Supplementary information for

Contrasting coordination modes of a tridentate bis(oxazoline)phosphine ligand in cobalt and iron vs. palladium complexes: unprecedented N,N-coordination for a N,P,N ligand.

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General considerations: All reactions were performed under purified nitrogen. Solvents were purified and dried under nitrogen by conventional methods. The ^{1}H NMR spectra were recorded at 300.13 MHz, $^{31}P\{^{1}H\}$ NMR spectra at 121.5 MHz, and $^{13}C\{^{1}H\}$ NMR spectra at 75.5 MHz on a FT Bruker AC300 instrument. IR spectra in the range of 4000-400 cm^{-1} were recorded on a Bruker IFS28FT spectrometer. Gas chromatographic analyses were performed on a Thermoquest GC8000 Top Series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 µm film thickness). Magnetic moments were determined by the Evans method[1-4] in CD_2Cl_2 using a solution of CH_3NO_2 in CD_2Cl_2 (20:80, v/v) as reference. Mass spectra were recorded with a Bruker Daltonics microTOF (ESI; positive mode; capillary voltage: 4.8 kV; nebulizer pressure: 0.2 bar; desolvation temperature: 180 °C; desolvation gas flow rate: 4.5 L/min). The ligands and complexes $NOPON^{Me}$, [Pd(Me)Cl(COD)], $[PdCl_2(NCPh)_2]$, $[Pd(NCMe)_4(BF_4)_2]$ have been synthesized according to the literature.[5-7]

Synthesis of bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine (NPN^{Me2})

A *n*-BuLi solution (64.0 mmol, 1.6 M in hexane) was added dropwise to a degassed solution of 2,5,5-trimethyl-2-oxazoline (7.24 g, 64.0 mmol) in 100 mL of THF at -78 °C. After the pale yellow mixture was stirred for 1 h at -78 °C, degassed chlorotrimethylsilane (6.95 g, 64.0 mmol) was added dropwise and stirring was maintained for 2 h. Liquid $PPhCl_2$ (5.73 g, 32.0 mmol) was added to the colourless solution at -78 °C. The solution was allowed to reach

room temperature overnight and a mixture of diethylether and toluene was added to precipitate the LiCl which was removed by filtration. Solvents were evaporated and the remaining yellow oil was dried for several hours under vacuum at 40 °C. This afforded the pure ligand as a yellow oil (yield: 4.4 g, 13.25 mmol, 41%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 and 1.13 (each 6H, 2s, CH_3), ABX spin system (A = B = H, X = P): 2.80 (2H, dd, J_{AB} = 14.1 Hz, $^{2}J_{XB}$ = 0.9 Hz, P-CH_2) and 2.92 (2H, dd, J_{AB} = 14.1 Hz, $^{2}J_{XA}$ = 4.6 Hz, P-CH_2), 3.78 (4H, s, O-CH_2), 7.31–7.35 (3H, m, aromatic H), 7.48–7.53 (2H, m, aromatic H); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 26.9 (d, $^{1}J_{PC}$ = 22.0 Hz, P-CH_2), 28.32 (s, CH_3), 28.41 (s, CH_3), 67.1 (s, O-CH_2), 79.2 (s, *C*-CH_3), 128.35 (d, $^{3}J_{PC}$ = 6.9 Hz, *m*-CH of aryl), 129.4 (s, *p*-CH of aryl), 132.2 (d, $^{2}J_{PC}$ = 20.2 Hz, *o*-CH of aryl), 135.2 (d, J_{PC} = 20.2 Hz, C-P of aryl), 162.4 (d, $^{2}J_{PC}$ = 4.7 Hz, *C*=N); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ -24.83. HRMS: Mass calcd. for $C_{18}H_{26}N_2O_2P$: 333.173. Found. 333.166 $[(N,P,N)+H]^{+}$.

Synthesis of [Co{bis(1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-1-ethylethyl)phenyl phosphonite}Cl_2] (1)

Anhydrous $CoCl_2$ (0.14 g, 1.1 mmol) was added to a solution of $NOPON^{Me2}$ (0.46 g, 1.1 mmol) in 30 mL of THF. The blue solution was stirred for 3 h at room temperature. After elimination of THF under reduced pressure, the blue powder was dried overnight under vacuum. Complex **1** was obtained as a blue powder without further purification (yield: 0.58 g, 1.05 mmol, 97%). The structure of **1** has been determined by X-ray diffraction on single crystals obtained by slow diffusion of toluene into a CH_2Cl_2 solution. IR (KBr): 1682 (s), 1627 (vs), 1465 (m), 1437 (m), 1366 (m), 1313 (m), 1258 (w), 1144 (s), 1177 (w), 1142 (m), 1119 (vs), 1021 (s), 979 (vs), 913 (m), 865 (w), 741 (s), 714 (w), 698 (w), 576 (w), 562 (w) cm^{-1}. Anal. calcd. for $C_{22}H_{33}Cl_2CoN_2O_4P$: C, 48.01; H, 6.04; N, 5.09. Found: C, 48.06; H, 5.92; N, 4.84.

Synthesis of [Co{bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl_2] (2)

Anhydrous $CoCl_2$ (0.24 g, 1.85 mmol) was added to a solution of bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine (NPN^{Me2}) (0.62 g, 1.85 mmol) in 50 mL of THF. The blue solution was stirred for 3 h at room temperature. After filtration of the solution and elimination of THF under reduced pressure, the blue powder was dried overnight under vacuum. Complex **2** was obtained as a blue powder without further purification (yield: 0.81 g, 1.75 mmol, 94%). The structure of **2** has been determined by X-ray diffraction on single crystals obtained by slow diffusion of toluene into a CH_2Cl_2 solution. IR (KBr): 1628 (vs),

1613 (vs sh), 1476 (w), 1462 (w), 1433 (w), 1422 (m), 1372 (s), 1321 (s), 1252 (w), 1222 (m), 1184 (m), 1136 (m), 1119 (m), 1012 (s), 1002 (s sh), 959 (vs), 924 (w), 839 (w), 798 (w), 773 (w), 744 (s), 699 (m) cm^{-1}. Anal. calcd. for $C_{18}H_{25}Cl_2CoN_2O_2P$: C, 46.77; H, 5.45; N, 6.06. Found: C, 46.47; H, 5.23; N, 5.70.

Synthesis of [Fe{bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl_2] (3)

To a solution of bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine (NPN^{Me2}) (1.99 g, 6.0 mmol) in 50 mL of CH_2Cl_2 was added a CH_2Cl_2 solution of $FeCl_2{\cdot}4H_2O$ (1.19 g, 6.0 mmol) and the mixture was stirred at room temperature overnight. The solvent was then eliminated under reduced pressure and 50 mL of diethylether was added to precipitate the white complex. Complex **3** was recovered by filtration, washed with diethylether and dried under vacuum (yield: 2.40 g, 5.2 mmol, 87%). The crystal structure of **3** has been determined on white single crystals obtained by slow diffusion of heptane into a CH_2Cl_2 solution of the complex. IR (KBr): 1624 (vs), 1460 (w), 1448 (w), 1433 (w), 1423 (w), 1371 (s), 1319 (s), 1220 (w), 1178 (m), 1133 (m), 1004 (m), 954 (m), 744 (m), 698 (m) cm^{-1}. Anal. calcd. for $C_{18}H_{25}Cl_2FeN_2O_2P$: C, 47.09; H, 5.45; N, 6.10. Found: C, 46.51; H, 5.58; N, 5.57.

Synthesis of [Pd(Me){bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl] (4)

To a solution of (2-oxazolin-2,5,5-trimethyl)phenylphosphine (NPN^{Me2}) (1.05 g, 3.15 mmol) in CH_2Cl_2 was added [Pd(Me)Cl(COD)] (0.84 g, 3.15 mmol) at room temperature and the pale yellow solution was stirred overnight. After elimination of the solvent under reduced pressure, a pale yellow powder was obtained. Complex **4** was washed with diethylether and dried under vacuum (yield: 1.34 g, 2.7 mmol, 87%). IR (KBr): 1659 (s), 1630 (s), 1463 (m), 1435 (m), 1366 (s), 1320 (s), 1261 (s), 1159 (s), 1103 (s), 951 (m), 801 (s), 747 (m), 692 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.74 (3H, s, Pd-CH_3) 1.27 (3H, s, CCH_3) 1.30 (3H, s, CCH_3) 1.56 (3H, s, CCH_3) 1.58 (3H, s, CCH_3), ABX spin system 1 (A = B = H, X = P) 2.98 (1H, $^2J_{AB}$ = 18.0 Hz, $^2J_{PA}$ = 11.1 Hz, PC$H_A$$H_B$), ABX spin system 2 (A = B = H, X = P) 3.06 (1H, $^2J_{AB}$ = 14.4 Hz, $^2J_{PA}$ = 7.5 Hz, PC$H_A$$H_B$), ABX spin system 2 (A = B = H, X = P) 3.23 (1H, $^2J_{AB}$ = 14.4 Hz, $^2J_{PB}$ = 12.9 Hz, PC$H_A$$H_B$), ABX spin system 1 (A = B = H, X = P) 3.78 (1H, $^2J_{AB}$ = 18.0 Hz, $^2J_{PB}$ = 11.1 Hz, PC$H_A$$H_B$), AB spin system 3.97 and 4.01 (2H, $^2J_{AB}$ = 8.1 Hz, overlapping signal of OCH_AH_B), AB spin system 4.13 and 4.16 (2H, $^2J_{AB}$ = 8.1 Hz, overlapping signal of OCH_AH_B), 7.67–7.84 (5H, m, aromatic H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ -4.3 (s, Pd-CH_3), 26.1 (d, $^1J_{PC}$ = 25.1 Hz, PCH_2), 27.6 (s, C-CH_3), 27.9 (s, C-CH_3), 28.2 (s, C-CH_3), 28.6 (s, C-CH_3), 30.0 (d, $^1J_{PC}$ = 30.0 Hz, PCH_2), 67.9 (s, NCCH_3), 68.4 (s,

N*C*CH_3), 79.6 (s, OCH_2), 83.5 (s, OCH_2), 129.2 (d, $^2J_{PC}$ = 11.3 Hz, *m*-CH of aryl), 129.3 (d, $^1J_{PC}$ = 48.6 Hz, C-P of aryl), 132.1 (s, *p*-CH of aryl), 132.7 (d, $^3J_{PC}$ = 13.5 Hz, *o*-CH of aryl), 159.4 (s, C=N from uncoordinated oxazoline), 169.5 (d, $^2J_{PC}$ = 18.5 Hz, C=N from coordinated oxazoline); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 26.56.

Synthesis of [Pd{bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl_2] (5)

To a solution of (2-oxazolin-2,5,5-trimethyl)phenylphosphine (NPN^{Me2}) (0.80 g, 2.4 mmol) in CH_2Cl_2 was added 0.92 g (2.4 mmol) of [$PdCl_2(NCPh)_2$] at room temperature and the red solution was stirred overnight. After elimination of the solvent under reduced pressure, a yellow powder was obtained. After it was washed with 20 mL of THF, this powder was dried overnight under vacuum (yield: 1.01 g, 2.0 mmol, 83%). IR (KBr): 1659 (s), 1630 (s), 1463 (m), 1435 (m), 1419 (w), 1366 (s), 1320 (s), 1261 (s), 1159 (s), 1103 (s), 951 (m), 801 (s), 747 (m), 692 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.22 (3H, s, CCH_3), 1.28 (3H, s, CCH_3), 1.67 (3H, s, CCH_3), 1.71 (3H, s, CCH_3), ABX spin system 1 (A = B = H, X = P): 3.23 (1H, $^2J_{AB}$ = 18.7 Hz, $^2J_{PA}$ = 12.7 Hz, PC$H_A$$H_B$ of coordinated oxazoline), ABX spin system 2 (A = B = H, X = P): 3.49 (1H, J_{AB} = 16.4 Hz, $^2J_{PA}$ = 12.4 Hz, PC$H_A$$H_B$ of uncoordinated oxazoline), ABX spin system 2 (A = B = H, X = P): 3.57 (1H, $^2J_{AB}$ = 16.4 Hz, $^2J_{PB}$ = 11.0 Hz, P$CH_A$$H_B$ of uncoordinated oxazoline), AB spin system 3.89 and 3.98 (each 1H, J_{AB} = 8.1 Hz, overlapping signal of OCH_AH_B), ABX spin system 1 (A = B = H, X = P): 4.04 (1H, $^2J_{AB}$ = 18.7 Hz, $^2J_{PB}$ = 11.7 Hz, P$CH_A$$H_B$ of coordinated oxazoline), AB spin system 4.25 and 4.34 (each 1H, $^2J_{AB}$ = 8.4 Hz, overlapping signal of OCH_AH_B), 7.67–7.84 (5H, m, aromatic H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 26.0 (d, $^1J_{PC}$ = 35.9 Hz, PCH_2), 27.4 (s, C-*C*H_3), 27.8 (s, C-*C*H_3), 28.2 (s, C-*C*H_3), 28.5 (s, C-*C*H_3), 29.1 (d, $^1J_{PC}$ = 33.3 Hz, PCH_2), 68.0 (s, N*C*CH_3), 69.9 (s, N*C*CH_3), 79.5 (s, OCH_2), 84.2 (s, OCH_2), 125.8 (d, $^1J_{PC}$ = 56.7 Hz, C-P of aryl), 129.3 (d, $^2J_{PC}$ = 12.0 Hz, *o*-CH of aryl), 132.5 (s, *p*-CH of aryl), 132.7 (d, $^3J_{PC}$ = 8.1 Hz, *m*-CH of aryl), 158.2 (d, $^2J_{PC}$ = 7.6 Hz, C=N from uncoordinated oxazoline), 173.9 (d, $^2J_{PC}$ = 51.6 Hz, C=N from coordinated oxazoline); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 19.40. Anal. calcd. for $C_{18}H_{25}Cl_2N_2O_2PPd$: C, 42.42; H, 4.94; N, 5.50. Found: C, 41.84; H, 4.59; N, 5.45.

Synthesis of [Pd(NCMe){bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}]$(BF_4)_2$ (6)

To a solution of (2-oxazolin-2,5,5-trimethyl)phenylphosphine (NPN^{Me2}) (0.45 g, 1.4 mmol) in CH_2Cl_2 was added 0.61 g (1.4 mmol) of [$Pd(NCMe)_4$]$(BF_4)_2$ at room temperature and the red

solution was stirred overnight. After elimination of the solvent under reduced pressure, an orange powder was obtained which was washed with 20 mL of diethylether and dried overnight under vacuum (yield: 0.82 g, 1.25 mmol, 90%). IR (KBr): 1613 (vs), 1465 (m), 1438 (w), 1422 (m), 1376 (m), 1329 (m), 1060 (vs), 864 (m), 748 (m), 691 (m) cm^{-1}. ^1H NMR (300 MHz, acetonitrile-d_3): δ 1.40 (6H, s, CCH_3), 1.45 (6H, s, CCH_3), ABX spin system (A = B = H, X = P), 3.54 (2H, $^2J_{AB}$ = 18.3 Hz, $^2J_{PA}$ = 16.0 Hz, PCH_AH$_B$), ABX spin system (A = B = H, X = P), 4.35 (2H, $^2J_{AB}$ = 18.3 Hz, $^2J_{PB}$ = 14.2Hz, PCH$_A$$H_B$), AB spin system 4.44 (2H, J_{AB} = 8.9 Hz, OCH$_A$$H_B$), AB spin system 4.57 (2H, J_{AB} = 8.9 Hz, OCH_AH$_B$), 7.65–8.04 (5H, m, aromatic H); $^{13}C\{^1H\}$ NMR (75.5 MHz, acetonitrile-d_3): δ 26.0 (s, C-CH_3), 26.5 (s, C-CH_3), 29.6 (d, $^1J_{PC}$ = 41.8 Hz, PCH_2), 68.4 (s, $C(CH_3)_2$), 83.4 (s, OCH_2), 121.7 (d, $^1J_{PC}$ = 66.7 Hz, C-P of aryl), 130.1 (d, $^2J_{PC}$ = 13.6 Hz, *o*-CH of aryl), 132.7 (d, $^3J_{PC}$ = 12.0 Hz, *m*-CH of aryl), 134.8 (d, $^4J_{PC}$ = 3.3 Hz, *p*-CH of aryl), 174.7 (d, $^2J_{PC}$ = 19.8 Hz, C=N); $^{31}P\{^1H\}$ NMR (121.5 MHz, acetonitrile-d_3): δ 43.92. Anal. calcd. for $C_{20}H_{28}B_2F_8N_3O_2PPd$: C, 36.76; H, 4.32; N, 6.43. Found: C, 37.04; H, 4.56; N, 6.33.

Oligomerization of Ethylene: All catalytic reactions were carried out in a magnetically stirred (900 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to protect the inner walls of the autoclave from corrosion. The cobalt complex ($4x10^{-2}$ mmol) was dissolved in 14 mL of cholorobenzene and injected into the reactor under an ethylene flux. Then 0.75 mL of a cocatalyst solution, corresponding to 6 equiv of $AlEtCl_2$, was added into the reactor. After injection of the catalytic solution and of the cocatalyst under a constant low flow of ethylene, the reactor was pressurized to 30 bar. This working pressure was maintained during the experiments through a continuous feed of ethylene from a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. Since negligeable conversions were observed at room temperature, the reaction mixture was heated to 80 °C immediately after injection of the cocatalyst. At the end of each test (35 min) a dry ice bath, and in the more exothermic cases also liquid N_2, was used to rapidly cool down the reactor, thus stopping the reaction. When the inner temperature reached 0 ºC, the ice bath was removed allowing the temperature to slowly rise to 10 ºC. The gaseous phase was then transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The products in the reactor were hydrolyzed in situ by the addition of ethanol (1 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation (20 °C, 0.8

mbar) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product.

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