ELSEVIER

Journal of Molecular Catalysis A: Chemical 98 (1995) 117–122

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Surface active phosphines for catalysis under two-phase reaction conditions. P(menthyl)[$(CH_2)_8C_6H_4$-*p*-SO_3Na]$_2$ and the hydroformylation of styrene

Tamás Bartik [1], Hao Ding, Berit Bartik [2], Brian E. Hanson *

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA

Received 30 May 1994; accepted 16 January 1995

Abstract

The novel optically active phosphine, bis(8-phenyloctyl)(Menth)phosphine, (Menth = 1*R*,3*R*,4*S*(−)menthyl) is synthesized and sulfonated under mild conditions to yield the corresponding sulfonated phosphine, disodium bis-(8-(*para*-sulfonatophenyl)octyl)(Menth)phosphine. The water soluble phosphine is used to generate an aqueous–methanol rhodium catalyst for the hydroformylation of styrene. The catalyst shows high catalytic activity, but virtually no optical induction. Normal to branch ratios for the hydroformylation of styrene are in the range 0.35 to 0.5. The catalytic data with TPPTS is given for comparison. TPPTS yields catalysts that are less active under two phase reaction conditions and slightly less selective for formation of 2-phenylpropanal.

A great deal of research interest has recently focused on the development of water soluble transition metal complexes as catalysts for the hydrogenation and hydroformylation of olefins [1–9]. In addition to the environmental benefits of water based processes, the ease of catalyst separation from water immiscible products provided by these complexes may reduce the cost of commercial homogeneous catalytic processes. With water soluble catalysts there is evidence that reaction occurs in the aqueous phase [4,9]. For this reason the application of water soluble hydroformylation catalysts has been limited to propylene, which has sufficient water solubility to provide good reaction rates [2]; reaction rates are low in a two phase system with higher olefins as the substrate.

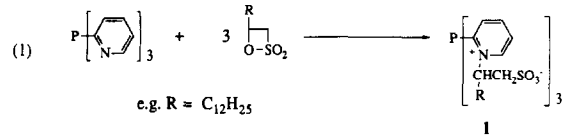
Several approaches have been taken to increase the reaction rate of a higher olefin with a water soluble hydroformylation catalyst. For example, in those catalysts that contain TPPTS, trisodium salt of trisulfonated triphenylphosphine, the sodium ion may be replaced by a quaternary ammonium cation [10]. This allows the catalysis to be done in a homogeneous reaction environment in a polar solvent such as an alcohol. Surfactants have been added to two phase reaction mixtures in order to increase reaction rates [11]. Another approach involves the immobilization of water soluble catalysts in a supported aqueous phase on a high surface area hydrophilic solid [12]. These supported aqueous phase catalysts have proven very effective for the application of

* Corresponding author.

[1] Research Group for Petrolchemistry of the Hungarian Academy of Sciences (Veszprém)

[2] FRG Research Fellow (Deutsche Forschungsgemeinschaft – Bonn) 1991–1993

SSDI 1381-1169(95)00012-7



Scheme 1.

water soluble catalysts to the hydroformylation of higher olefins.

Another modification that retains the two immiscible phases reaction format involves the use of surface active phosphines [13,14]. Although the mode of action in these systems is not known at this time, it is clear that significant rate enhancements can be observed. For example, the tripyridylphosphine has been modified as shown in Eq. 1 to yield a sulfonated surface active phosphine, **1** [13] (Scheme 1). Rhodium complexes of **1** in the presence of excess phosphine are thought to form micelles.

Recently we reported the aqueous phase hydroformylation of octene-1 with rhodium complexes of trisulfonated tris(ω-phenylalkyl)phosphines [14]. The results show an increase in reaction rate as the alkyl chain length, and hence the surface activity, increases.

Asymmetric hydroformylation is of importance due to the potential for the enantioselective preparation of compounds of pharmaceutical interest [15–19]. In this regard there has been some notable success with rhodium complexes of chelating chiral phosphites [18,19]. Here we report the preparation of a surface active monodentate phosphine that bears a chiral menthyl moiety, and its use in the hydroformylation of styrene. The catalytic results are reported in aqueous methanol which is immiscible with styrene and the phenylpropanal hydroformylation products.

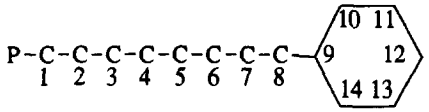
1. Experimental section

All reactions and analyses were carried out under an argon atmosphere by standard Schlenk techniques. All solvents used in experiments were freshly distilled under N_2 to remove oxygen. All chemicals were purchased from Aldrich and used without further purification.

The high pressure hydroformylation reactions were performed in 30 ml stainless steel reaction vessels equipped with high pressure gauges. The temperature of the catalytic reactions was controlled by an Omega CN 2000 temperature process controller and a silicon oil bath; n/b ratios and yields of the reactions were determined by gas chromatography on a Varian 3300 chromatograph equipped with an HP 1 column (25 m×0.32 mm×0.52 μm) and FID detector; the carrier gas was helium.

The enantiomeric excess (ee/%) of 2-phenylpropanal was determined by optical rotation by comparison with the reported rotation of 2-phenylpropanal [20].

Abbreviations:
Menth = 1*R*,3*R*,4*S*(−)menthyl. IR data; vs, very strong; w, weak; NMR; s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; carbon numbering scheme:



Preparation of 1-*Bromo*-8-*phenyl octane* (**2**). 1,8-Dibromooctane, 200 g (0.73 mol), and 200 ml of diethyl ether were placed into a three-neck flask equipped with reflux condenser and equal-pressure dropping funnel. After the addition of 200 ml of 1.8 M PhLi in cyclohexane the reaction was heated at reflux for 24 h. Lithium bromide was removed by filtration and the solvent removed by distillation. The resulting oil was vacuum distilled, and the fractions were checked by GC. The fraction collected at 160–165°C and 3 Torr contained $C_6H_5(CH_2)_8Br$; yield, 22 g (23% based on PhLi). Colorless oil, bp (3 Torr): 160–165°C. η_D^{20}: 1.5220. ^{1}H NMR δ ($CDCl_3$): 1.21–1.49 (m, 8H, C(3)H_2–C(6)H_2), 1.6 (quin, J_{HH}=6.6 Hz, 2H, C(7)H_2), 1.82 (quin, J_{HH}=7.4 Hz, 2H, C(2)H_2), 2.59 (t, J_{HH}=7.4 Hz, 2H, C(8)H_2), 3.37 (t, J_{HH}=6.6 Hz, 2H, C(1)H_2), 7.03–7.40 (m, 5H, C_6H_5). ^{13}C NMR δ ($CDCl_3$): 28.23 (s, *C*(4)H_2), 28.77 (s, *C*(5)H_2), 29.28 (s, *C*(3)H_2),

29.35 (s, $C(6)H_2$), 31.50 (s, $C(7)H_2$), 32.90 (s, $C(2)H_2$), 33.94 (s, $C(1)H_2$), 36.01 (s, $C(8)H_2C_6H_5$), 125.64 (s, $C(12)H(C_6H_5)$), 128.30 (s, $C(11)H+C(13)H(C_6H_5)$), 128.43 (s, $C(10)H+C(14)H(C_6H_5)$), 142.60 (s, $C(8)H_2C(9)(C_6H_5)$). MS m/z: $(M-H^+)=268$.

Synthesis of bis(8-phenyloctyl)menthyl phosphine (***3a***). Bis(8-phenyloctyl)menthyl phosphine was prepared from the reaction of $C_6H_5(CH_2)_8MgBr$ and $(Menth)PCl_2$ in ether [21]. After fractional crystallization from pentane at −80°C, the pure product is obtained as a colorless oil in 45% yield upon warming to room temperature. Colorless oil, d (g/ml): 1.095. $[\alpha]_D^{25}$ (CH_2Cl_2): −52.2°. ^{1}H NMR δ ($CDCl_3$): 0.65–1.72 (m, 47H, $2\times(C(1)H_2$–$C(7)H_2)+C_{10}H_{19}$(Menth)), 2.49 (t, $J_{HH}=8.1$ Hz, 4H, $C(8)H_2$), 7.15–7.22 (m, 10H, $2\times C_6H_5$). ^{13}C NMR δ ($CDCl_3$): 11.02 (s, CH_3CH(Menth)), 14.17, 15.25 (s, $(CH_3)_2CH$(Menth)), 26.72 (s br, $C(1)H_2P$), 27.51 (s br, $C(2)H_2C(1)H_2P$), 29.39 (m, $C(3)H_2$–$C(6)H_2$), 31.57 (s, $C(7)H_2$), 36.08 (s, $C(8)H_2C_6H_5$), 45.07 (d, $J_{PCP}=9.1$ Hz, CHP(Menth)), 125.63 (s, $C(12)H(C_6H_5)$), 128.30 (s, $C(11+13)H(C_6H_5)$), 128.42 (s, $C(10+14)H(C_6H_5)$), 142.91 (s, $C(8)H_2C(9)(C_6H_5)$). ^{31}P NMR δ ($CDCl_3$): −31.51 (s).

Synthesis of p,p-disulfonated bis(8-phenyloctyl)menthylphosphine (***3b***). The sulfonation of bis(8-phenyloctyl)menthyl phosphine (**3a**) was carried out in concentrated H_2SO_4. Typically 5 g (8.5 mmol) of **3a** was dissolved in portion in 20 ml of concentrated H_2SO_4 at room temperature. The sulfonation was complete after 2 h as determined by ^{1}H and ^{31}P NMR and was quenched by the slow addition of 20% NaOH at 0°C. The volume of the reaction solution was reduced to ca. 30 ml and then 300 ml of methanol was added and the mixture brought to reflux. After filtration the solid was further extracted with 200 ml of 10:1 hot methanol/water. The extracts were combined and reduced in volume to 50 ml. Addition of 250 ml of acetone yielded *p,p*-disulfonated bis(8-phenyloctyl)menthyl phosphine in ca. 90% purity. Further purification was achieved by recrystallization from ethanol. The yield of **3b** was 65% based on $(Menth)P[(CH_2)_8C_6H_5]_2$. White crystals, mp > 300°C. $[\alpha]_D^{25}$ (CH_3OH): −31.5. ^{1}H NMR δ (D_2O): 0.81–2.95 (m br, 51H, $2\times(CH_2)_8$+Menth), 6.91–7.15, 7.58–7.72 (m, 8H, $2\times C_6H_4$). ^{31}P NMR δ (D_2O): −31.60 (s). MS FAB (glycerol matrix) m/z: $(M+H)^+=753$; 731, 689, 651, 315, 205, 137, 115. (The FAB mass spectra show the molecular ion plus a proton. The fragmentation processes give peaks at $(+Na^+-H^+)$, $(-Na^++H^+)$, and $(-SO_3Na+H^+)$. The cleavage of the menthyl group results in a (menthene $-H^+$) fragment (137)).

Preparation of trans-L_2PdCl_2 ($L=(Menth)P[(CH_2)_8C_6H_5]_2$) (***4***). The bis(phosphine)–palladium complexes of the nonsulfonated ligands were prepared in chloroform at room temperature from $(PhCN)_2PdCl_2$ by literature procedures [22,23]. The purpose of the preparation of this compound was to estimate the steric size of the phosphine. The compound was isolated as an oil and thus was not subjected to analysis beyond recording its ^{31}P NMR spectrum. Only one signal was observed consistent with formation of the *trans* complex. ^{31}P NMR δ ($CDCl_3$): 14.18 (s).

Synthesis of $L_yNi(CO)_{4-y}$ ($L=(Menth)P[(CH_2)_8C_6H_5]_2$, $y=1$, 2) (***5a***, ***5b***). The complexes $LNi(CO)_3$ and $L_2Ni(CO)_2$ were prepared from the nonsulfonated ligand in CH_2Cl_2 following literature procedures [23–25]. The complexes were characterized by their infrared spectra in the carbonyl region and by ^{31}P NMR spectroscopy. Both of the nickel complexes **5a** and **5b** were isolated as oils; the compounds, **5a** and **5b** could be isolated free from one another, as judged by ^{31}P NMR spectroscopy, but not free of solvent. The purpose of preparation of **5a** was to estimate the Tolman electronic parameter by infrared spectroscopy. The purity of the complex was judged to be sufficient for this purpose.

$(Menth)P[(CH_2)_8C_6H_5]_2Ni(CO)_3$ (**5a**). IR (cm^{-1}, CH_2Cl_2) ν(CO): 2059.57 (w), 1980.47 (vs). ^{31}P NMR δ (CD_2Cl_2): 21.57 (s).

$\{(Menth)P(CH_2)_8C_6H_5]_2\}_2Ni(CO)_2$ (**5b**). IR (cm^{-1}, CH_2Cl_2) ν(CO): 1981.41 (vs), 1913.19 (bs). ^{31}P NMR δ (CD_2Cl_2): 21.03 (s).

Catalytic reactions. The following stock solutions were prepared for the catalytic hydroformylation reactions: Rh(acac)$(CO)_2$, 0.01 M in methanol, $(Menth)P[(CH_2)_8C_6H_4$-*p*-$SO_3Na]_2$, 0.05 M in H_2O; and TPPTS, 0.05 M in H_2O. The appropriate components of the reaction were combined at room temperature in a 30 ml stainless steel vessel under CO; nonane, 0.30 ml was added as an internal standard for GC analysis; H_2O an toluene were added to adjust both water and organic phases to 2 ml and a total volume of 4 ml. The vessel was then closed, pressurized with CO:H_2 (1:1) to 200 psig and placed in a silicon oil bath which had been set at reaction temperature (120°C). In all reactions, the stirring rate was kept at same value, 260 rpm. After the appropriate reaction time the vessel was removed from the bath, cooled to room temperature and depressurized. The organic phase, which was colorless, was taken for analysis. The organic phase, when reintroduced to the reactor, showed no activity for the hydroformylation of 1-octene indicating that the ligand system is fairly efficient at keeping the rhodium in aqueous–methanol.

2. Results

*Electronic and steric character of **3a**.* The electronic and steric character of **3a** was evaluated experimentally as described previously [23]. It is known, that the ν(CO) A_1 stretching frequency of $PR_3Ni(CO)_3$ complexes correlates with the electronic character of the phosphorus ligands [25]. Tolman defined the electronic parameter χ for PR_3 as:

$$\chi_{PR_3} = \nu(CO)A_1PR_3Ni(CO)_3 - \nu(CO)A_1(P(tBu)_3Ni(CO)_3$$

where the stretching frequencies are measured in CH_2Cl_2 [24,25]. We determined the electronic parameter of **3a** to be 3.47. Thus the new (Menth)$P[(CH_2)_8C_6H_5]_2$ phosphine has a basicity similar to that of tri-isopropyl phosphine ($\chi_{P(iPr)_3} = 3.45$).

The steric parameter, θ_{TOL} was determined spectroscopically by the ^{31}P NMR chemical shift correlation method described by Bartik and Himmler for the compounds, *trans*-L_2PdCl_2 [26]. In this manner the Tolman cone angle for **3a** was found to be 138°.

A comparison of the electronic (χ) and steric θ_{TOL} parameters for the series $P[(CH_2)_xC_6H_5]_3$ and $P[(CH_2)_x\ C_6H_4$-*p*-$SO_3Na]_3$ $x = 1, 2, 3, 6$ shows that the sulfonated and nonsulfonated phosphines that contain three or more methylene groups are nearly identical with respect to χ and θ_{TOL}. Therefore the χ and θ_{TOL} were determined for the nonsulfonated phosphine, **3a**, only.

Styrene hydroformylation. The time dependence for the styrene hydroformylation by Rh(acac)$(CO)_2$ and $(Menth)P[(CH_2)_8C_6H_4$-*p*-$SO_3Na]_2$ as the in situ catalyst is presented in Fig. 1a. In these reactions the ligand to rhodium ratio is 3:1. Good catalytic activity is observed. For comparison, similar catalytic data for the hydroformylation of styrene with TPPTS at the same ligand to rhodium ratio is shown as Fig. 1b. Reaction rates with TPPTS are clearly lower than that obtained with the surface active phosphine, **3b**. With both ligands, the normal to branch ratio drops slightly as styrene conversion increases.

The activity of the catalysts is presented as a function of ligand/Rh in Fig. 2 for both **2** and TPPTS. These data were generated a constant reaction time, 2 h for $(Menth)P[(CH_2)_8C_6H_4$-*p*-$SO_3Na]_2$ and 8 h for TPPTS. When L = TPPTS, yield of aldehyde reaches its maximum value at L/Rh = 3 and drops slightly as a function of L/Rh thereafter. $(Menthyl)P[(CH_2)_8C_6H_4SO_3Na]_2$ shows a different trend in conversion as a function of ligand concentration. The maximum yield of aldehydes, about 90%, is achieved at a L/Rh ratio of approximately two. The yield drops to about 50% at L/Rh of 5 and remains virtually unchanged throughout the remaining course of L/Rh variation.

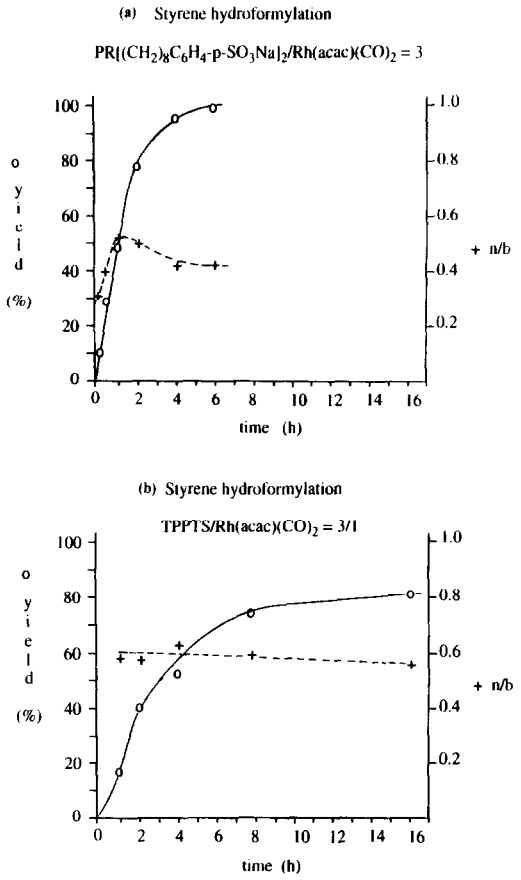


Fig. 1. (a) Yield of aldehydes and n/b ratio as a function of time in the two phase hydroformylation of styrene with $Rh(acac)(CO)_2$ and **3b** at a P/Rh ratio of 3. Styrene/Rh = 500; 120°C, 14 atm $CO:H_2$, 1:1. (b) Yield of aldehydes and n/b ratio as a function of time in the two phase hydroformylation of styrene with $Rh(acac)(CO)_2$ and TPPTS at a P/Rh ratio of 3. Styrene/Rh = 500; 120°C, 14 atm $CO:H_2$, 1:1.

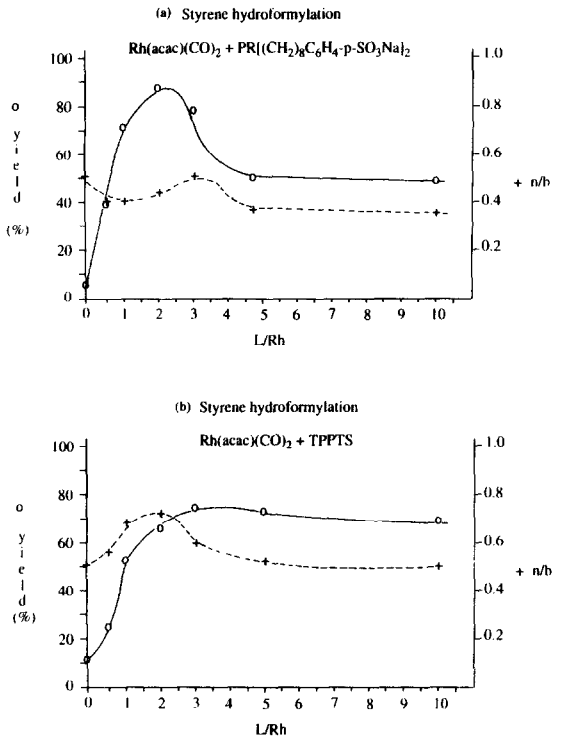


Fig. 2. a. Yield of aldehydes and n/b ratio as a function of ligand to rhodium ratio at a constant reaction time of 2 h with catalysts derived from $Rh(acac)(CO)_2$ and **3b**. Styrene/Rh = 500; 120°C, 14 atm $CO:H_2$, 1:1. (b) Yield of aldehydes and n/b ratio as a function of ligand to rhodium ratio at a constant reaction time of 8 h with catalysts derived from $Rh(acac)(CO)_2$ and TPPTS. Styrene/Rh = 500; 120°C, 14 atm $CO:H_2$, 1:1.

Reaction selectivity is indicated in Figs. 1 and 2 only as the n/b ratio. The possibility exists with the menthyl phosphine, **3b**, that optical induction in the formation of 2-phenylpropanal may lead to the preferential formation of one enantiomer. Thus the optical purity of the products was investigated. Unfortunately no significant enantiomeric excess was observed by optical rotation in any of the reactions with **3b** as the ligand.

3. Discussion

The initial turnover frequencies, as estimated from the initial slopes in Figs. 1a and 1b, are 245 mol aldehyde $(mol^{-1}\ Rh)\ h^{-1}$ and 100 mol aldehyde $(mol^{-1}\ Rh)\ h^{-1}$ for ligand **2** and TPPTS respectively at a L/Rh ratio of 3. While a difference in rate may be expected between a trialkylphosphine and a triarylphosphine for the rhodium catalyzed hydroformylation of olefins it can be argued that the higher rate is expected for the latter [21]. In the comparison above, the more surface active phosphine, **3b**, shows the higher rate, in spite of the fact that it is a trialkylphosphine.

The mechanism for the increase in rate is not clear at this time. It was argued that those sulfonated tripyridyl phosphines with a long alkyl chain, **1**, form micelles and thus show increased reaction rates over their nonsulfonated analogs [14]. In addition to increased reaction rates evidence for micelle formation was argued based on the increased solubility of water insoluble compounds in the reaction medium. When the aque-

ous/nonaqueous mixtures form stable emulsions the reaction rates decreased dramatically [14]. In the example presented here after reaction the nonaqueous and aqueous phases rapidly separate and the color associated with rhodium complex formation is exclusively in the aqueous phase. No evidence for the formation of an emulsion was observed. In favor of some degree of phosphine aggregation in the aqueous phase for **3b** is the fact that the water insoluble dye Orange–OT dissolves in dilute aqueous solutions of **3b** [27]. Studies are in progress to measure directly the degree of aggregation of this phosphine and related surface active phosphines in aqueous solution.

Although the phosphine is chiral no optical induction is observed in 2-phenylpropanal. This is not surprising in that monodentate chiral phosphines generally perform poorly in asymmetric hydroformylation [28].

Acknowledgements

We thank NSF (CTS-9101846) for support of this work. Berit Bartik gratefully acknowledges a fellowship from the Deutsche Forschungsgemeinschaft (1991–93).

References

[1] W.A. Herrmann and C.W. Kohlpaintner, Angew. Chem., Int. Ed. Engl., 32 (1993) 1524.
[2] E.G. Kuntz, CHEMTECH, 17 (1987) 570.
[3] A. Bényei and F. Joó, J. Mol. Catal., 58 (1990) 151.
[4] A.F. Borowski, D.J. Cole-Hamilton and G. Wilkinson, Nouv, J. Chem., 2 (1978) 137.
[5] P. Kalck, P. Escaffre, F. Serein-Spirau, A. Thorez, B. Besson, Y. Colleuille and R Perron, New J. Chem., 12 (1988) 687.
[6] A. Abatjoglou, US Pat. 5,196,596 (1993).
[7] M.K. Markiewicz and M.C. Baird, Inorg. Chim. Acta, 113 (1986) 95.
[8] C. Larpent, F. Brise-Le Menn and H. Patin, New J. Chem., 15 (1991) 361.
[9] I.T. Horváth, Catal. Lett., 6 (1990) 43.
[10] E. Kuntz, US Pat. 4,248,802 (1981).
[11] Y. Dror and J. Manassen J. Mol. Catal., 2 (1977) 219
[12] (a) J. P Arhancet, M.E. Davis and B.E. Hanson, J. Catal., 129 (1991) 94; (b) J. P Arhancet, M.E. Davis and B.E. Hanson, J. Catal., 129 (1991) 100.
[13] B. Fell and G. Pagadogianakis, J. Mol. Catal., 66 (1991) 143.
[14] T. Bartik, B. Bartik and B.E. Hanson, J. Mol Catal., 88 (1994) 43.
[15] I. Tóth, B.E. Hanson and I. Guo, Organometallics, 12 (1993) 848–852.
[16] G. Parrinello and J.K. Stille, J. Am. Chem. Soc., 109 (1987) 7122.
[17] L. Kollár, J. Bakos, I Tóth and B. Heil, J. Organomet. Chem., 370 (1989) 257.
[18] J.E. Babin and G.T. Whiteker, World Pat. WO93/03839, (1993)
[19] G.D. Cuny and S.L. Buchwald, J. Am. Chem. Soc., (1993) 114 2066.
[20] G. Consiglio, P. Pino, L. Flowers and C.K. Pittman, J. Chem. Soc., Chem. Commun., (1983) 612.
[21] G.M. Kosolapoff and L. Maier, Organic Phosphorus Compounds, Vol. 1, Wiley-Interscience, New York, 1972.
[22] T. Hayashi, M. Konishi and M. Kumada, Tetrahedron Lett., (1979) 1871.
[23] T. Bartik, B. Bartik, B.E. Hanson, I. Guo and I. Toth, Organometallics, 12 (1993) 164.
[24] W. Strohmeir and F.J. Muller, Chem. Ber., 100 (1967) 2812.
[25] C.A. Tolman, Chem. Rev., 77 (1977) 313.
[26] T. Bartik and T. Himmler, J. Organomet. Chem., 293 (1985) 343.
[27] A.W. Adamson, Physical Chemistry of Surfaces, 5th Ed., Wiley Interscience, p. 509.
[28] H.B. Kagan, in G. Wilkinson, F.G.A. Stone and E.W. Abel, (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, London, 1980, Chap. 53.