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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*-$Ph_2PCH{=}CHPPh_2)_2Fe(CO)_3$ (**1**) and (*cis*-$Ph_2PCH{=}CHPPh_2)Fe(CO)_3$ (**2**). Method A proceeds with the Me_3NO oxidative decarbonylation of (maleic acid)$Fe(CO)_4$, followed by a precipitation of maleate salt in the presence of either *trans*-$Ph_2PCH{=}CHPPh_2$ or *cis*-$Ph_2PCH{=}CHPPh_2$. Method B is a low temperature quenching of (*cis*-cyclooctene)$_2Fe(CO)_3$ with either *trans*-$Ph_2PCH{=}CHPPh_2$ or *cis*-$Ph_2PCH{=}CHPPh_2$. Complexes **1** and **2** have been characterized with spectroscopic methods and X-ray diffraction. X-ray crystallographic data for the title compounds: **1**, $C_{55}H_{44}FeO_3P_4 \cdot CH_2Cl_2$, monoclinic, space group $P2_1/c$, $a=11.532(2)$, $b=20.454(2)$, $c=22.652(6)$ Å, $\beta=104.49(2)°$, $V=5173(2)$ Å^3, $Z=4$; 2547 data with $I_o>2.5\sigma(I_o)$ were refined to $R=0.049$, $R_w=0.051$; **2**, $C_{29}H_{22}FeO_3P_2$, monoclinic, space group $P2_1/c$, $a=10.064(1)$, $b=15.164(2)$, $c=17.379(2)$ Å, $\beta=101.17(1)°$, $V=2602.2(5)$ Å^3, $Z=4$; 2274 data with $I_o>2.5\sigma(I_o)$ 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*-$Ph_2PCH{=}CHPPh_2$. Compound **2** has a trigonal-pyramidal Fe(0) center with one chelating *cis*-$Ph_2PCH{=}CHPPh_2$ 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. dppm, 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*-$Ph_2PCH{=}CHPPh_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$ would be expected to exhibit totally different coordination modes toward $Fe(CO)_3$. The 1:1 *trans*-$Ph_2PCH{=}CHPPh_2$ 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*-$Ph_2PCH{=}CHPPh_2$ to $Fe(CO)_3$ would form a chelated complex (*cis*-$Ph_2PCH{=}CHPPh_2)Fe(CO)_3$ which has been reported by King and Eggers from the UV irradiation of a mixture of $Fe_2(CO)_9$ and *cis*-$Ph_2PCH{=}CHPPh_2$ [2]. The *trans*-$Ph_2PCH{=}CHPPh_2$ 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*-$Ph_2PCH{=}CHPPh_2)_2Fe(CO)_3$ (**1**) from 1:1 *trans*-$Ph_2PCH{=}CHPPh_2$ to $Fe(CO)_3$ and an improved synthesis of (*cis*-$Ph_2PCH{=}CHPPh_2)Fe(CO)_3$ (**2**) from 1:1 *cis*-$Ph_2PCH{=}CHPPh_2$ 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 CH_2Cl_2 using CaF_2 optics on a Perkin-Elmer 882 spectrophotometer. The $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker MSL 200 spectrometer using 85% H_3PO_4 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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COE)$_2$Fe(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-Ph$_2$PCH=CHPPh$_2$)$_2$Fe(CO)$_3$, (1) and (cis-Ph$_2$PCH=CHPPh$_2$)Fe(CO)$_3$ (2)

Method A

(MA)Fe(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. $(CH_3)_3NO \cdot 2H_2O$ (167 mg, 1.5 mmol) in CH$_3$OH (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$_2$O$_3$, eluting with CH$_2$Cl$_2$/*n*-hexane) and recrystallization (CH$_2$Cl$_2$/*n*-hexane) to give **1** and **2**, respectively.

1 (L = *trans*-Ph$_2$PCH=CHPPh$_2$): yellow powder (297 mg, 31.8% yield). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 77.97(s), −6.75(s). IR (CH$_2$Cl$_2$): ν(CO) 1877 cm^{-1}. m.p. 79–81 °C. Mass (*m*/*z*) for $C_{55}H_{44}FeO_3P_4$: M^+ 932 (parent ion). *Anal.* Calc. for $C_{56}H_{46}Cl_2FeO_3P_4$: 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 CH$_2$Cl$_2$/*n*-hexane.

2 (L = *cis*-Ph$_2$PCH=CHPPh$_2$): orange–yellow powder (307 mg, 57.3% yield). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 116.9(s). IR (CH$_2$Cl$_2$): ν(CO) 1987(s), 1915(s), 1898(s) cm^{-1}. m.p. 139–140 °C. Mass (*m*/*z*) for $C_{29}H_{22}FeO_3P_2$: M^+ 536(parent ion). *Anal.* Calc. for $C_{29}H_{22}FeO_3P_2$: C, 64.93; H, 4.10. Found: C, 64.82; H, 3.98%. Crystals suitable

TABLE 1. Crystallographic data and refinement details for (*trans*-Ph$_2$PCH=CHPPh$_2$)$_2$Fe(CO)$_3$·CH$_2$Cl$_2$ (**1**) and (*cis*-Ph$_2$PCH=CHPPh$_2$)Fe(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	$C_{56}H_{46}Cl_2FeO_3P_4$	$C_{29}H_{22}FeO_3P_2$
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 Kα) (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	$-12 < h < 12$	$-10 < h < 10$
	$0 < k < 22$	$0 < k < 16$
	$0 < l < 24$	$0 < l < 18$
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] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{(1/2)}$.

for X-ray diffraction were grown by slow evaporation from CH_2Cl_2/*n*-hexane.

Method B

A solution of (*cis*-COE)$_2$Fe(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 CH_2Cl_2/*n*-hexane) and recrystallization (CH_2Cl_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 (trans-$Ph_2PCH{=}CHPPh_2)_2$-$Fe(CO)_3$ (1) and (cis-$Ph_2PCH{=}CHPPh_2)Fe(CO)_3$ (2)

A summary of crystal data and refinement details is given in Table 1. Diffraction intensities were measured 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 (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 e Å^{-3}) in the final difference map is found to be at (0.483, 0.298, 0.106) about 1.39 Å from P3*.

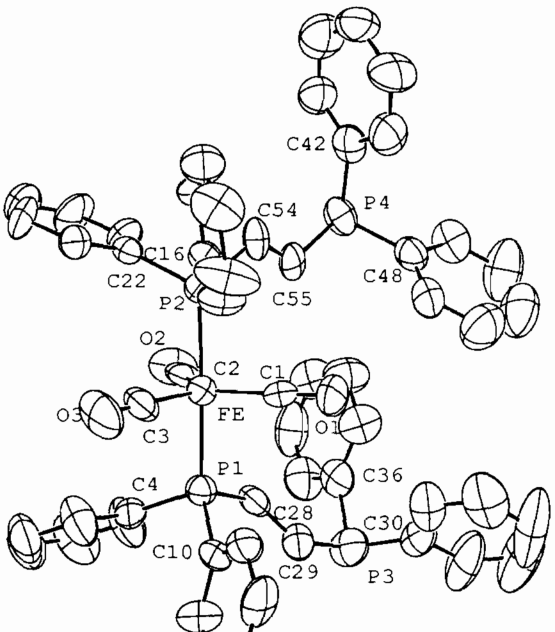

Fig. 1. ORTEP diagram of **1** with thermal ellipsoids at 50% probability. The atomic numbering sequence is attached. The H atoms are omitted for clarity. Selected bond lengths and angles: Fe–P(1) = 2.209(3), Fe–P(2) = 2.209(3), Fe–C(1) = 1.755(11), Fe–C(2) = 1.773(11), Fe–C(3) = 1.756(11), C(28)–C(29) = 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)°.

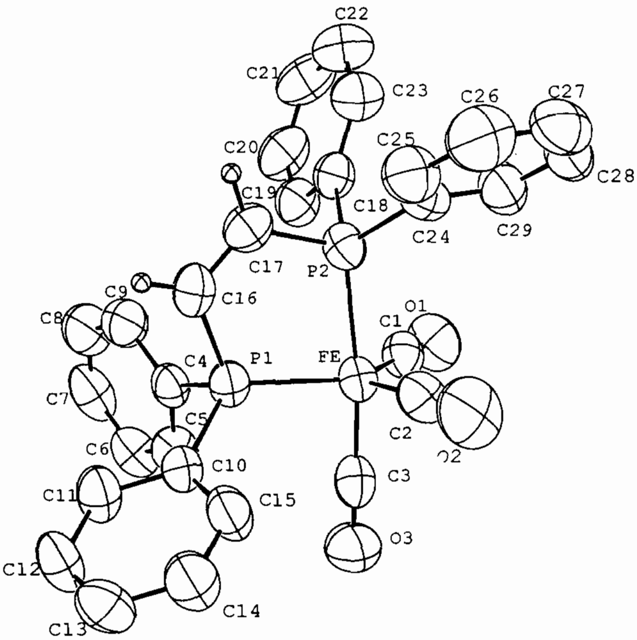

Fig. 2. ORTEP diagram of **2** with thermal ellipsoids at 50% probability. The atomic numbering sequence is attached. The H atoms except H(16) and H(17) are omitted for clarity. Selected bond lengths and angles: Fe–P(1) = 2.205(2), Fe–P(2) = 2.217(2), Fe–C(1) = 1.758(6), Fe–C(2) = 1.768(6), Fe–C(3) = 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)°.

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*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 (Å^2) for non-hydrogen atoms in (*trans*-$Ph_2PCH{=}CHPPh_2)_2Fe(CO)_3 \cdot CH_2Cl_2$ (**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)
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] $B_{iso} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

TABLE 3. Final atomic fractional coordinates and equivalent isotropic displacement coefficients (Å^2) for non-hydrogen atoms in (*cis*-$Ph_2PCH{=}CHPPh_2)Fe(CO)_3$ (**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] $B_{iso} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

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.

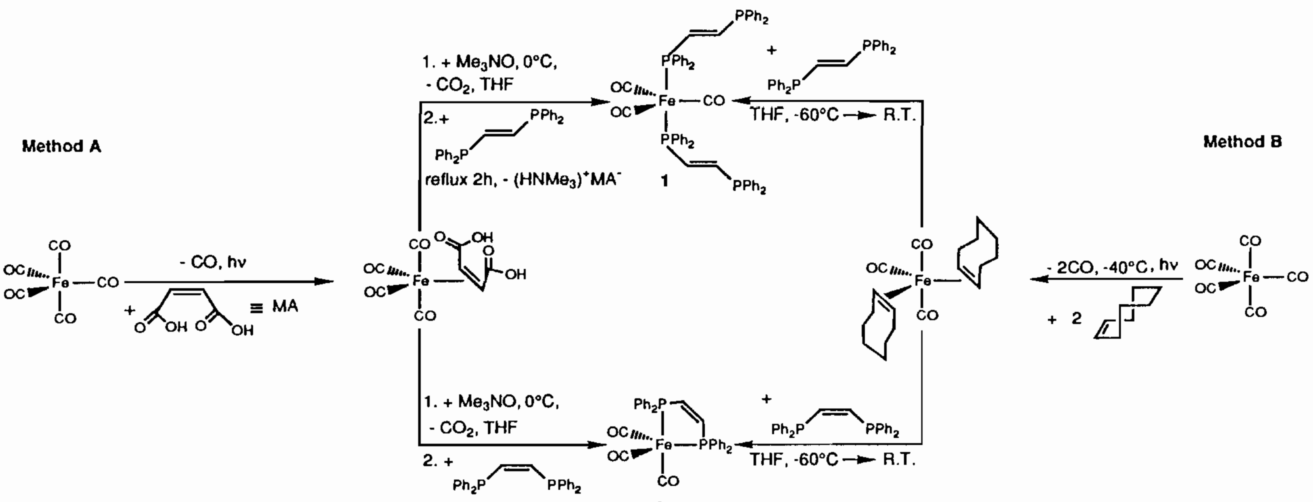
Method A proceeds with an oxidative decarbonylation, followed by the precipitation of a maleate salt in the presence of *trans*- or *cis*-$Ph_2PCH{=}CHPPh_2$ [10]. The oxidative decarbonylation step produces gaseous CO_2 and NMe_3, then the leaving ligand MA reacts with NMe_3 to form a salt $(HNMe_3)+MA^-$ in refluxing THF. Method B is a low temperature route by quenching (*cis*-COE)$_2$Fe$(CO)_3$ with *trans*- or *cis*-$Ph_2PCH{=}CHPPh_2$, respectively. Method B is a much neater and more efficient procedure in which (*cis*-COE)$_2$Fe$(CO)_3$ 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*-$Ph_2PCH{=}CHPPh_2$, either method results in **1** and for *cis*-$Ph_2PCH{=}CHPPh_2$, 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 $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ NMR spectrum of **1** shows two singlets of similar intensity at δ 77.97 for the coordinated P donor and at $\delta -6.75$ for the uncoordinated P donor. The P atoms of free *trans*-$Ph_2PCH{=}CHPPh_2$ resonate at δ −6.75. Since an uncoordinated $^{31}P\{^1H\}$ peak has been detected, **1** must have two unidentate diphosphine ligands. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows just one peak at δ 116.9, instead of two peaks corresponding to one axial and one equatorial. The ^{31}P peak for free *cis*-$Ph_2PCH{=}CHPPh_2$ is also at δ −6.75. The coordination shift for *cis*-$Ph_2PCH{=}CHPPh_2$ is much larger than that for *trans*-$Ph_2PCH{=}CHPPh_2$. 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 $^{31}P\{^1H\}$ 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*-$Ph_2PCH{=}CHPPh_2$, 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 $(PR_3)_2Fe(CO)_3$ structures, e.g. *trans*-$[(OMe)_3P]_2Fe(CO)_3$ [15], *trans*-$[(Me_2N)_3P]_2Fe(CO)_3$ [16] and *trans*-$P(OCH_2)_3PFe(CO)_3P(OCH_2)_3P$ [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 $[(trans\text{-}Ph_2PCH{=}CHPPh_2)Fe(CO)_3]_2$. 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 $\{[Ph_2P(CH_2)_5PPh_2]Fe(CO)_3\}_2$ [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, $[(trans\text{-}\mathrm{P{-}C{=}C{-}P})\mathrm{Fe(CO)_3}]_n$, 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 $[o\text{-}\mathrm{C_6H_4(PPh_2)_2}]\mathrm{Fe(CO)_3}$ [18], 87.9(1)° in $[\overline{\mathrm{OCCH{=}CHC(O)O}}(\mathrm{PPh_2})_2]\mathrm{Fe(CO)_3}$ [2e] and 84.4(1)° in $\mathrm{(CO)_3Fe}[\mu\text{-}\mathrm{(Ph_2P)_2C_6H_2(PPh_2)_2}]\text{-}\mathrm{Fe(CO)_3}$ [19]. These diphosphines all have two *cis* $\mathrm{PPh_2}$ moieties linked by a partial double bond or an aromatic C–C bond. The corresponding $\mathrm{Fe(CO)_3}$ 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 $[o\text{-}\mathrm{C_6H_4(PPh_2)_2}]\mathrm{Fe(CO)_3}$, 1.325(4) Å in $[\overline{\mathrm{OCCH{=}CHC(O)O}}(\mathrm{PPh_2})_2]\mathrm{Fe(CO)_3}$ and 1.412(7) Å in $\mathrm{(CO)_3Fe}[\mu\text{-}\mathrm{(Ph_2P)_2C_6H_2(PPh_2)_2}]\mathrm{Fe(CO)_3}$. The saturated counterpart $\mathrm{(dppe)Fe(CO)_3}$ 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 $\mathrm{(dppe)Fe(CO)_3}$ 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 $\mathrm{(dppe)Fe(CO)_3}$, 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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