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Synthesis and Crystal Structure of CpFe(CO)I(η^1-$Ph_2PCH_2P(O)Ph_2$)

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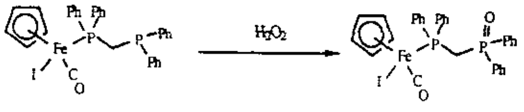
CpFe(CO)I(η^1-$Ph_2PCH_2P(O)Ph_2$) **2** was obtained in small yield from reaction of $[CpFe(CO)]_2[\mu\text{-}(Ph_2P)_2CH_2]$ with diiodine in benzene, or prepared in 82% yield on treating CpFe(CO)I(η^1-$Ph_2PCH_2PPh_2$) **1** with H_2O_2. Compound **2** crystallizes in the space group $P2_1/n$, with a = 8.441(2) Å, b = 10.054(2) Å, c = 33.343(8) Å, β = 92.33(2)°, Z = 4, V = 2827(1) Å^3, R_F = 0.057, and R_w = 0.056.

INTRODUCTION

The bidentate bisphosphine ligands, $R_2P(CH_2)_nPR_2$, are interesting to chemists because of their varied modes of coordination towards metal atoms.[1] The presence of bridging or capping ligands increases the stability of the metal atom framework and thus provides useful precursors of polynuclear clusters.[2]

Previously, Haines[3] showed that electrophilic attack of diiodine on Fe-Fe bond in $[CpFe(CO)]_2$(μ-dppe) afforded $[CpFe(CO)I]_2$(dppe), which we found to be subject to iodide substitution by metal carbonyl anions to generate heterotrimetallic complexes. In attempts to prepare the analogous dppm-bridged complex $[CpFe(CO)I]_2$(dppm), we heated $[CpFe(CO)]_2$(μ-dppm) with diiodine in benzene solution, but formed the known CpFe(CO)I(η^1-$Ph_2PCH_2PPh_2$) **1**,[3] and a green co-product CpFe(CO)I(η^1-$Ph_2PCH_2P(O)Ph_2$) **2** in small yield. We describe here the characterization and molecular structure of compound **2**, and conversion of **1** to **2** under oxidizing conditions (Eq. 1).



(1)

1 2

RESULTS AND DISCUSSION

The ^{1}H NMR and IR spectra of compound **1** agree with those reported by Haines.[3] The FAB mass spectrum of **2** gives the molecular ion signal at m/z = 676 (^{127}I, ^{56}Fe), and signals corresponding to loss of carbonyl and cyclopentadienyl groups. The ^{1}H NMR spectrum shows signals of the phenyl protons in the range 8.11-7.20 ppm, the Cp protons as a singlet at 4.35 ppm, and two complicated multiplets of diastereomeric methylene protons at 4.10 and 3.43 ppm. The $^{31}P\{^1H\}$ NMR spectrum reveals two doublets at 62.04 and 26.55 ppm ($^2J_{P\text{-}P}$ = 29 Hz), assigned to coordinated phosphorus and phosphoryl (P=O) atoms,[4] respectively, by comparison with compound **1** (63.16 and -25.28 ppm; $^2J_{P\text{-}P}$ = 56 Hz). The IR spectrum (KBr disc) includes strong absorptions at 1948 and 1199 cm^{-1}, assigned to ν(CO) and ν(P=O),[4,5] respectively.

Although the molecular structure of compound **1** has not been determined, it is expected to resemble that of compound **2**, shown in Fig. 1. From the center of the cyclopentadienyl group, coordination about iron is considered to be a distorted tetrahedron. The cyclopentadienyl group is bonded to the iron atom asymmetrically, with Fe-C bond distances ranging from 2.07(1) Å (Fe-C(28)) to 2.11(1) Å

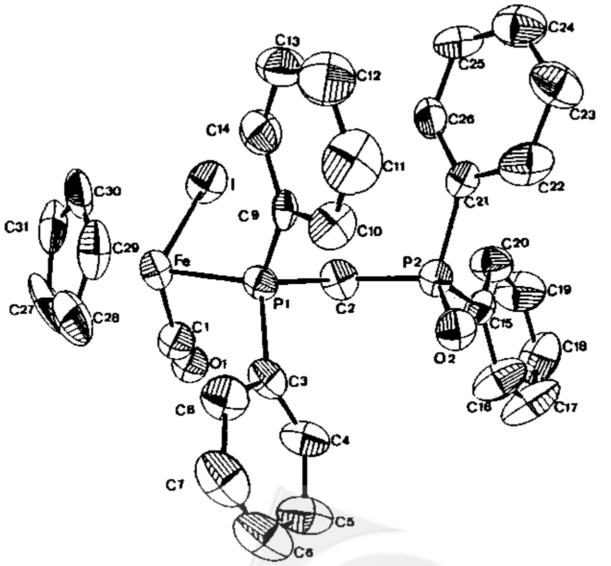


Fig. 1. Molecular structure of CpFe(CO)I(η^1-Ph_2PCH_2-$P(O)Ph_2$) **2**, showing the atomic labeling used in the text.

(Fe-C(30)). The P(2)-O(2) bond vector is opposite to the P(1)-Fe vector with torsional angles Fe-P(1)-C(2)-P(2) = 173.1(1)° and O(2)-P(2)-C(2)-P(1) = 39.1(4)°. The four phenyl groups are arranged according to steric demand, being staggered to each other. The enlarged ∠ P(1)-C(2)-P(2) angle 121.0(6)° is probably due to steric repulsions between two bulky phosphine moieties. The phosphoryl moiety is free of coordination with the P(2)-O(2) distance 1.485(8) Å, characteristic of a P=O double bond.[4c,5c,5d,6]

The formation of **2** is interesting because spontaneous oxidation of a dangling phosphine ligand is encountered in many cases,[4-7] but the mechanism leading to them is unclear.[6c] We made several tests to probe formation of **2**. Careful preparation and purification of **1** under dried nitrogen does not afford **2**. However, exposing the solution of **1** to air for 30 min shows formation of **2** in small proportions (*ca.* 7%), as evident from ^{31}P NMR, and the yield of **2** is not enhanced by extended exposure but leads to extensive decomposition over a period 24 h. Addition of water to the benzene solution of **1** under nitrogen also produced **2** in small yield. These results indicate that both O_2 and H_2O are influential in forming **2** but may not be directly. As phosphine compounds react with halogens, followed by hydrolysis in NaOH/H_2O solution to give phosphine oxides,[8] we suspect that partial decomposition of compound **1** might occur to release iodide or iodine atoms, which then attacked the dangling phosphine group; hydrolysis prompted by moisture would give **2**. However, as oxidation of phosphines is observed in several halogen-free complexes,[4a,6a] other unraveled routes are possible.

In attempts to increase the yield of compound **2**, we bubbled dioxygen through the solution of **1**, but achieved severe decomposition. Adding H_2O_2 (3% in water) in equimolar proportions to **1** in benzene solution at 25 °C afforded compound **2** in 82% yield. The peroxide reagent attacked the dangling phosphorus atom selectively without oxidizing the iron center. Nevertheless, oxidation of phosphine molecules by hydrogen peroxide is used to prepare phosphine oxides.[9,10]

EXPERIMENTAL SECTION

General Procedures

[CpFe(CO)]$_2$(μ-dppm) was prepared from [CpFe(CO)$_2$]$_2$ as described in the literature.[10] Iodine and bis(diphenylphosphino)methane (dppm) (Aldrich) were used as received. Thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). ^{1}H and ^{31}P{^{1}H} NMR spectra were measured (Varian VXR-300 spectrometer) at 300 MHz and 121.4 MHz, respectively. IR spectra were recorded on a Hitachi I-2001 spectrometer. Fast-atom-bombardment (FAB) mass spectra were obtained on a VG-5022 mass spectrometer.

Reaction of [CpFe(CO)]$_2$(μ-dppm) with I_2

A three-necked spherical flask (100 mL) was equipped with a magnetic stirring bar, a rubber serum stopper, a reflux condenser, and a nitrogen inlet. When the stopper was briefly removed, [CpFe(CO)]$_2$(μ-dppm) (200 mg, 0.29 mmol) and benzene (10 mL) were introduced against a nitrogen flow. The mixture was brought to reflux under nitrogen, and I_2 (89 mg, 0.35 mmol) in benzene (10 mL) solution was added dropwise over 15 min with a syringe. The resulting mixture was kept refluxing for 1 h, cooled to room temperature, and filtrated. The volatile materials were removed under vacuum and the residue separated by TLC, eluting with THF/hexane (1:4, v/v). Only CpFe(CO)I(η^1-$Ph_2PCH_2PPh_2$) (**1**) (6 mg, 4%) and CpFe(CO)I(η^1-$Ph_2PCH_2P(O)Ph_2$) (**2**) (14. mg, 8%) were isolated in small yields.

Much **1** was prepared according to Haine's method[3] by treating CpFe(CO)$_2$I with dppm ligand.

Table 1. Crystallographic Data and Refinement Details for Compound **2**

Empirical formula	$C_{31}H_{27}O_2P_2FeI$
Molar mass/g	676.24
Crystal system	monoclinic
Space group	$P2_1/n$
Radiation (λ/Å)	Mo K_α 0.70930
a/Å	8.441(2)
b/Å	10.054(2)
c/Å	33.343(8)
β/deg	92.33(2)
V/Å^3	2827.(1)
Z	4
T/K	298
D_{calc}/g cm^{-3}	1.589
μ/mm^{-1}	1.75
F(000)	1327.85
Scan parameters	2 (0.60 + 0.35 tan θ)
2θ max/deg	45.0
h, k, l range	-9, 9; 0, 10; 0, 35
No. of unique data	3675
No. of data with I>2σ(I)	1931
R_F[a]	0.057
R_w[a]	0.056
Goodness of fit	1.87

[a] $R_F = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w = \{\Sigma[\omega(|F_o|-|F_c|)^2]/\Sigma|F_o|^2]\}^{1/2}$

Table 2. Selected Bond Distances and Bond Angles for **2**

Bond distance/Å	
Fe-I	2.605(2)
Fe-P(1)	2.206(4)
Fe-C(1)	1.62(2)
Fe-C(27)	2.09(1)
Fe-C(28)	2.07(1)
Fe-C(29)	2.10(1)
Fe-C(30)	2.11(1)
Fe-C(31)	2.09(1)
P(1)-C(2)	1.82(1)
P(1)-C(3)	1.82(1)
P(1)-C(9)	1.82(1)
P(2)-C(2)	1.82(1)
P(2)-C(15)	1.80(1)
P(2)-C(21)	1.81(1)
P(2)-O(2)	1.485(8)
C(1)-O(1)	0.80(2)
Bond angle/deg	
I-Fe-P(1)	96.2(1)
I-Fe-C(1)	93.8(5)
P(1)-Fe-C(1)	89.9(5)
C(2)-P(2)-O(2)	115.5(5)
C(15)-P(2)-C(21)	106.7(6)
C(15)-P(2)-O(2)	111.5(5)
C(21)-P(2)-O(2)	112.6(5)
P(1)-C(2)-P(2)	121.0(6)
Fe-P(1)-C(2)	112.7(4)
Fe-P(1)-C(3)	112.0(4)
Fe-P(1)-C(9)	117.7(4)
C(2)-P(1)-C(3)	104.2(6)
C(2)-P(1)-C(9)	103.2(6)
C(3)-P(1)-C(9)	105.9(6)
C(2)-P(2)-C(15)	101.9(5)
C(2)-P(2)-C(21)	107.8(6)

Reaction of $CpFe(CO)I(\eta^1\text{-}Ph_2PCH_2PPh_2)$ with H_2O_2

$CpFe(CO)I(\eta^1\text{-}Ph_2PCH_2PPh_2)$ (400 mg, 0.61 mmol) was placed in a Schlenk flask (100 mL), equipped with a magnetic stirring bar and a rubber serum stopper, under a nitrogen atmosphere, and freshly distilled benzene (30 mL) was introduced with a syringe. An aqueous H_2O_2 solution (3%, 0.7 mL) was then added dropwise with a micro-syringe. The resulting mixture was stirred 2 h at 25 °C. The solvent was removed on a rotary evaporator and the residue subjected to TLC, eluting with dichloromethane. $CpFe(CO)I(\eta^1\text{-}Ph_2PCH_2P(O)Ph_2)$ (336 mg, 82%) was isolated from the major green band. Mass spectrum: m/z 676 (M^+, ^{56}Fe). IR (KBr disc): $\nu(CO)$ 1948, $\nu(P{=}O)$ 1199 cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): 8.11-7.20 (m, 20H, Ph), 4.35 (s, 5H, Cp), 4.15-4.04 (m, 1H, CH_2), 3.49-3.38 (m, 1H, CH_2) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 62.04 (d, P-Fe, $^2J_{P\text{-}P}$ = 29 Hz), 26.55 (d, P=O) ppm.

Table 3. Selected Atomic Coordinates of Compound **2**

Atom	x	y	z	B_{eq}
Fe	0.8075(2)	0.2869(2)	0.46135(5)	3.59(9)
I	1.0912(1)	0.1844(1)	0.46468(3)	4.78(5)
P1	0.7346(4)	0.2021(4)	0.4025(1)	2.9(2)
P2	0.8732(4)	0.1088(4)	0.3201(1)	3.0(2)
C1	0.864(2)	0.422(2)	0.4394(4)	3.9(5)
C2	0.898(1)	0.192(1)	0.3684(4)	3.4(6)
C3	0.588(1)	0.305(1)	0.3758(4)	3.4(6)
C4	0.629(2)	0.397(1)	0.3473(4)	4.5(7)
C5	0.520(2)	0.485(2)	0.3301(5)	5.6(8)
C6	0.367(2)	0.482(2)	0.3425(5)	5.9(9)
C7	0.322(2)	0.395(2)	0.3709(5)	5.7(9)
C8	0.434(1)	0.308(2)	0.3881(4)	4.4(7)
C9	0.654(1)	0.035(1)	0.4015(3)	2.7(6)
C10	0.540(2)	-0.009(1)	0.3729(4)	4.4(7)
C11	0.488(2)	-0.135(2)	0.3735(5)	6.2(9)
C12	0.547(2)	-0.226(2)	0.4013(5)	6.3(9)
C13	0.662(2)	-0.185(1)	0.4289(4)	4.9(8)
C14	0.714(2)	-0.055(1)	0.4294(4)	4.2(7)
C15	1.033(1)	0.178(1)	0.2930(3)	3.0(6)
C16	0.998(2)	0.280(2)	0.2670(4)	5.5(8)
C17	1.112(2)	0.338(2)	0.2458(5)	8(1)
C18	1.266(2)	0.300(2)	0.2508(4)	6.2(8)
C19	1.305(2)	0.203(2)	0.2768(4)	5.8(8)
C20	1.191(2)	0.140(1)	0.2978(4)	4.5(7)
C21	0.918(1)	-0.065(1)	0.3277(3)	2.8(6)
C22	0.850(2)	-0.152(2)	0.3003(4)	5.1(8)
C23	0.881(2)	-0.286(1)	0.3024(5)	5.5(8)
C24	0.977(2)	-0.334(2)	0.3323(4)	5.3(8)
C25	1.048(2)	-0.252(1)	0.3599(4)	4.4(7)
C26	1.016(2)	-0.117(1)	0.3577(4)	4.0(7)
C27	0.734(2)	0.407(2)	0.5082(5)	7(1)
C28	0.600(2)	0.358(2)	0.4845(5)	6.3(9)
C29	0.595(2)	0.222(2)	0.4854(4)	5.4(8)
C30	0.721(2)	0.181(2)	0.5103(4)	5.5(8)
C31	0.805(2)	0.292(2)	0.5239(4)	6.3(9)
O1	0.920(1)	0.4768(9)	0.4297(3)	3.9(5)
O2	0.7181(9)	0.1300(9)	0.2984(2)	3.8(4)
I′	0.92060	0.49750	0.42680	4.74
C1′	0.99800	0.21810	0.46350	3.95
O′	1.12320	0.17270	0.46500	3.95

X-ray diffraction measurements of $CpFe(CO)I(\eta^1\text{-}Ph_2PCH_2P(O)Ph_2)$

A dark green crystal of $CpFe(CO)I(\eta^1\text{-}Ph_2PCH_2P(O)Ph_2)$ with approximate dimensions 0.05 × 0.15 × 0.25 mm was mounted in a thin-walled glass capillary and aligned on the Nonius CAD-4 diffractometer. Diffraction data were collected with Mo K_α radiation (λ = 0.70930 Å) using $\theta/2\theta$ scan mode. Lattice parameters were determined from 25 randomly selected reflections with 2θ angle in the range 14.90-21.22°. All data were corrected for Lorentz and polarization effects and for effects of absorption. The structure was solved by the heavy-atom method and refined by least-square cycles; all non-hydrogen atoms were refined with anisotropic thermal parameters. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[11] The I atom and CO group were disordered in a 9:1 ratio. The data collection and refinement parameters are given in Table 1. Selected bond distances and bond angles are collected in Table 2. Atomic positional parameters are listed in Table 3.

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Key Words

Iron; Cyclopentadienyl; Phosphine.

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