Copolymerization of carbon monoxide with ethene catalyzed by bis-chelated palladium(II) complexes containing diphosphine and dinitrogen ligands†

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Several bis-chelated palladium(II) complexes, $[Pd(P\text{-}P)(N\text{-}N)_x](PF_6)_2$, containing binary combinations of diphosphine and dinitrogen ligands have been prepared and characterized. The diphosphine ligands comprise 1,3-bis(diphenylphosphino)propane (dppp), *meso*-2,4-bis(diphenylphosphino)pentane (*meso*-bdpp), *rac*-2,4-bis(diphenylphosphino)pentane (*rac*-bdpp) and 2,2′-bis(diphenylphosphinoethyl)pentane (Etdppp), while the dinitrogen ligands are either 2,2′-bipyridine (bipy; $x = 1$) or 1,8-naphthyridine (napy; $x = 2$). The structure of $[Pd(meso\text{-bdpp})(N,N'\text{-bipy})](PF_6)_2 \cdot CH_2Cl_2$ has been determined by an X-ray structural analysis. All the Pd(II) complexes have been tested as catalyst precursors for the copolymerization of carbon monoxide and ethene in methanol solution in either autoclaves or high-pressure sapphire NMR tubes. The combination of *meso*-bdpp and bipy at palladium, in conjuction with both 1,4-benzoquinone and *p*-toluenesulfonic acid, has shown the best catalytic performance. The different catalytic activities exhibited by the stereoisomers $[Pd(meso\text{-bdpp})(N,N'\text{-bipy})](PF_6)_2$ and $[Pd(rac\text{-bdpp})(N,N'\text{-bipy})](PF_6)_2$ has been interpreted in terms of the different spatial distribution of the phenyl rings around the metal center determined by the conformation of the six-membered metallaring.

The industrial importance of polyketone materials obtained by the alternating copolymerization of carbon monoxide and α-olefins is stimulating intense research activity aimed at designing new catalysts with improved efficiency and lower environmental impact.[1,2]

The diphosphine ligand 1,3-bis(diphenylphosphino)propane (dppp) is by far the ligand of choice in the Pd-catalyzed co- and terpolymerization of carbon monoxide and ethene or ethene–propene in MeOH [eqn. (1)].[1,3] In combination with dppp and a non-coordinating counter anion, dinitrogen chelating ligands such as 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) have recently been reported to form bis-chelated palladium(II) catalysts that, under comparable experimental conditions, are more efficient than monochelated dppp–Pd(II) systems.[4]

$$n\,C_2H_4 + n\,CO + MeOH \xrightarrow{cat} Et\text{-}(CCH_2CH_2\text{-}C(=O)\text{-})_{n-1}\text{-}OMe \qquad (1)$$

Besides creating facile access of CO and MeOH to the metal center *via* decoordination, the dinitrogen co-ligands have been suggested to modulate the proton concentration in the reaction mixtures with consequent beneficial effects on the activity of the catalysts as well as the molecular weight of the polyketones.[4,5]

In the course of a recent investigation,[6] we have found that the stereoselective introduction of methyl substituents in the 1,3-positions of dppp as in *meso*-2,4-bis(diphenylphosphino)-pentane (*meso*-bdpp)[7,8] results in the formation of palladium bis(trifluoroacetate) catalysts that can be more active than their dppp counterparts by *ca.* 50%. Conversely, ethyl substituents in the 2-position as in $Et_2C(CH_2PPh_2)_2$ (Etdppp) generate a catalyst that is less efficient than the dppp analog by *ca.* 20%. The different catalytic activities were interpreted in terms of both steric and electronic factors.[6]

Intrigued by the possibility of further improving the activity of soluble palladium catalysts for $CO\text{–}C_2H_4$ copolymerization, we decided to carry out a study in which different types of diphosphine ligands derived from dppp and different types of chelating dinitrogen ligands are systematically tested as ligands to palladium(II) so as to find the (P-P)–(N-N) combination exhibiting the best catalytic performance for $CO\text{–}C_2H_4$ copolymerization.

In this paper, we report the synthesis and catalytic activity of some bis-chelated palladium(II) complexes containing binary combinations of the diphosphine and dinitrogen ligands shown in Chart 1. The ligand 1,8-naphthyridine (napy), which is a better σ-donor and a poorer π-acceptor than bipy, has been selected for its capability to easily create a free coordination site at metal centers by changing its bonding mode from $\eta^2\text{-}N,N'$ to $\eta^1\text{-}N$.[9]

The combination of certain diphosphine and dinitrogen ligands at palladium, in conjuction with both 1,4-benzoquinone (BQ) and *p*-toluenesulfonic acid (TsOH), has been found

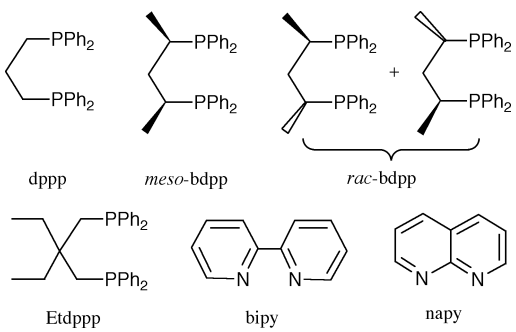


Chart 1

† *Non-SI unit employed*: 1 psi = 6.9×10^3 Pa.

to give higher productivities than dppp-based catalysts, without decreasing their spectacular chemo- and regioselectivity. High-pressure NMR experiments (HPNMR) under actual catalytic copolymerization conditions have been carried out in an attempt to elucidate the role of the dinitrogen ligands in the copolymerization mechanism catalyzed by the bis-chelated palladium complexes.

Experimental

Materials and methods

All reactions and manipulations were carried out under an atmosphere of nitrogen by using Schlenk-type techniques. The starting materials Pd(dppp) $(CO_2CF_3)_2$ (**1**),[6] [Pd(dppp)(*N*,*N*′-bipy)]$(PF_6)_2$ (**1a**),[4] napy,[9h] Pd(*meso*-bdpp)$(CO_2CF_3)_2$ (*meso*-**2**),[6] Pd(*rac*-bdpp)$(CO_2CF_3)_2$ (*rac*-**2**),[6] and Pd(Etdppp)$(CO_2CF_3)_2$ (**3**)[6] were prepared according to literature methods. Reagent grade MeOH was used in all copolymerization reactions. 1,1,1,3,3,3-Hexafluoropropan-2-ol- d_2(HFIP-d_2) was purchased from Cambridge Isotope Laboratories, Andover, MA. All other reagents and solvents were used as purchased from Aldrich, Fluka or Strem. Copolymerization reactions were performed with a 250 mL stainless steel autoclave, constructed at the ISSECC-CNR (Firenze, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure over all the catalytic reactions. Deuterated solvents for NMR measurements were dried over molecular sieves. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were obtained on either a Bruker ACP 200 (200.13, 50.32, and 81.01 MHz, respectively) or a Bruker AVANCE DRX-500 spectrometer equipped with a variable-temperature control unit accurate to ± 0.1 °C (500.13, 125.76, and 202.47 MHz, respectively). All chemical shifts are reported in ppm relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). The assignments of the signals resulted from 1D spectra, 2D ^{1}H-DQF-COSY, ^{1}H-NOESY, ^{1}H-ROESY and proton-detected 2D ^{1}H-^{13}C, ^{1}H-^{31}P correlations using non-spinning samples. 2D NMR spectra were recorded using pulse sequences suitable for phase-sensitive representations with TPPI. J_{HH} and J_{HP} coupling constants were obtained from ^{1}H and ^{1}H{^{31}P} heteronuclear decoupled 1D spectra and with the aid of computer simulation of the spectra using the gNMR program.[10] Standard pulse sequences were used for the ^{1}H-DQF-COSY,[11] ^{1}H-NOESY[12] and ^{1}H-ROESY[13] experiments; 1024 increments of size 2K (each with 16 scans) covering the full range in both dimensions (*ca.* 5900 Hz) were acquired with a relaxation delay of 1.5 s and a mixing time of 0.7 s. The ^{1}H-^{13}C correlations were recorded using the standard HMQC sequence[14] with no decoupling during acquisition; 1024 increments of size 2K (each with 16 scans) were collected covering the full range in both dimensions with a relaxation delay of 1.0 s. The ^{1}H-^{31}P correlations were recorded with the standard HMQC sequence with ^{1}H decoupling during acquisition; 128 increments of size 2K (each with 8 scans) were collected covering the full range in both dimensions with a relaxation delay of 1.0 s. The 10 mm sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure charging-head was constructed at the ISSECC-CNR (Firenze, Italy).[15]

Safety note: Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes.

General procedure for the synthesis of bis-chelated palladium complexes

To 5 mL of a methanol solution of Pd(P-P)$(CO_2CF_3)_2$ (P-P = dppp, *meso*-bdpp, *rac*-bdpp, Etdppp) and dinitrogen ligand N-N (napy, 2.3 equiv; bipy, 1.2 equiv) was added 5 mL of a methanol solution of NH_4PF_6 [eqn. (2)].

$$\text{Pd(P-P)(CO}_2\text{CF}_3)_2 + x\text{N-N} \xrightarrow[\text{MeOH}]{\text{NH}_4\text{PF}_6} [\text{Pd(P-P)(N-N)}_x](\text{PF}_6)_2$$

$$\text{bipy, } x = 1\text{; napy, } x = 2 \qquad (2)$$

The solution was allowed to stir for 5 min. The product precipitated on addition of 40 mL of petroleum ether. The solid was filtered on a sintered-glass frit and washed with petroleum ether before being dried in a stream of nitrogen.

[Pd(dppp)(*N*-napy)$_2$](PF$_6$)$_2$, 1b. **1** (150 mg, 0.20 mmol), 60 mg of napy (0.46 mmol) and 75 mg of NH_4PF_6 (0.46 mmol) were used. A white solid was obtained. Yield: 180 mg, 96%. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 2.31 (m, 2H, aliphatic chain), 2.87 (m, 4H, aliphatic chain), 7.1–8.0 (m, 24H, Ph and $H_{\beta\text{-}\beta'}$ napy), 8.01 (d, 4H, $J_{H_\gamma H_\beta} = J_{H_{\gamma'}H_{\beta'}} = 7.9$ Hz, $H_{\gamma\text{-}\gamma'}$ napy), 9.38 (br s, 4H, $H_{\alpha\text{-}\alpha'}$ napy). Anal. calcd (found) for $C_{43}H_{38}F_{12}N_4P_4Pd$: C, 48.31 (47.80); H, 3.58 (3.57); N, 5.24 (5.04).

[Pd(*meso*-bdpp)(*N*,*N*′-bipy)](PF$_6$)$_2$, *meso*-2a. *meso*-**2** (130 mg, 0.16 mmol), 31 mg of bipy (0.20 mmol) and 60 mg of NH_4PF_6 (0.37 mmol) were used. A white solid was obtained. Yield: 150 mg, 93%. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 1.06 (dd, 6H, $J_{HH} = 7.1$ Hz, $J_{HP} = 17.2$ Hz, CHC*H*$_3$), 1.81 (m, 1H, C*H*^{1}H), 2.4–2.9 (m, 3H, C*H*CH$_3$ and CH*H*^{2}), 7.08 (t, 2H, $J_{HH} = 6.6$ Hz, $H_{5\text{-}5'}$ bipy), 7.5–7.8 (m, 14H, Ph and $H_{6\text{-}6'}$ bipy), 7.9–8.2 (m, 10H, Ph and $H_{4\text{-}4'}$ bipy), 8.27 (d, 2H, $J_{HH} = 8.2$ Hz, $H_{3\text{-}3'}$ bipy). ^{13}C{^{1}H} NMR (125.76 MHz, CD_2Cl_2): δ 18.47 (CH*C*H$_3$), 27.96 (*C*HCH$_3$), 35.74 (CH$_2$), 135.76 (*o*-Ph^1), 130.28 (*m*-Ph^1), 133.81 (*p*-Ph^1), 133.47 (*o*-Ph^2), 130.93 (*m*-Ph^2), 134.23 (*p*-Ph^2), 124.22 ($C_{33'}$), 142.10 ($C_{44'}$), 126.33 ($C_{55'}$), 151.14 ($C_{66'}$). Anal. calcd (found) for $C_{39}H_{38}F_{12}N_2P_4Pd$: C, 47.17 (46.97); H, 3.86 (3.85); N, 2.82 (2.75). Crystals of *meso*-**2a**·CH_2Cl_2, suitable for an X-ray diffraction analysis, were grown by slow evaporation from a diluted dichloromethane solution of *meso*-**2a**. Anal. calcd (found) for $C_{40}H_{40}Cl_2F_{12}N_2P_4Pd$: C, 44.57 (44.33); H, 3.74 (3.61); N, 2.60 (2.51).

[Pd(*meso*-bdpp)(*N*-napy)$_2$](PF$_6$)$_2$, *meso*-2b. *meso*-**2** (200 mg, 0.26 mmol), 80 mg of napy (0.62 mmol) and 97 mg of NH_4PF_6 (0.60 mmol) were used. A white solid was obtained. Yield: 210 mg, 85%. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 1.19 (m, 6H, CHC*H*$_3$), 2.0–2.4 (m, 2H, CH$_2$), 2.94 (m, 2H, C*H*CH$_3$), 7.2–8.3 (m, 28H, Ph and $H_{\beta\text{-}\beta'}$, $H_{\gamma\text{-}\gamma}$ napy), 8.91 (br s, 4H, $H_{\alpha\text{-}\alpha}$ napy). Anal. calcd (found) for $C_{45}H_{42}F_{12}N_4P_4Pd$: C, 49.26 (49.20); H, 3.86 (3.83); N, 5.11 (5.09).

[Pd(*rac*-bdpp)(*N*,*N*′-bipy)](PF$_6$)$_2$, *rac*-2a. *rac*-**2** (250 mg, 0.32 mmol), 60 mg of bipy (0.38 mmol) and 120 mg of NH_4PF_6 (0.74 mmol) were used. A white solid was obtained. Yield: 250 mg, 79%. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 1.09 (dd, 6H, $J_{HH} = 7.0$ Hz, $J_{HP} = 16.3$ Hz, CHC*H*$_3$), 1.9–2.2 (m, 2H, CH$_2$), 2.80 (m, 2H, C*H*CH$_3$), 7.15 (t, 2H, $J_{HH} = 6.9$ Hz, $H_{5\text{-}5'}$ bipy), 7.5–8.0 (m, 18H, Ph and $H_{6\text{-}6'}$ bipy), 8.06 (td, 2H, $J_{HH} = 7.9$, 1.5 Hz, $H_{4\text{-}4'}$), 8.22 (d, 2H, $J_{HH} = 8.0$ Hz, $H_{3\text{-}3'}$), 8.39 (m, 4H, Ph). ^{13}C{^{1}H} NMR (125.76 MHz, CD_2Cl_2): δ 18.01 (CH*C*H$_3$), 31.02 (*C*HCH$_3$), 35.52 (CH$_2$), 135.87 (*o*-Ph^1), 131.46 (*m*-Ph^1), 135.22 (*p*-Ph^1), 132.65 (*o*-Ph^2), 130.58 (*m*-Ph^2), 133.60 (*p*-Ph^2), 124.18 ($C_{33'}$), 141.95 ($C_{44'}$), 126.98 ($C_{55'}$), 150.70 ($C_{66'}$). Anal. calcd (found) for $C_{39}H_{38}F_{12}N_2P_4Pd$: C, 47.17 (46.76); H, 3.86 (3.82); N, 2.82 (2.81).

[Pd(*rac*-bdpp)(*N*-napy)$_2$](PF$_6$)$_2$, *rac*-2b. *rac*-**2** (350 mg, 0.45 mmol), 140 mg of napy (1.08 mmol) and 169 mg of NH_4PF_6 (1.04 mmol) were used. A white solid was obtained. Yield: 390 mg, 89%. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 1.16 (m, 6H, CHC*H*$_3$), 1.8–2.2 (m, 2H CH$_2$), 3.15 (m, 2H, C*H*CH$_3$), 6.7–7.1 (m, 10H, Ph), 7.35 (dd, 2H, $J_{H\beta H\gamma} = 8.2$ Hz, $J_{H\beta H\alpha} = 5.1$ Hz, H_β napy), 7.69 (dd, 2H, $J_{H\beta' H\gamma'} = 8.2$ Hz, $J_{H\beta' H\alpha'} = 4.4$ Hz, $H_{\beta'}$

Table 1 Summary of crystallographic data for *meso*-**2a** · CH_2Cl_2

Formula	$C_{40}H_{40}Cl_2F_{12}N_2P_4Pd$
M	1077.96
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	16.085(9)
b/Å	14.361(2)
c/Å	19.564(3)
β/°	94.39(2)
U/Å^3	4506(2)
Z	4
T/K	298
μ/mm^{-1}	0.745
Reflections collected	81 522
Independent reflections	7906 ($R_{int} = 0.1003$)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0880$, $wR_2 = 0.2134$
R indices (all data)	$R_1 = 0.2424$, $wR_2 = 0.2730$

napy), 8.0–8.2 (m, 10H, Ph and $H_{\gamma-\gamma'}$ napy), 8.78 (m, 4H, Ph), 8.92 (m, 2H, H_α napy), 9.44 (dd, 2H, $J_{H\alpha'H\beta'} = 4.4$ Hz, $J_{H\alpha'H\gamma'} = 1.7$ Hz, $H_{\alpha'}$ napy). Anal. calcd (found) for $C_{45}H_{42}F_{12}N_4P_4Pd$: C, 49.26 (48.59); H, 3.86 (3.81); N, 5.11 (4.91).

[Pd(Etdppp)(*N*,*N*′-bipy)](PF$_6$)$_2$, 3a. 3 (47 mg, 59 μmol), 11 mg of bipy (71 μmol) and 23 mg of NH_4PF_6 (0.14 mmol) were used. A grey solid was obtained. Yield: 50 mg, 83%. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 0.54 (t, 6H, $J_{HH} = 7.2$ Hz, CH_2CH_3), 0.99 (q, 4H, $J_{HH} = 7.2$ Hz, CH_2CH_3), 2.44 (d, 4H, $J_{HP} = 7.8$ Hz, CH_2P), 7.05 (t, 2H, $J_{HH} = 7.1$ Hz, $H_{5-5'}$ bipy), 7.6–7.8 (br, 14H, Ph and $H_{6-6'}$ bipy), 8.04 (td, 2H, $J_{HH} = 7.8$, 1.3 Hz, $H_{4-4'}$ bipy), 8.1–8.3 (br, 10H, Ph and $H_{3-3'}$ bipy). Anal. calcd (found) for $C_{41}H_{42}F_{12}N_2P_4Pd$: C, 48.23 (48.11); H, 4.15 (4.05); N, 2.74 (2.61).

[Pd(Etdppp)(*N*-napy)$_2$](PF$_6$)$_2$, 3b. 3 (90 mg, 0.11 mmol), 32 mg of napy (0.25 mmol) and 41 mg of NH_4PF_6 (0.25 mmol) were used. A pale brown solid was obtained. Yield: 85 mg, 77%. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 0.49 (t, 6H, $J_{HH} = 7.3$ Hz, CH_2CH_3), 0.96 (q, 4H, $J_{HH} = 7.3$ Hz, CH_2CH_3), 2.56 (d, 4H, $J_{HP} = 8.1$ Hz, CH_2P), 7.4–8.0 (m, 24H, Ph and $H_{\beta-\beta'}$ napy), 8.06 (dd, 4H, $J_{H\gamma H\beta} = 8.3$, $J_{H\gamma H\alpha} = 1.8$ Hz, $H_{\gamma-\gamma'}$ napy), 9.07 (d, 4H, $J_{H\alpha H\beta} = 4.7$ Hz, $H_{\alpha-\alpha'}$ napy). Anal. calcd (found) for $C_{47}H_{46}F_{12}N_4P_4Pd$: C, 50.17 (49.98); H, 4.12 (4.08); N, 4.98 (4.70).

Copolymerization studies

Copolymerization of CO and ethene at constant pressure. Typically, a 100 mL solution of MeOH containing 0.01 mmol of catalyst, 0.8 mmol of BQ and the required acid was introduced by suction into a 250 mL autoclave previously evacuated by a vacuum pump. The autoclave was first pressurized with a 1 : 1 mixture of C_2H_4 and CO to 600 psi at room temperature and then heated to 85 °C. When the autoclave contents reached the desired temperature, they were stirred (1400 rpm) for 3 h. During the reaction the pressure level was kept constant at *ca.* 800 psi by continuous feeding of an equimolar mixture of C_2H_4 and CO from a high-pressure gas reservoir. The reaction was stopped by cooling the autoclave to room temperature by means of an ice-water bath. The pressure was then released. The polymer was filtered off, washed with methanol, and dried in a vacuum oven at 70 °C overnight.

***In situ* NMR study of the copolymerization of CO and ethene.** In a typical experiment, a 10 mm sapphire HPNMR tube was charged with the appropriate bis-chelated precursor (0.01 mmol), BQ (0.1 mol) and MeOH-d_4 (2 mL) under nitrogen. Under these conditions, all of the palladium complex did not generally dissolve. In all cases, however, the addition of 2 equiv. of TsOH led to complete dissolution of the complex. ^{1}H and ^{31}P{^{1}H} NMR spectra were acquired both before and after the addition of the acid. The tube was pressurized with a 1 : 1 mixture of CO and C_2H_4 to 600 psi at room temperature and then was heated to 85 °C. After *ca.* 2 h, the tube was cooled to room temperature and removed from the probehead. The formed copolymers appeared as off-white solids floating over yellow solutions.

Characterization of the copolymer. Irrespective of the catalyst precursor, the copolymer samples isolated were off-white powders with high melting points (246–256 °C).[1–4,6] These polyketones are insoluble in common organic solvents and dissolve appreciably only in highly polar solvents such as HFIP, *m*-cresol or trichlorobenzene, or in strong protic acids such as trifluoroacetic acid. The elemental analysis values are in agreement with an ethene : CO ratio of 1. Spectroscopically (IR and NMR), the polyketones obtained are identical with those previously isolated in methanol and for which a perfectly alternating structure was assigned.[1,3,4,6] In particular, the ^{1}H and ^{13}C{^{1}H} NMR spectra of the samples show the contemporaneous presence of both ketonic and ester end groups. The copolymers analyzed present average molecular weights (M_n), calculated by means of ^{1}H and ^{13}C{^{1}H} NMR spectroscopy in HFIP-d_2, in the range of 10 to 20 kg mol^{-1} depending on the reaction conditions.

X-Ray diffraction study of *meso*-2a · CH_2Cl_2

Selected crystallographic data for the compound is presented in Table 1. Experimental data were recorded at room temperature on a Enraf-Nonius CAD4 diffractometer using graphite-monochromated MoKa radiation. A set of 25 carefully centered reflections in the range $5.0° \leqslant \theta \leqslant 9.0°$, respectively, was used for determining the lattice constants. As a general procedure, the intensity of three standard reflections were measured periodically every 2 h for orientation and intensity control. This procedure revealed a minimum decay (2%) of intensities. The data were corrected for Lorentz and polarization effects. Atomic scattering factors were those tabulated by Cromer and Waber[16] with anomalous dispersion corrections taken from ref. 17. An empirical absorption correction was applied *via* ψ scan with transmission factors in the range 90.73–99.73. The computational work was performed with a Digital DEC 2000 workstation using the program SHELX96.[18]

The structure was solved *via* direct methods using the SIR92 program[19] and all non-hydrogen atoms were found through a series of F_o Fourier maps. Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters, and then, in the last least-square cycle, with anisotropic thermal parameters for all atoms except for the fluorine atoms of PF_6^-. All of the phenyl rings were treated as rigid bodies with D_{6h} symmetry and C–C distances fixed at 1.39 Å. Hydrogen atoms were introduced in calculated positions, but not refined.

CCDC reference number 440/131. See http://www.rsc.org/suppdata/nj/1999/929/ for crystallographic files in .cif format.

Results and discussion

Synthesis and characterization of palladium complexes with diphosphine and dinitrogen ligands

In Chart 2 are shown the complexes that have been employed as catalyst precursors for the copolymerization of CO and ethene.

The new bis-chelated derivatives [Pd(dppp)(*N*-napy)$_2$](PF$_6$)$_2$ (**1b**), [Pd(*meso*-bdpp)(*N*,*N*′-bipy)](PF$_6$)$_2$ (*meso*-**2a**), [Pd(*meso*-bdpp)(*N*-napy)$_2$](PF$_6$)$_2$ (*meso*-**2b**), [Pd(*rac*-bdpp)(*N*,*N*′-bipy)](PF$_6$)$_2$ (*rac*-**2a**), [Pd(*rac*-bdpp)(*N*-napy)$_2$](PF$_6$)$_2$ (*rac*-**2b**), [Pd(Etdppp)(*N*,*N*′-bipy)](PF$_6$)$_2$ (**3a**) and [Pd(Etdppp)(*N*-

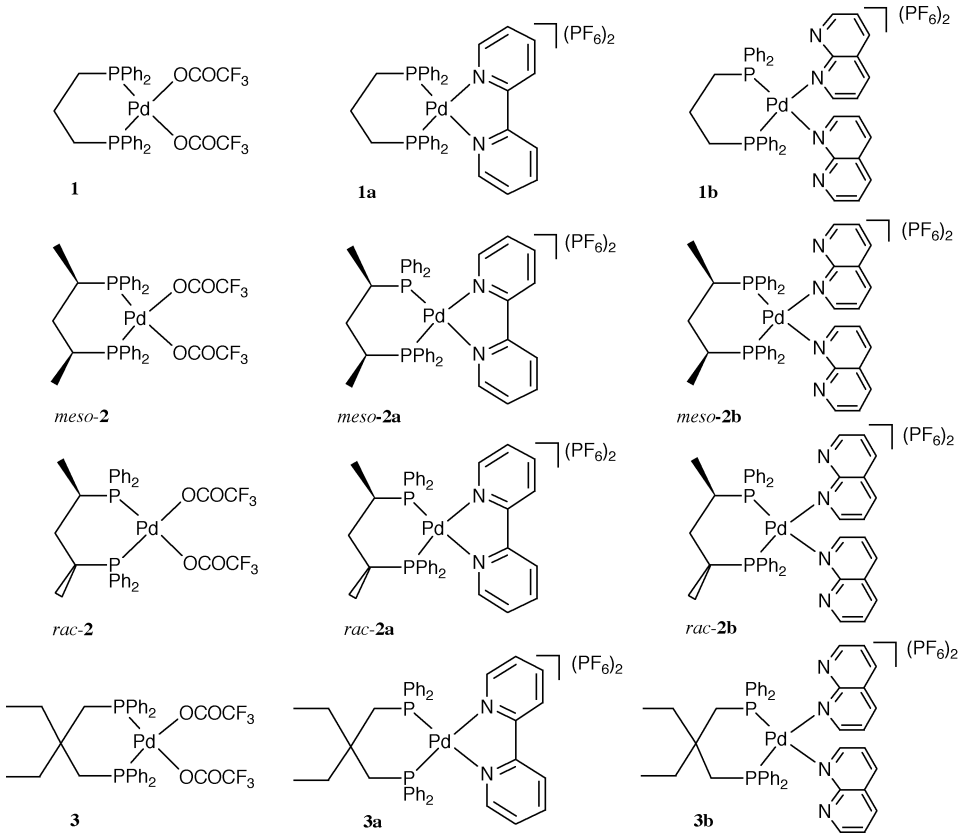


Chart 2

napy)$_2$](PF$_6$)$_2$ (**3b**) were synthesized following the synthetic protocol reported in the literature for [Pd(dppp)(*N*,*N*′-bipy)](PF$_6$)$_2$ (**1a**).[4] The latter complex and the monochelated trifluoroacetate derivatives Pd(dppp)(CO$_2$CF$_3$)$_2$ (**1**), Pd(*meso*-bdpp)(CO$_2$CF$_3$)$_2$ (*meso*-**2**), Pd(*rac*-bdpp)(CO$_2$CF$_3$)$_2$ (*rac*-**2**) and [Pd(Etdppp)(CO$_2$CF$_3$)$_2$ (**3**) were prepared for comparative purposes.[6]

The napy complexes contain two molecules of N-N ligand. Indeed, the ring strain in the four-membered metallaring has often been found to disfavor the η^2-*N*,*N*′ coordination mode of napy over the η^1-*N* one.[9] The bis(napy) complexes indeed form when only 1 equiv. of napy is reacted with Pd(P-P)(CO$_2$CF$_3$)$_2$. Overall, napy is a better ligand than bipy towards the present [Pd(P-P)]$^{2+}$ systems as shown by the fact that the addition of napy to methanol solutions of [Pd(P-P)(*N*,*N*′-bipy)](PF$_6$)$_2$ gives [Pd(P-P)(*N*-napy)$_2$](PF$_6$)$_2$ whereas the reverse reactions do not occur.

Single crystals of *meso*-**2a**·CH$_2$Cl$_2$ were analyzed by X-ray diffraction. Despite the low quality of the crystals, the structure was successfully solved and refined. The geometrical parameters obtained are sufficiently reliable to allow a sound discussion of the coordination geometry around the palladium center in the complex cation [Pd(*meso*-bdpp)(*N*,*N*′-bipy)]$^{2+}$. An ORTEP drawing is shown in Fig. 1(*a*), while relevant bond distances and angles are listed in Table 2.

The Pd atom has a square-planar coordination and is displaced by 0.008 Å from the P$_2$N$_2$ mean plane, the atoms of which are coplanar within ±0.19 Å. As is evident from inspection of Fig. 1(*b*), the six-membered chelate ring adopts a distorted conformation with pseudo-equatorial methyl groups. The overall geometry is quite similar to that found in [Pd(dppp)(*N*,*N*′-bipy)]$^{2+}$.[4] The bond angles around the metal center are the same as in the dppp derivative while all bond distances are slightly longer. In particular, one Pd–P distance

Table 2 Selected bond lengths (Å) and angles (°) in *meso*-**2a** · CH$_2$Cl$_2$

Pd–P1	2.267(3)	Pd–N1	2.122(11)
Pd–P2	2.286(3)	Pd–N2	2.136(10)
P1–Pd–P2	87.6(1)	P1–C1–C3	114.2(10)
P1–Pd–N1	169.1(3)	C1–C3–C2	120.8(12)
P1–Pd–N2	98.6(3)	C3–C2–P2	110.2(9)
P2–Pd–N1	98.2(3)	C5–C2–C3	112.4(13)
P2–Pd–N2	169.7(3)	C5–C2–P2	112.2(10)
N1–Pd–N2	77.1(5)		

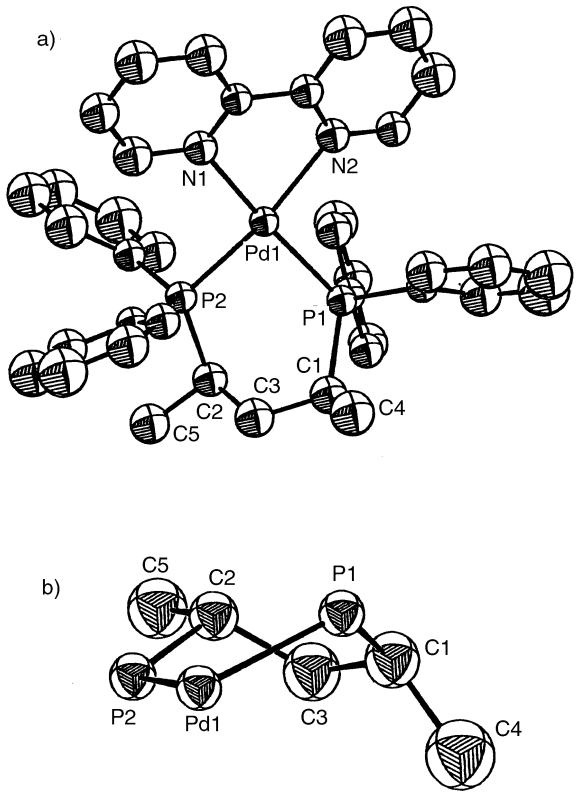


Fig. 1 (*a*) ORTEP drawing of the complex cation in *meso*-**2a**·CH$_2$Cl$_2$. (*b*) Simplified representation of the six-membered chelate ring.

in *meso*-**2a** appears longer than the other one [2.286(3) *vs.* 2.267(3) Å]. Like the dppp analog, [Pd(*meso*-bdpp)(*N*,*N*′-bipy)]$^{2+}$ is affected by steric strain in the diphosphine ligand as evidenced by both the large deviation from ideality of the bond angles in the alkyl chain and the displacements of P1 and P2 (−0.40 and 0.37 Å, respectively) from the PdN_2 plane.

The $^{31}P\{^1H\}$ NMR spectra of all bis-chelated complexes in CD_2Cl_2 consist of temperature-invariant singlets down to −80 °C (Table 3). From the spectra of the bipy complexes it is apparent that the two phosphorus donors are isochronous but not magnetically equivalent (see their different coupling to the H_6 hydrogen atom of bipy and to the central CH_2 group, Table 4). Due to the weaker donor properties of bipy as compared to napy, the bipy complexes exhibit lower field phosphorus resonances. The same occurs in MeOH-d_4 where the $^{31}P\{^1H\}$ NMR spectra of all compounds feature singlets at chemical shifts close to those in CD_2Cl_2.

All the bis-chelated complexes are stable as both the solid and in solution. Unlike the trifluoroacetate derivatives **1**, *meso*-**2**, *rac*-**2** and **3**, the bis-chelated complexes are quite stable in methanol at room temperature and no metallic palladium was observed inside the NMR tubes after 24 h. Heating methanol solutions at 85 °C for 3 h in NMR tubes showed all the napy compounds to be thermally stable, whereas the bipy derivatives decomposed, although very slowly, to give free bipy (5–10% after 3 h).

In both CD_2Cl_2 and MeOH-d_4, the bipy complexes show sharp, temperature-invariant ^1H NMR resonances that are shifted upfield, especially H_6, with respect to those of the free ligands.[4,5,20] Moreover, the hydrogens of bipy generate four signals of equal intensity indicating the equivalence of the two halves of the chelating ligand.[4,5,20] In an attempt to rationalize the different catalytic activity of *meso*-**2a** and *rac*-**2a** (*vide infra*), a detailed NMR study has been carried out on these two compounds in CD_2Cl_2. Selected ^1H NMR data are reported in Table 4.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of *meso*-**2a** display resonances due to a single set of CH and CH_3 groups, one diphenylphosphino group and one pyridyl unit. Two diastereotopic resonances feature the central CH_2 group (δ 1.81, CH^1H^2; 2.65, CH^1H^2). The overall pattern of the NMR resonances thus indicates that the complex assumes a time-averaged preferred conformation in which a reflection plane perpendicular to the coordination plane of the metal encompasses the methylene carbon, the Pd atom and the midpoint of the C–C bond connecting the two halves of bipy. A sketch of the molecule with the possible conformers is given in Fig. 2. The presence of a symmetry plane rules out a skew conformation for the six-membered chelate ring, while either boat or chair conformations may be equally plausible, each of which can bear equatorial or axial methyl groups.[7,21] Irrespective of the conformation, two phenyl rings are equatorial, while two are axial. In this way, the steric hindrance at the metal center in *meso*-**2a** is concentrated below the PPdP plane, leaving a complementary free space for coordination and reactivity. This concept has previously been developed for rationalizing the enantioselectivity of reactions catalyzed by chiral diphosphine ligands.[7,21,22]

The ^1H and $^{13}C\{^1H\}$ NMR spectra of *rac*-**2a** are quite similar to those of *meso*-**2a** except for the presence of a non-diastereotopic CH_2 group. This indicates that the complex in solution adopts a time-preferred conformation in which a C_2 axis passes through the Pd atom, the methylene carbon atom and the midpoint of the pyridyl–pyridyl C–C bond. A conformation of this type for six-membered chelate rings is known as "chiral skew"[7,21] and two possible conformers are possible,

Table 3 $^{31}P\{^1H\}$ NMR chemical shifts of palladium(II) complexes[a]

Trifluoroacetate complexes	δ	bipy complexes	δ	napy complexes	δ	Free ligand (δ)
1	12.1	**1a**	18.5	**1b**	7.6	−17.1
meso-**2**	30.5	*meso*-**2a**	32.1	*meso*-**2b**	26.0	−1.1
rac-**2**	25.5	*rac*-**2a**	35.7	*rac*-**2b**	28.5	0.1
3	19.6	**3a**	25.8	**3b**	16.5	−25.9

[a] All spectra were recorded at 81.01 MHz 20 °C in CD_2Cl_2 solutions.

Table 4 Selected ^1H NMR data for *rac*-**2a** and *meso*-**2a**[a]

	rac-**2a**		*meso*-**2a**	
Nucleus	δ	*J*/Hz	δ	*J*/Hz
$CHCH_3$	1.09 dd	$^3J_{HP}$ 16.3, $^3J_{HH}$ 7.0	1.06 dd	$^3J_{HP}$ 17.2, $^3J_{HH}$ 7.1
CH_2	2.11 ddt	$^3J_{HP}$ 23.3, $^3J_{HP'}$ 14.8, $^3J_{HH}$ 9.4	1.81 dtt	$^2J_{HH}$ 15.4, $^3J_{HP}$ 11.3, $^3J_{HH}$ 8.9 (CH^1)
			2.65 tdt	$^3J_{HP}$ 25.2, $^2J_{HH}$ 15.4, $^3J_{HH}$ 7.0 (CH^2)
$CHCH_3$	2.80 tqd	$^3J_{HH}$ 9.4, $^3J_{HH}$ 7.0, $^2J_{HP}$ 6.8	2.84 dddq	$^3J_{HH}$ 8.9, $^2J_{HP}$ 8.5, $^3J_{HH}$ 7.1, $^3J_{HH}$ 7.0
o-Ph^1	8.41		8.02[b]	
m-Ph^1	7.92		7.62	
p-Ph^1	7.96		7.74	
o-Ph^2	7.88		8.01[b]	
m-Ph^2	7.58		7.71	
p-Ph^2	7.62		7.78	
H3-3′	8.22 br d	$^3J_{HH}$ 8.0	8.27 br d	$^3J_{HH}$ 8.1
H4-4′	8.06 td	$^3J_{HH}$ 7.2, $^4J_{HH}$ 1.2	8.09 td	$^3J_{HH}$ 7.3, $^4J_{HH}$ 1.2
H5-5′	7.15 ddd	$^3J_{HH}$ 7.2, $^3J_{HH}$ 5.7, $^4J_{HH}$ 1.1	7.08 ddd	$^3J_{HH}$ 7.3, $^3J_{HH}$ 5.7, $^4J_{HH}$ 1.2
H6-6′	7.79 dddd	$^3J_{HH}$ 5.7, $^4J_{HP'}$ 4.6, $^4J_{HP}$ 3.0, $^4J_{HH}$ 1.2	7.68 dddd	$^3J_{HH}$ 5.7, $^4J_{HP'}$ 4.6, $^4J_{HP}$ 3.1, $^4J_{HH}$ 1.2

[a] 500.13 MHz, CD_2Cl_2, 20 °C. Abbreviations used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet. Unresolved multiplet unless otherwise specified. [b] Partially overlapped.

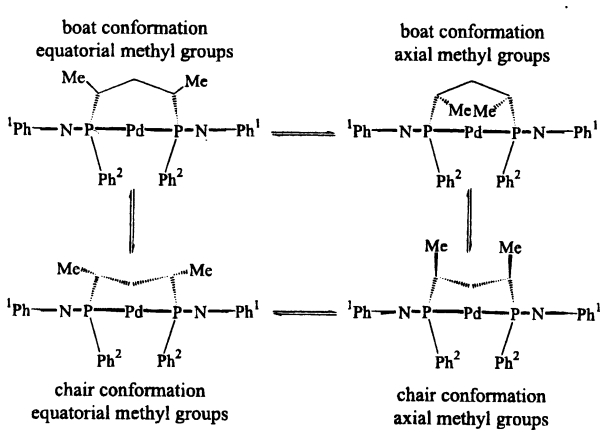
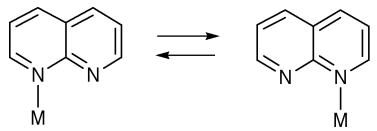


Fig. 2 Sketch of the four possible conformers of *meso*-**2a** in CD_2Cl_2 solution. View along the Pd–bipy axis with the amino ligand in the front.

bearing either pseudoaxial or pseudoequatorial methyl groups. Based on previous studies of rhodium (*S*,*S*)-bdpp complexes and other related metal complexes with diphosphine ligands,[7,21–23] a δ-skew conformation with equatorial methyl groups might be the preferred one also for *rac*-**2a**. A sketch of the molecule with the possible conformers is shown in Fig. 3. Again, two pairs of pseudo-equatorial and pseudo-axial phenyl rings feature either conformation. In this case, however, the crowded space (sterically hindered quadrants) is diagonally positioned with respect to the PPdP plane so that the free space at the metal center is more dispersed than in *meso*-**2a**.[7,21,22]

Unlike the bipy analogs, the napy complexes **1b**, *meso*-**2b** and **3b** are highly fluxional on the NMR time scale in either CD_2Cl_2 or MeOH-d_4 solution. The most relevant feature in the ^{1}H NMR spectrum of each compound is the presence of three signals for the napy protons, that is, one-fourth the number of chemically equivalent protons. The only dynamic process able to account for this NMR feature is a very fast interconversion of the bound and free nitrogen donors in each napy ligand [eqn. (3)]. Such a metal site exchange is indeed typical of η^1-*N* napy ligands and should have a very low energy barrier as the ^{1}H NMR spectra of **1b**, *meso*-**2b** and **3b** are temperature-invariant down to −80 °C.



(3)

Fig. 4 reports the ^{1}H NMR spectra in MeOH-d_4 of the napy complex **1b** in the aromatic hydrogen region at room

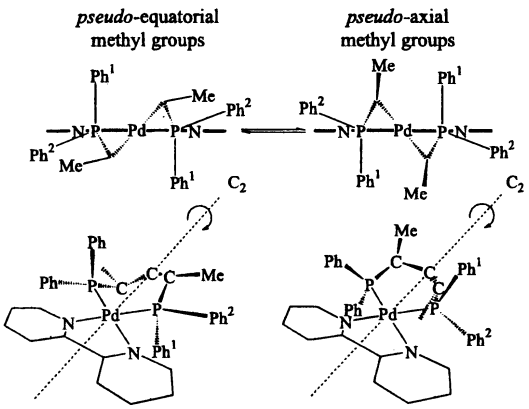


Fig. 3 Sketch of the two "skew" conformers of *rac*-**2a** in CD_2Cl_2 solution. (*Upper*) View along the C_2 axis, (*lower*) perspective view.

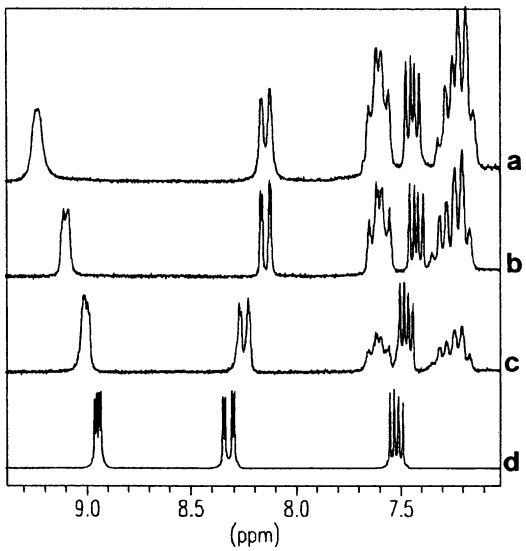


Fig. 4 Variable-temperature ^{1}H NMR spectra of **1b** (200.13 MHz, MeOH-d_4): (*a*) room temperature; (*b*) 85 °C; (*c*) 85 °C, after adding 1 equiv. of napy. (*d*) For comparative purposes, the ^{1}H NMR spectrum (MeOH-d_4, room temperature) of the napy ligand.

temperature (*a*), after 2 h at 85 °C (*b*) and at 85 °C in the presence of 1 equiv. of napy (*c*). The spectrum of the free ligand at room temperature is also reported for comparative purposes (*d*). Both the thermal stability and the fluxionality of the complex are evident. In particular, the exchange of coordinated and free ligand at 85 °C (*c*) suggests that coordination vacancies at the palladium center may be created by napy decoordination. At room temperature, the exchange of bound and free napy is almost negligible.

As shown in Fig. 5, *rac*-**2b** is the only bis-napy complex in the series to be stereochemically rigid on the NMR time scale in ambient temperature solution. The six hydrogen atoms of each equivalent napy ligand (*a*) are indeed visible at room temperature and their exchange takes place only at 85 °C (*d*). In light of the NMR analysis of *rac*-**2a** discussed above, the rigidity exhibited by *rac*-**2b** at room temperature might just be due to the "skew" conformation of the *rac*-bdpp–Pd metallaring that, by increasing the steric hindrance at the metal center, would increase the energy barrier to the metal site exchange shown in eqn. (3).

The napy and bipy complexes show different aptitudes to react with a protic acid, which is an important issue for

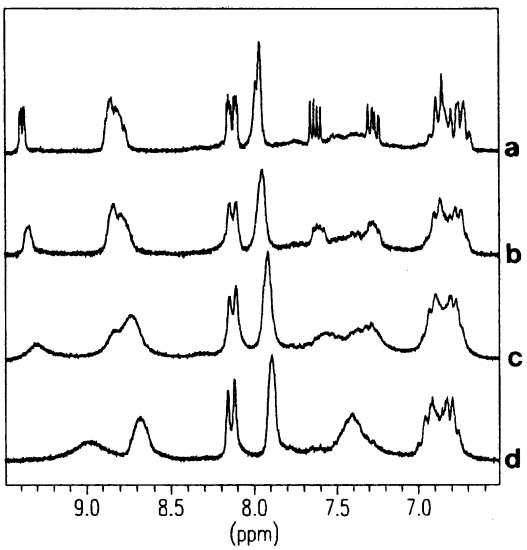


Fig. 5 Variable-temperature ^{1}H NMR spectra of *rac*-**2b** (200.13 MHz, MeOH-d_4): (*a*) room temperature; (*b*) 40; (*c*) 60; (*d*) 85 °C.

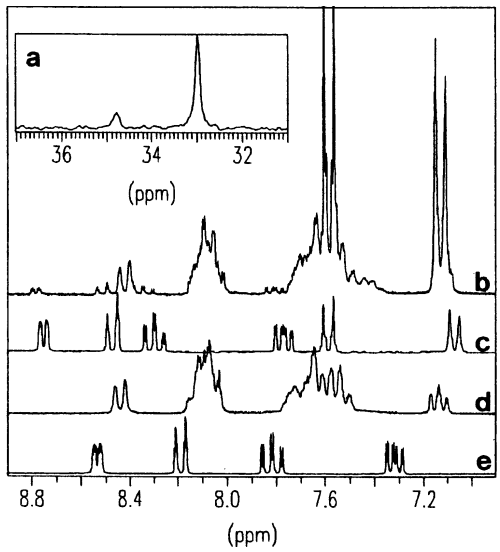


Fig. 6 (*a*) $^{31}P\{^{1}H\}$ (81.01 MHz) and (*b*) ^{1}H NMR (200.13 MHz) spectra of *meso*-**2a** in MeOH-d_4 at room temperature. For comparative purposes, the ^{1}H NMR spectra (MeOH-d_4, room temperature) of (*c*) [bipyH](OTs), (*d*) *meso*-**2a** and (*e*) bipy are shown.

rationalizing their catalytic behavior (*vide infra*). In Fig. 6 are shown the $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra at 20 °C of a MeOH-d_4 solution of *meso*-**2a** containing 2 equiv. of TsOH. For comparative purposes, the spectra of free bipy (*e*) and [bipyH](OTs) (*c*) in MeOH-d_4 are also reported. The $^{31}P\{^{1}H\}$ NMR spectrum of *meso*-**2a** (*a*) clearly shows that 15% of the starting complex (δ 33.1) converts to the bis-tosylate complex Pd(*meso*-bdpp)$(OTs)_2$ (δ 34.8) just after acquisition of the first spectrum.[6,24] This transformation proceeds by protonation of a corresponding amount of bipy to give free $[bipyH]^+$(*c*).[4,5] In the absence of acid, the complex is stable at 20 °C and no trace of free bipy was detected after 2 h (*d*).

A quite different NMR picture, consistent with the high stability of the bis-chelated structure in acidic media, is observed for the napy derivatives as exemplified by **1b** in Fig. 7. A sequence of variable-temperature $^{31}P\{^{1}H\}$ NMR spectra is reported on the left-hand side. Unlike the bipy analog, the addition of 2 equiv. of TsOH to **1b** at 20 °C does not lead to

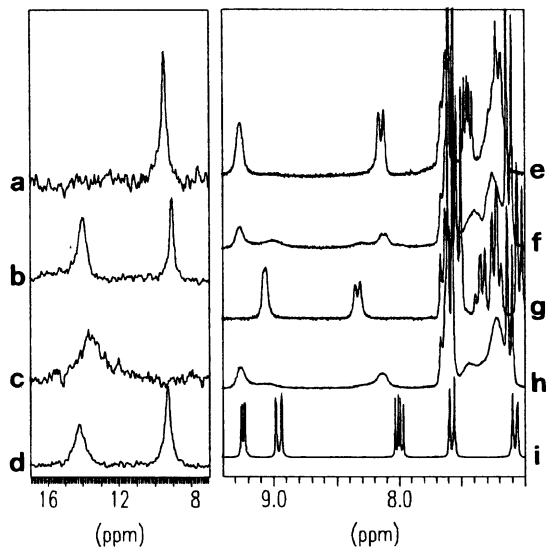


Fig. 7 Variable-temperature $^{31}P\{^{1}H\}$ (81.01 MHz, left hand side) and ^{1}H NMR (200.13 MHz, right side) spectra of **1b** in MeOH-d_4 : (*a* and *e*) room temperature; after adding 2 equiv. of TsOH, (*b* and *f*) at room temperature and (*c* and *g*) at 85 °C; (*d* and *h*) after cooling to room temperature. (*i*) For comparative purposes, the ^{1}H NMR spectrum (MeOH-d_4, room temperature) of [napyH](OTs).

the formation of the corresponding bis-tosylate complex (δ 18.0 in MeOH-d_4).[6,24] Instead, a new species is formed (*b*), which exhibits a broad signal at δ 14.1. This species is in a fast and reversible chemical exchange with the starting complex at high temperature, as shown by the unique broad signal observed in the spectrum at 85 °C (*c*) and by the signal separation at 20 °C (*d*). The parallel acquisition of ^{1}H NMR spectra (right-hand side) shows that no free $[napyH]^+$ is formed upon treatment of **1b** with TsOH. For comparative purposes, the spectrum of [napyH](OTs) (*i*) in MeOH-d_4 is also reported. The protonation of the napy ligand in **1b**, however, occurs already at 20 °C as indicated by both an effective line broadening of the resonances and the appearance of two humps centered at δ 9.0 and 8.3 for the α and γ hydrogen atoms, respectively, (*f*). At 85 °C, the napy and $[napyH]^+$ ligands are indistinguishable and only three rather sharp signals for the α, γ and β hydrogens atoms are observed (*g*).

Overall, this NMR analysis shows that the napy derivatives are more stable than the bipy analogs with respect to the complete dissociation of the dinitrogen ligand in either neutral or acidic MeOH solutions. The greater stability of the napy complexes is certainly due to the capability of napy to act as an excellent unidentate ligand, a feature that bipy does not seem to have. In particular, the ability of napy to act as a unidentate ligand seems to allow the protonated form $[napyH]^+$ to maintain good ligating properties. As we will see below, this characteristic of napy represents a catalytic drawback, however.

High pressure NMR studies

The copolymerization of ethene and CO catalyzed by the bis-chelated complexes [Pd(P-P)(N-N)]$(PF_6)_2$ in methanol was studied in an HPNMR tube under experimental conditions that were as close as possible to those employed in the batch reactions (see below). The most significant differences were a higher concentration of the catalyst precursor and a lower BQ-to-catalyst ratio for a better resolution and acquisition of the NMR spectra. However, the amount of the gaseous reagents contained in the headspace of the tubes was large enough to maintain a relatively high concentration of gases in solution during the course of the experiments as evidenced by the constant presence of the ethene resonance in the ^{1}H NMR spectra (singlet at δ 5.3). Indeed, despite the lower stirring rate as compared to the batch reactions, the mass transfer of gases from the headspace of the 10 mm NMR tubes is generally efficient enough to replenish the solution, which is being depleted in reagents by the catalyst.[6,25]

In a typical catalytic experiment, a MeOH-d_4 solution of a bis-chelated Pd(II) complex with either bipy or napy was pressurized in a 10 mm sapphire HPNMR tube with a 1 : 1 mixture of CO and C_2H_4 to 600 psi in the presence of 2 equiv. of TsOH and 10 equiv. of BQ. In all cases, the $^{31}P\{^{1}H\}$ NMR spectra at room temperature were identical with those of the precursors in the presence of 2 equiv. of acid. No remarkable differences were observed when the temperature of the probe-head was raised to 85 °C and the copolymer started to form. As in the absence of CO–C_2H_4, the $^{31}P\{^{1}H\}$ NMR spectra of both the bipy and napy complexes showed a single, broad resonance due to fast exchange with either the corresponding bis-tosylate derivative Pd(P-P)$(OTs)_2$ (bipy complexes) or the species that might contain a protonated napy ligand (napy complexes). With time and irrespective of the dinitrogen ligand, the NMR signals became narrower and shifted towards the position of the parent bis-chelated derivatives in pure methanol, as if the acidity was decreasing during the course of the catalysis. As an example, a sequence of selected $^{31}P\{^{1}H\}$ HPNMR spectra, recorded during the copolymerization reaction assisted by **1b**, is reported in Fig. 8. At room temperature (*a*), the starting complex (δ 9.2) and the species

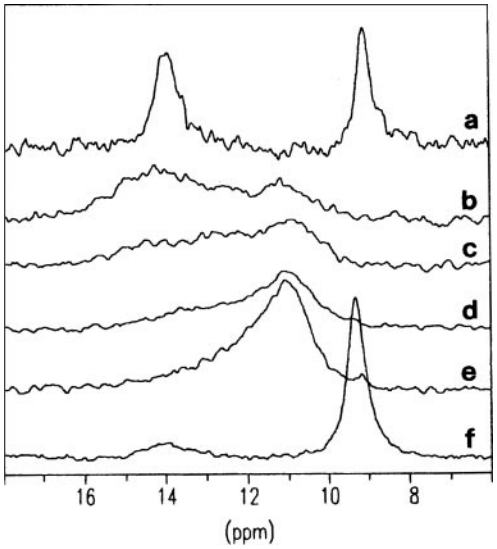


Fig. 8 Selected $^{31}P\{^{1}H\}$ HPNMR spectra (sapphire tube, MeOH-d_4, 81.01 MHz) recorded during a CO–C_2H_4 copolymerization reaction assisted by **1b** in the presence of 2 equiv. of TsOH, 10 equiv. of BQ and a CO–C_2H_4 pressure of 600 psi: (*a*) at room temperature at 85 °C after (*b*) 15, (*c*) 30, (*d*) 45 and (*e*) 60 min; (*f*) after cooling to room temperature.

that forms upon protonation of napy (δ 14.1) are separated although the broadness of the signals indicates that each species is not stereochemically rigid (*vide infra*). Under actual copolymerization conditions (*b–d*), the two species are apparently in fast exchange (*b*) but with time the concentration of the protonated species at δ 14.1 decreases (*c*, *d*) until the spectrum becomes similar to that of **1b** in the absence of acid (*e*, after *ca.* 1 h at 85 °C). The spectrum at room temperature (*f*) indeed shows that a remarkable decrease in the concentration of the protonated complex has occurred during the formation of the copolymer. A parallel ^{1}H NMR study fully confirmed the consumption of protons in the course of the catalysis. In particular, the signals of protonated napy had almost disappeared after 1 h with concomitant formation of hydroquinone (singlet at δ 6.5 due to the phenyl hydrogens).

The substitution of any other bis-chelated complex for **1b** gave a similar NMR picture suggesting that, also in the presence of an acid, the resting state of the catalyst in all reactions is constituted by $[Pd(P\text{-}P)(N\text{-}N)_x]^{2+}$ species ($x = 1$, bipy; 2, napy). Previous studies with $Pd(P\text{-}P)(TFA)_2$ precursors similarly showed that the only NMR-visible complexes during the copolymerization reactions were $Pd(P\text{-}P)X_2$ species in which X is the anion of the strong acid employed (generally TsOH).[6]

The observed reduction of BQ to hydroquinone also confirms that the Pd(II) catalysts with dinitrogen co-ligands tend to be reduced in copolymerization conditions, and thus the presence of an organic oxidant is required for high catalytic activity. An elegant study recently reported by Milani *et al.* has indeed demonstrated that Pd(0) complexes can be oxidized to Pd(II) by BQ in the presence of $[bipyH]^+$ with formation of hydroquinone and bipy. It was shown that this process can also regenerate the bis-chelated Pd(II) structure [eqn. (4)].[5]

$$Pd^{0}(bipy) + BQ + 2[bipyH]^{2+} \longrightarrow [Pd^{II}(bipy)_2]^{2+} + bipy + H_2BQ \quad (4)$$

Batch reactions

The catalytic performance of the bis-chelated Pd(II) complexes in the copolymerization of carbon monoxide with ethene in MeOH was investigated under identical conditions to those previously employed for the monochelated $Pd(P\text{-}P)(CO_2CF_3)_2$ precursors bearing diphosphine and trifluoroacetate ligands.[6] Accordingly, the reactions were carried out in the presence of TsOH as a non-esterifiable protic acid and of BQ as an organic oxidant. While the oxidant is certainly needed for the re-generation of the catalytically active Pd(II) complex *via* oxidation of the low-valent Pd(I) or Pd(0) species that may form under the reducing conditions of the copolymerization reaction,[26] the protic acid may serve to generate Pd–H moieties by oxidative addition to Pd(0) species and/or to convert catalytically inactive μ-OH dimers into reactive mononuclear species.[27]

Table 5 summarizes the results of catalytic reactions performed under different experimental conditions. Selected data for the trifluoroacetate complexes **1**, *meso*-**2**, *rac*-**2** and **3** have also been included for comparative purposes. In the absence of acid but with 80 equiv. of BQ, the activity of the trifluoroacetate catalysts was found to decrease in the order *meso*-**2** > *rac*-**2** > **1** > **3** (runs 1–4). The addition of 2 equiv. of TsOH led to a general increase of the catalytic activity by *ca.* 20% (runs 13–16), while no significant change in activity was observed when increasing the amount of acid from 2 to 20 equiv. (runs 25–28).

The substitution of bipy or napy for trifluoroacetate did not affect dramatically the reactivity trend. However, some interesting results have been obtained that deserve a specifc comment.

In the absence of TsOH, the dinitrogen co-ligands did not generally enhance the catalytic activity. A detrimental effect was in fact observed for the majority of both bipy (runs 5, 7, 8) and napy (runs 10–12) precursors. Only *meso*-**2a** proved to be much more efficient than the trifluoroacetate derivative *meso*-**2** (run 2 *vs.* run 6). The ligand combination *meso*-bdpp/bipy is

Table 5 Copolymerization of CO and ethene catalyzed by $Pd(P\text{-}P)(CO_2CF_3)_2$ and $[Pd(P\text{-}P)(N\text{-}N)_x](PF_6)_2$ complexes[a]

Complex	Run	Productivity[b] without acid	Run	Productivity with 2 equiv. TsOH	Run	Productivity with 20 equiv. TsOH
1	1	12.9	13	16.2	25	16.2
meso-**2**	2	19.1	14	24.0	26	24.2
rac-**2**	3	14.7	15	17.2	27	17.0
3	4	12.0	16	13.0	28	13.2
1a	5	11.7	17	24.3	29	24.5
meso-**2a**	6	25.6	18	25.7	30	23.3
rac-**2a**	7	9.7	19	16.1	31	—
3a	8	9.4	20	16.9	32	—
1b	9	13.6	21	21.0	33	16.9
meso-**2b**	10	15.4	22	20.5	34	20.2
rac-**2b**	11	9.5	23	14.2	35	—
3b	12	11.3	24	12.8	36	—

[a] Catalytic conditions: catalyst, 0.01 mmol; BQ, 0.8 mmol; methanol, 100 mL; initial $p(CO)$, 300 psi; initial $p(C_2H_4)$, 300 psi; temperature, 85 °C; time, 3 h. [b] Productivity expressed as kg copolymer (g Pd)$^{-1}$; each reaction was repeated three times.

apparently the optimal one among those investigated as the productivity obtained with *meso*-**2a** is the highest ever reported for any $[Pd(P\text{-}P)(N\text{-}N)]^{2+}$ catalyst precursor.[4] This finding is rather intriguing as one considers that the stereoisomer *rac*-**2a** is an average catalyst with a productivity of 9.7 kg copolymer (g Pd)$^{-1}$ (run 7). The same trend was exhibited by the pairs *meso*-**2**/*rac*-**2** (runs 2, 3) and *meso*-**2b**/*rac*-**2b** (runs 10, 11).

Irrespective of the dinitrogen ligand, the addition of 2 equiv. of TsOH to the catalytic mixtures increased the productivity remarkably (runs 17, 19–23), whereas 20 equiv. of acid did not lead to a further increase in productivity (runs 29, 30, 33, 34). In some reactions with 2 equiv. of TsOH, even a 100% increase was observed (runs 5, 7–9 *vs.* runs 17, 19–21) and the productivities were generally higher than those obtained with the trifluoroacetate derivatives. Again, *meso*-**2a** was the exception to the rule as the productivity did not appreciably change (run 18). In this case, however, we think that there is no chemical reason to account for the insensitivity of the productivity to the acid concentration. Indeed, a copolymer amount of *ca.* 27 g [productivity of *ca.* 25 kg copolymer (g Pd)$^{-1}$] seems to be the physical limit of our reactor ensemble as shown by the fact that reactions catalyzed by *meso*-**2a** in the presence of a much higher pressure of CO–C_2H_4 (up to 1000 psi) gave similarly 26–27 g of copolymer. Intuitively, this phenomenon may be accounted for by the nature of the copolyketone, which is a fluffy solid capable of adsorbing most of the solvent. After a certain amount of polyketone has been produced, the environment of the reaction apparently changes and the catalytic activity decreases and ultimately stops.

Milani *et al.* have recently shown that the bis-chelated palladium complex **1a** is a very efficient catalyst precursor for the copolymerization of ethene and carbon monoxide.[4] Under their conditions, no acid was apparently needed to produce 8.5 kg of polymer (g Pd h)$^{-1}$. In our hands, **1a** gives 3.9 kg of polymer (g Pd h)$^{-1}$ (run 5). Only in the presence of 2 equiv. of TsOH (run 17) did the complex become an efficient catalyst precursor with an activity [8.1 kg polymer (g Pd h)$^{-1}$] comparable to that obtained by Milani *et al.*[4] These authors proposed that, in copolymerization conditions, the bidentate bipy ligand dissociates either partially or completely from the palladium center to open up coordination sites for the reacting substrates. Our studies do agree with this hypothesis but also show that the protonation of **1a** may indeed facilitate the dissociation of bipy from the palladium center and eventually provide the free coordination sites required. The higher activity of **1a**, in the absence of acid, reported by Milani *et al.* may be due to the different experimental conditions, particularly the size of the reactor ensemble (2000 *vs.* 250 mL). On the other hand, in line with the results reported by Milani *et al.*, we have found that the molecular weights M_n of the copolymers produced with the bis-chelated precursors are higher than those obtained with the bis-trifluoroacetate derivatives, especially when an excess of acid is employed.

Conclusions

Under neutral conditions, the combination of diphosphine and dinitrogen ligands at palladium(II) does not generally result in the formation of more efficient catalyst precursors for the CO–C_2H_4 copolymerization than the traditional ones containing diphosphine and trifluoroacetate ligands.[4,6] In most cases, a detrimental effect is observed, due to the good coordinating capabilities of the dinitrogen ligands that hamper the creation of free sites at the metal center. However, in acidic media the dinitrogen ligands (here bipy and napy) exert a beneficial effect on both the productivity and the molecular weight of the polyketone. Depending on the dinitrogen ligand, the productivity can increase by up to 100% as compared to analogous diphosphine-trifluoroacetate precursors. The bipy complexes are generally more efficient than the napy ones. *In situ* NMR studies have shown that the acid protonates the dinitrogen ligand to create coordination vacancies. Consistent with the lower activity of the napy catalysts, this activation mechanism is less efficient for the napy precursors as the protonated form $[napyH]^+$, unlike $[bipyH]^+$, maintains residual nucleophilic properties. HPNMR studies in catalytic conditions have shown that the proton concentration in the catalytic mixtures decreases with time while the organic oxidant is contemporaneously reduced, thus confirming that a serious drawback for the CO–C_2H_4 copolymerization reactions is the propensity of palladium to reduce. Unfortunately, no species related to the catalytic cycle were seen by HPNMR spectroscopy, which showed uniquely $[Pd(P\text{-}P)(N\text{-}N)_x]^{2+}$ species ($x = 1$, bipy; 2, napy) to be the resting state in all the reactions.

A case apart is represented by the *meso*-**2a** catalyst, which is by far the most efficient in the series. Under neutral conditions, *meso*-**2a** is even more active than *meso*-**2**, whereas these two compounds exhibit comparable activity in acidic media.[4] This observation is hard to explain as bipy is a better ligand than trifluoroacetate and thus its presence in the palladium precursor should generate a lower number of active centers in solution. Under copolymerization conditions, however, one cannot exclude that bipy may stabilize catalytically active species, for example by favoring the oxidation of inactive Pd(0) to active Pd(II) (bipy is electrochemically active and may mediate the Pd/Pd(II) oxidation by BQ).[4–6] On the other hand, *meso*-**2a** is also much more efficient than its stereoisomer *rac*-**2a** and thus steric factors must indeed be important in differentiating the catalytic activity of these two complexes. As we have shown, the solution structures of *meso*-**2a** and *rac*-**2a** differ from each other for the conformation of the six-membered metallaring and ultimately for the spatial distribution of the phenyl rings around the metal center. In a CO–ethene copolymerization reaction, a less dispersed free space at the metal, like in $[Pd(meso\text{-}bddp)]$,$^{2+}$ may indeed be important to allow for the alternating coordination of the substrates and the rapid growth of the polymer. Indeed, it is in the ligand plane that the steric hindrance becomes a controlling factor in ethene coordination/insertion.[28]

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References

1 (*a*) A. Sen, *Acc. Chem Rev.*, 1993, **26**, 303; (*b*) C. E. Ash, *J. Mater. Educ.*, 1994, **16**, 1; (*c*) E. Drent and P. Budzelaar, *Chem Rev.*, 1996, **96**, 663; (*d*) A. Sommazzi and F. Garbassi, *Prog. Polym. Sci.*, 1997, **22**, 1547.

2 (*a*) M. J. Doyle, J. C. van Ravenswaay Classen, G. G. Rosenbrand and R. L. Wife, *U. S. Pat.* 4778876, 1988; (*b*) Z. Jiang and A. Sen, *Macromolecules*, 1994, **27**, 7215; (*c*) G. Verspui, G. Papadogianakis and R. Sheldon, *Chem. Commun.*, 1998, 401; (*d*) C. Bianchini, H. M. Lee, A. Meli, S. Moneti, V. Patinec, G. Petrucci and F. Vizza, *Macromolecules*, 1999, **32**, 3859.

3 (*a*) E. Drent, *Eur. Pat.* 121965, 1984; (*b*) E. Drent, *Eur. Pat.* 181014, 1986; (*c*) J. A. M. van Broekhoven, E. Drent and E. Klei, *Eur. Pat.* 213671, 1986; (*d*) J. A. M. van Broekhoven, E. Drent and E. Klei, *Eur. Pat.* 235865, 1987; (*e*) E. Drent, J. A. M. van Broekhoven and M. J. Doyle, *J. Organomet. Chem.*, 1991, **417**, 235; (*f*) N. Alperowicz, *Chem. Week*, 1995, Jan 25, 22; (*g*) A. X. Zhao and J. C. W. Chien, *J. Polym. Sci. Part A: Polym. Chem.*, 1992, **30**, 2735; (*h*) M. Brookhart, F. C. Rix and J. M. DeSimone, *J. Am. Chem. Soc.*,

1992, **114**, 5894; (*i*) F. C. Rix, M. Brookhart and P. S. White, *J. Am. Chem. Soc.*, 1996, **118**, 4746; (*j*) A. Sen and T.-W. Lai, *J. Am. Chem. Soc.*, 1982, **104**, 3520; (*k*) T.-W. Lai and A. Sen, *Organometallics*, 1984, **3**, 866; (*l*) Z. Jiang and A. Sen, *J. Am. Chem. Soc.*, 1995, **117**, 4455.
4 B. Milani, L. Vicentini, A. Sommazzi, F. Garbassi, E. Chiarparin, E. Zangrando and G. Mestroni, *J. Chem. Soc., Dalton Trans.*, 1996, 3139 and refs therein.
5 B. Milani, A. Anzilutti, L. Vicentini, A. Sessanta o Santi, E. Zangrando, S. Geremia and G. Mestroni, *Organometallics*, 1997, **16**, 5064.
6 C. Bianchini, H. M. Lee, A. Meli, S. Moneti, F. Vizza, M. Fontani and P. Zanello, *Macromolecules*, 1999, **30**, 4183.
7 P. A. MacNeil, N. K. Roberts and B. Bosnich, *J. Am. Chem. Soc.*, 1981, **103**, 2273.
8 J. Bakos, I. Tóth, B. Heil and L. Markó, *J. Organomet Chem.*, 1985, **279**, 23.
9 (*a*) H. Nakajima, H. Nagao and K. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1996, 1405; (*b*) M.-J. Bermejo, J.-I. Ruiz, X. Solans and J. Vinaixa, *Inorg. Chem.*, 1988, **27**, 4385; (*c*) M.-J. Bermejo, B. Martinez and J. Vinaixa, *J. Organomet Chem.*, 1986, **304**, 207; (*d*) K. R. Dixon, D. T. Eadie and S. R. Stobart, *Inorg. Chem.*, 1982, **21**, 4318; (*e*) R. W. Brookes and R. L. Martin, *Inorg. Chem.*, 1975, **14**, 528; (*f*) L. Sacconi, C. Mealli and D. Gatteschi, *Inorg. Chem.*, 1974, **13**, 1985; (*g*) R. L. Bodner and D. G. Hendricker, *Inorg. Chem.*, 1973, **12**, 33; (*h*) W. W. Paudler and T. J. Kress, *J. Org. Chem.*, 1967, **32**, 832.
10 P. H. M. Budzelaar, *gNMR V4.0*, Cherwell Scientific Publishing, Oxford, 1995.
11 A. Derome and M. Williamson, *J. Magn. Reson.*, 1990, **88**, 177.
12 (*a*) V. Sklener, H. Miyashiro, G. Zon, H. T. Miles and A. Bax, *FEBS Lett.*, 1986, **208**, 94; (*b*) J. Jeener, B. H. Meier, P. Bachmann and R. R. Ernst, *J. Chem. Phys.*, 1979, **71**, 4546.
13 A. Bax and D. G. Davis, *J. Magn. Reson.*, 1985, **63**, 207.
14 A. Bax, R. H. Griffey and B. L. Hawkins, *J. Magn. Reson.*, 1983, **55**, 301.
15 CNR (C. Bianchini, A. Meli and A. Traversi), *Ital. Pat.* FI A000025, 1997.
16 D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 1965, **18**, 104.
17 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, England, 1974, vol. IV.
18 G.M. Sheldrick, SHELX-96, Program for Structure Refinement, University of Göttingen, Germany, 1996.
19 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
20 B. Milani, E. Alessio, G. Mestroni, A. Sommazzi, F. Garbassi, E. Zangrando, N. Bresciani-Pahor and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1994, 1903.
21 J. Bakos, I. Tóth, B. Heil, G. Szalontai, L. Párkányi and V. Fülöp, *J. Organomet Chem.*, 1989, **370**, 263.
22 G. Zhu, P. Cao, D. Jiang and X. Zhang, *J. Am. Chem. Soc.*, 1997, **119**, 1799.
23 (*a*) M. Kojima, M. Fujita and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 898; (*b*) H. Boucher and B. Bosnich, *Inorg. Chem.*, 1976, **15**, 1471; (*c*) L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 1505.
24 (*a*) G. Consiglio, S. C. A. Nefkens and C. Pisano, *Inorg. Chim. Acta*, 1994, **220**, 273; (*b*) F. Benettolo, R. Bertani, G. Bombieri and L. Toniolo, *Inorg. Chim. Acta*, 1995, **233**, 5.
25 (*a*) C. Bianchini, V. Herrera, M. V. Jiménez, A. Meli, R. A. Sánchez-Delgado and F. Vizza, *J. Am. Chem. Soc.*, 1995, **117**, 8567; (*b*) C. Bianchini, D. Fabbri, S. Gladiali, A. Meli, W. Pohl and F. Vizza, *Organometallics*, 1996, **15**, 4604; (*c*) C. Bianchini, J. A. Casares, A. Meli, V. Sernau, F. Vizza and R. A. Sánchez–Delgado, *Polyhedron*, 1997, **16**, 3099; (*d*) C. Bianchini, A. Meli, V. Patinec, V. Sernau and F. Vizza, *J. Am. Chem. Soc.*, 1997, **119**, 4945; (*e*) C. Bianchini, A. Meli, S. Moneti and F. Vizza, *Organometallics*, 1998, **17**, 2636.
26 (*a*) P. H. Budzelaar, P. W. N. M. van Leeuwen and C. F. Roobeek, *Organometallics*, 1992, **11**, 23; (*b*) M. Portnoy and D. Milstein, *Organometallics*, 1994, **13**, 600; (*c*) I. Tóth and D. J. Elsevier, *Organometallics*, 1994, **13**, 2118; (*d*) M. Sperrle, V. Gramlich, and G. Consiglio, *Organometallics*, 1996, **15**, 5196.
27 C. Pisano, G. Consiglio, A. Sironi and M. Moret, *J. Chem. Soc., Chem. Commun.*, 1991, 421.
28 (*a*) Y. Koide, S. G. Bott and A. R. Barron, *Organometallics*, 1996, **15**, 2213; (*b*) T. A. Albright, R. Hoffmann, J. C. Thibeault and D. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801.

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