

Phosphinoalkyl nitriles as hemilabile ligands: New aspects in the homogeneous catalytic coupling of CO₂ and 1,3-butadiene¹

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Abstract

'In situ' catalysts prepared from $(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-C}_3\text{H}_5)$ **9** and phosphinoalkyl nitriles **10a–e** of the general formula $(i\text{-C}_3\text{H}_7)_2\text{P}-(\text{CH}_2)_n-\text{CN}$ have been used to catalyse the co-oligomerisation of 1,3-butadiene and carbon dioxide. The δ -lactone 2-ethylidene-6-heptene-5-olide **1** is formed, yielding up to 74%. Different solvent systems have been used of which pyridine provides the best result. The catalysis may also be performed without additional solvent. A minimum of five CH₂ units ($n = 5$) within the ligand is necessary to produce **1** with a selectivity higher than 29% in a solvent-free reaction. Therefore, phosphinoalkyl nitriles of the type described here are acting as hemilabile ligands in the catalytic cycle. © 1997 Elsevier Science B.V.

Keywords: Carbon dioxide; Co-oligomerisation; Palladium catalyst; Hemilabile P,N ligand

1. Introduction

Palladium complexes with suitable phosphine ligands are, as 'in situ' systems or as isolated compounds, well known as homogeneous catalysts for the telomerisation of conjugated dienes [1]. The co-oligomerisation of 1,3-butadiene and

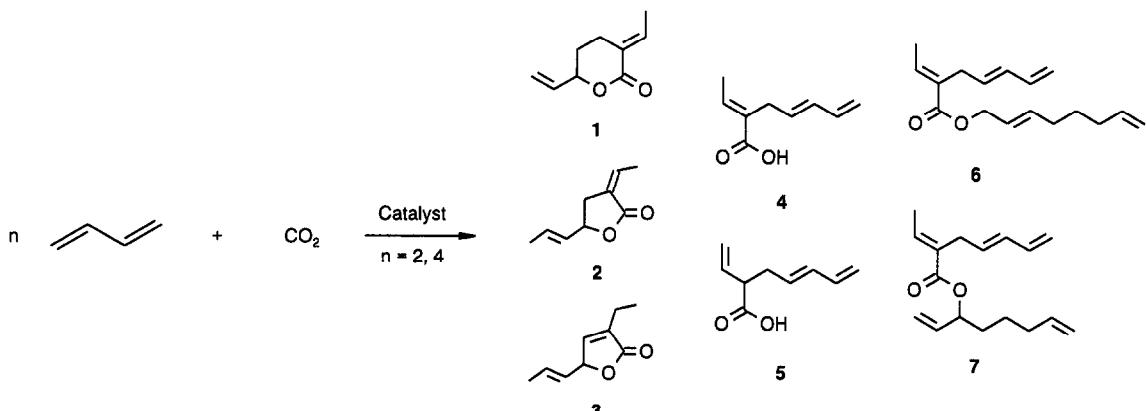
carbon dioxide, introducing carbon dioxide as a C₁ building block for organic synthesis, has attracted considerable interest since its initial discovery in 1976 by Sasaki and Inoue [2]. Studies of this catalytic system [3–8] have shown that the formation of several products **1–7** is possible as outlined in Scheme 1.

One key point of interest is the selective formation of **1**. Former attempts to find optimised catalysts and conditions have shown that phosphine ligands — particularly those with high σ -donator power and phosphorous linked residue of great steric hindrance, e.g. isopropyl and cyclohexyl — favour the catalysis [9]. It was suggested that the catalytic cycle starts with a complex $\text{Pd}(\text{PR}_2\text{R}')_2$ [10]. $\text{PR}_2\text{R}'$ symbolises a tertiary phosphine, or one part of a chelating

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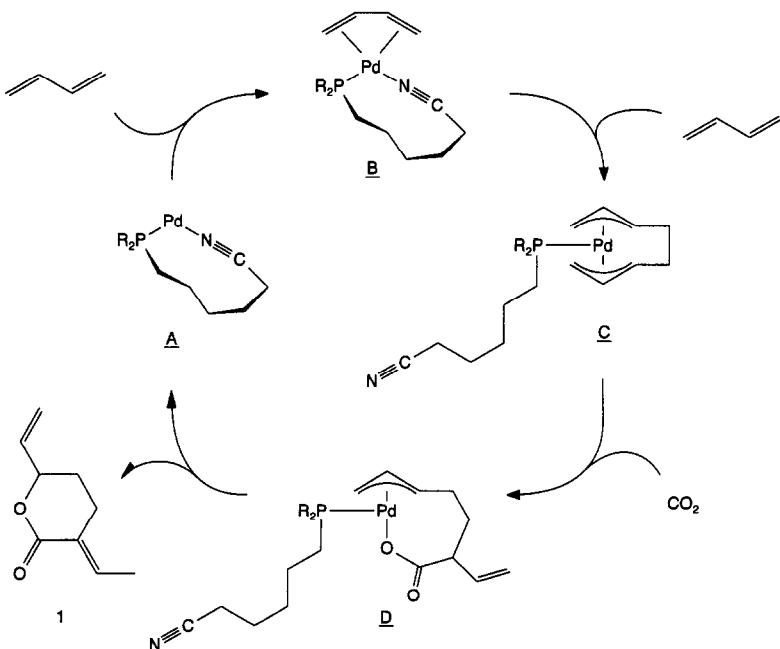
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Scheme 1.

diphosphine ligand. The successive coordination and linkage of two butadiene units with the simultaneous elimination of one phosphine ligand are followed by the insertion of carbon dioxide into a Pd,C bond. A cyclic metallacar-

boxylato species was also suggested as an intermediate in the formations of lactone **2**, acids **4**, **5** and esters **6**, **7** [11,12]. According to this mechanism, the δ -lactone **1**, which is the main product under specific conditions, is generated



R: isopropyl, cyclohexyl; R', R'': CH₃, n-alkyl.
[•] here: using a ligand with n-C₅H₉ chain.

Scheme 2.

by reductive elimination with reformation of the active species (compare also *A* to *D* in Scheme 2).

The published data show a significant ‘nitrile effect’: the use of alkyl nitriles as solvents was found to be essential for the formation of **1**. For example, the use of the ‘in situ’ catalyst $\{\text{Pd}(\text{acac})_2/\text{P}3(i\text{-C}_3\text{H}_7)_3\text{ 8}\}$ in acetonitrile yields 44% of **1**, whereas in benzene only 0.7% is formed under the same conditions [13]. The discussion of the results was based on the solubility of CO_2 in acetonitrile and the C_6H_5 acidity of this solvent [4]. On the other hand, nitrile complexes of palladium are well known: they are applied in several complex formations, whereas other ligands easily displace the weakly bonded nitrile. One can imagine that in the catalytic co-oligomerisation, palladium nitrile complexes play a role as well. Surprisingly, this fact has not been considered in the mechanistic interpretation. A preactivation of the palladium centre, as suggested more generally by Behr et al. [14], $[\text{Pd}(\text{NCR})_x(\text{PR}_3)_y]$, was not verified experimentally until today. However, it is important to understand the significance of the solvent in obtaining optimum results in the catalysis.

The purpose of our work is to demonstrate that the cooperation between strong and weak donor ligands is decisive to obtain an efficient

formation of **1**. To achieve this, a type of ligand which may be termed *hemiclable* [15] seemed to be the most suitable: within the ligand one phosphino moiety and one nitrile group are connected by an alkyl spacer. The alkyl spacer itself has no coordinating properties.

In an initial study, we described the ligand synthesis [16]. We were able to show that in tetrahydrofuran, the ‘in situ’ catalyst prepared from $(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-C}_3\text{H}_5)_2\text{ 9}$ and $(i\text{-C}_3\text{H}_7)_2\text{P}-(\text{CH}_2)_6-\text{CN}$ **10c** has an activity comparable to other known catalysts in acetonitrile.

In the present study, we report on the results of varying series of catalytic experiments. In particular, the influence of the chain length of the alkyl spacer is investigated. Additionally, we determine the optimum conditions for reaction temperature and reaction time.

2. Experimental section

All manipulations were carried out under dry argon atmosphere by standard Schlenk techniques. NMR spectra were acquired on a Bruker AC 200 spectrometer. Chemical shifts are referenced to internal or external TMS (^1H , ^{13}C), respectively, or external 85% H_3PO_4 (^{31}P). In experiments using non-deuterated solvents, a coaxial tube with D_2O was inserted as a lock.

Table 1

Catalytic co-oligomerisation in different solvents (refer to Section 2). ‘P’: $\text{P}(i\text{-C}_3\text{H}_7)_3$ **8**; ‘P \sqcap CN’: $(i\text{-C}_3\text{H}_7)_2\text{P}-(\text{CH}_2)_6-\text{CN}$ **10c**; Pd precursor: $(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-C}_3\text{H}_5)_2$ **9**

Solvent	Conversion of butadiene (%)		Selectivity to 1 (%)		Isolated yield of 1 (%)	
	‘P’	‘P \sqcap CN’	‘P’	‘P \sqcap CN’	‘P’	‘P \sqcap CN’
acetonitrile	85	> 95	39	61	32	58
benzene	> 3	> 44	2	78	— ^a	30
thf	> 4	> 24	< 1	62	— ^a	14
thf/pyridine (10/1)	> 5	> 49	2	70	— ^a	32
pyridine	> 12	100	3	74	— ^a	67
hexane	> 2	> 3	> 1	20	— ^a	— ^a
sc carbon dioxide ^b	> 4	> 3	< 1	< 1	— ^a	— ^a
— ^c	> 3	> 90	< 1	45	— ^a	39

^a The amount of **1** is not suitable for further distillation.

^b To reach supercritical conditions, 150 g CO_2 is introduced; the phase change being visible by using a reactor equipped with glassy windows.

^c No additional solvent is used, resulting in a liquid mixture of butadiene and CO_2 as reaction medium.

Table 2

Catalytic co-oligomerisation using ligands **10a–e** (refer to Section 2). Pd precursor: $(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-C}_3\text{H}_5)$ **9**

Ligand	Conversion of butadiene (%)		Selectivity to 1 (%)		Isolated yield of 1 (%)	
	Pd/ligand (2:1)	Pd/ligand (1:1)	Pd/ligand (2:1)	Pd/ligand (1:1)	Pd/ligand (2:1)	Pd/ligand (1:1)
$(i\text{-C}_3\text{H}_7)_2\text{P}-(\text{CH}_2)_3\text{-CN}$, 10a	> 22	> 17	22	19	— ^a	— ^a
$(i\text{-C}_3\text{H}_7)_2\text{P}-(\text{CH}_2)_5\text{-CN}$, 10b	> 76	> 66	40	36	29	26
$(i\text{-C}_3\text{H}_7)_2\text{P}-(\text{CH}_2)_6\text{-CN}$, 10c	> 90	> 83	45	40	39	31
$(i\text{-C}_3\text{H}_7)_2\text{P}-(\text{CH}_2)_7\text{-CN}$, 10d	> 87	> 80	44	39	37	33
$(i\text{-C}_3\text{H}_7)_2\text{P}-(\text{CH}_2)_{10}\text{-CN}$, 10e	> 74	> 63	32	30	23	20

^a The amount of **1** is not suitable for further distillation.

Assignments were confirmed by ^1H , ^1H - and ^1H , ^{13}C -COSY, ^{13}C -DEPT and selective $\{^{31}\text{P}\}$ decoupling of ^1H and ^{13}C spectra. For GC-MS analysis, a Hewlett Packard gas chromatograph 5890 equipped with a quadrupole mass analyser 5922 was used. Chromatograms were measured with helium on a 30 m HP5-MS capillary column. HPLC was performed with a Gynkotek system M480P/UVD340S on a C_{18} phase (25 \times 0.4 cm) with acetonitrile/ H_2O (10/90). IR spectra were recorded on a Perkin Elmer PC-16 spectrometer.

Solvents were distilled after purification using standard methods. Carbon dioxide (4.8) was used without modification. Butadiene (Fluka) was condensed immediately before use. $(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-C}_3\text{H}_5)$, **9**, was prepared by a method described in Ref. [17] and freshly sublimated. Materials needed for ligand synthesis are cited in a previous report [16].

2.1. General procedure for the catalytic experiments

$(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-C}_3\text{H}_5)$, **9**, typically between 0.1 and 1.0 mmol, is dissolved in butadiene at -50°C . This orange solution and the phosphine are transferred via a canula to a precooled 200 ml autoclave, equipped with a magnetic stirrer, internal thermometer, and Swagelock connections to external CO_2 and a vacuo/argon line. The reactor is locked and the content is stirred. At ambient temperature the autoclave is pressurised with CO_2 , then warmed in an oil bath. After stirring vigorously for a given reaction time, the oil bath is removed.

The unreacted gaseous components were removed carefully by stirring below 30°C under a slow argon stream. The selectivity to **1** is determined by $^1\text{H-NMR}$ of the raw product³. The accuracy is checked by quantitative GC-MS and quantitative HPLC to be $\pm 3\%$. The solution is then concentrated in vacuo of less than 10^{-1} mbar. Volatile byproducts, such as isomeric C_8H_{12} from dimerisation of butadiene as a side reaction, were removed also and not determined. Simple distillation following described procedures [13] yield **1** in ca. 90% of the above determined selectivity (Tables 1 and 2) and with purity higher than 95%. Further purification can be performed by multiple gentle distillation via a rotary column.

$^1\text{H-NMR}$ (CDCl_3) of **1** (assigned nucleus italic, coupling constants in Hz): 1.80 dt(3H, $\text{CH}-\text{CH}_3$, $^5J = 1.6$, $^3J = 7.2$), 1.95–2.21 m(2H, CH_2-CH_2), 2.32–2.71 m(2H, $\text{C}-\text{CH}_2$), 4.79 m(1H), 5.25 ddd(1H, *cis*- $\text{H}_2\text{C}=\text{CH}$, $^4J = 0.9$, $^3J_{cis} = 10.6$, $^2J = 1.1$), 5.32 ddd(1H, *trans*- $\text{H}_2\text{C}=\text{CH}$, $^4J = 0.9$, $^3J_{trans} = 17.2$, $^2J = 1.1$), 5.90 ddd(1H, $\text{H}_2\text{C}=\text{CH}$, $J_{trans} = 17.2$, $^3J_{cis} = 10.6$, $^3J = 5.4$), 7.13 tq(1H, CH_3-CH , $^4J = 2.5$, $^3J = 7.2$).

$^{13}\text{C-NMR}$ (CDCl_3) of **1**: 13.8 ($\text{CH}-\text{CH}_3$), 21.7 (CH_2-CH_2), 27.4 ($\text{C}-\text{CH}_2$), 78.7 (CH_2-CH), 116.6 ($\text{CH}-\text{CH}_2$), 125.8 ($\text{CH}=\text{C}$), 135.6 (CH_3-CH), 140.9 ($\text{CH}_2=\text{CH}$), 166.0 ($\text{C}=\text{O}$).

³ The selectivity of **1** was determined via ^1H by comparison of the integral values referenced to the O-CH proton (4.63–4.81 ppm, depending on the solvent). In cases where the selectivity was found to be less than 15%, the value was determined by quantitative GC-MS measurement.

All corresponding values of yield and selectivity to **1** were estimated by single experiments. Attempts to collect samples online were not successful because product formation was diminished.

The following phosphines were used: $P(i-C_3H_7)_3$ **8**, $(i-C_3H_7)_2P-(CH_2)_3-CN$ **10a**, $(i-C_3H_7)_2P-(CH_2)_5-CN$ **10b**⁴, $(i-C_3H_7)_2P-(CH_2)_6-CN$ **10c**, $(i-C_3H_7)_2P-(CH_2)_7-CN$ **10d**⁴, $(i-C_3H_7)_2P-(CH_2)_{10}-CN$ **10e**.

2.2. Catalysis using different solvents

Following the general procedure given above, the catalyst was synthesised from 0.037 g ($\eta^5-C_5H_5$)Pd($\eta^3-C_3H_5$) **9** (0.173 mmol), 0.079 g **10c** (0.346 mmol) in 18 g butadiene (0.333 mol), and 30 ml solvent. 20 g CO₂ (0.455 mol) were added resulting in a pressure of 12–16 bar at ambient temperature. Absolute values of butadiene and CO₂ were determined by differential weighing of the autoclave. Catalysis was performed at 60°C for 15 h. After the reaction, the solvent was removed by distillation in vacuo.

2.3. Catalysis using different phosphinoalkyl nitriles

Following the general procedure, the catalyst was synthesised from 0.074 g ($\eta^5-C_5H_5$)Pd(η^3-

C₃H₅) **9** (0.346 mmol) and one or two equivalents of phosphinoalkyl nitriles **10a–e** in 36 g butadiene (0.667 mol). 40 g CO₂ (0.910 mol) were added resulting in a pressure of 25–29 bar at ambient temperature. Absolute values of butadiene and CO₂ were determined by differential weighing of the autoclave. The catalysis was performed at 70°C for 20 h.

2.4. Catalysis using different temperatures and reaction times

Following the general procedure, the catalyst was synthesised from 0.037 g ($\eta^5-C_5H_5$)Pd($\eta^3-C_3H_5$) **9** (0.173 mmol), 0.079 g **10c** (0.346 mmol) in 18 g butadiene (0.333 mol). 20 g CO₂ (0.455 mol) were added resulting in a pressure of 10–13 bar at ambient temperature. Absolute values of butadiene and CO₂ were determined by differential weighing of the autoclave.

3. Results

Hemilabile ligands of the type described above have been prepared by several methods [18,19]. Following the recently published procedure, the synthesis of phosphinoalkyl nitriles with $n = 3$ and $n > 4$ can be easily achieved [16]. As mentioned earlier, we decided to use the diisopropylphosphino substituted alkyl nitriles. With 'in situ' catalysts prepared from ($\eta^5-C_5H_5$)Pd($\eta^3-C_3H_5$) **9** and different phosphines, we performed a series of experiments to co-oligomerise 1,3-butadiene and CO₂.

First, $(i-C_3H_7)_2P-(CH_2)_6-CN$ **10c** is compared to $P(i-C_3H_7)_3$ **8** which was often used in earlier works (Table 1) [9,12–14]. Under comparable conditions, e.g. a temperature of 60°C, a pressure of 13 bar CO₂ and acetonitrile as solvent, catalysis yields 49% (with **10c**) and 32% of **1** (with **8**), respectively. Other solvents cause dramatic effects: As the use of **8** strongly decreases the conversion of butadiene and the selectivity to the lactone, the catalyst prepared from **10c** still remains remarkably active. It is

⁴ **10b** and **10d** were prepared following the described procedure [16]. Both compounds gave correct elemental analysis data. **10b**: 1H -NMR (CDCl₃): H(⁰alkyl chain) 1.14–1.52 m(4CH₂ + H^{CH} = 10H), 2.19 t(2H, $^3J_{HH} = 7.0$); CH(CH₃)₂ 1.53 dsep($^3J_{HH} = 7.1$, $^2J_{HP} = 2.8$); H₃C^a 0.93 dd(H₃C^a + H₃C^b = 12H, $^3J_{HH} = 7.2$, $^3J_{HP} = 14.0$); H₃C^b 0.91 dd($^3J_{HH} = 7.0$, $^3J_{HP} = 11.1$). ^{13}C -NMR (CDCl₃): C(⁰alkyl chain) 30.2 d($^1J_{CP} = 12.1$), 21.0 d($^2J_{CP} = 17.5$), 27.3 d($^3J_{CP} = 19.0$), 22.1 d, 16.8 s; CN 119.1 s; CH(CH₃)₂ 23.0 d($^1J_{CP} = 12.1$); H₃C^a 19.9 d($^2J_{CP} = 14.1$); H₃C^b 18.5 d($^2J_{CP} = 9.0$). ^{31}P -NMR (CDCl₃): + 2.6 s. **10d**: 1H -NMR (CDCl₃): H(⁰alkyl chain) 1.05–1.45 m(5CH₂ + H^{CH} = 12H), 2.15 t(2H, $^3J_{HH} = 7.1$); CH(CH₃)₂ 1.47 dsep($^3J_{HH} = 7.1$, $^2J_{HP} = 2.6$); H₃C^a 0.85 dd(H₃C^a + H₃C^b = 12H, $^3J_{HH} = 7.0$, $^3J_{HP} = 13.5$); H₃C^b 0.82 dd($^3J_{HH} = 6.9$, $^3J_{HP} = 11.0$). ^{13}C -NMR (CDCl₃): C(⁰alkyl chain) 30.9 d($^1J_{CP} = 11.1$), 21.3 d($^2J_{CP} = 16.9$), 27.8 d($^3J_{CP} = 18.9$), 24.9 s, 25.1 s, 28.0 s, 16.7 s; CN 119.2 s; CH(CH₃)₂ 23.0 d($^1J_{CP} = 12.2$); H₃C^a 19.9 d($^2J_{CP} = 14.1$); H₃C^b 18.6 d($^2J_{CP} = 9.6$). ^{31}P -NMR (CDCl₃): + 3.4 s.

not surprising that pyridine and pyridine/tetrahydrofuran mixtures as solvents yield the highest amounts of **1**. Using longer reaction times for the catalysis, the isolable yield increases to 74%. This investigation is consistent with the well known influence of basic *N*-donors [20–22]⁵. Also pure tetrahydrofuran and benzene give reasonable yields of **1**. The less polar solvent hexane decreases formation of **1**. Under supercritical conditions (see footnote b in Table 1), no formation of **1** and only small amounts of butadiene oligomers are observed. Possibly this is due to low solubilities of the active species in these media.

The simultaneous use of butadiene as substrate and solvent is of particular interest. One may expect that chemical reaction engineering should be much easier. Under these ‘solvent-free’ conditions **1** is obtained in isolated yield of 39%.

Table 2 documents the dependence of the lactone yield from the chain length between the phosphino and the nitrile function in a solvent-free reaction.

It is clearly demonstrated that conversion rates higher than 60% and good selectivities are obtained only with chain lengths $n > 4$. Note the chelating coordination of a phosphinoalkyl nitrile: The usual coordination of nitriles is linear ‘end on’. The four atoms –Pd–N–C–C– tend to a linear geometry. This cannot be realised with phosphinoalkyl nitriles of shorter chain lengths. On the other hand, a chelating effect is probably not high, because, as predicted, large rings would be formed using ligands **10c–e**. We propose that a low energy barrier, in particular resulting in a fast ring opening (*B* to *C*) and closing (*D* to *A*), favours the catalysis as outlined in Scheme 2. From this point of view the preliminary discussed ‘nitrile effect’ probably is caused by similar nitrile coordination during the

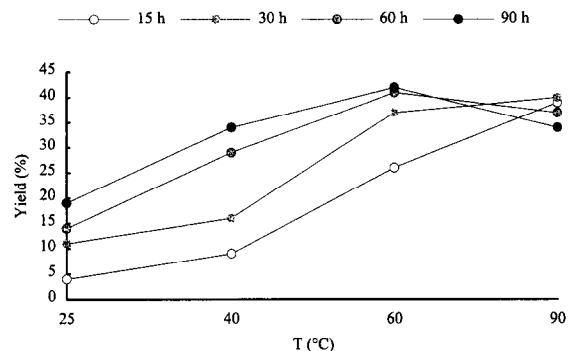


Fig. 1. Yields of **1** (%) in the catalytic co-oligomerisation (refer to Section 2). Ligand: $(i\text{-C}_3\text{H}_7)_2\text{P}-(\text{CH}_2)_6-\text{CN}$ **10c**; Pd-precursor $(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta\text{-C}_3\text{H}_5)$, **9**.

catalytic cycle. The key steps of the product formation only differ in the type of the supporting co-ligand.

The presumed hemilabile coordination mode is supported by another investigation: Changing the ratio palladium/phosphine of the ‘in situ’ catalyst from 0.5 to 1 causes no significant change in the formation of **1** (Table 2). This indicates that double phosphine coordinated palladium species instead of *A* and *B* (Scheme 2) are not present in the catalytic cycle.

Fig. 1 shows the dependence of the lactone yield on the temperature and reaction time. With the efficient ‘in situ’ catalyst prepared from **8** and **10c**, butadiene is already converted at room temperature. There is no remarkable change in the yield of **1** in the temperature range between 25 and 90°C if the reaction time is long enough. All these reactions produce bright yellow viscous liquids. These liquids consist of **1**, butadiene oligomers, traces of **6** and **7**, and of unreacted butadiene. Catalysis is highly sensitive towards traces of oxygen and results are also dependent on the procedure of mixing the components. Using temperatures above 120°C increases the rate of polymerization reactions according to previous investigations⁶. It should be noted that even with several replications, the variation

⁵ The authors also described the use of the phosphinoalkyl nitrile $\text{P}(\text{CH}_2\text{CN})_3$ together with $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ in the co-oligomerisation of butadiene and CO_2 to yield 1.5% of **1**.

⁶ See Refs. [13], pp. 29ff and [23]. Co-oligomerisation processes at higher temperatures are the subject of current research.

range of the lactone yield was found to be $\pm 6\%$.

4. Conclusions

A novel application of phosphinoalkyl nitriles for the homogeneous catalytic co-oligomerisation of 1,3-butadiene and carbon dioxide is introduced. Utilizing the ligands **10b–e** for catalyst preparation, the further use of acetonitrile as solvent is rendered unnecessary. More importantly, working without additional solvents offers new perspectives for a technical application. Furthermore we observed that within ligands $R_2P-(CH_2)_n-CN$ a minimum of five CH_2 units is necessary to obtain good yields of δ -lactone **1**. This observation also provides support for a hemilabile coordination mode of phosphinoalkyl nitriles during the catalytic formation of **1**. Studies concerning the use of alternative hemilabile ligands and further optimisation of the process parameters will be presented in the near future.

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