Electronic Supplementary Information for Dalton Transactions

Supplementary Material

Atropisomeric Phosphinines: Design and Synthesis

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Experimental section

General Considerations: All manipulations, except the preparation of pyrylium salts, were carried out under an argon atmosphere, using modified Schlenk techniques. All glassware was dried prior to use by heating under vacuum. All common solvents and chemicals were commercially available and purchased from Aldrich Chemical Co. and Merck. $P(SiMe_3)_3$[1], $P(CH_2OH)_3$[2] and 2,3-dimethylpropiophenone[3] were prepared according to the literature. The solvents were taken from custom-made solvent purification columns filled with Al_2O_3. The elemental analyses were obtained either from H. Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr (Germany) or were performed on a Perkin Elmer 2400, Series II CHNS/O Analyzer (Eindhoven University of Technology). ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 200 or 500 spectrometer and all chemical shifts are reported relative to the residual proton resonance in the deuterated solvents or referred to an 85% aqueous solution of H_3PO_4, respectively.

Preparation of compounds:

2,4-Diphenyl-5-methyl-6-(2,3-dimethylphenyl)-pyrylium tetrafluoro-borate (6):

Tetrafluoroboric acid (4.6 g, 27.1 mmol, 52% ethereal solution) was added at 70°C to a solution of benzylideneacetophenone (6.0 g, 28.6 mmol) and 2,3-dimethylpropiophenone **3** (2.32 g, 14.3 mmol) in 10 mL of 1,2-dichloroethane. The reaction mixture was heated for 6 hours and was subsequently allowed to cool down to room temperature. The red solution was diluted with Et_2O (150 mL) and a dark yellow oil was formed. The Et_2O-phase was decanted and the residue was dissolved in $CHCl_3$ (10 mL). Subsequently, Et_2O was added until a yellow precipitate was formed, which was filtered off. This procedure was repeated 2 more times. The yellow solid was stirred for overnight in Et_2O, filtered off and dried under vacuum. Yield: 2.40 g (5.5 mmol, 38%). Yellow crystals of **6** were obtained by slow recrystallization from MeOH. ^{1}H NMR (CD_3OD): δ (ppm) = 2.33, 2.35, 2.45 (3×s, 3×3H, -CH_3), 7.43 (m, 1H), 7.55 (m, 2H), 7.65-7.80 (m, 5H), 7.82-7.87 (m, 3H), 8.30 (m, 2H), 8.76 (s, 1H, H3). ^{19}F NMR (CD_3OD): δ (ppm) = -154.45, -154.50 (3:1). ^{13}C NMR (CD_3OD): δ (ppm) = 15.7, 15.8, 18.8 (-CH3), 110.0, 120.1, 126.2, 127.6, 128.2, 128.6, 129.0, 129.8, 131.0, 131.8, 133.5, 135.2, 136.1, 138.8, 153.8, 171.0, 173.0. Analysis Calcd for $C_{26}H_{23}BF_4O$ (M = 438.27 g/mol): C, 71.25; H. 5.29. Found: C, 71.64; H, 5.23.

2-(4-Methoxyphenyl)-4-phenyl-5-methyl-6-(2,3-dimethylphenyl)-pyrylium tetrafluoro-borate (7):

Pyrylium salt 7 was prepared according to the abvove-described procedure from tetrafluoroboric acid (4.0 g, 23.6 mmol, 52% ethereal solution), 4'-methoxychalcone (5.88 g, 24.7 mmol) and 2,3-dimethylpropiophenone **3** (2.00 g, 12.33 mmol) in 10 mL of 1,2-dichloroethane. The pyrylium salt was obtained as a dark orange solid. Yield: 1.89 g (4.04 mmol, 32.8%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 2.24, 2.26, 2.40 (3×s, 3×3H, -CH_3), 3.90 (s, -OCH_3), 7.06 (d, J = 9.0 Hz, 2H), 7.38 (m, 3H), 7.54 (m, 3H), 7.76 (m, 2H), 8.14 (d, J = 9.0 Hz, 2H), 8.23 (s, 1H). ^{19}F NMR ($CDCl_3$): δ (ppm) = -152.93, -152.98 (3:1).

^{13}C NMR (CD_3OD): δ (ppm) = 16.6, 17.1, 20.3 (-CH_3), 56.0 (-OCH_3), 115.9, 119.1, 120.5, 126.6, 128.1, 129.2, 129.3, 129.9, 131.3, 131.8, 133.6, 135.0, 135.7, 138.6, 166.2, 169.7, 170.7, 171.0. Analysis Calcd for $C_{27}H_{25}BF_4O_2$ (M = 468.30 g/mol): C, 69.25; H. 5.38. Found: C, 68.94; H, 5.47.

2-(4-Hydroxyphenyl)-4-phenyl-5-methyl-6-(2,3-dimethylphenyl)-pyrylium bromide (8):

To a solution of **7** (1 g, 2.14 mmol) in CH_2Cl_2 (20 mL) was added dropwise at T = -70 ºC a solution of BBr_3 in CH_2Cl_2 (1M) (11 mL, 11.0 mmol, 5 equiv.). The reaction mixture was slowly warmed up to room temperature and stirring was continued for 18 hours. Subsequently, the dark solution was poured onto ice and the mixture was stirred for 15 min. A small amount of a red precipitate was formed, which was filtered off. The organic phase was separated and dried over $MgSO_4$. The solution was concentrated until a dark red solid was formed, which was filtered off, washed several times with Et_2O and dried under vacuum. Yield: 0.7 g (1.56 mmol), 73 %. An orange solid was obtained by slow recrystallization from isopropanol. ^{1}H NMR ($CDCl_3$): δ (ppm) = 2.25, 2.26, 2.40 (3×s, 3×3H, -CH_3), 7.04 (d, *J* = 9.0 Hz, 2H), 7.38 (m, 3H), 7.57 (m, 3H), 7.72 (d, *J* = 9.0 Hz, 2H), 7.83 (m, 2H), 8.05 (s, 1H, H3), 10.43 (s, br, 1H, -OH). ^{13}C NMR (CD_3OD): δ (ppm) = 15.3, 15.6, 18.8 (-CH_3), 117.0, 118.6, 119.3, 126.1, 127.5, 128.3, 128.7, 128.9, 130.1, 131.4, 133.2, 135.4, 135.9, 138.7, 165.7, 169.1, 170.2, 171.3. Analysis Calcd for $C_{26}H_{23}BrO_2$ (M = 447.37 g/mol): C, 69.80; H. 5.18. Found: C, 69.98; H, 5.21.

2,4-Diphenyl-5-methyl-6-(2,3-dimethylphenyl)-phosphinine (1):

2.74 g (11.0 mmol, 3 equiv.) of $P(SiMe_3)_3$ was added drop wise at room temperature to a stirred solution of **7** (1.6 g, 3.65 mmol) in 15 mL of acetonitrile. The resulting dark reaction mixture was heated to T = 85°C and subsequently refluxed for 6 h. After cooling to room temperature, the volatiles were removed under vacuum. The residue was dissolved in CH_2Cl_2 and added to an appropriate amount of silica gel (ca. 3 g). Evaporation of the solvent was followed by flash chromatography over neutral alumina

with petroleum ether/ethyl acetate (5:1). Yield: 0.45 g (1.23 mmol, 34%) of a yellow solid.

Alternatively, **1** was synthesized from pyrylium salt 7 and $P(CH_2OH)_3$. To a solution of **7** (3.55 g, 8.1 mmol, 1 equiv.) in dry pyridine (20 mL) was added $P(CH_2OH)_3$ (1.8 g, 14.6 mmol, 1.8 equiv.) at room temperature. The solution was heated to T = 125ºC and stirring was continued for 3 h. Subsequently, the orange solution was concentrated to 50% of its original volume and degassed water (5 mL) was added. An orange solid was formed, which was isolated by decanting the liquid layer. The remaining solid was washed with a mixture of water and methanol (each 5 mL, 2×) and subsequently with methanol (5 mL, 1×). The product was dried under vacuum, dissolved in a minimum amount of a mixture of dichloromethane and petroleum ether (50:50) and flash chromatographed over silica with the same solvent mixture to remove traces of pyridine×HBF_4. After removal of the solvents in vacuo phosphinine **1** was obtained as a yellow solid. Yield: 700 mg (1.9 mmol, 24%). ^{1}H NMR (C_6D_6): δ (ppm) = 1.98, 2.04 (2×s, 2×3H, -CH_3), 2.06 (d, $^4J_{H\text{-}P}$ = 2.0 Hz, 3H, -CH_3), 6.96-7.09 (m, 3H), 7.11-7.24 (m, 8H), 7.63-7.68 (m, 2H), 7.95 (d, $^3J_{H\text{-}P}$ = 5.4 Hz, 1H, heteroarom.-H. ^{13}C NMR (C_6D_6): δ (ppm) = 16.5 (-CH_3), 19.2 (-CH3), 20.2 (-CH3), 15.3, 15.6, 18.8 (-CH_3), 125.0, 125.4, 129.2, 129.7, 130.1, 130.5, 133.9 (d,) 134.6 (d), 136.8, 137.4, 138.6 (d), 140.1 (d), 142.7 (d), 143.2 (d), 145.5 (d), 168.6 (d, $^1J_{C\text{-}P}$ = 52.5 Hz, C_α), 173.1 (d, $^1J_{C\text{-}P}$ = 50.6 Hz, C_α'). ^{31}P NMR (C_6D_6): δ (ppm) = 190.5. Analysis Calcd for $C_{26}H_{23}P$ (M = 366.44 g/mol): C, 85.22; H. 6.33. Found: C, 85.48; H, 6.51.

Phosphabarrelene (9):

To a suspension of phosphinine **1** (177.5 mg, 0.484 mmol, 1 equiv.) and magnesium turnings (26.0 mg, 1.07 mmol, 2.2 equiv.) in THF (3 mL) was added dropwise *ortho*-Fluorobromobenzene (178.0 mg, 1.02 mmol, 2.1 equiv.) at room temperature. The mixture was heated to T = 70º C and stirring was continued for 3.5 hours. After cooling down to room-temperature the dark-red solution was quenched with H_2O (0.5 mL) and all volatiles were removed in vacuo. Diethylether (4 mL) and dichloromethane (4 mL) was added and the organic phase was washed three times with H_2O (3×3 mL). The organic

phase was dried with Na_2SO_4 and the solvents were removed in vacuo. The red solid was dissolved in a mixture of petroleum ether and dichloromethane (50:50, 2 mL) and subsequently purified by flash chromatography over silica with the same solvent mixture (40 mL). The solvents were removed in vacuo and **9** was obtained as an orange solid (yield: 74.0 mg, 0.167 mmol, 35%). ^{1}H NMR (C_6D_6): δ (ppm) = 1.88, 1.94, 1.96, 1.99 (9H, -CH3), 6.72-7.25 (m, 13H), 7.56-7.80 (m, 4H), 8.22, 8.23 (2×d, 3JH-P = 5.6, 5.4 Hz, ratio 2:3, 1H, heterocyclic-H) (mixture of stereoisomers). ^{13}C NMR (C_6D_6): δ (ppm) = .16.5, 16.8 (-CH_3), 20.0, 20.2 (-CH_3), 20.8, 21.1 (-CH_3), 66.8, 66.9 (Csp^3-ring), 124.1, 124,3, 130.9, 131.4, 131.6, 132.1, 132.4, 133.4, 133.8, 136.9, 137.1, 138.6, 138.8, 139.0, 139.2, 139.4, 141.4, 141.6, 141.9, 142.0, 143.2, 143.5, 143.8, 144.1, 144.6, 144.8, 145.1, 145.9, 146.2, 152.2 (C-vinyl.), 153.1 (C-vinyl.), 154.6 (C-vinyl.), 155.0 (C-vinyl.), 155.8 (C-vinyl.), 156.2 (C-vinyl.) (mixture of stereoisomers). ^{31}PNMR (C_6D_6): δ (ppm) = -65.0, -66.4 (2:3, mixture of stereoisomers, figure 1). Analysis Calcd for $C_{32}H_{27}P$ (M = 442.54 g/mol): C, 86.85; H. 6.15. Found: C, 86.99; H, 6.23.

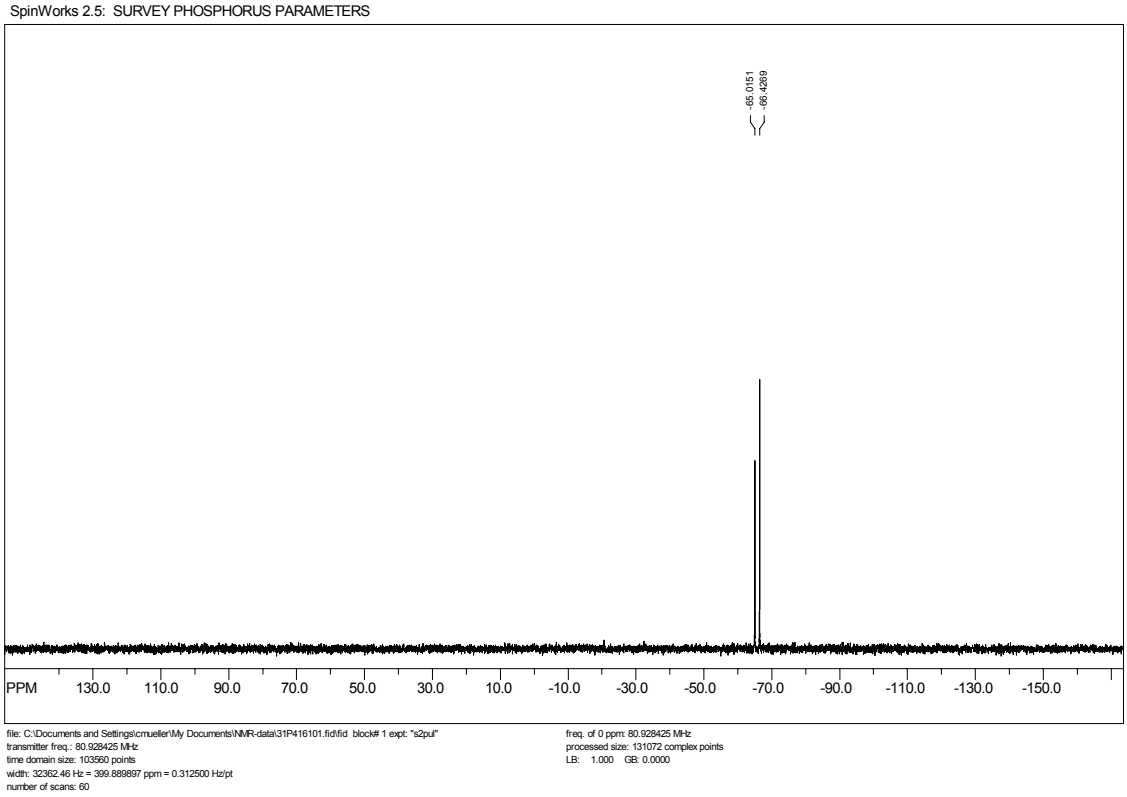

Figure 1: $^{31}P\{^{1}H\}$ NMR spectrum of stereoisomers of **9** at T = 25 ºC (C_6D_6).

Reaction of 9 with (*S*)-[PdCl{$C_6H_4CH(Me)NMe_2$}]$_2$

To a mixture of stereoisomers of **9** (11.1 mg, 0.025 mmol) was added (*S*)-[PdCl{$C_6H_4CH(Me)NMe_2$}]$_2$[4] (8.0 mg, 0.0125 mmol) and C_6D_6 (0.5 mL) at room temperature. An orange solution was formed and the $^{31}P\{^{1}H\}$ NMR spectrum was recorded (figure 2).

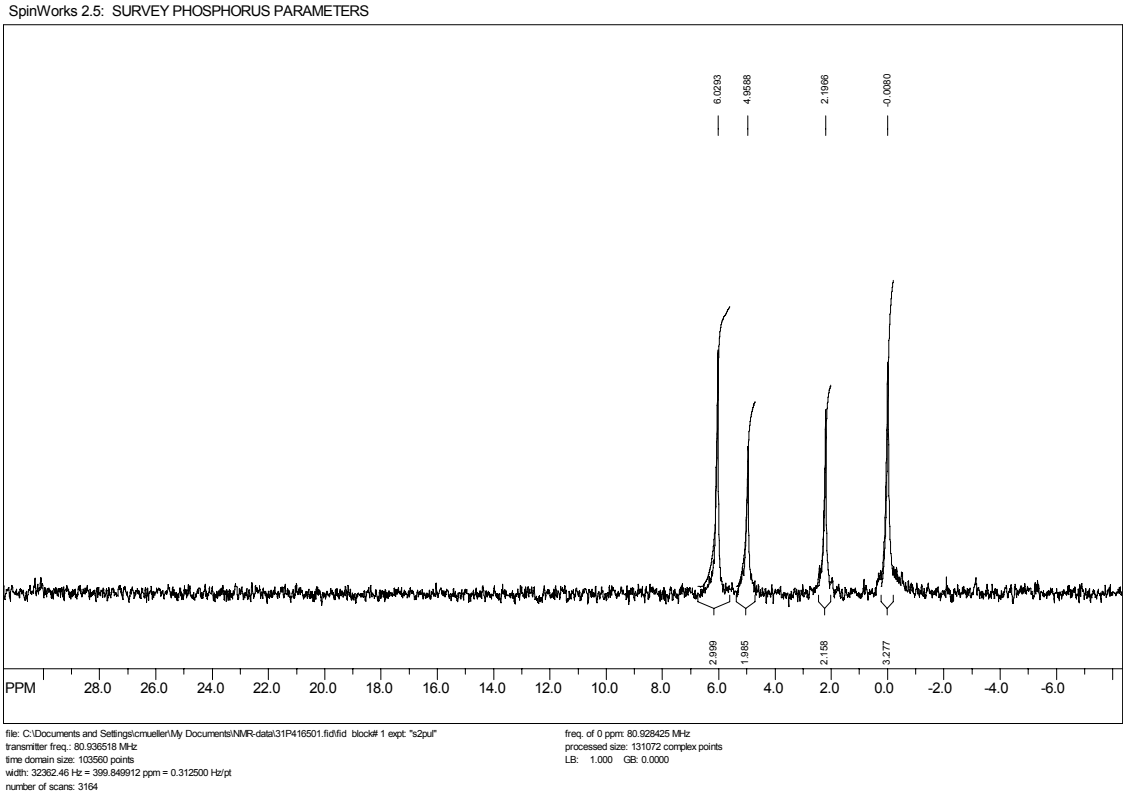

Figure 2: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **9** with (*S*)-$[PdCl\{C_6H_4CH(Me)NMe_2\}]_2$

HPLC Analysis

The HPLC analyses were performed using a Shimadzu LC-20AD Prominence solvent delivery module, conected to a Shimadzu DGU-20A5 Degasser, Spark Holland Marathon autosampler, Shimadzu SPD-20A Prominence UV-VIS-detector (set at 254 nm), and a Chiracel® OD-H column (Chiral Technologies Europe S.A.S., Illkirch-Cedex, France). The samples were eluted with *n*-Hexane at a flow-rate of 1 mL·min^{-1} at T = 20 ºC (t_1 = 19.31 min, t_2 = 23.81 min, figure 3).

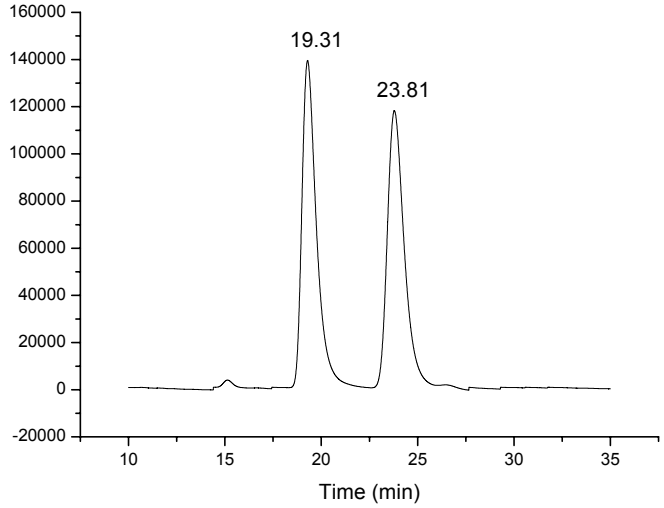

Figure 3: HPLC analysis of phosphinine **1** (Integration: 50.8:49.2).

X-ray crystal structure determination of 8

$[C_{26}H_{23}O_2]Br$, Fw = 447.35, red block, 0.42 x 0.27 x 0.15 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 8.1446(3), b = 18.5721(6), c = 14.4284(7) Å, β = 107.742(3)°, V = 2078.68(14) $Å^3$, Z = 4, D_x = 1.429 g/cm^3, μ = 1.997 mm^{-1}. 27152 Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 $Å^{-1}$ at a temperature of 150(2) K. Intensities were integrated with EvalCCD[5] using an accurate description of the experimental setup for the prediction of the reflection contours. The reflections were scaled and corrected for absorption using the program SADABS[6] (correction range 0.41-0.74). 4756 Reflections were unique (R_{int} = 0.0492), of which 3791 were observed [I>2σ(I)]. The structure was solved with automated Patterson methods using the program DIRDIF[7]. The structure was refined with SHELXL-97[8] against F^2 of all reflections. Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. The OH hydrogen atom was refined freely with isotropic displacement parameters; all other hydrogen atoms were refined with a riding model. 269 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0374/0.0871. R1/wR2 [all refl.]: 0.0545/0.0946. S = 1.047. Residual electron

density between -0.66 and 0.70 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program[9].

Theoretical Calculations:

The quantum-chemical calculations were all carried out within density functional theory using the Gaussian 03[10] program at the B3LYP/6-31G(d) level. Earlier, the hybride B3LYP method was reported to provide excellent descriptions of various reaction profiles and particularly of geometries, heats of reaction, activation energies, and vibrational properties of various molecules.[11] Full geometry optimization with subsequent frequency analysis was preformed for compounds **1,2,9** and for the respective transition state structures corresponding to the internal rotation of the 2,3-dimethylphenyl moiety. All of the minimum energy structures showed no imaginary frequencies, while transition state structures showed only a single imaginary frequency corresponding to the internal rotation around C_α-C_β-bond. All energies obtained from the DFT calculation used for the estimation of activation energies were corrected for the zero-point energies. The frequency calculations also provided us with the thermochemical analysis using the ideal gas approximation at a pressure of 1 atm and a temperature of 298.15 K. The values of $\Delta G^{\#}_{298}$ reported were calculated at these conditions.

The guess structures for the transition states were obtained from the relaxed potential energy surface scan via varying the dihedral angle corresponding to the internal rotation path. The resulting structures were then subject to full geometry optimization. In all cases considered, the low-energy path was the one involving the clockwise rotation of the 2,3-dimethylphenyl moiety in the conformers shown in Figure 1 of the manuscript (i.e. via interaction of the hydrogen atom at the 6 position of the substituted benzene ring and the methyl group at 2 position of the 2,3-dimethylphenyl moiety with, respectively, the lone pair on P-atom and the methyl group of the phosphinine ring).

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