

Palladium Catalyzed Alternating Cooligomerization of Ethylene and Carbon Monoxide to Unsaturated Ketones

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Dedicated to Prof. Dr. Dr. h.c. mult. Günther Wilke on the occasion of his 70th birthday

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Cationic palladium catalysts have been used to cooligomerize ethylene and carbon monoxide. At high ethylene/C \bullet ratios ($m/m = 10:1$) in methylene chloride as a solvent, unsaturated alternating cooligomers of the general structure $R[C(\bullet)CH_2CH_2]_mH$ ($m \geq 1$; $R = CH_2=CH-$, $CH_2=CHCH_2CH_2-$ and $CH_3CH=CHCH_2-$) were obtained for the first time. Single component catalyst precursors [(allyl)Pd(P^X)]⁺Y⁻ (P^X = Ph₂P(CH₂)_nC(=O)OR, Ph₂P(CH₂)₂P(=O)Ph₂, Ph₂P(CH₂)_nC=CHCH=CH₂, Ph₂P(CH₂)₂S(=O)Ph, $n = 1-3$, R = Me, Et; Y⁻ = BF₄⁻, SbF₆⁻) with bidentate P, O- and P, S-ligands as well as *in situ* catalysts with unfunctionalized phosphine ligands were used. With PⁿBu₃ as a ligand, selectivities for ethylvinylketone of 40% based on the CO converted were obtained. The hemilabile phosphino-ester and phosphinothiophene ligands behave like monodentate phosphines under catalytic conditions.

Introduction

Unsaturated ketones belong to a class of organic compounds of substantial synthetic interest, but their syntheses are often tedious. Potentially, an easy synthetic approach exists in the cooligomerization of olefins, especially ethylene, with carbon monoxide.

The first carbonylation reactions of olefins as pioneered by Roelen represent a milestone in the development of industrial, homogeneous transition metal based catalysis. Today, the oxo-synthesis represents the largest scale application of homogeneous catalysis.

In hydroformylation, as well as in other important carbonylation reactions of olefins, e.g. hydrocarboxylation and hydrocarbalkoxylation, the product contains one molecule of olefin and CO, respectively. Products containing more than one molecule of olefin can also be obtained. Roelen already observed the formation of diethylketone as a byproduct in the hydroformylation of ethylene [1], and many other examples are known [2]. Diethylketone can also be obtained selectively [3].

Multiple incorporation of carbon monoxide can also occur, yielding saturated oligoketones

$H[CH_2CH_2C(O)]_mEt$ or oligoketocarboxylic acids or esters $H[CH_2CH_2C(O)]_mOR$ ($m > 1$; R = H, alkyl). In addition to ethylene and carbon monoxide, the oligoketones contain two hydrogen atoms, usually originating from H₂ added or derived from water *via* the water-gas shift reaction. The oligoketocarboxylic acids or esters contain one molecule of water or alcohol, added or used as a solvent. In an early publication, Reppe and Magin have described the nickel catalyzed synthesis of such oligomers along with high-molecular-weight polymeric products [4]. With rhodium catalysts, oligoketones and oligoketoesters ($m = 1$ to approximately 4) can be obtained selectively under mild conditions [5]. Oligoketoesters can also be obtained with palladium catalysts [6, 7b].

The formation of unsaturated ketones, consisting only of olefin and carbon monoxide, has also been observed. Propenylpropylketones can be derived from propylene and carbon monoxide with rhodium [5b] and palladium catalysts [8]. Employing styrene, 1,5-diphenylpent-1-en-3-one can be obtained selectively [8, 9]. Considering the synthesis of unsaturated ketones from ethylene and CO, the transition metal catalyzed preparation of ethylvinylketone has been described under severe conditions with moderate selectivities, using ruthenium, copper or silver catalysts [10]. Drent has briefly noted, that ethylvinylketone can be ob-

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tained at low rates with $\text{Pd}(\text{OAc})_2/\text{PPh}_3$ /phenylphosphonic acid as a catalyst [11].

Recently, the copolymerization of olefins and CO, yielding alternating polyketones, has attracted much industrial [7] and academic [12] interest. Very active cationic palladium catalysts with chelating P,P- or N,N-ligands have been developed, and mechanistic considerations have contributed to the understanding of factors controlling chain growth and termination steps in this type of multiple carbonylation reactions.

For many years, we have been interested in transition metal catalysts with anionic chelating ligands. Exceptional results are obtained with bidentate P,O-ligands, which combine a hard and a soft donor atom. Such ligands are also applied commercially for the nickel catalyzed oligomerization of ethylene in the Shell higher olefin process [13]. Presently, we are also investigating nickel and palladium catalysts with comparable neutral ligands for C–C linkage reactions of olefins [14,15]. Well characterized cationic palladium allyl complexes with bidentate P,O- and P,S-ligands are used as catalyst precursors. These complexes are also well suited for mechanistic studies, especially with view of applying hemilabile bidentate functionalized phosphine ligands in homogeneous catalysis. In this paper, we wish to report the cooligomerization of ethylene and CO, yielding unsaturated low-molecular-weight alternating oligo-ketones. To the best of our knowledge, selective formation of these compounds from ethylene and CO has not been reported before. The preparation and stoichiometric reactions of the cationic complexes applied [16, 17] will be subject of a separate publication.

Results and Discussion

In homogeneous catalysis by transition metal complexes, two approaches exist: the use of isolated, well characterized complexes as single-component catalyst precursors, and the use of *in situ* catalysts. In this study, both methods were employed.

Cationic palladium allyl complexes with P,O- or P,S-ligands as catalyst precursors

Under identical pressures of ethylene and carbon monoxide and in methylene chloride as a sol-

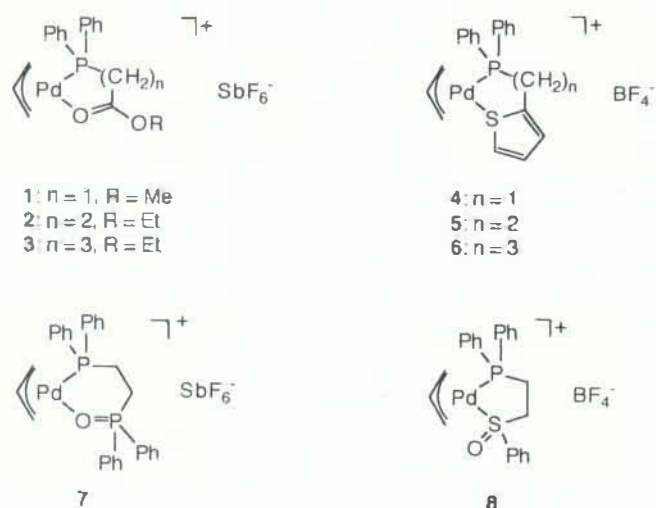


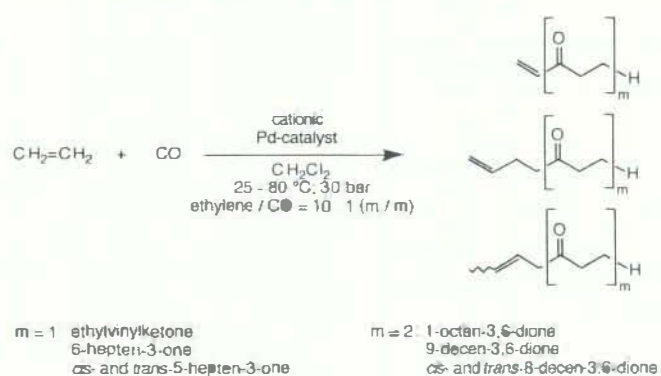
Fig. 1. Cationic palladium allyl complexes used as catalyst precursors.

vent, the complexes shown in Fig. 1 catalyze the copolymerization of ethylene and CO to alternating polyketone. Molecular weights of the products are approximately $\bar{M}_n = 2000\text{--}4000$ g/mol. Compared to cationic palladium catalysts with bidentate P,P-ligands in aprotic [18] or protic solvents [7,18], activities are moderate.

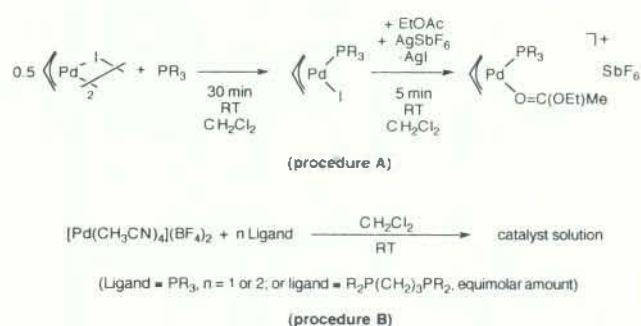
However, at high ethylene/CO ratios, oligomeric products with the structure shown in Scheme 1 are obtained*. Compounds with $m = 1, 2$ and 3 were separated and characterized by NMR, IR and mass spectroscopy. This data corresponds to literature-known spectroscopic data [19]. Products with $m > 3$ were not separated, but NMR-spectroscopy shows, that these higher oligomers and polymers also have the general structure shown in Scheme 1.

These products can be interesting intermediates for preparative organic chemistry, for which so far no simple high-yield syntheses are known. For ethylvinylketone even large-scale applications can be envisaged, e.g. for copolymers. 1,4-Diketones can be used for the synthesis of substituted cyclopentenones, which are a structural element of natural fragrances of the jasmin-type [20].

* In experiments carried out at high reaction temperatures ($\geq 110^\circ\text{C}$), in addition to the products shown in Scheme 1, a further isomer of the butenylketones was observed. For $m = 1$ and 2, this was identified as *trans*-4-hepten-3-one and *trans*-7-decen-3,6-dione, respectively.



Scheme 1. Cooligomerization of ethylene and CO.

Scheme 2. Preparation of *in situ* catalysts.

In standard work-up of the reaction mixtures obtained from catalysis, the products with $m \geq 3$ were divided into the fraction dissolved in the given amount of solvent (20 ml methylene chloride) and into the undissolved fraction, consisting of polyketones. Comparison of the amounts of

these two fractions can serve as a qualitative measure of the molecular weight of the products with $m \geq 3$.

Using complexes 1–6 (Table I) mainly low-molecular-weight products ($m = 1, 2$ and soluble oligoketones with $m \geq 3$) are obtained, whereas with 7 and 8 mainly insoluble polymers are obtained even at high ethylene/CO ratios.

The dependence on the temperature applied, shown for complex 3 in Table II, is typical for complexes 1–6. At temperatures of 50–65 °C, the optimum of activity and catalyst stability is observed, at higher temperatures rapid catalyst decomposition occurs. Complexes 7 and 8 require higher temperatures, 80 °C being the optimum. With all complexes, higher reaction temperatures favor the formation of low-molecular-weight products. As can be expected, chain-termination prevails over propagation (*cf.* Scheme 3).

Lowering the ethylene/CO ratio from 10:1 to 2:1 has the opposite effect (Table II): at low CO-concentrations, chain termination from an alkyl-species can compete with CO insertion, *i.e.* propagation, whereas at high CO partial pressures propagation prevails.

Figure 2 shows the course of reaction with complex 3. Because of the difficulty to draw a representative sample of the heterogeneous reaction mixture from an autoclave under the reaction conditions, data points for each reaction time were determined by a separate experiment. Deviations are inevitable, and this is considered the reason for a slight lowering of the TON for $m = 1$ and 2 after 14 h reaction time compared to 7 h.

Table I. Cooligomerization of ethylene and CO employing complexes 1–8 as catalyst precursors.

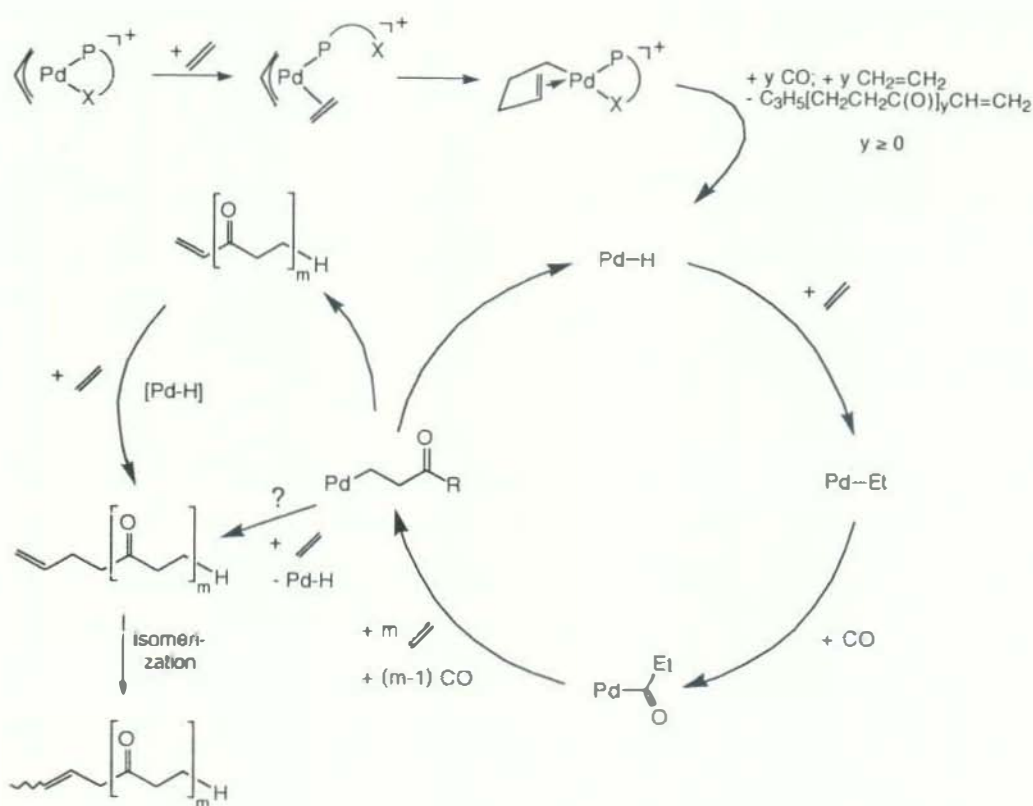
Catalyst Cat.	n [mmol]	Reaction conditions				Results					
		Temp. [°C]	Time [h]	Mass [g] C_2H_4	CO	Conv. of CO	TON/mol(substrate)/mol(Pd)		Sel. EVK[a]		
						insol.	sol.	total			
1	0.100	50	7	5.36	0.49	89%	44	140	235	419	3%
2	0.100	50	15	5.06	0.52	95%	159	120	134	413	2%
3	0.100	50	14	5.50	0.52	96%	66	171	207	444	10%
4	0.096	50	15	4.97	0.54	80%	67	167	154	388	5%
5	0.100	50	15	4.02	0.50	97%	164	110	134	408	3%
6	0.095	50	15	4.45	0.60	88%	135	224	55	414	2%
7	0.100	80	20	5.51	0.53	98%	299	60	22	381	0%
8	0.100	80	15	4.58	0.43	87%	172	84	16	272	0%

Solvent: 20 ml CH_2Cl_2 ; initial $p(\text{ethylene}) = 25$ bar; initial $p(\text{CO}) = 5$ bar. a) selectivity for ethylvinylketone, based on the CO converted.

Table II. Cooligomerization of ethylene and CO: influence of reaction conditions.

Catalyst Cat.	<i>n</i> [mmol]	Reaction conditions				Ratio C ₂ H ₄ / CO	Results Conv. of CO	TON/mol(substrate)/mol(Pd)			Sel. EVK[a]
		Temp. [°C]	Mass [g] C ₂ H ₄	CO	insol.			sol. <i>m</i> ≥ 3	<i>m</i> = 1,2	total	
3	0.102	r.t.	6.3	0.5	12	60%	86	84	68	238	5%
3	0.100	50	5.50	0.52	10	96%	66	171	207	444	10%
3	0.091	65	4.7	0.5	9	99%	36	203	259	498	8%
3	0.099	95	4.5	0.5	9	61%	3	106	191	300	13%
3	0.103	140	5.2	0.5	10	35%	2	54	115	171	18%
2	0.100	50	5.06	0.52	10	95%	159	120	134	413	2%
2	0.100	50	5.19	1.04	5	71%	491	33	3	527	0%
2	0.101	50	6.0	3.0	2	13%	256	12	0	268	0%

Solvent: 20 ml CH₂Cl₂; initial p(ethylene) = 25 bar; initial p(CO) = 5–30 bar; reaction time 15 h. a) selectivity for ethylvinylketone, based on the CO converted.



Scheme 3. Proposed mechanism for the cooligomerization of ethylene with CO, employing allyl complexes with hemilabile functionalized phosphine ligands as catalyst precursors.

The highest average reaction rate, TOF = 226 mol/mol·h, is observed in the one hour experiment. The decrease in rate with time is probably due to partial catalyst decomposition. Nevertheless, complete conversion of CO can be achieved after 14 h reaction time.

Due to the fact that the experiments shown in Fig. 2 were run in batchmode, the ethylene/CO ratio rises during the experiment because of the consumption of CO (simultaneous consumption of ethylene does not result in a significant change of the amount of ethylene, as it is present in a large

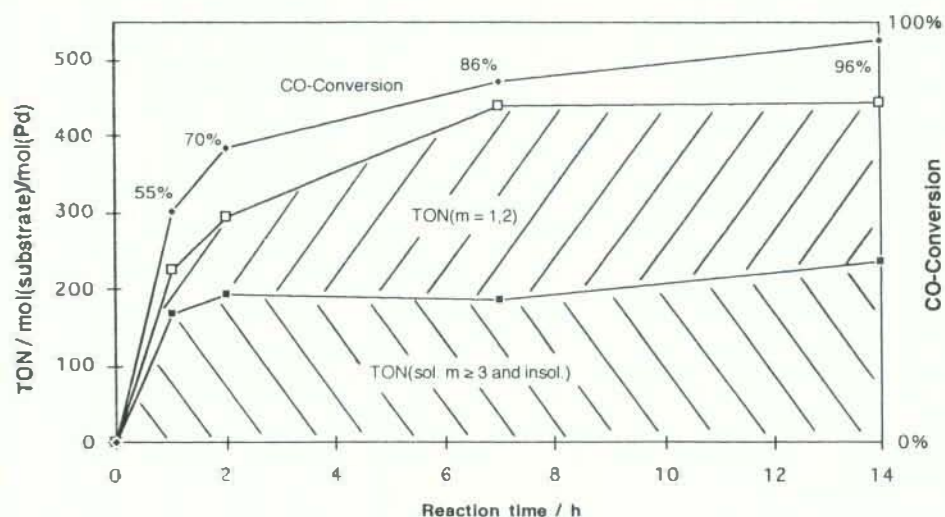


Fig. 2. Selectivity and conversion vs. reaction time (0.1 mmol complex **3** in 20 ml CH_2Cl_2 ; initial $p(\text{ethylene}) = 25$ bar and initial $p(\text{CO}) = 5$ bar; 50°C).

excess). As low CO concentrations favor the formation of low-molecular-weight products, only products with $m = 1$ or 2 are formed after half of the CO has been consumed. Also, within this product fraction products with $m = 1$ are then formed preferentially: after one hour the ratio ethylvinylketone/5- and 6-hepten-3-ones/1-octen-3,6-dione/8- and 9-decen-3,6-diones is 80:100:78:41, after complete conversion a ratio of 42:100:11:9 was obtained.

Considering the cooligomers with butenyl end-groups, depending on the reaction conditions and the catalyst precursor employed, either the terminal (*i.e.* 6-hepten-3-one for $m = 1$) or the internal (*i.e.* *trans*- and *cis*-5-hepten-3-one for $m = 1$) isomers can predominate. Generally, under conditions which favor formation of low-molecular-weight products, the internal isomers are obtained preferentially.

Using complex **7** (at 80°C), activities are slightly lower than those observed for **3** (29% CO conversion after 2 h; 46% after 4 h; complete conversion after 20 h), but insoluble polymeric material is obtained almost exclusively.

Allyl complexes with phosphino-thioether ligands $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{SR}$ ($n = 2$, $\text{R} \equiv \text{Me}$, Ph ; $n = 3$, $\text{R} \equiv \text{Ph}$) and *o*- $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{SR}$ ($\text{R} \equiv \text{Me}$, Pr , Ph) exhibit only low activities in the reaction of ethylene and CO. Activation of these complexes is slow. *E.g.*, in an experiment with $[(\text{C}_3\text{H}_5)\text{Pd}(\text{o-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{SPh})\text{-P,S}]\text{BF}_4$, stopped after 14 hours, 60% of the precursor complex were recovered unchanged.

Considering the coordination behaviour of the functionalized phosphine ligands applied during catalysis, it is conspicuous, that comparable results are obtained with the phosphino-ester complexes **1–3** as well as with the phosphino-thiophene complexes **4–6**. Neither the chain length n of the ligand backbone, nor the nature of the donor atom (O vs. S) have a strong impact on activity and selectivity. Also, with comparable *in situ* catalysts with unfunctionalized monodentate phosphines similar results are obtained (*vide infra*). This leads to the conclusion, that the P,O- and P,S-ligands in **1–6** behave like monodentate phosphines under catalytic conditions. These ligands are hemilabile in the sense, that the weaker donor atom (O,S) stabilizes the precursor complex and creates a free coordination site during the catalytic reaction. The markedly different selectivity with **7** and **8** can be attributed to bidentate coordination of the phosphino-phosphin oxide and the phosphino-sulfoxide ligand during catalysis. This interpretation is in accordance with stoichiometric experiments, using the catalyst precursors as model compounds [16,17]: the O-donor in **1–3** and the S-donor in **4–6** is quantitatively substituted by ethylene or CO upon bubbling the gas through a solution of the complex at room temperature and normal pressure. By contrast, with **7** and **8** the unchanged complexes prevail.

The allyl complexes **1**, **2**, **3** and **7** were also used as catalyst precursors in the absence of carbon monoxide. At 50°C under a constant pressure of

30 bar, ethylene is rapidly oligomerized with rates of up to 2000 mol/mol·h. With 1–3 butenes are obtained with >95% selectivity. By contrast, complex **7** yields significant amounts of hexenes (sel. 13%, 60% linear) and octenes (sel. 1%).

Cationic palladium catalysts modified by mono- or bidentate phosphines are known to catalyze selective dimerization of ethylene [11,21,22], whereas with bidentate N,N-ligands hexenes and higher oligomers were also obtained [11,22].

Addition of ethylvinylketone or 1-octen-3,6-dione to an ethylene oligomerization reaction, catalyzed by complex **2**, resulted in formation of 5- and 6-hepten-3-ones and 8- and 9-decen-3,6-diones, respectively, *i.e.* codimers of vinylketones and ethylene. The rate of homodimerization of ethylene, present in a large excess, was not significantly influenced. This observation suggests, that the butenylketones formed in cooligomerization of ethylene and CO are formed by codimerization of primarily formed vinylketones with ethylene, and not necessarily by subsequent insertion of two molecules of ethylene into a palladium-acyl bond.

Experiments with *in situ* catalysts

For rapid screening of ligands with different substituents attached to the P-donor and for comparison with complexes **1–8**, *in situ* catalysts with unfunctionalized phosphine ligands were used. Catalysts were prepared by the two routes shown in Scheme 2. Table III shows the results obtained with both catalyst systems, employing different ligands.

With allyl complexes prepared by route A, employing PPh₂Et as a ligand, results comparable to those using the isolated complex **3** were obtained. Stopping the experiment after 2 hours and 6 hours, respectively, activities and selectivities very similar to those observed for **3** (Fig. 2) were found. With P^{*n*}Bu₃ as a ligand, a slightly lower activity is observed in comparison to catalysts with aryl-substituted ligands. Remarkably, the share of oligo-ketones with *m* = 1 and 2 is relatively high, and contains predominantly vinylketones. A selectivity for the desired ethylvinylketone of about 40% based on the CO converted was obtained. Catalysts with the bulky secondary alkyl phosphine PCy₃ were almost inactive.

The use of catalysts prepared by route B for reacting ethylene and CO under identical pressures of both gases has already been described by Sen and others [6,18,21]. In aprotic solvents, high-molecular-weight alternating polyketones were obtained. β -Hydrogen abstraction, resulting in formation of vinyl end-groups, has been proposed as a termination step [18].

Employing catalysts prepared by route B at high ethylene/CO ratios (Table III), cooligomers can be obtained. These products are the same as those obtained with allyl complexes as catalyst precursors, *i.e.* unsaturated ketones of the general structure shown in Scheme 1 are formed exclusively.

With P^{*n*}Bu₃ as a ligand, again selectivities for ethylvinylketone of up to 40% are obtained. It was anticipated, that addition of more than one equivalent of phosphine ligand would stabilize the catalyst and also favor chain-termination by temporary blocking of coordination sites for propagation. Indeed, catalyst stability is improved, but selectivity is changed in favor of higher-molecular-weight products. With catalyst system B with one equivalent of P^{*n*}Bu₃, increasing the reaction temperature from 50 °C to 80 °C resulted in an increase of the selectivity for ethylvinylketone. With all other catalysts with monodentate ligands given in Table III, increasing the reaction temperature did not result in a significant improvement.

As expected, applying the bidentate P,P-ligand 1,3-bis(diphenylphosphino)propane (dppp), copolymer is formed exclusively even at high ethylene/CO ratios. With the alkyl-substituted diphosphine 1,3-bis(di-*iso*-propylphosphino)propane (dipp) cooligomers can be obtained, but rates and selectivities are only moderate.

Generalizing, results obtained with *in situ* catalysts prepared by route B and with allyl complexes, prepared *in situ* by route A or used as isolated complexes, are comparable. One is tempted to speculate that similar catalytically active species are formed during catalysis.

Mechanistic considerations

For the transition-metal catalyzed alternating cooligomerization and copolymerization of ethylene and CO in aprotic solvents, a hydride mechanism has been proposed by various authors [7b,11,12]. The initial palladium-hydride is

Table III. Cooligomerization of ethylene and CO by *in situ* catalysts.

Catalyst [a]		<i>n</i> [mmol]	Reaction conditions			Results					Sel. EVK[b]
Type	Ligand		Temp. °C	Mass [g] C ₂ H ₄	CO	Conv. of CO	TON/mol(substrate)/mol(Pd)		total		
						insol.	sol.	<i>m</i> ≥ 3	<i>m</i> = 1,2		
A	PPh ₂ Et	0.089	50	5.26	0.56	91%	39	242	198	479	9%
A	P ^{<i>n</i>} Bu ₃	0.114	50	5.1	0.5	74%	11	78	207	296	43%
A	PCy ₃	0.095	50	4.4	0.5	15%	23	32	1	56	0%
B	PPh ₂ Et 1 eq	0.108	50	4.4	0.5	87%	221	65	4	290	0%
B	PPh ₃ 1 eq	0.096	50	5.25	0.58	83%	183	48	238	469	6%
B	P(OPh) ₃ 1 eq	0.090	50	5.2	0.5	4%	17	0	0	17	0%
B	P ^{<i>n</i>} Bu ₃ 1 eq	0.080	50	4.5	0.5	22%	1	62	54	117	26%
B	P ^{<i>n</i>} Bu ₃ 1 eq	0.092	80	4.5	0.6	20%	1	34	88	123	41%
B	P ^{<i>n</i>} Bu ₃ 2 eq	0.112	50	5.35	0.55	69%	0	161	114	275	15%
B	P ^{<i>n</i>} Pr ₃ 2 eq	0.114	50	4.26	0.39	14%	0	26	17	43	9%
B	PCy ₃ 2 eq	0.104	50	4.95	0.53	13%	0	42	13	55	6%
[c]	dppp 1 eq	0.130	70	4.4	0.2	94%	103	0	0	103	0%
B	dipp 1 eq	0.100	50	4.89	0.58	18%	0	62	24	86	8%
B	dipp 1 eq	0.100	75	4.54	0.70	23%	0	82	55	137	8%

Solvent: 20 ml CH₂Cl₂; reaction time 15 h; initial p(ethylene) = 25 bar; initial p(CO) = 5 bar (experiment with dppp: p(ethylene) = 40 bar, p(CO) = 2 bar). a) A: metal component [(C₃H₅)PdI]₂, B: [Pd(CH₃CN)₄](BF₄)₂ + ligand (cf. Scheme 2). b) selectivity for ethylvinylketone, based on the CO converted. c) catalyst solution prepared by reacting [Pd(dppp)Cl₂] (suspension of 0.130 mmol in 20 ml CH₂Cl₂) with AgBF₄ (solution of 0.260 mmol in 0.5 ml CH₃CN) and subsequent filtration.

thought to be formed *via* the water-gas shift reaction from CO and trace impurities of water [11,12].

The structure of the oligomeric products obtained in this study is also consistent with a hydride mechanism. Stoichiometric reactions of the catalyst precursors with ethylene and CO [16] support the mode of activation depicted in the self-explanatory Scheme 3.

Conclusion

When working in methylene chloride as a solvent, the palladium catalyzed copolymerization of ethylene and CO can be directed towards formation of low-molecular-weight cooligomers by applying high ethylene/CO ratios. Unsaturated ketones of the general structure R[C(O)CH₂CH₂]_{*m*}H (R ≡ CH₂=CH-, CH₂=CHCH₂CH₂- and CH₃CH=CHCH₂-) are obtained (*i.e.* *m* = 1: ethylvinylketone, 5- and 6-hepten-3-ones; *m* = 2: 1-octen-3,6-dione, 8- and 9-decen-3,6-diones). Selectivities for ethylvinylketone of up to 43%, based on the CO converted, were observed using P^{*n*}Bu₃ as a ligand.

Cationic palladium allyl complexes with hemilabile bidentate ligands can be applied as single-component catalyst precursors. It is assumed that phosphino-ester and phosphino-thiophene ligands

behave like monodentate phosphines under catalytic conditions.

Experimental

All operations involving organometallic compounds and phosphine ligands were carried out under a dry argon atmosphere by standard Schlenk techniques. Methylene chloride was distilled from CaH₂ under argon. [Pd(CH₃CN)₄](BF₄)₂ was prepared according to [6]; [(C₃H₅)PdI]₂ was obtained from [(C₃H₅)PdCl]₂ [23] by halide exchange with NaI [24]. Phosphine ligands were obtained commercially or prepared by standard procedures. Cationic palladium complexes with bidentate P,O- or P,S-ligands were prepared according to [16] and [17], respectively. Ethylene (purity >99.5%) and carbon monoxide (purity >99.99%) were used as received. 1-Octen-3,6-dione was prepared by the procedure described in [25].

Gas chromatographic analyses were performed on a Siemens Sichromat with a 50 m Pona HP column. For GC-MS analyses a Varian 3700 gas chromatograph combined with a Varian MAT 112S mass spectrometer was used. GC-IR were performed on a Hewlett-Packard 5890 II gas chromatograph equipped with a HP 5965 A IR-detector. NMR spectra were obtained on Varian VXR 300 and Unity 500 spectrometers. IR-spectra were recorded on a Nicolet 510 P FT-spectrometer.

Preparation of *in situ* catalysts

Procedure A: To a solution of 0.05 mmol $[(C_3H_5)_2Pd]_2$ in 10 ml methylene chloride a solution of one equivalent of monodentate phosphine ligand in 10 ml methylene chloride was added. After stirring for 30 min, one equivalent of ethylacetate was added, and the yellow solution was transferred to a 50 ml round-bottom flask containing 1.01 equivalent of $AgSbF_6$. AgI precipitated immediately. After stirring for 5 min, the mixture was filtered over celite. A clear yellow filtrate was obtained.

Procedure B: To a suspension of 0.1 mmol $[Pd(CH_3CN)_4](BF_4)_2$ in 10 ml methylene chloride a solution of the appropriate amount of ligand in 10 ml methylene chloride was added. After stirring for a few minutes, a clear yellow to orange solution was obtained.

Cooligomerization and copolymerization of ethylene and carbon monoxide

Catalytic experiments were carried out in 75 ml V4A-steel autoclaves equipped with a magnetic stirrer bar. The catalyst solution was transferred to the autoclave under protective gas atmosphere *via* a syringe. Subsequently, the autoclave was purged and pressurized with ethylene, then CO was introduced and the autoclave was heated in an oil bath for the given reaction time. By weighing the autoclave, the amount of ethylene and CO was determined. After rapidly cooling to room temperature, unreacted gases were vented. CAUTION: vinylketones are highly toxic! The reaction mixture was filtered on a frit, the solid residue was dried in a stream of argon and weighed. The filtrate was distilled at 75 °C and 0.1 mbar. The distillate, which contains the oligoketones with $m = 1$ and 2, was analyzed by GC with *n*-heptane and *n*-dodecane as internal standards. The distillation residue was weighed, thus the amount of soluble cooligomers with $m \geq 3$ was determined.

Identification of ethylene-CO cooligomers and copolymers

For identification of the oligomeric products with $m = 1, 2$ and 3 a reaction mixture was analyzed by GC-MS and GC-IR. Also ethylvinylketone, a mixture of the isomeric 5- and 6-hepten-3-ones, 1-octen-3,6-dione and a mixture of 8- and 9-decen-3,6-diones were separated by vacuum dis-

tillation and identified by 1H and ^{13}C NMR. Ethylvinylketone and 1-octen-3,6-dione were also identified by GC analysis of a reaction mixture, to which a genuine sample of the compound had been added. The soluble product fraction with $m \geq 3$ was characterized by 1H and ^{13}C NMR in $CDCl_3$; the average chain length is $m = 4$ to 7. Spectroscopic data of the above compounds has been described in literature [19]. The complete data mentioned in this paragraph is given in [16].

The insoluble product fraction was analyzed by IR (KBr) and by 1H and $^{13}C\{^1H\}$ NMR in 1,1,1,3,3,3-hexafluoropropan-2-ol containing 10 vol.-% of C_6D_6 . Except for the signal of the polymer backbone (s with $\delta = 2.8$), 1H NMR spectra show ethyl end-groups (q with $\delta = 2.5$ and t with $\delta = 1.1$) and unresolved multiplets with $\delta = 6.3$ and 6.0, assigned to vinyl end groups. In the ^{13}C NMR spectra, except for the polymer backbone ($\delta = 215.1$ and 37.6), small signals with $\delta = 219.4, 206.7, 137.1, 133.5, 34.3$ and 8.4 are observed, which are also consistent with ethyl and vinyl end groups.

Oligomerization of ethylene

A solution of 0.05 mmol complex in 20 ml methylene chloride *supra* was introduced into a steel autoclave (*vide supra*). The autoclave was purged with ethylene, pressurized to 30 bar, and was then heated in an oil bath for 4 hours. During the reaction the pressure was kept constant by continuously feeding ethylene. After rapidly cooling the autoclave to room temperature, the gas phase was vented *via* a cold trap (-78 °C). By weighing the autoclave before pressurizing and after venting and by weighing the cold trap, the amount of ethylene converted was calculated. The reaction mixture was flash-distilled (200 °C; 0.1 mbar) from the catalyst. Selectivities for hexenes and higher oligomers were determined by GC with *n*-heptane as an internal standard.

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