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Supporting Information

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Self-Assembly of Bidentate Ligands for Combinatorial Homogeneous Catalysis: New A–T Base Pair Analogous Platforms stable in Methanol

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(38 pages)

I General

6-Diphenylphoshanyl-2-pivaloylamino-pyridine (6-DPPAP),[1] 3-diphenylphoshanyliso-quinolone (3-DPICon),[1] 2-amino-6-bromopyridine,[2] 1-amino-3-bromo-isoquinoline[3] and 2-bromo-4-aminothiazole hydrobromide[4] were synthesized according to literature procedures.

All reactions were carried out in dried glassware under an argon 5.0 atmosphere (Südwest-Gas). Air and moisture sensitive liquids and solutions were transferred *via* syringe. All reagents were commercially available unless otherwise noted. All solvents were dried and distilled by standard procedures. Organic solutions were concentrated under reduced pressure by rotary evaporation. Chromatographic purification of products was accomplished using flash chromatography[5] on a Merck silica gel Si 60® (200-400 mesh).

Nuclear magnetic resonance spectra were acquired on a Varian Mercury spectrometer (300 MHz, 121 MHz and 75 MHz for ^{1}H, ^{31}P and ^{13}C respectively), on a Bruker AMX 400 (400 MHz, 162 MHz and 100 MHz for ^{1}H, ^{31}P and ^{13}C respectively) and on a Bruker DRX 500 (500 MHz, 202 MHz and 125 MHz for ^{1}H, ^{31}P and ^{13}C respectively) and are referenced according to residual protio solvent signals. Data for ^{1}H-NMR are reported as follows: chemical shift (δ in ppm), multiplicity (s, singlet; br s, broad singlet; d, doublet; t, triplet; q,

quartet; m, multiplet; p, pseudo), coupling constant (Hz), integration. Data for ^{13}C-NMR are reported in terms of chemical shift (δ in ppm), multiplicity (if not a singlet), coupling constant (Hz).

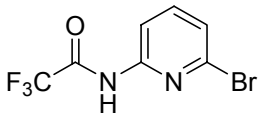
High-resolution mass spectra were obtained on a Finnigan MAT 8200 instrument. Elementary analysis was performed on an elementar vario (Fa. Elementar Analysensysteme GmbH).

Hydroformylation experiments were performed either with an Argonaut Endeavour® Catalyst Screening System or in a Premex stainless steel autoclave Medimex (100 ml). Synthesis gas (CO 3.7, H_2 4.3, 1:1) was obtained from Air liquide.

Caution: All operations involving carbon monoxide must be carried out in a well-ventilated fume hood. Use of a gas-leak detector for carbon monoxide is highly recommended.

II Experimental procedures and characterizations

1 6-Bromo-2-(trifluoroacetylamino)-pyridine:

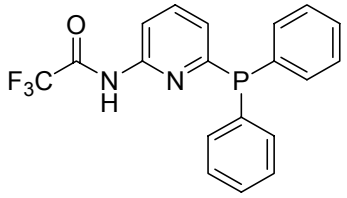


$C_7H_4BrF_3N_2O$
Mol. Wt.: 269.02

To a solution of 7.3 ml trifluoroacetic acid anhydride (10.92 g, 52.0 mmol, 3.0 eq.) in CH_2Cl_2 (40 ml) was added slowly at 0°C 7.2 ml triethylamine (5.26 g, 52.0 mmol, 3.0 eq.). After 5 min 3.00 g 2-amino-6-bromopyridine[2] (17.3 mmol, 1.0 eq.) was added and the solution was stirred at room temperature for 3 days. The conversion was monitored *via* TLC. After addition of 30 ml sat. aqueous $NaHCO_3$ solution, the aqueous layer was extracted with EtOAc (4×30 ml), the combined organic layers were dried ($MgSO_4$) and concentrated. The crude product was purified *via* flash chromatography (Cy:EtOAc 5:1) to yield 3.96 g of the title compound (14.7 mmol, 85%) as a yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.61 (br s, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.66 (pt, J = 8.0 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 155.0 (q, $J_{C,F}$ = 38.8 Hz, 1C), 148.9, 141.1, 139.9, 125.9, 115.4 (q, $J_{C,F}$ = 288.6 Hz), 111.9; **CHN** calcd. C: 31.25, H: 1.50, N: 10.41 found C: 31.40, H: 1.20, N: 10.36.

2 6-Diphenylphosphanyl-2-(trifluoroacetylamino)-pyridine (6-DPTFAAP) 2:

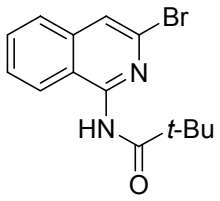


$C_{19}H_{14}F_3N_2OP$
Mol. Wt.: 374.30

To a solution of 2.22 g 6-bromo-2-(trifluoroacetylamino)-pyridine (8.3 mmol, 1.0 eq.) in thf (40 ml) was added at –100°C 10.3 ml *n*-BuLi (16.5 mmol, 1.6M in hexane, 2.0 eq.) over 15 min. The mixture was stirred for 15 min, then 1.5 ml $ClPPh_2$ (1.82 g, 8.3 mmol, 1.0 eq.) was added. The solution was allowed to warm to room temperature over 30 min, a few drops of H_2O were added and the solvent was removed under reduced pressure. The crude product was purified *via* flash chromatography (Cy:EtOAc 20:1) to yield 1.95 g of the title compound **2** (3.6 mmol, 52%) as a yellow foam.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.57 (br s, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.67 (dt, J = 7.8, 1.9 Hz, 1H), 7.41-7.34 (m, 10H), 6.94 (d, J = 7.3 Hz, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 163.2, 155.2 (q, $J_{C,F}$ = 37.8 Hz), 149.3 (d, $J_{C,P}$ = 13.1 Hz), 138.6, 134.3 (d, $J_{C,P}$ = 18.9 Hz), 132.2 (d, $J_{C,P}$ = 10.2 Hz), 129.5, 128.9 (d, $J_{C,P}$ = 7.3 Hz), 125.8 (d, $J_{C,P}$ = 13.1 Hz), 115.6 (q, $J_{C,F}$ = 289.2 Hz), 113.3; **^{31}P-NMR** (121 MHz, $CDCl_3$): δ –2.9; **CHN** calcd. C: 60.97, H: 3.77, N: 7.48 found C: 61.02, H: 3.51, N: 7.47.

3 1-Pivaloylamino-3-bromo-isoquinoline:

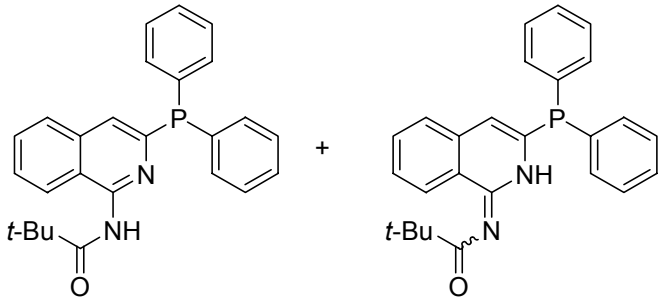


$C_{14}H_{15}BrN_2O$
Mol. Wt.: 307.19

To a solution of 4.1 ml triethylamine (2.95 g, 29.1 mmol, 5.0 eq.) and 1.30 g 1-amino-3-bromo-isoquinoline[3] (5.8 mmol, 1.0 eq.) in CH_2Cl_2 (50 ml) was added slowly at 0°C 3.6 ml pivaloylchloride (3.51 g, 29.1 mmol, 5.0 eq.). The solution was stirred for 24 h at room temperature. After addition of brine (20 ml) the aqueous layer was extracted with EtOAc (3×20 ml) and the combined organic layers were dried ($MgSO_4$) and concentrated. The crude product was purified *via* flash chromatography (Cy:EtOAc 5:1) to yield 1.17 g of the title compound (3.8 mmol, 65%) as a white solid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.35 (br s, 1H), 7.82 (d, J = 8.6 Hz, 1H), 7.74 (s, 1H), 7.68-7.63 (m, 2H), 7.55 (ddd, J = 8.3, 6.5, 1.6 Hz, 1H), 1.42 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 178.2, 150.3, 139.8, 132.2, 131.5, 127.4, 126.9, 125.8, 123.1, 122.5, 39.9, 27.7; **CHN** calcd. C: 54.74, H: 4.92, N: 9.12 found C: 54.52, H: 4.83, N: 9.27; **mp**: 183-185°C.

4 3-Diphenylphoshanyl-1-pivaloylamino-isoquinoline (3-DPPAICin) 3:



3 $C_{26}H_{25}N_2OP$ ***taut*-3**

Mol. Wt.: 412.46

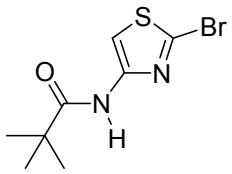
To a solution of 200 mg 1-pivaloylamino-3-bromo-isoquinoline (0.65 mmol, 1.0 eq.) in thf (12 ml) was added at −78°C 812 µl *n*-BuLi (1.3 mmol, 1.6M in hexane, 2.0 eq.). The mixture was stirred for 1 min, then 132 µl $ClPPh_2$ (157 mg, 0.72 mmol, 1.1 eq.) was added. The solution was allowed to warm to room temperature over 1 h, a few drops of H_2O were added and the solvent was removed under reduced pressure. The residue was redissolved in a 1:1 mixture (20 ml) of CH_2Cl_2 and H_2O, the aqueous layer was extracted with CH_2Cl_2 (3×20 ml) and the combined organic layers were dried ($MgSO_4$) and concentrated. The crude product was purified *via* flash chromatography using a CH_2Cl_2/EtOAc mixture to yield 201 mg of the title compound **3** (0.49 mmol, 75%) as a white solid.

NMR studies showed that the product exists as an equilibrium of tautomeric forms.

^{1}H-NMR (500 MHz, C_6D_6): δ 15.71 (br s, 1H, **taut**), 8.94 (br s, 1H, **taut**), 8.94 (br s, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.45-7.41 (br t, J = 7.5 Hz, 4H**, taut),** 7.38 (br t, J = 7.4 Hz, 4H), 7.28 (s, 1H), 7.19-7.15 (m, 3H und 2H **taut**), 7.10-7.03 (m, 2H und 4H **taut**), 6.98-6.88 (m, 4H und 4H **taut**), 1.46 (s, 9H, **taut**), 1.24 (s, 9H); **^{13}C-NMR** (125 MHz, C_6D_6): δ 193.8 (d, $J_{C,P}$ = 1.8 Hz), 178.0, 159.3, 154.1 (d, $J_{C,P}$ = 5.5 Hz), 152.1 (d, $J_{C,P}$ = 14.5 Hz), 138.5 (d, $J_{C,P}$ = 26.6 Hz), 138.0 (d, $J_{C,P}$ = 1.5 Hz), 136.8 (d, $J_{C,P}$ = 11.5 Hz), 136.6 (d, $J_{C,P}$ = 9.7 Hz), 134.5 (d, $J_{C,P}$ = 20.0 Hz), 134.1 (d, $J_{C,P}$ = 19.7 Hz), 132.7, 130.5, 129.8, 129.3 (d, $J_{C,P}$ = 6.7 Hz), 129.0, 128.8 (d, $J_{C,P}$ = 7.0 Hz), 128.3, 127.5, 127.2, 126.6, 126.5, 125.1, 123.6, 119.9 (d, $J_{C,P}$ = 29.1 Hz), 42.1, 39.7, 28.4, 27.6; **^{31}P-NMR** (162 MHz, C_6D_6): δ −7.8 (**taut**), −5.6; **edHSQC_N** (^{15}N-^{1}H heterocorrelation): ^{15}N (130 ppm), ^{1}H (8.94 ppm) and ^{15}N (158 ppm, **taut**), ^{1}H (15.71 ppm, **taut**-N-*H*); **CHN** calcd. C: 75.71, H: 6.11, N: 6.79 found C: 75.44, H: 6.09, N: 6.65; **mp**: 165-167°C.

The title compound exists as a mixture of tautomers (0.17M, C_6D_6) at a ratio of **3**:***taut*-3** 1.4:1.0.

5 2-Bromo-4-(pivaloylamino)-thiazole:

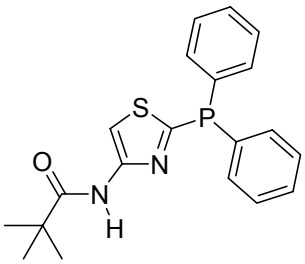


$C_8H_{11}BrN_2OS$
Mol. Wt.: 263.15

To a suspension of 2.00 g 2-bromo-4-aminothiazole hydrobromide[4] (7.7 mmol, 1.0 eq.) in CH_2Cl_2 (30 ml) was added slowly at 0°C 4.3 ml NEt_3 (3.11 g, 30.8 mmol, 4.0 eq.). The solution was stirred for 15 min at the same temperature then 1.4 ml pivaloylchloride (1.39 g, 11.5 mmol, 1.5 eq.) was added and the mixture was stirred overnight at room temperature.
The solvent was removed under reduced pressure and the residue was purified *via* flash chromatography (Cy:EtOAc 1:1). An analytically pure sample was obtained by bulb-to-bulb distillation at 155°C ($2.5\ 10^{-2}$ mbar). 1.41 g of the title compound (5.36 mmol, 70%) was isolated as a white solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.35 (br s, 1H), 7.56 (s, 1H), 1.27 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 176.1, 146.9, 134.2, 105.1, 39.3, 27.4; **CHNS** calcd. C: 36.51, H: 4.21, N: 10.65, S: 12.19 found C: 36.77, H: 4.12, N: 10.58, S: 12.07; **mp**: 76-78°C.

6 2-Diphenylphoshanyl-4-(pivaloylamino)-thiazole (2-DPPAT) 4:

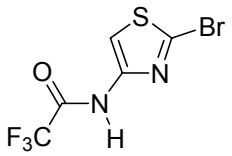


$C_{20}H_{21}N_2OPS$
Mol. Wt.: 368.43

To a solution of 300 mg 2-bromo-4-(pivaloylamino)-thiazole (1.14 mmol, 1.0 eq.) in thf (10 ml) was added at −100°C 1.5 ml *n*-BuLi (2.28 mmol, 1.52M in hexane, 2.0 eq.). The mixture was stirred for 90 min at −100°C then 211 µl $ClPPh_2$ (252 mg, 1.14 mmol, 1.0 eq.) was added. The solution was allowed to warm to room temperature over 1 h. After addition of sat. aqueous $NaHCO_3$ solution (10 ml) the aqueous layer was extracted with EtOAc (3×10 ml), the combined organic layers were dried ($MgSO_4$) and concentrated.
The crude product was purified *via* flash chromatography (Cy:EtOAc 10:1) to yield 201 mg of the title compound **4** (0.55 mmol, 48%) as a white solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.38 (br s, 1H), 7.80 (d, J = 1.3 Hz, 1H), 7.45-7.38 (m, 10H), 1.30 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 176.1, 168.9 (d, $J_{C,P}$ = 20.5 Hz), 150.3 (d, $J_{C,P}$ = 12.4 Hz), 135.1 (d, $J_{C,P}$ = 9.5Hz), 133.7 (d, $J_{C,P}$ = 20.3 Hz), 129.9, 128.8 (d, $J_{C,P}$ = 7.5 Hz), 106.1, 39.3, 27.6; **^{31}P-NMR** (121 MHz, $CDCl_3$): δ −11.1; **CHNS** calcd. C: 65.20, H: 5.75, N: 7.60, S: 8.70 found C: 65.00, H: 5.75, N: 7.40, S: 8.73; **mp**: 92-94°C.

7 2-Bromo-4-(trifluoroacetylamino)-thiazole:

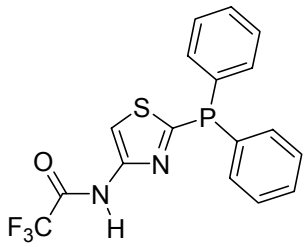


$C_5H_2BrF_3N_2OS$
Mol. Wt.: 275.05

To a solution of 2.43 g 2-bromo-4-aminothiazole hydrobromide[4] (9.3 mmol, 1.0 eq.) in CH_2Cl_2 (40 ml) was added simultaneously at 0°C 5.2 ml NEt_3 (3.78 g, 37.3 mmol, 4.0 eq.) and 3.0 ml trifluoroacetic acid anhydride (2.94 g, 14.0 mmol, 1.5 eq.) and the mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue was purified *via* flash chromatography (CH_2Cl_2). An analytically pure sample was obtained by bulb-to-bulb distillation at 120°C ($5.0\ 10^{-1}$mbar). 1.65 g of the title compound (6.00 mmol, 64%) was obtained as a white solid.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$): δ 12.68 (br s, 1H), 7.75 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 154.4 (q, $J_{C,F}$ = 38.2 Hz), 144.8, 135.5, 115.5 (q, $J_{C,F}$ = 287.6 Hz), 110.4; **HRMS**: calcd. 273.9023 found 273.9014; **mp**: 63-64°C.

8 2-Diphenylphoshanyl-4-(trifluoroacetylamino)-thiazole (2-DPTFAAT) 5:

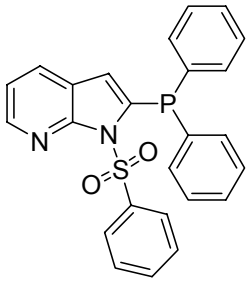


$C_{17}H_{12}F_3N_2OPS$
Mol. Wt.: 380.32

To a solution of 400 mg 2-bromo-4-(trifluoroacetylamino)-thiazole (1.45 mmol, 1.0 eq.) in thf (11 ml) was added at –100°C 1.8 ml *n*-BuLi (2.91 mmol, 1.60M in hexane, 2.0 eq.). The mixture was stirred for 3 min at this temperature then 269 µl $ClPPh_2$ (321 mg, 1.45 mmol, 1.0 eq.) was added and the reaction was allowed to warm to room temperature. The reaction mixture was quenched by addition of 50 µl degassed water and then concentrated in vacuo.
The crude product was purified *via* flash chromatography on deactivated (NEt_3) silica (Cy:EtOAc 10:1) to yield 214 mg of the title compound **5** (0.56 mmol, 39%) as a white foam.

^{1}H-NMR (400 MHz, C_6D_6): δ 8.35 (br s, 1H), 7.61 (d, J = 0.9 Hz, 1H), 7.48-7.41 (m, 5H), 7.08-7.04 (m, 5H); **^{13}C-NMR** (100 MHz, C_6D_6): δ 176.1 (d, $J_{C,P}$ = 25.1 Hz), 154.0 (q, $J_{C,F}$ = 38.4 Hz), 147.5 (d, $J_{C,P}$ = 10.6 Hz), 135.5 (d, $J_{C,P}$ = 10.1 Hz), 134.1 (d, $J_{C,P}$ = 20.8 Hz), 130.0, 129.1 (d, $J_{C,P}$ = 7.5 Hz), 115.9 (q, $J_{C,F}$ = 288.0 Hz), 109.0; **^{31}P-NMR** (162 MHz, C_6D_6): δ –9.9; **HRMS**: calcd. 380.0360 found 380.0368.

9 1-(Phenylsulfonyl)-2-(diphenylphoshanyl)-7-azaindole:

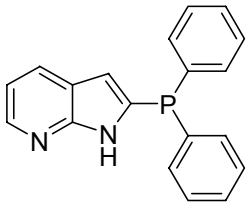


$C_{25}H_{19}N_2O_2PS$
Mol. Wt.: 442.47

To a solution of 300 mg 1-(phenylsulfonyl)-7-azaindole (1.16 mmol, 1.0 eq.) in thf (2.5 ml) was added at 0°C 1.0 ml LDA (1.27 mmol, 1.3M in thf, 1.1 eq.). The mixture was stirred for 30 min at the same temperature then 236 µl $ClPPh_2$ (282 mg, 1.27 mmol, 1.1 eq.) was added and the reaction mixture was allowed to warm to room temperature. The solvent was removed under reduced pressure and the crude product was purified *via* flash chromatography on deactivated (NEt_3) silica (Cy:EtOAc 7:1) to yield 434 mg of the title compound (0.98 mmol, 85%) as a white solid.

^{1}H-NMR (500 MHz, C_6D_6): δ 8.44 (dd, J = 4.8, 1.6 Hz, 1H), 8.21 (dd, J = 8.3, 1.0 Hz, 2H), 7.66 (dd, J = 7.8, 1.6 Hz, 1H), 7.53 (ptdd, J = 8.7, 6.9, 1.3 Hz, 1H), 7.49-7.38 (m, 12H), 7.15 (dd, J = 7.8, 4.8 Hz, 1H), 6.00 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 150.6, 145.0, 141.0 (d, $J_{C,P}$ = 26.8 Hz), 138.9, 136.1 (d, $J_{C,P}$ = 9.9 Hz), 134.2 (d, $J_{C,P}$ = 21.5 Hz), 133.8, 129.4, 128.8, 128.7 (d, $J_{C,P}$ = 7.5 Hz), 128.7, 128.6 (d, $J_{C,P}$ = 1.9 Hz), 122.0, 119.1, 115.7; **^{31}P-NMR** (162 MHz, $CDCl_3$): δ −17.8; **CHNS** calcd. C: 67.86, H: 4.33, N: 6.33, S: 7.25 found C: 67.58, H: 4.43, N: 6.31, S: 7.37; **mp**: 145-148°C.

10 2-(Diphenylphoshanyl)-7-azaindole (2-DPAIND) 7:



$C_{19}H_{15}N_2P$
Mol. Wt.: 302.31

To a solution of 434 mg 1-(phenylsulfonyl)-2-(diphenylphoshanyl)-7-azaindole (0.98 mmol, 1.0 eq.) in thf (5.0 ml) was added at room temperature 2.2 ml TBAF (2.20 mmol, 1.0M in THF, 2.2 eq.) and the reaction mixture was heated to reflux for 3 h. The conversion was monitored *via* TLC. The solvent was removed under reduced pressure and the residue was redissolved in a 1:1 mixture (15 ml) of CH_2Cl_2 and H_2O, the aqueous layer was extracted with CH_2Cl_2 (3×5 ml) and the combined organic layers were dried ($MgSO_4$) and concentrated. The crude product was purified *via* flash chromatography (toluene:EtOAc 7:1) to yield 160 mg of the title compound **7** (0.53 mmol, 54%) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.89 (br s, 1H), 7.90 (dd, J = 4.5, 1.5 Hz, 1H), 7.85 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.49-7.43 (m, 4H), 7.38-7.32 (m, 6H), 6.97 (dd, J = 8.0, 4.8 Hz, 1H), 6.54 (d, J = 2.6 Hz, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 151.1 (d, $J_{C,P}$ = 3.9 Hz), 143.2, 135.8 (d, $J_{C,P}$ = 8.0 Hz), 135.1 (d, $J_{C,P}$ = 14.0 Hz), 133.5 (d, $J_{C,P}$ = 19.8 Hz), 129.2, 128.9, 128.8 (d, $J_{C,P}$ = 7.3 Hz), 121.2 (d, $J_{C,P}$ = 5.8 Hz), 115.9, 110.3 (d, $J_{C,P}$ = 18.1 Hz); **^{31}P-NMR** (162 MHz, $CDCl_3$): δ –22.5; **CHN** calcd. C: 75.49, H: 5.00, N: 9.27 found C: 75.20, H: 5.11, N: 9.13; **mp**: 186-187°C.

III General procedure for the rhodium-catalyzed hydroformylation of 1-octene

1 General procedure for kinetic measurements of the rhodium-catalyzed hydroformylation of 1-octene

A solution of 1 mg [$Rh(CO)_2acac$], 10 eq. of ligand 1 and 10 eq. of a complementary ligand 2 in abs. toluene (10 ml) was stirred for 5 min at room temperature. The solution was transferred into a stainless steel autoclave via syringe under an atmosphere of argon. The reaction mixture was saturated with synthesis gas ($CO:H_2$ 1:1) by applying four cycles of careful evacuation and refilling. The autoclave was pressurized with 5 bar $CO:H_2$ (1:1) and kept for 30 min at 80°C. Afterwards 1-octene was added *via* a pressure lock and the autoclave was pressurized with 10 bar $CO:H_2$ 1:1. For the kinetic measurements samples were taken at the times indicated and analyzed by GC.

The turnover frequency of aldehyde formation (*TOF*) is defined as follows:

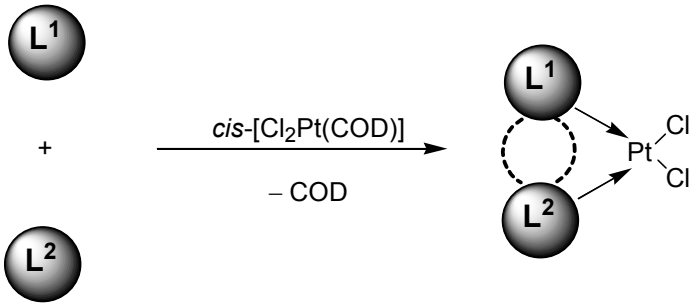
$$TOF = \frac{n(aldehyde)[mol]}{n(catalyst)[mol]} \cdot \frac{1}{t[h]}$$

2 General procedure for the hydroformylation of 1-octene in different solvents (MeOH, toluene)

To a solution of 1 mg [$Rh(CO)_2acac$] in 10 ml toluene or methanol in a schlenk tube were added 10 eq. of ligand 1 and 10 eq. of a complementary ligand 2 and 1000 eq. 1-octene. The solution was transferred into a stainless steel autoclave via syringe under an atmosphere of argon. The reaction mixture was saturated with synthesis gas ($CO:H_2$ 1:1) by applying four cycles of careful evacuation and refilling. The autoclave was pressurized with 10 bar $CO:H_2$ (1:1) and kept for 20 h at 80°C. Pressure and temperature were kept constant over the complete reaction time. After 20 h the autoclave was cooled down to room temperature, depressurized and the crude reaction mixture was analyzed by GC.

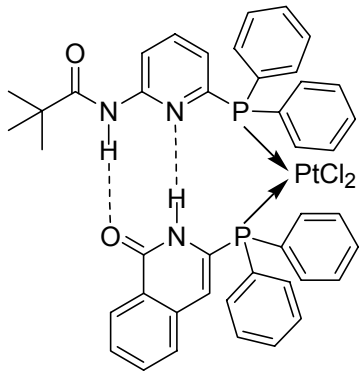
IV Heterodimeric platinum complexes

1 General procedure for the generation of heterodimeric platinum complexes



A solution of *cis*-[$Cl_2Pt(COD)$], 1.0 eq. ligand 1 and 1.0 eq. of a complementary ligand 2 in CH_2Cl_2 (5 ml) was stirred for 5 min at room temperature. The solvent was removed in vacuo and the residue was washed with *n*-pentane (8×5 ml). The remaining white solid was dried *in* vacuo.

1.1 *cis*-[Cl_2Pt(3-DPICon)(6-DPPAP)]



$C_{43}H_{39}Cl_2N_3O_2P_2Pt$
Mol. Wt.: 957.72

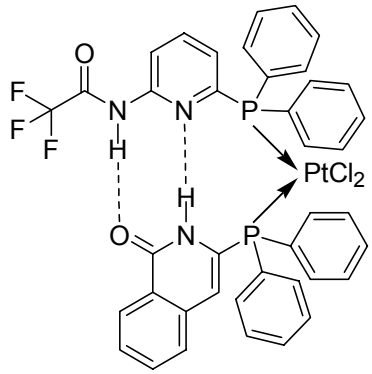
Following the general procedure the title compound was obtained from 30.0 mg *cis*-[$Cl_2Pt(COD)$] (80 μmol, 1.0 eq.), 29.1 mg 6-DPPAP (80 μmol, 1.0 eq.) and 26.3 mg 3-DPICon (80 μmol, 1.0 eq.).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 11.14 (br d, J = 5.4 Hz, 1H), 10.53 (s, 1H), 8.36 (dd, J = 8.5, 2.5 Hz, 1H), 8.20 (d, J = 7.5 Hz, 1H), 7.82 (dd, J = 12.6, 7.3 Hz, 4H), 7.71 (ddd, J = 7.9, 7.9, 4.4 Hz, 1H), 7.62-7.57 (m, 5H), 7.52-7.46 (m, 3H), 7.41-7.36 (m, 5H), 7.18 (d, J = 7.9 Hz, 1H), 6.99-6.95 (br m, 6H), 6.08 (d, J = 8.2 Hz, 1H), 1.33 (s, 9H); **^{13}C-NMR** (125 MHz,

$CDCl_3$): δ 178.5, 162.6 (d, $J_{C,P}$ = 7.5 Hz), 153.6 (d, $J_{C,P}$ = 19.3 Hz), 150.8, 150.1, 138.7 (d, $J_{C,P}$ = 8.6 Hz), 136.1 (d, $J_{C,P}$ = 10.8 Hz), 134.1 (d, $J_{C,P}$ = 11.8 Hz), 134.1 (d, $J_{C,P}$ = 9.7 Hz), 133.1, 132.0 (d, $J_{C,P}$ = 3.2 Hz), 130.7 (d, $J_{C,P}$ = 2.1 Hz), 129.6 (d, $J_{C,P}$ = 63.4 Hz), 128.8, 128.5 (d, $J_{C,P}$ = 11.8 Hz), 127.9 (d, $J_{C,P}$ = 11.8 Hz), 127.2, 127.1 (d, $J_{C,P}$ = 68.8 Hz), 126.9, 126.1, 124.9 (d, $J_{C,P}$ = 17.2 Hz), 116.8 (d, $J_{C,P}$ = 2.2 Hz), 115.4 (d, $J_{C,P}$ = 5.4 Hz), 40.2, 27.3; **^{31}P-NMR** (202 MHz, $CDCl_3$): δ 13.0 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3684.3 Hz), 11.3 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3507.1 Hz); **MS** (ESI; $C_{43}H_{39}Cl_2N_3O_2P_2Pt$ M = 956.15 g/mol): m/z = 886 (M^+–2HCl–H^+, 100) 922 (M^+–Cl^-, 13).

ROESY contact between ^{1}H-NMR signals at 10.53 and 11.14 ppm (H-bonds).

1.2 *cis*-[Cl_2Pt(3-DPICon)(6-DPTFAAP)]



$C_{40}H_{30}Cl_2F_3N_3O_2P_2Pt$

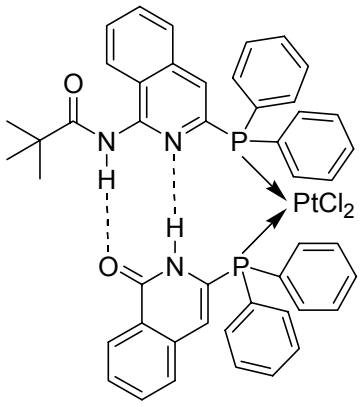
Mol. Wt.: 969.61

Following the general procedure the title compound was obtained from 30.0 mg *cis*-[Cl_2Pt(COD)] (80 µmol, 1.0 eq.), 29.9 mg 6-DPTFAAP (80 µmol, 1.0 eq.) and 26.3 mg 3-DPICon (80 µmol, 1.0 eq.).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 12.45 (s, 1H), 11.01 (d, J = 5.4 Hz, 1H), 8.41 (d, J = 8.2 Hz, 1H), 8.35 (ddd, J = 8.5, 2.5, 0.6 Hz, 1H), 7.77-7.63 (m, 6H), 7.59 (dt, = 7.5, 1.3 Hz, 1H), 7.51-7.46 (m, 6H), 7.37 (ddd, J = 8.5, 7.6, 2.8 Hz, 4H), 7.28 (ddd, J = 7.6, 4.4, 0.6 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.07 (m, 2H), 6.94 (br m, 4H), 6.18 (dd, J = 7.9, 1.6 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 162.8 (d, $J_{C,P}$ = 8.6 Hz), 156.6 (q, $J_{C,F}$ = 38.7 Hz), 152.9, 152.2, 151.1, 139.0 (d, $J_{C,P}$ = 7.5 Hz), 136.3 (d, $J_{C,P}$ = 9.7 Hz), 135.0 (pt, $J_{C,P}$ = 11.3 Hz), 133.5, 132.2 (d, $J_{C,P}$ = 3.2 Hz), 131.3 (d, $J_{C,P}$ = 2.1 Hz), 129.2, 128.5 (d, $J_{C,P}$ = 11.8 Hz), 127.9 (d,

$J_{C,P}$ = 10.7 Hz), 127.6, 127.5 (d, $J_{C,P}$ = 68.8 Hz), 126.9, 126.2, 125.9, 116.8 (d, $J_{C,P}$ = 3.2 Hz), 115.9 (q, $J_{C,F}$ = 288.0 Hz), 115.3 (d, $J_{C,P}$ = 4.3 Hz); **^{31}P-NMR** (202.294 MHz, $CDCl_3$): δ 16.0 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3691.6 Hz), 8.7 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3462.8 Hz); **MS** (ESI; $C_{40}H_{30}Cl_2F_3N_3O_2P_2Pt$ M = 969.61 g/mol): m/z = 897 (M^+–2HCl–H^+, 100) 921 (M^+–Cl^-, 22). ROESY contact between ^{1}H-NMR signals at 11.01 und 12.45 ppm (H-bonds).

1.3 *cis*-[Cl_2Pt(3-DPICon)(3-DPPAICin)]



$C_{47}H_{41}Cl_2N_3O_2P_2Pt$

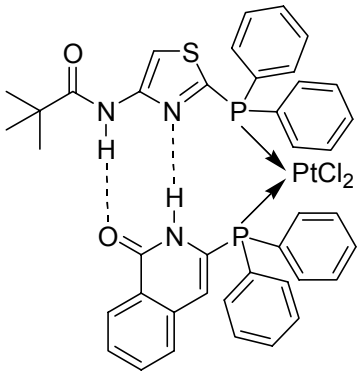
Mol. Wt.: 1007.78

Following the general procedure the title compound was obtained from 30.0 mg *cis*-[Cl_2Pt(COD)] (80 µmol, 1.0 eq.), 33.0 mg 3-DPPAICin (80 µmol, 1.0 eq.) and 26.3 mg 3-DPICon (80 µmol, 1.0 eq.).

^{1}H-NMR (500 MHz, CD_2Cl_2): δ 11.74 (br d, J = 5.7 Hz, 1H), 10.71 (s, 1H), 8.10 (d, J = 5.4 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H), 7.98-7.87 (m, 6H), 7.82 (dpt, J = 7.0, 1.3 Hz, 1H), 7.75 (ddd, J = 8.9, 7.0, 1.3 Hz, 1H), 7.65-7.58 (m, 5H), 7.56-7.52 (m, 2H), 7.50-7.40 (m, 5H), 7.20 (d, J = 7.9 Hz, 1H), 7.06 (ddd, J = 8.2, 7.9, 2.5 Hz, 4H), 6.93 (pt, J = 7.3 Hz, 2H), 6.13 (dd, J = 9.2, 1.6 Hz, 1H), 1.18 (s, 9H); **^{13}C-NMR** (125 MHz, CD_2Cl_2): δ 178.8, 163.5 (d, $J_{C,P}$ = 7.5 Hz), 153.7 (d, $J_{C,P}$ = 18.3 Hz), 141.9, 141.1, 137.7 (d, $J_{C,P}$ = 9.7 Hz), 136.4 (d, $J_{C,P}$ = 10.7 Hz), 135.7 (d, $J_{C,P}$ = 10.7 Hz), 133.7 (d, $J_{C,P}$ = 9.7 Hz), 133.4, 132.3 (d, $J_{C,P}$ = 2.2 Hz), 132.2, 130.8 (d, $J_{C,P}$ = 65.5 Hz), 130.7 (d, $J_{C,P}$ = 2.2 Hz), 129.3, 129.0, 129.0 (d, $J_{C,P}$ = 12.9 Hz), 129.0, 128.3 (d, $J_{C,P}$ = 10.8 Hz), 128.1, 127.9, 127.4 (d, $J_{C,P}$ = 70.9 Hz), 127.2, 127.0, 127.0, 126.3, 116.0 (d, $J_{C,P}$ = 6.5 Hz), 39.9, 27.3; **^{31}P-NMR** (202 MHz, CD_2Cl_2): δ 13.3 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3595.7 Hz), 10.4 (d, $^2J_{P,P}$ = 12.3 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3703.9 Hz); **MS** (ESI; $C_{47}H_{41}Cl_2N_3O_2P_2Pt$

M = 1007.78 g/mol): m/z = 454 (6), 935 (M^+–2HCl–H^+, 100) 972 (M^+–Cl^-, 13).
ROESY contact between ^{1}H-NMR signals at 10.71 und 11.74 ppm (H-bonds).

1.4 *cis*-[Cl_2Pt(3-DPICon)(2-DPPAT)]

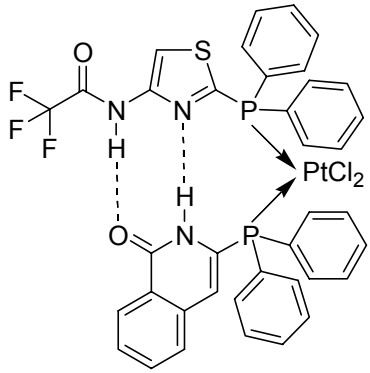


$C_{41}H_{37}Cl_2N_3O_2P_2PtS$
Mol. Wt.: 963.75

Following the general procedure the title compound was obtained from 45.0 mg *cis*-[Cl_2Pt(COD)] (120 µmol, 1.0 eq.), 44.2 mg 2-DPPAT (120 µmol, 1.0 eq.) and 39.5 mg 3-DPICon (120 µmol, 1.0 eq.).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 12.06 (d, J = 6.0 Hz, 1H), 10.72 (s, 1H), 8.51 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 1.3 Hz, 1H), 7.78-7.74 (m, 4H), 7.62 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H, Ar-H), 7.62 (ddd, J = 7.6, 7.3, 1.3 Hz, 1H), 7.45-7.27 (m, 13H), 7.12 (ddd, J = 8.2, 8.0, 2.8 Hz, 4H), 6.66 (dd, J = 8.8, 1.3 Hz, 1H), 1.47 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 178.1, 163.2, 156.8 (d, $J_{C,P}$ = 3.2 Hz), 156.2 (d, $J_{C,P}$ = 3.2 Hz), 151.2 (d, $J_{C,P}$ = 22.6 Hz), 136.6 (d, $J_{C,P}$ = 10.7 Hz), 135.0 (d, $J_{C,P}$ = 11.8 Hz), 134.3 (d, $J_{C,P}$ = 11.8 Hz), 133.3, 132.2 (d, $J_{C,P}$ = 2.2 Hz), 131.6 (d, $J_{C,P}$ = 2.2 Hz), 129.4 (d, $J_{C,P}$ = 72.0), 129.0, 128.7, 128.5 (d, $J_{C,P}$ = 4.3 Hz), 128.4 (d, $J_{C,P}$ = 3.2 Hz), 127.7 (d, $J_{C,P}$ = 67.7 Hz), 127.6 (d, $J_{C,P}$ = 14.0 Hz), 126.4, 114.5 (d, $J_{C,P}$ = 5.4 Hz), 109.1 (d, $J_{C,P}$ = 2.2 Hz), 39.8, 27.4; **^{31}P-NMR** (202 MHz, $CDCl_3$): δ 11.5 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3770.4 Hz), 10.6 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3512.0 Hz); **MS** (ESI; $C_{41}H_{37}Cl_2N_3O_2P_2PtS$ M = 963.75 g/mol): m/z = 891 (M^+–2HCl–H^+, 100).
ROESY contact between ^{1}H-NMR signals at 10.72 und 12.06 ppm (H-bonds).
Suitable single crystals for X-ray analysis were obtained from a solvent solution mixture of dichloromethane and *n*-pentane.[6]

1.5 *cis*-[Cl_2Pt(3-DPICon)(2-DPTFAAT)]



$C_{38}H_{28}Cl_2F_3N_3O_2P_2PtS$

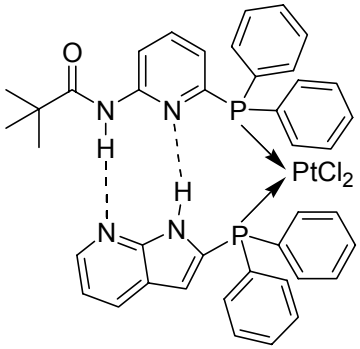
Mol. Wt.: 975.64

Following the general procedure the title compound was obtained from 20.0 mg *cis*-[Cl_2Pt(COD)] (54 µmol, 1.0 eq.), 20.3 mg 2-DPTFAAT (54 µmol, 1.0 eq.) and 17.6 mg 3-DPICon (54 µmol, 1.0 eq.).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 12.62 (s, 1H), 12.12 (d, J = 6.4 Hz, 1H), 8.56 (d, J = 7.3 Hz, 1H), 8.00 (d, J = 1.0 Hz, 1H), 7.75-7.70 (m, 5H), 7.66 (ddd, J = 8.5, 7.6, 1.3 Hz, 1H), 7.48-7.45 (m, 3H), 7.38-7.29 (m, 10H), 7.12 (ptd, J = 7.9, 2.8 Hz, 4H), 6.69 (dd, J = 7.1, 1.6 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 163.7 (d, $J_{C,P}$ = 8.6 Hz), 159.2 (d, $J_{C,P}$ = 3.2 Hz), 158.6 (d, $J_{C,P}$ = 3.2 Hz), 156.1 (q, $J_{C,F}$ = 38.7 Hz), 148.1 (d, $J_{C,P}$ = 22.6 Hz), 136.6 (d, $J_{C,P}$ = 9.7 Hz), 134.9 (d, $J_{C,P}$ = 11.8 Hz), 134.2 (d, $J_{C,P}$ = 10.7 Hz), 133.6, 132.4 (d, $J_{C,P}$ = 2.1 Hz), 131.7 (d, $J_{C,P}$ = 2.2 Hz), 129.2, 129.1 (d, $J_{C,P}$ = 50.5 Hz), 128.7 (d, $J_{C,P}$ = 11.8 Hz), 128.5 (d, $J_{C,P}$ = 11.8 Hz), 127.8, 127.6, 127.2 (d, $J_{C,P}$ = 66.6 Hz), 126.3, 115.8 (q, $J_{C,F}$ = 288.0 Hz), 115.1 (d, $J_{C,P}$ = 4.3 Hz), 111.9 (d, $J_{C,P}$ = 2.2 Hz); **^{31}P-NMR** (202 MHz, $CDCl_3$): δ 13.0 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3787.6 Hz), 10.3 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3494.8 Hz); **^{19}F-NMR** (235 MHz, $CDCl_3$): δ –74.4; **MS** (ESI; $C_{38}H_{28}Cl_2F_3N_3O_2P_2PtS$ M = 975.64 g/mol): m/z = 903 (M^+–2HCl–H^+, 100).

ROESY contact between ^{1}H-NMR signals at 12.12 und 12.62 ppm (H-bonds).

1.6 *cis*-[Cl_2Pt(2-DPAIND)(6-DPPAP)]



$C_{41}H_{38}Cl_2N_4OP_2Pt$

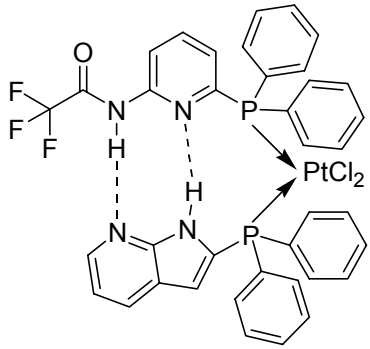
Mol. Wt.: 930.70

Following the general procedure the title compound was obtained from 30.0 mg *cis*-[Cl_2Pt(COD)] (80 µmol, 1.0 eq.), 29.1 mg 6-DPPAP (80 µmol, 1.0 eq.) and 24.2 mg 2-DPAIND (80 µmol, 1.0 eq.).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 12.26 (s, 1H), 10.27 (s, 1H), 8.47 (dd, J = 4.8, 1.3 Hz, 1H), 8.39 (dd, J = 8.9, 2.5 Hz, 1H), 7.72 (dd, J = 7.9, 1.3 Hz, 1H), 7.68-7.63 (m, 5H), 7.44-7.41 (m, 2H), 7.34-7.29 (m, 8H), 7.23 (dd, J = 7.3, 5.1 Hz, 1H), 7.14-7.09 (m, 3H), 6.84 (ddd, J = 8.5, 8.2, 2.2 Hz, 4H), 6.24 (dd, J = 3.5, 2.2 Hz, 1H), 1.52 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 178.1, 152.9 (d, $J_{C,P}$ = 19.3 Hz), 151.6, 150.9, 150.1 (d, $J_{C,P}$ = 10.8 Hz), 145.3, 138.4 (d, $J_{C,P}$ = 7.5 Hz), 135.0 (d, $J_{C,P}$ = 9.7 Hz), 134.6 (d, $J_{C,P}$ = 10.8 Hz), 131.5 (d, $J_{C,P}$ = 3.2 Hz), 130.8 (d, $J_{C,P}$ = 2.2 Hz), 129.9, 129.3 (d, $J_{C,P}$ = 70.9 Hz), 129.0 (d, $J_{C,P}$ = 62.3 Hz), 128.2 (d, $J_{C,P}$ = 11.8 Hz), 127.5 (d, $J_{C,P}$ = 10.8 Hz), 125.3 (d, $J_{C,P}$ = 16.1 Hz), 121.1 (d, $J_{C,P}$ = 7.5 Hz), 117.5 (d, $J_{C,P}$ = 2.2 Hz), 117.2, 110.4 (d, $J_{C,P}$ = 5.4 Hz), 40.3, 27.7; **^{31}P-NMR** (202 MHz, $CDCl_3$): δ 9.3 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3536.6 Hz), 2.9 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3667.0 Hz); **MS** (ESI; $C_{41}H_{38}Cl_2N_4OP_2Pt$ M = 930.70 g/mol): m/z = 592 (7), 958 (M^+–2HCl–H^+, 100), 895 (M^+–Cl^-, 90).

ROESY contact between ^{1}H-NMR signals at 10.27 und 12.36 ppm (H-bonds).

1.7 *cis*-[Cl_2Pt(2-DPAIND)(6-DPTFAAP)]



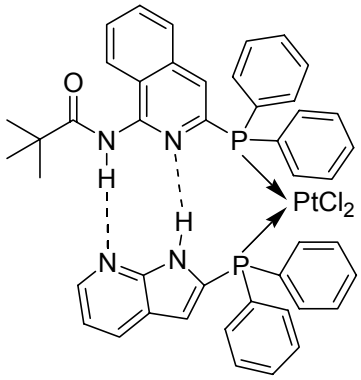
$C_{38}H_{29}Cl_2F_3N_4OP_2Pt$

Mol. Wt.: 942.59

Following the general procedure the title compound was obtained from 30.0 mg *cis*-[Cl_2Pt(COD)] (80 µmol, 1.0 eq.), 29.9 mg 6-DPTFAAP (80 µmol, 1.0 eq.) and 24.2 mg 2-DPAIND (80 µmol, 1.0 eq.).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 13.39 (s, 1H), 12.62 (s, 1H), 8.50 (dd, J = 5.1, 1.3 Hz, 1H), 8.41 (dd, J = 8.5, 2.5 Hz, 1H), 7.86 (dd, J = 8.2, 1.3 Hz, 1H), 7.79 (ddd, J = 8.5, 8.2, 4.1 Hz, 1H), 7.60-7.57 (br m, 4H), 7.44-7.41 (m, 2H), 7.32 (dpt, J = 7.6, 2.8 Hz, 4H), 7.28 (dd, J = 7.6, 4.4 Hz, 1H), 7.23-7.12 (m, 7H), 6.78 (br m, 4H), 6.39 (pt, J = 2.5 Hz, 1H); **^{13}C-NMR** (125.657 MHz, $CDCl_3$): δ 156.6 (q, $J_{C,F}$ = 38.7 Hz), 153.1, 152.4, 150.9 (d, $J_{C,P}$ = 19.3 Hz), 148.8 (d, $J_{C,P}$ = 11.8 Hz), 145.1, 139.1 (d, $J_{C,P}$ = 7.5 Hz), 135.1 (m), 134.2 (d, $J_{C,P}$ = 10.7 Hz), 131.6 (d, $J_{C,P}$ = 2.2 Hz), 131.0 (br s), 130.8, 129.4 (d, $J_{C,P}$ = 70.9 Hz), 128.2 (d, $J_{C,P}$ = 11.8 Hz), 128.1 (d, $J_{C,P}$ = 62.6 Hz), 127.5 (d, $J_{C,P}$ = 10.7 Hz), 126.4 (d, $J_{C,P}$ = 15.1 Hz), 121.9 (d, $J_{C,P}$ = 7.5 Hz), 117.7 (d, $J_{C,P}$ = 2.2 Hz), 117.3, 116.2 (d, $J_{C,F}$ = 288.0 Hz), 109.3 (d, $J_{C,P}$ = 4.3 Hz); **^{31}P-NMR** (202.294 MHz, $CDCl_3$): δ 7.2 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3426.1 Hz), 4.8 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3674.4 Hz); **MS** (ESI; $C_{38}H_{29}Cl_2F_3N_4OP_2Pt$ M = 942.59 g/mol): m/z = 870 (M^+–2HCl–H^+, 95), 907 (M_+–Cl^-, 100).

1.8 *cis*-[Cl_2Pt(2-DPAIND)(3-DPPAICin)]



$C_{45}H_{40}Cl_2N_4OP_2Pt$
Mol. Wt.: 980.76

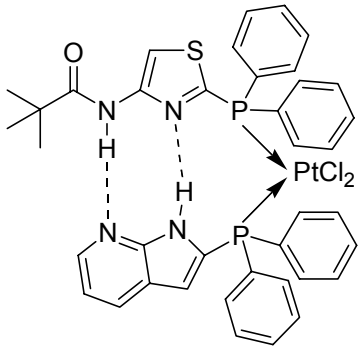
Following the general procedure the title compound was obtained from 30.0 mg *cis*-[Cl_2Pt(COD)] (80 µmol, 1.0 eq.), 33.0 mg 3-DPPAICin (80 µmol, 1.0 eq.) and 24.2 mg 2-DPAIND (80 µmol, 1.0 eq.).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 12.98 (br s, 1H), 10.78 (s, 1H), 8.42 (dd, J = 4.8, 1.3 Hz, 1H), 8.08-8.05 (m, 1H), 8.00 (d, J = 6.3 Hz, 1H), 7.78-7.67 (m, 7H), 7.63 (d, J = 7.9 Hz, 1H), 7.43-7.40 (m, 2H), 7.34-7.30 (m, 8H), 7.09-7.06 (m, 3H), 6.85 (ddd, J = 8.6, 7.9, 2.2 Hz, 4H), 6.15 (dd, J = 3.2, 2.2 Hz, 1H), 1.55 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 178.3, 152.1, 144.8, 142.8, 142.0, 137.3 (d, $J_{C,P}$ = 9.7 Hz), 134.7 (d, $J_{C,P}$ = 11.8 Hz), 134.5 (d, $J_{C,P}$ = 9.7 Hz), 131.6, 131.4 (d, $J_{C,P}$ = 3.2 Hz), 131.0 (br s), 130.5 (d, $J_{C,P}$ = 2.2 Hz), 131.0 (br s), 130.2 (d, $J_{C,P}$ = 65.6 Hz), 129.8, 129.3, 129.0, 128.2 (d, $J_{C,P}$ = 11.8 Hz), 127.8, 127.6, 127.6 (d, $J_{C,P}$ = 41.9 Hz), 127.5 (d, $J_{C,P}$ = 11.8 Hz), 124.4, 121.1 (d, $J_{C,P}$ = 7.5 Hz), 117.0, 110.6 (d, $J_{C,P}$ = 5.4 Hz), 40.0, 27.6; **^{31}P-NMR** (202 MHz, $CDCl_3$): δ 10.9 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3612.9 Hz), 2.1 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3686.7 Hz); **MS** (ESI; $C_{45}H_{40}Cl_2N_4OP_2Pt$ M = 980.76 g/mol): m/z = 454 (6), 908 (M^+–2HCl–H^+, 100) 945 (M_+–Cl^-, 60).

ROESY contact between ^{1}H-NMR signals at 10.78 und 12.98 ppm (H-bonds).

Suitable single crystals for X-ray analysis were obtained from a solvent solution mixture of dichloromethane and *n*-heptane.[7]

1.9 *cis*-[Cl_2Pt(2-DPAIND)(2-DPPAT)]

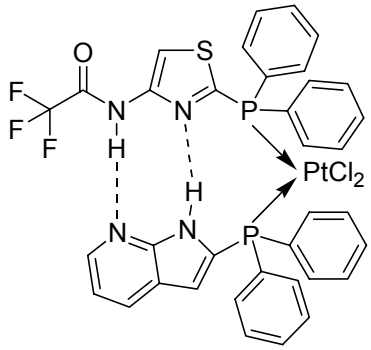


$C_{39}H_{36}Cl_2N_4OP_2PtS$
Mol. Wt.: 936.73

Following the general procedure the title compound was obtained from 30.0 mg *cis*-[Cl_2Pt(COD)] (80 µmol, 1.0 eq.), 29.5 mg 2-DPPAT (80 µmol, 1.0 eq.) and 24.2 mg 2-DPAIND (80 µmol, 1.0 eq.).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 12.44 (br s, 1H), 9.95 (s, 1H), 8.52 (dd, J = 7.9, 5.1 Hz, 1H), 7.98 (br d, J = 1.0 Hz, 1H), 7.91 (dd, J = 7.9, 1.3 Hz, 1H), 7.45-7.34 (m, 10H), 7.24-7.18 (m, 7H), 7.00-6.97 (m, 4H), 6.38 (d, J = 2.8 Hz, 1H), 1.50 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 176.9, 157.7, 157.0, 150.6 (d, $J_{C,P}$ = 26.5 Hz), 149.5 (d, $J_{C,P}$ = 10.8 Hz), 146.0 (br s), 134.7 (d, $J_{C,P}$ = 10.8 Hz), 133.9 (d, $J_{C,P}$ = 11.8 Hz), 131.5 (br s), 131.3 (d, $J_{C,P}$ = 2.2 Hz), 130.4, 129.0 (d, $J_{C,P}$ = 70.9 Hz), 128.2 (d, $J_{C,P}$ = 11.8 Hz), 128.0 (d, $J_{C,P}$ = 11.8 Hz), 127.5 (d, $J_{C,P}$ = 65.6 Hz), 120.8 (d, $J_{C,P}$ = 7.5 Hz), 117.2, 116.6 ($J_{C,P}$ = 5.4 Hz), 107.9, 39.6, 27.7; **^{31}P-NMR** (202 MHz, $CDCl_3$): δ 5.9 (d, $^2J_{P,P}$ = 14.8 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3535.0 Hz), .3 (d, $^2J_{P,P}$ = 14.7 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3608.0 Hz); **MS** (ESI; $C_{39}H_{36}Cl_2N_4OP_2PtS$ M = 936.73 g/mol): m/z = 901 (M^+–2HCl–H^+, 100); **Homoleptic complexes**: δ 7.3 (s, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3713.8 Hz), 0.6 (s, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3696.6 Hz); **MS** (ESI; $C_{40}H_{42}Cl_2N_4O_2P_2PtS_2$ M = 1002.85.73 g/mol): m/z = 966 (M^+–Cl–H^+, 11).
Ratio (homodimer:heterodimer:homodimer): 1.0:13.2:1.3.

1.10 *cis*-[Cl_2Pt(2-DPAIND)(2-DPTFAAT)]



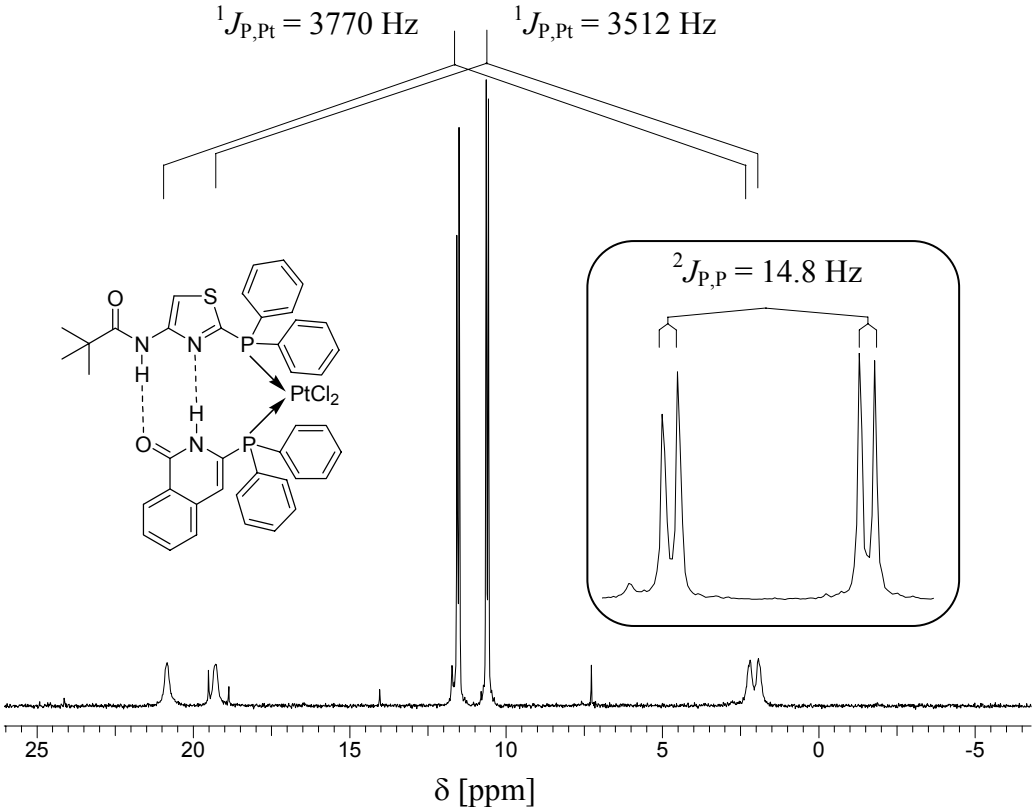
$C_{36}H_{27}Cl_2F_3N_4OP_2PtS$
Mol. Wt.: 948.62

Following the general procedure the title compound was obtained from 30.0 mg *cis*-[Cl_2Pt(COD)] (80 µmol, 1.0 eq.), 30.5 mg 2-DPPAAT (80 µmol, 1.0 eq.) and 24.2 mg 2-DPAIND (80 µmol, 1.0 eq.).

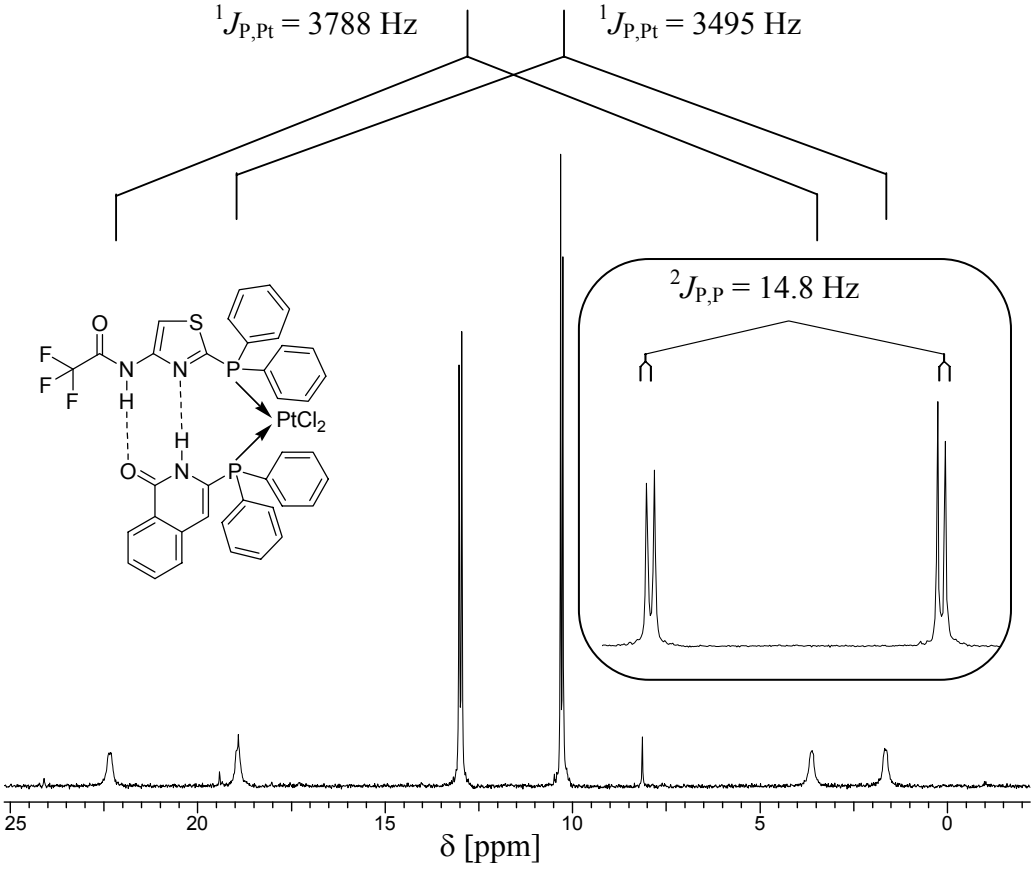
^{1}H-NMR (500 MHz, $CDCl_3$): δ 13.24 (br s, 1H), 12.90 (br s, 1H), 8.56 (d, J = 4.1 Hz, 1H), 8.11 (br d, J = 0.6 Hz, 1H), 8.05 (dd, J = 8.2, 1.3 Hz, 1H), 7.42-7.34 (m, 7H), 7.30-7.21 (m, 10H), 6.93-6.91 (m, 4H), 6.57 (dd, J = 3.1, 2.2 Hz, 1H); **^{13}C-NMR** (125. MHz, $CDCl_3$): δ 160.0, 159.3, 155.4 (q, $J_{C,F}$ = 39.8 Hz), 148.6 (br s), 147.9 (d, $J_{C,P}$ = 21.5 Hz), 145.9 (br s), 134.6 (d, $J_{C,P}$ = 10.8 Hz), 133.4 (d, $J_{C,P}$ = 10.7 Hz), 131.6 (d, $J_{C,P}$ = 2.2 Hz), 131.3 (d, $J_{C,P}$ = 2.2 Hz), 131.3, 128.9 (d, $J_{C,P}$ = 70.9 Hz), 128.3 (d, $J_{C,P}$ = 10.7 Hz), 128.0 (d, $J_{C,P}$ = 10.7 Hz), 126.7 (d, $J_{C,P}$ = 64.7 Hz), 121.6 (d, $J_{C,P}$ = 8.6 Hz), 117.4, 116.1 (d, $J_{C,F}$ = 286.9 Hz), 111.0 (d, $J_{C,P}$ = 3.2 Hz), 110.4; **^{31}P-NMR** (202 MHz, $CDCl_3$): δ 5.6 (d, $^2J_{P,P}$ = 17.2 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3539.0 Hz), 3.3 (d, $^2J_{P,P}$ = 17.2 Hz, flanked by ^{195}Pt isotope satellites as d, $^1J_{P,Pt}$ = 3608.0 Hz); **MS** (ESI; $C_{36}H_{27}Cl_2F_3N_4OP_2PtS$ M = 948.62 g/mol): m/z = 381 (11), 876 (M^+–2HCl–H^+, 76), 913 (M^+–Cl^-, 100).

C36H27Cl2F3N4OP2PtS
Mol. Wt.: 948.62

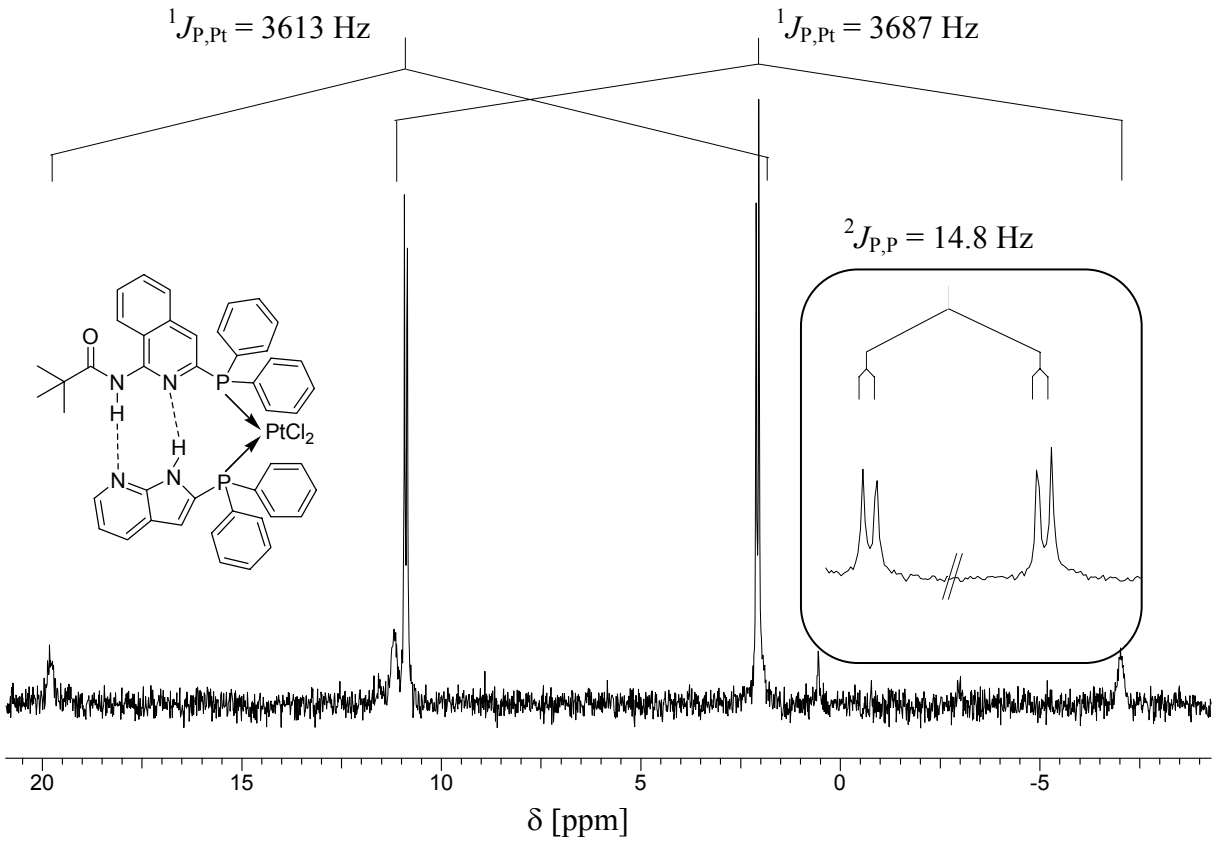
1.11 Examples of ^{31}P-NMRs



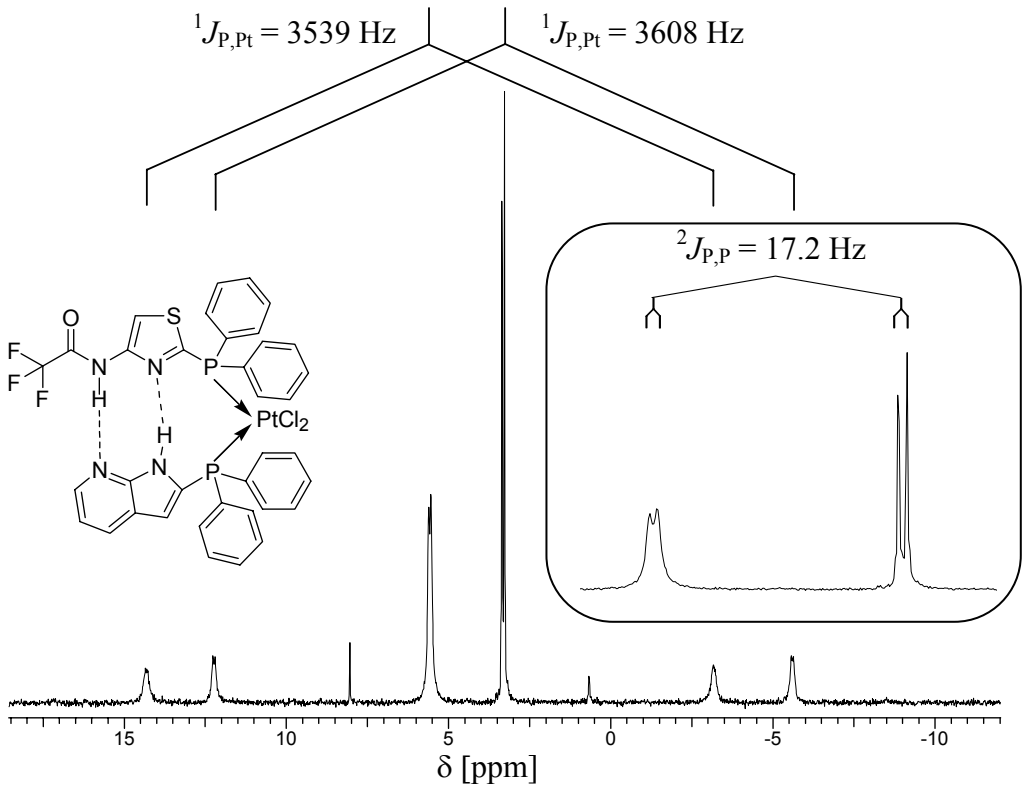
^{31}P-NMR-spectrum ($CDCl_3$, 121.5 MHz) of cis-*[Cl_2Pt(2-DPPAT)(3-DPICon)], obtained in situ from 1.0 eq.* cis-*[Cl_2Pt(1,5-COD)], 1.0 eq. 2-DPPAT* **4** *and 1.0 eq. 3-DPICon* **6**.



^{31}P-NMR-spectrum ($CDCl_3$, 121.5 MHz) of cis-*[Cl_2Pt(2-DPTFAAT)(3-DPICon)], obtained in situ from 1.0 eq.* cis-*[Cl_2Pt(1,5-COD)], 1.0 eq. 2-DPTFAAT* **5** *and 1.0 eq. 3-DPICon* **6**.



^{31}P-NMR-spectrum (CD_2Cl_2, 121.5 MHz) of cis-*[Cl_2Pt(3-DPAICin)(2-DPPAT)], obtained in situ from 1.0 eq.* cis-*[Cl_2Pt(1,5-COD)], 1.0 eq. 3-DPAICin* **3** *and 1.0 eq. 2-DPAIND* **7**.

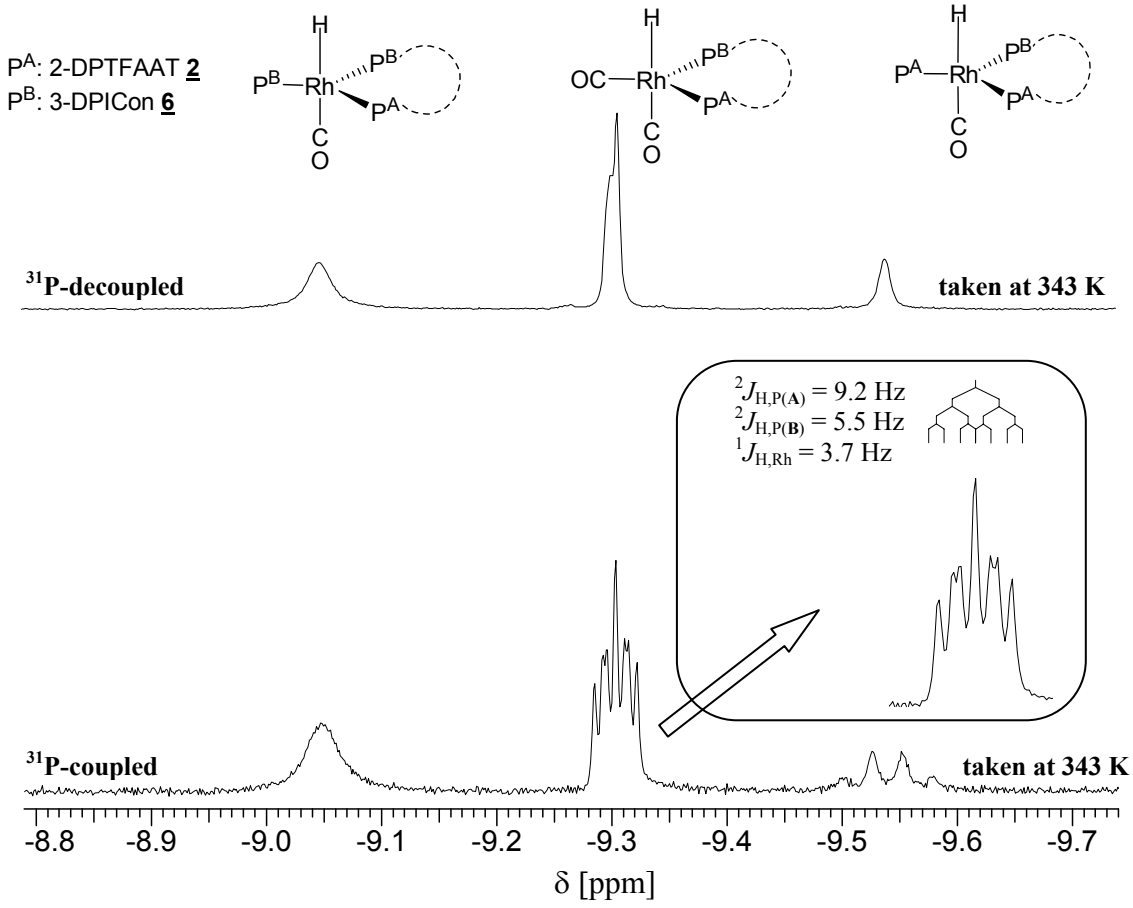


^{31}P-NMR-spectrum ($CDCl_3$, 121.5 MHz) of cis-*[Cl_2Pt(2-DPTFAAT)(2-DPPAT)], obtained in situ from 1.0 eq.* cis-*[Cl_2Pt(1,5-COD)], 1.0 eq. 2-DPTFAAT* **5** *and 1.0 eq. 2-DPAIND* **7**.

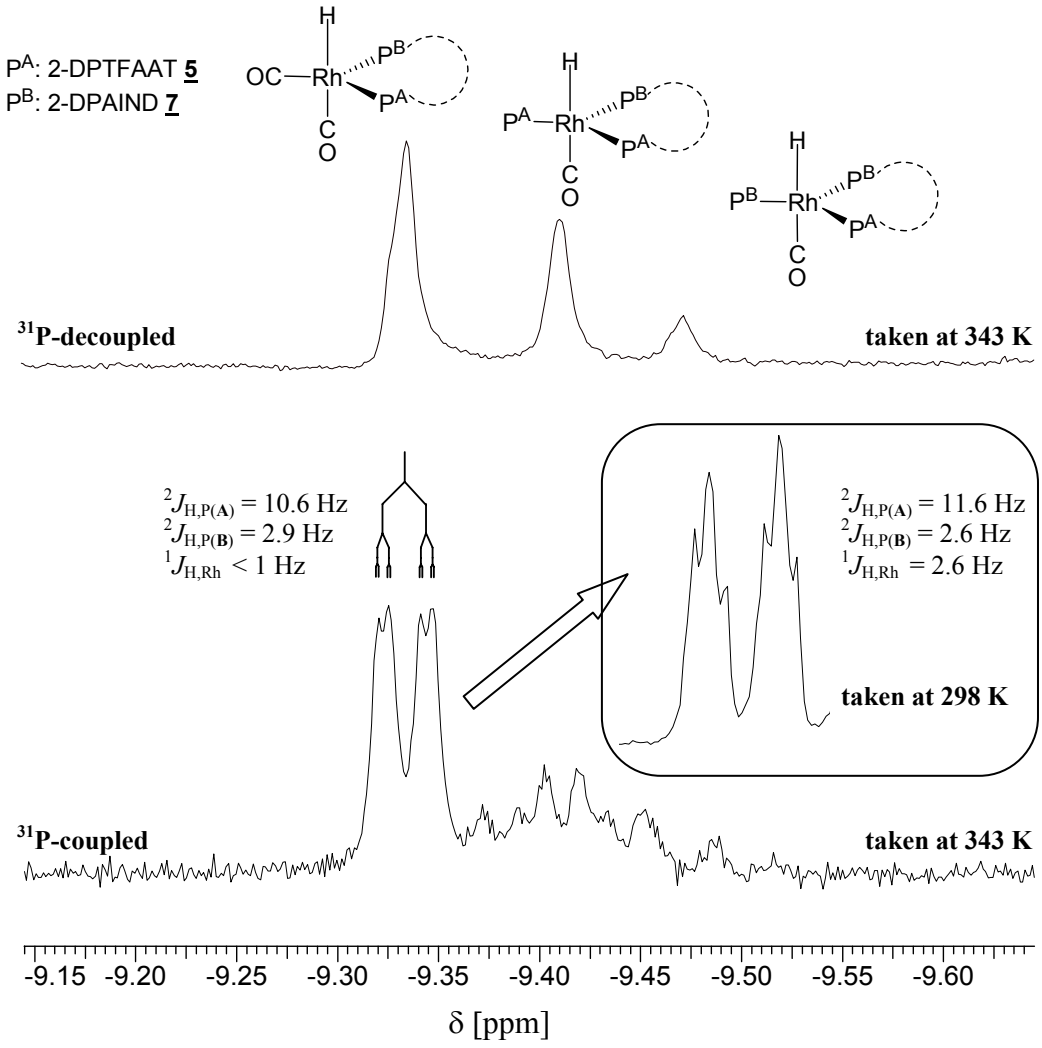
V Heteroleptic rhodium complexes

1 General procedure for the generation of heterodimeric rhodium complexes

1.0 mg $[Rh(CO)_2(acac)]$ ($3.80 \cdot 10^{-6}$ mol, 1.0 eq.) 1.1 eq. ligand 1 and 1.1 eq. of a complementary ligand 2 were transferred into an NMR tube and dissolved in d_6-benzene (1 ml). The NMR tube was placed into a stainless steel autoclave and the reaction mixture was saturated with synthesis gas ($CO:H_2$, 1:1) by applying three cycles of careful evacuation and refilling. Afterwards the autoclave was pressurized with 10 bar of synthesis gas and kept for 24 h at room temperature. After depressurization the solution was directly analyzed using NMR spectroscopy.



*^{1}H-NMR spectrum (hydride region, C_6D_6): Mixture of 1.0 eq. $[Rh(CO)_2acac]$, 1.1 eq. 2-DPTFAAT **5** and 1.1 eq. 3-DPICon **6** after 24 h under 10 bar $CO:H_2$ 1:1; NMR taken at 343 K.*

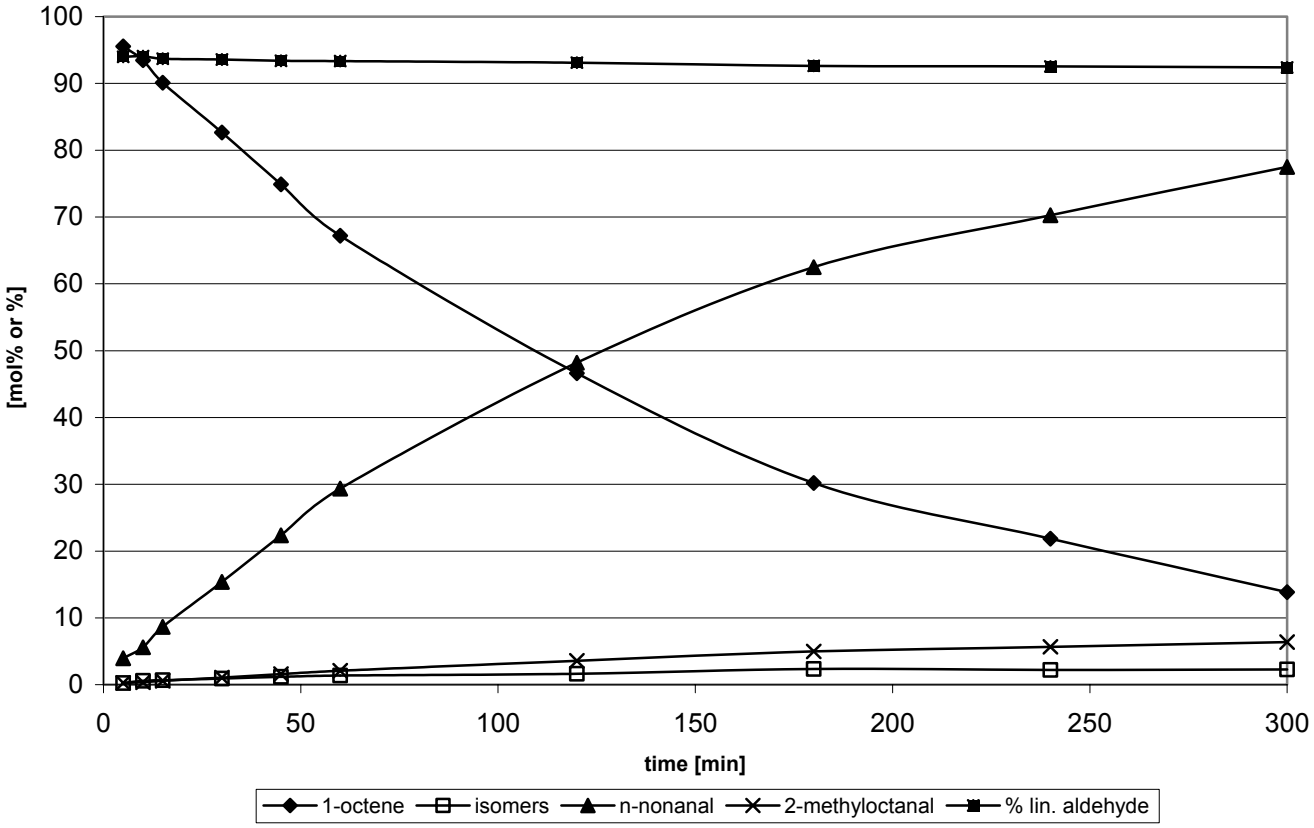


*^{1}H-NMR-spectrum (hydride region, C_6D_6): Mixture of 1.0 eq. [Rh(CO)$_2$acac], 1.1 eq. 2-DPTFAAT **5** and 1.1 eq. 2-DPAIND **6** after 24 h under 10 bar CO:H$_2$ 1:1; NMR taken at 343 K.*

entry	ligand P^A/P^B	$^1J_{(H,Rh)}$ [Hz]	$^1J_{(P,Rh)}$ [Hz]	$^2J_{(H,P)}$ [Hz]	$^2J_{(P,P)}$ [Hz]
1	2-DPTFAAT **5**/ 3-DPICon **6**	3.7	139.4/145.3	9.2 5.5	78.5
2	2-DPTFAAT **5**/ 2-DPAIND **7**	<1	152.6/156.3	10.6 2.9	113.8

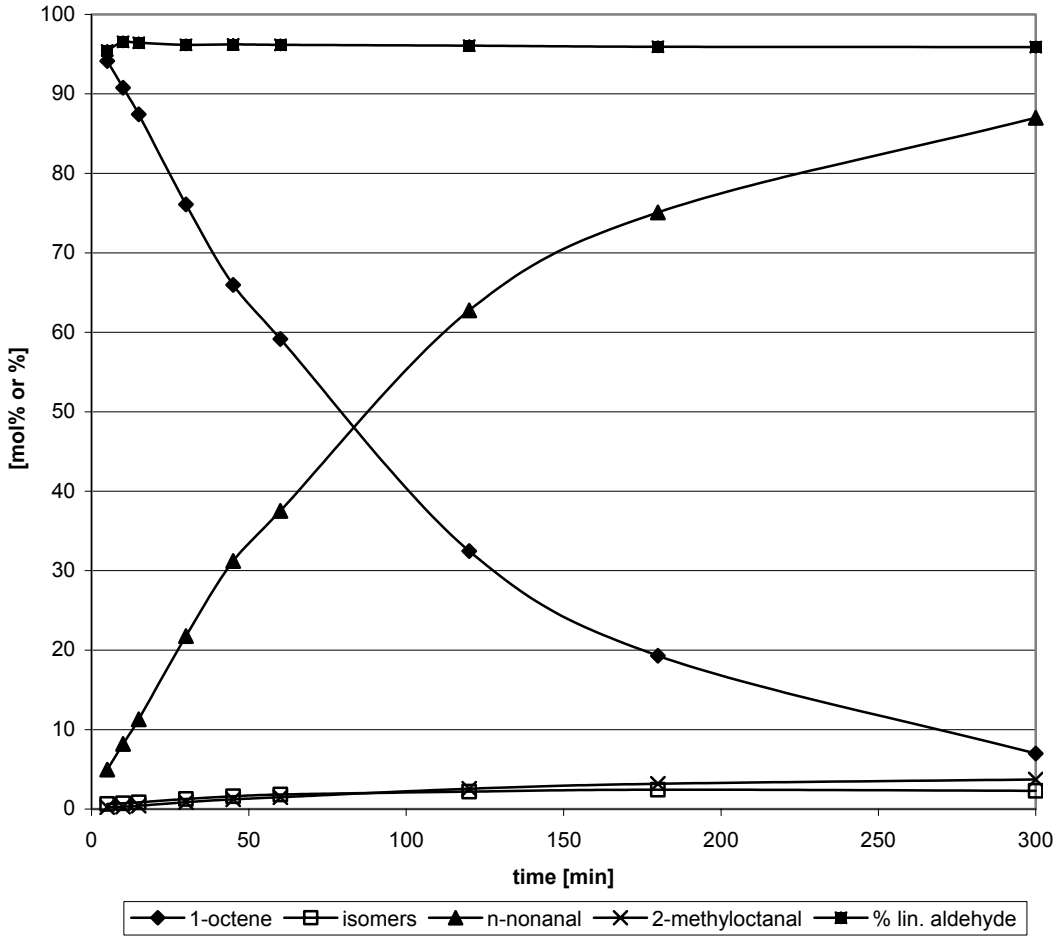
VI Kinetic data for the rhodium-catalyzed hydroformylation of 1-octene

1 6-DPPAP 1× 3-DPICon 6



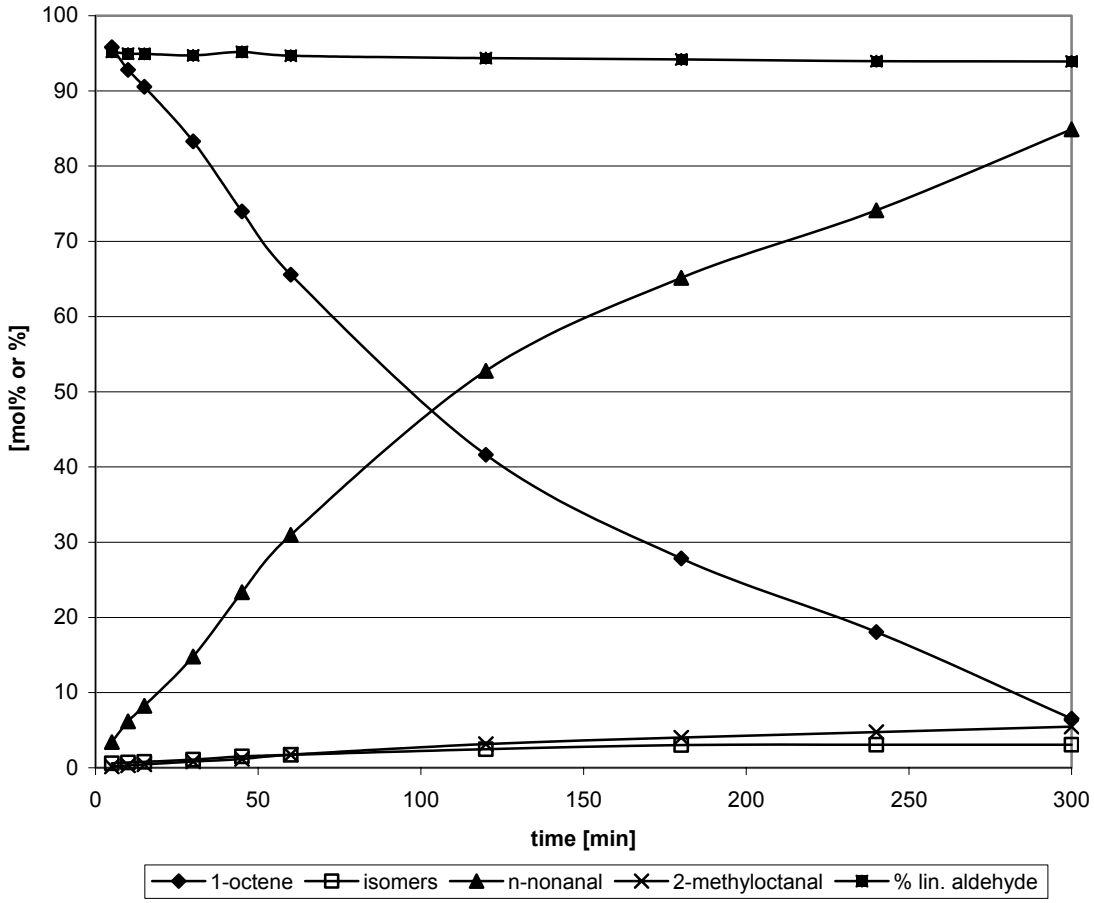
time [min]	**1-octene** [mol%]	**isomers** [mol%]	***n*-nonanal** [mol%]	**2-methyloctanal** [mol%]	**lin. aldhyd.** [%]	**TOF** [h^{-1}]
5	95.557	0.236	3.954	0.253	94.0	3786
10	93.468	0.579	5.602	0.351	94.1	2679
15	90.096	0.670	8.654	0.580	93.7	2770
30	**82.657**	**0.909**	**15.383**	**1.052**	**93.6**	**2465**
45	74.890	1.168	22.359	1.583	93.4	2394
60	67.203	1.356	29.350	2.092	93.3	2358
120	46.625	1.620	48.192	3.563	93.1	1941
180	30.183	2.340	62.506	4.971	92.6	1687
240	21.850	2.200	70.277	5.674	92.5	1424
300	13.839	2.274	77.500	6.389	92.4	1258

2 6-DPTFAAP 2× 3-DPICon 6



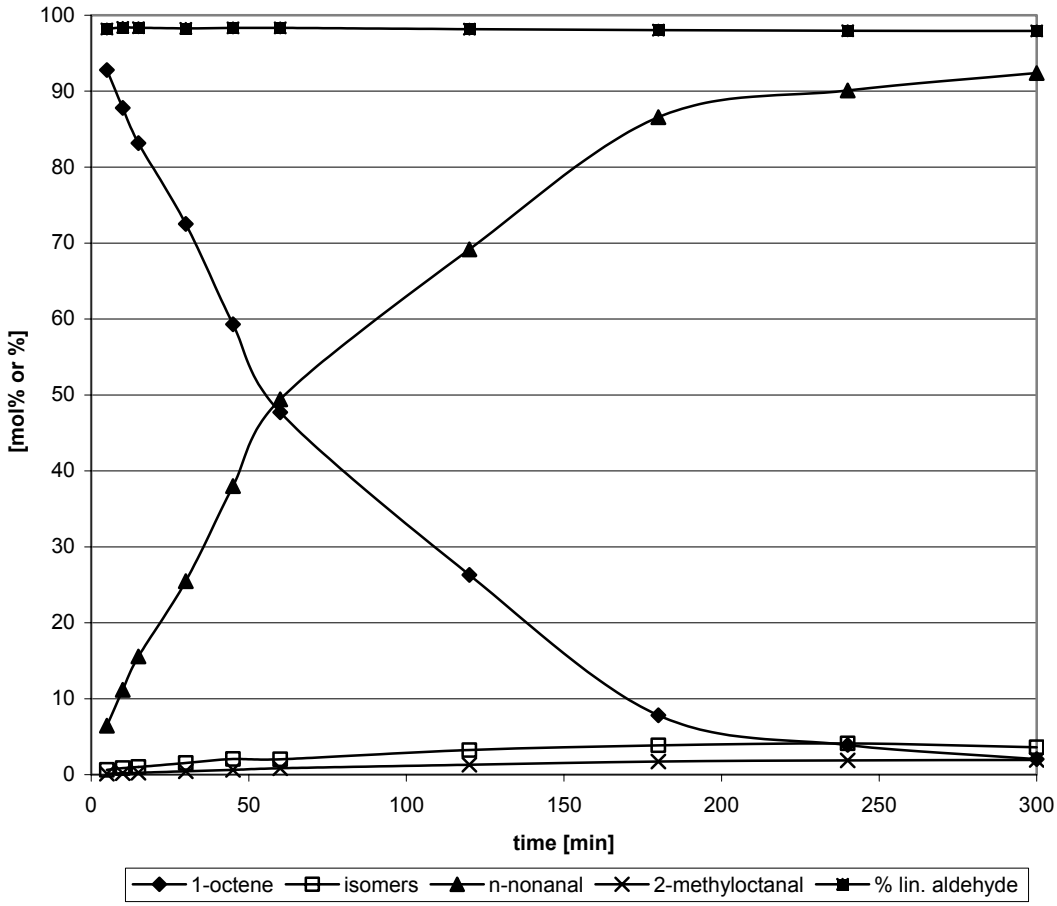
time [min]	**1-octene** [mol%]	**isomers** [mol%]	***n*-nonanal** [mol%]	**2-methyloctanale** [mol%]	**lin. aldhyd.** [%]	**TOF** [h^{-1}]
5	94.156	0.636	4.972	0.236	95.5	4687
10	90.762	0.732	8.204	0.293	96.6	3823
15	87.437	0.852	11.293	0.417	96.4	3513
30	76.086	1.276	21.774	0.865	**96.2**	**3396**
45	65.956	1.603	31.220	1.220	96.2	3244
60	59.155	1.827	37.532	1.487	96.2	2926
120	32.484	2.198	62.761	2.558	96.1	2449
180	19.304	2.433	75.088	3.176	95.9	1957
300	6.994	2.297	86.993	3.717	95.9	1361

3 3-DPAICin 3× 3-DPICon 6



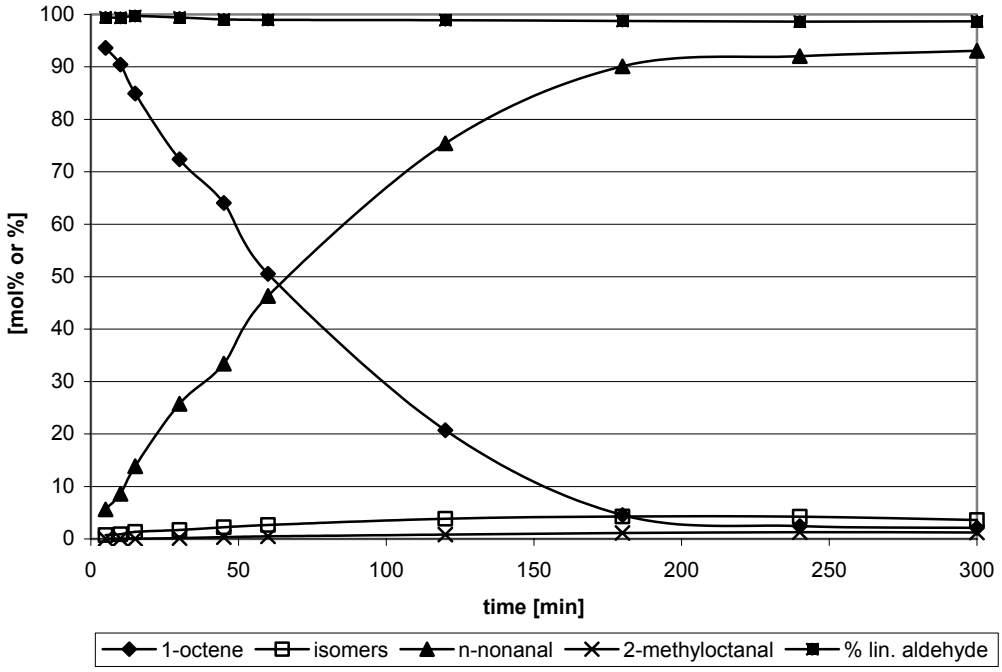
time [min]	**1-octene** [mol%]	**isomers** [mol%]	***n*-nonanal** [mol%]	**2-methyloctanal** [mol%]	**lin. aldhyd.** [%]	**TOF** [h^{-1}]
5	95.809	0.587	3.431	0.173	95.2	3243
10	92.791	0.707	6.175	0.328	95.0	2926
15	90.537	0.782	8.241	0.440	94.9	2604
30	**83.302**	**1.090**	**14.785**	**0.823**	**94.7**	**2341**
45	73.980	1.498	23.346	1.176	95.2	2452
60	65.562	1.731	30.973	1.734	94.7	2453
120	41.624	2.467	52.765	3.144	94.4	2097
180	27.835	3.011	65.137	4.017	94.2	1729
240	18.061	3.052	74.126	4.761	94.0	1479
300	6.550	3.069	84.892	5.490	93.9	1356

4 2-DPPAT 4× 3-DPICon 6



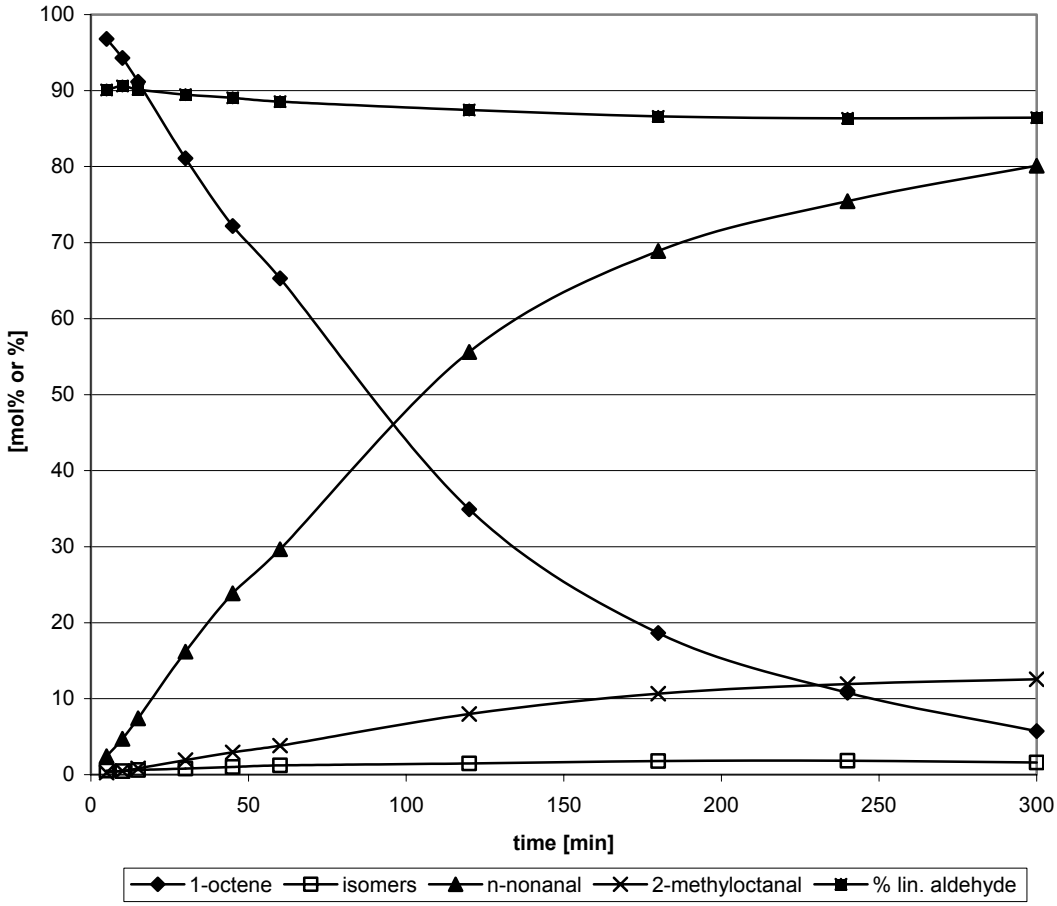
time [min]	**1-octene** [mol%]	**isomers** [mol%]	***n*-nonanal** [mol%]	**2-methyloctanal** [mol%]	**lin. aldhyd.** [%]	**TOF** [h^{-1}]
5	92.782	0.639	6.460	0.119	98.2	5921
10	87.790	0.860	11.169	0.182	98.4	5108
15	83.171	1.010	15.560	0.259	98.4	4746
30	72.531	1.536	25.483	0.450	**98.3**	**3890**
45	59.304	2.068	37.989	0.641	98.3	3863
60	47.722	2.020	49.422	0.836	98.3	3769
120	26.295	3.240	69.187	1.297	98.2	2643
180	7.820	3.873	86.574	1.733	98.0	2208
240	3.914	4.129	90.084	1.873	98.0	1724
300	2.048	3.616	92.391	1.945	97.9	1415

5 2-DPTFAAT 5× 3-DPICon 6



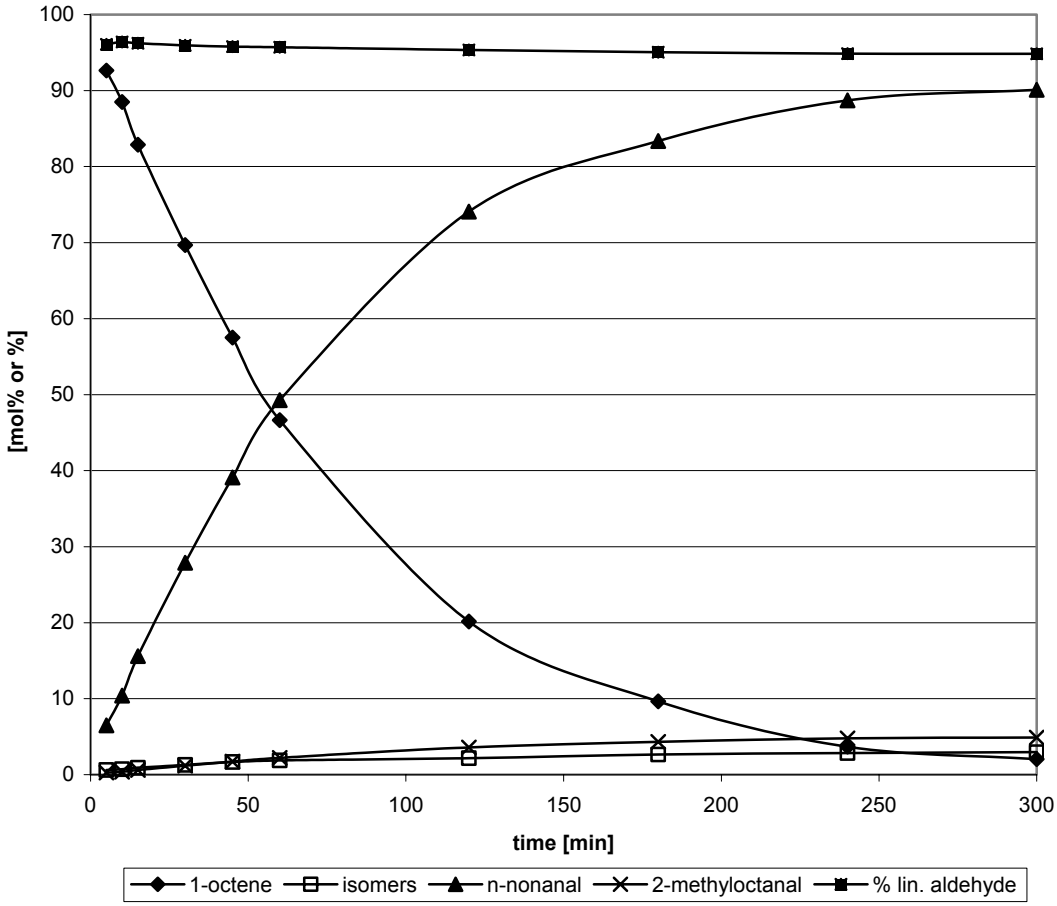
time [min]	**1-octene** [mol%]	**isomers** [mol%]	***n*-nonanal** [mol%]	**2-methyloctanal** [mol%]	**lin. aldhyd.** [%]	**TOF** [h^{-1}]
5	93.624	0.725	5.621	0.030	99.5	5086
10	90.443	0.879	8.623	0.055	99.4	3905
15	84.936	1.347	13.870	0.043	99.7	4174
30	72.360	1.717	25.767	0.152	99.4	**3888**
45	64.053	2.223	33.402	0.322	99.0	3372
60	50.542	2.658	46.319	0.481	99.0	3510
120	20.719	3.847	75.434	0.838	98.9	2860
180	4.537	4.250	90.088	1.125	98.8	2280
240	2.432	4.231	92.057	1.280	98.6	1750
300	2.091	3.593	93.091	1.224	98.7	1415

6 6-DPPAP 1× 2-DPAIND 7



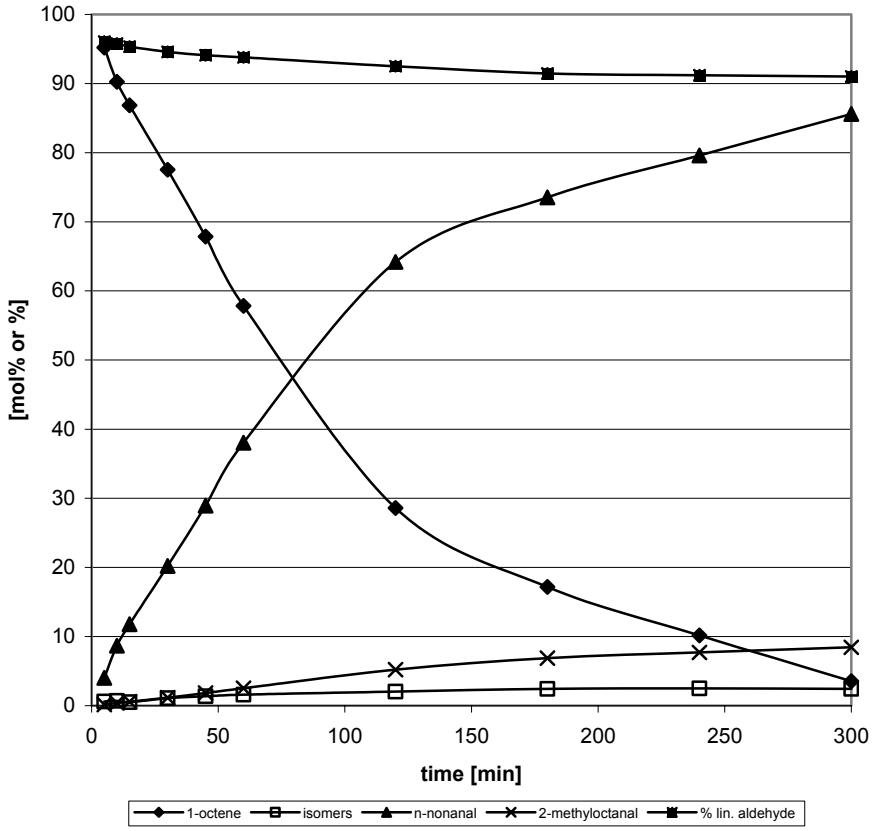
time [min]	**1-octene** [mol%]	**isomers** [mol%]	***n*-nonanal** [mol%]	**2-methyloctanal** [mol%]	**lin. aldhyd.** [%]	**TOF** [h^{-1}]
5	96.799	0.522	2.413	0.266	90.1	2411
10	94.307	0.468	4.734	0.491	90.6	2351
15	91.155	0.614	7.418	0.812	90.1	2469
30	**81.110**	**0.802**	**16.183**	**1.905**	**89.5**	**2713**
45	72.196	1.013	23.855	2.936	89.0	2679
60	65.304	1.209	29.652	3.835	88.5	2512
120	34.908	1.478	55.627	7.987	87.4	2386
180	18.652	1.777	68.919	10.652	86.6	1989
240	10.787	1.833	75.450	11.929	86.3	1638
300	5.736	1.593	80.112	12.560	86.4	1390

7 6-DPTFAAP 2× 2-DPAIND 7



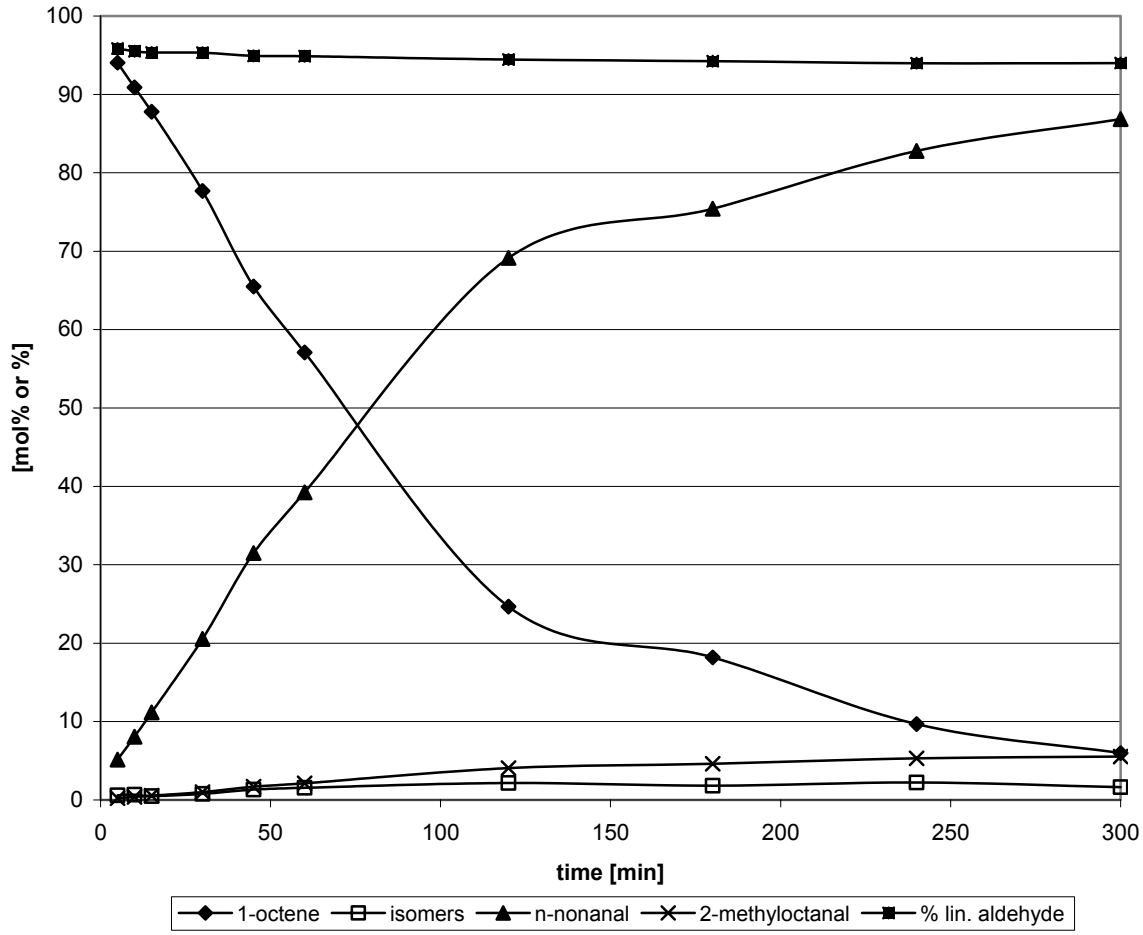
time [min]	**1-octene** [mol%]	**isomers** [mol%]	***n*-nonanal** [mol%]	**2-methyloctanal** [mol%]	**lin. aldhyd.** [%]	**TOF** [h^{-1}]
5	92.633	0.613	6.489	0.264	96.1	6078
10	88.493	0.711	10.409	0.388	96.4	4858
15	82.890	0.898	15.602	0.610	96.2	4864
30	**69.682**	**1.276**	**27.872**	**1.171**	**96.0**	**4356**
45	57.515	1.655	39.110	1.720	95.8	4083
60	46.647	1.864	49.277	2.212	95.7	3862
120	20.160	2.167	74.071	3.602	95.4	2913
180	9.650	2.648	83.364	4.338	95.1	2193
240	3.671	2.833	88.701	4.795	94.9	1753
300	2.035	2.967	90.108	4.890	94.9	1425

8 3-DPAICin 3× 2-DPAIND 7



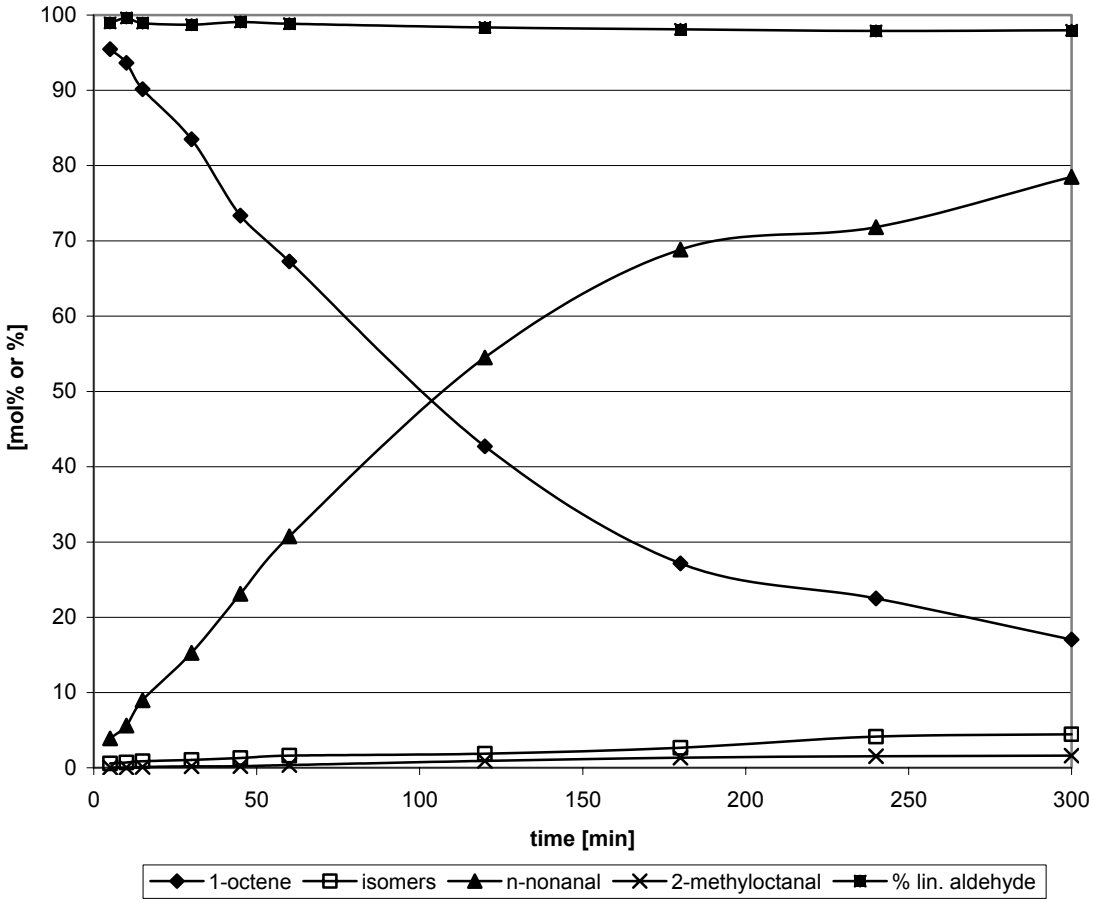
time [min]	**1-octene** [mol%]	**isomers** [mol%]	***n*-nonanal** [mol%]	**2-methyloctanal** [mol%]	**lin. aldhyd.** [%]	**TOF** [h^{-1}]
5	95.209	0.611	4.016	0.164	96.1	3762
10	90.254	0.700	8.665	0.382	95.8	4071
15	86.847	0.517	11.786	0.575	95.3	3708
30	77.542	1.089	20.212	1.157	**94.6**	**3205**
45	67.870	1.363	28.952	1.816	94.1	3077
60	57.838	1.584	38.060	2.517	93.8	3043
120	28.595	2.025	64.183	5.197	92.5	2602
180	17.180	2.418	73.527	6.875	91.4	2010
240	10.176	2.501	79.623	7.701	91.2	1637
300	3.533	2.417	85.601	8.448	91.0	1411

9 2-DPPAT 4× 2-DPAIND 7



time [min]	**1-octene** [mol%]	**isomers** [mol%]	***n*-nonanal** [mol%]	**2-methyloctanal** [mol%]	**lin. aldhyd.** [%]	**TOF** [h^{-1}]
5	94.041	0.592	5.145	0.223	95.9	4830
10	90.880	0.673	8.067	0.379	95.5	3801
15	87.783	0.499	11.174	0.544	95.4	3515
30	77.672	0.776	20.547	1.006	**95.3**	**3233**
45	65.500	1.330	31.487	1.683	94.9	3317
60	57.088	1.550	39.246	2.116	94.9	3102
120	24.654	2.153	69.136	4.058	94.5	2745
180	18.176	1.810	75.409	4.605	94.2	2000
240	9.689	2.220	82.800	5.291	94.0	1652
300	5.977	1.632	86.863	5.529	94.0	1386

10 2-DPTFAAT 5× 2-DPAIND 7



time [min]	**1-octene** [mol%]	**isomers** [mol%]	***n*-nonanal** [mol%]	**2-methyloctanal** [mol%]	**lin. aldhyd.** [%]	**TOF** [h^{-1}]
5	95.469	0.578	3.912	0.041	99.0	3558
10	93.663	0.695	5.620	0.022	99.6	2539
15	90.145	0.868	8.987	0.096	98.9	2725
30	83.512	1.037	15.253	0.198	98.7	2318
45	73.362	1.305	23.118	0.215	**99.1**	**2333**
60	67.277	1.613	30.754	0.355	98.9	2333
120	42.717	1.862	54.513	0.908	98.4	2078
180	27.159	2.646	68.865	1.329	98.1	1755
240	22.496	4.139	71.828	1.537	97.9	1376
300	17.052	4.452	78.496	1.622	98.0	1202

VII Literature

[1] Breit, B.; Seiche, W. *Angew. Chem.* **2005**, *117*, 1666-1669.

[2] Den Hertog, H. J; Wibaut, J. P. *Recl. Trav. Chim. Pays* **1932**, *51*, 381-387 and *ibid*. **1936**, *55*, 122-125.

[3] Sanders, G. M.; van Dijk, M.; Hertog, H. J. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 298-300.

[4] Johnson, F.; Nasutavicus, W. A. *J. Org. Chem.* **1963,** *28*, 1877-1883.

[5] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

[6] CCDC-631817 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[7] CCDC-63186 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.