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Dialkylaminophosphorus metal carbonyls

VIII. A new type of phosphorus-bridging carbonyl derivative containing three phosphorus atoms: crystal and molecular structure of $(^iPr_2NP)(^tBu_2PP)COFe_2(CO)_6$ *,**

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Abstract

Reduction of $(^iPr_2NP)_2COFe_2(CO)_6$ with Na/Hg in tetrahydrofuran at ambient temperature gives the anion $[^iPr_2NPCOPFe_2(CO)_6]^-$, which reacts with sterically hindered R_2PCl derivatives to give the new type of phosphorus-bridging carbonyl derivatives $(^iPr_2NP)(R_2PP)COFe_2(CO)_6$ ($R = {}^tBu$, Cx, ^iPr, and $^iPr_2N$). X-ray diffraction on $(^iPr_2NP)(^tBu_2PP)COFe_2(CO)_6$ (monoclinic, $P2_1/c$; *a* 8.901(1), *b* 29.590(7), *c* 12.136(4) Å; $\beta = 112.97(2)°$, $Z = 4$) indicates a phosphorus-bridging carbonyl structure very closely related to that of $(^iPr_2NP)_2COFe_2(CO)_6$ with Fe–Fe = 2.593(3) Å) and P–C–P = 85.7(4)°.

Introduction

The air-stable complex $(^iPr_2NP)_2COFe_2(CO)_6$ (I in Fig. 1, ^iPr = isopropyl) is the most readily available example of a phosphorus-bridging carbonyl derivative [2]. Recently [3] we reported that the sodium amalgam reduction of I in tetrahydrofuran gave an anion formulated as II. This anion could be trapped by Me_3SnCl to give the

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* We are pleased to dedicate this paper to Prof. F.G.A. Stone, F.R.S., in recognition of his many seminal contributions to organometallic chemistry. In addition, one of us (R.B.K.) would like to express his gratitude for the pivotal role that Gordon Stone played in his graduate education at Harvard University.

** For Part VII see ref. 1.

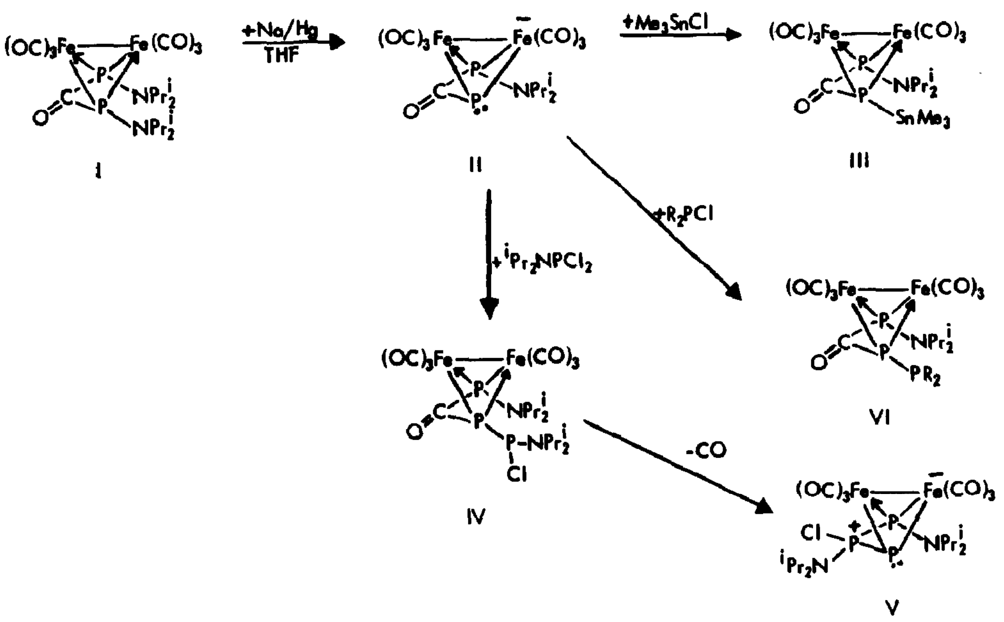

Fig. 1. Transformations of the anion obtained by the sodium amalgam reduction of $(^{i}Pr_2NP)_2$-$COFe_2(CO)_6$.

new unsymmetrical phosphorus-bridging carbonyl derivative $(^{i}Pr_2NP)(Me_3SnP)$-$COFe_2(CO)_6$ (**III** in Fig. 1), thereby suggesting the use of **II** as an intermediate for the preparation of new types of phosphorus-bridging carbonyl derivatives. However, suitable single crystals of neither **III** nor the $(Ph_3P)_2N^+$ salt of **II** could be obtained for structure determination by X-ray diffraction. The only structurally characterized reaction product of the anion **II** is $[(^{i}Pr_2NP)(^{i}Pr_2N)ClPP]Fe_2(CO)_6$ (**V** in Fig. 1) [3] obtained by reaction of **II** with $^{i}Pr_2NPCl_2$. Formation of **V** from **II** and $^{i}Pr_2NPCl_2$ can be postulated to proceed through an unsymmetrical phosphorus-bridging carbonyl derivative, **IV** [3]. This paper reports the preparation of stable analogues of **IV**, namely $(^{i}Pr_2NP)(R_2PP)COFe_2(CO)_6$ (**VI** in Fig. 1: $R = {}^{t}Bu$, Cx, $^{i}Pr_2N$) by reaction of the anion **II** with sterically demanding R_2PCl derivatives. The structure of the t-butyl derivative $(^{i}Pr_2NP)(^{t}Bu_2PP)COFe_2(CO)_6$ (**VI**: $R = {}^{t}Bu$) has been slowly to be very similar to that of the original $(^{i}Pr_2NP)_2COFe_2(CO)_6$ (**I**) indicating minimal perturbation of the phosphorus-bridging carbonyl framework upon substitution of one terminal diisopropylamino group in **I** by a di-t-butylphosphino group.

Experimental section

Microanalyses were performed by the Atlantic Microanalytical Laboratory, Atlanta, Georgia. Proton, carbon-13, and phosphorus-31 (Table 1) NMR spectra were taken on a JEOL FX-90Q multinuclear pulsed Fourier transform spectrometer using $CDCl_3$ solutions and internal Me_4Si or external 85% H_3PO_4 as references. Infrared spectra (Table 2) were run in the 2200–1600 cm^{-1} metal carbonyl region using hexane solutions and a Digilab FTS-60 Fourier transform infrared spectrometer. Melting and decomposition points were taken in capillaries and are uncorrected.

Table 1

Phosphorus-31 NMR spectra of $({}^{i}Pr_2NP)(R_2PP)COFe_2(CO)_6$ derivatives and related compounds

Compound [a]	Phosphorus-31 NMR, δ [b]		
	P(NR₂)	P(PR₂)	R₂P
$({}^{i}Pr_2NP)({}^{t}Bu_2PP)COFe_2(CO)_6$	211.5 d (125)	155.0 dd (484, 125)	71.4 d (484)
$({}^{i}Pr_2NP)(Cx_2PP)COFe_2(CO)_6$	211.2 d (117)	157.7 dd (448, 117)	30.2 d (448)
$({}^{i}Pr_2NP)({}^{i}Pr_2PP)COFe_2(CO)_6$	210.9 d (110)	154.6 dd (447, 110)	39.5 d (447)
$({}^{i}Pr_2NP)[({}^{i}Pr_2N)_2PP]COFe_2(CO)_6$	204.4 d (80)	181.4 dd (499, 80)	91.8 d (499)
$({}^{i}Pr_2NP)(Me_3SnP)COFe_2(CO)_6$	197.6 d (66)	114.1 d (66)	–
$({}^{i}Pr_2NP)_2COFe_2(CO)_6$	225.6 s	–	–

[a] Me = methyl; ⁱPr = isopropyl; ᵗBu = t-butyl; Cx = cyclohexyl. [b] s = singlet, d = doublet; coupling constants in Hz are given in parentheses.

The $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ starting material was prepared from commercial $Fe(CO)_5$, PCl_3, and ${}^{i}Pr_2NH$ through $Na_2Fe(CO)_4 \cdot 1.5C_4H_8O_2$ and ${}^{i}Pr_2NPCl_2$ using the published procedure [4,5]. The phosphorus halides R_2PCl (R = ᵗBu, Cx, ⁱPr, ${}^{i}Pr_2N$) were prepared by standard procedures [6–9]. Procedures for solvent purification and inert atmosphere handling are described elsewhere [4].

Preparation of $({}^{i}Pr_2NP)({}^{t}Bu_2PP)COFe_2(CO)_6$

A solution of $[{}^{i}Pr_2NPCOPFe_2(CO)_6]^-$ was prepared by stirring 8.5 g (15 mmol) of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ in 250 ml of tetrahydrofuran for 7 h at ambient temperature with the sodium amalgam from 2.6 g (113 mmol) of sodium and 16 ml of mercury. After removal of excess amalgam the solution was stirred for 2 days with 5.4 g (30 mmol) of ${}^{t}Bu_2PCl$ [6]. The phosphorus-31 NMR spectrum of the crude reaction mixture at this point indicated the presence of $({}^{i}Pr_2NP)({}^{t}Bu_2PP)COFe_2(CO)_6$, much unreacted ${}^{t}Bu_2PCl$ (δ 149.1), and small amounts of ${}^{t}bu_2P{-}P{}^{t}Bu_2$ (δ 42.0) and ${}^{t}Bu_2PH$ (δ 22.0). After removal of the solvent in vacuum, the residue was extracted with 1500 ml of hexane in three portions. Concentrations and cooling (−15°C) of the filtered hexane extracts gave 4.5 g (49% yield) of orange crystalline $({}^{i}Pr_2NP)({}^{t}Bu_2PP)COFe_2(CO)_6$, m.p. 120–121°C (dec.); proton NMR: δ 3.8–3.4 (multiplet: CH), 1.49 (doublet, $J = 12$ Hz, CH_3), and 1.28 (doublet, $J = 7$ Hz, CH_3); proton-decoupled carbon-13 NMR: δ 211.9 s (CO), 53.3 s (CH of isopropyl), 37.3 d (6) (C of t-butyl) 35.8 d (6) (C of t-butyl), 32.3 d (4) (CH_3 of t-butyl), 31.8 d (5) (CH_3 of t-butyl), and 22.7 s (CH_3 of isopropyl). Anal. Calcd. for $C_{21}H_{32}Fe_2NO_7P_3$: C, 41.0; H, 5.2; N, 2.3. Found: C, 41.1; H, 5.3; N, 2.3.

Table 2

Infrared ν(CO) frequencies of $({}^{i}Pr_2NP)(R_2PP)COFe_2(CO)_6$ derivatives and related compounds

Compound	Infrared ν(CO) frequencies, cm^{-1}	
	Terminal	Bridging
$({}^{i}Pr_2NP)({}^{t}Bu_2PP)COFe_2(CO)_6$	2058 m, 2018 s, 1992 s, 1973 s, 1958 s	1714 m
$({}^{i}Pr_2NP)(Cx_2PP)COFe_2(CO)_6$	2060 m, 2019 s, 1998 s, 1974 s, 1964 m	1721 m
$({}^{i}Pr_2NP)[({}^{i}Pr_2N)_2PP]COFe_2(CO)_6$	2056 m, 2015 s, 1994 s, 1970 m, 1960 m	1707 m
$({}^{i}Pr_2NP)(Me_3SnP)COFe_2(CO)_6$	2050 m, 2010 s, 1993 s, 1979 s, 1965 m	1715 m
$({}^{i}Pr_2NP)_2COFe_2(CO)_6$	2060 m, 2016 s, 1996 s, 1975 s, 1964 m	1720 m

Preparation of $(^iPr_2NP)(Cx_2PP)COFe_2(CO)_6$

A solution of $[^iPr_2NPCOPFe_2(CO)_6]^-$ in 250 ml of tetrahydrofuran prepared as above from 6.1 g (10.8 mmol) of $(^iPr_2NP)_2COFe_2(CO)_6$, 2.2 g (96 mmol) of sodium, and 15 ml of mercury was treated at −78 °C with 5.0 g (21.5 mmol) of dicyclohexylchlorophosphine [7]. After stirring overnight at room temperature, solvent was removed in vacuum and the residue was extracted with hexane. Concentration and cooling (−78 °C) of the filtered hexane extracts gave 0.8 g (11% yield) of orange $(^iPr_2NP)(Cx_2PP)COFe_2(CO)_6$, dec. 90 °C. The analytical sample was dried in vacuum overnight at room temperature but still appeared to contain solvent of crystallization. Anal. Calcd. for $C_{25}H_{36}Fe_2NO_7P_3$: C, 45.0; H, 5.4; N, 2.1. Calcd. for $C_{25}H_{36}Fe_2NO_7P_3 \cdot C_4H_8O$: C, 47.1; H, 6.0; N, 1.9. Found: C, 46.7; H, 6.1; N, 1.9.

Preparation of $(^iPr_2NP)(^iPr_2PP)COFe_2(CO)_6$

A solution of $[^iPr_2NPCOPFe_2(CO)_6]^-$ in 250 ml of tetrahydrofuran prepared as above from 4.0 g (7.1 mmol) of $(^iPr_2NP)_2COFe_2(CO)_6$, 1.6 g (69 mmol) of sodium, and 13 ml of mercury was stirred for 2 h at ambient temperature with 2.2 g (14.2 mmol) of $^iPr_2PCl$ [8]. Solvent was removed in vacuum and the residue was extracted with hexane. The phosphorus-31 NMR spectrum of the hexane solution indicated the presence of $(^iPr_2NP)(^iPr_2PP)COFe_2(CO)_6$ (Table 1). Concentration of this solution gave a solid which decomposed to a viscous mass at room temperature.

Preparation of $(^iPr_2NP)[(^iPr_2N)_2PP]COFe_2(CO)_6$

A solution of $[^iPr_2NPCOPFe_2(CO)_6]^-$ in 300 ml of tetrahydrofuran prepared as above from 4.3 g (7.5 mmol) of $(^iPr_2NP)_2COFe_2(CO)_6$, 2.2 g (96 mmol) of sodium, and 15 ml of mercury was treated at −78 °C with a solution of 4.0 g (15.0 mmol) of $(^iPr_2N)_2PCl$ [9] dissolved in 150 ml of tetrahydrofuran. After stirring overnight at room temperature solvent was removed in vacuum and the residue was extracted with hexane. Concentration and cooling (−78 °C) of the filtered hexane extracts gave 1.1 g (21% yield) of orange $(^iPr_2NP)[(^iPr_2N)_2PP]COFe_2(CO)_6$, m.p. 128–129 °C (dec.). Anal. Calcd. for $C_{25}H_{42}Fe_2N_3O_7P_3$: C, 42.8; H, 6.0; N, 6.0. Found: C, 42.2; H, 6.1; N, 6.0.

X-Ray structure determination of $(iPr_2NP)(tBu_2PP)COFe_2(CO)_6$

A single crystal of $(^iPr_2NP)(^tBu_2PP)COFe_2(CO)_6$ from hexane was mounted on a Syntex P_3 automated diffractometer. Unit cell dimensions (Table 3) 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 consisting of 3877 independent points after removal of space group forbidden and redundant data were collected at room temperature using a variable scan rate, a 2θ scan mode, and a scan width of 1.2° below K_{α_1} and 1.2° above K_{α_2} to a maximum 2θ value of 45°. Backgrounds were measured on each side of the scan for a combined time equal to the 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 (2326 with $I > 3.0\sigma(I)$) were used for solution of heavy atom positions by direct methods using MULTAN [10]. Cycles of least-squares refinement followed by difference Fourier analysis allowed

Table 3

Crystallographic and data collection parameters for $({}^{i}\mathrm{Pr}_2\mathrm{NP})({}^{t}\mathrm{Bu}_2\mathrm{PP})\mathrm{COFe}_2(\mathrm{CO})_6$

Formula	$C_{21}H_{32}NP_3Fe_2O_7$
M.W.	615.1
a	8.901(1) Å
b	29.590(7)
c	12.136(4)
α	90.0
β	112.97(2)
γ	90.0
V	2943.2(19) Å^3
$F(000)$	1272
μ(Mo-K_α)	11.807 cm^{-1}
λ(Mo-K_α)	0.71069 Å
D_{calc}	1.388 g cm^{-3}
Z	4
Space group	$P2_1/c$
Independent reflections measured	3877
Observed reflections	2326
Octants measured	$\pm h, +k, +l$
Temperature	25 °C
R/R_w	5.8/7.7%
G.O.F.	0.337

location of the remainder of the nonhydrogen positions. Refinement [11] of scale factor, positional, and isotropic thermal parameters for these atoms was carried out to convergence. Hydrogen positions were located from a difference Fourier synthesis. Final cycles of least-squares refinement allowed refinement of nonhydrogen positions with anisotropic thermal parameters. The final cycles of refinement

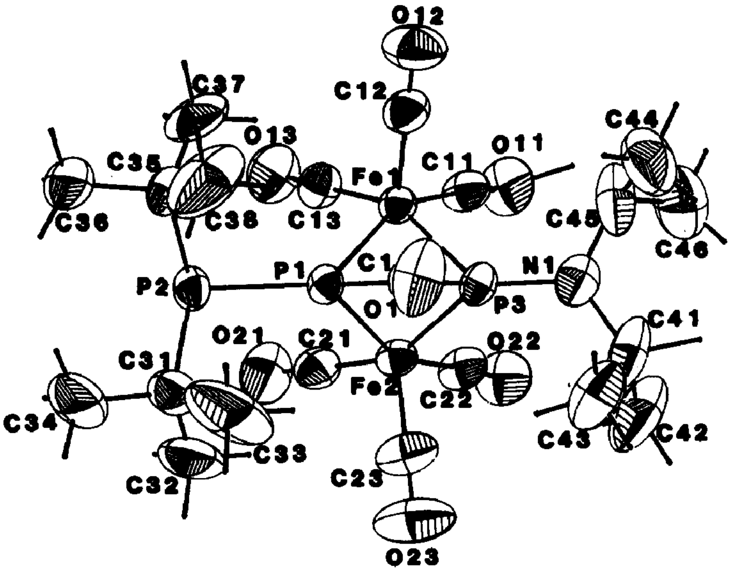

Fig. 2. ORTEP diagram of $({}^{i}\mathrm{Pr}_2\mathrm{NP})({}^{t}\mathrm{Bu}_2\mathrm{PP})\mathrm{COFe}_2(\mathrm{CO})_6$.

Table 4

Selected bond distances (Å) and angles (degrees) for $(^iPr_2NP)(^tBu_2PP)COFe_2(CO)_6$

Fe1–Fe2	2.593(3)	Fe1–P1–Fe2	70.1(1)
Fe1–P1	2.266(3)	Fe1–P3–Fe2	71.6(1)
Fe1–P3	2.209(4)	P1–C1–P3	85.7(4)
Fe2–P1	2.249(4)	P1–Fe1–P3	69.5(1)
Fe2–P3	2.221(4)	P1–Fe2–P3	69.6(1)
P1–P3	2.550(4)	Fe1–P1–P2	129.6(2)
P1–P2	2.199(4)	Fe2–P1–P2	127.6(2)
Fe1–C11	1.79(1)	P1–C1–O1	137.4(8)
Fe1–C12	1.75(1)	P3–C1–L1	136.8(8)
Fe1–C13	1.77(1)		
Fe2–C21	1.77(2)		
Fe2–C22	1.77(1)		
Fe2–C23	1.74(2)		
P1–C1	1.88(1)		
P3–C1	1.87(1)		
P3–N1	1.65(1)		
P2–C31	1.89(1)		
P2–C35	1.89(1)		
C1–O1	1.20(1)		

leading to an agreement factor $R = 5.8\%$ $[R_w = (\Sigma w \| F_o | - | F_c \| / \Sigma w | F_o |) \times 100]$ minimized the function $\Sigma(w \| F_o | - | F_c \|)^2$. Scattering factors were taken from Cromer and Mann [12]. Anomalous dispersion corrections were made for Fe and P [13]. In the final stages of refinement weights of $1/\sigma(F)^2$ were used leading to $R_w = 7.7\%$. Selected bond distances and angles are given in Table 4. Figure 2 shows an ORTEP diagram of the structure of $(^iPr_2NP)_2(^tBu_2PP)COFe_2(CO)_6$. Tables of positional parameters, all bond distances and angles, anisotropic thermal parameters, and F_{obs} and F_{calc} are available from the authors upon request.

Results and discussion

Reduction of $(^iPr_2NP)_2COFe_2(CO)_6$ (I) with sodium amalgam in tetrahydrofuran followed by reaction of the resulting $[^iPr_2NPCOPFe_2(CO)_6]^-$ anion (II) with a sterically hindered R_2PCl derivative results in a new type of phosphorus-bridging carbonyl derivative, namely $(^iPr_2NP)(R_2PP)COFe_2(CO)_6$ (VI). The course of this reaction is readily recognized by formation of the characteristic AMX pattern of VI in the phosphorus-31 NMR spectrum with $J_{A\text{-}X} \approx 0$ (Table 1). Isolable moderately air-stable orange solid products were obtained from $^tBu_2PCl$, Cx_2PCl, and $(^iPr_2N)_2PCl$. Treatment of II with $^iPr_2PCl$ also gave a crude reaction mixture exhibiting a phosphorus-31 NMR spectrum (Table 1) indicative of the formation of $(^iPr_2NP)(^iPr_2PP)COFe_2(CO)_6$ (VI: $R = {}^iPr$) but this product decomposed upon attempted isolation. Reactions of II with the less sterically hindered Ph_2PCl and $PhPCl_2$ gave complex mixtures indicated by their phosphorus-31 NMR spectra to contain several organophosphorus iron carbonyl derivatives. Pure products were not isolated from these reaction mixtures.

The formulation of these products as phosphorus-bridging carbonyl derivatives VI is suggested by their infrared ν(CO) spectra (Table 2), which all exhibit a band

1714 ± 7 cm^{-1} characteristic of a phosphorus-bridging carbonyl group in addition to a pattern of five terminal ν(CO) frequencies very similar to those in $(^iPr_2NP)_2COFe_2(CO)_6$ (I) [4]. A suitable single crystal of the t-butyl derivative $(^iPr_2NP)(^tBu_2PP)COFe_2(CO)_6$ (VI: R = ^{t}Bu) was obtained for structure determination by X-ray diffraction, which confirmed the proposed structure. The geometry of the Fe_2P_2CO unit in $(^iPr_2NP)(^tBu_2PP)COFe_2(CO)_6$ (VI: R = ^{t}Bu) is very similar to that in $(^iPr_2NP)_2COFe_2(CO)_6$ (I). Thus the P–C–P angle in VI (R = ^{t}Bu) is 85.7(4)° as compared with 84.4° (4) in I. In addition, the Fe–Fe distance in VI (R = ^{t}Bu) is 2.593(3) Å which is identical within experimental error to the 2.603(2) Å Fe–Fe distance in I.

The reaction of $(^iPr_2NP)_2COFe_2(CO)_6$ (I) with sodium amalgam in tetrahydrofuran followed by addition of R_2PCl results in the replacement of a diisopropylamino group with a dialkylphosphino group to give $(^iPr_2NP)(R_2PP)COFe_2(CO)_6$ (VI). In an attempt to carry this process one step further the reaction of $(^iPr_2NP)(^tBu_2PP)COFe_2(CO)_6$ (VI, R = ^{t}Bu) with sodium amalgam in tetrahydrofuran at ambient temperature was investigated. However, the phosphorus-31 NMR spectrum of the resulting yellow reaction solution exhibited the characteristic two doublets of the $[^iPr_2NPCOFe_2(CO)_6]^-$ anion [3] in addition to resonances from $^tBu_2P{-}P^tBu_2$ and $^tBu_2PH$. This indicates that the P–P bond in VI (R = ^{t}Bu) is cleaved by sodium amalgam in preference to the P–N bond, thereby excluding this method for the preparation of the unknown $(R_2PP)_2COFe_2(CO)_6$ derivatives.

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