Novel C_s-Symmetric 1,4-Diphosphine Ligands in the Copolymerization of Propene and Carbon Monoxide: High Regio- and Stereocontrol in the Catalytic Performance

by **Antonella Leone** and **Giambattista Consiglio***

Eidgenössische Technische Hochschule, Departement Chemie und Angewandte Biowissenschaften, ETH Hönggerberg, CH-8093 Zurich
(e-mail: consiglio@chem.ethz.ch)

New C_s-symmetric aryl 1,4-diphosphine ligands were synthesized and tested in the copolymerization of carbon monoxide and propene. The electronic properties of the two different P-atoms did not affect the high enantioselectivity of the catalyst precursors, thus resulting in high 'regio'- and 'stereoregular' copolymers.

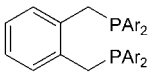
Introduction. – Cationic Pd complexes modified with diphosphine ligands are very active catalysts for the carbonylation of alkenes, a field of considerable industrial and academic interest [1][2]. This reaction makes a wide range of products accessible, starting with high-molecular-weight polyketones [3][4] to methyl propanoate [5], a key intermediate in the synthesis of methyl methacrylate (= methyl 2-methylprop-2-enoate). A detailed mechanistic study of the intermediates involved in the commercially important Pd-catalyzed methoxycarbonylation of ethene was reported [6]. The complex [Pd(dppb)(dba)][1]) was used to generate *in situ* the species involved in the catalytic cycle. The same type of ligand was employed in the Pd-catalyzed carbonylation of butadiene and of methyl pent-3-enoate [7–9].

We tested the performance of Pd complexes modified with 1,2-bis[di(aryl)phosphinomethyl]benzene ligands in the copolymerization of carbon monoxide (CO) and propene, investigating the relationship between the electronic characteristics of the catalytic system and the microstructure of the resulting copolymer [10]. In particular, we were interested in the factors influencing the insertion mode of propene, as this step of the catalytic process gives rise to different chain configurations. For ligands of the type **1a**, electronic factors strongly influence the regio- and enantioselectivity in the efficient and largely isotactic copolymerization of CO and propene. Oligomerization experiments [10] have shown that, under certain conditions, a highly regioselective secondary insertion of propene occurs. The catalytic systems $[Pd(P\text{^}P)(H_2O)_2)](CF_3SO_3)_2$[2]) modified with the ligands **1b** and **1c** show opposite regioselectivity in the insertion of propene, but similar isotacticity with regard to the copolymerization reaction. For these C_{2v}-symmetric ligands, the discrimination of the enantiotopic faces during the copolymerization process should be chain-end controlled. As chain-end

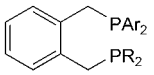
[1]) Abbreviations: dbbp = '1,2-bis[di(*tert*-butyl)phosphinomethyl]benzene'; dba = 'dibenzylideneacetone' (= (*E*,*E*)-1,5-diphenylpenta-1,4-dien-3-one).

[2]) The term (P^P) refers to a chelating diphoshine ligand.

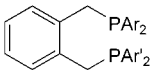
control and secondary insertion both lead to syndiotactic copolymers in the case of styrene [11], this may have enabled a syndiotactic structure to form in the copolymerization of propene and CO.



1a Ar = Ph
1b Ar = 2-MeO–C_6H_4
1c Ar = 3-CF_3–C_6H_4



2 Ar = Ph, R = cyclohexyl

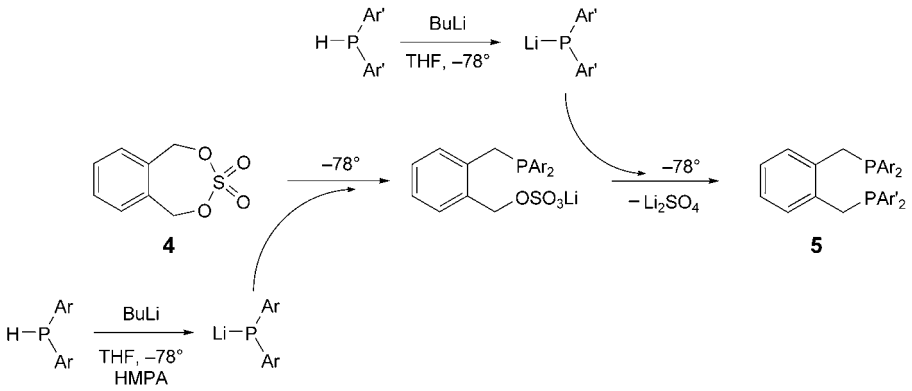


3a Ar = 4-MeO–C_6H_4, Ar' = Ph
3b Ar = Ph, Ar' = 3-CF_3–C_6H_4
3c Ar = 4-MeO–C_6H_4, Ar' = 3-CF_3–C_6H_4

Results and Discussion. – Keeping the same C backbone of the above ligands, different C_s-symmetric diphosphine ligands were synthesized to introduce two different phosphino moieties. From the results obtained with corresponding C_{2v}-symmetric diphosphines, the investigation of this new system appeared to be particularly interesting. We were interested in the question whether the regiochemistry of this reaction would be altered with such new ligands, possibly resulting in new copolymer structures.

The C_s-symmetric 1,4-diphosphine ligands **2** and **3** were synthesized according to a procedure reported in the literature [12]. The starting material was the cyclic sulfate **4** (*Scheme*), which was obtained upon treatment of 1,2-phenylenedimethanol with $SOCl_2$, followed by oxidation with $NaIO_4$ [13]. Cleavage of the C–O bond and opening of the sulfate occurred rapidly and quantitatively after adding a solution of $LiPAr_2$ at −78°. After reaching room temperature, the solution was cooled again to −78°. Addition of the second lithium phosphide, $LiPAr'_2$, introduced the nonequivalent moiety with substitution of the sulfate group. The yield of the chelate ligands **5** ranged from 55 to 75%.

Scheme



The catalyst-precursor complexes $[Pd(P\hat{}P')(OH_2)_2](OTf)_2$ were prepared according to the methods reported in the literature [14], and tested according to the protocol published elsewhere [15] (*Table 1*). Moreover, a series of experiments with *in situ*

Table 1. *Copolymerization of Carbon Monoxide and Propene with Preformed Catalyst Precursors [Pd(P^P′)(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$^{2})*. Reaction conditions: 0.03 mmol catalyst precursor, 75 ml THF and 4.5 ml MeOH, 1.73 mmol 1,4-naphtoquinone, 45 mmol propene, 80 bar CO, 44°.

Ligand	Reaction time [h]	Productivity [g (g(Pd) h)$^{-1}$]	M_n	'Regioregularity'[a])			'Stereoregularity'[b]) [%]
				hh	ht	tt	
2	16	58	3400	0	1	0	67
3a	20	126	5400	0.02	1	0.03	82
3b	25	123	15100	0.04	1	0.05	71
3c	25	15	1700	0.03	1	0.04	76

[a]) Relative intensity of ^{12}C-NMR signals centered at δ *ca.* 223, 219, and 214 ppm, resp. [b]) Intensity [%] of the most-intense band in the ht range of the carbonyl signals in the ^{13}C-NMR spectra; *h* and *t* refer to '*head*' and '*tail*', resp.

formation of the catalyst precursors were carried out, generating the catalyst from a suspension of Pd(AcO)$_2$ and the diphosphine ligand in CH_2Cl_2 (*Table 2*). The general features of the copolymers were found to be very similar for both the preformed Pd complexes and the *in situ* systems Pd(AcO)$_2$/P^P′/BF$_3$ · OEt$_2$.

The productivities of the preformed catalysts were similar to those reported for the C_{2v}-symmetric analogs previously tested [16]. However, there was a general improvement in the activity, especially in the case of **2** compared to the analog bearing only cyclohexyl groups at the two P-atoms. The productivity was higher for the catalyst precursors generated *in situ* (*Table 2*). This can be attributed either to the different solvent mixture or to a counter-ion effect. However, these factors do not affect the enantioselectivity of the cationic complex toward the insertion of the olefin, leading to copolymers with similar isotacticities.

Table 2. *Copolymerization of Carbon Monoxide and Propene with* in situ *Catalyst Precursors from Pd(AcO)$_2$, Ligand, and BF$_3$ · OEt$_2$.* Reaction conditions: 0.03 mmol Pd(AcO)$_2$; 0.036 mmol P^P′ ligand; 0.79 mmol BF$_3$ · OEt$_2$; 75 ml CH_2Cl_2 and 4.5 ml MeOH; 1.73 mmol 1,4-naphtoquinone; 45 mmol propene; 80 bar CO; 44°.

Ligand	Reaction time [h]	Productivity [g (g(Pd) h)$^{-1}$]	M_n	'Regioregularity'[a])			'Stereoregularity'[b]) [%]
				hh	ht	tt	
2	23	205	3800	0.01	1	0	77
3a	27	163	4800	0	1	0	72
3b	23	239	4100	0	1	0	79
3c	43	167	6900	0	1	0	74

[a]) Relative intensity of ^{13}C-NMR signals centered at δ *ca.* 223, 219, and 214 ppm, resp. [b]) Intensity [%] of the most intense band in the ht range of the carbonyl signals in the ^{13}C-NMR spectra; *h* and *t* refer to '*head*' and '*tail*' resp.

From a ^{13}C-NMR analysis (*Fig.*) of the produced copolymers, only one stereochemical arrangement, corresponding to an isotactic structure, was found. In contrast to what could have been expected, an essentially regular enchainment must, thus, have occurred. The 'stereoregularity' ranged from 67 to 82% for the isotactic pentad

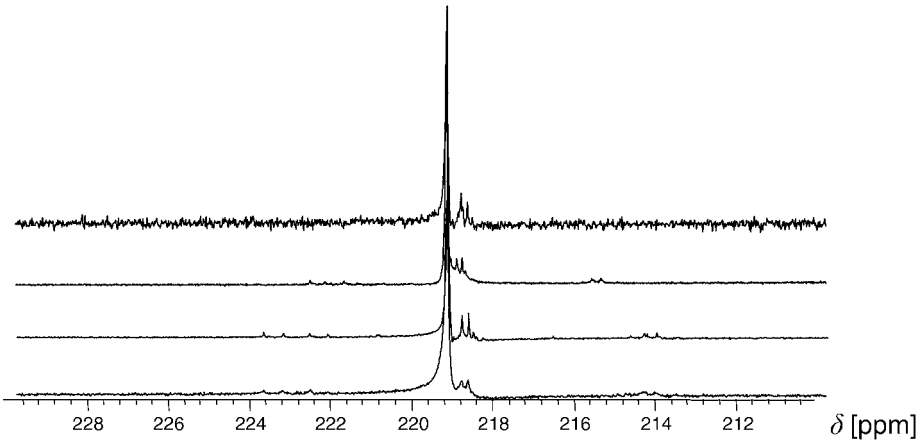


Figure. *^{13}C-NMR* ($(CF_3)_2C(D)OD$, 125 MHz) *of the poly(propene-alt-CO) copolymers prepared with the catalyst precursors [Pd(P^P′)(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$* (see *Table 1*). The chelating phosphine ligands P^P correspond to **2**, **3a**, **3b**, and **3c** (from top to bottom), resp.

(corresponding to a minimum content of 92 and 96% *l*-diads, resp. [17]), which is comparable to the values reported for the catalyst precursors modified with the corresponding C_{2v}-symmetrical 1,4-diphosphine ligands [16]. This shows that the insertion mode of the propene unit is not affected by a variation of the electronic character and basicity at the P-atom. The insertion mode of the olefin generates the same configuration along the polymer chain as observed for the C_{2v}-symmetric diphosphine ligands. The ligand **2** showed a remarkable improvement in 'stereoregularity', when compared with the C_{2v}-symmetric diphosphine ligand bearing only cyclohexyl substituents. The 'regioregularity' showed the predominance of ht (head-to-tail) enchainment, as expected for a basic ligand [18].

To elucidate the geometry of the species responsible for the insertion, a carbonylation study of the model complex [PdMe(P^P′)MeCN](OTf), where P^P′ is **3c**, was carried out. [PdMe(P^P′)Cl], with a stereoisomer ratio of 6.5 : 1, was transformed with AgOTf into a monocationic complex for which the ratio became 2 : 1. After bubbling CO into the reaction mixture, the acyl complex [PdC(O)Me(P^P′)MeCN](OTf) was formed as a mixture of stereoisomers in a ratio of 3.3 : 1. In all the cases, the major isomer has the Me group *trans* to the stronger electron-withdrawing substituents.

Even though two isomers may have been present, the copolymerization proceeded under high regio- and stereocontrol. This suggests that isomerization of the intermediates takes place very easily by exchanging the coordination site of the olefin and the growing polymer chain, thus implying site-selective coordination of the olefin. In fact, the HMQC ^{1}H, ^{31}P{H} correlation spectrum of the complex [PdMe(P^P′)-MeCN](OTf) displayed considerable fluctuation at room temperature.

Experimental Part

General. All reactions were carried out under Ar gas using standard *Schlenk* techniques. All solvents were purified according to standard procedures and deoxygenated prior to use. The precursor sulfate **4** was prepared according to the method of *Gao* and *Sharpless* [13]. The synthetic procedure for preparing the ligands was an adaptation of that described by *Fries et al.* [12]. The diaqua palladium complexes were prepared according to published methods [19].

^{1}H- and ^{31}P-NMR spectra were recorded on a *Bruker AMX-500* apparatus; δ in ppm rel. to Me_4Si (^{1}H or ^{13}C) or 85% H_3PO_4 (^{31}P), J in Hz. The copolymerization reactions were carried out in a 250-ml stainless-steel autoclave, which was placed in an oil bath equipped with a thermostat.

1,5-Dihydro-2,4,3-benzodioxathiepin 3,3-Dioxide (**4**). $SOCl_2$ (4 ml, 0.055 mol) was slowly added to benzene-1,2-dimethanol (6.1696 g, 0.0446 mol) in CCl_4 (30 ml) by means of a syringe. The resulting brownish soln. was refluxed for 1.5 h. After cooling to r.t., the mixture was concentrated on a rotary evaporator to give a brown oil. The latter was dissolved in a mixture of ice-cold CCl_4 (30 ml), MeCN (30 ml), and H_2O (45 ml), Then, $RuCl_3 \cdot n\ H_2O$ (82 mg, 0.308 mmol) and $NaIO_4$ (19 g, 0.089 mol) were added while stirring the mixture vigorously. The mixture was stirred at 25° for 1 h, diluted with H_2O (200 ml), and extracted with Et_2O (4 × 50 ml). The org. phase was dried (Na_2SO_4), filtered through *Celite* (to remove the Ru salts), and evaporated to dryness. Recrystallization from THF and hexane afforded 6.43 g (72%) of **4** as a pure, colorless crystalline solid, which was stored at −20° to avoid thermal decomposition. ^{1}H-NMR (500 MHz, $CDCl_3$, 25°): 5.43 (*s*, 2 CH_2); 7.35–7.37 (*m*, 2 arom. H); 7.44–7.46 (*m*, 2 arom. H). ^{13}C-NMR (125.7 MHz, $CDCl_3$, 25°): 73.61 (CH_2); 129.51, 130.05, 134.07 (arom. C). Anal. calc. for $C_8H_8O_4S$: C 47.99, H 4.03, O 31.69, S 16.08; found: C 48.03, H 4.24, O 31.75, S 15.98.

Dicyclohexyl ({2-[(diphenylphosphino)methyl]phenyl}methyl)phosphine (**2**). A 1.6M soln. of BuLi (8.40 ml, 13.44 mmol) in hexane was added to a soln. of dicyclohexylphosphine (2.21 g, 11.14 mmol) in THF (25 ml) at −78° in the presence of hexamethylphosphoramide (HMPA; 5 ml). The mixture was allowed to warm to 25°, stirred for 30 min at this temp., cooled to −78°, and then added dropwise to a soln. of **4** (2.22 g, 11.09 mmol) in THF (45 ml) precooled to −78°. The mixture was stirred for 30 min at this temp., stirred for 30 min at r.t., cooled again to −78°, and treated with a soln. of Ph_2Li (prepared from Ph_2PH (2.05 g, 11.04 mmol) in THF (25 ml) and 8.30 ml (13.28 mmol) of a 1.6M soln. of BuLi in hexane). The mixture was allowed to reach r.t., and then heated at 60° for 3 h. The solvent was removed under vacuum, and the residue was redissolved in Et_2O (50 ml). The soln. was quenched with H_2O (20 ml). The aq. phase was extracted with Et_2O (3 × 10 ml). The org. phase was separated, dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was recrystallized from degassed MeOH to afford **2** in 65% yield. White solid. ^{1}H-NMR (500 MHz, C_6D_6, 25°): 1.07–1.34 (br., 11 H, cyclohexyl); 1.49–1.87 (br., 11 H, cyclohexyl); 3.05 (br., CH_2P(cyclohexyl)$_2$); 3.89 (*d*, J(P,H) = 2.31, CH_2PPh_2); 6.79 (*d*, 1 arom. H, C_6H_4); 6.87 (*m*, 1 arom. H, C_6H_4); 6.99–7.09 (*m*, 7 arom. H, C_6H_4 and Ph); 7.24 (*m*, 1 arom. H, Ph); 7.42–7.48 (*m*, 3 arom. H, Ph). ^{31}P{^{1}H}-NMR (202.5 MHz, C_6D_6, 25°): −3.89 (br., P(cyclohexyl)$_2$); −13.8 (*d*, J(P,P) = 1.6, PPh_2). Anal. calc. for $C_{32}H_{40}P_2$: C 78.98, H 8.28; found: C 78.38, H 8.28.

Compounds **3a**–**c** were prepared as described for **2** and isolated as white air-sensitive solids in 56% (**3a**), 75% (**3b**), and 47% (**3c**) yield, resp.

REFERENCES

[1] A. S. Abu-Surrah, B. Rieger, *Top. Catal.* **1999**, *7*, 165.
[2] U. W. Meier, F. Hollmann, U. Thewalt, M. Klinga, M. Leskela, B. Rieger, *Organometallics* **2003**, *22*, 3905.
[3] E. Drent, P. H. M. Budzelaar, *Chem. Rev.* **1996**, *96*, 663.
[4] C. Bianchini, A. Meli, *Coord. Chem. Rev.* **2002**, *225*, 35.
[5] G. R. Eastham, R. P. Tooze, X. L. Wang, K. Whiston, *ICI*, WO9619434, 1996.
[6] W. Clegg, G. R. Eastham, M. R. J. Elsegood, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman, S. Zacchini, *Organometallics* **2002**, *21*, 1832.
[7] E. Drent, W. W. Jager, *Shell*, WO0056695, 1999.
[8] E. Drent, W. W. Jager, *Shell*, WO0172697, 2001.
[9] E. Drent, W. W. Jager, *Shell*, WO0168583, 2001.
[10] B. Sesto, G. Consiglio, *Chem. Commun.* **2000**, 1011.
[11] M. Barsacchi, G. Consiglio, L. Medici, G. Petrucci, U. W. Suter, *Angew. Chem., Int. Ed.* **1991**, *30*, 989.
[12] G. Fries, J. Wolf, M. Pfeiffer, D. Stalke, H. Werner, *Angew. Chem., Int. Ed.* **2000**, *39*, 564.

[13] Y. Gao, K. B. Sharpless, *J. Am. Chem. Soc.* **1988**, *110*, 7538.
[14] M. Sperrle, G. Consiglio, *J. Am. Chem. Soc.* **1995**, *117*, 12130.
[15] B. Sesto, G. Consiglio, *J. Am. Chem. Soc.* **2001**, *123*, 4097.
[16] B. Sesto, Dissertation No. 14218, ETH Zürich, 2001.
[17] S. Bronco, G. Consiglio, *Macromol. Chem. Phys.* **1996**, *197*, 355.
[18] A. Batistini, G. Consiglio, U. W. Suter, *Angew. Chem., Int. Ed.* **1992**, *31*, 303.
[19] M. Sperrle, V. Gramlich, G. Consiglio, *Organometallics* **1996**, *15*, 5196.

Received November 26, 2004