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Hydroformylation of styrene in the presence of rhodium-2,4,6-trialkylphenyl-phosphole in situ catalytic systems

György Keglevich [a], Tamás Kégl [b], Tungalag Chuluunbaatar [a], Beáta Dajka [c], Péter Mátyus [c], Balázs Balogh [c], László Kollár [d,e,*]

[a] *Department of Organic Chemical Technology, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*
[b] *Research Group for Petrochemistry of the Hungarian Academy of Sciences, H-8201 Veszprém, P.O. Box 158, Hungary*
[c] *Institute of Organic Chemistry, Semmelweis University, H-1092 Budapest, Hungary*
[d] *Department of Inorganic Chemistry, University of Pécs, H-7624 Pécs, P.O. Box 266, Hungary*
[e] *Research Group for Chemical Sensors of the Hungarian Academy of Sciences, H-7624, Pécs, Hungary*

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This paper is dedicated to Prof. Gábor Bernáth (University of Szeged, Hungary) on the occasion of his 70th birthday

Abstract

The hydroformylation of styrene was carried out in the presence of in situ rhodium catalysts containing 1-arylphospholes with different substituents in position 2 or 3. The aryl substituents were varied from phenyl to different sterically hindered 2,4,6-trialkylphenyls. The structures and Bird-indices (BIs) of the phospholes with different steric and electronic properties were determined by DFT calculations. High chemoselectivities towards hydroformylation, as well as regioselectivities towards the branched formyl regioisomer (2-phenyl-propanal) were obtained at a temperature of 40 °C. Similarly, high chemoselectivity was accompanied by a decreased regioselectivity at 100 °C. The phospholes with an exocyclic P-function in position 2 or 3 showed higher catalytic activity.

Keywords: Arylphospholes; Aromaticity; Rhodium-complexes; Hydroformylation; DFT calculations

1. Introduction

Hundreds of phosphorus containing ligands have already been tested in cobalt, rhodium- and platinum-catalysed hydroformylation reactions [1]. Both the hydroformylation of simple substrates like propene and the asymmetric hydroformylation (e.g. that of vinylaromatics resulting in α-phenylpropanals, the precursors of α-aryl-propionic acids which are of pharmacological importance) hold an enormous potential in synthesis. Due to their high practical importance, hydroformylation catalysts received particular attention. From theoretical reasons, to find an appropriate balance of chemo-, regio- and enantioselectivities (in asymmetric hydroformylation), as well as a satisfactory catalytic activity, the search for efficient hydroformylation catalysts still remains a challenge.

Although phosphines as ligands bound to various transition metals play a dominant role in the reaction concerned, phospholes have also been thoroughly investigated during the systematic structural variation of the ligands [2]. Simple monophospholes, such as

* Corresponding author. Tel.: +36-72-327622; fax: +36-72-501527.
E-mail address: kollar@ttk.pte.hu (L. Kollár).

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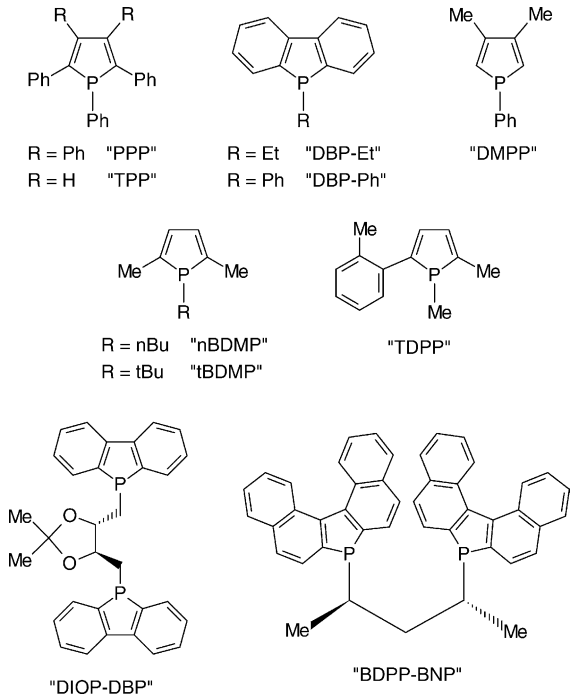


Fig. 1. Various mono- and bidentate phosphole ligands used in hydroformylation.

pentaphenyl-phosphole (PPP), 1-ethyl-dibenzophosphole (DBP-Et), 1-phenyl-dibenzophosphole (DBP-Ph) [3], 3,4-dimethyl-1-phenyl-phosphole (DMPP) [4,5], 1,2,5-triphenyl-phosphole (TPP) [6], 1-*n*-butyl-2,5-dimethylphosphole (*n*-BDMP) [4–6], 1-*tert*-butyl-2,5-dimethylphosphole (*t*-BDMP) [7], 1,2-dimethyl-5-*o*-tolylphosphole (TDPP) [8] and a diphosphole, 1,2-bis(dibenzophospholyl)ethane (DBP-$(CH_2)_2$-DBP) [9] (Fig. 1) have been used successfully as ligands in the synthesis of formyl derivatives. Rhodium as transition metal has been used almost exclusively in the in situ catalysts.

The fine tuning of the steric and electronic properties of the ligands led to the application of optically active derivatives possessing dibenzophospholyl (DBP) group as a substitute for diphenyl-phosphino group. DIOP–DBP [11–13] that holds dibenzophospholyl substituents instead of diphenyl-phosphino moieties attached to the chiral backbone of DIOP, was among the first chiral ligands that have been successfully used both in rhodium- and platinum-catalysed enantioselective hydroformylations (Fig. 1). In the past two decades both the dibenzophospholyl [10,14–19] and the binaphthophospholyl (BNP) [20] analogues of the most widely used chiral diphosphines (e.g. 2,4-bis(binaphthophospholyl)pentane, BDPP–BNP) have been synthesised and tested in homogeneous catalytic reactions (Fig. 1). Simple olefins, such as butene isomers and vinyl aromatics (styrene, 4-isobutylstyrene) have been used as substrates in hydroformylation.

All the papers published up till now describe phosphole ligands possessing either dibenzo (dinaphtho) annulation or common substituents in the phosphole ring including also substituents on the phosphorus. In the present paper, we describe the application of recently developed novel phosphole ligands in hydroformylation. Phospholes of considerably aromatic character due to the bulky 2,4,6-trialkylphenyl substituents at the phosphorus may tune both electronic and steric properties in the catalytically active complex. Therefore, structures of phospholes were also studied by density functional calculations.

2. Experimental

2.1. 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 TMS. GLC analyses were carried out with a HP-5890/II gas chromatograph using a 15 m HP-5 column (temperature program: initial temperature: 200 °C (2 min), rate: 10 °C/min, final temperature: 300 °C).

The catalytic precursor $[Rh(nbd)Cl]_2$ was prepared according to a known procedure [21]. 1-Phenyl-3,4-dimethylphosphole (**4**) was prepared as reported earlier [22] and used after distillation. The other phospholes (**1**–**3**, **5**–**11**) were synthesised as described previously [23–26]. Toluene was distilled under argon from sodium in the presence of benzophenone. Styrene was freshly distilled before use.

2.2. Hydroformylation experiments

In a typical experiment, a solution of 0.0125 mmol of $[Rh(nbd)Cl]_2$ and 0.05 mmol of monophosphole in 7.5 ml toluene containing 25 mmol of styrene was

transferred under argon 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 for the appropriate reaction time. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analysed by GC.

2.3. DFT calculations

All calculations were carried out by using Spartan program package (Spartan SGI, Version 5.1.1, Wavefunction Inc., 1998). Optimized structures at PM3 semiempirical level were used for full geometry optimization with the pBP/DN* model.

3. Results and discussion

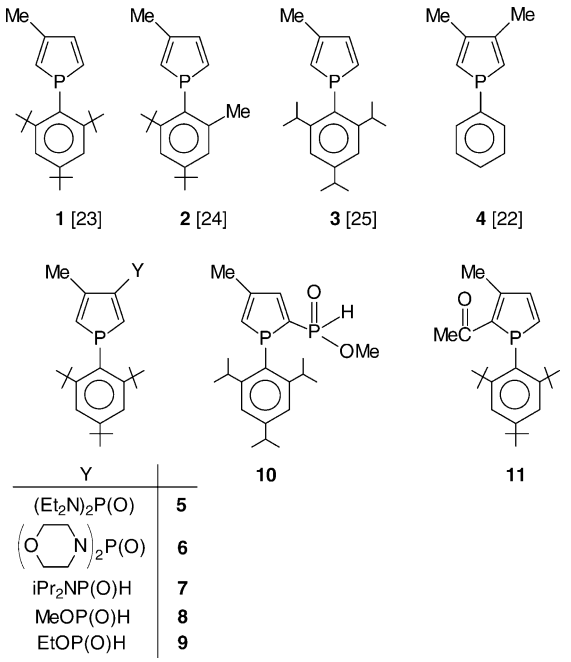
3.1. Hydroformylation in the presence of rhodium—phosphole in situ catalysts

Styrene as the model substrate was reacted in the presence of in situ rhodium catalysts containing different phospholes (**1**–**11**, Fig. 2) [22–26] with CO/H_2 (1/1) at 40 or at 100 °C at a pressure of 100 bar. The phosphole ligands applied differ thoroughly both in electronic and in steric properties and range from simple P-phenyl substituted Mathey phosphole (**4**) to sterically hindered phosphorylated trialkylphenyl-phospholes.

In addition to the formation of the two formyl regioisomers, 2-phenyl-propanal (**12**) and 3-phenyl-propanal (**13**), ethylbenzene (**14**) coming from hydrogenation was also expected (Eq. (1)):

$$\mathrm{PhCH{=}CH_2} \xrightarrow{CO/H_2} \underset{\mathbf{12}}{\mathrm{PhCH(CH_3)CHO}} + \underset{\mathbf{13}}{\mathrm{PhCH_2CH_2CHO}} + \underset{\mathbf{14}}{\mathrm{PhC_2H_5}} \quad (1)$$

All the in situ catalysts formed from $[Rh(nbd)Cl]_2$ and the above mentioned phospholes (**1**–**11**) were active under the given conditions (see Section 2). Practically, complete conversions have been obtained in most cases in up to 6 or 14 h at 100 or 40 °C, respectively (Table 1). The catalyst with ligand **4** that is the Mathey-phosphole is the only less active one providing a 61% conversion after 10 h even at 100 °C. The in situ catalysts containing ligands **3** and **5** show similarly low hydroformylation activity at 40 °C.



Y	
$(Et_2N)_2P(O)$	5
$\left(O\text{-}N\right)_2P(O)$	6
$iPr_2NP(O)H$	7
MeOP(O)H	8
EtOP(O)H	9

Fig. 2. P-arylphospholes of increased aromaticity used in the present work.

It is worth noting that the reaction can almost be considered as chemospecific towards the formation of aldehydes; the chemoselectivity of the reaction was excellent in all cases (higher than 97%, in most cases higher than 99%) by the prevailing formation of aldehydes (**13**, **14**) over ethylbenzene (**15**). All these high values fall in a narrow range, so considering also the experimental error, chemoselectivities cannot be considered for the discussion of a more detailed structure-selectivity relation.

At 40 °C high regioselectivities have been obtained by the prevailing formation of the branched aldehyde **13**. Unexpectedly, strong temperature dependence of the regioselectivity has been observed. While at 40 °C the predominance of the branched regioisomer (**13**) over the linear one (**14**) was overwhelming (>91%, in most cases above 95%), at 100 °C moderate regioselectivities (57–80%) have been obtained. Unexpectedly low, but reproducible branched to linear ratios

Table 1
Hydroformylation of styrene in the presence of $[Rh(nbd)Cl]_2 + 4$ L in situ catalysts (L = sterically hindered phosphole ligands[a]

L	Temperature (°C)	Reaction time (h)	Conversion (%)	R_C[b]	R_{br}[c]
1	100	6	99	98	66
1	40	14	67	97	91
2	100	6	99	97	51
2	40	14	81	98	86
3	100	10	97	99	81
3	40	14	31	99	95
4	100	10	61	98.5	58
4	40	14	33	99	99
5	100	6	99	99	62
5	40	14	53	99	97
6	100	6	98	99	57
6	40	14	99	99	96
7	100	6	90	99	72
7	40	14	97	99	95
8	100	2	98	99	75
8	40	14	95	99	99
9	100	2	99	99	80
9	40	14	96	99	95
10	100	2	98	99	62
10	40	14	98	99	98
11	100	2	92	98	63
11	40	14	95	97	95

[a] Reaction conditions: 0.025 mmol catalyst; Rh/*P* = 1/2; 25 mmol styrene; solvent toluene; $p(CO) = p(H_2) = 50$ bar.
[b] Chemoselectivity; (mol **13** + mol **14**)/(mol **13** + mol **14** + mol **15**) × 100.
[c] Regioselectivity; (mol **13**)/(mol **13** + mol **14**) × 100.

have been obtained with **2** as the ligand both at 40 and 100 °C (86 and 51%, respectively).

It is worthy of mention that using ligands **8**–**10**, the reaction time at 100 °C was as short as 2 h.

Although no close correlations between the catalytic activities and the ^{31}P NMR chemical shifts of the ring phosphorus (phosphole phosphorus), as well as between the regioselectivities and ^{31}P NMR chemical shifts have been obtained, some tendencies could still be observed.

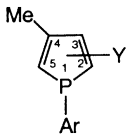
It can be clearly seen (especially at 40 °C) that the arylphospholes with positive ^{31}P NMR chemical shift of the ring phosphorus have higher catalytic activities. (Substituted phospholes **6**–**10** with δ_P of 3.1, 8.0, 11.3, 10.3 and 2.9, respectively, fall in this category.) At 40 °C, in up to 14 h nearly complete conversions have been obtained for the phospholes possessing positive δ_P values. The use of phospholes with negative chemical shifts (such as **3**, **4** and **5** with δ_P of −8.6, −2.5 and −1.8, respectively) resulted in 31–53% conversions in the same reaction time. The catalyst prepared from phosphole **1** with slightly negative chemical shift showed a medium catalytic activity.

3.2. Density functional theory calculations concerning the aromatic character of arylphospholes

Recent structural studies on phospholes have concluded that the aromatic character of these species may be significantly increased by the presence of a sterically demanding P-substituent [23–25]. The conjugation of the lone pair with the π-system may be increased due to flattening the tricoordinate phosphorous atom. Following this line of investigation, we also wished to study the structures of arylphospholes **1**, **3**, **5**, **7**–**10**. The geometry was optimized by the DFT method with LSDA/pBP86/DN* model [27]. In the previous study, it was found that the geometry of various heterocyclic compounds including phospholes could be obtained with high accuracy at this or comparable levels of the theory [28]. The Bird-index of aromaticity (BI), which is widely used for the characterization of aromaticity of heterocyclic compounds, was calculated from the equalization of bond lengths using the standard formula [29]. The out of plane (OOP) angle around the phosphorous (defined as the angle of the P–$C_{1'}$ bond with the C_2–P–C_5 plane) was also determined (Table 2). As expected, the BI seems to be in correlation with the OOP angle; compounds with smaller OOP angles are more aromatic (i.e. they possess a higher BI).

The phospholes with the highest aromaticity, possessing typically a bulky P-substitutent, have Bird-indices close to 50 or even higher [23,24]. The Bird-indices of trialkylphenyl-phospholes in the present series fall also in the range of 45–53. The steric bulk of the P-substituent plays the primary role in the aromaticity of phospholes, whereas other ring substituents are of less importance in this respect. In fact, the BI of the phosphole with tri(*tert*-butyl)phenyl substituent on the phosphorous (**1**) (48.3), is somewhat higher than that of the triisopropyl analogue **2** (47.8), although, their difference is smaller than that calculated from the X-ray data [23,24]. The introduction of a substituent into position 3 or 2 of the ring can also modify the aromaticity. The Bird-indices of

Table 2
^{31}P NMR and calculated data of arylphospholes **1**, **3**, **5**, **7**–**10**

	δ (^{31}P) $CDCl_3$	BI DFT (X-ray)	OOP angle (°)					
				Geometry (Å) DFT (X-ray)				
				P–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–P
1	−0.4	48.3 (54.9 [26])	46.5	1.779 (1.741)	1.378 (1.352)	1.452 (1.402)	1.380 (1.347)	1.786 (1.746)
3	−8.6	49.5 (40.4 [25])	47.8	1.783 (1.779)	1.379 (1.366)	1.450 (1.436)	1.379 (1.340)	1.777 (1.782)
5	−1.8	49.8	47.5	1.779	1.382	1.468	1.377	1.775
7	8.0	53.1	44.5	1.774	1.385	1.464	1.379	1.771
8	11.3	52.5	43.9	1.770	1.389	1.463	1.382	1.781
9	10.7	53.2	43.7	1.770	1.390	1.464	1.382	1.781
10	2.9	45.3	55.0	1.805	1.388	1.447	1.382	1.782

compounds **7** and **9** with their significantly higher values (>50) than that of the structurally related compound **8** (46.3) suggest that the introduction of a substituent into position 3 can affect the conjugation of the lone pair of phosphorous with the π-system of the ring. For the time being, arylphospholes **7** and **9** seem to be of the highest aromaticity of this family, with BI of 53.1 and 53.2, respectively.

In general, bond lengths are well reproduced at this level of theory (errors are less than 0.02 Å [28,30], accordingly, errors in the Bird-indices are less than ca. ±5–10%).

Taking the results of the hydroformylation experiments and the calculations into consideration, it might be concluded that aromatic trialkylphenyl-phospholes can be useful ligands in catalytic hydroformylation reactions. A substituent with a tetracoordinate phosphorous at position 2 or 3 may increase the catalytic activity; this effect may, however, be related only partly to the effect of the substituent on the aromaticity.

It is further a challenge for us to evaluate how other exocyclic P-functions, such as the phosphine oxido- or phosphine functions affect the extent of aromaticity and the catalytic activity of trialkyphenyl-phospholes.

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