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Synthesis and reactivity of $[(R^1R^2N)_2PH]Fe(CO)_4$ complexes. X-ray crystal structure of $[(Ph_2N)_2PH]Fe(CO)_4$

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Abstract

$KHFe(CO)_4$ reacts with tris(amino)phosphines by substitution at phosphorus leading to [bis(amino)phosphine]tetracarbonyliron complexes $[(R^1R^2N)_2PH]Fe(CO)_4$. The X-ray structure has been determined for $R^1 = R^2 = Ph$. Deprotonation of these complexes with KH affords stable potassium phosphidotetracarbonylferrates which can be alkylated or acylated at phosphorus. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

As part of our interest in the chemistry of hydridotetracarbonylferrates $M^+[HFe(CO)_4]^-$ [1], we have reported the reaction of $K^+[HFe(CO)_4]^-$ with phosphites and phosphines [2]. These reactions procee by CO exchange processes [3], providing highly selective routes to a large variety of ionic and neutral phosphane-substituted ironcarbonyl complexes [4–6].

In contrast, the reaction of $K^+[HFe(CO)_4]^-$ with tris(dimethylamino)phosphine does not proceed by CO substitution. Instead, substitution of an amino group at phosphorus is observed, affording $K_2Fe(CO)_4$ and the neutral irontetracarbonyl complex $[(Me_2N)_2PH]$ $(Fe(CO)_4$ [7]. This reaction provides a very easy, laboratory scale preparation of the Collman type reagents $M_2Fe(CO)_4$ (M = Na, K) for immediate use. It should also be an easy way to prepare ironcarbonyl-stabilized secondary bis(amino)phosphines.

We report here the synthesis of several of these complexes and the X-ray crystal structure of $[(Ph_2N)_2PH]Fe(CO)_4$, which is the first X-ray crystal structure of a bis(amino)phosphine coordinated to a transition metal, along with preliminary results on both the deprotonation of $[(R_2N)_2PH]Fe(CO)_4$ derivatives and the reactivity of the resulting phosphidotetracarbonylferrate complexes.

2. Results and discussion

2.1. Synthesis of $[(R^1R^2N)_2PH]Fe(CO)_4$ complexes

The reaction of $KHFe(CO)_4$ **1** with tris(amino) phosphines **2a–c** is conducted at room temperature in (r.t.) THF (Eq. (1)). For **2b**, the reaction is instantaneous, as indicated by an immediate white precipitate of $K_2Fe(CO)_4$, whereas for **2a** and **2c**, the reaction occurs only on evaporation of the solvent under reduced pressure. Classical work-up allows isolation of complexes **4a–c** in a 70–90% yield.

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$$\underset{1}{2KHFe(CO)_4} + \underset{2}{P(NR^1R^2)_3} \xrightarrow[-R^1R^2NH]{THF, RT} \underset{3}{\downarrow K_2Fe(CO)_4} + \underset{4}{[(R^1R^2N)_2PH]Fe(CO)_4} \quad (1)$$

a $R^1 = R^2 = Me$, 90%
b $R^1 = R^2 = {}^iPr$, 90%
c $R^1 = Et$, $R^2 = Ph$, 70%

Complex **4c** is reported for the first time. **4a** and **4b** have been previously prepared by reacting either $({}^iPr_2N)_2PH$ with $Fe(CO)_4(THF)$ (**4b**) [8] or $[PPh_4][HFe(CO)_4]$ with the corresponding bis(dialkylamino)chlorophosphine (**4a**, **4b**) [9].

The synthesis of complexes **4** from tris(amino)phosphines (Eq. (1)) thus appears as an interesting alternative to the above-mentioned procedures via a P–N bond activation process instead of a P–Cl one. Nevertheless, when tris(amino)phosphines are not readily accessible, the reaction shown in Eq. (2) [9] involving such a P–Cl bond activation is the best synthetic procedure and has been used to obtain **4c** and the previously unreported $[(Ph_2N)_2PH]Fe(CO)_4$, **4d**.

$$\underset{1}{KHFe(CO)_4} + (R^1R^2N)_2PCL \xrightarrow[-KCl]{THF, RT} \underset{4}{[(R^1R^2N)_2PH]\,Fe(CO)_4} \quad (2)$$

c $R^1 = Et$, $R^2 = Ph$, 72%
d $R^1 = R^2 = Ph$, 32%

$$\underset{4}{[(R^1R^2N)_2PH]Fe(CO)_4} + KH \xrightarrow{Et_2O, RT} \underset{5}{[\{(R^1R^2N)_2P\}Fe(CO)_4]^- K^+} \quad (3)$$

a $R^1 = R^2 = Me$
c $R^1 = Et$, $R^2 = Ph$
d $R^1 = R^2 = Ph$

2.2. X-ray crystal structure of 4d

The structure of **4d** has been determined by X-ray diffraction analysis (Table 1). A view of the molecular structure with atom labelling scheme is shown in Fig. 1. The Fe atom adopts an approximately trigonal-bipyramidal geometry with a nearly perfect trigonal plane of three CO ligands for which each C–Fe–C bond angle is 120°. The phosphorus atom and the fourth CO ligand occupy axial sites (P1–Fe–C2 = 176.6°). The Fe–P1 bond length (2.234(1) Å) is close to that found for $[(Me_2N)_3P]Fe(CO)_4$ (2.245 Å) and for $(Ph_3P)Fe(CO)_4$ (2.244 Å) [10]. The geometry at phosphorus is approximately tetrahedral, the average bond angle N1–P1–N2, Fe–P1–N1 and Fe–P2–N2 being 115°. The sum of the angles about nitrogen is equal to 360°. The most intriguing structural feature is that, although the geometry at each nitrogen atom is perfectly trigonal planar, the two P–N bond lengths are unexpectedly very different (P1–N2 = 1.670(3); P1–N1 = 1.739(4) Å) and in the range found for phosphorus–nitrogen compounds containing sp^2-type nitrogen atoms (1.66–1.68 Å [10,11]) and sp^3-type nitrogen atoms (1.73–1.74 Å [11]), respectively.

2.3. Reaction of $[(R^1R^2N)_2PH]Fe(CO)_4$ complexes 4 with KH

Several mechanistic proposals involving terminal phosphinidene complexes as intermediates [12] encouraged us to study the deprotonation of complexes **4** under non-reversible conditions.

Reaction of **4a,c,d** with excess KH in Et_2O or THF at r.t. results in the quantitative formation (^{31}P-NMR) of the air-sensitive phosphido complexes **5a,c,d** (Eq. (3)).

As verified for **5c**, complexes **5a,c,d** can alternatively be obtained by allowing $K_2Fe(CO)_4$ to react with the corresponding $(R^1R^2N)_2PCl$ in DMAC, according to the route reported from $Na_2Fe(CO)_4$ and Ar_2PCl [13].

In the case of **4b** ($R^1 = R^2 = {}^iPr$), the reaction with KH regenerates $[HFe(CO)_4]^-$ and $({}^iPr_2N)_2PH$, indicating that H^- acts as a competitive ligand for the $[Fe(CO)_4]$ moiety.

The phosphidotetracarbonylferrates **5** can be represented by the resonance forms shown in Scheme 1 and are characterized by a low-field ^{31}P-NMR signal in the range 220–230 ppm.

This deshielding suggests the participation of the amido-stabilized phosphinidene resonance form in the description of the complex. This proposal is supported by analogy with literature data on base-stabilized ironsilylene complexes, e.g. $[Fe(CO)_4\{SiMe_2–(NMe_2H)\}]$ [14], and by the behaviour of complex **5a**. Indeed, although complexes **5c** and **5d** are stable in THF, complex **5a** slowly decomposes at r.t. Thus, stirring a solution of **4a** in the presence of excess KH in THF leads to the clean formation of **5a** ($^{31}P\{^1H\}$-NMR). After 2 days at r.t. the

By contrast, the phosphido character (Scheme 1) of complexes **5** is revealed by their reaction with CH_3I or CH_3COCl to afford the expected alkyl- or acyl-bis(amino)phosphinetetracarbonyliron complexes **9c** and **10c** in good yield, as demonstrated for **5c** (Eq. (5)) Scheme 3.

These reactions are additional examples of the deprotonation-alkylation sequence of coordinated secondary phosphines known for a long time [15] and of the synthesis of coordinated acylphosphines [16].

3. Experimental section

3.1. General procedure and reagent syntheses

All manipulations were performed under argon using standard Schlenk tube and vacuum line techniques. THF (SDS) and diethylether (SDS) were dried and deaerated by distillation from sodium–benzophenone ketyl under argon. *n*-Pentane (SDS) was dried and deaerated by distillation from P_2O_5 under argon. Samples of $(Me_2N)_3P$ and KH as a dispersion in mineral oil were purchased from Fluka and Aldrich, respectively. Literature methods or methods adapted therefrom were used to prepare $(i\text{-}Pr_2N)_3P$, $(EtPhN)_3P$, $(i\text{-}Pr_2N)_2PCl$, $(EtPhN)_2PCl$, $(Ph_2N)_2PCl$ [17], solutions of $KHFe(CO)_4$ in THF [2] and $K_2Fe(CO)_4$ [7]. NMR spectra were recorded on Bruker AC-200 or Bruker AMX-400 spectrometers. $^{31}P\{^1H\}$-NMR-spectra were referenced to external H_3PO_4. ^1H-NMR spectra were referenced to the residual proton resonance of the deuterated solvents (SDS) ($CDCl_3$, $\delta_H = 7.27$; C_6D_6, $\delta_H = 7.15$; THF-d_8, $\delta_H = 3.60$ ppm). $^{13}C\{^1H\}$-NMR spectra were referenced to the carbon resonance of the solvents ($CDCl_3$, $\delta_C = 77.0$; C_6D_6, $\delta_C = 128.5$; THF-d_8, $\delta_C = 25.8$ ppm). Satisfactory C, H, N analysis ($\pm$ 0.6%) were obtained for complexes **4a–d**, **9c** and **10c** (Laboratory In-house Service, Perkin-Elmer 2400 apparatus).

Table 1
Crystal and collection data for complex **4d**

Crystal parameters	
Empirical formula	$C_{28}H_{21}FeN_2O_4P$
M (g)	536.31
Shape (color)	Plate (orange)
Size (mm)	$0.5 \times 0.5 \times 0.07$
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.051(1)
b (Å)	11.111(2)
c (Å)	13.827(2)
α (°)	100.66(1)
β (°)	109.50(2)
γ (°)	104.53(2)
V (Å^3)	1212.6(4)
Z	2
$F(000)$	4040
$D_{calc.}$ (g cm^{-3})	1.40
μ (Mo–K_α) (cm^{-1})	6.9
Data Collection	
Diffractometer	IPDS Stoe
Monochromator	Graphite
Radiation	Mo–K_α ($\lambda = 0.71073$)
Scan mode	ϕ
ϕ range (°)	$0 < \phi < 250$
ϕ incr. (°)	2
2θ range (°)	$2.9 < \theta < 48.4$
No. of rflns collected	8963
No. of unique rflns	3449
No. rflns used ($I > 3\sigma(I)$)	2337
Refinement	
R	0.053
R_w	0.059
Weighting scheme	Chebyshev
Coeff. Ar	3.17; −0.408; 2.59
Goodness-of-fit	1.10
L.s parameters	330

3.2. Preparation of complexes *4*

Complexes **4a** and **4b** were prepared from $KHFe(CO)_4$ and the corresponding tris(dialkylamino)phosphine, as previously described for $(Me_2N)_3P$ [7]. **4b** could also be prepared from $KHFe(CO)_4$ and $(i\text{-}Pr_2N)_2PCl$. **4a** and **4b** displayed similar NMR spectra as those previously reported [7,9].

4c: $(EtPhN)_2PCl$ (4.9 mmol) was added to a solution of $KHFe(CO)_4$ (5.0 mmol) in THF (15 ml) at r.t. After 10 min stirring, the solvent was evaporated and pentane (20 ml) was added. The liquid phase was cannulated into another Schlenk flask and evaporated to give $[(EtPhN)_2PH]Fe(CO)_4$ **4c** (oil, 72%). $^{31}P\{^1H\}$-NMR (162.0 MHz) (THF-d_8) δ (ppm) = 136.3; ^1H-NMR (400.1 MHz) (THF-d_8) δ (ppm) = 0.94 (t, 6H, CH_3CH_2, $^3J_{H-H} = 7.0$ Hz); 3.58 and 3.78 (ABC_3Y system, 4H, CH_3CH_2, $^3J_{H-P} = 8.9$ Hz, $^2J_{H-H} = 14.0$ Hz); 7.1–7.35 (10H, aromatic H); 8.0 (d, 1H, *H*P, $^1J_{H-P} = 454.3$ Hz; $^{13}C\{^1H\}$-NMR (50.3 MHz) (THF-d_8) δ (ppm) = 15.0 (d, CH_3CH_2, $^3J_{C-P} = 4$ Hz); 47.5 (d, CH_3CH_2, $^2J_{C-P} =$ 8 Hz); 127.1, 128.8, 130.6, 146. (d, $^2J_{C-P} = 3$ Hz) (aromatic C); 214.6 (d, *C*O, $^2J_{C-P} = 20$ Hz).

4d: $(Ph_2N)_2PCl$ (2.5 mmol) was added to a solution of $KHFe(CO)_4$ (4 mmol) in THF (15 ml) at r.t. After 5 h stirring, the solvent was evaporated and pentane (20 ml) was added. The liquid phase was cannulated into another Schlenk flask in which $[(Ph_2N)_2PH]Fe(CO)_4$ **4d** slowly crystallised as orange plates (32%). $^{31}P\{^1H\}$-NMR (81.0 MHz) ($CDCl_3$) δ (ppm) = 120.4; ^1H-NMR (200.1 MHz) ($CDCl_3$) δ (ppm) = 7.00–7.30 (20H, aromatic H); 8.77 (d, 1H, *H*P, $^1J_{H-P} = 444.0$ Hz; $^{13}C\{^1H\}$-NMR (50.3 MHz) ($CDCl_3$) δ (ppm) = 125.8, 127.3 (d, $J_{C-P} = 3$ Hz), 129.2, 145.9 (aromatic C); 212.6 (d, *C*O, $^2J_{C-P} = 20$ Hz).

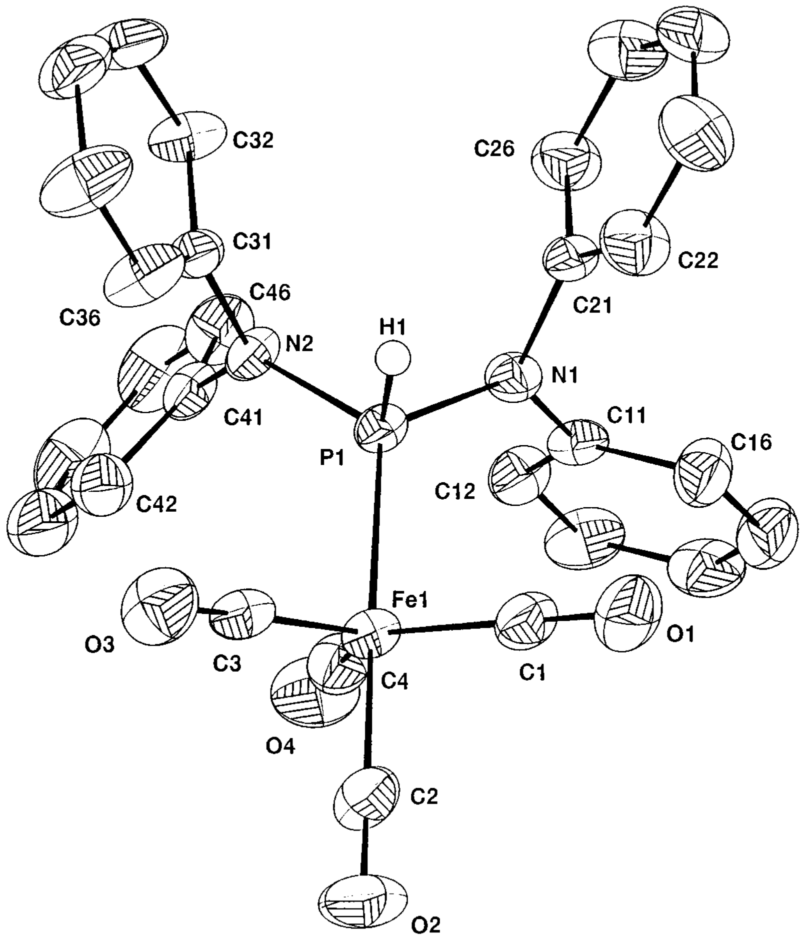


Fig. 1. Molecular structure of complex **4d** showing the atom numbering scheme.

*3.3. Synthesis of complexes **5a,c,d***

In a typical experiment, an excess of KH in mineral oil was washed with THF (3 × 2 ml) and the solvent was evaporated under vacuum until a mobile powder was obtained. A solution of **4c** (2 mmol) in diethyl ether (10 ml) was then added and the reaction mixture was stirred until gas evolution ceased. The supernatant phase was then cannulated into another Schlenk flask and the solvent removed under vacuum to afford **5c** (73%).

Complexes **5a** and **5d** were similarly prepared but only **5d** could be isolated (70% yield) (see text).

5a: $^{31}P\{^1H\}$-NMR (162.0 MHz) (THF-d_8) δ (ppm) = 231.2; ^1H-NMR (400.1 MHz) (THF-d_8) δ (ppm) = 2.47 (d, CH_3, $^3J_{H-P} = 9.0$ Hz); $^{13}C\{^1H\}$-NMR (50.3 MHz) (THF-d_8) δ (ppm) = 43.1 (d, CH$_3$, $^2J_{C-P} = 15$ Hz); 222.1 (d, CO, $^2J_{C-P} = 3$ Hz).

5c: $^{31}P\{^1H\}$-NMR (162.0 MHz) (THF-d_8) δ (ppm) = 231.2; ^1H-NMR (400.1 MHz) (THF-d_8) δ (ppm) = 1.09 (t, 6H, CH_3CH$_2$, $^3J_{H-H} = 6.8$ Hz); 3.58 and 3.78 (ABC$_3$ system, 4H, CH$_3$CH_2, $^2J_{H-H} = 15.0$ Hz); 6.85–7.15 (10H, aromatic H); $^{13}C\{^1H\}$-NMR (100.6 MHz) (THF-d_8) δ (ppm) = 14.6 (CH$_3$CH$_2$); 45.0 (d, CH$_3$$CH_2$, $^2J_{C-P} = 8$ Hz); 117.3 (d, $J_{C-P} = 2$ Hz), 120.0 (d, $J_{C-P} = 17$ Hz), 128.7, 151.7 (d, $^2J_{C-P} = 19$ Hz) (aromatic C); 220.3 (CO).

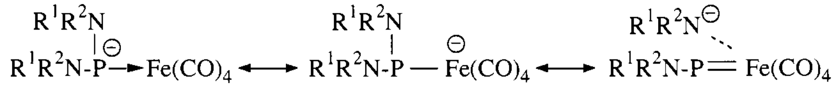
5d: $^{31}P\{^1H\}$-NMR (81.0 MHz) (C_6D_6) δ (ppm) = 208.3; $^{13}C\{^1H\}$-NMR (50.3 MHz) (C_6D_6) δ (ppm) = 118.5, 122.4, 126.7 (d, $J_{C-P} = 7.5$ Hz), 129.5, 130.6, 151.8 (d, $^2J_{C-P} = 3$ Hz) (aromatic C); 218.6 (d, CO, $J_{C-P} = 3$ Hz).

*3.4. Alternative generation of complex **5c***

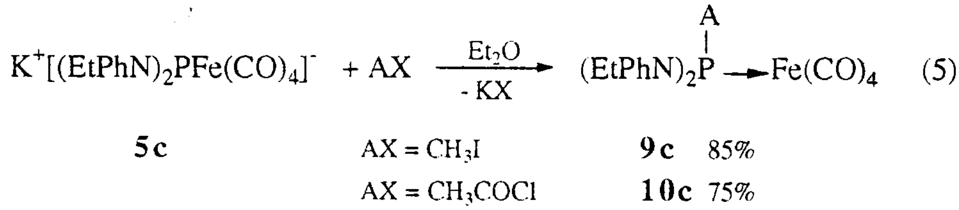
A solution of $(PhEtN)_2PCl$ (0.25 mmol) in DMAC (1.2 ml) was dropped by means of a syringe into a magnetically stirred solution of $K_2Fe(CO)_4$ (0.25 mmol) in DMAC (4 ml) at r.t. After 15 min, the $^{31}P\{^1H\}$-NMR spectrum of the crude solution indicated the quantitative formation of **5c**.

*3.5. Synthesis of complexes **9c** and **10c***

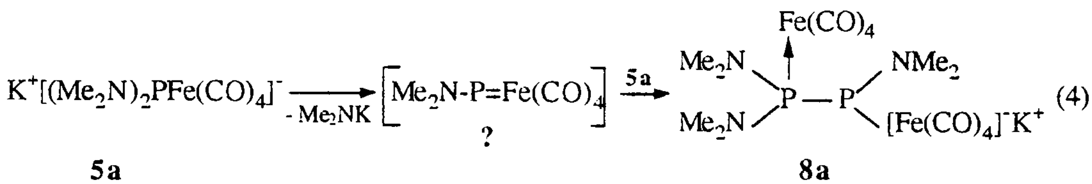
Methyl iodide (or acetyl chloride) (0.4 mmol) was added to a solution of **5c** (0.4 mmol) in diethyl ether (5 ml) at r.t. After a few min., the liquid phase was cannulated into another Schlenk flask and the solvent



Scheme 1.



Scheme 2.



Scheme 3.

evaporated under vacuum to afford **9c** or **10c** as solids in an 85 and 75% yield, respectively.

9c: $^{31}P\{^1H\}$-NMR (162.0 MHz) (C_6D_6) δ (ppm) = 135.7; ^1H-NMR (400.1 MHz) (C_6D_6) δ (ppm) = 0.85 (t, 6H, C*H*$_3$CH$_2$, $^3J_{H-H}=7.0$ Hz); 1.34 (d, 3H, C*H*$_3$P, $^2J_{H-P}=7.3$ Hz); 3.36 and 3.62 (ABC$_3$Y system, 4H, CH$_3$C*H*$_2$, $^3J_{H-P}=7.0$ Hz, $^2J_{H-H}=14.0$ Hz); 6.70–7.15 (5H, aromatic H); $^{13}C\{^1H\}$-NMR (100.6 MHz) (C_6D_6) δ (ppm) = 14.6 (*C*H$_3$CH$_2$); 25.9 (d, *C*H$_3$P, $^1J_{C-P}=49$ Hz); 47.9 (CH$_3$*C*H$_2$); 127.4, 129.6, 131.3, 143.8 (d, $^2J_{C-P}=4$ Hz) (aromatic C); 215.3 (d, *C*O, $^2J_{C-P}=20$ Hz).

10c: $^{31}P\{^1H\}$-NMR (162.0 MHz) (C_6D_6) δ (ppm) = 149.5; ^1H-NMR (200.1 MHz) (C_6D_6) δ (ppm) = 0.72 (t, 6H, C*H*$_3$CH$_2$, $^3J_{H-H}=7.0$ Hz); 1.89 (d, 3H, C*H*$_3$COP, $^3J_{H-P}=4.0$ Hz); 3.44 and 3.53, ABC$_3$Y system, 4H, CH$_3$C*H*$_2$, $^3J_{H-P}$ ca. 7 Hz, $^2J_{H-H}=14.0$ Hz); 7.00–7.30 (5H, aromatic H); $^{13}C\{^1H\}$-NMR (100.6 MHz) (C_6D_6) δ (ppm) = 14.3 (d, *C*H$_3$CH$_2$, $^3J_{C-P}=3$ Hz); 28.3 (d, *C*H$_3$COP, $^2J_{C-P}=48$ Hz); 48.7 (d, CH$_3$*C*H$_2$, $^2J_{C-P}=6$ Hz); 127.3, 129.8, 130.2, 143.6 (aromatic C); 211.9 (d, CH$_3$*C*OP, $^1J_{C-P}=25$ Hz); 214.0 (d, *C*O, $^2J_{C-P}=17$ Hz).

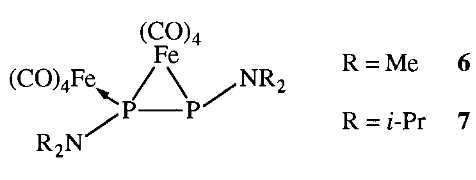


Fig. 2. Unsymmetrical diphosphene bis(irontetracarbonyl) complexes.

3.6. X-ray diffraction study of 4d

X-ray quality crystals were obtained by slow evaporation of a pentane solution. The data was collected on a Stoe Imaging Plate Diffraction System (IPDS). The crystal-to-detector distance was 80 mm. A total of 125 exposures (4 min per exposure) were obtained with $0<\phi<250°$ and with the crystals rotated through 2° in ϕ. Coverage of the unique set was over 95% complete to at least 24.2°. Crystal decay was monitored by measuring 200 reflexions per image. The final unit cell parameters were obtained by the least-squares refinement of 2000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collection. Owing to the rather low μx value, 0.35, no absorption correction was considered.

The structure was solved by direct methods (SIR92) [18] and refined by least-squares procedures on F_o. H atoms were located on difference Fourier maps, but those attached to C atoms were introduced in calculation in idealized positions ((d(CH) = 0.96 Å) and their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. The H atom attached to the phosphorus was refined isotropically. Least-squares refinements were carried out by minimizing the function $\Sigma w(|F_o|-|F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w=w'\{1\text{-}[\Delta F/6\sigma(F_o)]^2\}^2$ where $w'=1/\Sigma_1^n A_r T_r(x)$ with three coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ where x was $F_c/F_c(\max)$

[19]. Models reached convergence with $R = \Sigma(\|F_o| - |F_c\|)/\Sigma(|F_o|)$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, having values listed in Table 1. Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviation less than 0.1 and no significant features in final difference maps.

The calculations were carried out with the CRYSTALS package programs [20] running on a PC. The drawing of the molecule was realized with the help of CAMERON [21].

4. Supplementary material

Complete tables of interatomic distances, bond angles, fractional atomic coordinates with the equivalent thermal parameters for all atoms but H, anisotropic thermal parameters for non hydrogen atoms and atomic coordinates for H atoms have been deposited at the Cambridge Crystallographic Data Centre.

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