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Steric activation of chelate catalysts: efficient polyketone catalysts based on four-membered palladium(II) diphosphine chelates

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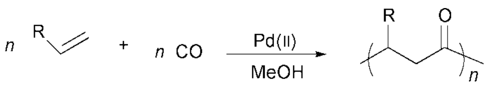
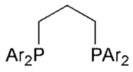
Palladium(II) complexes of ligands of the type $Ar_2PCH_2PAr_2$ and $Ar_2PN(Me)PAr_2$ (Ar = *ortho*-substituted phenyl group) are very efficient catalysts for copolymerisation of CO and C_2H_4.

The perfectly alternating polyketone made by palladium(II)-catalysed copolymerisation of CO and alkenes [eqn. (1)] has

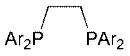


$$n\,RCH{=}CH_2 + n\,CO \xrightarrow[MeOH]{Pd(II)} [CH(R)CH_2C(O)]_n \qquad (1)$$

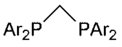
numerous potential applications.[1] Several types of palladium(II) chelates have been reported to be catalysts[1,2] but diphosphine chelates outperform all others in terms of activity and selectivity. Drent *et al.*[1] have shown that the CO/C_2H_4 copolymerisation catalytic activity of palladium(II) complexes of diphosphines of the type $Ar_2P(CH_2)_nPAr_2$ is a sensitive function of the backbone chain length, *n*, and the aryl group, Ar.



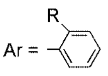
1a,b



2a



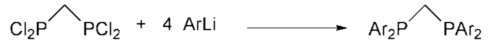
3a–e



a R = H
b R = OMe
c R = Me
d R = Et
e R = Pr^i

Thus it was shown that the 6-membered chelate derived from **1a** was an order of magnitude more active than the 5-membered analogue from **2a** and that the 4-membered chelate from **3a** was essentially inactive. It was also disclosed that the complex of **1b**, containing *ortho*-methoxy substituents, gave a polymer of significantly greater molecular weight than that obtained with the complexes of unsubstituted ligand **1a**.[3] The catalyst sensitivity to chelate ring size might be rationalised in terms of bite angle effects.[4] However, we show here that the activity of 4-membered Pd–P–C–P chelates is dramatically increased by the presence of bulky *ortho* substituents on the aryl groups and that polymerisation rates comparable to, or even exceeding, the best commercial catalysts are obtained with 4-membered Pd–P–N–P chelates.[5,6]

The diphosphine ligands **3b–e** were made from bis(dichlorophosphino)methane[7] according to eqn. (2) and fully



3a–e

$$Cl_2PCH_2PCl_2 + 4\,ArLi \longrightarrow Ar_2PCH_2PAr_2 \qquad (2)$$

characterised. The catalysts were tested for the production of ethene/propene/CO terpolymer over a 3 h period at 50 barg and 70 °C in dichloromethane using tris(pentafluorophenyl)borane promoter. In Table 1, the polymer yield is a measure of the productivity of the catalysts over 3 h. The polymerisation rate and catalyst half-life, as determined by fitting first order curves to the cumulative gas uptake profiles, are also given in Table 1. The borane activation method was reported recently and involves the transfer of a pentafluorophenyl group from boron to palladium to form a cationic $Pd–C_6F_5$ complex which is the catalytically active species.[6] The catalysts were formed by the reaction of palladium acetate and ligand *in situ* or using pre-formed palladium acetate complexes. The results obtained in terms of rate and productivity are the same (within the accuracy of our measurements) for both of these methods, indicating that the same catalytic species is formed in both cases (see Table 1, entries 3 and 4).

Polydispersities are consistently around the value of 2, as expected for a single site catalyst, and termonomer incorpora-

Table 1 Copolymerisation of CO and C_2H_4 results

Entry	Ligand[a]	Yield/g	Rate[b]/ g gPd^{-1} h^{-1}	Half-life[b]/ min	M_w	M_n	PDI	C_3H_6 incorp. (%)
1	**3a**[d]	0.2	[c]	[c]	58 000	24 000	2.4	6.0
2	**3b**[d]	1.5	1 029	44	81 000	31 000	2.6	6.0
3	**3c**	2.8	2 020	38	78 000	42 000	1.9	6.6
4	**3c**[d]	3.0	2 185	35	71 000	42 000	1.7	6.3
5	**3d**[d]	5.0	2 776	53	98 000	50 000	2.0	6.5
6	**3e**[d]	25.1	9 396	165	278 000	107 000	2.6	5.0
7	**3e**[e]	0.3	[c]	[c]	17 000	13 000	1.3	7.1
8	**5a**	0.4	[c]	[c]	[f]	[f]	[f]	[f]
9	**5b**	12.0	4 800	160	103 000	43 000	2.4	3.6[g]
10	**5c**	7.7	3 454	144	282 000	113 000	2.5	3.6[g]
11	**5d**	10.4	4 029	152	639 000	179 000	3.6	3.7[g]
12	**5e**	17.0	11 517	134	888 000	355 000	2.5	3.7[g]
13	**5e**[e]	0.2	[c]	[c]	20 000	9 300	2.1	4.9[g]

[a] Polymerisation conditions: 50 barg C_2H_4/CO, 20.0 g C_3H_6, CH_2Cl_2 diluent, 70 °C for 3 h using $B(C_6F_5)_3$ promoter (0.2 mmol). Catalyst solution formed *in situ* with $Pd(OAc)_2$ (0.01 mmol) and ligand (0.01 mmol). [b] Determined by fitting first order curve to cumulative gas uptake profile. [c] Rate too low to be determined. [d] Conditions as above, except $[Pd(OAc)_2(ligand)]$ (0.01mmol) complex was pre-formed. [e] Conditions as above, except methanol diluent and $HBF_4{\cdot}OMe_2$ promoter (0.05 mmol). [f] Only oligomeric products were formed. [g] 12.0 g Propene used.

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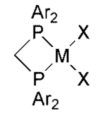
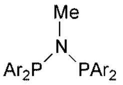
tion is largely unaffected by ligand structure. However, other aspects of the polymerisations are very sensitive to the structure of the ligand. Generally, polymerisation rate, catalyst stability and polymer molecular weight all increase with increasing steric bulk of the aryl *ortho* substituent (entries 1–6). These effects are very pronounced with the *o*-isopropylphenyl derivative **3e** (entry 6) where, compared with the *o*-ethylphenyl derivative **3d** (entry 5), the productivity has increased 5-fold and the molecular weight has doubled. Polymerisation under the methanolic conditions described by Drent[1] gave only a very low rate (entry 7), showing the importance of the activation method used. Indeed, even dppm (**3a**) produces polymer under our conditions, albeit in very low yield (entry 1). Derivative **3b** (entry 2), bearing polar methoxy substituents, gives some improvement over the performance of **3a**; however, productivity is less than one third that of the sterically similar *ortho* ethyl compound **3d**.

The correlation between the steric bulk of the *ortho* substituents and the catalytic performance of the 4-membered chelates led us to investigate further the source of this steric activation by carrying out solid state and solution structural studies of model chelates of general structure **4** (M = Pd, X = Cl, OAc; M = Pt, X = Cl). Most enlightening to the catalysis discussed here is the structure of the chelate complex **4e** (M = Pt, X = Cl), a model for the very active catalyst system derived from **3e**. The crystal structure of **4e** was determined (as its dichloromethane solvate) and is shown in Fig. 1.† It shows a flat 4-membered chelate ring with, as a consequence, isoclinal aryl groups, two of which have *ortho*-isopropyl groups orientated so as to block the axial sites at the metal. The NMR spectra for **4e** show that this species is fluxional. The ^{31}P NMR spectrum of **4e** in $CDCl_3$ at +20 °C is a singlet at −64.5 ppm [^1J(PtP), 3130 Hz] but this signal broadens as the temperature is lowered and at −60 °C, there appears to be a 1 : 1 mixture of two species which give rise to an AB pattern [δ_A −65.4, $^1J(PtP_A)$ 3045 Hz, δ_B −66.1, $^1J(PtP_B)$ 3337 Hz, $^1J(P_AP_B)$ 48 Hz] and a singlet [δ_C −68.4, ^1J(PtP) 3195 Hz]. The ^{1}H NMR signals for the isopropylgroups of **4e** are broad at ambient temperatures and at −60 °C this signal is resolved into overlapping complex multiplets. The ^{1}H and ^{31}P NMR spectra for the parent dppm complex **4a** (M = Pt, X = Cl) are invariant with temperature and therefore the changes in the NMR spectra with temperature observed with **4e** are associated with the presence of the bulky *ortho* substituents. Thus we tentatively assign the fluxionality of **4e** to interconversion of symmetrical and unsymmetrical rotamers arising from restricted rotation around the aryl–P bond.



4a–e



5a–e

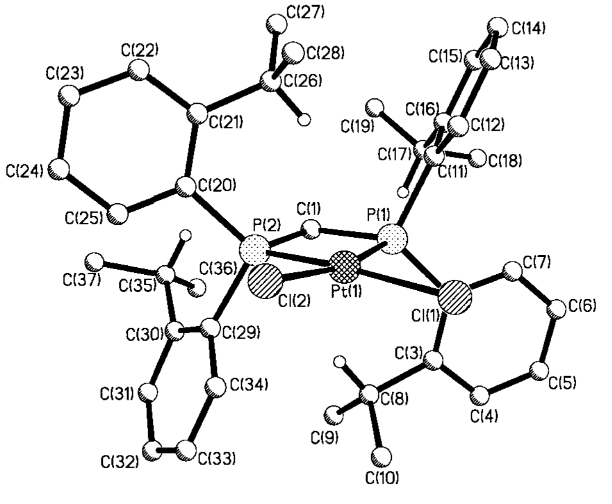
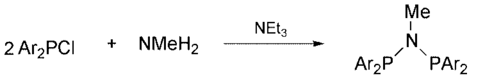


Fig. 1 Molecular structure and numbering scheme for **4b**. All but tertiary isopropyl hydrogen atoms have been omitted for clarity. Important molecular bond lengths (Å) and angles (°): Pt(1)–P(1) 2.2301(9), Pt(1)–P(2) 2.2202(9), Pt(1)–Cl(1) 2.3627(9), Pt(1)–Cl(2) 2.3465(9); P(1)–Pt(1)–P(2) 75.96(3), P(1)–C(1)–P(2) 94.54(13).

The success of bulky diarylphosphinomethane ligands prompted us to investigate other one-atom backbone diphosphines in which similar steric effects may be observed. Amino-bridged diphosphines offered such a suitably versatile ligand architecture. Although the chemistry of the simple ligands based on this structural motif has been studied,[8] the synthesis of bulky derivatives **5b–e** and their use in catalysis has not been explored. The methylamino-bridged diphosphines (**5a–e**) were made according to eqn. (3) and fully characterised.



$$2\,\mathrm{Ar_2PCl} + \mathrm{NMeH_2} \xrightarrow{\mathrm{NEt_3}} \mathrm{Ar_2P{-}N(Me){-}PAr_2} \qquad (3)$$

5a–e

The palladium(II) complexes of ligands **5a–e** were tested for polymerisation activity as before (entries 8–13) and the results largely parallel those obtained with (**3a–e**). Thus, polymerisation rate, catalyst stability and polymer molecular weight all increase with increasing steric bulk of the aryl *ortho* substituent (entries 8–13) and methanolic conditions give only very low activity (entry 13). In this case, the *ortho*-methoxy derivative **5b** (entry 9) shows comparable productivity to the ethyl derivative **5d**, albeit to give a lower molecular weight material. The N_1-backbone chelates are consistently superior to their C_1-backbone analogues and the polymerisation rate of the most active catalyst in this family, **5e**, exceeds that of even dppp (**1a**) under our conditions.[6] The molecular weight of the polymer produced by this system is also extremely high compared with other polyketone catalysts.[1,3,6]

Our studies have shown that 4-membered palladium(II) diphosphine chelates, hitherto considered to be inefficient polyketone catalysts, are in fact very active when sterically demanding derivatives are used.

Notes and references

† *Crystal data* for $4b\cdot CH_2Cl_2$: $C_{38}H_{48}Cl_4P_2Pt$, M = 903.59, monoclinic, space group $P2_1/c$ (no. 14), a = 12.942(2), b = 12.338(2), c = 23.711(7) Å, β = 98.64(2)°, U = 3743.1(15) Å^3, Z = 4, μ = 4.146 mm^{-1}, T = 173 K, 8581 unique data, $R1$ = 0.0220.

CCDC 155957. See http://www.rsc.org/suppdata/cc/b0/b010063n/ for crystallographic files in .cif or other electronic format.

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