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Homogeneous telomerization of 1,3-butadiene with alcohols in the presence of palladium catalysts modified by hybrid chelate ligands

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Abstract

1,3-Butadiene telomerization with methanol and higher alcohols was investigated in the presence of different palladium(0) and palladium(II) complexes based on hybrid chelate ligands. When P∩O ligands were used, the resulting palladium complexes displayed poor activity and low selectivity to telomers, also in the presence of alkoxide promoters. Even worse performances were found when ionic palladium(II) or neutral palladium(0) and palladium(II) complexes based on N∩N chelate ligands were employed in combination with alkoxide promoters. Better results were obtained by using ionic palladium(II) complexes with P∩N∩N ligands in combination with an alkoxide promoter. Very promising results were achieved when the telomerization reaction was catalyzed by palladium(0) complexes obtained in situ from $Pd(dba)_2$ and P∩N ligands. The data are discussed and interpreted in terms of different capability of the chelate ligands, depending on their size and donor power, to give palladium complexes with metal sites at low oxidation state characterized at the same time by a sufficient stability and coordinative unsaturation to promote high catalytic activity and selectivity.

Keywords: 1,3-Butadiene telomerization; Methanol; Higher alcohols; Palladium catalysts; Octadienyl ethers; Chelate ligands

1. Introduction

The telomerization of 1,3-butadiene with alcohols has recently gained increasing interest for the synthesis of linear octadienyl ethers because, after hydrogenation, they display special properties as components of diesel fuels, owing to their high cetane number and cold flow properties [1]. It is also well established [2–4] that homogeneous palladium complexes result the best catalysts, in terms of both activity and selectivity, for promoting the above reaction process (Scheme 1).

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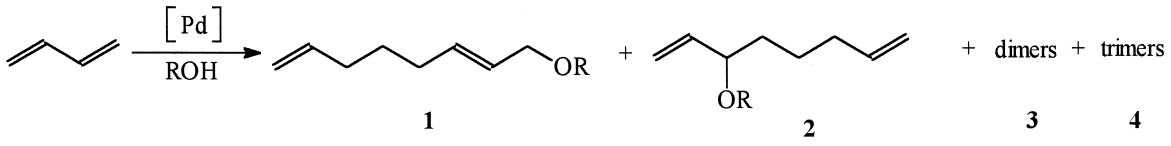


Scheme 1.

In this context, we have revisited [5] the homogeneous telomerization of 1,3-butadiene with alcohols catalyzed by palladium(0) complexes in the presence of monophosphine ancillary ligands with particular reference to the influence of the nature of the phosphine ligand as well as of the alcohol/diene molar ratio on the conversion and selectivity of the reaction. The use of alkyl phosphines seems to increase the selectivity to telomers, especially for higher linear alcohols; analogous results, accompanied also by an improvement of diene conversion, were obtained by increasing the alcohol/diene molar ratio. More recently, a detailed investigation of the influence of electronic as well as steric requirements of the phosphine ligand on the reaction course has allowed to conclude that the best performances, in terms of both activity and selectivity, are obtained by using palladium(0) complexes modified with ancillary phosphines having high basicity and low steric hindrance [6]. Finally, the 1,3-butadiene telomerization with alcohols catalyzed by homogeneous palladium(0) complexes based on diphosphine chelating ligands was also investigated [6]. In particular, the influence of the nature of diphosphine ligand, in terms of P∩P distance, basicity and steric hindrance, on catalyst performances was studied. Despite the lower activity of the above systems as compared with the corresponding catalysts based on monophosphine ligands, a higher selectivity to telomers was obtained when P∩P ligands able to afford larger than six-membered metallacyclo moieties were used. Moreover, an increase of activity was observed by decreasing the stability of the resulting metallacyclo catalytic species. This was achieved either by decreasing the basicity of the diphosphine ligand or by using the appropriate P∩P spacer to favour the formation of less stable four- and seven-membered metallacyclo palladium species. Finally, a decrease of the steric hindrance of the chelate ligand enhanced the selectivity of the palladium catalyst to telomers.

All the obtained results allowed to conclude that, whereas diphosphine chelating ligands caused in general an excessive stabilization of the resulting metal sites, thus implying a reduced activity in the 1,3-butadiene telomerization with alcohols, the corresponding monophosphine modified systems presented, at least under low P/Pd ratios, the drawback of catalyst decomposition and partial metal deposition. Therefore, in principle, a good compromise between stability and reactivity of the metal sites could be realized by the use of hemilabile chelate ligands characterized by both a strong donor centre, able to assure a permanent coordination to the palladium atoms thus stabilizing the active sites and favouring the selective synthesis of the telomers, and a labile donor centre capable, through association and dissociation equilibria, to give rise to the formation of unsaturated coordinative metal sites with high catalytic activity.

In this context, it appeared of interest to check the performances of palladium complexes, modified by hybrid ligands with P∩O donors as well as by N∩N chelating ligands, never used up to date in the 1,3-butadiene telomerization with alcohols. Finally, P∩N ligands appeared particularly attractive as they, from one side, would stabilize low oxidation state palladium species through the phosphino group, and from the other, assure a coordinative lability able to afford unsaturated active sites, via the amino group. Indeed, recent studies [7] indicated that P∩N chelating ligands were suitable systems for promoting the formation of carbon–carbon bonds by palladium catalysts.

2. Experimental

2.1. Materials

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

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

n-Hexane (Merck) was refluxed and distilled on Na/K alloy.

Tetrahydrofuran (THF) (Carlo Erba) was refluxed on Na/K alloy and distilled on $LiAlH_4$.

Toluene (Baker) and dioxane (Carlo Erba) were refluxed and distilled on sodium.

Anhydrous methanol (Baker) and ethanol (Carlo Erba) were obtained by refluxing the commercial product over Mg/I_2 and stored on molecular sieves (4 Å).

1-Propanol (Riedel-de Haën), 1-pentanol (Carlo Erba) and 1-octanol (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.

2,2′-Bipyridyl (bpy) (Carlo Erba) was used as received.

Sodium methoxide (Aldrich) and potassium *tert*-butoxide (Merck-Schuchardt) were dried under vacuum at 50°C and stored under dry argon.

Palladium(II) acetate [$Pd(OAc)_2$] (Aldrich) was used as received and stored under dry argon.

Palladium dibenzylideneacetone [$Pd(dba)_2$] was prepared as previously described [8].

Trans-bis-(η^1-benzoylmethylenetriphenyl phosphorane)-dichloro-palladium(II) [$PdCl_2Y_2$] was prepared, as previously reported [9], by reaction of $PdCl_2$ with (benzoylmethylene)triphenylphosphorane (DPPY), in turn synthesized according to the literature [10].

FT-IR (KBr pellet): 3050 (ν_{CH}, aromatic), 1627 ($\nu_{C=O}$), 1600 ($\nu_{C=C}$, aromatic), 1107 (ν_{P-Ph}), and 785, 690 (δ_{CH}, aromatic) cm^{-1}.

Cis-bis-[$Ph_2PCH{=}C(O)Ph$-κ^2P,O]-palladium(II) [$Pd(P\frown O)_2$] was synthesized [11] by reacting Na_2PdCl_4 with diphenylphosphinoacetone, in turn prepared according to the literature [11].

FT-IR (KBr pellet): 3055 (ν_{CH}, aromatic), 3021 ($\nu_{CH=}$), 1513, 1484 (ν_{CO} and $\nu_{C=C}$), 1101 (ν_{P-Ph}), and 747, 694 (δ_{CH}, aromatic) cm^{-1}.

^1H NMR (C_6D_6): $\delta = 8.06–6.95$ (m, 15H, aromatic protons) and 4.6 (s, 1H, $^2J_{P-H} = 2$ Hz, CH) ppm.

$\{^1H\}-^{31}P$ NMR (CH_2Cl_2/C_6D_6): $\delta = 37.0$ (s) ppm.

(η^3-C_4H_7)-[$Ph_2PCH_2C(O)Ph$-κ^1P]-chloro-palladium(II) [$Pd(P\frown O)$] was prepared [11] by reacting diphenylphosphinoacetophenone (DPAP) with bis-(η^3-C_4H_7)-di-μ-chloro-di-palladium(II), in turn synthesized according to the literature [12].

^1H NMR ($CDCl_3$): $\delta = 7.96–7.26$ (m, 15H, aromatic protons), 4.5 (d, 1H, $^2J_{P-H} = 8.3$ Hz, H^b), 4.4 (d, 2H, $^2J_{P-H} = 9.2$ Hz, P–CH_2), 3.45 (d, 1H, $^2J_{P-H} = 10.9$ Hz, H^a), 3.12 (s, 1H, H^c), 2.65 (s, 1H, H^d) and 1.92 (s, 3H, CH_3) ppm.

$\{^1H\}-^{31}P$ NMR ($CDCl_3$): $\delta = 17.7$ (s) ppm.

[(1,2,6-η^3)-(5-Methoxycyclooctenyl)-(bipyridyl-κ^2N,N')-palladium(II)] hexafluorophosphate (PdNN1) was prepared [13] from η^4-(cycloocta-1,5-diene)-dichloro-palladium(II), in turn synthesized according to the literature [14].

FT-IR (KBr pellet): 3130–3071 (ν_{CH}, aromatic and olefinic), 2929 (ν_{asCH_2}), 2828 (ν_{sCH_2}), 1605, 1598 ($\nu_{C=N}$ and $\nu_{C=C}$, bpy rings), 1440 (δ_{CH_2}), 1069 (ν_{C-OCH_3}), 838 (ν_{P-F}, PF_6^-), and 770 (δ_{CH}, bpy rings) cm^{-1}.

^{1}H NMR (DMSO-d_6): $\delta = 8.71$–7.88 (m, 8H, aromatic protons of bpy rings), 6.11, 5.84, (s, 2H, CH=, COD), 3.35 (s, 3H, CH_3) and 2.63–1.66 (m, 9H, CH_2, COD) ppm.

{^{1}H}–^{31}P NMR (DMSO-d_6): $\delta = -139.4$ (hept, $^1J_{P-F} = 711$ Hz, PF_6^-) ppm.

[(η^4-Cycloocta-diene)-(bipyridyl-$\kappa^2 N,N'$)-palladium(II)] bis-perchlorate (PdNN2) was prepared from PdNN1, according to the literature [14].

FT-IR (KBr pellet): 3130–3040 (ν_{CH}, aromatic and olefinic), 2934 (ν_{asCH_2}), 2839 (ν_{sCH_2}), 1603, ($\nu_{C=N}$ and $\nu_{C=C}$, bpy rings), 1440 (δ_{CH_2}), 1090 (ClO_4^-), and 774 (δ_{CH}, bpy rings) cm^{-1}.

^{1}H NMR (DMSO-d_6): $\delta = 9.1$–7.8 (m, 8H, aromatic protons of bpy rings), 5.51, (s, 4H, CH=, COD), and 2.3 (m, 8H, CH_2, COD) ppm.

Bipyridyl-dichloro-palladium(II) ($PdCl_2$bpy) was prepared according to the literature [15].

N,N-Dimethyl-2-diethylphosphino-aniline (Me_2AnPEt_2) was prepared, as previously described [16], starting from *N,N*-dimethyl-2-bromoaniline, in turn synthesized from 2-bromoaniline [17].

^{1}H NMR ($CDCl_3$): $\delta = 7.40$–6.72 (m, 4H, aromatic protons), 2.76 (s, 6H, N–CH_3), 1.68 (m, 4H, CH_3–CH_2–P), 1.02 (dt, 6H, CH_3–CH_2–P; $^3J_{H-H} = 7.4$ Hz, $^3J_{P-H} = 14.6$ Hz,) in ppm.

{^{1}H}–^{31}P NMR ($CDCl_3$): $\delta = -26.03$ ppm.

2-Diethylphosphino-1-methylpyrrole ($MePyPEt_2$) was synthesized from 1-methylpyrrole (Aldrich) by lithiation at the 2-position of the ring and successive reaction with diethyl chlorophosphine as follows.

Thirty-one milliliters of a 1.6 M *n*-hexane solution of ^{n}BuLi (49.6 mmol) were added dropwise at 0°C, under stirring and dry argon atmosphere, to 49.6 mmol of 1-methylpyrrole dissolved in 20 ml of anhydrous diethyl ether. The reaction mixture, after 1 h refluxing, was cooled at −78°C and slowly added with 24.6 mmol of fresh distilled diethyl chlorophosphine dissolved in 20 ml of anhydrous diethyl ether. The reaction mixture was subsequently kept at room temperature for 12 h; then, after filtration and removal of the solvent under vacuum, it was distilled to give 1.97 g (48% yield) of an uncoloured viscous liquid (b.p. = 70–72°C/0.7 mbar) which resulted pure $MePyPEt_2$.

^{1}H NMR ($CDCl_3$): $\delta = 6.79$ (s, 1H, aromatic H_3), 6.33 (s, 1H, aromatic H_2), 6.22 (t, 1H, aromatic H_1; $^3J_{P-H} \approx 3$ Hz), 3.77 (s, 3H, N–CH_3), 1.67 (q, 4H, CH_3–CH_2–P; $^3J_{H-H} = 7.5$ Hz), 1.04 (dt, 6H, CH_3–CH_2–P; $^3J_{H-H} = 7.4$ Hz, $^3J_{P-H} = 15.4$ Hz) in ppm.

{^{1}H}–^{31}P NMR ($CDCl_3$): $\delta = -43.19$ ppm.

2-Diethylphosphino-1-methyl-imidazole ($MeImiPEt_2$) was prepared with the same procedure as described for $MePyPEt_2$, starting from 64.2 mmol of 1-methylimidazole (Aldrich), 64.4 mmol of ^{n}BuLi and 32.1 mmol of diethyl chlorophosphine. $MeImiPEt_2$ (2.2 g, 61% yield) was obtained as uncoloured viscous liquid (b.p. = 82–84°C/0.7 mbar).

^{1}H NMR ($CDCl_3$): $\delta = 7.1$ (s, 1H, aromatic H_2), 6.87 (s, 1H, aromatic H_1), 3.70 (s, 3H, N–CH_3), 1.71 (m, 4H, CH_3–CH_2–P), 0.89 (dt, 6H, CH_3–CH_2–P; $^3J_{H-H} \approx 7.6$ Hz, $^3J_{P-H} \approx 14.8$ Hz,) in ppm.

{^{1}H}–^{31}P NMR ($CDCl_3$): $\delta = -40.7$ ppm.

[*N*-(2-Diphenylphosphinobenzylidene)]-[2-(2-pyridyl)ethyl]-amine (Ph_2PNN) was prepared, as previously described [18], by reacting 2-(2-aminoethyl)pyridine (Aldrich) with 2-(diphenylphosphino)benzaldehyde, in turn synthesized from 2-bromo-benzaldehyde (Aldrich) in a four-step reaction pathway [19].

^{1}H NMR ($CDCl_3$): $\delta = 8.81$ (d, 1H, H_7; $^4J_{P-H} \approx 4.6$ Hz), 8.44 (d, 1H, H_{14}; $^3J_{H-H} \approx 4.6$ Hz), 7.90 (dd, 1H, H_2; $^3J_{H-H} \approx 4.0$ Hz, $^4J_{P-H} \approx 7.3$ Hz), 7.45 (t, 1H, H_{12}; $^3J_{H-H} \approx 7.6$ Hz), 7.35–7.20 (m, 12H, $H_{o,m,p} + H_3 + H_{11}$), 7.02 (m, 1H, H_{13}), 6.98 (d, 1H, H_5; $^3J_{H-H} \approx 4.8$ Hz), 6.83 (dd, 1H, H_4; $^3J_{H-H} \approx 4.8$ and $^3J_{P-H} \approx 7.7$ Hz), 3.85 (t, 2H, H_8; $^3J_{H-H} \approx 7.3$ Hz), 2.94 (t, 2H, H_9; $^3J_{H-H} \approx 7.3$ Hz) in ppm.

{^{1}H}–^{31}P NMR ($CDCl_3$): $\delta = -14.1$ ppm.

Bis-(η^3-allyl)-di-μ-chloro-di-palladium(II) [(η^3-$C_3H_5PdCl)_2$] was synthesized from $PdCl_2$, NaCl and allyl chloride under CO atmosphere [12].

[(η^1-Allyl)-(*N*-(2-(diphenylphosphino)benzylidene)-(2-(2-pyridyl)ethylamine)-κ^3-*P*,*N*,*N*′] palladium(II) chloride [(Ph_2PNN)Pd(η^1-C_3H_5)Cl] was prepared, as previously described [18], by reacting (η^3-$C_3H_5PdCl)_2$ with Ph_2PNN.

^{1}H NMR ($CDCl_3$, 223 K): $\delta = 9.36$ (s, 1H, H_7), 8.49 (m, 1H, H_{14}), 8.08 (m, 1H, H_2), 7.95 (t, 1H, H_{12}), 7.86–7.28 (m, 14H, $H_{o,m,p} + H_3 + H_4 + H_{11} + H_{13}$), 7.09 (m, 1H, H_5), 5.62 (tt, 1H, $H_{2'}$), 4.49 (d, 2H, $H_{3'}$), 4.02 (t, 2H, H_8), 3.52 (t, 2H, H_9), 2.17 (dd, 2H, $H_{1'}$) in ppm.

{^{1}H}–^{31}P NMR ($CDCl_3$, 223 K): $\delta = +33.0$ (s) ppm.

2.2. Catalytic experiments and analyses

Catalytic experiments were usually 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 solvent and eventually the chelating ligand as well as the alkoxide promoter 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 up to the desired temperature in a thermostatted 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 analyzed.

In some experiments a mechanically stirred 150 ml stainless steel autoclave, equipped not only with an inner glass becker, a substrate inlet vessel and a sampling valve, but also with an internal thermocouple and a cooling coil with a circulating cold water, was adopted for a better control of the reaction temperature.

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

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

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

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

2.3. Physicochemical measurements

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

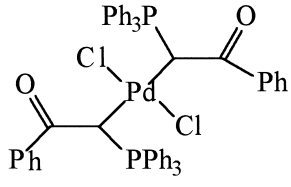
Quantitative analyses of telomerization products were performed by a HP 5890 gas chromatograph, equipped with a HP 3396 integrator, a flame ionization detector and a 50 m HP PONA capillary column (cross-linked methyl silicone gum). The identification of the telomerization products was carried out by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

^{1}H and {^{1}H}–^{31}P NMR spectra of the samples were carried out on a Varian Gemini 200 spectrometer operating at 200 MHz (^{1}H) and 80.95 MHz (^{31}P), tetramethylsilane (TMS) and 85% H_3PO_4 being used as internal and external standards, respectively.

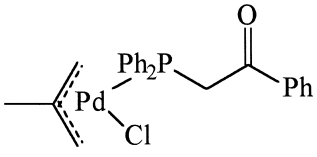
3. Results and discussion

3.1. Homogeneous 1,3-butadiene telomerization with methanol catalyzed by palladium complexes with P∩O chelating ligands

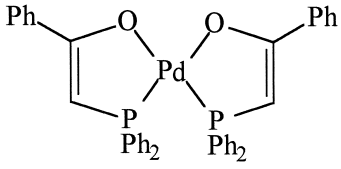
No examples are reported up to now concerning the oxidative addition of ylide ligands to palladium(0) derivatives, analogously to what known [20,21] for Ni(0) complexes. Indeed, the attempt to prepare a ylide P∩O palladium complex by reacting $Pd(dba)_2$ with (benzoylmethylene)triphenylphosphorane (BPPY) in the presence of a phosphine ancillary ligand completely failed, the deposition of metallic palladium being observed. Therefore, we have prepared, according to the literature [9], the *trans*-bis-(η^1-benzoylmethylenetriphenylphosphorane)-dichloro-palladium(II) ($PdCl_2Y_2$) where the ylide behaves as a monodentate ligand through the formation of a η^1-C-metal bond. However, the above ligand would stabilize, in principle, the metal complex during the catalytic cycle by means of a P∩O chelation, when an alkoxide promoter is added. Moreover, we have also synthesized, as previously described [11], the (η^3-C_4H_7)-[$Ph_2PCH_2C(O)Ph$-κ^1P]-chloro-palladium(II) [Pd(P∩O)] complex, where the β-ketophosphine DPAP behaves as a monodentate ligand through the phosphorus atom. However, it is known [21] that the above complex may evolve, under the action of a base, to the corresponding phosphino-enolate complex, where a P∩O chelate ligand is present. Finally, the *cis*-bis-[$Ph_2PCH{=}C(O)Ph$-κ^2P,O]-palladium(II) [$Pd(P\cap O)_2$] complex, where two P∩O chelate ligands are really present, was also prepared according to the literature [11]. Therefore, all the above complexes, whose proposed structures are reported below, were used as catalyst precursors in the 1,3-butadiene telomerization with methanol.



$PdCl_2Y_2$



Pd(P∩O)



Pd(P∩O)$_2$

As expected, the complex $PdCl_2Y_2$ in absence of any basic promoter resulted completely inactive in the telomerization reaction. Therefore, in all the successive experiments (Table 1) an alkoxide promoter was also used. The effect of reaction temperature and of the type of promoter was studied. As reported in runs 1–4, in the 50–80°C range and by adopting a MeONa/Pd molar ratio equal to 10, the maximum of catalyst activity was observed at 60°C. However, even under these conditions the $PdCl_2Y_2$ catalytic precursor displayed (run 2) both lower activity and chemoselectivity to telomers, as compared with catalysts based on $Pd(dba)_2$ and different diphosphine chelating ligands, previously described [6]. Indeed, in runs 1–4, despite a very high regioselectivity to the linear telomers **1**, a significant amount of dimers was obtained (18–28%), depending on the adopted temperature. Moreover, an appreciable amount of trimers and higher telomers was also observed in all the experiments. In order to improve the catalytic performances of $PdCl_2Y_2$, the MeONa/Pd ratio was varied. At a ratio value = 4 (run 5) a significant decrease of the C_4H_6 conversion was obtained, accompanied also by a remarkable lowering of the chemoselectivity to telomers. Moreover, in the presence of a MeONa/Pd = 20 (run 6), no significant improvement of activity was found, the chemoselectivity to telomers being lower than in run 2, where a MeONa/Pd ratio equal to 10 was

Table 1
Homogeneous 1,3-butadiene telomerization with methanol in the presence of the $PdCl_2Y_2$ catalytic precursor and different alkoxide (Alk) promoters[a]

Run	Alkoxide	Alk/Pd (mol/mol)	Temperature (°C)	C_4H_6 Conv. (%)	Selectivity (%)[b]			R[c] (%)
					1[d]	**2**[e]	**3**[f]	
1	MeONa	10	50	35.5	74.6	0.5	22.6	99.4
2	MeONa	10	60	51.0	78.1	2.8	18.1	96.6
3	MeONa	10	70	34.6	68.2	3.0	28.3	95.9
4	MeONa	10	80	33.9	72.0	3.0	25.0	96.0
5	MeONa	4	60	13.4	55.4	0.6	38.9	99.0
6	MeONa	20	60	51.2	70.0	2.2	26.6	97.0
7	^{t}BuOK	5	60	18.1	49.7	1.2	46.4	97.6
8	^{t}BuOK	10	60	28.0	62.8	2.7	33.0	95.9
9	^{t}BuOK	20	60	44.3	59.0	4.4	35.0	97.3
10	^{t}BuOK	50	60	53.3	68.2	1.5	28.6	97.8

[a] Reaction conditions: Pd: 0.1 mmol; Pd/P/MeOH/C_4H_6 = 1/2/3000/2000; solvent: *n*-hexane (20 ml); P_{N_2}: = 3 MPa; time: 5 h.
[b] When $\mathbf{1}+\mathbf{2}+\mathbf{3} < 100$, trimers and higher telomers are also present to some extent.
[c] Regioselectivity to the linear telomers **1**, expressed as $[\mathbf{1}/(\mathbf{1}+\mathbf{2})]\times 100$.
[d] *Cis*- and *trans*-1-methoxy-2,7-octadiene.
[e] 3-Methoxy-1,7-octadiene.
[f] Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.

employed. When MeONa was replaced by ^{t}BuOK (runs 7–10) a molar ratio alkoxide/Pd equal to 50 was necessary to reach substantially the same activity as in run 2 where a MeONa/Pd = 10 was adopted. Moreover, the comparison of runs 2 and 8 allows one to conclude that a lower chemoselectivity to telomers was obtained in the presence of ^{t}BuOK. Inferior performances of the catalyst were found when the ^{t}BuOK/Pd ratio was < 50 (runs 7–9). GC–MS analyses of the reaction products did not reveal the presence of the ^{t}BuO group in the telomers; however, ^{t}BuOH was detected, thus clearly indicating that ^{t}BuOK does not behave as either a reductive agent or a nucleophile, but only as a base capable to exchange with methanol to give MeOK which is responsible for the activation of the catalytic precursor. Finally, it is worth noting that in all the experiments deposition of metallic palladium was observed at the end of the reaction, thus suggesting that the above ylide ligand has no electronic requirements suitable for stabilizing the resulting catalyst. Therefore, it is likely that in the $PdCl_2Y_2$/alkoxide catalytic systems no donor phosphine group is permanently bound to the metal. The attempt to use in combination with $PdCl_2Y_2$ a strong reductive agent, such as $NaBH_4$, completely failed, the resulting catalyst being substantially inactive. The use of $AgNO_3$ as third component in addition to the $PdCl_2Y_2$/MeONa system, in order to favour the removal from the metal of the chloride ligand and hence the formation of the active species [2], not only did not give any improvement of the catalyst activity, but, on the contrary, substantially poisoned the catalyst, only traces of products being obtained.

When the Pd(P∩O) complex, combined with MeONa (runs 11 and 12, Table 2), was used in the C_4H_6 telomerization with methanol, a very low activity was observed, the C_4H_6 conversion being negligible and around 22% at 60 and 80°C, respectively. Analogous results were obtained with the $Pd(P\cap O)_2$/MeONa catalytic system (Table 2). Indeed, at 60°C the above system was substantially inactive (run 13), a very low activity being observed at higher temperatures (80°C, run 14 and 100°C, run 15), accompanied in this last case also by a quite low chemoselectivity to telomers ($< 68\%$). Therefore, we may conclude that all the above precursors, even under reaction conditions which may favour the formation of complexes with at least one P∩O chelating ligand, display unacceptable performances in the C_4H_6 homogeneous telomerization with methanol.

Table 2
1,3-Butadiene telomerization with methanol catalyzed by homogeneous systems obtained in situ from either Pd(P∩O) or Pd(P∩O)$_2$ and MeONa as promoter[a]

Run	Precursor	Temperature (°C)	C_4H_6 Conv. (%)	Selectivity (%)[b]			R[c] (%)
				1[d]	**2**[e]	**3**[f]	
11	Pd(P∩O)	60	<1	42.4	2.0	46.6	95.5
12	Pd(P∩O)	80	22.3	88.0	5.1	7.5	94.5
13	Pd(P∩O)$_2$	60	traces	–	–	–	–
14	Pd(P∩O)$_2$	80	7.6	85.4	6.5	4.8	92.9
15	Pd(P∩O)$_2$	100	3.0	61.7	6.0	30.2	91.1

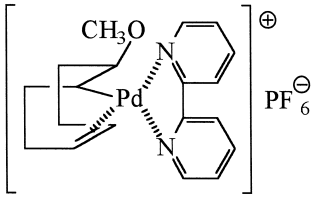
[a]Reaction conditions: Pd: 0.1 mmol; P/MeONa/MeOH/C_4H_6 = 1/10/6000/4000; P_{N_2}: = 3 MPa; solvent: *n*-hexane (20 ml); time: 4 h.
[b]When **1**+**2**+**3** < 100, trimers and higher telomers are also present to some extent.
[c]Regioselectivity to the linear telomers 1, expressed as [**1**/(**1**+**2**)]×100.
[d]*Cis*- and *trans*-1-methoxy-2,7-octadiene.
[e]3-Methoxy-1,7-octadiene.
[f]Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.

In particular, the scarce activity of the Pd(P∩O)/alkoxide system, as compared with that reported in the oligomerization of ethylene for η^3-allyl palladium complexes with phosphino-ester P∩O chelating ligands, where a hydride–palladium species was supposed to occur by hydrogen elimination from the allylic precursor [22], seems to suggest that the above system does not evolve to Pd–H species responsible for the 1,3-butadiene telomerization with alcohols.

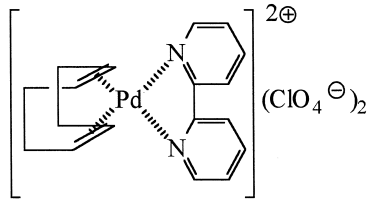
In conclusion all the data indicate that palladium complexes based on hybrid P∩O ligands are not suitable for 1,3-butadiene telomerization with methanol, O–Pd bond being probably responsible for a relevant stabilization of the palladium atoms in the (II) oxidation state.

3.2. Homogeneous 1,3-butadiene telomerization with methanol catalyzed by palladium complexes with N∩N chelating ligands

Taking into account that no data are available up to now about the catalytic activity of palladium complexes with N∩N chelating ligands in the telomerization reaction and considering that the above ligands are certainly more stable to oxidation reactions compared with the diphosphine analogs [23], the 1,3-butadiene telomerization with methanol was studied by using the ionic PdNN1 and PdNN2 complexes, based on the 2,2′-bipyridyl ligand and prepared according to the literature [13], both in absence and in presence of MeONa as promoter. The proposed structures of the above complexes are reported below:



PdNN1



PdNN2

The results were compared with those obtained by using $PdCl_2$(bpy) in the presence of MeONa and a palladium(0) catalytic system prepared in situ by adding 2,2′-bipyridyl to Pd(dba)$_2$.

When PdNN1 and PdNN2 were used in absence of MeONa as promoter, no activity was observed in the telomerization reaction. However, when a MeONa/Pd molar ratio equal to 10 was employed,

both PdNN1 and PdNN2 showed (runs 16 and 17, respectively, Table 3) a very low catalytic activity, the C_4H_6 conversion being lower than about 8% after a prolonged reaction time (18 h).

Moreover, the chemoselectivity to telomers was in both cases very low ($< 50\%$) and deposition of metallic palladium was also observed at the end of the reaction. Considering that oligomerization products were preferentially produced we may suggest that the reaction mechanism involved in the presence of the above complexes is different from that operating with palladium complexes modified by phosphine ligands. When $PdCl_2$(bpy) was employed in the presence of different amounts of MeONa (runs 18 and 19, Table 3) a higher activity was observed with respect to the preceding systems, an increase of the MeONa/Pd ratio from 5 to 10 enhancing the performances of the catalyst, although modest C_4H_6 conversions ($< 38\%$) and significant amounts of dimers ($> 36\%$) were still obtained. A similar situation occurred when the $Pd(dba)_2$/bpy system was used (run 20, Table 3). Indeed, the productivity of the above system resulted quite poor (C_4H_6 conversion = 22%) and the chemoselectivity to telomers, although slightly improved as compared with that of run 19, was lower than 70%.

In conclusion, the results concerning the catalytic performances of the above palladium complexes with N∩N chelating ligands appear significantly inferior as compared with the corresponding systems based on P∩P chelating ligands [6]. These findings may be explained assuming that amino groups are not able to sufficiently stabilize a metal complex at low oxidation state, due to their scarce π-electron withdrawing capability from an electron-rich metal site, contrarily to what occurs in the case of π-acid phosphine groups.

3.3. Homogeneous 1,3-butadiene telomerization with linear primary alcohols catalyzed by palladium(0) complexes modified with P∩N and P∩N∩N chelating ligands

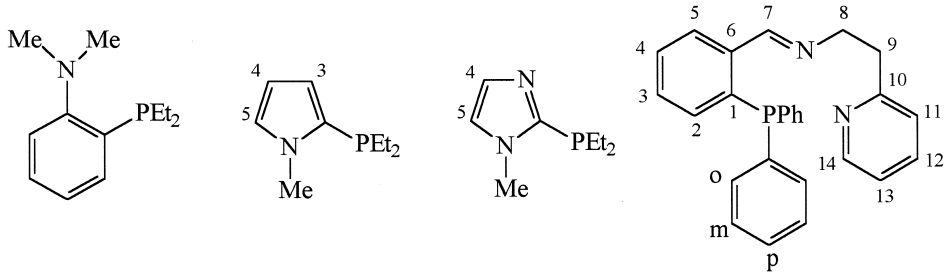
The results obtained in Section 3.2 seem to suggest that one phosphine donor group in the chelating ligand is required. Therefore a P∩N ligand, having at one extremity a basic σ-donor amino group, able to provide both a high nucleophilicity to the metal atom and a relative lability to the ligand with the formation of coordinative unsaturated metal species, would realize the best chelate system, the π-acid phosphino group present at the other extremity being capable to stabilize the metal complex itself. In this context, *N,N*-dimethyl-2-diethylphosphino-aniline (Me_2AnPEt_2) and novel 2-diethylphosphino-1-methylpyrrole ($MePyPEt_2$) as well as 2-diethylphosphino-1-methyl-imidazole (MeImi-

Table 3
Homogeneous 1,3-butadiene telomerization with methanol by palladium complexes modified with 2,2′-bipyridyl ligand in the presence of MeONa (Alk) as promoter[a]

Run	Precursor	Alk/Pd (mol/mol)	C_4H_6 Conv. (%)	Selectivity (%)[b]			R[c] (%)
				1[d]	**2**[e]	**3**[f]	
16	PdNN1	10	8.3	42.7	3.4	53.9	92.6
17	PdNN2	10	4.2	25.3	2.2	72.4	92.2
18	$PdCl_2$bpy	5	10.2	52.1	2.9	45.0	94.7
19	$PdCl_2$bpy	10	37.9	56.7	6.8	36.5	89.3
20	$Pd(dba)_2$ /bpy	0	22.0	64.1	4.4	31.5	93.5

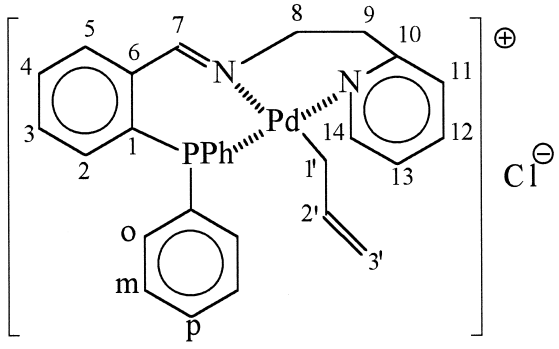
[a] Reaction conditions: Pd: 0.1 mmol; Pd/N/MeOH/C_4H_6 = 1/2/3000/2000; P_{N_2}: = 3 MPa; solvent: *n*-hexane (20 ml); $T = 60$°C; time: 18 h.
[b] When $\mathbf{1}+\mathbf{2}+\mathbf{3} < 100$, trimers and higher telomers are also present to some extent.
[c] Regioselectivity to the linear telomers **1**, expressed as $[\mathbf{1}/(\mathbf{1}+\mathbf{2})]\times 100$.
[d] *Cis*- and *trans*-1-methoxy-2,7-octadiene.
[e] 3-Methoxy-1,7-octadiene.
[f] Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.

PEt_2), were prepared and used in combination with $Pd(dba)_2$ for the preparation in situ of the catalytic systems. Indeed, Me_2AnPEt_2 is known [24,25] to give rise to palladium complexes where both N and P atoms are coordinatively bound to the same metal atom (five-membered metallacyclo moieties). Moreover, $MePyPEt_2$ and $MeImiPEt_2$, were designed in order to afford labile P∩N four-membered metallacyclo moieties, the occurrence of N∩N and P∩N∩N coordinative modes being substantially unlikely. Finally, a multidentate P∩N∩N ligand, such as [*N*-(2-diphenylphosphinobenzylidene)]-[2-(2-pyridyl)ethyl]-amine (Ph_2PNN), was also synthesized [18].



Me_2AnPEt_2 $MePyPEt_2$ $MeImiPEt_2$ Ph_2PNN

Indeed, in Ph_2PNN the imino group and the pyridine moiety would be able to increase the π-withdrawing character of the ligand, thus stabilizing palladium(0) species. Moreover, the intrinsic coordinative flexibility of the ligand would favour the interconversion during the catalytic cycle between palladium complexes where the above molecule may behave in principle as phosphino monodentate, P∩N bidentate as well as P∩N∩N tridentate ligands. It is also worth noting that in Ph_2PNN imino P∩N coordination mode to the metal affords six-membered metallacyclo moieties, whereas a much larger metallacyclo (10-membered) would be formed in the case of pyridino P∩N coordination mode of the ligand. Therefore, Ph_2PNN was reacted with bis-(η^3-allyl)-di-μ-chloro-dipalladium(II) to give [18] the ionic [(η^1-allyl)-(*N*-(2-(diphenylphosphino)benzylidene)-(2-(2-pyridyl)ethylamine)-κ^3-*P*,*N*,*N*′] palladium(II) chloride [(Ph_2PNN)Pd(η^1-C_3H_5)Cl] which was checked as catalytic precursor in the telomerization reaction in combination with sodium methoxide as promoter, in order to favour the formation of palladium(0) species.



(Ph_2PNN)Pd(η^1-C_3H_5)Cl

Indeed, analogous complexes were successfully applied in carbonylation and alkylation reactions [18].

Table 4
Homogeneous 1,3-butadiene telomerization with alcohols catalyzed by the $Pd(dba)_2$ /Me_2AnPEt_2 system[a]

Run	Chelate ligand	ROH	Temperature (°C)	C_4H_6 Conv. (%)	Selectivity (%)[b]			R_c	T.N.[d] (h^{-1})
					1[e]	**2**[f]	**3**[g]		
21	Me_2AnPEt_2	CH_3OH	60	56.6	90.4	6.6	2.9	93.2	283
22	Me_2AnPEt_2	CH_3OH	80	57.7	80.4	13.1	6.3	86.0	289
23[h]	DEPE[i]	CH_3OH	60	37.2	86.6	4.4	7.3	95.2	186
24	Me_2AnPEt_2	*n*-C_3H_7OH	60	32.8	83.0	3.6	13.0	95.8	164

[a]Reaction conditions: $Pd(dba)_2$: 0.15 mmol; $Pd/ROH/C_4H_6 = 1/3000/2000$ mol/mol; $P\cap N/Pd = 1$; solvent: *n*-hexane (20 ml); $P_{N_2} = 3$ MPa; time: 4 h.
[b]When $\mathbf{1}+\mathbf{2}+\mathbf{3} < 100$ trimers and higher telomers are also present to a some extent.
[c]Regioselectivity to the linear telomers **1**, expressed as $[\mathbf{1}/(\mathbf{1}+\mathbf{2})]\times 100$.
[d]Turnover number, expressed as mol (products)/[mol (Pd)×h].
[e]*Cis*- and *trans*-1-alkoxy-2,7-octadiene.
[f]3-Alkoxy-1,7-octadiene.
[g]Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.
[h]Ref. [6]; $P\cap P/Pd = 1$.
[i]DEPE = 1,2-bis(diethylphosphino)ethane.

When the $Pd(dba)_2/Me_2AnPEt_2$ system ($Pd/P\cap N = 1$) was used in the 1,3-butadiene telomerization with methanol, carried out at 60°C and by using a $MeOH/C_4H_6$ molar ratio equal to 1.5, (run 21, Table 4) a significant catalytic activity was observed (C_4H_6 conv. ≈ 57% after 4 h). Moreover, this was accompanied by very high chemoselectivity to telomers (97%) as well as regioselectivity to the linear telomers **1** (93.2%). An increase of the reaction temperature up to 80°C (run 22) did not substantially improve the activity of the catalyst, the C_4H_6 conversion remaining substantially the same; however a decrease of both chemo- and regioselectivity to telomers was observed.

It is worth noting that, when the C_4H_6 conversion is plotted as a function of the reaction time for runs 21 and 22 (Fig. 1), a sharp increase of the conversion in the first half an hour of the reaction occurs in both cases, a limiting value far enough from the reaction completeness being rapidly reached. These results seem to suggest that a quite fast catalyst deactivation occurs, this tendency being favoured by the temperature increase.

A comparison with the $Pd(dba)_2$/1,2-bis(diethylphosphino)ethane (DEPE) system under the same telomerization conditions [6] (run 23, Table 4), where the $P\cap P$ ligand is able to afford five-membered metallacyclo moieties as Me_2AnPEt_2, clearly indicates that the $P\cap N$ ligand gives rise to a catalytic

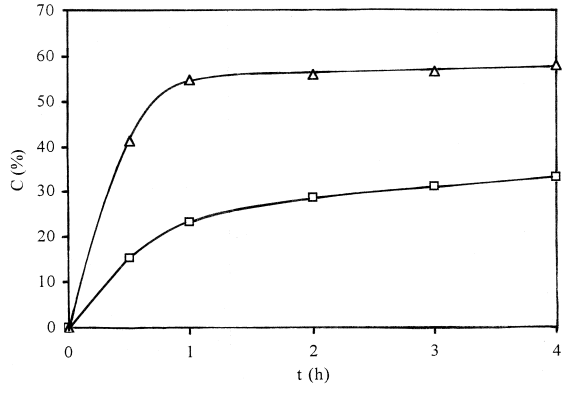


Fig. 1. Activity, expressed as C_4H_6 conversion (C) in %, as a function of reaction time: □ at 60°C (run 21) and △ at 80°C (run 22). Catalyst: $Pd(dba)_2$ /Me_2AnPEt_2.

system which displays better performances both in terms of activity [turnover number (T.N.) values after 4 h are 283 and 186, respectively] and selectivity. This may be probably addressed to the fact that, as expected, the P∩N ligand is characterized, through the amino group, by a higher coordinative lability with respect to the P∩P ligand, thus being more able to afford unsaturated active sites.

When methanol was replaced by a linear higher primary alcohol, such as 1-propanol (run 24, Table 4), a drop of C_4H_6 conversion was observed and a significant decrease of chemoselectivity to telomers was also found. An analogous behaviour was previously reported [6] when $Pd(dba)_2$ was used in combination with diphosphine chelate ligands.

With the aim to check the catalytic activity of systems derived in situ from $Pd(dba)_2$ and P∩N ligands potentially affording four-membered metallacyclo moieties, $MeImiPEt_2$ ligand was firstly tested. The 1,3-butadiene telomerization with methanol, carried out in the presence of the above-mentioned system showed (run 25, Table 5) lower activity as compared with that of the $Pd(dba)_2$/Me_2AnPEt_2 system under the same experimental conditions (run 21, Table 4). However, high values of chemo- and regioselectivity to telomers were still obtained, although slightly inferior as compared with those found in run 21. The lower activity of the catalytic system deriving from $MeImiPEt_2$ with respect to that from Me_2AnPEt_2 may be tentatively explained taking into account that in the former ligand the two nitrogen coordinative centres belong to an aromatic ring, thus depressing the catalytic activity, as previously observed for the bpy ligand.

The influence of the P∩N/Pd molar ratio on the catalyst performances was also examined (runs 26 and 27, Table 5). Indeed, on increasing the above ratio from 1 to 3 a maximum of catalyst activity was observed at the value equal to 2, where a 57.4% C_4H_6 conversion was reached. It is worth noting that in run 26 a significant improvement of chemo- (98.1%) and regio- (93.6%) selectivities to telomers was also obtained. However, a further increase of the P∩N/Pd molar ratio caused a detrimental effect on the selectivity of the process (run 27). An increase of the reaction temperature up to 100°C (run 28, Table 5) allowed to achieve a slightly higher C_4H_6 conversion (61.5%) but accompanied by a significant reduction of the chemoselectivity, almost 20% of dimers being formed. The comparison with the $Pd(dba)_2$/bis(diphenylphosphino)methane (DPPM) catalytic system, based on a P∩P chelate ligand able in principle to equally afford four-membered metallacyclo moieties (run

Table 5
Homogeneous 1,3-butadiene telomerization with methanol catalyzed by the $Pd(dba)_2$/$MeImiPEt_2$ system[a]

Run	Chelate ligand	Ligand/Pd (mol/mol)	Temperature (°C)	C_4H_6 Conv. (%)	Selectivity (%)[b]			R[c] (%)	T.N.[d] (h^{-1})
					1[e]	**2**[f]	**3**[g]		
25	$MeImiPEt_2$	1	60	42.1	82.2	12.5	5.1	86.8	210
26	$MeImiPEt_2$	2	60	57.4	91.8	6.3	1.9	93.6	287
27	$MeImiPEt_2$	3	60	35.1	75.1	20.9	3.9	78.2	176
28	$MeImiPEt_2$	1	100	61.5	69.9	9.7	18.2	87.8	307
29[h]	DPPM[i]	1	60	93.3	90.5	4.1	5.3	95.7	466

[a] Reaction conditions: $Pd(dba)_2$: 0.15 mmol; Pd/MeOH/C_4H_6 = 1/3000/2000 mol/mol; solvent: *n*-hexane (20 ml); P_{N_2} = 3 MPa; time: 4 h.
[b] When **1** + **2** + **3** < 100 trimers and higher telomers are also present to some extent.
[c] Regioselectivity to the linear telomers **1**, expressed as [**1**/(**1** + **2**)] × 100.
[d] Turnover number, expressed as mol (products)/[mol (Pd) × h].
[e] *Cis*- and *trans*-1-methoxy-2,7-octadiene.
[f] 3-Methoxy-1,7-octadiene.
[g] Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.
[h] Ref. [6].
[i] DPPM = Bis(diphenylphosphino)methane.

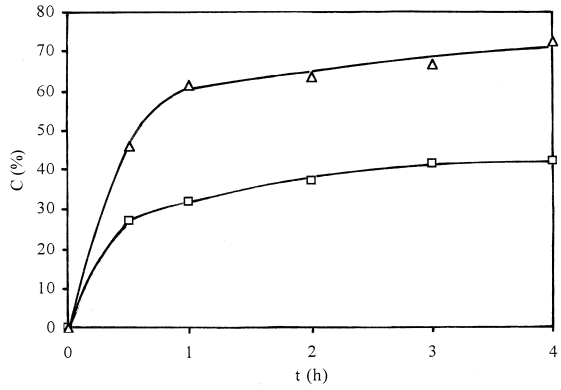


Fig. 2. Activity, expressed as C_4H_6 conversion (C) in %, as a function of reaction time: □ at 60°C (run 25) and △ at 100°C (run 28). Catalyst: $Pd(dba)_2$ /MeImiPEt$_2$.

29, Table 5), clearly indicates that the MeImiPEt$_2$ ligand gives rise to a catalytic system with lower activity under the same reaction conditions. However, it is worth noting that DPPM is not the diphosphine ligand strictly analogous to MeImiPEt$_2$, where ethyl groups and not phenyl moieties are bound to the phosphorus atom. Indeed, the higher basicity of diethyl phosphine moieties in chelate ligands usually reduces the catalytic activity of the resulting palladium catalysts [6]. When the C_4H_6 conversion was examined as a function of the reaction time for runs 25 and 28 (Fig. 2), a fast increase of the conversion in the first half an hour of reaction was observed for both experiments, a limiting value quite far from the complete C_4H_6 consumption being progressively reached. This behaviour, analogously to what found for the $Pd(dba)_2$/Me$_2$AnPEt$_2$ system, is in agreement with a quite rapid deactivation process of the catalyst, particularly in the case of experiments carried out at higher reaction temperatures.

Table 6
Homogeneous 1,3-butadiene telomerization with alcohols catalyzed by the $Pd(dba)_2$ /MePyPEt$_2$ system[a]

Run	Alcohol	P∩N/Pd (mol/mol)	ROH/C_4H_6 (mol/mol)	Temperature (°C)	C_4H_6 Conv. (%)	Selectivity (%)[b]			R[c]	T.N.[d] (h^{-1})
						1[e]	**2**[f]	**3**[g]		
30	CH_3OH	1	1.5	60	54.6	86.2	10.0	3.7	89.6	273
31	CH_3OH	2	1.5	60	51.5	83.4	12.4	3.7	87.1	258
32	CH_3OH	3	1.5	60	32.5	66.1	26.2	7.5	71.6	163
33	CH_3OH	2	1.5	70	43.2	89.6	9.3	0.9	90.6	216
34	CH_3OH	1	1.5	80	51.3	91.0	8.1	0.9	91.8	257
35	CH_3OH	1	1.5	100	61.3	89.0	9.1	1.7	90.7	306
36	C_2H_5OH	1	1.5	60	69.6	88.8	3.4	7.6	96.3	348
37	*n*-C_3H_7OH	1	1.5	60	61.0	87.5	3.6	8.6	96.1	305
38	*n*-C_3H_7OH	1	2.9	60	82.4	94.1	3.4	2.3	96.5	412
39	*n*-$C_5H_{11}OH$	1	1.5	60	77.5	83.8	2.9	12.9	96.7	387
40	*n*-$C_8H_{17}OH$	1	1.5	60	71.9	82.2	2.2	14.9	97.4	360

[a] Reaction conditions: $Pd(dba)_2$: 0.15 mmol; Pd/C_4H_6 = 1/2000 mol/mol; solvent: *n*-hexane (20 ml); P_{N_2} = 3 MPa; time: 4 h.
[b] When **1**+**2**+**3** < 100 trimers and higher telomers are also present to a some extent.
[c] Regioselectivity to the linear telomers **1**, expressed as [**1**/(**1**+**2**)]×100.
[d] Turnover number, expressed as mol (products)/[mol (Pd)×h].
[e] *Cis*- and *trans*-1-alkoxy-2,7-octadiene.
[f] 3-Alkoxy-1,7-octadiene.
[g] Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.

Therefore, in order to assure a single P∩N coordinative mode affording a four-membered metallacyclo moiety, the performances of the $Pd(dba)_2$/$MePyPEt_2$ system were checked.

When the 1,3-butadiene telomerization with methanol was performed in the presence of the above catalytic system, the effect of P∩N/Pd molar ratio (runs 30–32, Table 6) as well as of the reaction temperature (runs 33–35, Table 6) were investigated. The study of the first parameter indicates that the catalytic activity decreases going from 1 to 3 ligand/Pd ratios. However, the $Pd(dba)_2$/$MePyPEt_2$ system seems to be less sensitive to this parameter, as compared with the previous $Pd(dba)_2$/MeImi-PEt_2 system. A comparison of the two systems at 60°C with P∩N/Pd = 1 (run 30, Table 6 against run 25, Table 5) suggests that $Pd(dba)_2$/$MePyPEt_2$ is slightly more active, T.N. values in the two cases being 273 and 210, respectively. Moreover, the increase of the P∩N/Pd value causes an appreciable progressive reduction of both chemo- and regioselectivities to telomers.

The increase of the reaction temperature in the 60–100°C range does not significantly influence both activity and selectivity of the reaction process (compare runs 30 with 34 and 35).

For a better understanding of this last effect, the C_4H_6 conversion was plotted as a function of the reaction time (Fig. 3). In all the above experiments, after a rapid increase of the conversion in the first half an hour of reaction, a stationary value was reached, particularly in the case of experiments carried out at higher temperatures.

Taking into account that this phenomenon is common to all the investigated catalytic systems it appeared reasonable to assume that the deactivation of the catalyst could be due to the scarce temperature control during the reaction. Indeed, the temperature of the reaction mixture may reach at the beginning of the process (when the reaction rate is the highest) significantly higher values with respect to that predetermined of the thermostated oil bath which is reported as reaction temperature. Therefore, the 1,3-butadiene telomerization with methanol, catalyzed by the $Pd(dba)_2$/$MePyPEt_2$ system, was performed at two different temperatures (runs 41 and 42, Table 7) in an oil bath heated autoclave equipped with an inside water circulating cooling coil for an efficient heat transfer control and a thermocouple for measuring the effective reaction temperature. The data obtained clearly show that, when the reaction temperature is maintained constant by an efficient heat transfer control, the catalyst displays a very high activity, the C_4H_6 conversion being complete after one hour of reaction. Indeed, the T.N. value in run 42 (performed at 60°C) is more than one order of magnitude higher than that obtained in run 30 (Table 6) in absence of the above temperature control. Moreover, excellent chemo- (> 97%) and regio- (> 94%) selectivity values were obtained. The control of temperature

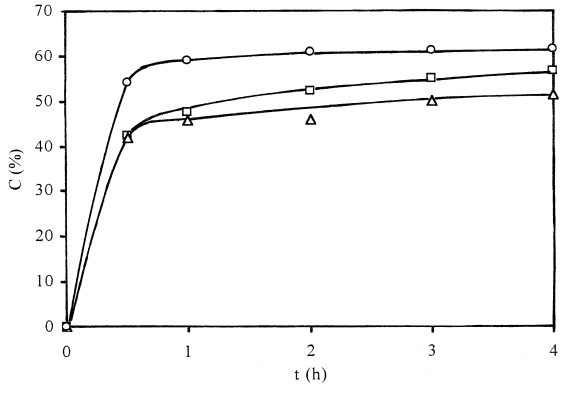


Fig. 3. Activity, expressed as C_4H_6 conversion (C) in %, as a function of reaction time: □ at 60°C (run 30), △ at 80°C (run 34) and O at 100°C (run 35). Catalyst: $Pd(dba)_2$ /$MePyPEt_2$.

Table 7
Homogeneous 1,3-butadiene telomerization with methanol at constant temperature, in the presence of the $Pd(dba)_2$/$MePyPEt_2$ system, by adopting an efficient heat transfer control[a]

	Run no. 41 (T = 45°C)				Run no. 42 (T = 60°C)			
	10 min	20 min	30 min	60 min	10 min	20 min	30 min	60 min
C_4H_6 Conv. (%)	49.1	69.5	83.7	98.2	63.8	86.3	93.6	100.0
1 (%)[b,c]	93.7	93.6	93.9	93.7	92.0	91.4	91.6	91.2
2 (%)[b,d]	4.7	4.7	4.8	4.7	5.5	5.5	5.4	5.5
3 (%)[b,e]	1.1	1.1	1.1	1.1	2.1	2.7	2.5	2.6
R (%)[f]	95.5	95.2	95.1	95.2	94.3	94.3	94.4	94.3
T.N.[g]	5890	4170	3350	1960	7660	5180	3740	2000

[a] Reaction conditions: $Pd(dba)_2$: 0.15 mmol; $Pd/P\cap N/MeOH/C_4H_6 = 1/1/3000/2000$ mol/mol; solvent: *n*-hexane (20 ml); $P_{N_2} = 3$ MPa; time: 4 h.
[b] When $\mathbf{1}+\mathbf{2}+\mathbf{3} < 100$ trimers and higher telomers are also present to a some extent.
[c] *Cis*- and *trans*-1-methoxy-2,7-octadiene.
[d] 3-Methoxy-1,7-octadiene.
[e] Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.
[f] Regioselectivity to the linear telomers **1**, expressed as $[\mathbf{1}/(\mathbf{1}+\mathbf{2})]\times 100$.
[g] Turnover number, expressed as mol (products)/[mol (Pd)×h].

allows also to maintain the above values substantially constant during the overall reaction time. Even better performances, in terms of selectivity values, were obtained at lower reaction temperature (45°C, see run 41), the percentage of the linear telomers **1** in the reaction mixture reaching values higher than 93%, never obtained before.

When primary higher alcohols were submitted to the 1,3-butadiene telomerization in the presence of the $Pd(dba)_2/MePyPEt_2$ system (runs 26–30, Table 6) higher C_4H_6 conversions (60–80%) and excellent chemoselectivities to telomers (in the 85–92% range) were obtained with respect to those found for methanol (run 24), contrarily to what occurred for the $Pd(dba)_2/P\cap P$ systems [6]. The higher activity of the former system would be partially explained assuming that $MePyPEt_2$ may behave as a hemilabile ligand in the sense that whereas the phosphino group is probably tightly bound to the metal, the amino group may exist as metal-bound and free ligand. In this situation the steric hindrance of the alcohol would not be so critical in affecting its reactivity. Moreover, the presence of a basic amino group in the close vicinity of the metal site could assist the insertion of the nucleophile, in the sense that it could enhance the nucleophilic character of the alcohol. A similar behaviour was previously invoked to explain the relevant role played by the $P\cap N$ ligand in the methoxycarbonylation of propyne catalyzed by palladium systems modified with 2-pyridyl-diphenylphosphine [26]. Considering that an efficient control of the reaction temperature should markedly enhance the performances of the catalyst also in the above cases, and that an increase of the alcohol/C_4H_6 molar ratio (compare runs 37 and 38, Table 6) appreciably enhances both productivity and selectivity of the process, this catalytic system appears to be very promising for obtaining in high yield and selectivity octadienyl ethers from linear higher alcohols.

Finally, the catalytic activity of the $(Ph_2PNN)Pd(\eta^1\text{-}C_3H_5)Cl$ complex was also checked in the 1,3-butadiene telomerization with methanol at 60°C. A preliminary experiment carried out in absence of a basic promoter did not give any catalytic activity. However, when $(Ph_2PNN)Pd(\eta^1\text{-}C_3H_5)Cl$ was used in combination with MeONa (run 43, Table 8) the resulting system displayed an appreciable activity, a quantitative C_4H_6 conversion being obtained after 18 h reaction. Moreover, a high chemoselectivity to telomers was found to occur ($\approx$ 93%). In order to have a deeper insight on the performances of the above catalytic system an experiment (run 44) was carried out under the same

Table 8
Homogeneous 1,3-butadiene telomerization with methanol by the $(Ph_2PNN)Pd(\eta^1\text{-}C_3H_5)Cl/MeONa$ [**A**] system[a]

Run	Catalyst	Time (h)	C_4H_6 Conv. (%)	Selectivity (%)[b]			R[c] (%)	T.N.[d]
				1[e]	**2**[f]	**3**[g]		
43	**A**	18	100	85.7	7.2	6.9	92.2	111
44	**A**	6	42.6	73.0	15.1	11.6	82.9	142
45	$Pd(dba)_2/Ph_2PNN$	6	4.3	70.6	6.0	23.0	92.2	14

[a] Reaction conditions: Pd: 0.10 mmol; Pd/P/N/MeOH/C_4H_6 = 1/1/2/3000/2000 mol/mol; solvent: *n*-hexane (20 ml); P_{N_2} = 3 MPa; T = 60°C.
[b] When **1** + **2** + **3** < 100 trimers and higher telomers are also present to a some extent.
[c] Regioselectivity to the linear telomers **1**, expressed as [**1**/(**1** + **2**)] × 100.
[d] Turnover number, expressed as mol (products)/[mol (Pd) × h].
[e] *Cis*- and *trans*-1-methoxy-2,7-octadiene.
[f] 3-Methoxy-1,7-octadiene.
[g] Mainly *cis*- and *trans*-1,3,7-octatriene and 4-vinyl-cyclohexene.

conditions as those adopted in run 43 except for the shorter reaction time (6 h) and the results compared with those obtained in an analogous experiment (run 45) performed in the presence of the catalytic system obtained in situ by reacting $Pd(dba)_2$ with the Ph_2PNN ligand in a 1 to 1 molar ratio. As reported in Table 8, the $(Ph_2PNN)Pd(\eta^1\text{-}C_3H_5)Cl/MeONa$ system displays lower activity and selectivity with respect to the $Pd(dba)_2/MeImiPEt_2$ and $Pd(dba)_2/MePyPEt_2$ systems (see runs 25 and 30, Tables 5 and 6, respectively). However, its activity is much higher than that of the $Pd(dba)_2/Ph_2PNN$ system which showed only 4.3% C_4H_6 conversion. It is noteworthy that the chemoselectivity of the $(Ph_2PNN)Pd(\eta^1\text{-}C_3H_5)Cl/MeONa$ system increases with increasing the reaction time, thus suggesting that the reduction by MeONa of Pd(II) to Pd(0) species in the above system is quite slow, in the early stages of the reactions the formation of dimers with respect to telomers being thus favoured. As far as the regioselectivity to linear telomers is concerned, an analogous trend was observed.

4. Conclusions

On the basis of the above results the following concluding remarks can be drawn.

(i) Palladium(II) complexes based on different P∩O ligands, when added with an alkoxide promoter to favour the formation in situ of catalytic species with a chelate P∩O moiety, in general display in the homogeneous telomerization of 1,3-butadiene with methanol lower activity and selectivity than the palladium(0) systems in the presence of chelate diphosphine ligands. Therefore, all the above examined systems do not appear to be suitable for 1,3-butadiene telomerization with alcohols, the Pd–O bond being probably responsible of an excessive stabilization of metal species in high oxidation state.

(ii) Ionic palladium complexes with N∩N (bpy) chelate ligands, such as PdNN1 and PdNN2, even in the presence of an alkoxide promoter, display very low catalytic activity in the homogeneous telomerization of 1,3-butadiene with methanol. Slightly better results were obtained with neutral palladium(0) and (II) systems based on the bpy chelating ligand. The above findings may be explained taking into account that amino groups are not able to stabilize palladium species at low oxidation state, probably owing to their scarce tendency to withdraw electrons from electron-rich metal sites, as compared with phosphine groups.

(iii) The catalysts obtained in situ by reacting $Pd(dba)_2$ with P∩N chelate ligands appear very promising in the 1,3-butadiene telomerization not only with methanol but also with higher alcohols. In particular, the new $MePyPEt_2$ ligand, especially when the reaction is performed under controlled heat exchange conditions, induces excellent performances of the catalyst, both in terms of activity as well as chemo- and regioselectivity to telomers. Indeed, the properly designed $MePyPEt_2$ behaves as a hemilabile chelate ligand affording palladium species characterized by both rather high stability at low oxidation state and reactivity.

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