# Supporting Information

# Interception of a $Rh^{(I)}$-$Rh^{(III)}$ Dinuclear Trihydride Complex Revealing the Dihydrogen Activation by $[Rh(CO)_2\{(R,R)\text{-Ph-BPE}\}]^+$

Delphine Crozet[a], David McKay[b], Christian Bijani[c], Aitor Gual[d], Cyril Godard[d], Carmen Claver[d], Laurent Maron[b], Martine Urrutigoïty*[a], and Philippe Kalck*[a]

*[a]* Laboratoire de Chimie de Coordination UPR CNRS 8241, composante ENSIACET, Université de Toulouse UPS-INP-LCC
4 allée Emile Monso BP 44362, 31030 Toulouse Cedex 4, France
E-mail : Philippe.Kalck@ensiacet.fr

*[b]* LPCNO, UMR 5215, Université de Toulouse-CNRS, INSA, UPS, 135 avenue de Rangueil, F-31077 Toulouse Cedex 4, France

*[c]* Laboratoire de Chimie de Coordination, CNRS UPR 8241,
Université de Toulouse UPS-INP-LCC
205, route de Narbonne, 31077 cedex 04, France

*[d]* Departament de Quimica Fisica i Inoranica
Universitat Rovira i Virgili, C/Marcel·li Domingo s/n
43007 Tarragona, Spain

# Contents

## SI.1 Experimental Section

**General Comments** : All reactions and manipulations were carried out under a dry oxygen-free nitrogen atmosphere by using standard Schlenk techniques. All solvents were carefully purified by appropriate procedures. THF-$d^8$, $CD_2Cl_2$, toluene-$d^8$, $CD_3OD$ were stored over molecular sieves under nitrogen. Air sensitive compounds were stored under argon.

**NMR data.** Standard NMR spectra were recorded either on a Bruker AV400 spectrometer equipped with a 5 mm triple resonance inverse probe with dedicated $^{31}P$ channel operating at 400.13 MHz for $^{1}H$, 161.97 for $^{31}P$, and 100.61 MHz for $^{13}C$. All chemical shifts for $^{1}H$ and $^{13}C$ are relative to TMS using $^{1}H$ (residual) or $^{13}C$ chemical shifts of the solvent as a secondary standard. $^{31}P$ chemical shifts were referenced to an external 85% $H_3PO_4$ sample.

**HP NMR spectroscopic study.** All high pressure NMR experiments were performed analogously, therefore only a typical procedure is described there. A 5 mm QPV NMR tube was charged under argon with 0.7 ml of a deuterated solvent solution of rhodium complex. Afterward, the NMR was charged with 7 bar $H_2$ (or with CO or $CO/H_2$) and HP-NMR spectra were recorded at room temperature or cooling the solution, according to the experiments carried out.

**Synthesis {1,2-Bis[(*R*,*R*)-2,5-diphenylphospholano]ethane}(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate.**

A solution of $[RhCl(COD)]_2$ dimer complex (50 mg, 0.10 mmol) and $AgBF_4$ silver salt (39mg, 0.2 mmol) in de-gassed dry acetone (15 mL), under an atmosphere of nitrogen was stirred at room temperature during 1h. Then the solution was filtered to remove the white AgCl precipitate and 1,2-Bis[(*R*,*R*)-2,5-diphenylphospholano]ethane (102.7 mg, 0.2 mmol) was added to the filtered solution under nitrogen atmosphere, and the solution was stirred during 2 hours. Concentration in vacuo gave an orange powder (156 mg, 96%).

**$^{1}H$ NMR (300 MHz, $CDCl_3$)**: δ = 1.17-1.36 (m, 4H), 1.64-1.78 (m, 4H), 2.01-2.07 (m, 2H), 2.19-2.31 (m, 4H), 2.48-2.62 (m, 6H), 3.44-3.52 (m, 2H), 3.55-3.62 (m, 2H), 4.30 (m, 2H), 5.41 (m, 2H), 6.82 (d, *J* = 9 Hz, 4H), 7.10 (t, *J* = 9 Hz, 4H), 7.13 (t, *J* = 9 Hz, 2H), 7.35 (d, *J* = 9 Hz, 4H), 7.4 (t, *J* = 9 Hz, 2H), 7.52 ppm (t, *J* = 11.2 Hz, 4H). **$^{31}P$ NMR (121 MHz, $CDCl_3$):** δ =78.41 ppm (d, $^{1}J_{Rh\text{-}P}$ = 153 Hz). **$^{13}C$ NMR (75.5 MHz, $CDCl_3$):** δ = 24.22 (m, bridge CH2), 26.91 (s), 31.37 (s), 31.57 (s), 32.96 (s), 47.06 (m, ring CH), 49.69 (m, ring CH), 94.21 (m), 101.43 (m), 126.94 (s), 127.45 (m), 127.88 (s), 128.62 (s), 128.67 (s), 129.36 (s), 135.33 (s), 139.06 ppm (s). **$^{103}Rh$ NMR (15.8 MHz, $CDCl_3$):** δ = - 8477 ppm

**Synthesis of (1), {1,2-Bis[(*R*,*R*)-2,5-diphenylphospholano]ethane}(dicarbonyl)rhodium(I) tetrafluoroborate.**

CO was bubbled through a solution of [Rh(COD){(*R*,*R*)-Ph-BPE}]$BF_4$ (50 mg, 0.062 mmol) in $CH_2Cl_2$ (15 mL) under stirring, at room temperature. After 30 min. the solution has turned from orange to yellow and was concentrated *in vacuo*. Adding $Et_2O$ (10 mL) under nitrogen allowed to precipitate a yellow powder, which could be isolated after filtration of the remaining solution, and after being dried *in vacuo* (44 mg, 95%).

**$^1$H NMR (500 MHz, THF-d$^8$, 298 K)**: δ = 1.85 (m, 2H, -P-C**H**H-C**H**H-P-), 2.02 (m, 2H, -P-C**H**H-C**H**H-P-), 2.36 (m, 2H, -$CH_2$-CH**H**- phospholane), 2.57 (m, 2H, -$CH_2$-CH**H**- phospholane), 2.63 (m, 2H, -$CH_2$-CH**H**- phospholane), 2.72 (m, 2H, -$CH_2$-CH**H**- phospholane), 3.93 (dd, 2H, -P-C**H**Ph-$CH_2$), 4.04 (dd, 2H, -P-C**H**Ph-$CH_2$-), 7.03 (m, 4H, -$C_6H_5$), 7.23 (m, 2H, -$C_6H_5$), 7.25 (m, 4H, -$C_6H_5$), 7.36 (m, 4H, -$C_6H_5$), 7.37 (m, 2H, -$C_6H_5$), 7.44 ppm (m, 4H, -$C_6H_5$). **$^{31}$P NMR (202 MHz, THF-d$^8$):** δ = 94 ppm (d, $^1J_{Rh\text{-}P}$ = 121 Hz). **$^{13}$C NMR (125.8 MHz, THF-d$^8$):** δ = 23.40 (-P-(**C**$H_2$)$_2$-P-), 31.87 (-(**C**$H_2$)$_2$- phospholane), 32.06 (-(**C**$H_2$)$_2$-phospholane), 48.0 (-P-**C**HPh-$CH_2$-), 48.7 (-P-**C**HPh-$CH_2$-), 126.64 (-$C_6H_5$), 127.53 (-$C_6H_5$), 127.7 (-$C_6H_5$), 128.30 (-$C_6H_5$), 128.58 (-$C_6H_5$), 129.15 (-$C_6H_5$), 134.31 (-C, Ph), 139.58 ppm (-C, Ph), 184.6 ppm (dd, CO ligands, $^1J_{Rh\text{-}C}$=61 Hz, $^2J_{Ptrans\text{-}CO}$=72 Hz, assigned with the $^{13}$CO labeled complex). **$^{103}$Rh NMR (15.8 MHz, THF-d$^8$):** δ = -8855 ppm. **IR** ($\nu_{CO}$, cm$^{-1}$): 2096, 2045.

**Synthesis of (2), [RhH(CO)$_2${(*R*,*R*)-Ph-BPE}]$BF_4$**

The rhodium precursor [Rh(acac)$(CO)_2$] (0.024 mmol, 6.2 mg) and the diphosphine ligand (*R*,*R*)-Ph-BPE (0.0264 mmol, 13 mg) were introduced in solution (1.5 mL solvent = $CD_2Cl_2$ or THF-$d_8$) in the autoclave under inert atmosphere, and stirred during 30 min. under 30 bar $CO/H_2$ (1:2) before being transferred in the 5 mm NMR tube.

**$^1$H NMR (500 MHz, THF-d$^8$, 298 K)**: δ = -9.74 (td, 1H, Rh-**H**), -0.5 (m, 2H, -P-C**H**H-C**H**H-P-), 1.73 (m, 2H, -P-C**H**H-C**H**H-P-), 2.13 (m, 2H, -$CH_2$-CH**H**- phospholane), 2.22 (m, 4H, -$CH_2$-CH**H**- phospholane), 2.28 (m, 2H, -$CH_2$-CH**H**- phospholane), 3.01 (dd, 2H, -P-C**H**Ph-$CH_2$), 3.32 (dd, 2H, -P-C**H**Ph-$CH_2$-), 7.04 (m, 4H, -$C_6H_5$), 7.09 (m, 4H, -$C_6H_5$), 7.22 (m, 2H, -$C_6H_5$), 7.26 (m, 2H, -$C_6H_5$), 7.28 (m, 4H, -$C_6H_5$), 7.32 ppm (m, 2H, -$C_6H_5$). **$^{31}$P NMR (202 MHz, THF-d$^8$):** δ = 97.9 ppm (dd, $^1J_{Rh\text{-}P}$ = 119 Hz, $^2J_{H\text{-}P}$=55 Hz). **$^{13}$C NMR (125,8 MHz, THF-d$^8$):** δ = 27.63 (-P-(**C**$H_2$)$_2$-P-), 31.78 (-(**C**$H_2$)$_2$- phospholane), 33.39 (-(**C**$H_2$)$_2$-phospholane), 50.82 (-P-**C**HPh-$CH_2$-), 57.87 (-P-**C**HPh-$CH_2$-), 125.95 (-$C_6H_5$), 126.18 (-$C_6H_5$), 127.66 (-$C_6H_5$), 127.77 (-$C_6H_5$), 128.15 (-$C_6H_5$), 128.82 (-$C_6H_5$), 136.8 (-C, Ph), 141.39 (-C, Ph), 196.85 ppm (dt, CO ligands, $^1J_{Rh\text{-}C}$ = 69.4Hz, assigned with the $^{13}$CO labeled complex). **$^{103}$Rh NMR (15.8 MHz, THF-d$^8$):** δ = -9041 ppm. **IR** (THF, $\nu_{CO}$, cm$^{-1}$): 1987, 1943.

**Reaction between equimolar amounts of 1 and 2 under $H_2$ pressure**

In a batch reactor specially adapted for the experiments, the complex **2** was prepared at room temperature from [Rh(acac)$(CO)_2$] and (R,R)-Ph-BPE under 30 bar $CO/H_2$ pressure in $CD_2Cl_2$. The monohydride complex is quantitatively obtained under these conditions, and is stable upon removal of the gas pressure. The pressure was then removed, and a solution containing an equimolar amount of the cationic complex **1** in $CD_2Cl_2$ was then added. The solution was transferred into the HP NMR tube, and pressurized under 7 bar $H_2$.

## SI.2 HP NMR experiments: complex 1 under 7 bar $H_2$ (THF-$d^8$)

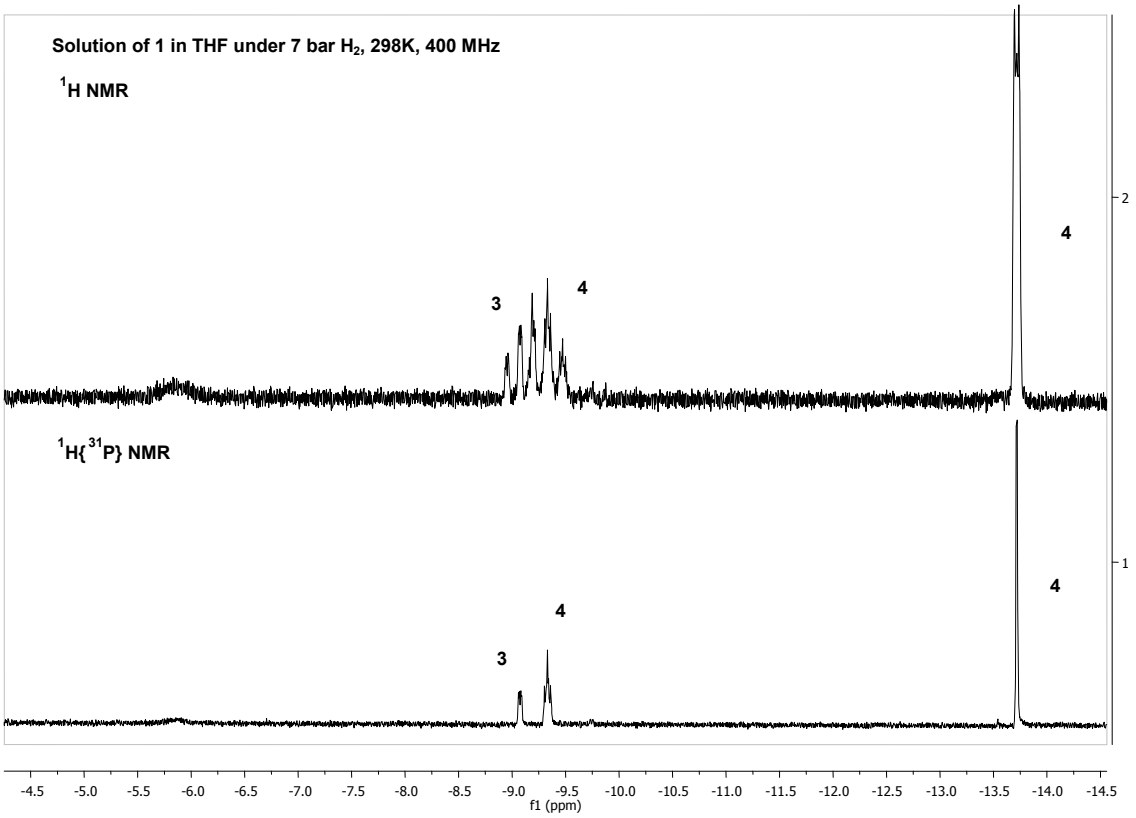



**Figure 1. $^1$H NMR spectrum of 1 under 7 bar $H_2$ (THF-$d^8$, 298K)**

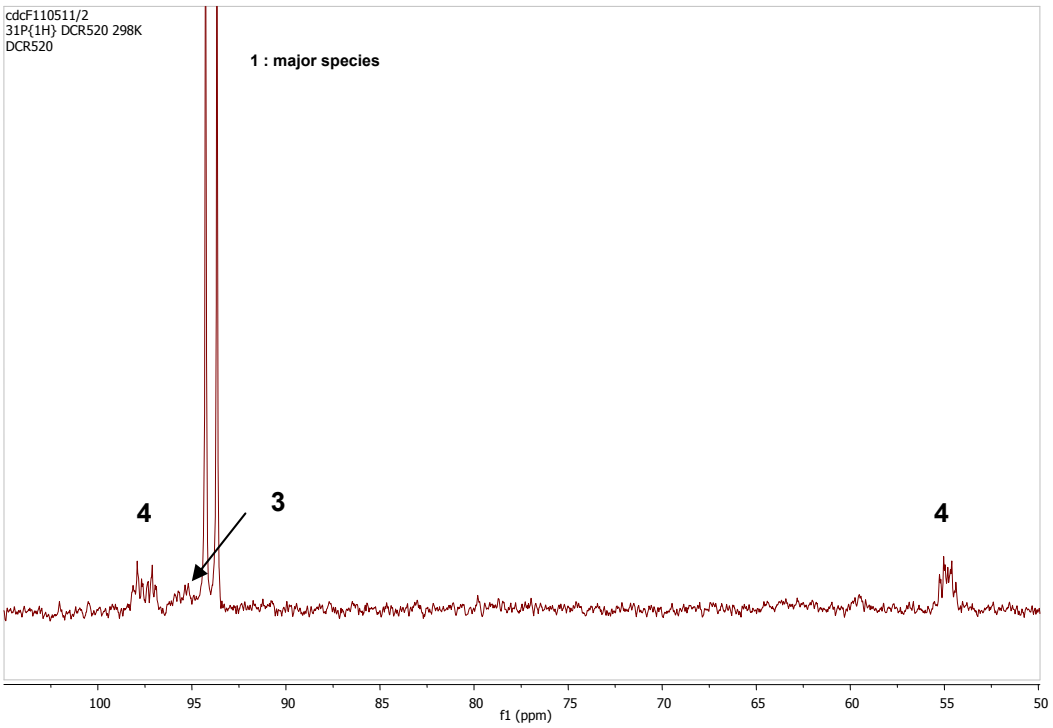



**Figure 2. $^{31}P\{^{1}H\}$ NMR spectrum of 1 under 7 bar $H_2$ (THF-$d^8$)**

## SI.3. HP NMR experiment: reaction of 1 and 2 under 7 bar $H_2$ ($CD_2Cl_2$, 298K)

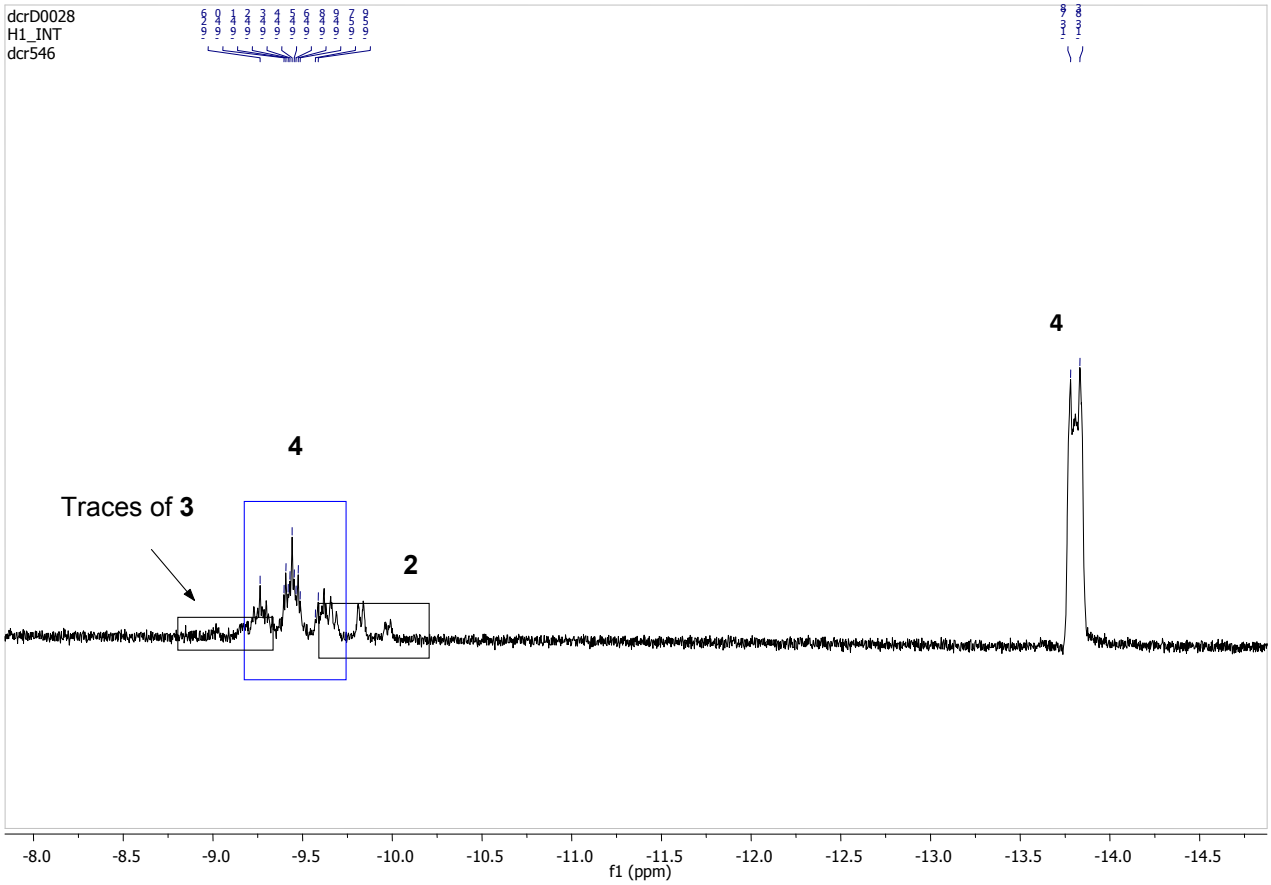



**Figure 3. $^1$H NMR spectrum, reaction of 1 and 2 under 7 bar $H_2$ ($CD_2Cl_2$, 298K)**

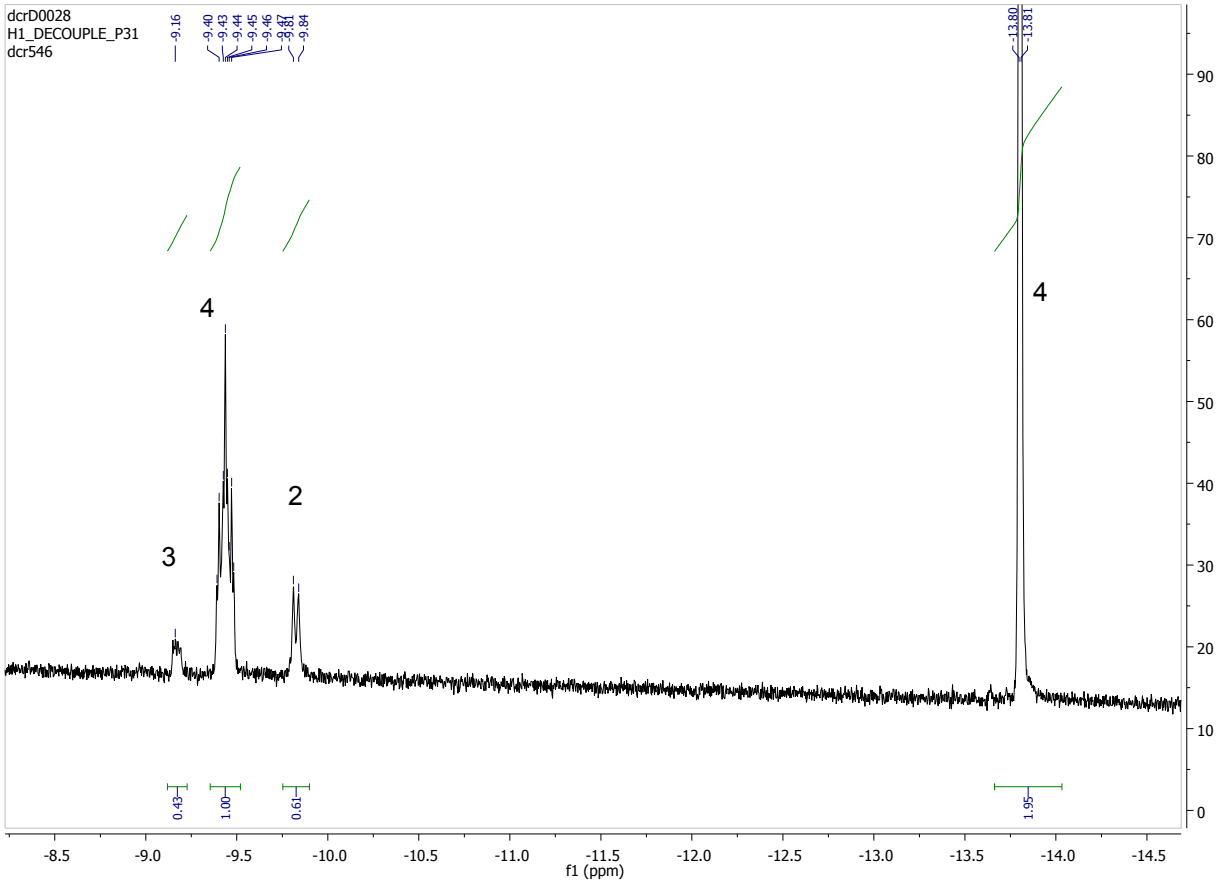



**Figure 4. $^{1}H\{^{31}P\}$ spectrum, reaction of 1 and 2 under 7 bar $H_2$ ($CD_2Cl_2$, 298K)**

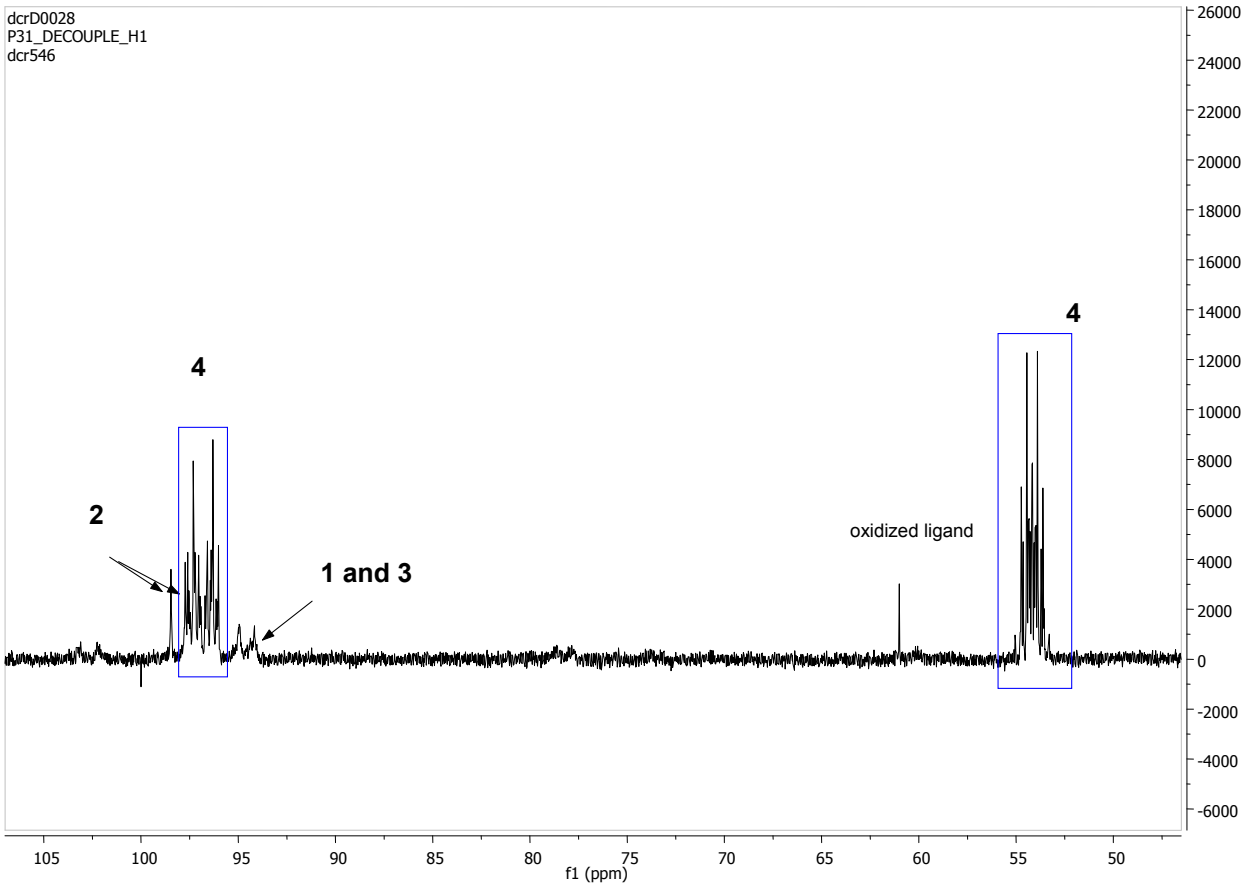
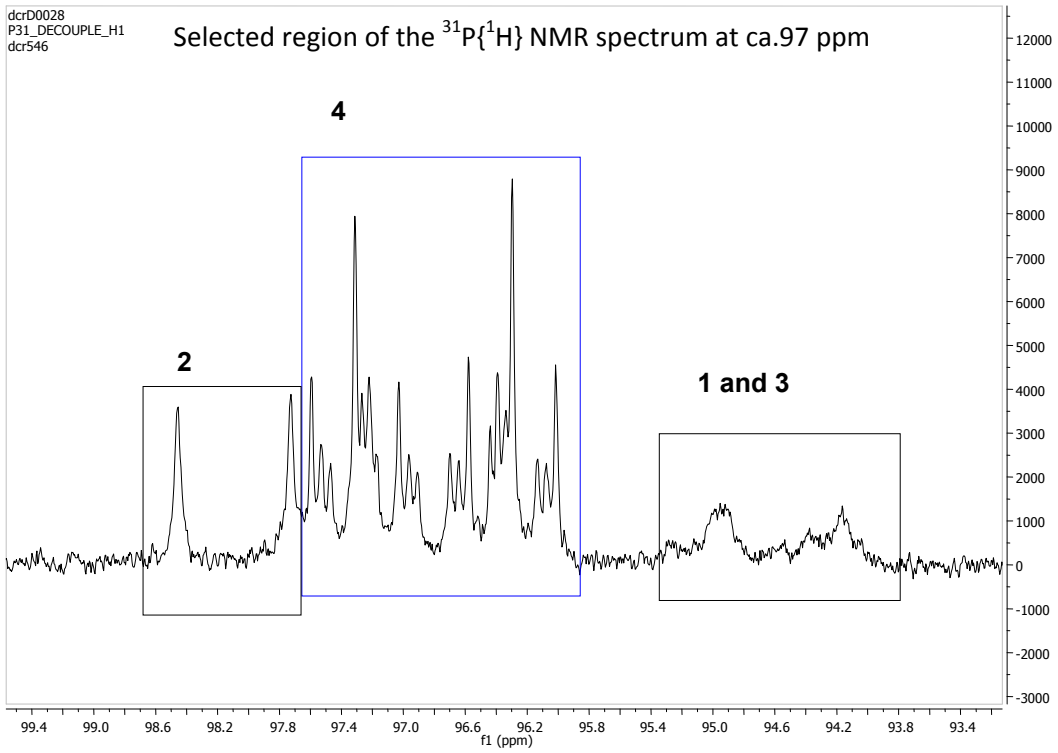
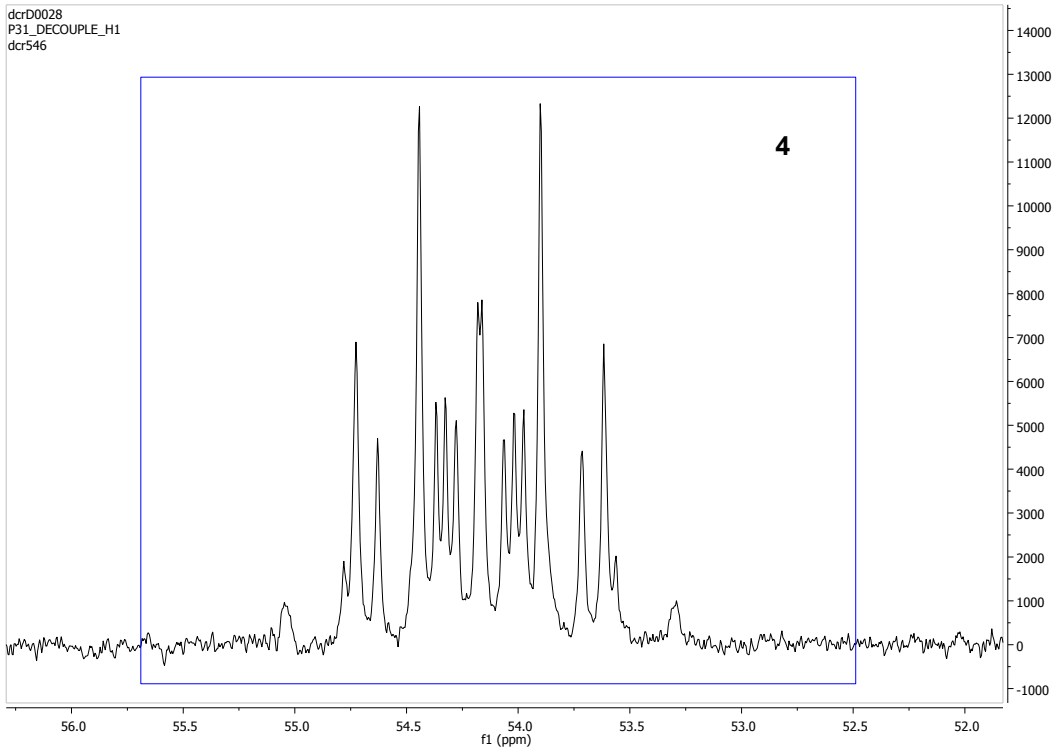



**Figure 5. $^{31}P\{^{1}H\}$ NMR spectrum, reaction of 1 and 2 under 7 bar $H_2$ ($CD_2Cl_2$, 298K)**

**Figure 6. Zoom on $^{31}P\{1H\}$ spectrum : 2$^{nd}$ order spectrum for 4**

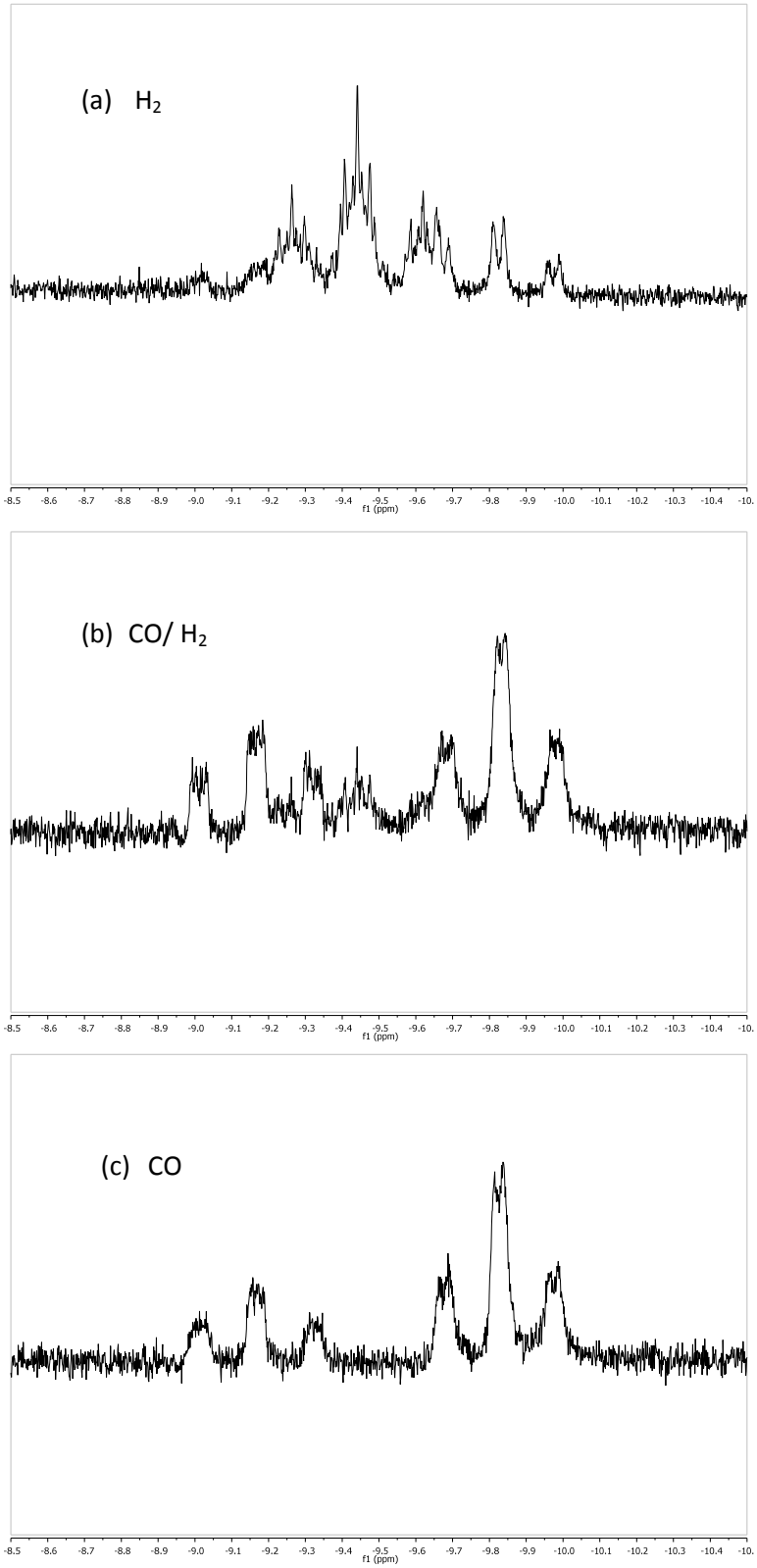



Selected region of the $^{31}P\{^{1}H\}$ NMR spectrum at ca. 54 ppm

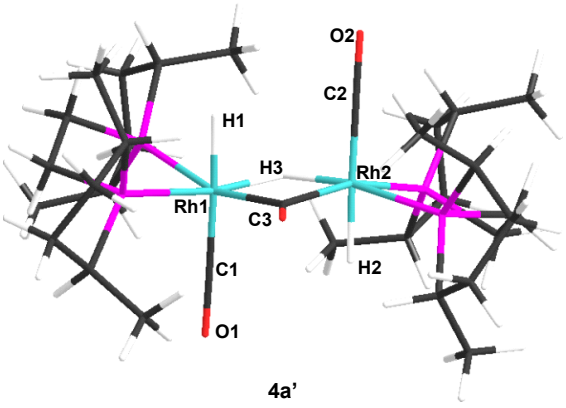


## SI.4. HP NMR experiment, behaviour of complex 4 in the presence of CO

**Figure 7. Behaviour of 4 in the presence of (a) 7 bar $H_2$, (b) 7 bar $CO/H_2$, (c) 7 bar CO. Hydride zone corresponding to the signals of 2, 3 and of the bridging H of complex 4 ($CD_2Cl_2$, 298K).**

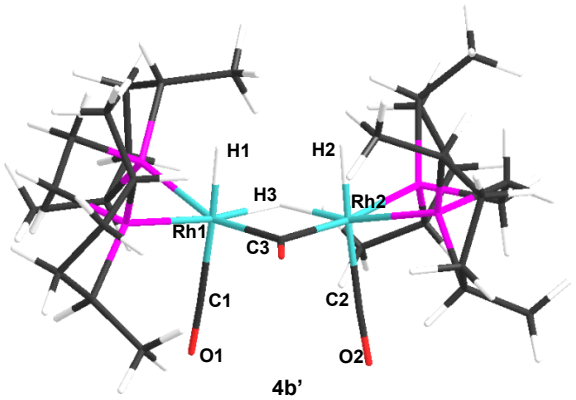


## SI.5. Computational Details




4a'

ΔG = 0.0 kcal.mol $^{-1}$




4b'

ΔG = +2.7 kcal.mol $^{-1}$

**Comparison of computed geometries of 4a' and 4b'**

Calculations were performed using Gaussian 03 Revision E.01,[1] adopting the B3PW91 functional.[2] 6-31G** basis sets[3] were used to describe C, H and O atoms whilst the Stuttgart-Dresden pseudopotential and associated basis sets were adopted for Rh and P.[4] For P, the basis sets were polarized with an additional d-function ($\zeta = 0.180$).[5] Geometry optimisations were performed without constraints and minima confirmed as such through analytical frequency calculations. Polarized Continuum Model calculations[6] were performed using THF as solvent ($\varepsilon = 7.58$) and UFF radii. Geometrical measurements were made using Mercury.[7]

In both species, the diphosphine ligand at each metal is inclined away from the respective terminal CO ligand. In **4a'** this inclination, $\theta = 100.8°$ (where $\theta$ is defined as the C1-Rh1-*c* angle and *c* as the P···P centroid of the adjacent diphosphine). In **4b'**, $\theta = 96.2°$, suggesting a less flexible structure. Distortion away from an octahedral geometry has the effect of rotating the diphosphine ligands in parallel in **4a'** but towards each other in **4b'**, leading to closer through-space contacts between carbon substituents of the diphosphine ligands in the latter. These steric effects are presumed to increasingly favour **4a** over **4b**, where (*R*,*R)*-Me-BPE is substituted for the larger (*R*,*R)*-Ph-BPE diphosphine ligand.

**References**

1. M. J. Frisch, G.W. Trucks, H. B. Schlegel, G. E. Scuseria,M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J.M.Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov,G. Liu,A. Liashenko, P. Piskorz, I. Komaromi, R. L.Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara,M.

Challacombe, P.M.W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision E.01)*, Gaussian, Inc., Wallingford, CT, 2004.

2. (a) J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (c) K. Burke, J. P. Perdew and W. Yang, *Electronic Density Functional Theory: Recent Progress and New Directions*, Plenum, New York, 1998.
3. (a) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (b) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
4. (a) A. Bergner, M. Dolg, H. Kuechle, H. Stoll and H. Preuss, *Mol. Phys.*, 1993, **80**, 1431; (b) M. Kaupp, P. v. R. Schleyer, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1991, **94**, 1360; (c) M. Dolg, H. Stoll, H. Preuss and R. M. Pitzer, *J. Phys. Chem.*, 1993, **97**, 5852.
5. A. Höllworth, M. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Syegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 237.
6. J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.
7. *Mercury*, version 1.4.2, Cambridge Crystallographic Data Center, Cambridge, UK, 2006.

## Computed Geometries

**4a'**

SCF (B3PW91) Energy = -1689.56890504
Enthalpy 0K = -1688.717100
Enthalpy 298K = -1688.665515
Free Energy 298K = -1688.806019
PCM (THF) Free Energy = -1689.535684

| | | | |
|---|---|---|---|
| Rh | -1.402964 | -0.115333 | -0.188208 |
| Rh | 1.403159 | -0.115238 | 0.188179 |
| C | -1.354678 | 0.054953 | -2.122412 |
| O | -1.340946 | 0.179957 | -3.264685 |
| H | 1.494300 | -0.229053 | -1.398328 |
| H | 0.000120 | 0.946014 | -0.000124 |
| C | 0.000119 | -1.586404 | 0.000073 |
| O | 0.000172 | -2.772618 | 0.000161 |
| H | -1.494190 | -0.229019 | 1.398307 |
| C | 1.354765 | 0.055474 | 2.122332 |
| P | 2.927182 | 1.730486 | -0.267427 |
| P | 3.275546 | -1.547941 | 0.039176 |
| C | 4.796222 | -0.431060 | -0.145319 |
| C | 4.491827 | 0.857493 | -0.897325 |
| H | 5.606415 | -0.984129 | -0.628786 |
| H | 5.113698 | -0.218684 | 0.881011 |
| H | 5.343713 | 1.542212 | -0.862816 |
| H | 4.280389 | 0.645487 | -1.950101 |
| C | 3.845934 | -2.766353 | 1.382597 |
| C | 3.310941 | -2.851439 | -1.356830 |
| C | 2.666547 | 3.058033 | -1.618697 |
| C | 3.466960 | 2.996138 | 1.081064 |
| C | 3.387035 | 4.291678 | -1.052351 |
| C | 1.192900 | 3.295300 | -1.931756 |
| H | 3.054519 | 5.204310 | -1.560623 |
| H | 4.466026 | 4.208171 | -1.230967 |
| C | 3.117822 | 4.359075 | 0.453980 |
| C | 4.926628 | 2.895970 | 1.516550 |
| H | 3.694342 | 5.160473 | 0.930071 |
| H | 2.059861 | 4.587952 | 0.627478 |
| C | 3.902789 | -4.126512 | -0.710372 |
| C | 4.032724 | -2.387832 | -2.618647 |
| H | 3.090243 | -4.815506 | -0.458426 |
| H | 4.549252 | -4.652002 | -1.421488 |
| C | 4.679415 | -3.764722 | 0.563662 |
| C | 2.682837 | -3.406087 | 2.135999 |
| H | 5.642785 | -3.311924 | 0.298263 |
| H | 4.906978 | -4.657925 | 1.157027 |
| H | 4.476258 | -2.207045 | 2.082682 |
| H | 2.254284 | -3.004979 | -1.592322 |
| H | 2.825705 | 2.795345 | 1.944091 |
| H | 3.168275 | 2.687740 | -2.518944 |
| H | 5.112517 | 3.603423 | 2.332212 |
| H | 5.185198 | 1.900300 | 1.889109 |
| H | 5.620233 | 3.146966 | 0.707980 |
| H | 3.065236 | -4.156132 | 2.837139 |
| H | 2.125452 | -2.664382 | 2.713357 |
| H | 1.974015 | -3.897614 | 1.464653 |
| H | 3.936153 | -3.151082 | -3.398133 |
| H | 3.604607 | -1.462494 | -3.017333 |
| H | 5.103318 | -2.230836 | -2.451728 |
| H | 1.095046 | 4.053306 | -2.717066 |
| H | 0.709187 | 2.378723 | -2.276877 |
| H | 0.641627 | 3.648059 | -1.054343 |
| P | -2.926819 | 1.730571 | 0.267250 |
| P | -3.275463 | -1.547804 | -0.039274 |
| C | -4.796100 | -0.430913 | 0.145499 |
| C | -4.491487 | 0.857704 | 0.897317 |
| H | -5.606096 | -0.983949 | 0.629338 |
| H | -5.113971 | -0.218667 | -0.880734 |
| H | -5.343336 | 1.542474 | 0.862889 |
| H | -4.279915 | 0.645736 | 1.950076 |
| C | -3.845939 | -2.766066 | -1.382671 |
| C | -3.311117 | -2.851463 | 1.356417 |
| C | -2.666260 | 3.058095 | 1.618510 |
| C | -3.466676 | 2.996239 | -1.081200 |
| C | -3.387956 | 4.291251 | 1.052667 |
| C | -1.192595 | 3.296394 | 1.930698 |

| | | | |
|---|---|---|---|
| H | -3.056241 | 5.204036 | 1.561192 |
| H | -4.466850 | 4.206668 | 1.231373 |
| C | -3.118967 | 4.359363 | -0.453673 |
| C | -4.925979 | 2.895003 | -1.517664 |
| H | -3.696421 | 5.160277 | -0.929446 |
| H | -2.061288 | 4.589481 | -0.627215 |
| C | -3.906394 | -4.125488 | 0.710862 |
| C | -4.029595 | -2.386533 | 2.619624 |
| H | -3.095717 | -4.817125 | 0.460156 |
| H | -4.554782 | -4.648360 | 1.422145 |
| C | -4.681402 | -3.763007 | -0.564028 |
| C | -2.682740 | -3.407550 | -2.134424 |
| H | -5.644388 | -3.308817 | -0.299661 |
| H | -4.909681 | -4.656124 | -1.157250 |
| H | -4.474887 | -2.206418 | -2.083724 |
| H | -2.254306 | -3.006995 | 1.589959 |
| H | -2.824718 | 2.796094 | -1.943857 |
| H | -3.167179 | 2.687356 | 2.519024 |
| H | -3.065211 | -4.157543 | -2.835578 |
| H | -2.123823 | -2.666805 | -2.711535 |
| H | -1.975250 | -3.899537 | -1.462004 |
| H | -3.933386 | -3.150140 | 3.398803 |
| H | -3.598636 | -1.462240 | 3.017685 |
| H | -5.100125 | -2.227061 | 2.454619 |
| H | -5.111909 | 3.602491 | -2.333284 |
| H | -5.183501 | 1.899210 | -1.890623 |
| H | -5.620301 | 3.145261 | -0.709480 |
| H | -1.094812 | 4.054413 | 2.716004 |
| H | -0.708027 | 2.380137 | 2.275463 |
| H | -0.642094 | 3.649634 | 1.052994 |
| O | 1.340815 | 0.180968 | 3.264550 |

**4b'**

SCF (B3PW91) Energy = -1689.56468361
Enthalpy 0K = -1688.712873
Enthalpy 298K = -1688.661338
Free Energy 298K = -1688.801672
PCM (THF) Free Energy = -1689.532002

| | | | |
|---|---|---|---|
| Rh | 0.000000 | 0.000000 | 0.000000 |
| Rh | 0.000000 | 0.000000 | 3.234000 |
| C | 2.499000 | 0.000000 | 0.000000 |
| O | 4.000000 | 0.000000 | 0.000000 |
| C | 2.499000 | 0.000000 | 3.234000 |
| O | 4.000000 | 0.000000 | 3.234000 |
| H | 0.000000 | 1.169178 | 1.669759 |
| C | 0.000000 | -1.767060 | 1.767060 |
| O | 0.000000 | -3.167060 | 1.767061 |
| H | -2.038400 | 0.000000 | 0.000000 |
| H | -2.038400 | 0.000000 | 3.234000 |
| P | 0.000000 | 2.009597 | 5.243597 |
| P | 0.000000 | -1.168460 | 5.803974 |
| C | 0.000000 | 0.033325 | 7.267051 |
| C | 0.645657 | 1.354808 | 6.892123 |
| H | 0.524543 | -0.426507 | 8.108574 |
| H | -1.046590 | 0.174613 | 7.551207 |
| H | 0.476009 | 2.110984 | 7.663733 |
| H | 1.724951 | 1.237560 | 6.747531 |
| C | -1.346382 | -2.433861 | 6.284501 |
| C | 1.380387 | -2.437547 | 6.164553 |
| C | 1.046648 | 3.573538 | 4.967072 |
| C | -1.641743 | 2.971060 | 5.582413 |
| C | 0.300793 | 4.593148 | 5.856377 |
| C | 1.213052 | 3.984959 | 3.586658 |
| H | 0.643993 | 5.607494 | 5.630358 |
| H | 0.548316 | 4.400854 | 6.907598 |
| C | -1.210226 | 4.458799 | 5.630280 |
| C | -2.368235 | 2.454078 | 6.725845 |
| H | -1.771051 | 4.990879 | 6.403707 |
| H | -1.470356 | 4.929228 | 4.677883 |
| C | 0.846414 | -3.273750 | 7.345949 |
| C | 2.706440 | -1.861867 | 6.277134 |
| H | 1.173754 | -4.310074 | 7.212386 |
| H | 1.303237 | -2.941050 | 8.281246 |
| C | -0.700997 | -3.186321 | 7.466778 |
| C | -1.746167 | -3.232835 | 5.142436 |
| H | -0.960252 | -2.656573 | 8.388461 |
| H | -1.146871 | -4.181739 | 7.553807 |
| H | -2.204569 | -1.844532 | 6.622410 |
| H | 1.352255 | -3.050513 | 5.255981 |
| H | -2.245753 | 2.788958 | 4.690011 |
| H | 2.032082 | 3.352773 | 5.390528 |
| H | -3.280270 | 3.031932 | 6.867964 |
| H | -2.623541 | 1.409829 | 6.551820 |
| H | -1.746514 | 2.532202 | 7.616509 |
| H | -2.513081 | -3.943415 | 5.447135 |
| H | -2.142928 | -2.581701 | 4.364924 |
| H | -0.882744 | -3.773447 | 4.757520 |
| H | 3.428508 | -2.650883 | 6.482055 |
| H | 2.966873 | -1.364926 | 5.343783 |
| H | 2.719851 | -1.137436 | 7.090117 |
| H | 1.825209 | 4.884758 | 3.547331 |
| H | 1.701650 | 3.188762 | 3.026958 |
| H | 0.237273 | 4.190348 | 3.148947 |
| P | 0.000000 | 2.009597 | -2.009597 |
| P | 0.000000 | -1.168460 | -2.569975 |
| C | 0.000000 | 0.033325 | -4.033051 |
| C | -0.645657 | 1.354808 | -3.658123 |
| H | -0.524543 | -0.426507 | -4.874574 |
| H | 1.046590 | 0.174613 | -4.317208 |
| H | -0.476009 | 2.110984 | -4.429733 |
| H | -1.724951 | 1.237560 | -3.513531 |
| C | 1.346382 | -2.433861 | -3.050501 |
| C | -1.380387 | -2.437547 | -2.930553 |
| C | -1.046648 | 3.573538 | -1.733072 |
| C | 1.641743 | 2.971060 | -2.348413 |
| C | -0.300793 | 4.593148 | -2.622377 |
| C | -1.213052 | 3.984959 | -0.352659 |
| H | -0.643993 | 5.607494 | -2.396359 |
| H | -0.548316 | 4.400854 | -3.673598 |
| C | 1.210226 | 4.458799 | -2.396280 |
| C | 2.368235 | 2.454078 | -3.491846 |
| H | 1.771051 | 4.990879 | -3.169707 |
| H | 1.470356 | 4.929228 | -1.443883 |
| C | -0.846414 | -3.273750 | -4.111949 |
| C | -2.706440 | -1.861867 | -3.043134 |
| H | -1.173754 | -4.310074 | -3.978386 |
| H | -1.303237 | -2.941050 | -5.047246 |
| C | 0.700997 | -3.186321 | -4.232779 |

| | | | |
|---|---|---|---|
| C | 1.746167 | -3.232835 | -1.908436 |
| H | 0.960252 | -2.656573 | -5.154461 |
| H | 1.146871 | -4.181739 | -4.319807 |
| H | 2.204569 | -1.844532 | -3.388410 |
| H | -1.352255 | -3.050513 | -2.021981 |
| H | 2.245753 | 2.788958 | -1.456012 |
| H | -2.032082 | 3.352773 | -2.156529 |
| H | 2.513081 | -3.943415 | -2.213134 |
| H | 2.142928 | -2.581702 | -1.130923 |
| H | 0.882743 | -3.773447 | -1.523521 |
| H | -3.428508 | -2.650883 | -3.248055 |
| H | -2.966874 | -1.364926 | -2.109783 |
| H | -2.719851 | -1.137436 | -3.856118 |
| H | 3.280270 | 3.031932 | -3.633965 |
| H | 2.623541 | 1.409829 | -3.317821 |
| H | 1.746514 | 2.532202 | -4.382509 |
| H | -1.825209 | 4.884758 | -0.313331 |
| H | -1.701650 | 3.188762 | 0.207041 |
| H | -0.237273 | 4.190348 | 0.085053 |

**2'**

SCF (B3PW91) Energy = -901.617500649
Enthalpy 0K = -901.183266
Enthalpy 298K = -901.156900
Free Energy 298K = -901.240328
PCM (THF) Free Energy = -901.626509

| | | | |
|---|---|---|---|
| C | 0.531000 | -1.296000 | -1.788000 |
| C | -0.800000 | -0.602000 | -2.048000 |
| H | 1.096000 | -1.425000 | -2.717000 |
| H | 0.379000 | -2.286000 | -1.348000 |
| H | -0.652000 | 0.372000 | -2.524000 |
| H | -1.444000 | -1.199000 | -2.701000 |
| Rh | -0.049000 | 0.338000 | 1.160000 |
| P | 1.568000 | -0.303000 | -0.556000 |
| P | -1.707000 | -0.282000 | -0.422000 |
| C | -3.158000 | 0.905000 | -0.768000 |
| H | -3.266000 | 1.457000 | 0.173000 |
| C | -2.816000 | -1.803000 | -0.100000 |
| H | -2.782000 | -2.351000 | -1.051000 |
| C | 2.605000 | 0.900000 | -1.631000 |
| H | 2.357000 | 0.619000 | -2.663000 |
| C | 3.054000 | -1.398000 | -0.087000 |
| H | 3.362000 | -1.008000 | 0.891000 |
| C | -4.361000 | -0.034000 | -0.932000 |
| H | -5.294000 | 0.517000 | -0.778000 |
| H | -4.388000 | -0.425000 | -1.958000 |
| C | -4.214000 | -1.186000 | 0.062000 |
| H | -4.982000 | -1.952000 | -0.087000 |
| H | -4.333000 | -0.813000 | 1.088000 |
| C | 4.058000 | 0.491000 | -1.336000 |
| H | 4.714000 | 0.816000 | -2.150000 |
| H | 4.402000 | 1.005000 | -0.428000 |
| C | 4.120000 | -1.021000 | -1.124000 |
| H | 3.921000 | -1.545000 | -2.068000 |
| H | 5.112000 | -1.341000 | -0.787000 |
| C | -2.945000 | 1.886000 | -1.914000 |
| H | -2.846000 | 1.372000 | -2.876000 |
| H | -3.810000 | 2.552000 | -1.990000 |
| H | -2.064000 | 2.518000 | -1.767000 |
| C | -2.392000 | -2.720000 | 1.037000 |
| H | -1.410000 | -3.169000 | 0.862000 |
| H | -2.355000 | -2.184000 | 1.990000 |
| H | -3.114000 | -3.537000 | 1.137000 |
| C | 2.317000 | 2.379000 | -1.421000 |
| H | 1.288000 | 2.643000 | -1.680000 |
| H | 2.500000 | 2.680000 | -0.384000 |
| H | 2.977000 | 2.980000 | -2.055000 |
| C | 2.756000 | -2.886000 | 0.041000 |
| H | 2.476000 | -3.329000 | -0.920000 |
| H | 3.650000 | -3.411000 | 0.392000 |
| H | 1.958000 | -3.085000 | 0.762000 |
| C | 1.134000 | 0.398000 | 2.664000 |
| C | -0.277000 | 2.281000 | 0.888000 |
| O | 1.803000 | 0.374000 | 3.588000 |
| O | -0.486000 | 3.401000 | 0.813000 |
| H | -0.088000 | -1.209000 | 1.468000 |
| H | -1.251000 | 0.358000 | 2.182000 |

**3'**

SCF (B3PW91) Energy = -901.212597110
Enthalpy 0K = -900.788550
Enthalpy 298K = -900.762271
Free Energy 298K = -900.845098
PCM (THF) Free Energy = -901.179883

| | | | |
|---|---|---|---|
| C | 0.174030 | -0.934263 | 0.258926 |
| C | 1.323278 | -0.028790 | -0.169064 |
| H | -0.499334 | -0.430689 | 0.961637 |
| H | 0.556427 | -1.839108 | 0.743015 |
| H | 0.939894 | 0.884103 | -0.636961 |
| H | 1.944905 | 0.263396 | 0.684078 |
| Rh | 0.871422 | -2.148621 | -2.882271 |
| P | -0.793576 | -1.506095 | -1.273608 |
| P | 2.374463 | -0.917578 | -1.484772 |
| C | 3.542351 | 0.434842 | -2.165233 |
| H | 3.861184 | 0.012563 | -3.126793 |
| C | 3.772018 | -1.731762 | -0.436718 |
| H | 3.543738 | -1.466947 | 0.603853 |
| C | -2.095836 | -0.103006 | -1.482437 |
| H | -1.906159 | 0.578127 | -0.642548 |
| C | -2.081472 | -2.747739 | -0.607883 |
| H | -2.347648 | -3.326208 | -1.501620 |
| C | 4.736475 | 0.441074 | -1.207939 |
| H | 5.598574 | 0.954798 | -1.651962 |
| H | 4.475370 | 0.992794 | -0.293680 |
| C | 5.060906 | -1.013990 | -0.868517 |
| H | 5.830275 | -1.092534 | -0.090907 |
| H | 5.464006 | -1.510939 | -1.761665 |
| C | -3.448583 | -0.797147 | -1.262259 |
| H | -4.218218 | -0.067341 | -0.983508 |
| H | -3.773870 | -1.255831 | -2.206026 |
| C | -3.281246 | -1.886291 | -0.202960 |
| H | -3.094905 | -1.430292 | 0.779802 |
| H | -4.187119 | -2.496655 | -0.101371 |
| C | 2.890404 | 1.785889 | -2.418235 |
| H | 2.601651 | 2.279318 | -1.483990 |
| H | 3.586175 | 2.454809 | -2.937702 |
| H | 1.998541 | 1.686595 | -3.045846 |
| C | 3.833413 | -3.245713 | -0.578932 |

| | | | |
|---|---|---|---|
| H | 2.905940 | -3.721834 | -0.249731 |
| H | 3.988925 | -3.534851 | -1.623231 |
| H | 4.658474 | -3.655563 | 0.016408 |
| C | -2.000504 | 0.666636 | -2.790820 |
| H | -1.020880 | 1.135711 | -2.917335 |
| H | -2.161680 | 0.009835 | -3.650423 |
| H | -2.760495 | 1.456643 | -2.823911 |
| C | -1.570610 | -3.701441 | 0.462717 |
| H | -1.319165 | -3.173077 | 1.388165 |
| H | -2.340682 | -4.441676 | 0.708462 |
| H | -0.685360 | -4.249227 | 0.125796 |
| C | 0.687466 | -4.017941 | -2.640853 |
| O | 0.586829 | -5.172343 | -2.579036 |
| C | 0.319050 | -1.256078 | -4.466957 |
| O | 0.037642 | -0.805277 | -5.497488 |
| H | 2.138222 | -2.528165 | -3.740960 |

**CO**

SCF (B3PW91) Energy = -113.258297204
Enthalpy 0K = -113.253238
Enthalpy 298K = -113.250878
Free Energy 298K = -113.272375
PCM (THF) Free Energy = -113.254923

| | | | |
|---|---|---|---|
| C | -0.033084 | 0.013350 | 2.235027 |
| O | -0.050778 | 0.017223 | 3.371896 |