2.56 (m, 8H), 0.76–1.16 (m, 24H); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 21.92$, 24.51, 30.07, 30.47, 32.93, 45.52, 126.02, 127.46, 127.91, 127.99, 128.94, 129.75, 130.67, 133.01, 137.92; ^{31}P NMR (145 MHz, $CDCl_3$): $\delta = 47$ (d, $J = 187$ Hz).

General method for enyne cycloisomerization: The enyne (0.4 mmol), [{Rh(BICP)Cl}$_2$] (5 mol%), and $ClCH_2CH_2Cl$ (2 mL) were introduced into a 25-mL Schlenk tube in a glovebox. The mixture was stirred for 1 min. To this mixture $AgSbF_6$ (5 mol%) was added, and a precipitate was observed. The mixture was stirred at room temperature, and the course of the reaction was monitored by TLC. The cyclization was normally complete within 2–6 h. The crude mixture was diluted with diethyl ether and filtered to remove silver chloride before purification by flash chromatography.

1e: ^{1}H NMR (360 MHz, $CDCl_3$): $\delta = 7.20$ (m, 1H), 7.11 (m, 1H), 7.06 (m, 1H), 6.95 (m, 1H), 6.14 (m, 1H), 5.63 (m, 1H), 5.18 (m, 1H), 5.14 (m, 1H), 4.50–4.63 (m, 2H), 4.06 (dd, $J = 7.4$, 7.4 Hz), 3.49 (dd, $J = 8.4$, 8.4 Hz), 3.42 (m, 1H); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 51.20$, 70.61, 72.74, 118.41, 121.32, 126.33, 127.12, 128.35, 130.12, 134.12, 136.72, 139.34, 145.92. MS: *m/z*: 220 [M^+]; HRMS (APCI) calcd for $C_{14}H_{13}ClO$ [M^++H]: 221.0733; found: 221.0724.

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Rhodium-Mediated Asymmetric Hydroformylation with a Novel Bis(diazaphospholidine) Ligand**

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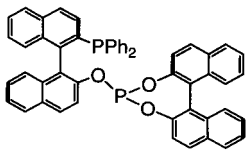
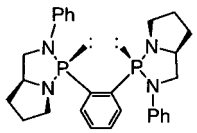
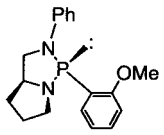
Asymmetric catalytic hydroformylation of alkenes is one of the most efficient and atom-economic of all the known processes for the synthesis of high-value chiral compounds. In one step, three readily available components (alkene, carbon monoxide, hydrogen) are combined in a C–C bond-forming process with no by-products other than unconverted reagents.[1] Asymmetric hydroformylation of vinyl acetate would convert this inexpensive bulk chemical in one step into a three-carbon synthetic building block which could be employed as an intermediate for the synthesis of many more complex molecules. Despite the scientific and commercial attractiveness of this process, few efficient catalysts are available for this reaction. Of those reported to date, BINAPHOS (**1**) and the closely related BIPHEMPHOS (**8**) are among the most efficient (Scheme 1).[2] As little as 0.20–0.25 mol% of a Rh^I complex of **1** facilitates the asymmetric



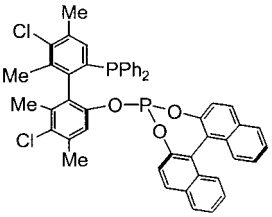
(*R*,*S*)-BINAPHOS (**1**)



ESPHOS (**6**)



SEMI-ESPHOS (**7**)



(*S*,*R*)-BIPHEMPHOS (**8**)

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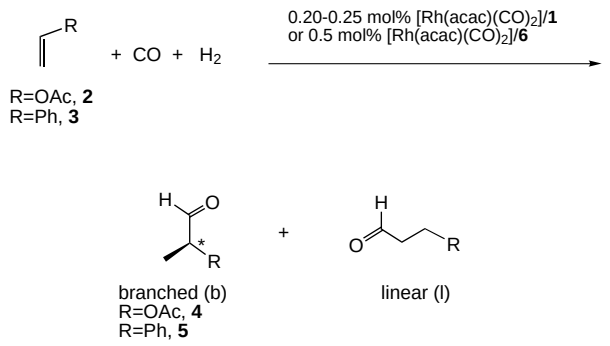

Scheme 1. Hydroformylation of vinyl acetate with rhodium(I) complexes of BINAPHOS (**1**) and ESPHOS (**7**). acac = acetylacetonate.

hydroformylation of vinyl acetate (**2**) and styrene (**3**) with high regio- and enantioselectivity (Table 1, entries 1 and 12). The branched-chain products **4** and **5** are formed in up to 94 and 92 % *ee*, respectively.

Recently, we reported the synthesis of, and preliminary studies on, a new class of chiral diazaphospholidine ligands.[3] The ligands can be prepared in both bidentate (ESPHOS; **6**)[4] or monodentate (SEMI-ESPHOS; **7**)[5] form. Both **6** and **7** are readily prepared by the reaction of the appropriate bis(dimethylamino) precursor with a diamine derived from glutamic acid. Although somewhat sensitive to decomposition by hydrolysis or alcoholysis, these heterocycles are stable to the neutral conditions commonly used in hydroformylation reactions. Given the attractiveness of hydroformylation with asymmetric catalysis, we chose to evaluate our ligands in this application.

Hydroformylation of vinyl acetate with 0.5 mol % of a rhodium(I) complex of ESPHOS gave excellent results (Table 1). The best results were achieved at a gas pressure of only 8 bar and 60 °C, which led to essentially quantitative (98.9 %) conversion after 5 h. The isolated product (90.3 %) was a mixture of branched and linear isomers in a ratio of 94.5:5.5, and the major product had 89 % *ee* (Table 1, entry 5). The temperature was lowered to 30 °C to establish whether the enantiomeric excess could be improved. This resulted in a dramatic decrease in the rate of reaction, so that a higher gas pressure was required to achieve measureable turnover, and in a lower yield (21.6 %), but the enantiomeric excess of the major product increased to 93 % (Table 1, entry 7). These results compare favorably with those achieved with BINAPHOS. Whilst the asymmetric induction achieved with **6** is marginally lower than for **1**, the branched:linear (b:l) ratio is superior (94.5:5.5 vs. 88:12), and the transformation was achieved at much lower gas pressures (8 bar vs. the lowest reported pressure of 20 bar[2g]) and reaction times (8 h vs. 13 h[2g]).

Further investigations revealed the crucial importance of the bidentate nature of **6** in the asymmetric hydroformylation process. The use of monodentate ligand **7** under the same conditions as for **6** gave very low yields of essentially racemic product, even when elevated temperatures and pressures were employed (Table 1, entries 8–10). Comparison with triphenylphosphane (Table 1, entry 11) underlines the specific requirement for bidentate ligands. In analogy with other C_2-symmetric ligands, it must be assumed that the origin of the high enantioselectivity results from the stereochemically well-defined environment which is created around the metal upon coordination of the ligand to a rhodium atom (Figure 1).

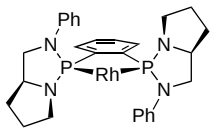

Figure 1. C_2-symmetric environment imposed by ESPHOS upon chelation to rhodium(I).

Having established that **6** is an excellent ligand for hydroformylation of vinyl acetate, we investigated the same reaction of styrene. Surprisingly, whilst rhodium(I) com-

Table 1. Asymmetric hydroformylation of alkenes with catalysis by rhodium complexes.[a]

Entry	Substrate	Ligand	P:Rh	T [°C]	p [bar]	t [h]	Conversion [%]	Aldehyde yield [%][b]	Aldehyde b:l[c]	Aldehyde *ee* [%]	Alcohol yield [%][d]	Alcohol *ee* [%]
1	**2**[e]	**1**[2e]	4.0	60	100	43	> 99	–	88:12	94(S)	–	–
2	**2**	**6**	1.5	80	40	3.0	100	34.9	94:6	76 (*S*)	58.8	84 (*S*)[h]
3	**2**	**6**	1.5	80	40	1.0	98.5	37.0	93:7	84 (*S*)	54.5	88 (*S*)
4	**2**	**6**	1.5	60	8	2.0	80.0	74.8	93.5:6.5	90 (*S*)	0.6	–
5	**2**	**6**	1.5	60	8	5.0	98.9	90.3	94.5:5.5	89 (*S*)	3.3	–
6	**2**	**6**	1.5	50	8	21	98.6	75.8	94:6	88 (*S*)	17.1	89 (*S*)
7	**2**	**6**	1.5	30	100	17	23.6	21.6	91.5:8.5	93 (*S*)	0	–
8	**2**	**7**[f]	3.0	80	40	8.0	4.2	1.1	25:75	–	–	–
9	**2**	**7**	2.0	80	40	20	10.2	2.5	25:75	–	–	–
10	**2**	**7**	2.0	120	100	6.0	21.8	14.7	70:30	< 2 (*R*)	0.5	–
11	**2**	PPh_3	3.0	80	40	4.5	99.7	73.6	81:19	0	4.1	0
12	**3**	**1**[2e]	4.0	60	100	36	> 99	–	86:14	92 (*S*)	–	–
13	**3**[g]	**6**	1.5	80	10	1.5	99.6	98.9	78:22	0	–	–
14	**3**	**7**	2.0	80	10	2.0	91.3	85.0	60:40	< 1	1.1	–
15	**3**	PPh_3	3.0	80	10	1.0	99.1	99.1	55:45	0	–	–

[a] Catalyst prepared in situ from $[Rh(acac)(CO)_2]$ (5×10^{-5} mol) and the phosphane in toluene (4 mL) containing styrene (1.0 g, 9.6×10^{-3} mmol) or vinyl acetate (1.0 g, 1.04×10^{-2} mmol); autoclave stirring speed = 500 rpm. [b] For vinyl acetate reactions, yield refers to 2-acetoxypropanal (1-acetoxypropanal decomposes under the reaction conditions to acetic acid and propenal), and for styrene reactions to 2-phenylpropanal plus 3-phenylpropanal. [c] Refers to aldehyde formation before aldehyde decomposition/hydrogenation. For vinyl acetate reactions, determined from the ratio of branched-chain product (aldehyde + alcohol) to acetic acid, and for styrene reactions from the ratio of branched-chain product (aldehyde + alcohol) to straight-chain product (aldehyde + alcohol). [d] For vinyl acetate reactions, this refers to 2-acetoxy-1-propanol plus 1-acetoxy-2-propanol, and for styrene reactions to 2-phenyl-1-propanol plus 3-phenyl-1-propanol. [e] Acetoxyacetone (0.3–0.6 %) is also a product. [f] Catalyst is unstable. [g] Acetophenone (< 1 %) is also a product. [h] The mixture consists of **8** (43 %, 82 % *ee*) and **9** (16 %, 84 % *ee*).

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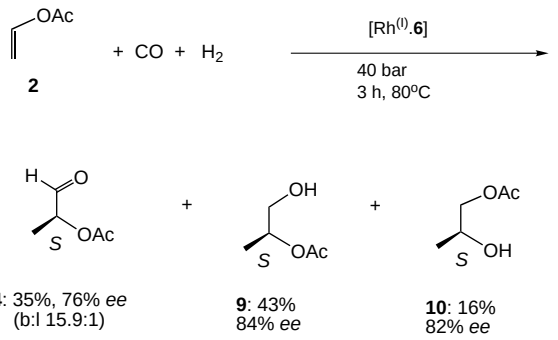
plexes of **6** and **7** are effective in styrene hydroformylation, the products in both cases were essentially racemic (Table 1, entries 13 and 14). This was unexpected, since most ligands are either good or bad for both substrates. It therefore appears that the presence of a coordinating group in the substrate is essential for high enantioselectivity when diazaphospholidines are used as ligands, somewhat analogous to asymmetric hydrogenation reactions with rhodium/diphosphane catalysts. However, it is possible that racemization may have followed an initially enantioselective reaction in the case of styrene, and we are currently investigating the causes of this unusual pattern of reactivity.

In some studies, we observed the formation of small quantities of alcohol products (from the reduction of the aldehyde **4**) when extended reaction times were employed in hydroformylation. Upon increasing the pressure and the temperature of the reaction, the alcohols **9** and **10** were formed in 43 and 16% yield, respectively, in both cases with 82–84% *ee* and identical configurations (Scheme 2; Table 1, entry 2). Clearly **9** is formed by the reduction of **4**, and **10** is a rearrangement product of **8**. This behavior contrasts with that



Scheme 2. Hydroformylation of vinyl acetate followed by reduction.

of other rhodium-based systems such as those containing **1** or BIPHEMPHOS (**8**), which show no activity for aldehyde hydrogenation. Such hydrogenations must be carried out in a separate step. The quantity of **4** that remained unreduced (35%) had an *ee* of 76%, which is presumably the result of aldehyde racemization over the extended reaction times. Since both **9** and **10** can be hydrolyzed to the same product, this process provides a direct approach to the asymmetric synthesis of 1,2-diols, which are important reagents and intermediates for fine-chemicals manufacture. We are therefore currently examining the extension of our hydroformylation process to the synthesis of diols and low molecular weight epoxides.

In conclusion, we have described a novel class of chelating phosphorus-donor ligands for asymmetric hydroformylation reactions. Our results demonstrate the need for a bidentate rather than a monodentate structure and an unprecedented requirement for a coordinating group in the substrate to achieve high enantioselectivity. In addition, the same catalyst system can perform the hydrogenation of the aldehyde product and thus provides a route to chiral 1,2-propanediol precursors.

Experimental Section

The preparation of the ligands **6** and **7** has been described.[3] The catalyst was prepared in situ from $[Rh(acac)(CO)_2]$ (5×10^{-5} mol) and the phosphane (1.5–4.0 equiv, see Table 1) in toluene (2 mL) in a miniautoclave fitted with a system for injection of substrate and for measuring kinetics at constant pressure. The autoclave was then flushed with CO/H_2 before pressurizing to several bar below the operating pressure. The temperature was raised with stirring to the desired operating temperature, styrene (1.0 g, 9.6×10^{-3} mmol) or vinyl acetate (1.0 g, 1.04×10^{-2} mmol) in toluene (2 mL) was injected, and the pressure was raised to the desired reaction pressure. The pressure was maintained with a mass flow controller. The autoclave stirring speed was 500 rpm. At the end of the reaction, the stirrer was stopped and the reactor cooled rapidly. The liquid products were analyzed by GC with a flame ionization detector (quantitative) and GC-MS (qualitative). The enantioselectivity of the reaction was determined by comparison with authentic product samples.

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arachno-$[Sn_8]^{6-}$ or *closo*-$[Li_2Sn_8]^{4-}$? Synthesis and Characterization of $A_4Li_2Sn_8$ (A = Rb, K)**

Svilen Bobev and Slavi C. Sevov*

Renewed interest in Zintl phases and Zintl ions in recent years has resulted in some major conceptual developments in these fields. Numerous isolated deltahedral clusters with unusual shapes, such as Tr_{11}^{7-}, Tr_4^{8-}, Tr_5^{7-}, Tr_6^{8-}, Tr_6^{6-}, and

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