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# 2-Bromophospholide Ions: Synthesis and Theoretical Study

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**Abstract:** DFT calculations at the B3LYP/6–311++G(3df,2p) level indicate that the 2-bromophospholide ion could be stable toward self-arylation as a result of the lowered nucleophilicity of the in-plane phosphorus lone pair (the corresponding $\sigma_P$ orbital is lowered by 0.7 eV compared with the corresponding orbital of the parent phospholide ion, and the negative charge at P is reduced from −0.435 to −0.369 e). Accordingly, the synthesis of 2-bromo-3,4-dimethylphospholide was successfully carried out by quantitative base-induced dealkylation of 2-bromo-1-(2-ethoxycarbonylethyl)-3,4-dimethylphosphole. This ion reacts with $FeCl_2$ to give the corresponding 2,2′-dibromo-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene as a poorly stable mixture of *meso-* and *rac*-diastereomers in 18% yield.

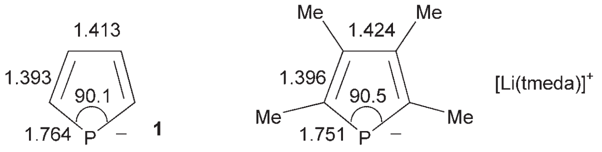
**Keywords:** density functional calculations • ferrocene derivatives • functional phospholyl anions • P heterocycles • phosphorus

## Introduction

Bromoferrocenes and, more generally halogenoferrocenes, are among the most useful synthons in ferrocene chemistry.[1] In phosphaferrocene chemistry, similar species are presently unknown and their absence is a drawback when designing an access to any functional derivative. This is all the more detrimental because such functional derivatives are finding increasing use in homogeneous and enantioselective catalysis.[2] Since 2-lithio-1-phosphaferrocenes cannot be made by metalation of phosphaferrocenes,[3] the only simple approach to 2-bromo-1-phosphaferrocenes seems to be via the still unknown 2-bromophospholide ions whose reaction with the appropriate iron precursors would yield the desired bromo derivatives. These ions would additionally provide a quite versatile entry into the chemistry of 2-functional phospholes and, through the 2*H*-phospholes resulting from their protonation,[4] to a variety of functional bicyclic phosphines. They would also provide access to a huge series of 2-bromo-1-phosphametallocenes derived from metals other than iron. However, the synthesis of such ions incorporating both a nucleophilic center ($P^-$) and an electrophilic center (C−Br) appears to be rather problematic. We describe hereafter their theoretical study explaining why they can display some stability, their successful synthesis, and their use for the preparation of the first 2,2′-dibromo-1,1′-diphosphaferrocene.

## Results and Discussion

Since the synthesis of 2-bromophospholide ions was obviously quite delicate, we decided first to investigate their properties by DFT calculations.[5] These calculations were performed at the B3LYP/6–311++G(3df,2p) level without the lithium counterion.[6a] The reliability of the results was first checked on the parent ion **1**. The computed geometrical parameters of **1** were compared to those recorded by X-ray analysis for $[Li(tmeda)][\eta^5\text{-}C_4Me_4P]$ (Scheme 1).[6b]



Scheme 1. Comparison of the distances [Å] and angles [°] in **1** and $[Li(tmeda)][\eta^5\text{-}C_4Me_4P]$.

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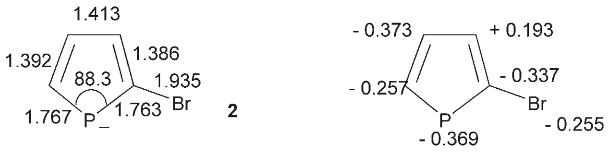
The agreement is quite satisfactory if we take into account the absence of the $\eta^5$-coordinated lithium ion in **1**. The highest occupied orbitals (HOMOs) of **1** are very similar to those proposed by Fenske and Kostic,[7] except for the ordering $\pi_P$(HOMO) > $\pi_C$ > $\sigma_P$ (in-plane lone pair). The $^{31}$P NMR parameters were calculated at the HF/6–311+G(2d,p) level. The absolute shielding of $H_3PO_4$ ($^{31}$P)[8] was taken from the literature. The agreement is satisfactory: $\delta(^{31}P) = 73.9$ versus 77.2 ppm for Li-**1** in THF.[9] Finally, the NICS(1)$_{tot}$ value[10] at −10.86 versus −11.3 for benzene (HF/6–311+G**) confirms the high aromaticity of the system in line with previous work.[11,12] This value can be compared to the value obtained by Schleyer (−11.03),[10] which was computed on the basis of a slightly different geometry (MP2(fc)/6–311+G**).

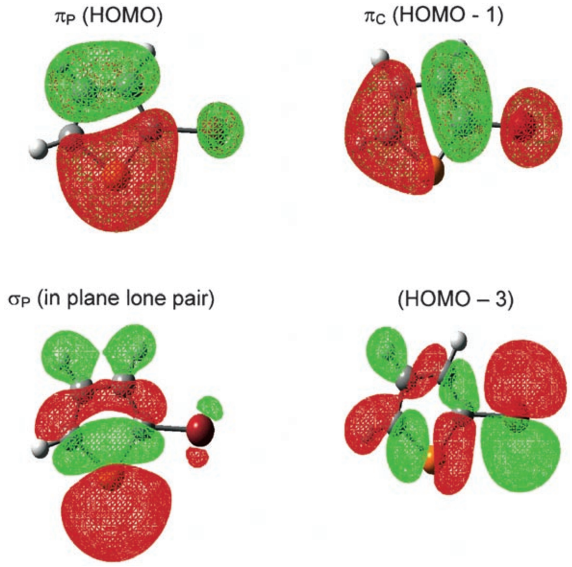
This rather positive picture gave us some confidence in the results obtained at the same level for the 2-bromophospholide ion **2**. The computed structure and the Mulliken population analysis of **2** are summarized in Scheme 2.



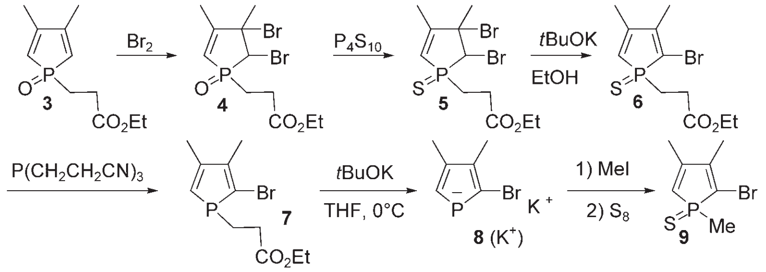
Scheme 2. Left: The computed distances [Å] and angles [°] in **2**; right: Mulliken population analysis for **2**.

The bromine substitution does not drastically modify the structure. The electron-withdrawing effect of the bromine atom is clearly seen in the population analysis. The $^{31}$P resonance is predicted to be shifted to low fields: **2**: $\delta(^{31}P) = 86.2$ ppm. The NICS value indicates some decrease of the delocalization at −10.19. The four highest occupied orbitals of **2** are shown in Scheme 3.

The three highest occupied orbitals of **2** are quite similar to those of **1**. They are just shifted to lower energies, $\pi_P$ by 0.52 eV, $\pi_C$ by 0.38 eV, and $\sigma_P$ by 0.70 eV. Thus, it is quite clear that **2** is a poorer $\pi$ donor than **1**, which is already a poorer donor than Cp$^-$, and the stability of the $\eta^5$ complexes of **2** might become a problem in some cases. These results also gave us some confidence in the potential stability of **2**. Such a species could indeed polymerize by self-arylation (P$^-$ + C–Br). The fact that the phosphorus lone pair is substantially lower in energy in **2** than in **1**, combined with the reduced charge at P (−0.435 in **1** versus −0.369 in **2**), suggests that **2** can be isolated in the absence of arylation catalysts. Accordingly, we first investigated the reaction of lithium in THF with the already described 1-phenyl-2-bromo-3,4-dimethylphosphole.[13] A complete debromination was observed and the sole product of the reaction is the 3,4-dimethylphospholide ion. Since a radical mechanism is involved in the cleavage of the P–Ph bond of phospholes by alkali metals,[14] this result is not very surprising. We thus decided to use an approach that avoids this radical mechanism. Instead it relies on the base-induced dealkylation of 1-(2-ethoxycarbonylethyl)-phospholes.[15] The necessary starting product **7** was prepared in 53% overall yield as shown in Scheme 4.



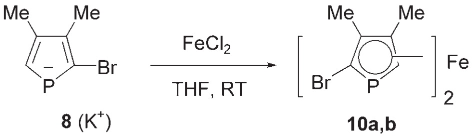
Scheme 3. Kohn–Sham orbitals of 2-bromophospholide (isovalue = 0.02).



Scheme 4. Synthesis of **8** and its conversion to **9**.

The reaction of the 3,4-dimethylphospholide ion with $BrCH_2CH_2CO_2Et$ in THF at −50 °C affords the expected functional phosphole ($\delta(^{31}P) = -6.8$ ppm) whose oxidation is performed by dry *meta*-chloroperbenzoic acid in dichloromethane at −50 °C (**3**: $\delta(^{31}P) = 57.2$ ppm). Contrary to what was observed with the P-phenyl derivatives,[13] the bromination of **3** mainly produces the 4,5-dibromo derivative **4** (Scheme 4). The 2,5-dibromo derivative is only a minor byproduct. The structure of **4** was easily established by inspection of the $^{13}$C NMR spectrum (CDCl$_3$). The CHBr group resonates at $\delta = 57.06$ ppm ($^1J_{C,P} = 60.3$ Hz), the CBr group at $\delta = 70.90$ ppm ($^2J_{C,P} = 17.4$ Hz), the =CH group at $\delta = 123.41$ ppm ($^1J_{C,P} = 91.6$ Hz), and the β-olefinic C atom at $\delta =$

167.25 ppm ($^2J_{\mathrm{C,P}}=11.9$ Hz). The negligible $^2J$(P,CHα) coupling means that the α-bromine is *cis* to the P=O group.[16] As expected, the $^{31}$P resonance of the 2-bromophosphole **7** is shifted downfield compared to that for the 2*H*-derivative (**7** $\delta(^{31}\mathrm{P})=6.5$ ppm in $CDCl_3$). The $^{13}$C resonance of the α-CBr group appears at higher field and displays a stronger coupling with phosphorus than the α-CH resonance: CBr: $\delta(^{13}\mathrm{C})=121.84$ ($^1J_{\mathrm{C,P}}=17.3$ Hz), CH: $\delta(^{13}\mathrm{C})=125.25$ ($^1J_{\mathrm{C,P}}=9.8$ Hz). The dealkylation reaction in which **7** is converted into **8** is quantitative and no debromination was observed. The anion **8** shows a $^{31}$P resonance at $\delta(^{31}\mathrm{P})=71.6$ ppm, that is, +15.8 ppm downfield from the 3,4-dimethylphospholide ion.[9] This downfield shift is in line with the prediction made for **2** versus **1** ($\Delta\delta=+12.3$). The characterization of **8** was completed by methylation and sulfurization, leading to **9**. In a preliminary non-optimized experiment, the reaction of **8** with $FeCl_2$ in THF at room temperature yielded the expected 2,2′-dibromo-1,1′-diphosphaferrocene as a 1:1 mixture of two diastereomers **10a,b** in 18 % yield. (Scheme 5)



Scheme 5. Synthesis of the phosphaferrocene derivatives **10a,b**.

The product appears not to be stable upon standing. It shows the expected $^{31}$P resonances at high fields [$\delta(^{31}\mathrm{P})=-67.8$ (dm, $^2J_{\mathrm{P,H}}=36.5$ Hz) and $-60.3$ ppm (d, $^2J_{\mathrm{P,H}}=36.3$ Hz) in $CD_2Cl_2$] versus $\delta=-72$ ppm for the non-brominated diphosphaferrocene.[17] In the mass spectrum (EI), the molecular peak (*m*/*z* 437) is also the base peak. The proton spectrum shows a doublet at $\delta=3.58$ ($^2J_{\mathrm{H,P}}=36.6$ Hz), and a doublet of multiplets at $\delta=3.71$ ($^2J_{\mathrm{H,P}}=36.6$ Hz). This positive result gives us confidence in the possible development of new avenues in phosphametallocene chemistry.

## Experimental Section

NMR spectra were recorded on a multinuclear Bruker Avance 300-MHz spectrometer operating at 300.13 for $^1$H, 75.47 for $^{13}$C, and 121.50 MHz for $^{31}$P. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane ($^1$H and $^{13}$C) and external 85 % aqueous $H_3PO_4$ ($^{31}$P). Mass spectra were obtained at 70 eV with an HP 5989B spectrometer by the direct inlet method. $P(CH_2CH_2CN)_3$ was purchased from Cytec Industries.

**1-(2-Ethoxycarbonylethyl)-3,4-dimethylphosphole oxide (3)**: 3,4-Dimethyl-1-phenylphosphole (10 g, 10 mL)[18] in dry THF (170 mL) was allowed to react with Li wire (0.5 % of Na) (0.8 g) at room temperature under nitrogen. The formation of the 3,4-dimethylphospholide was monitored by $^{31}$P NMR spectroscopy ($\delta(^{31}\mathrm{P})=53.9$ ppm). After completion of the cleavage reaction (ca.1.5 h), dry $AlCl_3$ (1.2 g) was slowly added at 0 °C and the reaction mixture stirred overnight. Ethyl 3-bromopropionate (9.25 mL) in THF (100 mL) was then added dropwise at −50 °C. The outcome of the reaction was monitored by $^{31}$P NMR spectroscopy (phosphole: $\delta(^{31}\mathrm{P})=-6.8$ ppm). The crude solution was evaporated, the residue dissolved in dry dichloromethane and cooled to −50 °C. Metachloroperbenzoic acid (13 g, dried over $MgSO_4$ in $CH_2Cl_2$) was added dropwise and the oxidation monitored by $^{31}$P NMR spectroscopy (**3**: $\delta(^{31}\mathrm{P})=57.2$ ppm). The crude solution was washed with an aqueous solution of sodium thiosulfate, then with an aqueous solution of sodium bicarbonate, then dried over $MgSO_4$. The phosphole oxide **3** tends to undergo a [4+2] Diels–Alder dimerization and must be used at once.

**Bromination of 3: synthesis of 4,5-dibromo-1-(2-ethoxycarbonylethyl)-3,4-dimethylphosphol-2-ene oxide (4)**: A mixture of pyridinium tribromide (21.5 g) and pyridine (20 mL) in dichloromethane (100 mL) was added dropwise at room temperature to a solution of **3** in dichloromethane (100 mL), prepared as described above. The reaction is instantaneous and can be monitored by $^{31}$P NMR spectroscopy (**4**: $\delta(^{31}\mathrm{P})=44.7$ ppm). The solution was washed with an aqueous solution of sodium thiosulfate, then with 3 N HCl (100 mL), then with water until neutral, and then dried over $MgSO_4$. The product displays a limited stability. It was purified by chromatography over silica gel with ethyl acetate as the eluent. $^{31}$P NMR ($CH_2Cl_2$): $\delta=44.1$ ppm; $^1$H NMR ($CDCl_3$): $\delta=1.19$ (t, 3H, Me (OEt)), 1.96 (s, 3H, Me), 2.19 (s, 3H, Me), 2.22 (m, 2H, $CH_2$), 2.70 (m, 2H, $CH_2$), 4.08 (q, 2H, $CH_2$ (OEt)), 4.60 (s, 1H, CHBr), 6.16 ppm (d, $^2J_{\mathrm{H,P}}=21$ Hz, 1H, CH=); $^{13}$C NMR ($CDCl_3$): $\delta=16.30$ (s, Me), 21.36 (d, $J_{\mathrm{C,P}}=15.5$ Hz, Me), 26.28 (d, $J_{\mathrm{C,P}}=74.2$ Hz, $PCH_2$), 28.77 (d, $J_{\mathrm{C,P}}=4.5$ Hz, $CH_2$), 34.04 (s, Me), 57.06 (d, $J_{\mathrm{C,P}}=60.3$ Hz, CHBr), 63.19 (s, $OCH_2$), 70.90 (d, $J_{\mathrm{C,P}}=17.4$ Hz, CBr), 123.41 (d, $J_{\mathrm{C,P}}=91.6$ Hz, CH=), 167.25 (d, $J_{\mathrm{C,P}}=11.9$ Hz, C=), 174.20 ppm (d, $J_{\mathrm{C,P}}=9.9$ Hz, C=O); MS: *m*/*z* (%): 388 ([*M*]$^+$, 20), 306 ([*M*−HBr], 65).

**4,5-Dibromo-1-(2-ethoxycarbonylethyl)-3,4-dimethylphosphol-2-ene sulfide (5)**: The sample of **4** obtained as described above was stirred overnight with $P_4S_{10}$ (12 g) in dichloromethane. Monitoring the reaction mixture by $^{31}$P NMR spectroscopy showed the complete transformation of **4** into **5** (**5**: $\delta(^{31}\mathrm{P})=56.7$ ppm). The solution was filtered over a layer of silica gel to remove unreacted $P_4S_{10}$, and the product was purified by chromatography with hexane/diethyl ether 80:20. $^{31}$P NMR ($CDCl_3$): $\delta=58.1$ ppm; $^1$H NMR ($CDCl_3$): $\delta=1.02$ (t, 3H, Me (OEt)), 1.76 (s, 3H, Me), 2.00 (d, $J_{\mathrm{H,P}}=1.5$ Hz, 3H, Me), 2.08 (m, 2H, $CH_2$), 2.57 (m, 2H, $CH_2$), 3.91 (q, 2H, $CH_2$ (OEt)), 4.59 (d, $J_{\mathrm{H,P}}=4.5$ Hz, 1H, CHBr), 5.96 ppm (d, $^2J_{\mathrm{H,P}}=24$ Hz, 1H, CH=); $^{13}$C NMR ($CDCl_3$): $\delta=12.82$ (s, Me), 18.29 (d, $J_{\mathrm{C,P}}=14.8$ Hz, Me), 25.92 (d, $J_{\mathrm{C,P}}=3.2$ Hz, $CH_2$), 27.05 (d, $J_{\mathrm{C,P}}=55.4$ Hz, $PCH_2$), 29.03 (s, Me), 57.42 (d, $J_{\mathrm{C,P}}=44$ Hz, CHBr), 59.84 (s, $OCH_2$), 68.72 (d, $J_{\mathrm{C,P}}=17.4$ Hz, CBr), 120.19 (d, $J_{\mathrm{C,P}}=75.3$ Hz, CH=), 160.62 (d, $J_{\mathrm{C,P}}=8.7$ Hz, C=), 170.66 ppm (d, $J_{\mathrm{C,P}}=10.2$ Hz, C=O); MS: *m*/*z* (%): 404 ([*M*]$^+$, 15), 324 ([*M*−HBr], 65).

**2-Bromo-1-(2-ethoxycarbonylethyl)-3,4-dimethylphosphole sulfide (6)**: A solution of *t*BuOK (6.5 g) in ethanol (150 mL) was added dropwise at 0 °C to the sample of **5** obtained as described previously in solution in dry dichloromethane (500 mL). After monitoring the reaction mixture by $^{31}$P NMR spectroscopy, hydrolysis was carried out with 3 N HCl at 0 °C. After decantation, extraction of the aqueous phase with dichloromethane, and washing of the organic phase with brine, the organic solution was dried over $MgSO_4$. $^{31}$P NMR ($CDCl_3$): $\delta=54.1$ ppm; $^1$H NMR ($CDCl_3$): $\delta=1.16$ (t, 3H, Me (OEt)), 1.98 (s, 3H, Me), 2.08 (s, 3H, Me), 2.16 (m, 2H, $CH_2$), 2.50 (m, 2H, $CH_2$), 4.02 (q, 2H, $CH_2$ (OEt)), 6.08 ppm (d, 1H, $^2J_{\mathrm{H,P}}=31$ Hz, CH=); $^{13}$C NMR ($CDCl_3$): $\delta=15.37$ (s, Me), 16.90 (d, $J_{\mathrm{C,P}}=12.8$ Hz, Me), 19.82 (d, $J_{\mathrm{C,P}}=15.8$ Hz, Me), 27.06 (d, $J_{\mathrm{C,P}}=53.6$ Hz, $PCH_2$), 28.41 (s, $CH_2$), 61.87 (s, $OCH_2$), 119.75 (d, $J_{\mathrm{C,P}}=83$ Hz, BrC=), 122.64 (d, $J_{\mathrm{C,P}}=77.7$ Hz, HC=), 150.10 (d, $J_{\mathrm{C,P}}=27.2$ Hz, =CMe), 154.92 (d, $J_{\mathrm{C,P}}=12.0$ Hz, =CMe), 172.53 ppm (d, $J_{\mathrm{C,P}}=14.3$ Hz, C=O); MS: *m*/*z* (%): 323 ([*M*]$^+$, 37).

**2-Bromo-1-(2-ethoxycarbonylethyl)-3,4-dimethylphosphole (7)**: The sample of **6** obtained as previously described was dissolved in toluene (200 mL), $P(CH_2CH_2CN)_3$ (11 g) was added and the mixture was refluxed for 4 h. After the mixture had been cooled, the solution was filtered through a sintered glass with a layer of silica gel. Evaporation of the solvent yielded orange crystals of **7** (8.2 g, 53 % overall yield from the starting phosphole). $^{31}$P NMR ($CDCl_3$): $\delta=6.5$ ppm; $^1$H NMR ($CDCl_3$): $\delta=1.11$ (t, 3H, Me (OEt)), 1.92 (d, $J_{\mathrm{H,P}}=2.5$ Hz, 3H, Me), 2.00 (dd, 3H, Me), 1.93–2.10 (m, 4H, $CH_2$), 3.97 (q, 2H, $CH_2$ (OEt)), 6.13 ppm (d, $^2J_{\mathrm{H,P}}=38.8$ Hz, 1H, CH=); $^{13}$C NMR ($CDCl_3$): $\delta=13.21$ (s, Me), 15.58 (s, Me), 16.84 (d, $J_{\mathrm{C,P}}=17.3$ Hz, $PCH_2$), 17.92 (s, Me), 28.20 (s, $CH_2$), 59.41

(s, $OCH_2$), 121.84 (d, $J_{C,P}=17.3$ Hz, BrC=), 125.25 (d, $J_{C,P}=9.8$ Hz, HC=), 145.65 (d, $J_{C,P}=9.8$ Hz, =CMe), 149.13 (d, $J_{C,P}=4.5$ Hz, =CMe), 171.58 ppm (d, $J_{C,P}=5.3$ Hz, C=O); MS: *m*/*z* (%): 290 ([*M*]$^+$, 100).

**2-Bromo-1,3,4-trimethylphosphole sulfide (9)**: Phosphole **7** (0.29 g, $1\times 10^{-3}$ mol) in THF (100 mL) was treated by *t*BuOK (0.12 g, $1\times 10^{-3}$ mol) at 0 °C. The reaction is instantaneous and can be monitored by $^{31}$P NMR spectroscopy (**8**: $\delta(^{31}P)=71.6$ ppm (d, $^2J_{P,H}=41.5$ Hz)). Methyl iodide (0.07 mL, $1.1\times 10^{-3}$ mol) was then added at 0 °C. The reaction is almost instantaneous and can be monitored by $^{31}$P NMR spectroscopy (2-bromo-1, 3,4-trimethylphosphole: $\delta(^{31}P)=-3.8$ ppm (d, $^2J_{P,H}=39.2$ Hz)). Sulfur (0.1 g) was then added and the mixture was heated at 40 °C for 1.5 h. After evaporation, the organic residue was chromatographed with dichloromethane. **9**: yellow solid, yield 0.15 g (63 %). $^{31}$P NMR ($CH_2Cl_2$): $\delta=48.4$ ppm; $^1$H NMR ($CDCl_3$): $\delta=1.72$ (d, $J_{H,P}=14$ Hz, 3H, P-Me), 1.96 (d, $J_{H,P}=2.1$ Hz, 3H, Me), 2.07 (dd, 3H, Me), 6.12 ppm (dd, $^2J_{H,P}=31.3$ Hz, 1H, CH=); $^{13}$C NMR ($CDCl_3$): $\delta=16.10$ (d, $J_{C,P}=10.3$ Hz, Me), 18.51 (d, $J_{C,P}=55.3$ Hz, PMe), 19.12 (d, $J_{C,P}=16.1$ Hz, Me), 120.92 (d, $J_{C,P}=85.4$ Hz, BrC=), 123.14 (d, $J_{C,P}=79.7$ Hz, HC=), 148.17 (d, $J_{C,P}=28$ Hz, =CMe), 153.78 ppm (d, $J_{C,P}=12.6$ Hz, =CMe); MS: *m*/*z* (%): 235 ([*M*]$^+$, 70), 157 ([*M*−Br], 100).

**2,2′-Dibromo-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (10 a,b)**: Phosphole **7** (0.33 g, $1.1\times 10^{-3}$ mol) in THF (100 mL) was treated by *t*BuOK (0.13 g, $1.1\times 10^{-3}$ mol) at room temperature. To this solution was added dry $FeCl_2$ (0.08 g). The reaction mixture was stirred for 0.5 h at room temperature. After evaporation, the residue was extracted with hexane/dichloromethane 90:10 and filtered on florisil. Yield 89 mg (18 %), orange oil. $^{31}$P NMR ($CD_2Cl_2$): $\delta=-67.8$ and $-60.3$ ppm; $^1$H NMR ($CD_2Cl_2$): $\delta=2.02$ (s, 6H, Me), 2.07 (s, 6H, Me), 2.12 (2 s, 12H, Me), 3.58 (d, $^2J_{H,P}=36.6$ Hz, 2H), 3.71 ppm (dm, $^2J_{H,P}=36.6$ Hz, 2H); MS: *m*/*z* (%): 437 ([*M*]$^+$, 100).

## Acknowledgements

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