ELSEVIER

Journal of Organometallic Chemistry 643–644 (2002) 32–38

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Site-selective phosphorylation of arylphospholes through reaction with phosphorus tribromide [1]

György Keglevich [a,*], Tungalag Chuluunbaatar [a], Beáta Dajka [a], Krisztina Ludányi [b], Gyula Parlagh [c], Tamás Kégl [d], László Kollár [e], László Tőke [f]

[a] *Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary*
[b] *Hungarian Academy of Sciences, Chemical Research Center, 1525 Budapest, Hungary*
[c] *Department of Physical Chemistry, Budapest University of Technology and Economics, 1521 Budapest, Hungary*
[d] *Research Group for Petrochemistry of the Hungarian Academy of Sciences, 8200 Veszprém, Hungary*
[e] *Department of Inorganic Chemistry, University of Pécs, 7624 Pécs, Hungary*
[f] *Research Group of the Hungarian Academy of Sciences at the Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary*

Received 21 May 2001; accepted 16 July 2001

Dedicated to Professor Dr François Mathey on the occasion of his 60th birthday

Abstract

The reaction of 1-(tri-*tert*-butylphenyl)phosphole (**1**) with phosphorus tribromide gave the 3-dibromophosphino intermediate (**2**) selectively that was useful in the synthesis of phosphonic amides **4**, H-phosphinic amide **6** and H-phosphinates **8**. A similar transformation of the 1-(triisopropylphenyl)phosphole (**9**) led to a 2-substitution furnishing phosphonic amides **12** or H-phosphinates **14**. The phosphorylated phospholes (**4**, **6**, **8**) were tested as ligands of transition metal complexes in hydroformylation.

Keywords: Arylphospholes; Phosphorylation; Selectivity; Hydroformylation

1. Introduction

Phospholes, perhaps the most representative class of P-heterocycles, have attracted much attention recently [2–4]; they are widely used as ligands in transition metal complexes applied in hydroformylations [5]. On the other hand, the controversy over the aromaticity of phospholes stimulated an intensive study of the problem [6]. It is now clear that the ''common or garden'' variety phospholes are not aromatic due to the pyramidal character of the phosphorus atom. The 1-(2,4,6-trialkylphenyl)phospholes exhibiting a flattened P-pyramid were found, however, to be of aromatic character. Both the bond-equalization in the hetero ring of phospholes and their reactivity in aromatic electrophilic substitutions encountered a significant electron delocalization [7–10].

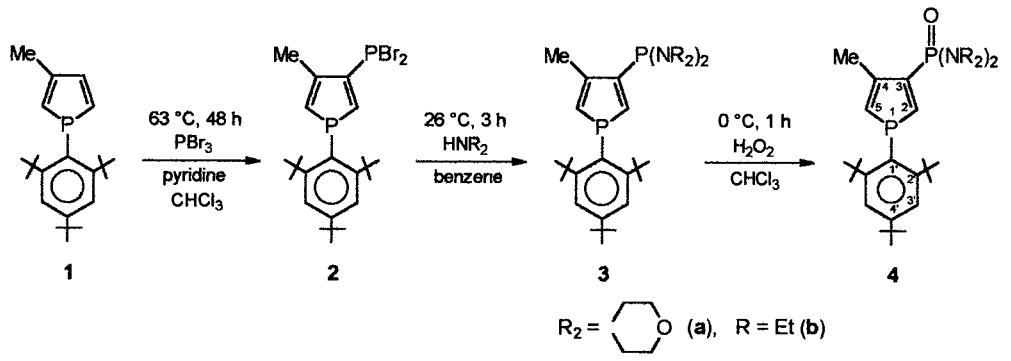
In this paper, we report a new reaction of trialkylphenylphospholes; their site-selective phosphorylation via reaction with phosphorus tribromide is a good means for the preparation of modified phospholes.

2. Results and discussion

The reaction of 1-(2,4,6-tri-*tert*-butylphenyl)-phosphole (**1**) with phosphorus tribromide, which was found to be an efficient reactant for the introduction of the dibromophosphino group into N-heterocycles [11–14], led to the 3-dibromophosphinophosphole (**2**) after 48 h reflux in chloroform, in the presence of one equivalent of pyridine. The unstable intermediate (**2**) was immediately converted to phosphonous amides (**3a**

* Corresponding author. Tel.: +36-1-463-1111/5883; fax: +36-1-463-3648.
E-mail address: keglevich@oct.bme.hu (G. Keglevich).
[1] Preliminary communication: [1].

0022-328X/02/$ - see front matter
PII: S0022-328X(01)01119-6



Scheme 1.

and **3b**) by reaction with morpholine or diethylamine in benzene solution. To obtain even more stable products, the phosphonous amides (**3a** and **3b**) were oxidized by hydrogen peroxide to phosphonic amides (**4a** and **4b**, respectively) (Scheme 1).

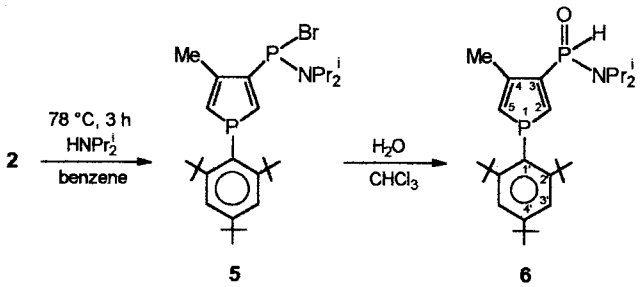
The power of the above reaction sequence is the site-selective substitution of the phosphole moiety in position 3. The reaction site must be controlled by the steric hindrance around the phosphorus atom. It is worthy of mention that the oxidation of intermediate **3** affected only the phosphonous function, the phosphorus atom of the phosphole ring remaining intact. This is obviously the consequence of the appropriate 3-substitution, as the trialkylphenylphospholes (e.g. **1** and **9**), are known to undergo oxidation to afford phosphole oxides that are subsequently dimerized [8,15]. The oxidation of sterically hindered phospholes (e.g. **1** and **9**) was, however, reported to proceed significantly slower than that of other phospholes [8,15].

Intermediates **3a** and **3b** were characterized by ^{31}P-NMR spectroscopy and their elemental composition was confirmed by high resolution mass spectrometry. The structure of products **4a** and **4b** obtained in ca. 56% yield after purification by column chromatography was supported by ^{31}P-, ^{13}C- and ^{1}H-NMR spectroscopy, as well as high resolution mass spectrometry. The ^{13}C-NMR spectral parameters are listed in Table 1. Species **3** and **4** were characterized by $^{3}J_{PP}$ couplings of ca. 34 and 22 Hz, respectively. The $^{1}J_{PC}$ coupling of ca. 155 Hz detected on C_3 of the phosphole ring of **4a** and **4b** was in agreement with the 3-substitution. The ^{1}H-NMR spectrum of phospholes **4** revealed a $^{2}J_{PH}$ coupling for both C_5–H and C_2–H (ca. 36 and 30 Hz, respectively), the latter signal also being coupled by the C_3–P atom ($^{3}J_{Ph}$ ca. 12).

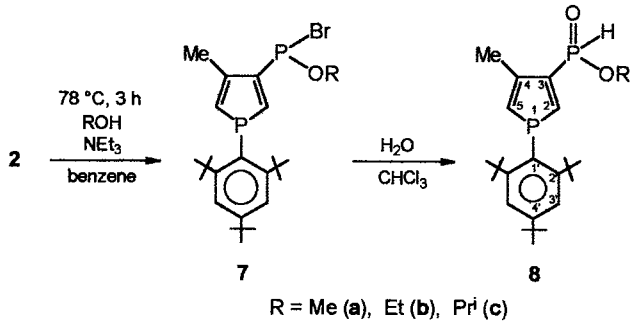
The reaction of dibromophosphine **2** with diisopropylamine, as a consequence of steric hindrance, led only to monosubstitution (Scheme 2). The H-phosphinic amide (**6**) obtained after hydrolysis was characterized by ^{31}P- and ^{13}C-NMR, as well as mass spectrometry. The ^{13}C-NMR spectral parameters are shown in Table 1. The P(O)H unit in compound **6** was supported by the $^{1}J_{PH}$ coupling of 499 Hz obtained from the proton coupled ^{31}P-NMR spectrum.

Intermediate **2** was also utilized in the synthesis of H-phosphinates; its reaction with simple alcohols in boiling benzene in the presence of triethylamine followed by hydrolysis gave rise to products **8a**–**c** (Scheme 3).

The phosphinates (**8a**–**c**) isolated in ca. 72% yield after chromatography were identified by ^{31}P-, ^{13}C- and ^{1}H-NMR, as well as high resolution mass spectrometry. The ^{13}C-NMR spectral parameters are listed in Table 1. The $^{3}J_{PP}$ couplings (ca. 27 Hz), the $^{1}J_{PC}$ couplings of ca. 130 Hz obtained on C_3 and the $^{2}J_{PH}$ couplings detected on C_2–H and C_5–H (ca. 26 and 36 Hz, respectively) were in accord with the 3-substitution. The P(O)H moiety of the products (**8a**–**c**) was confirmed by the $^{1}J_{PH}$ couplings of ca. 550 Hz obtained from the proton coupled ^{31}P-NMR spectrum.



Scheme 2.



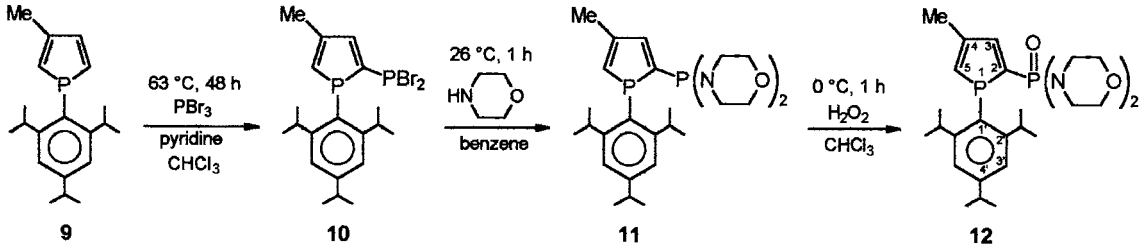
Scheme 3.

Table 1
^{13}C-NMR spectral parameters for substituted phospholes **4**, **6** and **8** in $CDCl_3$ solution

	δ_C (J_{PC}, J in Hz)														
	C_2	C_3	C_4	C_5	C_4–Me	$C_{2'}$	$C_{3'}$	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{2'}$–$C(CH_3)_3$	$C_{4'}$–$C(CH_3)_3$	$C_{2'}$–$C(CH_3)_3$	$C_{4'}$–$C(CH_3)_3$
4a	139.9 (14.6/8.6)	128.2 (21.4/154.5)	139.8 (23.2/15.2)	126.8 (13.2/21.0)	19.2 (6.2)	44.9 (-)	67.5 (5.8)	118.6 (4.6)	158.8 (11.7)	123.1 (10.5)	153.3 (2.4)	38.9 (3.5)	35.4 (-)	33.3 (3.5)	31.3 (-)
4b	138.8 (11.9/8.5)	132.0 (20.8/155.0)	140.4 (22.5/15.4)	126.4 (12.5/19.2)	18.8 (5.9)	39.0 (4.7)	14.3 (-)	119.7 (10.1)	158.8 (11.7)	123.0 (10.0)	152.8 (2.6)	38.8 (3.5)	35.1 (-)	33.3 (3.7)	31.2 (-)
6	141.8 (14.3/9.6)	129.8 (21.6/127.2)	137.7 (21.7/15.8)	126.5 (11.0/19.9)	18.1 (5.8)	46.1 (2.8)	23.3 (3.0)	118.7 (4.6)	158.8 (11.4)	123.0 (10.1)	153.1 (-)	38.7 (3.0)	35.3 (-)	33.3 (3.6)	31.2 (-)
8a	141.1 (18.4/10.7)	127.3 (22.3/129.6)	137.3 (21.4/17.0)	125.8 (12.0/23.8)	17.8 (7.7)	51.6 (6.3)	- (-)	117.5 (-)	158.9 (11.7)	123.0 (10.5)	153.5 (2.5)	38.7 (3.5)	35.3 (-)	33.2 (3.2)	31.1 (-)
8b	140.9 (17.8/10.4)	128.0 (22.2/129.8)	137.4 (21.5/16.9)	125.8 (12.0/23.0)	17.8 (5.6)	61.3 (6.3)	16.4 (6.7)	117.6 (-)	158.9 (11.8)	123.0 (10.7)	153.4 (2.6)	38.7 (3.5)	35.2 (-)	33.1 (3.4)	31.1 (-)
8c	140.9 (17.3/10.5)	128.6 (22.1/131.0)	137.5 (21.7/17.1)	126.0 (12.1/22.9)	18.0 (5.8)	70.5 (6.5)	24.1 (3.9)	117.9 (-)	159.1 (11.7)	123.2 (10.5)	153.5 (-)	38.8 (3.5)	35.4 (-)	33.3 (3.4)	31.1 (-)

Table 2
^{13}C-NMR spectral parameters for substituted phospholes **12** and **14** in $CDCl_3$ solution

	δ_C (J_{PC}, J in Hz)														
	C_2	C_3	C_4	C_5	C_4–Me	$C_{2''}$	$C_{3''}$	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{2''}$–$CH(CH_3)_2$	$C_{4''}$–$CH(CH_3)_2$	$C_{2''}$–$CH(CH_3)_2$	$C_{4''}$–$CH(CH_3)_2$
12	133.7 (151.4/19.9)	147.5 (17.3/6.1)	142.4 (18.4/14.6)	137.7 (5.6/5.2)	18.4 (3.6)	44.5 (-)	66.9 (6.9)	119.8 (-)	156.9 (14.7)	122.2 (11.1)	152.8 (-)	32.1 (15.9)	34.4 (-)	24.2 (-)	23.1 (-)
14	136.4 (152.0/13.9)	146.6 (19.8/8.0)	143.1 (19.3/12.5)	138.5 (6.1/2.2)	18.3 (4.0)	51.7 (6.2)	- (-)	118.1 (-)	157.1 (14.8)	122.2 (6.1)	152.8 (-)	34.3 (12.1)	34.3 (-)	23.7 (-)	23.6 (-)



Scheme 4.

Obviously, the reaction of 1-(2,4,6-triisopropylphenyl)phosphole (**9**) with phosphorus tribromide led to a 2-substitution, as the steric hindrance was not, in this case, significant. Reaction of intermediate **10** with morpholine furnished phosphonous amide **11**, whose oxidation, in turn, yielded phosphonic amide **12** (Scheme 4).

Phosphonous amide **11** was characterized by ^{31}P-NMR spectra and high resolution mass spectrometry. The structure of product **12** was confirmed by ^{31}P-, ^{13}C- and ^{1}H-NMR, as well as mass spectrometry. The ^{13}C-NMR spectral parameters are listed in Table 2. Species **11** and **12** were characterized by $^{2}J_{PP}$ couplings of 71 and 49 Hz, respectively.

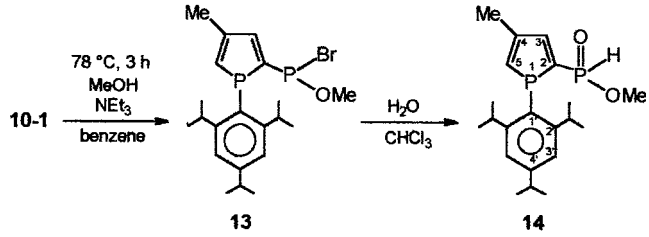
The reaction of the mixture of dibromophosphinophosphole (**10**) with methanol followed by hydrolysis resulted in the formation of H-phosphinate **14** (Scheme 5). The product (**14**) was identified by ^{31}P-, ^{13}C- and ^{1}H-NMR, as well as high resolution mass spectrometry. The ^{13}C-NMR spectral parameters are listed in Table 2. Product **14** exhibited a significant J_{PP} coupling of 58 Hz.

The substitution of triisopropylphenylphosphole **9** was not so efficient, as that of tri-*tert*-butylphenyl derivative **1**, products **12** and **14** were obtained in ca. 41% yield after chromatography. The side-reactions were not evaluated. It seems to be probable that the aromaticity of the phosphole ring promotes the reaction with phosphorus tribromide.

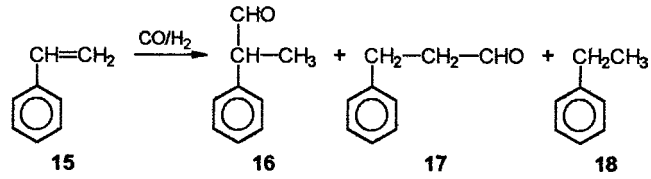
2.1. Hydroformylation in the presence of *4a*, *4b*, *6*, *8a* and *8b*

Styrene (**15**), as the model substrate, was reacted in the presence of in situ rhodium catalysts containing one of the sterically hindered phospholes **4a**, **4b**, **6**, **8a**, **8b** with CO/H_2 (1/1) at 100 °C at a pressure of 100 bar. Although the activity of the tested rhodium catalysts falls slightly behind the best rhodium–phosphine catalysts, the catalytic test of the hindered phosphole-based catalysts proved to be of interest from a theoretical point of view.

In addition to the formyl regioisomers, 2-phenyl-propanal (**16**) and 3-phenyl-propanal (**17**), the hydrogenation product, ethylbenzene (**18**) was also formed (Scheme 6). All the in situ catalysts formed from $[Rh(nbd)Cl]_2$ and the above phospholes are active under the given conditions (Table 3). Practically complete conversions have been obtained in up to 4 h at 100 °C. (The blank experiment with $[Rh(nbd)Cl]_2$ as the only catalyst shows that the addition of phospholes resulted in more active and more regioselective catalytic systems except for **4a**.) It is worth noting that the reaction can almost be considered to be chemospecific: the chemose-



Scheme 5.



Scheme 6.

Table 3
Hydroformylation of styrene (**15**) in the presence of $[Rh(nbd)Cl]_2$ + 4 L in situ catalysts (L = a sterically hindered phosphole ligand) [a]

L	Reaction time (h)	Conversion (%)	R_{br} [b] (%)
4a	3.5	95	57
4b	4	99	70
6	2.5	69	72
8a	2	98	75
8b	2	99	80
-	4	99	58

[a] Reaction conditions: 0.05 mmol catalyst; Rh/P = 1/2; 100 mmol styrene; toluene solvent; $p(CO) = p(H_2) = 40$ bar; 100 °C; the chemoselectivity (R_C = (mol **16** + mol **17**)/(mol **16** + mol **17** + mol **18**) × 100) was higher than 99% in all cases.

[b] Regioselectivity R_{br} = (mol **16**)/(mol **16** + mol **17**) × 100.

lectivity of the hydroformylation is excellent in all cases (higher than 99%) by the prevailing formation of aldehydes (**16**, **17**) over the hydrogenated side-product (**18**). Moderate regioselectivities (57–80%) have been obtained. However, the preliminary experiments at low temperature (40 °C) show high regioselectivities by the prevailing formation of the branched aldehyde (R_{br} > 99%). The systematic investigation of the temperature dependence of the catalytic characteristics, as well as that of the structure–reactivity relationship are in progress.

No reaction between the phospholes possessing P(O)H functionality (e.g. **8a**) and styrene has been observed either in the presence or in the absence of the rhodium-containing precursor, $[Rh(nbd)Cl]_2$. A five-membered ring H-phosphonate was, however, reported to react with 1-octene in the presence of a palladium complex [16].

In summary, it was found that the phospholes bearing a tri-*tert*-butylphenyl- or a triisopropylphenyl substituent on the phosphorus atom react with phosphorus tribromide in a site-selective manner to afford a 3- or a 2-substitution, respectively. The dibromophosphino derivatives are excellent intermediates in the preparation of phosphorylated phospholes that may be ligands in the transition metal catalysts of hydroformylation.

3. Experimental

3.1. General

The ^{31}P-, ^{13}C- and ^{1}H-NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7 and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 or Me_4Si. The couplings are given in Hz. Mass spectrometry was performed on a ZAB-2SEQ instrument.

3.2. General procedure for the phosphorylation of phospholes (*1* and *9*)

3.2.1. The preparation of dibromophosphinophospholes (*2* and *10*)

To 1.17 mmol of phosphole (**1** or **9**) in 50 ml of dry $CHCl_3$ was added 0.12 ml (1.26 mmol) of phosphorus tribromide and 0.10 ml (1.24 mmol) of Py and the solution was stirred at boiling point for 48 h under a nitrogen atmosphere. The volatile components were removed in vacuo to give **2** or **10**, respectively, practically in quantitative yield.

3.2.2. The preparation of diaminophosphorylphospholes (*4* and *12*)

The ca. 1.17 mmol of the intermediate (**2** or **10**) was taken up in 50 ml of dry benzene and treated with 4.7 mmol of morpholine or diethylamine at 0 °C. After stirring at room temperature (r.t.) for 3 h, the amine salt was filtered off and the solvent of the filtrate evaporated to yield **3a**,**b**, or **11**, respectively.

The 40 ml $CHCl_3$ solution of the ca. 1.17 mmol of phosphonous amide **3a**, **3b** or **11** was treated with 0.27 ml (2.34 mmol) of 30% H_2O_2 at 0 °C with intensive stirring. Then, the contents of the flask were stirred at r.t. for 1 h. The mixture was extracted with 3 × 20 ml of water, the organic phase was dried (Na_2SO_4) and the solvent evaporated. The crude product so obtained was purified by column chromatography (silica gel, 3% MeOH in $CHCl_3$) to furnish phosphorylphospholes **4a**,**b**, or **12**.

3.2.3. The preparation of alkoxy-H-phosphonylphospholes (*8* and *14*)

The solution of ca. 1.17 mmol of the intermediate **2** or **10**, 3.5 mmol of the alcohol (MeOH, EtOH or isopropanol) and 0.33 ml (2.34 mmol) of Et_3N in 50 ml of dry benzene was stirred at boiling point for 3 h. The amine salt was removed by filtration and the solvent of the filtrate evaporated. The residue was taken up in 40 ml of $CHCl_3$ and stirred with 1.5 ml of water for 10 min. The organic phase was dried (Na_2SO_4) and the solvent evaporated. The crude product so obtained was purified by column chromatography as above to afford **8a**–**c**, or **14**, respectively.

Product **6** was prepared similarly, using diisopropylamine instead of the alcohol.

3a: Yield: 79%; ^{31}P-NMR δ_P ($CDCl_3$) 3.4 (P_1), 90.7 (C_3–P), $^3J_{PP} = 33.6$; HR-FAB $[M+H]^+_{measured}$ = 544.3323, $C_{31}H_{50}N_2O_2P_2$ requires 544.3348.

4a: Yield: 60%; ^{31}P-NMR, δ_P ($CDCl_3$) 7.1 (P_1), 23.4 (C_3–P), $^3J_{PP} = 21.8$; ^{13}C-NMR, Table 1; ^{1}H-NMR δ_H ($CDCl_3$) 6.66 (dm, $J_{PH} = 35.5$, C_5–H), 7.37 (ddd, $J_{PH} = 28.1$, $J_{P'H} = 12.1$, $J_{HH} = 2.5$, C_2–H); HR-FAB $[M+H]^+_{measured} = 560.3292$, $C_{31}H_{50}N_2O_3P_2$ requires 560.3297.

3b: Yield: 71%; ^{31}P-NMR, δ_P ($CDCl_3$) −1.8 (P_1), 91.7 (C_3–P), $^3J_{PP} = 33.2$; HR-FAB $[M+H]^+_{measured}$ = 517.3731, $C_{31}H_{55}N_2P_2$ requires 517.3841.

4b: Yield: 52%; ^{31}P-NMR, δ_P ($CDCl_3$) 4.12 (P_1), 27.02 (C_3–P), $^3J_{PP} = 21.7$; ^{13}C-NMR, Table 1; ^{1}H-NMR δ_H ($CDCl_3$) 6.51 (dm, $J_{PH} = 36.2$, C_5–H), 7.16 (ddd, $J_{PH} = 31.3$, $J_{P'H} = 12.4$, $J_{HH} = 1.9$, C_2–H); HR-FAB $[M+H]^+_{measured} = 533.3701$, $C_{31}H_{55}N_2OP_2$ requires 533.3790.

8a: Yield: 71%; ^{31}P-NMR, δ_P ($CDCl_3$) 11.32 (P_1), 23.82 (C_3–P), $^3J_{PP} = 27.5$; ^{13}C-NMR, Table 1; ^{1}H-NMR δ_H ($CDCl_3$) 6.56 (dm, $J_{PH} = 35.8$, C_5–H), 7.66 (ddd, $J_{PH} = 26.5$, $J_{P'H} = 13.6$, $J_{HH} = 2.4$, C_2–H); HR-FAB $[M+H]^+_{measured} = 421.2355$, $C_{24}H_{39}O_2P_2$ requires 421.2425.

8b: Yield: 76%; ^{31}P-NMR, δ_P ($CDCl_3$) 10.72 (P_1), 21.32 (C_3–P), $^3J_{PP} = 27.2$; ^{13}C-NMR, Table 1; ^{1}H-NMR δ_H ($CDCl_3$) 6.55 (dm, $J_{PH} = 35.8$, C_5–H), 7.65 (ddd,

$J_{PH} = 25.4$, $J_{P'H} = 14.8$, $J_{HH} = 2.1$, C_2–H); HR-FAB $[M + H]^+_{measured} = 435.2502$, $C_{25}H_{41}O_2P_2$ requires 435.2582.

8c: Yield: 69%; ^{31}P-NMR, δ_P ($CDCl_3$) 10.02 (P_1), 18.82 (C_3–P), $^3J_{PP} = 26.9$; ^{13}C-NMR, Table 1; ^{1}H-NMR δ_H ($CDCl_3$) 6.54 (dm, $J_{PH} = 35.8$, C_5–H), 7.64 (ddd, $J_{PH} = 27.0$, $J_{P'H} = 13.6$, $J_{HH} = 2.2$, C_2–H); HR-FAB $[M + H]^+_{measured} = 449.2603$, $C_{26}H_{43}O_2P_2$ requires 449.2738.

6: Yield: 44%; ^{31}P-NMR, δ_P ($CDCl_3$) 8.02 (P_1), 5.02 (C_3–P), $^3J_{PP} = 26.5$; ^{13}C-NMR, Table 1; ^{1}H-NMR δ_H ($CDCl_3$) 6.62 (dm, $J_{PH} = 32.0$, C_5–H), 7.74 (ddd, $J_{PH} = 28.4$, $J_{P'H} = 13.2$, $J_{HH} = 2.4$, C_2–H); HR-FAB $[M + H]^+_{measured} = 490.3257$, $C_{29}H_{50}N_1OP_2$ requires 490.3368.

11: Yield: 90%; ^{31}P-NMR δ_P ($CDCl_3$) 0.2 (P_1), 94.1 (C_2–P), $^2J_{PP} = 70.6$; HR-FAB $[M + H]^+_{measured} = 502.2870$, $C_{28}H_{44}N_2O_2P_2$ requires 502.2878.

12: Yield: 38%; ^{31}P-NMR, δ_P ($CDCl_3$) 0.9 (P_1), 24.1 (C_2–P), $^2J_{PP} = 49.4$; ^{13}C-NMR, Table 2; ^{1}H-NMR δ_H ($CDCl_3$) 7.04 (dm, $J_{PH} = 38.2$, C_5–H), 7.42 (ddd, $J_{PH} = J_{P'H} \sim 13.0$, $J_{HH} = 1.2$, C_3–H); HR-FAB $[M + H]^+_{measured} = 518.2832$, $C_{28}H_{44}N_2O_3P_2$ requires 518.2827.

14: Yield: 43%; ^{31}P-NMR δ_P ($CDCl_3$) 2.92 (P_1), 22.52 (C_2–P), $^2J_{PP} = 58.4$; ^{13}C-NMR, Table 2; ^{1}H-NMR δ_H ($CDCl_3$) 6.82 (dm, $J_{PH} = 38.1$, C_5–H), 7.43 (ddd, $J_{PH} = J_{P'H} \sim 12.1$, $J_{HH} \sim 1$, C_3–H); HR-FAB $[M + H]^+_{measured} = 379.1878$, $C_{21}H_{33}O_2P_2$ requires 379.1956.

3.3. Hydroformylation experiments

In a typical experiment a solution of 0.0125 mmol of $[Rh(nbd)Cl]_2$, 0.05 mmol of substituted phospholes **4**, **6** or **8** in 7.5 ml toluene containing 25 mmol of styrene was transferred under Ar into a 20 ml stainless steel autoclave. The reaction vessel was pressurized to 100 bar total pressure ($CO/H_2 = 1/1$) and placed in an oil bath and the mixture was stirred with a magnetic stirrer. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analyzed by GC.

Acknowledgements

The authors thank the Hungarian National Science Foundation (OTKA T029039 and T035347) for financial support.

References

[1] Gy. Keglevich, T. Chuluunbaatar, A. Dobó, L. Tőke, J. Chem. Soc. Perkin Trans. 1 (2000) 1495.
[2] K.B. Dillon, F. Mathey, J.F. Nixon, Phosphorus: the Carbon Copy, from Organophosphorus to Phospha-Organic Chemistry, Wiley, Chichester, 1998, p. 203 chapter 8.
[3] L.D. Quin, Phospholes, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), C.W. Bird (Vol. Ed.), Comprehensive Heterocyclic Chemistry II, vol. 2, Pergamon, Oxford, 1996.
[4] L.D. Quin, in: F. Mathey (Ed.), Phosphorus–Carbon Heterocyclic Chemistry. The Rise of a New Domain, Elsevier, 2001 chapter 4, in press.
[5] I. Ojima, C.-Y. Tsai, M. Tzamarioudaki, D. Bonafoux, in: L.E. Overman et al. (Eds.), The hydroformylation reaction, Ch. 1, in: Organic Reactions, Vol. 56, Wiley, 2000, pp. 1–354.
[6] L. Nyulászi, Chem. Rev. 101 (2001) 1229.
[7] L.D. Quin, Gy. Keglevich, A.S. Ionkin, R. Kalgutkar, G. Szalontai, J. Org. Chem. 61 (1996) 7801.
[8] Gy. Keglevich, L.D. Quin, Zs. Böcskei, Gy.M. Keserű, R. Kalgutkar, P.M. Lahti, J. Organomet. Chem. 532 (1997) 109.
[9] Gy. Keglevich, Zs. Böcskei, Gy.M. Keserű, K. Újszászy, L.D. Quin, J. Am. Chem. Soc. 119 (1997) 5095.
[10] Gy. Keglevich, T. Chuluunbaatar, B. Dajka, A. Dobó, Á. Szöllősy, L. Tőke, J. Chem. Soc. Perkin Trans. 1 (2000) 2895.
[11] S.P. Ivonin, T.E. Terikovska, A.A. Chaikovskaya, A.P. Marchenko, G.N. Koydan, A.M. Pinchuk, A.A. Tolmachev, Heteroatom Chem. 10 (1999) 213.
[12] A.A. Tolmachev, S.P. Ivonin, A.A. Chaikovskaya, T.E. Terikovska, T.N. Kudrya, A.M. Pinchuk, Heteroatom Chem. 10 (1999) 223.
[13] A.A. Tolmachev, A.A. Yurchenko, A.S. Merculov, M.G. Semenova, E.V. Zarudnitskii, V.V. Ivanov, A.M. Pinchuk, Heteroatom Chem. 10 (1999) 585.
[14] S.P. Ivonin, A.A. Anishchenko, A.F. Kurochkin, A.A. Tolmachev, Heteroatom Chem. 9 (1998) 559.
[15] Gy. Keglevich, Zs. Böcskei, V. Harmat, L. Tőke, Heteroatom Chem. 8 (1997) 527.
[16] L.-B. Han, F. Mirzaei, C.-Q. Zhao, M. Tanaka, J. Am. Chem. Soc. 122 (2000) 5407.