

# [1,5] Sigmatropic Shifts in a 1,4-Diphospholylbenzene

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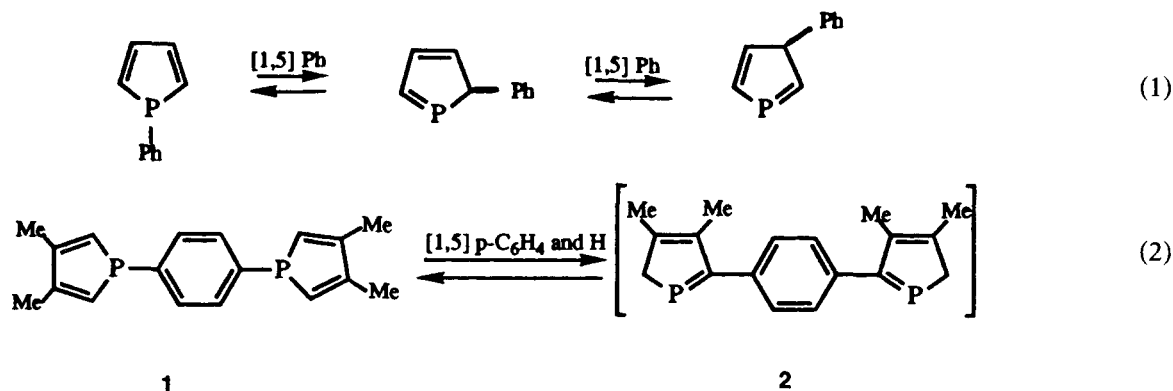
## ABSTRACT

The central phenylene ring of 1,4-bis(3,4-dimethylphosphol-1-yl)benzene undergoes [1,5] shifts around both phospholyl rings above 150°C to give 1,4-bis(3,4-dimethyl-5H-phosphol-2-yl)benzene, which can be trapped by toluene,  $[\text{CpFe}(\text{CO})_2]_2$ , or  $\text{Mn}_2(\text{CO})_{10}$  to yield the corresponding bis-1-phosphanorbornadiene, bis-phosphaferrocene, or bis-phosphacymantrene respectively.

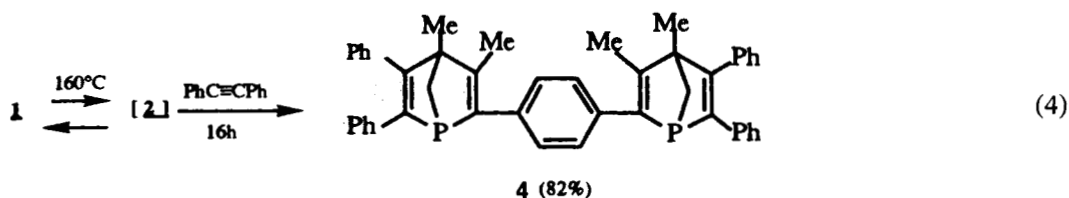
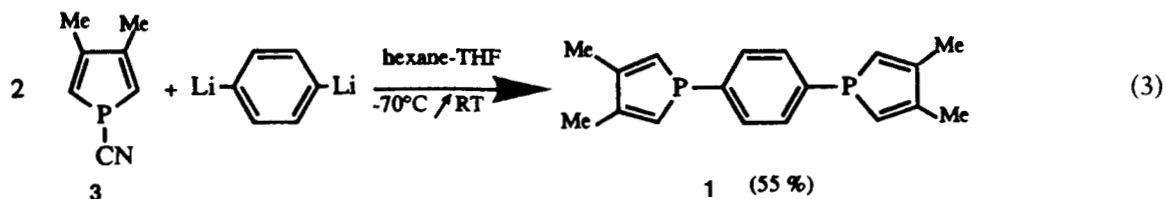
In several previous papers [1–5], we have demonstrated that a 1-phenyl substituent could migrate from the phosphorus atom to the carbon atoms of a phosphole ring via a series of [1,5] sigmatropic shifts (Equation 1). These relatively easy migrations can be correlated with the pyramidal struc-

ture of the phosphole nucleus. The pyramidity of phosphorus reduces the cyclic delocalization within the 1-*H*-phosphole system and allows some overlap between the  $\pi$ -dienic system and the  $\sigma$  orbital of the P—C exocyclic bond [6].

Recently, we became interested in all the possible techniques for building polyphosphole structures in order to create new polyphosphorus macrocycles, cages, and chains. Up to now, we have only been able to synthesize 2,2'-biphospholes [2, 7]. In such a context, it was tempting to link together two phosphole rings via a *para*-phenylene bridge and to check whether it would be possible to promote the [1,5] sigmatropic shifts of the *para*-phenylene substituent around both phosphole rings of **1** in order to create new species derived from the original C—C bonded tricyclic structure **2** (Equation 2). The starting phosphole **1** was obtained by reaction of the recently discovered 1-cyano-3,4-dimethylphosphole **3** [8] with 1,4-di-



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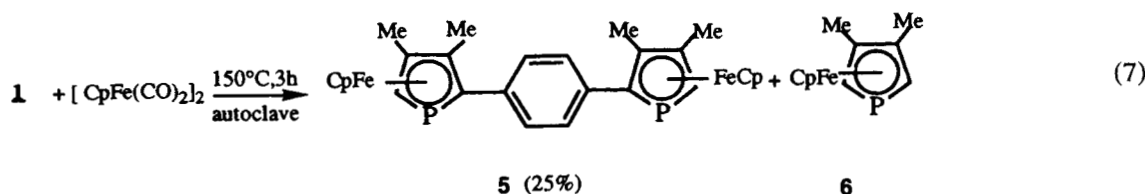
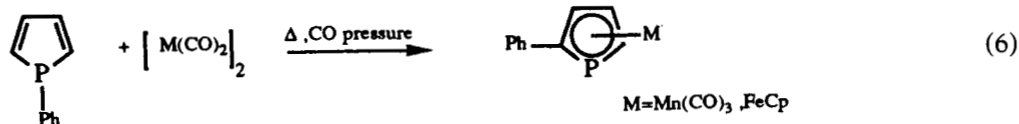
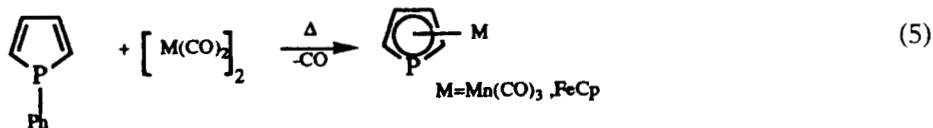
lithiobenzene [9] (Equation 3). As expected, the NMR parameters of **1** are very close to those of 1-phenyl-3,4-dimethylphosphole [10]. Upon heating with toluene at 160°C for 16 h, phosphole **1** is converted into the expected 1-phosphanorbornadiene **4** (Equation 4).

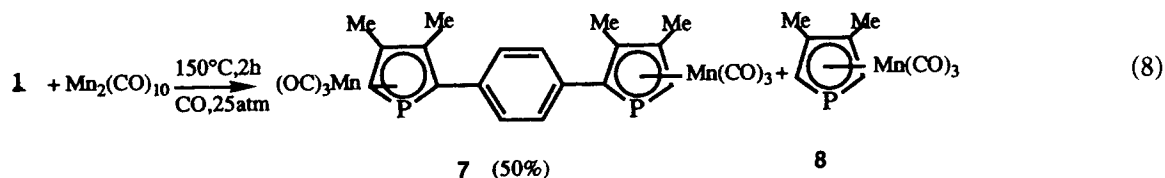
The formation of **4** unambiguously demonstrates the existence of the equilibrium depicted in Equation 2. The transient 2*H*-phosphole **2** is trapped by toluene to give the corresponding [4 + 2] cycloadduct as already shown for monocyclic phospholes [1]. The high yield of **4** establishes the practical usefulness of this kind of chemistry. It is interesting to remark that the main decomposition path of **4** in the mass spectrometer is the cycloreversion leading to **2**.

When heating a 1-phenylphosphole with Mn<sub>2</sub>(CO)<sub>10</sub> or [CpFe(CO)<sub>2</sub>]<sub>2</sub> under a stream of argon, the normal reaction path involves the cleavage of the P—Ph bond and the formation of the corresponding η<sup>5</sup>-phospholyl complex [11,12] (Equation 5).

When repeating the same experiment under CO pressure, the loss of CO leading to the η<sup>5</sup>-complex becomes more difficult and the [1,5] shift of the phenyl group competes with the cleavage of the P—Ph bond by the organometallic reagent. In such a case, the main product becomes the η<sup>5</sup>-2-phenylphospholyl complex [4,7] (Equation 6).

In an attempt to generalize this kind of chemistry to our biphosphole, we allowed **1** to react with [CpFe(CO)<sub>2</sub>]<sub>2</sub> at ca. 150°C under the autogenous pressure of CO (Equation 7). The main product was the bisphosphaferrocene **5** resulting from the η<sup>5</sup>-complexation of the transient 2*H*-phosphole **2**. 3,4-Dimethylphosphaferrocene **6** resulting from the cleavage of the P-aryl bonds of **1** was also formed. The molar ratio **5**/**6** was ca. 2/1. The NMR parameters of **5** are strikingly similar to those recorded for 2-phenyl-3,4-dimethylphosphaferrocene [12]. This kind of chemistry could be transposed to Mn<sub>2</sub>(CO)<sub>10</sub> using a higher pressure of CO (Equation 8). Here again, the molar ratio **7**/**8** was ca. 2/1. As ex-





pected, closely similar NMR parameters were found for **7** and 2-phenyl-3,4-dimethylphosphacymantrene [7].

If we summarize this first series of results, two general facts must be stressed. Firstly, the 1,4-disubstitution of the central phenylene ring is retained during the migrations. For each product, one type of phenylene protons and two types of phenylene carbons are observed in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. This is the expected consequence of the concertedness of the [1,5] shifts. Secondly, one main isomer is formed in each case. The other possible isomer resulting from the presence of two chiral phosphorus centers has been detected with certainty only in the case of **7** and represents ca. 20% of the total amount of product. Since this chemistry is selective and proceeds in reasonable to high yields, it offers some interesting synthetic opportunities, which we are currently exploring.

## EXPERIMENTAL

All reactions were performed under argon. Nuclear magnetic resonance spectra were recorded on multinuclear WP 80 SY and AC 200 Bruker spectrometers operating at 80.13 and 200.13 ( $^1\text{H}$ ), 20.15 and 50.32 ( $^{13}\text{C}$ ), and 32.44 ( $^{31}\text{P}$ ) MHz. Chemical shifts are in parts per million downfield from internal TMS ( $^1\text{H}$  and  $^{13}\text{C}$ ) and external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ), and coupling constants are in Hertz. Mass spectra were recorded on a Shimadzu GC-MS QP 1000 instrument at 70 eV under electronic impact. Elemental analyses were performed by the Service Central de Microanalyse du CNRS, France. Silica gel (70–230 mesh) was used for the chromatographic separations. All commercially available reagents were used as received from the suppliers.

### 1,4-Bis(3,4-dimethylphosphol-1-yl)benzene **1**

1-Cyano-3,4-dimethylphosphole **3** was prepared in toluene-THF from 3.8g ( $2 \times 10^{-2}$  mol) of 1-phenyl-3,4-dimethylphosphole according to [8]. 1,4-Dilithiobenzene ( $1 \times 10^{-2}$  mol) was prepared in hexane according to [9]. The solution of 1,4-dilithiobenzene was slowly added to the crude solution of **3** at  $-70^\circ\text{C}$ . The reaction mixture was warmed to room temperature. The solvent was evaporated. The residue was extracted with dichloromethane. The  $\text{CH}_2\text{Cl}_2$  solution was washed with water and dried with  $\text{Na}_2\text{SO}_4$ . After evapora-

tion of the solvent, the organic residue was chromatographed, first with hexane/ $\text{CH}_2\text{Cl}_2$  95/5 and, then, with hexane/ $\text{CH}_2\text{Cl}_2$  80/20. Phosphole **1** was recovered as white crystals mp  $162^\circ\text{C}$  (hexane/ $\text{CH}_2\text{Cl}_2$ ). Yield 3.3g (55%).

$^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -3.4; ( $\text{C}_6\text{D}_6$ ):  $\delta$  -5.0;  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  2.08 (dd,  $^4\text{J}(\text{H}-\text{H})$  0.88 Hz,  $^4\text{J}(\text{H}-\text{P})$  3 Hz, 12H, Me), 6.42 (dd,  $^2\text{J}(\text{H}-\text{P})$  38.6 Hz, 4H,  $=\text{CH}-\text{P}$ ), 7.19 (m, 4H, Ph). The multiplet at 7.19 collapses to a singlet upon irradiation of phosphorus, thus demonstrating the 1,4-disubstitution of the arene ring.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  17.76 (s, Me), 129.50 (s,  $\text{CH}(\text{Ph})$ ), 132.89 (d,  $^1\text{J}(\text{C}-\text{P})$  7.1 Hz, C ipso or  $\text{CH}-\text{P}$ ), 133.27 (d,  $^1\text{J}(\text{C}-\text{P})$  6.9 Hz,  $\text{CH}-\text{P}$  or C ipso), 149.79 (d,  $^2\text{J}(\text{C}-\text{P})$  8.4 Hz, Me-C); mass spectrum:  $m/z$  298 ( $\text{M}^+$ , 100%); Anal. Calcd. for  $\text{C}_{18}\text{H}_{20}\text{P}_2$ : C, 72.55; H, 7.10; Found: C, 72.34; H, 7.19.

### 1,4-Bis(3,4-dimethyl-5,6-diphenyl-1-phosphanorbornadien-2-yl)benzene **4**

Phosphole **1** (0.6g,  $2 \times 10^{-3}$  mol) and toluene (1.1g,  $6 \times 10^{-3}$  mol) were heated in a sealed tube at  $160^\circ\text{C}$  for 16 h. The crude product was dissolved in  $\text{CH}_2\text{Cl}_2$ . The extract was chromatographed with hexane/ $\text{CH}_2\text{Cl}_2$  50/50. Yield 1.1g (82%) of white crystals mp  $186^\circ\text{C}$  (hexane/ $\text{CH}_2\text{Cl}_2$  20/80).

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -11.3;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.34 (s, 6H, Me), 2.08 (s, 6H, Me), 2.03–2.27 (m, 4H,  $\text{CH}_2\text{P}$ ), 6.94–7.33 (m, 24H, Ph);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  16.11 (s, Me), 21.15 (s, Me), 65.09 (s,  $\text{CH}_2-\text{P}$ ), 72.62 (s, Me- $\text{C}_4$ ) [13]; mass spectrum:  $m/z$  654 ( $\text{M}^+$ , 5%), 476 ( $\text{M}^+-\text{Ph}_2\text{C}_2$ , 36%), 298 ( $\text{M}^+-2\text{Ph}_2\text{C}_2$ , 100%); Anal. Calcd. for  $\text{C}_{46}\text{H}_{40}\text{P}_2$ : C, 84.22; H, 6.16; P, 9.62; Found: C, 83.55; H, 6.07; P, 9.50.

### 1,4-Bis(3,4-dimethylphosphaferrocen-2-yl)benzene **5**

Phosphole **1** (1g,  $3 \times 10^{-3}$  mol),  $[\text{CpFe}(\text{CO})_2]_2$  (1.1g,  $3 \times 10^{-3}$  mol), and toluene (25 mL) were heated at  $150^\circ\text{C}$  for 3 h in an autoclave. After evaporation, the organic residue was chromatographed with hexane/ $\text{CH}_2\text{Cl}_2$  80/20. 3,4-Dimethylphosphaferrocene **6** was first eluted with ferrocene (ca. 0.3g). Then, **5** was recovered (0.4g, 25%) as orange crystals, very sensitive toward oxidation.

$^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -73.7;  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  2.26 (s, 12H, Me), 3.86 (d,  $^2\text{J}(\text{H}-\text{P})$  36.6 Hz, 2H,  $\text{CH}-\text{P}$ ), 4.17 (s, 10H, Cp), 7.20 (s, 4H, Ph);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  15.32 (s, Me), 17.32 (s, Me), 73.21 (s, Cp),

77.21 (d,  $^1\text{J}(\text{C}-\text{P})$  58.9 Hz, CH—P), 92.38 (s, C Me), 96.76 (d,  $^2\text{J}(\text{C}-\text{P})$  6.6 Hz, C Me), 100.51 (d,  $^1\text{J}(\text{C}-\text{P})$  57 Hz, C—P), 129.6 (d,  $^3\text{J}(\text{C}-\text{P})$  5.7 Hz, CH (Ph)), 138.72 (d,  $^2\text{J}(\text{C}-\text{P})$  18.2 Hz, C ipso); mass spectrum:  $m/z$  538 ( $\text{M}^+$ , 100%).

*1,4-Bis(3,4-dimethylphosphacymantren-2-yl)benzene 7*

Phosphole **1** (1g,  $3 \times 10^{-3}$  mol),  $\text{Mn}_2(\text{CO})_{10}$  (1.2 g,  $3 \times 10^{-3}$  mol), and toluene (25 mL) were heated at 150°C for 2 h in an autoclave under 25 bars of carbon monoxide. After evaporation, the organic residue was chromatographed with hexane/ $\text{CH}_2\text{Cl}_2$  90/10. 3,4-Dimethylphosphacymantrene **8** was first eluted (ca. 0.2 g). Then, **7** was recovered (0.85g, 50%).

$^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -38.13 (major), -37.64 (minor);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) major:  $\delta$  1.61 (s, 6H, Me), 1.67 (d,  $^4\text{J}(\text{H}-\text{P})$  1.6 Hz, 6H, Me), 3.93 (d,  $^2\text{J}(\text{H}-\text{P})$  35.3 Hz, 2H, CH—P), 6.95 (s, 4H, Ph);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ) major:  $\delta$  12.86 (s, Me), 15.25 (s, Me), 95.00 (d,  $^1\text{J}(\text{C}-\text{P})$  62.4 Hz, CH—P), 110.48 (d,  $^2\text{J}(\text{C}-\text{P})$  7.1 Hz, Me-C), 111.34 (d,  $^2\text{J}(\text{C}-\text{P}) \sim 3.5$  Hz, Me-C), 119.25 (d,  $^1\text{J}(\text{C}-\text{P})$  59.4 Hz, C—P), 130.05 (d,  $^3\text{J}(\text{C}-\text{P})$  5.9 Hz, CH (Ph)), 134.92 (d,  $^2\text{J}(\text{C}-\text{P})$  17.5 Hz, C ipso), 224.21 (s, CO); IR (decalin):  $\nu$  (CO) 2085 (w), 2015 (s), 1987 (s), 1950 (sh), 1940 (vs); mass spectrum:  $m/z$  574 ( $\text{M}^+$ , 19%), 490 ( $\text{M}^+ - 3\text{CO}$ , 100%), 406 ( $\text{M}^+ - 6\text{CO}$ , 87%); Anal. Calcd. for  $\text{C}_{24}\text{H}_{18}$

$\text{Mn}_2\text{O}_6\text{P}_2$ : C, 50.22; H, 3.16; Found: C, 49.91; H, 3.56.

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