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Enantioselective catalysis XVI: regio- and enantioselectivity in nickel-catalysed cross-coupling reactions of allylic substrates with Grignard reagents [1]

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Abstract

An investigation of the asymmetric synthesis of 3-phenyl-1-butene by the cross-coupling reaction of linear 2-butene-1-yl compounds and of branched 1-butene-3-yl substrates with phenylmagnesium halides is presented. Nickel and palladium complexes bearing chiral 3,4-bis(phosphanyl)pyrrolidine or 3-(diphenylphosphanyl)pyrrolidine ligands have been employed as catalysts. The quantitative analysis and the determination of enantiomeric composition of the catalytic samples were accomplished using enantioselective gas–liquid chromatography separations. Regio- and enantioselectivity can be influenced by the choice of the leaving group present in the allylic substrates and additionally by the choice of the ligand to nickel ratio in the case of monophosphane ligands. The influence of tertiary phosphanyl groups in three 3,4-bis(phosphanyl)pyrrolidine ligands, differing in basicity and molecular volume on chemical yield and on regio- and enantioselectivity is investigated. High chemical and optical yields (up to 83.5% ee) can be exclusively obtained with 3,4-bis(diphenylphosphanyl)pyrrolidine ligands. This conclusion contrasts with the results of another cross-coupling reaction yielding 3-phenyl-1-butene ((1-phenylethyl)magnesium halides and vinyl halides as starting compounds). In this catalysis nickel complexes bearing 3-(diphenylphosphanyl) pyrrolidine ligands were the most enantioselective catalysts. © 1998 Elsevier Science S.A.

Keywords: Enantioselective catalysis; Nickel-catalysed Grignard reagents; Cross-coupling

1. Introduction

Carbon–carbon bond formation by cross-coupling of main group organometallics with carbon electrophiles catalysed by transition metal complexes is a valuable tool in organic chemistry [1]. Among the transition metal compounds used for the efficient synthesis of substituted aryl, vinyl and allylic compounds, copper reagents and nickel and palladium phosphane complexes have proved to be the most effective. The enantioselective synthesis of 3-phenyl-1-butene (**3**) (Scheme 1) can be achieved with nickel and palladium complexes bearing chiral phosphanes [4]. This compound has synthetic utility as a starting material for the synthesis of commercial chiral products e.g. non-steroidal anti-inflammatory drugs [5]. The first approach to an enantioselective synthesis of **3** is the Grignard cross-coupling reaction of (1-phenylethyl)magnesium chloride (**1**), prepared from racemic 1-chloro-1-phenylethane and vinyl chloride (**2**) [6,7].

A second approach that will be investigated in this paper is the cross-coupling of either derivatives of 2-butene-1-ol (*E*-(**4**) and *Z*-(**4**)) or racemic derivatives of 1-butene-3-ol (**5**) with phenylmagnesium chloride (**7**). This enantioselective cross-coupling reaction has been investigated with nickel complexes bearing the C_2 symmetrical bisphosphane ligands CHIRAPHOS [8] and DPCP [9]. It yields mixtures containing both enantiomers of 3-phenyl-1-butene (**3**) in unequal amounts and isomeric 1-phenyl-2-butene (*E*-(**6**) and *Z*-(**6**)). We have used $NiCl_2$ complexes bearing either the C_2 symmetrical bisphosphane 3(*R*),4(*R*)-1-benzyl-3,4-bis(diphenylphosphanyl)pyrrolidine (compound **8**) [10] or the *P*,*N*-monophosphane 1-benzyl-3-(diphenylphosphanyl)-pyrrolidine (compound **9**) [11] as catalyst precursors in this study. The same complexes have been applied in the Grignard cross-coupling reaction [6], using **1** and **2** as starting com-

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[1] Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday.

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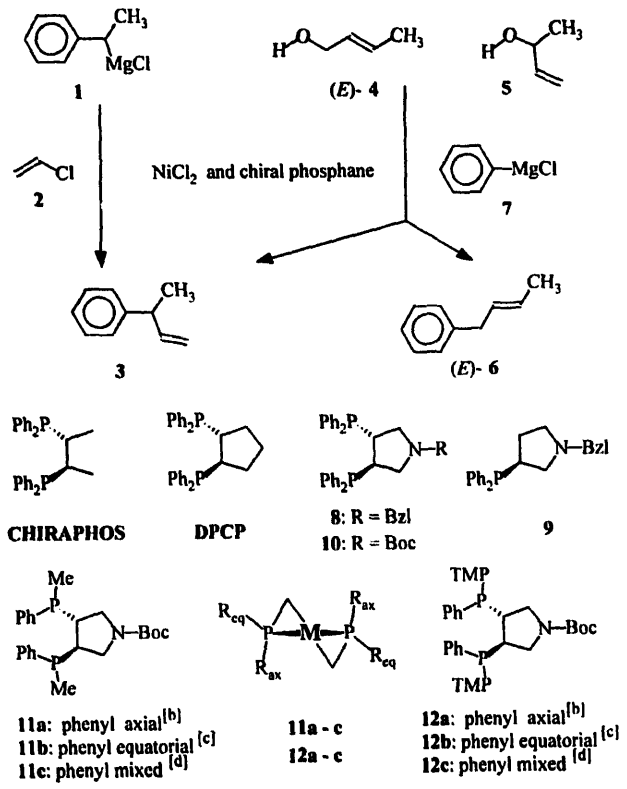


Scheme 1. Catalytic asymmetric cross-coupling of Grignard compounds (**1** or **7**) yielding chiral 3-phenyl-1-butene (**3**) and 1-phenyl-2-butene (**6**). For simplicity, the (*Z*)-isomers of 2-butene-1-yl compounds (**4** or **6**) are omitted. Chiral phosphane ligands, relevant for this paper are collected below, together with a front view of the five-membered chelate ring (λ-conformation) with axial (ax) and equatorial (eq) substituents, which are attached to both phosphorus atoms [a].

[a] The 2,4,6-trimethoxyphenyl substituent is abbreviated as TMP.

[b] The stereochemical descriptor for this ligand is P(*R*), 3(*R*), 4(*R*), P′(*R*), the transition metal complex, however, has the descriptor P(*S*), 3(*R*), 4(*R*), P′(*S*); see Refs. [2,3] for further discussion.

[c] The stereochemical descriptor for this ligand is P(*S*), 3(*R*), 4(*R*), P′(*S*), the transition metal complex, however, has the descriptor P(*R*), 3(*R*), 4(*R*), P′(*R*).

[d] The stereochemical descriptor for this ligand is P(*R*), 3(*R*), 4(*R*), P′(*S*), the transition metal complex, however, has the descriptor P(*S*), 3(*R*), 4(*R*), P′(*R*).

pounds. In the Grignard cross-coupling reaction the nickel complex with the β-aminoalkylmonophosphane ligand **9** is a much more enantioselective catalyst than the $NiCl_2$ complex with the C_2 symmetrical bisphosphane ligand **8**.

All bisphosphanes mentioned so far (CHIRAPHOS, DPCP and **8**) form upon coordination with a transition metal centre (M in Scheme 1) five-membered chelate rings which have a λ-conformation in the case of an (*R*,*R*)-configuration of the chiral centres in the ligand backbone [9]. The chiral array created by the four phenyl groups which are attached to the phosphorus atoms in this chelate ring is able to interact with coordinated substrate molecules. The phenyl groups can be classified as axial and equatorial substituents (see Scheme 1). Oxidative addition of allylic alcohol derivatives such as compounds **4** or **5** to Ni^0bisphosphane complexes were shown to form (η^3-allyl)Ni^{II}bisphosphane complexes. A 1-methylallyl (=crotyl) ligand which is coordinated η^3 to a chiral and C_2 symmetrical bisphosphane-nickel moiety can form four diastereomeric complexes [8,9,12]. These can be interconverted via π–σ–π isomerisations. This equilibrium of four diastereomeric complexes, together with those steps leading to products **3** and **6**, determine the regio- and enantioselectivity of this catalysis. The relative distribution of diastereomers should depend mainly on the chiral array of substituents attached to the phosphorus atom. This array can oe changed on going from a (diphenylphosphanyl)group in **8** and **10** to either a less bulky [methyl(phenylphosphanyl)] group in phosphanes **11a–c** or to a more bulky [2,4,6-trimethoxyphenyl)phenylphosphanyl] group in phosphanes **12a–c** [7]. The remaining phenyl groups in ligands **11a–c** and **12a–c** can act as both axial (e.g. **11a**) or both equatorial (e.g. **11b**) or mixed axial, equatorial (e.g. **11c**) substituents on phosphorus in the Ni-bisphosphane complexes. The relationship between the configuration of related Rh-bisphosphane complexes bearing additional chiral centres on phosphorus and enantioselectivity has been studied in detail for the enantioselective hydrogenation of α-(acetylamino)-cinnamic acid (see Ref. [2] (ligands **11a–c**) and Ref. [3]).

2. Experimental

2.1. Equipment

2.1.1. Quantitative analysis of catalytic samples

The quantitative analysis of catalytic samples, including enantiomer separation of 3-phenyl-1-butene (**3**) and separation of (*E*)-**6**/(*Z*)-**6** mixtures, was accomplished using gas–liquid chromatography (GLC) [13]. Instrumentation and retention data of sample components are collected below. Mesitylene was added as internal standard [13] to catalytic samples just before the reaction was terminated by hydrolysis (vide infra). The quantitative analysis (on column I) of samples containing mesitylene, 3-phenyl-1-butene (**3**) and 4-phenyl-1-butene has been developed for catalytic samples which were obtained by Grignard cross-coupling using **1** and **2** as starting compounds [6].

The gas chromatograph was a Chrompack, model 438 A; FID (250°C); split injector (200°C). The integration software was Kontron Data System 450-MT2, V1.02. The GLC column I was an FS-Cyclodex Beta-I/P® Phase II (60 m, 0.25 mm i.d., permethylated β-cyclodextrin/polysiloxane [2] [14]), 70°C isotherm, 0.85 bar H_2 pressure. Its retention data (as selectivity factors α [13]) are as follows: mesitylene $\alpha = 1$ with retention time $t_R = 14 \pm 1$ min; (*R*)-**3** $\alpha = 1.53$; (*S*)-**3** $\alpha = 1.56$; 4-phenyl-1-butene $\alpha = 1.99$; (*E*)-**6** $\alpha = 2.12$; (*Z*)-**6** $\alpha = 2.42$. The GLC column II was an FS-Lipodex®-E (50 m, 0.25 mm i.d., octakis-(2,6-di-*O*-pentyl-3-*O*-butyryl)-γ-cyclodextrin [3]), 50°C isotherm, 1.25 bar H_2 pressure. Its

[2] Column I is commercially available from CS-Chromatographie Services GmbH, 52379 Langerwehe, Germany; separation has Application No. CD 215b.

[3] Column II is commercially available from Machery Nagel GmbH, 52348 Düren, Germany.

retention data (as selectivity factors α [13]) are as follows: mesitylene $\alpha = 1$ with retention time $t_R = 18 \pm 1$ min; (*R*)-**3** and (*S*)-**3** $\alpha = 1.37$; 4-phenyl-1-butene $\alpha = 1.61$; (*E*)-**6** $\alpha = 2.10$; (*Z*)-**6** $\alpha = 2.27$.

'Relative molar response factors' f_{mol} [13] ($f_{mol} = 1$ for mesitylene, $f_{mol} = 0.922$ for (*R*)-**3**, (*S*)-**3**, 4-phenyl-1-butene, (*E*)-**6** and (*Z*)-**6**; see Ref. [6]) were used for the conversion of the recorded FID peak areas of eluted compounds into quantities (in mmol) of the corresponding sample components. The determinations of enantiomeric excess (% ee) values were reproducible to within less than ±0.5% (on column I) in the GLC analysis [6] and the determinations of sample components to within less than ±0.05 mmol (on column II). The separations done on columns I and II gave corresponding results in all cases. Column I was mainly used for the determination of enantiomeric excess (% ee) values (0.5–1 μl of sample injected), column II for the determination of the quantities of sample components (2–3 μl of sample injected).

2.1.2. NMR measurements

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were measured with three samples (samples A–C), containing different amounts (% estimates by GLC analysis) of 3-phenyl-1-butene (**3**), (*E*)-1-phenyl-2-butene ((*E*)-**6**) and (*Z*)-1-phenyl-2-butene ((*Z*)-**6**): sample A, pure **3**; sample B, 62% **3**, 34% (*E*)-**6**, 4% (*Z*)-**6**; sample C, 15% **3**, 66% (*E*)-**6**, 19% (*Z*)-**6**. We were not able to accomplish a quantitative analysis of catalytic samples on the basis of integration of ^{1}H NMR spectra. The spectral data of the compounds are presented below.

^{1}H NMR spectra at 297 K: Bruker DRX 250 (250.13 MHz), chemical shifts δ (in ppm) are referenced to the residual ^{1}H resonances of $CDCl_3$ versus TMS ($\delta = 7.24$). ^{13}C{^{1}H} NMR spectra measured with the DEPT 135 technique [15] at 297 K: Bruker DRX 250 (62.90 MHz), chemical shifts δ (in ppm) are referenced to ^{13}C resonances of $CDCl_3$ versus TMS ($\delta = 77.0$).

2.1.2.1. 3-Phenyl-1-butene (3)

^{1}H NMR: $\delta = 1.31$ [d, 3 H ($J = 7.2$ Hz), CH_3], 3.55–3.37 [m, 1 H, *CH* (C-3)], 5.00–5.10 [m, 2 H, *CH*2 (C-1)], 5.92–6.06 [m, 1 H, *CH* (C-2)], 7.11–7.28 [m, 5 H, *CH* (Ph)]. ^{13}C{^{1}H} NMR: $\delta = 21.20$ (s, CH_3), 43.65 (s, C-3), 113.50 (s, C-1), 126.60, 127.70, 128.87 [3 s, *CH* (Ph)], 143.68 (s, C-2).

2.1.2.2. (E)-1-Phenyl-2-butene ((E)-6)

^{1}H NMR [16]: $\delta = 1.67$ [d, 3 H ($J = 6$ Hz), CH_3], 3.29 [d, 2 H ($J = 6$ Hz), CH_2 (C-1)], 5.41–5.64 [m, 2 H, *CH* (C-2, C-3)], 7.11–7.28 [m, 5 H, *CH* (Ph)]. ^{13}C{^{1}H} NMR: $\delta = 18.31$ (s, CH_3), 39.76 (s, C-1), 115.87 (s, C-3), 120.58 (s, C-2), 126.30, 128.96, 129.60 [3 s, *CH* (Ph)].

2.1.2.3. (Z)-1-Phenyl-2-butene ((Z)-6)

^{1}H NMR: $\delta = 1.69$ [d, 3 H ($J = 6$ Hz), CH_3], 3.40 [m, 2 H ($J = 6$ Hz), CH_2 (C-1)], 5.51–5.74 [m, 2 H, *CH* (C-2, C-3)], 7.11–7.28 [m, 5 H, *CH* (Ph)]. ^{13}C{^{1}H} NMR: $\delta = 18.31$ (s, CH_3), 39.76 (s, C-1), 114.77 (s, C-3), 120.87 (s, C-2), 126.30, 128.96, 129.60 [3 s, *CH* (Ph)].

2.2. Starting compounds

Diethyl ether and tetrahydrofuran (THF) were dried and purified by distillation from $LiAlH_4$ solutions and kept under argon. All manipulations involving phosphanes and moisture sensitive compounds were conducted under dry argon.

2.2.1. Phenylmagnesium chloride (7)

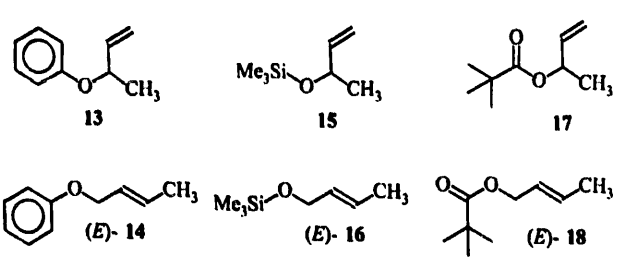
For the synthesis of a 2 M stock solution of phenylmagnesium chloride (**7**) in THF [17] magnesium turnings (Merck Schuchardt, 'according to Grignard' quality; 26 g, 1.08 mol) were stirred dry [18] for several days and were subsequently covered with a 20 ml aliquot of a mixture containing 1 mol of phenyl chloride (101.7 ml) and 250 ml THF. Initiation occurred upon gentle heating and the remaining mixture was added dropwise over 3 h. After completion of addition the reaction mixture was heated at 70°C for 3 h. The stirred mixture was diluted with 400 ml THF and was then filtered through Celite. On removal of a 2 ml aliquot from the clear filtrate we added 600 mg of mesitylene (5 mmol) and 2 N HCl (hydrolysis of the Grignard compound) to the analytical sample. The benzene content of diethyl ether extracts (100 ml), thus obtained, was assayed by quantitative GLC. Column II working at 40°C was used for this purpose. The recorded peak areas of benzene and mesitylene obtained in a GLC run with this sample were compared with those obtained in a GLC run with a standard solution containing 5 mmol amounts of benzene and mesitylene. On the basis of this analysis the THF solution was further diluted with THF until the concentration of the stock solution was reached.

2.2.2. Allylic substrates [19]

Quantitative analysis of substrate samples by ^{1}H NMR and GLC furnished the $E/(E+Z)$ ratios in the case of 2-butene-1-ol (**4**) and of derivatives thereof (**14**, **16** and **18** in Scheme 2) and the relative amounts of linear 2-butene-1-yl compounds and of branched 1-butene-3-yl compounds (**5**, **13**, **15** and **17** in Scheme 2).

2.2.2.1. Substrate I

This was prepared from crotyl bromide (equilibrium mixture [20]: 14% 1-butene-3-bromide, 69% (*E*)-2-butene-1-bromide, 17% (*Z*)-2-butene-1-bromide; $E/(E+Z) = 0.83$),



Scheme 2. Collection of 1-butene-3-yl derivatives (**13**, **15** and **17**) and 2-butene-1-yl compounds (**14**, **16** and **18**; (*Z*)-isomers are omitted for simplicity), present in substrates I, II, V and VI.

K_2CO_3 and phenol in acetone [21]. GLC analysis using column II at 100°C gave: 12% 3-phenoxy-1-butene (**13**; selectivity factor [13] $\alpha = 1$ with retention time $t_R = 13.3$ min); 73% (*E*)-1-phenoxy-2-butene ((*E*)-**14**; $\alpha = 1.82$); 15% (*Z*)-1-phenoxy-2-butene ((*Z*)-**14**; $\alpha = 1.88$); $E/(E+Z) = 0.83$ in accordance with the integrated ^{1}H NMR spectrum.

2.2.2.2. Substrate II

This was prepared from 2-butene-1-ol (crotyl alcohol (**4**), Merck Schuchardt), NaH and Me_3SiCl according to a published procedure [22]. The fraction boiling at 82°C (250 mbar) was used. GLC analysis using column II at 40°C gave: 33% 3-trimethylsiloxy-1-butene (**15**; selectivity factor [13] $\alpha = 1$ with retention time $t_R = 5.6$ min); 57% (*E*)-1-trimethylsiloxy-2-butene [23] ((*E*)-**16**; $\alpha = 1.13$); 10% (*Z*)-1-trimethylsiloxy-2-butene ((*Z*)-**16**; $\alpha = 1.17$); $E/(E+Z) = 0.85$ in close accordance with the integrated ^{1}H NMR spectrum.

2.2.2.3. Substrate III

2-Butene-1-ol (crotyl alcohol (**4**), Merck Schuchardt). GLC analysis using column I at 40°C gave: 86% (*E*)-2-butene-1-ol ((*E*)-**4**; selectivity factor [13] $\alpha = 1$ with retention time $t_R = 9.85$ min); 14% (*Z*)-2-butene-1-ol ((*Z*)-**4**; $\alpha = 1.18$); $E/(E+Z) = 0.86$ in close accordance with the integrated ^{1}H NMR spectrum.

2.2.2.4. Substrate IV

1-Butene-3-ol ((**5**), Merck Schuchardt). GLC analysis using column I at 40°C gave a racemic mixture of (*R*)-**5** and (*S*)-**5** with $\alpha = 0.43$ and $\alpha = 0.44$ ((*E*)-**4** as $\alpha = 1$).

2.2.2.5. Substrate V

This was prepared from 2-butene-1-ol ((**4**), Merck Schuchardt), NaH and pivaloyl chloride. GLC analysis using column I at 70°C gave: 86% (*E*)-2-butene-1-oxypivalate ((*E*)-**18**; selectivity factor [13] $\alpha = 1$ with retention time $t_R = 11.3$ min); 14% (*Z*)-2-butene-1-oxypivalate ((*Z*)-**18**; $\alpha = 0.93$); $E/(E+Z) = 0.86$ in close accordance with the integrated ^{1}H NMR spectrum.

2.2.2.6. Substrate VI

This was prepared from 1-butene-3-ol ((**5**), Merck Schuchardt), NaH and pivaloyl chloride. GLC analysis using column I at 70°C gave a racemic mixture of (*R*)-1-butene-3-oxypivalate ((*R*)-**17**) and (*S*)-1-butene-3-oxypivalate ((*S*)-**17**) with $\alpha = 0.64$ and $\alpha = 0.66$ ((*E*)-**18** as $\alpha = 1$).

2.3. Experimental procedures used for catalytic runs

2.3.1. Catalytic runs with nickel phosphane complexes (substrates I and II)

A mixture of either 50 μmol of $NiCl_2$ [6] and 55 μmol of bisphosphane ligand (see Table 1) or 55 μmol (**9**/Ni = 1), 110 μmol (**9**/Ni = 2) and 193 μmol (**9**/Ni = 3.5) amounts of **9**, respectively (see Table 2) was dissolved in 5 ml THF and stirred for 30 min. To this solution was added 741 mg (5 mmol) of substrate I or 722 mg (5 mmol) of substrate II and 15 ml of THF. Then 5 ml of the stock solution of Grignard compound **7** (10 mmol) were added via a syringe at −78°C and the Schlenk tube and the surrounding Dewar vessel containing 100 ml of isopropanol and 50 g of dry ice were allowed to attain room temperature overnight. After 120 h at room temperature 600 mg (5 mmol) of mesitylene and 2 ml THF were added and the reaction was terminated by addition of 20 ml of water. Then 2 N HCl was added until all solid components had dissolved and the aqueous phase was extracted with three 30 ml portions of diethyl ether. THF and diethyl ether were evaporated from the collected organic phases and the residue was dried at 40°C, 100 mbar for 30 min. The oil was dissolved in 80 ml diethyl ether and the solution was dried with K_2CO_3, filtered through Celite and the clear filtrate was made up to 100 ml and stored in a sealed bottle until GLC analysis was carried out.

2.3.2. Catalytic runs with nickel phosphane complexes in THF (substrates III–VI)

To the $NiCl_2$ phosphane (50 μmol Ni) solution in 5 ml THF (prepared as in Section 2.3.1) was added either 361 mg (5 mmol) of substrate III and IV, or 781 mg (5 mmol) of substrate V and VI, and 15 ml of THF. Then 20 ml of the stock solution of Grignard compound **7** (40 mmol) were added via a syringe at −78°C and the Schlenk tube and the surrounding Dewar vessel containing 100 ml of isopropanol and 50 g of dry ice were allowed to reach −10°C in 8 h. After 10 h at −10°C and 120 h at room temperature 600 mg (5 mmol) of mesitylene and 2 ml THF were added and the reaction was terminated by the addition of 20 ml of water. Further workup was done as before.

2.3.3. Catalytic runs with nickel monophosphane complexes in diethyl ether (substrates V and VI)

These catalytic runs were done as before (see Section 2.3.2) with the exception that THF was substituted by diethyl ether throughout. A stock solution of phenylmagnesium bromide in diethyl ether instead of phenylmagnesium chloride (**7**) was used.

2.3.4. Catalytic runs with the PdI_2 complex of 8 and $AgBF_4$

44 mg isolated PdI_2-**8** complex (50 μmol Pd) and 44 mg (226 μmol) $AgBF_4$ were stirred with 20 ml THF, containing a 5 mmol amount of substrates I–VI, for 30 min. Then the Grignard compound **7** was added (see Sections 2.3.1 and 2.3.2 for further experimental details).

3. Results and discussion

3.1. Catalysis with transition metal complexes of bisphosphane ligands

For the discussion of our catalytic results we summarise the mechanism of this cross-coupling reaction [9]. For sim-

Table 1
Catalytic results with nickel or palladium complexes of bisphosphane ligands (50 μmol of Ni or Pd) in THF [a]

Entry		I [b]	II [c]	III [d]	IV [e]	V [f]	VI [g]	Ligand
1	Yield [h] of 3	2.50	1.75	0.10	0.15	1.45	2.40	8 [i]
	ln(*R*/*S*) of 3	−2.10	−2.40	−0.90	−0.15	−1.80	−1.65	
	Yield [h] of 6	2.40	1.70	0.10	0.10	1.55	2.55	
	E/(*E*+*Z*) of 6	0.98	0.98	0.96	0.94	0.97	0.94	
2	Yield [h] of 3	3.20	2.90	0.15	1.25	2.90	2.10	10 [i]
	ln(*R*/*S*) of 3	−2.20	−2.30	−0.15	−0.05	−2.20	−1.50	
	Yield [h] of 6	1.75	1.65	0.05	0.35	1.70	2.95	
	E/(*E*+*Z*) of 6	0.96	0.96	0.96	0.95	0.96	0.74	
3	Yield [h] of 3	2.15	1.10	0.25	0.15	0.25	1.05	11a [i]
	ln(*R*/*S*) of 3	−0.60	−0.40	[l]	−0.40	−0.50	−0.35	
	Yield [h] of 6	1.45	0.60	0.10	0.20	0.45	3.00	
	E/(*E*+*Z*) of 6	0.96	0.96	0.94	0.72	0.89	0.65	
4	Yield [h] of 3	2.15	0.80	0.10	0.05	0.20	0.95	11b [i]
	ln(*R*/*S*) of 3	[l]	−0.15	−0.25	−0.25	−0.55	−0.55	
	Yield [h] of 6	2.55	0.95	0.05	0.05	0.80	3.25	
	E/(*E*+*Z*) of 6	0.98	0.98	0.94	0.92	0.91	0.73	
5	Yield [h] of 3	1.70	1.15	0.10	0.10	0.30	0.90	11c [i]
	ln(*R*/*S*) of 3	−0.55	−0.70	−0.60	−0.20	−0.65	−0.40	
	Yield [h] of 6	1.90	1.20	0.10	0.10	0.65	3.00	
	E/(*E*+*Z*) of 6	0.97	0.97	0.93	0.90	0.92	0.68	
6	Yield [h] of 3	0.95	0.45	0.05	0.10	0.10	0.70	12a [i]
	ln(*R*/*S*) of 3	0.55	−0.25	−0.05	−0.05	[l]	[l]	
	Yield [h] of 6	0.85	0.65	0.05	0.05	0.30	3.85	
	E/(*E*+*Z*) of 6	0.94	0.95	0.90	0.90	0.85	0.61	
7	Yield [h] of 3	1.00	0.35	0.05	0.05	0.45	1.05	12b [i]
	ln(*R*/*S*) of 3	−0.30	−0.35	−0.10	−0.10	−0.10	0.40	
	Yield [h] of 6	1.15	0.45	0.10	0.05	0.70	2.75	
	E/(*E*+*Z*) of 6	0.94	0.93	0.95	0.89	0.91	0.72	
8	Yield [h] of 3	0.50	0.25	0.10	0.15	0.15	0.75	12c [i]
	ln(*R*/*S*) of 3	−0.25	−0.35	−0.15	−0.15	0.25	−0.05	
	Yield [h] of 6	0.65	0.45	0.15	0.15	0.40	2.85	
	E(*E*+*Z*) of 6	0.91	0.95	0.93	0.93	0.85	0.64	
9	Yield [h] of 3	0.15	0.25	[m]	[m]	0.05	0.45	8 [k]
	ln(*R*/*S*) of 3	−0.05	−0.10			−0.25	[l]	
	Yield [h] of 6	0.45	0.35	0.05	0.05	0.75	3.30	
	E(*E*+*Z*) of 6	0.80	0.90	0.76	0.70	0.73	0.56	

[a] Catalytic runs with 5 mmol of allylic substrates (I–VI) and excess Grignard compound **7**.
[b] 12% of **13**, 73% of (*E*)-**14**, 15% of (*Z*)-**14**.
[c] 33% of **15**, 57% of (*E*)-**16**, 10% of (*Z*)-**16**.
[d] 86% of (*E*)-2-butene-1-ol [(*E*)-**4**], 16% of (*Z*)-**4**.
[e] 100% of 1-butene-3-ol (**5**).
[f] 86% of (*E*)-**18**, 16% (*Z*)-**18**.
[g] 100% of **17**.
[h] In mmol.
[i] $NiCl_2$ complexes as catalytic precursors.
[k] PdI_2 complex in the presence of a 4.5-fold excess of $AgBF_4$ as catalytic precursor.
[l] Racemic 3-phenyl-1-butene (**3**) obtained.
[m] Traces of 3-phenyl-1-butene (**3**).

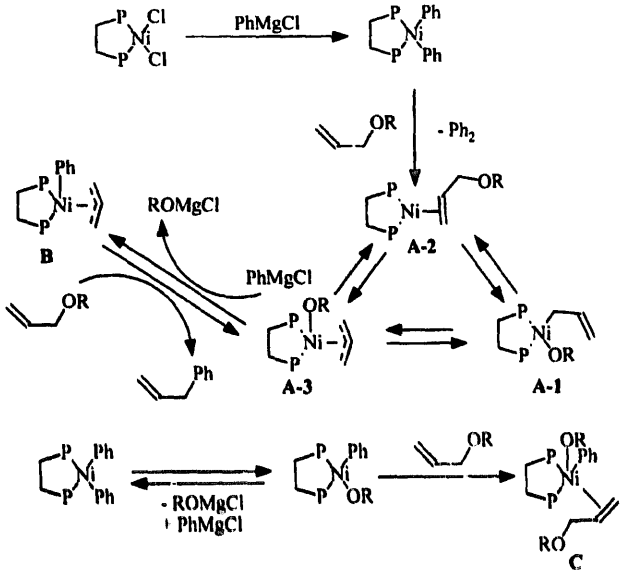
plicity, the mechanistic picture in Scheme 3 is presented with a simple allyl ligand instead of a 1-methylallyl (=crotyl) ligand. Complexes **A-1**, **A-2**, **B** and **C** have been intercepted and identified by $^{31}P\{^1H\}$ NMR and CD spectra. The η^3-allyl ligands in complexes **A-3** and **B** have two possible modes of coordination to the NiP_2X (X=OR, Ph) moiety. The first isomer (X and H atom on the (C-2) carbon atom *cis*) can interconvert to the second (rotational) isomer (X and H atom on the (C-2) carbon atom *trans*) [8].

An η^3-(1-methylallyl) ligand that is coordinated to an NiP'_2X (X=OR, Ph, $P'_2=C_2$ symmetrical chiral bisphosphane) moiety furnishes eight isomeric complexes. Each of the four diastereomeric complexes of the η^3-(1-methylallyl)NiP'_2 case discussed in Section 1 can form two rotational isomers. The $^{31}P\{^1H\}$ NMR spectra of reaction mixtures of cross-coupling reactions [9] showed two AB patterns which were assigned to a major and a minor diastereomer of a type **B** complex. These two diastereomers could

Table 2
Catalytic results with mixtures of $NiCl_2$ and P,N monophosphane **9** at different **9**/nickel ratios (50 μmol of Ni) in THF [a] or diethyl ether [b]

Entry		I	II	V	VI	V [b]	VI [b]	(9/Ni) ratio
1	Yield [c] of **3**	0.55	0.15	0.10	0.55	0.90	0.30	
	Yield [c] of **6**	0.80	0.20	0.30	2.95	1.20	0.30	1
	$E/(E+Z)$ of **6**	0.86	0.89	0.85	0.64	0.94	0.77	
2	Yield [c] of **3**	1.05	0.25					
	Yield [c] of **6**	1.15	0.35	[d]	[d]	[d]	[d]	2
	$E/(E+Z)$ of **6**	0.86	0.80					
3	Yield [c] of **3**	1.25	1.20			1.50	0.60	
	Yield [c] of **6**	1.50	2.75	[d]	[d]	1.90	0.50	3.5
	$E/(E+Z)$ of **6**	0.83	0.95			0.93	0.73	

[a] Catalytic runs with 5 mmol of allylic substrate (I, II, V and VI, cf. Table 1) and excess phenylmagnesium chloride (**7**); $\ln(R/S)$ values obtained are always smaller than a $\ln(R/S)$ value of -0.1.
[b] Catalytic runs with 5 mmol of allylic substrate (V and VI, see Section 2) and excess phenylmagnesium bromide.
[c] In mmol.
[d] Not performed.



Scheme 3. Mechanistic picture of the cross-coupling reaction with allylic substrates. The scheme contains a simplified achiral version of the nickel catalysed cross-coupling reaction. Additional features of the cross-coupling of 1-methylallylic moieties with PhMgCl, catalysed by nickel complexes bearing chiral bis(phosphanyl)ethane-type ligands are discussed in the text. Most complexes present during catalytic runs have been intercepted and identified by $^{31}P\{^1H\}$ NMR [9].

be either *syn/anti* isomers or both *anti* isomers [9]. The relative amounts of both diastereomers were dependent on the leaving group present in the allylic substrate used. The η^3-(1-methylallyl) complexes of type **A-3** could not be detected. They must be present in small portions in reaction mixtures [4], because the regio- and enantioselectivity of this cross-coupling reaction depends as well on the steric bulk of the leaving group (OR) of the allylic substrate [9].

The regioselectivity [9] and enantioselectivity [25] of the allylic cross-coupling reaction, yielding **3** and **6**, is dependent on temperature. Our experimental procedures consisted of a mixing period (up to 18 h below -10°C) and a subsequent reaction period (120 h at room temperature). Based on the results [9] that the cross-coupling reaction is very slow at temperatures below -10°C, we assume that the prevailing amount of products was formed at room temperature.

The results, obtained with a nickel-bisphosphane/substrate ratio of 100 (5 mmol substrate) and excess Grignard compound **7** are summarised in Table 1. Yields of both regioisomers 3-phenyl-1-butene (**3**) and 1-phenyl-2-butene (**6**) together with the $E/(E+Z)$ ratios of the linear product **6** are given. $\ln(R/S)$ values [5] are used as a measure for enantioselectivity instead of the more familiar % ee scale. These $\ln(R/S)$ values are proportional to changes of free enthalpy that are responsible for the observed enantioselectivity differences.

A comparison of our results (entries 1 and 2 in Table 1), obtained with nickel complexes bearing bisphosphanes **8** and **10**, with literature data can be mainly done in the case of catalytic runs using substrates I and II. The components **13**, (*E*)-**14** and (*Z*)-**14** of substrate I were reacted separately with Grignard compound **7** in the presence of the $NiCl_2$-CHIRAPHOS catalyst (see footnote 4 and Ref. [26]). This invariably gave 65% 3-phenyl-1-butene (**3**) (of 59 ± 1% ee equal to $\ln(R/S) = -1.35 \pm 0.05$) and 35% (*E*)-1-phenyl-2-butene ((*E*)-**6**). The same regioselectivity as with the $NiCl_2$-CHIRAPHOS catalyst is found in the case of our $NiCl_2$-**10** catalyst (entry 2). The analogous reaction, done with an (*E*)-**14** and (*Z*)-**14** mixture in the presence of an $NiCl_2$-DPCP catalyst [9] gave equal amounts of **3** (of 53% ee equal to $\ln(R/S) = -1.2$) and **6**. Our $NiCl_2$-**8** catalyst (entry 1) also gave equal amounts of **3** and **6**. The optical yield of branched isomer 3-phenyl-1-butene (**3**) $\ln(R/S) =$

[4] Consiglio and coworkers [24] provided direct evidence for common η^3-(1-methylallyl) intermediates of type **A-3**. They performed decarboxylations of 3-(phenoxycarbonyloxy)-1-butene or 1-(phenoxycarbonyloxy)-2-butene catalysed by nickel-CHIRAPHOS complexes. The nearly absent influence of different starting materials on regio- and enantioselectivity of products of 3-phenoxy-1-butene (**13**) and 1-phenoxy-2-butene (**14**) supports the appearance of such common intermediates (**A-3**).

[5] See Ref. [6] for further discussion of the $\ln(R/S)$ enantioselectivity scale. The $\ln(R/S)$ values of published results with CHIRAPHOS and DPCP complexes are always given for ligands of (*R,R*)-configuration.

−2.10 (equal to 78% ee) for the catalyst with ligand **8**; $\ln(R/S) = -2.20$ (equal to 80% ee) for the catalyst with ligand **10**) is improved in the case of our catalysts. The reactions done with substrate II [9] gave further improved enantioselectivity ($\ln(R/S) = -2.40$ (equal to 83.5% ee)). This demonstrates again that there is a dependence of enantioselectivity on the steric bulk of the leaving group.

Catalytic runs with substrates III (2-butene-1-ol (**4**)) and IV (1-butene-3-ol (**5**)) gave very small chemical yields [23] of **3** and **6** compared with catalytic runs with the corresponding ester derivatives (substrates V and VI). The nickel catalysed reaction of substrates V and VI yielding **3** and **6** is a fast reaction compared with the competing reductive cleavage reaction of those substrates by Grignard compound **7** yielding the magnesium alkoxides of 2-butene-1-ol (of **4**), 1-butene-3-ol (of **5**) and 1-bis(phenyl)neopentylalcohol. Pivalate anions (or reduction products thereof) improve enantioselectivity in catalytic runs with substrates V and VI compared with catalytic runs with substrates III and IV. The reduction of pivalate anions by Grignard compounds might be possible, when they are coordinated to nickel complexes (see Scheme 3). We therefore used a large excess of Grignard compound **7**, which would be sufficient for a complete reduction of pivalate anions (see Ref. [25]).

Enantioselectivity and chemical yields of catalytic runs with linear substrates (III or V) as starting compounds are different from catalytic runs with branched substrates (IV or VI). Improved chemical yields in the case of branched substrates in catalytic runs terminated before complete conversion can be explained on the basis of the results of Consiglio et al. [26]. They have shown that a complete conversion of the linear substrates (*E*)-**14** or (*Z*)-**14** to products takes roughly twice the time needed for a complete conversion of the branched substrate **13**. Furthermore, the optical purity of the branched product **3** did not depend on the extent of conversion. The enantioselectivity differences between linear substrates and branched substrates found in our investigation are significant (see Refs. [25,26] for related examples).

The catalytic run (entry 2) using branched substrate VI, Grignard compound **7** and catalytic amounts of $NiCl_2$-**10** as starting compounds gave large amounts of linear product **6** and an $E/(E+Z)$ ratio equal to 0.74 compared with $E/(E+Z)$ ratios of 0.97 ± 0.05 found for all other catalytic runs described so far. It is known [27] that 3-chloro-1-butene or ester derivatives of 1-butene-3-ol react with Grignard compound **7** or phenyllithium without any catalyst yielding 1-phenyl-2-butene (**6**) with an $E/(E+Z)$ ratio of 0.9 ± 0.1 (see $E/(E+Z)$ of our starting compounds **4**, **14**, **16** and **18**). This argument reveals that 1-phenyl-2-butene (**6**) products obtained in catalytic runs with $E/(E+Z)$ ratios smaller than 0.8 must be eliminated from transition metal centres. Such small $E/(E+Z)$ ratios were invariably obtained in catalytic runs using branched substrate VI, Grignard compound **7** and catalytic amounts of $NiCl_2$ complexes bearing bisphosphane ligands **10** and **11a–c** and **12a–c** as starting compounds. These ligands containing a (tert-butoxycarbonyl) group on the pyrrolidine nitrogen atom [7] can add two phenyl anions and eliminate a tert-butanolate anion. The $^{31}P\{^1H\}$ NMR spectroscopic investigation of reaction mixtures (see Ref. [9]) showed that measurable concentrations of $[P_2Ni]Ph_2$, $[P_2Ni]PhX$ (X = OR, halogen atom) and of complex **C** (see Scheme 3) were present throughout the catalytic run. The η^2-coordinated crotyl ligand in complexes of type **C** should be activated toward nucleophilic attack by a phenyl anion. This transition metal catalysed version of nucleophilic substitution of the branched 1-butene-3-yl substrate should yield $E/(E+Z)$ ratios differing from other reaction paths.

Chemical yields of cross-coupling products with substrates I and II are nearly quantitative when nickel complexes bearing ligands **8** or **10** are used. Nickel complexes bearing ligands **11a–c** give only 35–75% of cross-coupled products, those with ligands **12a–c** give 15–45% yield. The increased basicity of both types of ligands compared with ligand **10** and additionally the increased steric bulk in the case of ligands **12a–c** is obviously deleterious for an efficient conversion of our substrates to **3** and **6**. In catalytic runs with ligands **11a–c**, with a methyl and phenyl group attached to phosphorus, an optical induction which is close to zero was obtained for ligand **11b** (no phenyl group in axial position). A slightly enhanced optical induction was obtained for ligands **11a** and **11c** [$\ln(R/S) = -0.4$ (-0.7) (equal to 20% ee (29% ee))]. The branched product **3** is prevailing, as in catalytic runs with ligand **10**, only when two phenyl groups are in axial position (ligand **11a**). Nickel complexes bearing ligands **12b** and **12c**, with a bulky 2,4,6-trimethoxyphenyl group attached to phosphorus in either bisaxial or axial equatorial position give branched product **3** with $\ln(R/S) = -0.3 \pm 0.05$. The catalyst bearing ligand **12a** (both 2,4,6-trimethoxyphenyl groups situated in equatorial position) yields 3-phenyl-1-butene (**3**) with a reversed enantiomeric composition ($\ln(R/S) = 0.5$; substrate I). A series of catalytic runs, done with $NiCl_2$-DPCP [9] and $NiCl_2$-CHIRAPHOS catalysts [25,26] and Grignard compounds RMgX gave $\ln(R/S)$ values which were in the order: 1 (R = ethyl):3.5 (R = phenyl):6 (R = 2-naphthyl):0 (R = 1-naphthyl). The catalytic result with the 1-naphthyl Grignard compound was explained by an attack of a 1-naphthyl anion from outside the η^3-coordinated 1-methylallyl moiety and not within the inner sphere of the nickel complex as in the case of other Grignard compounds [9].

Catalytic runs with substrates III–VI and ligands **11a–c** and **12a–c** furnish examples that contradict the trends found for substrates I and II. Taking into account that very small free enthalpy variations are responsible for the observed differences in regio- or enantioselectivity, this result could be expected. Small yields of cross-coupling reactions with pivalate ester derivatives (substrates V and VI) indicate that the competing reductive cleavage reaction yielding magnesium alkoxides of 2-butene-1-ol (of **4**), 1-butene-3-ol (of **5**) and 1-bis(phenyl)neopentylalcohol is no longer a slow reaction (see earlier discussion).

We have used the PdI_2 complex bearing bisphosphane ligand **8** as catalyst precursor in several catalytic runs. The results collected in entry 9 (Table 1) were obtained by mixing the PdI_2 complex (50 μmol) with 220 μmol $AgBF_4$ and the substrate used before the Grignard compound was added. The catalytic results thus obtained were not different from those obtained without added $AgBF_4$. 1-Phenyl-2-butene (**6**), with low $E/(E+Z)$ ratios, was formed as the prevailing product in small yield [23]. We obtained extraordinarily large amounts of linear product **6** and an $E/(E+Z)$ ratio equal to 0.56 in the catalytic run using branched substrate VI and Grignard compound **7** as starting compounds. A comparison of the chemistry of palladium and nickel allyl complexes [28] reveals that the equilibrium between η^3-allyl complexes of type **A-3** (see Scheme 1) and η^1-allyl complexes of type **A-1** lies far on the side of η^3-allyl complexes in the case of nickel. Reductive elimination of cross-coupling products from palladium η^1-allyl complexes, present in large amounts in this case [28], could explain the different regioselectivity of palladium catalysis. We reach the conclusion that our palladium complex is not well suited for asymmetric cross-coupling reactions of Grignard compounds with allylic substrates [23]. In comparison with the nickel complex bearing the same chiral ligandm smaller amounts of branched product **3** with an optical purity close to zero are formed in the case of the palladium complex.

3.2. *Catalysis with $NiCl_2$ complexes of P,N-monophosphane ligand (9)*

In catalytic runs with $NiCl_2$ complexes of monophosphane ligand (**9**), we have maintained the nickel/substrate ratio of 100, but we have varied the ligand (**9**)/nickel ratio (see Table 2). 3-Phenyl-1-butene (**3**) was formed with very low optical induction (optimum 5% ee). We can now compare enantioselectivities, achieved with $NiCl_2$ complexes bearing either bisphosphane **8** or *P,N*-monophosphane **9**, in Grignard cross-coupling or allylic cross-coupling catalysis. Enantioselectivity obtained with $NiCl_2$-**8** (bisphosphane) complexes ($\ln(R/S) = -2.40$) is clearly superior to that obtained with $NiCl_2$-**8** (*P,N*-monophosphane) complexes ($\ln(R/S) = \pm 0.1$) in the case of allylic cross-coupling catalysis. Enantioselective Grignard cross-coupling catalysis, using **1** and **2** as starting compounds, can be best done with $NiCl_2$-**8** (*P,N*-monophosphane, (*S*)-configuration as in Scheme 1; $\ln(R/S) = 2.8$ [6]) complexes and not with $NiCl_2$-**8** ((*R,R*)-bisphosphane as in Scheme 1; $\ln(R/S) = -0.1$ [6]) complexes. In spite of the fact that the basic sequence of elementary steps, namely oxidative addition, transmetallation and reductive elimination of the cross-coupling product **3** is the same in both cases, the step which is responsible for enantioselection must be different.

Catalytic runs using 5 mmol of substrates I or II and 10 mmol of Grignard compound **7** as starting materials gave increasing amounts of products **3** and **6** when the **9**/nickel ratio was raised. The $E/(E+Z)$ ratios observed for the major product **6** are similar to the $E/(E+Z)$ ratios of the substrates used. These results can be explained on the basis of general principles of (η^3-allyl)-nickel chemistry. The most favourable reductive elimination of cross-coupled products (**3** and **6**) from a nickel centre [29] can be done from $L_2Ni(\eta^3$-allyl)Ph (L = monophosphane, total 18 e^- count) and from the corresponding bisphosphane complexes of type **B** (Scheme 3). The distribution [30] of $NiL_n(\eta^3$-allyl)Ph complexes ($n = 0, 1, 2$) and the catalytic results depend on the ligand/nickel ratio in catalysis with nickel monophosphane complexes. The improved selectivity and yield obtained at a **9**/nickel ratio of 3.5 compared with catalytic runs with a **9**/nickel ratio of 2 reveal that high concentrations of $L_2Ni(\eta^3$-allyl)Ph complexes are present at high **9**/nickel ratios only. These $L_2Ni(\eta^3$-allyl) complexes are also responsible for the interconversion of diastereomeric (η^3-allyl)Ni complexes via π–σ–π isomerisations (see Section 1). Our results agree with catalytic runs done with PPh_3 as monophosphane ligand [23,31], which revealed that π–σ–π isomerisations are slower in the case of the $Ni(PPh_3)_2$ catalyst compared with Ni-{1,2-bis(phosphanyl)ethane} type catalysts [28].

Allylic cross-coupling of substrates V and VI catalysed by $NiCl_2$-CHIRAPHOS [25] were not influenced by the choice of the ether solvent (diethyl ether or THF) used. Our catalytic results obtained with either phenylmagnesium chloride (**7**) in THF or with phenylmagnesium bromide in diethyl ether and $NiCl_2$-monophosphane (**9**) complexes are collected in Table 2. They show that this allylic cross-coupling is influenced either by the ether solvent or by the halide anion present in the Grignard compound. A solution of phenylmagnesium chloride (**7**) in diethyl ether cannot be prepared [17].

We conclude that the mechanistic picture (in Scheme 3) and general principles of allyl-nickel and allyl-palladium chemistry can explain the major part of our catalytic results. Nickel complexes bearing bisphosphane ligands are superior catalysts compared with palladium complexes bearing the same ligands. Nickel complexes bearing *P,N*-monophosphane ligands are as poor catalysts as are nickel complexes bearing simple monophosphanes [23,31]. There is no selectivity increase in the contribution of the nitrogen ligating site.

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