Copolymerization of Ethene and Carbon Monoxide with (Diphosphine)nickel Catalysts

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This work presents the results of the ethene–CO copolymerization with *in situ* generated catalysts based on atropisomeric 1,4-diphosphines and nickel(II). The influence of the reaction conditions and the NMR characterization of the copolymers are described.

Introduction. – Cationic palladium(II) complexes modified with bidentate ligands have been extensively applied in the alternating copolymerization of olefins and carbon monoxide for two decades [1]. Due to the high cost of the catalyst precursor, attempts have been made to employ the less expensive nickel as the catalyst metal. Nickel(II) complexes for the copolymerization found little success, even though lower insertion barriers for both CO and olefins were predicted [2][3]. So far, only a few nickel(II) complexes are known to catalyze the formation of polyketones from CO and ethene. Copolymerization of carbon monoxide and ethene on tetracyanonickelate(II) was already described by *Reppe* and *Magin* [4] in 1951 and by *Shryne* and *Holler* [5] in 1976, but the resulting polymers were never prepared on an industrial scale. In the mid 80s, the breakthrough in the polyketones catalytic process was achieved with a (diphosphine)palladium complex, which catalyzed the formation of a perfectly alternating 1:1 copolymer from ethene or propene and carbon monoxide under mild reaction conditions [1][6][7]. However, the interest in replacing palladium with the cheaper nickel remained.

Polyketone formation is catalyzed by arylnickel(II) compounds with P,O chelate ligands of the same type as those employed in the SHOP process (SHOP = *Shell* high olefin process) [8][9], in which ethene is oligomerized to higher olefins (*Fig. 1*).

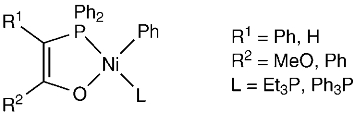
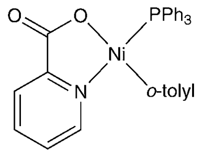


Fig. 1. *SHOP-Type catalysts for the copolymerization of ethene and carbon monoxide*

Arylnickel(II) compounds with N,O chelate ligands based on 4-substituted pyridine-2-carboxylate (pyca; *Fig. 2*) were reported to copolymerize carbon monoxide and ethene under mild conditions [10].



[Ni(o-tolyl)(pyca)PPh$_3$]

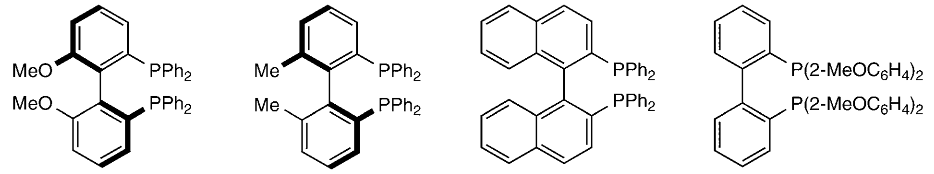
Fig. 2. *Example of an aryl(phosphine) nickel(II) complex containing a substituted N,O bidentate ligand*

An arylnickel(II) complex modified with the tripodal ligand hydrotris(3-phenyl-1*H*-pyrazol-1-yl)borate (Tp^{Ph}), [Ni(PPh$_3$)(o-tolyl)(Tp^{Ph})], catalyzed the copolymerization of ethene and carbon monoxide under mild conditions (60° and below 50 bar total pressure) [11]. Tp^{Ph} coordinates as a bidentate N,N-chelating ligand to the Ni-atom. In a following paper, the same group [12] proposed another N,N-chelating ligand of the semicorrine type as an alternative to the tripodal ligand Tp^{Ph}. The arylnickel(II) complex modified with this kind of ligand was almost twice as productive as [Ni(PPh$_3$)(o-tolyl)(Tp^{Ph})] in the copolymerization of carbon monoxide and ethene. A structurally similar class of N,O-chelating ligands, forming air-stable arylnickel(II) complexes, catalyzed the copolymerization of carbon monoxide and ethene with the highest efficiency reported for this kind of systems [12].

(Diphosphine)nickel(II) catalysts for the copolymerization of ethene and carbon monoxide are scarcely reported in the literature. Attempts to use aryl-substituted bidentate phosphines for the copolymerization of ethene and carbon monoxide resulted in low efficiency [13][14]. The use of the modified ligand o-MeO-dppe (= ethane-1,2-diylbis[bis(2-methoxyphenyl)phosphine]) afforded a 10-times increase in the catalyst productivity [14].

Results and Discussion. – *Atropisomeric Ligands in the Ni-Catalyzed Copolymerization of Carbon Monoxide and Ethene.* Atropisomeric chiral diphosphine ligands **1**–**4** (*Fig. 3*) based on the 1,1′-biphenyl or 1,1′-binaphthalene moieties were tested in the Ni-catalyzed copolymerization of ethene with carbon monoxide. All the ligands considered present similar structural features. The phosphine moieties of the ligands **1**–**3** are substituted with Ph groups, while ligand **4** ([1,1′-biphenyl]-2,2′-diylbis[bis(2-methoxyphenyl)phosphine]; bphmop) is substituted with 2-methoxyphenyl groups (o-MeOC$_6$H$_4$).

The steric hindrance displayed in the coordination sphere of the metal is comparable for the systems **1**–**4**. When electronic properties are considered, it is possible to



1 (S)-(MeO)$_2$bphp **2** (S)-Me$_2$bphp **3** (±)-binap **4** bphmop

Fig. 3. *Atropisomeric diphosphine ligands tested in this work*

arrange them according to their increase in basicity. (±)-Binap (**3**), based on the 1,1′-binaphthalene C-backbone, is the least basic ligand of the series. Among the biphenyl-based ligands, (*S*)-Me_2bphp (**2**) with two Me groups in positions 6 and 6′ of the aromatic C-backbone has a basicity comparable to that of (±)-binap (**3**) and is less basic than (*S*)-$(MeO)_2$bphp (**1**), substituted at the same position with MeO groups. While for the ligands **1**–**3** the differences in basicity concern the nature of the C-backbone, ligand **4** can profit from basic *o*-$MeOC_6H_4$ groups directly introduced at the phosphine moieties. Their influence in the catalytic activity will be discussed.

The catalyst for the copolymerization of ethene with carbon monoxide was generated *in situ* from $Ni(OAc)_2 \cdot 4\,H_2O$ and an excess of the P^P ligand in dry MeOH. After stirring the solution for *ca.* 30 min, an excess of HBF_4 was added. The solution of the catalyst was charged in the autoclave, which was pressurized first with ethene and then with carbon monoxide. As it was already reported, a deactivation of the catalyst occurs with exposure to an atmosphere of carbon monoxide by the formation of zerovalent (carbonyl)(phosphine)nickel complexes as well as reductive elimination products [11]. The reaction was carried out for 4 h at 80°.

Productivity. The atropisomeric ligands **1**–**4** displayed different activities in the copolymerization process (*Table 1*).

Table 1. *Productivity in the Copolymerization of Ethene with CO*[a])

Ligand		Productivity [g copolymer/($g_{Ni} \cdot h$)]
1	(*S*)-$(MeO)_2$bphp	6.3
2	(*S*)-Me_2bphp	1.5
3	(±)-binap	2.7
4	bphmop	15.3

[a]) Reaction conditions: ($Ni(OAc)_2 \cdot 4\,H_2O$ (0.1 mmol), P^P (0.12 mmol), 54% HBF_4 in Et_2O (3 ml), MeOH (50 ml); ethene pressure 40 bar, CO pressure 20 bar.

With the exception of **4**, the steric features in the coordination sphere are comparable for the ligands **1**–**3**. Therefore, the differences observed in the productivity should be explained considering the electronic properties of the ligands, which are tuned by a modification at the C-backbone. (±)-Binap (**3**) displayed an almost double catalytic activity with respect to (*S*)-bphp. The 1,1′-binaphthalene and the 6,6′-dimethyl-1,1′-biphenyl units of **2** and **3**, respectively, are electronically similar. The *o*-MeO groups in 6,6′-position of **1** increase the overall basicity of the ligand, which seems to bring about an improvement in the productivity. With the ligand **4**, a consistent improvement in the productivity of the copolymerization is observed. Introduction of *o*-$MeOC_6H_4$ groups at the P-atoms was already described in the patent literature [14] to improve the catalytic activity of nickel(II)-catalyzed copolymerization of ethene with carbon monoxide. The performance *o*-MeO-dppp (=propane-1,3-diylbis[bis(2-methoxyphenyl)phosphine]) and that of dppp (=propane-1,3-diylbis[diphenylphosphine]) were compared, and the presence of the *o*-MeO groups was crucial for the increase of the activity [14].

Influence of the Reaction Conditions. The dependence of the catalytic activity on the temperature was tested only with the ligand (*S*)-$(MeO)_2$bphp (**1**). No catalytic activity was observed for (*S*)-$(MeO)_2$bphp (**1**) at 20 and 40°, while only traces of polymer were formed at 60°. Temperature control is very important to assure the development of the catalytic process. Other active catalysts for the copolymerization of ethene with carbon monoxide were tested at 60° [10–12].

The influence of the pressure of carbon monoxide was studied carrying out different tests for (*S*)-$(MeO)_2$bphp (**1**). The catalysts were generated according to the method described in the *Exper. Part*. The ethene pressure was kept constant at 40 bar, while the CO pressure was systematically varied in the range 5–50 bar. The trend of the productivity in dependence on the CO pressure is displayed in *Fig. 4*.

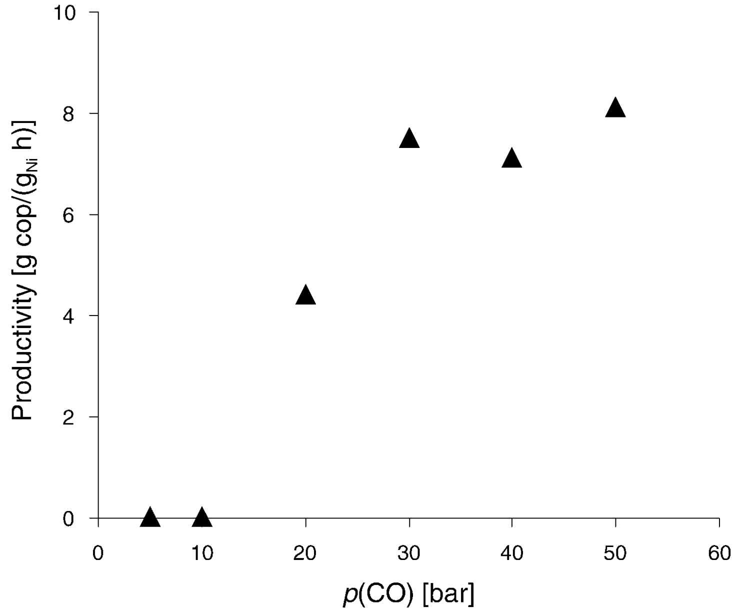


Fig. 4. *Productivity* [g copolymer/(g_{Ni}·h)] vs. *CO pressure* [bar]

The catalyst displayed no activity with CO pressure up to 10 bar (only traces of polymer were formed). Only when the ratio ethene/CO was 2 : 1 the catalyst achieved a remarkable activity. The highest productivity was reached with a CO pressure of 30 bar. A comparable activity within the experimental error was observed with the same pressure of ethene and CO over 40 bar. This result is consistent with what is reported in the patent literature, where similar pressures of ethene and CO pressure were employed [14].

The influence of the ethene pressure was investigated in a series of experiments were the CO pressure was kept constant at 20 bar and the ethene pressure varied in a range of 35 bar (from 5 to 40 bar). The catalyst was generated *in situ* from (*S*)-$(MeO)_2$-bphp (**1**), according to the usual procedure. When ethene pressure was low or it was equal to the pressure of CO, only traces of polymer were formed. Keeping the ethene pressure equal to 30 bar did not result in an appreciable activity. The influence of ethene pressure on the catalytic activity for this kind of systems is summarized in *Table 2*.

Table 2. *Influence of Ethene Pressure on Productivity.* The CO pressure was kept constant at 20 bar.

Ligand	Ethene pressure [bar]	CO pressure [bar]	Productivity [g copolymer/(g_{Ni} · h)]
1 (*S*)-$(MeO)_2$bphp	5	20	no activity
	10	20	no activity
	20	20	no activity
	30	20	no activity
	40	20	6.3

Apparently, the catalyst is active only when the pressure of ethene reaches a certain minimum. This is consistent with what is observed with the other recently published reports about Ni-catalysts for the ethene–CO copolymerization, where the ethene pressure employed was never below 40 bar [11] [12].

NMR Analysis of the Copolymers. In *Fig. 5*, a typical ^{1}H-NMR spectrum of a CO–ethene copolymer is reported. Beside the residual peaks of the solvent hexafluoro(D)-isopropyl (D)alcohol ($(CF_3)_2CDOD = (D_2)HFIP$), one can observe an *s* at δ 2.70, which results from the methylene groups of the polymer chain.

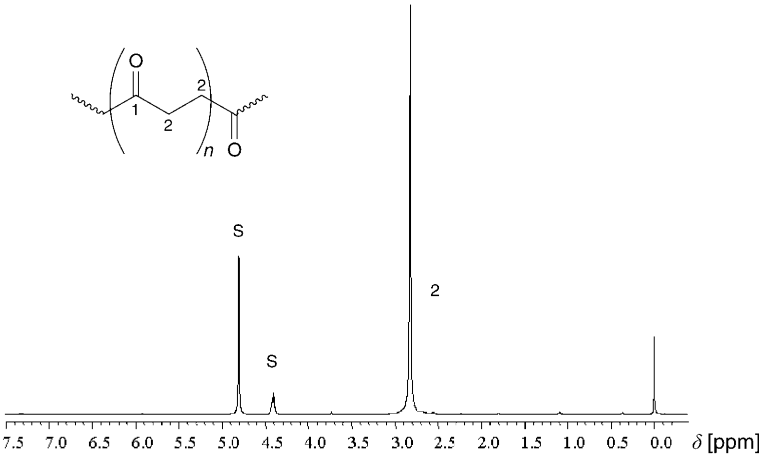


Fig. 5. *^{1}H-NMR Spectrum* ((D_2)HFIP, 500 MHz) *of a CO–ethene copolymer produced* via in situ *generation of the catalyst from the mixture of $Ni(OAc)_2 \cdot 4\, H_2O$, (*S*)-$(MeO)_2$bphp* (**1**) *and HBF_4 in MeOH.* S = residual peak of the deuterated solvent.

In *Fig. 6*, the ^{13}C-NMR carbonyl region of the ethene–CO copolymer obtained with (*S*)-$(MeO)_2$bphp (**1**) is reported.

A perfectly alternating structure resulted as established by the ^{13}C-NMR spectrum, *i.e.*, no double insertion of ethene is observed. The resonance at δ 37.8 is due to the backbone methylene C-atoms (2 in *Fig. 6*), while the carbonyl C-atom is found at δ 215.1 (1 in *Fig. 6*). The molecular masses M_n of the produced copolymers ranged between 10^4 and $1.5 \cdot 10^4$ g mol^{-1} (*Table 3*). The polymer chains were shorter than

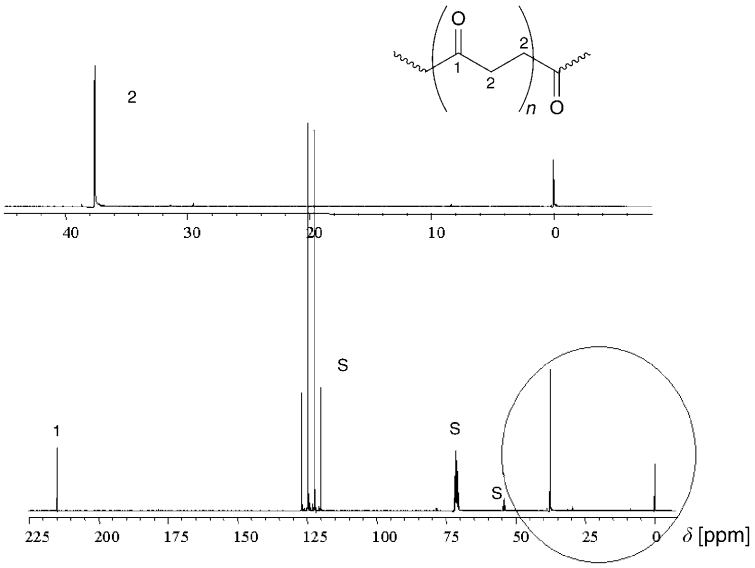


Fig. 6. *^{13}C-NMR Spectrum* ((D_2)HFIP/$CDCl_3$/CD_2Cl_2, 125 MHz) *of a CO–ethene copolymer produced* via in situ *generation of the catalyst from the mixture of* $Ni(OAc)_2 \cdot 4\,H_2O$, *(*S*)-*$(MeO)_2$*bphp (***1***) and* HBF_4 *in MeOH.* The detail of the alkyl region is displayed. S = residual peak of the deuterated solvent.

those found in ethene–CO copolymers obtained from Pd-catalyst, which are typically in the range $5.0 \cdot 10^4 - 10^5$ g mol^{-1}. This might be due to a shorter lifetime of the Ni-based catalysts, easily deactivated by reduction to Ni^0 species [11].

Table 3. M$_n$ *of the Ethene–CO Copolymers Produced with the Ligands* **1**–**4**[a])

Ligand	M_n [g mol^{-1}]
1 (*S*)-$(MeO)_2$bphp	12110
2 (*S*)-Me_2bphp	10650
3 (±)-binap	4030
4 bphmop	15530

[a]) Reaction conditions: $Ni(OAc)_2 \cdot H_2O$ (0.1 mmol), P^P (0.12 mmol), 54% HBF_4 in Et_2O (3 ml), MeOH (50 ml); ethene pressure 40 bar, CO pressure 20 bar.

The initiation step of the catalytic cycle occurs most probably *via* (methoxycarbonyl)nickel species. These species are formed through analogous pathways as those proposed [7] for palladium(II) catalysts, namely *via* either insertion of CO into a methoxynickel $[Ni(OMe)(P^\frown P)]^+$ or by direct attack of MeO on coordinated CO. The catalytic cycle will then proceed *via* insertion of the olefin into the Ni–COOMe bond. Evidence of this initiation pathway is the presence of ester end groups in the polymer chain [7][15].

In the ethene–CO copolymers, three types of end groups (alkyl, methoxycarbonyl, and ethenyl) can be observed, and their occurrence in the copolymers produced with each ligand can be determined from the analysis of the ^{1}H-NMR spectrum [16][17]. The alkyl end groups were identified with ^{1}H,^{1}H-COSY experiments. The Me group appeared as a *triplett* at δ 1.11 and gave a cross-peak with the CH_2 group (*q*) at δ 2.60. Methoxycarbonyl groups were identified at δ 3.70. No ethenyl end groups were observed. The distribution of the terminal groups in the copolymers obtained with the ligands **1**–**4** is reported in *Table 4*.

Table 4. *Relative Intensity*[a]) *of the End Groups in the Ethene–CO Copolymers Obtained with the Ligands* **1**–**4**

Ligand	Alkyl end groups	Methoxycarbonyl end groups
1 (*S*)-(MeO)$_2$bphp	0.89	1
2 (*S*)-Me$_2$bphp	1.17	0.83
3 (±)-binap	0.42	0.33
4 bphmop	0.67	0.47

[a]) Relative intensity of the integrals of the end groups in the ^{1}H-NMR ((D_2)HIFP) normalized to the total number of protons.

From the end-group distribution, the alkyl terminations are slightly prevailing in almost all the cases. They can arise either from an initiation (resulting from the ethene insertion into a $[Ni–H]^+$ initiator) or from a termination reaction (protonolysis). Methoxycarbonyl terminations are also present in comparable ratio, while no ethenyl end groups were observed. β-H Elimination is a negligible interruption pathway when ethene is copolymerized with CO.

Conclusions. – This work provides a contribution in the scarcely explored field of Ni-catalyzed copolymerization of ethene and carbon monoxide. The activity displayed by atropisomeric 1,4-diphosphines is only modest when compared to that of Ni-catalysts modified with N,N and N,O ligands. However, the results are interesting, when one considers the low affinity of the Ni-atom for phosphines and the large bite angles of the kind of ligands employed, *i.e.*, **1**–**4**. In particular, the influence of *o*-$MeOC_6H_4$ substituents at the phosphine moieties seems to be crucial to increase the activity of the catalysts. The *o*-MeO substituents offer the small Ni-center two further coordination sites.

Active (diphosphine)nickel(II) catalysts may be obtained from electron-donor diphosphine ligands substituted with *o*-$MeOC_6H_4$ substituents at the P-atoms. Moreover, the C-backbone should be suitably modified to favor the square-planar geometry of the complex, for instance by increasing the rigidity of the ligand.

Stabilization of the metal center and deactivation of the catalyst, resulting in low productivities, will have to be improved to develop efficient systems based on nickel(II) and diphosphine ligands for the copolymerization of ethene and carbon monoxide.

We thank *Hoffman-La Roche AG* for the generous supply of (*S*)-Me$_2$bphp and (*S*)-(MeO)$_2$bphp and the *Swiss National Science Foundation* for the financial support.

Experimental Part

General. (D$_2$)HFIP (=1,1,1,3,3,3-hexafluoro(2-D)propan-2-(D)-ol) was purchased from *Cambridge Isotope Laboratories*, Ni(OAc)$_2 \cdot 4$ H$_2$O from *Fluka*. 54% HBF$_4$ soln. in Et$_2$O from *Aldrich*, ethene (purity grade 3.5) from *Linde*, and carbon monoxide (purity grade 4.7) from *Pan Gas*. The ligands (*S*)-(6,6′-dimethoxy-[1,1′-biphenyl]-2,2′-diyl)bis[diphenylphosphine] ((*S*)-(MeO)$_2$bphp; **1**) and (*S*)-(6,6′-dimethyl-[1,1′-biphenyl]-2,2′-diyl)bis[diphenylphosphine] ((*S*)-Me$_2$bphp; **2**) were a gift of *Hoffmann-La Roche AG*.

Polymerization. Ni(OAc)$_2 \cdot 4$ H$_2$O (25 mg, 0.1 mmol) and the diphosphine ligand (0.12 mmol) were dissolved in dry MeOH (50 ml) and stirred for 0.5 h. The catalyst was generated *in situ* by adding 54% HBF$_4$ in Et$_2$O (0.3 ml; *ca.* 20 equiv.) to the mixture. The catalyst soln. was then transferred to a 300-ml stainless steel *Premex* autoclave. The soln. was pressurized with ethene (by means of a *Büchi* pressflow gas controller *200*) and carbon monoxide to the desired pressure, and then stirred mechanically for 4 h at 80°. At the end of the reaction, the autoclave was cooled to r.t., and the nonreacted gases were released. The polymer was filtered off, washed with MeOH and dried under high vacuum: 0.1–0.36 g. The copolymers were analyzed by means of NMR spectroscopy: *Figs. 5* and *6*.

Anal. calc. for (C$_3$H$_4$O)$_n$: C 64.27, H 7.19; found: C 64.42, H 7.18.

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