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METALLOCENEPHOSPHORAMIDES, 2.* AMIDES OF FERROCENEPHOSPHONOUS AND FERROCENEDIPHOSPHONOUS ACIDS

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METALLOCENEPHOSPHORAMIDES, 2.* AMIDES OF FERROCENEPHOSPHONOUS AND FERROCENEDIPHOSPHONOUS ACIDS

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The first examples of phosphorylated metallocenes containing P(III)-N bond were prepared. Two synthetic routes were developed: treating iron(II)bromide with phosphorylated sodium cyclopentadienide and the reaction of mono- and dilithiated ferrocenes with chlorides of diamidophosphorous acids. Two heterocyclic amides were obtained *via* chlorides of ferrocenediphosphonous acid.

Key words: Ferrocene; phosphoramides.

INTRODUCTION

Amides of phosphorous acid are effective phosphorylating reagents in respect to proton-containing nucleophiles such as alcohols, thiols, amines, etc. and were applied to the synthesis of phosphorylated sugars, lipids, nucleic acids and other complex molecules.^{2–4}

Phosphorilating with the amides makes it possible to join various phosphorus-containing moieties to the active proton-bearing nucleophilic center of the substrate. The creation of compounds of a new type (if the initial phosphoramide contains an organometallic group bonded to the phosphorus atom) may turn into a development of this synthetic method. Moreover phosphorus(III) atom being a potential ligand, additional transition metal centers may be inserted into the structure of this type. The goal of this work is the synthesis of the first metallocene-containing phosphoramides—amides of ferrocenephosphonous and ferrocenediphosphonous acids.

RESULTS AND DISCUSSION

The development of synthetic routes to phosphorylated metallocenes is not a new problem. However, there were only alkyl- and arylphosphinosubstituted metallo-

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enes among the substances of interest⁵ and metallocenes' phosphoramides have not been prepared yet.

There are two approaches to the metallocenephosphoramides which seem to be convenient: (i) From phosphordiamidous acid chloride and alkali-metallated metallocenes and (ii) from phosphorylated alkali-metal cyclopentadienide and corresponding transition-metal halide (Scheme I).

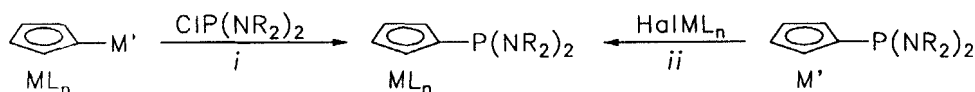
The first way (i) appears to be more simple. Nevertheless, it may be used only when the corresponding alkali-metal metallocenide is available, if exist at all. The second way (ii) is a more general one, but it requires the initial phosphorylated alkali-metal cyclopentadienides which have never been isolated before.

In order to work out both (i) and (ii) ways and to compare them we have tried to synthesize phosphorylated ferrocene, mono- and dilithiated derivatives of which being well known.

a) Synthesis of Diamidophosphorcyclopentadienide's Sodium Salts

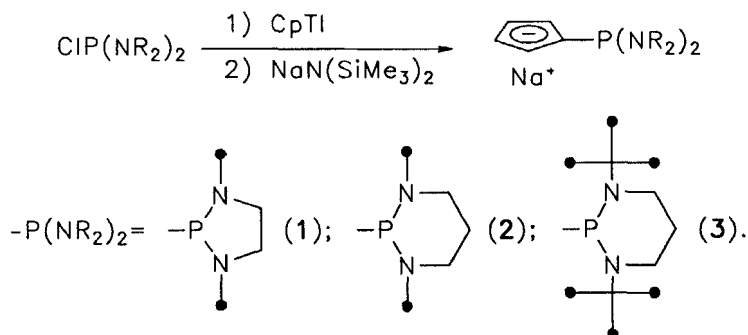
The sodium derivatives 1–3 were prepared by the reaction of thallium cyclopentadienide with the corresponding phosphordiamidous acid chloride followed by treatment of sodium hexamethyldisilazylamide. Since thallium cyclopentadienyl reacts with phosphorus(III) halides most smoothly,⁶ it was chosen to be the starting material (Scheme II).

Unfortunately, we have failed to distill the phosphorylated cyclopentadiene because of its high sensitivity to heating. As it turned out, it was the use of cyclic phosphoramides that made it possible to purify the resulting sodium salts by recrystallization. For instance, no crystalline product is observed if CIP(NEt₂)₂ is used.



M - transition metal

SCHEME I



SCHEME II

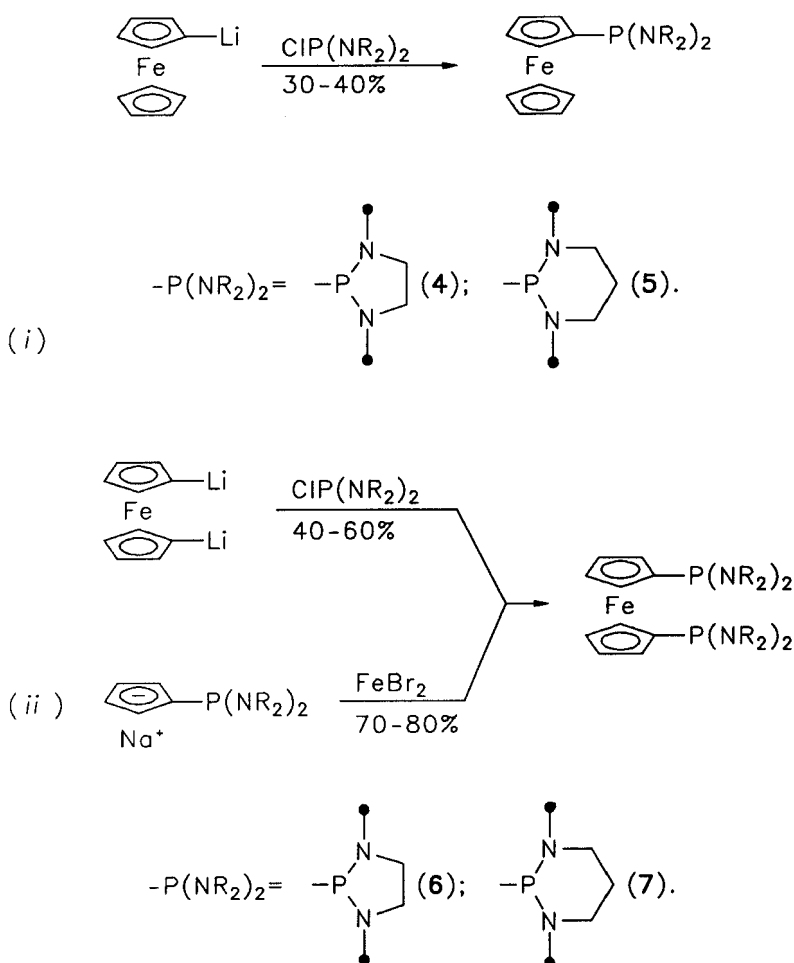
Compounds **1–3** are colourless air sensitive solids. They are easily soluble in THF and insoluble in non-polar inert solvents.

b) Synthesis Ferrocenephosphonous and Ferrocenediphosphonous Acids Amides

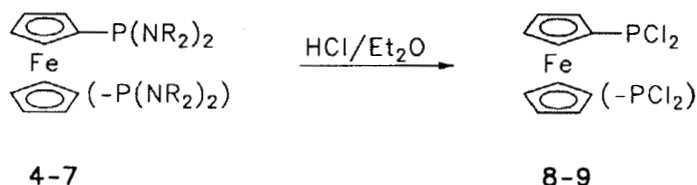
We have found that ferrocenediphosphonous acids amides can be obtained easily both from dilithiated ferrocene (*i*) or from sodium salts **1** and **2** (*ii*). Monophosphorilated compounds are formed if monolithiated ferrocene is used (*i*) (Scheme III).

Compounds **4–7** can be converted nearly quantitatively into the corresponding chlorides **8**⁷ and **9** (Scheme IV).

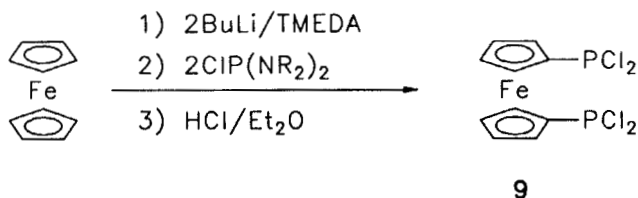
Isolation of diphosphorilated chloride **9** turned out to be so simple and convenient, that it was possible to carry out its preparation as the one pot synthesis from ferrocene (Scheme V).



SCHEME III



SCHEME IV

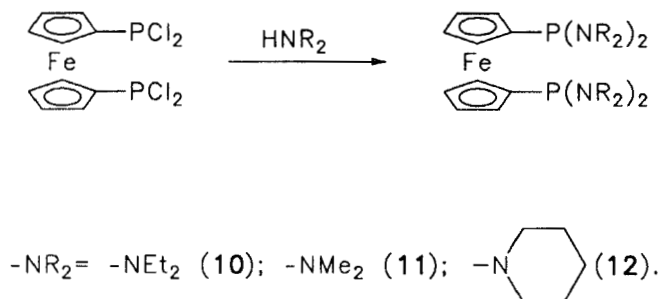


SCHEME V

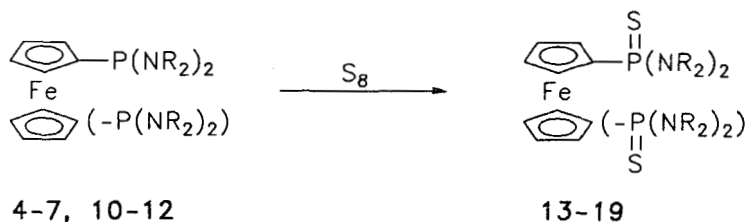
Using **9** and dimethylamine or piperidine we have prepared crystalline ferrocenediphosphonous acid amides **11** and **12** in high yields. Although no crystalline product was isolated when diethylamine was used, the ^{31}P NMR spectroscopy data ($\delta = 93.64$ ppm) indicate the quantitative formation of N,N-diethylamide **10** in reaction mixture. The same signal was observed in ^{31}P NMR spectra of the reaction mixture obtained when dilithiated ferrocene and $\text{CIP}(\text{NEt}_2)_2$ were reacted (Scheme VI).

It is remarkable that compounds **11** and **12** do not crystallize by the method (i). This may be a result of formation of co-products which prevent crystallization. Thus, the purity of initial materials and uniformity of transformations should be considered one of the most important factors in the chemistry of ferrocene phosphoramides and determines the great thoroughness in the choice of reagents and methods.

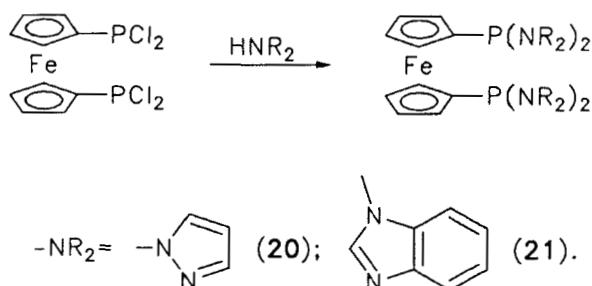
The obtained phosphoramides **4-7** and **11-12** are yellow-orange well-formed crystalline solids, unstable when exposed to air. To confirm the structure of those compounds we have isolated their sulfurated derivatives **13-19** which are, contrary to the amides of the phosphorus(III), stable in air and may be purified by chromatography (Scheme VII).



SCHEME VI



SCHEME VII



SCHEME VIII

It was shown recently that imidazolyl and pyrazolyl derivatives of trivalent phosphorus are considerably more reactive with respect to hydroxyl containing nucleophiles than their alkylamino-analogues.² That is why it was of interest to prepare these heterocyclic amides **20** and **21** from chloride **9** (Scheme VIII).

We have worked out the synthetic approach to ferrocenephosphoramides. Our further investigations will be directed to the problem of soft functionalization of such compounds.

TABLE I

NMR data of **1-3** (THF-d₈, 20°C, TMS for ¹H, ¹³C and 85% H₃PO₄ for ³¹P as a reference standard, *J* was calculated when possible)

Compound	NMR data
¹ H	5.90(m, <i>J</i> _{HP} =4.5Hz, αC-H(<i>Cp</i>), 2H); 5.80(m, <i>J</i> _{HP} =1.6Hz, βC-H(<i>Cp</i>), 2H); 3.20(m, C(4,5)-Ha, 2H); 2.75(m, <i>J</i> _{HP} =8.8Hz, C(4,5)-He, 2H); 2.33(d, <i>J</i> _{HP} =14.2Hz, Me, 6H)
1 ¹³ C	δ 115.57(d, <i>J</i> _{CP} =28.3Hz, C(1) <i>Cp</i>); 111.70(d, <i>J</i> _{CP} =22.4Hz, C(2) <i>Cp</i>); 107.29(d, <i>J</i> _{CP} =8.4Hz, C(3) <i>Cp</i>); 55.25(d, <i>J</i> _{CP} =8.8Hz, Me); 38.66(d, <i>J</i> _{CP} =22.0Hz, C(4,5)ring)
³¹ P	δ 108.37

TABLE I (Continued)

Compound	NMR data
2	^1H δ 5.99(m, $\alpha\text{C-H}(\text{Cp})$, 2H); 5.86(m, $\beta\text{C-H}(\text{Cp})$, 2H); 3.59(m, $J_{\text{HP}}=12.8\text{Hz}$, C(4,6)-He, 2H); 2.56(d, $J_{\text{HP}}=16.0\text{Hz}$, Me, 6H); 2.46(m, C(4,6)-Ha, 2H); 2.18(m, C(5)-He, 1H); 1.07(m, C(5)-Ha, 1H)
	^{13}C δ 118.13(d, $J_{\text{CP}}=26.3\text{Hz}$, C(1)Cp); 110.66(d, $J_{\text{CP}}=$ 21.1Hz, C(2)Cp); 106.26(d, $J_{\text{CP}}=8.2\text{Hz}$, C(3)Cp); 47.97(d, $J_{\text{CP}}=6.2\text{Hz}$, Me); 41.99(d, $J_{\text{CP}}=28.6\text{Hz}$, C(4,6)); 23.06(s, C(5))
	^{31}P δ 92.58
3	^1H δ 5.79(m, $\alpha\text{C-H}(\text{Cp})$, 2H); 5.71(m, $\beta\text{C-H}(\text{Cp})$, 2H); 3.60(m, C(4,6)-He, 2H); 2.79(m, $J_{\text{HP}}=3.3\text{Hz}$, C(4,6)-Ha, 2H); 1.60(m, C(5)-He, 1H); 1.24(d, $J_{\text{HP}}=1.5\text{Hz}$, <i>t</i> -Bu, 18H); 1.13(m, C(5)-Ha, 1H)
	^{13}C δ 116.10(d, $J_{\text{CP}}=15.1\text{Hz}$, C(1)Cp); 107.64(d, $J_{\text{CP}}=$ 16.6Hz, C(2)Cp); 105.80(d, $J_{\text{CP}}=7.6\text{Hz}$, C(3)Cp); 55.20(d, $J_{\text{CP}}=21.4\text{Hz}$, C(7,9)); 40.54(d, $J_{\text{CP}}=4.9$ Hz, C(4,6)); 31.30(d, $J_{\text{CP}}=13.9\text{Hz}$, Me); 30.78 (d, $J_{\text{CP}}=2.8\text{Hz}$, C(5))
	^{31}P δ 60.42

EXPERIMENTAL

All operations were performed under dry argon or in vacuum. The solvents were purified as usual. ^{31}P NMR spectra were recorded on JEOL FX-100 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer. The quantitative analysis was carried out on a Carlo Erba analyzer. Monobromoferrocene,⁸ ferrocenyllithium,⁹ ferrocenyldilithium¹⁰ were prepared as described in the literature. The NMR data of compounds 1–3 are listed in Table I. ^{31}P NMR spectra of compounds 4–21 and their analytical data are listed in Table II. The supposed structures of these compounds were confirmed with the ^1H NMR spectroscopy.

Synthesis of sodium salts 1–3. 3.6 mmol of corresponding chloride of phosphorous acid diamide in 3 ml of Et_2O are added to a suspension of 1 g (3.7 mmol) CpTiI in 10 ml Et_2O at -60°C . On adding the reaction mixture is stirred at -10°C for 1 h. The precipitate is filtered and the solution is treated dropwise with 5.8 ml of 0.6 M solution of $\text{NaN}(\text{SiMe}_3)_2$ in Et_2O . The compounds 1 and 2 begin to crystallize after several hours. In 2 or 3 days the solution was decanted, the crystals were washed with Et_2O and dried. The yields of 1–3 are 40–60%.

TABLE II
Analytical and ^{31}P NMR data of compounds 4–21

Compound	Formula	C	H	δ ^{31}P
		Found (Calc)	Found (Calc)	
4	$\text{C}_{14}\text{H}_{19}\text{FeN}_2\text{P}$	55.88 (55.63)	6.40 (6.35)	104.24
5	$\text{C}_{15}\text{H}_{21}\text{FeN}_2\text{P}$	56.80 (56.96)	6.67 (6.71)	88.28
6	$\text{C}_{18}\text{H}_{28}\text{FeN}_4\text{P}_2$	52.20 (51.68)	6.94 (6.76)	103.88
7	$\text{C}_{20}\text{H}_{32}\text{FeN}_4\text{P}_2$	53.81 (53.83)	7.37 (7.23)	87.87
8	$\text{C}_{10}\text{H}_9\text{Cl}_2\text{FeP}$	42.12 (41.72)	3.42 (3.15)	164.31
9	$\text{C}_{10}\text{H}_8\text{Cl}_4\text{FeP}_2$	30.45 (30.97)	2.09 (2.08)	161.90
10	$\text{C}_{26}\text{H}_{48}\text{FeN}_4\text{P}_2$	a		93.64
11	$\text{C}_{18}\text{H}_{32}\text{FeN}_4\text{P}_2$	50.57 (51.19)	7.36 (7.63)	95.74
12	$\text{C}_{30}\text{H}_{48}\text{FeN}_4\text{P}_2$	61.84 (61.86)	8.33 (8.31)	90.84
13	$\text{C}_{14}\text{H}_{19}\text{FeN}_2\text{PS}$	50.34 (50.29)	5.69 (5.74)	82.27
14	$\text{C}_{15}\text{H}_{21}\text{FeN}_2\text{PS}$	51.75 (51.72)	6.06 (6.10)	80.12
15	$\text{C}_{18}\text{H}_{28}\text{FeN}_4\text{P}_2\text{S}_2$	44.34 (44.82)	5.87 (5.86)	78.12
16	$\text{C}_{20}\text{H}_{32}\text{FeN}_4\text{P}_2\text{S}_2$	46.53 (47.06)	6.22 (6.33)	77.76
17	$\text{C}_{26}\text{H}_{48}\text{FeN}_4\text{P}_2\text{S}_2$	52.16 (52.17)	7.99 (8.08)	78.14
18	$\text{C}_{18}\text{H}_{32}\text{FeN}_4\text{P}_2\text{S}_2$	45.01 (44.45)	6.57 (6.63)	82.25
19	$\text{C}_{30}\text{H}_{48}\text{FeN}_4\text{P}_2\text{S}_2$	55.91 (55.72)	7.76 (7.48)	76.96
20	$\text{C}_{22}\text{H}_{20}\text{FeN}_8\text{P}_2$	50.84 (51.38)	4.14 (3.92)	65.69
21	$\text{C}_{38}\text{H}_{28}\text{FeN}_8\text{P}_2$	63.08 (63.38)	4.42 (3.95)	45.51

^aSatisfactory analysis can not be performed as the substance is an air sensitive liquid.

Synthesis of ferrocenephosphonous- and ferrocenediphosphonous acids' amides.

From mono- and dilithiated ferrocenes. a) 1.9 ml of 1.9 M solution of BuLi in hexane (3.63 mmol) are added to a cooled at -70°C solution of 1 g of monobromoferrocene (3.77 mmol) in 10 ml of Et_2O . The reaction mixture is allowed to warm gradually up to 0°C and stirred at this temperature within 1 h more. 3.6 mmol of corresponding chloride of phosphorous acid in 2 ml Et_2O is added then and the resultant mixture is stirred for 2 h at r.t. On filtering off the precipitate and removing the solvent the residual solid is recrystallized from pentane. Yields of 4–5 are about 30–40%.

b) The solution of dilithiated ferrocene obtained from 0.92 g (5 mmol) of ferrocene is treated under cooling with 10 mmol of corresponding chloride of phosphorous acid in 5 ml of THF. The mixture is stirred for 2 h at room temperature, then the solvent is removed. The residue is recrystallized from pentane. Yield 6–7 is about 40–60%.

From sodium derivatives 1 and 2. 0.53 g FeBr₂ (2.45 mmol) in 5 ml THF are slowly added to a solution of 4.9 mmol **1** or **2** in 5 ml THF under cooling. On stirring the mixture within 2 h at r.t. the solvent is removed and the residue is recrystallized from pentane. Yield of **6–7** is about 70–80%.

From ferrocenediphosphonous acid' tetrachloride 9. a) Amides **10–12**. A solution of 7 mmol triethylamine and 7 mmole of corresponding secondary amine (dimethylamine, diethylamine or piperidine) in 20 ml Et₂O are added slowly to a cooled at 0°C solution of 1 g **9** (3.5 mmol) in 10 ml of Et₂O. The mixture is stirred at 0°C within 15–20 min and then for 3 h more at r.t. The precipitating triethylamine hydrochloride is removed by filtration, the solvent is evaporated. The residue is recrystallized from pentane. The yield of **11** and **12** are 90–95%. We failed to crystallize the compound **10** prepared in this manner.

b) Heterocyclic amides **20** and **21**. Compounds **20** and **21** were prepared in a similar manner, but THF was used instead of Et₂O. After recrystallization from THF the yield obtained 60–70%.

Synthesis of chlorides 8 and 9. a) A solution of dilithiated ferrocene obtained from 3.7 g (20 mmol) of ferrocene is treated at 0°C with a slight excess of ClP(NEt₂)₂ (22 mmol) in 20 ml of Et₂O. The reaction mixture is stirred for 2 h at r.t. (an intensive signal with $\delta = 93.64$ ppm in ³¹P NMR spectrum of the reaction mixture). Then 40–50 ml 4 M HCl in Et₂O are added slowly under cooling at 0°C. After stirring the reaction mixture at r.t. within 2 h the precipitate is filtered and washed with Et₂O. The solution and washing Et₂O are combined, then the solvent is removed. The residue is recrystallized from pentane. Yield of **9**, 3.2 g (42%).

b) A 50% excess of HCl in Et₂O is added slowly to a solution of 5 mmol one of phosphoramides **4–12** in 5 ml of Et₂O. The subsequent operations are performed as described above. Yields of **8** and **9** are not less than 90%.

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