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Dialkylaminophosphorus metal carbonyls

X *. Phosphorus-bridging carbonyl expulsion in reactions of aldehydes and ketones with $(^{i}Pr_2NP)_2COFe_2(CO)_6$

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Abstract

Reactions of the phosphorus-bridging carbonyl derivative $(^{i}Pr_2NP)_2COFe_2(CO)_6$ with the aldehydes and ketones RR′C=O (R = R′ = H, Ph; R = Ph, R′ = H, Me; R + R′ = $(CH_2)_5$) in boiling toluene give derivatives of the type $[(^{i}Pr_2NP)_2OCRR']Fe_2(CO)_6$. X-ray diffraction of $[(^{i}Pr_2NP)_2OCHPh]Fe_2(CO)_6$ (triclinic, space group $P\bar{1}$; $a = 17.713(8)$, $b = 12.767(5)$, $c = 16.868(14)$ Å, $\alpha = 112.51(6)$, $\beta = 79.61(5)$, $\gamma = 68.73(5)°$, $Z = 4$) indicates expulsion of the phosphorus-bridging carbonyl followed by addition of the phosphorus atoms across the aldehyde or ketone carbonyl. The resulting central Fe_2P_2OC unit in the structure contains an Fe–Fe bond, four Fe–P bonds, no P–P bond, and a C–O single bond.

Introduction

Previous studies [2] on the chemical reactivity of the readily available [3,4] $(^{i}Pr_2NP)_2COFe_2(CO)_6$ (I) indicate that its phosphorus-bridging carbonyl group can either undergo reduction upon treatment with reagents such as $NaBH_4$, $LiAlH_4$, alkyllithiums, or sodium amalgam or expulsion upon treatment with protic reagents such as alcohols or hydrogen halides. We now report a new but related type of phosphorus-bridging carbonyl expulsion reaction upon treatment of I with a wide variety of aldehydes and ketones RR′C=O to give derivatives of the general type $[(^{i}Pr_2NP)_2OCRR']Fe_2(CO)_6$. In addition, we report the structure of the benzaldehyde derivative $[(^{i}Pr_2NP)_2OCHPh]Fe_2(CO)_6$, shown by X-ray diffraction to be II (R = H, R′ = Ph) in which the aldehyde is bonded to an Fe_2P_2 unit

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* For Part IX see ref. 1.

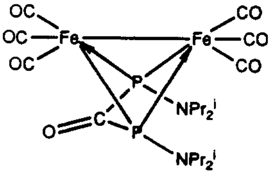
Table 1

Products from reactions of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ with aldehydes and ketones [a]

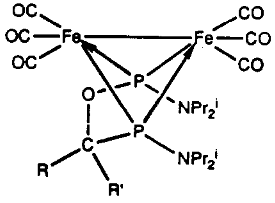
Aldehyde or ketone	Product	Isolated yield (%)	M.p. (°C)	Analyses (Found (calcd.) (%))		
				C	H	N
$(HCHO)_n$	$[({}^{i}Pr_2NP)_2OCH_2Fe_2(CO)_6$	21	148-150	40.0 (39.9)	5.3 (5.3)	5.0 (4.9)
PhCHO	$[({}^{i}Pr_2NP)_2OCHPh]Fe_2(CO)_6$	35	135-136	46.4 (46.3)	5.3 (5.3)	4.3 (4.3)
PhMeCO	$[({}^{i}Pr_2NP)_2OCMePh]Fe_2(CO)_6$	9	125	45.9 (47.2)	5.3 (5.5)	4.1 (4.2)
Ph_2CO	$[({}^{i}Pr_2NP)_2OCPh_2]Fe_2(CO)_6$	16 [b]	dec. 160	50.9 (51.4)	5.2 (5.3)	3.8 (3.9)
$(CH_2)_5CO$	$[({}^{i}Pr_2NP)_2OC(CH_2)_5]Fe_2(CO)_6$	40	165-166	44.9 (45.0)	6.0 (6.0)	4.3 (4.4)

[a] Me = methyl, ${}^{i}Pr$ = isopropyl, Ph = phenyl. [b] The indicated yield was obtained after chromatography (see Experimental section)

derived from I to form a novel chiral Fe_2P_2OC cage structure incorporating the carbonyl group from the aldehyde.



I



II

Experimental section

Microanalyses (Table 1) were performed by the Atlantic Microanalytical Laboratory, Atlanta, GA. Infrared spectra (Table 2) were run in the 2200–1400 cm^{-1} region using CH_2Cl_2 solutions and a Digilab FTS-60 Fourier transform infrared spectrometer. Phosphorus-31 (Table 2), proton (Table 3), and carbon-13 (Table 3) NMR spectra were taken on JEOL FX-90Q or Bruker AC-300 spectrometers

Table 2

Infrared $\nu(CO)$ frequencies and phosphorus-31 NMR spectra of $[({}^{i}Pr_2NP)_2OCRR']Fe_2(CO)_6$ derivatives

Compound	Infrared $\nu(CO)$ (cm^{-1})	Phosphorus-31 NMR (δ)		
		$NPFe_2O$	$NPFe_2C$	$J(P-P)$ (Hz)
$[({}^{i}Pr_2NP)_2OCH_2]Fe_2(CO)_6$	2054m, 2011s, 1991s, 1964s, 1955m	299.3	202.3	102
$[({}^{i}Pr_2NP)_2OCHPh]Fe_2(CO)_6$	2054m, 2010s, 1992s, 1964s, 1952m	296.1	221.2	116
$[({}^{i}Pr_2NP)_2OCMePh]Fe_2(CO)_6$	2053m, 2010s, 1990s, 1967m, 1954m	287.2	251.1	125
$[({}^{i}Pr_2NP)_2OCPh_2]Fe_2(CO)_6$	2052m, 2013s, 1987s, 1974m, 1957m	288.6	259.1	128
$[({}^{i}Pr_2NP)_2OC(CH_2)_5]Fe_2(CO)_6$	2052m, 2008s, 1988s, 1962m, 1952m	281.4	246.2	125

using $CDCl_3$ solutions and internal Me_4Si or external 85% phosphoric acid as references. Melting and decomposition points (Table 1) were taken in capillaries and are uncorrected.

The $(^iPr_2NP)_2COFe_2(CO)_6$ (I) starting material was prepared from commercial $Fe(CO)_5$, PCl_3, and $^iPr_2NH$ through $Na_2Fe(CO)_4 \cdot 1.5C_4H_8O_2$ and $^iPr_2NPCl_2$ using the published procedure [4,5]. The aldehydes and ketones were purchased from standard commercial sources. Procedures for solvent purification and inert atmosphere handling were similar to those described in earlier papers [4].

Reaction of paraformaldehyde with $(^iPr_2NP)_2COFe_2(CO)_6$

A solution of 0.25 g (8.3 mmoles of HCHO) of paraformaldehyde, 4.7 g (8.4 mmoles) of $(^iPr_2NP)_2COFe_2(CO)_6$, and 250 mL of toluene was boiled under reflux overnight. Solvent was then removed from the reaction mixture at ~ 25 °C/0.1 mmHg. Crystallization of the residue from hexane gave 1.0 g (22% yield) of air-stable yellow $[(^iPr_2NP)_2OCH_2]Fe_2(CO)_6$.

Reaction of benzaldehyde with $(^iPr_2NP)_2COFe_2(CO)_6$

A solution of 0.56 g (0.53 mL, 5.3 mmoles) of benzaldehyde, 3.0 g (5.4 mmoles) of $(^iPr_2NP)_2COFe_2(CO)_6$, and 100 mL of toluene was boiled under reflux for 3 h. Solvent was removed from the filtered golden yellow reaction mixture at ~ 25 °C/25 mmHg. The resulting gummy mass was washed with hexane to give 1.2 g (36% yield) of bright yellow $[(^iPr_2NP)_2OCHPh]Fe_2(CO)_6$.

Similar procedures were used for the reactions of acetophenone and cyclohexanone with $(^iPr_2NP)_2COFe_2(CO)_6$ to give $[(^iPr_2NP)_2OCMePh]Fe_2(CO)_6$ and $[(^iPr_2NP)_2OC(CH_2)_5]Fe_2(CO)_6$, respectively.

Reaction of benzophenone with $(^iPr_2NP)_2COFe_2(CO)_6$

A solution of 1.28 g (7.0 mmoles) of benzophenone, 4.0 g (7.2 mmoles) of $(^iPr_2NP)_2COFe_2(CO)_6$, and 300 mL of toluene was boiled 16 h under reflux. Toluene was then removed at ~ 25 °C/25 mmHg. The phosphorus-31 NMR spectrum of the crude reaction mixture indicated the presence of a minor component exhibiting an AX pattern with doublets ($J = 124$ Hz) centered at δ 284.6 and 246.7 in addition to $[(^iPr_2NP)_2OCPh_2]Fe_2(CO)_6$. For this reason a hexane solution of the crude product was chromatographed on a silica gel column, prepared in hexane. Elution of the initial yellow band with hexane followed by crystallization from hexane gave 0.8 g (16% yield) of $[(^iPr_2NP)_2OCPh_2]Fe_2(CO)_6$. The minor component apparently decomposed upon chromatography since the amounts that could be isolated by further elution of the chromatogram were insignificant.

X-Ray structure determination of $[(^iPr_2NP)_2OCHPh]Fe_2(CO)_6$

A single crystal of $C_{25}H_{34}Fe_2N_2O_7P_2$ from hexane was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table 4) were determined by least squares refinement of the best angular positions for fifteen independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$ Å). Data (8025 independent points after removal of redundant data) were collected at room temperature using a variable scan rate, a θ–2θ scan mode and a scan width of 1.2° below $K_{\alpha 1}$ and 1.2° above $K_{\alpha 2}$ to a maximum 2θ value of 45°. Backgrounds were measured at each side of the scan for a combined time

Table 3

Proton and carbon-13 NMR spectra of $[(^i\mathrm{Pr}_2\mathrm{NP})_2\mathrm{OCRR'}]\mathrm{Fe}_2(\mathrm{CO})_6$ derivatives [a]

Compound	Proton NMR spectrum (δ)				Carbon-13 NMR spectrum (δ)					
	Isopropyl		Other		Isopropyl		OCRR′	FeCO	R and R′	
	CH	CH_3	R and R′		CH	CH_3				
$[(^i\mathrm{Pr}_2\mathrm{NP})_2\mathrm{OCH}_2]$ $\mathrm{Fe}_2(\mathrm{CO})_6$	3.82 (sp)	1.29 (d, 7)	H:	3.45 (d, 6)	54.4	23.7	65.3 (d, 11)	213.1	-	
	3.73 (sp)	1.29 (d, 7)	H	3.42 (d, 6)	53.9					
$[(^i\mathrm{Pr}_2\mathrm{NP})_2\mathrm{OCHPh}]$ $\mathrm{Fe}_2(\mathrm{CO})_6$	3.92 (sp, 7)	1.35 (d, 7)	H:	4.59 (d, 6)	55.5	23.9		213.5	Ph:	137.2, 128.6
	2.54 (sp, 7)	1.19 (d, 7), 0.92 (d, 7)	Ph:	7.4–7.26 (m)	54.8					
$[(^i\mathrm{Pr}_2\mathrm{NP})_2\mathrm{OCMePh}]$ $\mathrm{Fe}_2(\mathrm{CO})_6$	4.00 (sp, 7)	1.43 (d, 7), 1.41 (d, 7)	Me:	1.98 (d, 9)	56.7	24.8 (d, 4)	84.2 (d, 10)	213.3	Me:	27.0 (d, 8)
	3.73 (m)	1.27 (d, 7), 1.22 (d, 7)	Ph:	7.45 (d, 7) 7.29 (m)	54.6	24.5 (d, 5)		213.0	Ph:	141.5 (d, 6) 127.8, 127.4, 126.2
$[(^i\mathrm{Pr}_2\mathrm{NP})_2\mathrm{OCPh}_2]$ $\mathrm{Fe}_2(\mathrm{CO})_6$	3.97 (sp, 7)	1.39 (d, 7)	Ph:	7.50 (d, 6)	57.7	25.0 (d, 4)	87.8 (dd, 8, 6)	212.9	Ph:	143.1, 143.0, 128.5, 128.3, 127.4
	3.57 (m)	1.29 (d, 7)		7.26 (m)	54.6	23.8 (d, 4)				
$[(^i\mathrm{Pr}_2\mathrm{NP})_2\mathrm{OC(CH}_2\mathrm{O}_5]$ $\mathrm{Fe}_2(\mathrm{CO})_6$	3.89 (m)	1.37 (d, 7)	$(CH_2)_5$:	1.80–1.50 (m)	57.0	25.3	84.6 (dd, 12, 8)	213.8	$(CH_2)_5$:	34.7, 24.0, 23.7, 23.5
	3.81 (m)	1.30 (d, 7)			54.1	25.2				

[a] d = doublet, dd = double doublet, sp = septet, m = multiplet.

Table 4

Crystal data for $C_{25}H_{34}Fe_2N_2O_7P_2$ (= [$^iPr_2NP)_2OCHPh]Fe_2(CO)_6$)

Formula	$C_{25}H_{34}O_7N_2P_2Fe_2$
MW	648.2
a, Å	17.713(8)
b, Å	12.767(5)
c, Å	16.868(14)
α, °	112.51(6)
β, °	79.61(5)
γ, °	68.73(5)
V, Å^3	3050(3)
$F(000)$	1344
μ(Mo-K_α), cm^{-1}	10.94
λ(Mo-K_α), Å	0.71069
C_{calc}, g cm^{-3}	1.411
Z	4
Space group	$P\bar{1}$
Observed reflections	3424
Octants measured	$\pm h, k, \pm l$
R/R_w, %	8.0/9.2
G.O.F.	0.65

equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections. As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. Observed reflections [3424 ($I > 3.0\sigma(I)$)] were used for solution of iron positions by direct methods using MULTAN80 [6]. P, C, N, and O positions were determined from a difference Fourier synthesis following refinement of the Fe positions. The asymmetric unit consists of two $C_{25}H_{34}Fe_2N_2O_7P_2$ units which are unrelated to each other by symmetry. Refinement [7] of scale factor, positional, and isotropic thermal parameters for all atoms was carried out to convergence. Hydrogen positions for isopropyl and phenyl hydrogen atoms were calculated using idealized geometry. These were included but not refined in final cycles of refinement with fixed isotropic thermal parameters. Final cycles of least squares refinement were completed with anisotropic thermal parameters [function minimized, $\Sigma\omega(|F_o| - |F_c|)^2$ leading to a final agreement factor, $R = 8.0\%$ [$R = (\Sigma\omega \| F_o| - |F_c\| / \Sigma\omega |F_o|) \times 100$]. Scattering factors were taken from Cromer and Mann [8]. Anomalous dispersion corrections were made for Fe and P [9]. In the final stages of refinement a weight of $1/\sigma(F)^2$ was used; $R_w = 9.2\%$.

An ORTEP diagram of the structure is given in Fig. 1. Non-hydrogen positional parameters are given in Table 5 and selected bond distances and angles are given in Table 6. Complete positional parameters, complete bond distances and angles, anisotropic thermal parameters, and structure factors (F_{obs} and F_{calc}) are available as supplementary material from the authors upon request.

Results

Reactions of ($^iPr_2NP)_2COFe_2(CO)_6$ (I) with diverse aldehydes and ketones RR′C=O (R = R′ = H, Ph; R = Ph, R′ = H, Me; R + R′ = $(CH_2)_5$) were found to

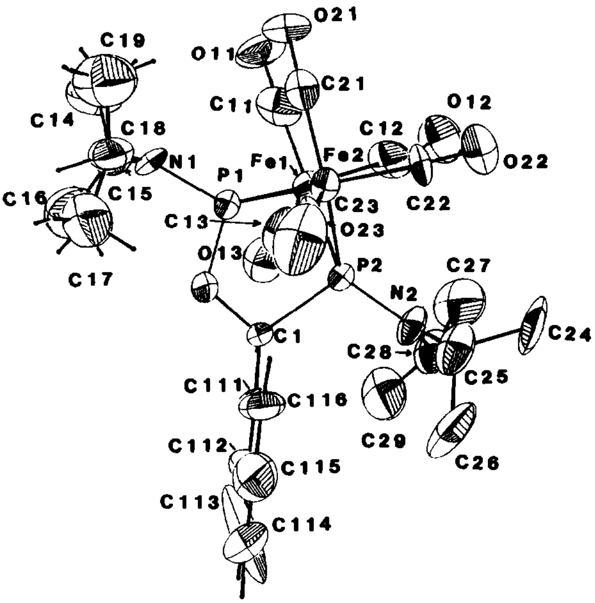


Fig. 1. ORTEP diagram of $[(^iPr_2NP)_2OCHPh]Fe_2(CO)_6$.

give air-stable yellow products of the general stoichiometries $[(^iPr_2NP)_2OCRR']Fe_2(CO)_6$ with expulsion of the phosphorus-bridging carbonyl group in I. These reactions proceeded readily in boiling toluene (~ 110 ° C) although with considerable side reactions leading to decomposition as indicated by the range of 9 to 40% in the isolated product yields (Table 1). However, an attempt to reduce the side reactions by running the reaction of $[(^iPr_2NP)_2OCRR']Fe_2(CO)_6$ (I) with benzaldehyde in the lower boiling tetrahydrofuran (~ 70 ° C) led to little reaction even after several days.

The infrared spectra of the $[(^iPr_2NP)_2OCRR']Fe_2(CO)_6$ derivatives (II) exhibit the expected five terminal $\nu(CO)$ frequencies for an $LFe_2(CO)_6$ derivative (Table 2) but no phosphorus-bridging carbonyl frequency around 1700 cm^{-1} indicating loss of the phosphorus-bridging carbonyl group in I during the course of the reaction. The phosphorus-31 NMR spectra (Table 2) exhibit an AX pattern with $|^1J(P-P)|$ in the range 102 to 128 Hz indicating that the equivalent phosphorus atoms in I have become non-equivalent upon reaction with an aldehyde or ketone. The proton and carbon-13 NMR spectra for the symmetrical $[(^iPr_2NP)_2OCR_2]Fe_2(CO)_6$ derivatives (II: $R = R' = H$, Ph, or $R_2 = (CH_2)_5$) exhibit two sets of isopropyl resonances of equal intensities also confirming the non-equivalence of the phosphorus atoms to which the two diisopropylamino groups are attached. The proton NMR spectra of the unsymmetrical $[(^iPr_2NP)_2OCRR']Fe_2(CO)_6$ derivatives (II: $R = Ph$, $R' = H$, Me) exhibit three or four sets of methyl doublets since each methyl group is diastereotopic because of the asymmetry originating from the asymmetric carbon atom arising from the aldehyde or ketone carbonyl group in structure II.

The structure (II) proposed for the $[(^iPr_2NP)_2OCRR']Fe_2(CO)_6$ derivatives was confirmed by X-ray crystallography on the benzaldehyde derivative ($R = Ph$, $R' =$

Table 5

Non-hydrogen positional parameters for $C_{25}H_{34}Fe_2N_2O_7P_2$ (= [$^iPr_2NP)_2OCHPh]Fe_2(CO)_6$) with esd's in parentheses

	x	*y*	*z*
Fe1	0.5917(2)	0.1930(3)	0.5365(2)
Fe2	0.5445(2)	0.4280(3)	0.6561(2)
Fe3	0.0447(2)	0.1842(3)	0.1564(2)
Fe4	0.0921(2)	0.2516(3)	0.0361(2)
P1	0.5370(3)	0.2788(5)	0.6870(3)
P2	0.6790(3)	0.2631(5)	0.5929(3)
P3	0.0364(3)	0.3726(5)	0.1870(3)
P4	0.1800(3)	0.1501(5)	0.0926(3)
O1	0.6103(7)	0.2273(13)	0.7273(8)
O2	0.1122(7)	0.3890(11)	0.2263(8)
O11	0.4294(10)	0.1985(19)	0.5149(12)
O12	0.6299(13)	0.2204(26)	0.3700(12)
O13	0.7003(12)	−0.0734(16)	0.4801(12)
O21	0.3620(10)	0.5243(23)	0.6685(15)
O22	0.5819(11)	0.5314(19)	0.5349(15)
O23	0.5241(11)	0.6284(17)	0.8269(14)
O31	0.0826(10)	−0.0795(15)	0.0360(13)
O32	0.0255(11)	0.1784(20)	0.3311(11)
O33	−0.1380(10)	0.2823(17)	0.1723(15)
O41	0.1325(11)	0.0181(18)	−0.1260(12)
O42	0.2020(12)	0.3543(19)	−0.0203(13)
O43	−0.0681(13)	0.3810(24)	0.0136(15)
N1	0.4492(9)	0.2864(18)	0.7495(12)
N2	0.7720(8)	0.2510(14)	0.5354(10)
N3	−0.0473(10)	0.5104(14)	0.2486(10)
N4	0.2692(9)	0.0161(14)	0.0379(10)
C1	0.6966(11)	0.1941(20)	0.6756(13)
C2	0.1998(13)	0.2810(19)	0.1719(13)
C11	0.4964(15)	0.1955(19)	0.5248(12)
C12	0.6181(14)	0.2088(23)	0.4347(13)
C13	0.6553(14)	0.0336(21)	0.5028(15)
C14	0.3730(18)	0.1584(26)	0.7043(21)
C15	0.4437(15)	0.1699(27)	0.7280(21)
C16	0.4882(22)	0.0883(31)	0.7592(24)
C17	0.4381(19)	0.4126(30)	0.9095(20)
C18	0.3970(13)	0.3927(33)	0.8434(17)
C19	0.3132(20)	0.4790(30)	0.8581(22)
C21	0.4330(15)	0.4869(26)	0.6636(17)
C22	0.5717(15)	0.4834(27)	0.5766(17)
C23	0.5354(13)	0.5436(17)	0.7553(18)
C24	0.7987(14)	0.4144(30)	0.5039(26)
C25	0.7830(12)	0.3706(20)	0.5742(15)
C26	0.8532(16)	0.3539(29)	0.6130(18)
C27	0.8361(18)	0.0895(32)	0.3687(18)
C28	0.8455(14)	0.1374(23)	0.4591(14)
C29	0.8852(16)	0.0273(27)	0.4767(18)
C31	0.0672(12)	0.0363(22)	0.0878(16)
C32	0.0346(13)	0.1824(20)	0.2612(14)
C33	−0.0672(16)	0.2440(28)	0.1670(20)
C34	−0.0608(16)	0.5536(31)	0.4093(17)
C35	−0.1012(15)	0.5477(30)	0.3421(16)
C36	−0.1891(15)	0.5690(31)	0.3609(20)
C37	−0.1322(18)	0.6759(35)	0.2089(21)

Table 5 (continued)

	x	y	z
C38	−0.0550(16)	0.6153(23)	0.2254(20)
C39	−0.0079(21)	0.6815(39)	0.2569(24)
C41	0.1166(13)	0.1173(22)	−0.0587(16)
C42	0.1578(15)	0.3185(28)	0.0030(18)
C43	−0.0068(18)	0.3344(35)	0.0255(19)
C44	0.2997(17)	−0.2076(24)	0.0017(22)
C45	0.2840(13)	−0.0806(19)	0.0736(15)
C46	0.3536(18)	−0.0908(25)	0.1140(17)
C47	0.3337(16)	−0.0576(30)	−0.1313(16)
C48	0.3467(14)	−0.0266(22)	−0.0429(14)
C49	0.3826(17)	0.0662(31)	−0.0196(19)
C111	0.7427(11)	0.2320(18)	0.7375(13)
C112	0.8183(15)	0.1480(26)	0.7340(18)
C113	0.8563(15)	0.1934(29)	0.7951(18)
C114	0.8280(19)	0.3044(33)	0.8534(18)
C115	0.7536(16)	0.3915(26)	0.8576(14)
C116	0.7110(12)	0.3594(21)	0.7987(14)
C211	0.2443(12)	0.2539(19)	0.2339(14)
C212	0.3200(14)	0.2627(22)	0.2303(15)
C213	0.3609(16)	0.2486(24)	0.2886(19)
C214	0.3270(17)	0.2208(26)	0.3531(18)
C215	0.2503(17)	0.2085(25)	0.3581(16)
C216	0.2089(14)	0.2276(26)	0.2997(17)

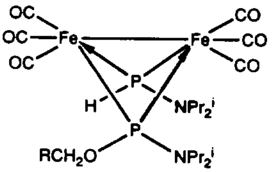
H). Characteristic features of the central Fe_2P_2OC unit include an Fe–Fe bond (2.589(4) Å and 2.609(6) Å in the two molecules), four Fe–P bonds per unit (2.190(6) to 2.243(7) Å), nonbonding $P \cdots P$ distances (2.614(8) Å and 2.628(6) Å in the two molecules) and C–O single bonds (1.43(2) and 1.45(2) Å in the two molecules). The individual molecules are chiral, i.e., there is no plane of symmetry. Furthermore, the two independent molecules of the asymmetric unit are enantiomers.

In a previous paper [2] the reactions of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ with the alcohols RCH_2OH (R = H, Me) were reported to result in expulsion of the carbonyl group to give the derivatives $({}^{i}Pr_2NPOCH_2R)({}^{i}Pr_2NPH)Fe_2(CO)_6$ (III). The compounds III are formally related to the derivatives $[({}^{i}Pr_2NP)_2OCHR]Fe_2(CO)_6$ (II: R′ = H) obtained from $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ and the aldehydes RCHO by addition of H_2. In an attempt to obtain the benzyl alcohol derivative $({}^{i}Pr_2NPOCH_2Ph)({}^{i}Pr_2NPH)Fe_2(CO)_6$ (III: R = Ph), the reaction of $[({}^{i}Pr_2NP)_2OCHPh]Fe_2(CO)_6$ with $LiAlH_4$ in boiling tetrahydrofuran for 16 hr was investigated. However, phosphorus-31 NMR of the reaction mixture indicated that no reaction had taken place. Similarly, an attempt to dehydrogenate the ethanol derivative $({}^{i}Pr_2NPOEt)({}^{i}Pr_2NPH)Fe_2(CO)_6$ (III: R = Me) to the corresponding acetaldehyde derivative $[({}^{i}Pr_2NP)_2OCHMe]Fe_2(CO)_6$ by treatment with an excess of activated manganese dioxide [10] in dichloromethane at room temperature was unsuccessful. Phosphorus-31 NMR of this reaction mixture after three days showed no evidence for any reaction.

Table 6

Selected bond distances (Å) and angles (°) for $C_{25}H_{34}Fe_2N_2O_7P_2$ (= [$^{i}Pr_2NP)_2OChPh]Fe_2(CO)_6$)

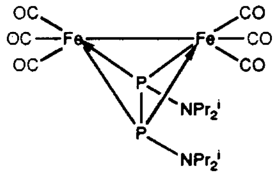
Fe1-Fe2	2.589(4)	P1-Fe1-P2	72.5(2)
Fe3-Fe4	2.609(6)	P1-Fe2-P2	72.4(2)
Fe1-P1	2.190(6)	Fe1-P1-Fe2	73.3(2)
Fe1-P2	2.231(7)	Fe1-P2-Fe2	70.8(2)
Fe2-P1	2.198(8)	Fe1-P1-N1	123.7(3)
Fe2-P2	2.229(5)	Fe2-P1-N1	127.4(8)
Fe3-P3	2.199(7)	Fe1-P1-O1	111.9(4)
Fe3-P4	2.244(1)	Fe2-P1-O1	111.4(7)
Fe4-P3	2.194(5)	O1-P1-N1	104.0(10)
Fe4-P4	2.243(7)	Fe1-P2-N2	128.6(6)
P1 · · · P2	2.614(8)	Fe2-P2-N2	128.3(7)
P3 · · · P4	2.628(6)	Fe1-P2-C1	102.3(8)
Fe1-C11	1.72(3)	Fe2-P1-C1	90.3(7)
Fe1-C12	1.80(3)	N2-P2-C1	110.5(9)
Fe1-C13	1.72(2)	P1-O1-C1	115(1)
Fe2-C21	1.80(2)	P2-C1-O1	103(1)
Fe2-C22	1.81(4)	O1-C1-C111	111(2)
Fe2-C23	1.68(2)	P2-C1-C111	120(2)
Fe3-C31	1.64(2)	P3-Fe3-P4	72.5(2)
Fe3-C32	1.75(3)	P3-Fe4-P4	72.6(2)
Fe3-C33	1.79(3)	Fe3-P3-Fe4	72.8(2)
Fe4-C41	1.67(2)	Fe3-P4-Fe4	71.1(2)
Fe4-C42	1.80(4)	Fe3-P3-N3	127.6(8)
Fe4-C43	1.77(3)	Fe4-P3-N3	128.4(7)
P1-N1	1.66(2)	Fe3-P3-O2	110.4(6)
P2-N2	1.67(2)	Fe4-P3-O2	110.5(4)
P3-N3	1.59(1)	O2-P3-N3	104.3(8)
P4-N4	1.61(1)	Fe3-P4-N4	128.1(8)
P1-O1	1.62(2)	Fe4-P4-N4	129.0(7)
P3-O2	1.64(1)	Fe3-P4-C2	110.6(6)
C1-O1	1.43(2)	Fe4-P3-C2	84.0(4)
C2-O2	1.45(2)	N4-P4-C2	109.3(9)
C1-P2	1.93(3)	P3-O2-C2	115.2(12)
C2-P4	1.90(2)	P4-C2-O2	103(1)
C11-O11	1.22(3)	O2-C2-C211	110(1)
C12-O12	1.15(4)	P4-C2-C211	117(2)
C13-O13	1.16(3)		
C21-O21	1.14(3)		
C22-O22	1.13(5)		
C23-O23	1.19(3)		
C31-O31	1.29(3)		
C32-O32	1.18(3)		
C33-O33	1.14(3)		
C41-O41	1.22(3)		
C42-O42	1.12(4)		
C43-O43	1.13(4)		



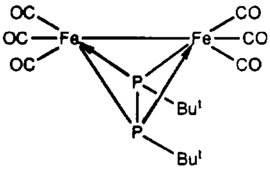
III

Discussion

The expulsion of the phosphorus-bridging carbonyl group in $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ (I) by reactions with aldehydes and ketones requires temperatures around 100 ° C (e.g., boiling toluene) like the corresponding reactions with alcohols discussed previously [2]. This suggests that the initial step of these reactions is expulsion of the phosphorus-bridging carbonyl group to give the diferradiphosphatetrahedrane intermediate $({}^{i}Pr_2NP)_2Fe_2(CO)_6$ (IV) analogous to the reported [11] tert-butylphosphorus derivative $({}^{t}BuP)_2Fe_2(CO)_6$ (V). The reactive P–P bond in IV can then add to the aldehyde or ketone carbonyl group to form the observed product II. However, our attempts to isolate the intermediate IV by heating $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ (I) in boiling toluene in the absence of another reactant provided no direct evidence for IV leading instead to complete decomposition of I. We thus suspect that at the temperature of its formation the tetrahedrane intermediate IV is too reactive to be isolated but instead decomposes completely in the absence of a trapping reagent such as an alcohol, aldehyde or ketone.



IV



V

Acknowledgments

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