ELSEVIER

Journal of Organometallic Chemistry 624 (2001) 105–109

Journal of Organo metallic Chemistry

www.elsevier.nl/locate/jorganchem

A new approach to β-functional phospholes. Application to the synthesis of a β-CH_2–CH_2-bridged diphosphole disulphide

Bernard Deschamps, François-Xavier Buzin, Adina Avarvari, François Nief, François Mathey *

Laboratoire 'Hétéroéléments et Coordination', UMR CNRS 7653, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

Received 18 September 2000; accepted 26 October 2000

Dedicated to Professor Jean-François Normant on the occasion of his 65th birthday

---

Abstract

Protection of both the dienic system and the lone pair of phosphorus of 1-phenyl-3,4-dimethylphosphole by complexation with iron carbonyl groups allow the regiospecific deprotonation of one β-methyl substituent by lithium diisopropylamide (LDA). The resulting anion exhibits versatile reactivity towards various electrophiles and can even undergo oxidative coupling with $CuCl_2$, thus providing an entry into the unprecedented β–β′-bridged biphosphole system. Finally, the protecting iron carbonyl moieties can be cleanly removed in a two-step procedure involving reaction with sulphur and cerium ammonium nitrate (CAN). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphole; Lithium diisopropylamide (LDA)

---

1. Introduction

As a result of their pyramidal structure [1], phospholes display a low aromaticity [2], hence their functionalization is difficult. Thus, many efforts have been devoted to the search for original access routes to functional phospholes. At present, the most versatile route involves 2-lithiophospholes obtained by metal–halogen exchange from 2-bromophospholes [3–6]. Conversely, the synthesis of β-functional phospholes [7] remains difficult. The only reported practical route relies on the palladium-catalyzed insertion of functional alkynes into phosphirenes [8,9]. In this paper, we report on a synthetic technology that allows us to partly fill this gap.

2. Results and discussion

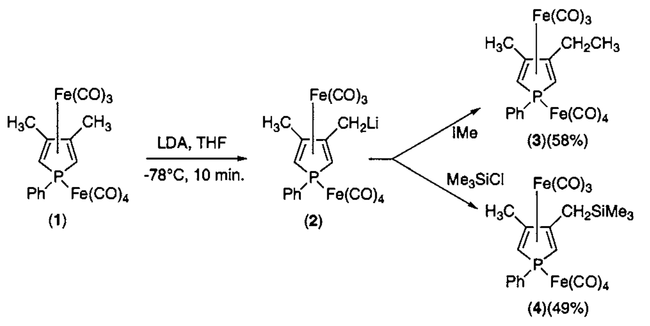
For some time, we have developed a route to functional phospholes involving the methyl metalation of 3,4-dimethylphosphole sulphides [10–12] or boranes [13]. The resulting allylic carbanions react either at the methyl or at the α-carbon of the ring. Although remarkably simple, this route to functional phospholes suffers from a major drawback: in many cases, mixtures of functional products are obtained, purification is difficult and yields are rather low. Some time ago, Semmelhack described the methyl metalation of (η^4-isoprene) iron tricarbonyl leading to the synthetic equivalent of an isoprene anion [14]. On this basis, we thought that the methyl metalation of 3,4-dimethylphosphole derivatives η^4-complexed on the diene subunit would yield localised anions that could thus be regioselectively functionalized. In order to check this hypothesis, we decided to investigate the metalation of complex **1** [15]. We chose lithium diisopropylamide (LDA) as the metalating agent by analogy with the work of Semmelhack. Our results were immediately positive (Eq. (1)).

---

* Corresponding author. Tel.: +33-1-69334079; fax: +33-1-69333029.

E-mail address: edchem@poly.polytechnique.fr (F. Mathey).

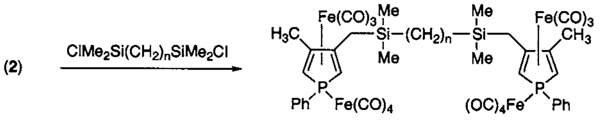
PII: S0022-328X(00)00834-2



(1)

For identification, the resulting carbanion **2** was allowed to react with methyl iodide and chlorotrimethylsilane. The resulting products **3** and **4** were characterised by NMR and mass spectrometry. In the starting product **1**, the two ring Hαs and Cαs appear at 2.98 ($^2J_{H-P} = 24.4$ Hz) and 49.54 ($^1J_{CP} = 38.7$ Hz), respectively on the ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$), whereas the Cβs resonate at 107.44 as a singlet. For **3**, practically no differentiation is visible between the two sides of the ring for Cα: δ 48.48 ($^1J_{CP} = 39.1$ Hz), the two Cβs appearing at 106.38 and 111.93. The $Fe(CO)_3$ and $Fe(CO)_4$ complexing groups resonate at 209.06 ($^2J_{CP} = 7.4$ Hz) and 214.38 ($^2J_{CP} = 19.9$ Hz), respectively. The ethyl CH_2 appears at 24.19 as a singlet. The mass spectrum confirms the formulation (M^+ at 510). For **4**, the differentiation between the two sides of the ring becomes more visible: Cα: δ 46.31 ($^1J_{CP} = 39.5$ Hz) and Cα′: δ 50.34 ($^1J_{CP} = 38.5$ Hz); Cβ: δ 105.26 and Cβ′: δ 112.61. The most significant feature of the ^{1}H spectrum concerns the two diastereotopic CH_2–Si protons: AB system: δ_A 1.57, δ_B 2.14, $^2J_{AB} = 13.4$ Hz.

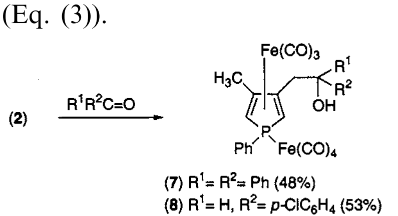
The reaction of carbanion **2** with Si–Cl bonds can serve to build bridges between two phosphole units as shown in Eq. (2).



(5) n = 2 (59%)
(6) n = 6 (56%)

(2)

The presence of two chiral phosphorus centres in **5** and **6** induces the possible formation of two diastereomers in both cases. In practice, we have been unable to detect these diastereomers. On the ^{31}P spectra, only one sharp resonance is visible for **5** and **6**. The carbanion **2** also cleanly reacts with carbonyl compounds (Eq. (3)).

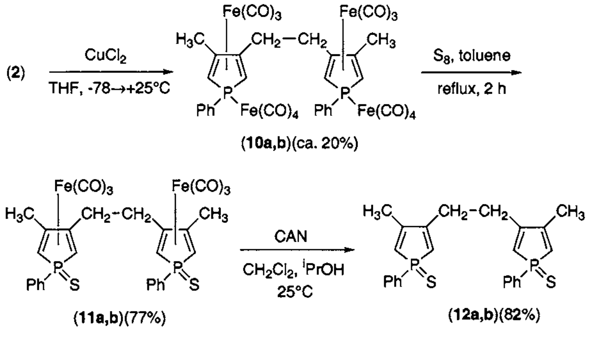


(3)

(7) $R^1 = R^2 = Ph$ (48%)
(8) $R^1 = H$, $R^2 = p\text{-}ClC_6H_4$ (53%)
(9) $R^1 = H$, $R^2 = (E)\text{-}PhCH{=}CH\text{-}$ (50%)

The main spectral characteristics of **7** are given here as an example. In the ^{1}H spectrum, the two αCH appear as two doublets: δ 3.02 ($^2J_{HP} = 24.1$ Hz) and 3.23 ($^2J_{HP} = 24.9$ Hz), and the diastereotopic exocyclic CH_2 protons as a AB system: δ_A 3.35, δ_B 3.68, $^2J_{AB} = 14.4$ Hz. In the ^{13}C spectrum (CD_2Cl_2), the exocyclic CH_2 appears as a singlet at 43.67, the α carbons as two doublets at 48.66 and 52.82 ($^1J_{CP} = 40.0$ and 37.3 Hz), the C–OH as a singlet at 78.75 and the β carbons as a singlet at 105.32 and a doublet at 111.67 ($^2J_{CP} = 1.9$ Hz). The mass spectrum shows the molecular peak at m/z 679 (M + 1, CI, NH_3).

Since the work of Manners [16], it is now known that strained ferrocenophanes readily polymerise under heating to give well-defined high quality ferrocene polymers. A priori, it seems possible to prepare phosphaferrocene polymers using a similar technique. Such polymers could act as ligands toward transition metal centres through their sp^2-lone pairs at phosphorus and interesting applications of this property could be envisaged. On that basis, we decided to use the regioselective functionalization of the β-methyl substituent for the creation of a β-CH_2–CH_2-bridged diphosphole ring system. This species could serve as an ideal starting point for the synthesis of a [2]ferrocenophane. The bridge can be created, albeit in modest yield, by oxidative coupling of two molecules of carbanion **2** (Eq. (4)).



(4)

The diphosphole complex **10** is formed as a 1:1 mixture of two diastereomers, δ ^{31}P 91.7 (**10a**) and 93.7 (**10b**) (THF). The CH_2CH_2 bridge appears as a singlet at 31.60 ($CDCl_3$) for **10a** and 30.55 (C_4D_8O) for **10b**. During the workup, **10b** is partly lost so that we have worked subsequently on a mixture enriched in **10a**. Refluxing **10** with sulphur in toluene destroys the $Fe(CO)_4$ complexing group. The major isomer **11a** appears at δ ^{31}P 70.0 (toluene), the minor corresponding to **10b** at 71.0. The ^{13}C spectrum of **11a** shows the $Fe(CO)_3$ group at 208.11 ($CDCl_3$) and no $Fe(CO)_4$ resonance. The main peaks in the mass spectrum are found at M′ = 374 (M–2$Fe(CO)_3$–2S) and 187 (M′/2, 100%). Treatment of **11** by cerium ammonium nitrate (CAN) in a dichloromethane/isopropanol mixture results in total decomplexation of the remaining iron carbonyl group thus affording diphosphole disulphide

12a,**12b**: δ ^{31}P 47.9 (**12a**, major) and 48.0 (**12b**, minor) in CH_2Cl_2. The CH_2 bridge of **12a** appears at 28.85 as a doublet ($J_{CP} = 15.7$ Hz) on the ^{13}C spectrum ($CDCl_3$). The Cα are now deshielded at 125.58 ($^1J_{CP} = 73.8$ Hz) and 127.13 ($^1J_{CP} = 75.4$ Hz). The mass spectrum shows the molecular peak at m/z 438.

From here, transformation of **12a**,**b** into the corresponding trivalent phospholes should be easily achieved by reduction of the P=S bond with a more basic phosphine, such as for instance $P(CH_2CH_2CN)_3$, as previously described; however the low yield of the coupling reaction hampers the practical use of this route to β-bridged diphospholes. But it is clear that the two-step decomplexation procedure allows using this metalation route as an effective access route to β-functional monophospholes.

3. Experimental

3.1. General

All reactions were performed under an inert atmosphere (nitrogen or argon). NMR spectra were measured on a multinuclear Bruker AC 200 spectrometer. Chemical shifts are expressed in ppm from internal TMS (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P); coupling constants are expressed in Hz. Mass spectra (Electron Impact, unless otherwise noted) were measured at 70 eV by the direct inlet method. Elemental analyses were performed at the Service de Microanalyse du CNRS, Gif sur Yvette, France.

3.2. Description of compounds

3.2.1. (1-Phenyl-3,4-dimethylphosphole)-heptacarbonyldiiron (1)

Complex **1** was prepared from 1-phenyl 3,4-dimethylphosphole and Fe_3CO_{12} as previously described [15]. Additional spectroscopic data:

NMR: ^{13}C{^{1}H} ($CDCl_3$): δ 16.75 (d, $^1J_{PC}$ 38, Cα), 107.44 (s, Cβ), 126.03 (d, $^2J_{CP}$ 10.4, C_{ortho}), 152.95 (d, $^3J_{CP}$ 8.3, C_{meta}), 129.31 (s, C_{para}), 152.95 (d, $^1J_{CP}$ 8.7, C_{ipso}), 209.42 (d, $^3J_{CP}$ 7.2, $Fe(CO)_3$), 214.82 (d, $^2J_{CP}$ 19.5, $Fe(CO)_4$); ^{31}P{^{1}H}: δ 92.65.

*3.2.2. General procedure for the synthesis of β-functional phosphole complexes: generation of anion **2** and its reaction with electrophiles*

To a solution of (1-phenyl-3,4-dimethyl-phosphole)-heptacarbonyldiiron (**1**, 0.25 g, 0.5 mmol) in THF (5 ml) at −78°C was added drop-wise one equivalent of lithium diisopropylamide (prepared by addition at −40° of 1.3 ml BuLi 1.6 M on 0.34 ml diisopropylamine in 5 ml of THF). The red mixture was stirred for 10 min. To the solution of anion **2** thus generated was added drop-wise the electrophilic reagent at −78°, and after 30 min the mixture was allowed to warm to room temperature (r.t.) and hydrolysed with a saturated solution of ammonium chloride. The solvent was removed and the residue extracted with dichloromethane, washed with water, dried with magnesium sulfate and purified by chromatography on silicagel with hexane–toluene 70:30 as eluent.

3.2.3. (1-Phenyl-3-ethyl-4-methyl-1H-phosphole)-heptacarbonyldiiron (3)

To anion **2** was added 0.04 g (4 mmol) of methyl iodide; 0.15 g of **3** (58% yield) were obtained.

NMR: ^{1}H (CD_2Cl_2) δ 0.85 (t, $^3J_{HH}$ 7.6, CH_3CH_2), 2.27 (s, CH_3) 2.72 (q, $^3J_{HH}$ 7.6, CH_2CH_3), 2.95 (d, $^2J_{HP}$ 24.4, Hα and Hα'), 6.92–7.35 (m, Ph); ^{13}C{^{1}H} (CD_2Cl_2): δ 14.28 (s, CH_3CH_2), 16.14 (s, CH_3), 24.19 (s, CH_2CH_3), 48.48 (d, $^1J_{CP}$ 39.1, Cα and Cα'), 106.38 (s, Cβ), 111.3 (s, Cβ'), 125.80–132.25 (m, Ph), 209.06 (d, $^2J_{CP}$ 7.4, $Fe(CO)_3$), 214.38 (d, $^2J_{CP}$ 19.9, $Fe(CO)_4$); ^{31}P{^{1}H} (THF) δ 90.20.

Mass spectrum: m/z 510 (M, 1%), 314 (M − 7CO, 100%).

Anal. Calc. for $C_{20}H_{15}Fe_2O_7P = 509.93$: C, 47.10; H, 2.96. Found: C, 47.26; H, 2.98%.

3.2.4. (1-Phenyl-3-methyl-4-trimethylsilylmethyl-phosphole)heptacarbonyldiiron (4)

To anion **1** was added 0.055 g of trimethylchlorosilane. The mixture was treated with 3 N HCl before extraction (instead of ammonium chloride); 0.14 g (50% yield) of **4** were obtained.

NMR ($CDCl_3$) ^{1}H δ −0.27 (s, $SiCH_3$), 1.57 (d, 1H, $^2J_{HH}$ 13.4, CH_2), 2.24 (1H, $^2J_{HH}$ 13.4, CH_2), 2.34 (s, =–CH_3), 2.95 (dd, $^2J_{HP}$ 30.8, $^4J_{HH}$ 2.8, Hα), 3.07 (dd, $^2J_{HP}$ 32.1, $^4J_{HH}$ 2.8, Hα'), 7.18–7.45 (m, Ph);^{13}C{^{1}H}: δ −1.74 (s, $SiCH_3$), 16.60 (s, –CH_3), 22.54 (s, –CH_2), 46.31 (d, $^1J_{CP}$ 39.5, Cα), 50.34 (d, $^1J_{CP}$ 38.5, Cα'), 105.26 (d, $^2J_{CP}$ 2.2, Cβ), 112.61 (d, $^2J_{CP}$ 3.6, Cβ'), 126–128 (Ph), 209.01 (d, $^2J_{CP}$ 7.6, $Fe(CO)_3$), 214.33 ($^2J_{CP}$ 18.7, $Fe(CO)_4$); ^{31}P{^{1}H} δ 84.68.

Mass spectrum: m/z 372 (M − 7CO, 100%).

Anal. Calc. for $C_{22}H_{21}Fe_2O_7PSi = 568.15$: C, 46.51; H, 3.73. Found: C, 46.71; H, 3.77%.

3.2.5. [1,2-Bis-{(4-methyl-1-phenyl-1H-phosphol-3-yl)-dimethylsilylmethyl}-ethane]tetradecacarbonyltetrairon (5)

To anion **1** was added 0.060 g of $ClSi(CH_3)_2$-$(CH_2)_2Si(CH_3)_2Cl$. Treatment with 3 N HCl (instead of ammonium chloride) was performed before extraction; 0.17 g (59% yield) of **5** was obtained.

NMR (CD_2Cl_2): ^{1}H: δ −0.43 (s, $SiCH_3$), −0.34 (s, $SiCH_3$), 0.14 (s, –CH_2CH_2–), 1.60 (d, $^2J_{HH}$ 13.5, –CH(A)H(B)–Si), 2.24 (d, $^2J_{HH}$ 13.5, –CH(A)H(B)–Si), 2.34 (s, –CH_3), 2.99 (dd, $^2J_{HP}$ 24.04, $^4J_{HH}$ 2.6, Hα), 3.11 (dd, $^2J_{HP}$ 25.52, $^4J_{HH}$ 2.6, Hα′), 7.10–7.40 (m, Ph); $^{13}C\{^1H\}$: δ −3.93 (s, $SiCH_3$), −3.66 (s, $SiCH_3$), 7.99 (s, CH_2CH_2), 17.36 (s, –CH_3), 21.26 (s, –CH_2), 47.16 (d, $^1J_{CP}$ 39.5, Cα), 52.21 (d, $^1J_{CP}$ 38.3, Cα′), 106.41 (s, Cβ), 113.53 (d, $^2J_{CP}$ 2.9, Cβ′), 126–129 (Ph), 210.01 (d, $^2J_{CP}$ 7.7, $Fe(CO)_3$), 215.28 (d, $^2J_{CP}$ 19.7, $Fe(CO)_4$); $^{31}P\{^1H\}$ (CD_2Cl_2) δ 83.46.

Anal. Calc. for $C_{44}H_{40}Fe_4O_{14}P_2Si_2 = 1134.30$: C, 46.59; H, 3.55. Found: C, 46.55; H, 3.57%.

*3.2.6. [1,6-Bis-{(4-methyl-1-phenyl-1H-phosphol-3-yl)-dimethylsilylmethyl}-hexane]tetradecacarbonyltetrairon **(6)***

To anion **1** was added 0.075 g of $ClSi(CH_3)_2(CH_2)_6Si(CH_3)_2Cl$. Treatment with 3 N HCl (instead of ammonium chloride) was performed before extraction; 0.18 g (56% yield) of **6** was obtained.

NMR (CD_2Cl_2): ^1H δ −0.34 (s, $SiCH_3$), −0.31 (s, $SiCH_3$), 0.18–0.34 (m, –$SiCH_2$–chain), 0.99–1.26 (m, CH_2 chain), 1.61 (d, $^2J_{HH}$ 13.5, –C*H*(A)H(B)–Si), 2.26 (d, $^2J_{HH}$ 13.5, –CH(A)*H*(B)–Si), 2.35 (s, –CH_3), 3.00 (dd, $^2J_{HP}$ 29.2, $^4J_{HH}$ 2.8, Hα), 3.12 (dd, 2H, $^2J_{HP}$ 30.7, $^4J_{HH}$ 2.8, Hα′), 7.11–7.45 (Ph); $^{13}C\{^1H\}$: δ −3.14 (s, $SiCH_3$), −3.02 (s, $SiCH_3$), 15.66 (s, CH_3), 17.41 (s, CH_2 chain), 22.02 (s, –CH_2), 24.21 (s, CH_2 chain), 33.98 (s, CH_2 chain), 47.27 (d, $^1J_{CP}$ 39.0, Cα), 52.35 (d, $^1J_{CP}$ 38.8, Cα′), 106.46 (s, Cβ), 113.89 (d, $^2J_{CP}$ 3.5, Cβ′), 126–132 (Ph), 210.07 (d, $^2J_{CP}$ 7.7, $Fe(CO)_3$), 215.37 (d, $^2J_{CP}$ 19.1, $Fe(CO)_4$); $^{31}P\{^1H\}$ δ 84.28.

3.2.7. [2-(4-Methyl-1-phenyl-1H-phosphol-3-yl)-1,1-diphenyl-ethanol]heptacarbonyldiiron (7)

To anion **1** was added benzophenone (0.090 g); 0.165 g of **7** were obtained (48% yield).

NMR (CD_2Cl_2): ^1H δ 1.82 (s, CH_3), 3.02 (d, $^2J_{HP}$ 24.1, Hα), 3.23 (d, 1H, $^2J_{HP}$ 24.9, Hα′), 3.35 (d, 1H, $^2J_{HH}$ 14.4, CH_2), 3.68 (d, 1H, $^2J_{HH}$ 14.4, CH_2), 6.97–7.39 (15H, Ph); $^{13}C\{^1H\}$ δ 16.58 (s, CH_3), 43.67 (s, CH_2), 48.66 (d, $^1J_{CP}$ 40.0, Cα), 52.82 (d, $^1J_{CP}$ 37.3, Cα′), 78.75 (s, COH), 105.32 (s, Cβ), 111.67 (d, $^2J_{CP}$ 1.9, Cβ′), 125–129 (Ph), 209.23 (d, $^2J_{CP}$ 7.5, CO), 214.66 (d, $^2J_{CP}$ 19.5, CO); $^{31}P\{^1H\}$ δ 84.70.

Mass spectrum (CI, NH_3): *m*/*z* 679 (M + 1, 88%), 662 (M − OH, 31%), 357 (M − 7CO − 2Ph, 37%).

Anal. Calc. for $C_{32}H_{23}Fe_2O_8P = 678.18$: C, 56.67; H, 3.42. Found: C, 56.32; H, 3.39%.

*3.2.8. [1-(4-Chlorophenyl)-2-(4-methyl-1-phenyl-1H-phosphol-3-yl)-ethanol]heptacarbonyldiiron **(8)***

To **1** was added 0.070 g (0.5 mmol) of *p*-chlorobenzaldehyde; 0.17 g of **8** were obtained (53% yield).

NMR: ^1H (CD_2Cl_2): δ 1.90 (s, CH_3), 2.55 (d, 1H, $^2J_{HH}$ 6.9, CH_2), 2.62 (d, 1H, $^2J_{HH}$ 6.9, CH_2), 2.99 (d, $^2J_{HP}$ 24.5, $^4J_{HH}$ 2.9, Hα), 3.1 (m, C*H*OH), 3.27 (d, $^2J_{HP}$ 24.6, $^4J_{H\text{–}H}$ 2.9, Hα′), 6.80–7.40 (m, Ar); $^{13}C\{^1H\}$ (CD_2Cl_2): δ 16.05 (s, CH_3), 41.85 (s, CH_2), 48.65 (d, $^1J_{CP}$ 39.1, Cα), 50.95 (d, $^1J_{CP}$ 38.5, Cα′), 74.20 (s, CHOH), 106.23 (s, Cβ), 108.59 (s, Cβ′), 125–133 (Ar), 208.95 (d, $^2J_{CP}$ 7.25, CO), 214.55 (d, $^2J_{CP}$ 19.71, CO); $^{31}P\{^1H\}$ (THF) δ 88.9.

Mass spectrum: *m*/*z* 608 (M − CO, 2%), 440 (M − 7CO, 20%).

*3.2.9. [1-(4-Methyl-1-phenyl-1H-phosphol-3-yl)-4-phenyl-(E)-but-3-en-2-ol]heptacarbonyldiiron **(9)***

To anion **1** was added 0.066 g (0.5 mmol) of cinnamaldehyde; 0.16 g (50% yield) of **9** were obtained.

NMR (CD_2Cl_2) ^1H: δ 2.27 (s, 3H, CH_3), 2.50 (d, $^2J_{HH}$ 6.0, H_A), 2.57 (d, $^2J_{HH}$ 6.0), 3.05 (dd, $^2J_{HP}$ 24.5, $^4J_{HH}$ 2.9, Hα), 3.24 (dd, $^2J_{HP}$ 24.5, $^4J_{HH}$ 2.8, Hα′), 3.2 (m, C*H*OH), 5.84 (dd, 1H, $^3J_{HH}$ 6.3, $^3J_{HH}$ 16.0, CHOH–C*H*=CH), 6.08 (d, $^3J_{HH}$ 16.0, CHOH–CH=C*H*), 7.15–7.60 (m, C_6H_5); $^{13}C\{^1H\}$: δ 16.90 (s, CH_3), 39.55 (s, CH_2), 48.65 (d, $^1J_{CP}$ 39.4, Cα), 50.55 (d, $^1J_{CP}$ 38.5, Cα′), 73.20 (s, CHOH), 106.55 (s, Cβ) , 108.75 (s, Cβ′), 126–134 (m, Ph), 209.05 (d, $^2J_{CP}$ 7.30, CO), 214.80 (d, $^2J_{CP}$ 19.7, CO); $^{31}P\{^1H\}$: 88.05.

Mass spectrum (CI, NH_3): *m*/*z* 629 (M + 1, 100%).

*3.2.10. [1,2-Bis-(4-methyl-1-phenyl-1H-phosphol-3-yl)-ethane]tetradecacarbonyltetrairon (**10a**, **10b**)*

To a stirred solution of **2** prepared as described above from **1** (5 g, 10 mmol), LDA (10.5 mmol) in THF (50 ml) at −78°C was added solid $CuCl_2$ (1.45 g, 10.5 mmol) in one portion. The reaction mixture was allowed to warm slowly to r.t. and filtered. The filtrate was evaporated to dryness and the residue chromatographed on silicagel. Elution with 1:1 hexane–toluene allowed for the recovery of unreacted **1**; further elution with 9:1 toluene–ethyl acetate afforded partially separated **10a** and **10b**, that were further purified by recrystallisation from toluene–THF. The overall yield of **10a** + **10b** is 1 g (1 mmol, 20%).

10a: NMR (C_4D_8O): ^1H: δ 2.27 (s,CH_3), 2.42 (s,CH_2), 3.12 (dd, $^2J_{HP}$ 24.5, $^4J_{HH}$ 2.4, Hα), 3.24 (dd, $^2J_{HP}$ 24.7, $^4J_{HH}$ 2.8, Hα′), 7.2 (m, Ph). $^{13}C\{^1H\}$: δ 15.60 (s, CH_3), 30.55 (s, CH_2), 48.94 (d, $^1J_{CP}$ 38.5, Cα), 49.93 (d, $^1J_{CP}$ 38.4, Cα′), 108.16 (d, $^2J_{CP}$ 2.9, Cβ), 109.50 (d, $^2J_{CP}$ 2, Cβ′), 126.46 (d, $^2J_{CP}$ 10.7, C_{ortho}), 128.96 (d, $^3J_{CP}$ 8.8, C_{meta}), 129.53 (s, C_{para}), 153.41 (d, $^1J_{CP}$ 9.6, C_{ipso}), 209.63 (d, $^3J_{CP}$ 7.6, Fe(CO)$_3$), 214.93 (d, Fe(CO)$_4$, $^2J_{CP}$ 19.2). $^{31}P\{^1H\}$: δ 94.58.

10b: NMR ($CDCl_3$): ^1H: δ 2.24 (s,CH_3), 2.36 (s,CH_2), 2.90 (dd, $^2J_{HP}$ 24.9, $^4J_{HH}$ 2.8, Hα), 2.97 (dd, $^2J_{HP}$ 24.7, $^4J_{HH}$ 2.8, Hα′), 7.15 (m, Ph). $^{13}C\{^1H\}$: δ 16.56 (s, CH_3), 31.60 (s, CH_2), 49.37 (d, $^1J_{CP}$ 39.6, Cα), 48.67 (d, $^1J_{CP}$ 38.2, Cα′), 106.72 (d, $^2J_{CP}$ 2.5, Cβ), 107.84 (d, $^2J_{CP}$ 2.1, Cβ′), 125.97 (d, $^2J_{CP}$ 10.7, C_{ortho}), 129.06 (d, $^3J_{CP}$ 8.9, C_{meta}), 129.65 (s, C_{para}), 152.63 (d, $^1J_{CP}$ 9.5, C_{ipso}), 208.76 (d, $^3J_{CP}$ 7.6, $Fe(CO)_3$), 214.52 (d, $^2J_{CP}$ 19.6, $Fe(CO)_4$). $^{31}P\{^1H\}$: δ 94.58.

Mass spectrum: m/z 934 ($M^+ - 2CO$, 3%), 878 ($M^+ - 4CO$, 7%), 598 ($M^+ - 14CO$, 57%), 276 (100%).

*3.2.11. [1,2-Bis-{(4-methyl-1-phenyl-1-thioxo-1H-phosphol-3-yl)}-ethane]hexacarbonyldiiron **(11)***

To a solution of **10** (1.48 g, 1.5 mmol) in toluene (5 ml) was added elemental sulphur (0.7 g, excess) and the reaction mixture was refluxed for 2.5 h. The solution was filtered and the black solid rinsed with THF. The filtrate was evaporated to dryness and chromatographed on silica-gel. Elution with 95:5 hexane–dichloromethane allowed the elimination of excess sulphur. Further elution with toluene and 9:1 toluene–ethyl acetate afforded **11** (830 mg, 1.16 mmol, 77%).

NMR ($CDCl_3$): ^1H: δ 2.17 (s, CH_3), 2.42 (s, CH_2), 2.76 (d, $^2J_{HP}$ 16.9, Hα), 2.78 (d, $^2J_{HP}$ 16.7, Hα'), 7.5 (m, Ph). $^{13}C\{^1H\}$: δ 16.29 (s, CH_3), 31.42 (s, CH_2), 51.35 (d, $^1J_{CP}$ 55.0, Cα), 52.72 (d, $^1J_{CP}$ 52.6, Cα'), 104.22 (d, $^2J_{CP}$ 13.8, Cβ), 104.72 (d, $^2J_{CP}$ 15.0, Cβ'), 129.23 (d, $^2J_{CP}$ 7.6, C_{ortho}), 129.44 (d, $^3J_{CP}$ 7.6, C_{meta}), 131.75 (s, C_{para}), 208.11 (d, $^3J_{CP}$ 5.7, $Fe(CO)_3$); C_{ipso} was not observed. $^{31}P\{^1H\}$: δ 68.79.

Mass spectrum: m/z 550 ($M^+ - 6CO$, 2%), 374 ($M^+ - 2Fe(CO)_3 - 2S$, 80%), 187 (100%).

*3.2.12. [1,2-Bis-{(4-methyl-1-phenyl-1-thioxo-1H-phosphol-3-yl)}ethane] **(12)***

To a solution of **11** (240 mg, 0.33 mmol) in 1:1 dichloromethane–isopropanol (10 ml) was added cerium ammonium nitrate (1.46 g, 2.66 mmol). The reaction mixture was stirred for 3 h at r.t. and the solvent evaporated to dryness. The residue was taken up in a 1:1 water–dichloromethane mixture and the aqueous phase was extracted with dichloromethane and evaporated to dryness. The residue was taken up in toluene, decanted and the resulting solution evaporated to dryness, whereupon the product crystallized. Solid **12** was rinsed with hexane and dried under vacuum (120 mg, 0.27 mmol, 82%).

NMR ($CDCl_3$): ^1H: δ 2.16 (d, $^4J_{HP}$ 1.1, CH_3), 2.73 (s, CH_2), 6.17 (d, $^2J_{HP}$ 28.1, Hα), 6.19 (d, $^2J_{HP}$ 29.9, Hα'), 7.37 ($3H_{ortho,\ para}$), 7.80 ($2H_{meta}$). $^{13}C\{^1H\}$: δ 18.00 (d, $^3J_{CP}$ 18.2, CH_3), 28.85 (d, $^3J_{CP}$ 15.7, CH_2), 125.60 (d, $^1J_{CP}$ 73.8, Cα), 127.13 (d, $^1J_{CP}$ 75.4, Cα'), 127.60 (d, $^1J_{CP}$ 80.9, C_{ipso}), 129.40 (d, $^2J_{CP}$ 12.3, C_{ortho}), 131.04 (d, $^3J_{CP}$ 12.3, C_{meta}), 132.73 (d, $^4J_{CP}$ 3.1, C_{para}), 153.76 (d, $^2J_{CP}$ 17.8, Cβ), 156.32 (d, $^2J_{CP}$ 17.1, Cβ'). $^{31}P\{^1H\}$: δ 45.49.

Mass spectrum: m/z 438 (M^+, 58%), 405 ($M^+ - S - 1$, 100%).

Acknowledgements

Financial support for this work by Ecole Polytechnique and CNRS is gratefully acknowledged. The authors also wish to thank Elf-Atochem for a thesis grant to François-Xavier Buzin.

References

[1] P. Coggon, A.T. McPhail, J. Chem. Soc. Dalton Trans. (1973) 1988.
[2] P.v.R. Schleyer, P.K. Freeman, H. Jiao, B. Goldfuss, Angew. Chem. Int. Ed. Engl. 34 (1995) 337.
[3] E. Deschamps, F. Mathey, Bull. Soc. Chim. Fr. 129 (1992) 486.
[4] E. Deschamps, L. Ricard, F. Mathey, Angew. Chem. Int. Ed. Engl. 33 (1994) 1158.
[5] E. Deschamps, L. Ricard, F. Mathey, J. Chem. Soc. Chem. Commun. (1995) 1561.
[6] S. Holand, F. Gandolfo, L. Ricard, F. Mathey, Bull. Soc. Chim. Fr. 133 (1996) 33.
[7] The first β-functional phosphole was described by Quin: L.D. Quin, S.G. Borleske, Tetrahedron Lett. (1972) 299.
[8] A. Marinetti, F. Mathey, Tetrahedron Lett. 28 (1987) 5021.
[9] A. Espinosa-Ferao, B. Deschamps, F. Mathey, Bull. Soc. Chim. Fr. 130 (1993) 695.
[10] F. Mathey, Tetrahedron 30 (1974) 3127.
[11] F. Mathey, Tetrahedron 32 (1976) 2395.
[12] B. Deschamps, F. Mathey, Organometallics 11 (1992) 1411.
[13] N.H. Tran Huy, F. Mathey, Organometallics 13 (1994) 925.
[14] M.F. Semmelhack, E.J. Fewkes, Tetrahedron Lett. 28 (1987) 1497.
[15] F. Mathey, G. Muller, J. Organomet. Chem. 136 (1977) 241.
[16] I. Manners, Angew. Chem. Int. Ed. Engl. 35 (1996) 1603.