

# Hydrovinylation of olefins catalyzed by cationic nickel complexes $[\text{Ni}(\text{2,4,6-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})\text{P}_2]\text{BF}_4$

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## Abstract

The hydrovinylation of several olefins and alkynes by the ionic nickel precursor *trans*- $[\text{Ni}(\text{2,4,6-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})(\text{P}(\text{CH}_2\text{Ph})_3)_2]\text{BF}_4$  in THF solution was studied. The activity of the catalytic system showed strong dependence on the nature of the substrate. Only conjugated diolefins and some strained mono-olefins led to hydrovinylation products with nearly complete conversion. Selectivity was also variable: for norbornene, *exo*-2-vinylnorbornane (94%) was obtained selectively, whereas isoprene gave a mixture of 9 hydrovinylation compounds. The turnover rate of the reaction at 25°C and 15 bar of initial pressure of ethylene with an olefin/[Ni] ratio of 1000/1 was 4300 h<sup>-1</sup> for norbornene and 30 h<sup>-1</sup> for isoprene. The chiral monodentate phosphines, (*cis*-myrtenyl)diphenylphosphine and myrtenyldiphenylphosphine, were obtained. The catalytic precursors containing these phosphines were being tested in the hydrovinylation of styrene and norbornene, and the enantiomeric excess obtained was between 3–7%. Diphenylacetylene was also found to be active in the hydrovinylation reaction; *cis*- and *trans*-3,4-diphenyl-1,3-hexadiene, products of a double vinylation of the triple bond were obtained. © 1997 Elsevier Science B.V.

**Keywords:** Codimerization; Hydrovinylation; Nickel; Ethylene; Olefins; Dienes

## 1. Introduction

The catalytic codimerization of olefins is an interesting method for the production of higher functionalized olefins which find extensive application as industrial intermediates [1–5]. The codimerization with ethylene is called hydrovinylation [6]. We have observed that simple compounds, such as  $[\text{Ni}(\text{2,4,6-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})(\text{PR}_3)_2]\text{BF}_4$ , are one-component precursors of active species in the catalytic prepara-

tion of 3-phenyl-1-butene, from styrene [7]. The extent of the hydrovinylation of the styrene derivatives depends on the position of the substituents in the styrene molecule.

However, this one component nickel system has not been tested with other olefins. In this work we complete the study of the scope of this system with a selected group of olefins and some related alkynes.

The detection of 2,4,6-trimethylstyrene from the crude reaction mixture, which is the expected product of the  $\beta$ -elimination after insertion of ethylene in the Ni-(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) bond, is a good indication of the formation of

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the initial hydride, the active species in the hydrovinylation process. These precursors can catalyze the dimerization of ethylene [8]. Therefore the formation of different amounts of butenes also acts as a test of the proper preparation of the species that are the active intermediates for both processes, and provides information about the relative competence between the olefin and ethylene present in the reaction medium for such active species.

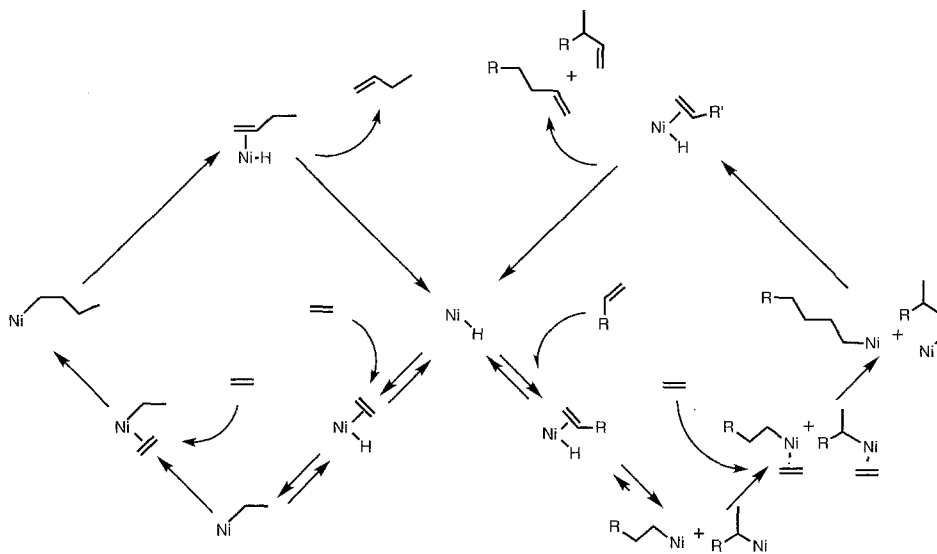
## 2. Results and discussion

The ionic compounds  $[\text{Ni}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})(\text{PR}_3)_2]\text{BF}_4$  ( $\text{PR}_3 = \text{P}(\text{CH}_2\text{Ph})_3$  and  $\text{P}(i\text{-Bu})_3$ ) catalyze the codimerization of styrene and ethylene in THF above  $20^\circ\text{C}$  [7]. Since these complexes can dimerize ethylene [8], variable amounts of butenes are also obtained. Comparison of the amounts of ethylene consumed at a reference time gave an idea about the competition for the active sites between ethylene and the olefin. The reaction rates for the dimerization of ethylene were always slower in the presence of olefins. In the experimental conditions used in this work at a

ratio olefin/ $\text{Ni} = 1000$  with the same amount of precursor a fall of about 5 bar of pressure was expected to complete the stoichiometric codimerization reaction; with a ratio olefin/ $\text{Ni} = 500$  the fall is  $\sim 2.5$  bar. As a reference, in reactions carried out at  $25^\circ\text{C}$  the gas pressure measured after 2 h in experiments starting with 15 bar ethylene were  $\sim 1$  and 3.5 bar for the dimerization of ethylene and codimerization with styrene, respectively.

The catalytic runs were carried out at 15 or 25 bar of initial ethylene pressure in a thermostatic cooling bath at several temperatures. However, at 25 bar, if the precursor was activated and the competition of the olefin with ethylene for the active hydride was not significant, a fast rise in temperature was observed between five and twenty minutes after initial pressurization due to the exothermic oligomerization of ethylene. After this non-controlled reaction, the catalytic species decomposed, and the final pressure reported is that observed when the initial temperature of  $25^\circ\text{C}$  was recovered (Scheme 1).

The precursor used with all the olefins was  $[\text{Ni}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})(\text{P}(\text{CH}_2\text{Ph})_3)_2]\text{BF}_4$ . In some cases other phosphine ligands,



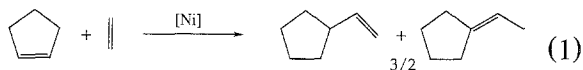
Scheme 1.

such as  $P(i\text{-Bu})_3$  and  $\text{PCy}_3$ , were also tested. Direct measurements by  $^{31}\text{P}$  NMR at room temperature of the solutions of the ionic nickel compounds in the presence of olefins always showed the same signal as that observed with the catalytic precursor, with the exception of 2-vinylpyridine, suggesting that in these conditions the olefins tested did not substitute the  $\text{CH}_3\text{CN}$  ligand.

### 2.1. Non-functionalized mono-olefins

(-)- $\alpha$ -Pinene, (+)-2-carene and (-)-camphene were tested at 15 bar and 25°C. In these cases no hydrovinylation reaction was observed, but dimerization of ethylene took place at a slower rate than in the absence of olefins. For instance with camphene, the ethylene pressure was still 5 bar after 3 h. With vinylcyclohexane neither of the two competitive reactions was observed, even when the pressure of ethylene was raised to 25 bar, but the precursor was not recovered. With cyclopentene, after 1 h in the same conditions, 4% of the initial olefin was

converted into two hydrovinylation products (Eq. (1)) in a ratio 3/2, but pressure fell to  $\sim 1$  bar, showing that the preferred reaction in this case was the dimerization of ethylene. In different conditions, a mixture of isomers of ethylcyclopentenes and ethylidencyclopentane has been reported using  $\text{PdCl}_2$  as catalytic precursor [9] (Table 1).



When norbornene was used a selective and fast reaction took place (Table 1, Eq. (2)). In this case the selectivity towards *exo*-2-vinyl-norbornane was nearly 95%. Isomerization products ( $\text{C}_9$ ), derivatives of double ethylene insertion ( $\text{C}_{11}$ ) and compounds containing two norbornene molecules and one of ethylene ( $\text{C}_{16}$ ) were present in low quantities. The dimerization of ethylene began after consumption of all the norbornene. The effect of the size of the  $\text{PCy}_3$  ligand was apparent either by the difficult  $\beta$ -elimination from the ethenyl complex, product

Table 1

Results of the hydrovinylation reaction of olefins catalyzed by  $\text{trans}[\text{Ni}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})(\text{P}(\text{CH}_2\text{Ph})_2)_2]\text{BF}_4$

Olefin	Conversion <sup>a</sup> (%)	Hydrovinylation <sup>b</sup> (%)	$P_{\text{initial}}$ (bar)	$P_{\text{final}}$ (bar)	Time (h)	$T_{\text{max}}$ (°C)
(-)- $\alpha$ -pinene			15	9	1/2	25
(+)-2-carene			15	12	3	25
(-)-camphene			15	5	3	25
Vinylcyclohexane			25	25	3	30
Allylbenzene			25	25	3	30
Cyclopentene	4	4	15	1	1	25
1,5-hexadiene	10–85 <sup>c</sup>	0.5–40	15–25	11–18	3–1/2	90
2,5-dimethyl-2,4-hexadiene	2	2	25	18	1/2	90
<i>cis,cis</i> -1,5-cyclooctadiene	19 <sup>c</sup>	2	15	5	3	25
Isoprene	20–95	20–95	15–25	6–5	6–1/2	25–130
Cyclopentadiene	0.5	0.5	15	15	3	25
Indene	3 <sup>c</sup>	3	15	6	3	25
Methyl acrylate <sup>d</sup>	10	10	25	24	3	25
Vinyl acetate <sup>d</sup>	3	3	25	25	3	40
2-vinylpyridine			15	15	3	25
Acrylonitrile			15	15	3	30
3,4-dihydro-2H-pyran			15	9	3	25

Conditions: [olefin]/[Ni] = 500; 10 ml of THF.

<sup>a</sup> Transformation of initial olefin.

<sup>b</sup> Codimerization products.

<sup>c</sup> See text.

<sup>d</sup> [olefin]/[Ni] = 1000.

Table 2

Hydrovinylation of norbornene with  $[\text{Ni}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})(\text{PR}_3)_2][\text{BF}_4]$ ; 1: R =  $\text{CH}_2\text{Ph}$ ; 2: R = *i*-Bu; 3: R = Cy

Run	Catalyst	Solvent	Time (min)	Conversion	Selectivity <sup>a</sup>	TOF/h	C <sub>9</sub>	C <sub>11</sub>	C <sub>16</sub>	P <sup>b</sup>
1	1	THF	14	99.9%	94.2%	> 4300	2.05%	1.3%	2.45%	9
2	2	THF	14	28.6%	95.3%	1240	0.2%	1.5%	3.0%	13
3	3	THF	14	87.5%	92.8%	3800	0.35%	5.1%	1.55%	7
4	2	THF	180	99.9%	94.8%	335	2.2%	0.8%	2.2%	8
5	1	$\text{CH}_2\text{Cl}_2$	180	41.6%	93.5%	141	1.0%	1.1%	4.4%	12
6	1	toluene	180	10.4%	95.3%	35	—	—	4.7%	14

Conditions: [Norbornene]/[Ni] = 1000; Initial pressure of 15 bar of ethylene; 25°C; 10 ml of solvent.

<sup>a</sup> Toward *exo*-2-vinylnorbornane.<sup>b</sup> Final ethylene pressure.

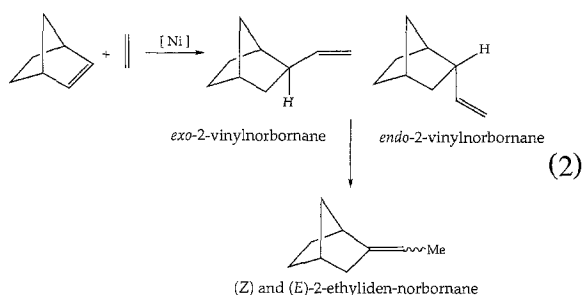
of the first vinylation, that led to a 5% of a compound containing two ethylene and one norbornene units and by the extension of the competitive reaction of dimerization (final pressure of 7 bar after 14 min). The results published about this reaction refers mainly to catalytic synthesis of pure enantiomers of the hydrovinylation products [1,10–13].

Norbornadiene has been mono-vinylated using  $[\text{Ni}(\text{acac})_2]/\text{Et}_x\text{Al}_2\text{Cl}_{6-x}/\text{dppe}$  with low selectivity at  $-30^\circ\text{C}$  [14].

The hydrovinylation reaction was very sensitive to the solvent (Table 2), but this was not observed in the reaction with styrene [7], probably because norbornene was more efficient competing with  $\text{CH}_3\text{CN}$  in a coordinating solvent.

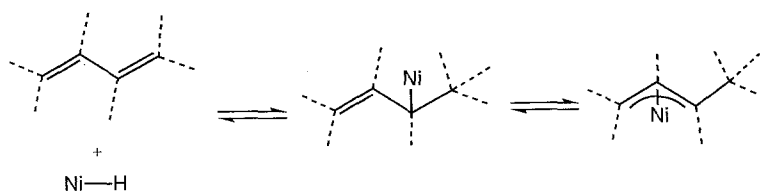
The organometallic precursor  $[\text{Ni}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})(\text{PCy}_3)_2][\text{BF}_4]$  was tested in the dimerization of ethylene and in the hydrovinylation of styrene in the same conditions. The selectivity towards 1-butene was 96% and the TOF found to be  $3680\text{ h}^{-1}$ , better than the results obtained with precursors containing  $\text{P}(\text{CH}_2\text{Ph})_3$  [8]. The hydrovinylation afforded 3-phenyl-1-butene with 90% selectivity and a

TOF of  $113\text{ h}^{-1}$ , which are lower than the values reported with  $\text{P}(\text{CH}_2\text{Ph})_3$  or  $\text{P}(\textit{i}\text{-Bu})_3$  due to the competence of the dimerization process [7].



## 2.2. Non-functionalized di-olefins

A group of dienes were tested in the hydrovinylation reaction. Conjugated dienes always showed activity with the extension depending on the steric hindrance of the diene and the accessibility of the allyl intermediate after insertion in the Ni–H bond (Scheme 2). The formation of these relatively stable allyl intermediates compared to the equivalent alkyl-nickel inter-



Scheme 2.

mediate could be the factor determining the chemoselectivity of the reaction, hydrovinylation versus dimerization (Scheme 1) and the selectivity observed [7,15].

The hydrovinylation of isoprene gave a mixture of five  $C_7H_{12}$  products in similar amounts when the reaction was performed at 25°C and 15 bar of initial ethylene pressure. The activity was relatively low: a conversion of 20% was observed in 6 h, with the dimerization process competing at lower rate (final pressure of 6 bar). Under 25 bar of initial pressure the temperature increased to 130°C, and in 1/2 h conversion of isoprene was almost complete (95%), with a final pressure of 5 bar. The selectivity to hydrovinylation products remained low (nine  $C_7H_{12}$  compounds were observed), and four  $C_9H_{16}$  compounds containing one isoprene and two ethylene units also appeared. This reaction has been previously described with different systems based on  $RhCl_3 \cdot 3H_2O$  [16],  $[Fe(acac)_3]/AlEt_3$  [17,18] or  $CoCl_2$ /phosphite [19], 4-methyl-1,4- and 5-methyl-1,4-hexadienes were obtained in ratios 50/50–80/20.

The hydrovinylation of 2,5-dimethyl-2,4-hexadiene was observed only when the initial ethylene pressure was 25 bar, the temperature reached 90°C and the conversion to 3-isopropyl-5-methyl-1,4-hexadiene was only ~2%; the final pressure was 18 bar after 1/2 h reaction. The difference with isoprene may be related to the decrease in the coordination ability of the olefin due to the steric hindrance of the substituents. When the reaction was carried out at 25°C and 15 bar of initial pressure with a nonconjugated linear diene such as 1,5-hexadiene, only 0.5% of hydrovinylation products and 9.5% of isomers of 1,3-, 1,4- and 2,4-hexadienes were obtained. However, at an initial pressure of 25 bar, the temperature reached 90°C and after 1/2 h the remaining pressure was 18 bar. 85% of the starting hexadiene was converted to a mixture of isomers of hexadiene (45%) and fourteen octadiene isomers (40%) products of the hydrovinylation reaction with low selectivity. Only 3-methyl-1,4-

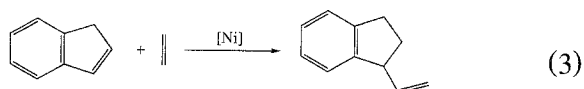
heptadiene and 3-ethyl-1,4-hexadiene were clearly identified. The hydrovinylation took place when the initial diene isomerized to reach conjugation, as proposed by Alderson et al. [16].

Cyclic non-conjugated diolefins such as *cis,cis*-1,5-cyclooctadiene, at 15 bar and 25°C, gave only 2% of hydrovinylation products, 3-ethenylcyclooctene and other isomer (ratio 9/1), which were probably formed from conjugated 1,3-cyclooctadiene since a 17% of 1,4- and 1,3-cyclooctadienes were recovered together with 81% of unreacted 1,5-cyclooctadiene. The final pressure of 5 bar after 3 h showed that the dimerization of ethylene was significant.

The conjugated cyclopentadiene can block the process due to the stability of the allyl intermediate. The reaction carried out at 15 bar of initial pressure gave after 3 h only 0.5% of 3-vinylcyclopentene, the final pressure remained at ~15 bar, but the final solution was yellow with a  $^{31}P$  NMR signal (12 ppm, broad, room temperature) different from that of the precursor, and contained 2,4,6-trimethylstyrene. Butenes were not detected.

The preparation of 3-vinylcyclopentene with enantiomeric excess of 95% has been reported by Wilke et al. [1,13], who used a chiral phosphine large enough to preclude stabilization of the allyl intermediate responsible for the selectivity.

Indene showed similarities with cyclopentadiene and styrene: the reaction was slow like that of cyclopentadiene, but selectivity was 100% for 1-ethenylindene (Eq. (3)). Competition for the dimerization reaction was high, in 3 h the pressure fell from 15 bar to 3 bar. The conversion was 3% in 3 h, but in 24 h, after replacing the initial pressure of ethylene three times, a 15% conversion was achieved.



Neither hydrovinylation nor dimerization was observed with allylbenzene; even 2,4,6-trimeth-

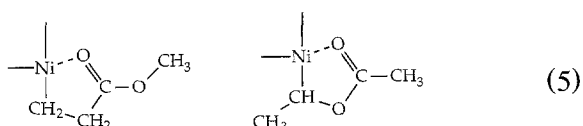
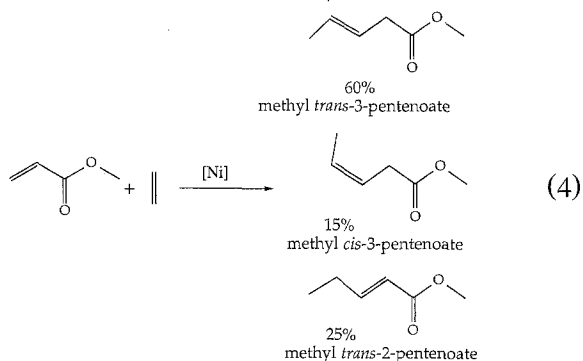
ylstyrene was not detected, as expected when the precursor remained intact.

### 2.3. Functionalized olefins

When the olefin contained a coordination atom such as nitrogen or oxygen, the competition for the labile position in the coordination sphere of the nickel complex was enough to block even the activation of the precursor, as observed with acrylonitrile or 2-vinylpyridine. The  $^{31}\text{P}$  NMR spectra of solutions of the precursor and these olefins showed a new signal at 8.5 ppm with 2-vinylpyridine, but no displacement with respect to the signal of the precursor with acrylonitrile (9.4 ppm). With 3,4-dihydro-2H-pyran the precursor was activated at 25°C and 15 bar of ethylene and dimerization took place slowly (final pressure 9 bar after 3h), but no vinylation was observed.

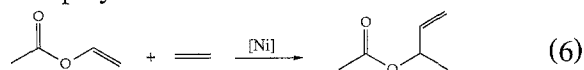
Brookhart et al. [20] did not observe the dimerization of 2-vinylpyridine with rhodium systems active with methyl acrylate.

The hydrovinylation reaction of methyl acrylate carried out under 25 bar of initial pressure and at 25°C showed a negligible contribution of the ethylene dimerization; after 3 h a final pressure of 24–25 bar was recorded, but detection of 2,4,6-trimethylstyrene suggest that the precursor was activated. Three isomers of the product of vinylation at the terminal carbon were obtained with low conversion ( $\sim 10\%$ ) (Eq. (4)). The absence of activity towards both reactions and the selectivity observed suggest the stabilization of species containing five-membered rings (Eq. (5)). At higher temperatures polymerization of methyl acrylate begins. Barlow using  $[\text{PdCl}_2(\text{PhCN})_2]$  at 105°C reported very similar selectivity in the same reaction [9]. The Rh and Ru salts used at high temperatures by Alderson [16] gave a mixture of hydrovinylation products and methyl acrylate dimers. Nickel complexes have been used in similar reactions such as the co-oligomerization of butadiene and methyl acrylate [21].



The structure of the proposed intermediates containing five and six-membered rings has been characterized in similar reactions with other metals and with analogous consequences [20,22–26].

Reactions performed with vinyl acetate under 25 bar of ethylene at 40°C gave only one product of hydrovinylation (Eq. (6)), although with a low conversion (3%) in 3 h. The results, like that observed with methyl acrylate, could be explained by the formation of five-membered ring intermediates (Eq. (5)), as expected when the vinyl addition takes place in the internal carbon of the olefin. Therefore, the conversion of the olefin and the rate of dimerization were consequently low. The product was identified through the fragment analysis of the mass spectra [27]. The reaction did not take place at temperatures lower than 40°C, but at 60°C thermal polymerization was observed.



### 2.4. Nickel precursors containing chiral phosphines

Precursors containing bidentate phosphines were not useful in the hydrovinylation reaction

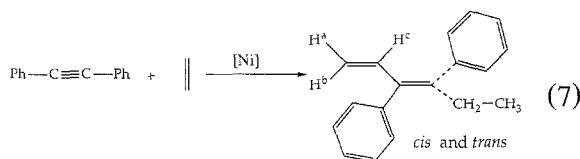
[7], therefore two monodentate chiral phosphines  $\text{PPh}_2\text{R}^*$  ( $\text{R}^* = \text{myrtenyl, cis-myrtanyl}$ ) were obtained. The preparation of analytically pure samples of the complete series of  $[\text{NiBr}_2(\text{PPh}_2\text{R}^*)_2]$ ,  $\text{trans-}[\text{NiBr}(\text{2,4,6-Me}_3\text{C}_6\text{H}_2)(\text{PPh}_2\text{R}^*)_2]$  and  $\text{trans-}[\text{Ni}(\text{2,4,6-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})(\text{PPh}_2\text{R}^*)_2]\text{BF}_4$  compounds were possible only with  $\text{PPh}_2(\text{cis-myrtanyl})$ . The compounds containing  $\text{PPh}_2(\text{myrtenyl})$  present high lability and poor stability in solution towards oxidation of the phosphine. Nevertheless, the catalytic test was carried out with both samples.

Styrene and norbornene were tested with the  $\text{trans-}[\text{Ni}(\text{2,4,6-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})\text{-}(\text{PPh}_2\text{R}^*)_2]\text{BF}_4$  precursors, and the results are collected in Table 3. Low asymmetric induction was observed, but the high activity of the precursor containing  $\text{PPh}_2(\text{cis-myrtanyl})$  was unexpected, since it seems that the intermediate hydrides are more stabilized by basic and bulky phosphines as observed in the dimerization of ethylene [8]. In the reaction with norbornene 29% of products containing two norbornene and one ethylene units ( $\text{C}_{16}$ ) were obtained.

Wilke et al. [1,12,13] have achieved high enantiomeric excess in these reactions using allyl-nickel systems containing a phosphine ligand and with twelve chiral centers. With norbornene at  $-65^\circ\text{C}$  and styrene or substituted styrenes at  $-70^\circ\text{C}$  a 53% ee to an isomer of the *exo*-form and the range 85–95.2% ee of 3-aryl-1-butenes were obtained respectively.

## 2.5. Reactions with alkynes

When alkynes such as phenylacetylene, diphenylacetylene or dimethyl-2-butindioate were tested, at  $30^\circ\text{C}$  with 25 bar of ethylene and a ratio alkyne/ $[\text{Ni}] = 300$ , a double vinylation product was observed only with diphenylacetylene (Eq. (7)). The 40% conversion was achieved in 3h (TOF  $40 \text{ h}^{-1}$ ). The activation of the precursor was not observed in the experiments with phenylacetylene or dimethyl-2-butindioate.



*cis*- and *trans*-isomers of 3,4-diphenyl-1,3-hexadiene were obtained in similar amounts (3/2) as could be suggested from their NMR spectra. Two ethyl groups appeared, at 0.8 (t,  $\text{CH}_3$ ), 2.25 (q,  $\text{CH}_2$ ) and 1.0 (t,  $\text{CH}_3$ ), 2.6 (q,  $\text{CH}_2$ ) ppm, both with  $^3J_{\text{HH}} = 7.5 \text{ Hz}$ . The signals of the olefinic protons of the two isomers appeared superimposed, the major isomer at 5.05 ppm ( $H^a$ ) and 5.20 ppm ( $H^b$ ), with the coupling constants:  $^3J_{\text{trans}} = 17.1 \text{ Hz}$ ,  $^3J_{\text{cis}} = 10.7 \text{ Hz}$  and  $^2J_{\text{gem}} = 1.8 \text{ Hz}$ , typical values for 1,3-dienes. The internal olefinic proton,  $H^c$ , expected about 6.5 ppm may be masked by the signals of the aromatic protons. Therefore the reaction performed could be interpreted as a

Table 3

Results of the hydrovinylation reaction with  $\text{trans-}[\text{Ni}(\text{2,4,6-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})(\text{PPh}_2\text{R}^*)_2]\text{BF}_4$  precursors

$\text{R}^*$	Olefin	% conversion (time)	% selectivity <sup>a</sup>	% ee	$P^b$
<i>cis</i> -Myrtanyl	styrene	100 (1/2 h)	96.6	7	8
Myrtenyl	styrene	25 (3 h)	96.7	3	12
<i>cis</i> -Myrtanyl	norbornene	56.5 (1 h)	65.0	4	12

Conditions:  $[\text{olefin}]/[\text{Ni}] = 1000$ ; Initial pressure of 15 bar of ethylene;  $25^\circ\text{C}$ ; 10 ml of THF.

<sup>a</sup> Towards 3-phenyl-1-butene or *exo*-2-vinylnorbornane.

<sup>b</sup> Final ethylene pressure.

double vinylation followed by a double-bond isomerization.

The same reaction with diphenylacetylene has been tested by Battiste using  $[\text{PdCl}_2(\text{PhCN})_2]$  as precursor giving *trans-trans*-3,4-diphenyl-2,4-hexadiene which evolves with time to indene isomers [28].

### 3. Concluding remarks

The ionic compounds of the type *trans*- $[\text{Ni}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)(\text{CH}_3\text{CN})(\text{PR}_3)_2]\text{BF}_4$  used as precursors in the hydrovinylation reaction showed good catalytic properties when conjugated dienes were used, including ring-substituted styrene derivatives. Moreover, strained olefins like norbornene showed good activity in the reaction. The selectivity with the conjugated dienes depends on the preferred stabilization of one of the allyl intermediates, as in the case of the styrene toward 3-phenyl-1-butene (97%) [7,15]; in the case of norbornene the selectivity to the *exo*-derivative may be steric in origin.

The precursor was activated by ethylene in the presence of many olefins but the quenching of the process was easily observed when some stable bidentate intermediates were formed, either by formation of a stable allyl complex, as in the case of cyclopentadiene, or by the formation of five-membered rings, as in the case of methyl acrylate or vinyl acetate, where the dimerization of ethylene was not observed in spite of the activation of the precursor. Therefore, the small amounts of hydrovinylation products obtained was coherent with this interpretation of the results.

## 4. Experimental

### 4.1. General remarks

Infrared spectra were recorded on a Nicolet 520 FT-IR spectrometer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were obtained using either a Varian

Gemini200 or a Bruker DRX250 spectrometer. Chemical shifts ( $\delta$  in ppm) are reported downfield relative to  $\text{Me}_4\text{Si}$  or  $\text{H}_3\text{PO}_4$  (85%) standards. Assignment of proton NMR signals was achieved with the help of COSY  $^1\text{H}$ - $^1\text{H}$  and COSY  $^1\text{H}$ - $^{13}\text{C}$  experiments carried out in a Varian VRX-500 spectrometer. GC analyses were performed on a Hewlett-Packard 5890 equipped with a 50 m ultra-2 cross-linked 5% phenyl-methyl silicone capillary column and an F.I.D. detector connected to an HP 3396A integrator. Mass spectra were obtained from a Hewlett-Packard 5890 chromatograph equipped with the same column coupled to a Hewlett-Packard 5971A Mass selective detector. Enantiomeric excess was determined by G.C. analysis with a 50 m FS-CYCLODEX- $\beta$  column.

All solvents were purified by standard methods. THF was distilled over sodium-benzophenone under nitrogen before use. Non-chiral phosphines were purchased or prepared according to described procedures [29]. Ethylene (99.95% Quality) was used as received. Olefins were used as received from Fluka or Aldrich.

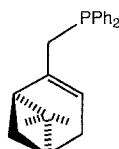
### 4.2. Preparations

#### 4.2.1. Synthesis of myrtenyldiphenylphosphine, $\text{PPh}_2(\text{myrtenyl})$

(a) Synthesis of myrtenyl bromide: 5.87 g (21.7 mmol) of  $\text{PBr}_3$  was added at  $0^\circ\text{C}$  to a suspension of (1*R*)-(-)-myrtenol (9.89 g, 65 mmol) and  $\text{CaH}_2$  in ether (140  $\text{cm}^3$ ). After stirring overnight at room temperature the mixture was hydrolyzed, and the organic phase was separated and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The product, a pale yellow liquid was obtained by evaporation of the solvent. (Yield: 11.19 g, 80%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 308 K):  $\delta$  (ppm) 0.83 (s, 3 H, Me), 1.31 (s, 3 H, Me), 2.00–2.50 (m, 6 H), 3.95 (s, 2 H,  $\text{CH}_2\text{Br}$ ), 5.65 (s, 1 H,  $\text{CH}=\text{C}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 308 K):  $\delta$  (ppm) 21.1, 26.0, 31.3, 31.5, 37.8, 37.9, 40.3, 44.8, 123.1, 144.1. Mass spectra ( $m/z$ ): 91 (100), 119 (9), 135 (21), 199 (0.4), 201 (0.4), 214 ( $\text{M}^+$ , 5), 216 (5).



(b) Synthesis of myrtenyldiphenylphosphine  $\text{PPh}_2(\text{myrtenyl})$ :  $7.12 \text{ cm}^3$  (11.4 mmol) of a solution of 1.6 M of  $^n\text{BuLi}$  in hexane was added to a solution of  $\text{HPPH}_2$  (2.13 g, 11.4 mmol) in THF ( $60 \text{ cm}^3$ ) at  $-78^\circ\text{C}$ , the temperature was allowed to rise to room temperature and the mixture was stirred for 1 h. Then, this solution was cooled to  $0^\circ\text{C}$ , and slowly added to a solution of myrtenyl bromide (2.45 g, 11.4 mmol) in THF ( $40 \text{ cm}^3$ ). After 1 h at room temperature the solution was hydrolyzed and the organic phase was separated and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The phosphine is a resin that was obtained by concentration to dryness. (Yield: 3.47 g, 95%).  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF, 240 K):  $\delta$  (ppm)  $-23.3$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 308 K):  $\delta$  (ppm) 0.69 (s, 3 H, Me), 1.17 (s, 3 H, Me), 1.85–2.35 (m, 6 H), 2.75 (m, 2 H,  $\text{CH}_2\text{P}$ ), 5.08 (m, 1 H,  $\text{CH}=\text{}$ ), 7.15–7.80 (m, 10 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 308 K):  $\delta$  (ppm) 21.3, 26.2, 31.3, 31.7, 37.9 (d,  $^1J_{\text{CP}} = 12.77$  Hz), 40.1, 40.4, 46.8 (d,  $^3J_{\text{CP}} = 6.44$  Hz), 119.1 (d,  $^3J_{\text{CP}} = 10.96$  Hz), 143.4 (d,  $^2J_{\text{CP}} = 6.39$  Hz); aromatic carbons: 128.1 (d,  $^3J_{\text{CP}} = 3.67$  Hz), 128.2 (d,  $^3J_{\text{CP}} = 3.67$  Hz), 128.4, 132.6 (d,  $^2J_{\text{CP}} = 2.72$  Hz), 133.0 (d,  $^2J_{\text{CP}} = 1.81$  Hz), 139.2 (d,  $^1J_{\text{CP}} = 13.73$  Hz). Mass spectra ( $m/z$ ): 108 (33), 183 (100), 265 (32), 291 (7), 305 (19), 320 ( $\text{M}^+$ , 29).



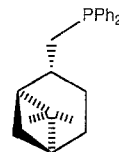
(1R)-Myrtenyldiphenylphosphine

#### 4.2.2. Synthesis of (*cis*-myrtanyl)diphenylphosphine, $\text{PPh}_2(\text{cis-myrtanyl})$

(a) Synthesis of *cis*-myrtanyl tosylate according to reported method [30]: To 7.7 g (40.4 mmol) of tosyl chloride was added a solution at  $0^\circ\text{C}$  of (–)-*cis*-myrtanol (5.67 g, 36.7 mmol) in dry pyridine ( $20 \text{ cm}^3$ ). The resulting mixture was stirred at room temperature for 16 hours

and hydrolyzed with HCl 2 M; after extraction with  $\text{CHCl}_3$ , the organic phase was dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the crude tosylate was purified by slow recrystallization from ether. (Yield: 10.55 g, 93%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 308 K):  $\delta$  (ppm) 0.79 (s, 3 H), 1.09 (s, 3 H), 1.15–2.40 (m, 9 H), 2.45 (s, 3 H), 3.93 (d, 2 H,  $^3J_{\text{HH}} = 7.86$  Hz), 7.35 (d, 2 H,  $^3J_{\text{HH}} = 8.30$  Hz), 7.79 (d, 2 H,  $^3J_{\text{HH}} = 8.30$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 308 K):  $\delta$  (ppm) 17.9, 21.6, 22.9, 25.5, 27.6, 32.5, 38.7, 40.0, 41.0, 42.4, 74.3, 127.9, 129.8, 133.4, 144.6.

(b) Synthesis of (*cis*-myrtanyl)diphenylphosphine,  $\text{PPh}_2(\text{cis-Myrtanyl})$ :  $6.08 \text{ cm}^3$  (9.74 mmol) of a solution of 1.6 M of  $^n\text{BuLi}$  in hexane was added to a solution of  $\text{HPPH}_2$  (1.82 g, 9.74 mmol) in THF ( $50 \text{ cm}^3$ ) at  $-78^\circ\text{C}$ , then, the solution was allowed to warm to room temperature and stirred for 1 h. Then, this solution was added over a solution of *cis*-myrtanyl tosylate (3.00 g, 9.73 mmol) in THF ( $40 \text{ cm}^3$ ). The solution was hydrolyzed with a deoxygenated aqueous  $\text{NH}_4\text{Cl}$  solution. The organic phase was separated and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The phosphine was obtained as a resin by concentration to dryness. (Yield: 2.83 g, 90%).  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF, 308 K):  $\delta$  (ppm)  $-20.7$ . Mass spectra ( $m/z$ ): 183 (81), 199 (100), 239 (25), 279 (36), 307 (9), 322 ( $\text{M}^+$ , 14).

(1S,2R,5S)-*cis*-Myrtanyldiphenylphosphine

#### 4.2.3. Synthesis of *trans*-dibromobis((*cis*-myrtanyl)diphenylphosphine)nickel(II) $[\text{NiBr}_2(\text{PPh}_2(\text{cis-myrtanyl}))_2]$

A solution of  $\text{PPh}_2(\text{cis-Myrtanyl})$  (2.10 g, 6.51 mmol) in THF ( $20 \text{ cm}^3$ ) was added to a solution of  $\text{NiBr}_2$  (0.71 g, 3.26 mmol) in ethanol

(10 cm<sup>3</sup>), the green complex precipitates after elimination of the THF. (Yield: 2.67 g, 95%). Analytical data: Calculated for C<sub>44</sub>H<sub>54</sub>Br<sub>2</sub>NiP<sub>2</sub>: %C = 61.21, %H = 6.30. Found: %C = 59.9, %H = 6.4.

#### 4.2.4. Synthesis of *trans*-bromomesitylbis(*cis*-myrtanyl)diphenylphosphine)nickel(II), [NiBr(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)(PPh<sub>2</sub>(*cis*-myrtanyl))<sub>2</sub>]

To a suspension of mesitylmagnesiumbromide in THF was added slowly a solution of [NiBr<sub>2</sub>(PPh<sub>2</sub>(*cis*-Myrtanyl))<sub>2</sub>] (1.45 g, 1.68 mmol) in THF (20 cm<sup>3</sup>) at 0°C. Addition was stopped when the solution acquired a yellow color. Five minutes later the solution was hydrolyzed with a deoxygenated aqueous 5% NH<sub>4</sub>Br solution. The organic phase was separated and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Addition of absolute ethanol caused the precipitation of a yellow complex. The compound was recrystallized from dichloromethane–ethanol. (Yield: 1.02 g, 67%). Analytical data: Calculated for C<sub>53</sub>H<sub>65</sub>BrNiP<sub>2</sub>: %C = 70.52, %H = 7.26. Found: %C = 69.7, %H = 7.1. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 308 K): δ (ppm) 14.1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 308 K): δ (ppm) 0.55 (s, 6 H), 0.98 (s, 6 H), 1.00–2.00 (m, 9 H), 2.07 (s, 3 H), 2.44 (s, 6 H), 3.72 (m, 2 H), 6.25 (s, 2 H), 7.20–7.70 (m, 20 H). [α]<sub>D</sub><sup>24</sup> = +13.6° (c = 0.11 g/100 cm<sup>3</sup>, CH<sub>2</sub>Cl<sub>2</sub>).

#### 4.2.5. Synthesis of *trans*-mesitylacetonitrilebis(*cis*-myrtanyl)diphenylphosphine)nickel(II) tetrafluoroborate, [Ni(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)(CH<sub>3</sub>CN)(PPh<sub>2</sub>(*cis*-myrtanyl))<sub>2</sub>] [BF<sub>4</sub>]

A slight excess of TIBF<sub>4</sub> (0.12 g, 0.41 mmol) was added to a solution of [NiBr(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)(PPh<sub>2</sub>(*cis*-Myrtanyl))<sub>2</sub>] (0.31 g, 0.34 mmol) in THF (25 cm<sup>3</sup>) and acetonitrile was added to the resulting suspension causing the immediate precipitation of TIBr, which was removed by filtration through celite. The yellow ionic compound was crystallized out after addition of *n*-hexane. (Yield: 0.23 g, 71%). Analytical data: Calculated for C<sub>55</sub>H<sub>68</sub>BF<sub>4</sub>NNiP<sub>2</sub>: %C = 69.49, %H = 7.21, %N = 1.47. Found: %C

= 66.6, %H = 7.3, %N = 1.4. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 240 K): δ (ppm) 17.95. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 240 K): δ (ppm) 0.72 (s, 6 H), 1.02 (s, 6 H), 1.10–2.10 (m, 9 H), 1.73 (s, 3 H), 2.11 (s, 3 H), 2.21 (s, 6 H), 3.75 (m, 2 H), 6.37 (s, 2 H), 7.10–7.60 (m, 20 H). [α]<sub>D</sub><sup>24</sup> = -2.5° (c = 0.10 g/100 cm<sup>3</sup>, CH<sub>2</sub>Cl<sub>2</sub>).

#### 4.2.6. Synthesis of *trans*-mesitylacetonitrilebis(tricyclohexylphosphine)nickel(II) tetrafluoroborate, [Ni(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)(CH<sub>3</sub>CN)(PCy<sub>3</sub>)<sub>2</sub>] [BF<sub>4</sub>]

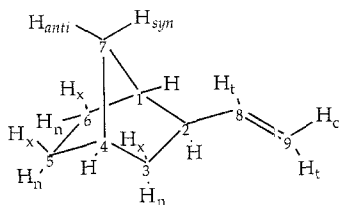
A slight excess of TIBF<sub>4</sub> (0.21 g, 0.69 mmol) was added to a solution of [NiBr(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>] (0.53 g, 0.65 mmol) in THF (70 cm<sup>3</sup>), acetonitrile was also added. After stirring at room temperature for 1 hour, TIBr was filtered off. The yellow ionic compound precipitated when THF was replaced by pentane. (Yield: 0.31 g, 55%). Analytical data: Calculated for C<sub>47</sub>H<sub>80</sub>BF<sub>4</sub>NNiP<sub>2</sub>: %C = 65.14, %H = 9.30, %N = 1.62. Found: %C = 63.8, %H = 9.4, %N = 1.5. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 308 K): δ (ppm) 18.5. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 308 K): δ (ppm) 0.70–2.10 (m, 66 H), 2.29 (s, 3 H), 2.58 (s, 3 H), 2.89 (s, 6 H), 6.47 (s, 2 H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 308 K): δ (ppm) 4.1, 19.9, 25.0, 26.8, 27.6, 30.2, 34.3 (t, <sup>2</sup>J<sub>CP</sub> = 7.98 Hz), 126.9, 128.2, 130.0, 142.0.

### 4.3. Hydrovinylation reactions

Hydrovinylation reactions were performed using a Berghof type reactor of 150 cm<sup>3</sup> capacity equipped with a magnetic stirring bar, two gas valves, a manometer, and a thermocouple. One of the gas valves allowed direct introduction of the solutions with a syringe into either a liner of Teflon, or directly over the steel. No significant change was observed when the type of container was changed. The reactions were also performed in a stainless-steel autoclave fitted with an external jacket connected to a thermostated *i*-butanol bath controlled to ±0.5°C.

A solution of ~25 mg of the organonickel

Table 4  
Proton and  $^{13}\text{C}$  NMR data for *exo*-2-vinylnorbornane



numbering scheme of *exo*-2-vinylnorbornane.

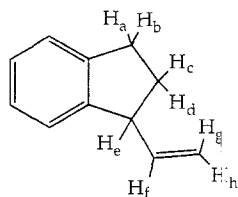
Atom numbering	$\delta(^{13}\text{C}\{^1\text{H}\})^a$	$\delta(^1\text{H})^b$
1	42.3 (31.4)	1.99 (d)
2	45.9 (48.5)	2.02 (dd)
3	37.2 (33.9)	$x = 1.37$ (m); $n = 1.22$ (m)
4	36.6 (30.0)	2.16 (broad)
5	29.7 (29.9)	$x = 1.42$ (m); $n = 1.09$ (m)
6	29.0 (29.4)	$x = 1.42$ (m); $n = 1.13$ (m)
7	35.6 (35.9)	$syn = 1.27$ (m); $anti = 1.025$ (m)
8	144.3 (143.7)	5.66 (ddd)
9	111.4 (111.8)	$t = 4.82$ (ddd), $c = 4.77$ (ddd)

Spectra in  $\text{CDCl}_3$ , chemical shift in ppm.

<sup>a</sup> Calculated values between brackets.

<sup>b</sup> Multiplicity of the signals; Coupling constants in Hz:  $^2J_{7syn7anti} = 10.0$ ;  $^3J_{7syn1} = ^3J_{7syn4} = ^4J_{7syn5n} = ^4J_{7syn6n} = 2.0$ ;  $^3J_{7anti1} = ^3J_{7anti4} = ^4J_{7anti3n} = 1.5$ ;  $^4J_{7anti2} = 2.5$ ;  $^3J_{8t} = 7.5$ ;  $^3J_{8t9t} = 17.0$ ;  $^3J_{8t9c} = 10.0$ ;  $^2J_{9t9c} = 2.0$ ;  $^4J_{9c2} = 1.0$ .

Table 5  
Proton NMR data for 1-ethenylnorbornane



numbering scheme of 1-ethenylnorbornane  
( $\delta$  in ppm, J in Hz,  $\text{CDCl}_3$ , 308 K)

$H_a, H_b = 1.8$ and $2.3$ (m)	$^3J_{ef} = 8.1$
$H_c, H_d = 2.9$ (m)	$^3J_{fg} = 17.3$
$H_e = 3.74$ (q)	$^3J_{fh} = 10.1$
$H_f = 5.84$ (m)	$^2J_{gh} = 1.7$
$H_g = 5.13$ (m)	
$H_h = 5.07$ (m)	
$H_{ar} = 7.0$ – $7.5$ (m)	

complex and the olefin in THF ( $10\text{ cm}^3$ ) was prepared under inert atmosphere. The ratios used were  $[\text{Ni}]/\text{olefin} = 1/1000$  or  $1/500$ . The solution was transferred via syringe under argon into the autoclave, which had previously been purged with successive applications of vacuum and argon. Ethylene was admitted until the desired initial pressure was reached and the required temperature for the experiment was then adjusted with an external thermostatic bath. The internal temperature was monitored by means of a thermocouple. Internal temperature or pressure as a function of time was registered with a Leeds and Northrup Speedomax Recorder.

After the time indicated in the text for every reaction, usually three hours, the reactor was cooled to  $-20^\circ\text{C}$  and vented slowly. The quantitative distribution of products fractions was determined by GC analysis. In some cases, the compounds were distilled from the reaction mixtures and characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and gas chromatography with mass selective detector (Tables 4 and 5).

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