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Ligand driven σ,π-η^3 structural rearrangements of organopalladium complexes: their relevance to the CO/styrene copolymerisation reaction

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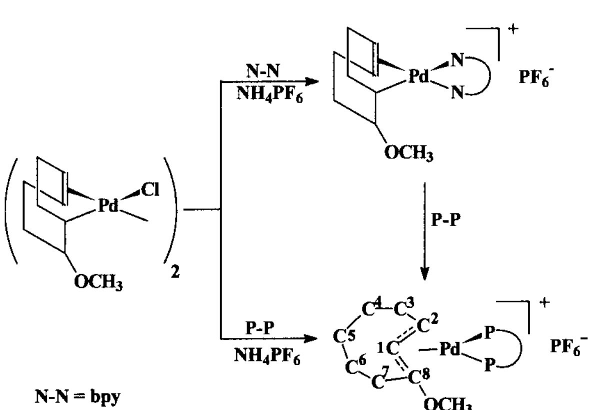
Received 10th July 2000, Accepted 11th August 2000

The crystal structure and the full characterisation in solution of a palladium(II)–π-allylic compound is reported; its chemical behaviour may shed some light on the mechanism of the CO/styrene copolymerisation promoted by Pd(II) complexes.

In the last few years much attention has been addressed to the CO/olefins co- and ter-polymerisation reactions yielding perfectly alternating polyketones.[1] This reaction is homogeneously catalysed by palladium-based systems modified by phosphorus- or nitrogen-donor chelating ligands (P–P or N–N).[1] Early studies showed that there is a close relationship between the nature of the olefin co-monomer and the ancillary ligand. In particular, Consiglio *et al.* reported that the catalytic system based on diphosphine ligands, such as 1,3-bis(diphenylphosphino)propane (dppp), the most active for the CO/ethylene copolymerisation, does not promote the CO/styrene one, yielding, instead, *E*-1,5-diphenylpent-1-en-3-one.[2] Despite the subsequent development of research in this area, the reason for this peculiar behaviour is still unclear.

We reported that the complexes [Pd(η^1,η^2-$C_8H_{12}OMe$)(bpy)][X] (**1**) [bpy = 2,2′-bipyridine, X = BPh_4^-, $CF_3SO_3^-$, BF_4^-, PF_6^-, SbF_6^-, B{3,5-$(CF_3)_2C_6H_3$}$_4^-$], synthesised through the reaction of [Pd(η^1,η^2-$C_8H_{12}OMe$)Cl]$_2$ with the N–N ligand in methanol,[3] promote the CO/styrene copolymerisation in methylene chloride under very mild reaction conditions (room temperature and atmospheric pressure).[4]

We have now found that the reaction of the [Pd(η^1,η^2-$C_8H_{12}OMe$)Cl]$_2$ precursor with the phosphorus-donor ligand dppp, instead of bpy, in methanol, results in a rearrangement of the organometallic fragment, yielding the product [Pd(η^3-$C_8H_{12}OMe$)(dppp)][PF_6] (**2**) (Scheme 1).† The same complex is also obtained starting from [Pd(η^1,η^2-$C_8H_{12}OMe$)(bpy)][PF_6] upon addition of dppp, either in methanol or in aprotic solvents (Scheme 1).‡ Addition of diethyl ether to an acetone solution of **2** yielded single crystals suitable for X-ray analysis.



Scheme 1

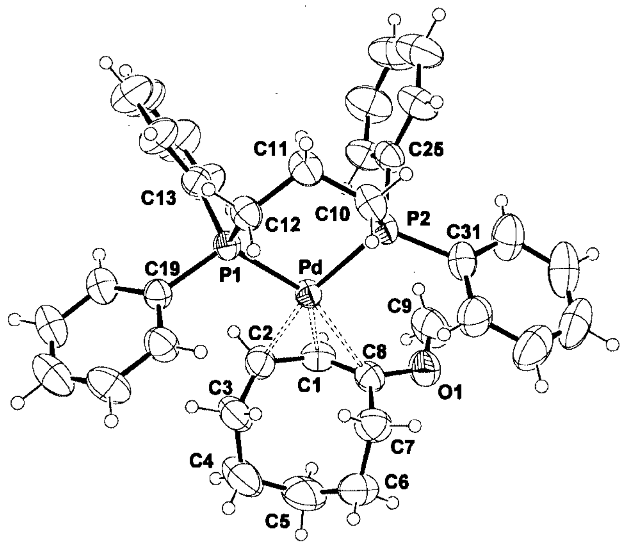


Fig. 1 ORTEP[20] view (40% thermal ellipsoids) of the complex cation **2**. Selected bond lengths (Å), angles (°) and torsion angles (°): Pd–C(1) 2.168(4), Pd–C(2) 2.162(5), Pd–C(8) 2.507(5), Pd–P(1) 2.287(1), Pd–P(2) 2.309(1), O(1)–C(8) 1.354(6), O(1)–C(9) 1.417(7), C(1)–C(2) 1.403(7), C(1)–C(8) 1.370(7); P(1)–Pd–P(2) 94.55(4), C(2)–Pd–C(8) 63.1(2), C(8)–O(1)–C(9) 118.8(4), C(8)–C(1)–C(2) 124.9(5), C(1)–C(2)–C(3) 126.8(5); C(2)–C(1)–C(8)–O(1) −176.6(5), C(9)–O(1)–C(8)–C(1) 13.5(8).

The molecular structure clearly indicates a π-allyl fragment in the complex cation as shown in the ORTEP view of Fig. 1.§ The phosphine ligand possesses a chelate angle of 94.55(4)° and the Pd–P separations of 2.287(1) and 2.309(1) Å fall in the expected range for P donors *trans* to an allylic ligand,[6–8] the slightly shorter bond length pertaining to phosphorus *trans* to allyl carbon C(8) (*vide infra*).

On the other hand, the allyl fragment exhibits several noteworthy features. It is unsymmetrically coordinated to the metal center with comparable values for the Pd–C(1) and Pd–C(2) bond distances [2.168(4) and 2.162(5) Å, respectively], while the third carbon atom is significantly further from the palladium [Pd–C(8) 2.507(5) Å]. The methoxy substituent, coplanar with the allyl group, exhibits a *syn* configuration, as evidenced by the C(9)–O(1)–C(8)–C(1) torsion angle of 13.5°. This planar arrangement favours the overlap of an oxygen lone pair with the allyl π-orbitals leading to a significant double bond character between the oxygen and the allyl carbon atom (the C(8)–O(1) bond distance of 1.354(6) Å is, in fact, intermediate between a carbon–oxygen double bond and a single one). A similar weaker interaction with the allyl carbon bound to a methoxy-group has already been detected in complexes with different coordination spheres, namely Rh [coordination

DOI: 10.1039/b005492p

distances of 2.179(4), 2.145(4), 2.233(4) Å],[9] and Mo [2.308(5), 2.228(5), 2.453(5) Å].[10]

In the present complex the strong π conjugation in the allyl-methoxy group and steric interactions between the methoxy and the phenyl group of the diphosphine [C(31)···O(1) distance of 3.45 Å] may account for the differences observed in the coordination Pd–allyl distances.

The π-homoallylic structure is retained in solution, as deduced from the ^{1}H and ^{13}C NMR analysis.† The main feature of the ^{1}H NMR spectrum of **2**, measured in CD_2Cl_2 at room temperature, is the lack of the two multiplets at 6.09 and 5.91 ppm typical for the olefin protons of the cyclooctene moiety.[4] They are replaced by a doublet (4.83 ppm) and a multiplet (3.92 ppm), coupled to each other, in agreement with the literature,[11] indicating the presence of two protons of an allylic fragment. The signal at lower field of the two is assigned to the proton bound to the carbon atom C1 (see Scheme 1 for the numbering system of η^3-$C_8H_{12}OMe$), as deduced by the clear NOE with the methoxy group, thus indicating that the *syn* configuration is also present in solution. In the ^{13}C NMR spectrum, the signals of carbon atoms bound to palladium (C1 and C2 at 85.6 and 69.2 ppm, respectively) have chemical shifts typical for an allylic system.[12] The signal of the third carbon atom (C8) of the allylic moiety is at 155.0 ppm, due to the bond with the oxygen atom of the methoxy group. This downfield shift has already been reported for a palladium–allylic system bearing such a substituent.[10,13] These three signals also show a different fine structure, thus confirming their different relative position with respect to the phosphorus atoms. Actually, both the resonances of C2 and C8 are a double doublet (even though that due to C8 is not very well resolved), indicating coupling with the *cis* and *trans* phosphorus atoms, respectively. On the other hand, the signal of C1 is a triplet suggesting a pseudoequivalence of the two phosphorus atoms with respect to it.

In the ^{1}H NMR spectrum, at room temperature, the signals of the propylenic bridge of dppp and those of the protons from H3 to H7 are broad. Decreasing the temperature (from 293 K to 213 K) resulted only in a further broadening, while the signals of the allylic moiety were not significantly affected by temperature, thus indicating that they are not involved in a dynamic process. The stability of the *syn* configuration seems to be a feature of π-allylic systems substituted with a methoxy group.[10]

The compound we obtained is the result of a rearrangement of the organometallic fragment from a σ,π-enyl cooordination mode to a π-allylic one, involving the C8-atom. Similar cyclic palladium–allylic systems are reported in the literature, but in no case is the C-atom bearing the alkoxy group part of the allylic fragment.[14] Therefore, the above rearrangement implies a migration of the C–C double bond. As a first step of the mechanism a β-hydrogen elimination from the carbon atom substituted with the methoxy group of the $C_8H_{12}OMe$ ligand, either on the starting dimer or on **1**, is proposed, in agreement with the literature.[15] Subsequent hydride-migrations/elimination reactions may occur yielding the final product. A similar mechanism was reported for the η^4-diene$\rightarrow\eta^3$-allyl rearrangement of the cycloocta-1,5-diene ligand in ruthenium–phosphine complexes.[16] Our results indicate that the $\sigma,\pi\rightarrow\eta^3$ rearrangement is induced by the diphosphine ligand.

When complex **2** was tested as a catalyst precursor for the CO/ethylene and CO/styrene copolymerisations, under the reaction conditions reported for complex **1**, no formation of polyketone was observed.¶

From a critical review of the literature, the following observations are summarised: 1. The diphosphine ligands (P–P) promote the CO/aliphatic olefins copolymerisation, but do not promote the CO/aromatic ones;[2] 2. The nitrogen-donor ligands (N–N) promote copolymerisation of CO with both aliphatic and aromatic olefins;[1,17] 3. The CO/styrene copolymerisation promoted by N–N ligands involves an equilibrium between a chelate and a π-benzylic intermediate;[18] 4. It is suggested that in the initiation step of the CO/styrene copolymerisation the Pd–styryl intermediate is so strongly stabilised by the π-benzylic coordination so as to prevent CO insertion;[1c] 5. A series of Pd–diphosphine complexes containing a benzyl ligand, synthesised on protonation of the corresponding styrene derivatives, shows that, in all cases, the π-benzylic linkage is the preferred coordination mode.[19]

On the basis of the above considerations and of the obtained results we propose that the inactivity of P–P ligands towards the CO/aromatic olefins copolymerisation may be due to the inertness of the π-allylic (or π-benzylic) fragment towards CO insertion.‖ Therefore, in this case the β-hydrogen elimination becomes the fastest reaction, yielding the compound *E*-1,5-diphenylpent-1-en-3-one,[2] instead of the polyketone.

Acknowledgements

This work was supported by Ministero dell'Università e della Ricerca Scientifica (MURST-Rome) grant no. 9903153427.

Notes and references

† Complex **2** was synthesised as previously reported,[4] by adding dppp instead of bpy. The solid obtained is yellow; yield 0.54 g, 86%. Found: C, 53.0; H, 5.02%. $C_{36}H_{41}OF_6P_3Pd$ requires: C, 53.84; H, 5.15%. δ_H (400 MHz; solvent CD_2Cl_2, referenced to the solvent peak *versus* TMS at δ 5.30; $T = 293$ K): 7.53–7.40 [20 H, m, Ph], 4.83 [1 H, d, H1], 3.92 [1 H, m, H2], 3.13 [3 H, s, OCH_3], 2.66 [4 H, br m, CH_2-P], 2.39 [1 H, br m, H_A7], 2.02 [1 H, br m, CH_{2A}-CH_2-P], 1.88 [1 H, br m, H_B7], 1.65 [1 H, br m, CH_{2B}-CH_2-P], 1.45–1.31 [8 H, br m, $H_{A,B}$6, $H_{A,B}$5, $H_{A,B}$4, $H_{A,B}$3]; δ_C (100.5 MHz; solvent CD_2Cl_2, referenced to the solvent peak *versus* TMS at δ 53.8; $T = 293$ K): 155.0 [dd, ^2J(C–P) = 3.7 Hz, C8], 134.0–129.0 [m, Ph], 85.6 [t, ^2J(C–P) = 5.5 Hz, C1], 69.2 [dd, ^2J(C–P) = 5.5 Hz, ^2J(C–P) = 31.2 Hz, C2], 56.5 [s, OCH_3], 37.5 [s, C7], 30.0 [d, C6 or C5 or C4 or C3], 28.0–27.0 [m, CH_2-P and C6 or C5 or C4 or C3], 26.0 [m, C6 or C5 or C4 or C3], 22.8 [s, C6 or C5 or C4 or C3], 18.5 [s, CH_2-CH_2-P]; δ_P (161.86 MHz; solvent CD_2Cl_2; H_3PO_4 as external reference; $T = 293$ K): 11.1 [d, $^2J(P_A$-$P_B) = 56.5$ Hz, P_A or P_B], 6.1 [d, $^2J(P_A$-$P_B) = 56.5$ Hz, P_A or P_B].

‡ The ligand dppp (0.28 g, 0.68 mmol) was added to a suspension of [Pd(η^1,η^2-$C_8H_{12}OMe$)(bpy)][PF_6] (0.31 g, 0.57 mmol) in methanol (20 mL), yielding a yellow solution. After a few minutes the product precipitated as a yellow solid. It was stirred at room temperature for 30 min, filtered off, washed with diethyl ether and dried under vacuum. Yield: 0.27 g, 60%. Found: C, 53.0; H, 4.89%. $C_{36}H_{41}OF_6P_3Pd$ requires: C, 53.84; H, 5.15%.

§ Crystallography. $C_{36}H_{41}F_6OP_3Pd$, $M = 803.00$, monoclinic, space group $P2_1/n$, $a = 10.716(2)$, $b = 18.008(2)$, $c = 18.978(4)$ Å, $\beta = 98.01(1)$°, $V = 3626.5(11)$ Å^3, $Z = 4$, $D_{calc} = 1.471$ g cm^{-3}, μ(Mo-Kα) = 0.703 mm^{-1}, $T = 293$ K, $R1 = 0.0490$, $wR2 = 0.1256$ for 8213 unique reflections. All the calculations were performed using the WinGX System, Ver 1.63.[5] CCDC reference number 186/2140. See http://www.rsc.org/suppdata/dt/b0/b005492p/ for crystallographic files in .cif format.

¶ When the complex **1** was used as precatalyst for the CO/ethylene copolymerisation under the same reaction conditions reported for the CO/styrene one,[4] a productivity of 19 g CP/g Pd was obtained.

‖ When complex **1** (30 mM, CD_2Cl_2, room temperature) was treated with carbon monoxide (1 atm) all of the signals in the ^{1}H NMR spectrum broadened and a red solid precipitated. On the other hand, when carbon monoxide was bubbled into a solution of **2** (30 mM, CD_2Cl_2, room temperature) no change in the ^{1}H NMR spectrum was observed.

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