Bis-alkoxycarbonylation of styrene by pyridinimine palladium catalysts

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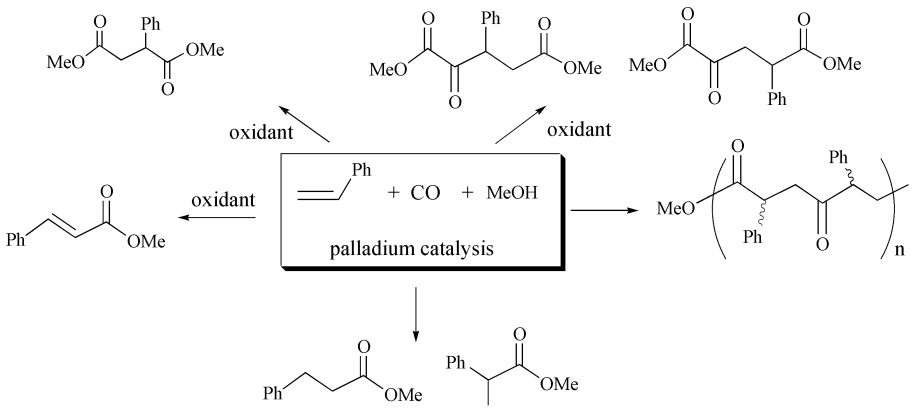
Pyridinimine-modified Pd(II) complexes of general formulae (N-N′)Pd(Y)$_2$ catalyze the methoxycarbonylation of styrene to give dimethyl phenylsuccinate as the largely major product [N-N′ = py-2-C(R)=N(2,6-R′C$_6$H$_3$), R = H, Me; R′ = Me, *i*-Pr; 6-Mepy-2-C(H)=N[2,6-(*i*-Pr)$_2$C$_6$H$_3$]; py-2-C(H)=N(C$_6$H$_5$); Y = acetate, trifluoroacetate]. The influence of various catalytic parameters on the overall conversion of styrene to carbonylated products and on the product selectivity has been studied by systematically varying the type of palladium initiator, the concentrations of organic oxidant (1,4-benzoquinone) and protic acid (*p*-toluenesulfonic acid), and the CO pressure. By an appropriate choice of the structure of the pyridinimine ligand and of the reaction parameters, turn-over numbers as high as 96 and selectivities in dimethyl phenylsuccinate as high as 98% were obtained. In particular, the overall conversion of styrene is controlled by the steric properties of the alkyl substituents on the imine aryl group, while the nature of the substituent (H or Me) on the imine carbon influences the selectivity. The addition of 2 equivalents of TsOH to the catalytic mixtures generally increased the styrene conversion but lowered the selectivity in dimethyl phenylsuccinate due to greater production of methyl 3,6-diphenyl-4-oxohexanoate. Further additions of TsOH (up to 6 equivalents) resulted in better selectivities and lower conversions for all precursors.

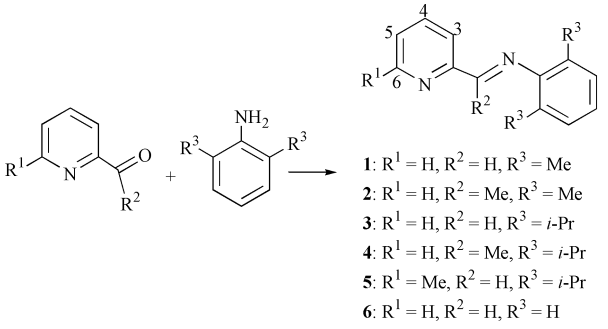
The alkoxycarbonylation of olefins is a metal-catalyzed reaction that transforms relatively cheap feedstocks (CO, olefins, alcohols) into esters, diesters and/or polyketones.[1,2] Effective and selective catalyst precursors for this industrially relevant reaction generally require the use of palladium(II) salts in conjunction with either tertiary phosphorus or nitrogen ligands.

In the case of styrene, the carbonylation in methanol in the presence of palladium initiators and of an organic oxidant, required to convert Pd^0 to Pd^{II}, may yield different types of products spanning from alternating polyketones, methyl cinnamate, phenylpropanoates, dimethyl phenylsuccinate, to dimethyl 2-oxo-phenylglutarates (Scheme 1).[2–5] The chemoselectivity is essentially driven by the nature of the supporting ligand.[2–5] Dinitrogen ligands, particularly those with rigid carbon backbones, form selective catalysts for the alternating copolymerization leading to polyketones,[2] while diphosphines generate effective systems for the single, double or triple carbonylation of styrene yielding esters, diesters or oxo-glutarates.[3,4] Miscellaneous catalytic systems containing (chiral) ligands with oxygen, sulfur, phosphorus and nitrogen donor atoms may be appropriately tuned so as to give a wealth of products with low to high chemo-, regio- and stereoselectivities.[2,4,6]

To the best of our knowledge, no palladium catalyst stabilized by a chelating dinitrogen ligand has ever been reported to catalyze the methoxycarbonylation of styrene, yielding phenyl cinnamate, dimethyl phenylsuccinate or other diesters. Therefore, we were truly surprised to discover that palladium(II) precursors with certain pyridinimine ligands (Scheme 2) were



Scheme 1 Products obtainable from the methoxycarbonylation of styrene by palladium catalysis.



Scheme 2 Synthesis, structure and numbering scheme of the ligands employed in this work.

able to catalyze the selective formation of dimethyl phenylsuccinate upon methoxycarbonylation of styrene. We expected to obtain alternating polyketones, in fact.[2,7]

Pyridinimines[8–21] constitute a numerous family of chelating dinitrogen ligands whose coordination chemistry closely resembles that of α-diimine ligands[8,9,21] and, like the latter, have been used in palladium and nickel catalysis, particularly in olefin oligomerization and polymerization,[9,15,16,21] co-oligomerization of ethylene with alkyl acrylates,[9,15,21] and CO/styrene copolymerization.[7] Due to the formation of stable metal complexes and the ease of functionalization, pyridinimine ligands have been also employed to study fundamental processes such as migratory insertions in Pd(alkyl)(CO) and Pd(acyl)(olefin) complexes.[18,19]

In this work, we describe the synthesis of new pyridinimines (N-N′) and of several palladium(II) complexes of general formulae (N-N′)Pd(Y)$_2$ (Y = acetate, trifluoroacetate), which have been employed as catalyst precursors to bring about the oxidative carbonylation of styrene in MeOH.

Experimental

General procedure

All manipulations were carried out under a nitrogen atmosphere using Schlenk-type techniques. All the solid compounds were collected on sintered-glass frits and washed with appropriate solvents before being dried in a stream of nitrogen. The solvents were distilled under nitrogen over $LiAlH_4$ (*n*-pentane, *n*-hexane, THF), CaH_2 (CH_2Cl_2) or Na (diethyl ether). MeOH employed in carbonylation runs was heated at reflux temperature over Mg shavings under an atmosphere of dry nitrogen and distilled just prior to use. Styrene was freshly distilled from $LiAlH_4$. All the other reagents and solvents were used as purchased from commercial suppliers. The palladium complex (COD)$PdCl_2$ (COD = 1,5-cyclooctadiene) was prepared as described in the literature.[22] Carbonylation reactions were performed with a 250 ml stainless steel autoclave, constructed at the ISSECC-CNR (Firenze, Italy), equipped with a magnetic drive stirrer, a Parr 4842 temperature and pressure controller. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded on a Perkin–Elmer 1600 Series FT-IR spectrophotometer. Deuterated solvents for NMR measurements were dried over molecular sieves. ^{1}H NMR spectra were collected on a Bruker ACP-200 (81.01 MHz). Chemical shifts are reported in ppm relative to TMS, referenced to the chemical shifts of residual solvent resonances. GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. The product composition was determined by using acetophenone as the internal standard. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a column identical to that used for GC analysis.

Syntheses of ligands

The pyridinimine ligands were synthesized following previously reported procedures that have been modified when necessary to improve the yield.[12–16]

py-2-C(H)=N(2,6-Me$_2$C$_6$H$_3$), 1.[13] A mixture of 2-pyridinecarboxaldeyde (1.7 g, 15.9 mmol) and 2,6-dimethylaniline (1.9 g, 15.9 mmol) in 20 ml of MeOH was heated at reflux temperature. After 4 h the solvent was removed under vacuum to give an yellow oil that was used without further purification. Yield: 60%. Anal. calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32; found: C, 79.85; H, 6.75; N, 13.25%. IR (neat, cm^{-1}): ν(C=N) 1645 (s). ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 6H, $Me_2C_6H_3$), 6.95–7.13 (m, 3H, *m*- and *p*-Ar), 7.42 [ddd, ^3J(HH) = 7.7, 4.9, ^4J(HH) = 1.4 Hz, 1H, H$_5$-py], 7.85 [td, ^3J(HH) = 7.7, ^4J(HH) = 1.8 Hz, 1H, H$_4$-py], 8.30 [ddd, ^3J(HH) = 7.7, ^4J(HH) = 1.4, ^5J(HH) = 1.0 Hz, 1H, H$_3$-py], 8.36 [s, 1H, C(H)=N], 8.73 [ddd, ^3J(HH) = 4.9, ^4J(HH) = 1.8, ^5J(HH) = 1.0 Hz, 1H, H$_6$-py].

py-2-C(Me)=N(2,6-Me$_2$C$_6$H$_3$), 2. A mixture of 2.0 g of 2-acetylpyridine (16.5 mmol) and 8.0 g of 2,6-dimethylaniline (66.0 mmol) was heated at 100 °C. After 4 days, the resulting residue was eluted on a neutral alumina column with ethyl acetate–*n*-hexane (5 : 95) as eluent. Evaporation of the solvents under reduced pressure gave a yellow oil. Yield: 42%. Anal. calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49; found: C, 80.43; H, 7.20; N, 12.41%. IR (neat, cm^{-1}): ν(C=N) 1644 (s). ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 6H, $Me_2C_6H_3$), 2.20 [s, 3H, C(Me)=N], 6.91–7.10 (m, 3H, *m*- and *p*-Ar), 7.40 [ddd, ^3J(HH) = 7.7, 4.9, ^4J(HH) = 1.3 Hz, 1H, H$_5$-py], 7.83 [td, ^3J(HH) = 7.7, ^4J(HH) = 1.8 Hz, 1H, H$_4$-py], 8.30 [ddd, ^3J(HH) = 7.7, ^4J(HH) = 1.3, ^5J(HH) = 0.9 Hz, 1H, H$_3$-py], 8.69 [ddd, ^3J(HH) = 4.9, ^4J(HH) = 1.8, ^5J(HH) = 0.9 Hz, 1H, H$_6$-py].

py-2-C(H)=N[2,6-(*i*-Pr)$_2$C$_6$H$_3$], 3.[16] 2-Pyridinecarboxaldeyde (0.26 g, 2.48 mmol) and 2,6-diisopropylaniline (4.4 g, 2.48 mmol) were dissolved in 10 mL of ethanol and the resulting mixture was heated at reflux temperature for 20 min. The solvent was removed under reduced pressure and the residue was chromatographed on basic alumina with *n*-pentane–ethyl acetate (3 : 1) as eluent. Recrystallization from *n*-pentane yielded pale yellow crystals, which were filtered off and washed with cold *n*-pentane. Yield: 62%. Anal. calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.32; N, 10.52; found: C, 81.08; H, 8.36; N, 10.42%. IR (Nujol mull, cm^{-1}): ν(C=N) 1649 (s). ^{1}H NMR ($CDCl_3$): δ 1.16 [d, ^3J(HH) = 7.0 Hz, 12H, CHMe_2], 2.97 [sept., ^3J(HH) = 7.0 Hz, 2H, CHMe$_2$], 7.05–7.23 (m, 3H, *m*- and *p*-Ar), 7.42 [ddd, ^3J(HH) = 7.7, 5.0, ^4J(HH) = 1.3 Hz, 1H, H$_5$-py], 7.86 [td, ^3J(HH) = 7.7, ^4J(HH) = 1.8 Hz, 1H, H$_4$-py], 8.27 [ddd, ^3J(HH) = 7.7, ^4J(HH) = 1.3, ^5J(HH) = 0.9 Hz, 1H, H$_3$-py], 8.31 [s, 1H, C(H)=N], 8.73 [ddd, ^3J(HH) = 5.0, ^4J(HH) = 1.8, ^5J(HH) = 0.9 Hz, 1H, H$_6$-py].

py-2-C(Me)=N[2,6-(*i*-Pr)$_2$C$_6$H$_3$], 4.[15] 2-Acetylpyridine (1.5 g, 1.24 mmol) and 2,6-diisopropylaniline (2.2 g, 1.24 mmol) were dissolved in 15 mL of MeOH containing a few drops of formic acid and the resulting mixture was heated at reflux temperature for 5 days. Partial evaporation of the solvent under reduced pressure led to the precipitation of yellow crystals, which were filtered off and washed with a small amount of cold MeOH. Yield: 62%. M.p.: 79–80 °C. Anal. calcd for $C_{19}H_{24}N_2$: C, 81.38; H, 8.63; N, 9.99; found: C, 81.40; H, 8.60; N, 10.01%. IR (Nujol mull, cm^{-1}): ν(C=N) 1649 (s). ^{1}H NMR ($CDCl_3$): δ

1.16 [d, ^3J(HH) = 7.0 Hz, 12H, CHMe_2], 2.23 [s, 3H, C(Me)=N), 2.76 [sept., ^3J(HH) = 7.0 Hz, 2H, CHMe$_2$], 7.01–7.21 (m, 3H, *m*- and *p*-Ar), 7.41 [ddd, ^3J(HH) = 7.7, 5.0, ^4J(HH) = 1.3 Hz, 1H, H_5-py], 7.83 [td, ^3J(HH) = 7.7, ^4J(HH) = 1.8 Hz, 1H, H_4-py], 8.37 [ddd, ^3J(HH) = 7.7, ^4J(HH) = 1.3, ^5J(HH) = 0.9 Hz, 1H, H_3-py], 8.70 [ddd, ^3J(HH) = 5.0, ^4J(HH) = 1.8, ^5J(HH) = 0.9 Hz, 1H, H_6-py].

6-Mepy-2-C(H)=N[2,6-(*i*-Pr)$_2$C$_6$H$_3$], 5. A mixture of 0.36 g of 6-methyl-2-pyridinecarboxadehyde (2.97 mmol) and 0.55 g of 2,6-diisopropylaniline (3.10 mmol) was heated at 100 °C for 1 h. The resulting residue was allowed to stand overnight at ambient temperature. The formed yellow solid was crystallized from MeOH and water (a few drops). Yield: 70%. M.p.: 73–76 °C. Anal. calcd for $C_{19}H_{24}N_2$: C, 81.38; H, 8.63; N, 9.99; found: C, 81.40; H, 8.60; N, 10.01%. IR (Nujol mull, cm^{-1}): ν(C=N) 1640 (s). ^{1}H NMR ($CDCl_3$): δ 1.18 [d, ^3J(HH) = 6.9 Hz, 12H, CHMe_2], 2.66 (s, 3H, Me-py), 2.98 [sept., ^3J(HH) = 6.9 Hz, 2H, CHMe$_2$], 7.08–7.21 (m, 3H, *m*- and *p*-Ar), 7.29 [d, ^3J(HH) = 8.2 Hz, 1H, H_5-py], 7.76 [t, ^3J(HH) = 8.2 Hz, 1H, H_4-py], 8.11 [d, ^3J(HH) = 8.2 Hz, 1H, H_3-py], 8.30 [s, 1H, C(H)=N].

py-2-C(H)=N(C$_6$H$_5$), 6.[12] This ligand was prepared as an oily material following a procedure analogous to that described for **1** starting from 2-pyridinecarboxaldyde (1.5 g, 14.0 mmol) and aniline (1.3 g, 14.0 mmol). Yield: 78%. Anal. calcd for $C_{12}H_{10}N_2$: C, 79.10; H, 5.53; N, 15.37; found: C, 79.00; H, 5.48; N, 15.21%. IR (Nujol mull, cm^{-1}): ν(C=N) 1623 (s). ^{1}H NMR ($CDCl_3$): δ 7.24–7.46 (m, 5H, Ph), 7.4 (masked by Ph, 1H, H_5-py), 7.81 [td, ^3J(HH) = 7.9, ^4J(HH) = 1.6 Hz, 1H, H_4-py], 8.21 [ddd, ^3J(HH) = 7.9, ^4J(HH) = 1.4, ^5J(HH) = 0.8 Hz, 1H, H_3-py], 8.62 [s, 1H, C(H)=N], 8.72 [ddd, ^3J(HH) = 4.9, ^4J(HH) = 1.6, ^5J(HH) = 0.8 Hz, 1H, H_6-py].

Synthesis of the palladium complexes

Bis-trifluoroacetate palladium complexes 1a–6a. In a typical reaction, the appropriate diimine ligand (1.1 mmol) dissolved in CH_2Cl_2 (10 ml) was added to a MeOH (10 ml) solution of $Pd(TFA)_2$ (1 mmol, TFA = trifluoroacetate). The mixture was allowed to stir for 10 min and then the volume was reduced under a steady stream of nitrogen until the product began to precipitate. Portionwise addition of diethyl ether (20 ml) completed the precipitation of the product, which was collected by filtration and washed with petroleum ether.

[py-2-C(H)=N(2,6-Me$_2$C$_6$H$_3$)]Pd(TFA)$_2$, 1a. Yellow microcrystals, yield 76%. Anal. calcd for $C_{18}H_{14}F_6N_2O_4Pd$: C, 39.83; H, 2.61; N, 5.16; found: C, 39.80; H, 2.50; N, 5.20%. ^{1}H NMR ($CDCl_3$): δ 2.43 (s, 6H, $Me_2C_6H_3$), 7.04–7.23 (m, 3H, *m*- and *p*-Ar), 7.79 [ddd, ^3J(HH) = 7.8, 5.6, ^4J(HH) = 1.1 Hz, 1H, H_5-py], 7.98 [dd, ^3J(HH) = 7.8, ^4J(HH) = 1.1 Hz, 1H, H_3-py], 8.08 [s, 1H, C(H)=N], 8.23 [td, ^3J(HH) = 7.8, ^4J(HH) = 1.3 Hz, 1H, H_4-py], 8.38 [dd, ^3J(HH) = 5.6, ^4J(HH) = 1.3 Hz, 1H, H_6-py]. Crystals suitable for an X-ray analysis were obtained by slow evaporation of the solvent from a diluted CH_2Cl_2 solution of **1a**.

[py-2-C(Me)=N(2,6-Me$_2$C$_6$H$_3$)]Pd(TFA)$_2$, 2a. Yellow microcrystals yield 74%. Anal. calcd for $C_{19}H_{16}F_6N_2O_4Pd$: C, 40.98; H, 2.90; N, 5.03; found: C, 40.85; H, 2.91; N, 5.00%. ^{1}H NMR ($CDCl_3$): δ 2.31 [s, 3H, C(Me)=N], 2.41 (s, 6H, $Me_2C_6H_3$), 7.07–7.25 (m, 3H, *m*- and *p*-Ar), 7.92 [ddd, ^3J(HH) = 7.7, 5.6, ^4J(HH) = 1.5 Hz, 1H, H_5-py], 8.02 [dd, ^3J(HH) = 7.7 ^4J(HH) = 1.5 Hz, 1H, H_3-py], 8.23 [td, ^3J(HH) = 7.7, ^4J(HH) = 1.5 Hz, 1H, H_4-py], 8.40 [dd, ^3J(HH) = 5.6, ^4J(HH) = 1.5 Hz, 1H, H_6-py]. Crystals suitable for an X-ray analysis were obtained by slow evaporation of the solvent from a diluted CH_2Cl_2 solution of **2a**.

{py-2-C(H)=N[2,6-(*i*-Pr)$_2$C$_6$H$_3$]}Pd(TFA)$_2$, 3a. Yellow microcrystals, yield 88%. Anal. calcd for $C_{22}H_{22}F_6N_2O_4Pd$: C, 44.12; H, 3.71; N, 4.68; found: C, 44.15; H, 3.70; N, 4.71%. ^{1}H NMR (CD_2Cl_2): δ 1.15 [d, ^3J(HH) = 6.8 Hz, 6H, CHMeMe′], 1.42 [d, ^3J(HH) = 6.8 Hz, 6H, CHMeMe′], 3.43 [sept., ^3J(HH) = 6.8 Hz, 2H, CHMeMe′], 7.28–7.44 (m, 3H, *m*- and *p*-Ar), 7.84 [ddd, ^3J(HH) = 7.9, 5.5, ^4J(HH) = 1.5 Hz, 1H, H_5-py], 7.97 [s, 1H, C(H)=N], 7.99 [ddd, ^3J(HH) = 7.9, ^4J(HH) = 1.5, ^5J(HH) = 0.7 Hz, 1H, H_3-py], 8.28 [td, ^3J(HH) = 7.9, ^4J(HH) = 1.5 Hz, 1H, H_4-py], 8.34 [ddd, ^3J(HH) = 5.5, ^4J(HH) = 1.5, ^5J(HH) = 0.7 Hz, 1H, py H-6]. Crystals suitable for an X-ray analysis were obtained by slow evaporation of the solvent from a diluted CH_2Cl_2 solution of **3a**.

{py-2-C(Me)=N[2,6-(*i*-Pr)$_2$C$_6$H$_3$]}Pd(TFA)$_2$, 4a. Yellow microcrystals, yield 90%. Anal. calcd for $C_{23}H_{24}F_6N_2O_4Pd$: C, 45.07; H, 3.95; N, 4.57; found: C, 45.10; H, 3.90; N, 4.60%. ^{1}H NMR ($CDCl_3$): δ 1.14 [d, ^3J(HH) = 6.9 Hz, 6H, CHMeMe′], 1.48 [d, ^3J(HH) = 6.6 Hz, 6H, CHMeMe′], 2.34 [s, 3H, C(Me)=N], 3.26 [sept., ^3J(HH) = 6.8 Hz, 2H, CHMeMe′], 7.15–7.43 (m, 3H, *m*- and *p*-Ar), 7.85 [ddd, ^3J(HH) = 7.7, 5.6, ^4J(HH) = 1.5 Hz, 1H, H_5-py], 7.92 [dd, ^3J(HH) = 7.7, ^4J(HH) = 1.5 Hz, 1H, H_3-py], 8.32 [td, ^3J(HH) = 7.7, ^4J(HH) = 1.5 Hz, 1H, H_4-py], 8.44 [dd, ^3J(HH) = 5.6, ^4J(HH) = 1.5 Hz, 1H, H_6-py].

{6-Mepy-2-C(H)=N[2,6-(*i*-Pr)$_2$C$_6$H$_3$]}Pd(TFA)$_2$, 5a. Yellow microcrystals, yield 93%. Anal. calcd for $C_{23}H_{24}F_6N_2O_4Pd$: C, 45.07; H, 3.95; N, 4.57; found: C, 45.10; H, 3.90; N, 4.60%. ^{1}H NMR (CD_2Cl_2): δ 1.14 [d, ^3J(HH) = 6.8 Hz, 6H, CHMeMe′], 1.42 [d, ^3J(HH) = 6.8 Hz, 6H, CHMeMe′], 2.71 (s, 3H, Me-py), 3.50 [sept., ^3J(HH) = 6.8 Hz, 2H, CHMeMe′], 7.16–7.43 (m, 3H, *m*- and *p*-Ar), 7.61 [dd, ^3J(HH) = 7.8, ^4J(HH) = 1.4 Hz, 1H, H_5-py], 7.76 [dd, ^3J(HH) = 7.8, ^4J(HH) = 1.4 Hz, 1H, H_3-py], 7.90 [s, 1H, C(H)=N], 8.09 [t, ^3J(HH) = 7.8 Hz, 1H, H_4-py].

[py-2-C(H)=N(C$_6$H$_5$)]Pd(TFA)$_2$, 6a. Yellow brown microcrystals, yield 86%. Anal. calcd for $C_{16}H_{10}F_6N_2O_4Pd$: C, 37.33; H, 1.96; N, 5.44; found: C, 37.50; H, 2.00; N, 5.40%. ^{1}H NMR ($CDCl_3$): δ 7.39–7.51 (m, 5 H, Ph), 7.75 [ddd, ^3J(HH) = 7.8, 5.7, ^4J(HH) = 1.4 Hz, 1H, H_5-py], 8.00 [dd, ^3J(HH) = 7.7, ^4J(HH) = 1.4 Hz, 1H, H_3-py], 8.20 [s, 1H, C(H)=N], 8.23 (m, 2H, H_4-py and H_6-py).

[py-2-C(H)=N(2,6-Me$_2$C$_6$H$_3$)]Pd(OAc)$_2$, 1b. To $Pd(OAc)_2$ (0.29 g, 1.30 mmol, OAc = acetate) dissolved in MeOH (10 ml) was added a solution of **1** (0.27 g, 1.30 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for half an hour and then concentrated to 5 ml under a steady stream of nitrogen. Portionwise addition of an 1 : 1 mixture of diethyl ether and *n*-pentane (20 ml) led to the precipitation of a yellow-orange product, which was filtered off and washed several times with *n*-pentane. Yield: 65%. Anal. calcd for $C_{18}H_{20}N_2O_4Pd$: C, 49.74; H, 4.60; N, 6.44; found: C, 49.20; H, 4.55; N, 6.40%. ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 3H, CH_3CO_2), 2.05 (s, 3H, CH_3CO_2), 2.44 (s, 6H, $Me_2C_6H_3$), 7.00–7.20 (m, 3H, *m*- and *p*-Ar), 7.72 [ddd, ^3J(HH) = 7.8, 5.6, ^4J(HH) = 1.1 Hz, 1H, H_5-py], 7.99 [dd, ^3J(HH) = 7.8, ^4J(HH) = 1.1 Hz, 1H, H_3-py], 8.11 [s, 1H, C(H)=N], 8.19 [td, ^3J(HH) = 7.8, ^4J(HH) = 1.3 Hz, 1H, H_4-py], 8.44 [dd, ^3J(HH) = 5.6, ^4J(HH) = 1.3 Hz, 1H, H_6-py].

[{py-2-C(H)=N(2,6-Me$_2$C$_6$H$_3$)}Pd(THF)$_2$](PF$_6$)$_2$, 1c. A solid sample of (COD)$PdCl_2$ (0.18 g, 0.63 mmol) was added to a stirred solution of **1** (0.13 g, 0.63 mmol) in THF (10 ml) at ambient temperature. After 20 min, solid $AgPF_6$ (0.35 g, 1.38 mmol) was added and the resulting slurry was stirred for 1 h.

The mixture was filtered on celite to remove AgCl and the yellow filtrate was concentrated to 5 ml. Addition of *n*-pentane (20 ml) led to the precipitation of a yellow microcrystalline solid, which was filtered off and washed with *n*-pentane. Yield: 68%. Anal. calcd for $C_{22}H_{29}F_{12}N_2O_2P_2Pd$: C, 35.25; H, 3.87; N, 3.73; found: C, 35.21; H, 3.85; N, 3.70%. ^{1}H NMR ($CDCl_3$): δ 1.82 (m, 8H, THF, $-CH_2CH_2-$), 2.42 (s, 6H, $Me_2C_6H_3$), 3.65 (m, 8H, THF $-CH_2OCH_2-$), 7.09–7.34 (m, 3H, *m*- and *p*-Ar), 8.02 [ddd, $^3J(HH) = 5.5$, $^4J(HH) = 1.5$, $^5J(HH) = 0.5$ Hz, 1H, H_6-py], 8.10 [ddd, $^3J(HH) = 7.7$, 5.5, $^4J(HH) = 1.5$ Hz, 1H, H_5-py], 8.12 [s, 1H, C(H)=N], 8.25 [ddd, $^3J(HH) = 7.7$, $^4J(HH) = 1.5$, $^5J(HH) = 0.5$ Hz, 1H, H_3-py], 8.40 [td, $^3J(HH) = 7.7$, $^4J(HH) = 1.5$ Hz, 1H, H_4-py].

Catalytic carbonylation of styrene

Typically, a MeOH solution (20 ml) of styrene (2 mmol) was introduced by suction into a 250 ml autoclave, previously evacuated by a vacuum pump, containing 0.01 mmol of catalyst precursor along with the desired amounts of 1,4-benzoquinone (BQ) and *p*-toluenesulfonic acid (TsOH). The autoclave was then pressurized with CO (generally 800 psi) at room temperature and heated to 80 °C. As soon as the reaction mixture in the autoclave reached the desired temperature, stirring (700 rpm) was applied for the desired time (generally 3 h). The reaction was stopped by cooling the autoclave to room temperature by means of an ice-water bath. The pressure was then released. The product composition was determined by GC using acetophenone as the internal standard.

X-Ray structure determinations

Suitable crystals were sealed in a glass capillary and transferred to a Enraf–Nonius CAD4 diffractometer. Data were collected at room temperature using Mo-Kα radiation ($\lambda = 0.71069$ Å). A set of 25 carefully centred reflections having $6.5 \leqslant \theta \leqslant 10.0°$ were used to determine the lattice constants. The intensities of three standard reflections were measured every 2 h for orientation and intensity control. This procedure revealed no decay of intensity. The data were corrected for Lorentz and polarization effects. Atomic scattering factors with anomalous dispersion correction were taken from the literature.[23] Absorption corrections were applied *via* ψ scans. The computational work was performed with a DIGITAL DEC 5000/200 workstation using the program SHELX-93.[24] The structures were solved by direct methods using the SIR92 program[25] and all of the 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 finally with anisotropic thermal parameters for all the atoms but the hydrogens. The phenyl rings were treated as rigid bodies with D_{6h} symmetry and hydrogen atoms were introduced at calculated positions.

CCDC reference numbers 178390–178392. See http://www.rsc.org./suppdata/nj/b1/b108804c/ for crystallographic data in CIF or other electronic format.

Results and discussion

Syntheses and properties of the pyridinimine ligands and of the corresponding palladium complexes

The pyridinimine ligands were conveniently prepared by condensation of either 2-pyridinecarboxaldeyde or 2-acetylpyridine with equimolecular amounts of the appropriate anilines (Scheme 2).[12–16] All the ligands were authenticated by elemental analysis and ^{1}H NMR and IR spectroscopies. Selected ^{1}H NMR data for all the ligands are presented in Table 1.

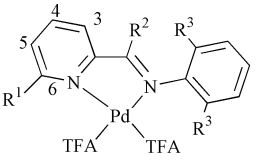
Table 1 Selected ^{1}H NMR data ($CDCl_3$) for the pyridinimine ligands and the corresponding palladium complexes

	H_5-py	H_3-py	H_4-py	H_6-py	Py-C(*R*)=N-Ar
1	7.42 ddd	8.30 ddd	7.85 td	8.73 ddd	8.36 s
1a	7.79 ddd	7.98 dd	8.23 td	8.38 dd	8.08 s
1b	7.72 ddd	7.99 dd	8.19 td	8.44 dd	8.11 s
1c	8.10 ddd	8.25 ddd	8.40 td	8.02 ddd	8.12 s
2	7.40 ddd	8.30 ddd	7.83 td	8.69 ddd	2.20 s
2a	7.92 ddd	8.02 dd	8.23 td	8.40 dd	2.31 s
3	7.42 m	8.27 d	7.86 t	8.73 d	8.31 s
3a	7.84 ddd	7.99 ddd	8.28 ddd	8.34 ddd	7.97 s
4	7.41 ddd	8.37 ddd	7.83 td	8.70 ddd	2.23 s
4a	7.85 ddd	7.92 dd	8.32 td	8.44 dd	2.34 s
5	7.29 d	8.11 d	7.76 t	—	8.30 s
5a	7.61 dd	7.76 dd	8.09 t	—	7.90 s
6	7.4[a]	8.21 ddd	7.81 td	8.72 ddd	8.62 s
6a	7.75 ddd	8.00 dd	8.23 m[b]	8.23 m[b]	8.20 s

[a] Masked by aryl hydrogen resonances. [b] Signals overlapped.

Reaction of the ligands **1**–**6** with $Pd(TFA)_2$ in MeOH–CH_2Cl_2 at room temperature, followed by addition of diethyl ether, yielded the corresponding neutral bis(trifluoroacetate) complexes (N-N′)$Pd(TFA)_2$ (**1a**–**6a**) in good yields (Scheme 3). The bis(acetate) derivative [py-2-C(H)=N(2,6-$Me_2C_6H_3$)]-$Pd(OAc)_2$ (**1b**) was obtained from **1** by substituting $Pd(TFA)_2$ for $Pd(OAc)_2$, while the cationic complex [{py-2-C(H)=N(2,6-$Me_2C_6H_3$)}$Pd(THF)_2$][PF_6]$_2$ (**1c**) was prepared by a more complex procedure involving the substitution of the diene ligand in (COD)$PdCl_2$ by the pyridinimine **1** in THF, followed by reaction of the dichloride intermediate with silver hexafluorophosphate. All the complexes are quite air stable in the solid state while they are stable in solutions of organic solvents such as CH_2Cl_2, acetone and MeOH only under a nitrogen atmosphere. The complexes have been characterized by elemental analysis and ^{1}H NMR spectroscopy (selected data are given in Table 1). Moreover, single-crystal X-ray structure determinations were performed for the TFA complexes **1a**–**3a**.

The ^{1}H NMR characteristics of the complexes are in line with those reported for related palladium(II) complexes containing bidentate pyridinimine ligands and therefore do not deserve any detailed analysis.[15,16,18,20] It may be worthwhile to stress, however, that the resonances of the protons in the 3 position are high-field shifted as compared to the free ligands, which has been attributed to the difference between free (*s-trans*) and coordinated (*s-cis*) conformations of the formal 1,4-diazabutadiene moiety (Schemes 2 and 3).[18a] In the free ligand, the electron density on the imino nitrogen largely deshields the vicinal H3 atom, in fact. Moreover, upon complexation to palladium, the isopropyl groups in **3a**, **4a**, and **5a** became magnetically inequivalent (doublets at *ca.* δ 1.15 and 1.45 *vs.* doublet at *ca.* δ 1.17 in the free ligands), which can be attributed to hindered rotation of the aryl rings.[15,16] This magnetic inequivalence was observed up to 80 °C in MeOH-d_4.



1a: R^1 = H, R^2 = H, R^3 = Me
2a: R^1 = H, R^2 = Me, R^3 = Me
3a: R^1 = H, R^2 = H, R^3 = *i*-Pr
4a: R^1 = H, R^2 = Me, R^3 = *i*-Pr
5a: R^1 = Me, R^2 = H, R^3 = *i*-Pr
6a: R^1 = H, R^2 = H, R^3 = H

Scheme 3 Structure and numbering scheme of the bis-trifluoroacetate complexes.

At higher temperature, rapid decomposition of the complexes occurred. In **1b**, the methyl resonance of the acetate coligand that is spatially closer to the imino aryl group is shifted upfield (δ 1.32 *vs.* 2.05) due to shielding by the aromatic π system.[15,16]

Crystallographic studies

Crystals suited for an X-ray analysis were obtained for **1a**, **2a**, and **3a** by slow evaporation of the solvent from diluted CH_2Cl_2 solutions. ORTEP drawings are shown in Fig. 1, while details of data collection/refinement and selected bond distances and angles are reported in Tables 2 and 3, respectively.

The overall molecular structure of the compounds investigated can be described as a square plane with the palladium centre coordinated by a chelating pyridinimine ligand and by two *cis* TFA groups. The palladium atom in **3a**, which features a ligand bearing *ortho i*-propyl substituents, lies in the coordination N_2O_2 plane [only 0.020(4) Å above], the atoms of which are coplanar within $\pm$0.096 Å. In contrast, the metal centre in the complexes containing 2,6-methyl substituents on the imino aryl group (**1a** and **2a**) is significantly displaced from the coordination plane [below by 0.553(4) and 0.41(3) Å, respectively], with average deviations of $\pm$0.566 Å for **1a** and $\pm$0.567 Å for **2a**.

The values of the chelating angles N1–Pd–N2 in **1a**–**3a** are comparable within the three compounds [from 79.7(3) to 81.1(3)°] and reflect the small bite sizes of the ligands.[15,16,18]

A feature common to all complexes is the almost perpendicular orientation of the mean plane defined by the imino aromatic ring with respect to the mean plane defined by the atoms N(1), N(2), and Pd. As a consequence of this orientation, the free space at palladium in the coordination plane is partly controlled by the imino aryl substituents.

The aromatic ring in **2a** [78.1(4)°] is more tilted towards the diazadiene backbone than in **1a** and **3a** [81.1(2) and 84.5(3)°, respectively],[15,16] which contrasts recent DFT studies on substituent effects in palladium-catalyzed olefin polymerization.[26] Indeed, one would expect a more vertical orientation of the aryl ring in **2a** as compared to **1a** due to the greater repulsion between the methyl substituent at the aryl group and the methyl substituent at the imino carbon atom.[26] This apparent contrast means that the aryl orientation in the solid state is determined also by the TFA co-ligands. Consistently, the Pd–O bonds are slightly longer and the N1–Pd–O1 angle is slightly larger [96.4(3)°] in **2a** than in **1a** [94.3(2)°] and **3a** [93.8(3)°].

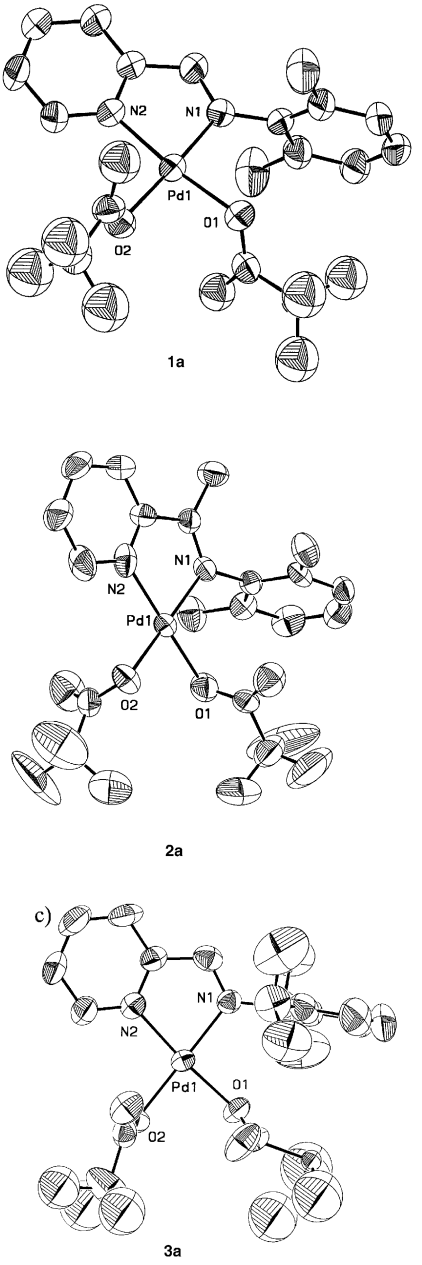


Fig. 1 ORTEP drawings of the pyridinimine palladium complexes **1a** (a), **2a** (b) and **3a** (c).

Table 2 Crystal data and structure refinement details for **1a**, **2a**, and **3a**

	1a	**2a**	**3a**
Empirical formula	$C_{18}H_{14}F_6N_2O_4Pd$	$C_{19}H_{16}F_6N_2O_4Pd$	$C_{22}H_{22}F_6N_2O_4Pd$
Formula weight	542.71	556.74	598.84
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	9.383(3)	8.481(4)	12.370(4)
b/Å	9.774(2)	20.641(4)	17.071(2)
c/Å	11.585(2)	12.241(3)	12.663(5)
α/°	85.90(2)	90.00	90.00
β/°	89.74(2)	98.80(2)	105.55(4)
γ/°	70.79(2)	90.00	90.00
U/Å^3	100.5(9)	2117.7(12)	2576.1(13)
Z	2	4	4
μ/mm^{-1}	0.994	0.957	0.781
Reflections collected	3700	3709	4725
Independent reflections	3508	3709	4509
R_{int}	0.0179	0.0200	0.0185
R_1 [$I>2\sigma(I)$]	0.0636	0.0667	0.0752
wR_2 (all data)	0.1755	0.2114	0.2123

Table 3 Selected bond distances (Å) and angles (°) for **1a**, **2a**, and **3a**

	1a	**2a**	**3a**
Pd–N(1)	1.989(5)	1.989(7)	1.987(8)
Pd–N(2)	1.989(5)	1.995(9)	1.984(8)
Pd–O(1)	2.000(5)	2.014(7)	2.006(6)
Pd–O(2)	2.000(5)	2.039(6)	2.026(6)
N(1)–Pd–N(2)	81.0(2)	79.7(3)	81.1(3)
N(2)–Pd–O(2)	96.0(2)	97.9(3)	98.2(3)
O(2)–Pd–O(1)	88.9(2)	86.4(3)	87.5(3)
N(1)–Pd–O(1)	94.3(2)	96.4(3)	93.8(3)
N(1)–Pd–O(2)	176.4(2)	174.7(3)	175.6(3)
N(2)–Pd–O(1)	173.7(2)	173.7(3)	171.4(3)

Catalytic carbonylation of styrene

The catalytic performance of the present pyridinimine palladium complexes in the carbonylation of styrene in MeOH was investigated under experimental conditions comparable with those previously employed for analogous reactions catalyzed by chelating diphosphine precursors of the formula $[(P\text{-}P)PdL_2]^{n+}$ (L = MeCN, bipy, $n = 2$; L = OAc, $n = 0$)[4] (see Experimental). In a second stage, various parameters such as the concentration of the protic acid, the CO pressure and the reaction time were varied in an attempt at optimizing the process as well as acquiring mechanistic information.

Unlike the reactions catalyzed by phosphine-modified palladium complexes,[4] extreme care was adopted to avoid the degradation of the metal precursors during the preparation of the catalytic systems. Therefore, MeOH was carefully dried and styrene was introduced into the reactor only after adding the organic oxidant (BQ). In fact, we noticed that the palladium precursors started decomposing to palladium metal and free ligand already at room temperature upon addition of excess styrene in commercial MeOH. It may be interesting to report that the decomposition of the precursors is accompanied by the formation of both PhC(O)Me and its hemiketal PhC(OH)(OMe)Me in almost equimolar concentrations. The formation of acetophenone may be explained by taking into account a sequence of reactions analogous to that leading to the production of acetaldehyde in the Wacker process, which involves an intramolecular nucleophilic attack by H_2O/OH^- at the double bond of coordinated ethylene.[27] The hemiketal is apparently formed by addition of alcohol to the acetophenone carbonyl group.[28,29]

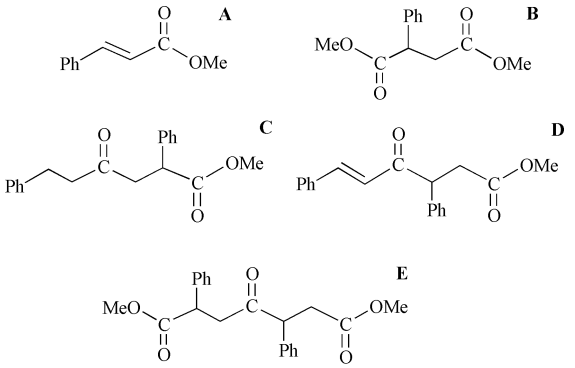
The precursor degradation in the presence of styrene was studied by ^1H NMR spectroscopy in commercial MeOH-d_4. It was thus discovered that the decomposition of the palladium(II) complexes is quite rapid ($t_{1/2}$ *ca.* 5 min) and is accompanied by the formation of both palladium metal and cationic bis-chelate complexes of the general formula $[(N\text{-}N')_2Pd]^{2+}$.[15,30,31] The production of partially deuterated acetophenone and its hemiketal was observed by GC/MS analysis. The formation of the bis-chelate complexes can be accounted for by the reaction of water with styrene leading to acetophenone and (N-N′)Pd(0) species.[27] These latter are known to decompose rapidly, in fact, yielding palladium metal that precipitates as a black powder and free ligand that reacts with the parent monochelate palladium(II) moiety to give the corresponding bis-chelate complex. An identical mechanism has been recently reported to explain the formation of bis-chelates $[(P\text{-}P)_2Pd]^{2+}$ in the course of styrene carbonylation reactions catalyzed by diphosphine-modified palladium(II) catalysts in MeOH.[4]

Adopting the precautions previously described decreased substantially the degradation of the precursors by a Wacker-type process as neither acetophenone nor its hemiketal was produced in appreciable amounts, as determined by GC. The results obtained by applying different reaction times were consistent with a good catalyst stability, at least within 3 h of reaction. However, some catalyst degradation invariably occurred, although in trace amounts, as black palladium metal was observed in all reactions, particularly in those carried out with a six-fold excess of acid.

Table 4 Carbonylation of styrene catalyzed by (N-N′)Pd(II) complexes[a]

Entry	Precursor	TsOH/equiv	Time/h	P_{CO}/psi	Conv (%)	**A** (%)	Sel **A** (%)	**B** (%)	Sel **B** (%)	**C**–**E** (%)	Sel **C**–**E** (%)	DMO/TON[b]
1	**1a**	0	1.5	800	35.1	1.5	4	29.8	85	3.8	11	9
2		0	3	800	44.3	1.0	2	37.7	85	5.6	13	20
3		2	3	800	57.3	1.1	2	47.2	82	9.0	16	11
4		4	3	800	50.2	0.5	1	46.6	93	3.1	6	4
5		6	3	400	51.2	1.2	2	48.1	94	1.9	4	0
6		6	3	800	41.3	0.2	0	40.0	97	1.1	3	3
7		6	3	1500	24.9	0.0	0	24.4	98	0.5	0	19
8	**1b**	0	3	800	4.0	0.0	0	3.4	85	0.6	15	42
9		2	3	800	52.2	0.7	1	39.0	75	12.5	24	15
10	**1c**	0	3	800	46.1	1.0	2	40.1	87	5.0	11	28
11		2	3	800	47.2	0.8	2	39.5	84	6.9	15	13
12	**2a**	0	1.5	800	21.5	0.4	2	15.7	73	5.4	25	6
13		0	3	800	42.9	0.4	1	31.9	74	10.6	25	16
14		2	3	800	53.4	0.7	1	37.3	70	15.4	29	9
15		4	3	800	42.4	0.3	1	36.1	85	6.0	14	4
16		6	3	800	37.6	0.2	1	35.8	95	1.6	4	2
17	**3a**	0	1.5	800	16.1	0.3	2	14.5	90	1.3	8	9
18		0	3	800	26.2	0.1	0	23.4	89	2.7	10	23
19		2	3	800	38.9	0.3	1	32.3	83	6.3	16	16
20		6	3	800	25.0	0.2	1	24.3	97	0.5	2	2
21	**4a**	0	1.5	800	13.9	0.2	1	10.5	76	3.2	23	8
22		0	3	800	23.0	0.6	3	16.9	73	5.5	24	19
23		2	3	800	36.1	0.2	1	22.8	63	13.1	36	12
24		6	3	800	19.0	0.2	1	17.8	94	1.0	5	2
25	**5a**	2	3	800	0.0	0.0	—	0.0	—	0.0	—	22
26	**6a**	2	3	800	1.9	0.0	0	1.6	84	0.3	16	14

[a] Pd(II) precursor (0.01 mmol); styrene (2 mmol); BQ (2 mmol); /MeOH (20 mL); 80 °C; 700 rpm. [b] Mol of dimethyl oxalate produced per mol of catalyst.



Scheme 4

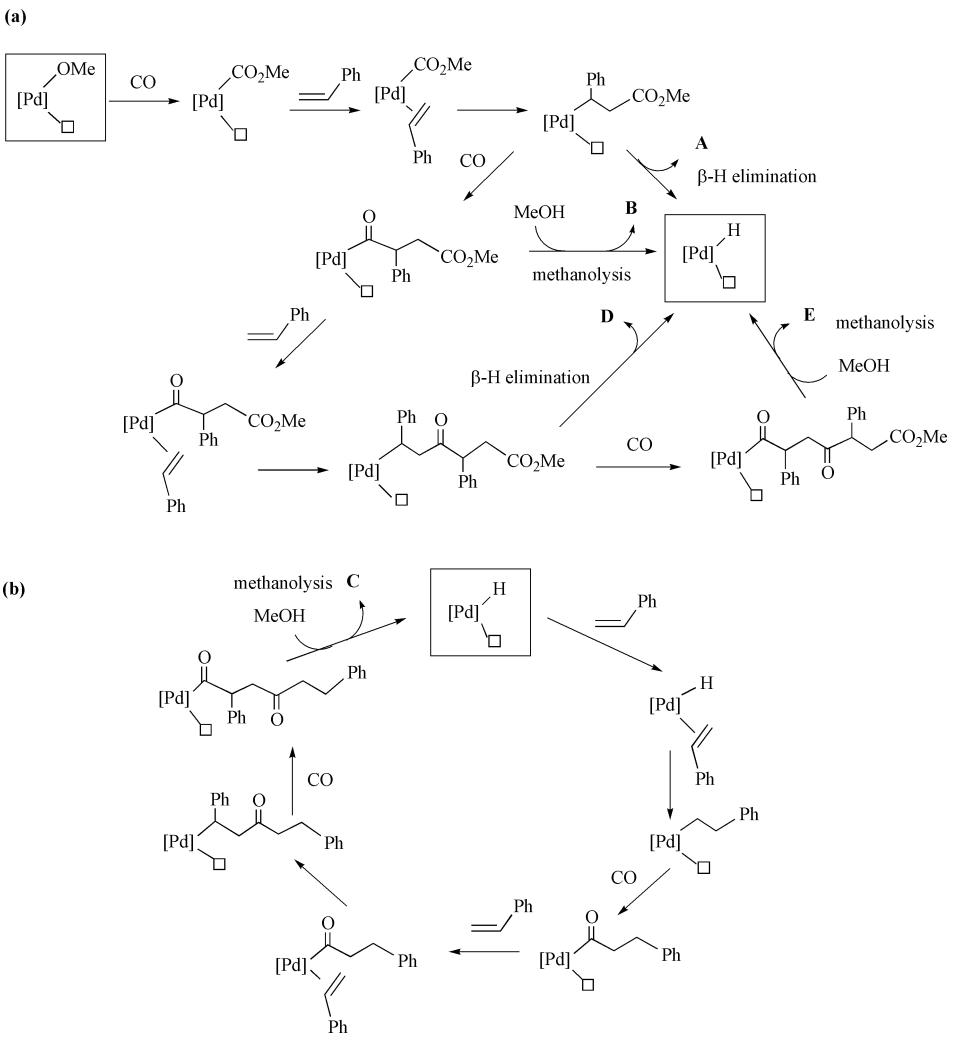
The catalytic results are summarized in Table 4. The reaction products are shown in Scheme 4: methyl cinnamate (**A**), dimethyl phenylsuccinate (**B**), methyl 2,6-diphenyl-4-oxohexanoate (**C**), methyl 3,6-diphenyl-4-oxohex-5-enoate (**D**), and dimethyl 2,5-diphenyl-4-oxoheptanedioate (**E**). These products were identified by comparing their GC retention times and GC/MS spectra with those of authentic samples.[3a,b,4]

Before reporting and commenting the results obtained, it may be worth giving a brief description of the commonly accepted mechanisms of styrene carbonylation by palladium(II) catalysis,[2] particularly as regards the formation of the products **A**–**E** (Scheme 5).

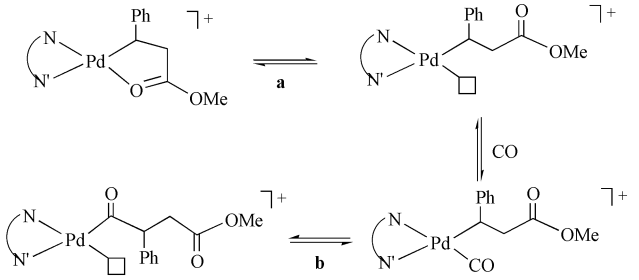
The formation of **A**, **B**, **D** and **E** upon carbonylation of styrene in MeOH implies a series of reactions that require the participation of methoxy initiators $[(N\text{-}N')Pd(OMe)]^+$ as well as the occurrence of termination steps leading to the generation of hydride species $[(N\text{-}N')PdH]^+$ *via* either β-H elimination (products **A** and **D**) or methanolysis (products **B** and **E**).[3a,b,4]

As for the formation of **C**,[3b] the catalytic cycle requires the occurrence of a 1,2-migratory insertion process[3a,b,g] in $[(N\text{-}N')Pd(H)(styrene)]^+$ and termination *via* methanolysis (Scheme 5b). Given the nature of the products obtained, the migratory insertion in $[(N\text{-}N')Pd(acyl)(styrene)]^+$ must occur with 2,1-regiospecificity.[2,3j,32–34] Secondary insertions of this type have been observed for a variety of styrene carbonylation reactions leading to alternating polyketones,[2] ketones or esters.[3,4] Secondary insertions of styrene have been also observed in homogeneous oligomerization[35] and polymerization reactions of olefins.[36]

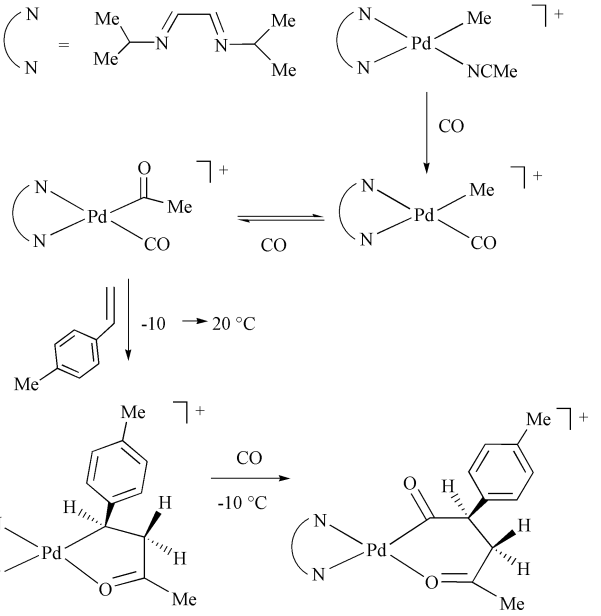
From a perusal of the catalytic data reported in Table 4, it is apparent that, in the absence of the Brønsted acid co-reagent, the ligands **1**–**4** give rise to efficient catalysts for the synthesis of the bis-alkoxycarbonylation product **B** with selectivities spanning from 73 to 90%. In particular, among the pyridinimines investigated, **1** showed itself to be appropriately tailored to provide the highest productivity in **B** (about 75 mol per mol of catalyst in 3 h, entry 2). The remaining products were the cinnamate **A** (max. 1.5%) and the oligomers **C**–**E** obtained by alternating insertion of styrene and carbon monoxide. Among the oligomers only **C** was produced in



Scheme 5 Proposed reaction schemes for the methoxycarbonylation of styrene with chelating dinitrogen-Pd(II) precursors; [Pd] = $[(N\text{-}N')Pd]^{2+}$, N-N′ = dinitrogen ligand. □ represents either a co-ligand or a solvent molecule.



Scheme 6



Scheme 7

appreciable amounts, **D** and **E** never being obtained in concentrations higher than 1%. For this reason, the quantitative data relative to the oligomeric products **C**–**E** have been collected together in Table 4.

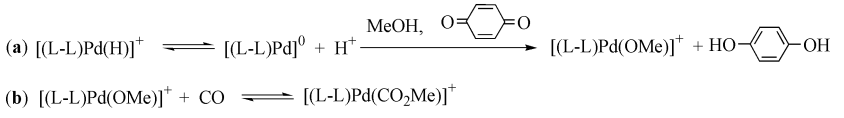
The selectivities in **A** were quite low indeed, in particular when compared to those found in analogous styrene carbonylation reactions in MeOH catalyzed by diphosphine-modified palladium complexes.[3a,b,f,4] The low selectivity in methyl cinnamate suggests that β-elimination is disfavoured over CO insertion in Pd–CH(Ph)CH_2CO_2Me intermediates stabilized by chelating dinitrogen ligands (Scheme 5a). There are two possible explanations for this eventuality. The first is that the greater electrophilic character of palladium(II) in the dinitrogen complexes might disfavour the β-elimination due to the formation of more stable β-chelate complexes (equilibrium **a**, Scheme 6).[2b,d] β-Keto chelate palladium complexes with diimine ligands have been isolated, in fact.[32,33] In particular, both β- and γ-chelates have been synthesized starting from the complex $[(Pr^iDAB)Pd(Me)(NCMe)]^+$ where Pr^iDAB is 1,4-diisopropyl-1,4-diazabuta-1,3-diene (Scheme 7).[32] Indeed, the electrophilic character of the palladium centre in the pyridinimine complexes is clearly shown by the occurrence of styrene oxidation by water yielding acetophenone (*vide infra*). An alternative explanation for the low selectivity in cinnamate is that the rate of migratory insertion in Pd(CO)(alkyl) is faster in the complexes stabilized by dinitrogen ligands[18,37] than in diphosphine analogues (equilibrium **b**, Scheme 6),[38] as a consequence of the greater electrophilicity of CO *trans* to nitrogen as compared to CO *trans* to phosphorus.[37a] As for the observed low selectivities in **D** and **E**, it may be simply pointed out that the chain growth in the pyridinimine complexes is disfavoured over termination by methanolysis leading to **B** (Scheme 5a).

From a perusal of Table 4, one may also realize that the overall yield in carbonylation products is controlled by the steric properties of the alkyl substituents on the imine aryl group, while the nature of the substituent (H or Me) at the imine carbon influences the selectivity of the carbonylation reaction. Indeed, the catalyst precursors **1a** and **2a**, bearing methyl groups at the 2,6 positions of the aryl group, gave more **B** (37.7 and 31.9%, respectively) as compared to the *i*-propyl-substituted precursors **3a** and **4a** (23.4 and 16.9%, respectively). In turn, the precursors **1a** and **3a**, containing the –C(H)=N– group, were appreciably more selective in **B** than the precursors with the –C(Me)=N– group (87_{av} *vs.* 74_{av}%). The greater activity of **1a** and **2a** as compared to **3a** and **4a** may be related to a more favourable steric control by the methyl substituents over the *i*-propyl ones on the insertion of CO and styrene into palladium-carbon bonds as well as the termination process by methanolysis (Scheme 5). The presence of *i*-propyl groups may stabilize certain intermediates, thus hindering the access of styrene, CO or MeOH to the palladium centre[39,40] and ultimately resulting in reduced rates of product formation.

The different selectivities observed in the reactions catalyzed by the complexes modified with the ligands **1**–**4** deserve a comment. In view of the results reported in Table 4 and of what was previously said on the relative abundance of the oligomeric products, the lower selectivity in **B** is essentially due to the greater production of oligomer **C**. Since **B** and **C** are formed in catalytic cycles that involve different initiators (Pd–OMe for **B** and Pd–H for **C**), the selectivity in **B** is effectively controlled by the ability of the catalysts to favour (or disfavour) the conversion of $[(N\text{-}N')PdH]^+$ to $[(N\text{-}N')Pd(OMe)]^+$. Exhaustive information may be found in the literature on the factors that promote the formation of either $[(L\text{-}L)Pd\text{–}H]^+$ or $[(L\text{-}L)Pd\text{–}OMe]^+$ in MeOH (L-L = chelating diphosphine or dinitrogen ligand).[2] It is generally agreed that the presence of an oxidant such as BQ favours the formation of the methoxy complexes. Furthermore, the reaction between $[(L\text{-}L)PdH]^+$ and CO/MeOH to give $[(L\text{-}L)PdCO_2Me]^+$ has been interpreted in terms of a series of equilibria and reactions that see the initial formation of an unstable Pd(0) species, later oxidized to Pd(II) by BQ (Scheme 8). It has been suggested that the latter process occurs with the intermediacy of palladium(0) complexes containing a molecule of BQ, either η^2 or η^4 bonded to the metal.[2b,30b,41]

A further evidence of the role played by BQ in shifting the equilibria of Scheme 8 to the right has been provided by the results obtained with the catalysts containing the pyridinimine ligands **1**–**6**. Control experiments have shown in fact that the use of 300 instead of 200 equivalents of BQ in an experiment carried out in the experimental conditions of entry 13 (Table 4) led to a drastic decrease (from 25 to 6%) in the selectivity in oligomer **C** whose formation requires a Pd–H initiator.

Given the complexity of the reaction sequence illustrated in Scheme 8, it is not easy to determine the factors accounting for



Scheme 8

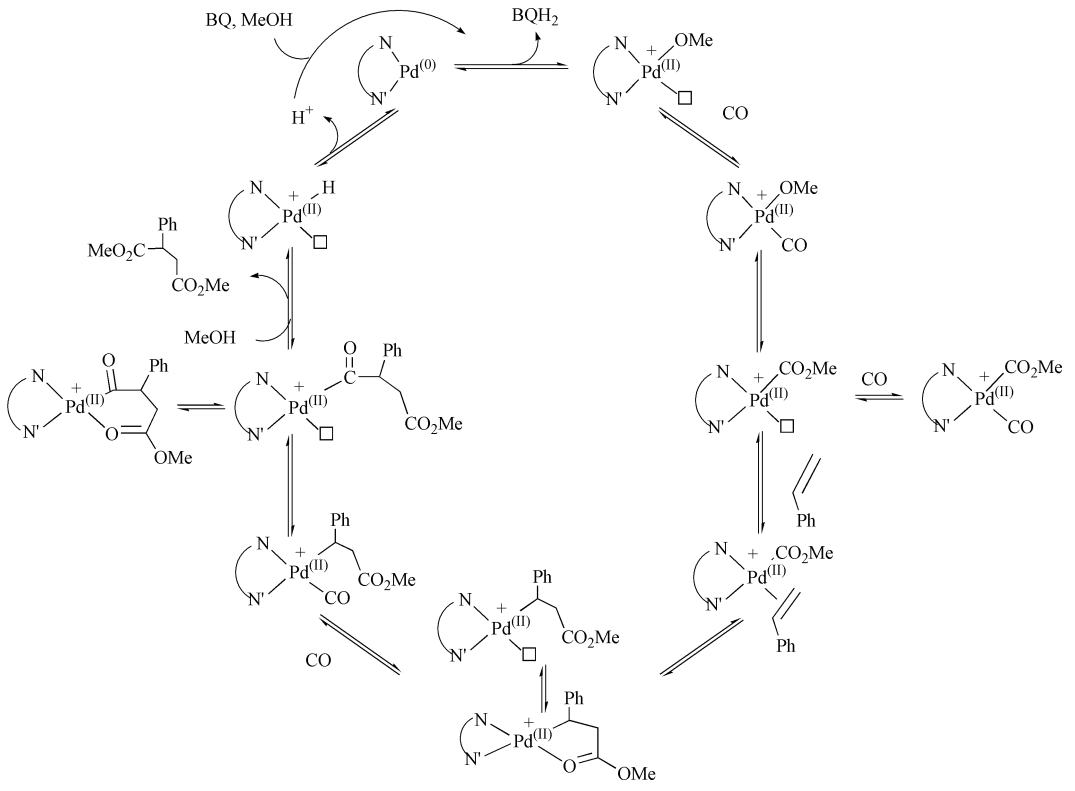
the decreased conversion of Pd–H into Pd–OMe with ligands **2** and **4** as compared to ligands **1** and **3**. Intuitively, we suggest that the methyl group on the imine carbon induces a sterically less favourable environment to the formation of BQ-containing intermediates, and hence to palladium(0) oxidation.

In the course of the catalyst screening, we have been also looking for yield and/or selectivity dependence on the nature of the co-ligands in the palladium precursors. Previous studies of styrene methoxycarbonylation by palladium-diphosphine catalysis had shown in fact that the substitution of acetate for weaker co-ligands such as MeCN can result in an inversion of selectivity from dimethyl phenylsuccinate to methyl cinnamate.[4] In contrast to palladium-diphosphine catalysts, the substitution of TFA (entry 2) for either acetate (entry 8) or THF (entry 10) in the pyridinimine-modified precursor **1a** gave no substantial selectivity change. It was found, however, that **1b** was less efficient than **1a** and **1c**, which may be accounted for by the greater nucleophilicity of acetate *vs.* trifluoroacetate and THF.[4,30*a*]

Unlike the co-ligand nature, an important role in determining both the catalytic activity and the selectivity seems to be played by the concentration of the protic acid co-catalyst. The addition of two equivalents of TsOH to the catalytic mixtures has been found to generally increase the styrene conversions as well as slightly decrease the selectivity in **B** due to increased production of **C**. Notwithstanding the decreased selectivity, the production of succinate **B** was greater than that obtained in the absence of added acid (*e.g.*, entry 3 *vs.* entry 2). It is also worth pointing out that precursors **1a** and **2a** were more efficient even in acidic media (57.3 and 53.4% conversion, respectively) than **3a** and **4a** (38.9 and 36.1% conversion, respectively). The increased conversion observed for all catalysts in the presence of TsOH might be simply due to a larger number of catalytically active sites as a consequence of the weaker coordinating properties of the tosylate anion as compared to carboxylate. A greater catalyst durability, occasioned by the higher oxidizing power of BQ in an acidic environment, may also contribute to enhance the catalyst productivity.[4,41*b*]

In order to gain further insight into the ligand requirements controlling the conversion and/or selectivity of the methoxycarbonylation reaction, some experiments have been carried out with pyridinimine **5**, containing *ortho*-*i*-propyl substituents on the imino phenyl ring and a methyl substituent at the 6 position of the pyridine ring, and with pyridinimine **6** with no substituent on either ring. Catalytic reactions carried out with these precursors in the presence of two equivalents of acid gave very low (**6a**, entry 26) or even no conversion (**5a**, entry 25). In particular, the latter catalyst completely decomposed in 3 h.

Taken together, the results obtained with the pyridinimine ligands **1**–**6** in the presence of 2 equivalents of TsOH allowed us to infer the following structure/activity relationship. The ligands bearing *o*-methyl substituents on the imine aryl group (*e.g.*, **1** and **2**) give rise to more active catalysts (entries 3 and 14) as compared to pyridinimine **6** that contains an unsubstituted phenyl ring (entry 26). On a qualitative basis, the increase in productivity may be associated to an increase in the steric hindrance provided by the imine phenyl. This hypothesis is indirectly supported by previous evidence according to which both the migratory insertion of Pd(Me)(CO)[18*a*] and the coordination of the olefin[42] in palladium(II) fragments stabilized by pyridinimine ligands is favoured when the latter contain alkyl substituents at the 2 or/and 6 position(s) of the phenyl group. A large steric hindrance such as in pyridinimines **3** and **4** containing *i*-propyl groups, however, reduced the catalytic activity, which may be related to hindered access to palladium of styrene, CO or MeOH. Consistently, when the pyridinimine ligand bears 2,6-*i*-propyl groups at the phenyl and a methyl group in the 6 position of the pyridine ring as in **5**, the production of styrene carbonylation products was practically suppressed (entry 25). A similar structure/activity relationship has been recently reported for the copolymerization of styrene and CO by 1,10-phenanthroline modified palladium(II) catalysts.[30*a*] In fact, a dramatic decrease in catalytic



Scheme 9 Proposed mechanism for the bis-methoxycarbonylation of styrene with pyridinimine precursors. □ represents either a co-ligand or a solvent molecule.

activity was observed when 2,9-dimethyl-1,10-phenanthroline was substituted for 1,10-phenanthroline. It cannot be ruled out, however, that the low activity of the pyridinimines **3** and **4** may be due to competitive formation of palladacycles *via* intramolecular C–H bond activation from an *i*-propyl group.[43]

Increasing the concentration of protic acid (from 2 to 4 to 6 equiv.) resulted for all precursors in a better selectivity in **B** accompanied by decreased conversions, however. In the presence of 6 equiv. of TsOH, **1a**–**4a** gave selectivities in the range 94–97% but with productivities even lower than those obtained in the absence of acid co-reagent. We do not have a clear-cut explanation accounting for the decreased activity and increased selectivity in **B** at high acid concentrations. The drop in activity in the presence of a large excess of TsOH may be actually related to an increased amount of water in the catalytic mixture. In fact, the acid is commercially available as the monohydrated salt and also promotes the esterification of the trifluoroacetate co-ligands by MeOH, yielding TFAMe and H_2O. As for the selectivity, we can only suggest that a high acid concentration, favouring the oxidizing properties of BQ,[4,41*b*] might favour the conversion of Pd–H to Pd–CO_2Me (Scheme 8).

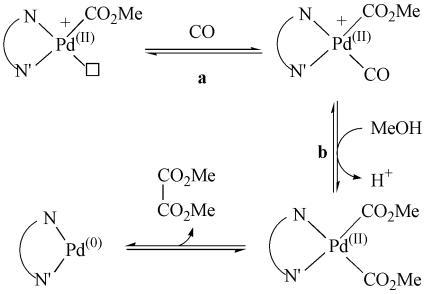
In an attempt at determining the influence of the CO pressure on the rate and selectivity of the methoxycarbonylation reaction catalyzed by the pyridinimine complexes, **1a** was employed as precursor together with 6 equiv. of TsOH in some experiments in which the initial CO pressure was varied from 400 to 1500 psi. Under these conditions, the conversion decreased from 51.2% to 24.4%, while the selectivity in **B** was practically unaffected. In actuality, a high CO concentration might disfavour the coordination of styrene to the fragment $[(N'\text{-}N)Pd\text{–}CO_2Me]^+$ in the early stages of the catalytic cycle (Scheme 5a), thus favouring the formation of the intermediate $[(N\text{-}N')Pd(CO)(CO_2Me)]^+$ that is a precursor to dimethyl oxalate (entries 5–7) (see below).

To conclude, incorporation of all of these data leads us to propose the mechanism shown in Scheme 9 for the bis-methoxycarbonylation of styrene with pyridinimine palladium(II) catalysts.

As for the coordination structure around palladium in the species reported in Scheme 9, we cannot state univocally whether the alkyl or acyl groups are *cis* or *trans* to either nitrogen donor atom. Previous studies in both the solid state and solution of the structure of $[(N\text{-}N')Pd(alkyl)(L)]^+$ and $[(N\text{-}N')Pd(acyl)(L)]^+$ complexes clearly show that the coordination geometry is variously controlled by the electronic and steric properties of both nitrogen donor atoms and the fourth co-ligand at palladium.[15,18]

Finally, it is worth saying a few words on the formation of small amounts of dimethyl oxalate (DMO) that almost invariably was found to contaminate the methoxycarbonylation of styrene (Table 4). The production of alkyl oxalates from alcohols is generally achieved by either homogeneous oxidative carbonylation by palladium(II) catalysis[44] or carbonylation of alkyl nitrites with Pd(0) catalysts in the homogeneous or heterogeneous phase.[45] In the former case, the reaction proceeds *via* formation of intermediates $L_nPd(COOR)_2$ that ultimately release the oxalate by reductive coupling.[44] In the present case, species with the formula $[(N\text{-}N')Pd\text{–}CO_2Me]^+$ may actually form from the carbonylation of Pd–OMe, and therefore it may be possible that the observed production of DMO occurs *via* the mechanism shown in Scheme 10. Oxidation by BQ of the Pd(0) complex that forms upon reductive elimination of the oxalate regenerates the catalytically active species (see Scheme 9).

In favour of a homogeneous process such as that proposed in Scheme 10 there is the evidence that the production of DMO increases with the CO pressure (entries 5–7) and decreases with the concentration of the protic acid (entries 2–5; 13–16, 18–20 and 22–24). Indeed, it is reasonable to think that the concentration of intermediate $[(N\text{-}N')Pd(CO)(CO_2Me)]^+$ (step **a** in Scheme 10) increases with the CO pressure, while a high concentration of acid would shift step **b** to the left.



Scheme 10 Reaction sequence for the production of dimethyl oxalate.

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