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Palladium(II) complexes with hemilabile etherdiphos ligands in the alternating copolymerization of carbon monoxide with olefins

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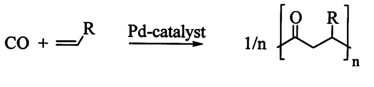
Abstract

The potentially hexadentate diphos ligands $(ROCH_2CH_2)_2P(CH_2)_3P(CH_2CH_2OR)_2$ (**1a-d**) (R = Et (**a**), *n*-Bu (**b**), *t*-Bu (**c**), Cy (**d**)) are accessible by photochemically induced hydrophosphination of the vinyl ethers $CH_2{=}CH{-}OR$ with the diprimary phosphine $H_2P(CH_2)_3PH_2$. Treatment of **1a–d** with $(PhCN)_2PdCl_2$ in CH_2Cl_2 leads to the dichlorodiphospalladium(II) complexes **2a–d**, from which the dicationic palladium(II) complexes **3a–d** were obtained by abstraction of the chlorides with $AgBF_4$ in CH_2Cl_2. In **3a–d** the etherdiphos ligands are coordinated in a $\eta^4(O,P;O',P')$ fashion. A rapid chemical exchange between the η^2-P∩O chelated and the η^1-P coordinated part of the ligands in **3a–d** was demonstrated by means of temperature-dependent $^{13}C\{^1H\}$ NMR spectroscopy. Both Pd–O bonds in **3a–d** are easily cleaved by polar solvents such as acetonitrile and water resulting in the formation of the adducts **3b**·$2CH_3CN$, **3c**·H_2O, and **3c**·$2H_2O$. The molecular structures of **2a** and **3c**·H_2O were determined by single crystal X-ray diffraction methods. Under a total pressure of 60 bar ethene/CO and propene/CO, respectively, **3a-d** are highly active catalysts in the copolymerization of olefins with carbon monoxide. GPC measurements revealed high molecular weights of these polyketones. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Palladium complexes; Hemilabile ligands; Copolymerization; Ethene; Propene; Carbon monoxide

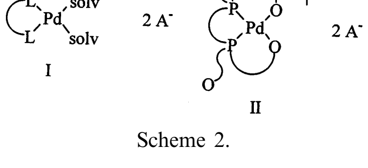
1. Introduction

The alternating copolymerization of carbon monoxide with α-olefins forming polyketones (Scheme 1) has attracted both academic and industrial interest, because of at least four reasons: (i) a plausible reaction mechanism which makes the alternation of the inserted monomers clear [1]; (ii) an easy and cheap access of the comonomers; (iii) the polymers engineering properties [2], and (iv) the potential of further derivatization of the carbonyl group [3]. A great variety of olefins [4] or imines [5] were employed and carbon monoxide was replaced by other polar building blocks, such as sulfur dioxide [6] or alkane-α,ω-dinitrite esters [7].



Scheme 1.

The copolymerization is commonly catalyzed by cationic palladium complexes, provided with bidentate phosphorus [8] or nitrogen [9] ligands (L∩L), weakly coordinating anions (A^-) [10], and solvent molecules (solv) (Scheme 2). Diphosphines with a hydrocarbon backbone consisting of three methylene groups belong to the most active palladium catalysts [8,11]. Upon polymerization conditions the solvent molecules are separated and the complex fragment is then transformed to the active form [1a].



Scheme 2.

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The introduction of bifunctional ether-phosphines [12] makes the external solvent molecules unnecessary. Hemilabile ligands of this type are provided with an ether-oxygen donor forming only weak metal–oxygen interactions while the phosphorus atom is strongly coordinated to the central atom. The oxygen-containing part of the ligand may be regarded as an intramolecular solvent stabilizing vacant coordination sites. Bis(ether-phosphine)palladium(II), ruthenium(II), and rhodium(I) complexes show fluxional behavior which can be studied by dynamic ^{31}P NMR spectroscopy [13]. Comparable hybrid palladium(II) complexes with monodentate phosphines have already been successfully employed in an interphase catalysis for the copolymerization of ethene with carbon monoxide [14]. Although in dicationic bis(chelated) palladium(II) complexes the phosphorus atoms initially are oriented in a *cis* fashion [15], in the course of the copolymerization a rearrangement to the inactive *trans* complexes takes place. Keim and co-workers demonstrated that palladium(II) complexes containing anionic hemilabile phosphine ligands enhance the catalytic activity leading to high molecular weight copolymers [16]. Therefore in this investigation hemilabile diphosphines were employed in the copolymerization of carbon monoxide with ethene and propene, respectively. The ability of the intramolecular ether moiety to stabilize electron deficient palladium species should suppress the decomposition of the catalyst which is associated with the formation of palladium.

2. Experimental

2.1. General remarks

All experiments were carried out under an atmosphere of argon, unless otherwise stated. Dichloromethane was distilled from calcium hydride, diethyl ether from sodium/benzophenone, *n*-hexane from $LiAlH_4$ and acetonitrile from P_4O_{10}. $PdCl_2$ was a gift from Degussa AG. Ethylvinyl ether, *n*-butylvinyl ether, *tert*-butylvinyl ether and cyclohexylvinyl ether were purchased from Aldrich. The diprimary phosphine 1,3-diphosphinopropane [17] and dppp [18] were synthesized according to literature methods. Propene, ethene and carbon monoxide were gifts from BASF AG. Elemental analyses were carried out on a Carlo Erba analyzer model 1106 and Elementar model Vario EL; Cl analyses were carried out according to Dirschel and Erne [19] and Schöniger [20]. Palladium was determined on a Perkin–Elmer Model 4000 atomic absorption spectrometer. The high resolution ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX 250 spectrometer at 296 K. Frequencies and standards are as follows: $^{13}C\{^{1}H\}$ NMR 62.90 MHz, $^{31}P\{^{1}H\}$ NMR 101.25 MHz. Chemical shifts in the ^{1}H, $^{31}P\{^{1}H\}$, and $^{13}C\{^{1}H\}$ spectra were measured relative to partially deuterated solvent peaks and to deuterated solvent peaks, respectively, which are reported relative to TMS. Mass spectra were acquired on a Finnigan MAT 711A modified by AMD 'Meß- und Datensysteme' (8 kV, 303 K) and reported as mass/charge (*m*/*z*). IR spectra were recorded on a Bruker IFS 48 FT-IR spectrometer. Molecular weights were determined by means of gel permeation chromatography (GPC), using a set-up consisting of a Perkin–Elmer Series 10 HPLC pump, a Perkin–Elmer LC 90 UV-detector, a PSS SDV linear XL column ($CHCl_3$) with a pore size of 10 μm or a PSS PFG linear XL column (1,1,1,3,3,3-hexafluoroisopropanol) with a pore size of 7 μm. All molecular weights refer to narrow distributed polymethylmethacrylate standards.

2.2. Preparation of the phosphine ligands **1a–d**. General procedure A

In a quartz Schlenk tube 1,3-diphosphinopropane and an excess of the corresponding olefin were magnetically stirred and the mixture was irradiated with the ultraviolet light of a mercury high pressure lamp. After 6 h excess olefin was removed under reduced pressure. Further purification was not necessary.

Hazards: The phosphines **1a–c** are pyrophoric in contact with cellulose.

2.3. 1,3-Bis[di(2-ethoxyethyl)phosphino]propane (**1a**)

1,3-Diphosphinopropane (891 mg, 8.25 mmol) and ethylvinyl ether (2.617 g, 36.3 mmol) were reacted according to procedure A to give 3.14 g (96%) of **1a**. MS (EI): *m*/*z* 396.1 (M^+). *Anal.* Calc. for $C_{19}H_{42}O_4P_2$ (396.2): C, 57.56; H, 10.68. Found: C, 57.10; H, 10.23%. ^{1}H NMR ($CDCl_3$): δ (ppm) 3.4 (m, $8H^4 + 4$ OCH_2CH_3[1]), 1.67 (m, $8H^3$), 1.49 (m, br, $2H^1 + 4H^2$), 1.13 (t, $^{3}J_{HH} = 6.9$ Hz, $4CH_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ (ppm) 68.2 (d, $^{3}J_{PC} = 16.5$ Hz, C^4), 66.0 (s, OCH_2CH_3), 29.4 ($N = 22.8$ Hz [2] [21], C^2), 28.0 (d, $^{1}J_{PC} = 13.4$ Hz, C^3), 22.4 (t, $^{2}J_{PC} = 14.5$ Hz, C^1), 15.1 (s, CH_3). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ (ppm) −37.4 (s). IR (CH_2Cl_2, cm^{-1}): $\nu_{as}(C_2O)$ 1096.

2.4. 1,3-Bis[di(2-*n*-butoxyethyl)phosphino]propane (**1b**)

1,3-Diphosphinopropane (1.012 g, 9.37 mmol) and *n*-butylvinyl ether (4.133 g, 41.3 mmol) were reacted according to procedure A to give 4.47 g (94%) of **1b**.

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[1] For the labeling of the hydrogen and carbon atoms see Scheme 3.

[2] AXX′ pattern, $N = |\,^{1}J_{PC} + ^{3}J_{PC}\,|$.

MS (EI): m/z 508.2 (M^+). *Anal.* Calc. for $C_{27}H_{58}O_4P_2$ (508.3): C, 63.75; H, 11.49. Found: C, 63.75; H, 11.38%. ^1H NMR ($CDCl_3$): δ (ppm) 3.47 (m, $8H^4$), 3.32 (t, $^3J_{HH} = 6.6$ Hz, $8OCH_2C_3H_7$), 2.0 (m, $2H^1$), 1.69 (m, $8H^3$), 1.48 (m, $4H^2 + 4CH_2C_2H_5$), 1.32 (m, $4CH_2CH_3$), 0.85 (t, $^3J_{HH} = 7.3$ Hz, $4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 70.6 (s, $OCH_2C_3H_7$), 68.4 (d, $^2J_{PC} = 18.2$ Hz, C^4), 31.7 (s, $CH_2C_2H_5$), 29.4 ($N = 22.9$ Hz ^{2}, C^2), 27.9 (d, $^1J_{PC} = 13.5$ Hz, C^3) 22.4 (t, $^2J_{PC} = 14.3$ Hz, C^1), 19.3 (s, CH_2CH_3), 13.9 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) -37.1 (s). IR (CH_2Cl_2, cm^{-1}): $\nu_{as}(C_2O)$ 1098.

2.5. 1,3-Bis[di(2-tert-butoxyethyl)phosphino]propane (1c)

1,3-Diphosphinopropane (1.251 g, 11.58 mmol) and tert-butylvinyl ether (5.104 g, 51.0 mmol) were reacted according to procedure A to give 5.46 g (93%) of **1c**. MS (EI): m/z 507.4 ($M^+ - H$). *Anal.* Calc. for $C_{27}H_{58}O_4P_2$ (508.3): C, 63.75; H, 11.49. Found: C, 63.25; H, 11.40%. ^1H NMR ($CDCl_3$): δ (ppm) 3.44 (m, $8H^4$), 1.9 (m, $2H^1$), 1.68–1.62 (m, $8H^3$), 1.39 (m, $4H^2$), 1.14 (s, $4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 72.8 (s, $C(CH_3)_3$), 59.5 (d, $^2J_{PC} = 22.1$ Hz, C^4), 29.7 ($N = 22.3$ Hz ^{2}, C^2), 28.9 (d, $^1J_{PC} = 12.8$ Hz, C^3), 27.5 (s, CH_3), 22.38 (t, $^2J_{PC} = 14.1$ Hz, C^1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) -37.2 (s). IR (CH_2Cl_2, cm^{-1}): $\nu_{as}(C_2O)$ 1195.

2.6. 1,3-Bis[di(2-cyclohexoxyethyl)phosphino]propane (1d)

1,3-Diphosphinopropane (974 mg, 9.02 mmol) and cyclohexylvinyl ether (5.010 g, 39.7 mmol) were reacted according to procedure A to give 5.4 g (98%) of **1d**. M.p. 49°C. MS (EI): m/z 611.4 ($M^+ - H$). *Anal.* Calc. $C_{35}H_{66}O_4P_2$ (612.4): C, 68.64; H, 10.78. Found: C, 68.60; H, 11.06%. ^1H NMR ($CDCl_3$): δ (ppm) 3.91–3.73 (m, $8H^4 + 4OCH$), 3.29–3.19 (m, $8H^3$), 2.70–1.13 (m, 46H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 76.8 (s, OCH), 64.9 (d, $^2J_{PC} = 20.5$ Hz, C^4), 31.7 (s, $OCHCH_2$), 29.0 ($N = 22.8$ Hz ^{2}, C^2), 27.8 (d, $^1J_{CP} = 13.5$ Hz, C^3), 25.3 (s, $OCHCH_2CH_2$), 23.5 (s, $OCHCH_2CH_2CH_2$), 21.9 (t, $^2J_{PC} = 15.2$ Hz, C^1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) -36.7 (s). IR (CH_2Cl_2, cm^{-1}): $\nu_{as}(C_2O)$ 1100.

2.7. Preparation of the dichlorodiphosphinepalladium(II) complexes 2a–f. General procedure B

Stirred solutions of the corresponding phosphine **1a–d** and $(PhCN)_2PdCl_2$ in each 20 ml of dichloromethane were reacted for 2 h at room temperature. Subsequently the solvent was removed in vacuo. Finally, the complexes **2a–d** were washed with cold n-hexane (-30°C, 3×20 ml) and recrystallized from toluene/n-hexane to give colorless, crystalline complexes.

2.8. Dichloro{1,3-bis[di(2-ethoxyethyl)phosphino]-propane-P,P′}palladium(II) (2a)

According to procedure B, **1a** (433 mg, 1.093 mmol) was reacted with $(PhCN)_2PdCl_2$ (381 mg, 0.993 mmol) to give 461 mg (81%) of **2a**. M.p. 114°C. MS (FD, 30°C): m/z 573.8 (M^+, ^{106}Pd). *Anal.* Calc. for $C_{19}H_{42}Cl_2O_4P_2Pd$ (573.6): C, 39.77; H, 7.38; Cl, 12.38; Pd, 18.56. Found: C, 40.01; H, 7.48; Cl, 12.30; Pd, 18.05%. ^1H NMR ($CDCl_3$): δ (ppm) 3.79 (m, $8H^4$), 3.45 (m, $4OCH_2CH_3$), 2.60 (m, $4H^3$), 2.24 (m, $4H^3$), 2.10 (m, $2H^1$), 1.85 (m, $4H^2$), 1.13 (t, $^3J_{HH} = 6.9$ Hz, $4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 66.8 (s, C^4), 66.4 (s, OCH_2CH_3), 28.8 ($N = 31.7$ Hz ^{2}, C^3), 22.9 ($N = 38.4$ Hz ^{2}, C^2), 19.2 (s, C^1), 15.2 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 17.1 (s). IR (KBr, cm^{-1}): $\nu_{as}(C_2O)$ 1100.

2.9. Dichloro{1,3-bis[di(2-n-butoxyethyl)phosphino]-propane-P,P′}palladium(II) (2b)

According to procedure B, **1b** (572 mg, 1.126 mmol) was reacted with $(PhCN)_2PdCl_2$ (390 mg, 1.024 mmol) to give 555 mg (79%) of **2b**. M.p. 85.5°C. MS (FD, 30°C): m/z 685.9 (M^+, ^{106}Pd). *Anal.* Calc. for $C_{27}H_{58}Cl_2O_4P_2Pd$ (685.7): C, 47.27; H, 8.52; Cl, 10.53; Pd, 15.53. Found: C, 47.09; H, 8.49; Cl, 10.48; Pd, 16.01%. ^1H NMR ($CDCl_3$): δ (ppm) 3.76 (m, $8H^4$), 3.34 (m, $4OCH_2C_3H_7$), (m, $4H^2$), 2.28 (m, $4H^2$), 2.14–1.76 (m, $2H^1 + 4H^2$), 1.45 (m, $4CH_2C_2H_5$), 1.27 (m, $4CH_2CH_3$), 0.85 (t, $^3J_{HH} = 7.2$ Hz, $4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 70.9 (s, $OCH_2C_3H_7$), 66.9 (s, C^4), 31.7 (s, $CH_2C_2H_5$), 28.7 ($N = 37.7$ Hz ^{2}, C^3), 22.7 ($N = 36.4$ Hz ^{2}, C^2), 19.2, 19.1 (s, $C^1 + CH_2CH_3$), 13.8 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 17.3 (s). IR (KBr, cm^{-1}): $\nu_{as}(C_2O)$ 1106.

2.10. Dichloro{1,3-bis[di(2-tert-butoxyethyl)phosphino]-propane-P,P′}palladium(II) (2c)

According to procedure B, **1c** (584 mg, 1.149 mmol) was reacted with $(PhCN)_2PdCl_2$ (397 mg, 1.035 mmol) to give 625 mg (88%) of **2c**. M.p. 175 °C. MS (FD, 30 °C): m/z 650.9 ($M^+ - Cl$, ^{106}Pd). *Anal.* Calc. for $C_{27}H_{58}Cl_2O_4P_2Pd$ (685.7): C, 47.27; H, 8.52; Cl, 10.53; Pd, 15.53. Found: C, 47.50; H, 8.67; Cl, 10.11; Pd, 15.40%. ^1H NMR ($CDCl_3$): δ (ppm) 3.78 (m, $8H^4$), 2.52 (m, $4H^3$), 2.28 (m, $4H^3$), 2.16–1.88 (m, $2H^1 + 4H^2$), 1.14 (s, $16CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 73.6 (s, $C(CH_3)_3$), 58.2 (s, C^4), 29.5 ($N = 35.8$ Hz ^{2}, C^3), 27.6 (s, CH_3), 23.0 ($N = 37.9$ Hz ^{2}, C^2), 19.1 (s, C^1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 16.3 (s). IR (KBr, cm^{-1}): $\nu_{as}(C_2O)$ 1195.

*2.11. Dichloro{1,3-bis[di(2-cyclohexoxyethyl)phosphino]-propane-P,P′}palladium(II) (**2d**)*

According to procedure B, **1d** (599 mg, 1.095 mmol) was reacted with $(PhCN)_2PdCl_2$ (375 mg, 0.978 mmol) to give 672 mg (87%) of **2d**. M.p. 159°C. MS (FD, 30°C): m/z 650.8 ($M^+ - Cl$, ^{106}Pd). *Anal.* Calc. for $C_{35}H_{66}Cl_2O_4P_2Pd$ (789.7): C, 53.20; H, 8.42; Cl, 8.97; Pd, 13.47. Found: C, 52.89; H, 7.90; Cl, 8.91; Pd, 13.25. ^1H NMR ($CDCl_3$): δ (ppm) 3.83 (m, 8H^4), 3.23 (m, 4OCH), 2.54 (m, 4H^3), 2.29 (m, 4H^3), 1.92–1.16 (m, 46H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 77.7 (s, OCH), 63.9 (s, C^4), 32.1 (s, OCHCH_2), 29.1 ($N = 34.7$ Hz ^{2}, C^3), 25.6, 23.8 (s, C_6H_{11}), 22.8 ($N = 37.0$ Hz ^{2}, C^2), 19.2 (s, C^1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 16.5 (s). IR (KBr, cm^{-1}): $\nu_{as}(C_2O)$ 1087.

*2.12. Preparation of the dicationic palladium(II) complexes **3a–d**. General procedure C*

To a solution of the corresponding dichloropalladium(II) complexes **2a–d** in 10 ml of CH_2Cl_2 a suspension of $AgBF_4$ in 10 ml of CH_2Cl_2 was added and the mixture was stirred for 1 h at room temperature. Subsequently the suspension was centrifuged, decanted and the solvent was removed in vacuo. The crude product was dissolved in CH_2Cl_2 and centrifuged again to remove traces of AgCl. Finally the solvent was removed under reduced pressure to give the dicationic complexes **3a–d**.

*2.13. {1,3-Bis[di(2-ethoxyethyl)phosphino]propane-O,P;O′,P′}palladium(II)bis(tetrafluoroborate) (**3a**)*

According to procedure C, **2a** (290 mg, 0.505 mmol) was reacted with $AgBF_4$ (198 mg, 1.02 mmol) to give 324 mg (95%) of **3a**. M.p. 43°C. MS (FD, 30°C): m/z 588.7 ($M^+ - BF_4$, ^{106}Pd). *Anal.* Calc. for $C_{19}H_{42}B_2F_8O_4P_2Pd$ (676.3): C, 33.73; H, 6.26; Pd, 15.73. Found: C, 33.71; H, 6.31; Pd, 15.45%. ^1H NMR (CD_2Cl_2): δ (ppm) 3.97–3.69 (m, 8H^4 + 4OCH_2CH$_3$), 2.50 (m, 8H^3), 2.38–2.23 (m, 2H^1 + 4H^2), 1.22 (t, $^3J_{HH} = 6.9$ Hz, 4CH$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 70.4 (s, OCH_2CH$_3$), 67.2 (s, C^4), 26.5 ($N = 36.5$ Hz ^{2}, C^3), 20.8–20.1 (m, C^2 + C^1), 15.0 (s, CH$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 46.2 (s). IR (CH_2Cl_2, cm^{-1}): $\nu_{as}(C_2O)$ 1106, $\nu(BF_4^-)$ 1061.

*2.14. {1,3-Bis[di(2-n-butoxyethyl)phosphino]propane-O,P;O′,P′}palladium(II)bis(tetrafluoroborate) (**3b**)*

According to procedure C, **2b** (336 mg, 0.49 mmol) was reacted with $AgBF_4$ (191 mg, 0.98 mmol) to give 375 mg (97%) of **3b**. M.p. 96°C. MS (FD, 30°C): m/z 700.8 ($M^+ - BF_4$, ^{106}Pd). *Anal.* Calc. for $C_{27}H_{58}B_2F_8O_4P_2Pd$ (788.4): C, 41.12; H, 7.41; F, 19.27; Pd, 13.49. Found: C, 40.54; H, 7.09; Pd, 14.06%. ^1H NMR (CD_2Cl_2): δ (ppm) 3.95–3.63 (m, 4OCH_2C$_3$H$_7$ + 8H^4), 2.51 (m, 8H^3), 2.37–2.22 (m, 2H^1 + 4H^2), 1.56 (m, 4OCH$_2$$CH_2C_2H_5$), 1.28 (m, 4$CH_2CH_3$), 0.86 (t, $^3J_{HH} = 7.2$ Hz, 4CH$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 74.3 (s, OCH_2C$_3$H$_7$), 67.2 (s, C^4), 31.5 (s, OCH$_2$$CH_2C_2H_5$), 26.3 ($N = 31.8$ Hz ^{2}, C^3), 20.7–20.0 (m, C^1 + C^2), 19.4 (s, CH_2CH$_3$), 14.1 (s, CH$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 43.2 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80°C): δ (ppm) 45.7 (br s), 19.6 (br s). IR (CH_2Cl_2, cm^{-1}): $\nu_{as}(C_2O)$ 1106, $\nu(BF_4^-)$ 1063 cm^{-1}.

A solution of **3b** (120 mg, 0.152 mmol) in 1 ml of dichloromethane reacts with excess acetonitrile to give the adduct **3b** · 2CH$_3$CN. ^1H NMR (CD_2Cl_2): δ (ppm) 3.75–3.62 (m, 8H^4), 3.39 (m, 4OCH_2C$_3$H$_7$), 2.35 (m, 8H^3), 2.16–1.89 (m, 2H^1 + 4H^2 + CH$_3$CN), 1.47 (m, 4CH_2C$_2$H$_5$), 1.28 (m, 4CH_2CH$_3$), 0.82 (t, $^3J_{HH} = 7.5$ Hz, 4CH$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 117.7 (s, CN), 71.6 (s, OCH_2C$_3$H$_7$), 65.8 (s, C^4), 32.0 (s, CH_2C$_2$H$_5$), 28.5 ($N = 43.1$ Hz ^{2}, C^3), 20.5–18.9 (m, C^1 + C^2 + CH_2CH$_3$), 14.0 (s, CH$_3$), 1.8 (s, CH_3CN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 21.0 (s). IR (CH_2Cl_2, cm^{-1}): ν(CN) 2325, 2297, $\nu(C_2O)$ 1100, $\nu(BF_4^-)$ 1065.

*2.15. {1,3-Bis[di(2-tert-butoxyethyl)phosphino]propane-O,P;O′,P′}palladium(II)bis(tetrafluoroborate) (**3c**)*

According to procedure C, **2c** (357 mg, 0.521 mmol) was reacted with $AgBF_4$ (203 mg, 1.043 mmol) to give 374 mg (91%) of **3c**. M.p. 67.6 °C. MS (FD, 30 °C): 700.9 ($M^+ - BF_4$, ^{106}Pd). *Anal.* Calc. for $C_{27}H_{58}B_2F_8O_4P_2Pd$ (788.4): C, 41.12; H, 7.41; Pd, 13.49. Found: C, 40.56; H, 7.25; Pd, 13.81%. ^1H NMR (CD_2Cl_2): δ (ppm) 3.83–3.74 (m, 8H^4), 2.40 (m, 8H^3), 2.27–2.05 (m, 2H^1 + 4H^2), 1.22 (s, 16CH$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 79.6 (s, OC(CH$_3$)$_3$), 59.2 (s, C^4), 27.4–26.7 (m, CH$_3$ + C^3), 20.2 ($N = 41.7$ Hz ^{2}, C^2), 19.2 (s, C^1). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −80°C): δ (ppm) 84.9 (br, PdOC(CH$_3$)$_3$), 75.8–74.6 (br, OC(CH$_3$)$_3$), 62.7 (br, PdOC^4), 56.0 (br, C^4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 40.3 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80°C): δ (ppm) 45.7 (br s), 43.8 (br s), 37.8 (br s), 19.5 (br s). IR (CH_2Cl_2, cm^{-1}): $\nu_{as}(C_2O)$ 1191 cm, $\nu(BF_4^-)$ 1048.

3c reacts stepwise with water to give **3c** · H$_2$O and **3c** · 2H$_2$O. Whereas **3c** · H$_2$O is obtained from a concentrated solution of **3c** in CH_2Cl_2 layered with n-hexane in a Schlenk tube which is sealed with a rubber plug, **3c** · 2H$_2$O is formed if the same solution (without n-hexane) is exposed to atmospheric humidity for 5 min.

3c · H$_2$O: MS (FD, 30°C): m/z 632.3 ($M^+ - 2BF_4$, ^{106}Pd). ^1H NMR (CD_2Cl_2): δ (ppm) 3.87–3.77 (m, 8H^4), 2.45 (m, 8H^3), 2.32–2.22 (m, 2H^1 + 4H^2), 1.24 (s, 16CH$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 78.9 (s, C(CH$_3$)$_3$), 59.0 (s, C^4), 27.5–26.8 (m, CH$_3$ + C^3), 20.5 ($N = 41.9$ Hz ^{2}, C^2), 19.2 (s, C^1). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 36.7 (s).

3c·$2H_2O$: MS (FD, 30 °C): *m*/*z* 650.4 ($M^+ - BF_4$, ^{106}Pd). ^1H NMR (CD_2Cl_2): δ (ppm) 3.77 (m, $8H^4$), 3.07 (m, br, H_2O), 2.36 (m, $8H^3$), 2.19–1.97 (m, $2H^1 + 4H^2$), 1.19 (s, $16CH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 77.4 (s, $C(CH_3)_3$), 58.9 (s, C^4), 29.0 ($N = 31.7$ Hz ^{2}, C^3), 28.7 (s, CH_3), 22.4 ($N = 42.5$ Hz ^{2}, C^2), 19.9 (s, C^1). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 25.5 (s). IR (CH_2Cl_2, cm^{-1}): ν(H_2O) 3624, ν(C_2O) 1190, ν(BF_4^-) 1076.

2.16. {1,3–Bis[di(2-cyclohexoxyethyl)phosphino]-propane-O,P;O′,P′}palladium(II)bis(tetrafluoroborate) (**3d**)

According to procedure C, **2d** (311 mg, 0.508 mmol) was reacted with $AgBF_4$ (198 mg, 1.018 mmol) to give 438 mg (97%) of **3d**. M.p. 82°C. MS (FD, 30°C): *m*/*z* 805.1 ($M^+ - BF_4$, ^{106}Pd). *Anal.* Calc. for $C_{35}H_{66}B_2F_8O_4P_2Pd$ (892.4): C, 47.08; H, 7.45; Pd, 11.93. Found: C, 47.19; H, 7.36; Pd, 11.50%. ^1H NMR (CD_2Cl_2): δ (ppm) 3.86 (m, $8H^4$), 3.51 (m, 4OCH), 2.49 (m, H^3), 2.25–2.13 (m, $4H^2 + 2H^1$), 1.98–1.05 (m, 44H, C_6H_{11}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 82.4 (s, OCH), 64.0 (s, C^4), 32.4 (s, OCH*C*H_2), 27.2 ($N = 31.2$ Hz ^{2}, C^3), 25.7, 24.9 (s, C_6H_{11}), 20.6 ($N = 42.1$ Hz ^{2}, C^2), 20.1 (s, C^1). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −80°C): δ (ppm) 85.0 (br, PdOCH), 78.8 (br, OCH), 65.7 (br, PdOC^4), 62.0 (br, C^4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 44.1 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C): δ (ppm) 47.6 (br s), 43.0 (br s), 19.7 (br s). IR (CH_2Cl_2, cm^{-1}): $\nu_{as}(C_2O)$ 1099, ν(BF_4^-) 1065.

2.17. Copolymerization of ethene and propene with carbon monoxide

For all high pressure reactions a computer controlled autoclave system was applied. A solution of the corresponding palladium(II) complex **3a–d** (0.01 mmol) in CH_2Cl_2 (30 ml) and CH_3OH (2 ml) as activator [22] was placed in a 100-ml magnetically-stirred steel autoclave which was charged with 30 bar of ethene and 30 bar of carbon monoxide. The reaction temperature was adjusted by a thermostat. Finally, the gases were released after the appropriate reaction time. The copolymer was collected by filtration and dried in vacuo.

The copolymerization of propene with carbon monoxide was carried out in a 250-ml mechanically-stirred steel autoclave with electrical heating, and air cooling. The evacuated autoclave was charged with a solution of the corresponding dicationic palladium(II) complex **3a–d** (0.01 mmol) in CH_2Cl_2 (100 ml) and CH_3OH (2 ml) as activator. The mixture was saturated with propene (20°C, 20 min) and pressurized with 51 bar of carbon monoxide. At the end of the reaction period the gases were released. The propene/carbon monoxide copolymers were obtained by evaporation of the solvent. The reproducibility of the catalytic activity is about 10% (ethene/CO copolymerization) and 5% (propene/CO copolymerization).

2.18. X-ray structural determination of **2a** and **3c**·H_2O (see Section 5)

Single crystals of **2a** were obtained by slow diffusion of n-hexane into a concentrated solution of **2a** in CH_2Cl_2. Crystals of **3c**·H_2O were grown within several weeks by slow diffusion of water into a Schlenk tube sealed with a rubber plug containing a CH_2Cl_2 solution of **3c** layered with n-hexane. The crystals were mounted on a glass fiber and transferred to a P4 Siemens diffractometer, using graphite-monochromated Mo Kα radiation. The lattice constants were determined by 17 (**2a**) or 20 (**3c**·H_2O) precisely centered high-angle reflections and refined by least-squares methods. The structures were solved by Patterson methods [23] and refined by full-matrix least-squares using SHELXL97 [24]. All non-hydrogen atoms were refined anisotropically (based on F^2). Hydrogen atoms were placed in calculated positions ($d(CH_3) = 0.98$ Å; $d(CH_2) = 0.99$ Å; $d(CH) = 1.00$ Å). The H atoms of the water molecule in **3c**·H_2O were located on a difference Fourier map and refined isotropically. The final cell parameters and specific data collection parameters for **2a** and **3c**·H_2O are summarized in Table 1.

3. Results and discussion

3.1. Synthesis of the ligands **1a–d** and complexes **2a–d**, **3a–d**

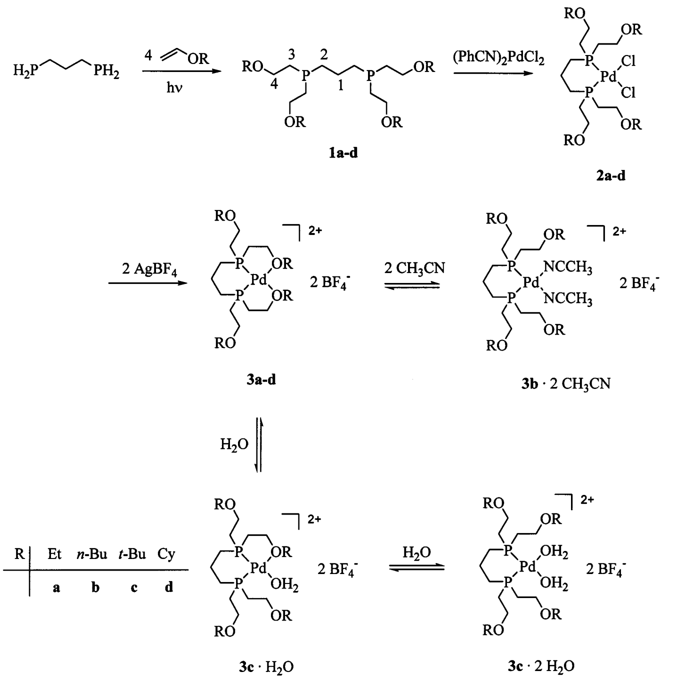
With some modifications the etherdiphos ligands **1a–d** were prepared according to Ref. [25]. The diprimary phosphine $H_2P–(CH_2)_3–PH_2$ [17] was photochemically hydrophosphinated with an excess of vinyl ether (Scheme 3). This procedure is much more convenient, since the reaction, as monitored by $^{31}P\{^1H\}$ spectroscopy, is quantitative and no by-products occur. In a simple purification step excess olefin can be removed in vacuo. All phosphines are colorless, air-sensitive, and oily (**1a–c**) or solid (**1d**) products, which are readily soluble in common organic solvents. They were characterized by means of MS, IR, and NMR spectra (Section 2).

By treatment of $(PhCN)_2PdCl_2$ with **1a–d** in dichloromethane at room temperature, the air-stable, colorless palladium(II) complexes **2a–d** are formed (Scheme 3). Recrystallization from toluene/n-hexane affords crystalline products; the molecular structure of

Table 1
Summary of crystallographic data and parameters for data collection and refinement of **2a** and **3c** · H_2O

	2a	**3c** · H_2O
Formula	$C_{19}H_{42}Cl_2O_4P_2Pd$	$C_{27}H_{60}B_2F_8O_5P_2Pd$
Formula weight	573.8	806.1
Color	colorless plate	colorless plate
Crystal dimension (mm)	0.45 × 0.20 × 0.10	0.1 × 0.4 × 0.45
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ No. 14	$P2_1/n$ No. 14
a (Å)	8.885(4)	10.126(5)
b (Å)	22.81(2)	36.328(9)
c (Å)	12.753(5)	11.035(4)
β (°)	93.10(2)	113.45(2)
V (Å^3)	2580(2)	3724(2)
Z	4	4
$d_{calc.}$ (g cm^{-1})	1.477	1.439
T (°C)	−100	−100
F(000)	1192	1680
μ(Mo Kα) (mm^{-1})	1.071	0.657
Scan type	ω	ω
2θ limits (°)	4–55	4–50
Data collected: h, k, l	−11–2, −1–29, ±16	−12–3, ±43, ±12
Number of reflections measured	7744	17415
Number of unique data with $I \geq 2\sigma(I)$	5235	5516
Number of variables	254	415
Goodness-of-fit	1.988	1.997
R_1 [a]	0.0416	0.0474
wR_2 [b]	0.1088	0.1169

[a] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{0.5}$.



Scheme 3.

2a was exemplarily determined by an X-ray structural analysis (vide infra). Spectroscopic data of **2a–d** are summarized in Section 2.

Intramolecular coordination of two ether moieties to the metal center succeeded by reacting **2a–d** with two equivalents of $AgBF_4$ in CH_2Cl_2 at 20°C, leading to the dicationic, colorless, hygroscopic etherdiphospalladium(II) complexes **3a–d**. Without cleavage of a Pd–O bond they are soluble in medium polar organic solvents, like CH_2Cl_2. Because of the ring contribution Δ_R [26], the ^{31}P resonances in the $^{31}P\{^1H\}$ NMR spectra are shifted about 30 ppm to lower field compared to **2a–d**. The $\eta^4(O,P;O',P')$ coordination mode in **3a–d** is responsible for a center of chirality at both phosphorus atoms resulting in three diastereomers [(*R*,*R*), (*S*,*S*), *meso*]. However, at room temperature only one ^{31}P singlet is observed, because of a rapid chemical exchange process between the coordinated ($P \frown O$) and the non-coordinated ($P \sim O$) ether oxygen atoms. Compared to **2a–d** the signals of both carbon atoms adjacent to the ether function in the $^{13}C\{^1H\}$ NMR spectra of **3a–d** are shifted to lower field. This is a further hint for the $\eta^4(O,P;O',P')$ coordination. Instead of two signals for each coordinated (C4′, C5′) and non-coordinated (C4, C5) ether moiety, only two averaged resonances for the four carbon atoms are observed. The dynamic behavior was studied by temperature-dependent $^{13}C\{^1H\}$ NMR experiments. The exchange of both types of ether oxygen atoms is decelerated by cooling the sample which results in a line broadening of the above-mentioned resonances of the carbon nuclei. Below the coalescence temperature of about −60°C for **3c** and **3d**, these signals split in pairs, revealing coordinated and non-coordinated oxygen atoms (Fig. 1). In the case of **3a** and **3b**, this splitting was not observed, because of their low coalescence temperatures (below −80°C). The inversion of the six-membered ring formed by the ligand backbone is also affected at low temperatures and is illustrated by the line broadening of the bridging carbon atoms C1 and C2. Due to chemical exchange and conformational processes the singlets in the $^{31}P\{^1H\}$ NMR spectra of **3c** and **3d** split in several resonances at −80°C, while those of **3a** and **3b** only broaden.

Although no kinetic parameters were determined [13a], complexes **3a–d** can be classified into two groups. The Pd–O bonds in **3c** and **3d** are much stronger compared to **3a** and **3b**, leading to a higher coalescence temperature. Obviously because of the higher basicity the tert-butyl and cyclohexyl groups strengthen the Pd–O contact.

Both Pd–O bonds in **3a–d** are easily ruptured with coordinating solvents like acetonitrile or water. If for

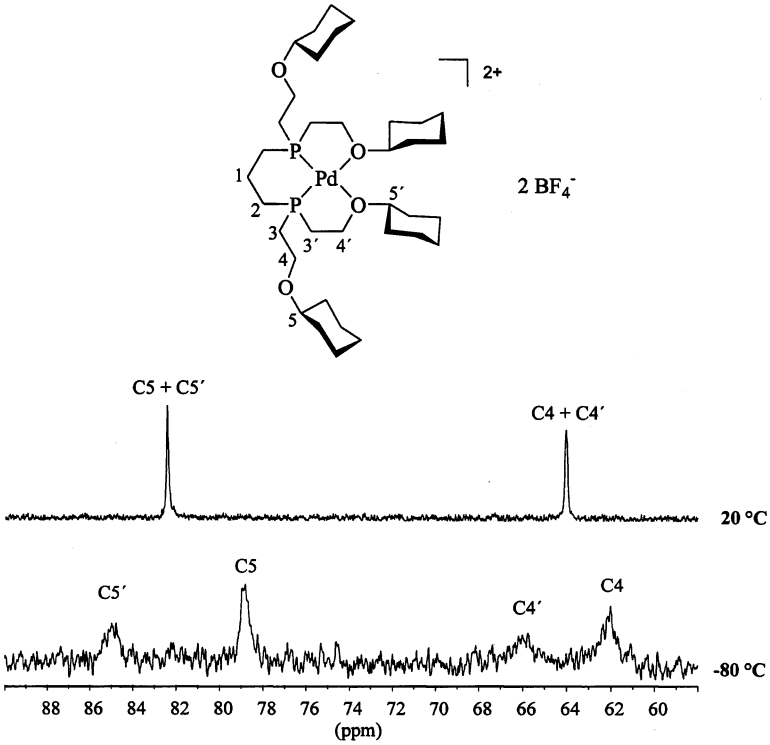


Fig. 1. Temperature-dependent $^{13}C\{^1H\}$ NMR spectrum of **3d**.

example **3b** or **3c** is treated with CH_3CN or exposed to atmospheric humidity, the adducts **3b** · $2CH_3CN$, **3c** · H_2O, and **3c** · $2H_2O$ are obtained, respectively. However, these complexes cannot be isolated by simple removal of the solvent, because of the reversibility of the reaction, in particular in the case of the acetonitrile complexes. Due to the Pd–O cleavage of the five-membered chelate rings the incorporation of water and acetonitrile in **3c** and **3b**, respectively results in a shift of the singlets in the $^{31}P\{^1H\}$ NMR spectra of **3c** · H_2O, **3c** · $2H_2O$, and **3b** · $2CH_3CN$ to higher field [26]. The IR spectrum of **3b** · $2CH_3CN$ (in CH_3CN) exhibits two strong C≡N absorptions at 2325 and 2297 cm^{-1}, which are typical for the expected *cis* configuration.

3.2. Crystal structures of 2a and 3c · H_2O

The resultant data of **2a** best fit the centrosymmetric monoclinic space group $P2_1/c$ (No. 14). Crystallization occurs with four formula units per unit cell ($Z = 4$). A perspective view of compound **2a** (Fig. 2) shows the crystallographic numbering scheme. Due to the backbone the square planar geometry about the Pd atom is slightly distorted with a P1–Pd1–P2 angle of 95.45(4)°. Noticeable is the plane formed by the seven atoms Cl1, Cl2, Pd1, P1, P2, C1, and C3. The distance between atom C2 and this plane is 0.757(4) Å. The Pd–P (Pd1–P1 = 2.241(1) Å, Pd1–P2 = 2.243(1) Å) and Pd–Cl (Pd1–Cl1 = 2.365(1) Å, Pd1–Cl2 = 2.365(1) Å) distances are equal within experimental error. In Table 2 a selection of bond lengths and angles of **2a** is summarized.

The formulation of **3c** · H_2O readily follows from the results of the single crystal diffraction analysis (Fig. 3). Selected interatomic parameters are collected in Table 3. The square planar coordination about the palladium by the four donor functions P1, P2, O1, O11 is extremely distorted, caused on the one hand by the bicyclic ring system and on the other hand by the hydrogen bridge between O11 and O3 (O11–H1E··· O3 = 2.630(5) Å [27]). The six-membered ring of the bicyclic system is arranged in a chair conformation. The Pd and the C2 atoms are located 0.795(3) Å above and − 0.721(6) Å below the plane that is formed by the atoms P1, P2, C1, and C3. The five-membered chelate ring reveals a twisted conformation. Remarkable is the rather shortened Pd–P1 bond length with 2.205(1) Å and the enlarged O1–Pd–O11 angle with 96.42(12)°.

3.3. Copolymerization of carbon monoxide with ethene and propene

Dicationic palladium(II) complexes of the type **3a–d** proved to be highly active catalysts in the copolymerization of carbon monoxide with ethene and propene,

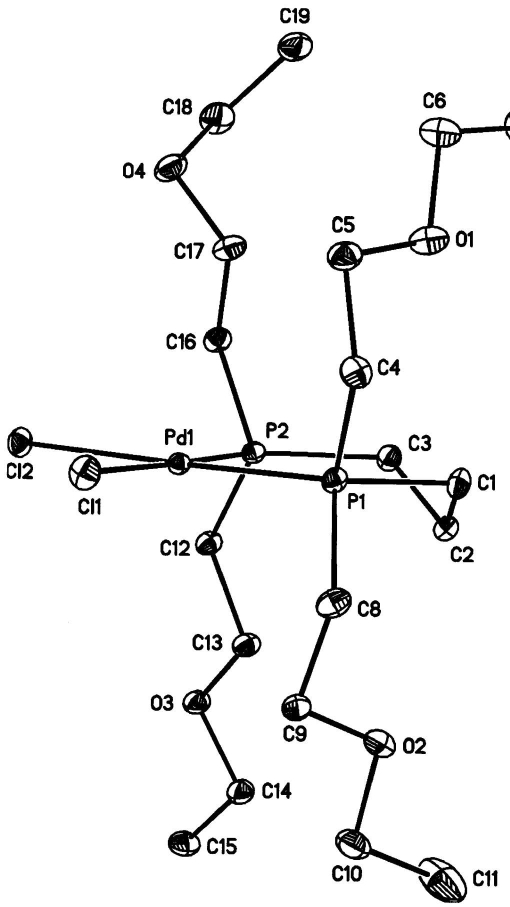


Fig. 2. ORTEP plot of the palladium(II) complex **2a**.

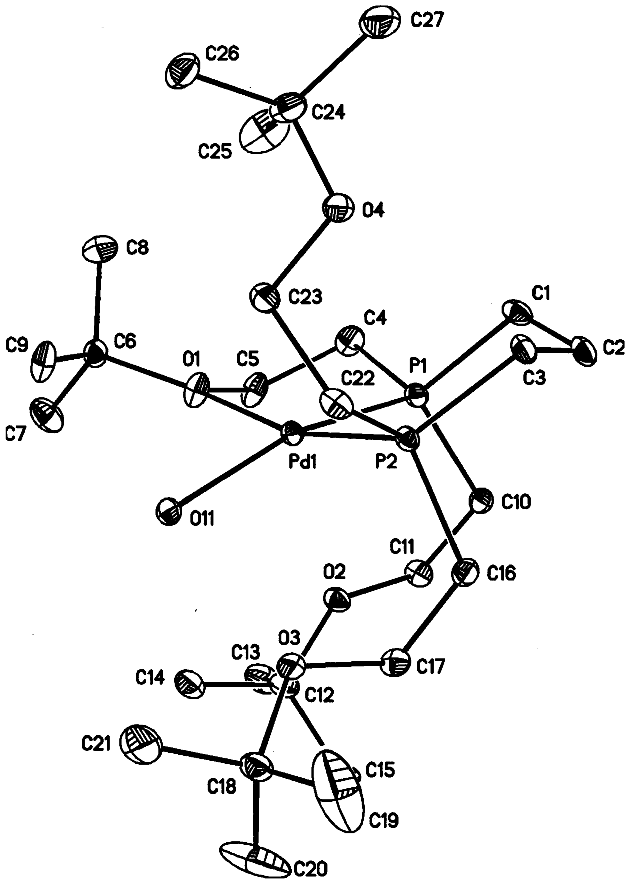


Fig. 3. ORTEP plot of the palladium(II) complex **3c** · H_2O.

respectively. However, they do not catalyze the copolymerization of styrene with carbon monoxide. Optimal reaction conditions are achieved at a total pressure of 60 bar using dichloromethane as solvent and a small amount of methanol as activator. All catalysts were stable under the reaction conditions and no precipitation of palladium occurred. In order to compare the catalytic efficiency of **3a–d** with the performance of a standard, the industrially employed complex $[(dppp)Pd(NCCH_3)_2][BF_4]_2$ **[(dppp)Pd]** was incorporated in the investigations [8].

Upon copolymerization of ethene with carbon monoxide at 25 °C the highest activities were obtained with **3b** and **3c** followed by **3d** and **3a**. A rise of the temperature leads to an overall increased activity (Fig. 4 and Table 4). While the efficiency of **3b–d** and **(dppp)Pd** is similar at 60°C, **3a** still remains somewhat moderate in this series. The resulting copolymer represents a colorless, flocky material with high melting points ranging from 254–266°C [28]. The molecular weight of the ethene/CO copolymer, obtained with catalyst **3a** is the lowest at 25°C, while with complex **3d** a much higher molecular weight was determined (Table 4, run 1–5). The expected decrease of the M_w values was observed at 60°C. However, at this temperature **(dppp)Pd** clearly produces the highest molecular weight, followed by the more bulky etherdiphospalladium(II) catalysts **3c–d** (Table 4, run 6–10). In the IR spectra a carbonyl absorption at 1691 cm^{-1} is observed. In the

Table 2
Selected interatomic distances (Å) and angles (°) for **2a**

Bond lengths			
Pd(1)–P(1)	2.2409(11)	Pd(1)–Cl(1)	2.3647(11)
Pd(1)–P(2)	2.2425(10)	Pd(1)–Cl(2)	2.3649(11)
Bond angles			
P(1)–Pd(1)–P(2)	95.45(4)	P(1)–Pd(1)–Cl(1)	86.48(4)
P(2)–Pd(1)–Cl(2)	87.14(4)	Cl(1)–Pd(1)–Cl(2)	90.90(4)

Table 3
Selected interatomic distances (Å) and angles (°) for **3c** · H_2O

Bond lengths			
Pd(1)–P(1)	2.2055(12)	Pd(1)–O(1)	2.254(3)
Pd(1)–P(2)	2.2327(13)	Pd(1)–O(11)	2.154(3)
Bond angles			
P(1)–Pd(1)–P(2)	89.71(5)	P(2)–Pd(1)–O(11)	92.60(10)
P(1)–Pd(1)–O(1)	84.22(9)	O(1)–Pd(1)–O(11)	96.40(13)

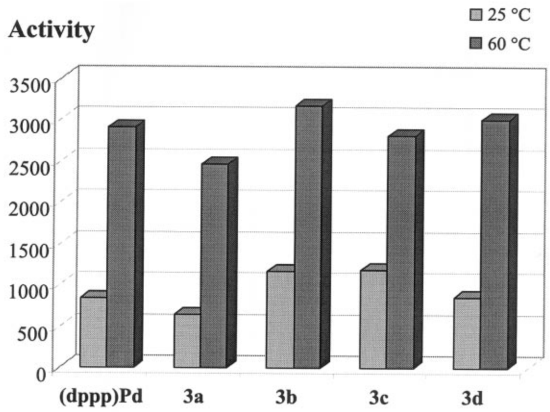


Fig. 4. Catalytic activity (g polymer)(g Pd h)$^{-1}$ in the ethene/CO copolymerization.

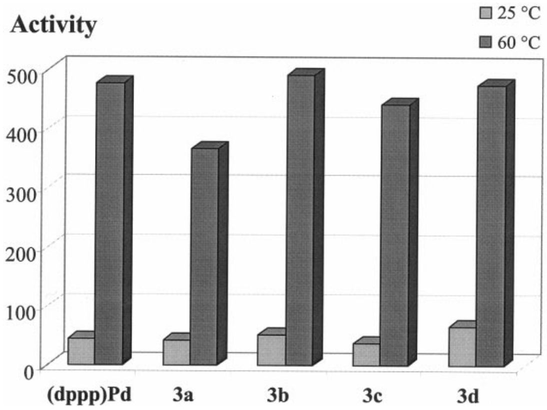


Fig. 5. Catalytic activity (g polymer)(g Pd h)$^{-1}$ in the propene/CO copolymerization.

inverse gated decoupled ^{13}C NMR spectra of the copolymers (in 1,1,1,3,3,3-hexafluoroisopropanol) no end groups were found. The integrals of the ^{13}C signals of the carbonyl and methylene groups (212 and 35 ppm, respectively [28]) are in a ratio of 1:2 which is consistent with the strict alternation of the copolymers. No additional resonances were observed.

With the exception of lower reaction rates comparable relations are established in the propene/carbon monoxide copolymerization for both temperatures (25 and 60°C). However, in contrast to ethene/CO copolymerization at 25°C, **3d** is the best catalyst in this sequence (Fig. 5 and Table 4). With all catalysts **3a–d**, colorless, viscous solutions of the copolymers were formed from which thin, brittle films were grown by slow evaporation of the solvent. At 25 °C **3a–d** produce ultra-high molecular weight propene/CO copolymers. Although **(dppp)Pd** is a similar active catalyst, chain transfer reactions are more frequent, which is corroborated by the much lower molecular weight and the broader molecular weight distribution (Table 4, run 11–15). Rising the polymerization temperature to 60°C results in decrease of the molecular weight, but **3a–d** remain superior to **(dppp)Pd**. In the DSC spectra only

Table 4
Results of the copolymerization of carbon monoxide with ethene and propene, respectively

Run	Precatalyst	Olefin [a]	Temperature (°C)	Reaction time (h)	Activity [b]	TON (cycles)	H–T units [c] (%)	M_w [d] (10^3 g mol^{-1})	M_w/M_n
1	**3a**	Ethene	25	2	645	2453	–	261.1	2.5
2	**3b**	Ethene	25	2	1166	4434	–	473.7	5.1
3	**3c**	Ethene	25	2	1189	4520	–	510.0	4.1
4	**3d**	Ethene	25	2	852	3238	–	686.9	1.9
5	**(dppp)Pd**	Ethene	25	2	840	3194	–	554.0	2.0
6	**3a**	Ethene	60	2	2469	9389	–	41.1	4.5
7	**3b**	Ethene	60	2	3174	12072	–	49.9	3.2
8	**3c**	Ethene	60	2	2803	10659	–	76.5	2.3
9	**3d**	Ethene	60	2	3007	11435	–	53.4	3.1
10	**(dppp)Pd**	Ethene	60	2	2904	11043	–	245.5	7.0
11	**3a**	Propene	25	24	43	1563	100	181.5	2.2
12	**3b**	Propene	25	24	53	1922	100	181.6	2.2
13	**3c**	Propene	25	24	37	1355	96	247.0	1.5
14	**3d**	Propene	25	24	65	2373	98	244.1	1.4
15	**(dppp)Pd**	Propene	25	24	45	1643	57	108.2	3.4
16	**3a**	Propene	60	4	365	2221	100	25.3	3.8
17	**3b**	Propene	60	4	489	2975	100	33.9	3.4
18	**3c**	Propene	60	4	441	2682	98	29.8	3.4
19	**3d**	Propene	60	4	474	2885	100	34.0	3.4
20	**(dppp)Pd**	Propene	60	4	476	2896	58	8.5	4.1

[a] Ethene: the polymerization was carried out in 30 ml of CH_2Cl_2, 2 ml of methanol and 30 bar of ethene, and CO each; propene: 100 ml of CH_2Cl_2, 2 ml of methanol, saturated with 9 bar of propene in 20 min and 51 bar of CO.

[b] Activity in g of copolymer × (g of Pd × h)$^{-1}$.

[c] H–T units: regioregularity in mol% of head-to-tail units.

[d] Molecular weight of the ethene/CO and propene/CO copolymers determined by GPC.

weak glass transitions (−5 to 10°C) and little distinct melting points (120–150°C) were observed. Inverse gated decoupled ^{13}C NMR spectra point to an almost regioregular microstructure which is realized if alkyl substituted diphospalladium(II) complexes are applied in the propene/CO copolymerization [29].

The catalytic activities of the catalysts in the copolymerization of carbon monoxide with ethene and propene cannot be correlated with the dynamic behavior of the complexes **3a–d**. Obviously the ether oxygen atoms do not compete with the substrate molecules for the empty coordination sites at the palladium centers [1]. Remarkably the complexes with the weakest Pd–O bonds belong to the most (**3b**) and least (**3c**) active catalysts in this series. If one would expect a specific effect of the hemilabile P$\cap$O ligand, the increase of the polymerization temperature should result in a significant enhancement of the catalytic activity of **3a–d** compared to [(dppp)Pd(NCCH$_3$)$_2$][BF$_4$]$_2$, which is not observed. Such an implication should be observed if the oxygen donors exert an impact on the coordination of the comonomers. Yet the copolymerization is influenced by steric effects of the ligand. From the polymerization of olefins with β-diiminepalladium(II) and -nickel(II) complexes it is known that bulky substituents are necessary to suppress chain transfer and termination reactions [30]. The lower catalytic activity of **3a** may be attributed to the lack of steric bulk.

If the oxygen function is replaced by a methylene group, the corresponding diphospalladium(II) complexes show a higher activity in the 1-alkene/CO copolymerization compared to etherdiphospalladium(II) species. In a systematic study [31], the steric and electronic properties of diphospalladium(II) complexes are optimized with respect to the catalytic performance by variation of the length of the phosphorus attached alkyl chains. This observation clearly demonstrates that not only steric, but also electronic effects play an important role in this type of catalysis.

4. Conclusions

A series of potentially hexadentate etherdiphos ligands **1a–d** (Scheme 3) was prepared by an improved synthesis derived from a patent [25]. The oxygen containing part of these ligands protects empty coordination sites in the coordinatively unsaturated dicationic etherdiphospalladium(II) complexes **3a–d**. They represent a new type of diphospalladium(II) precatalysts in the copolymerization of olefins with carbon monoxide, in which external solvent molecules (e.g. acetonitrile) are replaced for an intramolecular donor. The complexes reveal remarkable catalytic activities and polyketones with high molecular weights are obtained. A rapid chemical exchange between the η^2-P$\cap$O chelated and the η^1-P coordinated part of the ligands in **3a–d**, in other words, the strength of the Pd–O bond is not responsible for the catalytic activity of these complexes in the copolymerization of carbon monoxide with ethene and propene, respectively. Obviously the catalytic activity is influenced by steric effects, since **3b–d** with the more bulky ligands **1b–d** are superior to **3a**. However, also electronic impacts can not be ruled out.

5. Supplementary material

Crystallographic data (excluding structural factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 134578 (**2a**) and CCDC 134579 (**3c**·H$_2$O). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336 033; e-mail: deposit@ccdc.cam.ac.uk.

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