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New diphosphine ligands based on diphenyl ether for the Pd-catalyzed CO/ethene copolymerization†

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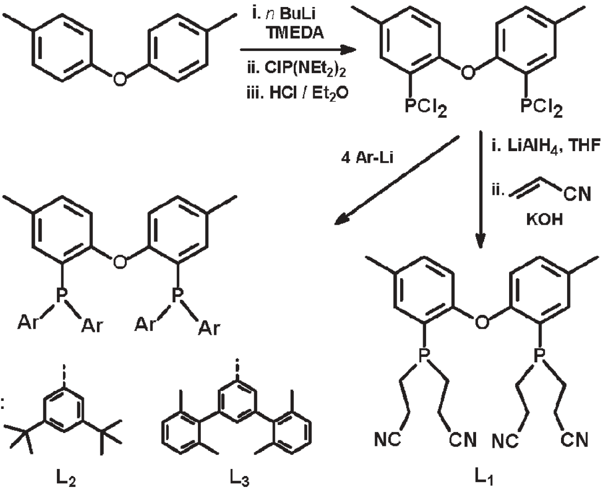
The catalytic activity and selectivity of palladium(II) complexes of new, flexible bidentate ligands in the CO/ethene copolymerization reaction have been found to change considerably with the steric properties of the ligands.

The palladium-catalyzed carbonylation of ethene is a reaction of great potential from an industrial point of view and it has also attracted academic interest for many years.[1] With this process, a wide range of products can be obtained, ranging from methyl propanoate, a useful starting material for the preparation of methyl methacrylate,[2] to thermoplastic polymers, called polyketones, which have valuable chemico-physical properties.[3] Studies carried out by van Leeuwen[4] *et al.* on alcoholysis of acyl palladium(II) complexes in methanol point out that complexes bearing rigid bulky diphosphines, which adopt trans coordination, showed no alcoholysis, while complexes containing flexible ligands that are cis or can adopt cis coordination do undergo alcoholysis and it was concluded that a *cis* geometry was needed for an intramolecular ester formation. When the steric bulk of the diphosphine is increased, the reaction rate is enhanced. Other authors have recently asserted that the methanolysis of acyl–Pd(II) complexes proceeds *via* an intramolecular mechanism.[5] In this paper, we focus on flexible bidentate diphosphines with variable steric bulk containing a diphenyl ether (DPE) backbone. Indeed, the variation of the steric hindrance allows modulation of the bite angle and the flexibility of the ligand (*i.e.* the geometry of coordination, cis or trans) which strongly influence the rates of the insertion and termination reactions. Our aim is to understand the influence of the steric properties of the ligand in the CO/C_2H_4 copolymerization. The synthesis of the ligands has been carried out using 4,4′-dimethyldiphenyl ether as starting material, according to Scheme 1.

Ortho-lithiation and subsequent reaction with $ClP(NEt_2)_2$ gave the diethylamino phosphane, which by reaction with HCl, afforded the 2,2′-bis(dichlorophosphino)-4,4′-dimethyldiphenyl ether. Reduction with $LiAlH_4$ to the corresponding 2,2′-bis(phosphino)-4,4′-dimethyldiphenyl ether and double Michael addition to acrylonitrile gave the desired cyanoethylphosphane **L$_1$**. Coupling of the 2,2′-bis(dichlorophosphino)-4,4′-dimethyldiphenyl ether with aryllithio derivatives on the other hand afforded the more bulky ligands **L$_2$** and **L$_3$**, respectively. DPEphos was used as a reference in our studies.[6]

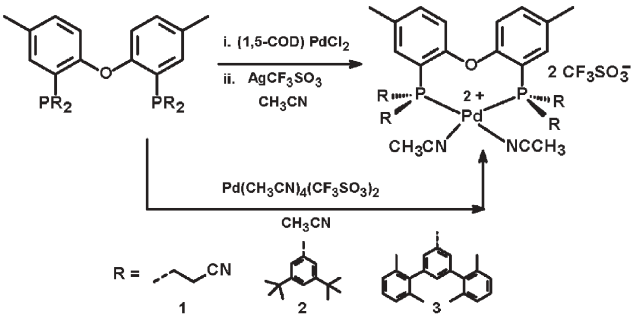


Scheme 1

The palladium(II) bis-acetonitrile complexes $[(P,P)Pd(CH_3CN)_2]^{2+}$ $2[CF_3SO_3]^-$ were used for the catalytic reactions. The triflate ion is a non-coordinating anion towards palladium in methanol. The desired complexes can be prepared in a straightforward manner either by reaction of the precursor $Pd(CH_3CN)_4(CF_3SO_3)_2$ with ligand **L$_1$**, **L$_2$** or **L$_3$**, or by reaction of the ligand with (1,5-COD)$PdCl_2$ and subsequent reaction with $AgCF_3SO_3$, according to Scheme 2.

Single crystals suitable for X-ray diffraction‡ of the compound (**L$_2$**)$PdCl_2$ could be obtained by crystallization from pentane and the molecular structure[7] is depicted in Fig. 1. The compound is a *cis*-complex exhibiting a P–Pd–P angle of 97.67(3)°.

Catalytic experiments with the new complexes were carried out under mild conditions and the results have been summarized in



Scheme 2

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b5/b503764f/
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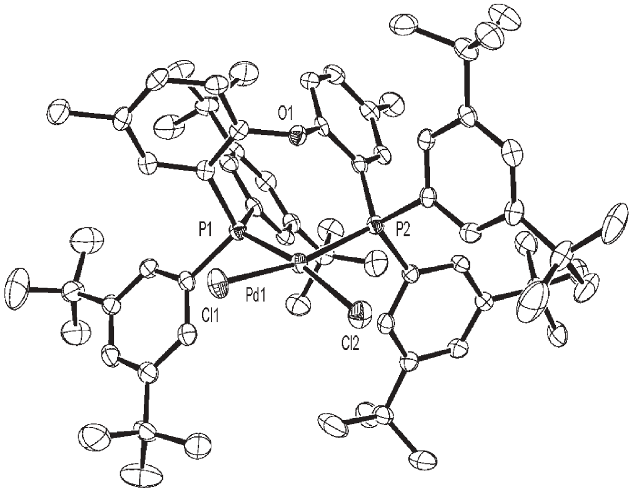

Fig. 1 X-ray crystal structure of the complex ($\mathbf{L_2}$)$PdCl_2$. Displacement ellipsoids shown at the 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–P(1): 2.2738 (11), Pd–P(2): 2.2416(11), P(1)–Pd–P(2): 97.67(3), Cl(1)–Pd–Cl(2): 91.26(4).

Table 1. Ligands $\mathbf{L_2}$ and $\mathbf{L_3}$ show increasing steric bulk due to the *tert*-butyl and the phenyl substituents in meta position of the aromatic ring. This might give rise to different bite angles of the ligands, which consequently affects the product distribution.

Indeed, as shown in Table 1, the product distribution is dramatically different going from ligand $\mathbf{L_1}$, the least hindered diphosphine, to ligand $\mathbf{L_3}$, the bulkiest one; the former gives only polymers, while the latter gives mainly methyl propanoate and a small amount of low molecular weight oligomers. As expected, there is a competition between chain growth and chain termination rates: the bisphosphine $\mathbf{L_1}$ which contains cyanoethyl moieties and considered electronically as being in between arylphosphines and arylphosphites,[8] but sterically much less demanding, is expected to adopt a *cis*-coordination to the palladium centre which favours multiple insertion reactions of carbon monoxide and ethene, while the bulky ligand $\mathbf{L_3}$ may disfavour the formation of long chains.

A recent study concerning reductive elimination reactions of palladium(II) complexes with mono- or bidentate phosphines showed that an increase of the steric hindrance led to higher reaction rates by many orders of magnitude, while changes in electronic properties gave only small changes in rate.[9]

Table 1 Comparative catalytic results for complexes **1–3**

Entry	Ligand	CF_3SO_3H (equiv)	MP[a]	Olig[a]
1	L_1	0	n.d.	20
2	DPEphos*	0	267.0	28
3	DPEphos	20	498.5	34
4	L_2	0	91.7	153
5	L_2	20	133.7	165
6	L_3	0	119.7	9
7	L_3	20	395.9	6

[a] Grams of product per gram of Pd per hour. MP: methyl propanoate, Olig: precipitated fraction. *DPEphos = 2,2′-bis(diphenylphosphino)diphenyl ether. [b] Conditions: catalyst: 0.02 mmol, MeOH: 10 mL, p(CO) = p(ethene): 25 bar (*T*: 25 °C), Reaction time: 2 h, *T*: 60 °C, 1100 rpm, stainless steel reactor with volume of 75 mL.

Entries 1, 2 and 6 in Table 1, show that the growing steric bulk of the ligand favours the formation of short oligomers *i.e.* there is an increase of termination rate respect to the insertion rate. Ligand $\mathbf{L_3}$, the most sterically demanding of all ligands, gives mainly products of methoxycarbonylation of alkene instead of polymers. However, entry 4 and 5, which corresponds to complex $[(\mathbf{L_2})Pd(NCCH_3)_2]^{2+}$ in absence and in presence of triflic acid respectively, shows higher productivity in polyketones compared to complexes $[(DPEphos)Pd(NCCH_3)_2]^{2+}$ and $[(\mathbf{L_3})Pd(NCCH_3)_2]^{2+}$ while less methyl propionate is produced. This behaviour was not expected on the basis of previous studies. It should be noted here that the low overall activity of the complex $[(\mathbf{L_1})Pd(NCCH_3)_2]^{2+}$ might be due to intra- or intermolecular coordination of the pendant cyano group to a Pd center, which is currently under investigation.

The CO/ethene copolymers, obtained from the catalytic experiments, were analysed by ^1H and ^{13}C NMR and by Maldi-Tof-MS in order to characterize the end groups of the polymer chains. The analysis reveals that each chain has a methyl ester (E) and an ethylketone (K) end group (EK), and neither ketone-ketone (KK) nor ester-ester end-groups (EE) were detected. In addition, the structure of the polymer is perfectly alternating (see supplementary material†).

In order to analyze the molecular weight distribution of the polyketones, the logarithm of intensities of the peaks obtained by Maldi-Tof and the weight fraction have been plotted *versus* the mass (*m*/*z*). The resulting curve shows the behaviour of a Schulz–Flory curve and the Schulz–Flory constant, α, was found to be equal to 0.90 (Fig. 2).

In conclusion, the steric bulk of the new, fluxional ligands control the rates of reaction and the molecular weight of the final products of the CO/C_2H_4 copolymerization. The trend toward more MP with increasing cone angles is the same as that found for diphosphines containing $C_{1–3}$ bridges.[1]

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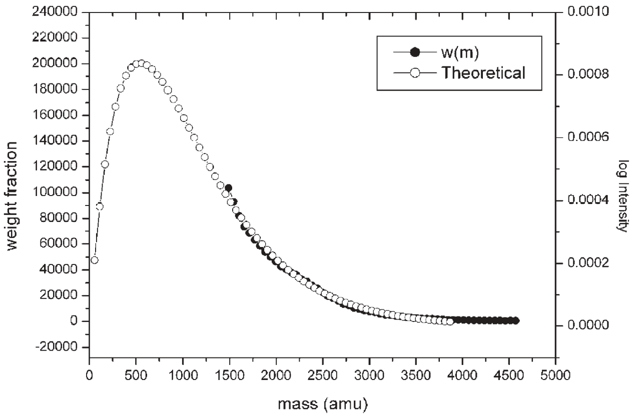

Fig. 2 Weight fraction distribution for CO/ethene copolymer obtained in the presence of complex $[(\mathbf{L_2})Pd(NCCH_3)_2(CF_3SO_3)_2]$ entry 4, Table 1, a) theoretical curve calculated according to Schulz–Flory distribution, b) curve obtained from experimental data.

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‡ CCDC 267390. See http://www.rsc.org/suppdata/cc/b5/b503764f/ for crystallographic data in CIF or other electronic format.

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7 Crystal data: $C_{70}H_{96}Cl_2OP_2Pd$, M_r = 1192.71, orthorhombic, space group *Pbca*, a = 25.241 (3), b = 20.053 (4), c = 26.004 (2) Å, V = 13162 (3) $Å^3$, T = 150 K, Z = 8, D_{calcd} = 1.204 g cm^{-3}, F(000) = 5072, μ (MoKα) = 0.452 mm^{-1}, crystal dimensions 0.02 × 0.22 × 0.24 mm. Of 164826 reflections measured, 8606 unique reflections were used in the refinement. Final R = 0.0363 (wR2 = 0.0874) S = 1.02.

8 The χ-value of L_1 is considered to be *ca.* 17, thus in between arylphosphines (∼13) and arylphosphites (∼22). See also: C. A. Streuli, *Anal. Chem.*, 1960, **32**, 985; W. M. A. Henderson and C. A. Streuli, *J. Am. Chem. Soc.*, 1960, **82**, 5791.

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