Stereocontrol mechanism in CO/*p*-methylstyrene copolymerisation catalysed by aryl-α-diimine Pd(II) complexes†

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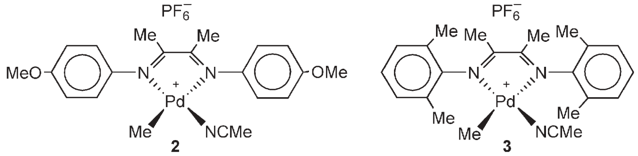
Structural analysis of the first steps of isotactic CO/*p*-methylstyrene copolymerisation, catalysed by aryl-α-diimine Pd(II) complexes, highlights the influence of steric effects on the stereoselectivity of olefin insertion.

In the last ten years, α-diimine ligands having a 1,4-diaza-1,3-butadiene or acetanaphthene skeleton have been widely employed in olefin polymerisation catalysed by late transition metal complexes.[1] In particular, Brookhart and co-workers have found that Pd(II) and Ni(II) aryl-substituted α-diimine complexes are highly active catalysts for the conversion of ethylene and α-olefins, into high molecular weight polymers.[2] Polar monomers can be copolymerised with ethylene,[3] but only very few examples of olefin/carbon monoxide copolymerisation, using this type of catalyst, were reported.[2b] Recently, we have described the catalytic behaviour in CO/*p*-methylstyrene copolymerisation of a series of α-diimine Pd complexes of general formula [Pd(η^1,η^2-$C_8H_{12}OMe$)(Ar–N=C(R)–C(R)=N–Ar)]X **1** with *ortho* or *para* substituents on the aryl rings. The microstructure of the resulting polyketones ranged from atactic to stereoblock isotactic, depending on the substituents on the aryls.[4] These results are rather peculiar since isotactic CO/vinylarene copolymers are generally obtained with palladium complexes bearing enantiomerically pure C_2-symmetric ligands, while achiral C_{2v} or C_s nitrogen ligands produce highly syndiotactic polyketones.[5] In the case of aryldiimine palladium complexes a chain-end control mechanism should be responsible for the production of isotactic copolymer due to the achiral nature of the catalysts; however, unlike the case of planar nitrogen ligands,[6] the same olefin enantioface is selected within each stereoblock.[4] Moreover, we found that the isotacticity strongly increases using ligands with bulky groups in the phenyl *ortho*-positions and in the backbone; these factors contribute to orientate the aryl rings perpendicularly with respect to the coordination plane of the complex.[4] With the aim of understanding how this steric arrangement is able to determine an enantioselective insertion of the olefin, we have investigated the first intermediates of the copolymerisation process. For this purpose we simplified the structure of complexes **1**, replacing the bulky methoxycyclooctenyl fragment with a methyl group and an acetonitrile molecule, namely complexes **2** and **3** were synthesised (Scheme 1) (ESI†). Complex **2** was used since similar catalysts, with electron-donating substituents in *para* position of the phenyl ring, showed an higher catalytic activity without significantly influencing the polyketone microstructure.[4]



Scheme 1

Complexes **2** and **3** were tested as catalysts in the CO/*p*-methylstyrene copolymerisation under mild conditions (P_{CO} = 1 atm, T = 17 °C) (ESI†). While an improvement of the yields was achieved in comparison to those previously reported with analogous complexes bearing the same α-diimine ligand,[4] the stereochemistry of the resultant polyketones remained unchanged. In particular, atactic copolymer was obtained with *para*-methoxy substituted complex **2** and isotactic copolymer (ll triad 74%) was obtained with *ortho*-dimethyl substituted catalyst **3**. For model studies about the first steps of the process,[7] we used complexes **6** and **7** (Scheme 2) directly since it was previously observed that methyl acetonitrile Pd complexes with α-diimine ligands give origin, under CO atmosphere and in copolymerisation conditions, to the corresponding methyl carbonyl derivatives that are the real catalytic initiators.[8b,c] In addition, the less coordinating tetraarylborate counterion was chosen to favour alkene insertion in the stoichiometric reactions. Fast insertion of *p*-methylstyrene in the Pd–acetyl bond, deriving from methyl migration in **6** and **7**, leads to the quantitative formation of **8** and **9**, respectively (Scheme 2). The NMR characterisation of these compounds reveals that the *p*-methylstyrene unit is coordinated in an η^3-allyl fashion involving one double bond of the aryl ring. The presence of this kind of coordination is highlighted by the considerable upfield shifts of the aromatic protons and of C-*ipso* and C-*ortho* of the styrene unit. In agreement with such a structure, both H^a and H^b are shielded by the anisotropy effects of the aryl ring of the ligands.‡ Intermediates, obtained from analogous reactions with less hindered nitrogen ligands, are generally described as five-membered metallacycles with the carbonyl oxygen linked to palladium.[8,9] While the two previously reported η^3-allyl products derived from styrene insertion in Pd–acyl bond were observed only in solution,[10] in the case of the aryldiimine complex **9** we were also able to confirm the above described structure by solid-state X-ray

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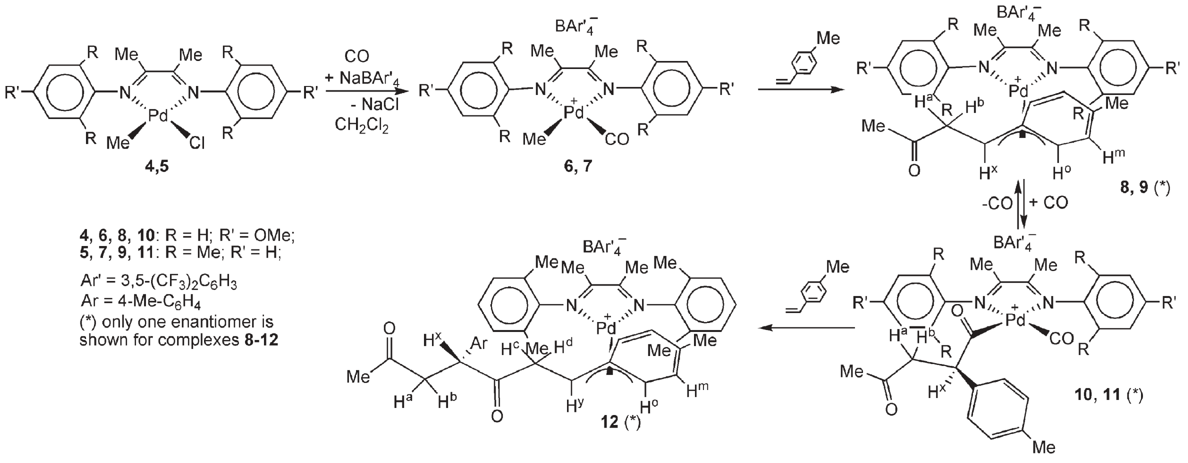
† Electronic supplementary information (ESI) available: Synthesis and characterisation of compounds **2** ,**3**, **6–12** and copolymerisation reactions. See DOI: 10.1039/b707107h



Scheme 2

analysis (Fig. 1). In the crystal lattice there are two independent metal complexes, **9a** and **9b**, which are almost completely superimposable except for the orientation of the –COMe group.§ Atoms N(1), N(2), C(21) and C(28) of **9a** (N(1′), N(2′), C(21′) and C(28′) of **9b**) are disposed in a distorted square-planar arrangement about the palladium ion, which is 0.06 Å in **9a** (0.03 Å in **9b**) out of the mean plane defined by the four donors. The latter forms an angle of 78.8(1)° in **9a** (83.2(1)° in **9b**) with the phenyl ring of the *p*-methylstyrene fragment plane. The bond length Pd(1)–C(21) in **9a** (Pd(1′)–C(21′), **9b**) is significantly longer in respect to the other palladium-carbon bond distances (see caption of Fig. 1), being, in both the independent complexes, Pd(1)–C(28) and Pd(1′)–C(28′) the shortest. Finally, as already observed,[11] the xylyl rings of the diimine moiety are almost perpendicular to the metal coordination plane. To investigate the next step of the copolymerisation process, $CDCl_3$ solutions of **8** or **9** were saturated with carbon monoxide, by bubbling the gas for 5 min, resulting in the formation of equilibrium mixtures of compounds **8/10** or **9/11**, respectively (Scheme 2). The equilibrium ratios appear to be strongly affected by the temperature and by the nature of the ligand: at −20 °C and with the *para*-methoxy substituted ligand the reaction is completely shifted toward the carbonylated product **10**, while at the same temperature with the *ortho*-dimethyl substituted aryldiimine ligand a 70 : 30 ratio of **9** : **11** was observed. A six-membered chelate structure with the acetyl linked to palladium[12] was ruled out for compound **10** since the C=O stretching frequency (at 1721 cm^{-1}) and the corresponding ^{13}C resonance (at 205.1 ppm) of the terminal carbonyl group are sensibly different from those of a palladium O-coordinated acetyl moiety (around 1620 cm^{-1} and 230 ppm).[8,9] Analogous NMR evidence was also found for complex **11**. Moreover, NMR data of intermediates **10** and **11** gave an insight into the preferred conformation of the growing chain. Protons H^a and H^b (at around 2.7 and 1.7 ppm) appear strongly shielded in comparison with those of an analogous complex bearing an isopropyl-α-diimine ligand (3.5 and 2.6 ppm).[8b] This observation suggests that also in **10** and **11** both H^a and H^b are located in the shielding cone of the aromatic ring of the nitrogen ligand.‡ Moreover NOE experiments carried out on complex **10** by saturating H^x resulted in a considerable enhancement (3%) of the resonance due to aromatic protons of the nitrogen ligand, in agreement with a relatively short distance. On the basis of these experimental data, we deduce that the growing chain assumes the preferential conformation sketched in Scheme 2. We suggest that the next styrene insertion goes through an intermediate having a structure analogous to **10** and **11**, but with the olefin in place of CO. The geometry of this intermediate is crucial in the choice of the enantioface of the styrene unit. The four **I–IV** forms (Scheme 3) are in principle possible by arranging the olefin double bond perpendicular to the Pd coordination plane. In the case of *ortho*-substituted aryldiimine ligands, the forms **II** and **III** appear to be strongly disfavoured because of the steric hindrance between the phenyl rings of styrene and of the ligand; moreover, structure **IV** is also disfavoured due to steric interactions between the olefin and the aryl of the last inserted styrene unit. Thus, the preferred coordination of the olefin is likely to be that of intermediate **I**: this hypothesis is in agreement with the high isotacticity of the copolymer synthesized with this kind of ligands. Instead, in the case of aryldiimine ligands without *ortho*-substituents, it is probable that intermediates **II** and **III**, due to a minor steric hindrance, become energetically comparable to **I**: this assumption justifies the formation of atactic copolymers with these ligands. An analogous influence of aryldiimine ligands on the stereochemistry of alkene coordination was previously observed in

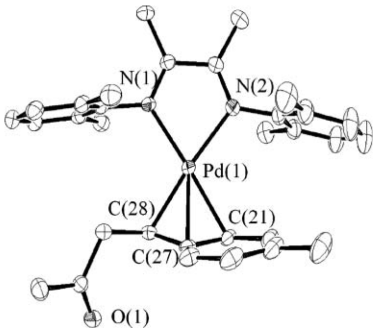
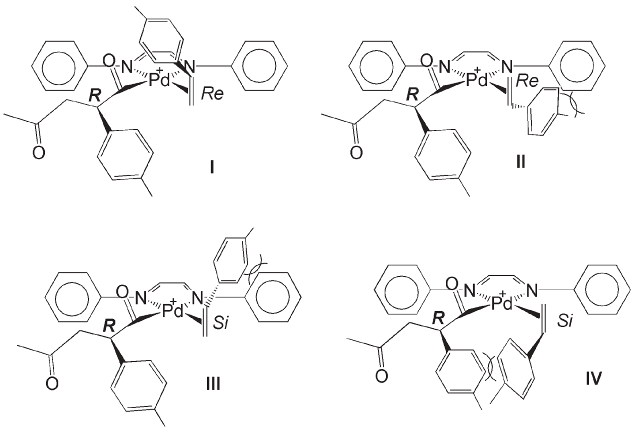


Fig. 1 ORTEP view (30% thermal ellipsoids) of the complex cation $(C_{31}H_{37}N_2OPd)^+$. Given the similarity of the two independent cations, only complex **9a** has been reported. Selected bond lengths (Å) for **9a** and **9b** (′ labels refer to complex **9b**): Pd(1)–N(1) 2.107(3), Pd(1)–N(2) 2.131(3), Pd(1)–C(21) 2.228(4), Pd(1)–C(27) 2.198(4), Pd(1)–C(28) 2.118(4), Pd(1′)–N(1′) 2.116(3), Pd(1′)–N(2′) 2.129(3), Pd(1′)–C(21′) 2.240(4), Pd(1′)–C(27′) 2.183(4), Pd(1′)–C(28′) 2.139(5).



Scheme 3 Possible intermediates for the enantioselective coordination of the second styrene unit in complexes **10** and **11**.

[Pt(Me)(η^2-olefin)(N–N)]$^+$ complexes.[13] To verify the stereoselectivity of the olefin insertion, complex **9** was dissolved in $CDCl_3$ saturated with CO and a second equivalent of *p*-methylstyrene was added. After 20 days at −20 °C the solvent was evaporated, yielding an orange powder which was found to be a mixture of the two η^3-allyl complexes **9** : **12** in a 25 : 75 ratio; NMR spectra reveal that the product of double olefin insertion **12**‡ exists in just one diastereoisomeric form that should correspond to a *RR* or *SS* configuration (Scheme 2), considering the isotacticity of the copolymer obtained with the catalyst bearing the *ortho*-dimethyl substituted aryldiimine ligand. The same experimental procedure with complex **8**, afforded a mixture of several compounds as shown by the complicated NMR spectrum. This is probably due to the non-stereoselective formation of products of double and multiple insertion. In summary, in this work the first intermediates of the CO/*p*-methylstyrene copolymerisation catalysed by aryl-α-diimine Pd complexes have been studied. Insertion of styrene in the Pd–acyl bond generates stable η^3-allyl species. Moreover, for the first time we determined the conformation of the growing chain in the acyl palladium intermediates responsible for the selection of the olefin enantioface. This result prompted us to propose, for the copolymerisation catalysed by these complexes, a novel mechanism which could be regarded as a ligand-assisted chain-end stereocontrol.

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Notes and references

‡ Selected IR and NMR data for compounds **8–12** (for labels refer to Scheme 2, *J* values are given in Hz).

8: IR (film): ν_{max}/cm^{-1} 1718.9 (C=O). NMR: δ_H (200 MHz; $CDCl_3$; Me_4Si; 253 K) 6.75 (2H, d, *J* = 7.3, H^m), 6.40 (2H, d, *J* = 7.3, H^o), 3.15 (1H, dd, *J* = 2.5, 9.6, H^x), 2.57 (1H, dd, *J* = 9.6, 18.9, H^a), 1.51 (1H, dd, *J* = 2.5, 18.9, H^b). δ_C (50 MHz; $CDCl_3$; Me_4Si; 253 K) 209.3 (s, (*C*=O)Me), 133.8 (s, CH^m), 118.9 (s, C-*ipso*), 109.8 (s br, CH^o), 53.1 (s, CH^x), 43.7 (s, CH^aH^b).

9: IR (film): ν_{max}/cm^{-1} 1718.8 (C=O). NMR: δ_H (200 MHz; $CDCl_3$; Me_4Si; 293 K) 6.54 (2H, d, *J* = 7.3, H^m), 6.33 (2H, d, *J* = 7.3, H^o), 3.17 (1H, dd, *J* 4.1, 18.7, H^b). δ_C (50 MHz; $CDCl_3$; Me_4Si; 293 K) 209.3 (s, (*C*=O)Me), 134.5 (s, CH^m), 116.8 (s, C-*ipso*), 106.1 (s br, CH^o), 55.5 (s, CH^x), 40.6 (s, CH^aH^b).

10: IR (CD_2Cl_2): ν_{max}/cm^{-1} 2130.3 (C≡O), 1720.5 (Pd(C=O) and (C=O)Me) cm^{-1}. NMR: δ_H (200 MHz; $CDCl_3$; Me_4Si; 223 K) 4.29 (1H, dd, *J* = 1.5, 10.0, H^x), 2.77 (1H, dd, *J* = 10.0, 18.6, H^a), 1.84 (1H, dd, *J* = 1.5, 18.6, H^b). δ_C (50 MHz; $CDCl_3$; Me_4Si; 223 K) 205.1 (s, *C*=OMe), 60.5 (s, CH^x), 45.1 (s, CH^aH^b).

11: NMR: δ_H (200 MHz; $CDCl_3$; Me_4Si; 253 K) 4.20 (1H, dd, *J* = 1.9, 10.2, H^x), 2.72 (1H, dd, *J* = 10.2,18.6, H^a), 1.67 (1H, dd, *J* = 1.9, 18.6, H^b). δ_C (50 MHz; $CDCl_3$; Me_4Si; 253 K) 204.5 (s, *C*=OMe), 59.9 (s, CH^x), 44.6 (s, CH^aH^b).

12: NMR: δ_H (200 MHz; $CDCl_3$; Me_4Si; 293 K) 6.59 (2H, d, *J* = 7.6, H^m), 6.45 (2H, d, *J* = 7.6, H^o), 3.84 (1H, dd, *J* = 2.9, 11.2, H^x), 3.36 (1H, dd, *J* = 11.2, 18.4, H^a), 2.81 (1H, dd, *J* = 4.3, 11.2, H^y), 2.60 (1H, dd, *J* = 2.9, 18.4, H^b), 2.53 (1H, dd, *J* = 11.2, 17.4, H^c), 1.27 (1H, dd, *J* = 4.3, 17.4, H^d). δ_C (50 MHz; $CDCl_3$; Me_4Si; 253 K) 134.4 (s, CH^m), 117.3 (s, C-*ipso*), 106.3 (s br, CH^o), 56.1 (s, CH^y), 52.6 (s, CH^x), 47.6 (s, CH^aH^b), 39.7 (s, CH^cH^d).

§ Rms value for the coordination sphere superimposition: 0.03 Å. Dihedral angle which defines the orientation of the –COMe group: −20.9(5)° for **9a** *vs.* 40.2(6)° for **9b**. *Crystal data* for **9**: $(C_{31}H_{37}N_2OPd)^+(C_{32}H_{12}BF_{24})^-$, M = 1423.27, triclinic, space group $P\bar{1}$, (no. 2), a = 15.903(3), b = 17.905(4), c = 23.331(4) Å, α = 104.04(2), β = 91.16(1), γ = 100.14(2)°, V = 6331(2) Å^3, T = 150 K, Z = 4, μ(Cu-Kα) = 3.383 mm^{-1}, 176884 reflections measured, 24149 unique (R_{int} = 0.0362). The final R value for all data was 0.0637. CCDC 647672. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707107h

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