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# Cationic $\eta^3$-allyl complexes. 21. Telomerization of buta-1,3-diene with Z–H compounds mediated by group 10 complexes

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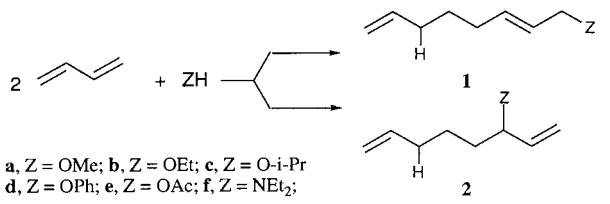
**Abstract**

Cationic ($\eta^3$-allyl) complexes of general formula $[(\eta^3\text{-allyl})M(ligand)_2]^+Y^-$, where $Y^-$ is a non-coordinating anion ($BF_4^-$, $ClO_4^-$, $BF_4^-$) have been examined in telomerization reactions of buta-1,3-diene with representative nucleophiles. No reaction are observed for nickel complexes, due to their high reactivity versus nucleophiles. With palladium complexes, the reaction only occurs with alcohols and provides an increased selectivity for telomers with more than two diene units, leading to $C_{16}$, $C_{24}$ and even higher ethers. Although much less reactive, platinum complexes can also produce higher telomers when hydrogenosilanes are used. It is proposed, at least in the case of palladium, that the formation of $C_{16}$ and $C_{24}$ ethers arises from the coupling of $C_8$ units within dimeric palladium intermediates with the telogen acting as a bridging ligand. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Buta-1,3-diene telomerization; Allyl complexes; Functionalized hexadecatetraenes; Palladium; Platinum

## 1. Introduction

Telomerization reactions of dienes are reported to provide, in good yields, linear dimerization products with a 1,6 or 3,6 addition of the telogen which is generally a compound with active hydrogen (e.g. water [1], alcohols [2], amines [3], carboxylic acids [4], etc.) (Eq. (1)).




**a**, Z = OMe; **b**, Z = OEt; **c**, Z = O-i-Pr
**d**, Z = OPh; **e**, Z = OAc; **f**, Z = $NEt_2$;

The reaction is known to proceed smoothly with group 10 metals. Neutral ($\eta^3$-allyl) palladium complexes have been reported to be catalyst precursors or reaction intermediates in the catalytic transformation of unsaturated substrates [5]. It has been also recognized that cationic ($\eta^3$-allyl) metal species may play a central role in such reactions, although they are not used as such as catalyst precursors [6]. Also, our approach to new catalytic reactions of unsaturated hydrocarbons was to design ad hoc cationic ($\eta^3$-allyl) complexes and to examine their activity in telomerization reactions. For these precursors, one can predict: (i) an easier coordination of substrates and reactants via dissociation of labile ligands L; (ii) an increased activity of donor substrates owing to the greater electrophilic character of the metal center; and (iii) the occurrence of reactions specific to the monohapto ⇄ trihapto and masked hydride behaviors of the allyl ligand [7].

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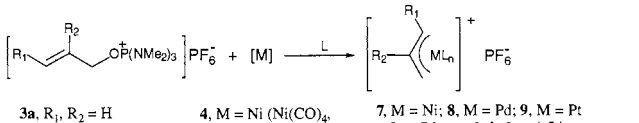
We have already reported on efficient and economic methods for the synthesis of cationic ($\eta^3$-allyl) complexes of nickel [8], palladium [9] and platinum [10] using the general reaction between allyloxyphosphonium salts like **3** with the corresponding molecular group 10 zerovalent precursors **4**–**6** (Eq. (2)).



**3a**, $R_1$, $R_2$ = H
**3b**, $R_1$ = H, $R_2$ = Me
**3c**, $R_1$ = H, $R_2$ = Ph
**3c**, $R_1$ = Me, $R_2$ = H

**4**, M = Ni ($Ni(CO)_4$, $Ni(cod)_2$
**5**, M = Pd ($Pd(dba)_{1.5}$)
**6**, M = Pt ($Pt(dba)_3$)

**7**, M = Ni; **8**, M = Pd; **9**, M = Pt
**a**, L = CO, n = 2; **b**, $L_n$ = 1.5 hmpa
**c**, $L_n$ = dba, hmpa; **d**, $L_n$ = cod
**e**, L = $P(OPh)_3$, n = 2; **f**, L = $PPh_3$, n = 2
**g**, L = $PBu_3$, n = 2; **h**, L = $PCy_3$, n = 2

In this paper we present examples of unexpected transformations of mixtures of buta-1,3-diene and active hydrogen compounds (i.e. alcohols, amines, water and silanes) and provide relevant mechanistic insights on the formation of these compounds. A preliminary account of part of this work has been published [11].

## 2. Results and discussion

### 2.1. Nickel complexes

Complexes **7** are catalysts for the oligomerization of buta-1,3-diene [12]. The strong electrophilic character of the nickel center enhances its reactivity toward nucleophiles ([8]a). This could be extended to the $\eta^3$-allyl ligand. However, reaction of buta-1,3-diene with methanol or diethylamine leads to low conversions of the diene and to the decomposition of the complex used (e.g. **7a**, **7f**) to $Ni^{2+}$ salts: the catalytic behavior of these compounds was therefore not studied further.

### 2.2. Palladium complexes

In the case of alcohols it is known that octadienyl ethers are the main reaction products together with octatrienes [2]. In very few instances higher telomers containing three or four buta-1,3-diene units were observed [13]. By reacting buta-1,3-diene with methanol in the presence of complex **8c** or **8d** dissolved in dichloromethane, a mixture of $H(C_4H_6)_nOMe$ ethers is formed instead (Table 1). Noteworthy are the preferred formation of $C_{16}$ telomers and the presence as minor components of telomers with an odd number of taxogen units. The telomers with 2 ($C_8OMe$), 4 ($C_{16}OMe$), and 6 ($C_{24}OMe$) buta-1,3-diene units were characterized by conventional spectroscopic techniques and hydrogenation followed by comparison with authentic samples (Section 4). Thus, 1-methoxy-2,7-octadiene **1a**, 3-methoxy-1,6,10,15-hexadecateraene **9a** and 3-methoxy-1,6,10,14,18,23-tetracosahexaene **10a** were identified: for the higher telomers, only small amounts ($< 3\%$) of 1-methoxy adducts were detected. Catalytic activity and product selectivities are not modified by the use of other cationic allylpalladium complexes or their generation in situ.

Several parameters have a drastic influence on buta-1,3-diene conversion and product distributions. As shown in Table 1, conversions are always higher than 90% in the solvents examined except for acetonitrile which inhibits the reaction. The highest yield of $C_{16}OMe$ is observed when toluene is used. However, no correlation can be found with any solvent parameter. Reagent ratios, temperature and reaction time have a greater influence on conversion and selectivity. As expected, an increase of the molar ratio $MeOH/C_4H_6$ leads to a greater selectivity in $C_8OMe$ ethers (Table 2). It is noteworthy that the highest selectivity for $C_{16}OMe$ ethers is not observed for the ratio $MeOH/C_4H_6 = 1/4$ but around 1/2. Interestingly, 1-methoxyhexadecatetraene is build in noticeable amounts as the methanol content in the reaction medium increases. An increase in the reaction temperature allows a higher conversion of buta-1,3-diene but at the expense of the telomers. Fig. 1 indicates a steady decrease of the ethers $C_8OMe$, but optimal temperature for the formation of the higher ethers $C_{16}OMe$ and $C_{24}OMe$. Octatrienes and hexadecapentaenes are not formed at the expense of the telomers. Finally, reaction time has a drastic influence on the product distribution. As shown in Fig. 2, the highest selectivities are observed at the shortest time, hence at the lowest buta-1,3-diene conversions. Furthermore, $C_8OMe$ ethers selectivities slightly decrease with increased reaction times. The yield of $C_{16}OMe$ and $C_{24}OMe$ ethers reaches a plateau after 4 h. At longer reaction times, large amounts of higher oligomers are produced.

The catalytic reaction observed with methanol proceeds well with other aliphatic alcohols and with phenol. Table 3 sums up typical examples. Chemical

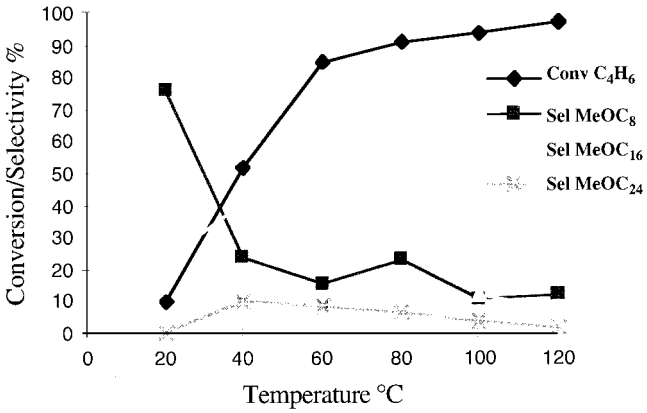



Fig. 1. Influence of the reaction temperature on buta-1,3-diene conversion and ether distributions (reaction conditions: [Pd] = 0.25 mmol, $C_4H_6$ = 300 mmol, $CH_2Cl_2$ = 10 ml, reaction time = 20 h).

Table 1
Telomerization of buta-1,3-diene with methanol: influence of the nature of complexes and solvents

| Run | Catalyst or solvent | Conversion (%) | Yield (%) | | Selectivity (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_4H_6$ | $C_{16}{}_{16}OMe$ | $C_{24}OMe$ | 1-$MeOC_8$ | 3-$MeOC_8$ | $MeOC_{12}$ | 1-$MeOC_{16}$ | 3-$MeOC_{16}$ | $MeOC_{20}$ | $MeOC_{24}$ | $C_8$ | $C_{16}$ |
| 1 | **8d** | 76 | 20 | 7 | 22 | 1 | 2 | 3 | 23 | 5 | 9 | 2 | 3 |
| 2 | $Pd_2(dba)_3 \cdot CHCl_3$ + **3b** | 60 | 23 | 3 | 19 | 1 | 2 | 2 | 36 | 6 | 6 | 2 | 3 |
| 3 | $Pd_2(dba)_3$ + **3b** | 94 | 21 | 6 | 10 | 1 | 1 | 2 | 20 | 5 | 7 | 3 | 5 |
| 4 | $Pd_2(dba)_3$ + **3b**[a] | 97 | 14 | 6 | 13 | 4 | 3 | 2 | 12 | 7 | 6 | 2 | 4 |
| 5 | $Pd_2(dba)_3$ + **3b**[b] | 76 | 11 | 6 | 7 | 1 | 1 | 3 | 12 | 3 | 9 | 3 | 4 |
| 6 | $Pd_2(dba)_3$ + **3b**[c] | 0 | — | — | — | — | — | — | — | — | — | — | — |
| 7 | $Pd_2(dba)_3$ + **3d** | 94 | 20 | 6 | 11 | 1 | 1 | 2 | 19 | 5 | 7 | 2 | 5 |
| 8 | $Pd_2(dba)_3$ + **3c**[d] | 76 | 14 | 6 | 13 | 4 | 3 | 2 | 12 | 7 | 6 | 2 | 4 |
| 9 | — | 91 | 28 | 6 | 19 | 1 | 2 | 2 | 28 | 5 | 7 | 4 | 2 |
| 10 | Cyclohexane | 88 | 24 | 5 | 27 | 2 | 1 | 2 | 26 | 3 | 5 | 2 | 1 |
| 11 | Toluene | 94 | 32 | 8 | 19 | 1 | 1 | 2 | 32 | 2 | 9 | 2 | 3 |
| 12 | Toluene[e] | 97 | 21 | 3 | 20 | <1 | 2 | 2 | 20 | 3 | 4 | 1 | 1 |
| 13 | Tetrahydrofurane | 100 | 22 | 10 | 7 | 1 | <1 | 2 | 19 | 2 | 10 | 2 | 4 |
| 14 | *t*-Butanol[f] | 94 | 24 | 7 | 20 | 2 | 1 | 3 | 23 | 1 | 7 | 2 | 2 |
| 15 | Acetone | 94 | 18 | 8 | 8 | 1 | 1 | 2 | 17 | 4 | 9 | 3 | 3 |
| 16 | Dimethylformamide | 97 | 24 | 9 | 10 | 1 | <1 | 3 | 22 | 2 | 9 | 3 | 3 |
| 17 | Acetonitrile | 0 | — | — | — | — | — | — | — | — | — | — | — |

Reaction conditions: [Pd] = 0.25 mmol, $C_4H_6$ = 300 mmol, MeOH = 75 mmol, solvent = 10 ml, temperature = 80°C, reaction time = 20 h; runs 9–17 were performed in presence of a catalyst generated from $Pd_2(dba)_3$ + **3b**.
[a] Y = $BF_4$ instead of $PF_6$; [b] Y = $ClO_4$ instead of $PF_6$; [c] Y = $BPh_4$ instead of $PF_6$; [d] Y = $ClO_4$ instead of $PF_6$; [e] catalyst isolated as the 1,5-cod complex **8d**; [f] presence of 1-*t*-butoxy-octa-2,7-diene (3%).

Table 2
Telomerization of buta-1,3-diene with methanol: influence of methanol/buta-1,3-diene ratio and temperature

| Run | $MeOH/C_4H_6$ | Temperature (°C) | Conversion (%) | Yield (%) | | Selectivity (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $C_4H_6$ | $C_{16}OMe$ | $C_{24}OMe$ | 1-$MeOC_8$ | 3-$MeOC_8$ | $MeOC_{12}$ | 1-$MeOC_{16}$ | 3-$MeOC_{16}$ | $MeOC_{20}$ | $MeOC_{24}$ | $C_8$ | $C_{16}$ |
| 17 | 2/1 | 80 | 98 | 23 | 5 | 29 | 3 | 3 | 6 | 18 | 2 | 5 | 2 | 4 |
| 18 | 1/1 | 80 | 95 | 27 | 5 | 28 | 2 | 2 | 4 | 24 | 2 | 5 | 2 | 3 |
| 19 | 1/2 | 80 | 91 | 27 | 7 | 22 | 1 | 2 | 3 | 27 | 4 | 7 | 2 | 4 |
| 3 | 1/4 | 80 | 94 | 21 | 6 | 10 | 1 | 1 | 2 | 20 | 5 | 7 | 3 | 5 |
| 20 | 1/6 | 80 | 85 | 18 | 7 | 8 | <1 | 1 | 1 | 20 | 5 | 8 | 2 | 4 |
| 21 | 1/8 | 80 | 76 | 19 | 7 | 6 | <1 | <1 | <1 | 24 | 4 | 10 | 2 | 3 |
| 22 | 1/2 | 25 | 10 | 4 | <1 | 76 | — | — | — | 23 | | 1 | | |
| 23 | 1/2 | 40 | 52 | 21 | 5 | 23 | <1 | — | <1 | 40 | 1 | 10 | 1 | 1 |
| 24 | 1/2 | 60 | 85 | 27 | 8 | 15 | 1 | <1 | 1 | 31 | 2 | 9 | 1 | 2 |
| 25 | 1/2 | 100 | 94 | 11 | 4 | 9 | 2 | 2 | 3 | 9 | 5 | 4 | 5 | 7 |
| 26 | 1/2 | 120 | 97 | 8 | 2 | 9 | 3 | 3 | 2 | 6 | 5 | 2 | 6 | 5 |

Reaction conditions: [Pd] = 0.25 mmol, $C_4H_6$ = 300 mmol, $CH_2Cl_2$ = 10 ml, reaction time = 20 h.

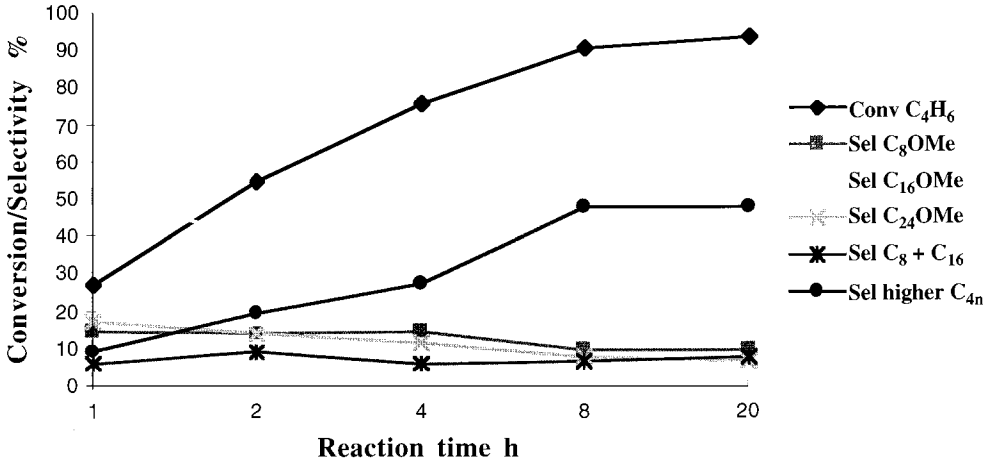



Fig. 2. Influence of the reaction time on buta-1,3-diene conversion and ether distributions (reaction conditions: [Pd] = 0.25 mmol, $C_4H_6$ = 300 mmol, $CH_2Cl_2$ = 10 ml, temperature = 80°C).

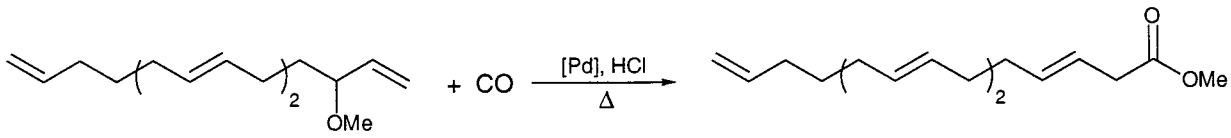
ionization mass spectra, $^1$H-NMR spectra and comparison of the hydrogenated products with the corresponding saturated $C_{4n}$OR ethers were used to ascertain the structures. Inspection of Table 3 shows the expected decrease in buta-1,3-diene conversion which was accounted for by the increase in the steric hindrance of the alkyl group [1]: Me ~ Et > *i*-Pr ≫ *t*-Bu. However, 1-*t*-butyloctadienylether which is not obtained with conventional catalysts according to the literature [14] is now produced in noticeable amounts. The high reactivity of phenol is in agreement with published results, but the poor reactivity of allyl alcohol requires further investigation. Higher telomers are produced except for *t*-butanol and allyl alcohol. It is worth noting that large amounts of $C_{12}$OPh ether are obtained: this may reflect another mechanistic route to this compound.

In the case of other telogens like secondary amines and carboxylic acids, the catalytic reaction does not run in the same way. Only octadienyl amines or esters were obtained. With diethylamine, the product of nucleophilic attack on the ($\eta^3$-allyl) ligand of **8d** is detected. With acetic acid, dodecatetraenes are also formed. In fact, complex **8d** is converted into bis[($\eta^3$-methyl-2-allyl)acetatopalladium] which is known for converting buta-1,3-diene into $C_8$ and $C_{12}$ oligomers ([12]a).

Transformations of the telomers into other products will provide new entries to long-chain unsaturated compounds. The presence of an allyl function offers several opportunities like dimerization and carbonylation. Reaction of the telomers with acetic acid in the presence of palladium acetate gives rise to unsaturated linear and branched hydrocarbons with twice the number of carbon atoms (Eq. (3)) [15].

$$2\ C_8^2OMe + 2\ AcOH \xrightarrow[\Delta]{Pd(OAc)_2} C_{16}^5 + 2\ AcOMe + 2\ H_2O$$

The telomers are smoothly converted into the corresponding esters by carbonylation. It is noteworthy that in the case of the 3-MeO$C_{16}$ ether, the carbonylation reaction gives rise to the 1-MeO(O)C$C_{16}$ ester (Eq. (4)) [16].




However, one-pot synthesis of this compound starting from buta-1,3-diene, methanol and carbon monoxide could not be achieved. In fact, the first step, telomerization, requires an ionic complex and the second step, carbonylation, occurs only in the presence of chloride ions [17].

Addition of two equivalents of phosphane ligands to the catalytic system formed in situ or the use of well defined complexes like **8f** and **8g** gives rise to telomers and, mostly, oligomers (Table 4). $^1$H-NMR analysis of the reaction products indicates that compounds with more than two buta-1,3-diene units are methoxy-1 telomers which exhibit branching in the oligomeric chain since two vinyl groups are present (see Section 4). Hydrogenation of these telomers confirms the occurrence of branching with one ethyl group. For the $C_{16}$ telomer, analysis of the CI-MS spectra indicates that the backbone of this compound corresponds to 1-methoxy-6-ethyltetradecane, therefore suggesting structure **11** or **12**.

Table 4
Telomerization of buta-1,3-diene with methanol: effect of added phosphanes and phosphane complexes

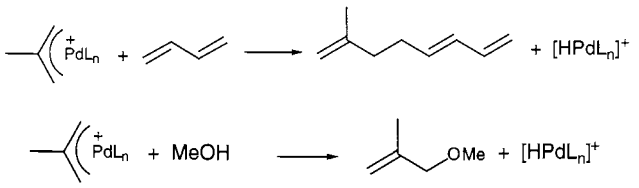
| Run | Complex or ligand | $MeOH/C_4H_6$ | Conversion (%) | Yield (%) | | Selectivity% | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $C_4H_6$ | $C_{16}OMe$ | $C_{24}OMe$ | 1-$MeOC_8$ | 3-$MeOC_8$ | 1-$MeOC_{16}$ | 3-$MeOC_{16}$ | $MeOC_{24}$ | $C_8$ | $C_{16}$ | $C_{24}$ |
| 32 | **8e** | 1/4 | 0 | — | — | — | — | — | — | — | — | — | — |
| 33 | **8f** | 1/4 | 100 | 10 | 5 | 14 | 1 | 9 | 1 | 5 | 10 | 6 | 5 |
| 34 | **8f** | 1/1 | 100 | 10 | 0 | 78 | 5 | 10 | 0 | 0 | 5 | 0 | 0 |
| 35 | **8g** | 1/4 | 100 | 3 | 0 | 31 | 2 | 3 | 0 | 0 | 60 | 3 | 0 |
| 36 | **8g** | 1/1 | 100 | 2 | 0 | 71 | 7 | 2 | 0 | 0 | 19 | 0 | 0 |
| 37 | 2 $P(OPh)_3$ | 1/4 | 0 | — | — | — | — | — | — | — | — | — | — |
| 38 | 2 $PPh_3$ | 1/4 | 97 | 10 | 6 | 20 | 1 | 9 | $<1$ | 6 | 10 | 5 | 6 |
| 39 | 2 $PBu_3$ | 1/4 | 0 | — | — | — | — | — | — | — | — | — | — |
| 40 | 2 $PCy_3$ | 1/4 | 100 | 7 | 2 | 19 | 1 | 6 | 1 | 2 | 41 | 10 | 3 |

Reaction conditions: [Pd] = 0.25 mmol, $C_4H_6$ = 300 mmol (except runs 32, 34 and 36: 150 mmol), $CH_2Cl_2$ = 10 ml, temperature = 80°C, reaction time = 20 h.

(ii) Reaction of 1,3,6- and 1,3,7-octatrienes with methanol in the presence of the same complex **8d** does not occur.

(iii) Reaction of 1-methoxyoct-2-ene (obtained by selective hydrogenation of the terminal double bond of 1-methoxyocta-2,7-diene in the presence of $Ru(PPh_3)_3Cl_2$ (see Section 4)) only provides, under the same conditions as (i), small amounts of octa-1,3-dienes in addition to the starting compound.

We therefore suggest that the key step of the reaction involves a coupling of two $C_8$ units generated from methoxy-1-octa-2,7-diene or methoxy-3-octa-1,7-diene. These octadienyl ethers are formed either through a zerovalent or a hydridopalladium species (Eqs. (8) or (9)). The hydridopalladium could arise from the reaction of the cationic ($\eta^3$-allyl)palladium complex with buta-1,3-diene (Eq. (8)) or from nucleophilic attack of methanol on the allyl ligand (Eq. (9)). The zerovalent palladium entity could be formed by reductive elimination within the intermediate **16** resulting from deprotonation of methanol coordinated to a cationic ($\eta^3$-allyl)palladium species (Eq. (10)). It should be pointed out that an equilibrium can occur between the zerovalent palladium species and proton and the cationic hydridopalladium species [20].



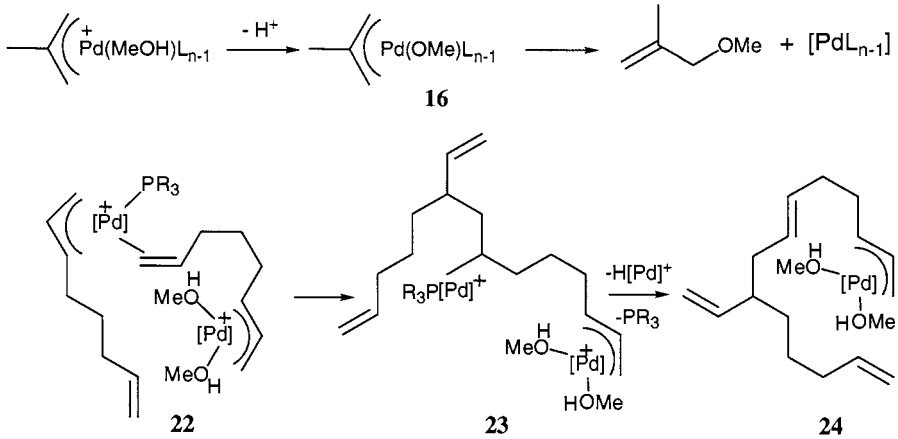

As already reported [17], a $\eta^3$-octatrienyl unit is formed by the attack of a zerovalent palladium species on the protonated methoxyoctadiene. The corresponding cationic ($\eta^3$-allyl) complex **17a** is solvated with methanol and under the reaction conditions used can be in equilibrium with a dimer **18a** arising from the formation of methanol bridges (Scheme 1).

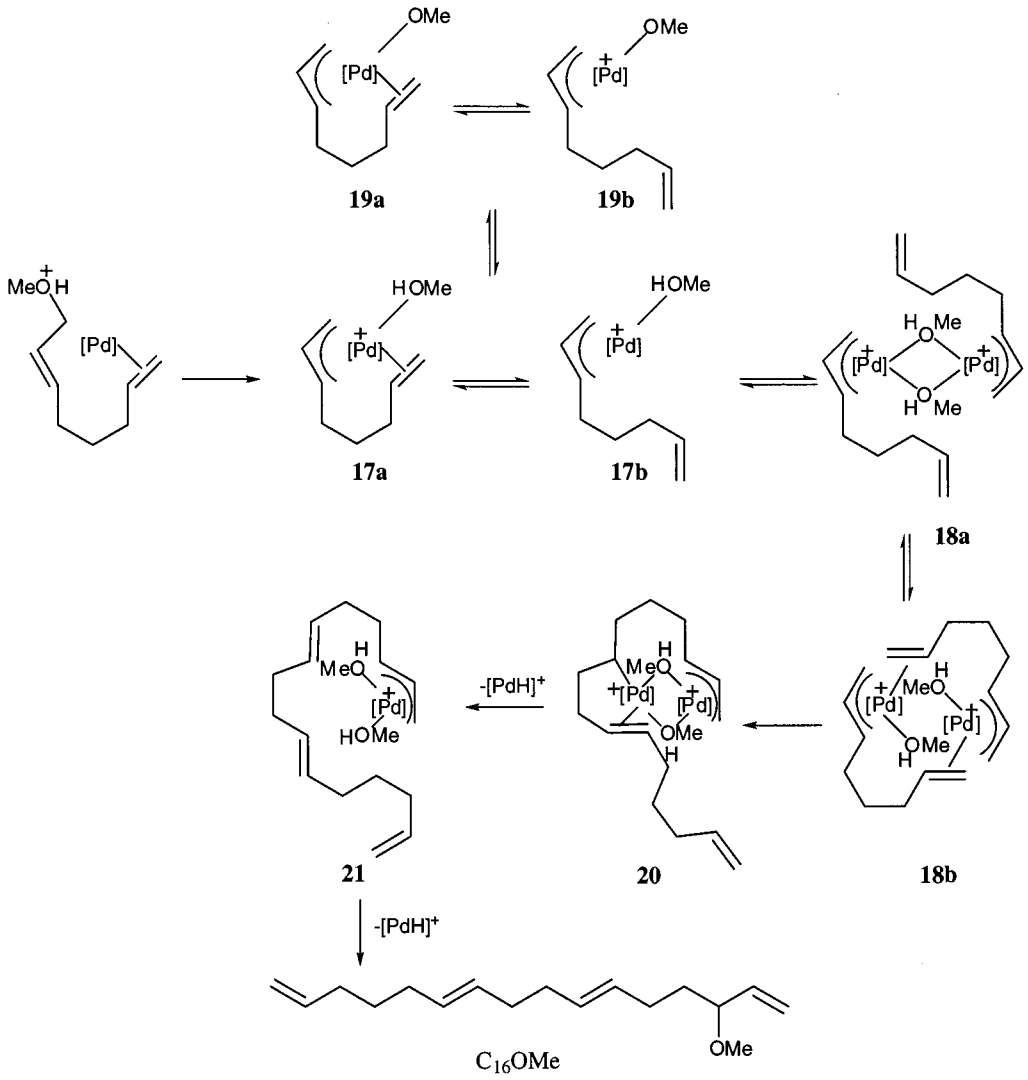
Other equilibria can take place, like: (i) the deprotonation of one or both methanol ligands leading to a less charged species (i.e. **19a**); further dimerization can be possible at that stage; and (ii) the coordination of the pendent double bond of an octatrienyl ligand to the other palladium center leading to a new type of dimer (i.e. **18b**).

Carbon–carbon coupling is possible with complex **18b**, leading to the intermediate **20** which, through $\beta$-elimination evolves the hexadecatetraenyl ligand **21**. Methanol (or methoxy ligand) is suitably well positioned in this complex for a nucleophilic attack at C-3 position of the $\eta^3$-allyl ligand, therefore producing the expected telomer. Interaction of **21** with an octatrienyl species **17b** will provide the route to the formation of $C_{24}OMe$ telomers.

This mechanistic proposal requires two equivalents of methanol for four moles of buta-1,3-diene, in complete agreement with the experimental observation of highest $C_{16}OMe$ selectivity for a $MeOH/C_4H_6$ ratio of 1/2. The formation of the 1-methoxy isomer by increasing the methanol amount will be explained by external attack of the solvent at the less hindered C-1 position. This proposal also explains the lack of formation of $t$-$BuOC_{16}$ ethers owing to the steric inhibition for dimerization. Finally, the low stability of the reaction intermediates, especially the dimers, requires low reaction temperatures and short reaction times.

In the presence of phosphane ligands, the equilibria monomer dimer are not in favor of the latter form(s). Hence, the amount of $C_8OMe$ ethers is higher and the regioselectivity of the C–C coupling is changed owing to the steric hindrance introduced by the phosphane in the intermediate **22**, analogous to **18b**. The C–C coupling now generates an intermediate with a branched vinyl group (i.e. **23**), where the attack of methanol may occur on the terminal carbon of the remaining $\eta^3$-allyl ligand (Eq. (11)).






Scheme 1.

### 2.3. Platinum complexes

Platinum precursors are much less active than palladium ones in telomerization reactions of buta-1,3-diene in the presence of ZH compounds. This trend is observed too for cationic complexes like **9d**. Moreover, inspection of Table 5 shows that only methoxyoctadienes are obtained in that case. Diethylamine also acts as a telogen, giving diethyloctadienylamines.However, the use of acetic acid does not lead to the formation of acetoxyoctadienes. In fact **9d** is converted into platinum acetate which is inactive for this reaction under the conditions used. Water also acts as a nucleophile but only but-2-enol is produced with large amounts of $C_{4n}$ oligomers in the presence of carbon dioxide. No adduct is formed in the absence of carbon dioxide which is not used under supercritical conditions. The absence of higher telomers could be explained by a faster attack of the alcohol molecule on the $\eta^3$-allyl ligand of **17** therefore leading to a low concentration of cationic platinum complexes which prevents the formation of dimeric intermediates like **18**.

Platinum compounds are well known as catalysts for hydrosilylation [21] and its use for the telomerization of buta-1,3-diene with hydrogenosilanes as been reported ([22]a). In the present case, $C_4$, $C_8$ and $C_{16}$ adducts are obtained in the presence of triethylsilane (Table 5). No $C_{12}$ adducts are observed.If the reaction is performed in the presence of triphenylphosphane, only the $C_4$ adducts (*cis* and *trans*) are observed. The products were identified by MS and NMR, and by comparison of the hydrogenated derivatives with authentic samples prepared by the conventional hydrosilation route: no branched telomers are formed in this case. The $C_4$ adduct are presumably formed by the 1,4 addition of triethylsilane on buta-1,3-diene catalyzed by a cationic platinum hydride complex generated according to the process depicted in Eq. (8). The formation of the higher

Table 5
Telomerization of buta-1,3-diene with different telogens in the presence of platinum complexes

| Run | Complex | Z–H | Conversion (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | $C_4H_6$ | 1-$ZC_4$ | 1-$ZC_8$ | 1-$ZC_{16}$ | $C_8$ |
| 41 | **9d** | MeOH | 70 | 0 | 92 | 0 | 8 |
| 42 | **9d** | AcOH | 0 | — | — | — | — |
| 43 | **9d** | $Et_2NH$ | 40 | 0 | 89 | 0 | 11 |
| 44 | **9d** | $H_2O$[a] | 10 | 5 | 0 | 0 | 95 |
| 45 | **9d** | $Et_3SiH$ | 83 | 76 | 15 | 9 | <1 |
| 46 | **9d** + 1$PPh_3$ | $Et_3SiH$ | 92 | 96 | <1 | 0 | 3 |

Reaction conditions: [Pt] = 0.25 mmol, $C_4H_6$ = 300 mmol, ZH = 75 mmol, $CH_2Cl_2$ = 10 ml, temperature = 80°C (except run 45, 25°C), reaction time = 24 h.
[a] Under pressure of $CO_2$ (20 bar).

telomers should proceed via another pathway than that proposed in Scheme 1. Indeed, inspection of NMR spectra indicates that there are no vinyl groups in the $C_8$ and $C_{16}$ telomers formed with triethylsilane. A stepwise addition process of one $C_4$ ($Et_3SiC_8$) and one $C_8$ unit ($Et_3SiC_{16}$) will be in agreement with the observations reported in the literature ([22]b). However, no $C_{12}$ telomers are observed. Further work is needed for understanding this specific reaction.

## 3. Conclusions

The isoleptic cationic ($\eta^3$-allyl)metal complexes of the nickel group exhibit very differentiated behavior in telomerization reactions of buta-1,3-diene with different types of telogens. Due to their electrophilic nature, nickel complexes are transformed into $Ni^{2+}$ species which are inactive in catalysis. The palladium complexes are also sensitive to telogens like amines, water and carboxylic acids. However the use of alcohols provide an access to higher telomers with four, six, and certainly higher even numbers of buta-1,3-diene units. The formation of these new telomers can be explained by the coupling of two $C_8$ units ($C_{16}$ telomers), one $C_{16}$ and one $C_8$ unit ($C_{24}$ telomers), etc. within binuclear palladium complexes with alcohol or alkoxy bridges. Finally, the peculiar behavior of the platinum complexes for telomerization of buta-1,3-diene with triethylsilane may arise from another process than that depicted for palladium and protic solvents. Further work on catalytic formation of higher functionalized buta-1,3-diene oligomers is in progress [23].

## 4. Experimental

### 4.1. General

Schlenk tube technique was used with purified argon as inert gas. Solvents were distilled according to the literature. Buta-1,3-diene was dried on Molecular Sieves 3A before use. Alcohols were distilled over the corresponding alcoholates (methanol, ethanol, *i*-propanol) or calcium hydride (*t*-BuOH). The phosphorus ligands were either crystallized (triphenylphosphane, tricyclohexylphosphane) or distilled under reduced pressure (triphenylphosphite, tributylphosphane).

### 4.2. Syntheses

Zerovalent palladium complexes, allyloxytris(dimethylamino)phosphonium salts **3** and complexes **7**, **8** and **9** were prepared according to the literature [8–10].

Authentic samples of the following $C_8$ telomers with alcohols were prepared for GC, MS and NMR comparison: 1-methoxyocta-2,7-octadiene ([22]a), 1-ethoxy octa-2,7-octadiene [14], 1-*i*-propoxy octa-2,7-octadiene [14], 1-phenoxyocta-2,7-octadiene [24], 1-methoxyoct-2-ene is prepared by selective hydrogenation of 1-methoxy-2,7-octadiene in the presence of $Ru(PPh_3)_3Cl_2$ [25].

### 4.3. Characterization of the higher telomers

#### 4.3.1. 3-Methoxyhexadecatetraene

The reaction mixture (10 g) from repetitions of run 9 was percolated through a column of Kieselgel 60 (Merck) and then submitted to a first distillation (1 torr) leading to a distillate (7.2 g) containing octa-1,3,7-triene, 1-methoxy-octa-2,7-diene and 3-methoxy-octa-1,7-diene. The residue is distilled under $10^{-2}$ torr to give fractions enriched (>95%) in 3-methoxyhexadecatetraene (Eb 55–60°C, 1.5 g) and 3-methoxytetracosahexadecatetraene (Eb 155–160°C, 0.7 g).

MS (EI, 70 eV): 248 (0.5, $M^{+\cdot}$), 216 (0.6, $M^{+\cdot} - CH_3OH$), 107 (43, $C_8H_{11}^+$), 93 (14, $C_7H_9^+$), 79 (86, $C_6H_7^+$), 71 (100, $C_4H_7O^+$), 67 (61, $C_5H_7^+$), 55 (31, $C_4H_7^+$), 45 (7, $C_2H_5O^+$), 41 (64, $C_3H_5^+$).

IR (KBr): 1640 ($\nu_{C=C}$), 1100 ($\nu_{C-O}$, ether), 990 and 920 ($\delta_{C-H}$, terminal vinyl), 970 $cm^{-1}$ ($\delta_{C-H}$, *trans*-disubstituted double bond).

NMR (80 MHz, $CDCl_3$): $\delta$ 1.3–1.7 (m, 4H), 1.8–2.3 (m, 10H), 3.30 (s, 3H), 3.55 (q, $^3J = 6$ Hz, 1H), 4.9–6.0 ppm (m, 10H).

This product is hydrogenated (20 bar, 25°C) with $PtO_2$ (0.02 g) in pentane (25 ml). The retention time (GC) and MS spectra of the hydrogenated product are identical to those of 3-methoxyhexadecane.

IR (KBr): 1095 $cm^{-1}$($\nu_{C-O}$, ether).

NMR (80 MHz, $CDCl_3$): $\delta$ 0.8–1.0 (m, 6H), 1.1–1.6 (m, 26H), 3.05 (q, $^3J = 5$ Hz, 1H), 3.30 (s, 3H) ppm.

*4.3.2. 3-Methoxytetracosahexadecatetraene*

MS (EI, 70 eV): 324 (1.8, $M^{+\cdot} - CH_3OH$), 107 (45, $C_8H_{11}^+$), 93 (20, $C_7H_9^+$), 79 (71, $C_6H_7^+$), 71 (52, $C_4H_7O^+$), 67 (70, $C_5H_7^+$), 55 (30, $C_4H_7^+$), 45 (4, $C_2H_5O^+$), 41 (41, $C_3H_5^+$).

IR (KBr): 1640 ($\nu_{C=C}$), 1090–1100 ($\nu_{C-O}$, ether), 990 and 915 ($\delta_{C-H}$, terminal vinyl), 970 $cm^{-1}$ ($\delta_{C-H}$, *trans*-disubstituted double bond).

NMR (80 MHz, $CDCl_3$): $\delta$ 1.3–1.7 (m, 4H), 1.9–2.2 (m, 18H), 3.25 (s, 3H), 3.50 (q, $^3J = 7$ Hz, 1H), 4.8–5.9 ppm (m, 14H).

*4.3.3. 1-Methoxyhexadecatetraene*

A fraction enriched in 1-methoxyhexadecatetraene is obtained through chromatography of Kieselgel 60 (Merck), starting from a mixture of 1-$MeOC_{16}$, 3-$MeOC_{16}$ and $C_{16}$ (respectively, 15, 55 and 30% based on GC analysis, 1 g). Elution with cyclohexane–ethyl acetate (95:5) provides $C_{16}$ (0.1 g), a mixture of the three components (0.6 g) and a mixture of 1-$MeOC_{16}$ and 3-$MeOC_{16}$ (80:20, 0.25 g).

MS (EI, 70 eV): 248 (0.4, $M^{+\cdot}$), 216 (0.7, $M^{+\cdot} - CH_3OH$), 107 (28, $C_8H_{11}^+$), 93 (27, $C_7H_9^+$), 79 (51, $C_6H_7^+$), 71 (20, $C_4H_7O^+$),67 (100, $C_5H_7^+$), 55 (60, $C_4H_7^+$), 45 (29, $C_2H_5O^+$), 41 (38, $C_3H_5^+$).

IR (KBr): 1640 ($\nu_{C=C}$), 1100 ($\nu_{C-O}$, ether), 1000 and 910 ($\delta_{C-H}$, terminal vinyl), 970 $cm^{-1}$ ($\delta_{C-H}$, *trans*-disubstituted double bond).

NMR (80 MHz, $CDCl_3$): $\delta$ 1.2–1.8 (m, 4H), 1.8–2.2 (m, 10H), 3.25 (s, 3H), 3.80 (D, $^3J = 4$ Hz, 2H), 4.8–6.0 ppm (m, 9H).

*4.3.4. 1-Methoxy-6-vinyltetradecatriene*

The reaction mixture (10 g) from repetitions of run 34 was percolated through a column of Kieselgel 60 (Merck) and then submitted to a first distillation (1 torr) leading to a distillate (8.5 g) containing octa-1,3,7-triene, 1-methoxy-octa-2,7-diene and methoxy-3-hexadecatetraene as identified by GC. A fraction of this distillate (3.7 g) is submitted to a second distillation (1 torr) leading to a residue (Eb 125–130°C, 0.5 g) which contains mainly 1-methoxy-6-vinyltetradecatriene (> 98%).

MS (EI, 70 eV): 216 (0.4, $M^{+\cdot} - CH_3OH$), 107 (26, $C_8H_{11}^+$), 93 (27, $C_7H_9^+$), 85 (28, $C_5H_9O^+$), 79 (49, $C_6H_7^+$), 71 (20, $C_4H_7O^+$), 67 (100, $C_5H_7^+$), 55 (54, $C_4H_7^+$), 45 (39, $C_2H_5O^+$), 41 (43, $C_3H_5^+$).

IR (KBr): 1640 ($\nu_{C=C}$), 1120–1100 ($\nu_{C-O}$, ether), 990 and 910 ($\delta_{C-H}$, terminal vinyl), 970 $cm^{-1}$ ($\delta_{C-H}$, *trans*-disubstituted double bond).

NMR (80 MHz, $CDCl_3$): $\delta$ 1.20–1.70 (m, 4H), 1.90–2.25 (m, 9H), 3.32 (s, 3H), 3.85 (d, $^3J = 4$ Hz, 2H), 4.8–5.1 (m, 4H), 5.3–6.0 ppm (m, 6H).

This product is hydrogenated (20 bar, 25°C) with $PtO_2$ (0.02 g) in pentane (25 ml). The retention time (GC) and MS spectra of the hydrogenated product are different from those of 1-methoxyhexadecane.

MS ($m/z$, CI, $NH_3$): 274 (100, $M + NH_4^+$), 255 (46, $MH^+$), 148 (99, $M - C_9H_{19} + NH_4^+$), 111 (13, $C_8H_{15}^+$), 101 (20, $C_5H_{10}OCH_3^+$), 71 ($C_4H_7O^+$), 58 ($C_3H_6O^+$), 45 ($C_2H_5O^+$).

*4.3.5. Telomers with ethanol*

The reaction mixture from run 27 was percolated through a column of Kieselgel 60 (Merck).

GC-MS ($m/z$, CI with $NH_3$). For 1-$EtOC_8$: 172 (100, $M + NH_4^+$), 126 (11, $M - EtOH + NH_4^+$), 109 (32, $M^+ - EtO$). For 1-$EtOC_{16}$: 280 (100, $M + NH_4^+$), 217 (10, $M^+ - EtO$). For 3-$EtOC_{16}$: 280 (100, $M + NH_4^+$), 234 (3, $M - EtOH + NH_4^+$), 217 (64, $M^+ - EtO$). For 3-$EtOC_{24}$: 388 (100, $M + NH_4^+$), 325 (60, $M^+ - EtO$).

Distillation of the reaction mixture from run 27 gives a fraction containing 1-ethoxy-octa-2,7 diene and 3-ethoxy-octa-1,7-diene (80:20, 0.2 g) and a fraction of $C_{16}$ compounds which is separated on a column of Kieselgel 60 (Merck) with cyclohexane-ethyl acetate (98:2) into three fractions: $C_{16}$ (0.04 g), $C_{16} + EtOC_{16}$ (0.41 g) and 1-$EtOC_{16}$ + 3-$EtOC_{16}$ (20:80, 0.25 g) which were examined by IR and NMR.

IR (KBr): 1640 ($\nu_{C=C}$), 1100 ($\nu_{C-O}$, ether), 990 and 920 ($\delta_{C-H}$, terminal vinyl), 970 $cm^{-1}$ ($\delta_{C-H}$, *trans*-disubstituted double bond).

NMR (80 MHz, $CDCl_3$): $\delta$ 1.00–1.75 (m, ca. 3.5H), 1.55 (t, $^3J = 7$ Hz, ca. 3H), 1.80–2.40 (m, ca. 10.5H), 3.00–3.70 (m, ca. 3H), 3.85 (d, $^3J = 4$ Hz, ca. 0.5H), 4.80–6.00 ppm (m, ca.10H).

*4.3.6. Telomers with i-propanol*

The reaction mixture from run 28 was percolated through a column of Kieselgel 60 (Merck).

GC-MS ($m/z$, CI with $NH_3$). For 1-*i*-PrO–$C_8$: 186 (100, $M + NH_4^+$), 126 (58, $M - i\text{-PrOH} + NH_4^+$),109 (98, $M^+ - i$-PrO). For 1-*i*-PrO–$C_{16}$: 294 (100, $M + NH_4^+$), 234 (5, $M - i\text{-PrOH} + NH_4^+$), 217(67, $M^+ - i$-PrO). For 3-*i*-PrO–$C_{16}$: 294 (20, $M + NH_4^+$), 234 (5, $M - i\text{-PrOH} + NH_4^+$), 217(100, $M^+ - i$-PrO). For 3-*i*-PrO–$C_{24}$: 402 (32, $M + NH_4^+$), 325 (100, $M^+ - i$-PrO).

Distillation (1 torr) of part of the reaction mixture from run 28 gives a fraction containing 1-*i*-propoxy-octa-2,7 diene (Eb 30–35°C, 0.5 g) and a fraction of $C_{16}$ compounds (Eb 100–106°C) which is separated on

a column of Kieselgel 60 (Merck) with cyclohexane, then cyclohexane–ethyl acetate (98:2) into two fractions: $C_{16}$ (0.1 g) and 1-*i*-$PrOC_{16}$ + 3-*i*-$PrOC_{16}$ (30:70, 0.65 g) which were examined by IR and NMR.

IR (KBr): 1640 ($\nu_{C=C}$), 1120 and 1150 ($\nu_{C-O}$, ether), 990 and 910 ($\delta_{C-H}$, terminal vinyl), 970 $cm^{-1}$ ($\delta_{C-H}$, *trans*-disubstituted double bond).

NMR (80 MHz, $CDCl_3$): $\delta$ 1.15 (d, $^3J = 7$ Hz, ca. 6H), 1.25–1.70 (m, ca. 3.5H), 1.80–2.30 (m, ca. 11H), 3.40–3.80 (heptuplet, $^3J = 6$ Hz, ca. 2H), 3.85 (d, $^3J =$ 6Hz, ca. 0.5H), 4.80–6.00 ppm (m, ca.10H).

### 4.3.7. Telomers with t-butanol

The reaction mixture from run 29 was percolated through a column of Kieselgel 60 (Merck).

GC-MS ($m/z$, CI with $NH_3$): 200 (14, $M + NH_4^+$), 126 (17, $M - t$-$BuOH + NH_4^+$),109 (100, $M^+ - t$-BuO).

### 4.3.8. Telomers with allyl alcohol

The reaction mixture from run 30 was percolated through a column of Kieselgel 60 (Merck) and distilled under reduced pressure (1 torr). The telomer recovered (Eb 36°C, 0.1g) was examined by MS, IR and NMR.

MS (EI, 70 eV): 166 (0.1, $M^{+\bullet}$), 57 (10, $C_3H_5O^+$), 41 (41, $C_3H_5^+$).

IR (KBr): 1640 ($\nu_{C=C}$), 1060 ($\nu_{C-O}$, ether), 990 and 910 ($\delta_{C-H}$, terminal vinyl), 970 $cm^{-1}$ ($\delta_{C-H}$, *trans*-disubstituted double bond).

NMR (80 MHz, $CDCl_3$): $\delta$ 1.2 (s, 9H), 1.30–1.70 (m, 2H), 1.80–2.20 (m, 4H), 3.80 (d, $^3J = 4$ Hz, 2H), 4.80–5.10 (m, 2H), 5.40–6.00 ppm (m, 3H).

### 4.3.9. Telomers with phenol

The reaction mixture from run 31 was percolated through a column of Kieselgel 60 (Merck).

GC-MS ($m/z$, EI, 70 eV). For 1-PhO–$C_8$: 202 (6, $M^{+\bullet}$), 94 (100, $PhOH^+$), 77 (10, $C_6H_5^+$). For 3-PhO–$C_8$: 202 (6, $M^{+\bullet}$), 94 (62, $PhOH^{+\cdot}$), 77 (20, $C_6H_5^+$). For 1-PhO–$C_{12}$: 256 (5, $M^{+\bullet}$), 94 (92, $PhOH^+$), 77 (23, $C_6H_5^+$). For1-PhO–$C_{16}$: 310 (3, $M^{+\bullet}$), 94 (43, $PhOH^+$), 77 (15, $C_6H_5^+$).

Distillation under reduced pressure (1 torr) gives 1-phenoxyocta-2,7-diene (Eb 85°C, 0.2g) which was examined by GC, IR and NMR.

IR (KBr): 1640 ($\nu_{C=C}$), 1600 and 1500 ($\nu_{C=C}$), 1230 ($\nu_{C-O}$, ether), 990 and 910 ($\delta_{C-H}$, terminal vinyl), 970 ($\delta_{C-H}$, *trans*-disubstituted double bond), 750 and 690 $cm^{-1}$ ($\delta_{C-H}$, phenyl).

NMR (80 MHz, $CDCl_3$): $\delta$ 1.3–1.7 (m, 2H), 1.80–2.20 (m, 4H), 4.40 (d, $^3J = 4$ Hz, 2H), 4.85–5.15 (m, 2H), 5.40–6.00 (m, 3H), 6.7–7.4 ppm (m, 5H).

### 4.3.10. Telomers with triethylsilane

The reaction mixture from run 45 is distilled under reduced pressure (1, then $10^{-2}$ torr). The first fraction (1 torr, Eb 42–45°C, 9.7 g) corresponds to a mixture of *cis*- and *trans*-triethylsilylbut-2-ene (55:45).

MS ($m/z$, EI, 70 eV): 170 (39, $M^{+\bullet}$), 144 (77, $C_4H_7SiEt_2^+$), 115 (100, $Et_3Si^+$), 85 (47, $C_4H_7SiH_2^+$), 55 (8, $C_4H_7^+$).

IR (KBr): 1646 ($\nu_{C=C}$ *cis* isomer), 1660 ($\nu_{C=C}$ *trans* isomer), 960 ($\delta_{C-C}$ *cis* isomer), 750 ($\delta_{C-C}$, *trans* isomer).

NMR (250 MHz, $CDCl_3$): 0.55 (m, 6H), 0.94 (m, 9H), 1.37–1.65 (m, 2H), 1.55 (m, 3H), 5.35 ppm (m, 2H).

The second fraction ($10^{-2}$ torr, Eb 85–90°C, 1.6 g) mostly contains 1-triethylsilylocta-2,7-diene (> 95%).

MS ($m/z$, EI, 70 eV): 224 (2.5, $M^{+\bullet}$), 195 (6, $C_8H_{12}SiEt_2^+$), 169 (17, $C_4H_6SiEt_3^+$), 115 (74, $Et_3Si^+$), 108 (10, $C_8H_{12}^+$), 87 (100, $HEt_2Si^+$), 59 (38, $H_2EtSi^+$), 55 (3, $C_4H_7$).

NMR (250 MHz, $CDCl_3$): 0.56 (m, 6H), 0.94 (m, 9H), 1.43–1.65 (m, 2H), 2.03 (m, 3H), 5.34 ppm (m, 8H).

The third fraction ($10^{-2}$ torr, Eb 160–175°C, 0.3 g) mostly contains 1-triethylsilylhexadecatetraene (> 95%).

MS ($m/z$, EI, 70 eV): 223 (1, $C_8H_{12}SiEt_3^+$), 169 (1.5, $C_4H_6SiEt_3^+$), 163 (10.5, $C_{12}H_{19}$), 115 (100, $Et_3Si^+$), 87 (77, $HEt_2Si^+$),83 (2, $C_4H_7Si^+$), 55 (2, $C_4H_7$).

NMR (250 MHz, $CDCl_3$): 0.54 (m, 6H), 0.94 (m, 9H), 1.43–1.65 (m), 2.1 (m), 5.45–5.26 ppm (m).

## 4.4. Catalytic runs

All catalytic runs are performed in a 100 ml glass-lined stainless steel autoclave equipped with a double mantle for oil circulation and a magnet bar. The cover of the autoclave is supplied with three valves for, respectively, introduction of gases, introduction of liquids (ball valve) and sampling, a manometer (0–50 bar) and a safety valve adjusted to 50 bar.

For catalyst precursors prepared ex situ, the appropriate amount of cationic ($\eta^3$-allyl) complex is placed under argon in the autoclave which is tightly closed and submitted to three vacuum–argon cycles. The appropriate volume of solvent is then introduced with a glass syringe, with eventually the dissolved phosphane, and the mixture is agitated for 5 min. The autoclave is cooled down to $-10$°C. The telogen is introduced with a glass syringe and then the corresponding amount of buta-1,3-diene is distilled from a calibrated thick-wall glass bottle. The autoclave is connected to an oil-circulating bath and heated at a given temperature for the given time. Slow degassing allows the determination of the buta-1,3-diene consumed during the reaction. The autoclave is opened and the reaction mixture is processed as indicated above.

For catalyst precursors prepared in situ, the appropriate amounts of palladium complex and allyloxytris-(dimethylamino)phosphonium salt are placed under

argon in a Schlenk tube which is then submitted to three vacuum–argon cycles. The corresponding volume of solvent is then introduced with a glass syringe and the mixture is agitated until a yellow solution is obtained. Eventually the phosphane dissolved in a small amount of solvent is added and the mixture agitated during 5 min. The solution is removed with a glass syringe and transferred to the autoclave.

In the case of telomerization of buta-1,3-diene with water, after addition of the diene, the autoclave is pressurized with carbon dioxide (20 bar, Air Liquide N35).

### *4.5. Model reactions*

#### *4.5.1. Dimerization of methoxyoctadienes*

In a Schlenk tube are added successively under argon: **8d** (0.25 mmol, 108 mg), dichloromethane (5 ml), methanol (5 ml) and a mixture of 1- and 3-methoxyoctadienes (15:85, 100 mmol, 14 g). The mixture is refluxed under argon for 4 h (precipitation of palladium). The solvents are distilled off and the reaction products are examined by GC which indicates: octa-1,3,7-triene (6%), 1-$MeOC_8$ (24%), 3-MeO-$C_8$ (traces), $MeOC_{12}$ (2%), $C_{16}$ (3%), 1-$MeOC_{16}$ (2%), 3-$MeOC_{16}$ (25%), $MeOC_{20}$ (3%), $MeOC_{24}$ (5%).

#### *4.5.2. Reaction with 1-methoxyoct-2-ene*

In a Schlenk tube are added successively under argon: **8d** (0.125 mmol, 54 mg), dichloromethane (2.5 ml), methanol (2.5 ml) and 1-methoxyoct-2-ene (50 mmol, 7 g). The mixture is refluxed under argon for 4 h (precipitation of palladium). The solvents are distilled off and the reaction products are examined by GC which only shows the starting material with traces of octadienes.

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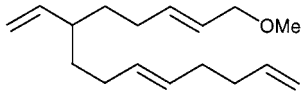
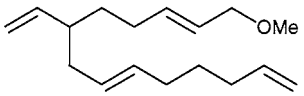
Table 3
Telomerization of buta-1,3-diene with alcohols: influence of the nature of the telogen

| Run | ROH | Conversion (%) | Yield (%) | | | Selectivity (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_4H_6$ | $ROC_8$ | $ROC_{16}$ | $ROC_{24}$ | 1-$ROC_8$ | 3-$ROC_8$ | $ROC_{12}$ | 1-$ROC_{16}$ | 3-$ROC_{16}$ | $ROC_{20}$ | $ROC_{24}$ | $C_8$ | $C_{16}$ |
| 11 | MeOH | 94 | 19 | 32 | 8 | 19 | 1 | 1 | 2 | 32 | 2 | 9 | 2 | 3 |
| 27 | EtOH | 94 | 9 | 20 | 8 | 11 | <1 | 2 | 2 | 20 | 9 | 9 | 2 | 3 |
| 28 | *i*-PrOH | 79 | 18 | 14 | 4 | 22 | — | — | 4 | 14 | — | 5 | 3 | 2 |
| 29 | *t*-BuOH | 38 | 7 | — | — | 17 | — | — | — | — | — | — | 4 | — |
| 30 | $C_3H_5OH$ | 45 | 4 | — | — | 10 | — | — | — | — | — | — | — | — |
| 31 | PhOH | 97 | 21 | 11 | — | 20 | 2 | 12 | 3 | 8 | — | — | 3 | — |

Reaction conditions: [Pd] = 0.25 mmol, $C_4H_6$ = 300 mmol, ROH = 75 mmol, toluene = 10 ml, temperature = 80°C, reaction time = 20 h.

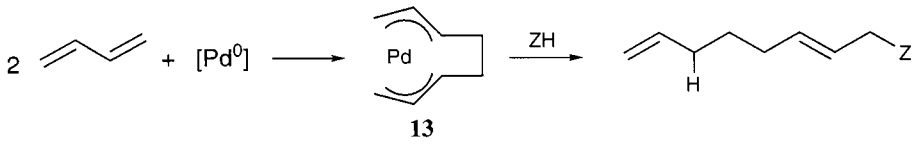



**11**



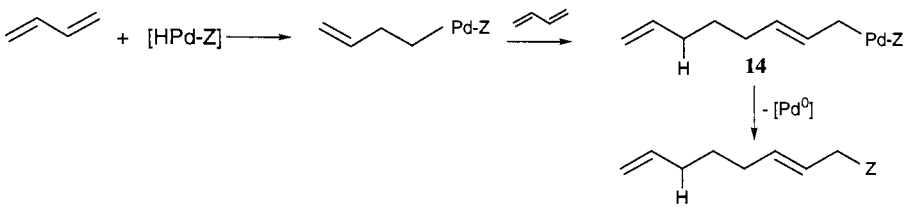

**12**

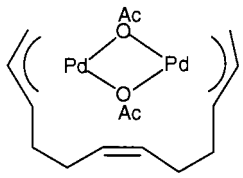
Two reaction pathways were proposed for the telomerization of buta-1,3-diene with alcohols [18]. The first one involves oxidative coupling of two diene units leading to a bis($\eta^3$-allyl) complex **13** (Eq. (5)).




**13**

The second one corresponds to stepwise addition of two diene units on a hydridopalladium species, leading to a ($\eta^1$-allyl)palladium compound **14** (Eq. (6)).




**15**

The process depicted by Eq. (5) seems to be preferred in the case of alcohols [19]. The greater $C_{16}$OMe and $C_{24}$OMe selectivities observed at low conversion of buta-1,3-diene indicate that the catalytic species able to induce this reaction, does evolve during the early stages of the process. Furthermore, the corresponding yields are not modified after 4 h of reaction, suggesting that higher oligomers of buta-1,3-diene are generated in a second stage, after catalyst deactivation for telomerization. The main pathway of palladium-catalyzed reaction of buta-1,3-diene is dimerization. Trimerization to form dodeca-1,3,6,10-tetraene takes place with the dimeric complex **15** in the absence of phosphane ligands ([13]a). Although tetramerization is even detected with this compound, the results reported here show that $C_{8n}$ linear chains coming from buta-1,3-diene are selectively formed. Thus, none of the active species proposed in the literature gives satisfactory explanations for the build-up of $C_{16}$ and $C_{24}$ chains.

Three experiments indicates the role of preformed $C_8$ chains in the formation of these higher telomers:

(i) The reaction takes place with 1-methoxy-octa-2,7-diene in the presence of **8d** and a 1:1 mixture of dichloromethane and methanol (Eq. (7)). A product distribution typical of the telomerization described above is achieved. The conversion is higher in the presence of buta-1,3-diene which may stabilize the active species.