trimethylphosphite group seemed an ideal indicator ligand to demonstrate the relative π-back bonding abilities of the carbonyl and nitrosonium ligands. We report here the preparation of the isoelectronic nitrosyl complex $[(\eta^5\text{-}C_5H_5)Fe(P\{OMe\}_3)(NO)(I)BF_4$ (**3**) and the crystal structures of **2** and **3**.

0022-328X/92/$05.00

Experimental

Crystallographic studies

Structure of 2

Dark red needles were obtained by crystallisation from a dichloromethane/diethyl ether solution. A suitable crystal specimen was obtained by cutting a large crystal, mounted on a glass fibre with epoxy resin. Precession photographs and intensity data were collected on a Nicolet R3m/V diffractometer using graphite monochromatized Mo-K_α X-rays.

Crystal data. $C_9H_{14}O_4PFeI$, $M = 399.9$, monoclinic, space group $P2_1/c$, $a = 7.161(3)$, $b = 25.490(9)$, $c = 7.802(3)$ Å, $\beta = 107.92(4)°$, $U = 1355.0(10)$ Å^3, $D_c = 1.96$ g cm^{-3} for $Z = 4$, $F(000) = 776$, μ(Mo-K_α) = 34.79 cm^{-1}, $T = -42$°C, crystal size 0.40 × 0.25 × 0.20 mm. Cell dimensions were obtained from 42 centred reflections with 2θ values from 23 to 37°. Intensity data in the range $3 < 2\theta < 65°$ were collected using an ω scan technique. The intensities of three reflections measured periodically showed a decrease of less than 1% over the data collection. An empirical absorption correction was applied using an azimuthal scan technique. A total of 5333 reflections were collected of which 4895 were independent, and 3264 for which $I > 3\sigma(I)$ were used in the refinement. A small number of reflections in the range $60 < 2\theta < 65°$ were omitted from the calculations due to anomalous intensities caused by interference of the brass pin connecting the glass fibre to the goniometer head. The structure was solved by standard heavy atom routines and refined by full matrix least squares methods. All non-hydrogen atoms were given anisotropic temperature factors. Hydrogen atoms were placed in the model at calculated positions and allowed to ride on their respective carbon atoms. The highest peak in the final difference map was 2.16 e Å^{-3} and associated with the

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for 2

	x	y	z	U_{eq} [a]
I(1)	1185(1)	530(1)	3888(1)	41(1)
Fe(1)	2797(1)	1011(1)	1755(1)	25(1)
C(1)	5367(10)	922(3)	1072(12)	74(3)
C(2)	4951(11)	445(3)	1781(9)	67(3)
C(3)	3137(12)	273(3)	628(10)	59(3)
C(4)	2459(11)	614(3)	−711(9)	61(2)
C(5)	3833(15)	1027(3)	−445(10)	72(4)
C(6)	739(9)	1420(2)	864(8)	44(2)
O(4)	−486(7)	1676(2)	275(7)	64(2)
P(1)	4252(2)	1575(1)	3770(2)	31(1)
O(1)	4857(8)	2076(2)	2890(5)	56(2)
C(7)	5994(11)	2502(3)	3941(9)	67(3)
O(2)	6428(7)	1431(2)	5102(6)	61(2)
C(8)	6696(10)	988(3)	6230(8)	53(2)
O(3)	3401(7)	1765(2)	5330(6)	57(2)
C(9)	1455(11)	1983(3)	4908(11)	68(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

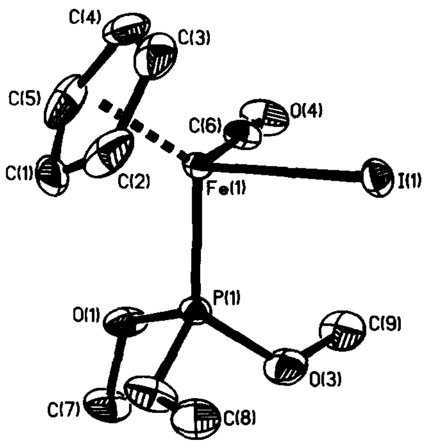


Fig. 1. Molecular structure of $[(\eta^5\text{-}C_5H_5)Fe(P\{OMe\}_3)(CO)(I)]$ (2).

iodine atom. At convergence $R = 4.71\%$ and $R_w = 5.24\%$, $w = [\sigma^2(F) + 0.0012F^2]^{-1}$, $S = 1.39$ for a data/parameter ratio 22.5 : 1, $\Delta/\sigma < 0.001$.

Calculations were performed using SHELXTL-PLUS on a Micro VAX II. The final positional parameters are given in Table 1.

Structure of 3

Dark red-black blocks were obtained by crystallisation from a dichloromethane/diethyl ether solution. A suitable crystal was mounted on a glass fibre with epoxy resin. Precession photographs and intensity data were collected on a Nicolet R3m/V diffractometer using graphite monochromatized Mo-K_α X-rays.

Crystal data. $C_8H_{14}BNO_4F_4PFeI$, $M = 488.7$, triclinic, space group $P\bar{1}$, $a =$ 7.1533(14)0, $b = 10.259(2)$, $c = 11.067(3)$ Å, $\alpha = 90.38(2)$, $\beta = 90.96(2)$, $\gamma = 92.54(2)°$, $U = 811.3(3)$ Å^3, D_c 2.00 g cm^{-3} for $Z = 2$ $F(000) = 472$, μ(Mo-K_α) = 29.58 cm^{-1}, $T = 23$°C, crystal size $0.35 \times 0.30 \times 0.25$ mm. Cell dimensions were obtained from 41 centred reflections with 2θ values from 22 to 38°. Intensity data in the range $3.5 < 2\theta < 60°$ were collected using a θ–2θ scan technique. The intensities of three reflections measured periodically showed a decrease of less than 1% over the data collection. An empirical absorption correction was applied using an azimuthal scan technique. A total of 4979 reflections were collected of which 4625 were independent, and 2792 for which $I > 3\sigma(I)$ were used in the refinement. A small number of reflections in the range $55 < 2\theta < 60°$ were omitted from the calculations due to anomalous caused by interference of the brass pin connecting the glass fibre to the goniometer head. The structure was solved by standard heavy atom routines and refined by full matrix least squares methods. All non-hydrogen atoms were given anisotropic temperature factors. Hydrogen atoms were placed in the model at calculated positions and allowed to ride on their respective carbon atoms. There was rotational disorder in the BF_4^- group which could not be satisfactorily modelled. The highest peak in the final difference map was 1.27 e Å^{-3} and associated with the BF_4^- group. At convergence $R = 6.20\%$, $R_w = 6.37$, $w = [\sigma^2(F) + 0.0002F^2]^{-1}$, $S = 3.80$ for a data/parameter ratio 14.6 : 1, $\Delta/\sigma < 0.012$.

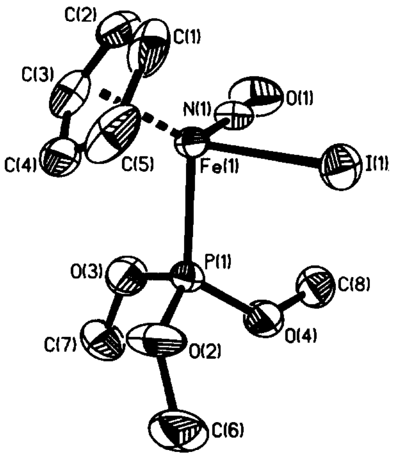


Fig. 2. Molecular structure of the cation in [(η^5-C_5H_5)Fe(P{OMe}$_3$)(NO)(I)]BF_4 (3).

Calculations were performed using SHELXTL-PLUS on a Micro VAX II. The final positional parameters are given in Table 2.

Syntheses and spectra

All reactions and preparations were carried out under nitrogen by standard Schlenk-tube techniques. Diethyl ether, benzene, and light petroleum ether (b.p.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 3

	x	y	z	U_{eq} [a]
I(1)	1702(1)	493(1)	2244(1)	73(1)
Fe(1)	−765(1)	2102(1)	1520(1)	45(1)
C(1)	1141(18)	2925(12)	297(14)	111(5)
C(2)	−648(20)	2982(10)	−187(8)	91(4)
C(3)	−1656(16)	3705(10)	553(10)	87(4)
C(4)	−671(21)	4158(9)	1476(9)	90(4)
C(5)	1179(19)	3651(12)	1361(12)	107(5)
N(1)	−2381(9)	987(6)	1119(5)	56(2)
O(1)	−3529(11)	274(8)	802(6)	101(3)
P(1)	−1724(3)	2313(2)	3393(2)	53(1)
O(2)	−409(12)	3200(8)	4184(5)	103(3)
C(6)	−96(19)	3150(14)	5456(10)	119(5)
O(3)	−3701(10)	2926(7)	3252(6)	94(3)
C(7)	−4886(16)	3301(11)	4201(10)	97(4)
O(4)	−2045(12)	1110(6)	4201(6)	92(3)
C(8)	−2972(14)	−94(9)	3879(9)	84(4)
B(1)	4845(8)	3395(6)	7874(6)	72(4)
F(1)	3376(12)	3389(10)	7222(9)	217(7)
F(2)	4798(13)	4298(11)	8656(9)	216(7)
F(3)	4943(16)	2309(9)	8401(13)	313(12)
F(4)	6263(13)	3585(14)	7221(8)	318(14)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

40–60°C) were dried over sodium wire and distilled. Dichloromethane was dried over phosphorus pentoxide and distilled. Chloroform was allowed to stand over magnesium sulphate in the dark prior to use. Analar grade acetone was used as supplied. Chromatography was performed on neutral alumina (Grade IV) under nitrogen. Infrared spectra were recorded on a Perkin–Elmer 1710 FTIR instrument. Nuclear magnetic resonance spectra were recorded on Jeol EX90 (89.56 MHz, ^{1}H; 36.25 MHz, ^{31}P) and Bruker AC300 (300.13 MHz, ^{1}H; 121.49 MHz, ^{31}P; 75.47 MHz, ^{13}C) spectrometers. Elemental analyses were by Butterworth Laboratories, London. Fast atom bombardment (FAB) mass spectra were obtained on a Kratos Concept S1 spectrometer.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(I)]$ (**1**) was prepared from $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(Br)]$ and sodium iodide in acetone. Nitrosonium tetrafluoroborate was obtained from Lancaster Synthesis and was washed rapidly with ice cold dichloromethane under nitrogen prior to immediate use.

$[(\eta^5\text{-}C_5H_5)Fe(P\{OMe\}_3)(CO)(I)]$ (2) [5]

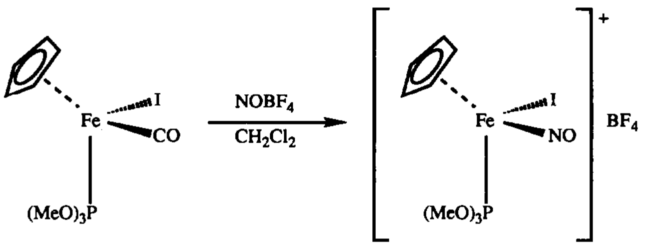
A mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(I)]$ (**1**) (1.80 g, 5.92 mmol) and trimethylphosphite (3.0 cm^3, 25.5 mmol) in benzene (75 cm^3) was stirred under reflux for 24 h. The volume was reduced to approximately 20 cm^3 and the dark solution was chromatographed using light petroleum ether to elute the excess ligand and dichloromethane to elute the product. Removal of the solvent under reduced pressure and crystallisation of the crude material from dichloromethane/light petroleum ether gave brown microcrystalline **2**, yield 1.80 g (76%). IR (nujol): ν_{max} 1960s cm^{-1} (CO). ^{1}H NMR (CDCl$_3$): δ 4.67 (d, J(PH) 0.9 Hz, 5H, C_5H_5), 3.71 (d, J(PH) 11.4 Hz, 9H, P(OMe)$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 206.9 (s, CO), 82.9 (d, J(PC) 2.0 Hz, C_5H_5), 53.6 (d, J(PC) 5.4 Hz, P(OMe)$_3$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 181.0 ppm.

$[(\eta^5\text{-}C_5H_5)Fe(P\{OMe\}_3)(NO)(I)BF_4$ (3)

Nitrosonium tetrafluoroborate (0.15 g, 1.28 mmol) was added to a cooled (0°C) solution of **2** (0.20 g, 0.50 mmol) in dichloromethane (30 cm^3) with stirring. After 15 min the reaction mixture was filtered and concentrated under reduced pressure (approx. 10 cm^3). Addition of diethylether (approx. 25 cm^3) and cooling to -30°C gave red-black blocks of **3**, yield 0.13 g (71%). Anal. Found: C, 19.67; H, 2.75; N, 2.54. $C_8H_{14}BNO_4F_4PFeI$ calc.: C, 19.66; H, 2.89; N, 2.87%. IR (nujol): ν_{max} 1872s cm^{-1} (NO). ^{1}H NMR (CDCl$_3$): δ 6.08 (s, 5H, C_5H_5), 3.95 (d, J(PH) 11.7 Hz, 9H, P(OMe)$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 99.3 (s, C_5H_5), 57.1 (d, J(PC) 8.7 Hz, P(OMe)$_3$) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 137.8 ppm. MS (FAB): m/z 402 $\{M-BF_4\}^+$.

Results and discussion

Treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(I)]$ (**1**) with trimethylphosphite in refluxing benzene and subsequent chromatographic purification gave the known brown microcrystalline $[(\eta^5\text{-}C_5H_5)Fe(P\{OMe\}_3)(CO)(I)]$ (**2**). Crystalline samples of **2** such as those used for the structural determination appear red-black in natural light. The spectroscopic parameters measured for **2** were in reasonable agreement with those reported by Schumann [6].



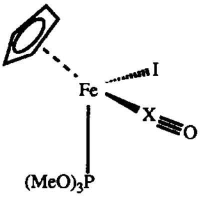
(2) (3)

Following the report by Treichel [1] that $[(\eta^5\text{-}C_5H_5)Fe(P\{OPh\}_3)(CO)(I)]$ could be reacted with $NOPF_6$ to produce $[(\eta^5\text{-}C_5H_5)Fe(P\{OPh\}_3(NO)(I)]PF_6$, we treated **2** with nitrosonium tetrafluoroborate in dichloromethane at 0°C. Red-black crystals of $[(\eta^5\text{-}C_5H_5)Fe(P\{OMe\}_3)(NO)(I)]BF_4$ (**3**) were obtained after work-up. The infrared spectrum of **3** contained a strong band at 1872 cm^{-1} assignable to $\nu(NO)$ while the ^1H NMR spectrum of **3** in $CDCl_3$ consisted of a singlet at δ 6.08 and a doublet at δ 3.95 ($J(PH) = 11.7$ Hz) due to the cyclopentadienyl and methoxy protons, respectively. The $^{31}P\{^1H\}$ NMR spectra of **2** and **3** each consisted of a singlet resonance due to the trimethylphosphite ligand at δ 181.0 for **2** and at δ 137.8 for **3**; the free ligand resonates at δ 140.0 [7].

The structures of **2** and **3** are shown in Figs. 1 and 2. Both **2** and **3** contain pseudo-octahedral geometry at the iron atom with the angle sums for the non-carbocyclic ligands being 279.0(5)° and 282.0(5)°, respectively. Selected bond lengths and bond angles for **2** and **3** are shown in Table 3.

The bonding scheme for phosphorus centred ligands (PX_3) to low oxidation state transition metals established by Orpen and Connelly [8] is clearly applicable when comparing the metal to phosphorus bond lengths in **2** and **3**; the π-acceptor orbitals are a combination of a phosphorus 3*d* orbitals and the P–X σ^* orbitals of

Table 3
Selected bond lengths (Å) and bond angles (°) for **2** and **3**



	CO (**2**)	NO^+ (**3**)
Fe–I	2.605(1)	2.591(1)
Fe–P	2.149(2)	2.206(2)
Fe–X	1.764(6)	1.643(6)
X–O	1.077(7)	1.125(10)
Fe–Cg [a]	1.738	1.736
P–Fe–X	92.9(2)	95.5(2)
P–Fe–I	93.3(1)	90.1(1)
X–Fe–I	92.8(2)	96.4(2)
Fe–X–O	177.3(7)	176.1(7)

[a] Cg denotes the geometric centre of the cyclopentadienyl ring.

e symmetry. Accordingly the greater the degree of metal to phosphorus back donation into π-symmetry orbitals the greater will be the weakening and elongation of the ligand P–X bonds; the metal to phosphorus bond will also strengthened and shortened. The trimethylphosphite ligand is sterically compact and should allow these electronic effects to be clearly observed. The increase in the metal to phosphorus bond length in **3** compared with **2** (2.149(2) versus 2.206(2) Å) is a consequence of the reduced electron density of the metal centre in (**3**) relative to **2** caused by the positive charge and the superior π-accepting ability of the nitrosyl group. This reduction in metal π-back donation has increased the metal to phosphorus bond length. Comparison of the phosphorus–oxygen bond lengths in the trimethylphosphite ligands supports this description; the averaged P–O bond lengths are 1.598(6) and 1.552(8) Å, respectively, for **2** and **3** indicating that there is a smaller π-acceptor component in **3** than in **2**.

The effect of the positive charge in **3** would be expected to reduce all metal to ligand bond lengths for σ and π-donor ligands relative to those observed for **2**, and a small effect is indeed observed for the iodide and cyclopentadienyl ligands.

Acknowledgements

We thank the European Social Fund for a studentship (J.E.K.) and Johnson-Matthey Chemicals Ltd. for a generous loan of $RuCl_3$.

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