New structurally rigid palladium catalysts for the alternating copolymerization of carbon monoxide and ethene†

Claudio Bianchini,*[a] Hon Man Lee,[a] Andrea Meli,[a] Werner Oberhauser,[a] Francesco Vizza,[a] Peter Brüggeller,[b] Rainer Haid[b] and Christoph Langes[b]

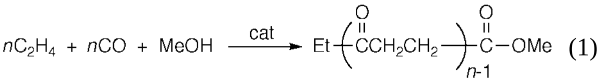
[a] *Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, ISSECC-CNR, 50132 Firenze, Italy. E-mail: bianchin@fi.cnr.it*

[b] *Institut fuer Allgemeine, Anorganische und Theoretische Chemie der Universitaet Innsbruck, Innrain 52a, Innsbruck, Austria*

Received (in Cambridge, UK) 20th December 1999, Accepted 28th March 2000

Decreasing the flexibility of the $Ph_2PCH_2CH_2PPh_2$ (dppe) backbone by making the central carbon atoms part of a cyclobutane ring leads to the formation of Pd(II) catalysts for CO/ethene copolymerization that are more efficient than those of dppe by a factor of ten.

Polyketones obtained by alternating copolymerization of carbon monoxide and olefins are important innovative materials prepared on industrial scale by homogeneous palladium catalysis [eqn. (1)].[1]

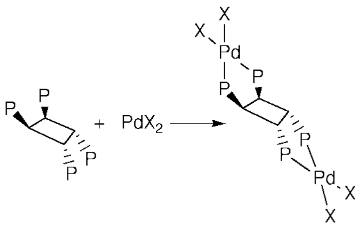


$$n\mathrm{C_2H_4} + n\mathrm{CO} + \mathrm{MeOH} \xrightarrow{\text{cat}} \mathrm{Et}\left(\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2}\right)_{n-1}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{OMe} \qquad (1)$$

The diphosphine 1,3-bis(diphenylphosphino)propane (dppp) is the ligand of choice for the copolymerization of CO and ethene;[2,3] indeed, dppp forms Pd(II) catalysts that are more efficient than those with the lower homologue 1,2-bis(diphenylphosphino)ethane (dppe) by almost one order of magnitude.[1–3] The ability of the chelate ring size (as determined by the number of carbon atoms separating the PPh_2 groups) to modulate the flexibility of the Pd(P–P) moiety is the factor that, most commonly, is invoked to account for the dramatically different activity of the dppp and dppe catalysts.[3–5] In particular, several studies have tried to correlate the greater catalytic activity of the dppp complexes to the higher flexibility of the dppp backbone as compared to that of dppe.[3–5]

In this work, we prove experimentally that efficient Pd catalysts are formed also with diphosphine ligands containing two carbon atoms between the PPh_2 donors on the condition, however, that ligand *flexibility* is substantially *reduced*.

Reaction of the tetraphosphine *cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane[6] (*cyclo*-tetraphos) with 2 equiv. of either $Pd(CO_2Me)_2$ or $PdCl_2$ in CH_2Cl_2 yielded the bimetallic complexes Pd_2(*cyclo*-tetraphos)$(OCOMe)_4$ **1** and Pd_2(*cyclo*-tetraphos)Cl_4 **2**, respectively.‡ The latter complex was quantitatively transformed into the acetonitrile derivatives $[Pd_2$(*cyclo*-tetraphos)$(MeCN)_4]Y_4$, **3** Y_4 (Y = PF_6 or BF_4) by treatment with AgY in acetonitrile solution.



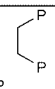
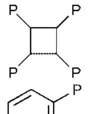
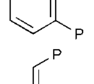
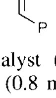
1 X = CO_2Me
2 X = Cl

Under standard copolymerization conditions (Table 1),[2,3] **1** and **3** $(PF_6)_4$ give rise to the same catalyst system with a productivitiy of 10 kg of polyketone (g of Pd)$^{-1}$ (entry 2). This productivity value is higher than that obtained with Pd(dppe)$(OCOMe)_2$ **4** by a factor of *ten* (entry 1) and is comparable with that of the industrial catalyst Pd(dppp)$(OCOMe)_2$.[2,3] The increase in productivity using either **1** or **3**$(PF_6)_4$ in the place of **4** is not accompanied by a change in the average molecular weights of the copolymers (*ca.* 6 kg mol^{-1}).[3,7]

A single-crystal X-ray analysis has been carried out on **3**$(BF_4)_4\cdot 2MeCN\cdot 3.4CH_2Cl_2$.§ As is shown in Fig. 1, a perfectly planar cyclobutane ring connects two equivalent $(-PPh_2)_2Pd(NCMe)_2$ moieties in each of which the Pd(II) centres adopts a slightly distorted square-planar coordination. The bond angles and distances in the cyclobutane ring are close to those of an ideal square. The P–Pd–P chelate angle and the Pd–P distances are in the usual range for dppe Pd(II) complexes with nitrogen ligands.[8] The two symmetry-related metalla-rings in **3** adopt an envelope conformation. As a consequence, each phosphorous centre of the asymmetric unit exhibits one equatorial and one axial phenyl group with the two axial phenyl rings being related by a mirror plane. The conformation of the metalla-ring and the mutual disposition of the phenyl substituents represent the most striking difference between **3** and square-planar dppe complexes in which the ligand generally assumes a twisted conformation and the phenyl groups can be all equatorial.[8,9] Therefore, in terms of steric hindrance (quadrant effect),[10] each palladium centre in **3** has a larger space for coordination and reactivity than in dppe complexes.

Since the envelope conformation of each metalla-ring is maintaned in solution, at least on the NMR time scale, the remarkable increase in catalytic activity of the *cyclo*-tetraphos

Table 1 Alternating CO/C_2H_4 copolymerization catalyzed by Pd(P–P)$(OCOMe)_2$[a]

Complex	P–P Ligand	Entry	Copolymer productivity[b]
4		1	1.1
1, **3**		2	9.8
5		3	6.4
6		4	5.5

[a] *Conditions*: catalyst (0.01 mmol based on Pd), MeOH (100 mL), 1,4-benzoquinone (0.8 mmol), *p*-toluenesulfonic acid (0.2 mmol), initial $p(C_2H_4)$ (300 psi), initial p(CO) (300 psi), temperature (85 °C), time (3 h), stirring rate (1400 rpm). [b] Productivity expressed as kg of polymer (g Pd)$^{-1}$.

---

† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b0/b000376j/ for crystallographic data in .cif format.

DOI: 10.1039/b000376j

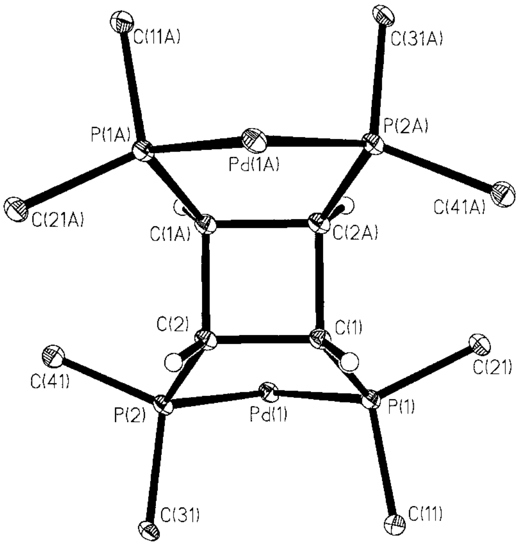


Fig. 1 ORTEP drawing of **3**$(BF_4)_4 \cdot 2MeCN \cdot 3.4CH_2Cl_2$ (coordinated MeCN ligands are omitted for clarity). Selected bond lengths (Å) and angles (°): Pd–P(1) 2.2484(8), Pd–N(1) 2.070(3), Pd–P(2) 2.2505(8), Pd–N(2) 2.077(3), P(1)–Pd–P(2) 82.81(3), N(1)–Pd–N(2) 89.35(12), N(1)–Pd–P(1) 93.94(9), N(2)–Pd–P(1) 174.63(9), N(1)–Pd–P(2) 176.72(9), N(2)–Pd–P(2) 93.85(9).

complex as compared to the dppe derivative may reasonably be associated to the substantial rigidity of the former that ultimately controls the steric hindrance at the metal centre. In an attempt to verify this hypothesis, the structurally rigid complexes Pd(*o*-dppbe)$(OCOMe)_2$ **5** and Pd(*cis*-dppen)$(OCOMe)_2$ **6** have been prepared and employed as catalyst precursors for CO/C_2H_4 copolymerization under the same experimental conditions [*o*-dppbe = *o*-bis(diphenylphosphino)benzene, *cis*-dppen = *cis*-bis(diphenylphosphino)ethylene].‡ Neither **5** and **6** are as efficient as **1** or **3** in the copolymerization reaction (likely due to the different electronic nature of the phosphine donors), but still the productivities are *ca.* six times higher than that of the dppe precursor **4**, yielding copolymers with comparable chain lengths.[3,7]

In conclusion, we have shown here that high rigidity of the control ligand is a structural feature that improves CO/olefin copolymerization Pd(II) catalysts. Recent studies with dppp-based catalysts are consistent with the present results as it has been found that the introduction of methyl substituents into the dppp backbone has beneficial effects on the copolymerization rate.[11] Conformational rigidity has also been invoked to account for the higher activity of the C_4-bridged bis(tetramethylphosphole) complex $[(Me_4C_4P)_2X]Pd(CO_2Me)_2$ [X = $CH_2(C_6H_4)CH_2$] as compared to C_2- [X = $(CH_2)_2$] and C_3-bridged [X = $(CH_2)_3$] analogs. The copolymerization activity of the *o*-xylene-bridged bis(phosphole)-based complex is, however, quite low [300 g of polymer (g Pd)$^{-1}$ h^{-1}].[12]

Shell International Chemicals B. V. (Amsterdam) is gratefully acknowledged for financing a post-doctoral program to H. M. L. at ISSECC-CNR.

Notes and references

‡ *Selected spectroscopic data*: **1**: δ_P(CD_2Cl_2, 81.01 MHz) 67.0 (s). δ_H(CD_2Cl_2, 200.13 MHz) 1.46 (s, 12H, $OCOCH_3$), 4.26 (pseudo t, $^2J_{HP}$ 7.0 Hz, 4H, CH), 7.15–7.64 (m, 40H, aromatic protons). δ_C(CD_2Cl_2, 50.32 MHz) 24.0 (s, $OCOCH_3$), 38.7 (s, CH), aromatic carbons [129.9 (s), 132.6 (s), 134.7 (s), 135.4 (s)], 177.1 (s, $OCOCH_3$). **3**$(PF_6)_4$: δ_P(CD_3CN, 81.01 MHz) 79.3 (s). δ_H(CD_3CN, 200.13 MHz) 4.6 (s, 4H, CH), 3.0 (s, 12H, CH_3CN), 7.3–8.2 (m, 40H, aromatic protons). IR ν(KBr)/cm^{-1} 1656s (C–N). **4**: δ_P(CD_2Cl_2, 81.01 MHz) 58.9 (s). δ_H(CD_2Cl_2, 200.13 MHz) 1.66 (s, 6H, $OCOCH_3$), 2.23 (d,$^2J_{HP}$ 22.0 Hz, 4H, CH_2), 7.52–7.83 (m, 20H, Ph). δ_C(CD_2Cl_2, 50.32 MHz) 23.5 (s, $OCOCH_3$), 27.5 (AXX′ system, $^1J_{CP}$ 36.6, $^2J_{CP}$ 12.8 Hz, CH_2), aromatic carbons [129.6 (s), 131.4 (s), 132.8 (s), 134.1 (s)], 176.6 (s, $OCOCH_3$). **5**: δ_P(CD_2Cl_2, 81.01 MHz) 56.9 (s) δ_H(CD_2Cl_2, 200.13 MHz) 1.60 (s, 6H, $OCOCH_3$), 7.18–7.80 (m, 24H, aromatic protons). δ_C(CD_2Cl_2, 50.32 MHz) 23.5 (s, $OCOCH_3$), aromatic carbons (128.9–134.6), 176.5 (s, $OCOCH_3$). **6**: δ_P(CD_2Cl_2, 81.01 MHz) 65.5 (s). δ_H(CD_2Cl_2, 200.13 MHz) 1.70 (s, 6H, $OCOCH_3$), 7.08 (AA′XX′ system, $^2J_{HP}$ 60.0, $^3J_{HP}$ 13.0 Hz, 2H, CH), 7.44–7.84 (m, 20H, aromatic protons). δ_C(CD_2Cl_2, 50.32 MHz) 23.4 (s, $OCOCH_3$), aromatic carbons [129.7 (s), 129.9 (s), 132.8 (s), 133.7 (s), 133.9 (s)], 146.2 (dd, $^1J_{CP}$ 48.4, $^2J_{CP}$ 27.0 Hz, CH), 176.4 (s, $OCOCH_3$).

§ *Crystal data* for **3**$(BF_4)_4 \cdot 2MeCN \cdot 3.4CH_2Cl_2$: M = 1889.65, triclinic, space group $P\bar{1}$, a = 12.180(2), b = 12.702(2), c = 15.338(3) Å, α = 110.35(1), β = 105.72(1), γ = 101.78(1)°, U = 2021.2(6) Å^3, T = 173 K, Z = 1, D_c = 1.552 g cm^{-3}, μ = 0.863 mm^{-1}, λ(Mo-Kα) = 0.71069 Å, F(000) 947, Crystal size 1.0 × 0.8 × 0.6 mm, 8779 independent reflections (R_{int} = 0.0186), 10 006 reflections collected. Refinement method: full-matrix least squares on F^2, Goodness-of-fit on F^2 = 1.052, Final R indices [$I > 3\sigma(I)$] R_1 = 0.0454, wR_2 = 0.1251. CCDC 182/1583.

1 A. Sen, *Acc. Chem Res.*, 1993, **26**, 303; C. E. Ash, *J. Mater. Educ.*, 1994, **16**, 1; E. Drent and P. Budzelaar, *Chem Rev.*, 1996, **96**, 663; A. Sommazzi and F. Garbassi, *Prog. Polym. Sci.*, 1997, **22**, 1547.
2 E. Drent, EP-A 121965, 1984; E. Drent, EP-A 181014, 1986; J. A. M. van Broekhoven, E. Drent and E. Klei, EP-A 213671, 1987; J. A. M. van Broekhoven, E. Drent and E. Klei, EP-A 235865, 1987.
3 E. Drent, J. A. M. van Broekhoven and M. J. Doyle, *J. Organomet. Chem.*, 1991, **417**, 235.
4 F. Y. Xu, A. X. Zhao and J. C. W. Chien, *Macromol. Chem.*, 1993, **194**, 2579; Y. Koide, S. G. Bott and A. R. Barron, *Organometallics*, 1996, **15**, 2213.
5 G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen and C. F. Roobeek, *J. Organomet. Chem.*, 1992, **430**, 357; G. P. C. Dekker, C. J. Elsevier, K. Vrieze and P. W. N. M. van Leeuwen, *Organometallics*, 1992, **11**, 1598.
6 W. Oberhauser, C. Bachmann, T. Stampfl, R. Haid, C. Langes, H. Kopacka, A. Rieder and P. Brüggeller, *Inorg. Chim. Acta*, 1999, **290**, 167.
7 The average molecular weights (M_n) were calculated by means of ^1H NMR spectroscopy in 1,1,1,3,3,3-hexafluoropropan-2-ol-d_2.
8 G. J. Palenik, M. Mathew, W. L. Steffen and G. Beran, *J. Am. Chem. Soc.*, 1975, **97**, 97.
9 W. L. Steffen and G. J. Polenik, *Inorg. Chem.*, 1976, **15**, 2432; W. A. Hermann, W. R. Thiel, C. Brosman, K. Ofile, T. Piermeier and W. Scherer, *J. Organomet. Chem.*, 1993, **461**, 51.
10 J. Bakos, I. Toth, B. Heil, G. Szalontai, L. Párkányi and V. Fülöp, *J. Organomet. Chem.*, 1989, **370**, 263; N. Rahmouni, J. A. Osborne, A. De Cian, J. Fischer and A. Ezzamarty, *Organometallics*, 1998, **17**, 2470.
11 C. Bianchini, H. M. Lee, A. Meli, S. Moneti, F. Vizza, M. Fontani and P. Zanello, *Macromolecules*, 1999, **32**, 4183.
12 S. Doherty, G. R. Eastham, R. P. Tooze, T. H. Scanlan, D. Williams, M. R. J. Elsegood and W. Clegg, *Organometallics*, 1999, **18**, 3558.