

Supporting Information

## **How Solvents Affect the Stability of Cationic Rh(I) Diphosphine Complexes: A Case Study of Acetonitrile Coordination**

Nora Jannsen,<sup>\*a</sup> Christian Fischer,<sup>b</sup> Carmen Selle,<sup>a</sup> Cornelia Pribbenow,<sup>a</sup> Hans-Joachim Drexler,<sup>a</sup>  
Fabian Reiß,<sup>a</sup> Torsten Beweries,<sup>\*a</sup> Detlef Heller<sup>\*a</sup>

<sup>a</sup> Leibniz Institut für Katalyse e.V., Albert-Einstein-Straße 29a, 18059 Rostock, Germany.

<sup>b</sup> Universität Greifswald, Institut für Biochemie, Felix Hausdorff-Straße 4, 17489 Greifswald, Germany.

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## Experimental

### General

All manipulations were carried out using standard Schlenk techniques under oxygen- and moisture-free conditions. MeOH was dried over magnesia, MeCN over calcium hydride and freshly distilled under argon prior to use. THF was distilled from sodium benzophenone ketyl prior to use. Deuterated solvents (CD<sub>3</sub>OD and CD<sub>3</sub>CN) were dried over calcium hydride, distilled under argon and the oxygen was removed in six freeze-thaw-pump cycles. [Rh(acac)(NBD)], [Rh(acac)(COD)] (Sigma Aldrich, 99%), [Rh(DUANphos)(NBD)]BF<sub>4</sub> (gifted by Xumu Zhang), BINAP (Strem, 98%), DIOP (Strem, 99.5%), DIPAMP (Strem, 98%), DPEphos(TCI, 98%), DPPE (Fluka, 99%) and DPPP (Fluka, 97%) were used as received.

### UV-vis spectroscopic measurements

#### Dip Optrode/Cary Spectrometer

All [Rh(PP)(NBD)]BF<sub>4</sub> exchange reactions were investigated under anaerobic conditions using a Cary 4000 spectrometer (Varian) connected to a fiber-optical sensor in a temperature controlled vessel (298 K).

#### Stopped flow/diode array

For the fast COD-MeCN exchanges, a J&M Tidas MMS/100-1 diode array and a Bio-Logic  $\mu$ -SFM-20 stopped flow unit were used. A wavelength range from 360-500 nm was detected, with an integration time of 32 ms per spectrum. The complex concentration was varied from 2.50 to 6.70 mmolL<sup>-1</sup>, and the MeCN concentration from 1.19 to 6.33 molL<sup>-1</sup>. Spectra were obtained at 283, 288, 298 and 308 K.

### NMR Spectroscopy

#### High Field NMR Spectroscopy

<sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on Bruker 300 Fourier and AV400 spectrometers at room temperature (297-298 K) or at low temperature (203-273 K). Chemical shifts ( $\delta$ ) are reported in parts per million (ppm), internally referenced to the chosen deuterated solvent and externally referenced, respectively, to tetramethylsilane (TMS) for <sup>1</sup>H NMR or 85% H<sub>3</sub>PO<sub>4</sub> solution for <sup>31</sup>P NMR. Coupling constants are given in Hertz (Hz). All <sup>31</sup>P NMR spectra were recorded with proton decoupling.

#### Low Field NMR Spectroscopy

The low field NMR measurements were performed on a Magritek Spinsolve 80. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm), internally referenced to the chosen deuterated or non-deuterated solvent. Shimming was performed before each experiment on 90% deuterated water.

#### Static measurements

<sup>31</sup>P NMR (128 or 256 scans; 154 ppm bandwidth; 40 ppm centre frequency; 15 s repetition time; 90° pulse angle; with NOE; with proton decoupling).

#### Reaction monitoring

<sup>31</sup>P NMR (128 scans; 154 ppm bandwidth; 40 ppm centre frequency; 15 s repetition time; 90° pulse angle; with NOE; with proton decoupling).

### Synthesis of Diolefin Complexes

#### General Procedure for Synthesis of [Rh(PP)(diolefin)]BF<sub>4</sub> Complexes

All [Rh(PP)(diolefin)]BF<sub>4</sub> (PP=BINAP, DPPE, DPPP, DIOP, DPEphos; diolefin=COD, NBD) complexes were synthesised according to the synthesis developed by Schrock and Osborn.<sup>1</sup> 0.1 mmol [Rh(acac)(diolefin)] was dissolved in 5 mL thf and cooled to -78 °C. A solution of 0.1 mmol PP in thf was added dropwise to the cooled complex solution. After one hour, 100  $\mu$ L HBF<sub>4</sub> were added and the mixture was stirred at -78 °C for further 30 min. The solution was layered with diethyl ether and the resulting crystals washed three times with diethyl ether and dried in vacuum.

## Synthesis of Solvate Complexes

### General Procedure for Synthesis of [Rh(PP)(solvate)<sub>2</sub>]BF<sub>4</sub> Complexes

[Rh(PP)(diolefin)]BF<sub>4</sub> (0.01 mmol) were dissolved in 1.0 mL of solvent and hydrogenated for a precise prehydrogenation time.<sup>2</sup> The hydrogen was removed in six freeze-thaw-pump cycles.

### Synthesis of [Rh(BINAP)(MeCN)<sub>2</sub>]BF<sub>4</sub>

[Rh(BINAP)(NBD)]BF<sub>4</sub> (45.2 mg, 0.05 mmol) was dissolved in 2.0 mL of MeOH. The orange solution was hydrogenated for 5 min and the hydrogen was removed in six freeze-thaw-pump cycles. The solvent was removed in vacuum and the oily residue was dissolved in 1.0 mL of thf. 20  $\mu$ L (0.4 mmol) of MeCN were added turning the red solution yellow. Small yellow needles grew overnight, suitable for X-ray analysis.

<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN): 7.85-7.78 (4H, m); 7.70 (4H, br s); 7.64-7.60 (4H, m); 7.54 (6H, ddt); 7.50-7.40 (2H, m); 7.36 (2H, ddd); 7.04 (2H, ddd); 6.88-6.80 (2H, m); 6.77-6.69 (4H, m); 6.55-6.49 (2H, m); 1.65-1.82 (CH<sub>3</sub>CN, br s).

<sup>31</sup>P NMR (122 MHz, CD<sub>3</sub>CN): 44.7 ( $J_{P-Rh}$  = 177 Hz).

### Synthesis of [Rh(DPEphos)(MeCN)<sub>2</sub>]BF<sub>4</sub>

[Rh(DPEphos)(COD)]BF<sub>4</sub> (16.7 mg, 0.02 mmol) was dissolved in 5 mL of MeOH. The yellow solution was hydrogenated for 150 s. From the deep red solution, the hydrogen was removed in six freeze-thaw-pump cycles. The solution was dried in vacuum and the oily residue was dissolved in 1.0 mL of thf. MeCN (10  $\mu$ L, 0.2 mmol) was added turning the red solution yellow. Small yellow needles grew overnight, suitable for X-ray analysis.

<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN): 7.58-7.48 (8H, m); 7.47-7.37 (10H, m); 7.37-7.30 (2H, m); 6.96-6.93 (2H, m); 6.93-6.85 (4H, m); 6.69-6.61 (2H, m); 1.65-1.82 (CH<sub>3</sub>CN, br s).

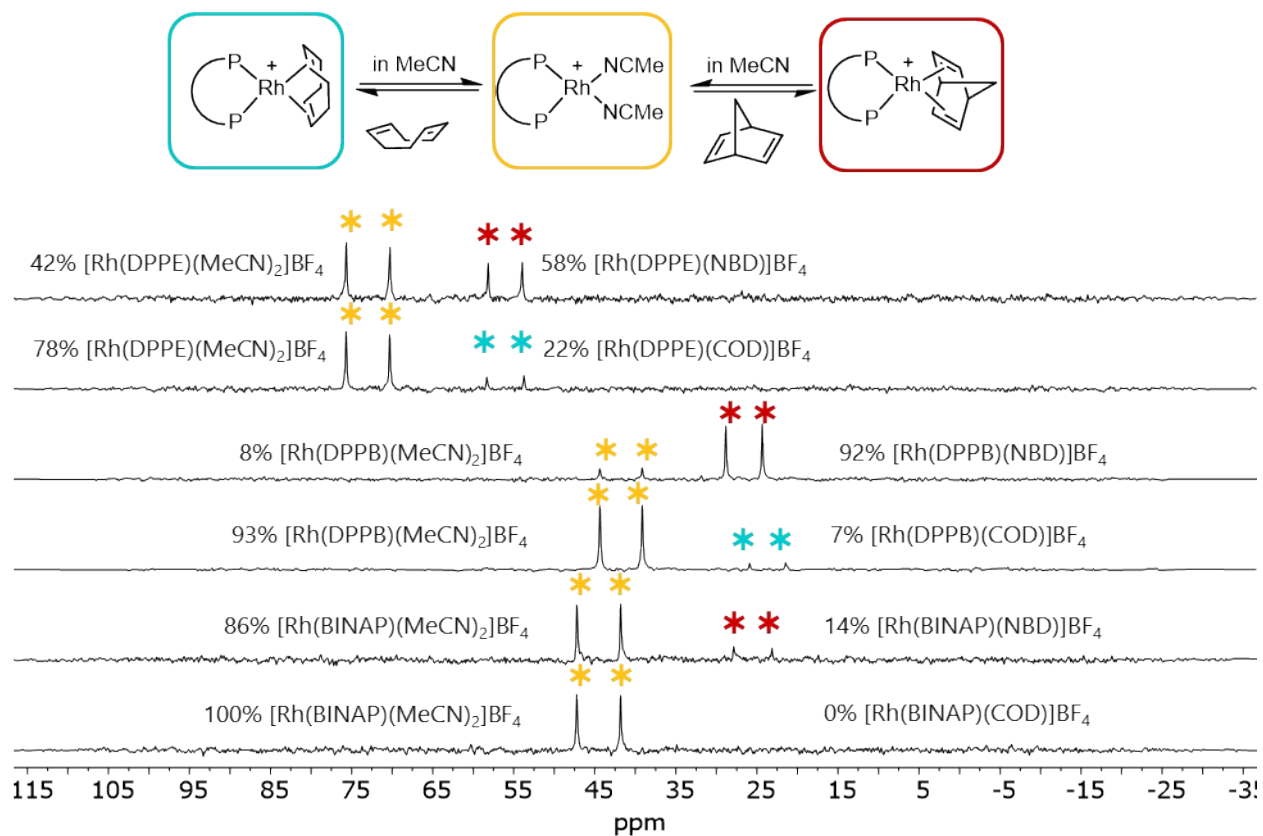
<sup>31</sup>P NMR (122 MHz, CD<sub>3</sub>CN): 34.4 ( $J_{P-Rh}$  = 181 Hz).

### Synthesis of the Catalyst Substrate Complex [Rh(DIPAMP)(MAC)]BF<sub>4</sub>

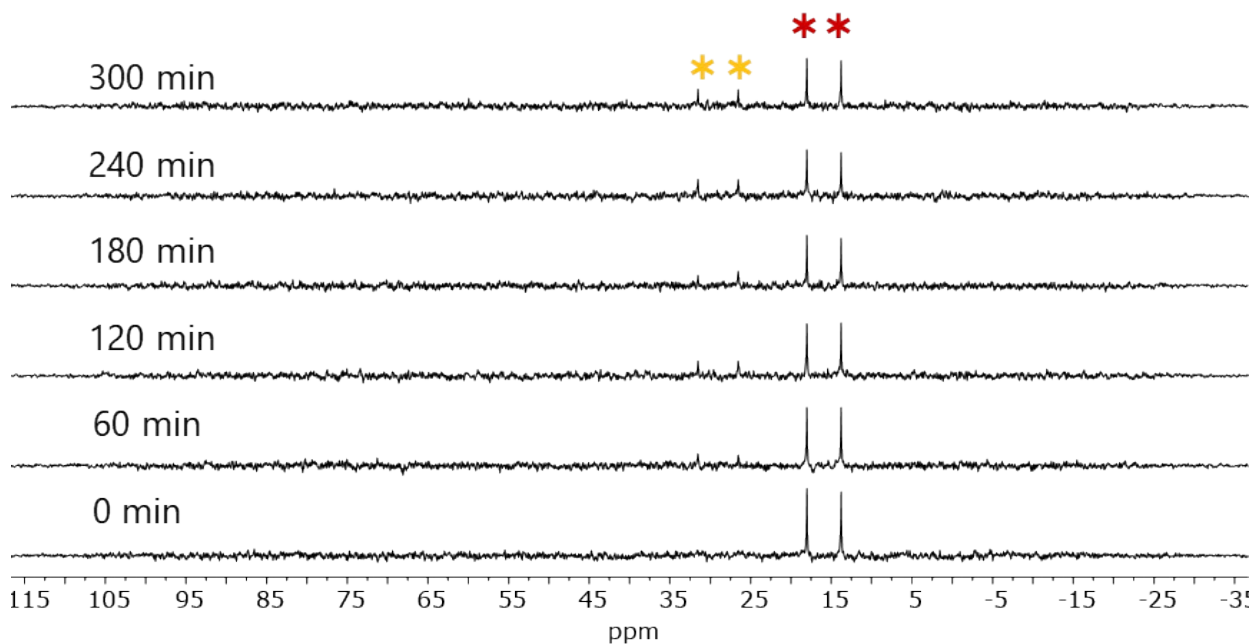
[Rh(DIPAMP)(MAC)]BF<sub>4</sub> was synthesised according to the procedure established by Heller *et al.*<sup>3</sup> [Rh(DIPAMP)BF<sub>4</sub>]<sub>2</sub> (13.0 mg, 0.01 mmol) and methyl *Z*- $\alpha$ -acetamidocinnamate (MAC, 21.9 mg, 0.1 mmol) were dissolved in 1.0 mL of *i*PrOH and layered with 5 mL of diethyl ether. Dark red single crystals were formed overnight.

<sup>31</sup>P NMR (122 MHz, CD<sub>3</sub>OD): major: 70.9 (dd,  $J_{P-Rh}$  = 161 Hz,  $J_{P-Rh}$  = 39 Hz), 47.4 (dd,  $J_{P-Rh}$  = 150 Hz,  $J_{P-Rh}$  = 39 Hz); minor: 68.8 (dd,  $J_{P-Rh}$  = 156 Hz,  $J_{P-Rh}$  = 36 Hz), 44.0 (dd,  $J_{P-Rh}$  = 160 Hz,  $J_{P-Rh}$  = 37 Hz).

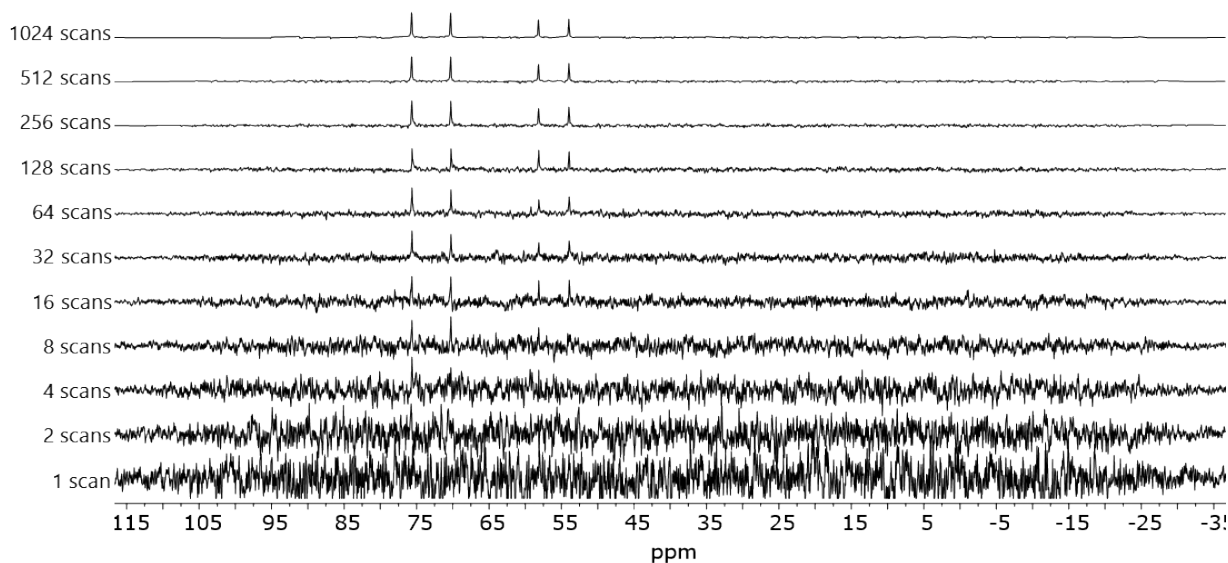
## Additional Figures and Tables



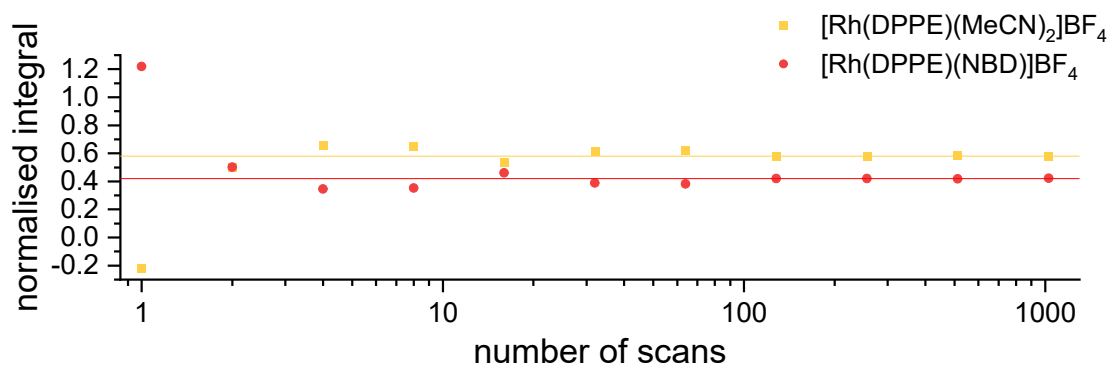
**Figure S 1:** LF  $^{31}\text{P}$  NMR (33 MHz, 297 K) spectra of different diolefin complexes  $[\text{Rh}(\text{PP})(\text{diolefin})]\text{BF}_4$  (diolefin = NBD, COD) in MeCN.



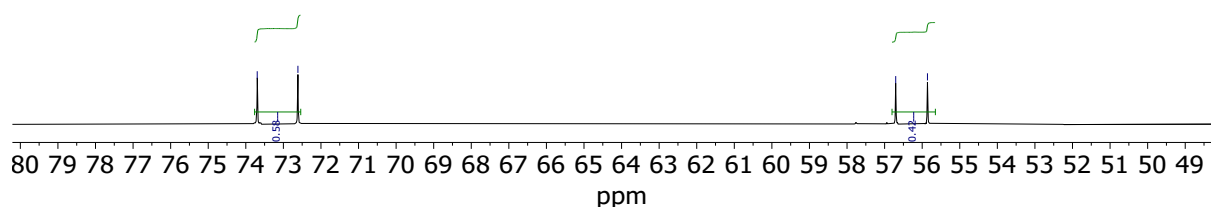
**Figure S 2:** LF  $^{31}\text{P}$  NMR (33 MHz, 297 K) monitoring of the reaction of  $0.01 \text{ mmol } [\text{Rh}(\text{DPPP})(\text{NBD})]\text{BF}_4$  in  $1.0 \text{ mL MeCN}$  forming 32% of  $[\text{Rh}(\text{DPPP})(\text{MeCN})_2]\text{BF}_4$ .



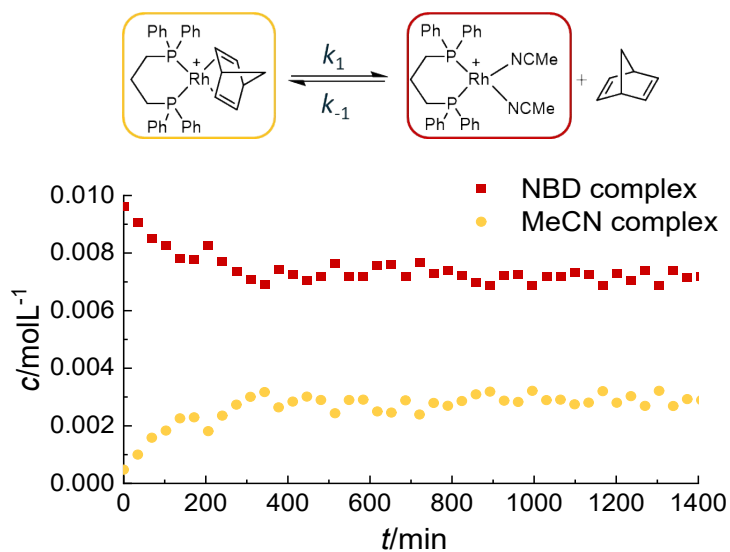
**Figure S 3:** Variation of scans from 1-1024 for 0.07 mmol  $[\text{Rh}(\text{DPPE})(\text{NBD})]\text{BF}_4$  in 0.7 mL  $\text{MeCN-}d_3$  (33 MHz, 297 K).



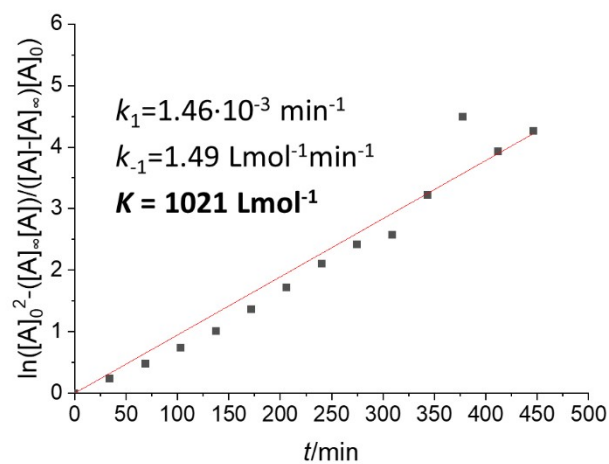
**Figure S 4:** Normalised integrals from the spectra in **Figure S 3**, the straight lines represent the normalised integrals from  $^{31}\text{P}\{^1\text{H}\}$  quant (Figure S 3).



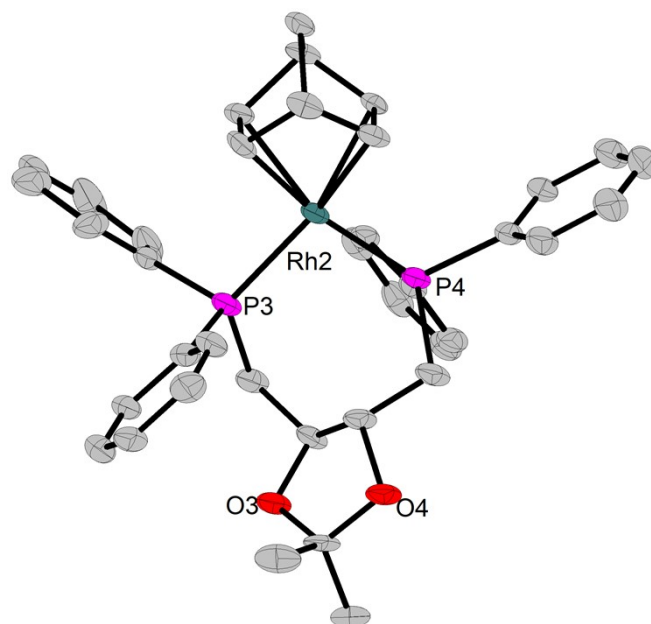
**Figure S 5:** High field (162 MHz, 297 K)  $^{31}\text{P}\{^1\text{H}\}$  quant NMR spectrum for validation of integrals in LF (33 MHz) NMR spectra.



**Figure S 6:** Concentration-time plot of the reaction of 0.01 mmol  $[\text{Rh}(\text{DPPP})(\text{NBD})]\text{BF}_4$  \* in 1.0 mL MeCN followed by LF  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy (33 MHz, 297 K). Concentrations are calculated from the ratios in  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra.

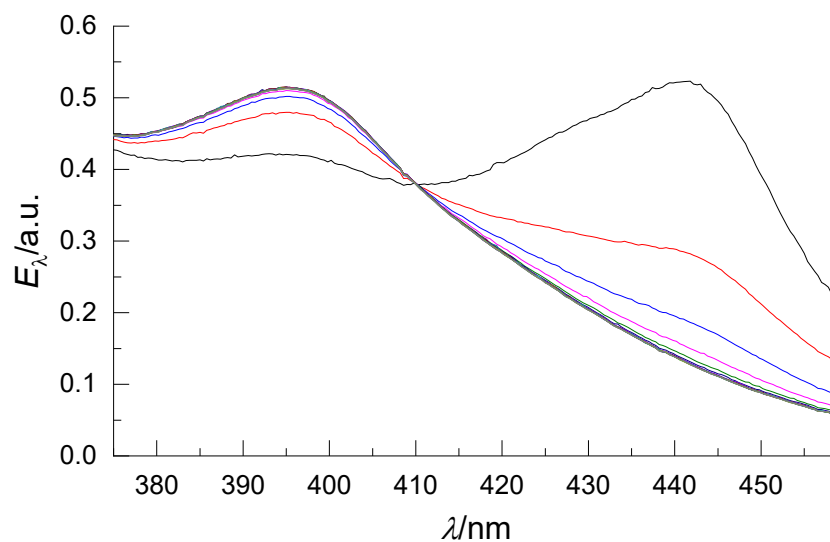


**Figure S 7:** Linearisation of LF  $^{31}\text{P}\{^1\text{H}\}$  NMR (33 MHz, 297 K) spectroscopic reaction monitoring.

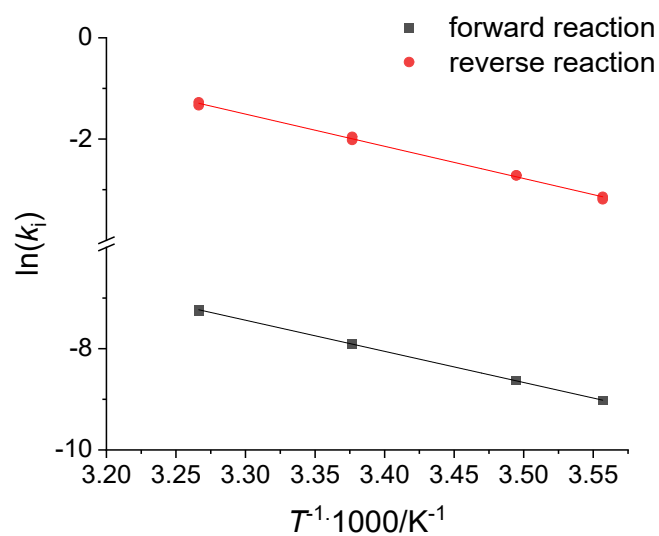


**Figure S 8:** Molecular structure of  $[\text{Rh}(\text{S,S})\text{-DIOP}(\text{NBD})]\text{BF}_4$  (ellipsoid representations, 30%). One  $[\text{Rh}(\text{S,S})\text{-DIOP}(\text{NBD})]^+$  molecule, hydrogen atoms, residual solvent molecules and  $\text{BF}_4^-$  anion are omitted for clarity. Selected bond lengths and angles: Rh2-P3 2.326(2) Å, Rh2-P4 2.296(2) Å, P3-Rh2-P4 94.73(7)°.

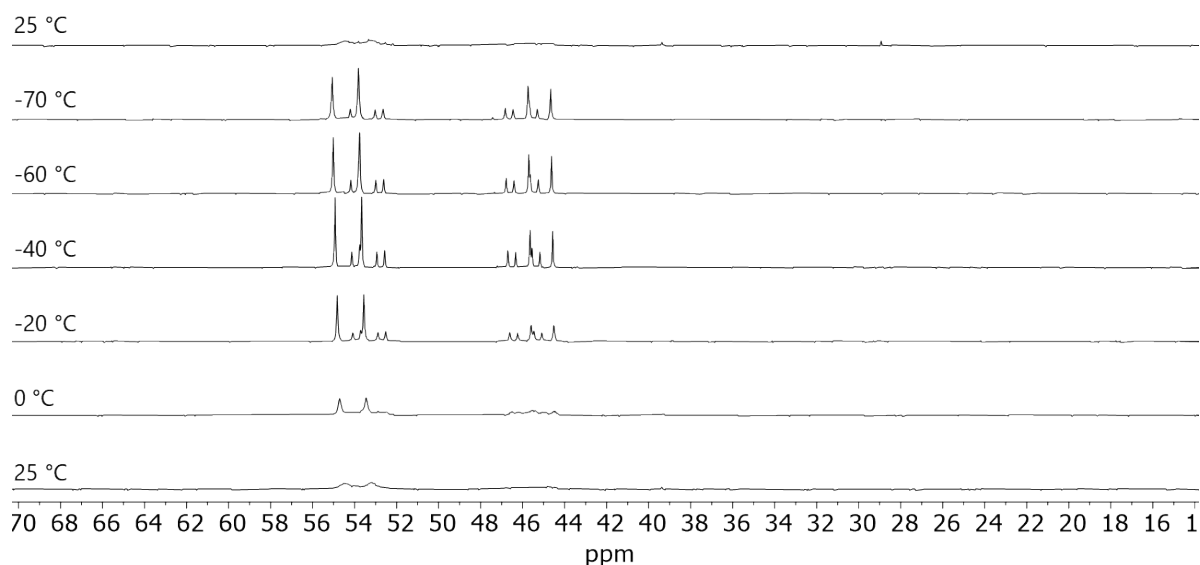




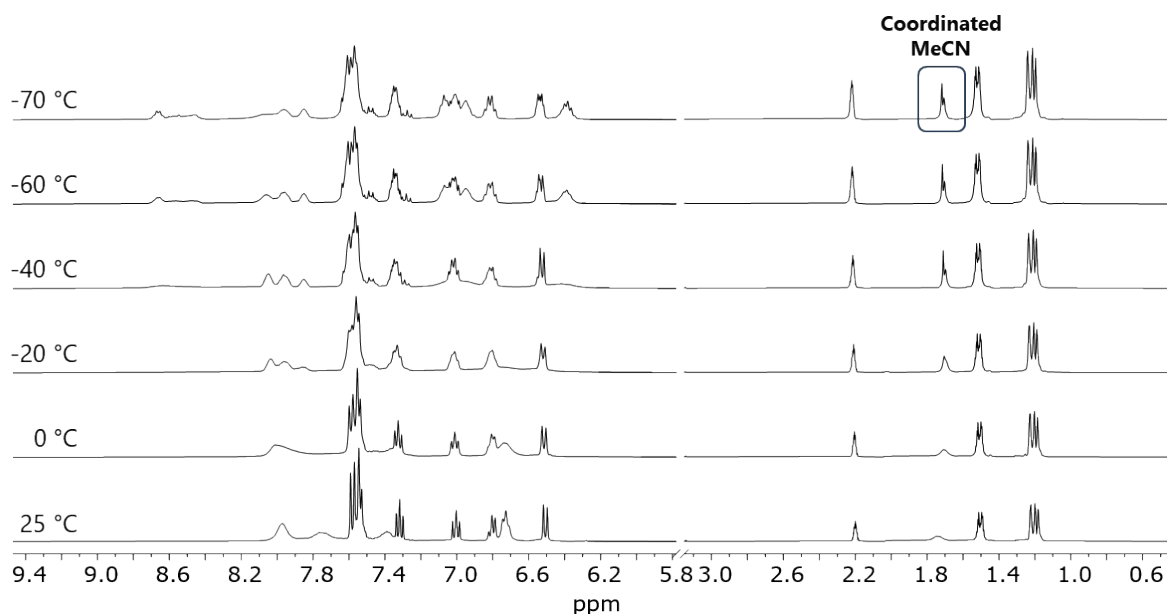
**Figure S 9:** UV-vis spectra of  $[\text{Rh}(\text{DIOP})(\text{COD})]\text{BF}_4$  in MeCN (25 °C) followed with a dip optrode setup.



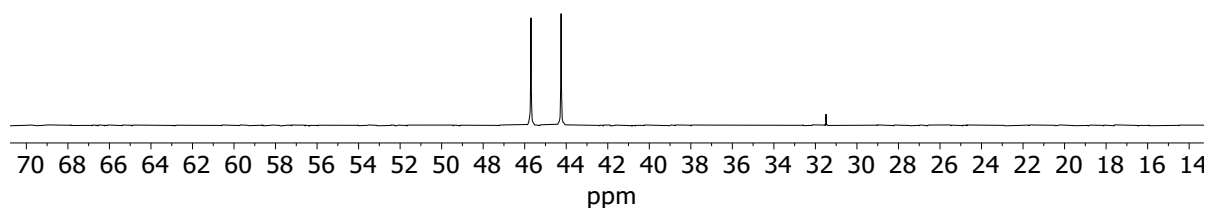
**Figure S 10:** Arrhenius plot of the forward and reverse rate constant of the reaction  $[\text{Rh}(\text{DIOP})(\text{COD})]\text{BF}_4 \rightleftharpoons [\text{Rh}(\text{DIOP})(\text{MeCN})_2]\text{BF}_4 + \text{COD}$ .



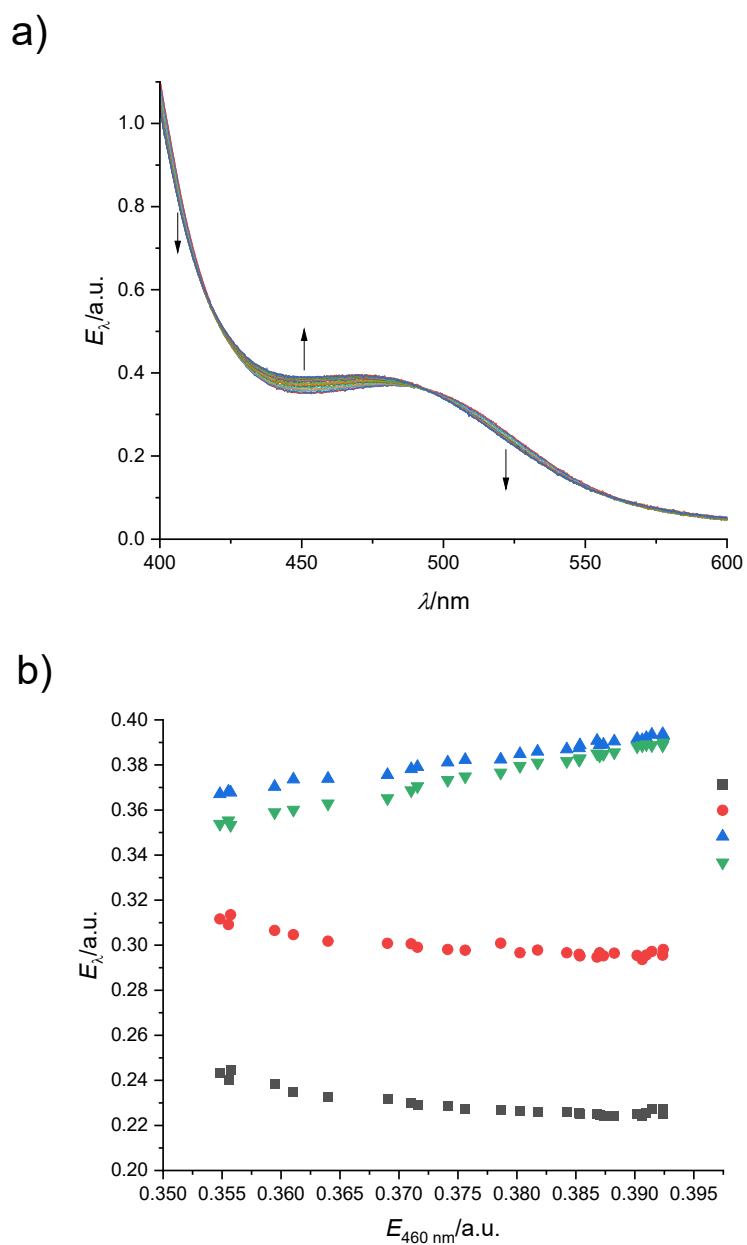
**Figure S 11:**  $^{31}\text{P}$  NMR spectra (162 MHz) of  $[\text{Rh}(\text{BINAP})(\text{MeOH})_2]\text{BF}_4 + 1 \text{ MeCN}$  at different temperatures (bottom to top: cooling down from 25 °C to -70 °C, last spectrum after warming to room temperature).



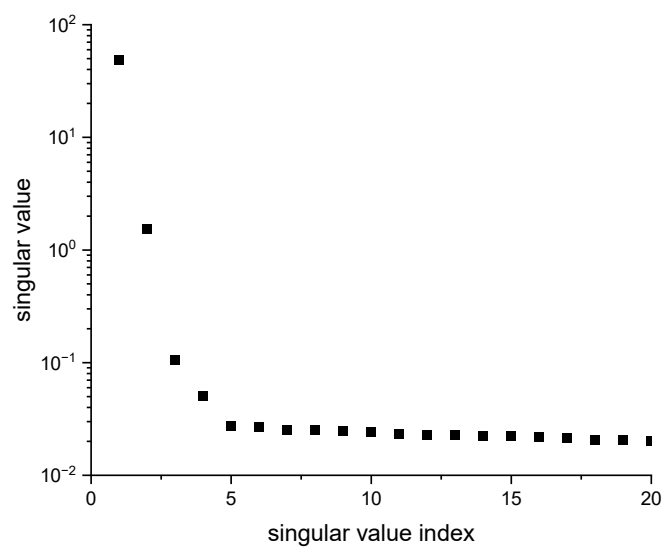
**Figure S 12:**  $^1\text{H}$  NMR spectra (400 MHz) at different temperatures (25 °C to -70 °C). The coordinated MeCN is marked with a blue frame.



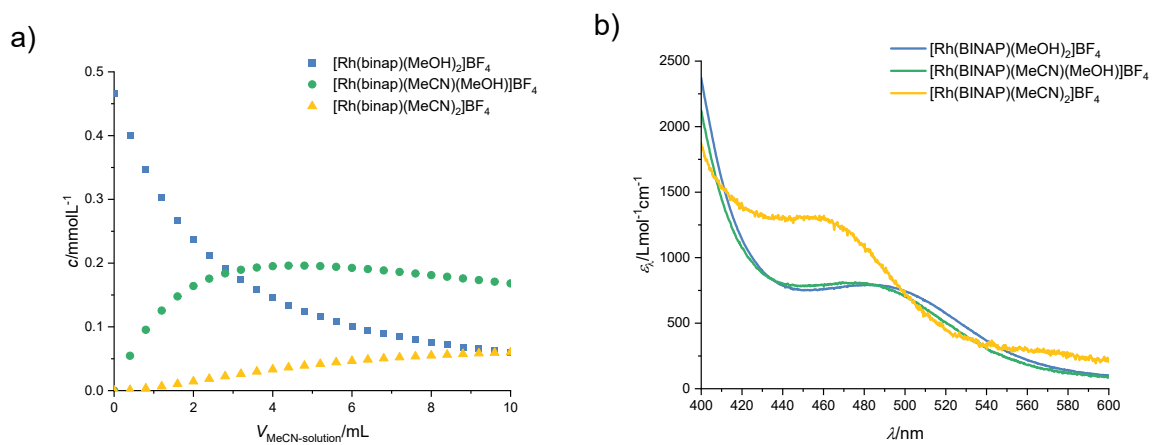
**Figure S 13:**  $^{31}\text{P}$  NMR spectra (122 MHz) of  $[\text{Rh}(\text{BINAP})(\text{MeOH})_2]\text{BF}_4 + 1 \text{ MeCN}$  after further addition of MeCN.



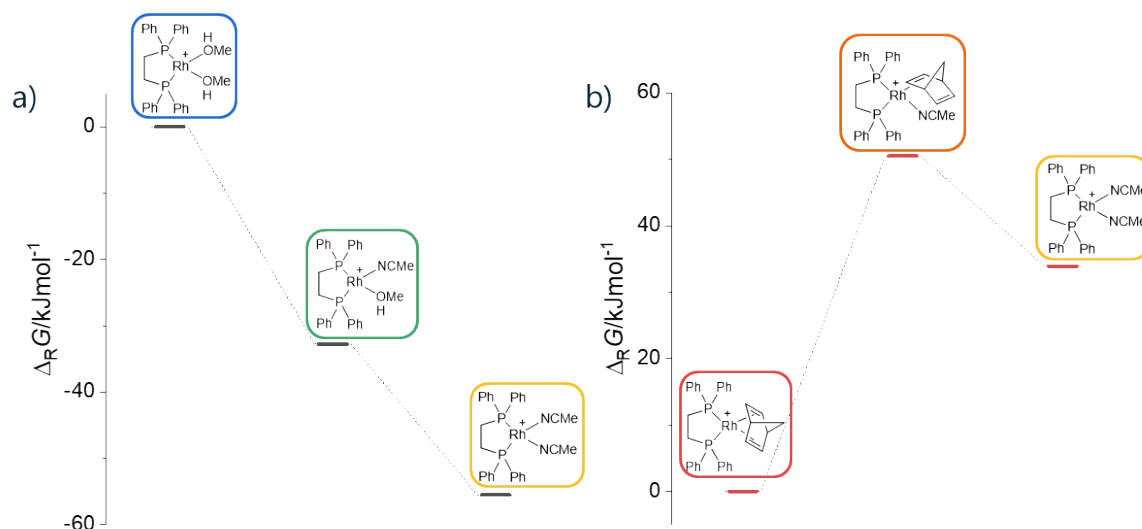
**Figure S 14:** (a) Corrected (regarding dilution) reaction spectra and (b) extinction diagram of the titration of  $0.470 \text{ mmol}\cdot\text{L}^{-1}$   $[\text{Rh}(\text{BINAP})(\text{MeOH})_2]\text{BF}_4$  with a  $7.49 \text{ mM}$  solution of MeCN in MeOH at  $25^\circ\text{C}$ .



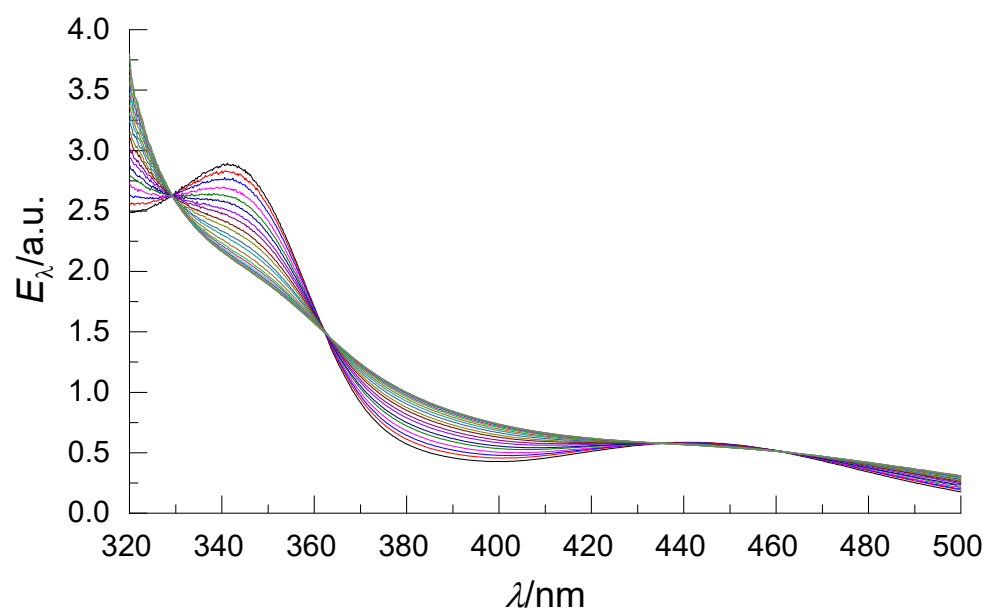
**Figure S 15:** Singular value decomposition of the UV-vis spectroscopic titration (Figure S15).



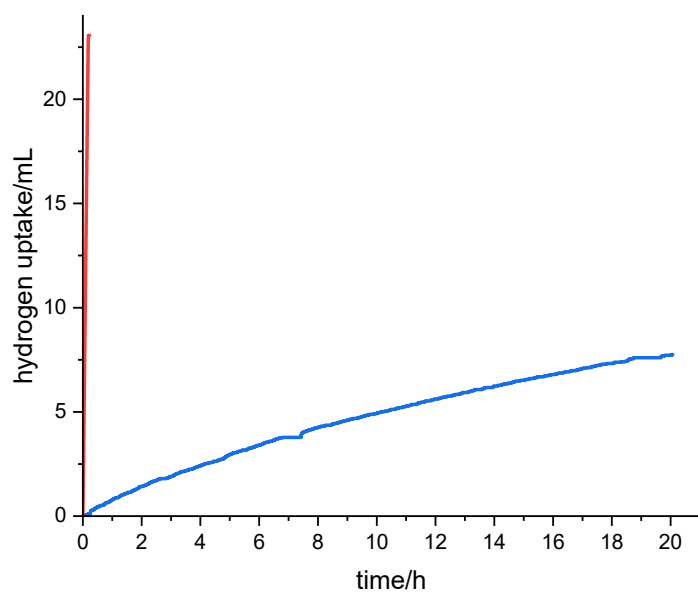
**Figure S 16:** (a) Concentration profile during the titration of  $[\text{Rh}(\text{BINAP})(\text{MeOH})_2]\text{BF}_4$  with MeCN (see Figure S15) and (b) pure component spectra of all Rh containing species.



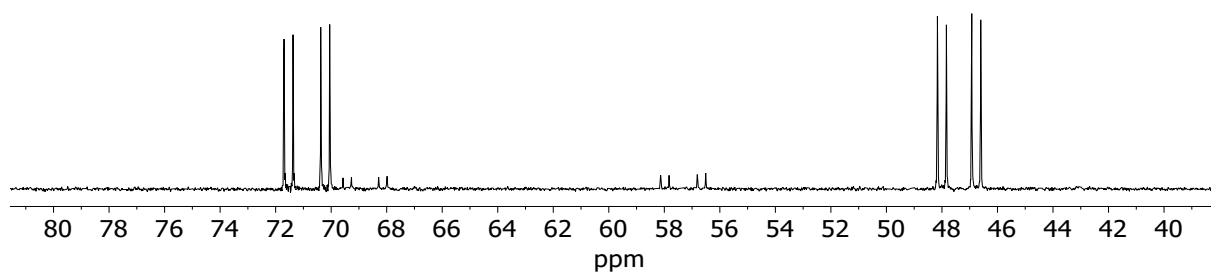
**Figure S 17:** Gibbs free energy profile for the reaction of a)  $[\text{Rh}(\text{DPPE})(\text{MeOH})_2]^+$  \* and b)  $[\text{Rh}(\text{DPPE})(\text{NBD})]^+$  \* with MeCN (b3lyp/def2svp/gd3bj/SMD=MeOH//b3lyp/def2tzvp/gd3bj/SMD=MeOH).



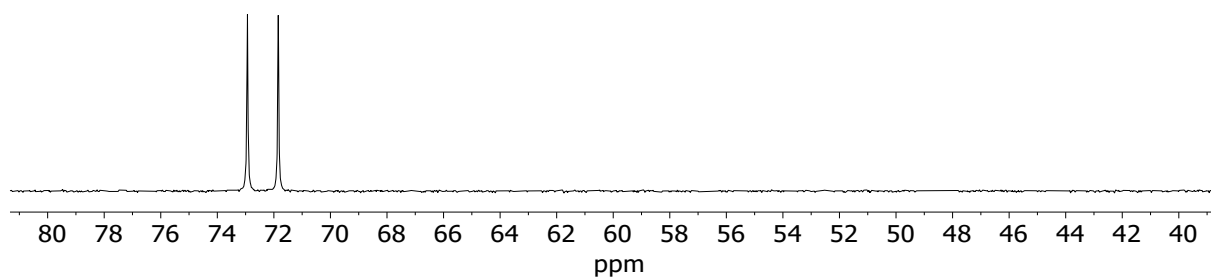
**Figure S 18:** Adjusted UV-vis spectra of the titration of  $6.8 \cdot 10^{-3}$  mmol  $[\text{Rh}(\text{DIPAMP})(\text{MeOH})_2]\text{BF}_4$  in 16.65 mL with a  $4.3 \cdot 10^{-3}$  M solution (100  $\mu\text{L}$  each step) of MAC at 25 °C.



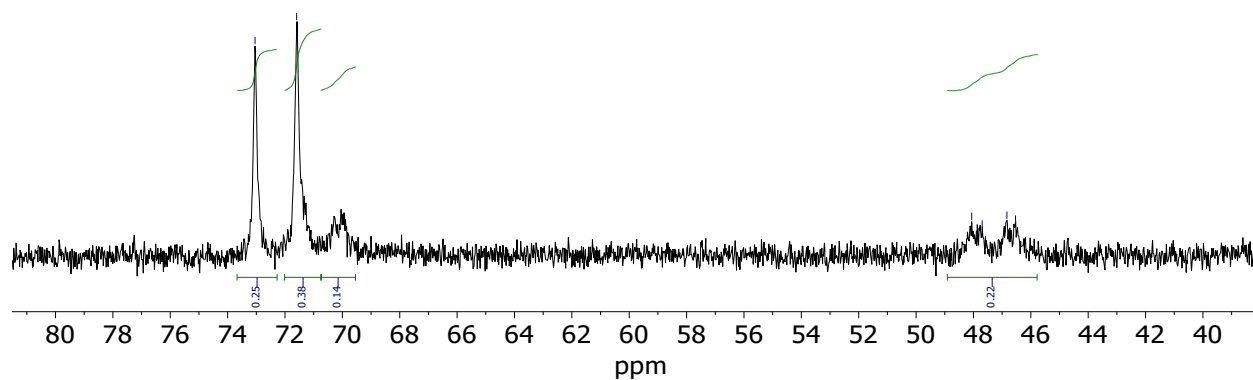
**Figure S 19:** Hydrogenation of 1.00 mol MAC with 0.01 mmol  $[\text{Rh}(\text{DIPAMP})(\text{solvent})_2]\text{BF}_4$  in different volumetric ratios of MeOH and MeCN. red: conversion in 15 mL MeOH, blue: in 7.5 mL MeOH/7.5 mL MeCN.



**Figure S 20:**  $^{31}\text{P}$  NMR spectrum (122 MHz, 297 K) of  $[\text{Rh}(\text{DIPAMP})(\text{MAC})]\text{BF}_4$  as major and minor complex in  $\text{MeOH-}d_4$ .

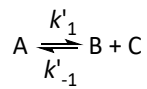


**Figure S 21:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (122 Hz, 297 K) of the conversion of 0.01 mmol  $[\text{Rh}(\text{DIPAMP})(\text{MeOH})_2]\text{BF}_4$  with 1.00 mmol MAC in 0.5 mL  $\text{MeOH-}d_4$  and 0.5 mL  $\text{MeCN-}d_3$ .



**Figure S 22:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (122 Hz, 297 K) of the conversion of 0.01 mmol  $[\text{Rh}(\text{DIPAMP})(\text{MeOH})_2]\text{BF}_4$  with 1.00 mmol MAC and 1.05 mmol MeCN.

## Derivation of Equation 4



$\frac{dX}{dt}$

$$= X = k_1([A]_0 - X) - k_{-1}X^2 = k_1[A]_0 - X(k_1 + k_{-1}X)$$

$$\Delta E_\lambda = E_{\lambda,t} - E_{\lambda,0} = l(e_{\lambda,A}([A] - [A]_0) + e_{\lambda,B}([B] - [B]_0) + e_{\lambda,C}([C] - [C]_0))$$

$$= l(e_{\lambda,A}(-X) + e_{\lambda,B}(X) + e_{\lambda,C}(X))$$

$$= l(X)(-e_{\lambda,A} + e_{\lambda,B} + e_{\lambda,C})$$

$$X = \frac{E_{\lambda,t} - E_{\lambda,0}}{l(-e_{\lambda,A} + e_{\lambda,B} + e_{\lambda,C})}$$

in which  $Q_\lambda = l(-e_{\lambda,A} + e_{\lambda,B} + e_{\lambda,C})$

$$\frac{d}{dt} \frac{E_{\lambda,t} - E_{\lambda,0}}{Q_\lambda} = k_1[A]_0 - k_1X - k_{-1}X^2 = k_1[A]_0 - k_1 \left( \frac{E_{\lambda,t} - E_{\lambda,0}}{Q_\lambda} \right) - k_{-1} \left( \frac{E_{\lambda,t} - E_{\lambda,0}}{Q_\lambda} \right)^2$$

$$\frac{d}{dt} (E_{\lambda,t} - E_{\lambda,0}) = k_1[A]_0 Q_\lambda - k_1 (E_{\lambda,t} - E_{\lambda,0}) - \frac{k_{-1}}{Q_\lambda} (E_{\lambda,t} - E_{\lambda,0})^2$$

$$E_{\lambda,t} - E_{\lambda,0} = k_1[A]_0 Q_\lambda (t - t_0) - \frac{k_{-1}}{Q_\lambda} \int_{t_0}^t (E_{\lambda,t} - E_{\lambda,0})^2 dt$$

with  $\zeta = k_1[A]_0 Q_\lambda$ ;  $\zeta_1 = k_1$  and  $\zeta_2 = k_{-1} Q_\lambda^{-1}$ :

$$E_{\lambda,t} - E_{\lambda,0} = \zeta \int_{t_0}^t (E_{\lambda,t} - E_{\lambda,0}) dt - \zeta_2 \int_{t_0}^t (E_{\lambda,t} - E_{\lambda,0})^2 dt$$

$X$	extent of reaction
$t$	time
$k$	rate constant
$[A], [B], [C]$	concentration
$E_\lambda$	extinction
$\varepsilon_\lambda$	extinction coefficient
$l$	path length of the beam of light through the material sample



## Comparison of Evaluation Methods for UV-vis Spectroscopic Data

Other possibilities represent the singular value decomposition (SVD)<sup>4</sup> with further solution of the factorisation problem as well use of the program ReactLab™ Kinetics.<sup>5</sup> Table S1 compares the results of all three methods for the measurement shown in Table S1. To our delight, only minor differences for the rate constants of the forward and reverse reaction could be observed. It can thus be concluded that all three methods can be equally used to evaluate the present reactions.

**Table S1:** Comparison of different methods for analysis of the UV-vis spectroscopic monitoring of the reaction of [Rh(DPPP)(NBD)]BF<sub>4</sub> in MeCN (Figure 3). For one experiment rate constants  $k_1$  and  $k_{-1}$  and the corresponding  $K'_{\text{NBD complex}}$  are listed.

	$k_1/\text{min}^{-1}$	$k_{-1}/\text{Lmol}^{-1}\text{min}^{-1}$	$K' = k_1 / \text{Lmol}^{-1}$
<b>ζ method</b>	$1.87 \cdot 10^{-3} \pm 9.80 \cdot 10^{-7}$	$1.30 \pm 2.64 \cdot 10^{-3}$	694
<b>SVD</b>	$1.88 \cdot 10^{-3} \pm 1.21 \cdot 10^{-6}$	$1.26 \pm 6.05 \cdot 10^{-5}$	668
<b>ReactLab™ Kinetics</b>	$1.87 \cdot 10^{-3} \pm 1.08 \cdot 10^{-6}$	$1.28 \pm 2.49 \cdot 10^{-3}$	685

## X-Ray Structure Elucidation

X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at low temperature. Diffraction data were collected at 150(2) K on a Bruker Kappa APEX II Duo diffractometer using Mo-K $\alpha$  radiation [Rh(DPEphos)(MeCN)<sub>2</sub>]BF<sub>4</sub> or Cu-K $\alpha$  radiation [Rh(BINAP)(MeCN)<sub>2</sub>]BF<sub>4</sub> or at 200(2) K on a STOE-IPDS diffractometer using Mo-K $\alpha$  radiation [Rh(DIOP)(NBD)]BF<sub>4</sub>. The structures were solved by iterative (SHELXT)<sup>6</sup> or direct methods (SHELXS-97)<sup>7</sup> and refined by full matrix least square techniques against F<sup>2</sup> (SHELXL-2014)<sup>8</sup>. Semi-empirical absorption corrections were applied (SADABS/Bruker or X-SHAPE/Stoe).<sup>9</sup> The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed into theoretical positions and were refined by using the riding model. Contributions of solvent molecules were removed in [Rh(DIOP)(NBD)]BF<sub>4</sub> and [Rh(BINAP)(MeCN)<sub>2</sub>]BF<sub>4</sub> from the diffraction data with PLATON / SQUEEZE.<sup>10</sup> DIAMOND (Crystal Impact GbR) was used for structure representations.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk

**Table S1:** Crystallographic details of [Rh(BINAP)(MeCN)<sub>2</sub>]<sub>2</sub>BF<sub>4</sub>, [Rh(DPEphos)(MeCN)<sub>2</sub>]<sub>2</sub>BF<sub>4</sub> and [Rh(DIOP)(NBD)]<sub>2</sub>BF<sub>4</sub>.

Compound	[Rh(BINAP)(MeCN) <sub>2</sub> ] <sub>2</sub> BF <sub>4</sub>	[Rh(DPEphos)(MeCN) <sub>2</sub> ] <sub>2</sub> BF <sub>4</sub>	[Rh(DIOP)(NBD)] <sub>2</sub> BF <sub>4</sub>
Chem. Formula	C <sub>48</sub> H <sub>38</sub> BF <sub>4</sub> N <sub>2</sub> P <sub>2</sub> Rh	C <sub>40</sub> H <sub>34</sub> BF <sub>4</sub> ON <sub>2</sub> P <sub>2</sub> Rh·C <sub>4</sub> H <sub>8</sub> O	C <sub>38</sub> H <sub>40</sub> O <sub>2</sub> BF <sub>4</sub> P <sub>2</sub> Rh
Formula weight [g/mol]	894.46	882.45	780.36
Colour	yellow	yellow	red
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub>
<i>a</i> [Å]	11.3861(5)	9.0262(7)	18.996(4)
<i>b</i> [Å]	12.0671(5)	29.400(2)	11.954(2)
<i>c</i> [Å]	16.2841(7)	15.1648(12)	18.381(4)
$\alpha$ [°]	90	90	90
$\beta$ [°]	93.728(3)	98.944(2)	118.24(3)
$\gamma$ [°]	90	90	90
<i>V</i> [Å <sup>3</sup> ]	2232.66(17)	3975.4(5)	3677.1(16)
<i>Z</i>	2	4	4
$\rho_{\text{calcd.}}$ [g/cm <sup>3</sup> ]	1.331	1.474	1.410
$\mu$ [mm <sup>-1</sup> ]	4.190	0.569	0.604
<i>T</i> [K]	150(2)	150(2)	200(2)
Measured reflections	42099	90110	51868
Independent reflections	6603	8315	14148
Reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	6048	6527	10891
<i>R</i> <sub>int</sub>	0.0670	0.0678	0.0336
<i>F</i> (000)	912	1808	1600
<i>R</i> <sub>1</sub> ( <i>R</i> [ <i>F</i> <sup>2</sup> >2 $\sigma$ ( <i>F</i> <sup>2</sup> )])	0.0363	0.0344	0.0387
w <i>R</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> )	0.0885	0.0840	0.0978
GooF	1.072	1.062	1.002
No. of Parameters	517	553	824
CCDC #	2176529	2176531	2176530

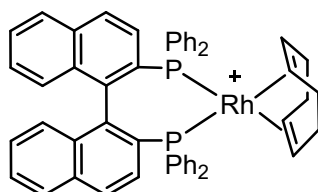
## DFT Calculated Structures and Energies

### General

All calculations were performed in Gaussian 16.<sup>11</sup> The optimisations were carried out using the b3lyp method,<sup>12</sup> the def2svp<sup>13</sup> basis set and gd3bj<sup>14</sup> empirical dispersion, followed by a single point calculation using a def2tzvp<sup>13</sup> basis set (b3lyp/gd3bj). Moreover, the SMD<sup>15</sup> correction was applied for MeCN or MeOH. Vibrational frequencies were also calculated (def2svp) to include the zero-point vibrational energies in the thermodynamic parameters and to characterise all structures as minima on the potential energy surface.

### Structures and Energies of Diolefin Complexes

#### [Rh(BINAP)(COD)]<sup>+</sup>



SMD=MeCN

HF=-2802.429933

Sum of electronic and thermal Enthalpies=-2801.573369

Sum of electronic and thermal Free Energies=-2801.698409

SMD=MeOH

HF=-2802.422573

Sum of electronic and thermal Enthalpies=-2801.565872

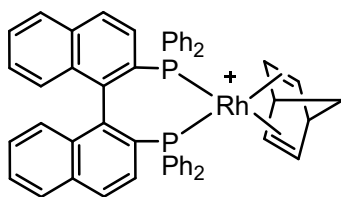
Sum of electronic and thermal Free Energies=-2801.690458

Rh	2.04654800	-0.00006700	0.00000900
P	0.37196600	1.65050000	0.24841400
P	0.37181300	-1.65051600	-0.24844100
C	3.55421300	1.50182600	-0.69194500
H	2.95906600	2.35796900	-1.03455300
C	3.73533700	1.37532300	0.67975100
H	3.23885800	2.12280400	1.29604300
C	4.81550800	0.59320000	1.40357800
H	5.06515500	1.13329500	2.33176500
H	5.73918500	0.56466600	0.80709500
C	4.36329700	-0.83143300	1.77278600
H	5.24144600	-1.46007100	2.02503100
H	3.74221800	-0.79310700	2.68459000
C	3.55419700	-1.50209600	0.69186000
H	2.95897400	-2.35817700	1.03449300
C	3.73525700	-1.37559500	-0.67983500
H	3.23866700	-2.12301100	-1.29611600
C	4.81542200	-0.59351500	-1.40370900
H	5.06501700	-1.13362700	-2.33190100
H	5.73912200	-0.56499900	-0.80726200
C	4.36323600	0.83112900	-1.77290800
H	5.24139100	1.45973700	-2.02520100
H	3.74210900	0.79281400	-2.68468100
C	-1.10401200	1.12461200	1.23943100
C	-1.23517000	1.54297800	2.59348400
H	-0.56506900	2.29681900	2.99983200
C	-2.20446500	1.01833400	3.41593300
H	-2.27914000	1.34995400	4.45556100

C	-3.11747800	0.04616600	2.93511300
C	-4.10229400	-0.53649800	3.77955400
H	-4.13881500	-0.22879400	4.82872800
C	-4.99250200	-1.46700200	3.28563800
H	-5.74690700	-1.91125600	3.94154700
C	-4.93000500	-1.85004000	1.92265200
H	-5.63489600	-2.59166100	1.53564800
C	-3.97950500	-1.30631400	1.08340800
H	-3.93414200	-1.62912600	0.04277700
C	-3.04072800	-0.34681300	1.56036000
C	-2.01600300	0.20620900	0.71894400
C	-2.01603900	-0.20602600	-0.71893700
C	-3.04075700	0.34705500	-1.56032400
C	-3.97945100	1.30662300	-1.08334600
H	-3.93402000	1.62945000	-0.04272300
C	-4.92995400	1.85039400	-1.92255700
H	-5.63477900	2.59206900	-1.53553500
C	-4.99253500	1.46733800	-3.28553400
H	-5.74694400	1.91162600	-3.94141600
C	-4.10240500	0.53677200	-3.77947500
H	-4.13899500	0.22905000	-4.82864100
C	-3.11758700	-0.04593900	-2.93506700
C	-2.20465800	-1.01817700	-3.41590700
H	-2.27940000	-1.34981400	-4.45552400
C	-1.23537100	-1.54287800	-2.59348500
H	-0.56534400	-2.29677800	-2.99984500
C	-1.10413300	-1.12450400	-1.23944200
C	-0.28720500	2.20325700	-1.36406400
C	-1.35292200	3.11287900	-1.45165900
H	-1.81850500	3.50026200	-0.54185400
C	-1.83021000	3.51287000	-2.70088000
H	-2.66629000	4.21491700	-2.76266900
C	-1.25693400	2.99801000	-3.86933300
H	-1.64230100	3.30258200	-4.84684300
C	-0.19697900	2.08833600	-3.78692100
H	0.24775200	1.67684800	-4.69751400
C	0.29019000	1.69505700	-2.53767200
H	1.10867800	0.97257100	-2.46013700
C	0.96630400	3.18930200	1.06731600
C	0.98060300	4.42773000	0.40780600
H	0.58633900	4.51964000	-0.60498800
C	1.50827200	5.56158600	1.03681800
H	1.51129400	6.51769600	0.50517500
C	2.02684000	5.47472100	2.33081000
H	2.43505100	6.36314000	2.82161100
C	2.03475100	4.24028400	2.99076400
H	2.45432100	4.15521600	3.99731700
C	1.52271800	3.10576500	2.35958400
H	1.57746200	2.14218800	2.87275900
C	-0.28739200	-2.20322800	1.36403800
C	-1.35314800	-3.11280400	1.45164200
H	-1.81873600	-3.50018900	0.54183900
C	-1.83045300	-3.51276000	2.70086700
H	-2.66656000	-4.21477300	2.76266400
C	-1.25715700	-2.99790800	3.86931400
H	-1.64254200	-3.30244700	4.84682800
C	-0.19716100	-2.08828300	3.78689300
H	0.24758900	-1.67680600	4.69748200
C	0.29002800	-1.69504100	2.53763900

H	1.10855400	-0.97259700	2.46009700
C	0.96600700	-3.18937900	-1.06732200
C	0.98016400	-4.42779300	-0.40778600
H	0.58586600	-4.51963900	0.60500200
C	1.50772600	-5.56171600	-1.03676600
H	1.51063700	-6.51781500	-0.50510300
C	2.02632400	-5.47493100	-2.33075200
H	2.43444700	-6.36340400	-2.82152900
C	2.03437200	-4.24050900	-2.99073300
H	2.45396700	-4.15550500	-3.99728200
C	1.52244300	-3.10592400	-2.35958700
H	1.57729700	-2.14236400	-2.87278100

**[Rh(BINAP)(NBD)]<sup>+</sup>**



SMD=MeCN

HF=-2761.852725

Sum of electronic and thermal Enthalpies=-2761.05099

Sum of electronic and thermal Free Energies=-2761.172266

SMD=MeOH

HF=-2761.844966

Sum of electronic and thermal Enthalpies=-2761.043122

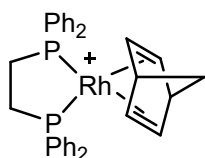
Sum of electronic and thermal Free Energies=-2761.164016

Rh	-2.06239900	-0.00002000	0.00000300
P	-0.41964900	1.66238700	-0.26033100
P	-0.41963400	-1.66241400	0.26030000
C	-3.79563500	1.36629700	0.26358000
H	-3.49069300	2.35530700	0.60973600
C	-3.79749700	0.90086400	-1.04740900
H	-3.49786500	1.44857300	-1.93886100
C	-4.66199000	-0.37417500	-1.06685000
H	-5.00289600	-0.71188800	-2.05256300
C	-3.79568000	-1.36629500	-0.26340200
H	-3.49079600	-2.35531600	-0.60957900
C	-3.79741600	-0.90085700	1.04758600
H	-3.49772100	-1.44856900	1.93901400
C	-4.66188800	0.37419300	1.06710400
H	-5.00270000	0.71191300	2.05284800
C	-5.72545600	0.00001700	0.00017400
H	-6.35544600	0.85635900	-0.29869400
H	-6.35543300	-0.85631400	0.29909900
C	1.06474400	1.15318000	-1.23540400
C	1.20237400	1.58614300	-2.58366800
H	0.53796700	2.35225000	-2.97926100
C	2.16639000	1.05718300	-3.40970300
H	2.24901900	1.39774800	-4.44582500
C	3.06505200	0.06817900	-2.93530000
C	4.04567400	-0.51639400	-3.78357200
H	4.08795200	-0.19773900	-4.82925900
C	4.92544600	-1.46092600	-3.29780400

H	5.67674400	-1.90579100	-3.95684200
C	4.85662300	-1.85681900	-1.93879900
H	5.55388900	-2.60865900	-1.55772800
C	3.90958700	-1.31258200	-1.09604400
H	3.85934500	-1.64493500	-0.05861000
C	2.98048700	-0.33945800	-1.56458000
C	1.95976800	0.21430600	-0.71841600
C	1.95974400	-0.21432000	0.71849000
C	2.98041100	0.33946400	1.56470400
C	3.90947900	1.31264800	1.09623000
H	3.85925600	1.64503400	0.05880500
C	4.85645800	1.85690700	1.93903600
H	5.55370000	2.60879400	1.55801300
C	4.92525200	1.46097600	3.29803200
H	5.67650500	1.90585800	3.95711000
C	4.04550900	0.51638600	3.78374000
H	4.08776400	0.19770300	4.82941900
C	3.06494600	-0.06820800	2.93541500
C	2.16630900	-1.05726400	3.40976000
H	2.24891500	-1.39785200	4.44587600
C	1.20233500	-1.58623300	2.58368000
H	0.53793800	-2.35236800	2.97923400
C	1.06473000	-1.15323000	1.23542700
C	-1.08148200	3.17995600	-1.05547100
C	-1.14315800	4.40827300	-0.37767200
H	-0.72960000	4.50629900	0.62712700
C	-1.74236800	5.52033300	-0.97938100
H	-1.78186700	6.46907600	-0.43603300
C	-2.28587200	5.42201600	-2.26304400
H	-2.75176600	6.29367200	-2.73203800
C	-2.23978600	4.19906000	-2.94175500
H	-2.67097900	4.10706900	-3.94282600
C	-1.65334600	3.08460400	-2.33867000
H	-1.64608500	2.13182900	-2.87348400
C	0.21507400	2.20584900	1.36415000
C	1.27773200	3.11698400	1.46817200
H	1.74793600	3.51571900	0.56560700
C	1.74655700	3.50293800	2.72516600
H	2.58093400	4.20567700	2.80060600
C	1.16742700	2.97272600	3.88377800
H	1.54737500	3.26518300	4.86710800
C	0.10707400	2.06497300	3.78460900
H	-0.34395800	1.64437200	4.68792000
C	-0.37240100	1.68645100	2.52791700
H	-1.19383000	0.96775200	2.43518700
C	0.21512600	-2.20575700	-1.36420200
C	-0.37229400	-1.68623000	-2.52793900
H	-1.19369900	-0.96750700	-2.43516900
C	0.10721300	-2.06464900	-3.78465000
H	-0.34377300	-1.64394800	-4.68793800
C	1.16753600	-2.97243200	-3.88386700
H	1.54750800	-3.26481000	-4.86721200
C	1.74660700	-3.50277300	-2.72528500
H	2.58096200	-4.20553500	-2.80076300
C	1.27775500	-3.11692000	-1.46827100
H	1.74791100	-3.51575800	-0.56572700
C	-1.08145100	-3.18005300	1.05531900
C	-1.14312600	-4.40830100	0.37739700
H	-0.72957800	-4.50622200	-0.62741800

C	-1.74232100	-5.52042600	0.97899900
H	-1.78182200	-6.46911300	0.43555500
C	-2.28580600	-5.42224400	2.26268100
H	-2.75168700	-6.29395100	2.73159400
C	-2.23971100	-4.19935800	2.94151800
H	-2.67088500	-4.10747300	3.94260800
C	-1.65328700	-3.08483700	2.33854000
H	-1.64601600	-2.13212000	2.87345800

**[Rh(DPPE)(NBD)]<sup>+</sup>**



SMD=MeCN

HF=-2070.755013

Sum of electronic and thermal Enthalpies=-2070.165928

Sum of electronic and thermal Free Energies=-2070.266977

SMD=MeOH

HF=-2070.748671

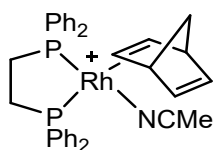
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Sum of electronic and thermal Free Energies=-2070.260345

P	1.53809400	-0.04207900	-0.78790100
P	-1.53778600	0.04209000	-0.78848600
C	0.67377400	0.36488200	-2.38378500
H	0.51925800	1.45606500	-2.42374800
H	1.30005100	0.07093300	-3.24220600
C	-0.67286700	-0.36478200	-2.38407000
H	-0.51833500	-1.45596100	-2.42406700
H	-1.29881900	-0.07076400	-3.24270400
C	2.19854700	-1.72063200	-1.08178800
C	1.59532600	-2.80856800	-0.43072700
H	0.77815000	-2.62191000	0.27471200
C	2.03477600	-4.11181300	-0.68560900
H	1.56008700	-4.95546800	-0.17614400
C	3.08083600	-4.33229700	-1.58735600
H	3.42802700	-5.35106600	-1.78430900
C	3.68589500	-3.24938700	-2.23841300
H	4.50420000	-3.42114300	-2.94403700
C	3.24576800	-1.94701600	-1.99052000
H	3.72093300	-1.10515400	-2.50252700
C	2.97782700	1.06233600	-0.62686700
C	4.10683100	0.62424800	0.08775600
H	4.15874200	-0.40490400	0.45361400
C	5.16859500	1.49931200	0.33120600
H	6.04438100	1.14711800	0.88430100
C	5.11238700	2.81934700	-0.13041400
H	5.94488500	3.50314200	0.05997600
C	3.98709600	3.26256400	-0.83363500
H	3.93570800	4.29390500	-1.19498000
C	2.92098500	2.39180800	-1.07796500
H	2.04377700	2.75814200	-1.61702400
C	-2.97749500	-1.06242200	-0.62789200
C	-2.92052900	-2.39185100	-1.07910000

H	-2.04321700	-2.75811600	-1.61803600
C	-3.98665400	-3.26266600	-0.83503300
H	-3.93516500	-4.29397300	-1.19646100
C	-5.11208400	-2.81955200	-0.13197100
H	-5.94459000	-3.50339600	0.05821400
C	-5.16842000	-1.49956000	0.32975700
H	-6.04431400	-1.14744600	0.88273100
C	-4.10664300	-0.62444000	0.08657200
H	-4.15865200	0.40467500	0.45252300
C	-2.19828400	1.72059000	-1.08260100
C	-3.24528700	1.94686600	-1.99161000
H	-3.72025200	1.10495200	-2.50371900
C	-3.68545800	3.24919500	-2.23964900
H	-4.50359500	3.42086600	-2.94548800
C	-3.08065600	4.33217000	-1.58846300
H	-3.42788000	5.35090600	-1.78553100
C	-2.03481600	4.11179400	-0.68643600
H	-1.56032900	4.95550000	-0.17686600
C	-1.59532600	2.80859100	-0.43140500
H	-0.77832700	2.62202100	0.27426300
Rh	-0.00015700	0.00006600	0.94105700
C	1.20624900	0.70044900	2.66986800
C	1.21716300	-0.68793200	2.67387500
C	-1.21806800	0.68813200	2.67345900
H	2.01389200	1.36400900	2.35440400
C	-0.00758900	1.13097000	3.52602300
H	2.03482900	-1.34244200	2.36682700
C	0.00641200	-1.13073300	3.52607200
H	-2.03562100	1.34263200	2.36609200
C	-1.20715100	-0.70024600	2.66951200
H	-0.01217700	2.17254900	3.86844400
C	-0.00075700	0.00014100	4.59064800
H	0.01088900	-2.17229800	3.86853800
H	-2.01468100	-1.36382200	2.35379000
H	0.90612200	0.00534000	5.22066400
H	-0.90783600	-0.00503300	5.22037800

[Rh(DPPE)(NBD)(MeCN)]<sup>+</sup>



SMD=MeOH

HF=-2203.571361

Sum of electronic and thermal Enthalpies=-2202.930243

Sum of electronic and thermal Free Energies=-2203.042731

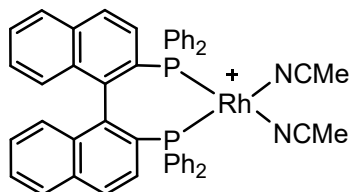
C	0.11098700	-3.16627800	-2.66356000
H	-0.82295500	-3.69797700	-2.46718900
C	0.33295100	-2.20129700	-3.56835900
H	-0.37985100	-1.77301900	-4.27662800
C	1.74165000	-1.67416600	-3.33314800
H	2.18699500	-1.09013000	-4.14989700
C	1.82231600	-0.98512100	-1.93629600
H	2.47954500	-0.12120200	-1.80934200
C	1.60767100	-1.99535100	-1.00291900
H	2.05784100	-2.07686100	-0.01299200



C	1.37221600	-3.29724600	-1.82014400
H	1.47301300	-4.21990000	-1.23289700
C	2.43792800	-3.01497700	-2.93065500
H	3.45723700	-2.87322300	-2.53169600
H	2.44689500	-3.77234700	-3.73434200
Rh	0.07393200	-0.38902600	-0.59854600
P	-1.50625300	0.39507200	0.92496000
P	1.52786400	0.65806400	0.80763700
C	-0.70093000	1.53817500	2.14789600
C	-2.21913400	-0.94797000	1.94038800
C	-2.92588100	1.30710100	0.22372000
C	0.70425200	1.01080900	2.43598600
C	3.15277200	-0.06828100	1.21336200
C	1.88027100	2.33604400	0.16214400
H	-0.65544600	2.53939700	1.68797400
H	-1.30819200	1.61353300	3.06445200
C	-1.86891000	-2.27839300	1.66367600
C	-3.09105600	-0.66794300	3.00691900
C	-4.20505400	0.73565500	0.14166500
C	-2.68905400	2.55502400	-0.38099900
H	0.65589900	0.06668000	3.00419800
H	1.30515800	1.73180700	3.01490600
C	3.23455000	-1.08904300	2.17675000
C	4.30259200	0.28670100	0.48931300
C	2.69382300	3.23912100	0.86657800
C	1.26109600	2.74639200	-1.02900200
H	-1.18251100	-2.48845700	0.83703300
C	-2.38513800	-3.31895200	2.44309000
C	-3.60397500	-1.70885100	3.78386400
H	-3.37676400	0.36462700	3.22853800
H	-4.40059700	-0.24264300	0.58685800
C	-5.23683000	1.41066400	-0.51932900
C	-3.72324900	3.22812100	-1.03449500
H	-1.68949000	3.00030800	-0.35491100
H	2.34458400	-1.39854700	2.73188200
C	4.45195800	-1.72828500	2.42411600
C	5.51771400	-0.35917300	0.73601900
H	4.25387900	1.07122500	-0.26994300
H	3.18375000	2.92974300	1.79471000
C	2.88511300	4.53480200	0.38113200
C	1.45096400	4.04564800	-1.51130100
H	0.62702400	2.03566100	-1.57111300
H	-2.10647500	-4.35359400	2.22199800
C	-3.25184100	-3.03518600	3.50282900
H	-4.28210500	-1.48475400	4.61284200
H	-6.22986700	0.95486100	-0.57781400
C	-5.00038700	2.65761100	-1.10532100
H	-3.52930100	4.20064200	-1.49696300
H	4.50562700	-2.51711900	3.18044600
C	5.59592300	-1.36496500	1.70453800
H	6.40760400	-0.07276500	0.16744700
H	3.52170200	5.23338500	0.93258500
C	2.26283700	4.93992800	-0.80672800
H	0.96276200	4.35846900	-2.43913000
H	-3.65477600	-3.84856400	4.11409400
H	-5.80866400	3.18417800	-1.62167000
H	6.54802900	-1.86857400	1.89732300
H	2.41291800	5.95662400	-1.18274200
N	-1.57191900	-0.89744400	-1.76391600

C	-2.60154300	-0.96565600	-2.28692300
C	-3.88396800	-1.05692400	-2.95890300
H	-4.25863200	-0.04337500	-3.18244700
H	-3.77693700	-1.62289300	-3.90083700
H	-4.61139900	-1.57037800	-2.30710300

### Structures and Energies of Solvate Complexes



SMD=MeCN

HF=-2755.894355

Sum of electronic and thermal Enthalpies=-2755.125157

Sum of electronic and thermal Free Energies=-2755.257056

SMD=MeOH

HF=-2755.8852

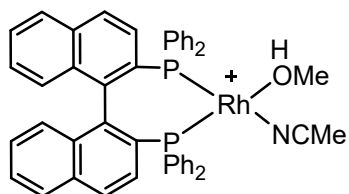
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P	-0.49210700	1.60710400	-0.25647900
C	0.95999300	-1.04959600	1.26527600
C	1.01433900	-1.38208500	2.64732600
H	0.28804300	-2.07744900	3.06714300
C	1.96930000	-0.83665600	3.47381100
H	1.99002500	-1.09580000	4.53631500
C	2.93945000	0.06592300	2.96690500
C	3.92013200	0.65739300	3.81048900
H	3.91137400	0.40817800	4.87572600
C	4.86236500	1.52402900	3.29707000
H	5.61353500	1.97368000	3.95306300
C	4.85624100	1.83642600	1.91476300
H	5.60110300	2.52943600	1.51272600
C	3.90987700	1.28588600	1.07536800
H	3.90721200	1.55345300	0.01814000
C	2.92324100	0.38564300	1.57026700
C	1.90904900	-0.17997900	0.72598800
C	1.90851800	0.18441400	-0.72637900
C	2.92360900	-0.37919100	-1.57092100
C	3.91200800	-1.27767100	-1.07633500
H	3.91006300	-1.54536400	-0.01913700
C	4.85919200	-1.82638600	-1.91600100
H	5.60541600	-2.51807100	-1.51420500
C	4.86444200	-1.51382200	-3.29827500
H	5.61628900	-1.96202300	-3.95448300
C	3.92050700	-0.64886100	-3.81139200
H	3.91105100	-0.39955300	-4.87660100
C	2.93891700	-0.05929700	-2.96752900
C	1.96697000	0.84151200	-3.47413400
H	1.98697900	1.10080200	-4.53661500

C	1.01109000	1.38496900	-2.64741300
H	0.28332600	2.07890700	-3.06703800
C	0.95761400	1.05217800	-1.26540300
C	0.22927300	-2.30883700	-1.27234900
C	1.32247200	-3.18926000	-1.24021100
H	1.77855700	-3.46162700	-0.28489300
C	1.84337000	-3.70258400	-2.42927500
H	2.70095500	-4.38041900	-2.39826300
C	1.28576700	-3.33114200	-3.65822900
H	1.70550500	-3.72326400	-4.58932900
C	0.19750300	-2.45267200	-3.69542500
H	-0.23536800	-2.15356800	-4.65449000
C	-0.33253500	-1.94592200	-2.50554800
H	-1.17455400	-1.24663400	-2.52190600
C	-1.18112700	-3.05053200	1.16933700
C	-1.07752700	-4.36939300	0.70575300
H	-0.51494500	-4.59520700	-0.20141300
C	-1.71060800	-5.41300000	1.39260800
H	-1.62511800	-6.43609200	1.01439400
C	-2.44916300	-5.15078800	2.54903900
H	-2.94446700	-5.96745800	3.08266000
C	-2.56142300	-3.83506600	3.01627000
H	-3.14621400	-3.61764500	3.91494000
C	-1.94151200	-2.79319200	2.32580100
H	-2.06705000	-1.76404900	2.67431200
C	0.22400200	2.30899900	1.27269000
C	1.31482900	3.19236900	1.24085600
H	1.77007200	3.46642300	0.28561900
C	1.83442800	3.70656400	2.43011000
H	2.69018200	4.38671800	2.39934100
C	1.27790500	3.33308900	3.65894000
H	1.69665600	3.72592500	4.59018300
C	0.19198400	2.45171100	3.69582500
H	-0.24003400	2.15104700	4.65478700
C	-0.33678100	1.94407600	2.50576000
H	-1.17695600	1.24256400	2.52186400
C	-1.18809300	3.04833300	-1.16863900
C	-1.08763300	4.36719300	-0.70437400
H	-0.52546900	4.59388400	0.20283500
C	-1.72335300	5.40961900	-1.39058200
H	-1.64030500	6.43271400	-1.01183400
C	-2.46142800	5.14622200	-2.54704500
H	-2.95879500	5.96196600	-3.08016500
C	-2.57055400	3.83047600	-3.01496000
H	-3.15495400	3.61211000	-3.91365500
C	-1.94803400	2.78974200	-2.32511800
H	-2.07118400	1.76047900	-2.67412100
C	-4.31854800	2.31820700	-0.06252000
C	-5.23098300	3.44327000	-0.14354000
H	-5.52010700	3.60913000	-1.19564000
H	-6.13614600	3.24549200	0.45545600
H	-4.73089000	4.34960400	0.23907200
C	-4.31326300	-2.32787500	0.06167500
C	-5.22310000	-3.45505800	0.14244900
H	-5.51899800	-3.61629400	1.19337700
H	-6.12467700	-3.26303700	-0.46378000
H	-4.71777700	-4.36191500	-0.23198100
N	-3.55990100	1.44663400	-0.02351900
N	-3.55664600	-1.45453300	0.02278800

**[Rh(BINAP)(MeCN)(MeOH)]<sup>+</sup>**



SMD=MeOH

HF=-2738.840754

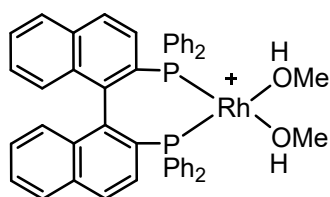
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Sum of electronic and thermal Free Energies=-2738.193877

Rh	-1.77480900	1.19001700	-0.15365700
P	0.42888300	1.66447200	-0.38551600
P	-1.31951200	-0.95504400	0.26742300
O	-2.37776600	3.32549800	-0.35470000
H	-3.34689200	3.33839200	-0.46024600
C	-2.00785300	4.23572700	0.68658500
H	-2.38069400	5.24787000	0.44806200
H	-0.90962800	4.25825100	0.72832200
H	-2.40718100	3.91079700	1.66362400
C	1.37610700	0.35229300	-1.28348300
C	1.63176900	0.50438800	-2.67413000
H	1.40151000	1.44848600	-3.16842900
C	2.16087800	-0.52641600	-3.41606300
H	2.34241600	-0.39615900	-4.48702300
C	2.47757200	-1.77015200	-2.81106100
C	2.99903000	-2.85577000	-3.56760400
H	3.15182400	-2.71786000	-4.64223900
C	3.30633300	-4.05558700	-2.96070500
H	3.70694000	-4.88542700	-3.55057500
C	3.09976800	-4.21635600	-1.56806900
H	3.33852900	-5.17187600	-1.09157400
C	2.58596200	-3.18371200	-0.81132700
H	2.41391800	-3.33241600	0.25543700
C	2.25832700	-1.93082400	-1.40410900
C	1.69244300	-0.84947400	-0.64874600
C	1.45636300	-1.04687000	0.81665200
C	2.59241600	-1.06163000	1.69449400
C	3.92360200	-0.88520700	1.21942900
H	4.09726400	-0.74444200	0.15196000
C	4.99405800	-0.87169700	2.08951100
H	6.00711100	-0.72924500	1.70165400
C	4.79177500	-1.02579900	3.48346700
H	5.64891800	-1.00565200	4.16315800
C	3.51593100	-1.19808000	3.97815500
H	3.34432000	-1.31717200	5.05220300
C	2.39437400	-1.22596200	3.10408600
C	1.07508100	-1.40889700	3.59275100
H	0.92179100	-1.55258000	4.66639400
C	-0.00100100	-1.40576300	2.73578100
H	-1.00024800	-1.55452700	3.14437700
C	0.17127700	-1.20817900	1.33762600
C	1.39118800	1.98646400	1.13677100
C	2.78723000	2.13262000	1.11505500

H	3.33288100	2.04421500	0.17184000
C	3.48600100	2.36733100	2.30069100
H	4.57448600	2.47126200	2.27778800
C	2.79859000	2.44345500	3.51733600
H	3.35015400	2.61238400	4.44708200
C	1.40763700	2.29526600	3.54485600
H	0.86788200	2.34426100	4.49522000
C	0.70525800	2.07128100	2.35785900
H	-0.38069300	1.93560200	2.36998900
C	0.62230600	3.17426600	-1.41904900
C	1.47346400	4.23755400	-1.08424900
H	2.09091100	4.19160700	-0.18556900
C	1.53069400	5.37804600	-1.89339800
H	2.19678200	6.20138700	-1.61807200
C	0.74184000	5.46744300	-3.04353300
H	0.78894200	6.36023500	-3.67456100
C	-0.11625500	4.41372200	-3.38036800
H	-0.74392500	4.47867500	-4.27423200
C	-0.18315200	3.28064700	-2.56828300
H	-0.87191500	2.46931900	-2.82164600
C	-1.05273100	-2.05786600	-1.16936900
C	-0.62892100	-3.38633100	-1.00636300
H	-0.43955600	-3.78215200	-0.00489900
C	-0.42784600	-4.19994000	-2.12268900
H	-0.08841400	-5.23101200	-1.98909000
C	-0.63587200	-3.68997900	-3.40940600
H	-0.46220700	-4.32476300	-4.28351900
C	-1.05790400	-2.36674400	-3.57689800
H	-1.21275600	-1.96196900	-4.58146200
C	-1.27064600	-1.55408900	-2.45996400
H	-1.58414800	-0.51223600	-2.57908800
C	-2.71549200	-1.72135200	1.19752600
C	-3.35180400	-2.90009400	0.78451300
H	-2.98524800	-3.45395000	-0.08125500
C	-4.48006800	-3.37288600	1.46675700
H	-4.96894700	-4.29103300	1.12704400
C	-4.98167900	-2.67648700	2.56864800
H	-5.86479100	-3.04630900	3.09848100
C	-4.35527300	-1.49484800	2.98473300
H	-4.74735800	-0.93516200	3.83925400
C	-3.23929200	-1.01656200	2.29798000
H	-2.78449600	-0.06913800	2.60146500
N	-3.81008900	0.79199100	-0.15681300
C	-4.91660200	0.45770800	-0.10728200
C	-6.28628300	-0.00829200	-0.01306600
H	-6.31971600	-1.08901700	-0.23501900
H	-6.66736600	0.16158100	1.00866600
H	-6.92342200	0.53148800	-0.73454600

[Rh(BINAP)(MeOH)<sub>2</sub>]<sup>+</sup>



SMD=MeOH

HF=-2721.800001

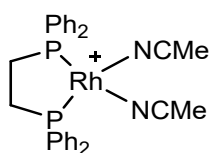
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Sum of electronic and thermal Free Energies=-2721.145265

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P	0.85929100	-1.40758300	-0.41431200
O	3.66216200	1.98015800	0.12126600
H	4.46186300	1.44508200	-0.05160900
O	4.07155100	-0.76328800	-0.18242600
H	4.10106800	-1.27028900	-1.01727400
C	3.60105800	3.06805800	-0.80559900
H	4.47312700	3.73213300	-0.66538200
H	2.68198300	3.63102400	-0.58871200
H	3.57353900	2.70465900	-1.84784000
C	4.39884600	-1.63043900	0.91042100
H	5.41866700	-2.03367900	0.77743400
H	3.67568500	-2.46110600	0.98673300
H	4.36055700	-1.02184400	1.82573800
C	-0.95661900	0.75320000	1.35871300
C	-1.02265600	0.91549500	2.77008300
H	-0.38991300	1.65605000	3.26035400
C	-1.86767100	0.14559800	3.53560100
H	-1.89901800	0.27671500	4.62127500
C	-2.70683800	-0.82895500	2.93596200
C	-3.56404800	-1.65462900	3.71455300
H	-3.56685800	-1.52658900	4.80121000
C	-4.37382500	-2.59594100	3.11403900
H	-5.02965000	-3.22722800	3.72104100
C	-4.35433600	-2.74923500	1.70547700
H	-4.99296400	-3.50194400	1.23361400
C	-3.52638300	-1.96798800	0.92603800
H	-3.50968100	-2.11434300	-0.15471000
C	-2.67809100	-0.98505500	1.51159100
C	-1.78168100	-0.18098400	0.72997400
C	-1.74743000	-0.38333900	-0.75372400
C	-2.84746400	0.09633700	-1.54071700
C	-3.96352000	0.76453600	-0.96092900
H	-3.99645600	0.91200700	0.11930900
C	-4.99272700	1.24269800	-1.74522400
H	-5.83751700	1.75741800	-1.27786500
C	-4.95769400	1.08709700	-3.15323100
H	-5.77664200	1.47828900	-3.76428100
C	-3.89104900	0.44619400	-3.74821400
H	-3.85029400	0.31996000	-4.83432000
C	-2.82110300	-0.06712300	-2.96427600
C	-1.71958100	-0.73736900	-3.55714000
H	-1.70668600	-0.87963400	-4.64178100
C	-0.67990100	-1.20396500	-2.78611000
H	0.14954600	-1.71921800	-3.27126800
C	-0.67155200	-1.01855700	-1.37616900
C	-0.48668500	2.38841400	-1.00473800
C	-1.70337300	3.07034700	-0.84487200
H	-2.16341700	3.14620600	0.14398500
C	-2.34391800	3.63176400	-1.95111400
H	-3.29632700	4.15321300	-1.82003200
C	-1.78266300	3.50408600	-3.22665000
H	-2.29444300	3.93113700	-4.09434800
C	-0.57166400	2.82310600	-3.39213600

H	-0.13483600	2.71264700	-4.38914600
C	0.07644700	2.27063900	-2.28422100
H	1.01422700	1.71937100	-2.40420000
C	0.89384600	3.01434200	1.49415300
C	0.50084000	4.34472000	1.28628900
H	-0.16865200	4.60244000	0.46386300
C	0.97454500	5.36041400	2.12455000
H	0.66276000	6.39442000	1.94837700
C	1.84223100	5.05855900	3.17784100
H	2.21106700	5.85493400	3.83150400
C	2.24497500	3.73427400	3.38793300
H	2.93028000	3.49021500	4.20524400
C	1.78190700	2.72178100	2.54616100
H	2.11599700	1.69077000	2.69688900
C	0.27815000	-2.41569600	0.99960500
C	-0.64322700	-3.46123400	0.83038400
H	-1.04077200	-3.68616600	-0.16307300
C	-1.07187300	-4.20331500	1.93257600
H	-1.79739100	-5.01022300	1.79524800
C	-0.59339000	-3.89924900	3.21225200
H	-0.94213900	-4.47230400	4.07664700
C	0.32514600	-2.85832900	3.38588000
H	0.69473300	-2.61226500	4.38581200
C	0.76287800	-2.12101200	2.28237500
H	1.46704400	-1.29301600	2.40870200
C	1.82256800	-2.57276900	-1.46813600
C	1.97585400	-3.93456000	-1.17237000
H	1.45281400	-4.37815700	-0.32333100
C	2.81333500	-4.73831100	-1.95524500
H	2.92478200	-5.79881400	-1.70985300
C	3.50849000	-4.19236400	-3.03712200
H	4.16528700	-4.82304100	-3.64373500
C	3.36731700	-2.83183100	-3.33683500
H	3.91071500	-2.39349600	-4.17916100
C	2.53427100	-2.02747700	-2.55633300
H	2.44161600	-0.96021000	-2.78274100

[Rh(DPPE)(MeCN)<sub>2</sub>]<sup>+</sup>



SMD=MeCN

HF=-2064.795571

Sum of electronic and thermal Enthalpies=-2064.238302

Sum of electronic and thermal Free Energies=-2064.348657

SMD=MeOH

HF=-2064.787545

Sum of electronic and thermal Enthalpies=-2064.230304

Sum of electronic and thermal Free Energies=-2064.340822

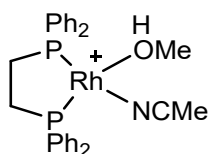
Rh	0.00000100	-0.00001500	0.96146800
P	1.51451300	-0.02223200	-0.71067300
P	-1.51450900	0.02222800	-0.71067500
C	0.67503900	0.36038900	-2.32563100
H	0.53048000	1.45205800	-2.38421400

H	1.30950100	0.05134400	-3.17242800
C	-0.67503500	-0.36038200	-2.32563500
H	-0.53047600	-1.45205100	-2.38423000
H	-1.30949500	-0.05132700	-3.17243000
C	2.29536100	-1.65344500	-1.00112400
C	1.90246300	-2.74886400	-0.21742500
H	1.15303200	-2.59997500	0.56686200
C	2.45907000	-4.01272900	-0.44307700
H	2.14786800	-4.86227200	0.17205400
C	3.40993100	-4.18727800	-1.45332500
H	3.84661200	-5.17490900	-1.63019300
C	3.80410400	-3.09725700	-2.24053700
H	4.54778100	-3.23217400	-3.03167600
C	3.24939900	-1.83515900	-2.01714600
H	3.56496100	-0.98666500	-2.63176200
C	2.90215600	1.15465400	-0.52440800
C	4.13895200	0.73210800	-0.00960700
H	4.32057600	-0.32810200	0.18261300
C	5.14475400	1.66442900	0.26437200
H	6.10376000	1.32287900	0.66531700
C	4.92612300	3.02541100	0.02712500
H	5.71452500	3.75363800	0.23943900
C	3.69303700	3.45311600	-0.47934500
H	3.51351200	4.51669400	-0.66280800
C	2.68270300	2.52550100	-0.74593600
H	1.71596800	2.87753800	-1.11696700
C	-2.90216800	-1.15464200	-0.52441800
C	-2.68273200	-2.52549300	-0.74594000
H	-1.71599800	-2.87754700	-1.11695800
C	-3.69308000	-3.45309400	-0.47935500
H	-3.51356800	-4.51667500	-0.66281200
C	-4.92616500	-3.02537000	0.02710300
H	-5.71457800	-3.75358600	0.23941300
C	-5.14477900	-1.66438500	0.26434600
H	-6.10378300	-1.32282100	0.66528200
C	-4.13896100	-0.73207900	-0.00962700
H	-4.32057300	0.32813500	0.18258900
C	-2.29534400	1.65345000	-1.00111300
C	-3.24938800	1.83517500	-2.01712700
H	-3.56496000	0.98668500	-2.63174400
C	-3.80408600	3.09727700	-2.24051000
H	-4.54776600	3.23220200	-3.03164400
C	-3.40989900	4.18729200	-1.45329700
H	-3.84657500	5.17492800	-1.63015700
C	-2.45903200	4.01273200	-0.44305600
H	-2.14782100	4.86227100	0.17207700
C	-1.90243400	2.74886300	-0.21741100
H	-1.15299900	2.59996500	0.56687100
N	1.53858100	0.03654600	2.35861200
N	-1.53857400	-0.03658800	2.35861600
C	-2.50346200	-0.11467300	2.99244600
C	2.50346400	0.11462500	2.99244900
C	-3.73428000	-0.22386200	3.75385800
H	-3.54212000	-0.02015800	4.82112100
H	-4.47112200	0.50347700	3.37162500
H	-4.14539400	-1.24246600	3.64617000
C	3.73426900	0.22383700	3.75387800
H	4.47112800	-0.50349300	3.37165800
H	4.14537100	1.24244500	3.64618900



H 3.54209800 0.02013300 4.82113900

[Rh(DPPE)(MeCN)(MeOH)]<sup>+</sup>



SMD=MeOH

HF=-2047.742038

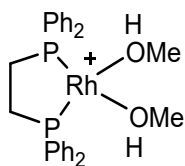
Sum of electronic and thermal Enthalpies=-2047.17891

Sum of electronic and thermal Free Energies=-2047.288702

Rh	-0.04506700	-0.11576300	0.99176700
P	1.31597700	-0.00235800	-0.75602000
P	-1.68171000	0.00092200	-0.54516200
C	0.36449800	0.40237200	-2.30374300
H	0.20135000	1.49271200	-2.32698900
H	0.94448400	0.12317100	-3.19848900
C	-0.97397600	-0.33595100	-2.22999700
H	-0.81942500	-1.42359300	-2.32736300
H	-1.67132000	-0.01263300	-3.02040900
C	2.17241300	-1.57044200	-1.17079800
C	1.92521400	-2.71529000	-0.39918500
H	1.23600800	-2.64661700	0.44877800
C	2.54845100	-3.92751200	-0.71562400
H	2.34990500	-4.81632000	-0.10903000
C	3.42093800	-4.00122400	-1.80554800
H	3.90950700	-4.94855700	-2.05373500
C	3.67044300	-2.86132400	-2.58094500
H	4.35332600	-2.91677800	-3.43425100
C	3.04915000	-1.65082400	-2.26646800
H	3.25389500	-0.76271500	-2.87217200
C	2.65641200	1.23738900	-0.61594700
C	3.94769500	0.86033000	-0.21195700
H	4.19569800	-0.19574400	-0.07970900
C	4.92407500	1.83194600	0.02984600
H	5.92601600	1.52494400	0.34519900
C	4.62204100	3.18797800	-0.13088600
H	5.38746300	3.94739500	0.05542800
C	3.33503800	3.57050100	-0.52733700
H	3.09020500	4.62991100	-0.65038400
C	2.35457700	2.60283800	-0.75989400
H	1.34627400	2.91914300	-1.04232300
C	-3.09447600	-1.13515400	-0.29828800
C	-3.00138500	-2.48192200	-0.69108900
H	-2.11777600	-2.84372400	-1.22392900
C	-4.03517100	-3.37459000	-0.39690500
H	-3.95606900	-4.41817100	-0.71635000
C	-5.16430400	-2.93873800	0.30620200
H	-5.97159000	-3.64024800	0.53733700
C	-5.25520900	-1.60449900	0.71532400
H	-6.13304900	-1.25771100	1.26903000
C	-4.22680900	-0.70547000	0.41590700

H	-4.30899400	0.33589700	0.73857900
C	-2.43741200	1.66121000	-0.72737900
C	-3.46878100	1.89775400	-1.65214700
H	-3.86530600	1.07514900	-2.25515300
C	-3.99578000	3.18248800	-1.80108100
H	-4.79905000	3.36067500	-2.52255100
C	-3.49807500	4.24010400	-1.02862200
H	-3.91291800	5.24582100	-1.14748400
C	-2.47244300	4.01025800	-0.10658400
H	-2.08163200	4.83411900	0.49823200
C	-1.94293000	2.72373300	0.04391300
H	-1.13589600	2.53086900	0.75907000
O	-1.51936900	-0.28704300	2.65139500
H	-2.18313200	-0.95292900	2.39356700
C	-1.07961500	-0.54299200	3.98933400
H	-1.95042800	-0.58115200	4.66776700
H	-0.51432700	-1.48981000	4.05398900
H	-0.42795900	0.29309700	4.28262400
N	1.60408900	-0.13752100	2.25747500
C	2.62489000	-0.07855600	2.79976500
C	3.91931500	0.01169000	3.44821700
H	4.61259700	-0.71823700	2.99535700
H	4.32909900	1.02801600	3.31519100
H	3.82066900	-0.20272900	4.52636800

**[Rh(DPPE)(MeOH)<sub>2</sub>]<sup>+</sup>**



SMD=MeOH

HF=-2030.698943

Sum of electronic and thermal Enthalpies=-2030.129769

Sum of electronic and thermal Free Energies=-2030.23275

Rh	0.06434900	0.28352300	1.04193200
P	1.49263700	0.08402300	-0.62321400
P	-1.48833600	0.00873700	-0.52162700
C	0.64243000	0.37654200	-2.24693000
H	0.47563300	1.46115900	-2.35693300
H	1.26377300	0.03181800	-3.09007000
C	-0.69004100	-0.36853000	-2.16727700
H	-0.52468300	-1.45891300	-2.19408400
H	-1.36190000	-0.11127900	-3.00134400
C	2.25414600	-1.57290500	-0.82994200
C	1.86518000	-2.61428400	0.02605500
H	1.13680100	-2.40745400	0.81681300
C	2.40271900	-3.89647900	-0.13228700
H	2.09342800	-4.70332700	0.53898300
C	3.33218300	-4.14365700	-1.14722500
H	3.75325200	-5.14598100	-1.27256800
C	3.72582800	-3.10734200	-2.00383500
H	4.45445200	-3.29865900	-2.79757500
C	3.18951600	-1.82705100	-1.84724400
H	3.50588300	-1.02102500	-2.51653300

C	2.91008800	1.23686800	-0.50301200
C	4.12396800	0.82099700	0.07163900
H	4.27175200	-0.22720500	0.34377200
C	5.15248200	1.74269100	0.29495500
H	6.09281000	1.40597300	0.74187200
C	4.98126200	3.08549500	-0.05448200
H	5.78769200	3.80489700	0.11687400
C	3.77212000	3.50787600	-0.62020300
H	3.63026200	4.55842900	-0.89139200
C	2.73862800	2.59309700	-0.83421900
H	1.79131700	2.94290300	-1.25421400
C	-2.68153800	-1.36905400	-0.29153600
C	-2.15974100	-2.67083500	-0.17851400
H	-1.08237200	-2.83893700	-0.27511600
C	-3.00671200	-3.75360400	0.06589600
H	-2.58938400	-4.76192400	0.14718300
C	-4.38420200	-3.54793300	0.21448200
H	-5.04755400	-4.39543900	0.41238600
C	-4.90745500	-2.25561900	0.11306100
H	-5.98226200	-2.08715000	0.23172300
C	-4.06135400	-1.16982700	-0.13917600
H	-4.48390900	-0.16512800	-0.21090700
C	-2.53180900	1.48884900	-0.82570600
C	-3.34785300	1.60222900	-1.96413200
H	-3.39464800	0.78874700	-2.69388100
C	-4.11729600	2.75071800	-2.16832100
H	-4.74771100	2.83036700	-3.05923900
C	-4.08321000	3.79463500	-1.23608700
H	-4.68519500	4.69389900	-1.39906300
C	-3.27889700	3.68591000	-0.09713200
H	-3.25016800	4.49827900	0.63539900
C	-2.50479700	2.53907600	0.10601300
H	-1.87055900	2.45118500	0.99281300
O	-1.24801500	0.50673400	2.81997100
H	-1.24116400	1.45484200	3.04732400
O	1.70994700	0.71753900	2.51459500
H	2.40233300	1.24047800	2.06851000
C	-2.58513300	0.00590900	2.89419400
H	-2.98116000	0.13991500	3.91703500
H	-3.24478600	0.51516500	2.17080000
H	-2.54144400	-1.06649700	2.65696200
C	2.31004300	-0.42170100	3.14201900
H	3.03840000	-0.09283400	3.90527000
H	1.50001600	-0.98408500	3.62998500
H	2.81208200	-1.06875700	2.40202500

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