

A structural study on bis{*trans*-[bis(diphenylphosphino)ethylene]}-tricarbonyliron(0) and *cis*-[bis(diphenylphosphino)ethylene]-tricarbonyliron(0)

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Abstract

Two routes have been employed in the synthesis of (*trans*-Ph₂PCH=CHPh₂)₂Fe(CO)₃ (**1**) and (*cis*-Ph₂PCH=CHPh₂)Fe(CO)₃ (**2**). Method A proceeds with the Me₃NO oxidative decarbonylation of (maleic acid)Fe(CO)₄, followed by a precipitation of maleate salt in the presence of either *trans*-Ph₂PCH=CHPh₂ or *cis*-Ph₂PCH=CHPh₂. Method B is a low temperature quenching of (*cis*-cyclooctene)₂Fe(CO)₃ with either *trans*-Ph₂PCH=CHPh₂ or *cis*-Ph₂PCH=CHPh₂. Complexes **1** and **2** have been characterized with spectroscopic methods and X-ray diffraction. X-ray crystallographic data for the title compounds: **1**, C₅₅H₄₄FeO₃P₄·CH₂Cl₂, monoclinic, space group *P*2₁/*c*, *a* = 11.532(2), *b* = 20.454(2), *c* = 22.652(6) Å, β = 104.49(2)°, *V* = 5173(2) Å³, *Z* = 4; 2547 data with *I*_o > 2.5σ(*I*_o) were refined to *R* = 0.049, *R*_w = 0.051; **2**, C₂₉H₂₂FeO₃P₂, monoclinic, space group *P*2₁/*c*, *a* = 10.064(1), *b* = 15.164(2), *c* = 17.379(2) Å, β = 101.17(1)°, *V* = 2602.2(5) Å³, *Z* = 4; 2274 data with *I*_o > 2.5σ(*I*_o) were refined to *R* = 0.035, *R*_w = 0.037. Complex **1** has a trigonal-pyramidal Fe(0) center with two diaxially-coordinated, unidentate *trans*-Ph₂PCH=CHPh₂. Compound **2** has a trigonal-pyramidal Fe(0) center with one chelating *cis*-Ph₂PCH=CHPh₂ occupying one axial and one equatorial site.

Introduction

Compounds of the type (diphosphine)Fe(CO)₃ have been reported for a number of diphosphines, e.g. dpmm, dppe, dppp, forming chelate rings with size 4, 5, 6, etc. [1]. It is our aim to see to what extent other diphosphines exhibiting geometric differences affect the structure of bonding around a Fe(0) center. With the double-bond fixed phosphine orientations, the diphosphines *trans*-Ph₂PCH=CHPh₂ and *cis*-Ph₂PCH=CHPh₂ would be expected to exhibit totally different coordination modes toward Fe(CO)₃. The 1:1 *trans*-Ph₂PCH=CHPh₂ to Fe(CO)₃ would be expected to form an adduct with oligomeric nature because two P donors are not able to coordinate to the same Fe(CO)₃. The 1:1 *cis*-Ph₂PCH=CHPh₂ to Fe(CO)₃ would form a chelated complex (*cis*-Ph₂PCH=CHPh₂)Fe(CO)₃ which has been reported by King and Eggers from the UV irradiation of a mixture of Fe₂(CO)₉ and *cis*-Ph₂PCH=CHPh₂ [2]. The *trans*-Ph₂PCH=CHPh₂ reaction with iron carbonyls has not been reported, however. The published synthetic procedures generally involve the reaction of a diphosphine with iron carbonyls

under various conditions [3]. In some cases, iron carbonyls are activated first. Here we report the synthesis of (*trans*-Ph₂PCH=CHPh₂)₂Fe(CO)₃ (**1**) from 1:1 *trans*-Ph₂PCH=CHPh₂ to Fe(CO)₃ and an improved synthesis of (*cis*-Ph₂PCH=CHPh₂)Fe(CO)₃ (**2**) from 1:1 *cis*-Ph₂PCH=CHPh₂ to Fe(CO)₃, with two different methods each. We also present the X-ray structure determinations of **1** and **2**.

Experimental

All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques, and all solvents were distilled from an appropriate drying agent [4]. IR spectra were recorded in CH₂Cl₂ using CaF₂ optics on a Perkin-Elmer 882 spectrophotometer. The ³¹P{¹H} NMR spectra were obtained on a Bruker MSL 200 spectrometer using 85% H₃PO₄ as external standard. Mass spectra were obtained on a VG system, model 70-2503 spectrometer. Microanalytical data were obtained with the use of a Perkin-Elmer 240 C elemental analyzer. The melting points were measured on a Yanaco micro melting point apparatus. (MA)Fe(CO)₄, MA = maleic acid, and (*cis*-

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$\text{COE}_2\text{Fe}(\text{CO})_3$, *cis*-COE = *cis*-cyclooctene, were prepared according to the literature procedures [5, 6]. Other reagents were obtained from commercial sources, e.g. Aldrich, Merck, and used without further purification.

Preparation of *trans*- $\text{Ph}_2\text{PCH}=\text{CHPPH}_2)_2\text{Fe}(\text{CO})_3$ (1) and (*cis*- $\text{Ph}_2\text{PCH}=\text{CHPPH}_2)_2\text{Fe}(\text{CO})_3$ (2)

Method A

(MA) $\text{Fe}(\text{CO})_4$ (284 mg, 1 mmol) and the diphosphine L (396 mg, 1 mmol) were dissolved in THF (50 ml) and stirred for 1/2 h at 0 °C. $(\text{CH}_3)_3\text{NO} \cdot 2\text{H}_2\text{O}$ (167 mg, 1.5 mmol) in CH_3OH (1 ml)/THF (15 ml) was added dropwise to the solution over a period of 2 h. The color of solution changed from yellow to dark brown. The solution was then refluxed at 70 °C for 2 h before filtration and evaporation to dryness under vacuum. The resultant yellow crystals were purified by

chromatography (Al_2O_3 , eluting with $\text{CH}_2\text{Cl}_2/n$ -hexane) and recrystallization ($\text{CH}_2\text{Cl}_2/n$ -hexane) to give 1 and 2, respectively.

1 (L = *trans*- $\text{Ph}_2\text{PCH}=\text{CHPPH}_2$): yellow powder (297 mg, 31.8% yield). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 77.97(s), -6.75(s). IR (CH_2Cl_2): $\nu(\text{CO})$ 1877 cm^{-1} . m.p. 79–81 °C. Mass (m/z) for $\text{C}_{55}\text{H}_{44}\text{FeO}_3\text{P}_4$: M^+ 932 (parent ion). Anal. Calc. for $\text{C}_{56}\text{H}_{46}\text{Cl}_2\text{FeO}_3\text{P}_4$: C, 66.08; H, 4.52. Found: C, 65.45; H, 4.81%. Crystals suitable for X-ray diffraction were grown by slow evaporation from $\text{CH}_2\text{Cl}_2/n$ -hexane.

2 (L = *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPH}_2$): orange–yellow powder (307 mg, 57.3% yield). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 116.9(s). IR (CH_2Cl_2): $\nu(\text{CO})$ 1987(s), 1915(s), 1898(s) cm^{-1} . m.p. 139–140 °C. Mass (m/z) for $\text{C}_{29}\text{H}_{22}\text{FeO}_3\text{P}_2$: M^+ 536 (parent ion). Anal. Calc. for $\text{C}_{29}\text{H}_{22}\text{FeO}_3\text{P}_2$: C, 64.93; H, 4.10. Found: C, 64.82; H, 3.98%. Crystals suitable

TABLE 1. Crystallographic data and refinement details for (*trans*- $\text{Ph}_2\text{PCH}=\text{CHPPH}_2)_2\text{Fe}(\text{CO})_3 \cdot \text{CH}_2\text{Cl}_2$ (1) and (*cis*- $\text{Ph}_2\text{PCH}=\text{CHPPH}_2)_2\text{Fe}(\text{CO})_3$ (2)

	1	2
Space group	$P2_1/c$	$P2_1/c$
a (Å)	11.532(2)	10.064(1)
b (Å)	20.454(2)	15.164(2)
c (Å)	22.652(6)	17.379(2)
β (°)	104.49(2)	101.17(1)
V (Å ³)	5173(2)	2602.2(5)
Empirical formula	$\text{C}_{56}\text{H}_{46}\text{Cl}_2\text{FeO}_3\text{P}_4$	$\text{C}_{29}\text{H}_{22}\text{FeO}_3\text{P}_2$
Crystal dimensions (mm)	0.50 × 0.25 × 0.24	0.54 × 0.22 × 0.15
FW	1017.61	536.28
Z	4	4
$F(000)$	2103.76	1103.85
D_{calc} (g cm^{-3})	1.307	1.369
Temperature (K)	298	298
μ (mm^{-1})	0.56	0.73
λ (Mo $K\alpha$) (Å)	0.7093	0.7093
2θ (max)	45	45
Diffractometer	Nonius CAD-4	Nonius CAD-4
Scan mode	$\theta/2\theta$	$\theta/2\theta$
Data ranges	$-12 < h < 12$ $0 < k < 22$ $0 < l < 24$	$-10 < h < 10$ $0 < k < 16$ $0 < l < 18$
Unique reflections	6750	3397
Observations	2547 $I_o > 2.5\sigma(I_o)$	2274 $I_o > 2.5\sigma(I_o)$
Absorption corrections	yes	yes
Transmission factors	0.940–0.998	0.939–0.999
Total atoms	112	57
Parameters	595	404
Weights ^a	counting statistics	counting statistics
Weight modifier	0.0001	0.0001
R^b	0.049	0.035
R_w^c	0.051	0.037
Goodness of fit	1.63	1.51
Max Δ/σ	0.016	0.114
Peaks in D-map (e Å ⁻³)		
highest	0.570	0.260
deepest	-0.260	-0.200

^a $w = 1/[\sigma(F_o)^2 + 0.0001(F_o)^2]$, $\sigma(F_o)$ from counting statistics. ^b $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^c $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

for X-ray diffraction were grown by slow evaporation from $\text{CH}_2\text{Cl}_2/n$ -hexane.

Method B

A solution of $(\text{cis-COE})_2\text{Fe}(\text{CO})_3$ (360 mg, 1 mmol) in THF (30 ml) was stirred for 10 min at -60°C before dropwise adding the diphosphine L (396 mg, 1 mmol) in THF (15 ml). After keeping the temperature at -60°C for 2 h more, the solution was then allowed to warm up to room temperature. The solution was then filtered and evaporated to dryness under vacuum, resulting in yellow solids **1** and **2**, respectively.

1 was further purified by chromatography (Al_2O_3 , eluting with $\text{CH}_2\text{Cl}_2/n$ -hexane) and recrystallization ($\text{CH}_2\text{Cl}_2/n$ -hexane) to give a yellow powder (516 mg, 55.3% yield).

2 was washed with n -hexane (3×30 ml) resulting in an orange-yellow powder (465 mg, 86.7% yield).

Structure analyses of $(\text{trans-Ph}_2\text{PCH=CHPh})_2\text{-Fe}(\text{CO})_3$ (**1**) and $(\text{cis-Ph}_2\text{PCH=CHPh})_2\text{Fe}(\text{CO})_3$ (**2**)

A summary of crystal data and refinement details is given in Table 1. Diffraction intensities were measured

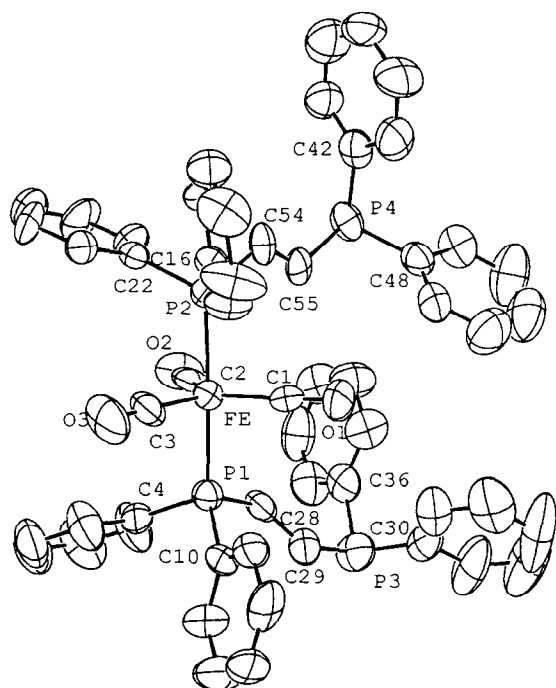


Fig. 1. ORTEP diagram of **1** with thermal ellipsoids at 50% probability. The atomic numbering sequence is attached. The H atoms are omitted for clarity. Selected bond lengths and angles: Fe–P(1) = 2.209(3), Fe–P(2) = 2.209(3), Fe–C(1) = 1.755(11), Fe–C(2) = 1.773(11), Fe–C(3) = 1.756(11), C(28)–C(29) = 1.336(15), C(54)–C(55) = 1.340(15) Å; P(1)–Fe–P(2) = 175.64(12), P(1)–Fe–C(1) = 91.9(3), P(1)–Fe–C(2) = 86.4(3), P(1)–Fe–C(3) = 90.3(3), P(2)–Fe–C(1) = 91.1(3), P(2)–Fe–C(2) = 89.4(3), P(2)–Fe–C(3) = 90.9(3), C(1)–Fe–C(2) = 118.3(5), C(1)–Fe–C(3) = 121.0(5), C(2)–Fe–C(3) = 120.6(5)°.

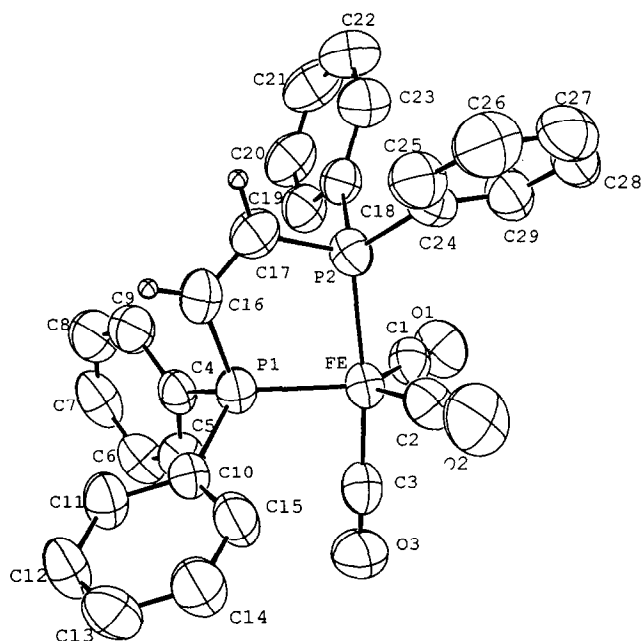


Fig. 2. ORTEP diagram of **2** with thermal ellipsoids at 50% probability. The atomic numbering sequence is attached. The H atoms except H(16) and H(17) are omitted for clarity. Selected bond lengths and angles: Fe–P(1) = 2.205(2), Fe–P(2) = 2.217(2), Fe–C(1) = 1.758(6), Fe–C(2) = 1.768(6), Fe–C(3) = 1.751(6), C(16)–C(17) = 1.337(8) Å; P(1)–Fe–P(2) = 83.91(6), P(1)–Fe–C(1) = 126.7(2), P(1)–Fe–C(2) = 115.5(2), P(1)–Fe–C(3) = 89.1(2), P(2)–Fe–C(1) = 91.1(2), P(2)–Fe–C(2) = 91.8(2), P(2)–Fe–C(3) = 172.7(2), C(1)–Fe–C(2) = 117.7(3), C(1)–Fe–C(3) = 91.4(3), C(2)–Fe–C(3) = 93.2(3)°.

with background counts made for half the total scan time on each side of the peak. Three standard reflections, remeasured after every hour, showed no significant decrease in intensity during data collection. Data were corrected for Lorentz–polarization and absorption (empirical psi corrections). The structures were solved by direct methods MULTAN [7]. Calculations and full-matrix least-squares refinements were performed utilizing the NRCVAX program package [8] with anisotropic thermal parameters for all non-hydrogen atoms. Scattering factor curves of Fe, Cl, P, O, C and H were taken from the International Tables [9]. The hydrogen parameters of **1** were calculated ($\text{C–H} = 1.00$ Å). For **1**, a solvent CH_2Cl_2 was also located at the anisotropic convergence. For **2**, the hydrogen atoms were located in a D -map at the anisotropic convergence and included in the refinement isotropically. The final refinement converged to $R = 0.049$ and $R_w = 0.051$ for **1**, and to $R = 0.035$ and $R_w = 0.037$ for **2**. For **1**, the largest peak ($0.57 \text{ e } \text{Å}^{-3}$) in the final difference map is found to be at (0.483, 0.298, 0.106) about 1.39 Å from P3*.

*An attempt to refine this position as an oxygen atom has resulted in unreasonably large thermal parameters ($U_{ij} = 0.37, 0.65, 0.49, 0.09, 0.11$ and 0.15) even at 30% occupancy. This residual peak may be rationalized with a very minor co-crystallization of the corresponding phosphine oxide in the crystal.

TABLE 2. Final atomic fractional coordinates and equivalent isotropic displacement coefficients (\AA^2) for non-hydrogen atoms in (*trans*-Ph₂PCH=CHPh₂)₂Fe(CO)₃·CH₂Cl₂ (**1**)

Atom	x	y	z	B_{iso}^a
FE	0.86282(13)	0.03664(7)	0.20272(6)	3.49(7)
P1	0.80914(26)	0.10907(13)	0.12855(13)	3.80(14)
P2	0.90428(23)	-0.04014(13)	0.27349(11)	3.49(14)
P3	0.54872(31)	0.26467(17)	0.15523(17)	6.32(20)
P4	0.64036(27)	-0.00145(17)	0.38793(13)	5.00(17)
Cl1	0.64672(47)	0.82959(24)	0.03358(22)	13.82(38)
Cl2	0.89172(49)	0.85027(25)	0.03670(23)	14.77(40)
O1	0.9076(8)	0.1380(4)	0.2959(3)	6.7(5)
O2	0.6194(6)	-0.0138(4)	0.1606(3)	6.6(5)
O3	1.0546(7)	-0.0091(4)	0.1507(4)	7.7(5)
C1	0.8891(10)	0.0980(5)	0.2586(5)	4.1(6)
C2	0.7157(10)	0.0049(5)	0.1775(4)	4.4(6)
C3	0.9780(11)	0.0086(6)	0.1711(5)	5.0(7)
C4	0.7549(10)	0.0725(5)	0.0535(4)	4.0(6)
C5	0.8304(11)	0.0425(7)	0.0260(6)	7.6(9)
C6	0.7876(15)	0.0132(7)	-0.0323(7)	8.3(10)
C7	0.6694(15)	0.0140(8)	-0.0595(6)	8.2(10)
C8	0.5959(12)	0.0447(9)	-0.0329(7)	9.1(11)
C9	0.6387(13)	0.0737(7)	0.0240(6)	7.4(9)
C10	0.9144(10)	0.1697(5)	0.1147(5)	4.1(6)
C11	1.0166(11)	0.1848(5)	0.1584(5)	5.1(7)
C12	1.0925(11)	0.2343(6)	0.1470(7)	7.0(9)
C13	1.0703(14)	0.2653(7)	0.0933(7)	7.1(9)
C14	0.9679(15)	0.2511(7)	0.0503(6)	8.1(10)
C15	0.8924(11)	0.2034(6)	0.0603(5)	6.4(8)
C16	1.0591(9)	-0.0486(5)	0.3182(4)	3.7(6)
C17	1.0924(10)	-0.0993(5)	0.3586(5)	4.4(6)
C18	1.2097(12)	-0.1051(6)	0.3927(5)	5.8(7)
C19	1.2927(10)	-0.0593(7)	0.3866(5)	6.7(8)
C20	1.2617(10)	-0.0077(7)	0.3478(5)	7.2(8)
C21	1.1459(11)	-0.0025(6)	0.3149(5)	5.6(7)
C22	0.8658(10)	-0.1235(5)	0.2435(4)	3.5(6)
C23	0.7482(10)	-0.1457(5)	0.2336(5)	5.0(7)
C24	0.7185(12)	-0.2053(6)	0.2074(6)	6.9(9)
C25	0.8001(17)	-0.2442(6)	0.1898(6)	8.4(11)
C26	0.9151(14)	-0.2218(6)	0.1989(6)	7.1(9)
C27	0.9493(10)	-0.1617(6)	0.2243(5)	4.8(6)
C28	0.6810(10)	0.1553(5)	0.1377(4)	4.4(6)
C29	0.6767(9)	0.2203(5)	0.1414(4)	4.7(6)
C30	0.6180(12)	0.3094(6)	0.2232(6)	5.7(8)
C31	0.5638(14)	0.3651(8)	0.2334(8)	10.5(13)
C32	0.6045(19)	0.4026(10)	0.2832(13)	13.9(20)
C33	0.7086(18)	0.3851(11)	0.3223(11)	13.5(18)
C34	0.7681(12)	0.3282(9)	0.3156(7)	9.0(11)
C35	0.7205(14)	0.2903(7)	0.2648(7)	7.4(9)
C36	0.4684(11)	0.2006(6)	0.1822(6)	5.4(7)
C37	0.4953(11)	0.1752(7)	0.2407(7)	6.7(8)
C38	0.4323(14)	0.1241(7)	0.2565(6)	7.5(9)
C39	0.3384(13)	0.0975(7)	0.2158(8)	7.4(10)
C40	0.3074(13)	0.1215(9)	0.1583(8)	8.4(10)
C41	0.3714(14)	0.1733(8)	0.1414(6)	7.3(9)
C42	0.7338(10)	-0.0459(6)	0.4524(5)	4.9(7)
C43	0.8310(12)	-0.0188(6)	0.4943(6)	6.6(8)
C44	0.8977(11)	-0.0573(7)	0.5419(6)	7.3(8)
C45	0.8690(15)	-0.1208(7)	0.5472(6)	7.6(10)
C46	0.7688(15)	-0.1467(7)	0.5062(7)	8.1(10)
C47	0.7049(11)	-0.1098(7)	0.4590(6)	6.1(8)
C48	0.6413(11)	0.0827(6)	0.4130(5)	5.0(7)

(continued)

TABLE 2. (continued)

Atom	x	y	z	B_{iso}^a
C49	0.5553(11)	0.1023(7)	0.4427(6)	6.3(8)
C50	0.5457(14)	0.1653(9)	0.4597(9)	10.1(12)
C51	0.6207(17)	0.2098(8)	0.4500(8)	9.3(11)
C52	0.7070(15)	0.1950(8)	0.4212(7)	9.1(11)
C53	0.7175(12)	0.1313(7)	0.4032(5)	6.6(8)
C54	0.8244(8)	-0.0390(5)	0.3339(4)	4.1(5)
C55	0.7316(9)	0.0007(5)	0.3331(4)	4.2(6)
C56	0.7745(16)	0.8754(7)	0.0654(6)	10.8(12)

$$^a B_{\text{iso}} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

TABLE 3. Final atomic fractional coordinates and equivalent isotropic displacement coefficients (\AA^2) for non-hydrogen atoms in (*cis*-Ph₂PCH=CHPh₂)Fe(CO)₃ (**2**)

Atom	x	y	z	B_{iso}^a
FE	0.25127(6)	0.71730(4)	0.12135(4)	4.20(3)
P1	0.27985(12)	0.82590(7)	0.20722(6)	4.27(6)
P2	0.12453(12)	0.65971(8)	0.19962(7)	4.47(6)
O1	0.4094(3)	0.5556(2)	0.1249(2)	7.0(2)
O2	0.0221(4)	0.7328(2)	-0.0096(2)	8.8(2)
O3	0.4339(4)	0.8076(2)	0.0365(2)	8.3(2)
C1	0.3474(5)	0.6200(3)	0.1259(3)	4.9(2)
C2	0.1101(5)	0.7278(3)	0.0435(3)	5.4(3)
C3	0.3604(5)	0.7719(3)	0.0697(3)	5.4(3)
C4	0.4395(4)	0.8308(3)	0.2777(2)	4.2(2)
C5	0.5555(5)	0.8491(3)	0.2516(3)	5.3(3)
C6	0.6795(6)	0.8537(4)	0.3026(4)	6.3(3)
C7	0.6872(7)	0.8384(4)	0.3803(4)	6.7(4)
C8	0.5736(7)	0.8181(4)	0.4075(3)	7.3(4)
C9	0.4480(6)	0.8140(3)	0.3567(3)	6.0(3)
C10	0.2586(4)	0.9395(3)	0.1719(2)	4.0(2)
C11	0.3147(5)	1.0108(3)	0.2161(3)	5.4(3)
C12	0.2922(6)	1.0962(3)	0.1889(3)	6.1(3)
C13	0.2103(6)	1.1122(3)	0.1180(3)	5.9(3)
C14	0.1545(6)	1.0428(4)	0.0736(3)	6.2(3)
C15	0.1793(5)	0.9581(3)	0.0995(3)	5.7(3)
C16	0.1538(5)	0.8178(3)	0.2678(3)	5.0(3)
C17	0.0813(5)	0.7452(3)	0.2632(3)	5.1(3)
C18	0.1939(5)	0.5780(3)	0.2741(2)	4.6(2)
C19	0.3285(5)	0.5842(4)	0.3112(3)	5.6(3)
C20	0.3799(6)	0.5294(5)	0.3730(3)	6.9(4)
C21	0.2999(7)	0.4670(4)	0.3977(3)	7.6(4)
C22	0.1667(7)	0.4591(4)	0.3619(4)	7.4(4)
C23	0.1137(6)	0.5156(4)	0.3006(3)	6.1(3)
C24	-0.0350(5)	0.6115(3)	0.1505(2)	4.7(2)
C25	-0.1560(5)	0.6550(4)	0.1480(3)	6.0(3)
C26	-0.2746(6)	0.6201(5)	0.1061(4)	7.8(4)
C27	-0.2736(8)	0.5422(5)	0.0678(4)	7.8(4)
C28	-0.1551(8)	0.4983(4)	0.0685(3)	7.0(4)
C29	-0.0342(6)	0.5330(4)	0.1098(3)	6.0(3)

$$^a B_{\text{iso}} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

Selected bond distances and angles of **1** and **2** are given in the captions of Figs. 1 and 2, and the final atomic fractional coordinates are given in Tables 2 and 3, respectively.

Results and discussion

Synthesis

Two different procedures have been employed in this study for the synthesis of (diphosphine)Fe(CO)₃. The overall scheme is shown in Scheme 1.

Method A proceeds with an oxidative decarbonylation, followed by the precipitation of a maleate salt in the presence of *trans*- or *cis*-Ph₂PCH=CHPPh₂ [10]. The oxidative decarbonylation step produces gaseous CO₂ and NMe₃, then the leaving ligand MA reacts with NMe₃ to form a salt (HNMe₃)⁺MA⁻ in refluxing THF. Method B is a low temperature route by quenching (cis-COE)₂Fe(CO)₃ with *trans*- or *cis*-Ph₂PCH=CHPPh₂, respectively. Method B is a much neater and more efficient procedure in which (cis-COE)₂Fe(CO)₃ serves as a nice Fe(CO)₃ transfer reagent at temperatures well below 0 °C. Examples of *cis*-COE exchange by other ligands are the synthesis of (diene)Fe(CO)₃ [11], (diphosphacyclobutadiene)Fe(CO)₃ [12], metal clusters containing fragment of Fe(CO)₃ [13], and (chelate-P,S)Fe(CO)₃ [14]. For *trans*-Ph₂PCH=CHPPh₂, either method results in **1** and for *cis*-Ph₂PCH=CHPPh₂, either method gives **2**. The yields of **1** are 31.8% and 55.3%; those of **2** are 57.3% and 86.7% for methods A and B, respectively.

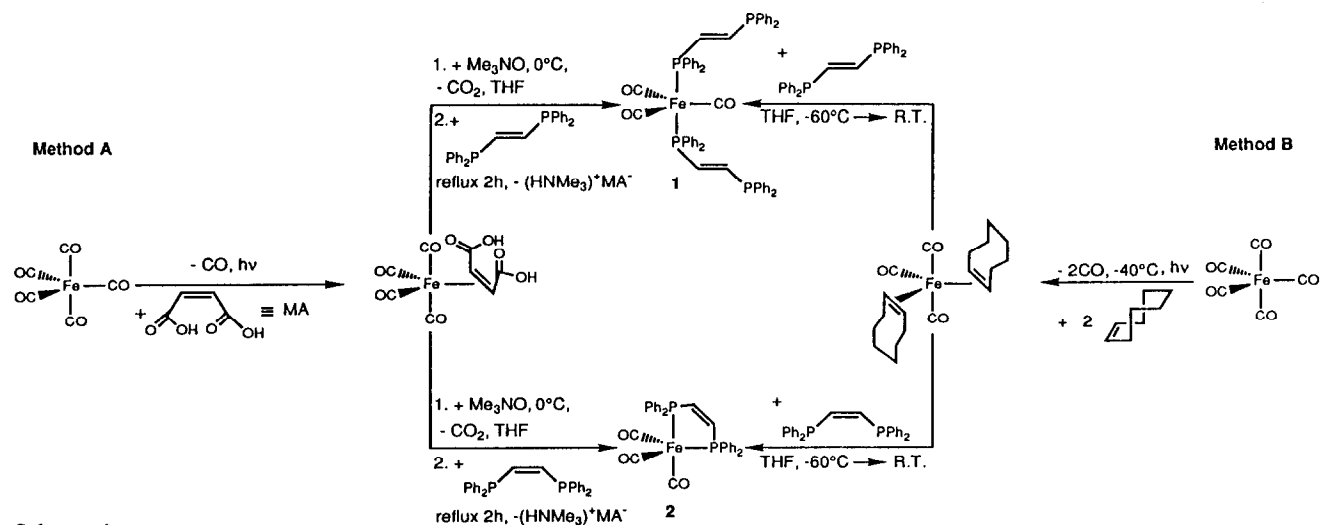
Spectroscopy

Both **1** and **2** have been characterized with ³¹P{¹H} NMR, IR, m.p., EA, mass, and X-ray structure analysis. With one ν(CO) band in the IR spectrum, **1** is expected to have two P atoms coordinated diaxially at *trans* positions around a *tbp* Fe(0) center, whereas with three ν(CO) absorptions in the IR spectrum, **2** is expected to have one P atom axial and the other P atom equatorial. The ³¹P{¹H} NMR spectrum of **1** shows two singlets of similar intensity at δ 77.97 for the coordinated P

donor and at δ -6.75 for the uncoordinated P donor. The P atoms of free *trans*-Ph₂PCH=CHPPh₂ resonate at δ -6.75. Since an uncoordinated ³¹P{¹H} peak has been detected, **1** must have two unidentate diphosphine ligands. The ³¹P{¹H} NMR spectrum of **2** shows just one peak at δ 116.9, instead of two peaks corresponding to one axial and one equatorial. The ³¹P peak for free *cis*-Ph₂PCH=CHPPh₂ is also at δ -6.75. The coordination shift for *cis*-Ph₂PCH=CHPPh₂ is much larger than that for *trans*-Ph₂PCH=CHPPh₂. It is also reasoned that the fluxional exchange of **2** between its axial and the equatorial P donors is so fast that the time scale of ³¹P{¹H} NMR is unable to differentiate.

Structure

Figure 1 shows the X-ray structure of **1**, in which the *tbp* Fe(0) center is seen to be coordinated by two unidentate *trans*-Ph₂PCH=CHPPh₂, each ligand has one P coordinating to the Fe(0) center and the other P dangling. The Fe-P distances are both 2.209(3) Å. The angle P(1)-Fe-P(2) is 175.64(12)°. The two P-Fe bonds are 2.2(5) and 8.0(5)°, respectively, from a perfectly staggered conformation. The overall P...P geometry is 6.0(6)° from the fully eclipsed conformation. This is the general geometry in known (PR₃)₂Fe(CO)₃ structures, e.g. *trans*-[(OMe)₃P]₂Fe(CO)₃ [15], *trans*-[(Me₂N)₃P]₂Fe(CO)₃ [16] and *trans*-P(OCH₂)₃PFe(CO)₃P(OCH₂)₃P [17]. The P...P distances in the *trans*-P=C=C-P moiety have been calculated to be 4.519(4) and 4.543(4) Å, respectively, which are probably too short to form a dimeric [(*trans*-Ph₂PCH=CHPPh₂)Fe(CO)₃]₂. For two diphosphines to bridge two Fe(CO)₃ groups in a dimeric form, a P...P distance of 7.539(3) Å has been found in {[Ph₂P(CH₂)₅PPh₂]Fe(CO)₃]₂ [1e]. The planar groups P(1)-C(28)-C(29)-P(3) and P(2)-C(54)-C(55)-P(4) in **1** are *cis* to each other with an inter-planar angle of



Scheme 1.

56.3(13)°. The torsional angle of C(28)–P(1)···P(2)–C(54) is 6.5(5)°. Should these inter-planar constraints also exist in a cyclic oligomer, [(*trans*-P–C=C–P)Fe(CO)₃]_n, *n* would be approximately 3 or 6, taking molecular inter-planar angles of 120 (180–60) or 60°, respectively. This static oligomer is unfavorable to the entropy consideration and to the fluxional behavior around *tbp* Fe(0) centers. Other structural parameters for the ligands are in the expected range for distances and angles involving P or C atoms.

The X-ray structure of **2** as shown in Fig. 2 reveals a *tbp* Fe(0) center with the chelating diphosphine occupying one axial and one equatorial site, consistent with a *cis* form. The P(1)–Fe–P(2) angle is 83.92(5)°, compared with 85.81(3)° in [*o*-C₆H₄(PPh₂)₂]Fe(CO)₃ [18], 87.9(1)° in [OCCH=CHC(O)O(PPh₂)₂]Fe(CO)₃ [2e] and 84.4(1)° in (CO)₃Fe[μ-(Ph₂P)₂C₆H₂(PPh₂)₂]Fe(CO)₃ [19]. These diphosphines all have two *cis* PPh₂ moieties linked by a partial double bond or an aromatic C–C bond. The corresponding Fe(CO)₃ complexes have a slightly distorted *tbp* around the Fe(0) center. In this series, **2** exhibits the smallest diphosphine bite angle, attributable to the shortest C–C length (1.315(7) Å). The C–C bond lengths are 1.385(4) Å in [*o*-C₆H₄(PPh₂)₂]Fe(CO)₃, 1.325(4) Å in [OCCH=CHC(O)O(PPh₂)₂]Fe(CO)₃ and 1.412(7) Å in (CO)₃Fe[μ-(Ph₂P)₂C₆H₂(PPh₂)₂]Fe(CO)₃. The saturated counterpart (dppe)Fe(CO)₃ shows a tremendously different geometry: its P–Fe–P angle is 84.1(1)° [1b], seemingly the same as that in **2**, but its largest angle of P–Fe–C is only 143.3(2)°, significantly different from the axial P–Fe–C angle 172.5(2)° in **2**.

The application of the τ test [20, 21] has revealed that **2** and (dppe)Fe(CO)₃ conform to different bonding geometries ($\tau=0$ defines a perfect square pyramid, *sp*, and $\tau=1$, a regular *tbp*). Using the largest angle around a penta-coordinate Fe(0) center as α and the second largest angle as β yields $\tau=(\alpha-\beta)/60$. For **2** the geometry is pseudo-*tbp*: the τ value being 0.76. For (dppe)Fe(CO)₃, however it is pseudo-*sp*: the τ value being 0.35.

In complex **2**, P(1)–C(16)–C(17)–P(2) is planar to within 0.02 Å and Fe is displaced from the plane by 0.490(4) Å, forming an enveloped five-membered heterocyclic ring. Other structural parameters for the ligands are in the expected range for distances and angles involving P or C atoms.

Supplementary material

For the two structures **1** and **2**, listings of positional and anisotropic thermal parameters and complete bond distances and angles (13 pages); and listings of *F_o*/*F_c* (36 pages) are available from author L.-K.L.

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