

Quantitative formation of the intermediate of alkene insertion in the copolymerization of *p*-methylstyrene and carbon monoxide catalyzed by $[(\text{Pr}^i\text{DAB})\text{Pd}(\text{Me})(\text{NCMe})]^+\text{BAR}_4^-$

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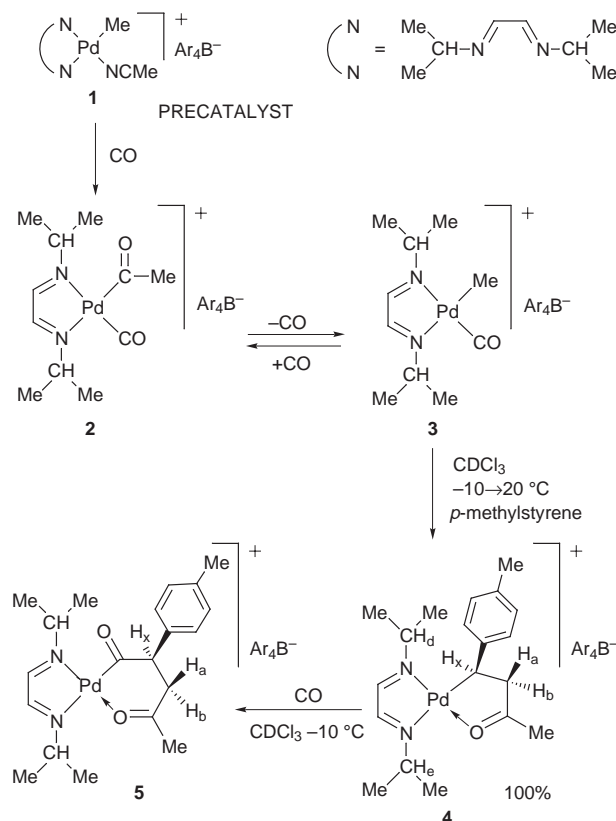
The intermediate after the first CO and *p*-methylstyrene insertion in the chain growth process of the copolymerization of these monomers has been quantitatively obtained from $[(\text{Pr}^i\text{DAB})\text{Pd}(\text{Me})(\text{NCMe})]^+[\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4\text{B}]^-$ in CHCl_3 at 20 °C.

In recent years there has been increasing interest in carbon monoxide olefin copolymerization.¹ We and others have found that ionic Pd complexes with non-coordinating anions and chiral nitrogen ligands, such as bioxazolines, are active precatalysts for the copolymerization of styrene and carbon monoxide, to yield isotactic optically active polymers.^{2,3} The use of achiral nitrogen ligands, however, leads to syndiotactic copolymers.⁴

From our recent study, the objective of which was to test the catalytic properties of various nitrogen ligands with different π -acceptor capacity,⁵ the complex $[(\text{Pr}^i\text{DAB})\text{Pd}(\text{Me})(\text{NCMe})]^+[\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4\text{B}]^-$ **1** (Pr^iDAB = 1,4-diisopropyl-1,4-diaza-but-1,3-diene) proved to be a very active precatalyst in the copolymerization of styrene and 4-methylstyrene with carbon monoxide, giving alternating syndiotactic polyketones under very mild conditions (1 bar CO and 0 °C). In addition, the complex **1** is a convenient starting point for modelling the first steps of the polymer chain growth, as described here.

By exposure of the precatalyst solution **1** to a CO atmosphere, under conditions used for the copolymerization reaction, the corresponding acetyl carbonyl complex **2**[‡] was obtained, which reversibly releases one CO group; bubbling nitrogen through a CH_2Cl_2 solution at -15 °C resulted in the formation of **3**, and exposure of the solution of **3** to CO atmosphere led to the regeneration of **2**[‡] (Scheme 1). The structure of **3**[§] was confirmed by the presence, in the ¹³C NMR spectrum, of the Pd-CO resonance at δ 174.8 and by the absence of the acetyl signals.

We then focused our attention on the next step, the olefin insertion, to see whether our catalytic system would allow quantitative insertion and isolation of the reaction product. We performed the reaction using directly the more reactive compound **3** which was isolated as a white powder from **2**. By adding an equimolar amount of *p*-methylstyrene at -10 °C to a slightly yellow CHCl_3 solution of **3** and heating gently to 20 °C, a colour change to dark orange occurred. The new compound formed in 100% yield corresponds to the 5-membered palladacycle **4**, in agreement with the NMR evidence.[¶] In particular, in the carbonyl region of the ¹³C NMR spectrum, the resonance of a typical acetyl group at δ 224.9 is present, while the Pd-CO signal has disappeared. This result is confirmed by the IR spectrum, which shows an absorption at 1721 cm^{-1} for the acetyl CO coordinated to Pd.^{‡,6f} Moreover, the CH₂ and CH signals are detected in the DEPT ¹³C NMR spectrum. The CH-CH₂ fragment is confirmed by the corresponding three-spin pattern observed in the ¹H NMR spectrum, where the relatively high value of the geminal coupling $J_{ab} = -19.7$ Hz is typical of a CH₂ linked to a CO group, while the values of the two vicinal couplings, $J = 8.3$ and 3.5 Hz, are representative of two



Scheme 1

substantially different dihedral angles. Evidence for two non-equivalent isopropyl groups is given by the two different CH chemical shifts observed in both the ¹H and ¹³C NMR spectra. Moreover, the two methyl groups, within each isopropyl group, are non-equivalent due to the dissymmetry introduced by the styrene monomeric unity. The signals of the two *meta* aromatic hydrogens are assigned on the basis of NOEs with the adjacent methyl, while the remaining *ortho* aromatic hydrogens show NOEs with CH_x. The *ortho* hydrogens also show NOEs with CH_d, thus allowing the assignment of the latter. Moreover the NOE observed between the *ortho* hydrogens and CH_a but not CH_b is in agreement with an orientation of the phenyl group closer to CH_a. Therefore the conformation across the CH-CH₂ bond is as depicted in the Newmann projection in Fig. 1, in agreement also with the values of $J_{ax} = 8.3$ and $J_{bx} = 3.5$ Hz,

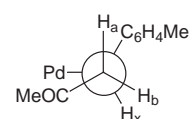


Fig. 1

due to nearly *anti* and *gauche* relationships, respectively. This suggests that the conformation of the pentatomic ring is slightly folded.

Insertions of different alkenes into metal–acyl bonds have already been reported^{6,1j} but to the best of our knowledge there are in the literature only two examples of reaction of styrene with a palladium–acyl complex. After insertion, the reaction products have been described either as a mixture of allylic and chelate structures in very rapid equilibrium^{1c} or as an allylic intermediate.⁷ Therefore it appears that the quantitative formation of 5-membered palladacycle **4** as the only observable species is unprecedented. Compound **4** can be isolated as a relatively stable dark red oil by removing the solvent under reduced pressure; in CHCl₃ solution it proved to be stable up to 50 °C.

In the next step, CO was bubbled through a solution of **4** in CHCl₃ at –10 °C for 15 min, yielding the six-membered chelate complex **5** in solution. Evidence for the insertion of CO comes from the doubling of the CO signals in the ¹³C NMR spectrum and in the IR spectrum. The deshielding observed for both the proton and carbon resonances of the CH group of the CH–CH₂ fragment shows that the CO has inserted into the Pd–CH bond, as expected.^{1j}

In conclusion, the results of this work show that by using the proper ligand it has been possible for the first time to quantitatively obtain and determine the conformation of the first intermediate in the syndiotactic copolymerization of CO and styrene derivatives, *i.e.* the 5-membered palladacycle **4**; it results from the insertion of *p*-methylstyrene into the Pd–acyl bond formed in **3** as a result of α -methyl migration. Furthermore, it has been possible to obtain the new complex **5** which represents the second step of the copolymerization reaction.

We are currently exploring the use of the isolable complex **4**, as a preformed catalyst, for the synthesis of syndiotactic copolymers.

We thank Professor C. J. Elsevier (University of Amsterdam) for helpful discussions. This work was supported by Ministero dell'Università e della Ricerca Scientifica e Tecnologica and Consiglio Nazionale delle Ricerche.

Notes and References

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‡ Selected data for **2**: $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2, -75\text{ }^\circ\text{C})$ 7.98 and 7.92 (s, 1 H each, CH=N), 7.65 (s, 8 H, Ar-H_o), 7.47 (s, 4 H, Ar-H_p), 3.72 [m, 2 H, CH(CH₃)₂], 2.67 (s, 3 H, COCH₃), 1.10 [d, J_{HH} 6.1, 12 H, CH(CH₃)₂]; $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2, -75\text{ }^\circ\text{C})$ 214.5 (COCH₃), 172.9 (Pd–CO), 164.1 and 160.5 (C=N), 162.1 (q, $^1J_{\text{CB}}$ 49.4, Ar-C_i), 134.9 (Ar-C_o), 128.9 (q, $^2J_{\text{CF}}$ 31.4, Ar-C_m), 124.7 (q, $^1J_{\text{CF}}$ 272.6, CF₃), 117.9 (Ar-C_p), 63.8 and 59.5 [CH(CH₃)₂], 41.6 (COCH₃), 23.2 and 22.0 [CH(CH₃)₂]; $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 2137 (Pd–CO), 1750 (COCH₃), 1611 (C=N). Compound **2** can also be synthesized directly by reaction of Pr⁺DABPdMeCl and Na⁺BAR₄[–] in the presence of CO.

§ Selected data for **3**: $\delta_{\text{H}}(\text{CDCl}_3, -20\text{ }^\circ\text{C})$ 7.96 and 7.92 (s, 1 H each, CH=N), 7.69 (s, 8 H, Ar-H_o), 7.54 (s, 4 H, Ar-H_p), 4.13 and 3.77 [sept, 1 H each, CH(CH₃)₂], 1.36 (s, 3 H, Pd–CH₃), 1.25 [d, J_{HH} 6.7, 12 H, CH(CH₃)₂]; $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2, 0\text{ }^\circ\text{C})$ 174.8 (Pd–CO), 165.8 and 160.1 (C=N), 161.5 (q, $^1J_{\text{CB}}$ 49.6, Ar-C_i), 134.6 (Ar-C_o), 128.7 (q, $^2J_{\text{CF}}$ 30.0, Ar-C_m), 124.3 (q, $^1J_{\text{CF}}$ 272.5, CF₃), 117.5 (Ar-C_p), 63.4 and 56.3 [CH(Me)₂], 22.7 and 21.8 [CH(CH₃)₂], 5.7 (Pd–CH₃); $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 2130 (Pd–CO), 1610 (C=N). Compound **3** was isolated as a white powder.

¶ Selected data for **4**: $\delta_{\text{H}}(\text{CDCl}_3, -3\text{ }^\circ\text{C})$ 7.80 and 7.78 (s, 1 H each, CH=N), 7.71 (s, 8 H, Ar-H_o), 7.54 (s, 4 H, Ar-H_p), 7.20 and 7.00 (d, 2 H each, Ph-H_o, Ph-H_m), 3.88 [sept, 1 H, CH_d(CH₃)₂], 3.68 [sept, 1 H, CH_e(CH₃)₂], 3.76 (dd, J_{HH} 8.3 and 3.5, 1 H, CH_κ–CH₂), 3.04 (dd, J_{HH} 19.7 and 8.3, 1 H, CH–CH₂), 2.70 (dd, J_{HH} 19.4 and 3.5, 1 H, CH–CH₂), 2.39 (s, 3 H, CO–CH₃), 2.19 (Ph–CH₃), 1.29, 1.17 and 1.09 [d, J_{HH} 6.4, 12 H, CH(CH₃)₂]; $\delta_{\text{C}}(\text{CDCl}_3, -20\text{ }^\circ\text{C})$ 224.9 (COCH₃), 161.7 (q, $^1J_{\text{CB}}$ 49.2, Ar-C_i), 161.2 and 157.1 (C=N), 139.9 (Ph-C_i), 134.8 (Ar-C_o), 132.1 (Ph-C_o), 130.8 (Ph-C_p), 128.8 (q, $^2J_{\text{CF}}$ 31.5, Ar-C_m), 124.5 (q, $^1J_{\text{CF}}$ 272.4, CF₃), 119.9 (Ph-C_m), 117.6 (Ar-C_p), 62.1 and 59.5 [CH(Me)₂], 52.0 (CH–CH₂), 47.0 (CH–CH₂), 29.2 (COCH₃), 22.8, 22.0, 21.4 and 21.3 [CH(CH₃)₂], 21.9 (Ph–CH₃); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1721 (CO), 1610 (C=N).

|| Selected data for **5**: $\delta_{\text{H}}(\text{CDCl}_3, -20\text{ }^\circ\text{C})$ 7.80 (s, 2 H, CH=N), 7.73 (s, 8 H, Ar-H_o), 7.58 (s, 4 H, Ar-H_p), 7.22 (s, 4 H, Ph-H_o, Ph-H_m), 4.65 (dd, J_{HH} 10.6 and 2.0, 1 H, CH–CH₂), 3.79 [br s, 2 H, CH(CH₃)₂], 3.60 (dd, J_{HH} 18.7 and 11.3, 1 H, CH–CH₂), 2.80 (d, J_{HH} 18.7, 1 H, CH–CH₂), 2.33 (s, 3 H, Ph–CH₃), 2.29 (s, 3 H, CO–CH₃), 1.21 and 1.10 [d, J_{HH} 6.1, 12 H, CH(CH₃)₂]; $\delta_{\text{C}}(\text{CDCl}_3, -20\text{ }^\circ\text{C})$ 211.7 and 207.1 (CO–CH₃, CO–CH), 161.7 (q, $^1J_{\text{CB}}$ 49.6, Ar-C_i), 140.4 (Ph-C_i), 134.8 (Ar-C_o), 130.9 (Ph-C_o), 129.5 (Ph-C_m), 128.8 (q, $^2J_{\text{CF}}$ 30.5, Ar-C_m), 124.5 (q, $^1J_{\text{CF}}$ 272.7, CF₃), 117.8 (Ar-C_p), 61.9 (CH–CH₂), 46.2 (CH–CH₂), 30.1 (CO–CH₃), 22.5 [CH(CH₃)₂], 21.2 (Ph–CH₃); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1722 (br, CO), 1610 (C=N).

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Received in Liverpool, UK, 9th February 1998; 8/01158C