

# Telomerization of 1,3-butadiene with alcohols catalyzed by homogeneous palladium(0) complexes in the presence of mono- and diphosphine ligands

Federica Benvenuti<sup>a</sup>, Carlo Carlini<sup>a,\*</sup>, Massimo Lami<sup>b</sup>, Mario Marchionna<sup>b</sup>,  
Renata Patrini<sup>b</sup>, Anna Maria Raspolli Galletti<sup>a</sup>, Glauco Sbrana<sup>a</sup>

<sup>a</sup> *Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Risorgimento 35, I-56126 Pisa, Italy*

<sup>b</sup> *Snamprogetti, Via Maritano 26, I-20097 San Donato Milan, Italy*

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## Abstract

The homogeneous telomerization of 1,3-butadiene with alcohols for the selective synthesis of linear octadienyl ethers in the presence of catalysts prepared in situ from palladium(0) bis-dibenzylidene-acetone and different mono- and diphosphine ancillary ligands is described. With monophosphines, a correlation between basicity as well as steric hindrance of the ligand and activity and selectivity of the resulting catalyst was found. When diphosphines were used, the effect of the bite of the chelating ligand, as well as its basicity and steric hindrance on the activity and selectivity of the process was studied and discussed in terms of the relative stability of the metallacyclo moieties involved in the catalytic cycle. The above results have allowed to gain more light on the reaction mechanism. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Telomerization; 1,3-Butadiene; Alcohols; Palladium(0)-dibenzylidene-acetone; Monophosphines; Diphosphines; Homogeneous catalysts; Octadienyl ethers

## 1. Introduction

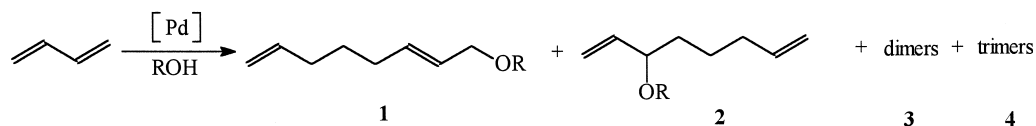
Catalytic telomerization of dienes with nucleophiles has recently received a particular attention in order to provide both fine chemicals [1,2] and petrochemicals. In the latter direction, a significant effort was devoted to study the palladium-catalyzed telomerization of 1,3-butadiene with water and alcohols to produce, after hydrogenation, either a precursor for plasticizers [3–5] or high cetane components for the

formulation of environmentally-friendly diesel fuels [6].

In this context, we have recently re-investigated [7] the telomerization of 1,3-butadiene with alcohols (Scheme 1) by using palladium(0) homogeneous catalysts in the presence of monophosphines as ancillary ligand, paying particular attention to the influence of the alcohol/diene molar ratio, the excess of alcohol favouring the selective synthesis of octadienyl ethers (**1** and **2**) against octatrienes (**3**) and butadiene trimers (**4**) or higher telomers.

Moreover, the effect of the nature of the phosphine ligand on the catalytic activity, as

\* Corresponding author. Tel.: +39-50-918-222; Fax: +39-50-918-260; E-mail: carlini@cci.unipi.it



Scheme 1.

well as on the selectivity of the process to the telomers was preliminarily investigated [7], the results suggesting that alkyl phosphines are to be preferred for improving the catalyst performances as also suggested by many other authors [2]. However, a more detailed investigation about the influence of the electronic properties and the steric requirements of the phosphine ligand on the catalyst performances is required in order to have a deeper insight on both mechanistic aspects of the telomerization reaction and the optimization of the catalyst formulation.

Finally, taking into account that chelating ligands may strongly affect the reactivity and selectivity of homogeneous palladium systems in different reactions, depending on the size of the resulting metallacyclo moiety, typical examples being offered by olefins/carbon monoxide copolymerizations [8], carbonylation [9], formylation [10] and reduction [11] reactions, as well as by Heck coupling reactions involving aryl halogenides [12], it appeared also to be of great interest to investigate how the structure of the chelate diphosphine ligand could modify the catalytic performances of homogeneous palladium(0) systems in the telomerization of 1,3-butadiene with alcohols. In this context, our interest to the study of diphosphine ligands was also related to the possibility to have some further information on the mechanistic aspects of the reaction.

## 2. Experimental

### 2.1. Materials

All manipulations as well as catalytic reactions were carried out under dry purified argon or nitrogen using standard Schlenk techniques.

All solvents, after drying, were stored on molecular sieves (4 Å), under dry inert atmosphere.

*n*-Hexane (Merck) was refluxed, distilled on Na/K alloy and stored on molecular sieves (4 Å), under dry argon.

Anhydrous methanol (Baker) and ethanol (Carlo Erba) were obtained by refluxing the commercial product over Mg/I<sub>2</sub> and stored on molecular sieves (4 Å).

1-Propanol (Riedel-de Haën), 1-butanol (Carlo Erba), 1-pentanol (Carlo Erba) and 1-hexanol (Fluka) were distilled on sodium under dry argon and stored on molecular sieves (4 Å).

1,3-Butadiene (99%) (Rivoira) was flash distilled prior to use in order to avoid contamination from 4-vinyl-cyclohexene and peroxides.

Bis(diphenylphosphino)methane (DPPM), 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), 1,4-bis(diphenylphosphino)butane (DPPB) all purchased from Aldrich, 1,2-bis(diethylphosphino)ethane (DEPE) and 1,2-bis(dicyclohexylphosphino)ethane (DCPE), both from Strem, were used as received and stored under nitrogen.

Commercial monophosphines such as, triphenylphosphine (Φ<sub>3</sub>P) (Aldrich), triethylphosphine (Et<sub>3</sub>P) (Strem), tricyclohexylphosphine (Cy<sub>3</sub>P) (Strem), triisopropylphosphine (Pr<sub>3</sub><sup>i</sup>P) (Strem) tri-*n*-butylphosphine (Bu<sub>3</sub><sup>n</sup>P) (Strem), tri-*n*-hexylphosphine (Hex<sub>3</sub><sup>n</sup>P) (Tokyo Kasei), *n*-butyl-diphenylphosphine (Φ<sub>2</sub>PBu<sup>n</sup>) (K&K) and di-*n*-butyl-phenylphosphine (ΦPBu<sub>2</sub><sup>n</sup>) (Strem), were used as received and stored under argon.

Ethyl-di-*n*-dodecylphosphine (Dod<sub>2</sub><sup>n</sup>PEt) was prepared, according to a general procedure [13], by reaction of ethyl-dichlorophosphine (Strem) with *n*-dodecyl-magnesium chloride.

Palladium bis-dibenzylidene-acetone [Pd(dba)<sub>2</sub>] was prepared as previously described [14].

## 2.2. Catalytic experiments and analyses

Catalytic experiments were carried out in a 150 ml mechanically stirred stainless steel autoclave, equipped with an inner glass beaker, a substrate inlet vessel, and a sampling valve.

In a typical procedure, the desired amount of the alcohol, palladium catalyst precursor, benzene (as internal standard for GC analysis), *n*-hexane as the solvent and the phosphine ligand were introduced under dry argon in the nitrogen purged autoclave. Then, 1,3-butadiene was charged and the system pressurized with nitrogen up to 3 MPa. The autoclave was heated to the desired temperature in a thermostated oil bath. Products samples were periodically removed via the liquid sampling valve, collected in pre-cooled capped vials and immediately analysed by GC. At the end of the reaction, the autoclave was cooled at room temperature and, after removing unreacted 1,3-butadiene, the products were analyzed.

Selectivities to octadienylethers **1** and **2** as well as to dimers **3**, as reported in the Tables, were evaluated as:

$$\left[ \frac{2(\text{moles of the individual product})}{(\text{moles of converted } C_4H_6)} \right] \times 100.$$

Selectivities to trimers **4** and telomers containing three butadiene units, as reported in the Tables, were evaluated as:

$$\left[ \frac{3(\text{moles of the individual product})}{(\text{moles of converted } C_4H_6)} \right] \times 100$$

## 2.3. Physico-chemical measurements

GC/MS spectra of the telomerization products were performed by a Hewlett-Packard 5995 A spectrometer.

Quantitative analyses of telomerization products were performed by a HP 5890 gas chromatograph, equipped with a HP 3396 integrator, a flame ionization detector and a 50 m HP PONA capillary column (cross-linked methyl-silicone gum). The identification of the telomerization products was carried out by GC/MS and NMR analyses.

## 3. Results and discussion

### 3.1. Homogeneous 1,3-butadiene telomerization with methanol catalyzed by Pd(dba)<sub>2</sub> in the presence of different monophosphines: effect of the nature of the ligand and of activation procedure

The steric and electronic properties of a phosphine ligand were evaluated by means of the well-known Tolman's parameters [15], the cone angle  $\vartheta$  for the former requirement and the  $\chi$  value for the latter [16]. Even if the method for the determination of  $\vartheta$  in asymmetric phosphines, such as R<sub>2</sub>R'P and RR'R''P is controversial [17], and recently, innovative approaches have been proposed [18] in order to overcome the intrinsic limitations of the original model defined by Tolman, however, the differences in  $\vartheta$  values, depending on the determination procedure used, resulted in modest entity. Therefore, the Tolman model was adopted for its simplicity and diffuse use in the literature, the values of  $\vartheta$  for asymmetric phosphines of the RR'R''P type being calculated according to an approximate estimation [17] based on the following equation:

$$\vartheta = \frac{2}{3} \sum_{i=1}^3 \vartheta_i / 2$$

where each  $\vartheta_i$  represents the cone angle of the corresponding symmetric phosphine (R<sub>i</sub>)<sub>3</sub>P. The  $\chi$  parameter is related to the overall donor/acceptor properties of the considered phosphine,

higher values of  $\chi$  being connected with less basic properties of the ligand.

With the aim to find a correlation between activity and selectivity of the catalyst, and the nature of the phosphine ligand used, in terms of basicity and steric hindrance, as evaluated by  $\chi$  and  $\vartheta$  parameters, the 1,3-butadiene telomerization with methanol was performed under the same experimental conditions by using Pd(dba)<sub>2</sub> as catalyst precursor, in the presence of different phosphine ligands (Table 1).

A more immediate representation of the influence of the phosphine basicity on the catalyst activity is shown in Fig. 1, where the C<sub>4</sub>H<sub>6</sub> conversion is plotted as a function of the  $\chi$  parameter. Indeed, it is evident that the catalytic systems, which display higher activity, are characterized by a high basicity and hence, by low values of the  $\chi$  parameter. In particular, in the Bu<sub>x</sub><sup>n</sup>PΦ<sub>3-x</sub> phosphine series (runs 1–4) the progressive substitution of an alkyl group with a phenyl moiety, characterized by higher electron-withdrawing properties, is accompanied by a linear decrease of the activity of the resulting catalyst. However, steric hindrance of

the phosphine ligand also plays a certain role on the activity of the resulting palladium catalyst, the very high bulkiness of Cy<sub>3</sub>P slightly lowering the diene conversion with respect to less hindered basic phosphines (Et<sub>3</sub>P, Pr<sub>3</sub><sup>i</sup>P).

On the other hand, the highest selectivities to telomers were obtained when the phosphine ligands in the coordination sphere of the palladium atom give rise to a limited steric hindrance (runs 3–5 and 8,9), as nicely shown in Fig. 2, where the selectivity of the catalyst is plotted as a function of the  $\vartheta$  parameter. In particular, phosphine ligands (Cy<sub>3</sub>P and Pr<sub>3</sub><sup>i</sup>P) characterized by a very high cone angle parameter afford catalytic systems (runs 6 and 7) with a lower selectivity to telomers (about 80%).

The optimal P/Pd molar ratio to be used resulted in and were strictly related to the nature of the phosphine ligand, more basic alkyl phosphines (Bu<sub>3</sub><sup>n</sup>P) requiring a value near 1, whereas for less basic phosphines (Φ<sub>3</sub>P), a value near 2 is necessary (Fig. 3). However, it is noteworthy to point out that the productivity of the two catalytic systems reported in Fig. 3 cannot be quantitatively compared, owing to the different

Table 1

1,3-Butadiene telomerization with methanol catalyzed by homogeneous systems obtained in situ by reacting Pd(dba)<sub>2</sub> with different monophosphine ligands<sup>a</sup>

Run	Phosphine ligand	C <sub>4</sub> H <sub>6</sub> conversion (%)				Selectivity (%) <sup>b,c</sup>		R <sup>b,d</sup> (%)	$\vartheta$ (°)	$\chi$ (cm <sup>-1</sup> )
		0.5 h	1 h	2 h	3 h	1 <sup>e</sup> + 2 <sup>f</sup>	3 <sup>g</sup>			
1	Φ <sub>3</sub> P	76	86	93	95	93.7	6.1	93.9	145	12.9
2	Φ <sub>2</sub> PBu <sup>n</sup>	83	91	96	97	95.7	4.2	94.1	141	10.0
3	ΦPBu <sub>2</sub> <sup>n</sup>	89	96	98	99	96.8	3.1	93.8	136	7.1
4	Bu <sub>3</sub> <sup>n</sup> P	96	99	100	100	97.2	2.6	94.0	134	4.2
5	Et <sub>3</sub> P	99	100	100	100	97.9	2.0	94.4	132	5.4
6	Pr <sub>3</sub> <sup>i</sup> P	100	100	100	100	76.0	22.5	93.3	160	3.1
7	Cy <sub>3</sub> P	95	99	100	100	81.6	17.9	92.4	170	0.3
8	Hex <sub>3</sub> <sup>n</sup> P	89	98	100	100	97.3	2.0	95.4	135	3.8
9	Dod <sub>2</sub> <sup>n</sup> PEt	98	99	100	100	96.7	2.2	94.1	134	4.0

<sup>a</sup>Reaction conditions: Pd(dba)<sub>2</sub>: 0.1 mmol; solvent: *n*-hexane (20 ml); T = 60°C; P<sub>N<sub>2</sub></sub> = 3.0 MPa; Pd/PR<sub>3</sub>/MeOH/C<sub>4</sub>H<sub>6</sub> = 1/2/3000/2000 mol/mol; time: 3 h.

<sup>b</sup>Determined at 0.5 h.

<sup>c</sup>When 1 + 2 + 3 < 100 trimers are also present to some extent.

<sup>d</sup>Regioselectivity to linear telomers evaluated as [1/(1 + 2)] × 100.

<sup>e</sup>*Cis*- and *trans*-1-methoxy-2,7-octadiene.

<sup>f</sup>3-Methoxy-1,7-octadiene.

<sup>g</sup>Mainly, *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.

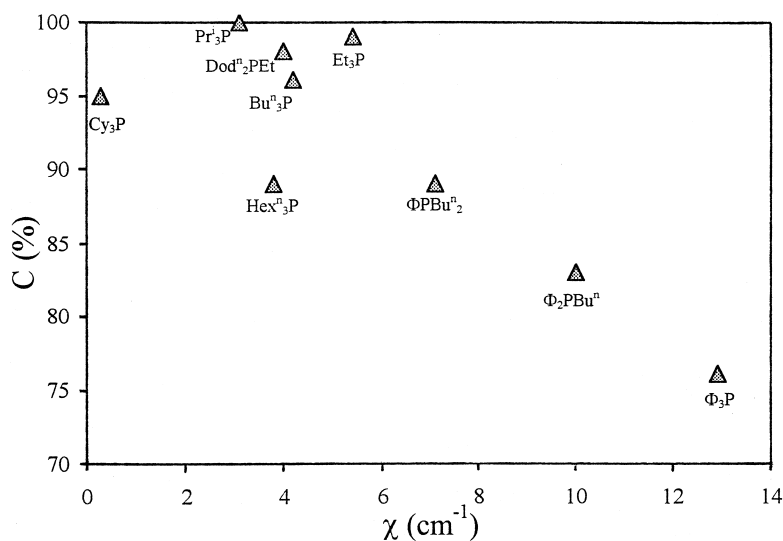


Fig. 1. Homogeneous 1,3-butadiene telomerization with methanol catalyzed by Pd(dba)<sub>2</sub> in the presence of different ancillary monophosphine ligands: influence of the electronic parameter ( $\chi$ ) on 1,3-butadiene conversion (C), determined at 0.5 h reaction time. Reaction conditions: Pd(dba)<sub>2</sub>: 0.1 mmol; Pd/P/MeOH/C<sub>4</sub>H<sub>6</sub> = 1/2/3000/2000 mol/mol; *n*-hexane: 20 ml; P<sub>N<sub>2</sub></sub> = 3 MPa.

conditions adopted, in terms of palladium and reagents concentration.

Furthermore, it was also observed, carrying out the telomerization of 1,3-butadiene with methanol with the Pd(dba)<sub>2</sub>/Bu<sup>n</sup><sub>3</sub>P catalytic sys-

tem at very low concentrations, thus operating under strict kinetic control, that 1,3-butadiene pre-treatment had a favourable effect on reaction rate whereas methanol pre-treatment resulted in an inhibiting effect (Fig. 4). It is also

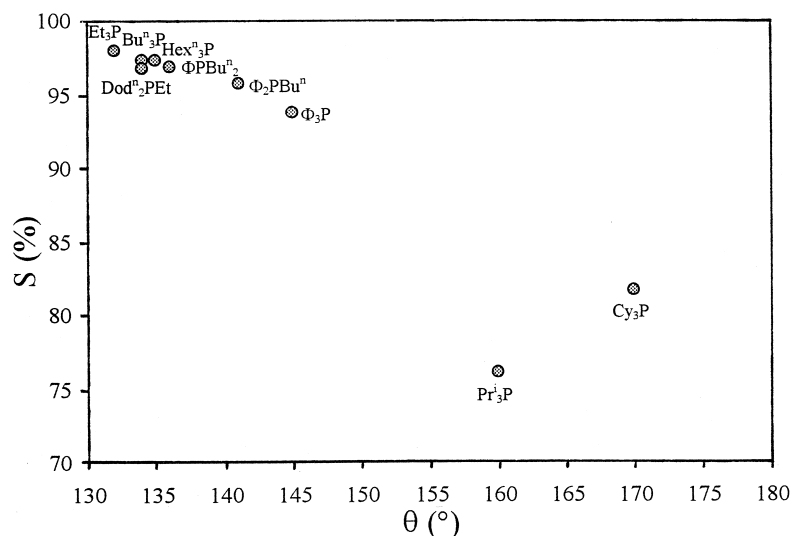


Fig. 2. Homogeneous 1,3-butadiene telomerization with methanol catalyzed by Pd(dba)<sub>2</sub> in the presence of different ancillary monophosphine ligands: influence of the steric parameter ( $\theta$ ) on the chemoselectivity to telomers (S), determined at 0.5 h reaction time. Reaction conditions: Pd(dba)<sub>2</sub>: 0.1 mmol; Pd/P/MeOH/C<sub>4</sub>H<sub>6</sub> = 1/2/3000/2000 mol/mol; *n*-hexane: 20 ml; P<sub>N<sub>2</sub></sub> = 3 MPa.

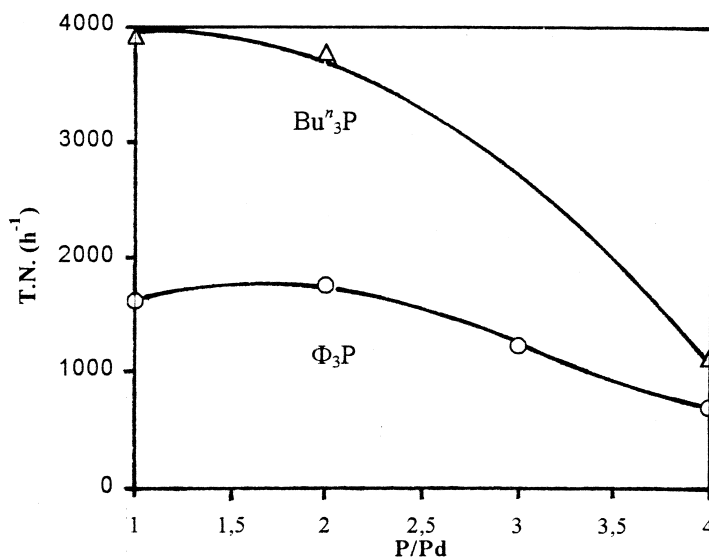


Fig. 3. Effect of the P/Pd molar ratio on productivity to telomers, expressed as mol (products)/mol (Pd) × h (T.N.), in the homogeneous 1,3-butadiene telomerization with methanol catalyzed by the Pd(dba)<sub>2</sub>/Bu<sup>n</sup><sub>3</sub>P (a) and Pd(dba)<sub>2</sub>/PΦ<sub>3</sub> (b) systems. Reaction conditions: Pd(dba)<sub>2</sub>/Bu<sup>n</sup><sub>3</sub>P system: Pd(dba)<sub>2</sub>: 0.05 mmol; Pd/MeOH/C<sub>4</sub>H<sub>6</sub> = 1/30,000/19,000 mol/mol; T = 60°C; P<sub>N<sub>2</sub></sub> = 3 MPa, time: 5 h. Pd(dba)<sub>2</sub>/PΦ<sub>3</sub> system: Pd(dba)<sub>2</sub>: 0.1 mmol; Pd/C<sub>4</sub>H<sub>6</sub>/MeOH = 1/1000/1500 mol/mol; n-hexane: 20 ml; T = 60°C; P<sub>N<sub>2</sub></sub> = 3 MPa; time: 0.5 h.

noteworthy to point out that the catalytic performances can be improved by the use of a recycled catalyst from previous runs.

In this context, the use of chelating diphosphine ligands, such as R<sub>2</sub>P-(CH<sub>2</sub>)<sub>n</sub>-PR<sub>2</sub>, in combination with Pd(dba)<sub>2</sub> could give not only

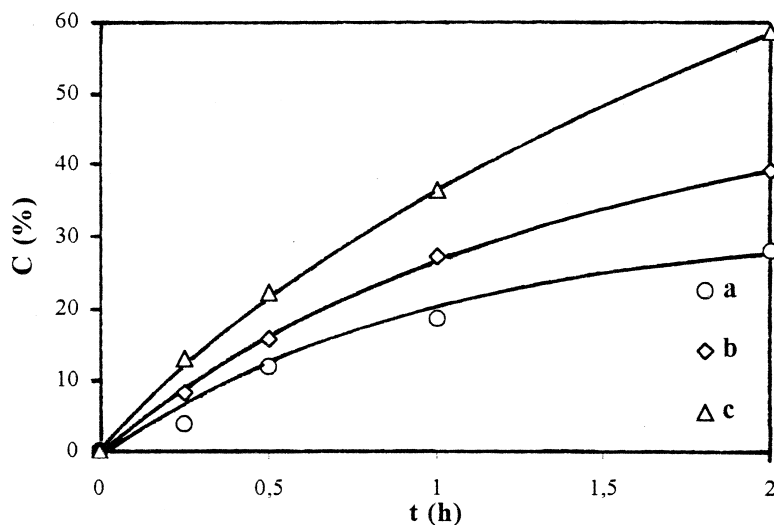


Fig. 4. Effect of methanol/1,3-butadiene pre-treatment on the reaction rate [C<sub>4</sub>H<sub>6</sub> conversion (C) vs. time] of the homogeneous 1,3-butadiene telomerization with methanol catalyzed by the Pd(dba)<sub>2</sub>/Bu<sup>n</sup><sub>3</sub>P system. Reaction conditions: Pd(dba)<sub>2</sub>: 0.068 mmol; Pd/P/C<sub>4</sub>H<sub>6</sub>/MeOH = 1/2/15,000/22,500 mol/mol; P<sub>N<sub>2</sub></sub> = 3 MPa; T: 60°C. (a) Pre-treatment for 45 min with only methanol; (b) typical run without pre-treatment; (c) pre-treatment for 45 min with only 1,3-butadiene.

further insights about the mechanistic aspects of the telomerization reaction but also would allow to modulate the activity and selectivity of the process by varying the bite of the resulting metallacyclo moiety.

### 3.2. Homogeneous 1,3-butadiene telomerization with alcohols catalyzed by $Pd(dba)_2/R_2P-(CH_2)_n-PR_2$ systems

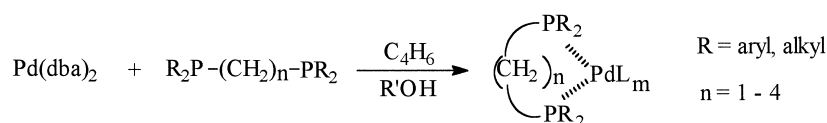
Telomerization reactions were carried out at 60°C by using *n*-hexane as the solvent and molar ratios MeOH/ $C_4H_6$  as well as  $C_4H_6/Pd = 1.5$  and 2000, respectively, i.e., under experimental conditions analogous to those adopted for the monophosphine ligands. The catalytic systems were prepared in situ from  $Pd(dba)_2$  and different bidentate phosphine ligands (P/Pd = 2 mol/mol), the formation of a metallacyclo moiety being assumed to occur, at least initially [19], according to Scheme 2.

It may be supposed that the stability of the above metallacyclo moiety strongly depends on the size of the ring, 5- and 6-membered systems, i.e., those originated by chelating diphosphines with *n* equal to 2 and 3, being the most stable. On the other hand, metallacyclo moieties with larger size, due to the higher coordinative flexibility of the ligand, may co-exist with situations of mono-coordination. Moreover, bis(diphenylphosphino)methane (DPPM) is characterized by a strong tendency to give binuclear palladium species, owing to its preferential bridge coordinative mode [20,21]. Nevertheless, complexes are known in which the two phosphorus atoms of DPPM are bound to the same palladium atom, although characterized by distorted P–Pd–P angles, as compared with the usual square planar geometry [19,22–24].

The data reported in Table 2 (runs 10–13) indicate that, after 4 h of reaction time, the systems based on DPPE and DPPP (*n* = 2 and 3) display (runs 11 and 12) a lower activity [turnover number (T.N.) values in the 330–230  $h^{-1}$  range] as compared with those (runs 10 and 13) obtained in the presence of DPPM and DPPB (*n* = 1 and 4), their T.N. values being  $> 450 h^{-1}$ . It is noteworthy that the  $Pd(dba)_2/DPPM$  system is characterized by a relative longer induction period. Moreover, the catalytic systems derived from DPPM and DPPB resulted also more regioselective, the percentage of the linear telomers **1** (*R* =  $CH_3$ ) being almost 96%, against values lower than 94% for the other systems. In the above series the  $Pd(dba)_2/DPPB$  system afforded the best performances, in terms of productivity, chemoselectivity to telomers and regioselectivity to linear telomers.

The comparison of the above systems with the catalysts based on  $Pd(dba)_2$  and monophosphine ligands (runs 1 and 2, Table 2) allows one to conclude that the former systems usually display lower catalytic activity (see T.N. values at 0.5 h reaction time). However, when a diphosphine ligand with a large coordinative flexibility, such as DPPB, is chosen, the resulting catalyst shows (run 13) an analogous activity to that found for the system in the presence of the corresponding monophosphine ligand (run 2).

As far as the effect of the basicity and steric hindrance of the diphosphine ligand on the activity and selectivity of the telomerization process is concerned, the results of run 11 are compared to those obtained in runs 14 and 15 (Table 2), where chelating ligands with the same bite of DPPE (*n* = 2) but with different sub-



Scheme 2.

Table 2

1,3-Butadiene telomerization with methanol catalyzed by homogeneous systems obtained in situ by reacting Pd(dba)<sub>2</sub> with different R<sub>2</sub>P-(CH<sub>2</sub>)<sub>n</sub>-PR<sub>2</sub> chelating diphosphine ligands<sup>a</sup>

Run	Chelating ligand		C <sub>4</sub> H <sub>6</sub> conversion (%)		Selectivity <sup>b,c</sup> (%)			R <sup>d</sup> (%)	T.N. <sup>e</sup> (h <sup>-1</sup> )	
	R	n	0.5 h	4 h	1 <sup>f</sup>	2 <sup>g</sup>	3 <sup>h</sup>		0.5 h	4 h
10	Ph	1	31.0	93.3	90.4	4.1	5.3	95.7	1240	467
11	Ph	2	35.3	64.2	91.5	6.2	2.1	93.7	1410	326
12	Ph	3	26.6	46.0	85.7	7.1	6.8	92.4	1060	230
13	Ph	4	82.8	99.9	93.4	4.1	2.5	95.8	3310	500
14	Et	2	12.8	37.2	86.6	4.4	7.3	95.2	640	186
15	Cy	2	3.1	11.1	65.4	4.5	24.3	93.6	155	56
1	Φ <sub>3</sub> P		76.0	–	88.0	5.7	6.1	93.9	3040	–
2	Φ <sub>2</sub> PBu <sup>h</sup>		83.0	–	90.0	5.7	4.2	94.1	3320	–

<sup>a</sup>Reaction conditions: Pd(dba)<sub>2</sub>: 0.1 mmol; Pd/P/MeOH/C<sub>4</sub>H<sub>6</sub> = 1/2/3000/2000; solvent: *n*-hexane (20 ml); P<sub>N<sub>2</sub></sub> = 3 MPa; T = 60°C; time: 4 h.

<sup>b</sup>Determined after 4 h for runs 10–15 and after 0.5 h for runs 1–2.

<sup>c</sup>When 1 + 2 + 3 < 100, trimers and higher telomers are also present to some extent.

<sup>d</sup>Regioselectivity to the linear telomers 1, expressed as [1/(1 + 2)] × 100.

<sup>e</sup>Turnover number, expressed as mol (products)/mol (Pd) × h.

<sup>f</sup>*Cis*- and *trans*-1-methoxy-2,7-octadiene.

<sup>g</sup>3-Methoxy-1,7-octadiene.

<sup>h</sup>Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.

stituents on both the phosphorus atoms were used. Indeed, the replacement of the phenyl rings by ethyl (DEPE) and cyclohexyl (DCPE) groups allowed to increase the basicity and the steric hindrance of the ligand.

The obtained data clearly indicate that, moving from phenyl to ethyl and to cyclohexyl groups in the diphosphine ligand, the activity of the resulting catalytic systems was progressively reduced, T.N. values (at 4 h reaction time) decreasing from 326 to 186 and 56 h<sup>-1</sup>, in that order. Therefore, the above findings may be

explained by assuming that by increasing the basicity of the ligand, a more stable metallacyclo moiety is formed, thus, decreasing the activity of the resulting catalysts. Moreover, it is worth noting that in the runs 11, 14 and 15, the chemoselectivity to telomers is strongly affected by the nature of the chelating ligand, the increase of steric hindrance causing a drop of chemoselectivity, whereas regioselectivity values are very close to each other.

The effects of the temperature and of the P/Pd molar ratio were also studied in order to

Table 3

Homogeneous 1,3-butadiene telomerization with methanol catalyzed by Pd(dba)<sub>2</sub>/DPPP system: influence of the reaction temperature<sup>a</sup>

Run	T (°C)	C <sub>4</sub> H <sub>6</sub> conversion (%)					S <sup>b</sup> (0.5 h)		S <sup>b</sup> (4 h)		R <sup>c</sup> (%)	
		0.5 h	1 h	2 h	3 h	4 h	1 <sup>d</sup> + 2 <sup>e</sup>	3 <sup>f</sup>	1 <sup>d</sup> + 2 <sup>e</sup>	3 <sup>f</sup>	0.5 h	4 h
12	60	26.6	38.9	43.2	44.7	46.0	95.3	4.5	92.8	6.8	94.9	92.4
16	80	39.2	46.6	57.8	64.9	75.1	85.5	14.4	83.4	16.3	93.3	92.6
17	100	59.0	81.7	95.8	97.2	100	77.0	22.8	72.1	27.3	94.4	92.6

<sup>a</sup>Reaction conditions: Pd(dba)<sub>2</sub>: 0.1 mmol; Pd/P/MeOH/C<sub>4</sub>H<sub>6</sub> = 1/2/3000/2000; solvent: *n*-hexane (20 ml); P<sub>N<sub>2</sub></sub> = 3 MPa; time: 4 h.

<sup>b</sup>Selectivity (%); when 1 + 2 + 3 < 100, trimers and higher telomers are also present to some extent.

<sup>c</sup>Regioselectivity to linear telomers 1, expressed as [1/(1 + 2)] × 100.

<sup>d</sup>*Cis*- and *trans*-1-methoxy-2,7-octadiene.

<sup>e</sup>3-Methoxy-1,7-octadiene.

<sup>f</sup>Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.



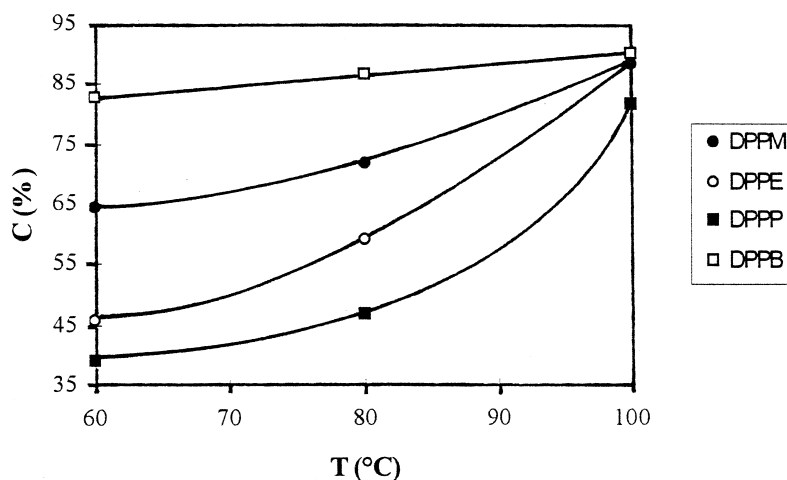


Fig. 5. Effect of temperature on activity [ $C_4H_6$  conversion (C) vs.  $T$  ( $^{\circ}C$ )] of the homogeneous 1,3-butadiene telomerization with methanol catalyzed by  $Pd(dba)_2/Ph_2P-(CH_2)_n-PPh_2$  systems. Reaction conditions:  $Pd(dba)_2$ : 0.1 mmol;  $Pd/P/MeOH/C_4H_6 = 1/2/3000/2000$  mol/mol;  $n$ -hexane: 20 ml;  $P_{N_2} = 3$  MPa; time: 1 h.

optimize the reaction conditions. Therefore, the  $Pd(dba)_2/Ph_2P-(CH_2)_n-PPh_2$  ( $n = 1-4$ ) systems were examined in the 1,3-butadiene telomerization with methanol by varying the reaction temperature from 60 to 100 $^{\circ}C$  and the P/Pd molar ratio from 0.5 to 4. As an example, the telomerization experiments carried out in the presence of the  $Pd(dba)_2/DPPP$  system at different temperatures are reported in Table 3 (runs 12, 16 and 17).

The data clearly show that the increase of temperature enhances the activity of the catalyst, thus making it possible to reach an almost quantitative conversion of 1,3-butadiene. However, the productivity improvement is accompanied by a strong decay of selectivity to telomers. Analogous results were obtained with the other  $Pd(dba)_2/Ph_2P-(CH_2)_n-PPh_2$  systems, the most remarkable effect being observed for DPPE and DPPP ligands (Figs. 5 and 6).

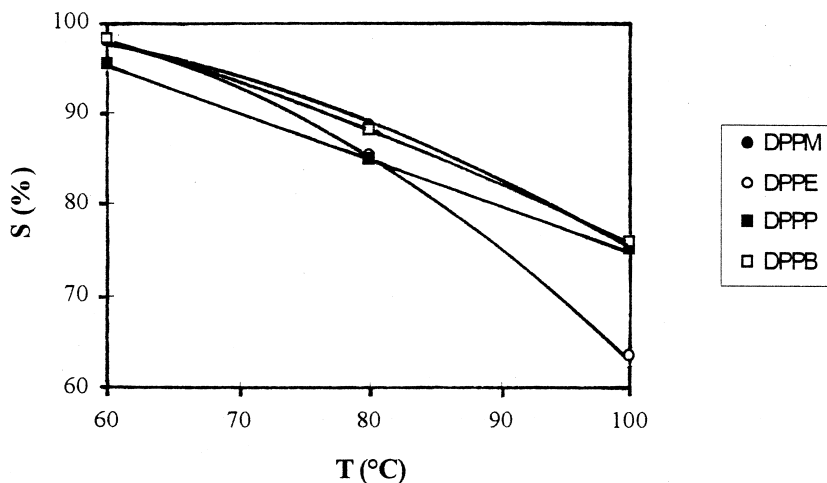


Fig. 6. Effect of temperature on selectivity to telomers [chemoselectivity ( $S$ ) vs.  $T$  ( $^{\circ}C$ )] of the homogeneous 1,3-butadiene telomerization with methanol catalyzed by  $Pd(dba)_2/Ph_2P-(CH_2)_n-PPh_2$  systems. Reaction conditions:  $Pd(dba)_2$ : 0.1 mmol;  $Pd/P/MeOH/C_4H_6 = 1/2/3000/2000$  mol/mol;  $n$ -hexane: 20 ml;  $P_{N_2} = 3$  MPa; time: 1 h.

Table 4

Homogeneous 1,3-butadiene telomerization with methanol catalyzed by the Pd(dba)<sub>2</sub>/DPPB system: influence of the P/Pd molar ratio<sup>a</sup>

Run	P/Pd (mol/mol)	C <sub>4</sub> H <sub>6</sub> conversion (%)					Selectivity <sup>b,c</sup> (%)			R <sup>b,d</sup> (%)
		0.5 h	1 h	2 h	3 h	4 h	1 <sup>e</sup>	2 <sup>f</sup>	3 <sup>g</sup>	
18	0.5	17.8	33.2	41.5	46.4	51.6	71.8	9.2	17.4	88.6
19	1	39.8	59.4	71.5	78.7	80.7	92.4	3.9	3.3	96.0
13	2	31.3	60.5	79.2	89.8	93.3	90.4	4.1	5.3	95.7
20	4	2.6	3.1	5.7	8.4	10.4	82.2	12.5	5.3	86.8

<sup>a</sup>Reaction conditions: Pd(dba)<sub>2</sub>: 0.1 mmol; Pd/MeOH/C<sub>4</sub>H<sub>6</sub> = 1/3000/2000; solvent: *n*-hexane (20 ml); P<sub>N<sub>2</sub></sub> = 3 MPa; T = 60°C.<sup>b</sup>Determined after 4 h.<sup>c</sup>When 1 + 2 + 3 < 100, trimers and higher telomers are also present to some extent.<sup>d</sup>Regioselectivity to the linear telomers 1, expressed as [1/(1 + 2)] × 100.<sup>e</sup>*Cis*- and *trans*-1-methoxy-2,7-octadiene.<sup>f</sup>3-Methoxy-1,7-octadiene.<sup>g</sup>Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.

As far as the influence of the P/Pd ratio on the catalytic performances is concerned, the data of telomerization experiments carried out at 60°C and catalyzed by the Pd(dba)<sub>2</sub>/DPPB are reported, as an example, in Table 4 (runs 13, 18–20). The results clearly indicate that the above catalytic system displays a maximum of activity when a P/Pd molar ratio is equal to 2, i.e., a 1 to 1 Pd chelating ligand was adopted. An analogous trend was observed also for the other Pd(dba)<sub>2</sub>/Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>*n*</sub>-PPh<sub>2</sub> systems (Fig. 7).

Indeed, the above behaviour may be explained assuming that, on increasing the P<sup>∧</sup>P ligand amount until a P/Pd molar ratio is equal to 4 was reached, the content of non catalytically active tetraphosphinic coordinatively saturated palladium species is progressively enhanced, thus causing a dramatic decay of activity. On the other hand, when a defect of ligand is used the stabilization of palladium intermediates to give the active species is reduced, deposition of metallic palladium being also observed, thus justifying the decrease of activity.

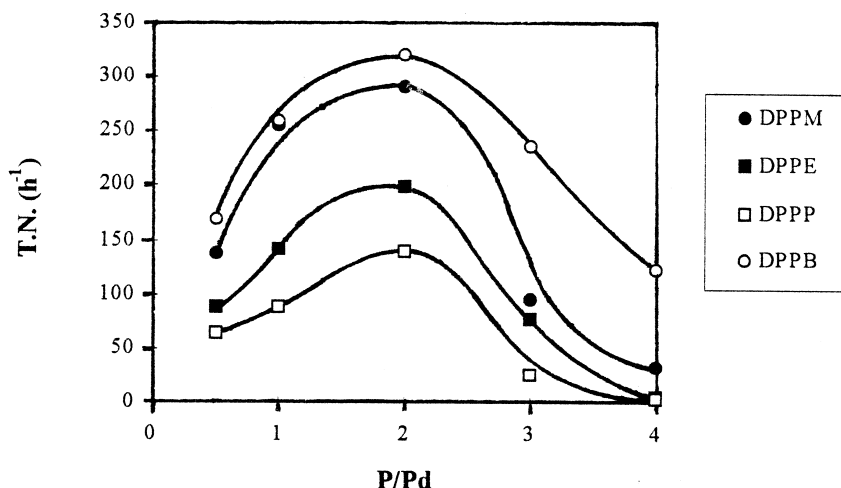


Fig. 7. Effect of the P/Pd molar ratio on productivity to telomers, expressed as mol (products)/mol (Pd) × h (T.N.), in the homogeneous 1,3-butadiene telomerization with methanol catalyzed by Pd(dba)<sub>2</sub>/Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>*n*</sub>-PPh<sub>2</sub> systems. Reaction conditions: Pd(dba)<sub>2</sub>: 0.1 mmol; Pd/P/MeOH/C<sub>4</sub>H<sub>6</sub> = 1/2/3000/2000 mol/mol; *n*-hexane: 20 ml; T = 60°C; P<sub>N<sub>2</sub></sub> = 3 MPa; time: 4 h.

Table 5

Influence of the methanol/ $C_4H_6$  ratio in the homogeneous 1,3-butadiene telomerization with methanol catalyzed by the  $Pd(dba)_2/DPPM$  system<sup>a</sup>

Run	MeOH/ $C_4H_6$ (mol/mol)	$C_4H_6$ conversion (%)	Selectivity (%) <sup>b</sup>			$R^c$ (%)
			<b>1</b> <sup>d</sup>	<b>2</b> <sup>e</sup>	<b>3</b> <sup>f</sup>	
21	3.0	95.1	89.0	5.8	4.8	93.9
10	1.5	93.3	90.5	4.1	5.4	95.7
22	1.0	59.4	82.3	7.9	9.3	91.3

<sup>a</sup>Reaction conditions:  $Pd(dba)_2$ : 0.1 mmol;  $Pd/P/MeOH = 1/2/3000$ ; solvent: *n*-hexane (20 ml);  $P_{N_2} = 3$  MPa; time: 4 h;  $T = 60^\circ C$ .

<sup>b</sup>When **1** + **2** + **3** < 100, trimers and higher telomers are also present to some extent.

<sup>c</sup>Regioselectivity to the linear telomers **1**, expressed as  $[1/(1+2)] \times 100$ .

<sup>d</sup>*Cis*- and *trans*-1-methoxy-2,7-octadiene.

<sup>e</sup>3-Methoxy-1,7-octadiene.

<sup>f</sup>Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.

In particular, under these conditions, a drop of selectivity to telomers was also observed, as shown in run 18.

The influence of the MeOH/ $C_4H_6$  molar ratio on the performances of the catalyst was also studied in the case of the  $Pd(dba)_2/DPPM$  system and the results are reported in Table 5. The obtained data (runs 21, 10 and 22) clearly indicate, as expected [7], that on increasing the MeOH/ $C_4H_6$  ratio, an increase of the diene conversion was obtained; moreover, an improvement of chemoselectivity to telomers was also observed, although the highest regioselectivity to the linear telomers **1** was found when a MeOH/ $C_4H_6$  equal to 1.5 was adopted.

Finally, 1,3-butadiene telomerization with higher primary alcohols was studied, in the presence of the  $Pd(dba)_2/Ph_2P-(CH_2)_n-PPh_2$  systems, varying the length of the alkyl substituent of the alcoholic substrate. The data reported in Table 6 for the  $Pd(dba)_2/DPPM$  system (runs 10, 23–27) indicate that the  $C_4H_6$  conversion (at 4 h reaction time) drastically decreases from methanol to 1-propanol and then it reaches an almost steady value. However, some experiments carried out at longer reaction time (18 h) (runs 24 and 25) allow to conclude that it is possible to reach almost quantitative  $C_4H_6$  conversions also when higher alcohols are used as substrate. Moreover, the chemoselectivity to telomers appreciably decreases from methanol to 1-propanol and then it remains substantially constant on further increasing the length of the alcohol. An analogous behaviour was substantially observed when  $Pd(dba)_2$  was used in combination with other diphosphine ligands (Table 7).

It is noteworthy that the influence of the bulkiness of the alcohol on the activity and selectivity of the catalyst is much more evident when DPPE was used as  $P^{\cap}P$  ligand. This behaviour is in accordance with the high stability of the  $Pd(dba)_2/DPPE$  system, due to the

Table 6

Homogeneous 1,3-butadiene telomerization with different primary alcohols catalyzed by  $Pd(dba)_2/DPPM$  systems<sup>a</sup>

Run	Alcohol	$C_4H_6$ conversion (%)		Selectivity <sup>b,c</sup> (%)			$R^{b,d}$ (%)
		4 h	18 h	<b>1</b> <sup>e</sup>	<b>2</b> <sup>f</sup>	<b>3</b> <sup>g</sup>	
10	CH <sub>3</sub> OH	93.3	n.d.	90.4	4.1	5.3	95.7
23	C <sub>2</sub> H <sub>5</sub> OH	46.0	n.d.	79.4	3.6	17.0	95.7
24	<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	37.8	100	70.6	2.4	25.9	96.7
25	<i>n</i> -C <sub>4</sub> H <sub>9</sub> OH	36.9	100	69.3	2.5	28.2	96.6
26	<i>n</i> -C <sub>5</sub> H <sub>11</sub> OH	33.2	n.d.	60.2	4.3	35.5	93.4
27	<i>n</i> -C <sub>6</sub> H <sub>13</sub> OH	40.5	n.d.	70.3	0.7	29.0	99.0

<sup>a</sup>Reaction conditions:  $Pd(dba)_2$ : 0.1 mmol;  $Pd/P/ROH/C_4H_6 = 1/2/3000/2000$ ; solvent: *n*-hexane (20 ml);  $P_{N_2} = 3$  MPa;  $T = 60^\circ C$ .

<sup>b</sup>Determined after 4 h.

<sup>c</sup>When **1** + **2** + **3** < 100, trimers and higher telomers are also present to some extent.

<sup>d</sup>Regioselectivity to the linear telomers **1**, expressed as  $[1/(1+2)] \times 100$ .

<sup>e</sup>*Cis*- and *trans*-1-alkoxy-2,7-octadiene.

<sup>f</sup>3-Alkoxy-1,7-octadiene.

<sup>g</sup>Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.

Table 7

Homogeneous 1,3-butadiene telomerization with different primary alcohols catalyzed by Pd(dba)<sub>2</sub>/Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>n</sub>-PPh<sub>2</sub> systems<sup>a</sup>

Run	P <sup>∧</sup> P ligand	Alcohol	C <sub>4</sub> H <sub>6</sub> conversion (%)		Selectivity <sup>b,c</sup> (%)		R <sup>b,d</sup> (%)
			0.5 h	4 h	1 <sup>e</sup> + 2 <sup>f</sup>	3 <sup>g</sup>	
11	DPPE	CH <sub>3</sub> OH	35.3	64.2	97.7	2.1	93.7
28	DPPE	C <sub>2</sub> H <sub>5</sub> OH	14.2	30.1	74.9	24.3	96.9
29	DPPE	<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	4.6	39.7	30.6	68.8	95.8
30	DPPE	<i>n</i> -C <sub>6</sub> H <sub>13</sub> OH	4.2	22.1	23.2	76.5	96.0
13	DPPB	CH <sub>3</sub> OH	82.8	99.9	97.5	2.5	95.8
31	DPPB	C <sub>2</sub> H <sub>5</sub> OH	35.2	83.0	84.2	13.6	97.5
32	DPPB	<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	34.4	78.4	73.3	26.2	97.8
33	DPPB	<i>n</i> -C <sub>6</sub> H <sub>13</sub> OH	21.9	36.0	66.3	33.1	98.6

<sup>a</sup>Reaction conditions: Pd(dba)<sub>2</sub>: 0.1 mmol; Pd/P/ROH/C<sub>4</sub>H<sub>6</sub> = 1/2/3000/2000; solvent: *n*-hexane (20 ml); P<sub>N<sub>2</sub></sub> = 3 MPa; T = 60°C; reaction time: 4 h.

<sup>b</sup>Determined after 4 h.

<sup>c</sup>When 1 + 2 + 3 < 100, trimers and higher telomers are also present to some extent.

<sup>d</sup>Regioselectivity to the linear telomers 1, expressed as [1/(1 + 2)] × 100.

<sup>e</sup>*Cis*- and *trans*-1-alkoxy-2,7-octadiene.

<sup>f</sup>3-Alkoxy-1,7-octadiene.

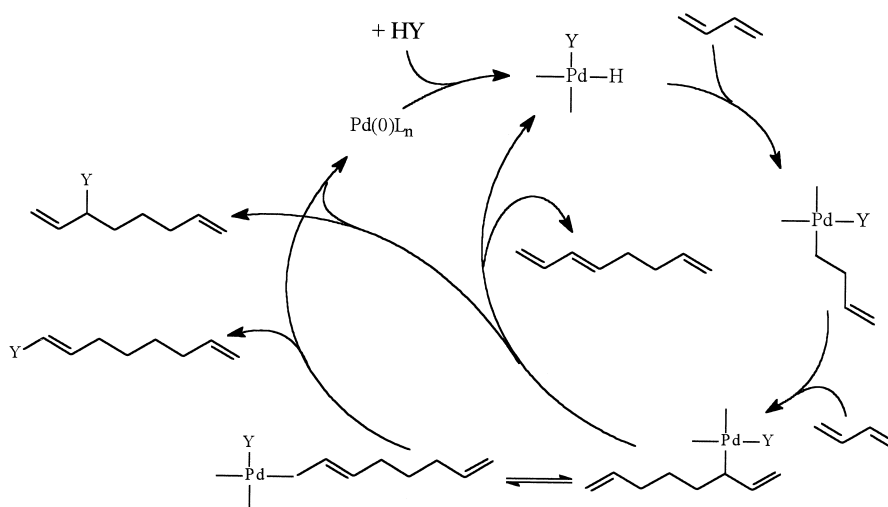
<sup>g</sup>Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.

formation of 5-membered metallacyclo moieties, and hence, with the low activity of the resulting catalyst.

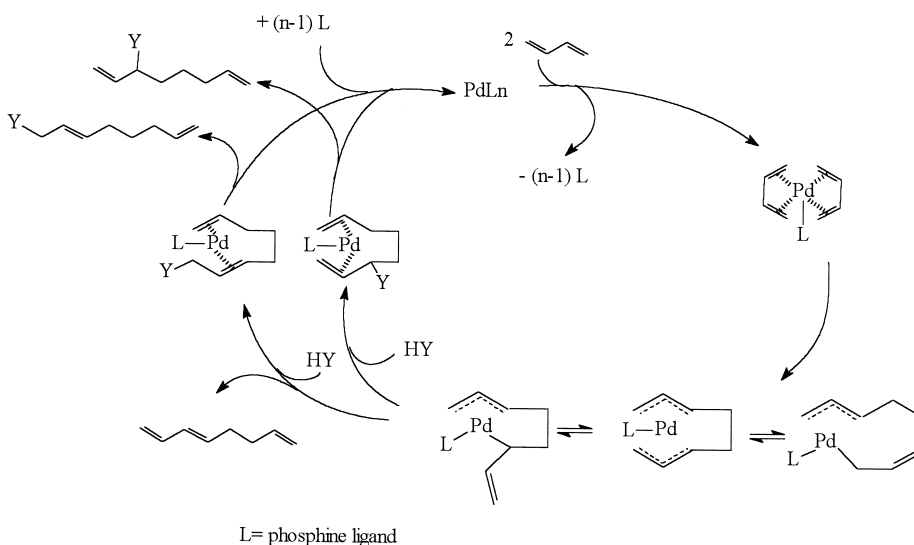
### 3.3. Mechanistic implications

The present study allows us to point out some considerations. If a palladium hydride intermediate would be responsible for the formation of the telomers, as previously proposed [25] according to Scheme 3, the presence of strongly

basic chelate ligands would increase the nucleophilic character of the site, as suggested by Portnoy and Milstein [26], and hence, favour the oxidative addition of the alcohol to a Pd(0) species. In this respect, a diphosphine chelate ligand with proper size, basicity and steric requirements would exert a positive effect on the activity of the resulting metallacyclo catalytic moiety toward the formation of telomers. However, the results collected in the present paper concerning the use of these chelate ligands dis-



Scheme 3.



Scheme 4.

play in general a detrimental effect. Moreover, the observation that the pre-treatment of  $\text{Pd}(\text{dba})_2/\text{R}_3\text{P}$  catalysts by 1,3-butadiene has a favourable effect on the reaction rate, whereas the analogous pre-treatment by methanol causes an inhibiting effect, seems to confirm that a bis-allyl palladium(0) and not a Pd(II) hydride species is involved in the reaction mechanism, as previously proposed by Döhning et al. [27] and tentatively represented in Scheme 4. Indeed, the bis-allyl intermediate is favoured by 1,3-butadiene pre-coordination and also by a rather low P/Pd molar ratio because its formation strictly requires a ligand dissociation step. Accordingly, strongly basic monodentate phosphines, characterized also by a low steric hindrance, give the best results, in terms of activity and selectivity of the telomerization process, because they are not only able to stabilize the palladium species but also may be employed with a low P/Pd molar ratio.

#### 4. Conclusions

On the basis of the obtained results some concluding remarks can be drawn below.

(1) When the catalyst for the 1,3-butadiene telomerization with primary alcohols was prepared in situ from  $\text{Pd}(\text{dba})_2$  and monophosphines, a rather strict correlation between basicity, as well as steric hindrance of the ligand and activity and selectivity of the resulting catalyst was found.

(2) The use of diphosphine chelate ligands in combination with  $\text{Pd}(\text{dba})_2$  evidenced that the catalytic activity is strongly dependent on the size of the resulting metallacyclo palladium species, 5- and 6-membered systems displaying the lowest catalytic activity, according to their highest stability.

(3) When primary higher alcohols were used in the 1,3-butadiene telomerization, a progressive reduction of activity and selectivity up to a limiting value was observed on increasing the length of the alkyl residue.

(4) Catalyst pre-treatment by 1,3-butadiene significantly improved the catalytic activity, whereas the analogous pre-treatment by methanol resulted detrimentally for the telomerization rate. These effects, up to now never evidenced, suggest that the active catalytic species involved in the reaction would be a bis-allyl palladium(0) intermediate.

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