Dialkylaminophosphorus metal carbonyls XIII [*]. Structure of a tertiary alcohol $[(^{i}Pr_2NP)_2C(OH)R]Fe_2(CO)_6$ and the effect of carbon hybridization on the geometry of the CP_2Fe_2 cage

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 $(^{i}Pr_2NP)_2COFe_2(CO)_6$ with benzyllithium (from $PhCH_2SnPh_3 + n$-BuLi) gives the corresponding tertiary alcohol $(^{i}Pr_2NP)_2C(CH_2Ph)(OH)Fe_2(CO)_6$, which has been characterized structurally by X-ray diffraction (monoclinic; space group, $P2_1/a$; $a = 9.797(1)$, $b = 16.593(1)$ and $c = 19.671(2)$ Å; $\beta = 101.564(9)°$; $Z = 4$). A comparison of the geometries of the CP_2Fe_2 cages in the series $(^{i}Pr_2NP)_2C(CH_2Ph)(OH)Fe_2(CO)_6$ and $[(^{i}Pr_2NP)_2CHSiMe_3]Fe_2(CO)_6$ with $P-C(sp^3)-P$ bridges and $(^{i}Pr_2NP)_2COFe_2(CO)_6$, $(^{i}Pr_2NP)(^{t}Bu_2PP)COFe_2(CO)_6$, and $(^{t}BuP)_2COFe_2(CO)_6$ with $P-C(sp^2)-P$ bridges indicates that changing the P bridging (i.e. cage) carbon atom from sp^3 hybridization to sp^2 hybridization increases the P–C–P bond angle from 78–80 to 84–86°, the P–Fe–P bond angles from 64–67 to 69–70°, and the non-bonding P $\cdots$ P distance from 2.44 to 2.53–2.55 Å while having relatively little effect on the P–C, Fe–P and Fe–Fe distances.

Keywords: Iron; Dialkylaminophosphorus metal carbonyls; Alcohol; Stereochemistry; Cage compound; Phosphorus

1. Introduction

Our first detailed report [2] on the chemical reactivity of the phosphorus-bridging carbonyl derivative $(^{i}Pr_2NP)_2COFe_2(CO)_6$ (**I**) included its reactions with the organolithium compounds RLi (R = Me or *n*-Bu) to give the corresponding tertiary alcohols $(^{i}Pr_2NP)_2$-$CR(OH)Fe_2(CO)_6$ (**II**). However, none of these tertiary alcohols was characterized structurally by X-ray diffraction. We have now obtained the closely related tertiary alcohol $(^{i}Pr_2NP)_2C(CH_2Ph)(OH)Fe_2(CO)_6$ (**II**)(R = CH_2Ph) by an analogous reaction of $(^{i}Pr_2NP)_2COFe_2$-$(CO)_6$ (**I**) with the benzyllithium obtained by transmetallation of $PhCH_2SnPh_3$ with *n*-butyllithium [3,4] and report here the structure of this tertiary alcohol. In addition, we review available structural data on CP_2Fe_2 cages in iron carbonyl derivatives and make some observations on the geometry of these cages relative to the carbon hybridization.

2. Experimental section

The general experimental conditions are the same as described in an earlier paper of this series [2]. The $(^{i}Pr_2NP)_2COFe_2(CO)_6$ was prepared by the published procedure [5] and the other reagents were commercial products (Aldrich Chemical Company).

2.1. Preparation of $(^{i}Pr_2NP)_2C(CH_2Ph)(OH)Fe_2(CO)_6$

A solution of 0.8 g (1.8 mmol) of $PhCH_2SnPh_3$ in 25 ml of diethyl ether was treated at $-78°C$ with 2.5 ml of 1.6 M *n*-butyllithium in hexane (4.0 mmol) and the mixture slowly allowed to warm to room temperature.

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[*] For part XII, see [1]. This paper is dedicated to Professor Henri Brunner in recognition of his many contributions to organometallic chemistry.

[*] Corresponding author.

Table 1
Crystal data for (^{i}Pr$_2$NP)$_2$C(CH$_2$Ph)(OH)Fe$_2$(CO)$_6$ (II) (R = CH$_2$Ph)

Empirical formula	C$_{26}$H$_{36}$N$_2$O$_7$P$_2$Fe$_2$
Molecular weight	663.23
Crystal dimensions (mm)	0.40×0.20×0.20
Crystal system	Monoclinic
Space group	$P2_1/a$ (No. 14)
a (Å)	9.797(1)
b (Å)	16.593(1)
c (Å)	19.671(2)
β (°)	101.564(9)
V (Å^3)	3132.8(5)
$F(000)$	1380
μ(Cu Kα) (cm^{-1})	87.62
D_{calc} (g cm^{-3})	1.406
Z	4
Number of total reflections	6786
Number of observed reflections	3860
Octants collected	$+h, +k, \pm l$
R	0.056
R_w	0.079
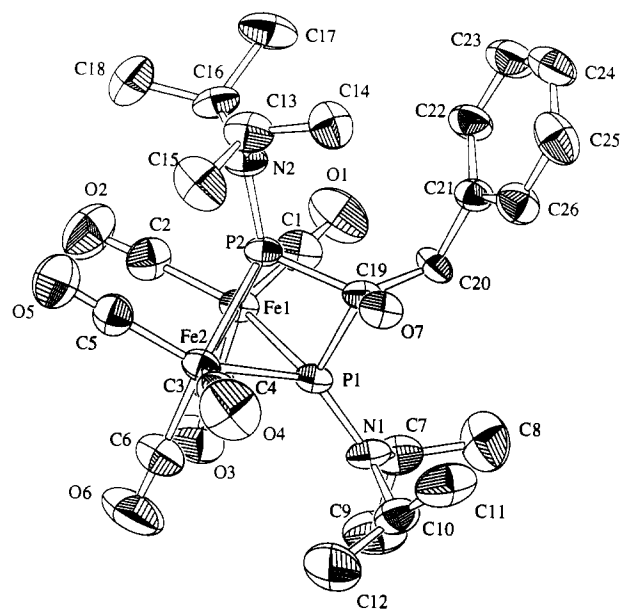
Fig. 1. ORTEP diagram for the structure of (^{i}Pr$_2$NP)$_2$C(CH$_2$Ph)(OH)-Fe$_2$(CO)$_6$ (II R = CH$_2$Ph).

After adding 1.12 g (2.0 mmol) of (^{i}Pr$_2$NP)$_2$COFe$_2$-(CO)$_6$, the reaction mixture was stirred overnight at room temperature. Solvent was then removed in vacuum and the residue extracted with hexane. Concentration of the hexane extract gave brownish crystals. The product was purified by dissolving in a minimum of a CH$_2$Cl$_2$–hexane mixture and passing the solution through a 1.2 cm layer of silica gel on a Schlenk filter. Concentration of the filtrate and cooling gave 0.4 g (33% yield) of yellow crystalline (^{i}Pr$_2$NP)$_2$C-(CH$_2$Ph)(OH)Fe$_2$(CO)$_6$ (II) (R = CH$_2$Ph) (melting point, 158–160°C). IR (hexane): ν(CO) 2051s, 2006s, 1990s, 1957m, and 1939 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 192.0 (singlet, relative to H$_3$PO$_4$) ppm. ^{1}H NMR (CDCl$_3$) δ 7.2–7.4 (benzenoid CH; obscured partially by CDCl$_3$), 4.40 (singlet OH), 3.51 (triplet, 5 Hz; benzyl CH$_2$), 3.41 (septet, 7 Hz; isopropyl CH), 1.04 (doublet, 7 Hz), 0.93 (doublet, 7 Hz; isopropyl CH$_3$) ppm. Anal. Found: C, 47.2; H, 5.4; N, 4.1. C$_{26}$H$_{36}$-Fe$_2$N$_2$P$_2$O$_7$: Calc.: C, 47.1; H, 5.4; N, 4.2%.

2.2. Structure determination of (^{i}Pr$_2$NP)$_2$C(CH$_2$Ph)-(OH)Fe$_2$(CO)$_6$

A yellow prismatic crystal of C$_{26}$H$_{36}$N$_2$O$_7$P$_2$Fe$_2$ = (^{i}Pr$_2$NP)$_2$C(CH$_2$Ph)(OH)Fe$_2$(CO)$_6$ from CH$_2$Cl$_2$–
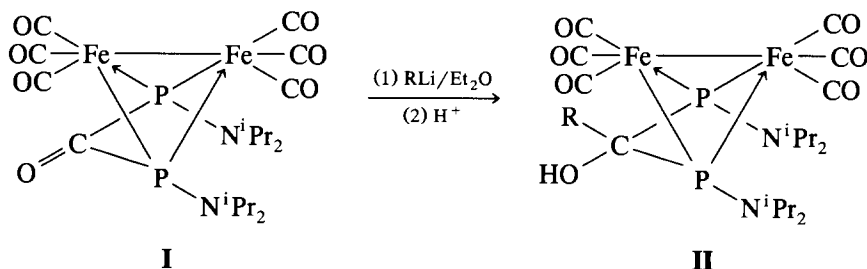
hexane having approximate dimensions 0.40 × 0.20 × 0.20 mm was fixed in a random orientation on a glass fiber and mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite crystal monochromator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $10.00° < 2\theta < 40.00°$. Intensity data using Cu Kα radiation (λ = 1.541 84 Å) were collected at a temperature of 23 ± 1°C over a θ range of 2–75° using the ω–2θ technique. Of the 7097 reflections which were collected, 6786 were unique (R_{int} = 0.030). The intensities of three representative reflections were measured after every 120 min of X-ray exposure time. No decay correction was applied. The linear absorption coefficient μ for Cu Kα radiation is 87.6 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.81 to 0.99. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient, 1.289 86 × 10^{-6}).

The structure was solved by direct methods [6] and expanded using Fourier techniques [7]. All non-hydrogen atoms were refined anisotropically. The final cycle

I   (1) RLi/Et$_2$O   (2) H$^+$ II

Table 2
Selected bond distances (Å) for $(^iPr_2NP)_2C(CH_2Ph)(OH)Fe_2(CO)_6$ (II) (R = CH$_2$Ph)

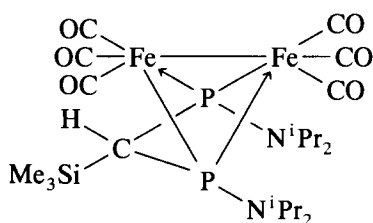|			
Fe(1)–Fe(2)	2.613(2)	Fe(1)–P(1)	2.216(2)
Fe(1)–P(2)	2.219(2)	Fe(1)–C(1)	1.756(8)
Fe(1)–C(2)	1.788(9)	Fe(1)–C(3)	1.768(8)
Fe(2)–P(1)	2.227(2)	Fe(2)–P(2)	2.260(2)
Fe(2)–C(4)	1.758(8)	Fe(2)–C(5)	1.764(9)
Fe(2)–C(6)	1.792(9)	P(1)–N(1)	1.665(6)
P(1)–C(19)	1.911(6)	P(2)–N(2)	1.656(6)
P(2)–C(19)	1.903(7)	O(1)–C(1)	1.145(9)
O(2)–C(2)	1.149(9)	O(3)–C(3)	1.156(9)
O(4)–C(4)	1.149(9)	O(5)–C(5)	1.147(9)
O(6)–C(6)	1.136(9)	O(7)–C(19)	1.412(7)
N(1)–C(7)	1.518(9)	N(1)–C(10)	1.488(9)
N(2)–C(13)	1.516(9)	N(2)–C(16)	1.504(9)

of full-matrix least-squares refinement was based on 3860 observed reflections ($I > 3\sigma(I)$) and 353 variable parameters and converged (largest parameter shift was 0.03 times its estimated standard deviation) with unweighted and weighted agreement factors of $R = 0.056$ and $R_w = 0.079$. Neutral atom scattering factors were taken from Cromer and Waber [8]. Anomalous dispersion effects were included in F_{calc} [9], the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [10]. The values for the mass attenuation coefficients are those of Creagh and Hubbel [11]. All calculations were

Table 3
Selected bond angles (°) for $(^iPr_2NP)_2C(CH_2Ph)(OH)Fe_2(CO)_6$ (II) (R = CH$_2$Ph)
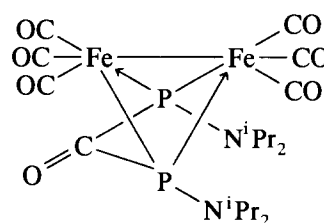
Fe(2)–Fe(1)–P(1)	54.17(6)	Fe(2)–Fe(1)–P(2)	55.05(5)
Fe(2)–Fe(1)–C(1)	153.2(3)	Fe(2)–Fe(1)–C(2)	95.1(3)
Fe(2)–Fe(1)–C(3)	98.7(3)	P(1)–Fe(1)–P(2)	66.82(7)
P(1)–Fe(1)–C(1)	107.6(3)	P(1)–Fe(1)–C(2)	149.3(3)
P(1)–Fe(1)–C(3)	92.6(3)	P(2)–Fe(1)–C(1)	101.3(3)
P(2)–Fe(1)–C(2)	96.6(3)	P(2)–Fe(1)–C(3)	152.7(3)
C(1)–Fe(1)–C(2)	100.7(4)	C(1)–Fe(1)–C(3)	102.0(4)
C(2)–Fe(1)–C(3)	92.8(4)	Fe(1)–Fe(2)–P(1)	53.77(5)
Fe(1)–Fe(2)–P(2)	53.58(5)	Fe(1)–Fe(2)–C(4)	153.7(3)
Fe(1)–Fe(2)–C(5)	98.7(3)	Fe(1)–Fe(2)–C(6)	96.9(3)
P(1)–Fe(2)–P(2)	65.93(7)	P(1)–Fe(2)–C(4)	104.6(3)
P(1)–Fe(2)–C(5)	150.9(3)	P(1)–Fe(2)–C(6)	95.9(3)
P(2)–Fe(2)–C(4)	106.5(3)	P(2)–Fe(2)–C(5)	90.8(3)
P(2)–Fe(2)–C(6)	150.3(3)	C(4)–Fe(2)–C(5)	98.5(4)
C(4)–Fe(2)–C(6)	100.6(4)	C(5)–Fe(2)–C(6)	97.1(4)
Fe(1)–P(1)–Fe(2)	72.07(7)	Fe(1)–P(1)–N(1)	126.5(2)
Fe(1)–P(1)–C(19)	97.5(2)	Fe(2)–P(1)–N(1)	135.6(2)
Fe(2)–P(1)–C(19)	95.3(2)	N(1)–P(1)–C(19)	117.7(3)
Fe(1)–P(2)–Fe(2)	71.37(6)	Fe(1)–P(2)–N(2)	127.3(2)
Fe(1)–P(2)–C(19)	97.6(2)	Fe(2)–P(2)–N(2)	132.9(2)
Fe(2)–P(2)–C(19)	94.4(2)	N(2)–P(2)–C(19)	120.2(3)
P(1)–N(1)–C(7)	118.6(5)	P(1)–N(1)–C(10)	123.9(5)
P(2)–N(2)–C(13)	123.6(5)	P(2)–N(2)–C(16)	119.7(5)
Fe(1)–C(1)–O(1)	178.7(8)	Fe(1)–C(2)–O(2)	176.7(8)
Fe(1)–C(3)–O(3)	177.5(8)	Fe(2)–C(4)–O(4)	179.4(9)
Fe(2)–C(5)–O(5)	178.8(8)	Fe(2)–C(6)–O(6)	178.3(9)
P(1)–C(19)–P(2)	79.6(3)	P(1)–C(19)–O(7)	115.9(4)
P(1)–C(19)–C(20)	112.3(4)	P(2)–C(19)–O(7)	114.7(5)
P(2)–C(19)–C(20)	123.0(5)	O(7)–C(19)–C(20)	108.9(5)

Table 4
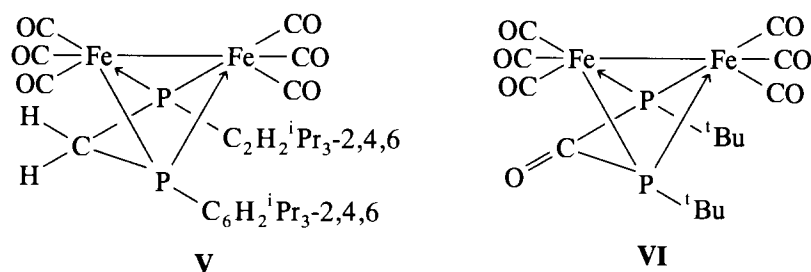Geometries of CP$_2$Fe$_2$ cages in organophosphorus iron carbonyl derivatives

	Value for the following compounds					
	II (R = CH$_2$Ph)	III	V	I	VI	IV
P–C–P (°)	79.6(3)	78.5(5)	83.7(4)	84.4(4)	84.6(6)	85.7(4)
P–Fe–P (°)	66.82(7)	65.1(1)	65.70(6)	69.60(9)	69.0(1)	69.5(1)
	65.93(7)	64.8(2)	65.97(6)	69.48(9)	68.9(1)	69.6(1)
P–C (Å)	1.903(7)	1.88(1)	1.836(6)	1.884(9)	1.875(9)	1.88(1)
	1.911(6)	1.91(1)		1.895(10)	1.878(9)	1.87(1)
Fe–P (Å)	2.219(2)	2.226(3)	2.258(2)	2.227(3)	2.228(4)	2.266(3)
	2.216(2)	2.228(3)	2.250(2)	2.220(3)	2.228(4)	2.209(4)
	2.260(2)	2.239(4)		2.224(3)	2.228(4)	2.249(4)
	2.227(2)	2.230(4)		2.230(3)	2.236(4)	2.221(4)
Fe–Fe (Å)	2.613(2)	2.612(3)	2.574(2)	2.603(2)	2.623(2)	2.593(3)
P $\cdots$ P (Å)	2.442(2)		2.445(3)		2.525(4)	2.550(4)

III

IV

V

VI

3. Results and discussion

The reaction of $(^iPr_2NP)_2COFe_2(CO)_6$ (**I**) with the benzyllithium obtained from $PhCH_2SnPh_3$ and n-BuLi to give the tertiary alcohol $(^iPr_2NP)_2C(CH_2Ph)(OH)Fe_2(CO)_6$ (**II**) (R = CH_2Ph) is completely analogous to the previously reported reactions of $(^iPr_2NP)_2COFe_2(CO)_6$ (**I**) with methyllithium and n-butyllithium [2]. The spectroscopic properties of $(^iPr_2NP)_2C(CH_2Ph)(OH)Fe_2(CO)_6$ (**II**) (R = CH_2Ph) are completely analogous to those of the related tertiary alcohols prepared previously. In particular, the IR spectrum shows the same five $\nu(CO)$ frequencies in similar positions within ±4 cm^{-1}. The $^{31}P\{^1H\}$ spectrum of $(^iPr_2NP)_2C(CH_2Ph)(OH)Fe_2(CO)_6$ (**II**) (R = CH_2Ph) exhibits a single singlet, indicating equivalence of both phosphorus atoms. The $\delta = 192.0$ ppm ^{31}P chemical shift can be compared with the ^{31}P chemical shifts of $\delta = 187.4$ and 189.4 for the related tertiary alcohols **II** (R = Me and n-Bu respectively).

The structure **II** (R = CH_2Ph) for $(^iPr_2NP)_2C(CH_2Ph)(OH)Fe_2(CO)_6$ has been confirmed by X-ray diffraction (Fig. 1). Of particular interest is the comparison of the shape and dimensions of the CP_2Fe_2 cages in the diisopropylaminophosphorus derivatives **II** (R = CH_2Ph) and $[(^iPr_2NP)_2CHSiMe_3]Fe_2(CO)_6$ (**III**) [13] with sp^3 carbon atoms bridging the two phosphorus atoms and **I** and $(^iPr_2NP)(^tBu_2PP)COFe_2(CO)_6$ (**IV**) [14] with sp^2 carbonyl carbon atoms bridging the two phosphorus atoms (Table 4). In this connection the compounds with P–C(sp^3)–P bridges (**II** and **III**) have P–C–P bond angles in the range 78–80° and P–Fe–P bond angles in the range 64–67° whereas the compounds with P–C(sp^2)–P bridges (**II** and **IV**) have wider P–C–P bond angles (84–86°) and P–Fe–P bond angles (69–70°) although these bond angles remain acute in all cases (Table 4). This widening of P–C–P bond angles in the CP_2Fe_2 cage in going from sp^3 to sp^2 carbon bridges also appears to be accompanied with an increase in the formally non-bonded P $\cdots$ P distances from 2.442(2) Å in **II** (R = CH_2Ph) to 2.525(4) Å in **IV**. In **IV** this formally non-bonded P $\cdots$ P distance in the CP_2Fe_2 unit can be compared with the 2.199(4) Å formal P–P single bond from the terminal $^tBu_2P$ unit to a CP_2Fe_2 phosphorus atom. The P–C, Fe–P and Fe–Fe bond lengths in the CP_2Fe_2 cages in the series of compounds **I**, **II** (R = CH_2Ph), **III** and **IV** do not appear to be affected significantly by the hybridization of the P–C–P carbon atom.

Structural data are also available in the literature for the CP_2Fe_2 cages in the compounds $(2,4,6-^iPr_3C_6H_2P)_2CH_2Fe_2(CO)_6$ (**V**) [15] and $(^tBuP)_2COFe_2(CO)_6$ (**VI**) [16]. The bond lengths and angles in the CP_2Fe_2 cage of **VI** are similar within experimental error to those of **I**, indicating relatively little effect in substituting terminal $tert$-butyl groups for terminal $^iPr_2N$ groups. However, the shape of the CP_2Fe_2 cage in **V** with terminal bulky aryl groups is significantly different from that of the CP_2Fe_2 cages in **II** (R = CH_2Ph) and **III** despite the presence of P–C(sp^3)–P bridges in all cases. The CP_2Fe_2 cage of **V** thus has a wide P–C–P angle (83.7(4)°) close to those found in the phosphorus-bridging carbonyls **I**, **IV** and **VI** despite an sp^3 bridging carbon atom in **V** and sp^2 bridging carbon atoms in **I**, **IV** and **VI**. This widening of the P–C–P bond angle in **V** appears to be a geometric consequence of the relatively short P–C cage bonds in **V** (1.836(6) Å) compared with the P–C cage bonds (1.87–1.91 Å) in the other compounds.

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performed using the teXsan [12] crystallographic software package of Molecular Structure Corporation.

The crystal data for $(^iPr_2NP)_2C(CH_2Ph)(OH)Fe_2(CO)_6$ (**II**) (R = CH_2Ph) are summarized in Table 1 and its structure is depicted in Fig. 1. Bond distances and angles are given in Tables 2 and 3 respectively.

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