

Letter

Telomerization of butadiene with methanol catalysed by cationic palladium complexes containing a bidentate phosphinoamino ligand

Marino Basato ^{a,*}, Laura Crociani ^b, Federica Benvenuti ^c,
Anna Maria Raspolli Galletti ^c, Glauco Sbrana ^c

^a *Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, CNR, Dipartimento di Chimica Inorganica Metallorganica e Analitica, Università di Padova, via Marzolo 1, I-35131 Padova, Italy*

^b *Istituto di Chimica e Tecnologia dei Materiali Avanzati, C.N.R., C.so Stati Uniti, 4, I-35127 Padova, Italy*

^c *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, I-56126 Pisa, Italy*

Received 2 November 1998; accepted 1 February 1999

Abstract

The cationic complexes $[\text{Pd}(\eta^3\text{-allyl})(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{NMe}_2))] \text{PF}_6$ (**1**) and $[\text{PdMe}(\text{PPh}_3)(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{NMe}_2))] \text{CF}_3\text{SO}_3 \cdot \text{C}_6\text{H}_6$ (**2**) catalyse, without any added phosphine, the telomerization reaction of 1,3-butadiene with methanol, showing high chemio- (> 95%) and regioselectivity towards the linear 1-methoxy-2,7-octadiene (> 93%). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Telomerization; 1,3-Butadiene; Palladium catalysts; Cationic palladium complexes; Phosphinoamines

1. Introduction

Telomerization reactions of dienes with different hydrogen active compounds like water, alcohols, amines, carboxylic acids to provide products of dimerization and simultaneous addition of nucleophile are well known in homogeneous catalysis [1–3]. A great deal of attention has recently been focused on the telomerization of 1,3-butadiene with water, as the resulting product can be hydrogenated to give *n*-octanol,

a useful raw material for plasticizers [4]; otherwise this reactivity might also be attractive for industrial production of *n*-octyl-amine from 1,3-butadiene and ammonia [5], and of linear ethers from dienes and alcohols, interesting high cetane oxygenated components for formulation of environmentally friendly diesel fuels [6].

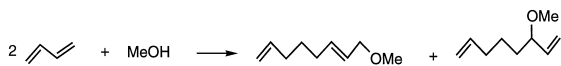
2. Discussion

In most cases, the catalyst is a complex mixture of either a zero- or a bi-valent palladium precursor with low coordinating anions and/or ligands with phosphine ancillary functions; the catalytic efficiency and distribution of

* Corresponding author. Tel.: +39-49-827-5217; Fax: +39-49-827-5223; E-mail: basato@chim02.unipd.it

products is strongly dependent both on the steric and electronic character of phosphine ligands and on the P/Pd ratio. Most studies have been centred on the prototype reaction of 1,3-butadiene with methanol and very high conversion and selectivity towards 1-methoxy-2,7-octadiene can be reached with alkyl phosphines and Pd(dba)₂ (dba = dibenzylideneacetone) in 2/1 ratio [7]. A mechanism is generally proposed which involves in the crucial steps the complexation of two dienes to a Pd(0) complex and their oxidative cyclization to give a bis-η³-allylpalladium (II) species, which then undergoes protonolysis and nucleophilic attack to the terminal position of coordinated octadienyl chain [8].

We have found that the recently published [9] cationic complexes [Pd(η³-allyl){Ph₂P(*o*-C₆H₄-NMe₂)}]PF₆ (**1**) and [PdMe(PPh₃){Ph₂P(*o*-C₆H₄-NMe₂)}]CF₃SO₃ · C₆H₆ (**2**) catalyse, *without any added phosphine*, the telomerization reaction



with high efficiency and selectivity (Tables 1 and 2 and Fig. 1).¹

In all cases, the conversion increases with time thus indicating a high stability of the catalytic system. The turnover number, after 12 h at 60°C, is always greater than 1700 mol of reacted 1,3-butadiene/mol of catalyst and reaches a turnover frequency of 466 mol/(mol h) for complex **1** in the presence of MeONa as co-catalyst. The differences in conversion using

¹ Complexes were synthesised as previously reported [9]. Catalytic runs were performed in a stirred stainless steel autoclave, equipped with a liquid sample valve and internal thermocouple. The thermostatted autoclave containing the complex, anhydrous methanol, *n*-hexane and benzene, as internal standard, was added with freshly distilled butadiene and pressurized with nitrogen (2 MPa). Samples were periodically collected in pre-cooled (-70°C) capped vials and analysed by gas chromatography on a HP 5890 instrument.

Table 1

Telomerization of 1,3-butadiene with methanol catalysed by the cationic complexes [Pd(η³-allyl){Ph₂P(*o*-C₆H₄NMe₂)}]PF₆ (**1**) and [PdMe(PPh₃){Ph₂P(*o*-C₆H₄NMe₂)}]CF₃SO₃ · C₆H₆ (**2**); Conversions with time^a

Complex	Conversion (%) ^b with time			
	3 h	6 h	9 h	12 h
1 ^c	58.24	71.87	95.77	98.85
1	38.63	46.25	62.12	71.32
1 ^d	42.36	54.02	68.09	85.47
2 ^c	43.43	60.73	75.35	79.43
2	32.90	41.30	55.80	70.90

^a Solvent: *n*-hexane (20 ml); C₄H₆/MeOH/Pd = 2400/6000/1; Pd = 5 × 10⁻⁵ mol; T = 60°C.

^b [(moles C₄H₆ in products)/(moles C₄H₆ initial)] × 100.

^c In the presence of MeONa (MeONa/Pd 10/1).

^d T = 80°C.

complex **1** or **2** alone are small, although the former appears to be slightly more efficient. A higher reaction temperature (80°C) slightly increases the conversion, but it reduces the selectivity (Table 2).

In general, the selectivity towards telomers is good (> 92%, at 60°C) and constant with time, the major by-products being C₈-dienes. Complex **1** is more selective and its selectivity reaches a value greater than 97% in the absence of MeONa. The linearity of the products is also high and scarcely dependent on the type of catalytic system (regioselectivity 93–94%).

These results can be compared with those obtained with other cationic palladium complexes [Pd(η³-allyl)L_n]PF₆ (L = (Me₂N)₃P(O), dba, PPh₃, PBU₃, cod), where in all cases mixtures of C₈- and higher weight telomers are produced [10]. The presence of the 2-(diphenylphosphino)-dimethylaniline ligand in the coordination sphere of complexes **1** and **2** clearly plays a fundamental role in determining their selectivity towards the C₈ telomer.

The close similarity in the catalytic behaviour between complexes **1** and **2** suggests that the mechanism involves essentially the same intermediates. We propose the formation of the cationic hydride complex [(P[∧]N)PdH]⁺ (P[∧]N = Ph₂P(*o*-C₆H₄NMe₂)), resulting from the insertion of a butadiene unit on the coordinated

Table 2

Telomerization of 1,3-butadiene with methanol catalysed by $[\text{Pd}(\eta^3\text{-allyl})(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{NMe}_2))] \text{PF}_6$ (**1**) and $[\text{PdMe}(\text{PPh}_3)(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{NMe}_2))] \text{CF}_3\text{SO}_3 \cdot \text{C}_6\text{H}_6$ (**2**); Selectivities after 3 and 12 h^a

Complex	Selectivity (%) after 3 h				Selectivity (%) after 12 h			
	Telomers ^b (lin. tel.) ^c	Dimers	Trimers	high tel.	Telomers ^b (lin. tel.) ^c	Dimers	Trimers	high tel.
1 ^d	95.91 (92.94)	4.06	0.02	0.01	96.04 (92.95)	3.91	0.05	0.01
1	97.32 (93.01)	2.66	0.01	0.01	97.03 (93.22)	2.91	0.02	0.04
1 ^e	91.21 (93.25)	8.72	0.03	0.04	89.73 (93.12)	10.15	0.05	0.07
2 ^d	93.47 (93.65)	6.49	0.03	0.00	92.04 (93.95)	7.88	0.02	0.04
2	95.37 (93.50)	4.63	0.00	0.00	94.84 (95.05)	5.06	0.02	0.05

^aSolvent: *n*-hexane (20 ml); $\text{C}_4\text{H}_6/\text{MeOH}/\text{Pd} = 2400/6000/1$; $\text{Pd} = 5 \times 10^{-5}$ mol; $T = 60^\circ\text{C}$.

^b $[2(\text{moles of telomer})/(\text{moles of converted } \text{C}_4\text{H}_6)] \times 100$.

^cRegioselectivity to the linear telomers *cis* and *trans*-1-methoxy-2,7-octadiene, expressed as percentage of linear over total telomers.

^dIn the presence of MeONa (MeONa/Pd 10/1).

^e $T = 80^\circ\text{C}$.

allyl (**1**) or methyl (**2**) group, followed by β -elimination of a C_7 -triene or a C_5 -diene. Insertion of dienes into allyl- or alkyl-palladium bonds are well-known processes [8,11]. The hydrido palladium (II) complex could, in principle, undergo coordination and insertion of a molecule of 1,3-butadiene, opening in this way the catalytic cycle (hydrido route, [12]), or undergo reductive elimination of H^+ to give as effective catalyst the subcoordinated palladium (0) complex $[(\text{P}^\cap\text{N})\text{Pd}]$ (oxidative cyclization route [8]). To shed light on this point, we have used as catalytic system a 1/1 molar mixture of $\text{Pd}(\text{dba})_2$ and $\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{NMe}_2)$. Under the same experimental conditions, the rate of telomerization is about twice that observed with the

cationic complexes **1** and **2**, the conversion being complete in 6 h at 60°C , but the chemio- and regioselectivities are very similar (Table 3).

3. Conclusion

On these bases, we believe that in all cases, the telomerization is catalysed by the palladium (0) complex $[(\text{P}^\cap\text{N})\text{Pd}]$: this is easily formed by a ligand exchange process in the $\text{Pd}(\text{dba})_2/\text{P}^\cap\text{N}$ system or by H^+ reductive elimination from a hydrido complex, when the palladium (II) cationic precursors are used. This reduction is favoured by the presence of MeO^- , which, in fact, has a positive effect on the telomerization rate. In this view, the observed differences in catalytic activity seem to be simply related to a higher concentration of active sites, starting from a palladium (0)-based system.

The obtained results confirm the importance of the phosphinoamine P^\capN ligands in stabiliz-

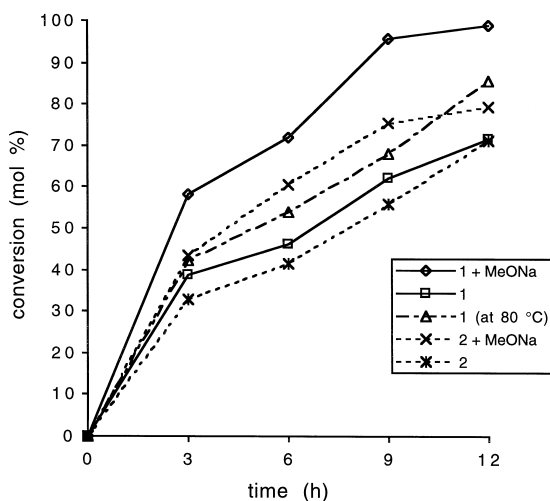


Fig. 1.

Table 3

Telomerization of 1,3-butadiene with methanol catalysed by the system $\text{Pd}(\text{dba})_2/\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{NMe}_2)$ in 1/1 Pd/P molar ratio^a

Time (h)	1.00	2.00	3.00	4.00	5.00	6.00
C_4H_6 conversion	44.88	62.21	74.18	89.67	96.80	99.54
Selectivity	94.20	96.50	96.52	96.70	96.69	96.48
Linear/total ethers	93.84	93.48	93.50	94.15	94.14	93.46
Dimers	5.76	3.33	3.45	3.20	3.21	3.42

^aSolvent: *n*-hexane (20 ml); $\text{C}_4\text{H}_6/\text{MeOH}/\text{Pd} = 2400/6000/1$; $\text{Pd} = 5 \times 10^{-5}$ mol; $T = 60^\circ\text{C}$.

ing palladium centres, which behave as very active and selective catalysts in the telomerization of butadiene with methanol [13]. The cationic allyl and methyl palladium (II) complexes **1** and **2** are very stable and easy to handle compounds, which represent a valid single component alternative to the mixtures of Pd(OAc)₂ or Pd(dba)₂ with phosphine ligands, usually employed as catalyst precursors in this type of reactions.

Acknowledgements

We thank Progetto Strategico 'Tecnologie Chimiche Innovative', CNR, for partial financial support of this research.

References

- [1] A. Behr, Aspects of Homogeneous Catalysis, in: R. Ugo (Ed.), Vol. 5, Reidel, Dordrecht, 1984, p. 3.
- [2] N. Yoshimura, Applied Homogeneous Catalysis with Organometallic Compounds, in: B. Cornils, W.A. Herrmann (Eds.), Vol. 1, VCH, Weinheim, 1996, p. 351.
- [3] J. Tsuji, Palladium Reagents and Catalysts, Wiley, Chichester, 1995, p. 423.
- [4] E. Monflier, P. Bordaudecq, J.L. Couturie, J. Kervennal, I. Suisse, A. Mortreux, Appl. Catal. A: Gen. 131 (1995) 167.
- [5] T. Prinz, W. Keim, B. Driessen-Hölscher, Angew. Chem., Int. Ed. Engl. 35 (1996) 1708.
- [6] M. Marchionna, R. Patrini, F. Giavazzi, G.C. Pecci, Preprints 212th National Meeting of the American Chemical Society, Div. Petrol. Chem. 41 (1996) 585.
- [7] F. Benvenuti, C. Carlini, M. Lami, M. Marchionna, R. Patrini, A.M. Raspolli Galletti, G. Sbrana, J. Mol. Catal. A: Chemical, in press.
- [8] L.S. Hegedus, Transition Metal in the Synthesis of Complex Organic Molecules, University Science Book, Mill Valley, CA, 1994, p. 262.
- [9] L. Crociani, G. Bandoli, A. Dolmella, M. Basato, B. Corain, Eur. J. Inorg. Chem. (1998), 1811.
- [10] P. Grenouillet, D. Neibecker, J. Poirier, I. Tkatchenko, Angew. Chem. Int. Ed. Engl. (1982), 767.
- [11] B.M. Trost, J.I. Luengo, J. Am. Chem. Soc. 110 (1988) 8239.
- [12] P.M. Maitlis, in: The Organic Chemistry of Palladium, Vol. 2, Academic Press, New York, 1971, p. 46.
- [13] F. Benvenuti, C. Carlini, M. Marchionna, R. Patrini, A.M. Raspolli Galletti, G. Sbrana, J. Mol. Catal. A: Chemical 140 (1999) 139.