

# Dialkylaminophosphorus metal carbonyls. 14. Stereochemistry of some HX additions to the $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ unit from $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ <sup>1</sup>

V. Kumar, D.W. Lee, M.G. Newton, R.B. King \*

Department of Chemistry, University of Georgia, Athens, GA 30602, USA

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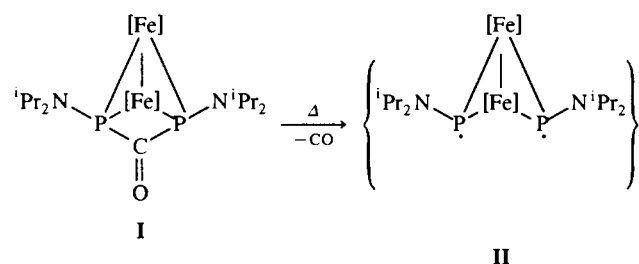
## Abstract

Reaction of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with aniline in boiling hexane results in addition of aniline to the  $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  unit to give yellow  $(^i\text{Pr}_2\text{NPNHPh})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ , shown by X-ray diffraction to have a syn orientation of the two  $^i\text{Pr}_2\text{N}$  groups. However, the  $(\text{XPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  adducts ( $\text{X} = \text{Cl}, \text{OEt}, \text{OCH}_2\text{SiMe}_3$ ) of  $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  with HCl and ROH ( $\text{R} = \text{Et}, \text{CH}_2\text{SiMe}_3$ ) respectively, are shown by X-ray diffraction to have an anti orientation of the two  $^i\text{Pr}_2\text{N}$  groups.

**Keywords:** Dialkylaminophosphorus derivatives; Stereochemistry; Irons; Carbonyls

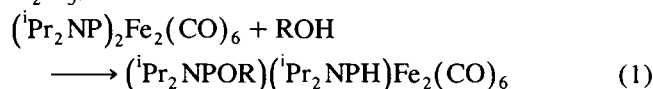
## 1. Introduction

Expulsion of the phosphorus-bridging carbonyl group in  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  (**I**:  $[\text{Fe}] = \text{Fe}(\text{CO})_3$  here and elsewhere) occurs at temperatures around 100 °C (e.g. boiling toluene) to give a reactive  $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  unit, possibly the diradical **II** formed according to the following reaction:



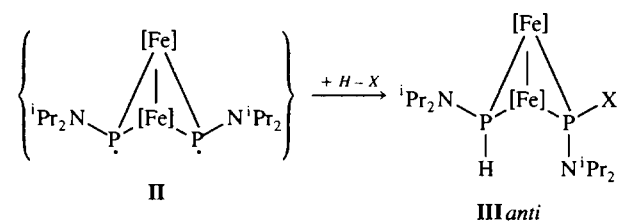
The  $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  unit can be trapped by addition across the C=O bonds of aldehydes, ketones, or anhydrides [2,3], the C≡N bonds of nitriles, and the C=C bond of acrylonitrile. In addition, alcohols have

been shown [4] to add to this reactive  $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  unit according to the following equation ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ ):

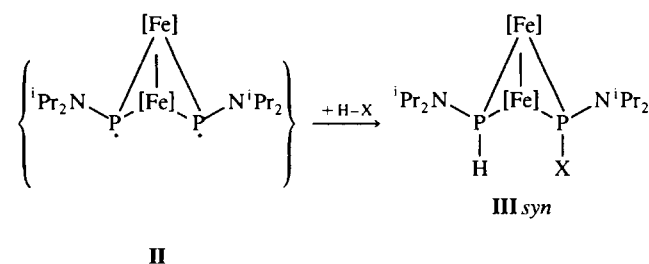


Such addition reactions can proceed according to either syn or anti stereochemistry as follows ( $\text{X} = \text{OR}$ ):

*Anti stereochemistry:*



*Syn stereochemistry:*



\* Corresponding author.

<sup>1</sup> This paper is dedicated to Professor Marvin Rausch in recognition of his many contributions to organometallic chemistry. For part 13 of this series see Ref. [1]. Portions of this paper were presented at the 208th National Meeting of the American Chemical Society, Washington, DC, August, 1994.

Table 1  
Infrared  $\nu(\text{CO})$  frequencies and  $^{31}\text{P}$  NMR spectra of  $(^i\text{Pr}_2\text{NPX})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  and related compounds

Compound <sup>a</sup>	Infrared $\nu(\text{CO})(\text{cm}^{-1})$ <sup>a</sup>	$^{31}\text{P}$ NMR ( $\delta$ ) <sup>b</sup>		
		PX	PH or PY	$J(\text{P}-\text{P})(\text{Hz})$
$(^i\text{Pr}_2\text{NPNHPh})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$	2041s, 2021m, 2004vs, 1974s, 1961s, 1943m	205.6d	152.1d	110
$(\text{EtOPN}^i\text{Pr}_2\text{X})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ <sup>c</sup>	2055m, 2015s, 1987s, 1977s, 1961s, 1954m	265.8d(264.4d)	146.6d(146.1d)	127(128)
$(\text{MeOPN}^i\text{Pr}_2\text{X})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ <sup>d</sup>	2050m, 2012s, 1987s, 1977s, 1962s, 1952m	270.5d	145.7d	128
$(\text{Me}_3\text{SiCH}_2\text{OPN}^i\text{Pr}_2\text{X})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$	2044m, 2004s, 1982s, 1975s, 1959s, 1948m	273.7d	146.5d	126
$(\text{ClPN}^i\text{Pr}_2\text{X})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$	2057m, 2022s, 1994s, 1981m, 1967s, 1958m	265.7d	142.1d	121
$(\text{BrPN}^i\text{Pr}_2\text{X})(\text{BrPH})\text{Fe}_2(\text{CO})_6$ <sup>d</sup>	2080m, 2045s, 2026s, 2002s, 1993s	242.1d	151.1d	136
$(\text{EtOPN}^i\text{Pr}_2\text{X})(\text{BrPH})\text{Fe}_2(\text{CO})_6$ <sup>d</sup>	2068m, 2030s, 2010s, 1990s, 1980m	246.8d	159.5d	137

<sup>a</sup> Infrared  $\nu(\text{CO})$  frequencies were measured in  $\text{CH}_2\text{Cl}_2$  solution. Me = methyl; <sup>i</sup>Pr = isopropyl, Ph = phenyl. <sup>b</sup>  $^{31}\text{P}$  NMR spectra were taken in  $\text{CDCl}_3$  solution: d = doublet. <sup>c</sup>  $^{31}\text{P}$  NMR data on the  $(\text{EtOPN}^i\text{Pr}_2\text{X})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  obtained in this work are in agreement within experimental error with data from Ref. [4] (given in parentheses). <sup>d</sup> Data from Ref. [4].

Syn stereochemistry is preferred if loss of the phosphorus-bridging carbonyl and addition of the H–X unit are concerted processes, since the pair of sites initially vacated by loss of the phosphorus-bridging carbonyl are necessarily in syn positions. However, if the  $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  intermediate has a sufficiently long lifetime, the diisopropylamino groups on its three-coordinate phosphorus atoms can occupy intermediate positions so that either syn or anti addition of the H–X unit is possible. In fact, formation of the anti isomer reduces the steric hindrance between the bulky diisopropylamino groups.

This paper reports the structures of four products obtained by additions of protic reagents, H–X, to the  $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  unit generated by extrusion of the phosphorus-bridging carbonyl in  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  (**I**). In this connection the reaction of  $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  with aniline in boiling hexane was found to proceed in a manner analogous to the previously reported reactions with alcohols to give  $(^i\text{Pr}_2\text{NPNHPh})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ , shown by X-ray diffraction to have syn stereochemistry (**III**<sub>syn</sub>). However, the  $(^i\text{Pr}_2\text{NPX})(\text{HPN}-^i\text{Pr}_2)\text{Fe}_2(\text{CO})_6$  (X = OEt,  $\text{OCH}_2\text{SiMe}_3$ , Cl) adducts of  $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  with the alcohols ROH (R = Et,  $\text{Me}_3\text{SiCH}_2$ ) and HCl respectively, have been shown by X-ray diffraction to have anti stereochemistry (**III**<sub>anti</sub>).

These observations suggest that the  $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  intermediate (**II**) is long enough lived that its reactions with many HX substrates are slow enough for the diisopropylamino groups to rearrange to the less hindered anti positions.

## 2. Experimental section

The general experimental conditions are the same as an earlier paper of this series [3]. Infrared  $\nu(\text{CO})$  frequencies and  $^{31}\text{P}$  NMR spectra of the products are given in Table 1, proton-decoupled  $^{13}\text{C}$  NMR spectra are given in Table 2, and proton NMR spectra are given in Table 3.

### 2.1. Reaction of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with aniline

A solution of 1.12 g (2.0 mmol) of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ , 1.0 ml (1.0 g, 11 mmol) of aniline, and 50 ml of hexane was boiled under reflux for 36 h. Concentration of the reaction mixture followed by crystallization from hexane gave 0.2 g (18% yield) of  $(^i\text{Pr}_2\text{NPNHPh})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ , m.p. 119 °C (dec.). Anal. Found: C, 45.5; H, 5.5; N, 6.5.  $\text{C}_{24}\text{H}_{35}\text{Fe}_2\text{N}_3\text{O}_6\text{P}_2$ . Calc. C, 45.3; H, 5.5; N, 6.6%.

Table 2  
Proton-decoupled  $^{13}\text{C}$  NMR spectra of  $(^i\text{Pr}_2\text{NPX})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  and related compounds <sup>a</sup>

Compound	Isopropyl groups		Terminal CO	Other
	CH	$\text{CH}_3$		
$(^i\text{Pr}_2\text{NPNHPh})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$	52.9, 48.5	23.6, 22.0	213	PhNH: 129, 120, 117
$(\text{EtOPN}^i\text{Pr}_2\text{X})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$	53.2, 48.6	23.5, 21.9	214	EtO: 65.4, 15.7
$(\text{MeOPN}^i\text{Pr}_2\text{X})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ <sup>c</sup>	53.3, 48.5	23.6, 21.8	214	MeO: 56.8
$(\text{Me}_3\text{SiCH}_2\text{OPN}^i\text{Pr}_2\text{X})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$	53.3, 48.6	23.6, 21.8	213.8	$\text{Me}_3\text{SiCH}_2\text{O}$ : 62, –3.2
$(\text{ClPN}^i\text{Pr}_2\text{X})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$	55, 48	23, 22	212	—
$(\text{BrPN}^i\text{Pr}_2\text{X})(\text{BrPH})\text{Fe}_2(\text{CO})_6$ <sup>c</sup>	55.8	21.7	210	—
$(\text{EtOPN}^i\text{Pr}_2\text{X})(\text{BrPH})\text{Fe}_2(\text{CO})_6$ <sup>c</sup>	53.4	23.6	211	EtO: 66.3, 15.7

<sup>a</sup> Spectra taken in  $\text{CDCl}_3$  solutions using  $\text{Me}_4\text{Si}$  as internal standard. <sup>b</sup>  $^{13}\text{C}$  NMR data on the  $(\text{EtOPN}^i\text{Pr}_2\text{X})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  obtained in this work are in agreement within experimental error with data from Ref. [4]. <sup>c</sup> Data from Ref. [4].

An attempt to carry out the reaction of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with aniline in a similar manner, but using boiling toluene in the presence of molecular sieves rather than boiling hexane, led to complete decomposition without the isolation of any product.

### 2.2. Isolation of $(\text{EtOPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ from the reaction of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with diethyl succinate

A mixture of 2.26 g (4.0 mmol) of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ , 0.88 ml (0.92 g, 5.3 mmol) of diethyl succinate, 5.1 ml (5.1 mmol) of 1 M potassium *t*-butoxide in *t*-butanol, and 50 ml of hexane was boiled under reflux for 3 days. Concentration of the reaction mixture followed by crystallization from hexane gave 0.6 g (27% yield) of  $(\text{EtOPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ . Anal. Found: C, 40.9; H, 5.9; N, 4.7.  $\text{C}_{20}\text{H}_{34}\text{Fe}_2\text{N}_2\text{O}_7\text{P}_2$ . Calc.: C, 40.8; H, 5.8; N, 4.8%.

A similar reaction of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with diethyl succinate in boiling hexane for 72 h in the absence of potassium *t*-butoxide failed to give any product, indicating the essential role of the strong base in liberating the ethanol from the diethyl succinate in this reaction.

### 2.3. Isolation of $(\text{Me}_3\text{SiCH}_2\text{OPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ from the reaction of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with $\text{Me}_3\text{SiCH}_2\text{Li}$

A solution of 2.26 g (3.9 mmol) of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  in about 100 ml of hexane at  $-78^\circ\text{C}$  was treated with 3.9 ml (3.9 mmol) of a 1 M solution of  $\text{Me}_3\text{SiCH}_2\text{Li}$  and the reaction mixture stirred overnight at room temperature. The  $^{31}\text{P}$  NMR spectrum of the reaction mixture at this point indicated only unchanged  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ . The reaction mixture was then boiled overnight under reflux. The  $^{31}\text{P}$  NMR spectrum after the boiling indicated conversion of the  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  to a variety of products. The

reaction mixture was then treated with 0.35 ml (4.9 mmol) of acetyl chloride. After boiling under reflux for 2 h, the reaction mixture was hydrolyzed with saturated aqueous ammonium chloride. Concentration of the organic layer followed by chromatography twice on alumina and repeated crystallization from hexane gave 0.25 g (7% yield) of  $(\text{Me}_3\text{SiCH}_2\text{OPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ , m.p.  $96^\circ\text{C}$ . Anal. Found: C, 41.0; H, 6.2; N, 4.5.  $\text{C}_{22}\text{H}_{40}\text{Fe}_2\text{N}_2\text{O}_7\text{P}_2\text{Si}$ . Calc.: C, 40.9; H, 6.2; N, 4.3%.

Reaction of 1.12 g (2.0 mmol) of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with 0.25 ml (2.0 mmol) of  $\text{Me}_3\text{SiCH}_2\text{OH}$  in 25 ml of boiling hexane for 24 h was shown to give  $(\text{Me}_3\text{SiCH}_2\text{OPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  with a  $^{31}\text{P}$  NMR spectrum identical to that reported in Table 1.

### 2.4. Isolation of $(\text{CIPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ from the reaction of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with acetyl chloride

A solution of 1.12 g (2.0 mmol) of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ , 0.3 ml (0.33 g, 4.2 mmol) of redistilled acetyl chloride, and 30 ml of hexane was boiled under reflux for 12 h. At this point a  $^{31}\text{P}$  NMR spectrum exhibited a small resonance at  $\delta$  148. The reaction mixture was then treated with an additional 0.2 ml (0.22 g, 2.8 mmol) of acetyl chloride and the boiling continued. The  $^{31}\text{P}$  NMR spectrum of the final reaction mixture showed doublets at approximately  $\delta$  145 and 250. Concentration and cooling gave 0.4 g (36% yield) of  $(\text{CIPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ , dec.  $126^\circ\text{C}$ . Anal. Found: C, 37.5; H, 5.1; N, 4.8.  $\text{C}_{18}\text{H}_{29}\text{ClFe}_2\text{N}_2\text{O}_6\text{P}_2$ . Calc. C, 37.3; H, 5.0; N, 4.8%.

### 2.5. Reaction of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with thionyl chloride

A mixture of 1.12 g (2.0 mmol) of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ , 0.14 ml (0.23 g, 1.9 mmol) of thionyl chloride, and 30 ml of hexane was boiled under reflux for 24 h.

Table 3  
Proton NMR spectra of  $(^i\text{Pr}_2\text{NPX})(^i\text{Pr}_2\text{NPY})\text{Fe}_2(\text{CO})_6$  and related compounds <sup>a</sup>

Compound	Isopropyl groups		P–H	Other
	CH	CH <sub>3</sub>		
$(^i\text{Pr}_2\text{NPNHPh})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$	3.91sp(7), 3.46sp(7)	1.26d(7), 1.11d(7)	5.66dd(403,15)	PhNH: m7.21t(8), p6.85t(7), o6.78d(8)
$(\text{EtOPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ <sup>b</sup>	3.5m(7)	1.25d(7), 1.19d(7)	5.70dd(398,23)	EtO: 3.81m, 1.57s
$(\text{MeOPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ <sup>c</sup>	4.0–3.3	1.28d(7), 1.20d(7)	5.8dd(400,24) <sup>d</sup>	MeO: 3.59d(13)
$(\text{Me}_3\text{SiCH}_2\text{OPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$	3.8m, 3.5m	1.28d(7), 1.19d(7)	5.6dd(390,25)	$\text{Me}_3\text{SiOCH}_2$ : 3.42d(7), 0.08(s)
$(\text{CIPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$	3.82m(6), 3.51m(8)	1.28d(7), 1.19d(6)	5.62dd(407,19)	—
$(\text{BrPN}^i\text{Pr}_2)(\text{BrPH})\text{Fe}_2(\text{CO})_6$ <sup>c</sup>	4.4–3.6	1.35d(7)	4.50dd(416,5)	—
$(\text{EtOPN}^i\text{Pr}_2)(\text{BrPH})\text{Fe}_2(\text{CO})_6$ <sup>c</sup>	3.85sp(7)	1.25d(7)	4.66dd(404,7)	EtO: 3.9, 1.25t(7)

<sup>a</sup> Proton NMR spectra obtained in  $\text{CDCl}_3$  solutions using tetramethylsilane as internal standard; d = doublet, dd = double doublet, t = triplet, sp = septet, o = *ortho* protons, m = *meta* protons, p = *para* protons. Coupling constants are given in parentheses. <sup>b</sup> Proton NMR data on the  $(\text{EtOPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  obtained in this work are in agreement within experimental error with data from Ref. [4] (given in parentheses).

<sup>c</sup> Data from Ref. [4]. The P–H resonance was erroneously reported there as  $\delta$  2.8 rather than the correct value of  $\delta$  5.8.

Concentration of the filtered reaction mixture and cooling gave yellow  ${}^1\text{Pr}_2\text{NP}(\text{S})\text{Cl}_2$ ,  ${}^{31}\text{P}$  NMR,  $\delta$  51.0. Anal. Found: C, 31.2; H, 6.0; N, 5.7.  $\text{C}_6\text{H}_{14}\text{Cl}_2\text{NPS}$ . Calc.: C, 30.8; H, 6.0; N, 6.0%.

2.6. Determination of the structures of  $({}^1\text{Pr}_2\text{NPNHPh})({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ ,  $(\text{EtOPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ ,  $(\text{Me}_3\text{SiCH}_2\text{OPN}{}^1\text{Pr}_2)-({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ , and  $(\text{CIPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$

Crystals of  $({}^1\text{Pr}_2\text{NPNHPh})({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  (orange blocks),  $(\text{EtOPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  (yellow needles),  $(\text{Me}_3\text{SiCH}_2\text{OPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  (yellow needles), and  $(\text{CIPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  (yellow cubes) from hexane were fixed in a random orientation on a glass fiber and mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite crystal monochromator. Cell dimensions were determined by least squares refinement of the angular positions of 25 independent reflections for each sample in the  $10\text{--}20^\circ$   $\theta$  range during the normal alignment procedure. Intensity data were collected over a  $\theta$  range of  $2\text{--}75^\circ$  using the  $\omega\text{--}2\theta$  technique with a variable scan width and scan range using Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). A semi-empirical absorption correction [5] was applied to each data set. Table 4 provides information relevant to the crystal cells and data collections.

The structures were solved by direct methods [6] for  $(\text{Me}_3\text{SiCH}_2\text{OPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NH})\text{Fe}_2(\text{CO})_6$ , or by Fourier

techniques [7] for  $(\text{EtOPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ , and expanded using Fourier techniques. All non-hydrogen atoms were located in several difference Fourier maps and then refined by full-matrix least squares, first isotropically, then anisotropically. Hydrogens were not included in the analysis of the structures. The final unweighted  $R$  values were 0.053, 0.067, 0.056, and 0.057 for  $({}^1\text{Pr}_2\text{NPNHPh})({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ ,  $(\text{EtOPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ ,  $(\text{Me}_3\text{SiCH}_2\text{OPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NH})\text{Fe}_2(\text{CO})_6$ , and  $(\text{CIPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  respectively.

The structures of  $({}^1\text{Pr}_2\text{NPNHPh})({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ ,  $(\text{EtOPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ ,  $(\text{Me}_3\text{SiCH}_2\text{OPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NH})\text{Fe}_2(\text{CO})_6$ , and  $(\text{CIPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  are depicted in Figs. 1 to 4 respectively. Bond lengths and angles of  $({}^1\text{Pr}_2\text{NPNHPh})({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ ,  $(\text{EtOPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ ,  $(\text{Me}_3\text{SiCH}_2\text{OPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NH})\text{Fe}_2(\text{CO})_6$ , and  $(\text{CIPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  are listed in Tables 5–12.

### 3. Results

Most of the reactions giving  $({}^1\text{Pr}_2\text{NPX})({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  derivatives reported in this paper were unsuccessful attempts to effect transformations on the carbonyl group in  $({}^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ , analogous to known transformations on the carbonyl groups of organic ketones,  $\text{R}_2\text{C}=\text{O}$ . Instead, such reactions on  $({}^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  were often found to give novel

Table 4

Crystal data for  $({}^1\text{Pr}_2\text{NPNHPh})({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ ,  $(\text{EtOPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ ,  $(\text{Me}_3\text{SiCH}_2\text{OPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NH})\text{Fe}_2(\text{CO})_6$ , and  $(\text{CIPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$

	$({}^1\text{Pr}_2\text{NPNHPh})\text{Fe}_2(\text{CO})_6$	$(\text{EtOPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$	$(\text{Me}_3\text{SiCH}_2\text{OPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NH})\text{Fe}_2(\text{CO})_6$	$(\text{CIPN}{}^1\text{Pr}_2)({}^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$
Empirical formula	$\text{Fe}_2\text{P}_2\text{O}_6\text{N}_3\text{C}_{24}\text{H}_{35}$	$\text{Fe}_2\text{P}_2\text{O}_7\text{N}_2\text{C}_{26}\text{H}_{43}$	$\text{Fe}_2\text{N}_2\text{P}_2\text{SiO}_7\text{C}_{22}\text{H}_{39}$	$\text{Fe}_2\text{P}_2\text{O}_6\text{ClN}_2\text{C}_{18}\text{H}_{29}$
Formula weight	621.19	669.28	645.29	578.53
Crystal color, habit	orange, blocks	yellow, needle	yellow needle	yellow, cubes
Crystal dimensions ( $\text{mm}^3$ )	$0.20 \times 0.20 \times 0.10$	$0.50 \times 0.10 \times 0.10$	$0.50 \times 0.10 \times 0.05$	$0.30 \times 0.30 \times 0.40$
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)	$Pbca$ (No. 61)
$a$ ( $\text{\AA}$ )	12.4254(6)	9.477(2)	9.226(1)	11.073(1)
$b$ ( $\text{\AA}$ )	9.9831(5)	24.784(2)	36.788(1)	16.870(4)
$c$ ( $\text{\AA}$ )	24.5994(8)	12.173(1)	9.9553(4)	28.067(6)
$\beta$ (deg)	98.570(5)	104.525(9)	107.625(5)	90
$V$ ( $\text{\AA}^3$ )	3017.3(2)	2767.7(6)	3220.3(3)	5242(1)
$F(000)$	1292.00	1404.00	1685.00	2384.00
$\mu$ (Cu K $\alpha$ ) ( $\text{cm}^{-1}$ )	90.32	99.18	110.60	112.66
$D_{\text{calcd}}$ ( $\text{g cm}^{-3}$ )	1.367	1.606	1.664	1.466
$Z$	4	4	4	8
No. of total reflections	6629	4866	6636	6006
No. of observed reflections	2112	2557	2446	1842
Octants collected	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, +l$
$R$	0.053	0.067	0.056	0.057
$R_w$	0.071	0.085	0.073	0.075

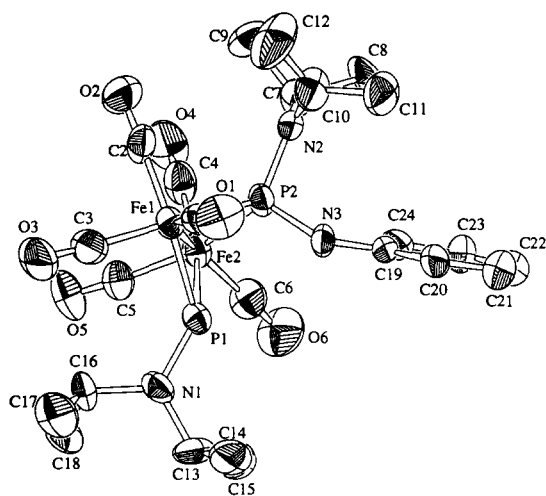


Fig. 1. ORTEP diagram for the structure of  $(i\text{Pr}_2\text{NPNHPh})(i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ .

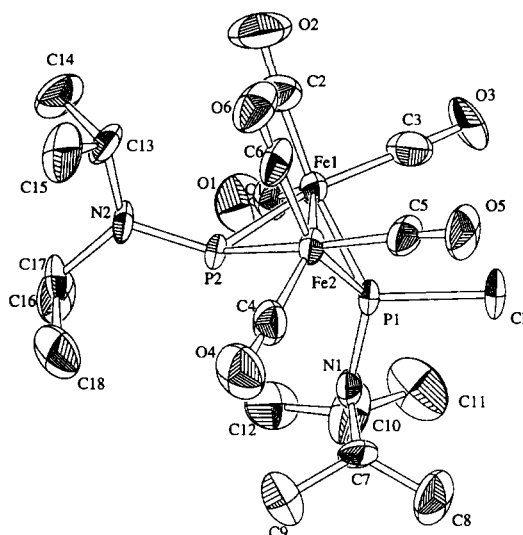


Fig. 4. ORTEP diagram for the structure of  $(\text{CINiPr}_2)(i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ .

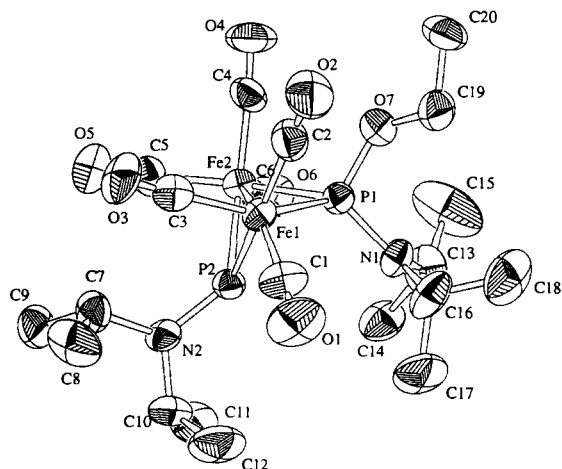


Fig. 2. ORTEP diagram for the structure of  $(\text{EtOPNiPr}_2)(i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ .

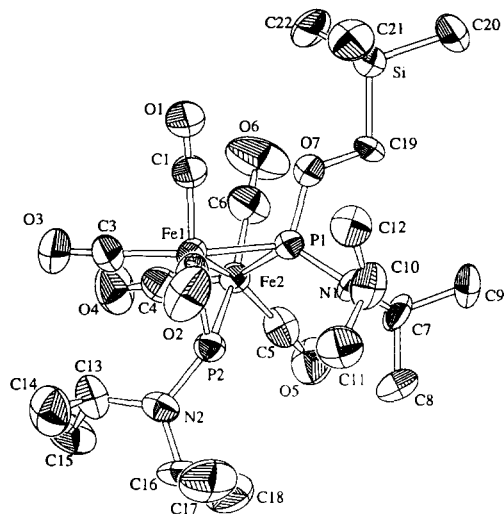


Fig. 3. ORTEP diagram for the structure of  $(\text{Me}_3\text{SiCH}_2\text{OPNiPr}_2)(i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ .

Table 5  
Selected bond lengths (Å) for  $(i\text{Pr}_2\text{NPNHPh})(i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$

Fe1–Fe2	2.639(3)	Fe1–P1	2.206(4)
Fe1–P2	2.244(4)	Fe1–C1	1.75(1)
Fe1–C2	1.80(2)	Fe1–C3	1.79(1)
Fe2–P1	2.246(4)	Fe2–P2	2.234(4)
Fe2–C4	1.80(1)	Fe2–C5	1.80(1)
Fe2–C6	1.76(2)	P1–N1	1.657(10)
P2–N2	1.70(1)	P2–N3	1.720(9)
O1–C1	1.14(1)	O2–C2	1.13(1)
O3–C3	1.14(1)	O4–C4	1.13(1)
O5–C5	1.12(1)	O6–C6	1.15(2)

Table 6  
Selected bond angles (deg) for  $(i\text{Pr}_2\text{NPNHPh})(i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$

Fe2–Fe1–P1	54.3(1)	Fe2–Fe1–P2	53.7(1)
Fe2–Fe1–C1	145.2(5)	Fe2–Fe1–C2	93.8(5)
Fe2–Fe1–C3	113.2(5)	P1–Fe1–P2	78.8(1)
P1–Fe1–C1	105.6(5)	P1–Fe1–C2	147.1(5)
P1–Fe1–C3	94.7(5)	P2–Fe1–C1	97.8(4)
P2–Fe1–C2	88.8(4)	P2–Fe1–C3	166.8(5)
C1–Fe1–C2	106.2(7)	C1–Fe1–C3	95.0(7)
C2–Fe1–C3	90.7(6)	Fe1–Fe2–P1	53.0(1)
Fe1–Fe2–P2	54.1(1)	Fe1–Fe2–C4	110.8(5)
Fe1–Fe2–C5	98.7(4)	Fe1–Fe2–C6	141.2(5)
P1–Fe2–P2	78.2(1)	P1–Fe2–C4	162.5(5)
P1–Fe2–C5	90.4(4)	P1–Fe2–C6	94.0(5)
P2–Fe2–C4	97.4(5)	P2–Fe2–C5	152.0(4)
P2–Fe2–C6	104.8(5)	C4–Fe2–C5	85.8(6)
C4–Fe2–C6	103.5(7)	C5–Fe2–C6	101.4(7)
Fe1–P1–Fe2	72.7(1)	Fe1–P1–N1	129.9(4)
Fe2–P1–N1	126.9(4)	Fe1–P2–Fe2	72.2(1)
Fe1–P2–N2	124.0(4)	Fe1–P2–N3	108.7(4)
Fe2–P2–N2	125.4(4)	Fe2–P2–N3	121.0(4)
N2–P2–N3	103.1(5)	P1–N1–C13	121.8(8)
P1–N1–C16	121.2(9)	P2–N2–C7	119.2(9)
P2–N2–C10	118.0(9)	P2–N3–C19	125.5(8)
Fe1–C1–O1	179(1)	Fe1–C2–O2	177(1)
Fe1–C3–O3	174(1)	Fe2–C4–O4	172(1)
Fe2–C5–O5	176(1)	Fe2–C6–O6	177(1)

Table 7  
Selected bond lengths (Å) for (EtOPN<sup>i</sup>Pr<sub>2</sub>)(<sup>i</sup>Pr<sub>2</sub>NPH)Fe<sub>2</sub>(CO)<sub>6</sub>

Fe1–Fe2	2.637(2)	Fe1–P1	2.219(3)
Fe1–P2	2.227(3)	Fe1–C1	1.78(1)
Fe1–C2	1.81(1)	Fe1–C3	1.84(1)
Fe2–P1	2.218(3)	Fe2–P2	2.198(3)
Fe2–C4	1.79(1)	Fe2–C5	1.80(1)
Fe2–C6	1.76(1)	P1–O7	1.608(8)
P1–N1	1.680(8)	P2–N2	1.630(9)
O1–C1	1.12(1)	O2–C2	1.14(1)
O3–C3	1.10(1)	O4–C4	1.14(1)
O5–C5	1.14(1)	O6–C6	1.14(1)
O7–C19	1.40(1)		

Table 8  
Selected bond angles (deg) for (EtOPN<sup>i</sup>Pr<sub>2</sub>)(<sup>i</sup>Pr<sub>2</sub>NPH)Fe<sub>2</sub>(CO)<sub>6</sub>

Fe2–Fe1–P1	53.52(8)	Fe2–Fe1–P2	52.92(8)
Fe2–Fe1–C1	144.3(4)	Fe2–Fe1–C2	109.1(4)
Fe2–Fe1–C3	95.6(4)	P1–Fe1–P2	77.0(1)
P1–Fe1–C1	111.2(4)	P1–Fe1–C2	89.1(4)
P1–Fe1–C3	145.9(4)	P2–Fe1–C1	94.2(4)
P2–Fe1–C2	161.7(4)	P2–Fe1–C3	96.3(4)
C1–Fe1–C2	102.0(6)	C1–Fe2–C3	102.5(6)
C2–Fe1–C3	88.5(5)	Fe1–Fe2–P1	53.54(8)
Fe1–Fe2–P2	53.91(8)	Fe1–Fe2–C4	95.1(4)
Fe1–Fe2–C5	108.8(4)	Fe1–Fe2–C6	150.2(3)
P1–Fe2–P2	77.6(1)	P1–Fe2–C4	88.8(4)
P1–Fe2–C5	162.2(4)	P1–Fe2–C6	102.1(4)
P2–Fe2–C4	148.4(4)	P2–Fe2–C5	93.1(4)
P2–Fe2–C6	108.7(4)	C4–Fe2–C5	91.6(5)
C4–Fe2–C6	102.0(5)	C5–Fe2–C6	95.1(5)
Fe1–P1–Fe2	72.9(1)	Fe1–P1–O7	117.9(3)
Fe1–P1–N1	121.4(3)	Fe2–P1–O7	108.8(3)
Fe2–P1–N1	126.4(3)	O7–P1–N1	106.7(4)
Fe1–P2–Fe2	73.17(10)	Fe1–P2–N2	127.2(3)
Fe2–P2–N2	129.1(3)	P1–O7–C19	127.2(8)
P1–N1–C13	124.2(8)	P1–N1–C16	118.7(7)
P2–N2–C7	120.9(7)	P2–N2–C10	122.6(7)
Fe1–C1–O1	177(1)	Fe1–C2–O2	178(1)
Fe1–C3–O3	177(1)	Fe2–C4–O4	177(1)
Fe2–C5–O5	175(1)	Fe2–C6–O6	176.7(10)

Table 9  
Selected bond lengths (Å) for (Me<sub>3</sub>SiCH<sub>2</sub>OPN<sup>i</sup>Pr<sub>2</sub>)(<sup>i</sup>Pr<sub>2</sub>NPH)Fe<sub>2</sub>(CO)<sub>6</sub>

Fe1–Fe2	2.653(2)	Fe1–P1	2.214(3)
Fe1–P2	2.213(3)	Fe1–C1	1.77(1)
Fe1–C2	1.74(1)	Fe1–C3	1.81(1)
Fe2–P1	2.204(3)	Fe2–P2	2.206(3)
Fe2–C4	1.82(1)	Fe2–C5	1.75(1)
Fe2–C6	1.77(1)	P1–O7	1.648(7)
P1–N1	1.698(8)	P2–N2	1.664(9)
Si–C19	1.90(1)	Si–C20	1.90(1)
Si–C21	1.88(1)	Si–C22	1.88(1)
O1–C1	1.14(1)	O2–C2	1.16(1)
O3–C3	1.12(1)	O4–C4	1.13(1)
O5–C5	1.16(1)	O6–C6	1.15(1)
O7–C19	1.46(1)		

Table 10  
Selected bond angles (deg) for (Me<sub>3</sub>SiCH<sub>2</sub>OPN<sup>i</sup>Pr<sub>2</sub>)(<sup>i</sup>Pr<sub>2</sub>NPH)Fe<sub>2</sub>(CO)<sub>6</sub>

Fe2–Fe1–P1	52.91(9)	Fe2–Fe1–P2	52.99(9)
Fe2–Fe1–C1	106.4(4)	Fe2–Fe1–C2	146.4(4)
Fe2–Fe1–C3	100.6(4)	P1–Fe1–P2	77.6(1)
P1–Fe1–C1	87.7(4)	P1–Fe1–C2	109.3(4)
P1–Fe1–C3	150.7(5)	P2–Fe1–C1	159.2(4)
P2–Fe1–C2	98.3(5)	P2–Fe1–C3	96.7(4)
C1–Fe1–C2	100.3(6)	C1–Fe1–C3	89.1(6)
C2–Fe1–C3	99.9(6)	Fe1–Fe2–P1	53.27(8)
Fe1–Fe2–P2	53.22(9)	Fe1–Fe2–C4	99.4(4)
Fe1–Fe2–C5	144.9(4)	Fe1–Fe2–C6	107.5(4)
P1–Fe2–P2	77.9(1)	P1–Fe2–C4	150.6(4)
P1–Fe2–C5	108.7(4)	P1–Fe2–C6	88.7(4)
P2–Fe2–C4	94.3(4)	P2–Fe2–C5	96.4(4)
P2–Fe2–C6	160.7(4)	C4–Fe2–C5	100.3(5)
C4–Fe2–C6	90.6(6)	C5–Fe2–C6	101.2(6)
Fe1–P1–Fe2	73.8(1)	Fe1–P1–O7	110.0(3)
Fe1–P1–N1	126.3(3)	Fe2–P1–O7	115.9(3)
Fe2–P1–N1	121.8(3)	O7–P1–N1	106.4(4)
Fe1–P2–Fe2	73.8(1)	Fe1–P2–N2	128.0(4)
Fe2–P2–N2	128.1(4)	C19–Si–C20	107.1(5)
C19–Si–C21	109.0(5)	C19–Si–C22	108.8(5)
C20–Si–C21	110.5(6)	C20–Si–C22	109.7(6)
C21–Si–C22	111.7(6)	P1–O7–C19	122.7(6)
P1–N1–C7	118.4(7)	P1–N1–C10	121.3(7)
P2–N2–C13	120.4(8)	P2–N2–C16	121.9(8)
Fe1–C1–O1	176(1)	Fe1–C2–O2	174(1)
Fe1–C3–O3	175(1)	Fe2–C4–O4	178(1)
Fe2–C5–O5	179(1)	Fe2–C6–O6	178(1)
Si–C19–O7	106.4(7)		

(<sup>i</sup>Pr<sub>2</sub>NPX)(<sup>i</sup>Pr<sub>2</sub>NPH)Fe<sub>2</sub>(CO)<sub>6</sub> derivatives, the stereochemistry of which has been established by X-ray diffraction.

### 3.1. Reaction of (<sup>i</sup>Pr<sub>2</sub>NP)<sub>2</sub>COFe<sub>2</sub>(CO)<sub>6</sub> with aniline

The reaction of (<sup>i</sup>Pr<sub>2</sub>NP)<sub>2</sub>COFe<sub>2</sub>(CO)<sub>6</sub> with aniline was an attempt to eliminate water to give (<sup>i</sup>Pr<sub>2</sub>NP)<sub>2</sub>(C=NPh)Fe<sub>2</sub>(CO)<sub>6</sub> with a phosphorus-bridging phenyl isocyanide group according to the following equation:

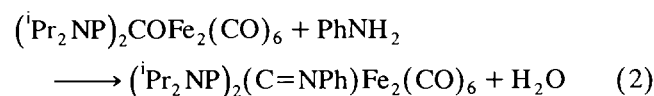


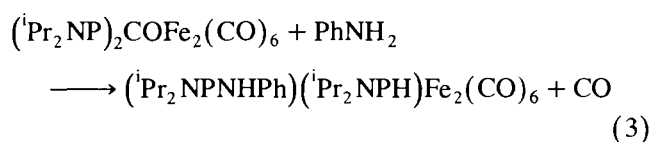
Table 11  
Selected bond lengths (Å) for (CIPN<sup>i</sup>Pr<sub>2</sub>)(<sup>i</sup>Pr<sub>2</sub>NPH)Fe<sub>2</sub>(CO)<sub>6</sub>

Fe1–Fe2	2.683(3)	Fe1–P1	2.202(4)
Fe1–P2	2.223(4)	Fe1–C1	1.76(2)
Fe1–C2	1.78(2)	Fe1–C3	1.83(2)
Fe2–P1	2.201(4)	Fe2–P2	2.215(4)
Fe2–C4	1.78(2)	Fe2–C5	1.78(2)
Fe2–C6	1.77(2)	C11–P1	2.119(4)
P1–N1	1.67(1)	P2–N2	1.665(10)
O1–C1	1.14(2)	O2–C2	1.14(2)
O3–C3	1.13(2)	O4–C4	1.13(2)
O5–C5	1.15(2)	O6–C6	1.15(2)

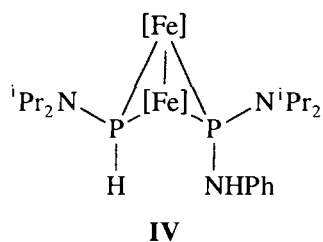
Table 12  
Selected bond angles (deg) for  $(\text{CIPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$

Fe2–Fe1–P1	52.5(1)	Fe2–Fe1–P2	52.7(1)
Fe2–Fe1–C1	143.1(6)	Fe2–Fe1–C2	97.1(6)
Fe2–Fe1–C3	113.1(6)	P1–Fe1–P2	76.6(1)
P1–Fe1–C1	112.7(6)	P1–Fe1–C2	147.3(6)
P1–Fe1–C3	90.8(6)	P2–Fe1–C1	93.0(6)
P2–Fe1–C2	95.0(6)	P2–Fe1–C3	165.0(6)
C1–Fe1–C2	99.1(8)	C1–Fe1–C3	99.4(8)
C2–Fe1–C3	91.4(8)	Fe1–Fe2–P1	52.5(1)
Fe1–Fe2–P2	52.9(1)	Fe1–Fe2–C4	141.7(6)
Fe1–Fe2–C5	112.5(6)	Fe1–Fe2–C6	98.7(5)
P1–Fe2–P2	76.7(1)	P1–Fe2–C4	109.5(6)
P1–Fe2–C5	91.3(6)	P1–Fe2–C6	148.9(6)
P2–Fe2–C4	92.4(6)	P2–Fe2–C5	165.0(6)
P2–Fe2–C6	95.5(5)	C4–Fe2–C5	100.2(8)
C4–Fe2–C6	100.7(8)	C5–Fe2–C6	90.1(7)
Fe1–P1–Fe2	75.1(1)	Fe1–P1–C11	114.6(2)
Fe1–P1–N1	126.4(5)	Fe2–P1–C11	114.3(2)
Fe2–P1–N1	122.1(5)	C11–P1–N1	103.2(4)
Fe1–P2–Fe2	74.4(1)	Fe1–P2–N2	128.2(5)
Fe2–P2–N2	127.5(5)	P1–N1–C7	116(1)
P1–N1–C10	124(1)	P2–N2–C13	120.7(9)
P2–N2–C17	119.2(9)	Fe1–C1–O1	177(1)
Fe1–C2–O2	175(1)	Fe1–C3–O3	177(1)
Fe2–C4–O4	176(1)	Fe2–C5–O5	175(1)
Fe2–C6–O6	177(1)		

In the initial reaction, performed in boiling toluene, molecular sieves were added in order to remove the water produced; under these conditions the reaction mixture decomposed completely without the formation of any tractable metal carbonyl derivatives. Under milder conditions (boiling hexane without molecular sieves) the reaction of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with aniline led to extrusion of the phosphorus-bridging carbonyl group to give  $(^i\text{Pr}_2\text{NPNHPh})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  according to the following equation:

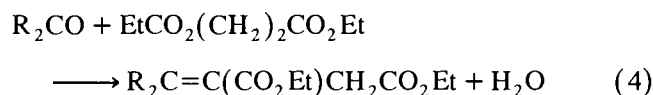


This product was shown by X-ray diffraction to have the syn stereochemistry (IV and Fig. 1). Apparently the PhNH and H units from the aniline occupy the sites vacated by the extruded phosphorus-bridging carbonyl group without any rearrangement of the stereochemistry of the intermediate biradical II.

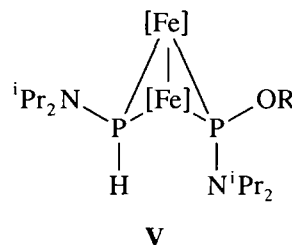


### 3.2. Reaction of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with diethyl succinate

Ketones or aldehydes without a C–H hydrogen adjacent to the carbonyl group undergo the Stobbe condensation [8] with diethyl succinate in the presence of potassium *t*-butoxide as a strong base according to the following equation (e.g. R = C<sub>6</sub>H<sub>5</sub>):

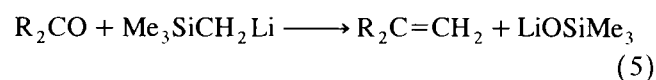


An attempt to effect an analogous reaction with the phosphorus-bridging carbonyl derivative  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  led instead to formation of yellow  $(\text{EtOPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ , which was shown by NMR spectroscopy to be identical to the known [4] product of this stoichiometry from the reaction of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with ethanol in boiling toluene. The structure of this product was confirmed by X-ray diffraction, which also indicated the anti stereochemistry (V; R = Et, and Fig. 2) in contrast to IV obtained from  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  and aniline. The ethanol required for the conversion of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  to  $(\text{EtOPN}^i\text{Pr}_2)(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  in the diethyl succinate reaction can be liberated from the diethyl succinate by transesterification with *t*-butanol catalyzed by the strongly basic potassium *t*-butoxide.



### 3.3. Reaction of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with trimethylsilylmethyl lithium

Ketones without a C–H hydrogen adjacent to the carbonyl group undergo methylenation with Me<sub>3</sub>SiCH<sub>2</sub>Li to give the corresponding olefin with elimination of trimethylsiloxide according to the following equation (Peterson reaction) [9]:

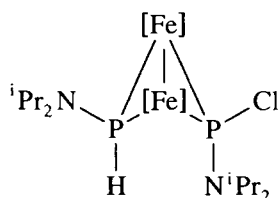


However, a similar reaction of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with Me<sub>3</sub>SiCH<sub>2</sub>Li in boiling hexane like the previously [10] attempted Wittig reaction of  $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with R<sub>3</sub>P=CH<sub>2</sub> (R = Me, Me<sub>2</sub>N, Ph, *p*-MeC<sub>6</sub>H<sub>4</sub>) did not result in methylenation of the phosphorus-bridging

carbonyl group to give the olefinic  $[(^1\text{Pr}_2\text{NP})_2\text{C}=\text{CH}_2]\text{Fe}_2(\text{CO})_6$ . Instead the reaction of  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with  $\text{Me}_3\text{SiCH}_2\text{Li}$  was found to give a low yield of yellow  $(\text{Me}_3\text{SiCH}_2\text{OPN}^1\text{Pr}_2)(^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ , which is formally derived from addition of the alcohol  $\text{Me}_3\text{SiCH}_2\text{OH}$  to the  $(^1\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  unit (**II**) resulting from extrusion of the phosphorus-bridging carbonyl group from  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ . The same product was also formed more rationally by reaction of  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with  $\text{Me}_3\text{SiCH}_2\text{OH}$  in boiling hexane. The formation of small quantities of  $(\text{Me}_3\text{SiCH}_2\text{OPN}^1\text{Pr}_2)(^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  from the reaction of  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with  $\text{Me}_3\text{SiCH}_2\text{Li}$  in boiling hexane can be related to the conversion of some of the  $\text{Me}_3\text{SiCH}_2\text{Li}$  to the alkoxide  $\text{Me}_3\text{SiCH}_2\text{OLi}$  by adventitious oxygen. X-ray diffraction of  $(\text{Me}_3\text{SiCH}_2\text{OPN}^1\text{Pr}_2)(^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  (Fig. 3) established the anti stereochemistry (**V**;  $\text{R} = \text{Me}_3\text{SiCH}_2$ ) similar to the ethoxy derivative  $(\text{EtOPN}^1\text{Pr}_2)(^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  (**V**;  $\text{R} = \text{Et}$ ) discussed above.

#### 3.4. Reaction of $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with acetyl chloride

Reaction of  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with excess hydrogen halides (e.g.  $\text{HBr}$ ) [4], even under mild conditions, results not only in extrusion of the phosphorus-bridging carbonyl group but also in cleavage of one of the P–N bonds to give  $(\text{BrPN}^1\text{Pr}_2)(\text{BrPH})\text{Fe}_2(\text{CO})_6$ . This P–N bond cleavage reaction can be suppressed if only a limited amount of hydrogen halide is used. In this connection reaction of  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with the limited amount of hydrogen chloride produced by hydrolysis of acetyl chloride with adventitious water was found to result in simple  $\text{HCl}$  addition to the  $(^1\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  unit (**II**) produced by extrusion of the phosphorus-bridging carbonyl group. The resulting  $(\text{ClPN}^1\text{Pr}_2)(^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  product has been shown by X-ray diffraction to have the same anti stereochemistry (**VI**) as found in the alcohol addition products (**V**). An attempt to substitute thionyl chloride for acetyl chloride in this reaction led instead to complete decomposition of the metal carbonyl derivative to give  $^1\text{Pr}_2\text{NP}(\text{S})\text{Cl}_2$ , identical to the previously reported product [3] from the reaction of  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with  $\text{S}_2\text{Cl}_2$  in boiling toluene.



**VI**

#### 3.5. Spectroscopic studies

The infrared and NMR spectra of all the compounds discussed in this paper (Tables 1–3) are in accord with their structures. Thus the  $^{31}\text{P}$  NMR spectra of all of the  $(^1\text{Pr}_2\text{NPX})(^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  derivatives exhibit two doublets with  $J(\text{P}–\text{P})$  in the range 110–130 Hz. The  $^1\text{Pr}_2\text{NPH}$  phosphorus atom appears in the chemical shift range  $\delta$  142 to 152 (Table 1). The proton and proton-decoupled  $^{13}\text{C}$  NMR spectra of all of the  $(^1\text{Pr}_2\text{NPX})(^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  derivatives clearly exhibit two non-equivalent isopropyl groups (Tables 2 and 3) in contrast to related compounds containing only a single diisopropylamino group such as  $(\text{BrPN}^1\text{Pr}_2)(\text{BrPH})\text{Fe}_2(\text{CO})_6$  and  $(\text{EtOPN}^1\text{Pr}_2)(\text{BrPH})\text{Fe}_2(\text{CO})_6$ . The P–H hydrogens exhibit double doublets in the proton NMR spectra with a large  $^1J(\text{P}–\text{P})$  coupling of about 400 Hz and a small  $^3J(\text{P}–\text{H})$  coupling of about 20 Hz. The P–H hydrogens in  $^1\text{Pr}_2\text{NPH}$  units exhibit chemical shifts around  $\delta$   $5.7 \pm 0.1$ , whereas those in  $\text{BrPH}$  units exhibit chemical shifts around  $\delta$   $4.6 \pm 0.1$ .

#### 4. Discussion

This work indicates that extrusion of the phosphorus-bridging carbonyl group from  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  to give a reactive  $(^1\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  unit followed by  $\text{HX}$  addition does not necessarily give products with the syn stereochemistry of the leaving phosphorus-bridging group. In fact of the four  $(^1\text{Pr}_2\text{NPX})(^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  derivatives investigated in this work, only the derivative from aniline, namely  $(^1\text{Pr}_2\text{NPNHPh})(^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ , was found to have syn stereochemistry. The remaining three derivatives, namely  $(\text{XPN}^1\text{Pr}_2)(^1\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$  ( $\text{X} = \text{Cl}, \text{OEt}, \text{OCH}_2\text{SiMe}_3$ ), were found to have anti stereochemistry. This suggests rearrangement of the intermediate  $(^1\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  (**II**) from the syn conformation initially formed by extrusion of the phosphorus-bridging carbonyl group in  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  to an anti conformation in order to reduce steric hindrance of the two bulky diisopropylamino groups prior to addition of the  $\text{HX}$  derivative.

Another observation from this work is the inability of the phosphorus-bridging carbonyl group in  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  to undergo many reactions which are established methods for converting the carbon–oxygen double bond of a ketonic carbonyl group to a carbon–carbon double bond. Thus the olefination of  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  to give  $[(^1\text{Pr}_2\text{NP})_2\text{C}=\text{CH}_2]\text{Fe}_2(\text{CO})_6$  fails using either the Peterson reaction with  $\text{Me}_3\text{SiCH}_2\text{Li}$  or the Wittig reaction with  $\text{R}_3\text{P}=\text{CH}_2$  [10]. In addition, the Stobbe condensation of  $(^1\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with diethyl succinate also fails to convert the  $\text{C}=\text{O}$  bond of the phosphorus-bridging carbonyl to a  $\text{C}=\text{C}$  bond.



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