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Reactions of lithium bis(μ-phenylphosphido)-bis(tricarbonyliron), $(\mu\text{-PhPLi})_2\text{Fe}_2(\text{CO})_6$, with organic halides. A novel anionic rearrangement of a chelating diphosphido ligand

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Abstract

Reactions of $(\mu\text{-PhPLi})_2\text{Fe}_2(\text{CO})_6$ with various organic mono- and di-halides resulted in alkylation of the phosphorus atoms. The use of α,ω-dihalides gave products with an organic bridge between the two phosphorus atoms. Deprotonation of the complex where the organic bridge is an *o*-xylylene group at −20 °C gives an anion (**16**) which undergoes a novel rearrangement via intramolecular attack at an iron atom to produce **19**.

Introduction

In a previous paper [1] we have described the chemistry of the dianion obtained by cleavage of the S–S bond of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ with LiBEt_3H. Reactions with diverse organic mono- and di-halides, inorganic and organometallic halides were reported. In the context of this research, the phosphorus analogs of $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]^{2-}$, complexes of the type $[(\mu\text{-RP})_2\text{Fe}_2(\text{CO})_6]^{2-}$, were of interest to us. Treichel and coworkers [2] had reported such species in 1972, prepared by the deprotonation of $(\mu\text{-RPH})_2\text{Fe}_2(\text{CO})_6$ ($\text{R} = \text{CH}_3$, Ph) complexes [3] with methyllithium in THF. They carried out only a limited study of the reactivity of the $(\mu\text{-PhPLi})_2\text{Fe}_2(\text{CO})_6$ complex toward two organic halides, iodomethane and 1,3-dibromopropane, obtaining the expected products, $(\mu\text{-PhPCH}_3)_2\text{Fe}_2(\text{CO})_6$ and $(\mu\text{-PhP(CH}_2)_3\text{PPh})\text{Fe}_2(\text{CO})_6$, respectively, in moderate yield.

We report here further studies of the chemistry of the $(\mu\text{-PhPLi})_2\text{Fe}_2(\text{CO})_6$ reagent which establish it to be rather less reactive than the sulfur analog, $(\mu\text{-LiS})_2\text{Fe}_2(\text{CO})_6$. Concurrent with our work, Stelzer and coworkers [4] carried out an independent investigation of the $[(\mu\text{-PhP})_2\text{Fe}_2(\text{CO})_6]^{2-}$ anion. Their interests, however, lay in other directions.

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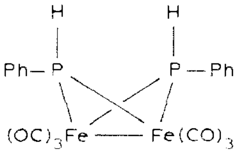
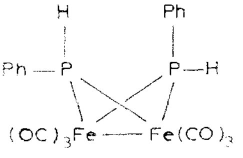
Results and discussion

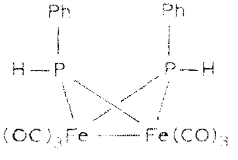
We were able to obtain reasonable (40–50%) yields of (μ-PhPH)$_2$Fe$_2$(CO)$_6$ using the procedure of Treichel et al. [3] provided that the yellow-orange crystals of this compound and its solutions were not exposed to air at any time. Stelzer et al. [4] developed a better, high-yield procedure which involved reaction of PhPH$_2$ with Fe(CO)$_5$ in octane solution at 100–105 °C. In either preparation, a mixture of three isomers (by ^{31}P NMR), **1a**, **1b** and **1c** (in 50/45/5 ratio by the Stelzer procedure), is



(**1a**)



(**1b**)

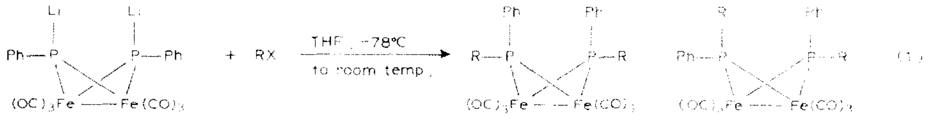


(**1c**)

formed. These isomers are configurationally stable in solution at room temperature. (Note, however, the previously reported [5] fluxional behavior of various (μ-R$_2$P)$_2$Fe$_2$(CO)$_6$ complexes which occurs above room temperature.)

The deprotonation of the **1a**, **1b**, **1c** mixture using CH$_3$Li as the base proceeded smoothly, as had been reported by Treichel et al. [2]. Stelzer and coworkers [4] found that the ^{31}P NMR spectrum of the (μ-PhPLi)$_2$Fe$_2$(CO)$_6$ reagent in THF or diethyl ether showed a temperature-invariant singlet at δ(P) 141.6 ppm and they proposed that the dianion has a planar structure in solution.

In our initial studies, we examined the reactions of (μ-PhPLi)$_2$Fe$_2$(CO)$_6$ with some simple organic halides (eq. 1). These reactions of the lithium phosphide

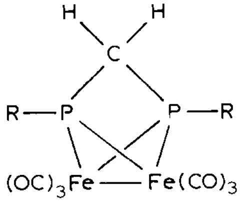


(**2a**) (**2b**)

(**2a**, **2b**: R = CH$_3$, X = I, 95% yield, **a**/**b** = 1.4;
R = PhCH$_2$, X = Br, 98% yield, **a**/**b** = 1.1;
R = CH$_2$=CHCH$_2$, X = Br, 96% yield, **a**/**b** ~ 20)

reagent with the organic halides were accompanied by a color change from red to yellow or orange. Workup by column chromatography and recrystallization gave the products as yellow or yellow-orange, air-stable solids. As indicated in eq. 1, two isomers were present. Isomer ratios were determined by ^{31}P NMR spectroscopy. Assignment of the symmetrical isomers as the axial, axial diphenyl species is based on an unpublished X-ray crystal structure determination of the **2a** isomer (R = CH$_3$) by Dahl and Huntsman [6]. Alternately, the [(μ-PhP)$_2$Fe$_2$(CO)$_6$]$^{2-}$ ion may be generated in situ. In one such reaction, in which a mixture of the (μ-PhPH)$_2$Fe$_2$(CO)$_6$ isomers and iodomethane in THF solution was treated with triethylamine at room temperature, the product yield (**2a**/**2b** (R = CH$_3$) = 0.93) was 99%.

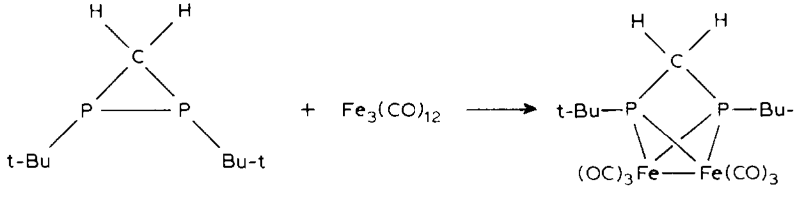
Of greater interest were the reactions of α,ω-dihalides with (μ-PhPLi)$_2$Fe$_2$(CO)$_6$. We were not able to prepare RPCH$_2$PR-bridged Fe$_2$(CO)$_6$ complexes, **3**, by reaction of CH_2I_2 with $(\mu\text{-RPLi})_2Fe_2(CO)_6$. This reaction was not straightforward,



(**3a** : R = Ph ;
3b : R = t-Bu)

giving as the only isolable product $(\mu\text{-PhPCH}_3)_2Fe_2(CO)_6$ (two isomers) in 13% yield. Possibly, an electron transfer process is involved in this conversion.

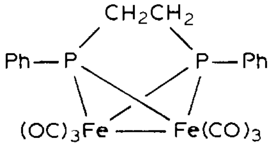
We were able to prepare the desired $RPCH_2PR$-bridged (R = t-Bu) complex, **3b**, by an alternate route as shown in eq. 2. Unfortunately, the yield of **3b** after workup was only 10% and this precluded study of its potentially interesting reactivity.



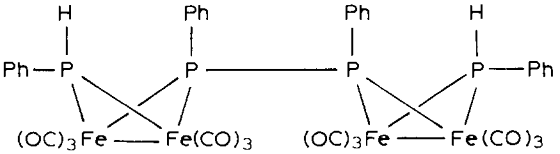
(**3b**)

(2)

The reaction of $(\mu\text{-PhPLi})_2Fe_2(CO)_6$ with 1,2-dibromoethane in diethyl ether resulted in formation of two products: the ethylene-bridged complex, **4**, in 23% yield and the P–P coupled "dimer", **5**, whose structure was confirmed by its ^1H and ^{31}P



(**4**)



(**5**)

NMR spectra and its combustion analysis and field desorption mass spectrum. The reaction of organophosphide anions with 1,2-dibromoethane to give P–P bonded products is a well-known reaction [7], and we had hoped that such P–P bond formation would occur intramolecularly [8*]. Formation of a second P–P bond after the first had coupled two molecules together was not observed, possibly because the "right" isomer for such coupling was not present. In any case, the intermediate dianion **5** (P–Li in place of P–H) either abstracted hydrogen from the solvent or, more likely, was converted to **5** during workup by column chromatography.

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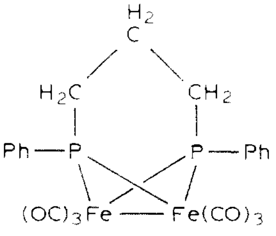
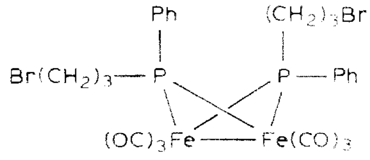
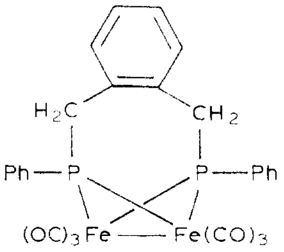
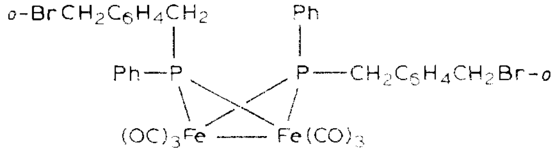
* Reference numbers with asterisks indicate notes in the list of references.

A similar reaction of $(\mu\text{-PhPLi})_2Fe_2(CO)_6$ with 1,3-dibromopropane gave, as reported earlier by Treichel et al. [2], the trimethylene-bridged compound **6** in 33% yield [9*]. The major product, however, was the unbridged species **7**. That the particular isomer shown was present was demonstrated by its 250 MHz proton NMR spectrum which showed six separate multiplets for the six different CH_2 groups. In similar manner, $(\mu\text{-PhPLi})_2Fe_2(CO)_6$ reacted with α,α'-dibromo-*o*-xylene to give both a bridged (**8**) and an unbridged (**9**) product in yields of 37% and 25%, respectively. These products also were prepared in comparable yield by the reaction of $(\mu\text{-PhPH})_2Fe_2(CO)_6$ with α,α'-dibromo-*o*-xylene in the presence of triethylamine. The fact that both bridged and unbridged products can be obtained from this reaction as well as from that with 1,3-dibromopropane would seem to suggest that the initial interaction of these difunctional electrophiles with $(\mu\text{-PhPLi})_2Fe_2(CO)_6$ can occur so as to given two intermediates, one in which the organic fragment derived from the electrophile is in the axial position relative to the cluster framework, and one in which it is in the equatorial position. The axially-substituted intermediate can then react in an intramolecular fashion to give the bridged product. The intermediate with the equatorially-substituted haloalkyl group cannot undergo this type of reaction, and instead reacts with a second equivalent of electrophile to give the disubstituted product. This site-specific reactivity is also observed in the reactions of $(\mu\text{-PhPH})_2Fe_2(CO)_6$ with electrophilic olefins and acetylenes and more conclusive evidence for this type of mechanism will be presented in a later paper.


(**6**)


(**7**)


(**8**)


(**9**)

A third synthesis of **8** which avoided formation of by-product **9** involved the in situ preparation of α,α'-bis(phenylphosphino)-*o*-xylene (**10**) by reaction of PhPHK with α,α'-dibromo-*o*-xylene in xylene solution, followed by addition of an excess of

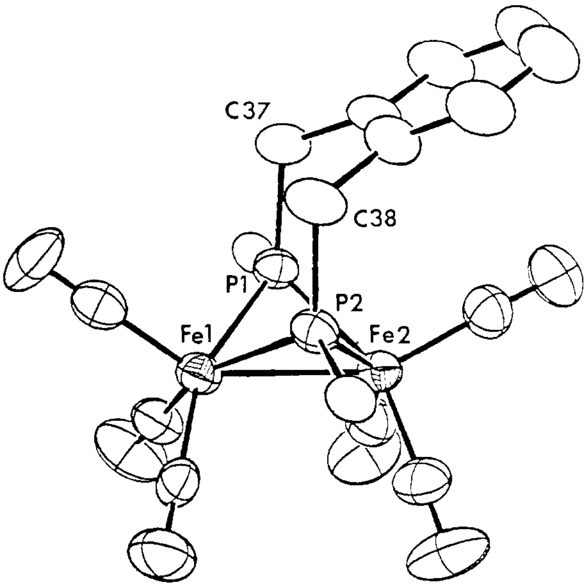
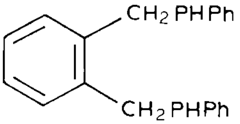
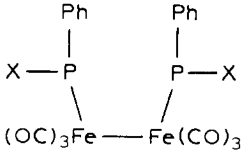


Fig. 1. Molecular structure of compound **8** (ref. 10).



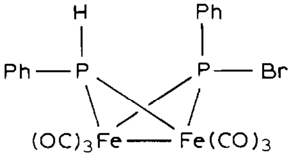
(**10**)



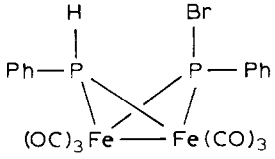
(**11a** : X = Cl ;
11b : X = Br)

$Fe_2(CO)_9$. This mixture was heated at reflux for several days; subsequent workup gave **8** in 40% yield. The structure of **8** was confirmed by X-ray crystallography (Fig. 1) [10].

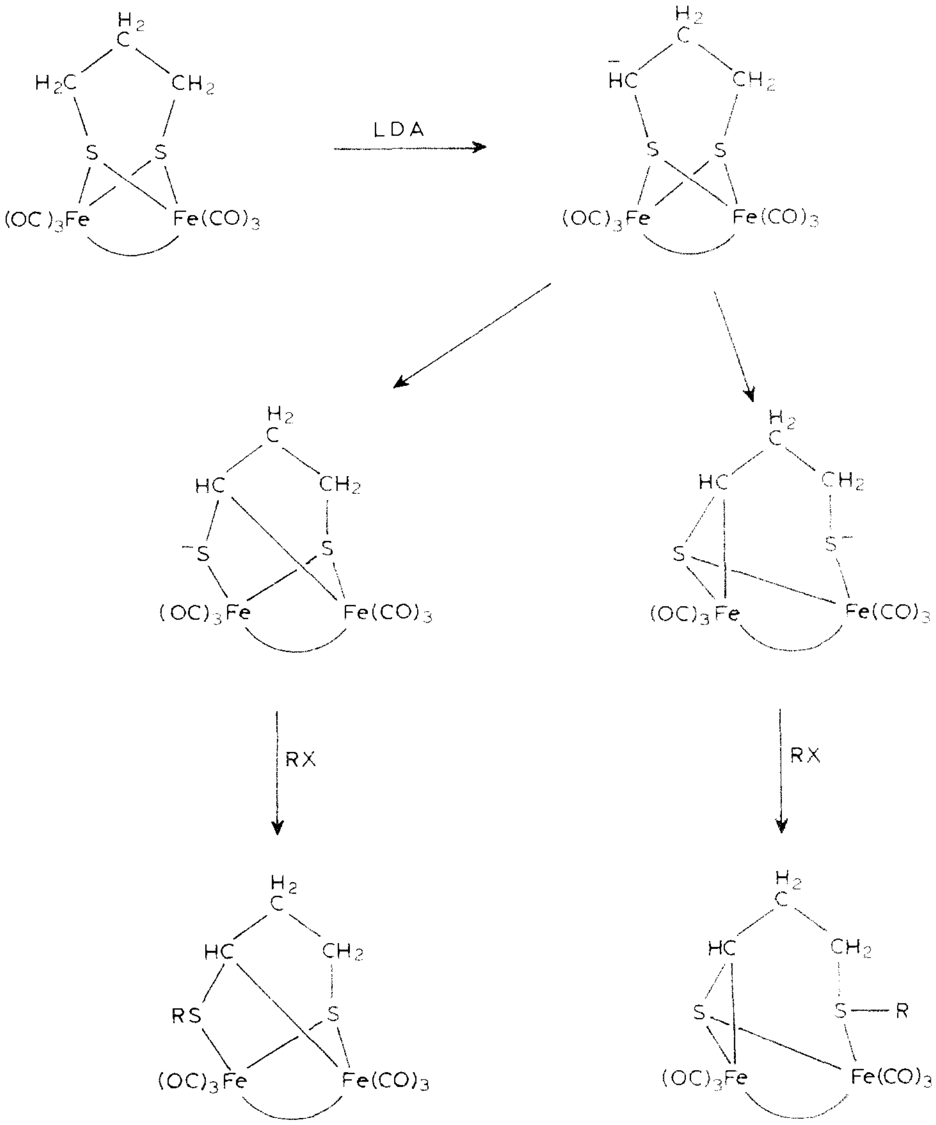
Also investigated were the reactions of $(\mu\text{-}PhPH)_2Fe_2(CO)_6$ with CCl_4 and CBr_4 (although radical, not anionic intermediates are involved), since such reactions should provide a facile access to complexes of the type $(\mu\text{-}PhPX)_2Fe_2(CO)_6$. The conversion $>$P–H + $CX_4 \rightarrow >$P–X represents a known synthesis of phosphorus halides [11]. The reaction of $(\mu\text{-}PhPH)_2Fe_2(CO)_6$ with an excess of CCl_4 at room temperature gave the dichloro compound **11a** in 82% yield. This compound has been prepared by De by the reaction of $PhPCl_2$ with $Fe(CO)_5$ and its structure was determined by X-ray crystallography [12]. In similar fashion, $(\mu\text{-}PhPH)_2Fe_2(CO)_6$ reacted with an excess of CBr_4 to give a mixture of **11b** and the unsymmetrical isomer (axial,equatorial diphenyl). When only one molar equivalent of CBr_4 was used in such a reaction, a mixture of **12a** and **12b** resulted in 75% yield.



(**12a**)



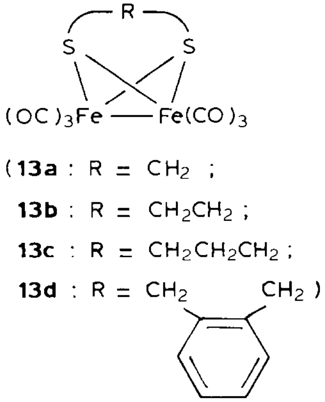
(**12b**)



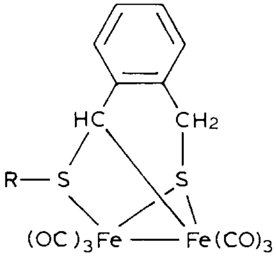
Scheme 1

An investigation of the deprotonation of the *o*-xylylidene-bridged complex **8** proved to be of some interest. In a separate study [13], we investigated the deprotonation of similar $Fe_2(CO)_6$ complexes containing organosulfur ligands, **13**, and found that anionic rearrangements occurred with **13a**, **13c** and **13d**. Scheme 1 shows the chemistry which occurred in the case of **13c**. In the case of **13d**, the anionic rearrangement resulted in formation of **14**.

Treatment of a solution of **8** in THF at −78 °C with a molar equivalent of n-butyllithium resulted in a color change from yellow to dark green. Addition of an excess of iodomethane caused an immediate color change back to yellow. The

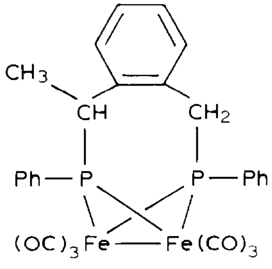


(**13a** : R = CH_2 ;
13b : R = CH_2CH_2 ;
13c : R = $CH_2CH_2CH_2$;
13d : R = CH_2 CH_2)

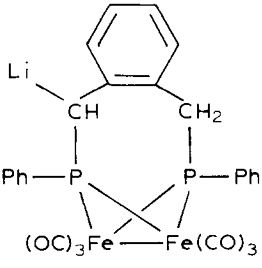


(**14**)

product which was isolated in 92% yield was not the rearrangement product analogous to **14**, rather it was **15**, i.e., the C-methylated, diastereomeric unrearranged product. Thus under these reaction conditions the lithium reagent **16** is



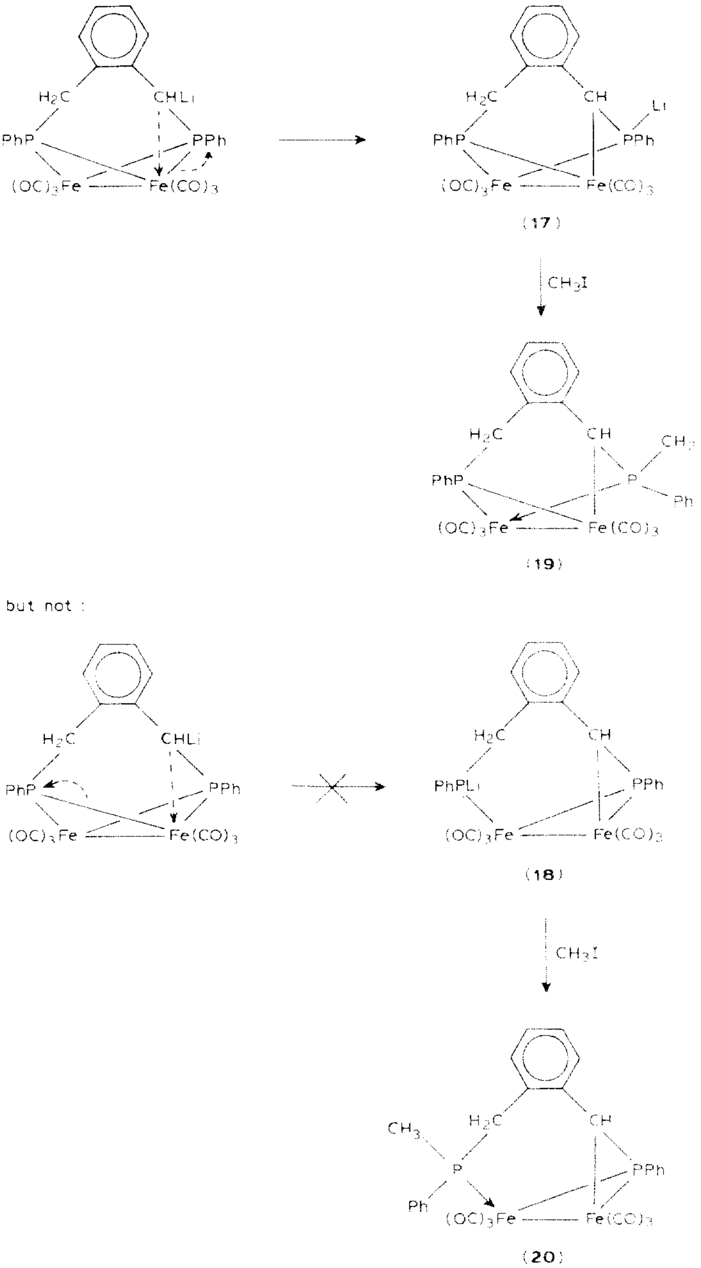
(**15**)



(**16**)

stable. In another experiment, the n-BuLi/**8** reaction mixture was warmed to −20 °C; this resulted in a green-to-red color change. As before, an excess of iodomethane was added (at −78 °C). A gradual color change to orange-red was noted as the reaction mixture was warmed to room temperature. The product of this reaction was not **15**, but was isomeric with **15**, so at higher temperature (−20 °C vs. −78 °C) the anionic rearrangement observed in the case of the sulfur analog **13d** must have taken place.

In principle, two different anionic products could be expected of such a rearrangement (Scheme 2), depending on which Fe–P bond is cleaved in the process, **17** or **18**. These, on reaction with CH_3I, would give the P-methyl derivatives **19** and **20**, respectively. The former, **19**, was considered as the more likely since it did not contain a strained three-membered ring, but the IR and NMR spectra did not distinguish conclusively between the two possibilities. In the proton NMR spectra of the methylated rearrangement product the methine and methyl proton resonances were not coupled to one another as they are in the spectrum of **15** and the methine



Scheme 2

proton in the NMR spectrum of the methylated rearrangement product was coupled to both phosphorus nuclei. The ^{31}P NMR spectrum of this product showed an AX quartet at 30.8, 182.5 ppm with a $J(P-P)$ coupling of only 19.5 Hz. The signal at 30.8 ppm is at far too high field to be assigned to a phosphido bridge between two metal centers and, in fact, is in the range where metal-coordinated tertiary phos-

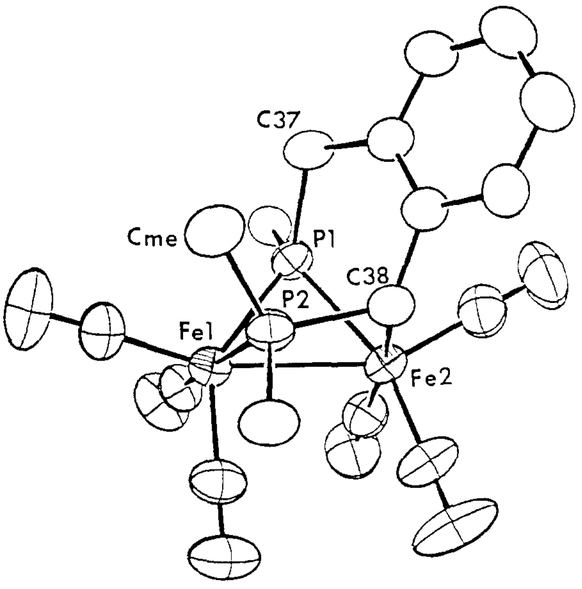


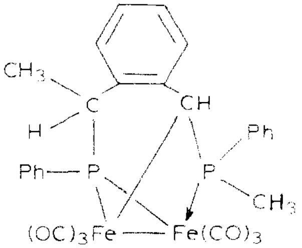
Fig. 2. Molecular structure of compound **19** (ref. 10).

phine resonances appear [14]. The small coupling constant indicates a decreased sharing of common metal *d* orbitals between the two phosphorus atoms. Both the ^{1}H and ^{31}P NMR spectra showed the presence of a single isomer, indicating that this reaction is both chemoselective and diastereoselective.

An X-ray diffraction study [10] conclusively proved the rearranged methylation product to be the more likely **19** (Fig. 2). In this structure one of the phosphido bridges in **8** has been replaced by what may be regarded as a bridging phosphaalkene ($Ph(CH_3)P{=}CHR$) unit. In line with this idea, we note that the P(2)–C(38) distances in **8** and in **19** are 1.876(9) and 1.820(4) Å, respectively [10], i.e., this P–C distance has become markedly shorter in the rearranged methylation product. In fact, this distance, 1.820(4) Å, is essentially the same as the observed P–C distance (1.814(4) Å) in an η^2-phosphaalkene complex of platinum(0), $(Ph_3P)_2Pt[2,6\text{-}(CH_3)_2C_6H_3P{=}C_{12}H_8]$ [15].

In addition to **19**, two other derivatives were prepared by treating anion **17** with iodoethane and with allyl bromide. In these reactions one equivalent of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was added to the reaction mixture after addition of the halide at −78 °C. This appeared to accelerate the reaction and it also resulted in precipitation of the lithium halide as the TMEDA complex.

The reaction of complex **19** with n-butyllithium also was investigated to see if a second anionic rearrangement could be induced. At −78 °C, a dark green solution resulted when n-butyllithium was added to a yellow THF solution of **19**. The yellow color was regenerated when an excess of iodomethane was added at −78 °C and the product, which was isolated in 95% yield, was **21**. This complex exists as a 1/1 mixture of two diastereomers as evidenced by its ^{1}H and ^{31}P NMR spectra. There



(21)

was spin–spin coupling between the carbon-bonded CH_3 protons and the methine proton adjacent to the phosphido group, indicating that deprotonation of the CH_3 group of **19** had occurred. Warming such a green solution to room temperature produced a color change to orange-red. However, the addition of CH_3I and the usual workup gave a yellow oil which TLC showed to contain three new products. These could not be resolved by column chromatography or fractional crystallization.

In conclusion, we have shown that the facile anionic intramolecular rearrangement observed in the case of the sulfur ligand complexes **13a**, **13c** and **13d** also occurs in the case of the deprotonation product of **8**, the PhP analog of **13d**. However, both the unrearranged *C*-methylated as well as the rearranged *P*-methylated products can be isolated, depending on the reaction temperature used.

While this rearrangement is novel for phosphido-bridged $Fe_2(CO)_6$ complexes, similar intramolecular attack at a metal atom by a carbanion generated in a neutral tertiary phosphine ligand has been reported previously [16].

Experimental

General comments

All reactions were carried out under an atmosphere of prepurified tank nitrogen unless otherwise stated. Tetrahydrofuran (THF), benzene and diethyl ether were distilled from sodium/benzophenone ketyl. Methylcyclohexane was distilled from lithium aluminum hydride. Reagent grade pentane, dichloromethane and carbon tetrachloride were deoxygenated by bubbling nitrogen through them for 15 min prior to use. Triethylamine and diethylamine were distilled from BaO before use. All other reagents were purified by appropriate methods. The progress of the reactions was monitored by thin layer chromatography (TLC) (J.T. Baker Silica Gel 1B). Since these reactions usually yielded products which could be separated easily, full scale chromatography was often not required. Instead, filtration chromatography, in which the reaction products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100 mesh silicic acid (ca. 100 ml) in a 350 ml glass-frit filter funnel, was used in some cases. The eluting solvent then was passed through with suction filtration.

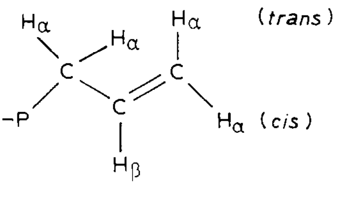
Infrared spectra were obtained using either a Perkin–Elmer Model 457A or 1430 double-beam grating spectrophotometer. Proton NMR spectra were recorded on a Varian Associates T60, Hitachi–Perkin–Elmer R-20B, JEOL-FX-90Q or Bruker WM-250 spectrometer. Proton chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Chloroform or dichloromethane generally was used as an internal standard. The ^{31}P NMR spectra were recorded on a JEOL FX-90Q spectrometer operating at 36.2 MHz in the Fourier transform mode. The spectrometer was locked externally on the deuterium signal of D_2O. The values are reported in δ(P) units ppm downfield from 85% aqueous H_3PO_4 using external Ph_3P (in the same solvent as the sample) as reference at -6.0 ppm. EI mass spectra were obtained with a Varian MAT-44 instrument operating at 40 or 70 eV or on a Finnigan 3200 instrument operating at 70 eV. Molecular ions were assigned on the basis of the most abundant natural isotope(s). FD mass spectra were obtained at the MIT Mass Spectrometry Facility using a MAT 731 spectrometer operating in the positive ion mode. Melting points were determined on analytically pure samples using a Büchi Capillary Melting Point Apparatus and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Organolithium reagents were purchased from Alfa Division, Morton Thiokol, organic halides from Aldrich. Phenylphosphine was prepared by $LiAlH_4$ reduction of phenyldichlorophosphine [17]. Bis(μ-phenylphosphido)bis(tricarbonyliron) (mixed **1a**, **1b**, **1c**) was prepared initially by the method of Treichel et al. [3], later by the method of Stelzer and coworkers [4]. The mixture of isomers was used in all subsequent reactions.

Reaction of (μ-PhPLi)$_2$Fe$_2$(CO)$_6$ with monohalides

In a dry box, a 200 ml round-bottomed, three-necked flask equipped with a stir-bar and serum caps was charged with 0.648 g (1.30 mmol) of (μ-PhPH)$_2$Fe$_2$(CO)$_6$. Tetrahydrofuran (THF), 50 ml, was added and the resulting solution was cooled to -78 °C. Subsequently, 1.80 ml (2.60 mmol) of 1.45 *M* $CH_3Li/LiBr$ in diethyl ether was added in four portions over a 15 min period, causing a yellow-to-red color change. To this solution was added 0.79 ml (9.10 mmol) of allyl bromide. The reaction mixture was stirred at -78 °C for 30 min and for 1 h at room temperature. The resulting orange solution was evaporated at reduced pressure to leave an orange solid. Column chromatography (silicic acid; elution with 20% CH_2Cl_2/pentane) gave 0.719 g (96% yield) of (μ-PhPCH$_2$CH=CH$_2$)$_2$Fe$_2$(CO)$_6$ (**2a**,**2b**, R = CH$_2$=CHCH$_2$) as an air-stable, yellow-orange solid, melting range 127–137 °C (sealed capillary) (from pentane). The ^{31}P NMR spectrum ($CDCl_3$) showed a singlet at δ(P) 125, consistent with the presence of the symmetrical isomer **2a**. Minor peaks in the spectrum indicated the presence also of ~ 5% of the other isomers.

Anal. Found: C, 49.54; H, 3.52. $C_{24}H_{20}O_6P_2Fe_2$ calcd.: C, 49.87; H, 3.49%. IR (CH_2Cl_2): ν(C=C) 1640, terminal CO, 2053(s), 2016(vs), 1982(s), 1968(s) cm^{-1}.



^{1}H NMR (250 MHz, $CDCl_3$): δ 2.97 (d of t, $J(H_\alpha-H_\beta)$ 7.35 Hz, $J(H_\alpha-H_\gamma)$ 4.6 Hz, 2H, CH_2CH=CH$_2$), 4.64 (d, $J(H_\beta-H_\gamma)$ 17 Hz, 1H, CH$_2$CH=CH_2 (*trans*-H)), 4.83 (d, $J(H_\beta-H_\gamma)$ 10 Hz, 1H, CH$_2$CH=CH_2 (*cis*-H), 5.32 to 5.52 (m, 1H, CH$_2$CH=CH$_2$), and 6.74 to 7.11 ppm (m, 5H, *Ph*P). Mass spectrum, *m/z* (rel. intensity): 578(2, M^+), 550 (3, M^+ − CO), 522(1, M^+ − 2CO), 494(2, M^+ − 3CO), 466(4, $M^+ -$ 4CO), 438(5, $M^+ -$ 5CO), 410(14, $M^+ -$ 6CO), 292(32, $C_6H_5C_3H_5P_2Fe_2$), 251(24, $C_6H_5P_2Fe_2$), 174(49, P_2Fe_2), 143(11, PFe_2), 112(15, Fe_2), 87(5, PFe), 56(100, Fe).

Prepared in similar manner were: $(\mu\text{-PhPCH}_3)_2Fe_2(CO)_6$, 1.4/1 **2a/2b** isomer mixture by ^{1}H and ^{31}P NMR, air-stable yellow solid, melting range 103–150 °C, in 95% yield.

IR (pentane), terminal CO region: 2054(s), 2015(vs), 1989(s), 1969(vs), 1961(m) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.78 (4 line pattern, J(P–H) 11.8 and 2.3 Hz, axial methyl of **2b**, 1.94 (t, J(P–H) 6 Hz, methyls of **2a**, 2.01 (4 line pattern, J(P–H) 11.8 and 3.3 Hz, equatorial methyl of **2b** and 6.77 to 7.68 ppm (complex m, *Ph*PMe); isomer ratio for **2a/2b** = 1.4. ^{31}P NMR ($CDCl_3$): δ(P) 124.2(s, isomer **2a**, 58.3%) and 132.3(s, isomer **2b**, 41.7%).

$(\mu\text{-PhPCH}_2\text{Ph})_2Fe_2(CO)_6$, 1.11/1 **2a/2b** isomer mixture, air-stable yellow solid, melting range 177–197 °C, in 98% yield.

Anal. Found: C, 56.61; H, 3.61. $C_{32}H_{24}O_6P_2Fe_2$ calcd.: C, 56.67; H, 3.57%. IR (pentane): terminal CO, 2052(s), 2016(vs), 1985(vs), 1972(vs), 1961(m), 1950(w), 1933(w) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.20 (d, J(P–H) 9 Hz, equatorial CH_2Ph in **2b**), 3.53 (t, J(P–H) 4 Hz, CH_2Ph of **2a**), 3.69 (d, J(P–H) 7 Hz, axial CH_2Ph of **2b**), 6.46–7.43 (Ph). ^{31}P NMR ($CDCl_3$): δ(P) 142.3 (s, isomer **2a**, 53%), 145.3 and 147.8 (AB quartet, J 129 Hz, isomer **2b**, 47%.

Reaction of $(\mu\text{-PhPLi})_2Fe_2(CO)_6$ with diiodomethane

Using the procedure above, the lithium reagent was prepared from 0.810 g (1.63 mmol) of $(\mu\text{-PhPH})_2Fe_2(CO)_6$. To the resulting red THF solution was added at −78 °C 0.13 ml (1.63 mmol) of CH_2I_2. The dark-red reaction mixture as stirred at −78 °C for 30 min and at room temperature for 16 h. Evaporation at reduced pressure was followed by extraction of the red-brown residue with boiling pentane. Evaporation of the extracts left a yellow-orange solid in an oil. Column chromatography (silicic acid) 10% CH_2Cl_2/hexanes gave a yellow band followed by several other minor bands. From the leading yellow band 0.117 g (13%) of $(\mu\text{-PhPCH}_3)_2Fe_2(CO)_6$ (1.11/1 **2a/2b** isomer mixture) was obtained. No other pure compounds were isolated.

Reaction of $(\mu\text{-PhPLi})_2Fe_2(CO)_6$ with 1,2-dibromoethane

To a solution of $(\mu\text{-PhPLi})_2Fe_2(CO)_6$ in Et_2O prepared as described above from 1.26 mmol of $(\mu\text{-PhPH})_2Fe_2(CO)_6$ was added 0.22 ml (2.52 mmol) of $Br(CH_2)_2Br$ by syringe. After it has been stirred for 0.5 h at −78 °C and 1 h at room temperature the solution was red-orange. Volatiles were removed in vacuo to give a red-brown, tarry residue which was extracted with 20% dichloromethane/petroleum ether until the washings were colorless. After filtration of the extracts and removal of solvent the orange-red residue was chromatographed on a silicic acid column. Elution with 10% CH_2Cl_2/hexanes yielded a yellow band, and 30% CH_2Cl_2/hexanes an orange band.

From the yellow band was isolated 0.152 g (0.29 mmol, 23%) of yellow crystals of $(\mu\text{-PhPCH}_2CH_2PPh)Fe_2(CO)_6$ (**4**), which was recrystallized from petroleum ether, m.p. 191–193 °C.

Anal. Found: C, 45.98; H, 2.80. $C_{20}H_{14}O_6Fe_2P_2$ calcd.: C, 45.85; H, 2.69%. IR ($CHCl_3$): terminal CO, 2052(s), 2013(s), 1990(vs), 1966(vs), cm^{-1}. ^{1}H NMR (90

MHz, $CDCl_3$): δ 2.15 (pseudo t, *J*(P–H) 1.9 Hz, $(CH_2)_2$, 4H) and 7.42–7.84 ppm (complex m, *Ph*P, 10H. ^{31}P NMR ($CHCl_3$): δ_p 165.4 ppm (s). Mass spectrum, *m/z* (relative intensity): 524 (36, M^+), 496 (31, $M^+ -$ CO), 468 (29, $M^+ -$ 2CO), 440 (37, $M^+ -$ 3CO), 412 (52, $M^+ -$ 4CO), 384 (54, $M^+ -$ 5CO), 356 (100, $M^+ -$ 6CO), 328 (92, $Ph_2P_2Fe_2$), 272 (44, Ph_2P_2Fe), 174 (56, P_2Fe), 56 (39, Fe).

The orange band gave 0.280 g (0.46 mmol, 37%) of orange crystals of **5**, which was recrystallized from CH_2Cl_2/petroleum ether. Anal. Found: C, 43.30; H, 2.39. $C_{36}H_{22}O_{12}Fe_4P_4$ calcd.: C, 43.51; H, 2.23%. Mass spectrum FD (24 mA, acetone) *m/z*: 994 (M^+) Calcd: 993.8. IR ($CHCl_3$): terminal CO, 2056(s), 2028(vs), 2000(m), 1988(sh), 1969(sh), cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 4.46, 5.95 (both five-line patterns, *J*(P(1)–H) 372.4 Hz, P*H*, 2H) and 7.18–7.89 (complex m, *Ph*P, 20H). ^{31}P NMR ($CHCl_3$): δ(P) 81.2, 148.5 ppm (both q, *J*(P(1)–H) 92.7 Hz, *J*(P(2)–H) 53.8 Hz).

Reaction of $(\mu$-$PhPLi)_2Fe_2(CO)_6$ with 1,3-dibromopropane

To a red THF solution of $(\mu$-$PhPLi)_2Fe_2(CO)_6$ prepared as above from 0.677 mmol of $(\mu$-$PhPH)_2Fe_2(CO)_6$ was added 0.41 ml (4.10 mmol, an excess) of $Br(CH_2)_3Br$ by syringe. After it had been stirred for 0.5 h at −78°C and 1 h at room temperature, the reaction mixture was orange-red. Volatiles were removed in vacuo to give a red-brown, tarry residue which was extracted with 30% dichloromethane/petroleum ether until the washings were colorless. After filtration of the extracts and evaporation of solvent, the orange-red residue was chromatographed on a silicic acid column. Elution with 20% CH_2Cl_2/hexanes separated a yellow band, and 40% CH_2Cl_2/hexanes an orange band.

From the first band was obtained 0.240 g (0.45 mmol, 33%) of yellow crystals of $(\mu$-$PhP(CH_2)_3PPh)Fe_2(CO)_6$ (**6**), which was recrystallized from pentane, m.p. 185–188°C, (lit. [2] 184–187°C). IR ($CHCl_3$): terminal CO, 2051(s), 2012(vs), 1985(vs), 1965(s), cm^{-1}.

^1H NMR (90 MHz, $CDCl_3$): δ 2.00 (m, $(CH_2)_3$, 6H) and 7.35–7.75 (complex m, *Ph*P, 10H). ^{31}P NMR ($CHCl_3$): δ(P) 130.2 ppm (s). Mass spectrum, *m/z* (relative intensity): 538 (20, M^+), 510 (24, $M^+ -$ CO), 482 (19, $M^+ -$ 2CO), 454 (24, $M^+ -$ 3CO), 426 (28, $M^+ -$ 4CO), 398 (23, $M^+ -$ 5CO), 370 (66, $M^+ -$ 6CO), 328 (22, $Ph_2P_2Fe_2$), 112 (50, Fe_2), 56 (100, Fe).

The orange band gave 0.483 g (0.65 mmol, 48%) of orange crystals of $(\mu$-$Br(CH_2)_3PPh)_2Fe_2(CO)_6$ (**7**), which was recrystallized from pentane, m.p. 96–97.5°C.

Anal. $C_{24}H_{22}O_6Fe_2P_2Br_2$ calcd.: C, 38.96; H, 3.00%. Found: C, 39.12; H, 3.10. IR ($CHCl_3$): terminal CO, 2060(s), 2019(vs), 1992(s), 1973(s), cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 0.95, 1.45, 1.90, 2.35 (all m, PCH_2CH_2, all 2H), 2.47 (t, *J*(H–H) 7.0 Hz, $BrCH_2$, 2H), 3.27 (t, *J*(H–H) 6.7 Hz, $BrCH_2$, 2H) and 7.37–7.63 ppm (complex m, *Ph*P, 10H). ^{31}P NMR ($CHCl_3$): δ(P) 141.3 ppm (s).

Reaction between (bis-μ-phenylphosphido)bis(tricarbonyliron) and α,α′-dibromo-o-xylene in the presence of triethylamine

In a dry box, a 500 ml Schlenk flask equipped with a stirbar and a serum cap was charged with 2.01 g (4.04 mmol) of $(\mu$-$PhPH)_2Fe_2(CO)_6$. THF (170 ml) was added and the resulting solution cooled to −78°C. α,α′-Dibromo-*o*-xylene (1.63 g, 6.20 mmol) was added as a solid against a counterflow of nitrogen. Next, 2.5 ml, (1.75

mmol, an excess) of Et_3N was added by syringe, causing an orange-to-red color change. After it had been stirred for 0.5 h at −78 °C and 12 h at room temperature, the solution was orange and contained a white precipitate. Solvent was removed on a rotary evaporator and the resulting brown tarry residue extracted with 50% CH_2Cl_2/petroleum ether. The extracts were filtered through a short plug of silicic acid and the solvent removed on a rotary evaporator to yield an orange crystalline solid. Chromatography (silicic acid, 30% CH_2Cl_2/petroleum ether) separated first a yellow and then an orange band.

From the yellow band was isolated 1.113 g (1.85 mmol, 46%) of (μ-$PhPCH_2C_6H_4CH_2PPh)Fe_2(CO)_6$ (**8**), which was recrystallized from pentane, m.p. 242–244 °C.

Anal. Found: C, 52.08; H, 3.10. $C_{26}H_{18}O_6Fe_2P_2$ calcd.: C, 52.04; H, 3.02%. IR ($CHCl_3$): terminal CO, 2047(s), 2010(vs), 1983(s), 1967(s), cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 3.11–3.68 (broad m, CH_2, 4H), and 7.02–7.73 ppm (complex m, *Ph*P and $CH_2C_6H_4CH_2$, 14H). ^{31}P NMR ($CHCl_3$): δ(P) 136.2 ppm (s).

The orange band yielded 0.873 g (1.01 mmol, 25%) of (*o*-$BrCH_2C_6H_4CH_2PPh)_2Fe_2(CO)_6$ (**9**), which was recrystallized from CH_2Cl_2/petroleum ether, m.p. 144–146 °C.

Anal. Found: C, 47.63; H, 3.16. $C_{34}H_{26}O_6Fe_2P_2Br_2$ calcd.: C, 47.26; H, 3.03%. IR ($CHCl_3$): terminal CO, 2050(s), 2006(vs), 1981(s), 1962(s), cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 2.27 and 3.85 (both d, *J*(P–H) 9.91, 7.4 Hz, respectively, *a*- and *e*- PCH_2, 4H), 3.23 and 3.64 (both s, *a*- and *e*-$BrCH_2$, 4H), and 6.68–7.72 ppm (complex m, *Ph*P and $CH_2C_6H_4CH_2$, 14H). ^{31}P NMR ($CHCl_3$): δ(P) 141.2, 145.7 ppm (AB quartet, *J*(P–P) 129.0 Hz).

Reaction between potassium phenylphosphide and α,α′-dibromo-o-xylene, followed by reaction of the product with diiron nonacarbonyl

In a dry box, a 200 ml Schlenk flask was charged with 2.46 g (16.6 mmol) of PhPHK (prepared by the method of Issleib and Jacob [18]) and 30 ml of THF and the resulting slurry was cooled to −20 °C. A solution of *a,a′*-dibromo-*o*-xylene (2.20 g, 8.3 mmol) in 20 ml of THF was added through a small-bore cannula, causing a color change from yellow-orange to colorless. The resulting solution was stirred for 30 min at room temperature. Subsequently, the solvent was removed at reduced pressure and the residue was extracted with 60 ml of toluene. The toluene extracts were filtered through a pad of Celite. Examination by ^{31}P NMR spectroscopy showed the presence of one major product (δ(P) −28.5) and two minor ones (δ(P) −47.6 and −124.9, the latter due to $PhPH_2$). The toluene solution was added under nitrogen to a 200 ml three-necked flask (equipped with a stir-bar, a reflux condenser, a gas inlet/outlet tube and a rubber septum) which contained 5.0 g (13.7 mmol) of $Fe_2(CO)_9$ and the mixture was heated at reflux for 4 days. A small amount of silicic acid was added to the flask and volatiles then were removed at reduced pressure. The residue was extracted with 10% CH_2Cl_2/petroleum ether and the extract submitted to filtration chromatography (silicic acid). Elution with 30% CH_2Cl_2/petroleum ether gave a yellow band from which 1.98 g (40%) of complex **8**, m.p. 242–244 °C (dec), was isolated.

Reaction between (bis-μ-phenylphosphido)bis(tricarbonyliron) and iodomethane in the presence of triethylamine

In a dry box, a 200 ml flask equipped with a stir-bar and a serum cap was charged with 0.620 g (1.245 mmol) of (μ-PhPH)$_2$Fe$_2$(CO)$_6$. THF (50 ml) and 0.47 ml (7.47 mmol, 6 ×) of MeI (Aldrich) were added. Subsequently, 0.87 ml (6.23 mmol, 5 ×) of Et$_3$N (Baker) was added over a 2 min period by syringe causing a yellow-to-red color change. After the reaction mixture had been stirred for 0.5 h, the solution became yellow and contained a white solid (Et$_3$NH$^+$ I$^-$). This solution was filtered, and then solvent was removed on a rotary evaporator, leaving an orange solid. This solid was chromatographed (silicic acid/20% CH$_2$Cl$_2$/pentane) to give 0.650 g (1.23 mmol, 99% yield) of (μ-CH$_3$PPh)$_2$Fe$_2$(CO)$_6$, as an air-stable, yellow solid, melting range 102–159 °C. It was identified by comparison of its IR and ^{31}P NMR spectra (**2a**/**2b** 0.93) with those of an authentic sample.

In situ reaction between 1,2-di-butyl-1,2-diphosphirane and triiron dodecacarbonyl

1,2-Di-t-butyl-1,2-diphosphirane was prepared according to the method of Baudler and Saykowski [19] in the presence of Fe$_3$(CO)$_{12}$. In a dry box, a 200 ml three-necked, round-bottomed flask equipped with a stir-bar, a dropping funnel and a reflux condenser was charged with 1.34 g (4.6 mmol) of K$_2$(t-BuP)$_2$ · 0.5 THF and 1.0 g (1.98 mmol) of Fe$_3$(CO)$_{12}$. Methylcyclohexane (30 ml) was added by syringe and the reaction mixture was cooled to 0 °C. A solution of CH$_2$Cl$_2$ (0.43 ml, 6.71 mmol, an excess) in 20 ml of methylcyclohexane was transferred to the dropping funnel and added to the reaction solution over a period of 40 min. The reaction mixture then was stirred for 14 h at room temperature and 2 h at reflux. The brown mixture was cooled to room temperature, filtered through a short pad of silicic acid, and the solvent was removed to give a red-brown gum. Chromatography (silicic acid, 2.5 × 30 cm, pentane) yielded a bright yellow band. After removal of solvent, the ^{31}P NMR spectrum (in CHCl$_3$ solution) of the resulting yellow solid showed it to be a mixture of a product with δ(P) 115.8 ppm (s) and (t-BuP)$_4$ (δ(P) -57.1 ppm). The product was dissolved in a mixture of 5 ml of benzene and 5 ml of Et$_2$O (under nitrogen) and 3.0 ml (a large excess) of CH$_3$I was added [20*]. The resulting solution then was stirred for 3 days at room temperature, after which time the reaction mixture had become quite cloudy. Volatiles were removed in vacuo, the residue dissolved in pentane and filtered through a pad of silicic acid. After removal of solvent, the ^{31}P NMR spectrum showed only a trace of (t-BuP)$_4$ remaining. By this method, 0.1455 g (0.31 mmol, 10%) of yellow crystals of μ-[CH$_2$(t-BuP)$_2$]Fe$_2$(CO)$_6$ (**3b**) was obtained, m.p. 150–152 °C (pentane). Anal. Found: C, 38.38; H, 4.35. $C_{15}H_{20}O_6Fe_2P_2$ calcd.: C, 38.34; H, 4.29%. IR (CHCl$_3$): 3040(br), 2435(m), 1515(w), 1417(m), 1365(w), 1234(w), 1175(m), 1037(m), 928(m), 805(w), 606(m) cm^{-1}. Terminal carbonyl region: 2042(s), 2000(vs), 1973(s), 1954(s), 1940(sh) cm^{-1}. ^{1}H NMR (90 MHz, CDCl$_3$): δ 1.23 (t, J(P–H) 9.8 Hz, t-C$_4H_9$, 18H) and 3.95 ppm (t, J(P–H) 12.0 Hz, CH_2, 2H). ^{31}P NMR (CHCl$_3$): δ(P) 115.8 ppm(s).

Reaction between (bis-μ-phenylphosphido)bis(tricarbonyliron) and carbon tetrachloride

A 200 ml Schlenk flask equipped with a stir-bar and a serum cap was charged with 0.566 g (1.14 mmol) of (μ-PhPH)$_2$Fe$_2$(CO)$_6$. Methanol (110 ml) and CCl$_4$ (5 ml, an excess) were added and the resulting solution was stirred overnight at room temperature to give an orange solution with a small amount of yellow precipitate. Volatiles were removed in vacuo and the yellow-orange residue redissolved in pentane and chromatographed (silicic acid/pentane). Elution with 30% CH$_2$Cl$_2$/pentane yielded a yellow-orange band which, upon removal of solvent, gave 0.526 g

(0.93 mmol, 82%) of $(\mu\text{-PhPCl})_2Fe_2(CO)_6$ (**11a**), as air-stable yellow crystals, m.p. 176–178 °C (sealed capillary) (from pentane).

Anal. Found: C, 38.14; H, 1.81. $C_{18}H_{10}Cl_2Fe_2O_6P_2$ calcd.: C, 38.14; H, 1.78%. IR (CH_2Cl_2): terminal CO, 2075(s), 2047(vs), 2020(s), 1991(s), cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.75–8.0 ppm (m, *Ph*P). ^{31}P NMR ($CHCl_3$), δ(P) 245.5 ppm (s) (lit. [12] δ(P) 245.2 ppm (acetone)). Mass spectrum, *m/z* (relative intensity): 567 (7, M^+), 539 (2, $M^+ - CO$), 511 (13, $M^+ - 2CO$), 483 (24, $M^+ - 3CO$), 455 (7, $M^+ - 4CO$), 427 (99, $M^+ - 5CO$), 399 (100, $M^+ - 6CO$).

An alternate synthesis of **11a** used the reaction of $(\mu\text{-PhP})_2Fe_2(CO)_6$ with *N*,*N*-dichlorocyclohexylamine.

A solution of $(\mu\text{-PhPLi})_2Fe_2(CO)_6$ was prepared as described above from 1.04 mmol of $(\mu\text{-PhPH})_2Fe_2(CO)_6$ in diethyl ether at −78 °C. To the red solution of this reagent (at −78 °C) was added by cannula a solution of 0.25 ml (1.77 mmol) of $C_6H_{11}NCl_2$ in 15 ml of Et_2O and the resulting solution was stirred for 0.5 h at −78 °C and 1 h at room temperature. Volatiles were removed on a rotary evaporator and the residue chromatographed (silicic acid/pentane). 10% CH_2Cl_2/pentane eluted a bright yellow band which, upon removal of solvent, gave 0.357 g (0.63 mmol, 71%, based on available $C_6H_{11}NCl_2$) of $(\mu\text{-PhPCl})_2Fe_2(CO)_6$ (**11a**), which, after recrystallization from pentane, was identified by comparison of its melting point and ^{31}P and infrared spectra with those of an authentic sample (prepared by reaction of $(\mu\text{-PhPH})_2Fe_2(CO)_6$ and CCl_4 as described above).

Reaction of bis(μ-phenylphosphido)bis(tricarbonyliron) with carbon tetrabromide

(a) 1/2 molar ratio. A 200 ml Schlenk flask equipped with a stir-bar and a serum cap was charged with 0.643 g (1.29 mmol) of $(\mu\text{-PhPH})_2Fe_2(CO)_6$. Dichloromethane (40 ml) was added to give an orange solution to which was added 0.870 g (2.62 mmol) of CBr_4 as a solid against a counterflow of nitrogen. The resulting solution was stirred overnight at room temperature to give an orange solution with a small amount of yellow precipitate. Pentane (150 ml) was added and the orange solution chromatographed (silicic acid/pentane). Elution with 25% CH_2Cl_2/pentane yielded a yellow-orange band which, upon removal of solvent, gave 0.803 g (1.22 mmol, 94%) of $(\mu\text{-PhPBr})_2Fe_2(CO)_6$ (**1b**), as an air-stable yellow solid. Recrystallization from pentane gave pure material, m.p. 111–113 °C (sealed capillary).

Anal. Found: C, 33.18; H, 1.67. $C_{18}H_{10}Br_2Fe_2O_6P_2$ calcd.: C, 32.97; H, 1.54%. IR (CH_2Cl_2): terminal CO, 2075(s), 2047(vs), 2020(s), 1994(vs), cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.1–7.9 ppm (m, *Ph*P). ^{31}P NMR ($CHCl_3$): δ(P) 247.3, 233.0 (AB quartet, *J*(P–P) 122 Hz, asymmetric isomer, 66.2%), 233.0 ppm (s, symmetric isomer, **11b**, 33.8%). Mass spectrum, *m/z* (relative intensity): 496 (3.2, $M^+ - 2Br$), 468 (4.8, $M^+ - 2Br - CO$), 440 92.6, $M^+ - 2Br - 2CO$), 412 (2.1, $M^+ - 2Br - 3CO$), 384 (4.1, $M^+ - 2Br - 4CO$), 356 (27.4, $M^+ - 2Br - 5CO$), 328 (22.1, $M^+ - 2Br - 6CO$), 251 (15.4, PhP_2Fe_2), 174 (100.0, P_2Fe_2), 143 (9.0, PFe_2), 112 (1.7, Fe_2), 56 (14.7, Fe).

(b) 1/1 molar ratio. A similar reaction was carried out between 1.22 mmol each of $(\mu\text{-PhPH})_2Fe_2(CO)_6$ and CBr_4 in 35 ml of CH_2Cl_2 at room temperature overnight to give a yellow-orange solution and a bright yellow precipitate. Solvent was removed on a rotary evaporator and the yellow-orange residue recrystallized from CH_2Cl_2/pentane, m.p. 157–160 °C (sealed capillary) to give 0.53 g (0.92

mmol, 75%) of (μ-PhPH)(μ-PhPBr)$Fe_2(CO)_6$ (**12**), as air-stable yellow-orange crystals.

Anal. Found: C, 37.47; H, 2.01. $C_{18}H_{11}BrFe_2O_6P_2$ calcd.: C, 37.48; H, 1.92%. IR (CH_2Cl_2): terminal CO, 2070(s), 2039(vs), 1993(s), cm^{-1} ^1H NMR (250 MHz, $CDCl_3$): δ 4.46 (dd, J(P(1)–H) 400.8 Hz, J(P(2)–H) 30.2 Hz, P–*H* of isomer *a*, 0.87H), 5.62 (dd, J(P(1)–H) 37.1 Hz, J(P(2)–H) 28.5 Hz, P–*H* of isomer *b*, 0.13H) and 6.81–7.85 ppm (complex m, *Ph*P, 10H). ^{31}P NMR ($CHCl_3$): δ(P) 65.8, 228.7 (AX quartet, J(P–P) 137 Hz, isomer *b*, 11.2%), 90.1, 264.3 ppm (AX quartet, J(P–P) 151 Hz, isomer *a*, 88.6%). Mass spectrum, m/z (relative intensity): 521 (< 0.8, $M^+ - 2CO$), 493 (0.8, $M^+ - 3CO$), 465 (0.3, $M^+ - 4CO$), 437, $M^+ - 5CO$), 409 (5.2, $M^+ - 6CO$), 31 (7.1, BrP_2PhFe_2), 251 (1.2, P_2PhFe_2), 174 (6.1, P_2Fe_2), 143 (2.2, PFe_2), 112 (4.8, Fe_2), (100.0, Fe).

*Deprotonation of complex **8**; iodomethane quench*

(a) Quench at −78 °C. A flame-dried 50 ml Schlenk flask was charged with 0.144 g (0.24 mmol) of complex **8**, evacuated and refilled with nitrogen three times. THF (15 ml) was added and the resulting solution cooled to −78 °C. Next, 0.117 ml (0.24 mmol) of 2.05 *M* n-BuLi in hexane was added by syringe, causing a yellow-to-dark green color change. The solution was stirred for 0.5 h after which time MeI (0.5 ml, 7.9 mmol, an excess) was added by syringe, causing an immediate color change back to yellow. After the solution had been stirred for 0.5 h at −78 °C and 1 h at room temperature, solvent was removed on a rotary evaporator. The resulting orange tarry residue was extracted with 30% CH_2Cl_2/petroleum ether and the extracts filtered through a short pad of silicic acid. Removal of solvent yielded 0.1360 g (0.22 mmol, 92%) of **15** which was recrystallized from petroleum ether, giving crystals with m.p. 219–221 °C.

Anal. Found: C, 52.94; H, 3.38. $C_{27}H_{20}O_6Fe_2P_2$ calc: C, 52.81; H, 3.28%. IR ($CHCl_3$): terminal CO, 2049(s), 2005(vs), 1984(s), 1966(s), cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.00 and 1.63 (both dd, J(H–H) 7.3, 7.5 Hz, J(P–H) 16.3, 16.3 Hz, respectively, CH_3 of both diastereomers, 3H), 2.99–3.15 (overlapping dd's, both diastereotopic CH_2 of one diastereomer, 1H) and 3.86, 4.15 (both dd, J(H–H) 14.2, 14.2 Hz, J(P–H) 14.0, 11.9 Hz, respectively, diastereotopic CH_2 of one diastereomer, 1H), 3.46 and 3.65 (both m, J(H–H) 7.5, 7.3 Hz, respectively, C(*H*) Me of both diastereomers, 1H) and 6.83–7.77 ppm (complex m, *Ph*P and $CH_2C_6H_4CH_2$, 14H). ^{31}P NMR ($CHCl_3$): δ(P) 136.5, 152.0 (AX quartet, J(P–P) 166.0 Hz, one diastereomer) and 137.0, 154.3 ppm (AX quartet, J(P–P) 170.9 Hz, other diastereomer).

(b) Quench at −20 °C. In similar manner, a solution of 0.2446 g of **8** in 20 ml of THF at −78 °C was treated with 0.205 ml (0.42 mmol) of 2.05 *M* n-BuLi in hexane, causing a yellow-to-dark green color change. The solution was warmed to −20 °C for 1 h after which time the color had changed to cherry red. The solution was cooled to −78 °C again and 1.0 ml (15.9 mmol, an excess), of CH_3I was added. After it had been stirred for 0.5 h at −78 °C and 1 h at room temperature, the solution was orange-red. Solvent was removed in vacuo and the resulting residue extracted with 40% CH_2Cl_2/petroleum ether. The extracts were filtered through a short pad of silicic acid and the solvent evaporated to give yellow-orange crystals. Chromatography (silicic acid, 2.5 × 20 cm, 40% CH_2Cl_2/hexanes) eluted a bright yellow band which, after removal of solvent and subsequent recrystallization from

CH_2Cl_2/petroleum ether gave 0.133 g (0.22 mmol, 53%) of **19**, m.p. 208–210 °C.

Anal. Found: C, 52.80; H, 3.39. $C_{37}H_{20}O_6Fe_2P_2$ calcd.: C, 52.81; H, 3.28%. IR ($CHCl_3$): 3020(br), 2420(m), 1583(w), 1390(w), 1181(w), 1102(w), 1031(w), 928(w), 880(w), 590(m); terminal carbonyl region: 2047(s), 2005(vs), 1981(vs), 1958(s), 1942(sh), cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 1.02 (d, J(P–H) 8.3 Hz, CH_3, 3H), 3.21 (dd, J(P(1)–H) 10.5 Hz, J(P(2)–H) 17.8 Hz, *H*–C, 1H), 3.85 (d, J(P–H) 12.2 Hz, CH_2, 2H) and 7.01–7.77 ppm (complex m, *Ph*P and $CH_2C_6H_4CH_2$, 14H). ^{31}P NMR ($CHCl_3$): δ(P) 30.8, 182.5 ppm (AX quartet, J(P–P) 19.5 Hz).

*Deprotonation of **8**; other quenches at −20 °C*

(a) Iodoethane. Using the procedure above, 0.2303 g (0.38 mmol) of **8** was treated at −78 °C in THF solution with 19 ml (0.39 mmol) of 2.05 *M* n-BuLi in hexane, causing a yellow-to-dark green color change. The solution was warmed to −20 °C for 1 h after which time the color had changed to cherry red. The solution was cooled to −78 °C and 1.0 ml (12.5 mmol, an excess) of EtI and 0.06 ml (0.40 mmol) of TMEDA were added. After it had been stirred for 0.5 h at −78 °C and 12 h at room temperature, the solution was orange-red and contained a white precipitate. Solvent was removed in vacuo and the residue extracted with 40% CH_2Cl_2/petroleum ether. The extracts were filtered through a short pad of silicic acid and the solvent evaporated to give an orange solid. Chromatography (silicic acid, 2.5 × 25 cm, 10% CH_2Cl_2/hexanes) separated two yellow bands. The first band contained starting material, **8**, 0.104 g (45% recovery). The second band gave 0.073 g (32%) of the P-ethyl analog of **19**, m.p. 214–217 °C (from petroleum ether).

Anal. Found: C, 53.52; H, 3.64. $C_{28}H_{22}O_6Fe_2P_2$ calcd.: C, 53.54; H, 3.53%. IR (CH_2Cl_3): terminal CO, 2045(s), 2002(vs), 1983(s), 1961(m), 1942(sh), cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ −0.14–0.183 (m, CH_2CH_3, 3H), 1.31–1.55 (m, CH_2CH_3, 2H), 3.26 (dd, J(P(1)–H) 17.6 Hz, J(P(2)–H) 10.8 Hz, *H*–C, 1H), 3.89 (d, JP–H) 12.7 Hz, CH_2, 2H) and 7.01–7.91 ppm (complex m *PhP* and $CH_2C_6H_4CH_2$, 14H). ^{31}P NMR ($CHCl_3$): δ(P) 40.9, 182.9 ppm (AX quartet, J(P–P) 24.4 Hz).

(b) Allyl bromide. Using the above procedure (0.40 mmol of **8**), but adding allyl bromide rather than iodoethane, gave a 30% recovery of starting **8** and 0.1724 g (66%) of the yellow, crystalline P-allyl analog of **19**, m.p. 198–200 °C (from petroleum ether).

Anal. Found: C, 54.59; H, 3.70. $C_{29}H_{22}O_6Fe_2P_2$ calcd.: C, 54.41; H, 3.46%. IR($CHCl_3$): terminal CO, 2047(s), 2008(vs), 1985(s), 1965(s), 1948(sh) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 2.04–2.15 nd 2.34–2.42 (both m, $CH_2CH{=}CH_2$, 2H), 3.23 (dd, J(P(1)–H) 17.6 Hz, J(P(2)–H) 11.5 Hz, *H*–C, 1H), 3.72–3.97 (complex m, P–CH_2 and CH_2–$CH{=}CH_2$, 3H), 4.31–4.39 (m, CH_2–$CH{=}CH_2$, 2H) and 6.99–7.87 ppm (complex m, *Ph*P and $CH_2C_6H_4CH_2$, 14H). ^{31}P NMR ($CHCl_3$): δ(P) 37.4, 182.9 ppm (AX quartet, J(P–P) 24.4 Hz).

*Deprotonation of complex **19**; iodomethane quench*

(a) At −78 °C. A flame-dried 50 ml Schlenk flask was charged with 0.0952 g (0.16 mmol) of **19**, evacuated and refilled with nitrogen three times. THF (12 ml) was added and the resulting solution cooled to −78 °C. Next, 0.075 ml (0.17 mmol) of 2.25 *M* n-BuLi in hexane was added by syringe, causing a yellow-to-dark green color change. The solution was stirred for 0.5 h after which time CH_3I (0.5 ml, 7.9

mmol), was added. After it had been stirred for 0.5 h at −78 °C, the solution was yellow-orange. The solution was stirred for an additional 1 h at room temperature. Solvent was removed on a rotary evaporator, the resulting tarry residue extracted with 20% CH_2Cl_2/petroleum ether and the extracts filtered through a short pad of silicic acid. Removal of solvent followed by chromatography (silicic acid, 2.5 × 20 cm, 10% CH_2Cl_2/hexanes) yielded 0.095 g (0.15 mmol, 95%) of yellow crystals of **21**, which after recrystallization from petroleum ether had m.p. 186–188 °C.

Anal. Found: C, 53.82; H, 3.63. $C_{28}H_{22}O_6Fe_2P_2$ calcd.: C, 53.54; H, 3.53%. IR (CH_2Cl_2): 1605(br), 1535(w), 1400(br), 1392(m), 1100(m), 933(m), 600(m); terminal carbonyl region: 2045(s), 2002(vs), 1983(s), 1960(m), 1935(sh) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.01–1.15 (m, P-CH_3 and CH–CH_3 of one diastereomer, 4.5 H), 1.40, 3.02 (both dd, J(H–H) 7.3, 12.1 Hz, J(P–H) 14.8, 17.9 Hz, respectively, *H*-C of both diastereomers, 1H), 1.98 (dd, J(H–H) 7.3 Hz, J(P–H) 14.8 Hz, CH–CH_3 of other diastereomer, 1.5 H), 3.43, 4.10 (both dt, J(H–H) 7.0, 7.4 Hz, J(P–H) 20.0, 22.1 Hz, CHCH_3 of both diastereomers, 1H) and 6.94–7.90 (complex m, *Ph*P and $CH_2C_6H_4CH_2$, 14H). ^{31}P NMR ($CHCl_3$): δ(P) 24.0, 181.2 (AX quartet, J(P–P) 19.5 Hz, one diastereomer) and 31.8, 191.5 ppm (AX quartet, J(P–P) 24.4 Hz, other diastereomer.

(b) At room temperature. The deprotonation was carried out as described above using 0.33 mmol of **19**. The resulting dark-green solution was warmed to room temperature for 1 h after which time the color had changed to burgundy red. The solution was cooled to −78 °C and 0.5 ml (7.9 mmol, an excess) of CH_3I was added. After it had been stirred for 0.5 h at −78 °C and 1 h at room temperature, the solution was orange. Solvent was removed in vacuo and the resulting residue extracted with 30% CH_2Cl_2/petroleum ether. The extracts were filtered through a short pad of silicic acid and the solvent evaporated to give a yellow oil. Chromatography (silicic acid, 2.5 × 20 cm, 25% CH_2Cl_2/hexanes) eluted a bright yellow band which, after removal of solvent, gave 0.109 g (0.17 mmol, 51%) of yellow oil and crystals, which by ^{31}P NMR, was shown to be a mixture of three complexes. Repeated attempts at chromatography and fractional recrystallization failed to isolate any of these complexes in pure form and further workup was not pursued. The ^{31}P NMR spectrum of the mixture of complexes was recorded:

^{31}P NMR ($CHCl_3$): δ 20.8, 81.5 (AX quartet, J(P–P) 19.8 Hz, complex **1**), 38.4, 95.3 (AX quartet, J(P–P) 51.0 Hz, complex **2**) and 88.3, 103.4 ppm (both s, complex **3**).

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