Electronic Supporting Information for

Tunable Coordination of a *Tropos* Phosphite for Fine-Tuning of the Rh Catalyzed Asymmetric Addition of Phenylboronic Acid to Cyclohexenone

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Experimental

Materials. TLC analyses were performed on silica gel 60 sheets; chromatography separations were carried out on adequate dimension columns using silica gel 60 (70-230 mesh). Toluene and dioxane were refluxed over sodium and distilled before the use. Water and the solution of 1M KOH were degassed before the use. Unless otherwise specified the reagents were used without any purification $[Rh\mu Cl(C_2H_4)_2]_2$ was prepared according to literature procedure.[1] Phosphites **1**, **1a** and **1b** were synthesized as described elsewhere[2] and matched the reported characteristics.

NMR Spectroscopy ^1H (300 MHz), ^{13}C (75 MHz) and ^{31}P (121.5 MHz) NMR spectra were recorded in $CDCl_3$,[D_8]toluene or [D_6]benzene on a Varian INOVA-300 spectrometer. The following abbreviations are used: s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet, br = broad. -NMR spectra were recorded at 75 MHz on a Varian INOVA-300 NMR spectrometer. ^1H and ^{13}C-NMR chemical shifts are referred to TMS as external standard. ^{31}P NMR chemical shifts are referred to H_3PO_4 as external standard. The temperature was controlled to ±0.1°C by means of the Varian unity control.

Analyses

Elemental analyses were performed at *Laboratorio di Microanalisi* Faculty of Pharmacy University of Pisa**.** HPLC analyses were performed on a JASCO PU-980 intelligent HPLC pump equipped with a JASCO UV-975 detector. GC analyses were performed on a Perkin-Elmer Autosystem XL chromatograph equipped with a BP-1 dimethyl polysiloxane column (25 m × 0.25 mm × 0.25 μm), using nitrogen as transport gas. Peak identification was performed using independently synthesized samples.

Size exclusion chromatography (SEC) measurements were carried out with a HPLC pump equipped with a 50 μm Rheodyne loop, a Waters 515 oven at 35 °C, and a Waters 2410 refractive index detector. A PL 5 μm gel MIXED-C column was used. Chloroform and 1 mL/min were adopted as the eluent and the elution rate, respectively. Monodispersed polystyrene samples (*M*w 1940, 10 050, 96 000, 483 000, 1 730 000, and 3 065 000) were used for the calibration curve.

Preparation of monosubstituited complex $[Rh\mu Cl(C_2H_4)(1)]_2$

$[Rh\mu Cl(C_2H_4)_2]_2$ (5.78 mg, 0.015 mmol) was added to a solution of **1** (19.94 mg, 0.03 mmol in dry toluene (0.5 mL) under nitrogen atmosphere and the mixture was stirred for 24 h at room temperature. The solvent was removed at reduced pressure affording a yellow powder. Elemental

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[1] R. Cramer, J. A. McCleverty, J. Bray, *Inorganic Syntheses*.1990, **28**, 86.

[2] A. Iuliano, S. Facchetti, G. Uccello-Barretta, *J. Org. Chem.* 2006**, 71**, 4943; A. Iuliano, P. Scafato, *Tetrahedron: Asymmetry*, 2003, **14**, 611

analysis (calc. for $C_{82}H_{110}Cl_2O_{14}P_2Rh_2$): C 59.91% (59.39%), H 6.61% (6.69%), Cl 4.32% (4.28%) P 3.80% (3.74%)

^{1}H-NMR: see figure 3.

^{13}C-NMR (75 MHz, [D_8]toluene, ppm): 173,6; 169,3; 149,7; 130,1; 130,0; 129,8; 129,2; 126,2; 125,4; 123,1; 121,7; 81,1; 75,3; 74,0; 73,9; 52,5; 50,8; 48,0; 46,8; 42,0; 36,0; 35,7; 35,6; 35,1; 34,8; 34,7; 34,4; 34,1; 33,9; 32,7; 32,5; 32,0; 31,1; 28,0; 27,6; 27,4; 27,4; 27,3; 27,2; 27,0; 26,9; 26,8; 26,4; 26,0; 23,9; 23,5; 23,1; 22,9; 22,8; 21,0; 20,9; 19,2; 14,1; 12,4.

Preparation of disubstituited complex $[Rh\mu Cl(1)_2]_2$

$[Rh\mu Cl(C_2H_4)_2]_2$ (5.78 mg, 0.015 mmol) was added to a solution of **1** (39.88 mg, 0.06 mmol) in dry toluene (0.5 mL) under nitrogen atmosphere and the mixture was stirred for 0.5 h at room temperature. The solvent was removed at reduced pressure affording a yellow powder. Elemental analysis (calc. for $C_{156}H_{204}Cl_2O_{28}P_4Rh_2$): C 64.81% (63.99%), H 6.93% (7.02%), Cl 2.49% (2.42%) P 4.31% (4.23%)

^{1}H-NMR: see figure 4.

^{13}C NMR (75 MHz, [D_6]benzene, ppm): 173.6; 169.5; 150.8; 150.6; 131.0; 130.5; 129.6; 129.1; 128.6; 127.0; 126.8; 126.5; 125.5; 125.3; 80.4; 74.6 (3-C bearing to one species); 74.9 (3-C bearing to the other species); 50.8; 47.3; 47.1; 46.1;46.0; 42.2; 39.9; 36.4; 35.1;34.1; 33.0; 31.8; 31.3; 28.2; 27.9; 26.6; 24.4; 23.5; 22.8; 21.2; 20.8; 12.4.

General procedure for the asymmetric Rh(I) catalyzed addition of phenylboronic acid to cyclohexenone

(R)-3-phenylcyclohexan-1-one 2

Under nitrogen atmosphere 1,4-dioxane (1 mL) was added to $[Rh\mu Cl(C_2H_4)_2]_2$. (1.5 mol %) and **1** (3 or 6 mol %). The mixture was stirred for 30 min (1:1 Rh:**1** catalyst) or 24 h (1:2 Rh:**1** catalyst) and then water (0.1 mL), 1M KOH (0.5 mL), phenylboronic acid (2 eq) and 2-cyclohexen-1-one (1 mmol) were added. The mixture was stirred at 25°C and the reaction was monitored by GC. After complete conversion, the mixture was poured into 1 M $NaHCO_3$ and extracted three times with diethyl ether. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and evaporated to yield the crude product. Chromatography on silica gel (hexane:EtOAc 70:30) gave (R)-3-phenylcyclohexan-1-one (**2**) as a colorless oil.[3]

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.73-1.89 (m, 2H); 2.07-2.13 (m, 2H); 2.34-2.59 (m, 4H); 2.95 (m, 1H); 7.08-7.44 (m, 4H); 7.54 (m, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ): 25.5; 32.7; 41.1; 44.7; 48.9; 126.5; 126.7; 128.6; 144.3; 211.0.

The e.e. was determined by HPLC analyses on Chiralcel OD-H, 220 nm, 1.0 mL/min, hexane–2-propanol 99:1, , t_R = 15.43 min (S), 16.97 min (R)[4]

(1R,3R)-1,3-diphenylcyclohexanol 3

Under nitrogen atmosphere 1,4-dioxane (1 mL) was added to [RhμCl(C_2H_4)$_2$]$_2$. (1.5 mol %) and **1** (3 or 6 mol %). The mixture was stirred for 30 min (1:1 Rh:**1** catalyst) or 24 h (1:2 Rh:**1** catalyst) and then water (0.1 mL), 1M KOH (0.5 mL), phenylboronic acid (3 eq) and 2-cyclohexen-1-one (1 mmol) were added. The mixture was stirred at 60°C and the reaction was monitored by GC. After complete conversion, the mixture was poured into 1 M $NaHCO_3$ and extracted three times with diethyl ether. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and evaporated to yield the crude product. Chromatography on silica gel (hexane:EtOAc 70:30) gave (1R,3R)-1,3-diphenylcyclohexanol (**3**) as a colorless oil.[5]

^{1}**H-NMR** (300 MHz, $CDCl_3$, δ): 1.45-1.62 (m, 1H); 1.80-2.15 (m, 7H); 3.11-3.23 (m, 1H); 7.18-7.39 (m, 8H); 7.54-7.60 (m, 2H).

^{13}**C-NMR** (75 MHz, $CDCl_3$, δ): 22.5; 33.4; 38.5; 39.8; 46.8; 74.1;124.6; 126.3; 127.1; 127.2; 128.5; 128.6; 146.9; 149.5.

The e.e. was determined by HPLC analyses on Chiralcel OD-H, 220 nm, 1.0 mL/min, hexane–2-propanol 95:5, T=25°C, t_R = 10.87 min (1S,3S), 19.54 min (1R,3R).[5]

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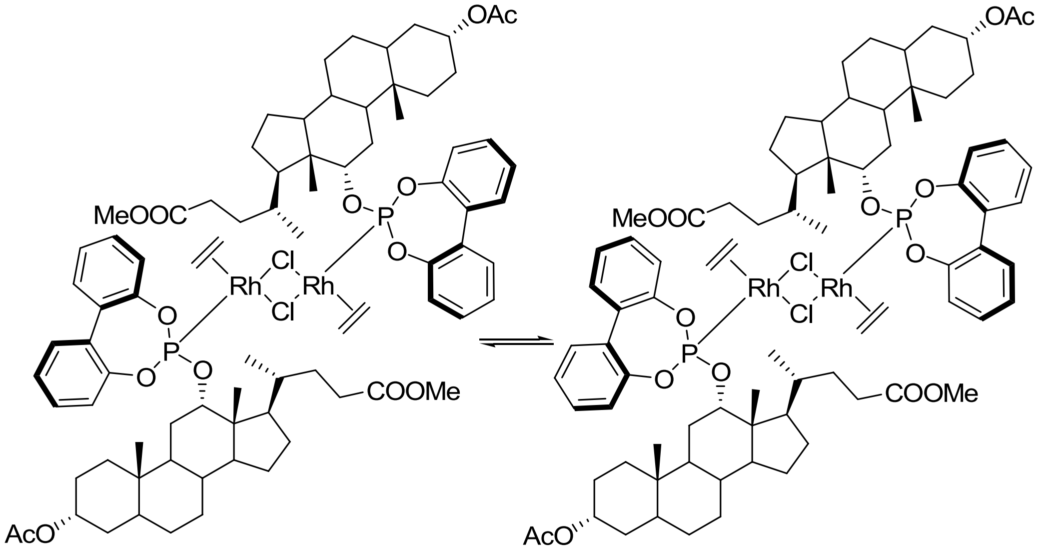
[3] Y. Takaya, M. Ogasawara, T. Hayashi, *J. Am .Chem. Soc.* 1998, **120**, 5579.

[4] P. Kasak, V. B. Arionb, M. Widhalma, *Tetrahedron: Asymmetry* 2006, **17**, 3084.

[5] K. Vandyck, B. Matthys, M. Willen, K. Robeyns, L. Van Meervelt, J. Van der Eycken, *Org. Lett.* 2006, **8**, 363.



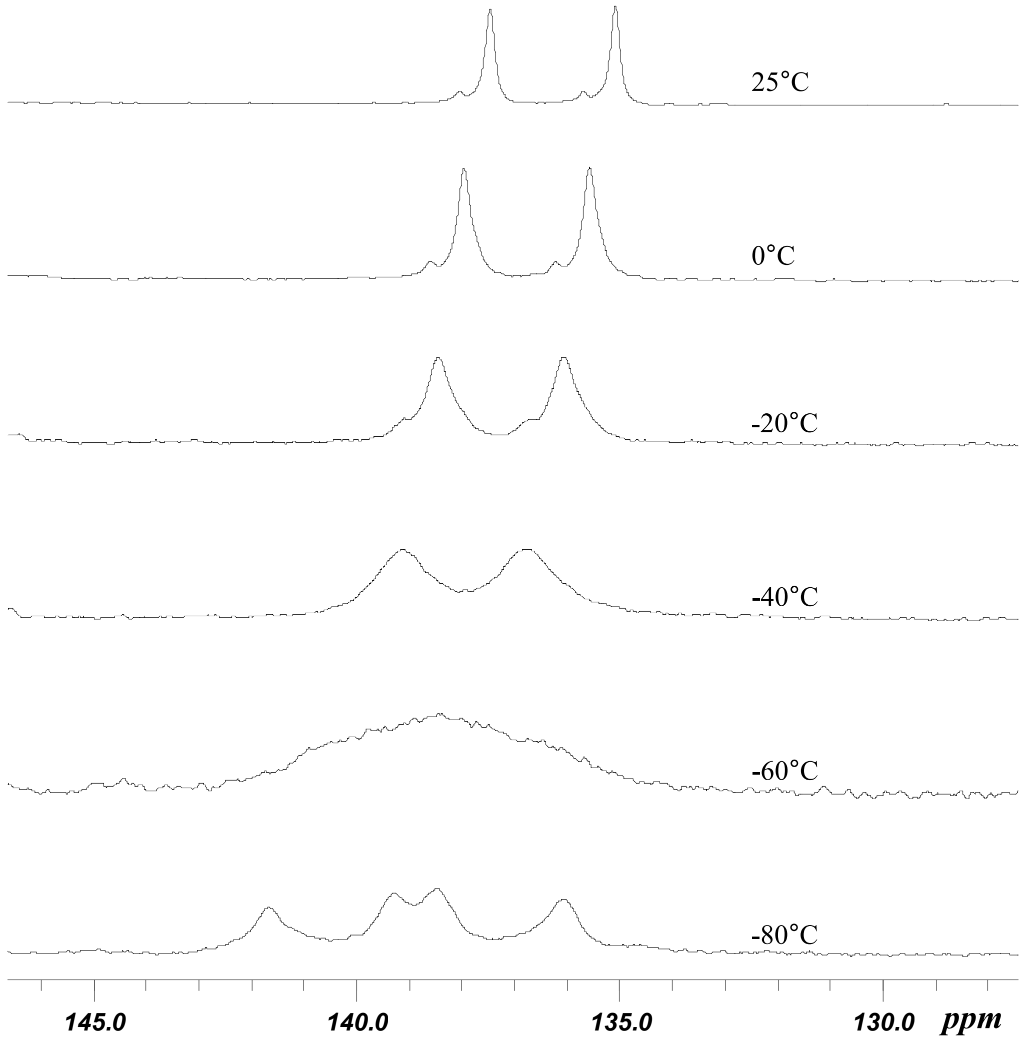


Figure S1. *VT* ^{31}P NMR spectra (121.4 MHz,[D$_8$]toluene) of the monosubstituted complex $[\mathrm{Rh}\mu\mathrm{Cl}(\mathrm{C_2H_4})(\mathbf{1})]_2$

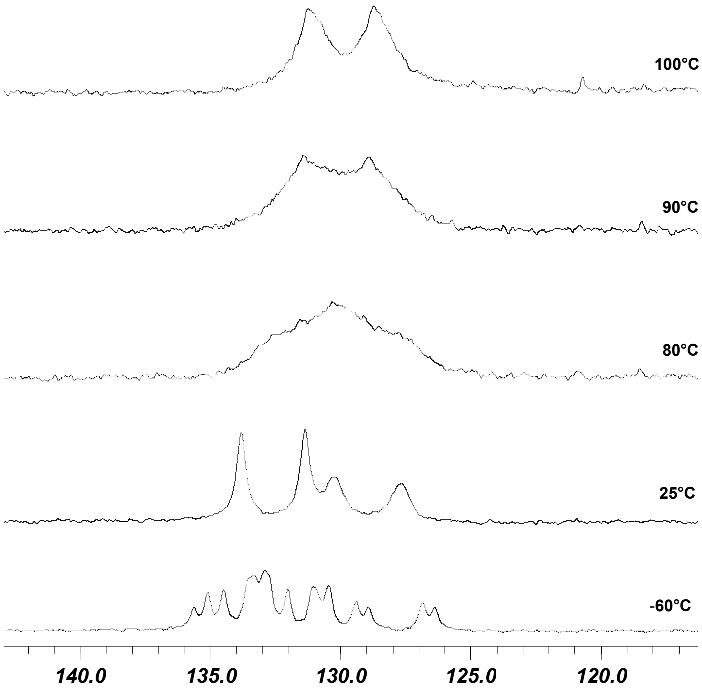


Figure S2. *VT* ^{31}P NMR spectra (121.4 MHz, [D$_8$]toluene) of the disubstituted complex **1**/[RhμCl(C$_2$H$_4$)$_2$]$_2$.

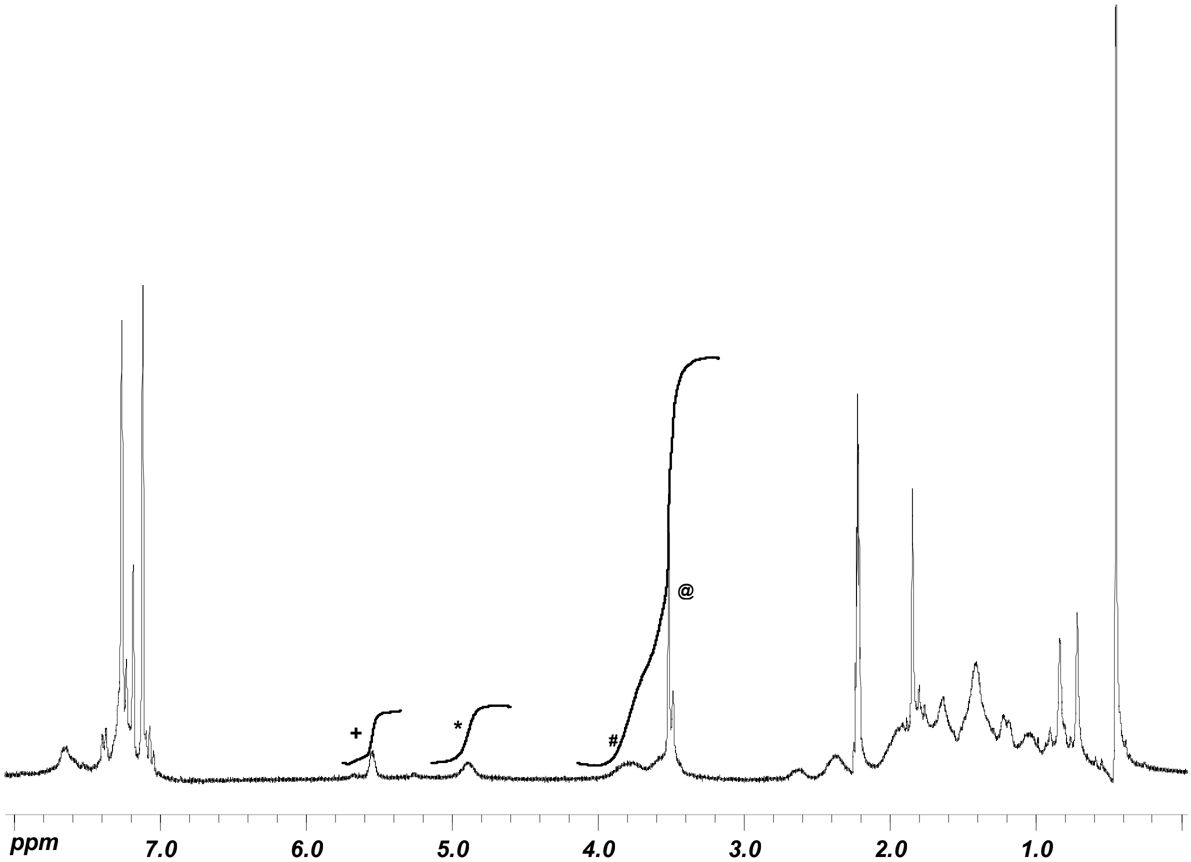


Figure S3. ^{1}H NMR spectrum (300 MHz, [D$_8$]toluene of the monosubstituted complex [RhμCl(**1**) (C$_2$H$_4$)]$_2$. (+) = 12-C$\underline{H}$; (*) = 3-C\$$\underline{H}$; (#)= coordinated ethene (attribution was been made by CO ligand exchange that caused disappearance of this signal while a singlet at 5.21 ppm due to free ethene came out); (@) = OC$\underline{H}_3$.

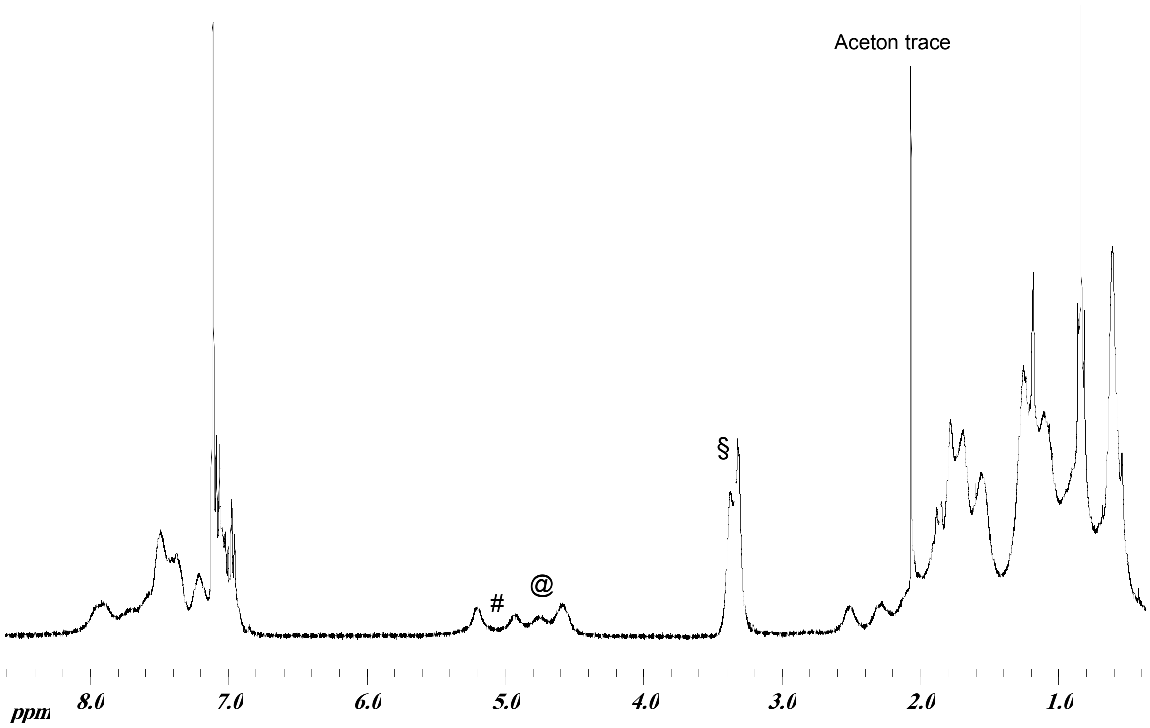


Figure S4. ^{1}H NMR spectrum (300 MHz, [D$_6$]benzene, 25 °C) of slow equilibrating species of the disubstituted complex **1**/[RhμCl(C_2H_4)$_2$]$_2$: (#) = 12-C$\underline{H}$; (@) = 3-C$\underline{H}$; (§) = OC$\underline{H}_3$.

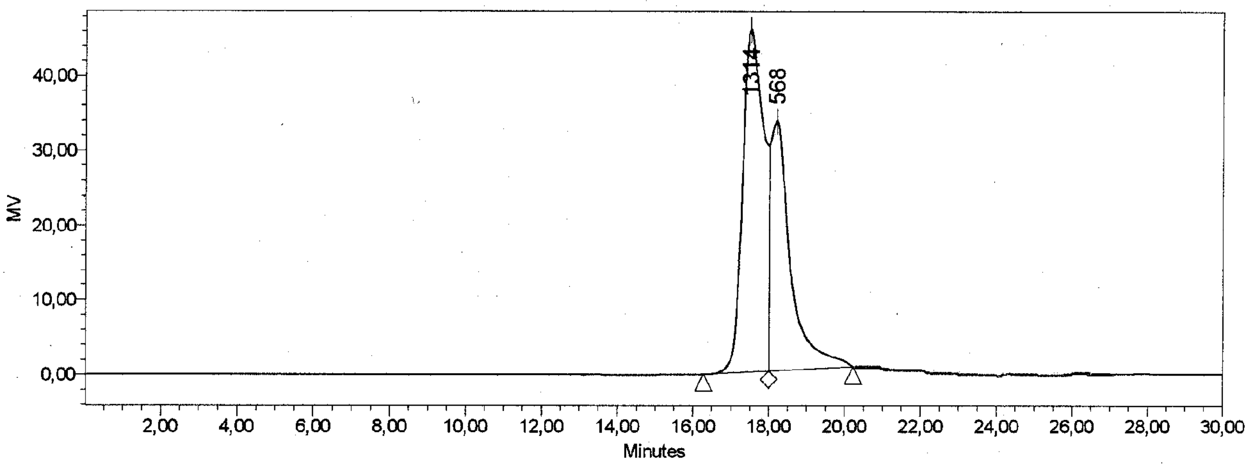


Figure S5: SEC chromatogram (polystyrene standard) of slow equilibrating species of the disubstituted complex **1**/[RhµCl$(C_2H_4)_2]_2$. Numeric values are not the real values of the molecular weight, due to the use of polystyrene as standard