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Synthesis and Characterization of Isomeric Binuclear Double-Bridged Alkylidene–Tetraphenyldiphosphine and Diphenylphosphido–Methylenediphenylphosphine Iron Nitrosyl Complexes

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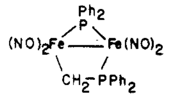
The dianion $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$ reacts as −78 °C with $RCHI_2$ in THF solution to afford the methylenediphenylphosphine complexes $(NO)_2Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH(R)PPh_2)Fe(NO)_2$ (R = H (**1**), Me (**2**)), in addition to $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$. The corresponding reactions of the monoanion $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]^-$ with $RCHI_2$ commence at ca. −63 °C and yield the μ-alkylidene complexes $(NO)_2Fe(\mu\text{-}CH(R))(\eta^2\text{-}(P,P')\text{-}\mu\text{-}Ph_2PPPh_2)Fe(NO)_2$ (R = H (**3**), Me (**4**)), as well as $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$. There is no reaction at 25 °C between $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]^-$ and $CH_2(OTs)_2$ (Ts = $S(O)_2C_6H_4Me\text{-}p$), and $(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$ and $CH_2(OTs)_2$ at −78 °C apparently afford $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2CH_2OTs)]^-$, which does not convert to **3** during prolonged stirring at 25 °C. Upon heating at 40–60 °C in THF solution, **3** and **4** isomerize to **1** and **2**, respectively, the conversion being faster for **4**. The rearrangement of **3** to **1** was found to be first order in **3**, with $k = 5.2 \times 10^{-5}$ s^{-1} at 60 °C. Complexes **1**–**4** were characterized by a combination of elemental analyses, FAB mass spectrometry, and IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy; the structures of **1** and **3** were determined by single-crystal X-ray diffraction analysis. Crystals of **1** are monoclinic of space group $P2/n$ with $a = 25.15$ (2) Å, $b = 8.458$ (9) Å, $c = 25.67$ (2) Å, $\beta = 96.06$ (6)°, and $Z = 8$. The structure was solved and refined to $R = 0.060$ and $R_w = 0.061$ by using 2882 independent reflections. There are two crystallographically independent but quite similar molecules of **1**. Crystals of **3** are monoclinic of space group Cc with $a = 9.809$ (2) Å, $b = 15.741$ (3) Å, $c = 17.320$ (3) Å, $\beta = 91.63$ (2)°, and $Z = 4$. The structure was solved and refined to $R = 0.032$ and $R_w = 0.034$ by using 2470 independent reflections. The Fe–P–C–Fe and Fe–P–P–Fe rings of **1** and **3**, respectively, are puckered.

Introduction

We recently reported[1] that reduction of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ with $LiBEt_3H$ affords the monoanion $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]^-$, which can be deprotonated at low temperature to $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$. The product dianion isomerizes upon slight warming to $[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]^{2-}$. Protonation and alkylation of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$ or $[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]^{2-}$ with 2 equiv of CF_3COOH or RI, respectively, resulted in a disintegration of the binuclear structure to yield mononuclear complexes $Fe(NO)_2(PPh_2X)_2$ (X = H or R). No neutral diiron compounds could be isolated or detected, except for $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$. The fragmentation of the binuclear network in these reactions apparently proceeds by reductive elimination of H or R and μ-PPh_2. If the occurrence of such a reductive elimination could be prevented, then neutral diiron nitrosyl complexes other than $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ might be obtainable. In that vein, particularly attractive to us appeared the possibility of bridging the terminal PPh_2 ligand and the $Fe(NO)_2$ iron in $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$ by a CH_2 group, instead of protonating or alkylating at each nucleophilic center. This would generate a $\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH_2PPh_2$ structure of expected greater resistance to fragmentation.

To ascertain whether such a diiron nitrosyl complex would be stable, we examined the reaction of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$ with CH_2I_2. As reported earlier,[2] the corresponding reaction of $[(CO)_3Fe(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe(CO)_2(PPh_2)]^{2-}$ with CH_2I_2 does afford isolable $(CO)_3Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH_2PPh_2)Fe(CO)_3$. We then discovered that the reaction in question indeed furnished $(NO)_2Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH_2PPh_2)Fe(NO)_2$ (**1**), but along with a small amount of $(NO)_2Fe(\mu\text{-}CH_2)(\eta^2\text{-}(P,P')\text{-}\mu\text{-}Ph_2PPPh_2)Fe(NO)_2$ (**3**). This result prompted an investigation of reactions of the other binuclear nitrosyl (μ-phosphido)iron anions with the methylene-transfer reagents $CH(R)I_2$ (R = H, Me) and CH_2-



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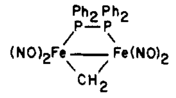

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Table I. Spectroscopic Data for Complexes 1–4[a]

	NMR, δ			
complex	$^{31}P\{^1H\}$[b]	$^{13}C\{^1H\}$[c]	^1H[c]	IR $\nu(NO)$,[b] cm^{-1}
1[d]	232.9 (d, μ-P), −1.6 (d, C*P*Fe, J_{PP} = 56 Hz)	138.4–128.4 (4 Ph), −30.3 (t, CH_2, J_{PC} = 7.8 Hz)	7.0 (m, 4 Ph), 1.4 (dd, CH_2, $^2J_{PH}$ = 3.8 Hz, $^3J_{PH}$ = 1.8 Hz)	1790 (w), 1750 (st), 1732 (st)
2[e]	221.0 (d, μ-P), 9.1 (d, C*P*Fe, J_{PP} = 57 Hz)	*h*	7.4 (m, 4 Ph), 1.8 (m, CH, Me)	1780 (w), 1750 (st), 1725 (st)
3[f]	−24.7 (s)	177.7 (t, CH_2, J_{PC} = 13 Hz), 134.6–127.9 (4 Ph)[i]	10.7 (t, CH_2, $^3J_{PH}$ = 3.2 Hz), 7.4 (m, 4 Ph)	1775 (me), 1745 (st), 1715 (st)
4[g]	−18.6 (s)	215.3[j] (CH), 134–128 (4 Ph), 41.5 (s, Me)	12.4 (m, CH), 7.4 (m, 4 Ph), 3.3 (m, Me)	1785 (me), 1740 (st), 1708 (st)

[a] At room temperature. Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, w = weak, me = medium, st = strong. [b] In THF solution. [c] In $CDCl_3$ solution unless otherwise indicated. [d] Anal. Calcd for $C_{25}H_{22}Fe_2N_4O_4P_2$: C, 48.72; H, 3.60. Found: C, 48.76; H, 3.69. Mass spectrum: *m/e* 616 (P^+). [e] Anal. Calcd for $C_{26}H_{24}Fe_2N_4O_4P_2$: C, 49.56; H, 3.84. Found: C, 48.95; H, 3.50. [f] Anal. Calcd for $C_{25}H_{22}Fe_2N_4O_4P_2$: C, 48.72; H, 3.60. Found: C, 48.91; H, 3.74. Mass spectrum: *m/e* 616 (P^+). [g] Anal. Calcd for $C_{26}H_{24}Fe_2N_4O_4P_2$: C, 49.56; H, 3.84. Found: C, 49.04; H, 3.43. [h] Not measured. [i] In THF-d_8 solution. [j] Multiplicity not determined because of poor signal-to-noise ratio.

$(OTs)_2$. Herein we report results of our study, including the complete characterization of complexes 1 and 3 by single-crystal X-ray diffraction. Some aspects of this research have been communicated in a preliminary form.[3]

Experimental Section

General Procedures and Measurements. All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of purified N_2 by using standard procedures.[4] Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN. Chromatographic separations and purifications were effected on columns packed with alumina (ca. 150 mesh, 6% H_2O). Melting points were measured in vacuo on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 337 or 283B spectrophotometer and were calibrated with polystyrene. ^1H NMR spectra were obtained on a Varian Associates EM 360L spectrometer. ^{31}P NMR spectra were recorded on a Bruker HX-90 spectrometer at 36.43 MHz in the Fourier transform mode. Chemical shifts are given with reference to 85% H_3PO_4 and are reproducible to ±0.1 ppm. ^{13}C NMR spectra were obtained on a Bruker WP-80 spectrometer at 20.11 MHz. ^2H NMR spectra were collected on a Bruker WM-300 spectrometer at 46.07 MHz and were standardized against the absolute frequency of the instrument. Ultraviolet (UV)–visible spectra were recorded on a Cary 14 spectrophotometer equipped with a thermostated cell holder. Mass spectra were obtained by use of the fast atom bombardment (FAB) technique on a Kratos MS-30 spectrometer by Mr. C. R. Weisenberger.

Materials. THF was distilled from Na and benzophenone under an atmosphere of N_2 immediately before use. Other solvents were purified according to procedures described by Perrin, Armarego, and Perrin.[5]

$LiBEt_3{}^*H$ (Super Hydride (*H = H), Super Deuteride (*H = D), 1.0 M in THF) and *n*-BuLi (1.6 M in hexanes) were obtained from Aldrich. Other reagents were purchased from various commercial sources and used as received. 1,1-Diiodoethane[6] and $CH_2(OTs)_2$ (Ts = $S(O)_2C_6H_4Me$-*p*)[7] were synthesized as described in the literature.

The preparation of the binuclear anionic complexes $Na_2[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]$, $Li[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2{}^*H)]$ (*H = H, D), $Li_2[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]$, and $Li[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2Me)]$ was effected as reported earlier.[1]

Reaction of $Na_2[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]$ with CH_2I_2. The title complex (0.20 g, 0.15 mmol) was dissolved in 2.0 mL of THF in an NMR tube, and the resulting solution was cooled to −78 °C (dry ice–acetone bath) and treated with 0.10 mL (1.2 mmol) of CH_2I_2. $^{31}P\{^1H\}$ NMR spectra of the reaction mixture were periodically recorded as the temperature gradually increased to ca. 25 °C.

Reaction of $Li[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2{}^*H)]$ (*H = H, D) with CH_2I_2. A solution of the title complex, prepared by treatment of 0.50 g (0.83 mmol) of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ in 50 mL of THF with 1.2 mL (1.2 mmol) of 1.0 M solution of $LiBEt_3H$ in THF at room temperature, was cooled to −78 °C. After 1.0 mL (12 mmol) of CH_2I_2 had been introduced by syringe, the resulting reaction mixture was allowed to warm to room temperature over 10 h. The solvent was removed under reduced pressure, and the red-brown residue was chromatographed on a 20 × 1-cm column. Elution with petroleum ether removed from the column a small red band which, after evaporation of the solvent, afforded 0.01 g (2% yield) of a red solid, mp 138–139 °C, shown to be $(NO)_2Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH_2PPh_2)Fe(NO)_2$ (1). Elution with diethyl ether then removed from the column a large red band which yielded 0.18 g (35%) of bright red $(NO)_2Fe(\mu\text{-}CH_2)(\eta^2\text{-}(P,P')\text{-}\mu\text{-}Ph_2PPPh_2)Fe(NO)_2$ (3) after solvent removal. This solid was recrystallized from diethyl ether–petroleum ether, washed with petroleum ether (2 × 10 mL), and dried under reduced pressure. Further elution, with CH_2Cl_2, produced yet another red band which was collected and evaporated to dryness to give 0.18 g (36% yield) of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$, identified by its $^{31}P\{^1H\}$ NMR spectrum. Chemical analyses and spectroscopic data for 1 and 3 are furnished in Table I.

Reaction between $Li[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2{}^*H)]$ and CH_2I_2 was also examined by $^{31}P\{^1H\}$ (*H = H) and ^2H (*H = D) NMR spectroscopy. A solution of $Li[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2{}^*H)]$, generated by treatment of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ (0.10 g, 0.17 mmol) in THF (2.0 mL) with 1.0 *M* $LiBEt_3{}^*H$ (0.17 mL of solution in THF, 0.17 mmol) at room temperature in an NMR tube, was cooled to −78 °C. To this solution was then added CH_2I_2 (0.10 mL, 1.2 mmol), and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture were periodically recorded as the temperature gradually increased to ca. 25 °C. A ^2H NMR spectrum was obtained at room temperature.

Reaction of $Li[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]$ with $MeCHI_2$. A solution of the title complex, prepared by treatment of 0.50 g (0.83 mmol) of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ in 50 mL of THF with 0.83 mL (0.83 mmol) of 1.0 M solution of $LiBEt_3H$ in THF at room temperature, was cooled to −78 °C. After 0.80 mL (6.0 mmol) of $MeCHI_2$ had been added, the resulting mixture was allowed to warm to room temperature and was worked up as described above for the corresponding reaction with CH_2I_2. Again, three red bands were separated by chromatography; they yielded, in the indicated order, $(NO_2Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH(Me)PPh_2)Fe(NO)_2$ (2) (0.01 g, 1%), $(NO)_2Fe(\mu\text{-}CH\text{-}$

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(Me))(η^2-(P,P')-μ-Ph_2PPPh_2)Fe$(NO)_2$ (**4**) (0.18 g, 34%), and $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ (0.15 g, 30%). Chemical analyses and spectroscopic data for **2** and **4** are provided in Table I.

Reaction of Li[$(NO)_2$Fe(μ-PPh_2)(μ-NO)Fe(NO)(PPh_2Me)] with CH_2I_2. A solution of Li[$(NO)_2$Fe(μ-PPh_2)(μ-NO)Fe(NO)(PPh_2H)], generated by treatment of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ (0.10 g, 0.17 mmol) in THF (2.0 mL) with 1.0 M $LiBEt_3H$ (0.17 mL of solution in THF, 0.17 mmol) at room temperature in an NMR tube, was cooled to −78 °C. This solution was converted to that of the title complex by addition first of 1.6 M n-BuLi (0.10 mL of solution in hexanes, 0.17 mmol) and then of MeI (10 μL, 0.17 mmol). After treatment with CH_2I_2 (0.10 mL, 1.2 mmol), the reaction mixture was stirred for 1 h and then allowed to warm to room temperature. A $^{31}P\{^1H\}$ NMR spectrum was recorded at 25 °C.

Reaction of Li_2[$(NO)_2$Fe(μ-PPh_2)(μ-NO)Fe(NO)(PPh_2)] with CH_2I_2. A solution of the title complex was prepared by treatment of 0.50 g (0.83 mmol) of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ in 50 mL of THF with 0.83 mL (0.83 mmol) of 1.0 M solution of $LiBEt_3H$ in THF at 25 °C, cooling to −78 °C, and addition of 0.52 mL (0.83 mmol) of 1.6 M solution of n-BuLi in hexanes. After 0.10 mL (12 mmol) of CH_2I_2 had been introduced by syringe, the resulting reaction mixture was allowed to warm to room temperature over 10 h. Workup, including chromatography, was similar to that described above for the crude mixture from the reaction of Li[$(NO)_2$Fe(μ-PPh_2)(μ-NO)Fe(NO)(PPh_2H)] with CH_2I_2 and yielded $(NO)_2$Fe(μ-PPh_2)(η^2-(C,P)-μ-CH_2PPh_2)Fe$(NO)_2$ (**1**) (0.15 g, 29%), $(NO)_2$Fe(μ-CH_2)(η^2-(P,P')-μ-Ph_2PPPh_2)Fe$(NO)_2$ (**3**) (0.02 g, 4%), and $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ (0.15 g, 30%).

This reaction was also followed by low-temperature $^{31}P\{^1H\}$ NMR spectroscopy. A THF solution of Li_2[$(NO)_2$Fe(μ-PPh_2)(μ-NO)Fe(NO)(PPh_2)] was prepared from 0.10 g (0.17 mmol) of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ and equimolar amounts of $LiBEt_3H$ and n-BuLi at −78 °C as already described. To this solution was added 0.10 mL (1.2 mmol) of CH_2I_2, and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture were periodically recorded as the temperature gradually increased to 25 °C.

Reaction of Li_2[$(NO)_2$Fe(μ-PPh_2)(μ-NO)Fe(NO)(PPh_2)] with $MeCHI_2$. A THF solution of the title complex was prepared by treatment of 0.50 g (0.83 mmol) of $Fe_2(NO)_4(\mu\text{-}PPh_2)$ with equimolar amounts of $LiBEt_3H$ and n-BuLi at −78 °C as already described. After 0.80 mL (6.0 mmol) of $MeCHI_2$ had been added, the resulting reaction mixture was allowed to warm to room temperature over 10 h. Workup, including chromatography, as described for the crude mixture from the reaction of Li[$(NO)_2$Fe(μ-PPh_2)(μ-NO)Fe(NO)(PPh_2H)] with CH_2I_2, yielded $(NO)_2$Fe(μ-PPh_2)(η^2-(C,P)-μ-CH(Me)PPh_2)Fe$(NO)_2$ (**2**) (0.10 g, 20%), $(NO)_2$Fe(μ-CH(Me))(η^2-(P,P')-μ-Ph_2PPPh_2)Fe$(NO)_2$ (**4**) (0.02 g, 4%), and $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ (0.18 g, 36%).

Reaction of Li_2[$(NO)_2$Fe(μ-PPh_2)(μ-NO)Fe(NO)(PPh_2)] with $CH_2(OTs)_2$. A THF solution of the title complex, generated from 0.10 g (0.17 mmol) of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ and equimolar amounts of $LiBEt_3H$ and n-BuLi at −78 °C as already described, was treated with 0.10 g (0.28 mmol) of $CH_2(OTs)_2$. The resulting reaction mixture was allowed to warm to 25 °C and stirred at that temperature for 48 h. $^{31}P\{^1H\}$ NMR spectra of the solution were recorded at 25 °C.

Thermal Conversion of $(NO)_2$Fe(μ-CH_2)(η^2-(P,P')-μ-Ph_2PPPh_2)Fe$(NO)_2$ (3) to $(NO)_2$Fe(μ-PPh_2)(η^2-(C,P)-μ-CH_2PPh_2)Fe$(NO)_2$ (1). Thermal conversion of **3** to **1** was followed by visible absorption spectroscopy in THF solution at 60 °C. Concentrations of the two complexes in the range 10^{-4}–10^{-3} M at any time of the reaction were calculated by measuring the increasing absorbance (A) at 380 and 520 nm of the solution and using the equations

$$A_{380} = \epsilon_{1(380)}bc_1 + \epsilon_{3(380)}bc_3$$

$$A_{520} = \epsilon_{1(520)}bc_1 + \epsilon_{3(520)}bc_3$$

where b is the path length of the cell, c_1 and c_3 are the concentrations of **1** and **3**, respectively, and $\epsilon_{1(380)}$, $\epsilon_{1(520)}$, $\epsilon_{3(380)}$, and $\epsilon_{3(520)}$ are the molar absorptivities of **1** and **3** at the indicated wavelengths. The four values of ϵ were determined from the visible absorption spectra (which are essentially featureless) of standard solutions of **1** and **3**: $\epsilon_{1(380)} = 6029$, $\epsilon_{1(520)} = 2403$, $\epsilon_{3(380)} = 5161$, and $\epsilon_{3(520)} = 1475$ M^{-1} cm^{-1}.

Table II. Crystallographic Data for 1 and 3

	1	3
mol formula	$Fe_2C_{25}H_{22}N_4O_4P_2$	$Fe_2C_{25}H_{22}N_4O_4P_2$
mol wt	616.1	616.1
cryst system	monoclinic	monoclinic
space group	$P2/n$	Cc
a, Å	25.15 (2)	9.809 (2)
b, Å	8.458 (9)	15.741 (3)
c, Å	25.67 (2)	17.320 (3)
β, deg	96.06 (6)	91.63 (2)
V, Å^3	5431 (9)	2673.2 (9)
Z	8	4
D(calcd), g cm^{-3}	1.507	1.531
cryst size, mm	0.21 × 0.19 × 0.52	0.25 × 0.31 × 0.46
λ(Mo Kα), Å	0.7107	0.71069
μ(Mo Kα), cm^{-1}	12.2	12.4
scan type	$\theta/2\theta$	$\omega/2\theta$
θ range, deg	3.5–24	3.0–28
intensity monitors	1[a]	3[b]
unique data with $I > n\sigma(I)$; n	2882; 2[c]	2470; 3
R[d]	0.060	0.032
R_w[e]	0.061	0.034

[a] Measured after each 100 reflections. [b] Measured after each hour. [c] Intensities have been collected and processed with a $P2/c$ cell: $a = 25.67$ Å, $b = 8.458$ Å, $c = 33.99$ Å, and $\beta = 132.62°$. This can be transformed into the above $P2/n$ cell by the matrix 1,0,1/0,1,0/−1,0,0. [d] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [e] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_c^2]^{1/2}$.

Crystallographic Analyses of $(NO)_2$Fe(μ-PPh_2)(η^2-(C,P)-μ-CH_2PPh_2)Fe$(NO)_2$ (1) and $(NO)_2$Fe(μ-CH_2)(η^2-(P,P')-μ-Ph_2PPPh_2)Fe$(NO)_2$ (3). Crystals of **1** suitable for X-ray diffraction were obtained by slow addition of hexane to a saturated diethyl ether solution and cooling at −10 °C for 24 h. Crystals of **3** were grown by slow treatment of a saturated THF solution with diethyl ether followed by storage at ca. 5 °C for 48 h.

Space group and cell parameters for compounds **1** and **3** were obtained by using Weissenberg and precession photographs. Unit cell parameters of **1** were refined and the intensity data collected on an AED-Siemens diffractometer using Zr-filtered Mo Kα radiation, whereas those of **3** were refined and collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. Crystallographic data of interest are summarized in Table II. In both cases, the intensities were corrected for Lorentz and polarization factors. For **3**, anomalous dispersion corrections were also applied. No absorption or extinction corrections were made because of the small size of the crystals used and the sufficiently small values of the linear absorption coefficients (μ).

The structure of **1** was solved by using the MULTAN direct methods procedure that allowed location of the iron and phosphorus atoms. All other atoms were then located through the usual combination of structure factor calculations and Fourier syntheses. Refinement by blocked full-matrix least-squares techniques, assigning anisotropic temperature factors only to Fe and P atoms because of the low number of observed intensities, converged to $R = 0.060$. Phenyl rings were refined as rigid groups. Hydrogen atoms were included at calculated positions ($B = 7.0$ Å^2). The final weighting scheme was $w = A/(\sigma^2(F) + BF^2)$, with $A = 0.7625$ and $B = 0.003682$.

The structure of **3** was solved by the heavy-atom method. In the space group Cc one of the iron atoms of **3** has indeterminate x and z coordinates which were set at 0.000. The coordinates of the other iron atom, Fe(2), were located from a Patterson map, and this position was used to phase a Fourier map that revealed all other non-hydrogen atoms. Hydrogen atoms were included at calculated positions and held fixed ($B = 5.0$ Å^2) during the

Table III. Positional and Thermal Parameters of Non-Hydrogen Atoms of Molecule A of 1 with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}/B, Å^2
Fe(1)	0.0677 (1)	−0.0062 (2)	0.2020 (1)	3.0 (1)
Fe(2)	0.0610 (1)	0.1655 (3)	0.1269 (1)	3.3 (1)
P(1)	0.0406 (2)	0.2474 (5)	0.1776 (1)	2.9 (2)
P(2)	0.0714 (2)	−0.0981 (5)	0.1217 (2)	3.3 (3)
N(1)	−0.0028 (6)	−0.0861 (15)	0.1836 (5)	4.3 (3)
N(2)	0.1378 (6)	0.0113 (14)	0.2638 (5)	4.3 (3)
N(3)	−0.0106 (7)	0.2033 (16)	0.0683 (5)	5.3 (4)
N(4)	0.1354 (7)	0.2399 (16)	0.1514 (5)	5.4 (4)
O(1)	−0.0509 (7)	−0.1418 (15)	0.1770 (5)	7.2 (4)
O(2)	0.1866 (7)	0.0210 (15)	0.3118 (5)	7.2 (4)
O(3)	−0.0650 (8)	0.2358 (18)	0.0241 (6)	9.4 (5)
O(4)	0.1892 (7)	0.3005 (16)	0.1665 (5)	8.5 (4)
C(1)	0.0973 (8)	−0.1856 (18)	0.1794 (6)	4.2 (4)
C(2)	0.0984 (3)	0.3968 (10)	0.2292 (3)	2.5 (3)
C(3)	0.1701 (3)	0.3959 (10)	0.2559 (3)	3.1 (4)
C(4)	0.2159 (3)	0.5066 (10)	0.2960 (3)	3.8 (4)
C(5)	0.1901 (3)	0.6181 (10)	0.3093 (3)	4.2 (4)
C(6)	0.1184 (3)	0.6190 (10)	0.2826 (3)	4.3 (4)
C(7)	0.0726 (3)	0.5083 (10)	0.2425 (3)	3.1 (4)
C(8)	−0.0490 (5)	0.3130 (11)	0.1446 (4)	2.8 (3)
C(9)	−0.0842 (5)	0.4174 (11)	0.1016 (4)	4.0 (4)
C(10)	−0.1528 (5)	0.4673 (11)	0.0755 (4)	4.8 (4)
C(11)	−0.1861 (5)	0.4127 (11)	0.0925 (4)	4.0 (4)
C(12)	−0.1509 (5)	0.3083 (11)	0.1356 (4)	4.2 (4)
C(13)	−0.0823 (5)	0.2584 (11)	0.1616 (4)	3.6 (4)
C(14)	−0.0116 (5)	−0.1893 (10)	0.0629 (4)	3.4 (4)
C(15)	−0.0120 (5)	−0.2940 (10)	0.0310 (4)	5.2 (5)
C(16)	−0.0748 (5)	−0.3684 (10)	−0.0122 (4)	6.4 (6)
C(17)	−0.1372 (5)	−0.3381 (10)	−0.0235 (4)	5.5 (5)
C(18)	−0.1368 (5)	−0.2333 (10)	0.0084 (4)	5.1 (5)
C(19)	−0.0740 (5)	−0.1589 (10)	0.0516 (4)	4.4 (4)
C(20)	0.1367 (5)	−0.1520 (11)	0.1175 (4)	3.6 (5)
C(21)	0.1509 (5)	−0.0499 (11)	0.0935 (4)	4.7 (4)
C(22)	0.1995 (5)	−0.0933 (11)	0.0895 (4)	6.3 (6)
C(23)	0.2341 (5)	−0.2388 (11)	0.1095 (4)	5.5 (5)
C(24)	0.2199 (5)	−0.3409 (11)	0.1335 (4)	5.7 (5)
C(25)	0.1712 (5)	−0.2975 (11)	0.1375 (4)	4.5 (4)

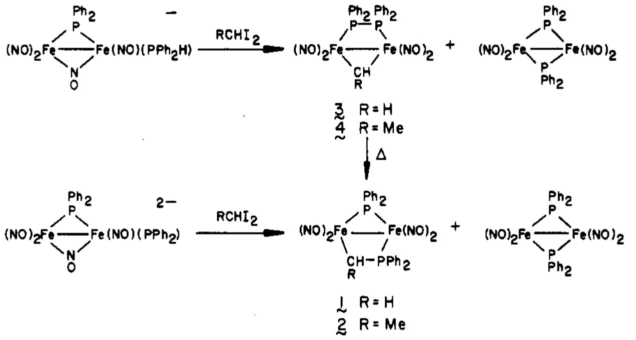
anisotropic full-matrix least-squares refinement which converged to $R = 0.032$ ($w = 1$). Atomic scattering factors and anomalous dispersion terms were taken from the literature.[8] Data processing for 1 was performed by programs of the X-RAY 70 system,[9] whereas all other calculations were carried out with the SHELX 76 system.[10] All calculations for 3 were done by using computer programs from the Enraf-Nonius SDP package.

The final positional parameters for non-hydrogen atoms of 1 are listed in Tables III and IV, respectively, for the two crystallographically independent molecules A and B; those of 3 are listed in Table V. Listings of temperature factors, hydrogen atom coordinates, and structure factors for both compounds are available as supplementary material.[11]

Table IV. Positional and Thermal Parameters of Non-Hydrogen Atoms of Molecule B of 1 with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}/B, Å^2
Fe(1)	0.5173 (1)	0.7270 (3)	0.6112 (1)	3.4 (1)
Fe(2)	0.4433 (1)	0.5339 (3)	0.6267 (1)	3.5 (1)
P(1)	0.4916 (2)	0.4678 (5)	0.5939 (2)	3.4 (2)
P(2)	0.4161 (2)	0.7937 (5)	0.6179 (2)	3.5 (2)
N(1)	0.4855 (7)	0.8164 (17)	0.5560 (6)	5.7 (4)
N(2)	0.6004 (7)	0.7204 (15)	0.6613 (5)	5.0 (4)
N(3)	0.3658 (7)	0.4561 (15)	0.5869 (5)	4.7 (4)
N(4)	0.5022 (7)	0.5051 (16)	0.6899 (5)	5.4 (4)
O(1)	0.4702 (7)	0.8867 (16)	0.5190 (5)	8.0 (4)
O(2)	0.6646 (7)	0.7212 (15)	0.6943 (5)	7.7 (4)
O(3)	0.3068 (7)	0.4028 (16)	0.5561 (5)	7.8 (4)
O(4)	0.5435 (7)	0.4662 (17)	0.7365 (6)	8.9 (5)
C(1)	0.4900 (7)	0.9025 (18)	0.6380 (6)	4.1 (4)
C(2)	0.5659 (5)	0.3308 (11)	0.6294 (4)	3.4 (4)
C(3)	0.6162 (5)	0.3338 (11)	0.6852 (4)	4.4 (4)
C(4)	0.6729 (5)	0.2282 (11)	0.7136 (4)	5.9 (5)
C(5)	0.6793 (5)	0.1196 (11)	0.6862 (4)	5.6 (5)
C(6)	0.6290 (5)	0.1166 (11)	0.6304 (4)	5.4 (5)
C(7)	0.5723 (5)	0.2222 (11)	0.6020 (4)	4.3 (4)
C(8)	0.4314 (5)	0.3980 (11)	0.5252 (3)	3.2 (4)
C(9)	0.3962 (5)	0.2545 (11)	0.5126 (3)	4.4 (4)
C(10)	0.3513 (5)	0.1970 (11)	0.4604 (3)	4.6 (4)
C(11)	0.3414 (5)	0.2830 (11)	0.4207 (3)	4.1 (4)
C(12)	0.3765 (5)	0.4265 (11)	0.4333 (3)	4.4 (4)
C(13)	0.4215 (5)	0.4840 (11)	0.4855 (3)	3.3 (4)
C(14)	0.3386 (5)	0.8558 (10)	0.5498 (3)	3.5 (4)
C(15)	0.3031 (5)	0.9944 (10)	0.5420 (3)	4.2 (4)
C(16)	0.2445 (5)	1.0437 (10)	0.4903 (3)	5.2 (5)
C(17)	0.2214 (5)	0.9544 (10)	0.4464 (3)	4.9 (5)
C(18)	0.2569 (5)	0.8158 (10)	0.4543 (3)	4.5 (4)
C(19)	0.3155 (5)	0.7665 (10)	0.5060 (3)	4.1 (4)
C(20)	0.3949 (5)	0.8509 (10)	0.6581 (4)	3.8 (4)
C(21)	0.3563 (5)	0.7467 (10)	0.6619 (4)	6.3 (5)
C(22)	0.3368 (5)	0.7906 (10)	0.6900 (4)	7.6 (6)
C(23)	0.3559 (5)	0.9388 (10)	0.7143 (4)	6.2 (5)
C(24)	0.3945 (5)	1.0430 (10)	0.7105 (4)	6.5 (6)
C(25)	0.4140 (5)	0.9991 (10)	0.6824 (4)	5.5 (5)

Scheme I



Results and Discussion

Synthesis of $(NO)_2Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH(R)\text{-}PPh_2)Fe(NO)_2$ (R = H (1), Me (2)) and $(NO)_2Fe(\mu\text{-}CH(R))(\eta^2\text{-}(P,P')\text{-}\mu\text{-}Ph_2PPPh_2)Fe(NO)_2$ (R = H (3), Me (4)). A $^{31}P\{^1H\}$ NMR spectrum at ca. −78 °C of a THF solution of $(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$ and added CH_2I_2 revealed the formation of complex 1 by the presence of doublet (J_{PP} = 56 Hz) signals at δ 209.6 and 3.3. When this reaction was commenced at −78 °C and allowed to proceed with warming to room temperature over 10 h, 1 and $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ were isolated as major products and 3 was isolated as a minor product (4% yield). The corresponding reaction of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$ with $MeCHI_2$ afforded 2 and $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$, in addition to a small amount of 4. These reactions are therefore analogous to that of the carbonyl anion $[(CO)_3Fe(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe(CO)_2(PPh_2)]^{2-}$ with CH_2I_2, which yields $(CO)_3Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH_2PPh_2)Fe(CO)_3$ and $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$.[2] The formation of 3 and 4 as minor products from $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$ and $RCHI_2$ (R = H and Me, respectively) apparently arises from an incomplete deprotonation of $(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]^-$ to the binuclear dianion. We demonstrated (vide

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(8) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(9) Stewart, J. M.; Kundal, F. A.; Baldwin, J. C. *The X-ray System*; University of Maryland: College Park, MD, 1970.

(10) Sheldrick, G. M. *SHELX Crystallographic Program System*; University Chemical Laboratory: Cambridge, U.K., 1976.

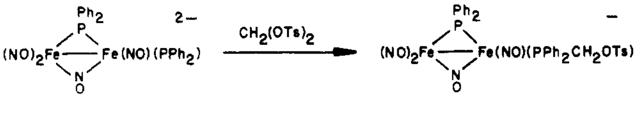
(11) See paragraph at end of paper regarding supplementary material.

Table V. Positional and Thermal Parameters of Non-Hydrogen Atoms of 3 with Estimated Standard Deviations in Parentheses

atom	x	y	z	B, Å^2
Fe(1)	0.000	0.08801 (4)	0.000	3.27 (1)
Fe(2)	0.16078 (8)	0.08762 (4)	0.13128 (4)	3.65 (1)
P(1)	−0.0061 (1)	0.22817 (7)	0.03476 (7)	3.01 (2)
P(2)	0.1941 (1)	0.22337 (8)	0.09242 (7)	3.07 (2)
O(1)	−0.2744 (5)	0.0352 (4)	−0.0116 (4)	8.5 (2)
O(2)	0.1281 (5)	0.0749 (3)	−0.1409 (2)	6.4 (1)
O(3)	0.0016 (8)	0.0975 (4)	0.2643 (3)	11.0 (2)
O(4)	0.4297 (5)	0.0239 (4)	0.1490 (3)	8.1 (1)
N(1)	−0.1628 (5)	0.0580 (3)	−0.0025 (3)	5.1 (1)
N(2)	0.0887 (5)	0.0814 (3)	−0.0789 (3)	4.07 (9)
N(3)	0.0612 (6)	0.0951 (3)	0.2063 (3)	5.6 (1)
N(4)	0.3168 (5)	0.0506 (3)	0.1402 (3)	5.0 (1)
C(1)	0.0746 (8)	−0.0020 (3)	0.0690 (5)	4.20 (9)
C(2)	−0.0198 (5)	0.3099 (3)	−0.0383 (3)	3.35 (9)
C(3)	−0.0988 (7)	0.3815 (4)	−0.0291 (4)	5.7 (1)
C(4)	−0.1076 (9)	0.4422 (4)	−0.0876 (5)	7.8 (2)
C(5)	−0.0363 (9)	0.4328 (4)	−0.1539 (4)	6.8 (2)
C(6)	0.0424 (8)	0.3645 (4)	−0.1632 (4)	5.9 (2)
C(7)	0.0502 (7)	0.3023 (4)	−0.1060 (3)	4.7 (1)
C(8)	−0.1329 (5)	0.2545 (3)	0.1066 (3)	3.42 (9)
C(9)	−0.1111 (6)	0.2992 (5)	0.1716 (4)	7.5 (2)
C(10)	−0.2169 (7)	0.3225 (6)	0.2174 (4)	7.9 (2)
C(11)	−0.3439 (5)	0.2991 (5)	0.1997 (4)	5.2 (1)
C(12)	−0.3684 (6)	0.2550 (7)	0.1378 (5)	9.1 (2)
C(13)	−0.2632 (7)	0.2319 (6)	0.0887 (4)	8.3 (2)
C(14)	0.2290 (5)	0.3077 (3)	0.1634 (3)	3.13 (9)
C(15)	0.2776 (5)	0.2841 (4)	0.2354 (3)	4.0 (1)
C(16)	0.3041 (6)	0.3444 (4)	0.2918 (3)	5.1 (1)
C(17)	0.2816 (6)	0.4282 (4)	0.2753 (4)	5.3 (1)
C(18)	0.2324 (6)	0.4528 (4)	0.2042 (4)	5.2 (1)
C(19)	0.2041 (5)	0.3928 (3)	0.1476 (3)	3.8 (1)
C(20)	0.3145 (5)	0.2388 (3)	0.0163 (3)	3.49 (9)
C(21)	0.3464 (7)	0.3197 (3)	−0.0109 (3)	4.8 (1)
C(22)	0.4443 (7)	0.3294 (4)	−0.0673 (4)	6.1 (1)
C(23)	0.5056 (7)	0.2590 (5)	−0.0987 (4)	6.0 (1)
C(24)	0.4750 (6)	0.1797 (4)	−0.0713 (4)	5.3 (1)
C(25)	0.3784 (5)	0.1697 (3)	−0.0150 (3)	4.0 (1)

infra) that the monoanion does react with $RCHI_2$ to yield 3 and 4. The deprotonation of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]^-$ is difficult to conduct with quantitative precision on this small a reaction scale and at such low temperatures. These and related reactions of binuclear iron nitrosyl species that were examined in our study are presented in Scheme I.

The formation of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ noted in the aforementioned reactions also occurs in the corresponding protonation and alkylation (with alkyl halides) reactions[1] and suggests a significant contribution of a radical pathway. To probe mechanistic aspects of these reactions further, we treated $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$ with $CH_2(OTs)_2$ at −78 °C and allowed the reaction mixture to warm to room temperature. A $^{31}P\{^1H\}$ NMR spectrum of the solution showed two doublets at δ 164.6 and 43.4 (J_{PP} = 20 Hz) to suggest the formation of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2CH_2OTs)]^-$ similar



to other P-alkylated binuclear monoanions reported earlier.[1] Prolonged stirring at room temperature did not convert this species to 1, implying that the alkylation at the $Fe(NO)_2$ iron may require a radical (from CH_2I) rather than an ionic (from CH_2OTs) process.

Since $(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$ readily isomerizes to $[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]^{2-}$ upon warming to ca. −70 °C[1] we examined the reaction of the latter dianion with CH_2I_2 to ascertain whether it might be responsible for the formation of the products isolated when the former dianion was treated with CH_2I_2. However, $^{31}P\{^1H\}$ NMR spectra of the reaction mixture showed $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ as the only product. Its formation may be rationalized by an electron-transfer mechanism. Consistent with this proposal, $[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]^{2-}$ does not react with $CH_2(OTs)_2$ in THF solution at 25 °C over 48 h.

The reaction of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]^-$ with CH_2I_2 in THF was followed by ^{31}P NMR spectroscopy as the solution was allowed to gradually warm from −78 to 25 °C. The formation of 3 was observed to commence at ca. −63 °C and was essentially complete at −33 °C. When a reaction conducted in this manner was terminated at 25 °C after 10 h, 3 and $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ were isolated upon workup as major products and 1 was isolated as a minor product (2% yield). Use of $MeCHI_2$ in place of CH_2I_2 furnished 4 and $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$, in addition to a trace amount of 2. The minor products 1 and 2 almost certainly arise by rearrangement of 3 and 4, respectively, during reaction at ambient temperatures and/or workup (vide infra).

The formation of 3 and 4 by reaction of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]^-$ with CH_2I_2 and $MeCHI_2$, respectively, represents a very unusual transformation. Especially surprising is the coupling of two PPh_2 groups under such mild conditions. Normally, the reverse of this process is operative; thus, reactions of P_2R_4 with metal carbonyls and nitrosyls commonly afford phosphido-bridged binuclear complexes.[12]

Although available experimental evidence does not permit extensive mechanistic conclusions to be drawn, we tentatively favor a radical pathway for the foregoing reactions. The involvement of radicals is suggested by the formation of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ in moderate yield (30–36%), along with 3 or 4. Moreover, reactions of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]^-$ with alkyl halides have been shown to proceed by a radical mechanism.[1] Finally, no reaction was observed by ^{31}P NMR spectroscopy when a THF solution of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]^-$ and $CH_2(OTs)_2$ in excess was stirred for 72 h at 25 °C.[13]

The alkylidene bridge in 3 and 4 may result from an addition of RCHI (R = H, Me) to the $Fe(NO)_2$ iron of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]^-$, followed by dissociation of PPh_2H and oxidative addition of FeCH(R)I to the other iron center. Several pathways are possible for the coupling of two PPh_2 groups to form η^2-(P,P')-μ-Ph_2PPPh_2; however, it would not be productive to discuss them here for lack of experimental evidence. Nevertheless, it is relevant that when the reaction of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2D)]^-$ with CH_2I_2 in THF was examined by ^2H NMR spectroscopy at 25 °C, a signal was observed at δ 7.3. This signal is assigned to DI, the elim-

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[12] (a) Hieber, W.; Kummer, R. *Z. Anorg. Allg. Chem.* **1966**, *344*, 292. (b) Hayter, R. G.; Williams, L. F. *Inorg. Chem.* **1964**, *3*, 717.

[13] However, relative rate constants for reactions of transition-metal nucleophiles with alkyl iodides and tosylates do not in general provide unambiguous mechanistic evidence; see, for example: Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541. We thank a reviewer for alerting us to that point.

ination of which may give rise to the coupling of PPh_2 groups. That the presence of PPh_2H is important to the formation of 3 and 4 is further illustrated by the behavior of $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2Me)]^-$ toward CH_2I_2. This reaction afforded $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ and $Fe(NO)_2(PPh_2Me)_2$, both identified in solution by ^{31}P NMR spectroscopy.

Spectroscopic Properties of New Complexes. Complexes 1 and 2 were isolated as red solids that are stable to air. Complexes 3 and 4 are deep red solids of moderate stability to air; they display rather low solubility in nonpolar solvents and decompose upon storage in solution of chlorinated solvents.

Spectroscopic properties and elemental analyses of these complexes are provided in Table I. Complexes 1 and 2 each show two doublet signals at δ 232.9 and −1.6 (1) and δ 221.0 and 9.1 (2) in their $^{31}P\{^1H\}$ NMR spectra. The low-field resonances are assigned to the μ-PPh_2 phosphorus, and their position indicates the presence of iron–iron bonding.[14] The higher field resonances are those of the η^2-(*C*,*P*)-μ-$CH(R)PPh_2$ (R = H, Me) phosphorus. The presence of the $FeCH_2P$ fragment in 1 is suggested by the position of the CH_2 $^{13}C\{^1H\}$ NMR signal at δ −30.3, which occurs in the high-field region characteristic for η^2-(*C*,*P*)-$CH(X)PR_2$ (X = H, CN) in mononuclear and metal–metal-bonded binuclear complexes.[2,15,16] The upfield chemical shift of the $FeC\mathit{H}(R)P$ protons at δ 1.4 (1) and 1.8 (2), and the splitting pattern of the signal at δ 1.4, further support the assigned structures. The IR spectra of 1 and 2 each exhibit three ν(NO) bands; four are predicted from their structures.

The μ-alkylidene complexes 3 and 4 each show only one $^{31}P\{^1H\}$ NMR signal of the η^2-(*P*,*P*′)-μ-Ph_2PPPh_2 ligand, the chemical shift of which is close to that of free Ph_2PPPh_2 at δ −15.2 (in benzene solution).[17] The μ-*C*HR (R = H, Me) carbon appears at δ 177.7 and 215.3 in the $^{13}C\{^1H\}$ NMR spectra of 3 and 4, respectively, which is essentially in the range reported for μ-alkylidene complexes with a supporting metal–metal bond.[18] The position of the ^1H NMR signal of the μ-C*H*R protons of 3 and 4 at δ 10.7 and 12.4, respectively, also accords with observed values for similar compounds.[18] Both complexes display three IR ν(NO) bands, which is the number predicted on the basis of C_{2v} molecular symmetry of the simplified $(NO)_2Fe(\mu\text{-}C)(\eta^2\text{-}(P,P')\text{-}\mu\text{-}PP)Fe(NO)_2$ structure.

Conversion of $(NO)_2Fe(\mu\text{-}CH(R))(\eta^2\text{-}(P,P')\text{-}\mu\text{-}Ph_2PPPh_2)Fe(NO)_2$ (R = H (3), Me (4)) to $(NO)_2Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH(R)PPh_2)Fe(NO)_2$ (R = H (1), Me (2)). Upon warming to 40–60 °C in THF solution, complexes 3 and 4 undergo isomerization to 1 and 2, respectively (Scheme I). The isomerization of 4 occurs more readily than that of 3. The rearrangement of 3 to 1 was found by ^{31}P NMR spectroscopy to be substantially complete in 5 h at 60 °C. Longer reaction times or higher temperatures lead also to the formation of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$. By contrast, complex 1 is stable for several hours in THF solution at 75 °C.

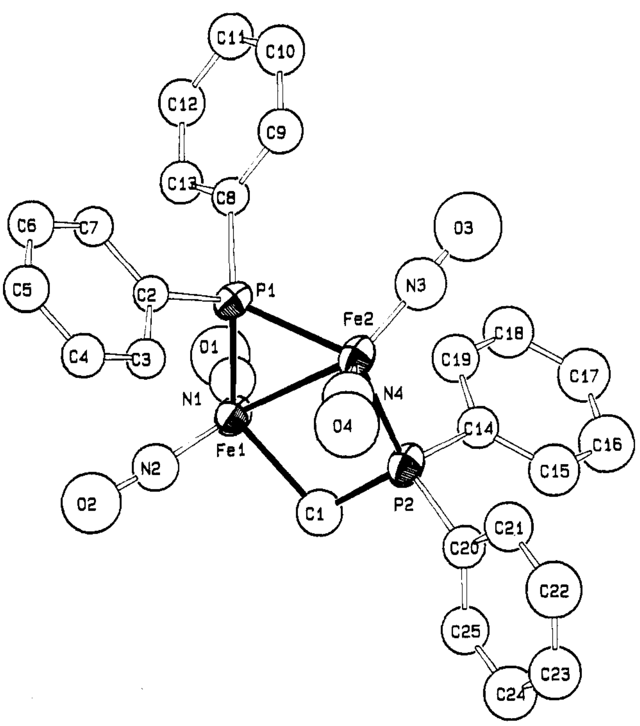

Figure 1. ORTEP plot of molecule A of 1, showing atom numbering scheme. Atoms are drawn at the 50% probability level.

The conversion of 3 to 1 was investigated kinetically by visible spectroscopy at 60 °C (Experimental Section). The reaction is first-order in 3, with $k = 5.2 \times 10^{-5}\ s^{-1}$. No temperature dependence of the isomerization was studied, since the conversion occurs slowly at lower temperatures and is complicated by decomposition at higher temperatures.

The observed kinetics suggests that 3 probably isomerizes by an intramolecular process. This process may be initiated by P–P bond cleavage, followed by the coupling of PPh_2 and CH_2. However, other mechanisms are also possible.

Attempted Reactions of $(NO)_2Fe(\mu\text{-}CH_2)(\eta^2\text{-}(P,P')\text{-}\mu\text{-}Ph_2PPPh_2)Fe(NO)_2$ (3). Binuclear μ-alkylidene–carbonyl–η^5-cyclopentadienyl complexes of cobalt, iron, and ruthenium react with one or more of the following reagents: Ph_3CPF_6 (hydride abstraction),[19] SO_2 (insertion),[20] HC≡CH and $H_2C=CH_2$ (addition to μ-alkylidene).[21] It was therefore of interest to ascertain whether complex 3 would also engage in some of these reactions.

However, all of our efforts in that vein have been unsuccessful. There was no detectable reaction between 3 and SO_2 at −10 °C and between 3 and each of CF_3COOH and Ph_3CPF_6 at room temperature. Under thermal or photochemical conditions, 3 did not react with HC≡CH or $H_2C=CH_2$ at ca. 25 °C; at higher temperatures, it isomerized to 1 instead.

Crystal and Molecular Structures of $(NO)_2Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH_2PPh_2)Fe(NO)_2$ (1) and

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Table VI. Selected Bond Distances (Å) and Angles (deg) for 1 with Estimated Standard Deviations in Parentheses

	molecules	
	A	B
	Bond Distances	
Fe(1)-Fe(2)	2.836 (4)	2.812 (5)
Fe(1)-P(1)	2.234 (4)	2.249 (5)
Fe(1)-N(1)	1.61 (2)	1.64 (2)
Fe(1)-N(2)	1.60 (1)	1.59 (1)
Fe(1)-C(1)	2.06 (2)	2.10 (2)
Fe(2)-P(1)	2.223 (7)	2.226 (8)
Fe(2)-P(2)	2.267 (5)	2.264 (5)
Fe(2)-N(3)	1.58 (1)	1.61 (1)
Fe(2)-N(4)	1.61 (2)	1.60 (1)
P(1)-C(2)	1.83 (1)	1.82 (1)
P(1)-C(8)	1.83 (1)	1.82 (1)
P(2)-C(14)	1.83 (2)	1.83 (2)
P(2)-C(20)	1.83 (2)	1.85 (2)
P(2)-C(1)	1.75 (2)	1.78 (2)
N(1)-O(1)	1.19 (2)	1.19 (3)
N(2)-O(2)	1.21 (2)	1.21 (2)
N(3)-O(3)	1.20 (2)	1.20 (2)
N(4)-O(4)	1.21 (2)	1.21 (2)
	Bond Angles	
Fe(2)-Fe(1)-P(1)	50.3 (2)	50.7 (2)
Fe(2)-Fe(1)-C(1)	81.7 (6)	82.2 (6)
Fe(2)-Fe(1)-N(1)	119.9 (5)	127.3 (6)
Fe(2)-Fe(1)-N(2)	117.6 (7)	111.4 (7)
P(1)-Fe(1)-C(1)	132.0 (6)	132.8 (6)
P(1)-Fe(1)-N(1)	105.9 (5)	108.7 (5)
P(1)-Fe(1)-N(2)	100.9 (4)	100.9 (5)
N(1)-Fe(1)-N(2)	121.2 (9)	120.6 (10)
N(1)-Fe(1)-C(1)	98.4 (8)	96.7 (8)
N(2)-Fe(1)-C(1)	100.7 (7)	99.3 (7)
Fe(1)-Fe(2)-P(1)	50.6 (1)	51.4 (1)
Fe(1)-Fe(2)-P(2)	68.2 (2)	66.3 (2)
Fe(1)-Fe(2)-N(3)	123.4 (8)	133.6 (6)
Fe(1)-Fe(2)-N(4)	114.1 (6)	101.3 (7)
P(1)-Fe(2)-P(2)	118.1 (2)	113.8 (2)
P(1)-Fe(2)-N(3)	103.5 (8)	105.6 (7)
P(1)-Fe(2)-N(4)	107.3 (7)	107.1 (8)
P(2)-Fe(2)-N(3)	101.4 (5)	101.0 (5)
P(2)-Fe(2)-N(4)	105.3 (6)	104.5 (5)
N(3)-Fe(2)-N(4)	122.2 (9)	125.0 (9)
Fe(1)-P(1)-Fe(2)	79.0 (2)	77.8 (2)
Fe(1)-P(1)-C(2)	117.6 (4)	117.2 (3)
Fe(1)-P(1)-C(8)	117.5 (3)	119.7 (4)
Fe(2)-P(1)-C(2)	119.5 (5)	121.0 (5)
Fe(2)-P(1)-C(8)	118.4 (4)	116.5 (5)
C(2)-P(1)-C(8)	104.2 (5)	104.1 (5)
Fe(2)-P(2)-C(1)	107.5 (6)	107.5 (6)
Fe(2)-P(2)-C(14)	112.8 (3)	114.8 (3)
Fe(2)-P(2)-C(20)	114.5 (4)	112.1 (4)
C(1)-P(2)-C(14)	108.7 (7)	107.5 (7)
C(1)-P(2)-C(20)	108.0 (8)	110.6 (8)
C(14)-P(2)-C(20)	105.1 (6)	104.3 (6)
Fe(1)-N(1)-O(1)	171 (1)	172 (1)
Fe(1)-N(2)-O(2)	173 (2)	171 (2)
Fe(2)-N(3)-O(3)	178 (1)	178 (1)
Fe(2)-N(4)-O(4)	176 (1)	173 (1)
Fe(1)-C(1)-P(2)	98.6 (7)	92.9 (7)

$(NO)_2Fe(\mu\text{-}CH_2)(\eta^2\text{-}(P,P')\text{-}\mu\text{-}Ph_2PPPh_2)Fe(NO)_2$ (3). There are two crystallographically independent but quite similar molecules of 1 (A and B). Major differences involve Fe–Fe–N bond angles (Table VI). It seems likely that these are due to different intramolecular steric interactions determined by the different puckering of the Fe–Fe–P–C ring (vide infra), attributable to packing effects. An ORTEP drawing of one of the two molecules (A) is presented in Figure 1, together with the numbering scheme used to define bond lengths and angles in both molecules (Table VI).

In each molecule, the two iron atoms are bridged by a diphenylphosphido group and by a methylenediphenylphosphine in a highly distorted trigonal-bipyramidal coordination environment of the metal centers. The bridging ligands roughly lie in a plane perpendicular to the plane defined by the two $Fe(NO)_2$ groups. In fact, the Fe–P–C–Fe ring is puckered, with torsion angles around the P–C bond of 19 and 32°, respectively, in molecules A and B. Similar puckered structures have been observed in related complexes such as those reported in Table VII.

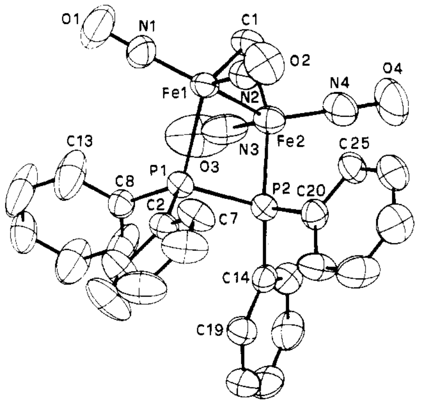

Figure 2. ORTEP plot of 3, showing atom numbering scheme. Atoms are drawn at the 50% probability level.

The average Fe–N and N–O bond distances[22] are 1.61 [2] and 1.20 [1] Å, respectively, comparable within experimental errors with the values found in 3 (vide infra) and in other Fe–NO systems.[23]

The Fe–N–O groups are essentially linear with angles ranging from 171 to 178°. The Fe–P(1) average bond distance of 2.23 [1] Å compares well with the values found in double-bridged compounds: e.g., 2.233 [6] Å in $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$,[24] 2.238 (1) Å in $(CO)_3Fe(\mu\text{-}PPh_2)(\mu\text{-}Cl)Fe(CO)_3$[25] and 2.231 [7] Å in $(CO)_3Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH(CN)PPh_2)Fe(CO)_3$.[15] The Fe–P(2) bond distance involving a bridging phosphine of 2.266 [2] Å is slightly longer than that of 2.243 [6] Å found in $(CO)_3Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH(CN)PPh_2)Fe(CO)_3$[15] but close to the value of 2.253 (3) Å found in $(CO)_3Fe(\mu\text{-}CO)(\eta^2\text{-}(P,P')\text{-}\mu\text{-}Ph_2PCH_2PPh_2)Fe(CO)_3$.[26] The Fe–C(1) mean distance of 2.08 [2] Å is comparable with that of 2.104 [1] Å found in $(CO)_3Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH(CN)PPh_2)Fe(CO)_3$[15] and is in the range of values reported for Fe–C σ bonds.[27]

The average P(2)–C(1) bond distance of 1.765 [16] Å is significantly shorter than the average P–C(Ph) distance of 1.831 [9] Å. It is interesting to note that this value is

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[22] The standard deviation for the mean values reported were calculated by the "scatter formula" $[{}_1^N\sum_i(d_i - \bar{d})^2/(N-1)]^{1/2}$ and are given in square brackets.

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Table VII. Structural Parameters for $M'(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH(R')PR_2)M$ Complexes[22]

M	M′	R′	R	M–M′, Å	P–C, Å	M–P–C, deg	M′–C–P, deg	
Fe	Fe	H	Ph	2.824 [17]	1.765 [16]	107.5 [0]	96 [4]	*a*
Fe	Fe	CN	Ph	2.807 [7]	1.796 [4]	106.8 [4]	93 [1]	*b*
Co	Co	H	Me	2.428 (2)	1.707 (10)	107.8 (3)	88.0 (4)	*c*
Co	Co	H	Me	3.846 (1)	1.797 (7)	112.1 (2)	117.6 (4)	*d*
Pd	Pd	CO_2Et	Ph	3.88	1.81 (2)	111.6 (6)	105 (1)	*e*
W	Os	OMe	Ph	3.022 (1)	1.85 (1)	103.3 (3)	100.5 (5)	*f*
Rh	Zr	H	Ph	4.37 [2][i]	1.809 [1]	113.8 [1]	127 [1][i]	*g*
Cr	Zr	H	Ph	*j*	1.815 [2]	118 [2]	128 [6]	*h*

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close to that of 1.762 [1] Å found in $(CO)_3Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(P,P')\text{-}\mu\text{-}Ph_2PC(CN)PPh_2)Fe(CO)_3$,[15] where the P–C(CN) bonds have a partial π-bonding contribution. Furthermore, it lies in the upper range of values reported for P=C distances in phosphorus-stabilized ylides.[28] It is also in the range of $P\text{–}CH_2$ distances (mean 1.77 [3] Å) found in several metal complexes containing the $Me_2P(CH_2)_2$ ligand, which seems to retain some of the ylidic character of the $P\text{–}CH_2$ bonds.[29] In this respect, it is worthy of note that in $L_2Co(\mu\text{-}PMe_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH_2PMe_2)CoL_2$ (L = PMe_3), the P–C bond distance of 1.707 (10) Å and the Co–C–P bond angle of 88.0 (4)° are consistent with a type of bonding which is best described as a P-metalated phosphorane coordinated to the second Co atom via its ylide function.[30]

Unfortunately, there are few structural data concerning metal complexes with $\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH(R')PR_2$ ligands to allow any detailed discussion of the bonding nature of these ligands. Anyhow, available data (Table VII) show that, when there is a metal–metal bond, the P–C distance is invariably below 1.83 Å and the M′–C–P angle is close to 90°. This suggests a distorted sp^2 hybridization of the C atom which would allow a d-p π orbital overlap.[31] The P–C–C(CN) bond angle of 117 [1]° found in $(CO)_3Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH(CN)PPh_2)Fe(CO)_3$,[15] together with its other bond parameters (Table VII), would support this hypothesis.

The Fe–Fe distances of 2.836 (4) and 2.812 (5) Å in molecules A and B, respectively, rank among the longer known iron–iron bond distances. They are close to those found in the binuclear iron carbonyl complexes $(CO)_3Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,P)\text{-}\mu\text{-}CH(CN)PPh_2)Fe(CO)_3$ (2.807 [7] Å)[15] and $(\eta^3\text{-}C_3H_5)(CO)_2Fe(\mu\text{-}PPh_2)Fe(CO)_3(PPh_2C_3H_5)$ (2.802 (2) Å).[2]

An ORTEP plot of the molecular structure of **3** is shown in Figure 2, together with the atom numbering scheme. Selected bond lengths and angles are listed in Table VIII.

Table VIII. Selected Bond Distances (Å) and Angles (deg) for 3 with Estimated Standard Deviations in Parentheses

Bond Distances			
Fe(1)–Fe(2)	2.730 (1)	P(1)–P(2)	2.179 (1)
Fe(1)–P(1)	2.288 (1)	P(1)–C(2)	1.807 (4)
Fe(1)–N(1)	1.665 (4)	P(1)–C(8)	1.832 (4)
Fe(1)–N(2)	1.644 (4)	P(2)–C(14)	1.834 (4)
Fe(1)–C(1)	1.979 (5)	P(2)–C(20)	1.811 (4)
Fe(2)–P(2)	2.267 (1)	N(1)–O(1)	1.158 (5)
Fe(2)–N(3)	1.652 (5)	N(2)–O(2)	1.157 (6)
Fe(2)–N(4)	1.640 (4)	N(3)–O(3)	1.178 (6)
Fe(2)–C(1)	1.953 (5)	N(4)–O(4)	1.191 (5)
Bond Angles			
Fe(2)–Fe(1)–P(1)	78.57 (3)	N(4)–Fe(2)–C(1)	100.6 (2)
Fe(2)–Fe(1)–N(1)	123.5 (2)	Fe(1)–P(1)–P(2)	93.28 (6)
Fe(2)–Fe(1)–N(2)	112.7 (2)	Fe(1)–P(1)–C(2)	120.3 (1)
Fe(2)–Fe(1)–C(1)	45.7 (2)	Fe(1)–P(1)–C(8)	114.9 (1)
P(1)–Fe(1)–N(1)	104.4 (2)	P(2)–P(1)–C(2)	113.2 (1)
P(1)–Fe(1)–N(2)	107.3 (1)	P(2)–P(1)–C(8)	108.5 (2)
P(1)–Fe(1)–C(1)	122.9 (2)	C(2)–P(1)–C(8)	106.0 (2)
N(1)–Fe(1)–N(2)	119.4 (2)	Fe(2)–P(2)–P(1)	91.89 (6)
N(1)–Fe(1)–C(1)	98.6 (2)	Fe(2)–P(2)–C(14)	120.6 (1)
N(2)–Fe(1)–C(1)	105.2 (2)	Fe(2)–P(2)–C(20)	116.4 (1)
Fe(1)–Fe(2)–P(2)	80.53 (3)	P(1)–P(2)–C(14)	115.5 (1)
Fe(1)–Fe(2)–N(3)	108.3 (2)	P(1)–P(2)–C(20)	105.1 (1)
Fe(1)–Fe(2)–N(4)	126.5 (2)	C(14)–P(2)–C(20)	106.1 (2)
Fe(1)–Fe(2)–C(1)	46.4 (2)	Fe(1)–N(1)–O(1)	173.4 (6)
P(2)–Fe(2)–N(3)	105.1 (2)	Fe(1)–N(2)–O(2)	167.6 (4)
P(2)–Fe(2)–N(4)	102.7 (2)	Fe(2)–N(3)–O(3)	173.0 (6)
P(2)–Fe(2)–C(1)	125.5 (2)	Fe(2)–N(4)–O(4)	178.1 (5)
N(3)–Fe(2)–N(4)	121.5 (3)	Fe(1)–C(1)–Fe(2)	87.9 (1)
N(3)–Fe(2)–C(1)	103.3 (2)		

The two $Fe(NO)_2$ groups are bridged by a methylene ligand and a tetraphenyldiphosphine. The average Fe–N and N–O distances are 1.65 [1] and 1.17 [2] Å, respectively, comparable within experimental errors with those of **1**. The Fe–N–O groups are linear (bond angles ranging from 173.0 (6) to 178.1 (5)°), with the greatest deviation for the Fe–N(2)–O(2) angle which is 167.6 (4)°. The two Fe–C and the two Fe–P bond lengths are slightly different: Fe(1)–C(1) = 1.979 (3), and Fe(2)–C(1) = 1.953 (5) Å; Fe(1)–P(1) = 2.288 (1) and Fe(2)–P(2) = 2.267 (1) Å. The Fe–C distances are in the range of values found in Fe–C(μ-alkylidene) compounds (1.92 (6)–2.083 (5) Å).[18,32] The Fe–P distances are comparable with the Fe–P(2) distances in **1**. The P–P bond distances of 2.179 (1) Å is shorter than that in the free ligand Cy_2PPCy_2 (2.215 (3) Å,[33] but in the range found for compounds containing P–P bonds, 2.17–2.24 Å.[34]

The Fe–P–P–Fe ring is puckered, with a torsion angle around the P–P bond of 34.0°, attributable to nonbonded steric interactions. The Fe–Fe bond distance of 2.730 (1) Å is about 0.1 Å shorter than in **1**, reflecting the different

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electronic environments of the metal atoms in the two compounds.

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Supplementary Material Available: Listings of structure factors for complexes 1 and 3 (30 pages). Ordering information is given on any current masthead page. Listings of temperature factors and hydrogen atom coordinates for 1 and 3 are given in the supplementary material provided with ref 3.

Functional Trimethylphosphine Derivatives. 24.[†] (Phosphinomethyl)aluminum Compounds: Bis- and Tris(dimethylphosphino)methyl Ligands in Tetrahedral and Octahedral Aluminum Phosphine Complexes and X-ray Structure of $Al[(PMe_2)_2C(SiMe_3)]_3$

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The bis- and tris(phosphino)methanides $Li[CX(PMe_2)_2]$ (**5a,b**) react with Me_2AlCl to give the tetrahedral, monomeric phosphine complexes $Me_2Al[(PMe_2)_2CX]$ (**6a,b**) (**a**, X = PMe_2; **b**, X = $SiMe_3$) with the four-membered chelate rings AlPCP. **6a,b** disproportionate in solution to $AlMe_3$ and the homoleptic complexes $Al[(PMe_2)_2CX]_3$ (**7a,b**) with hexacoordinated aluminum (AlP_6). **7a,b** are also obtained directly from $AlCl_3$ and **5a,b**. In contrast, the sterically less hindered bis(phosphino)methanide $Li[CX(PMe_2)_2]$ (**2**, X = H) yields $\{Me_2Al[CX(PMe_2)_2]\}_n$ (**4**) with Me_2AlCl. **4** exists in solution as an equilibrium mixture of dimeric (six-membered ring, AlCPAlCP, $n = 2$) and monomeric (three-membered ring, AlCP, $n = 1$) species. **4** forms aluminates with LiMe ($[Me_3AlCH(PMe_2)_2Li(TMEDA)_{3/2}]$ (**8**)) and **2** ($\{Me_2Al[CH(PMe_2)_2]_2Li(OEt_2)_2\}$ (**9**)). In **8**, the aluminate acts as a monodentate phosphine ligand to Li, whereas in **9** each of the two bis(phosphino)methyl groups acts as a monodentate ligand to Li, thus forming a six-membered ring (LiPCAlCP). The characterization of the compounds is based on ^1H, ^{13}C, ^{31}P, and ^{27}Al NMR as well as on an X-ray structure determination of **7b**. Crystals of **7b** are rhombohedral of space group $R\bar{3}c$ with $a = b = 12.964$ (2) Å, $c = 43.575$ (5) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 6342.3$ Å^3, and $d_{calcd} = 1.019$ g/cm^3 for $z = 6$ at 22 °C. Crystals of **7b** are rhombohedral of space group $R\bar{3}c$ with $a = b = 12.964$ (2) Å, $c = 43.575$ (5) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 6342.3$ Å^3, and $d_{calcd} = 1.019$ g/cm^3 for $Z = 6$ at 22 °C. Refinement converged at $R_w = 0.069$ for 67 refined parameters and 898 observables ($F_o \geqslant 4.0\ \sigma(F_o)$). **7b** is a trischelate with the ligands bound exclusively by Al–P bonds (Al–P = 2.495 (2) Å). Crystallographic D_3 symmetry is imposed on the molecule. The AlP_6 coordination geometry is almost halfway between octahedral and trigonal prismatic as manifested by a trigonal twist angle of 35.9° which compares with 60° for a regular octahedron and 0° for regular TP geometry. The observed distortion is induced by the small ligand bite.

Introduction

The ambidentate nature of phosphinomethanide anions I is well-documented. Depending on the nature of the

$[CH_2PR_2]^-$	$[CH(PR_2)_2]^-$	$[C(PR_2)_3]^-$
I	II	III

electrophile and on the reaction conditions, reaction is observed at either the carbon or the phosphorus atom or at both ligand sites simultaneously.[1] On going from I to II and III, i.e., with increasing number of phosphino substituents at the carbanion, its nucleophilicity should decrease both for steric and electronic reasons, thus favoring P reactivity. It was this argument, which led to the central role of phosphinomethanides in a new concept for the preparation of main group element phosphine complexes.[2] Within this concept, the anionic charge of the phosphine ligand proved to be a key for the accessibility of neutral, halogen-free and, in some cases, homoleptic phosphine complexes of main group elements. Thus, in the reaction of III with $SnCl_2$, neutral monomeric phosphine complexes of Sn(II) were obtained.[3] These reactions also revealed the dominant role of steric effects in compounds with phosphinomethanide ligands. In contrast to Sn(II) (soft metal/soft P donor), the hard metal center Al(III) is less

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[†] Part 23: see ref 2. Also part 6 of the series: Phosphine Complexes of Main Group Elements. Part 5: see ref 3b.

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