Bull Soc Chim Fr (1996) 133, 541-545

Synthesis of 2-functional phospholide anions from 1-phenylphosphole precursors

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(Received 23 February 1996; accepted 20 April 1996)

Summary — Several transformations have been performed upon the 2-substituents of 1-phenyl-3,4-dimethylphospholes. The 2-CO_2H compound has been converted into the 2-CN derivative **3**. Subsequent cleavage of the P–Ph bond of **3** by potassium in DME yielded the 2-cyanophospholide **4** which has been fully characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The ^{13}C data suggest a significant conjugation between the CN and the ring. The cleavage of the P–Ph bond of phospholes bearing 2-SMe, 2-$SiMe_3$ or 2-$SnMe_3$ groups by lithium in THF is also shown to give the corresponding phospholides **8**, **11** and **12**. Their reaction with $FeCl_2$ furnishes the respective 1,1′-diphosphaferrocenes **9**, **15** and **16**.

phosphole / phospholide anion / heteroaromaticity / 1,1′-diphosphaferrocene

Résumé — Synthèse d'anions phospholures 2-fonctionnels à partir de 1-phénylphospholes. *Une série d'anions phospholure fonctionnels a été préparée à partir des 1-phényl-3,4-diméthylphospholes adéquatement substitués sur la position 2. Le composé 2-CO_2H a été transformé en son dérivé 2-CN* **3**. *L'anion 2-cyanophospholure* **4**, *préparé par coupure de la liaison P-Ph de* **3** *par le potassium dans le DME, a été totalement caractérisé par spectroscopie RMN ^{1}H, ^{13}C et ^{31}P. Les données ^{13}C suggèrent une importante conjugaison entre le groupe CN et le cycle. La coupure par le lithium dans le THF de la liaison P-Ph de phospholes portant des groupements 2-SMe, 2-$SiMe_3$ et 2-$SnMe_3$ conduit de la même façon aux anions phospholure* **8**, **11** *et* **12**. *Leur réaction avec $FeCl_2$ permet la synthèse des 1,1′-diphosphaferrocènes correspondants.*

phosphole / anion phospholure / hétéroaromaticité / 1,1′-diphosphaferrocène

Introduction

The phospholide anions are, together with phosphinines, the only known monophosphorus monocycles that display a sizeable and proven aromaticity [1]. Nevertheless, it remains very difficult to develop a versatile chemistry to functionalize preformed phospholides because all of their known reactions take place at the phosphorus [2]. To prepare functionalized phospholides, it is therefore necessary to install the desired substitution pattern at the α or β positions of a phosphole, prior to transformation into the phospholide. As the synthesis of phospholide anions traditionally involves the alkali metal-induced cleavage of the P–Ph bond of 1-phenylphospholes [3], two approaches are possible, depending upon the stability of the desired functionality towards treatment by an alkali metal. The traditional approach can be used when it is stable, as we have already shown for the 2-PPh_2 derivative [4]. In cases where the substituent is sensitive to an alkali metal, treatment of a P–CH_2CH_2–CO_2Et substituted phosphole by a base may be useful, as was illustrated in the synthesis of a phospholide bearing a 3-CO_2Et functionality [5]. Unfortunately, this second approach employs a multistep synthesis which proceeds in low overall yield and, at the moment, is restricted to the less interesting 3-functional phospholides. In this work, we return to the initial route and systematically investigate the compatibility of several important functionalities with alkali-metal-induced P–C bond cleavage. Several new 2-functional phospholides are thus prepared and characterized.

Results and discussion

We started our investigation with the derivatives of the easily accessible 1-phenyl-3,4-dimethylphosphole-2-carboxylic acid **1** [6]. This acid **1** was first converted into its chloride using the Ph_3P-CCl_4 reagent. Ammonolysis of the chloride in aqueous solution then yielded the amide **2**, of which dehydration gave the nitrile **3** (eq 1).

The low reactivity of the phosphorus lone pair in compounds **1**–**3** is nicely illustrated by its inertness with respect to CCl_4 at ca 70–80 °C. The high-field shift of the C_2CN resonance is the most significant spectroscopic characteristic of **3**. At 114.11 ppm in

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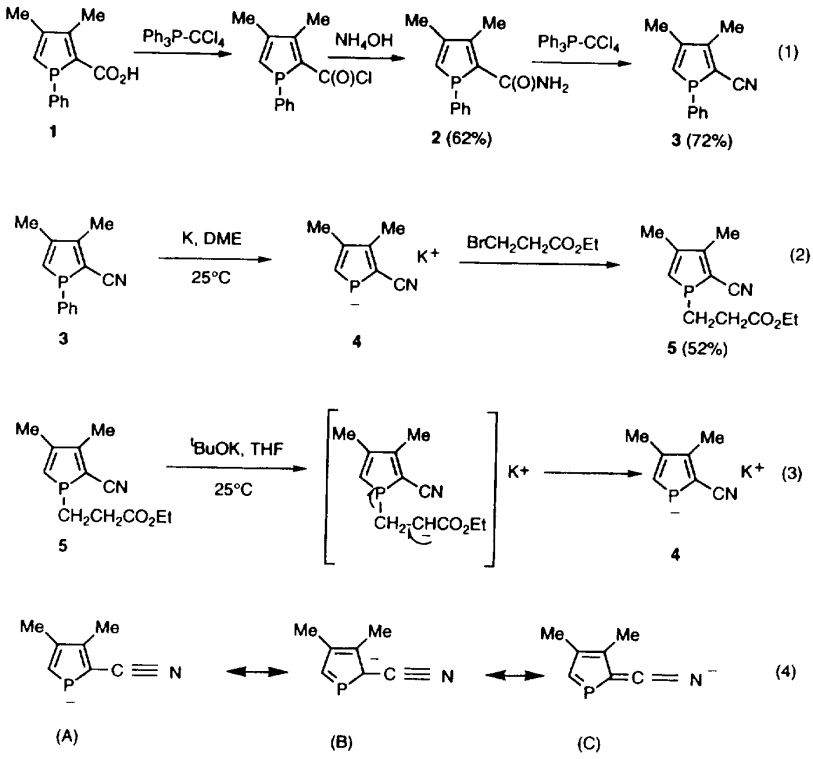


$CDCl_3$, it appears at 15.36 ppm upfield from the C_2 resonance in 1-phenyl-3,4-dimethylphosphole [7]. Correspondingly, the C_5 resonance of **3** is shifted downfield by 5.68 at 135.15 ppm. Unquestionably, these data reflect a significant polarization within the dienic system of **3**. Conversely, the CN resonance is quite normal at 116.86 ppm (compare 118.8 ppm in PhCN) and the large $^2J(P\cdots CN)$ coupling of 23.3 Hz is comparable with that observed for almost any α-substituent of the phosphole ring [7].

The cleavage of the P–Ph bond of **3** was achieved in classical fashion with potassium in 1,2-dimethoxyethane. It yielded the expected phospholide anion **4** which was characterized by a very low-field ^{31}P resonance (113.7 ppm). Unfortunately, the presence of phenylated by-products precluded any serious ^1H and ^{13}C NMR characterization of **4**. Both to demonstrate that the CN functionality was not destroyed during the reaction with potassium and to permit a more complete characterization of **4**, we allowed it to react with $BrCH_2CH_2CO_2Et$. The anticipated phosphole **5** was thus produced in fair yield (eq 2).

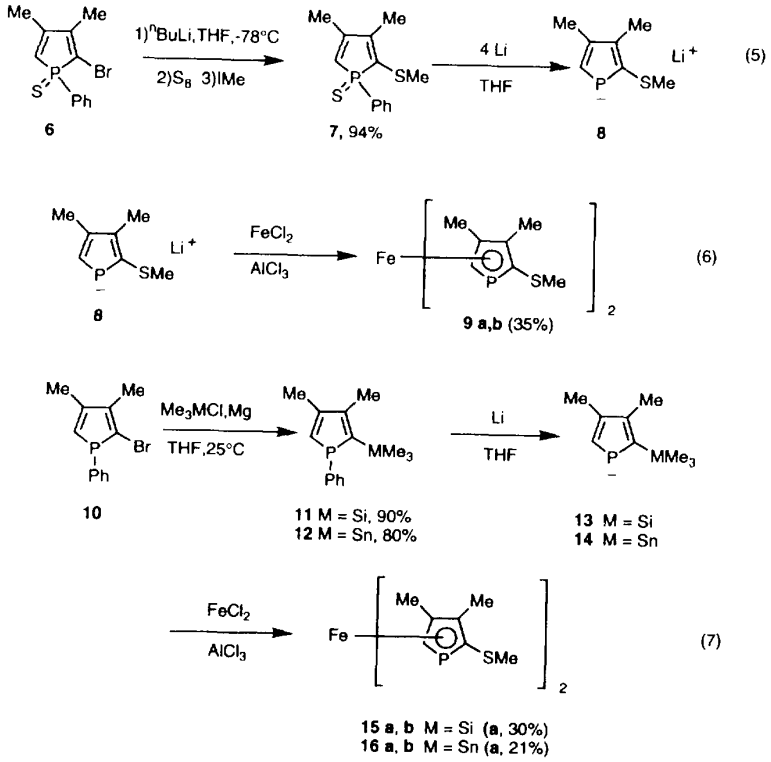
In the ^{13}C spectrum of **5**, the cyano group resonates at 116.40 [^2J(C–P) = 23.24 Hz] and C_2 appears at 111.26 [^1J(C–P) = 2.84 Hz]. Thus, the formula of **4** is clearly established. Subsequent treatment of **5** by *t*BuOK, according to our procedure for the synthesis of a 3-CO_2Et-substituted phospholide [5], produced a purer sample of **4**. Clean ^1H and ^{13}C spectra were obtained by running the reaction in THF-d_8 (eq 3).

The ^{13}C spectrum of **4** is particularly informative. The upfield shift of the C_2 resonance is rather spectacular: δ (C_2) 104.24, ^1J(C–P) = 35.4 Hz. Correspondingly, C_5 is displaced to low fields: δ (C_5) 139.01, ^1J(C–P) = 37.9 Hz. For comparison, the 2-unsubstituted 3,4-dimethylphospholide shows δ (C_α) 128.68, ^1J(C–P) = 44 Hz. Thus, the influence of the cyano group on the π-electron localization seems to be stronger in the anion **4** than in the neutral phosphole **3**. Moreover, the cyano resonance is shifted to very low field: δ (CN) 129.99, ^2J(C–P) = 28.5 Hz. These data suggest a significant contribution of the mesomeric formulation (C) to the electronic structure of **4** (eq 4).

The withdrawal of cyclic electronic density into the cyano group is probably responsible for the failure of $FeCl_2$ to react with **4** to give the corresponding 1,1′-diphosphaferrocene [8].

Our next target was the 2-methylthio derivative. The 2-bromophosphole sulfide **6** [6] was lithiated and sequentially treated with sulfur and methyl iodide. This procedure cleanly afforded the functionalized sulfide **7** (eq 5). Treatment of **7** with an excess of lithium induced simultaneous P=S reduction and P–Ph cleavage to give the expected 2-methylthiophospholide **8** (eq 5).

The ^{31}P resonance of a THF solution of **8** appears at 67 ppm, in the conventional range for such anions. Since the electronic characteristics of the phospholide **8** were obviously less perturbed than in **4**, we did not examine its spectroscopic data in detail, but characterized it by derivatization. Unlike **4**, **8** reacted readily with $FeCl_2$ to give the corresponding 1,1′-diphosphaferrocene **9** as a mixture of the two possible isomers (eq 6). The two isomers were not separated but their formula was unambiguously established by a combination of mass, ^1H, ^{13}C and ^{31}P NMR spectroscopy (see ref [8] for comparison).



Finally, we were able to develop a similar chemistry for the 2-trimethylsilyl and 2-trimethylstannyl derivatives. The appropriate starting phospholes **11** and **12** were easily obtained via direct reaction of the corresponding 2-bromophosphole **10** [6] with silyl and stannyl chlorides in the presence of magnesium in THF (eq 7). The phospholes, which were characterized briefly (for fuller details, see ref [6]), were cleaved cleanly to the corresponding phospholides **13** and **14** by lithium in THF (eq 7).

The ^{31}P resonances of **13** and **14** appear in the normal range at +93 and +89 ppm, respectively. As with **8**, both react with $FeCl_2$ to give the corresponding 1,1′-diphosphaferrocenes **15** and **16**, as a mixture of isomers in each case. The major isomers (a) were isolated in the pure state by chromatography and characterized straightforwardly.

Despite its brutality, the classical synthesis of phospholide anions by cleavage of the P–Ph bonds of 1-phenylphospholes with alkali metals [3] is thus compatible with several useful functional groups (CN, SMe, $SiMe_3$ and $SnMe_3$). A preliminary investigation of the chemistry of functional phospholides is therefore possible.

Experimental section

Spectroscopic determinations were made using the following instrumentation: Bruker AC 200 SY (NMR), Hewlett Packard 5989B (MS).

Merck silica gel $60F_{254}$ was used for analytical and preparative TLC. DME and THF were distilled from sodium diphenylketyl just before use; these solvents were stored under N_2.

1-Phenyl-3,4-dimethylphosphole-2-carboxamide **2**

A mixture of 6.7 g (25.5 mmol) triphenylphosphine, 20 mL CCl_4 and 60 mL THF was refluxed together for 0.5 h. The solution was cooled at room temperature and 2.5 g (8.5 mmol) **1** was added. The consumption of **1** was followed by ^{31}P NMR. When the reaction was complete (about 1.5 h), 4.5 mL (11 mmol) of a concentrated solution of ammonia was added and the mixture stirred for 15 min. The precipitate was filtered and the solution extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent removed. The mixture was chromatographed with hexane/ether (80:20) as eluent to give 1.55 g (62%) of **2**.

^1H NMR (DMSO) δ: 2.10 (dd, $^4J_{HP}$ = 3.6 Hz, CH_3), 2.23 (d, $^4J_{HP}$ = 3.5 Hz, CH_3), 6.68 (d, $^2J_{HP}$ = 38.6 Hz, =CH).

^{13}C NMR ($CDCl_3$) δ: 17.02 (s, CH_3), 19.34 (d, $^3J_{CP}$ = 2.9 Hz, CH_3), 130.19 (d, $^3J_{CP}$ = 8.8 Hz, Ph, *meta*), 130.78 (d, $^1J_{CP}$ = 8.6 Hz, Ph, C *ipso*), 131.36 (s, Ph, *para*), 132.68 (s, C_2), 135.00 (d, $^2J_{CP}$ = 19.3 Hz, Ph, *ortho*), 138.50 (d, $^1J_{CP}$ = 4.7 Hz, C_5), 151.74 (d, $^2J_{CP}$ = 5.7 Hz, C_3 or C_4), 156.67 (d, $^2J_{CP}$ = 12.3 Hz, C_4 or C_3), 169.38 (d, $^2J_{CP}$ = 20.0 Hz, CO).

^{31}P NMR ($CDCl_3$) δ: 4.4.

Mass spectrum *m/z*: 231 (M^+, 38%), 203 (M^+ - CO, 100%).

Anal $C_{13}H_{14}NOP$ calc: C, 67.53; H, 6.06; N, 6.06. Found: C, 67.64; H, 6.21; N, 5.77.

1-Phenyl-2-cyano-3,4-dimethylphosphole **3**

A mixture of 1.3 g (5 mmol) triphenylphosphine, 4 mL CCl_4 and 12 mL THF was refluxed for 30 min. Compound **2** (0.38 g, 1.65 mmol) was added. The formation of **3** was complete within 1 h. The mixture was cooled at room temperature, the solvent removed and the crude mixture chromatographed with hexane/ether (80:20) as eluent to give 0.25 g (72%) of **3**.

^{1}H NMR ($CDCl_3$) δ: 2.15 (dd, $^4J_{HP}$ = 3.2 Hz, CH_3), 2.32 (d, $^4J_{HP}$ = 4.8 Hz, CH_3), 6.73 (d, $^2J_{HP}$ = 39.0 Hz, =CH).

^{13}C NMR ($CDCl_3$) δ: 17.09 (s, CH_3), 17.48 (s, CH_3), 114.11 (s, C_2), 116.86 (d, $^2J_{CP}$ = 23.3 Hz, CN), 127.97 (d, $^1J_{CP}$ = 13.7 Hz, Ph, C *ipso*), 128.83 (d, $^3J_{CP}$ = 8.1 Hz, Ph, C *meta*), 130.15 (s, Ph, C *para*), 133.26 (d, $^2J_{CP}$ = 20.6 Hz, Ph, C *ortho*), 135.15 (d, $^1J_{CP}$ = 5.5 Hz, C_5), 148.58 (d, $^2J_{CP}$ = 2.3 Hz, C_3 or C_4), 162.47 ($^2J_{CP}$ = 14.6 Hz, C_4 or C_3).

Mass spectrum m/z: 213 (M^+, 100%).

IR ν 2 192 cm^{-1} (CN).

Anal $C_{13}H_{12}NP$ calc: C, 73.24; H, 5.63; N, 6.57. Found: C, 73.01; H, 5.74; N, 6.56.

1-[2-(Ethoxycarbonyl)ethyl]-2-cyano-3,4-dimethylphosphole **5**

Phosphole **3** (0.6 g, 2.2 mmol) was stirred with 0.22 g (5.6 mmol) of potassium in DME (10 mL) for 1.5 h. The mixture was cooled at 0 °C and 0.43 mL (2.8 mmol) $BrCH_2CH_2COOEt$ was added. After 0.5 h, DME was removed and the mixture chromatographed with CH_2Cl_2/AcOEt (90:10) to give 0.32 g (52%) of **5**.

^{1}H NMR ($CDCl_3$) δ: 1.25 (t, $^3J_{HH}$ = 7.2 Hz, $COOCH_2CH_3$), 2.12 (d, $^4J_{HP}$ = 1.1 Hz, CH_3), 2.16–2.30 (m, CH_3, PCH_2CH_2), 4.12 (q, $^3J_{HH}$ = 7.2 Hz, $COOCH_2CH_3$), 6.60 (d, $^2J_{HP}$ = 39.0 Hz, HC=P).

^{13}C NMR ($CDCl_3$) δ: 13.72 (s, $COOCH_2CH_3$), 16.78 (s, CH_3), 17.15 (s, CH_3), 18.02 (d, $^2J_{CP}$ = 22.01 Hz, PCH_2), 29.63 (s, CH_2CO), 60.20 (s, OCH_2), 111.26 (d, $^1J_{CP}$ = 2.80 Hz, C_2), 116.40 (d, $^2J_{CP}$ = 23.1 Hz, CN), 134.23 (d, $^1J_{CP}$ = 8.70 Hz, C_5), 148.93 (s, C_4 or C_3), 162.92 (d, $^2J_{CP}$ = 13.46 Hz, C_3 or C_4), 171.75 (d, $^3J_{CP}$ = 5.92 Hz, CO).

^{31}P NMR ($CDCl_3$) δ: 12.11.

Potassium 2-cyano-3,4-dimethylphospholide **4**

Phosphole **5** (0.24 g, 1 mmol) was dissolved in THF-d_8 (0.5 mL) and potassium *tert*-butylate (0.11 g, 1 mmol) was added at room temperature. The anion **4** was immediately formed and ^{31}P, ^{1}H and ^{13}C spectra recorded.

^{1}H NMR (THF-d_8) δ: 2.20 (s, CH_3), 2.32 (s, CH_3), 6.88 (d, $^2J_{HP}$ = 42.0 Hz, HC=P).

^{13}C NMR (THF-d_8) δ: 15.80 (s, CH_3), 16.68 (s, CH_3), 104.24 (d, $^1J_{CP}$ = 35.4 Hz, C_2), 128.99 (d, $^2J_{CP}$ = 28.5 Hz, CN), 130.05 (d, $^3J_{CP}$ = 7.8 Hz, C_3 or C_4), 135.46 (d, $^3J_{CP}$ = 6.0 Hz, C_4 or C_3), 139.01 (d, $^1J_{CP}$ = 37.9 Hz, C_5).

^{31}P NMR (THF-d_8) δ: 111.86.

1-Phenyl-2-methylthio-3,4-dimethylphosphole 1-sulfide **7**

n-Butyllithium (6.5 mL, 1.55 M, 10 mmol) was slowly added to 3.0 g (10 mmol) of **6** in freshly distilled dry THF (30 mL) at −78 °C. The solution turned deep red. After 30 min, 0.33 g (10 mmol) sulfur was added. Then, after 10 min, 1.0 mL (13 mmol) iodomethane was added. The mixture was warmed to room temperature. Solvent was removed and the crude mixture was chromatographed with toluene to give 2.52 g (94%) of **7**.

^{1}H NMR ($CDCl_3$) δ: 2.07 (d, $^4J_{HP}$ = 1.2 Hz, CH_3), 2.11 (d, $^4J_{HP}$ = 1.2 Hz, CH_3), 2.26 (s, SCH_3), 5.98 (d, $^2J_{HP}$ = 31.4 Hz, HC=).

^{13}C NMR ($CDCl_3$) δ: 14.18 (d, $^3J_{CP}$ = 14.2 Hz, CH_3), 14.78 (d, $^3J_{CP}$ = 3.2 Hz, CH_3), 17.70 (d, $^3J_{CP}$ = 17.8 Hz, SCH_3), 122.50 (d, $^1J_{CP}$ = 82.0 Hz, C_5), 127.20 (d, $^1J_{CP}$ = 78.1 Hz, Ph, C *ipso*), 128.29 (d, J_{CP} = 13.24 Hz, Ph, *meta* or *ortho*), 130.01 (d, J_{CP} = 11.23 Hz, Ph, *ortho* or *meta*), 131.54 (s, Ph, *para*), 132.49 (d, $^1J_{CP}$ = 74.9 Hz, C_2), 146.79 (d, $^2J_{CP}$ = 27.4 Hz, C_3 or C_4), 153.79 (d, $^2J_{CP}$ = 15.1 Hz, C_4 or C_3).

^{31}P NMR ($CDCl_3$) δ: 50.4.

Mass spectrum m/z: 288 (M^+, 100%).

1-Phenyl-2-trimethylsilyl-3,4-dimethylphosphole **11**

A mixture of 2.0 g (6.7 mmol) of **10**, 0.4 g (16.7 mmol) magnesium and 1.82 g (16.7 mmol) chlorotrimethylsilane in THF (15 mL) was stirred for 3 h at room temperature. After filtration, THF was removed and the crude material was extracted by hexane. After evaporation, 1.56 g (90%) of **11** was isolated.

1-Phenyl-2-trimethylstannyl-3,4-dimethylphosphole **12**

A mixture of 2.0 g (6.7 mmol) of **10**, 0.4 g (16.7 mmol) magnesium and 3.72 g (16.7 mmol) trimethyltin chloride in 15 mL THF was stirred for 15 h at room temperature. After filtration, THF was removed and the crude material extracted by hexane. After evaporation, 1.88 g (80%) of **12** was obtained.

^{1}H NMR ($CDCl_3$) δ: 2.15 (broad s, CH_3), 6.4 (d, $^2J_{HP}$ = 38.4 Hz, =CH).

^{31}P NMR (THF) δ: 15.2 ($^2J_{PSn}$ = 217.5 Hz).

2,2′-Bis-(methylthio)-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene **9**

Sulfide **7** (2.52 g, 9.5 mmol) was stirred with 0.28 g (40 mmol) lithium in THF (15 mL) for 1.5 h. The mixture was cooled to 0 °C and 0.21 g (1.6 mmol) aluminium chloride was added. Then, it was allowed to warm to room temperature, and 0.6 g (4.8 mmol) iron(II) chloride was added. After 0.5 h, THF was removed, and the crude mixture was chromatographed in hexane to give 0.62 g (35%) of two isomers (**9a**/**9b** = 70:30).

^{1}H NMR (CD_2Cl_2) **9a**: δ 2.09 (d, $^4J_{HP}$ = 0.9 Hz, CH_3), 2.18 (s, SCH_3), 3.59 (d, $^2J_{HP}$ = 36.0 Hz, HC=). **9b**: δ 2.12 (s, CH_3), 2.19 (s, SCH_3), 3.74 (d, $^2J_{HP}$ = 36.0 Hz, HC=).

^{13}C NMR (CD_2Cl_2) **9a**: δ 12.30 (s, CH_3), 15.76 (s, CH_3), 21.56 (d, $^3J_{CP}$ = 11.0 Hz, SCH_3), 81.66 (d, $^1J_{CP}$ = 65.5 Hz, C_5, $C_{5'}$). **9b**: δ 12.72 (s, CH_3), 16.36 (s, CH_3), 21.44 (d, $^3J_{CP}$ = 10.7 Hz, SCH_3), 82.32 (d, $^1J_{CP}$ = 62.3 Hz, C_5, $C_{5'}$).

^{31}P NMR (CD_2Cl_2) **9a**: δ −65.2. **9b**: δ −60.9.

Mass spectrum m/z 370 (M^+, 100%).

2,2′-Bis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene **15**

Phosphole **11** (0.28 g, 1.05 mmol) was stirred with 0.05 g (3.5 mmol) lithium in THF (5 mL) for 1.5 h. The mixture was cooled at 0 °C and 0.03 g (7.2 mmol) aluminium chloride was added. Then, it was allowed to warm to room temperature and 0.07 g (0.55 mmol) iron(II) chloride was added. After 0.5 h, THF was removed and a mixture of 2 isomers (**15a** and **15b**) was obtained. By chromatography in hexane, it was possible to isolate 0.07 g (30%) of pure isomer **15a**.

^{1}H NMR (CD_2Cl_2) **15a**: δ 0.19 (s, $SiCH_3$), 2.23 (s, CH_3), 2.27 (s, CH_3), 3.94 (d, $^2J_{HP}$ = 35.6 Hz, HC=).

^{13}C NMR (CD_2Cl_2) **15a**: δ 1.93 (d, $^3J_{CP}$ = 2.5 Hz, $SiCH_3$), 17.29 (s, CH_3), 85.32 (d, $^1J_{CP}$ = 62.99 Hz, C_5, $C_{5'}$), 88.19

(d, $^1J_{CP}$ = 79.51 Hz, C_2, $C_{2'}$), 100.80 (s, C_3, $C_{3'}$ or C_4, $C_{4'}$), 102.69 (s, C_3, $C_{3'}$ or C_4, $C_{4'}$).

^{31}P NMR (hexane) **15a**: δ −35.26. **15b**: δ −48.28.

Mass spectrum m/z: 422 (M^+, 100%).

2,2'-Bis(trimethylstannyl)-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene **16**

Phosphole **12** (1 g, 2.85 mmol) was stirred with 0.04 g (5.7 mmol) lithium in THF (5 mL) for 1.5 h. The mixture was cooled at 0 °C and 0.07 g (0.53 mmol) aluminium chloride was added. Then, it was allowed to warm to room temperature and 0.18 g (1.4 mmol) iron(II) chloride was added. After 0.5 h, THF was removed and a mixture of isomers was obtained. By chromatography in hexane on florisil, it was possible to isolate 0.18 g (21%) of isomer **16a**.

^{1}H NMR ($CDCl_3$) δ 0.31 (s, $Sn(CH_3)_3$), 2.28 (s, CH_3), 2.31 (s, CH_3), 3.95 (d, $^2J_{HP}$ = 34.6 Hz, HC=).

^{13}C NMR (C_6D_6) δ: 0.74 (s, $Sn(CH_3)_3$), 18.45 (s, CH_3), 18.88 (s, CH_3), 86.70 (d, $^1J_{CP}$ = 66.9 Hz, C_5, $C_{5'}$).

^{31}P NMR (CH_2Cl_2) δ: −42.44 ($^2J_{PSn}$ = 226.3 Hz).

Mass spectrum m/z: 604 (M^+, 6%), 589 ($M^+ - CH_3$, 15%).

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