

2-Diphenylphosphino-1,3-diphospholide anions

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Abstract

The title compounds are easily obtained in four steps from 4,5-disubstituted 1,3-diphenyl-1,3-diphosphacyclopent-4-enes (**1**). Metallation of the P–CH₂–P unit of **1** followed by reaction with Ph₂PCl allows a diphenylphosphino group to be grafted onto **1** at the C₂ carbon. After removal of the remaining C₂H proton by a base, selective cleavage of the two P₁–Ph and P₃–Ph bonds by lithium in THF affords the corresponding 2-diphenylphosphino-1,3-diphospholide ions (**5**). In one case, the reaction of n-butyllithium with **1a** leads to an opening of the five-membered ring via a nucleophilic attack at phosphorus. A bis-(phosphino)methanide ion (**8**) is thus obtained. Its chemistry has been investigated briefly.

Keywords: 1,3-Diphosphacyclopent-4-ene; 1,3-Diphospholide anions; 2-Diphenylphosphino-1,3-diphospholide ions; bis-(Phosphino)methanide ion; 1,3-Diphospha-ferrocene

1. Introduction

Phosphinocyclopentadienide anions are bidentate ligands which are frequently employed to promote interactions between two different metals [1]. Additionally, an electronic analogy between cyclopentadienide and phospho- or polyphosphacyclopentadienides is quite obvious [2], and a wide range of η^5 -complexes is accessible for most members of the phosphacyclopentadienide series [3]. As a consequence, the development of synthetic routes to the phosphino derivatives of phospho- and polyphosphacyclopentadienides becomes attractive. These ligands display three types of coordinating center, each having quite discrete behavior: the PR₂ group has σ -donor properties, the cyclic P atoms have π -acceptor properties and the five-membered ring shows Cp-like

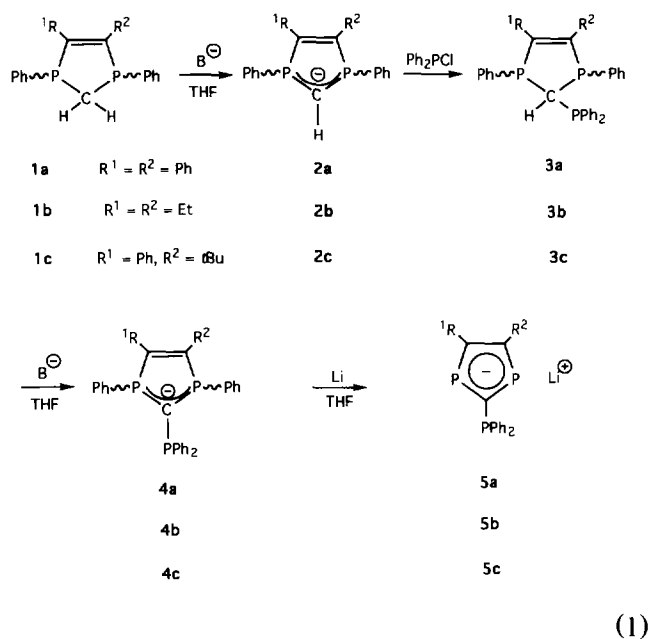
characteristics. We have previously developed access to the 2-phenylphosphinophospholide ions [4] and here present an extension of this methodology to the synthesis of 2-diphenylphosphino-1,3-diphospholide ions.

2. Results and discussion

Our synthetic approach is a variation of a route which we devised for the transformation of 4,5-disubstituted 1,3-diphenyl-1,3-diphosphacyclopent-4-enes into 1,3-diphospholide anions. This methodology involved metallation of the P–CH₂–P unit, which serves to strengthen the ring by a partially delocalizing electron density over the 2-position and, subsequently, a selective lithium-induced cleavage of the two external *cis* or *trans* P–Ph bonds to afford the desired 1,3-diphospholides [5]. In the modified scheme presented here, the first-formed [P–CH–P][–] anions are allowed to react with diphenylchlorophosphine in order to graft the PPh₂ substituent onto the C₂ carbon. Remetallation then gives the substituted [P–C(PPh₂)–P][–] anions,

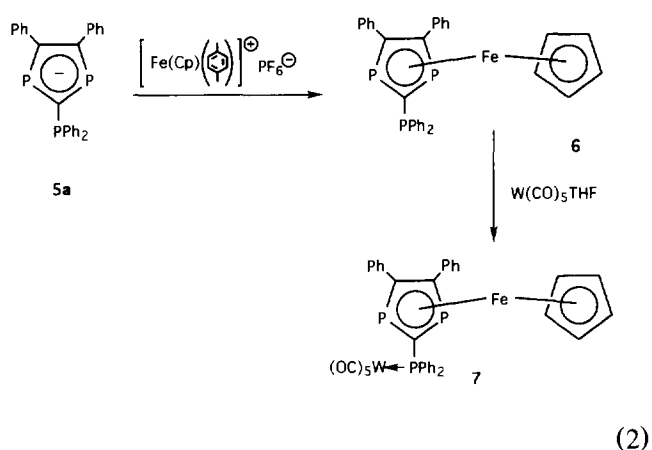
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whose reaction with lithium affords the expected 2-(di-phenylphosphino)-1,3-diphospholides:

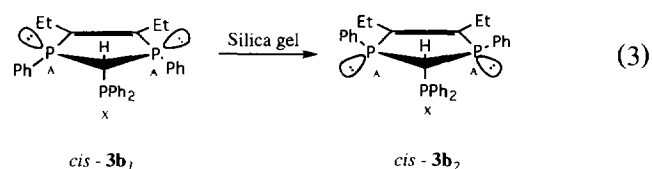


For **1a** ($R^1 = R^2 = \text{Ph}$), a careful choice of metallating agent B^- is important. Lithium dialkylamides ($R_2\text{NLi}$) are acceptable, but *n*-butyllithium may induce ring-cleavage reactions which will be discussed in more detail below. Deprotonation of pure **1a** with LDA at 20°C gives anion **2a** as a mixture of *cis* and *trans* isomers in a 15:85 ratio ($\delta_{31\text{P}} = 67.74$ for the *cis* and 97.42 for the *trans* isomer). After heating at 50°C for 1 h, this ratio evolves to 1:1, thus demonstrating that the *cis* isomer is the thermodynamic product. The composition of these mixtures was easily established by protonation, because the resulting *cis* and *trans* **1a** show characteristic ^1H NMR patterns for the P–CH₂–P unit. The reaction of **2a** (*cis:trans* 15:85) with Ph_2PCl leads to pure *trans* **3a**, as shown by the ABX pattern for the three different phosphorus atoms in the ^{31}P NMR spectrum. A combined analysis of the ^1H and ^{31}P NMR spectra of **3a**, using the classical relationship between $^2J_{(\text{H}-\text{C}-\text{P})}$ and the H–C–P lone pair dihedral angle [6], demonstrates that the PPh_2 phosphorus (X) is strongly coupled (ca. 200 Hz) to the cyclic phosphorus (A or B) when the X–C–A(B) lone pair dihedral angle α approaches 0°. When α is close to 120°, the $^2J_{(\text{A}(\text{B})-\text{X})}$ coupling is low (ca. 20 Hz). This observation was employed to establish the stereochemistry of the various isomers of **3a–c**. The reaction of Et_2NLi with *trans* **3a** leads to the anion *trans* **4a** which, upon heating, isomerizes to give *cis* **4a**. Both anions display an $\text{A}_2\text{X } ^{31}\text{P}$ NMR spectrum: *trans* **4a** $\delta_{\text{A}} + 98.8$, $\delta_{\text{X}} - 4.5$, $^2J_{(\text{AX})} = 128$ Hz; *cis* **4a** $\delta_{\text{A}} + 58.3$, $\delta_{\text{X}} + 12.1$, $^2J_{(\text{AX})} = 211$ Hz. The equivalence of the two ring phosphorus atoms in

trans **4a** and the formation of only one *cis* isomer suggest that the CP_3 carbon is planar in these anions. This hypothesis is supported by the X-ray crystal structure analysis of $\text{Li}[\text{C}(\text{PMe}_2)_3] \cdot \text{THF}$, which has a quasi-planar central carbon, Σ_{PCP} angles 350.8° [7]. Both *trans* and *cis* **4a** react with lithium in THF to give the substituted 1,3-diphospholide **5a**, which is easily identified by its characteristic $\text{A}_2\text{X } ^{31}\text{P}$ spectrum: $\delta_{\text{A}} + 224.6$, $\delta_{\text{X}} - 13.1$, $^2J_{(\text{AX})} = 133$ Hz. For additional characterization, **5a** was also converted into the corresponding 1,3-diphospha-ferrocene **6** and its $\text{P}_X-\text{W}(\text{CO})_5$ complex **7**:



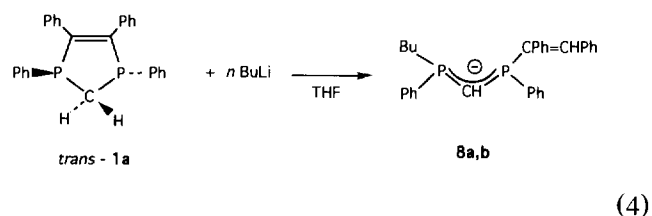
A first difference in the diethyl series ($R^1 = R^2 = \text{Et}$) concerns the *cis:trans* ratio. *Cis* isomers dominate throughout the series. Secondly, **2b** can be obtained by reaction of *n*-butyllithium with **1b**, as described for the corresponding non-functionalized diphospholide [5]. The reaction of Ph_2PCl with *cis*-**2b** leads to a kinetic *cis*-**3b₁** isomer whose PPh_2 lies on the same side of the ring as the phenyl 1,3-substituents; the $^2J_{(\text{AX})}$ coupling is low at 13 Hz. When chromatographed on silica gel, *cis*-**3b₁** epimerizes to the thermodynamic isomer *cis*-**3b₂**, where the PPh_2 and the phenyl 1,3-substituents lie on opposite sides of the ring. This epimerisation is obviously favored by some steric decompression:



In *cis*-**3b₂**, the $^2J_{(\text{AX})}$ coupling of 200 Hz is high. In **4b**, the comparably large $^2J_{(\text{AX})}$ coupling of 210 Hz confirms the *cis*-disposition of the two 1,3-phenyl substituents. It should be noted that some cleavage of the ring– PPh_2 bond was observed during the final step leading to **5b**.

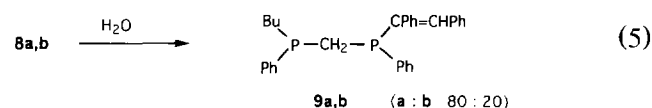
In the last case ($R^1 = \text{Ph}$, $R^2 = {}^1\text{Bu}$), the interpretation of the NMR spectra is more difficult, but the overall behavior of the system resembles that for $R^1 = R^2 = \text{Ph}$. The product phospholide anion **5c** shows two ^{31}P ring resonances at +188.4 and +205.7 with a $^2J_{(\text{P}-\text{P})}$ coupling of only 17 Hz. As in the diethyl case, some cleavage of the ring– PPh_2 bond in the last step leads to traces of the non-functionalized 1,3-diphospholide.

We have already noted that *n*-butyllithium cleaves the ring of **1a**, acting as a nucleophile rather than a base. The product is a bis-(phosphino)methanide ion:



The unexpected initial attack at phosphorus leads to the preferential cleavage of the $\text{P}_1\text{--C}_5$ bond. The vinyl anion which is generated by this process then deprotonates the $\text{P--CH}_2\text{--P}$ unit to give the more stable delocalised bis-(phosphino)methanide **8**. The existence of this anion as a 1 : 1 mixture of two isomers is probably the result of the chirality of the two phosphorus centers. Both isomers show huge $^2J_{(\text{P}-\text{P})}$ coupling constants: **8a** δ_{P} +18.1 and -11.4 , $^2J_{(\text{P}-\text{P})} = 405$ Hz; **8b** δ_{P} +17.7 and -11.6 , $^2J_{(\text{P}-\text{P})} = 399$ Hz. It is known from the literature [8] and from this work (see the data for the anions **4**) that the $^2J_{(\text{P}-\text{P})}$ couplings can reach very high absolute values in (polyphosphino)methanide ions. Even in this light, however, the data for **8a,b** were sufficiently extraordinary to require a check of the structure of **8** by an investigation of some of its chemical transformations.

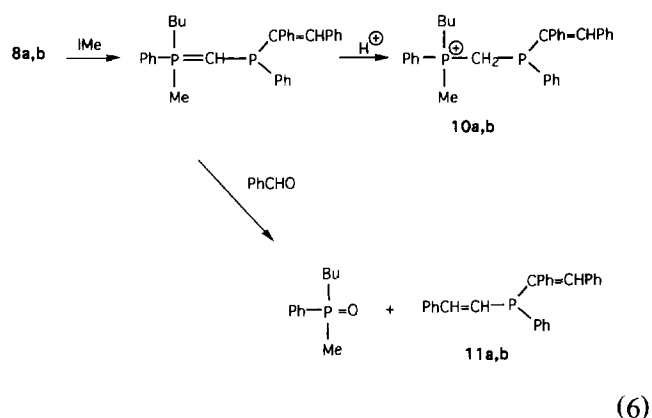
Protonation, which occurs at carbon, gives the diphosphine **9** as a mixture of two diastereomers:



The $^2J_{(\text{P}-\text{P})}$ couplings (122 and 118 Hz) are within the range of literature values for such species [9]. The presence of only one $=\text{CH}$ resonance in the ^{13}C spectrum (δ +139.0, $^2J_{(\text{C}-\text{P})} = 42$ Hz) confirms that the two isomers reflect the presence of two chiral phosphorus centers rather than *Z/E* stereoisomerism at the $\text{C}=\text{C}$ double bond.

It is well known that phosphinomethanide ions are ambident nucleophiles which can react either at carbon

or at phosphorus [10]. Here, methyl iodide reacts at the phosphorus centers to give a complex mixture of five phosphorus ylids. The $^2J_{(\text{P}-\text{P})}$ couplings of 130–154 Hz are again in line with the published data on similar species [11]. The majority of these ylids result from the attack of IMe on the more nucleophilic Bu--P center, as shown by the subsequent chemistry given in Eq. (6):



The reaction with aldehydes offers some potential for the synthesis of unusual divinylphosphines. According to inspection of their NMR spectra, the two isomers of **11** arise from the *Z/E* stereoisomerism at the newly created $\text{HC}=\text{CH}$ double bond.

3. Experimental section

All reactions were performed under argon; the solvents were purified, dried and degassed by standard techniques. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13, 50.32 and 81.01 MHz respectively. All chemical shifts are reported in parts per million downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra (EI) were obtained at 70 eV by the direct inlet method. Elemental analyses were performed by the ‘‘Service d’analyse du CNRS’’. (Note: in the following P_A and P_B refer to the phosphorus atoms in the ring and P_X to the chain; pt, pseudo-triplet.)

3.1. Compounds **1a** and **c**

Compound **1a** is obtained in 72% yield as a mixture of two *cis* and *trans* isomers (20 : 80) by the procedure previously given for **1b** [5]. The major (*trans*) isomer was isolated as a white solid, m.p. 147°C. Anal. Found: C, 79.28; H, 5.51. $\text{C}_{27}\text{H}_{22}\text{P}_2$ Calc.: C, 79.40; H, 5.43%. ^{31}P NMR (CDCl_3): δ +51.9. ^1H NMR (CDCl_3): δ 2.4 (part AA' of AA'XX', 2H, $\Sigma^2J_{\text{HP}} = 15.2$ Hz, PCH_2P). 7–7.5 (m, 20H, phenyl). ^{13}C NMR (CDCl_3): δ 23.64 (t,

$^1J_{CP} = 19$ Hz, PCP), 126.8–138.1 (m, phenyl), 149.2 (s, PC). The *cis* isomer is a colorless oil. ^{31}P NMR (CDCl_3): $\delta +27.5$. ^1H NMR (CDCl_3): δ 2.42 (part B of ABXX', 1H, $^2J_{H_A H_B} = 14$ Hz, $^2J_{H_B P_X} = 4.1$ Hz, $\text{PCH}_A H_B \text{P}$), 3.12 (part A of ABXX', 1H, $^2J_{H_A P_X} = 27$ Hz, $\text{PCH}_A H_B \text{P}$), 7.1–7.9 (m, 20H, phenyl). ^{13}C NMR (CDCl_3): δ 22.7 (t, $^1J_{CP} = 24.5$ Hz, PCP), 128.7–139.7 (m, phenyl), 148.07 (pt, $\Sigma^1 J_{CP} + ^2 J_{CP} = 0$ Hz, PC).

Compound **1c** is obtained as a mixture of two isomers *cis*:*trans* (55:45) in a procedure slightly modified from that for **1b** [5]. The cleavage of the 1,2-dihydrodiphosphete is performed with two equivalents of sodium. Yield 53%. ^{31}P NMR (CDCl_3): $\delta +56.3$ and $+40.9$ ($^2J_{PP} = 22$ Hz, *trans* isomer); $+37.0$ and 23.8 ($^2J_{PP} = 15$ Hz, *cis* isomer). ^1H NMR (CDCl_3): δ 0.96 (d, 9H, $^4J_{PH} = 0.9$ Hz, ^1Bu , *cis* isomer), 1.02 (s, 9H, ^1Bu , *trans* isomer), 1.97 (part A of ABXY, 1H, $^2J_{H_A H_B} = 14.3$ Hz, $^2J_{H_A P_X} = 20.1$ Hz, $^2J_{H_A P_Y} = 0.8$ Hz, $\text{PCH}_A H_B \text{P}$, *trans* isomer), 2.12 (part B of ABXY, 1H, $^2J_{H_A H_B} = 13.8$ Hz, $^2J_{H_B P_X} = ^2J_{H_B P_Y} = 3.8$ Hz, $\text{PCH}_A H_B \text{P}$, *cis* isomer), 2.3 (part B of ABXY, 1H, $^2J_{H_B P_Y} = 20.7$ Hz, $^2J_{H_B P_X} = 6.2$ Hz, $\text{PCH}_A H_B \text{P}$, *trans* isomer), 2.72 (part A of ABXY, 1H, $^2J_{H_A P_X} = 26.8$ Hz, $^2J_{H_A P_Y} = 27.4$ Hz, $\text{PCH}_A H_B \text{P}$, *cis* isomer), 7–7.9 (m, 15H, phenyl, *cis* and *trans* isomers). ^{13}C NMR (CDCl_3): δ 21.6 (t, $^1J_{CP_X} = ^1J_{CP_Y} = 22$ Hz, PCP, *cis* isomer), 24.12 (dd, $^1J_{CP_X} = 15.2$ Hz, $^1J_{CP_Y} = 20.3$ Hz, PCP, *trans* isomer), 32.55 (d, $^3J_{CP} = 7$ Hz, ^1Bu , *cis* or *trans* isomer), 32.41 (d, $^3J_{CP} = 7$ Hz, ^1Bu , *trans* or *cis* isomer), 38.19 (pt, $\Sigma^2 J_{CP} + ^3 J_{CP} = 20$ Hz, CMe_3 , *cis* or *trans* isomer), 38.56 (pt, $\Sigma^2 J_{CP} + ^3 J_{CP} = 24$ Hz, CMe_3 , *trans* or *cis* isomer), 125–143 (m, phenyl, *cis* and *trans* isomers), 139.6 (pt, $\Sigma^1 J_{CP} + ^2 J_{CP} = 0$ Hz, CPh, *cis* or *trans* isomer), 139.7 (pt, $\Sigma^1 J_{CP} + ^2 J_{CP} = 2$ Hz, :CPh, *trans* or *cis* isomer), 150.4 (pt, $\Sigma^1 J_{CP} + ^2 J_{CP} = 20$ Hz, :C ^1Bu , *cis* or *trans* isomer), 153.4 (pt, $\Sigma^1 J_{CP} + ^2 J_{CP} = 22$ Hz, :C ^1Bu , *trans* or *cis* isomer).

3.2. Compounds **3a**, **b** and **c**

A solution of 10 mmol of $^i\text{Pr}_2\text{NLi}$ (0.7 M) in hexane/THF was added dropwise to 7 mmol of **1a** or **1c** in 15 ml of dry THF at -50°C and the reaction mixture was subsequently warmed slowly to room temperature. **2a** showed one ^{31}P resonance at $+97.42$ for the *trans* isomer and $+67.74$ for the *cis* isomer. ^{31}P NMR of **2c** showed two AB systems, one at $+60.7$ and $+86.7$, with $^2J_{PP} = 6$ Hz for the *cis* isomer, and the other at $+79.2$ and $+101.9$, with $^2J_{PP} = 34$ Hz for the *trans* isomer. The mixture of **2a** or **2c** or **2b** [5] was added dropwise to 20 mmol of Ph_2PCI (previously degassed under vacuum in order to eliminate HCl) in 5 ml of dry THF at -80°C . The reaction mixture was slowly warmed to room temperature and the solvents evaporated.

3a was crystallized from 200 ml of methanol as a pale yellow solid, yield 62%. Anal. Found: C, 79.34; H, 5.46. $\text{C}_{39}\text{H}_{31}\text{P}_3$ Calc.: C, 79.05; H, 5.27%. Mass spectrum: m/z 592 (M^+ , 24%), 407 ($\text{M}-\text{PPh}_2$, 100%). ^{31}P NMR (CD_2Cl_2): $\delta +63.1$ (dd, $^2J_{P_A P_B} = 20.5$ Hz, $^2J_{P_A P_X} = 165.5$ Hz, P_A), $+59.4$ (dd, $^2J_{P_B P_X} = 28.4$ Hz, P_B), -18.4 (dd, P_X). ^1H NMR (CD_2Cl_2): δ 3.56 (ddd, 1H, $^2J_{HP_A} = 5.1$ Hz, $^2J_{HP_B} = 18$ Hz, $^2J_{HP_X} = 2.5$ Hz, CHP_3), 6.9–7.6 (m, 30H, phenyl). ^{13}C NMR (CD_2Cl_2): δ 34.06 (q, $^1J_{CP} = 28$ Hz, CP_3), 126–139.5 (m, phenyl), 147.5 (pt, $\Sigma^1 J_{CP} + ^2 J_{CP} = 30$ Hz, :CPh), 153.1 (pt, $\Sigma^1 J_{CP} + ^2 J_{CP} = 19$ Hz, :CPh).

3b: the residue was chromatographed on silica gel with hexane/toluene (70:30) as eluant, to give **3b** in the form of a pale yellow oil as a mixture of two *cis* isomers. Yield 75%. ^{31}P NMR (CD_2Cl_2): $\delta +36.5$ (d, $^2J_{P_A P_X} = 13.5$ Hz, P_A), -22.1 (t, P_X) for **3b**₁ (kinetic isomer); $\delta +29.3$ (d, $^2J_{P_A P_X} = 200$ Hz, P_A), -9.5 (pt, P_X) for **3b**₂ (thermodynamic isomer). ^1H NMR (CD_2Cl_2): δ 0.96 (t, 6H, $^3J_{HH} = 7.5$ Hz, CH_3), 1.02 (t, 6H, $^3J_{HH} = 7.5$ Hz, CH_3), 1.96 (m, 4H, CH_2), 2.42 (m, 4H, CH_2), 3.06 (dt, 1H, $^2J_{HP_A} = 3.4$ Hz, $^2J_{HP_X} = 1.5$ Hz, CHP_3 , **3b**₂), 3.95 (t, 1H, $^2J_{HP_A} = 22.1$ Hz, $^2J_{HP_X} = 0$ Hz, CHP_3 , **3b**₁), 6.9–7.4 (m, $2 \times 20\text{H}$, phenyl). ^{13}C NMR (CD_2Cl_2): δ 15.43 (d, $\Sigma^3 J_{CP} + ^4 J_{CP} = 7.1$ Hz, CH_3), 16.0 (pt, $\Sigma^3 J_{CP} + ^4 J_{CP} = 7$ Hz, CH_3), 24.33 (pt, $\Sigma^2 J_{CP} + ^3 J_{CP} = 0$ Hz, CH_2), 24.42 (pt, $\Sigma^2 J_{CP} + ^3 J_{CP} = 0$ Hz, CH_2), 38.1–39.1 (m, CHP_3 , both isomers), 126–140 (m, phenyl), 149.64 (pt, $\Sigma^1 J_{CP} + ^2 J_{CP} = 11$ Hz, :C-Et), 150.7 (pt, $\Sigma^1 J_{CP} + ^2 J_{CP} = 10$ Hz, :C-Et).

3c: the residue was chromatographed on silica gel with hexane/toluene (rising gradient from 70:30 to 60:40). **3c**, a pale yellow oil, was obtained as a 1:1:1 mixture of three isomers in 56% yield.

The *trans* isomer was crystallized from 50 ml of methanol, m.p. 147°C . Anal. Found: C, 77.17; H, 6.38. $\text{C}_{37}\text{H}_{35}\text{P}_3$ Calc.: C, 77.60; H, 6.16%. ^{31}P NMR (CDCl_3): $\delta +58.2$ (dd, $^2J_{P_A P_B} = 18.5$ Hz, $^2J_{P_A P_X} = 181.4$ Hz, P_A), $+66.9$ (dd, $^2J_{P_B P_X} = 18$ Hz, P_B), -16.4 (dd, P_X). ^1H NMR (CDCl_3): δ 1.06 (s, 9H, ^1Bu), 3.40 (d, 1H, $^2J_{HP} = 18$ Hz, CHP_3), 6.9–7.6 (m, 25H, phenyl). ^{13}C NMR (CDCl_3): δ 32.43 (d, $^3J_{CP} = 7.3$ Hz, ^1Bu), 32.64–33.27 (m, CP_3), 38.42 (pt, $\Sigma^2 J_{CP} + ^3 J_{CP} = 21$ Hz, CMe_3), 125–141 (m, phenyl), 149.73 (pt, $\Sigma^1 J_{CP} + ^2 J_{CP} = 24$ Hz, :C-Ph), 160.10 (ddd, $^1J_{CP} = 22$ Hz, $^2J_{CP}$ and $^3J_{CP} = 9$ Hz and 4 Hz, :C ^1Bu).

Both *cis* isomers are only characterized in ^{31}P NMR (CDCl_3): $\delta +39.3$ (d, $^2J_{P_A P_X} = 18.2$ Hz, P_A), $+56.9$ (d, $^2J_{P_B P_X} = 12$ Hz, P_B), -21.1 (dd, P_X); $+34.9$ (dd, $^2J_{P_A P_B} = 8.7$ Hz, $^2J_{P_A P_X} = 216$ Hz, P_A), $+46.5$ (dd, $^2J_{P_B P_X} = 200.6$ Hz, P_B), -8.8 (dd, P_X).

3.3. Compounds **4a–c** and **5a–c**

A solution of Et_2NLi (0.7 M) in hexane/THF (4 mmol) was added dropwise to 2 mmol of **3a** or **c** in 10

ml of dry THF at -80°C . The reaction mixture was warmed slowly to room temperature. After evaporation of the solvents and Et_2NH under vacuum, **4a** and **c** were obtained as a mixture of two isomers.

4a. ^{31}P NMR (THF): δ +98.8 (d, $^2J_{\text{P}_A\text{P}_X} = 128$ Hz, P_A), -4.5 (t, P_X) for the *trans* isomer and +58.3 (d, $^2J_{\text{P}_A\text{P}_X} = 211$ Hz, P_A), +12.1 (t, P_X) for the *cis* isomer.

4c. ^{31}P NMR (THF): δ +78.2 (dd, $^2J_{\text{P}_A\text{P}_B} = 23$ Hz, $^2J_{\text{P}_A\text{P}_X} = 110$ Hz, P_A), +99.6 (dd, $^2J_{\text{P}_B\text{P}_X} = 140$ Hz, P_B), -4.0 (dd, P_X) for the *trans* isomer and +44.6 (dd, $^2J_{\text{P}_A\text{P}_B} = 23.2$ Hz, $^2J_{\text{P}_A\text{P}_X} = 66.6$ Hz, P_A), 81.1 (dd, $^2J_{\text{P}_B\text{P}_X} = 365.4$ Hz, P_B), 15.0 (dd, P_X) for the *cis* isomer.

The anion **4b** was prepared by the same procedure with one equivalent of BuLi in hexane at -80°C . ^{31}P NMR (THF): δ +44.0 (d, $^2J_{\text{P}_A\text{P}_X} = 210$ Hz, P_A), +12.6 (t, P_X).

Anions **4a,b** or **c** were dissolved in 10 ml of dry THF and stirred with 50 mg of lithium at room temperature for 16 h. NH_4Cl (100 mg) was added at room temperature and, after stirring for 15 min, the 2-phosphino-1,3-diphospholide anions (**5**) could be identified by ^{31}P NMR and used without further purification.

5a. ^{31}P NMR (THF): δ +224.6 (d, $^2J_{\text{P}_A\text{P}_X} = 133$ Hz, P_A), -13.1 (t, P_X).

5b. ^{31}P NMR (THF): δ +213.2 (d, $^2J_{\text{P}_A\text{P}_X} = 110$ Hz, P_A), -56.9 (t, P_X).

5c. ^{31}P NMR (THF): δ +188.4 (dd, $^2J_{\text{P}_A\text{P}_B} = 17$ Hz, $^2J_{\text{P}_A\text{P}_X} = 111$ Hz, P_A), +205.7 (dd, $^2J_{\text{P}_B\text{P}_X} = 73$ Hz, P_B), -63 (dd, P_X).

3.4. Compound 6

The 2-phosphino-1,3-diphospholide anions **5a** (2 mmol), prepared as above, were treated with $[\text{CpFe}(\text{C}_8\text{H}_{10})]\text{PF}_6$ [12] (1 g, 2.7 mmol) at 50°C for 2 h. The solvent was evaporated and the residue flash chromatographed through a short silica gel column in CH_2Cl_2 . The solvent was evaporated and the residue chromatographed again on silica gel with toluene. M.p. 205°C , yield 13%. Mass spectrum: m/z 558 (M^+ , 10%). ^{31}P NMR (CD_2Cl_2): δ +20.1 (d, $^2J_{\text{P}_A\text{P}_X} = 84$ Hz, P_A), -12.4 (t, P_X). ^1H NMR (CD_2Cl_2): δ 4.38 (s, 5H, Cp), 7–7.4 (m, 20H, phenyl). ^{13}C NMR (CD_2Cl_2): δ 76.7 (s, 5C, Cp), 96.1 (dt, $^1J_{\text{CP}_A} = 87$ Hz, $^1J_{\text{CP}_X} = 30$ Hz, CP_3), 114.8 (pt, $\sum^1J_{\text{CP}} + ^2J_{\text{CP}} = 74$ Hz, $:\text{C}-\text{Ph}$), 127–141 (m, phenyl).

3.5. Compound 7

A solution of $\text{W}(\text{CO})_5\text{THF}$ in THF (110 ml, 0.03 M) was prepared by photolysis of $\text{W}(\text{CO})_6$ in THF and added to the crude solution of **6**. The mixture was then stirred for 2 h at room temperature. Solvent was evaporated in vacuo and the residue chromatographed quickly through a short silica gel column in CH_2Cl_2 . After

removal of solvent, the residue was rechromatographed on silica gel using hexane/toluene (70:30) as eluant. Yield 4%. Mass spectrum: m/z 854 ($\text{M}-\text{CO}$, 2%), 798 ($\text{M}-3\text{CO}$, 5%), 742 ($\text{M}-5\text{CO}$, 6%), 558 ($\text{M}-\text{W}(\text{CO})_5$, 100%). ^{31}P NMR (CD_2Cl_2): δ +28.6 (d, $^2J_{\text{P}_A\text{P}_X} = 70$ Hz, P_A), +14.7 (t, $^1J_{\text{P}_X\text{W}} = 250$ Hz, P_X). ^1H NMR (CD_2Cl_2): δ 4.27 (s, 5H, Cp), 7–7.5 (m, 20H, phenyl). ^{13}C NMR (CD_2Cl_2): δ 77.14 (s, Cp), 97.2 (dt, $^1J_{\text{CP}_A} = 88$ Hz, $^1J_{\text{CP}_X} = 17$ Hz, CP_3), 115.42 (pt, $\sum^1J_{\text{CP}} + ^2J_{\text{CP}} = 75$ Hz, PCCP), 125–141 (m, phenyl), 198.6 (dt, $^2J_{\text{CP}} = 6$ Hz, $^4J_{\text{CP}} = 3$ Hz, CO_{eq}), 200.0 (d, $^2J_{\text{CP}_X} = 22$ Hz, CO_{ax}).

3.6. Compounds 8a,b and 9a,b

One equivalent of BuLi in hexane (1.6 M) was added dropwise to a solution of 2 mmol of **1a** in 10 ml of dry THF at -50°C . The reaction mixture was slowly warmed to room temperature and the formation of **8a,b** was checked by ^{31}P NMR (THF): δ +18.1 (d, $^2J_{\text{PP}} = 405$ Hz), -11.4 for **8a**; +17.7 (d, $^2J_{\text{PP}} = 399$ Hz), -11.6 for **8b**.

Distilled water (0.1 ml) was added to the mixture of **8a,b** (2 mmol) at -20°C . The solvent was evaporated, and the residue chromatographed on silica gel in hexane/toluene (70:30). **9a,b** (80:20) were obtained in 64% yield. Mass spectrum: m/z 466 (M^+ , 17%), 409 ($\text{M}-\text{Bu}$), 287 ($\text{M}-\text{PhCCPh}$), 178 (PhCCPh , 100). ^{31}P NMR (CDCl_3): δ -9.7 (d, $^2J_{\text{PP}} = 122$ Hz), -30.7 (d), major isomer; -10.0 (d, $^2J_{\text{PP}} = 118$ Hz), -31.0 (d), minor isomer. ^1H NMR (CDCl_3): δ 0.83 (t, 3H, $^3J_{\text{HH}} = 6.8$ Hz, CH_3), 1.2–1.4 (m, 4H, CH_2CH_2), 1.7–1.9 (m, 2H, CH_2P), 2.03–2.1 (m, 2H, PCH_2P), 6.7–7.5 (m, 21H, $:\text{CH}$ and phenyl), major isomer. ^{13}C NMR (CDCl_3): δ 13.7 (s, CH_3), 24.25 (d, $J_{\text{CP}} = 12$ Hz, CH_2), 27.92 (d, $J_{\text{CP}} = 13$ Hz, CH_2), 28.6 (dd, $J_{\text{CP}} = 10.6$ Hz, $J_{\text{CP}} = 7.1$ Hz, CP), 24.0 (t, $^1J_{\text{CP}} = 22$ Hz, CP_2), 126–133 (m, phenyl), 139.0 (d, $^2J_{\text{CP}} = 42$ Hz, $\text{PC}:\text{CH}$), 136.34 (d, $J_{\text{CP}} = 14$ Hz, $:\text{C}$), 137.17 (dd, $J_{\text{CP}} = 7.5$ Hz, $J_{\text{CP}} = 15.6$ Hz, $:\text{C}$), 138.55 (d, $J_{\text{CP}} = 6$ Hz, $:\text{C}$), 142.2 (dd, $J_{\text{CP}} = 5.4$, $J_{\text{CP}} = 21$ Hz, $:\text{C}$), major isomer.

3.7. Compounds 10a,b

Pure methyl iodide (125 μl) was added to a mixture of **8a,b** (2 mmol) at -40°C . The mixture was hydrolysed, then dried on MgSO_4 and chromatographed on a short silica gel column with ethylacetate, yield 60%, as a 1:1 mixture of two diastereomers.

10a,b. Mass spectrum: m/z 481 (M^+ , 5%), 480 ($\text{M}-\text{H}$, 12%), 301 ($\text{M}-\text{PhCH}:\text{CHPh}$, 80%). ^{31}P NMR (CDCl_3): δ 29.0 (d, $^2J_{\text{PP}} = 65$ Hz, P^+), -14.8 (P) first isomer, 29.0 (d, $^2J_{\text{PP}} = 65$ Hz, P^+), -15.7 (P) second isomer. ^1H NMR (CDCl_3): δ 0.78–0.92 (m, 6H, CH_2CH_3), 1.25–1.45 (m, 8H, CH_2CH_2), 2.27 (d, 3H, $^2J_{\text{HP}} = 13.4$ Hz, CH_3P), 2.36 (d, 3H, $^2J_{\text{HP}} = 13.2$ Hz,

CH_3P), 2.6–2.8 (m, 4H, CH_2P), 2.88 (part B of ABX, 1H, $^2J_{\text{H}_A\text{H}_B} = 15.1$ Hz, $^2J_{\text{H}_B\text{P}_X} = 15.2$ Hz, $\text{P}^+\text{CH}_A\text{H}_B$ of first isomer), 3.07 (part B of ABX, 1H, $^2J_{\text{H}_A\text{H}_B} = 15.2$ Hz, $^2J_{\text{H}_B\text{P}_X} = 15.3$ Hz, $\text{P}^+\text{CH}_A\text{H}_B$ of second isomer), 3.67 (part A of ABX, 1H, $^2J_{\text{H}_A\text{P}_X} = 13$ Hz, $\text{P}^+\text{CH}_A\text{H}_B$ of first isomer), 3.82 (part A of ABX, 1H, $^2J_{\text{H}_A\text{P}_X} = 12.8$ Hz, $\text{P}^+\text{CH}_A\text{H}_B$ of second isomer), 6.7 (d, 1H, $^3J_{\text{HP}} = 11.8$ Hz, :CH), 6.85 (d, 1H, $^3J_{\text{HP}} = 8.8$ Hz, :CH), 6.9–7.7 (m, 40H, phenyl). ^{13}C NMR (CDCl_3): δ 6.9 (d, $^1J_{\text{CP}} = 55$ Hz, CH_3P^+), 13.38 (s, CH_2CH_3), 19.27 (pt, CP_2), 22.98 (d, $^1J_{\text{CP}} = 54$ Hz, CH_2P_X), 23.52 (d, $^2J_{\text{CP}} = 3$ Hz, $\text{CH}_2\text{CH}_2\text{P}_X$), 118.4 (d, $^1J_{\text{CP}} = 85$ Hz, C_{ipso} PhP_X), 127.6–138.7 (m, phenyl).

3.8. Compounds 11a,b

Pure methyl iodide (125 μl) was added to a mixture of **8a,b** (2 mmol) at -40°C . Pure benzaldehyde (125 μl) was added at -80°C , the mixture was stirred for 30 min at -80°C and then slowly warmed to room temperature. The solvent was evaporated and the residue chromatographed on silica gel with hexane/toluene (80 : 20).

11a,b were obtained in a 1 : 1 mixture as a colorless oil with 77% yield. Mass spectrum: m/z 390 (M^+ , 50%). ^{31}P NMR (CDCl_3): δ 1.0 and -11.8 . ^1H NMR (CDCl_3): δ 6.47 (dd, 1H, $^3J_{\text{HH}} = 12.8$ Hz, $^2J_{\text{HP}} = 2.8$ Hz, :CHP of Z isomer), 6.94 (dd, 1H, $^3J_{\text{HH}} = 17.2$ Hz,

$^2J_{\text{HP}} = 3.4$ Hz, :CHP of E isomer), 7.1–7.8 (m, 22H, :CHPh and phenyl).

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