

Catalytic Hydrophosphination of Styrenes

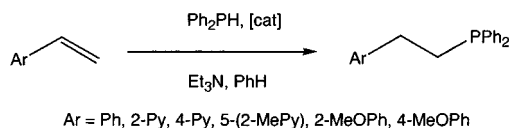
Mstislav O. Shulyupin, Marina A. Kazankova, and Irina P. Beletskaya*

Department of Chemistry, Moscow State University, Leninskie Gory,
GSP-3 Moscow, Russian Federation

beletska@org.chem.msu.ru

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ABSTRACT



The first example of intermolecular hydrophosphination of styrenes catalyzed by Ni and Pd complexes is described. The reaction of Ph_2PH with styrene, 4-vinylpyridine, 2-vinylpyridine, 4-methoxystyrene, 2-methoxystyrene, and 5-vinyl-2-methylpyridine in benzene under $\text{Ni}[\text{P}(\text{OEt})_3]_4$ catalysis proceeds with high yield and selectivity to give only anti-Markovnikov product.

Tertiary phosphines are an important class of organic compounds widely employed both as ligands for transition metals complexes and in various catalytic processes.¹ Though in common applications triarylphosphines are usually used, the more electron-rich alkyldiarylphosphines may bring special advantages in more demanding cases.^{2,3} The ligands Ph_2PAlk are obtained by coupling $\text{Ph}_2\text{P}^+\text{Hal}^-$ with organolithium or magnesium compounds or by the reaction between phosphide anion and an alkylhalide.⁴ However, from the point of view of “green chemistry” and the “atom efficiency” principle, the cleanest route toward such phosphines is the

addition of P–H reagents to olefins. This reaction can be carried out in the presence of radical initiators, in the acid- or base-catalyzed process,⁵ or in the presence of transition metal catalysts and lanthanides.⁶

Here, we report the first example of the addition of secondary phosphine across the double bond of aryl (heteroaryl)ethenes catalyzed by Ni and Pd complexes. Recently, it was shown that diphenylphosphine addition across an unactivated triple bond is catalyzed by these complexes.⁷

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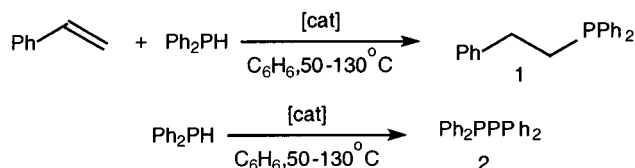
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We screened numerous readily available nickel and palladium complexes (NiCl_2 , NiBr_2 , $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$, $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$, $\text{Ni}(\text{acac})_2$, $\text{Ni}(\text{cod})_2$, $\text{Ni}[\text{P}(\text{OEt})_3]_4$, $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$) and found that Ni(II) complexes catalyze the oxidative dimerization of Ph_2PH to form tetraphenyldiphosphine, whereas with the Ni(0) complexes the reaction of hydrophosphination of styrene takes place.

Scheme 1



The catalytic system has a dramatic influence on the structure of the products of the reaction. The use of $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ results in a fast oxidative reaction (Table 1,

Table 1. Hydrophosphination of Styrene Catalyzed by Pd and Ni Complexes in Benzene^a

entry	catalyst, 5%	temp °C/h	conversion ^b	ratio of 1:2 (%) ^b	
				1	2
1	$\text{Ni}(\text{PPh}_3)_2\text{Br}_2$	50/5	100	0	100
2	$\text{Ni}(\text{PPh}_3)_2\text{Br}_2$	130/28	100 ^c	50	50
3	$\text{Ni}[\text{P}(\text{OEt})_3]_4$	90/40	85	95	5
4	$\text{Ni}[\text{P}(\text{OEt})_3]_4$	130/40	95	90	10
5	$\text{Ni}[\text{P}(\text{OEt})_3]_4$	130/40	95 ^c	100	0
6	$\text{Ni}[\text{P}(\text{OEt})_3]_4$	130/20	100 ^{c,d}	100	0
7	$\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$	90/40	75	100	0

^a Reaction conditions: styrene 1.5 mmol, Ph_2PH 1.5 mmol, catalyst 5% mol, benzene 2 mL, sealed tube. ^b Based on ^{31}P and ^1H NMR. ^c One equivalent of Et_3N was added. ^d Two equivalents of styrene was used.

entry 1) leading to tetraphenyldiphosphine.⁸ We suppose that diphenylphosphine is oxidized by Ni(II) to form Ph_2PPPh_2 and HBr . The latter carries on the catalytic cycle, reacting with Ni(0) to regenerate Ni(II) again. That is why the addition of Et_3N to neutralize HBr suppresses the oxidation of phosphine (Table 1, entry 2). When the Ni(0) complex was used instead of Ni(II) complex, only small amounts of Ph_2PPPh_2 were formed (Table 1, entry 3), but when the temperature was raised, the amount of Ph_2PPPh_2 increased (Table 1, entry 4). The addition of Et_3N completely suppressed the side reaction (Table 1, entry 5). The acceleration of the addition reaction was observed when an excess of styrene was added

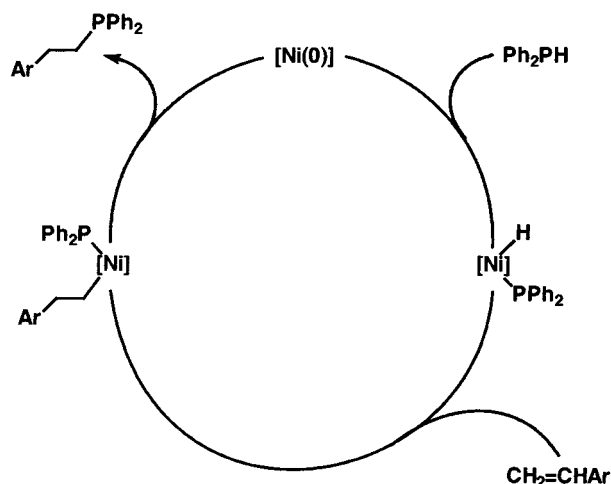
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(Table 1, entry 6). Thus we have found that heating a mixture of 2 equiv of styrene, 1 equiv of diphenylphosphine, and 1 equiv of Et_3N with 5 mol % tetrakis(triethyl phosphite)nickel in benzene in a sealed tube at 130 °C for 20 h provided the desired $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Ph}$ in quantitative yield.

A possible mechanism of hydrophosphination is presented in Scheme 2. To test the scope of the reaction several styrenes were employed under optimal conditions (Table 2).

Scheme 2



So we have designed a new catalytic system for the hydrophosphination of styrenes.¹¹

Table 2. Hydrophosphination of $\text{ArCH}=\text{CH}_2$ with Ph_2PH Catalyzed by $\text{Ni}[\text{P}(\text{OEt})_3]_4$ ^a

Entry	Ar	Adduct	Yield, % ^b
1	Ph		>99 ⁹
2	4-MeOPh		>99
3	2-MeOPh		>99
4	4-Py		>99
5	5-(2-MePy)		>95
6	2-Py		>99 ¹⁰

^a Reaction conditions: 5 mol % $\text{Ni}[\text{P}(\text{OEt})_3]_4$, benzene, 2 equiv of styrene, 1 equiv of Et_3N 130 °C, 20 h. ^b Based on ^{31}P NMR.

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(11) **General Procedure.** A mixture of 1.5 mmol of Ph₂PH, 3 mmol of alkene, 1.5 mmol of Et₃N, and 5 mol % of Ni[P(OEt)₃]₄ in 2 mL of the benzene was placed in an NMR tube and sealed. The tube was heated in an oil bath at 130 °C, and the reaction was followed using ³¹P NMR measurements. After completion of the reaction (disappearance of the signal of Ph₂PH at δ_p -40.6 ppm) the solvents were evaporated in a vacuum. The residue was recrystallized from a hexane/THF mixture and purified by column chromatography (hexane/benzene 3:1). Diphenyl(2-phenylethyl)-phosphine (**1**): ¹H NMR (400 MHz, C₆D₆) 2.31–2.36 (m, 2H), 2.74–2.80 (m, 2H), 7.06–7.21 (m, 11H), 7.48–7.52 (m, 4H); ³¹P{H} NMR (162.6 MHz, C₆D₆) -16.1 (s). [2-(4-Methoxyphenyl)ethyl](diphenyl)phosphine (**3**): ¹H NMR (400 MHz, C₆D₆) 2.33–2.37 (m, 2H), 2.74–2.80 (m, 2H),

Supporting Information Available: Experimental procedures and compound characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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3.43 (s, 3H), 6.79–6.86 (m, 4H), 7.15–7.21 (m, 6H), 7.50–7.54 (m, 4H); ³¹P{H} NMR (162.6 MHz, C₆D₆) -16.3 (s). [2-(2-Methoxyphenyl)ethyl]-(diphenyl)phosphine (**4**): ¹H NMR (400 MHz, C₆D₆) 2.45–2.49 (m, 2H), 2.97–3.03 (m, 2H), 3.36 (s, 3H), 6.61 (d, 1H), 6.91 (t, 1H), 7.08–7.20 (m, 8H), 7.54–7.58 (m, 4H); ³¹P{H} NMR (162.6 MHz, C₆D₆) -15.6 (s). 4-[2-(Diphenylphosphino)ethyl]pyridine (**5**): ¹H NMR (400 MHz, C₆D₆) 2.65–2.69 (m, 2H), 2.99–3.05 (m, 2H), 6.69–6.71 (m, 2H), 7.09–7.18 (m, 6H), 7.53–7.57 (m, 4H), 8.56–8.58 (m, 2H); ³¹P{H} NMR (162.6 MHz, C₆D₆) -16.1 (s). 5-[2-(Diphenylphosphino)ethyl]-2-methylpyridine (**6**): NMR (400 MHz, C₆D₆) 2.27–2.31 (m, 2H), 2.46 (s, 3H), 2.60–2.67 (m, 2H), 6.97–7.01 (m, 2H), 7.25–7.35 (m, 6H), 7.39–7.45 (m, 4H), 8.27 (s, 1H); ³¹P{H} NMR (162.6 MHz, C₆D₆) -16.5 (s). 2-[2-(Diphenylphosphino)ethyl]-pyridine (**7**): ¹H NMR (400 MHz, C₆D₆) 2.65–2.69 (m, 2H), 2.99–3.05 (m, 2H), 6.68–6.71 (m, 2H), 7.06–7.14 (m, 7H), 7.53–7.57 (m, 4H), 8.56–8.58 (m, 1H); ³¹P{H} NMR (162.6 MHz, C₆D₆) -15.8 (s).