Supporting information

For

A 2,2',6,6'-Tetraphosphinobiphenyl

Content

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1. General remarks

All reactions handling sensitive chemicals were carried out under an argon inert gas atmosphere using standard Schlenk and cannula techniques. Diethyl ether was purified by distillation from sodium/benzophenone ketyl. Dry ethanol was obtained from Acros. 6,6'-dibromo-4,4'-dimethyl-2,2'-diiodobiphenyl[10] was synthesized following published procedures. All other chemicals were purchased by commercial suppliers and were used without further purification. Elemental analyses were performed using a Thermo FlashAE 1112 analyser. Infrared spectra were recorded with a Nicolet IR200 FT-IR spectrometer. Mass spectra were recorded on a Bruker micrOTOF-QIIa mass spectrometer operating in ESI mode. All NMR spectra have been recorded on a 500 MHz Bruker AVANCE III spectrometer. Proton spectra are referenced to the residual protons of the deuterated solvent (d_7-dmf: δ = 8.18 ppm formyl proton; C_6D_6 : δ = 7.16 ppm); $^{31}P\{^1H\}$ NMR spectra are referenced to 85% H_3PO_4 as external standard. Temperature of the sample has been measured by the internal sensor of the probe head and is not corrected. Before accumulating data probe head and spectrometer were allowed to equilibrate for 10 min at the desired temperature.

2. Syntheses protocols

2.1 Synthesis of diphosphane **4**:

To a solution of **3** (400 mg, 0.676 mmol, 1.0 equiv.) in diethyl ether (6 mL) was added at -95°C within 5min a solution of *n*-BuLi (0.887 mL, 1.6 M *n*-hexane, 1.42 mmol, 2.1 equiv.). The resulting slightly opaque mixture was stirred for 25min at -95°C, and then a solution of *i*-Pr_2PCl (216.6 mg, 14.2 mmol) in diethyl ether (5 mL) was added. The mixture was allowed to attain ambient temperature within 2h. At ca. -65C°, the precipitation of a white solid started. After stirring for 3h at ambient temperature, the mixture was reduced to dryness under reduced pressure (oil pump vacuum) for 1h in order to remove butylbromide, then a new portion of Et_2O (5 mL) was added. The mixture was quenched by addition of 10 ml of degassed H_2O, extracted with diethyl ether (3 X 10 mL) under Ar. The combined organic extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The crude material obtained was purified by flash column chromatography on silica gel using THF as eluent, then concentrated under reduced pressure. The resulting colorless oil was recrystallized from EtOH to yield 292 mg (73 % based on **3**) of **4** as white crystals. M.p.: 192°C. $^{1}H\{^{31}P\}$ NMR (500 MHz, C_6D_6, 25 °C): δ = 7.41 (s, Ar-H, 2H); 7.22 (s, Ar-H, 2H); 2.17 (sep; ^{3}J(H,H) = 6.8 Hz, C*H*(Me)$_2$, 2H); 2.07 (sep; ^{3}J(H,H) = 7.4 Hz, C*H*(Me)$_2$, 2H); 2.01 (s, biphen-CH_3, 6H), 1.23 (d; ^{3}J(H,H) = 7.0 Hz, CH(*Me*)$_2$, 6H), 1.115 (d; ^{3}J(H,H) = 6.9 Hz, CH(*Me*)$_2$, 6H); 1.08 (d; ^{3}J(H,H) = 7.2 Hz, CH(*Me*)$_2$, 12H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6, 25 °C): δ = 144.2 (m, central *C*-*C*); 141.1 (m, Ar-*C*-P(*i*Pr)$_2$; 138.7 (Ar-*C*-Me); 133.7 (Ar-*C*-H); 131.8 (Ar-*C*-H); 127.3 (t, *J*(C,P) = 4.5 Hz, Ar-*C*-Br); 25.35 (dd, *J*(C,P) = 7.0/9.5 Hz, *C*H(Me)$_2$); 22.3 (t, *J*(C,P) = 10 Hz, CH(*C*H$_3$)$_2$); 22.1 (m, *C*H(Me)$_2$); 22.0 (d, *J*(C,P) = 11 Hz, CH(*C*H$_3$)$_2$); 20.85 (biphen-*C*H$_3$); 20.4 (t, *J*(C,P) = 11 Hz, CH(*C*H$_3$)$_2$); 17.75 (t, *J*(C,P) = 2.5 Hz, CH(*C*H$_3$)$_2$). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, C_6D_6, 25 °C): δ = 2.01 ppm. IR (KBr): 1452 (s), 1309 (s), 2942 (s), 2815 (s), 1589 (s), 1134 (s), 3052 (s). ESI-TOF MS: calcd (*m*/*z*) for $[C_{26}H_{38}Br_2P_2+H]^+$ (100%) 573.0873 found 573.076 $[C_{26}H_{38}Br_2P_2+H]^+$ with expected isotopic pattern. EA calcd (%) for $C_{26}H_{38}Br_2P_2$ (572.335 g·mol^{-1}): C 54.56, H 6.69; found C 54.13, H 6.82.

2.2 Syntheses of tetraphosphane **2**:

Method A:

n-BuLi (2.5 M in n-hexane, 0.887 mL, 2.19 mmol, 2.1 equiv.) was added at -95 °C dropwise over a period of 5 min. to a solution of **3** (400 mg, 1.0 mmol) in diethyl ether (6 mL). The mixture was stirred for 25 min at -95 °C, and then a solution of *i*-Pr_2PCl (432 mg, 2.84 mmol) in in diethyl ether (6 mL) was added at this temperature. The mixture was allowed to attain ambient temperature within 2h, at approximately -65 °C the precipitation (LiCl) of a white solid started. After stirring for 3 h at ambient temperature, the solvent was reduced to dryness under reduced pressure (oil pump vacuum) for 1 h to remove *i*-Pr_2PCl, *i*-Pr_2P-*n*-Bu as well as buthylbromide, and then a new portion of diethyl ether (6 mL) was added. After stirring for 2 h at ambient temperature, the mixture was filtered under Ar, and washed twice with diethyl ether (3 mL). At -95 °C *n*-BuLi (2.5 M in n-hexane, 0.887 mL, 2.19 mmol, 2.1 equiv.) was added. The mixture was stirred for 35 min at -95 °C and 1h at ambient temperature, chilled to -95 °C again and a solution of *i*-Pr_2PCl (432 mg, 2.84 mmol)) in diethyl ether (5 ml) was added. The resulting mixture was stirred for 45 min at -95 °C allowed to attain r.t. and stirred overnight, the mixture was quenched by

addition of degased H_2O (10 ml), and extracted with diethyl ether (3 × 10 mL) under Ar. The combined organic extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The crude material obtained was purified by flash column chromatography on silica gel using dichloromethane as eluent, concentrated under reduced pressure to obtain a colorless oil which was recrystallized from EtOH to afford 361 mg (82 % based on **3**) of **2** as white powder. Interestingly, **2** is only sparingly soluble in DMSO but well soluble in ether or hexane.. M.p.: 206 °C. $^1H\{^{31}P\}$ NMR (500 MHz, C_6D_6, 25 °C): δ = 7.58 (s, Ar-H, 4H); 2.53 (s, biphen-CH_3, 6H); 2.29 (dt; ^3J(H,H) = 7.2 Hz, ^3J(H,H) = 6.7 Hz, C*H*(Me)$_2$, 8H); 1.14 (d, ^3J(H,H) = 7.2 Hz, *Me*, 24H), 1.13 (d, ^3J(H,H) = 6.7 Hz, *Me*, 24H); $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6, 25 °C): δ = -4.08; $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 25 °C): δ = 148.9 (m, central *C*-*C*); 139.1 (m, Ar-*C*-P(*i*Pr)$_2$; 134.8 (Ar-*C*-Me); 133.2 (Ar-*C*-H); 23.4 ppm (m, *C*H(Me)$_2$); 23.1 (m, Me, *i*Pr); 21.5 (biphen-*C*H_3); 18.8 ppm(Me, *i*Pr). IR (KBr): 1457 (s), 1358 (s), 2975, 2947, 2915 (s), 2865 (s), 1583 (s), 1150 (s), 3046 (s). ESI-TOF MS: calcd (*m*/*z*) for $[C_{38}H_{66}P_4+H]^+$ 647.4193 found 647.405 $[C_{38}H_{66}P_4+H]^+$ with expected isotopic pattern. Elemental analysis calcd (%) for $C_{38}H_{66}P_4$·1/2 CH_2Cl_2 (572.335 g·mol^{-1}): C 67.09, H 9.80; found C 67.08, H 9.60.

Method B

To a solution of 200 mg (0.349 mmol, 1 equiv.) of **4** in diethyl ether (5 mL) was added at -95 °C during a period of 5 min a solution of *n*-BuLi (0.436 ml, 1.6 M n-hexane, 0.698 mmol, 2.0 equiv.). The resulting mixture was stirred for 30 min at -95 °C and 1h at ambient temperature, after cooling to -95 °C a solution of (106 mg, 0.698 mmol) of *i*-Pr$_2$PCI was added. The resulting mixture was stirred for 45 min at -95 °C, allowed to warm to r.t. and stirred overnight. The mixture was quenched by addition of 10 ml degassed H_2O, extracted with diethyl ether (3 × 10 mL) under Ar. The combined organic extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The resulting colorless oil was recrystallized from EtOH to afford 218.5 mg (96%) of **2** as white powder.

*2.3 Synthesis of complex **5**:*

One equivalent of ligand **2** (46 mg, 0.0712 mmol) was dissolved in CH_2Cl_2 (5 mL), and 2 equivalents of palladium acetate (32 mg, 0.1424 mmol) in CH_2Cl_2 (5 mL) were added dropwise at ambient temperature. The yellow brown suspension was stirred for 6h at room temperature. The reaction mixture was washed a couple of times with sodium chloride solution and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure, recrystallized from chloroform to yield complex **5** as yellow powder (60 mg, 84 % based on **2**). M.p.: 208 °C. ^1H NMR (500 MHz, d_7-dmf, 100°C): δ = 8.25 (d, ^3J(P,H) = 10 Hz, Ar-H, 4H); 4.04 (dsep; ^2J(P,H) = 10.4, ^3J(H,H) = 7.1 Hz, C*H*(Me)$_2$, 4H); 2.85 (s, biphen-CH_3, 6H); 2.15 (dsep; ^2J(P,H) 8.7, ^3J(H,H) 7.1 Hz, C*H*(Me)$_2$, 4H); 1.97 (dd, ^3J(P,H) = 17.0, ^3J(H,H) = 7.2 Hz, *Me*, 12H), 1.81 (dd, ^3J(P,H) = 15.0, ^3J(H,H) = 7.1 Hz, *Me*, 12H); 1.47 (dd, ^3J(P,H) = 20.6, ^3J(H,H) = 7.2 Hz, *Me*, 12H), 1.40 (dd, ^3J(P,H) = 14.0, ^3J(H,H) = 7.2 Hz, *Me*, 12H); $^{31}P\{^1H\}$ NMR (202.5 MHz, d_7-dmf, 100°C): δ = 53.9 ppm. IR (KBr): 1447 (s), 1385 (s), 2965 (s), 2865 (s), 1627 (s), 1173 (s), 3039 (s). ESI-TOF MS: calcd (*m*/*z*) for $[C_{38}H_{66}P_4Pd_2Cl_3\text{-}Cl+H]^+$ 966.1333 found 966.102 $[C_{38}H_{66}P_4Pd_2Cl_3\text{-}Cl+H]^+$ with expected isotopic pattern. Elemental analysis calcd (%) for $C_{38}H_{66}P_4Pd_2Cl_2$·1/2 $CHCl_3$ (1001.477 g·mol^{-1}): C 43.58, H 6.32; found C 43.39, H 6.35.

3. NMR spectra (Figure S1-S4)

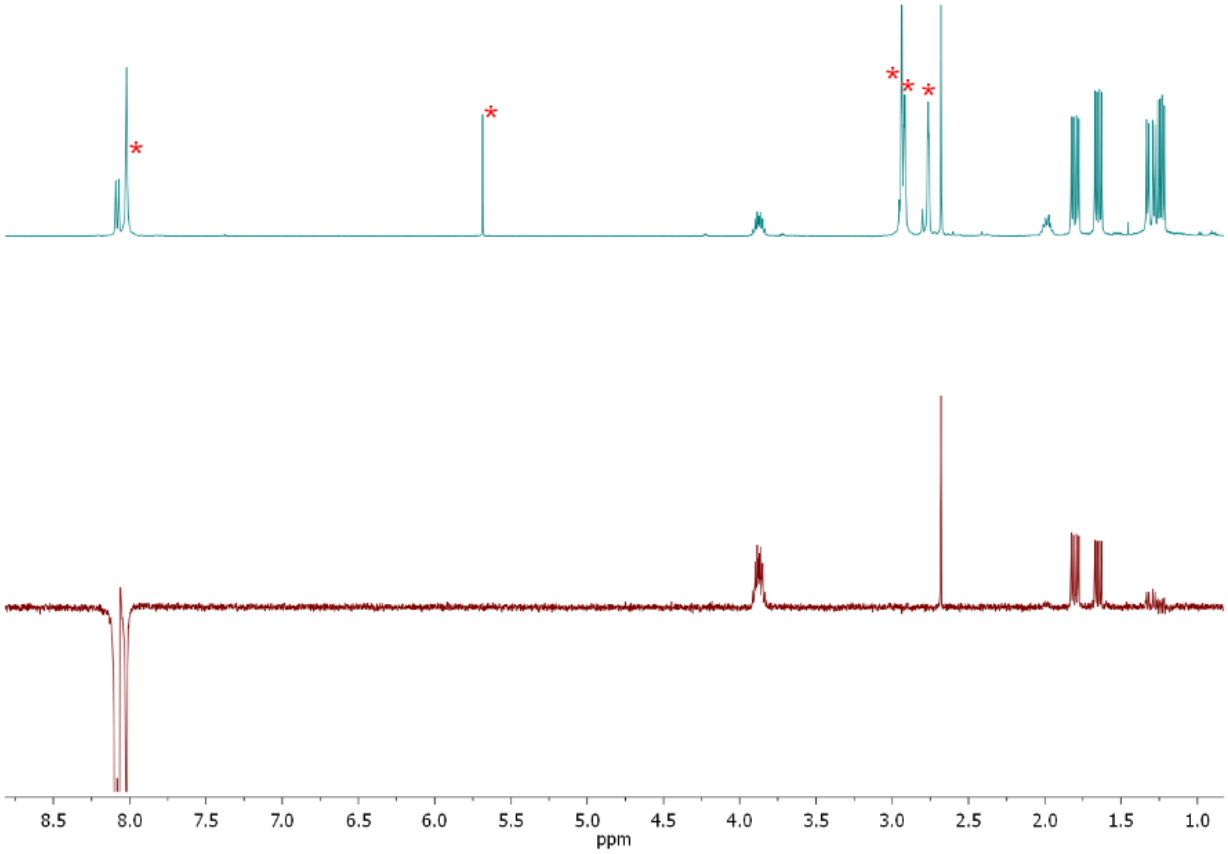

Figure S1: Standard proton nmr spectrum of complex **5** (top) in d_7-dmf and ^{1}H selective NOE spectrum [S1] (buttom) with irradiation at the aromatic proton at δ = 8.25 a mixing time of 0.5 sec and 64 transients recorded in d_7-dmf at 373K. Peaks marked with * are water, residual solvent protons, and CH_2Cl_2.

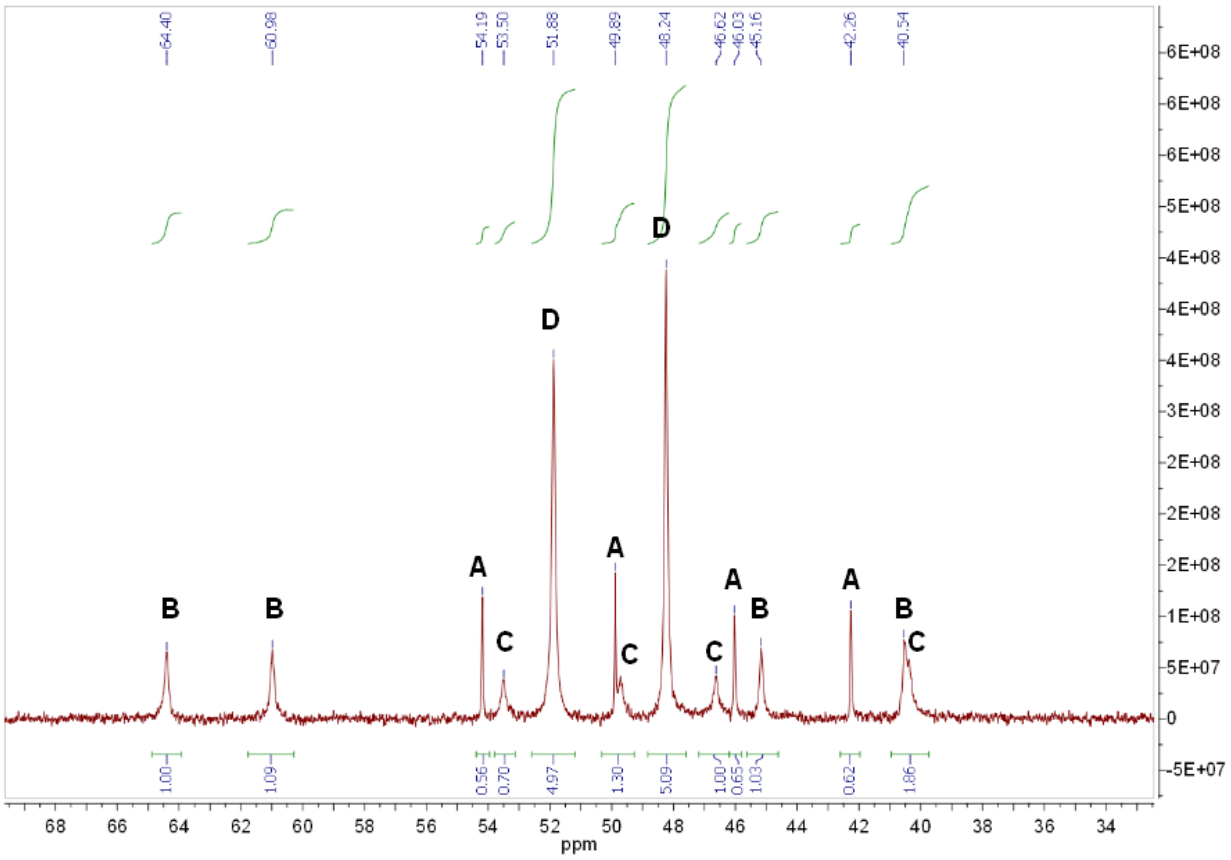

Figure S2: $^{31}P\{^{1}H\}$ NMR spectrum of complex **5** in d_7-dmf at 223K, signals were grouped based on the signal intensity and line broadening.

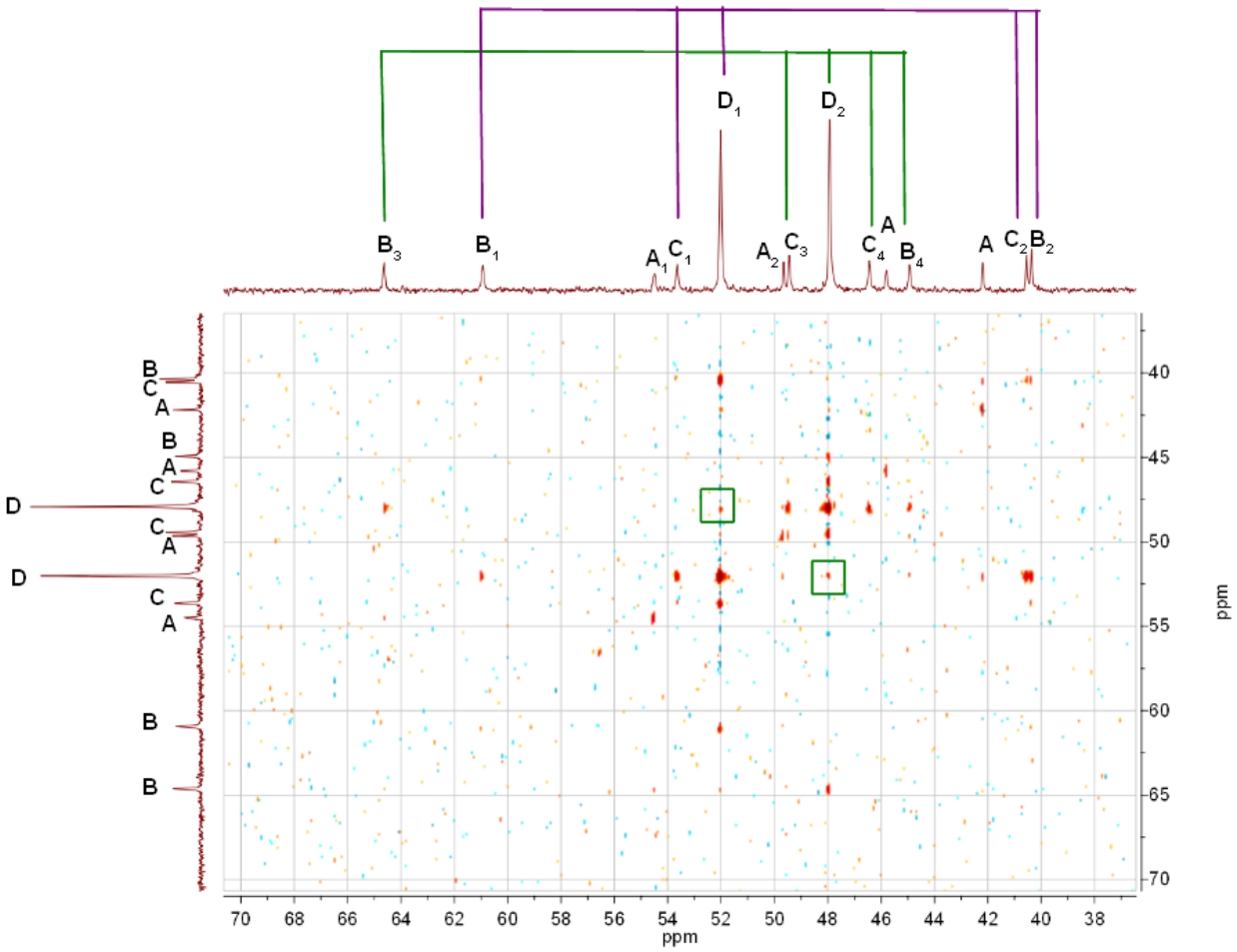

Figure S3: $^{31}P\{^{1}H\}$ EXSY spectrum[S2] of complex **5** at 208K in d_7-DMF/CH_2Cl_2 mixture (ratio 1:2), the cross peaks for the P-P exchange within conformer D is marked with green boxes, note that this cross peaks would have higher intensity due to the dominant conformer D if the P-P exchange would be comparable fast within D ($D_1 \leftrightarrow D_2$). The colored lines on the top should indicate the correlation between the exchanging signals. This spectrum has been recorded with 2048 transients in F2 and 128 transients in F1 and a mixing time of 0.6 sec. Conformer A does not show exchange signals in this spectrum.

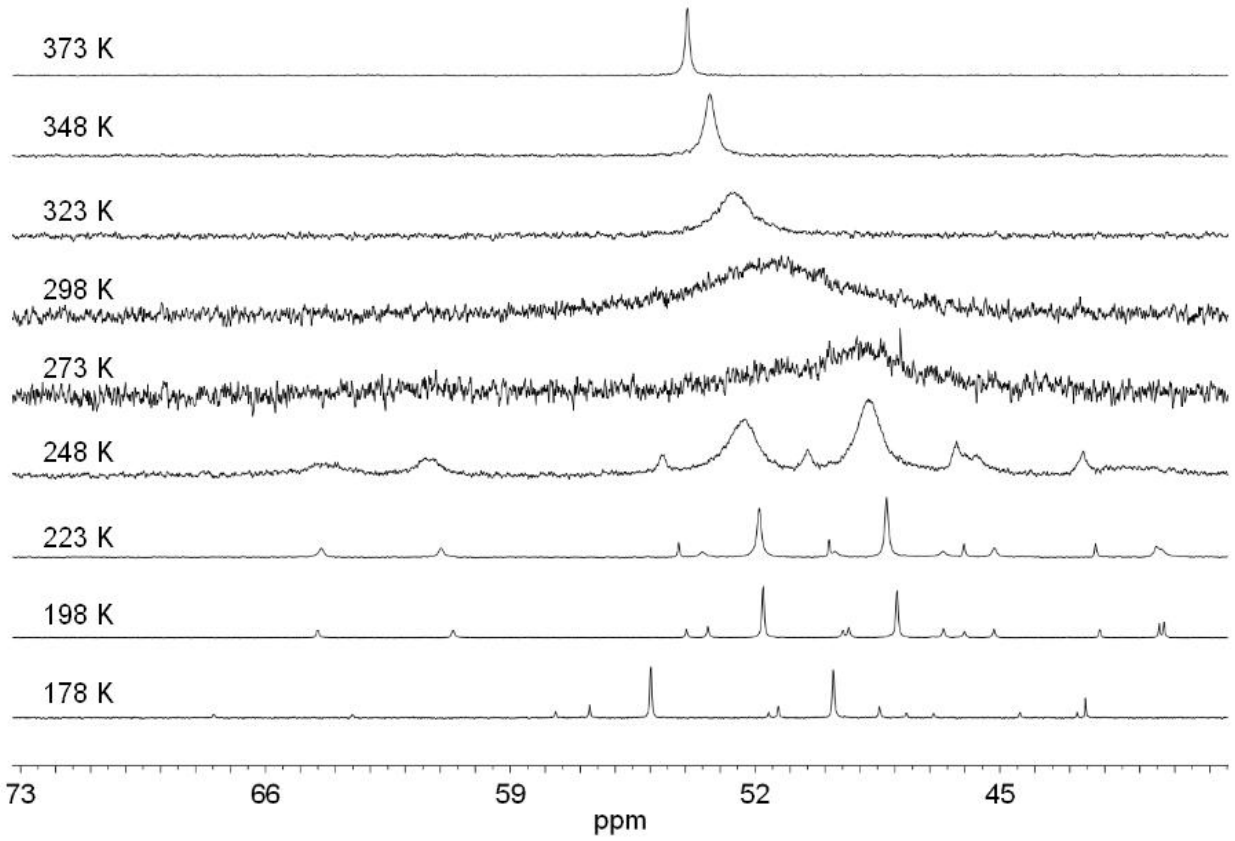

Figure S4: Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of complex **5** in d_7-dmf solution at 178, 198, 223, 248, 273, 298, 323, 348, and 373 K, respectively (from bottom to top); the spectra have been scaled in order to make the broad signals visible, spectrum at 178 K has been recorded in CD_2Cl_2/d_7-dmf mixture.

4. Single crystal X-ray analyses of complex 5 (Figure S5)

Due to the many conformers present at ambient temperature crystals of **5** are notoriously difficult to grow, although best solvent for recrystallization is chloroform this only yields twined crystals yielding diffraction data not suitable for structure refinement. Diffusion of pentane vapors to a solution of **5** in CH_2Cl_2/MeOH yields crystals suitable for collection of reasonable data for refinement. Reflection data have been collected on an Oxford Gemini S diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The structures have been solved by direct methods (SIR92)[S3] and refined against $IF_o I^2$ with the SHELXS 97[S4] and SHELXL 97[S5], respectively. *Ortep-3 for Windows*[S6] was employed for structure presentation. The crystal structure includes two molecules of complex **5**, five molecules of CH_2Cl_2 and one molecule of methanol (60% occupation). Not unexpected the molecules of complex **5** show disorder, however this disorder is restricted to one molecule of complex **5**. Especially the disorder of the isopropyl groups around the disordered P6 could not be resolved adequately; therefore this part of the molecule (C59-C64) has been refined isotropic with only 50% occupation (C59 and C59A), 33%

occupation for (C60-C62 and C60A to C64A) and 25% occupation (C63 and C63), respectively. The dichloromethane solvent molecules show also some disorder therefor Cl14 and Cl15 have been refined in a split model to Cl14 and Cl4A (57.2(5)%/42.8(5)% occupation) and Cl15 and Cl5A (71.5(15)%/ 28.5%(15) occupation), respectively. Moreover the fragment Cl8 and Pd4 show minor disorder and therefor are split into Cl8 and Cl8A (77.4(4)%/ 22.6(4)% occupation), Pd4 and Pd4A (77.4(4)%/ 22.6(4)% occupation) respectively. Interestingly the other molecule of complex **5** does not show any disorder and all non-hydrogen atoms have been refined anisotropic, moreover all hydrogen atoms belonging to this molecule have been clearly detected in difference Fourier synthesis but have been placed geometrically and hydrogens bound to methyl carbons have been placed geometrically with torsion angle taken from residual electron density, therefore the position of those hydrogen atoms could be clearly located. CCDC 832393 contains the supplementary crystallographic data for structure refinement on complex **5**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Empirical formula: $[C_{38}H_{66}Cl_4P_4Pd_2]$ * $[C_{35}H_{66}Cl_4P_4Pd_2]$ * $5[CH_2Cl_2]$ * $0.5[CH_3OH]$; formula weight ($g \cdot mol^{-1}$): 4837.92; T(K) : 153(2); crystal system: monoclinic; space group: P1 21/c 1; a(Å): 23.3722(4); b(Å): 11.6540(2); c(Å): 38.7341(6); α(°): 90; β(°): 99.158(2); γ(°): 90; V(Å^3): 10415.9(3); Z: 2; ρ ($g \cdot cm^{-3}$): 1.542; μ (cm^{-1}): 1.304; reflections collected: 51728; independent Reflections/R_{int}: 18391/ 0.0329; Reflections with I > 2σ(I): 14043; Parameters/restrains : 1095/43; $\Theta_{min/max}$(°): 3.10/ 25.05; Completeness to Θ(%): 99.8; wR_2 (all reflections F^2)[a]): 0.1058; R_1 ($I > 2\sigma(I)$)[a]): 0.0377; *GooF*[b]): 1.072; extrema ΔF ($e \cdot Å^{-3}$): 1.687/-0.879; absorption correction: 'multi-scan'; $T_{min/max}$: 0.79940/1.0000; Definition of R indices: $R_1 = (\Sigma || F_o | - | F_c ||) / \Sigma | F_o |$ $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.. [b] = $\{\Sigma[w(F_o^2 - F_c^2)^2] / (N_o - N_p)\}^{1/2}$.

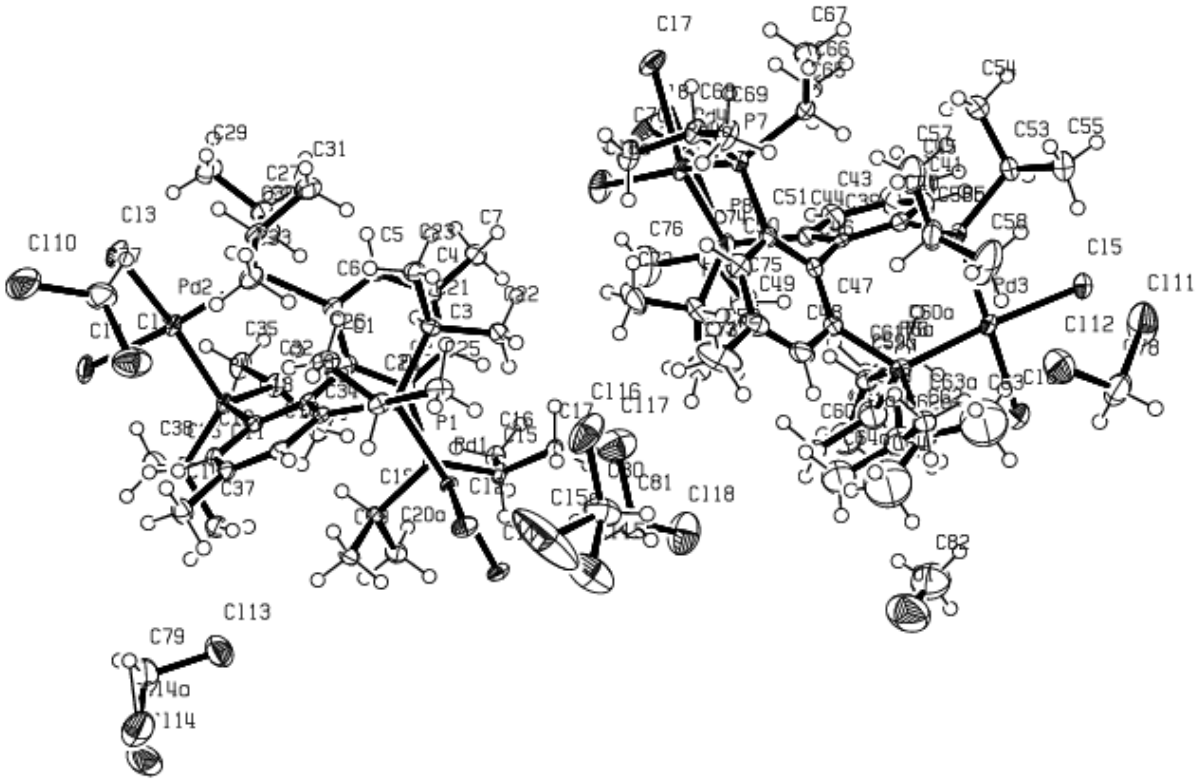

Figure S5: Ortep drawing of the complete asymmetric unit of crystals of complex **5**. Bond lengths (Å): Pd1-Pd2 7.7430(4), Cl1-Pd1 2.3738(9), Cl2-Pd1 2.3628(9), Cl3-Pd2 2.3640(9), Cl4-Pd2 2.3327(12), P1-Pd1 2.2744(9), P2-Pd1 2.2782(9), P3-Pd2 2.2993(11), P4-Pd2 2.2492(9), C36-P4 1.851(4), C32-P4 1.853(4), C30-P3 1.855(4), C27-P3 1.857(4), C24-P2 1.860(4), C21-P2 1.873(4), and bond angle (˚): P1-Pd1-P2 91.46(3), P1-Pd1-Cl2 170.51(4), P2-Pd1-Cl2 95.37(3), P1-Pd1-Cl1 86.78(3), P2-Pd1-Cl1 176.01(4), Cl2-Pd1-Cl1 85.98(3), P4-Pd2-P3 92.80(4), P4-Pd2-Cl4 90.84(4), P3-Pd2-Cl4 172.56(4), P4-Pd2-Cl3 167.49(4), P3-Pd2-Cl3 89.65(4), Cl4-Pd2-Cl3 88.18(4).

[S1] Stefan Berger, Sigmar Braun, *200 and More NMR Experiments - a practical course*, 2nd Edition, Wiley-VCH Wheinheim, **2004**, ISBN: 3-527-31067-3.

[S2] according to Stefan Berger, Sigmar Braun, *200 and More NMR Experiments - a practical course*, 2th Edition, Wiley-VCH Wheinheim, **2004**, ISBN: 3-527-31067-3 but with waltz16 proton composite pulse decoupling during acquisition.

[S3] A. Altomare,G. Cascarano,C. Giacovazzo, A. Guagliardi, *J. Appl. Cryst.* **1993**, *26*, 343-350.

[S4] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 467-473.

[S5] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, **1997**.

[S6] Ortep-3 for Windows: L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565-565.