C–C single bond. Whereas the substrates presently employed benefit from relief of the structural strain,[11] the construction of seven-membered ring lactone skeletons fused to aromatic rings is of synthetic value because of the presence of these subunits in biologically active compounds.

Experimental Section

7b: To a mixture of [Rh(cod)$_2$]BF$_4$ (6.0 mg, 15 µmol) and tris(*p*-methoxyphenyl)phosphane (9.6 mg, 36 µmol) in *m*-xylene (5 mL) under N$_2$ at room temperature were successively added 2-(2-hydroxy-5-methylphenyl)cyclobutanone (**6b**, 52.9 mg, 0.30 mmol) and *m*-xylene (5 mL). After the N$_2$ atmosphere was replaced with CO, the mixture was heated at 100 °C for 6 h. The reaction mixture was cooled and then passed through a pad of Florisil to remove the insoluble materials. The eluent was evaporated under vacuum, and the residue was subjected to preparative TLC (silica gel, ethyl acetate/hexane 1/5) to afford **7b** (47.3 mg, 91 %) as a colorless oil. ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 2.36$ (s, 3H), 3.05 (d, $J = 6.6$ Hz, 2H), 6.03 (dt, $J = 9.9, 6.6$ Hz, 1H), 6.83 (d, $J = 9.9$ Hz, 1H), 7.09–7.20 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): $\delta = 20.6$, 34.2, 120.9, 122.8, 126.7, 129.9, 130.1, 134.5, 148.3, 169.0; IR (neat): $\tilde{\nu} = 1752$ cm^{-1}; elemental analysis calcd for C$_{11}$H$_{10}$O$_2$: C 75.84, H 5.79; found: C 75.97, H 5.77.

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[4] The cyclobutanone **1a** was prepared by [2+2] cycloaddition of *o*-(methoxymethoxy)styrene with dichloroketene and the subsequent treatment with zinc in acetic acid.

[5] A cationic rhodium(I) complex having two PCyPh$_2$ ligands per rhodium atom is postulated as the catalytic species. No reaction occurred in the absence of the rhodium catalyst.

[6] The ratio of **4a** to **5a** changed little (68:32–75:25), when other catalyst systems like [Rh(cod)$_2$]BF$_4$/PPh$_3$, [Rh(cod)$_2$]BF$_4$/P(*p*-methoxyphenyl)$_3$, and [Rh(cod)(Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$)]BF$_4$ were used.

[7] The reactions previously reported[2] normally failed to occur under a CO atmosphere.

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[10] The formation of the corresponding α,β-unsaturated isomer was not observed.

[11] With less strained substrates like 2-(2-hydroxyphenyl)cyclopentanone, an analogous reaction failed to occur.

Ligand Electronic Effect in Enantioselective Palladium-Catalyzed Copolymerization of Carbon Monoxide and Propene[**]

Céline Gambs, Stanislav Chaloupka,
Giambattista Consiglio,[*] and Antonio Togni[*]

The alternating copolymerization of olefins with carbon monoxide (CO) catalyzed by cationic palladium(II) complexes modified by diphosphane ligands has attracted considerable interest due to the potential use of the produced polyketones as new materials.[1–7] Recently, a terpolymer derived from ethene, propene, and CO has become commercially available under the trade name of Carilon.

When propene is used as the substrate, control of regio- and stereoselectivity of the olefin insertion is required to obtain stereoregular alternating copolymers.[8, 9] Recently, a few examples of successful, highly enantioselective CO/propene copolymerizations have been reported, using either in situ or preformed Pd^{II} complexes containing chiral phosphorus ligands.[10–12] Among the catalysts studied the most active ever reported to date (productivity of about 905 g g(Pd)$^{-1}$ h^{-1}) contained (*R*)(*S*$_p$)-1-[2-(diphenylphosphanyl)ferrocenyl]ethyldicyclohexylphosphane (Josiphos) as the modifying ligand.[13, 14] With this system both a very high regioregularity (> 99 % head-to-tail enchainments) and stereoregularity (> 96 % of isotactic diads) were achieved. Thus, despite contrasting proposals,[15] and a precedent example of a system with low catalytic activity,[16] the best combination of donor groups in the chelate diphosphane ligand seems to be that of two electronically nonequivalent ligand fragments: a basic PCy$_2$ group to ensure high regioselective incorporation of propene and a slightly acidic PPh$_2$ donor.

Since planar-chiral ferrocenyl ligands represent a system that is synthetically easy to modify, and 1) in view of investigating possible electronic effects on both the copolymer structure and the performance of the catalyst, and 2) to gain insight on the role of electronic differentiation of the two binding sites in these ligands,[17, 18] we prepared a series of related chiral diphosphanes **1a–g** (Scheme 1) according to already published general methods.[19–22] Here we report extremely active Pd^{II} systems bearing chiral ferrocenyl diphosphanes **1b–d** for highly enantioselective alternating copolymerization of propene and carbon monoxide.

Thus, in typical experiments, in situ Pd^{II} systems prepared by reacting Pd(OAc)$_2$ with ligands **1a–g** and BF$_3$·Et$_2$O in CH$_2$Cl$_2$–MeOH were investigated (Scheme 2). In fact, ^{31}P

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[*] Prof. G. Consiglio
Laboratorium für Technische Chemie der ETH Zürich
Universitätstrasse 6, 8092 Zürich (Switzerland)
Fax: (+41) 1-632-11-62
E-mail: consiglio@tech.chem.ethz.ch

Prof. A. Togni, C. Gambs, S. Chaloupka
Laboratorium für Anorganische Chemie der ETH Zürich
Universitätstrasse 6, 8092 Zürich (Switzerland)
Fax: (+41) 1-632-10-90
E-mail: togni@inorg.chem.ethz.ch

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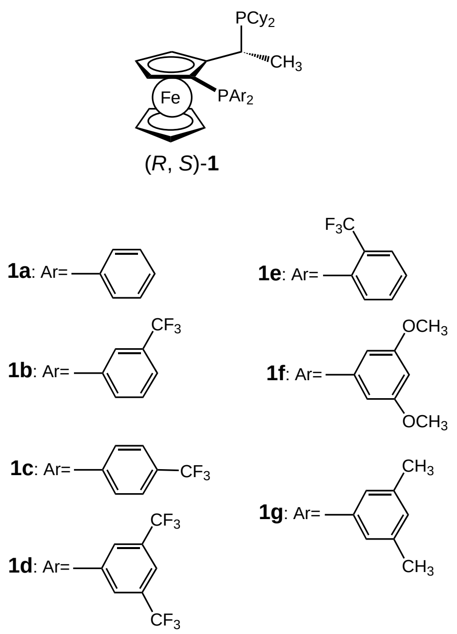
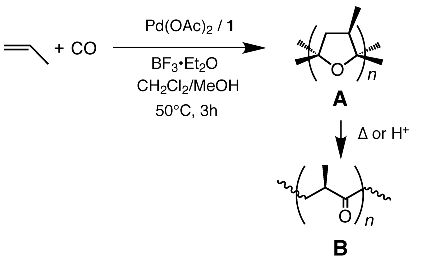


Scheme 1. Modified ferrocenyl ligands of the Josiphos-type used in the Pd-catalyzed CO/propene copolymerization.



Scheme 2. CO/propene copolymerization catalyzed by Pd^{II} systems.

NMR studies on the catalyst mixture containing Josiphos indicated first the formation of the $[Pd(Josiphos)(OAc)_2]$ adduct and, following the addition of the Lewis acid $BF_3 \cdot Et_2O$, the generation of a dicationic Pd^{II} species $[Pd(Josiphos)(L)_2]^{2+}$ (L = solvent molecule).[23] Noncoordinating dichloromethane was the solvent of choice, and small amounts of methanol were required as activator. The results of CO/propene copolymerization reactions are presented in Table 1.

Table 1. CO/propene copolymerizations.[a]

Ligand	Productivity $[g\,g(Pd)^{-1}h^{-1}]$	Regio-regularity [%]	Stereo-regularity (l-diads) [%]	$[\alpha]_D$[b]	$\Delta\varepsilon$ (CD)[c]	M_n[d]
1a	369	> 99	94–95	−24.5	0.84	9410
1b	1044	> 99	97.5	−27.4	1.20	14710
1c	1160	> 99	96.8	−29.8	1.23	10670
1d	1797	> 99	97.5	−34.6	1.26	13990
1e	–[e]	–[f]	–[f]	–[f]	–[f]	–[f]
1f	50	99	90–92	−21.5	0.76	9530
1g	223	> 99	93–94	−16.0	0.49	10360

[a] Reaction conditions: $Pd(OAc)_2$ (0.02 mmol), **1a**–**g** (0.024 mmol), $BF_3 \cdot Et_2O$ (0.040 mmol), CH_2Cl_2/CH_3OH (25/2 mL), propene (11 g), $p(CO) = 75$ bar, $T = 50\,^{\circ}C$, $t = 3$ h. [b] Measured in HFIP. [c] Measured in HFIP; 1–2 $mg\,mL^{-1}$ concentration range. [d] Determined by integration of end groups in the ^1H NMR spectrum. [e] Very low. [f] Not determined.

Under the reaction conditions applied the copolymers grow exclusively as poly[spiro-2,5-(3-methyltetrahydrofuran)] (**A**), which is known to be formed in the presence of protic solvents (Figure 1).[10, 12] Highly regio- and stereoregular CO/Propene copolymers have been obtained with all the ligands tested with the exception of **1e**. The degree of regio- and stereoselectivity was evaluated from the ^{13}C NMR spectrum in $[D_2]$1,1,1,3,3,3-hexafluoropropan-2-ol ($[D_2]$HFIP), in which the copolymer exists as a poly[2-methyl-3-oxopropane-1,3-diyl] (**B**), in the region of resonances of the carbonyl groups (Figure 2). Signals of carbonyl carbons of head-to-head and tail-to-taildiads were completely absent;[8] moreover, the sharpness of the carbonyl band, which was attributed to an isotactic pentad,[24] and the high optical activity of the copolymers are consistent with a highly isotactic structure.[25, 26]

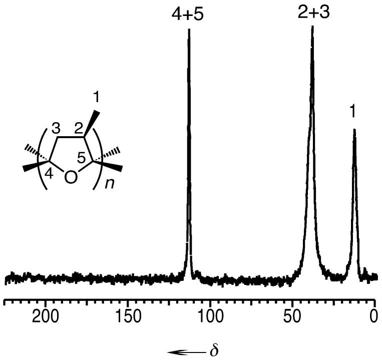


Figure 1. ^{13}C MAS solid-state NMR spectrum of poly[spiro-2,5-(3-methyltetrahydrofuran)] **A**, at room temperature.

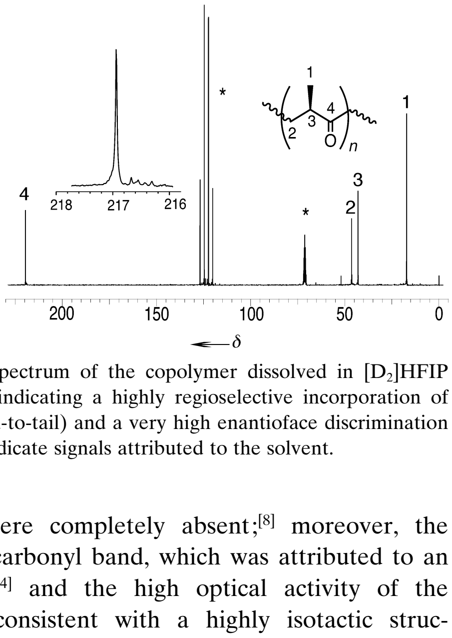


Figure 2. ^{13}C NMR spectrum of the copolymer dissolved in $[D_2]$HFIP (insert: CO region), indicating a highly regioselective incorporation of propene (> 99 % head-to-tail) and a very high enantioface discrimination (> 96 %). Asterisks indicate signals attributed to the solvent.

Increasing the electronic differentiation of the two P atoms causes drastic changes in the catalyst activity. The highest productivity (1797 g polymer per gram Pd per hour $[g\,g(Pd)^{-1}h^{-1}]$) is obtained with ligand **1d**, a 3,5-bis(trifluoromethyl)phenylphosphane derivative. On the other hand, its analogue **1f**, bearing the electron-donating methoxy groups instead of the electron-withdrawing trifluoromethyl groups, showed very low productivity ($50\,g\,g(Pd)^{-1}h^{-1}$). Thus, the effect of an enhanced π-acidity of the arylphosphane, which decreases the electron density at palladium, results in an increase of reaction rate. Steric effects are also evident. When the trifluoromethyl substituent is located in the *ortho* position (**1e**) only low-molecular-weight oligomers are obtained in a very low yield. Thus, placing the CF_3 group in the phenyl *meta* or *para* positions (**1b**–**d**) does not drastically influence the steric properties of the ligands and constitutes the modification of choice for the formation of highly efficient systems for the CO/propene copolymerization reaction.

Whereas electronic effects on the stereoselectivity of several different catalytic asymmetric reactions have been observed before,[21, 22, 27–29] a comparable influence on the catalytic activity has been reported in particular for Rh-catalyzed hydroformylation.[30–33] Because of the C_1 symmetry of the ligands, we believe that the isomeric intermediates containing CO and/or the olefin coordinated to Pd display significantly different reactivities. When the complex $[(\mathbf{1d})PdMe]^+$ is placed under a CO atmosphere the product $[(\mathbf{1d})Pd(CO)COMe]^+$ is formed through a highly regioselective coordination of the acyl moiety *trans* to the PAr_2 group.[16] The electrophilicity of the metal center, and hence that of the coordinated substrates should be higher in the case of the ligands bearing more electron-withdrawing PAr_2 groups. This also should coincide with a lower binding energy of the substrate. In contrast to other catalytic systems,[34] in fact, the kinetic order of the copolymerization with respect to carbon monoxide is positive. The crucial assumption sustaining the electronic effect on activity is that the configurational isomers in which the monomers are coordinated *trans* to the PAr_2 groups should be more reactive by virtue of their increased electrophilicity in this position. Furthermore, it has to be noted that in catalytic polyketone synthesis the electrophilicity of the metal center needs to be carefully balanced in order for olefins to compete with CO as ligands. Thus, for ligands containing a basic PAr_2 group, such as **1f**, CO is likely to bind more strongly to the Pd^{II} center, leading to a drastic decrease of the overall rate.

In conclusion, Pd^{II} systems combined with sterically very similar chiral ferrocenyl ligands **1a**–**g** (except **1e**) produce almost completely isotactic copolymers from propene and CO in a highly enantioselective fashion. Only small variations in enantioface discrimination were observed, whereas drastic changes in catalytic activity were noted by changing the electronic properties of the PAr_2 substituent.

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Versatile Indole Synthesis by a 5-*endo-dig* Cyclization Mediated by Potassium or Cesium Bases[**]

Alain Louis Rodriguez, Christopher Koradin, Wolfgang Dohle, and Paul Knochel[*]

The addition of heteroatomic nucleophiles to triple bonds is an important reaction that often requires a high activation energy.[1] Intramolecular additions proceed more readily and a recent hydroamination of *o*-chlorostyrenes followed by

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[*] Prof. Dr. P. Knochel, Dr. A. L. Rodriguez, Dipl.-Chem. C. Koradin, Dipl.-Chem. W. Dohle
Department Chemie, Universität München
Butenandtstraße 5–13, 81377 München (Germany)
Fax: (+49) 89-2180-7680
E-mail: Paul.Knochel@cup.uni-muenchen.de

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