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Supporting Information

Effector controlled transition metal catalysis to regulate the selectivity and activity of a hydroformylation catalyst

Shao-Tao Bai,[a] Vivek Sinha,[a] Alexander M. Kluwer,[b] Pim R. Linnebank,[a] Zohar Abiri,[b] Paweł Dydio,[a†] Martin Lutz,[c] Bas de Bruin[a] and Joost N. H. Reek*[a,b]

[a] Homogeneous Supramolecular and Bio-inspired Catalysis, Van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam (UvA), Science Park 904, 1098 XH Amsterdam, The Netherlands. Email: j.n.h.reek@uva.nl

[b] InCatT B.V. Science Park 904, 1098 XH Amsterdam, The Netherlands

[c] Bijvoet Center for Biomolecular Research, Utrecht University, The Netherlands

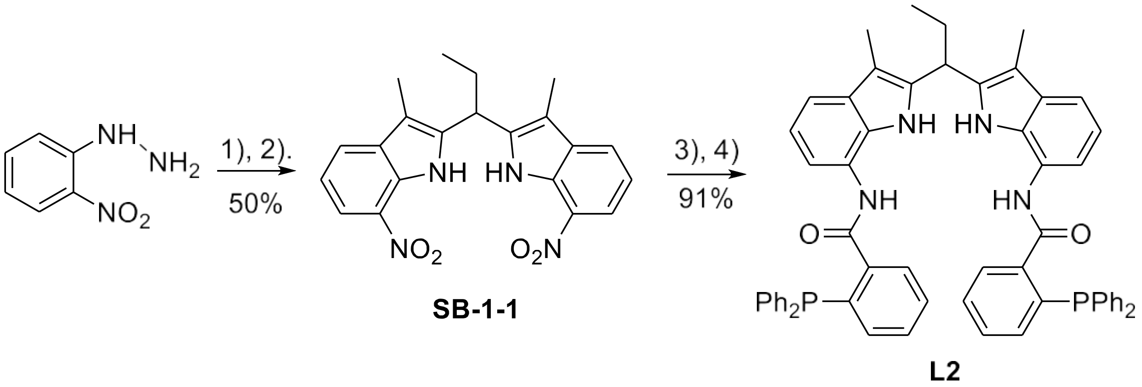
[†] Present address: Complex Systems in Synthesis & Catalysis, University of Strasbourg, CNRS UMR 7006, 8 Rue Gaspard Monge, 67000, Strasbourg, France

Table of Contents

General Information

All reactions involving air- or moisture sensitive materials were carried out under nitrogen atmosphere using standard Schlenk techniques or in the Glovebox. THF, pentane, hexane and toluene were distilled from sodium-benzophenone under nitrogen atmosphere; dichloromethane and methanol were distilled from CaH_2 under nitrogen atmosphere; triethylamine was distilled from KOH pellets under nitrogen atmosphere. CD_2Cl_2 and *N,N*-diisopropylethylamine were dried over molecular sieves (3Å) and degassed by three freeze-pump-thaw cycles. ^{1}H NMR, ^{13}C NMR, ^{31}P{^{1}H} NMR, ^{1}H DOSY NMR, ^{1}H{^{31}P} NMR, VT NMR and ^{1}H{sel^{31}P} NMR spectra were measured on Bruker AMX 300 MHz, Bruker AMX 400 MHz or Bruker AMX 500 MHz. ^{1}H NMR chemical shifts are given in ppm, and were calibrated using the residual solvent as internal reference ($CHCl_3$ 7.26 ppm, CH_2Cl_2 5.32 ppm). ^{13}C NMR chemical shifts were reported in ppm with the solvent peaks used as internal reference ($CHCl_3$ 77.16 ppm, CH_2Cl_2 53.84 ppm). Infrared (IR) spectra were recorded on a Thermo Nicolet Nexus FT-IR spectrometer. Mass spectra were collected on an AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer (JEOL, Japan). X-ray crystal diffraction data was collected on a Bruker Kappa ApexII diffractometer equipped with sealed tube and Triumph monochromator ($\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max} = 0.65$ Å^{-1}. If not stated otherwise, syngas referred to a 1:1 mixture of H_2 and CO, and the pressure refers to a sum pressure of both. All reagents were purchased from commercial suppliers and used without further purification, unless otherwise noted.

Synthesis of OrthoDIMPhos L2



Scheme S1. 1) C_2H_5CHO, CH_3CO_2H, reflux 2 h; 2) C_2H_5CHO, conc. HCl, reflux 2 h; 3) 1 bar H_2, Pd/C, MeOH/THF, RT; 4) 2-(Diphenylphosphino)benzoic acid, 4-pyrrolidinopyridine, 4-Dimethylaminopyridine, *N,N'*-diisopropylcarbodiimide, RT.

1,1-Bis-(3-methyl-7-nitro-1H-indol-2-yl)-propane (**SB-1-1**)

A mixture of 2-nitrophenylhydrazine, moistened with 30% water, as received from Sigma Aldrich (60 g, 0.38 mol, 1.0 eq.), propionaldehyde (50 mL, 0.70 mol, 1.8 eq.), acetic acid (2.0 mL, 0.03 mol, 0.09 eq.) and ethanol (0.5 L) was refluxed for 2 hours. After completion (monitored by TLC), the volatiles were removed under vacuum. The yellow solid residue was carefully suspended in concentrated aqueous HCl (35-37%, 0.6 L) by sonication for 1 hour (!!!in the fume hood). After adding 100 mL ethanol into the mixture, the suspension was carefully (!) warmed up to 100 ^{o}C while vigorously stirring. Propionaldehyde (45 mL, 0.63 mol, 1.7 eq.) was added dropwise via syringe controlled by injection pump for 1.5 hours while the heating was continued. After cooling down, the reaction mixture was poured into a beaker containing water (1 L) and $CHCl_3$ (300 mL). The mixture was carefully neutralized with solid Na_2CO_3 until pH 7 (careful!! CO_2 formation). After phase separation, the water phase was extracted with $CHCl_3$ (2x400 mL). The combined organic phase was dried over $MgSO_4$, filtrated and evaporated. The oil like black residue was re-dissolved in hot 1,2-dichloroethane (50 mL) and slowly cooled down. The solid was filtered off, washed thoroughly with hexane, until almost all the black impurities were removed (be patient!!), and then with small amount DCM or cold methanol, yielding 50% of the desired compound **SB-1-1**, as orange crystals. The spectroscopic data was identical to the data reported in literature[1].

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 2H, indole-$\underline{NH}$), 8.09 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.9 Hz, 2H), 4.52 (t, *J* = 8.0 Hz, 1H, $\underline{CH}CH_2CH_3$), 2.40 – 2.49 (m, 8H, $Ar\underline{CH_3}$ and $CH\underline{CH_2}CH_3$), 1.07 (t, *J* = 7.3 Hz, 3H, $CHCH_2\underline{CH_3}$).

2,2'-(Propane-1,1-diyl)bis(*N*-(2-(diphenylphosphaneyl)phenyl)-3-methyl-1H-indol-7-amine) (**L2**)

1,1-Bis-(3-methyl-7-nitro-1H-indol-2-yl)-propane (**SB-1-1**) (1.21 g, 3.08 mmol, 1.0 eq.) was suspended in methanol/THF (1/1, 50 mL) and 10% palladium on charcoal was added (0.39 g). The reaction mixture was vigorously stirred under H_2 atmosphere with a balloon. The progress of the reaction was monitored by TLC, and after completion (around 2 hours), the catalyst was quickly filtered off. The filtrate was evaporated, and the crude diamine was directly used in the subsequent reaction without further purification. To a solution of the crude diamine, 2-

(diphenylphosphino)benzoic acid (2.27 g, 7.40 mmol, 2.4 eq.), 4-dimethylaminopyridine (151 mg, 1.2 mmol, 0.4 eq.) and 4-pyrrolidinopyridine (228 mg, 1.54 mmol, 0.5 eq.) in dry dichloromethane (100 mL), *N,N'*-diisopropylcarbodiimide (1.43 mL, 9.25 mmol, 3 eq.) was added dropwise via syringe over 5 minutes while stirring at 0 °C under N_2 atmosphere. After overnight reaction (monitored by TLC), the urea precipitate was filtered off, and the solvent was evaporated. The solid residue was purified by column chromatography on silica gel (100 g) with a pentane/dichloromethane (1:3) mixture to dichloromethane as an eluent. Re-dissolve the product with a minimum amount of dichloromethane followed by adding pentane slowly until precipitates appearing. After sonification for 5 minutes, the pure ligand OrthoDIMphos (**L2**) was obtained as white powder after filtration. Yield 91%.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.49 (s, 2H, $\underline{NH}$-indole), 8.10 (s, 2H, $\underline{NH}$-amide), 7.36 – 6.87 (m, 34H), 4.48 (t, *J* = 8.0 Hz, 1H, $\underline{CH}CH_2CH_3$), 2.29 (s, 6H, $Ar\underline{CH_3}$), 2.27 – 2.21 (m, 2H, $CH\underline{CH_2}CH_3$), 0.98 (t, *J* = 8.0 Hz, 3H, $CH\underline{CH_2}CH_3$).

^{31}P NMR (162 MHz, CD_2Cl_2) δ -11.00.

^{13}C NMR (100 MHz, CD_2Cl_2) δ 167.65, 142.37, 142.10, 137.17, 137.09, 136.44, 136.26, 136.08, 135.90, 134.55, 134.12, 134.03, 133.92, 133.84, 131.70, 130.50, 129.11, 128.87, 128.80, 128.71, 128.58, 127.75, 121.60, 119.04, 116.28, 114.76, 107.99, 36.93, 28.77. 12.63, 8.87.

HR MS (ESI$^+$): calcd. for $C_{59}H_{50}N_4O_2P_2$ $[M]^+$ 908.3409; found 908.3105.

Characterization of the square planar dimeric Rh-complexes [Rh(L2)(CO)(BF_4)]$_2$ and [Rh(effector$\subset$L2)(CO)]$_2$ formed in solid and solution

Preparation of the square planar dimeric Rh-complex: A flamed-dried 5 mL Schlenk flask equipped with a Teflon stirring bar was charged with OrthoDIMPhos **L2** (4.000 mg, $4.40*10^{-3}$ mmol, 1 eq.) and [Rh(nbd)$_2$BF$_4$] (1.647 mg, $4.40*10^{-3}$ mmol, 1 eq.) followed by the addition of 1.0 mL dried and degassed CD_2Cl_2 via syringe through septum under nitrogen atmosphere. After stirring for 2 hours, the yellow solution was transferred into a high pressure (HP) NMR tube under nitrogen atmosphere, which was then taken to run a series NMR experiments. Then the tube was purged three times with 5 bar CO followed by pressurized at 5 bar CO. After around 10 minutes, the dimeric Rh-complex was formed as indicated by a series spectroscopy experiments. The crystal suitable for X-ray analysis was grown in the NMR tube or separated reaction tubes using dichloromethane over one week by adding a thin layer of dried and degassed pentene on the top under nitrogen atmosphere. The dimeric Rh-complex was thoroughly characterized by (^{1}H, ^{31}P{^{1}H }, ^{1}H-^{1}H COSY, ^{1}H DOSY) NMR, FT-IR, X-ray spectroscopy.

X-ray crystal structure determination of the square planar dimer [Rh(**L2**)(CO)(BF_4)]$_2$

[$C_{120}H_{100}N_8O_6P_4Rh_2$]($BF_4$)$_2$ · 6CH_2Cl_2, FW = 2762.95, yellow block, 0.42 × 0.34 × 0.13 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 12.7098(3), b = 15.9386(4), c = 17.4664(6) Å, α = 70.142(1), β =

74.739(1), γ = 69.740(1) °, V = 3079.21(15) Å^3, Z = 1, d_{calc} = 1.490 g/cm^3, μ = 0.65 mm^{-1}. 55669 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1}. The Eval15 software was used for intensity integration.[3] Absorption correction and scaling were performed with Sadabs[4]. (0.69-0.75 correction range). 14154 Reflections were unique (R_{int} = 0.020) of which 12375 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using the program SHELXT[5]. Structure refinement was done with SHELXL-2013.[5] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. N-H hydrogen atoms were located in difference-Fourier maps and refined freely with isotropic displacement parameters. All other hydrogen atoms were introduced in calculated positions and refined with a riding model. The co-crystallized CH_2Cl_2 solvent molecules were refined with a disorder model. 832 Parameters were refined with 145 restraints (concerning distances, angles and displacement parameters in the disordered CH_2Cl_2). R1/wR2 [I>2σ(I)] = 0.0373/0.1026. R1/wR2 [all refl.] = 0.0440/0.1073. S = 1.040. Residual electron density between -1.41 and 2.32 e/Å^3. Structure calculations and checking for higher symmetry were performed with PLATON.[6] For detials check CCDC 1877079.

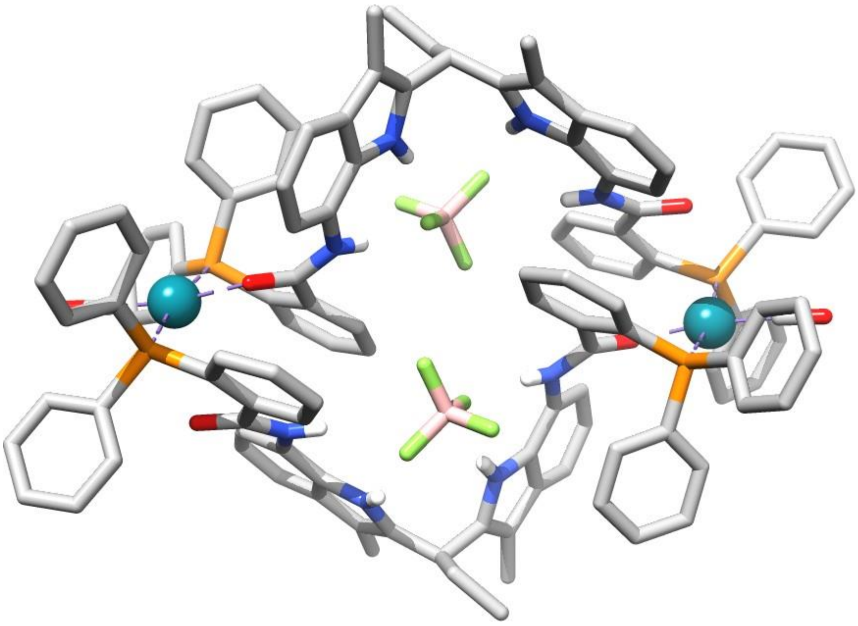


Fig S1. X-ray crystal structure of the dimeric Rh-complex [Rh(**L2**)(CO)(BF_4)]$_2$ (hydrides besides NHs are omitted for clarity; dissolved solvent molecules are omitted for clarity; BF_4^- binds in the DIM-receptors; the carbonyl-O coordinates to the Rh center).

The X-ray crystal structure reveals that the carbonyl-O partakes in the formation of the square planar dimeric complex. Furthermore, the P-O ditopic binding contributes to the stability of this dimeric complex and thus no monomeric complex is observed experimentally. The two BF_4^- counterions weakly bind in the DIM-receptors. CO ligand is in the *trans* position to the carbonyl-O ligand. The two phosphorus atoms from each ligand coordinate in mutual *trans* position.

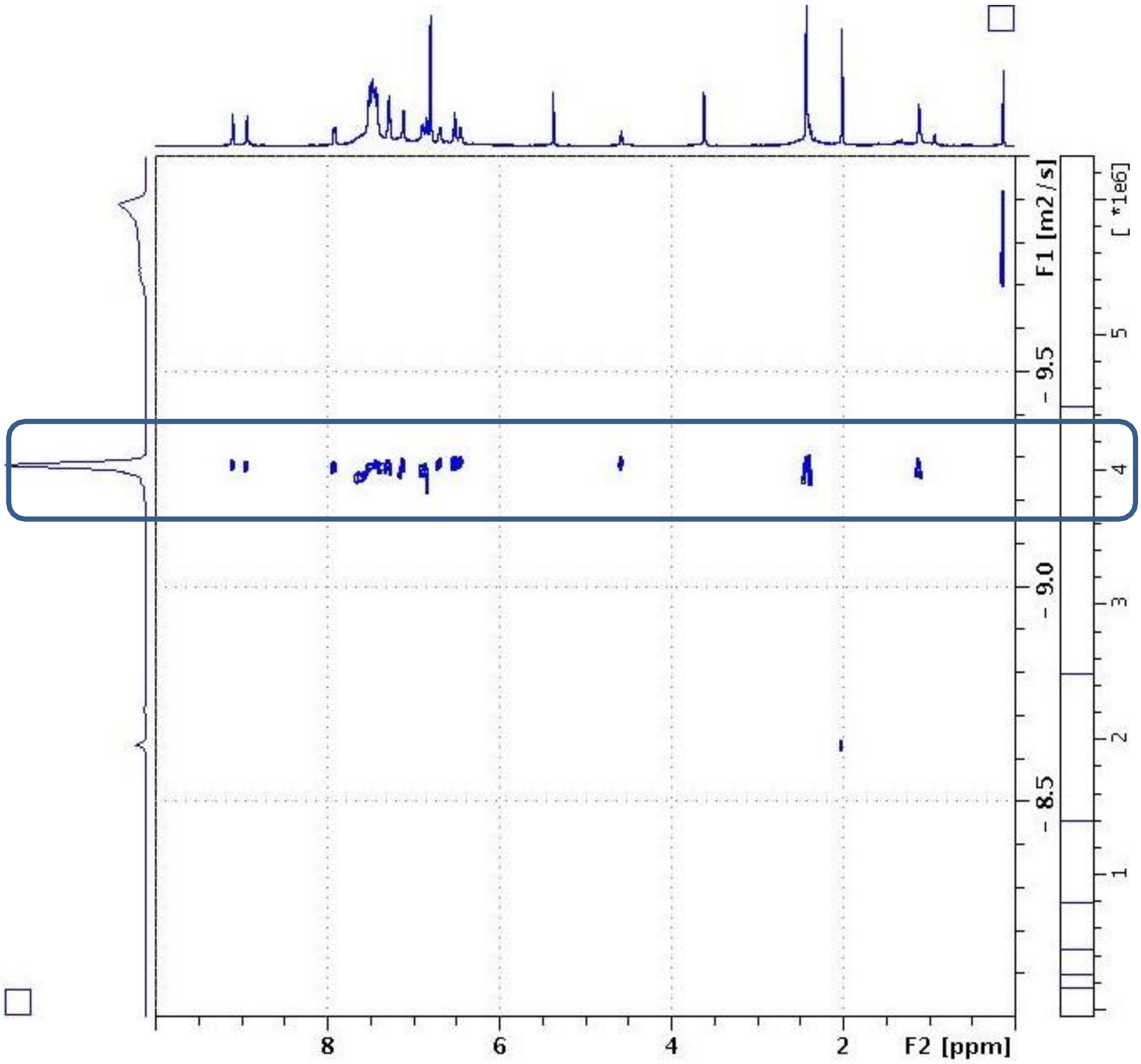


Fig S2. ^{1}H DOSY NMR spectra of the dimeric complex [Rh(**L2**)(CO)(BF$_4$)]$_2$.

One single species formed with a large size was confirmed by the DOSY experiments (log D=-9.27 m^2/s, r_H=1.02 nm), indicating a dimeric structure.

Stoke-Einstein equation: rH=k.T/(D.6π.η)

(K = the Boltzmann constant, T=the absolute temperature, η=the fluid viscosity, rH=the hydrodynamic radius, D=diffusion constant)

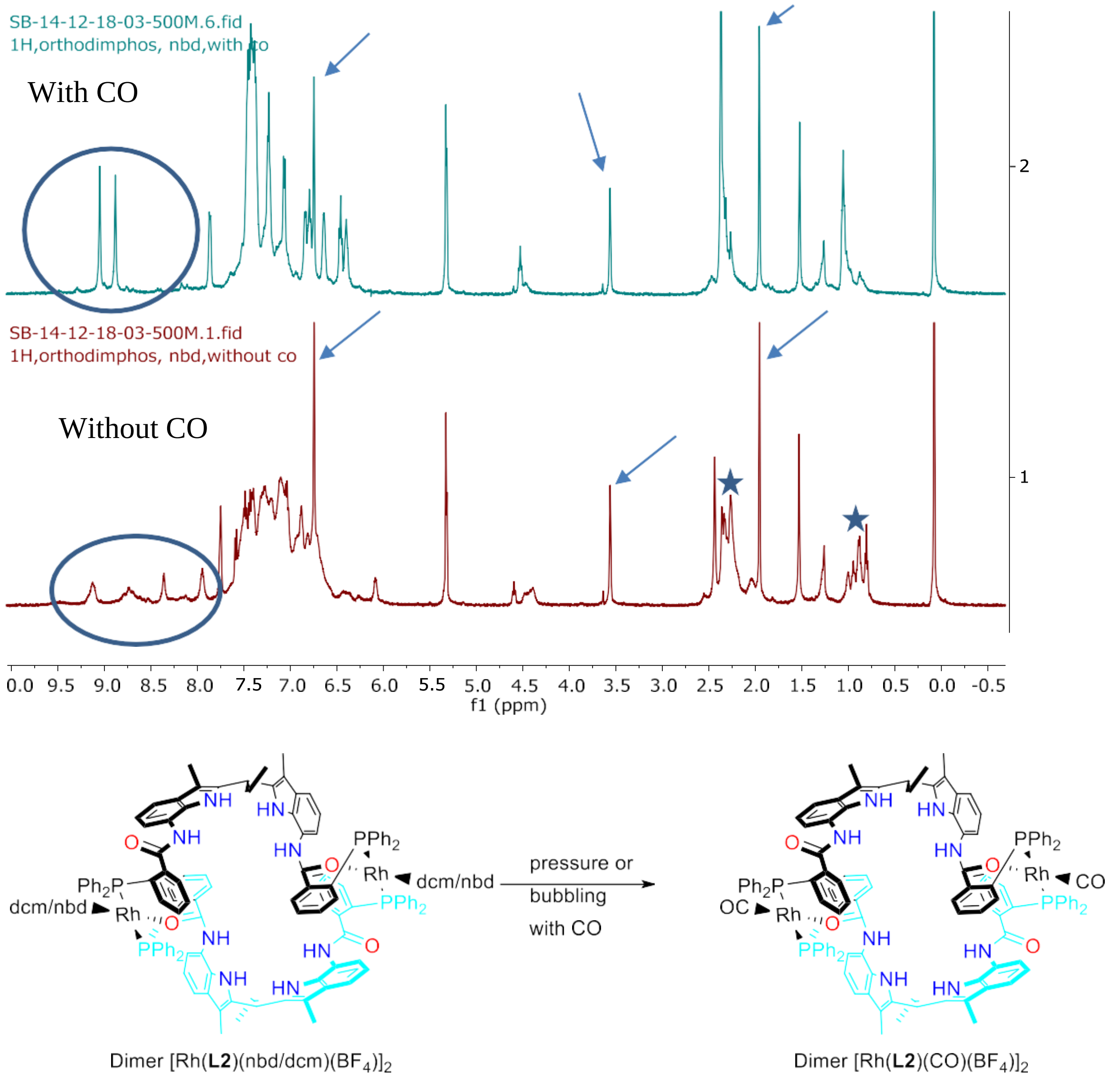


Fig S3. ^{1}H NMR spectra of the dimeric Rh-complexes [Rh(**L2**)(dcm/nbd)(BF$_4$)]$_2$ (the bottom spectra, the chemdraw structure is shown in the bottom left without the coordination of CO, and also the BF$_4^-$ counterions are omitted in the structure) and [Rh(**L2**)(CO)(BF$_4$)]$_2$ (the top spectra, the chemdraw structure is shown in the bottom right with the coordination of CO, and also the BF$_4^-$ counterions are omitted in the structure). Free nbd ligands in solution are indicated by arrows and partially coordinated nbd ligands are indicated by stars; the NH protons of the DIM-receptor are indicated by cycles.

The free nbd ligands in solution suggests that the coordinated nbd ligands are initially partially substituted by the carbonyl-O of the ligand (and also probably the solvent) without CO presence, and later fully substituted by the carbonyl-O of the ligand and the CO ligand in the presence of CO. Furthermore, in the absence of CO, due to dynamic coordination of the nbd ligand or the solvent or carbonyl-O, the NH protons of the DIM-receptors are broad and less defined (indicated in blue cycle). In contrast, in the presence of CO, the nbd or the solvent coordinating to the Rh center is fully replaced by CO ligand. This strong coordination CO ligand stabilizes the dimeric complex, and as such the NH protons of the DIM-receptor become well-defined signals with 1:1 ratio at 9.05 ppm and 8.89 ppm (indicated in blue cycle)**.**

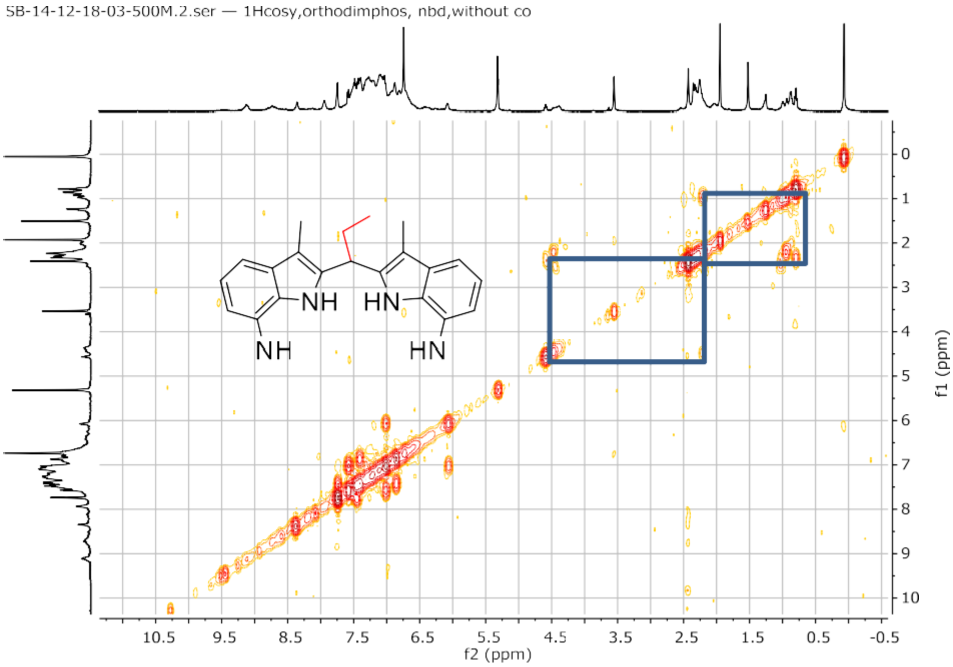


Fig S4. ^{1}H-^{1}H COSY NMR spectra of the dimeric Rh-complex [Rh(**L2**)(dcm/nbd)(BF$_4$)]$_2$ (without CO coordination, and the CH$_3$CH$_2$CH-protons of the dimeric complex are indicated by squares.)

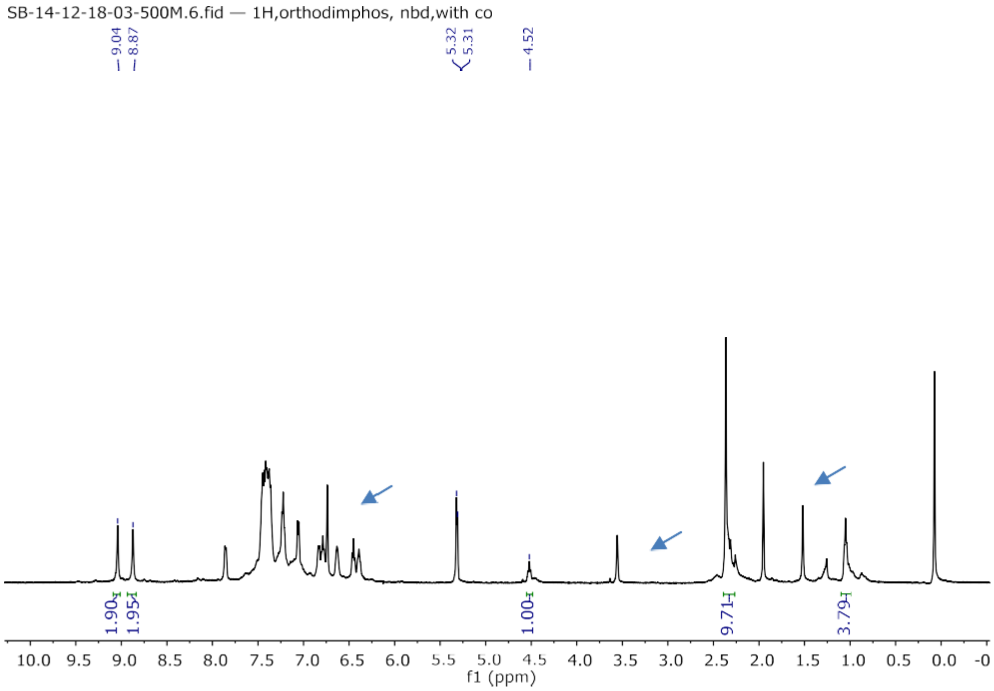


Fig S5. ^{1}H NMR spectra of the dimeric Rh-complex [Rh(**L2**)(CO)(BF$_4$)]$_2$ (with the pressure of CO, free nbd ligands in solution are indicated by arrows, and the indole-NHs and amide-NHs are at 9.04 ppm and 8.87 ppm with 2:2 ratio, respectively)

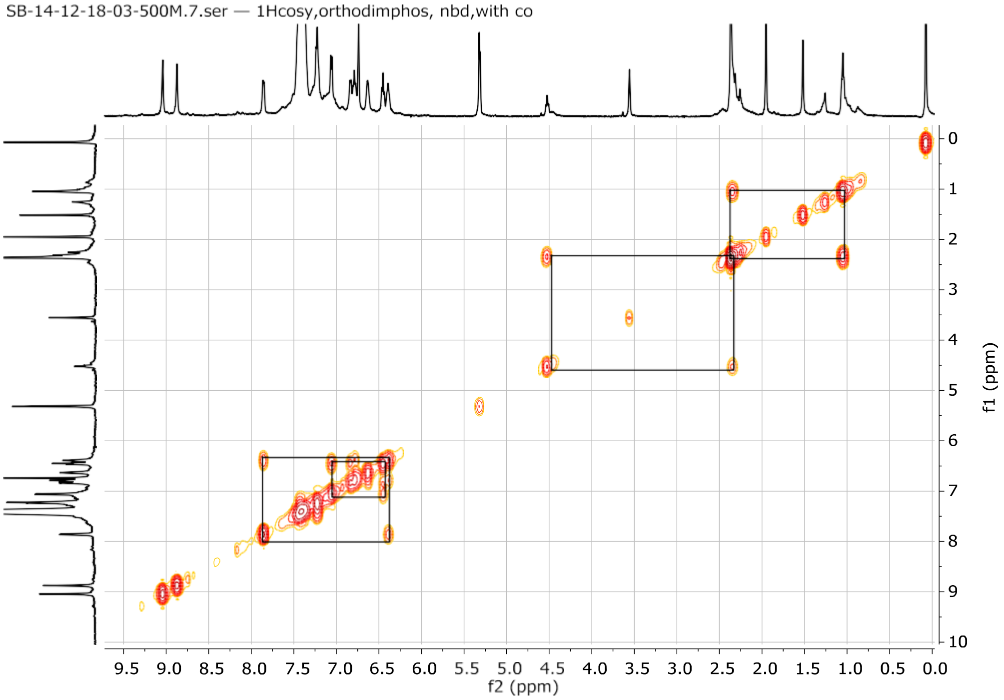


Fig S6. ^{1}H-^{1}H COSY NMR spectra of the dimeric Rh-complex [Rh(**L2**)(CO)(BF$_4$)]$_2$ (with the pressure of CO, and distinguishable protons in the aliphatic region and the aromatic region are indicated by squares.)

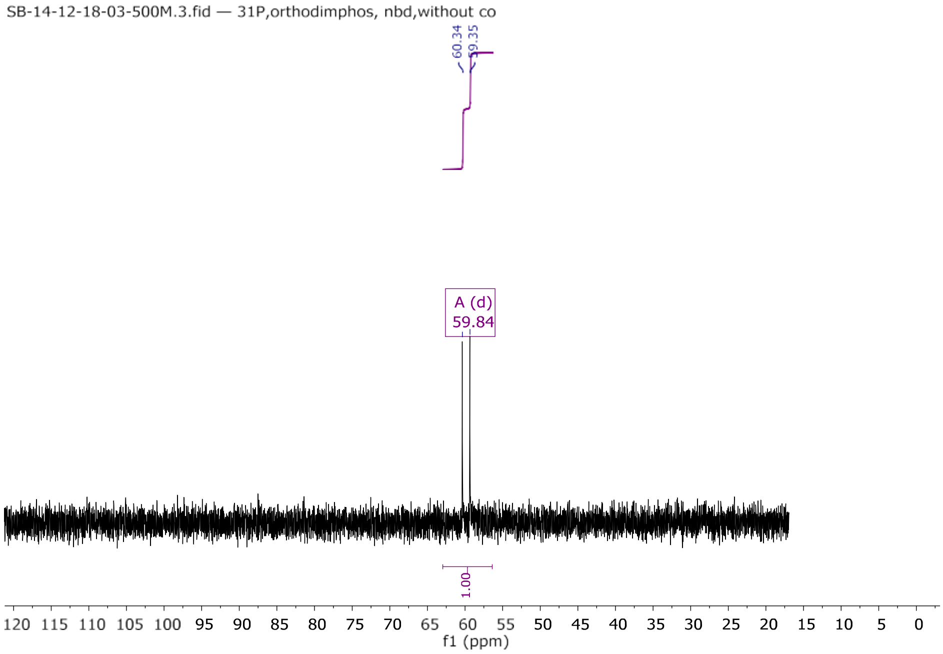


Fig S7.^{13}P{^{1}H} NMR spectra of the dimeric Rh-complex [Rh(**L2**)(nbd/dcm)(BF$_4$)]$_2$ (δ 59.84 (d, *J* = 201.2 Hz), without the coordination of CO)

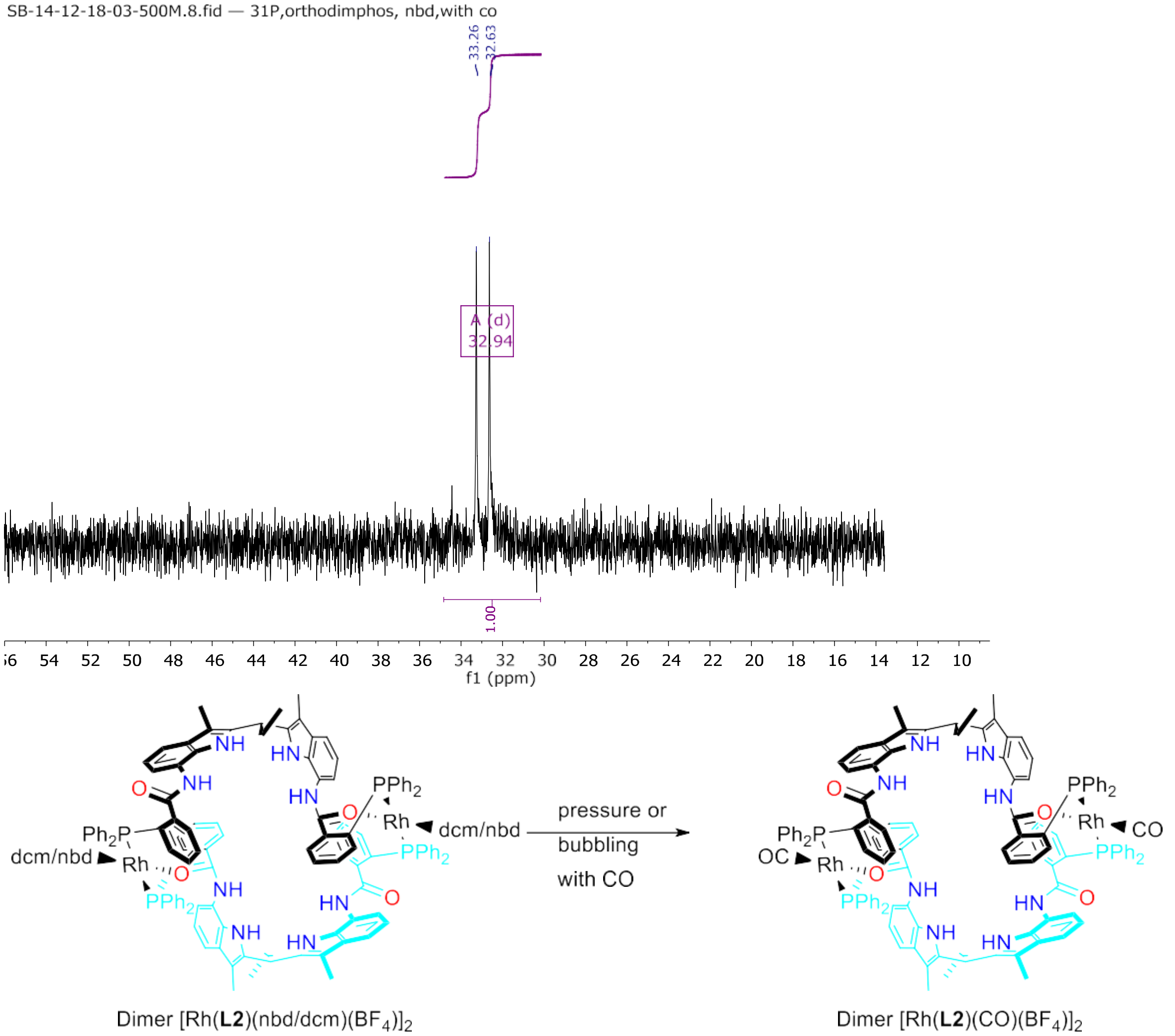


Fig S8. $^{31}P\{^{1}H\}$ NMR spectra of the dimeric Rh-complex [Rh(**L2**)(CO)(BF_4)]$_2$ (δ 32.94 (d, *J* = 127.8 Hz), with the pressure of CO; when CO coordination, the phosphorus signals shifts from 60 ppm to 33 ppm)

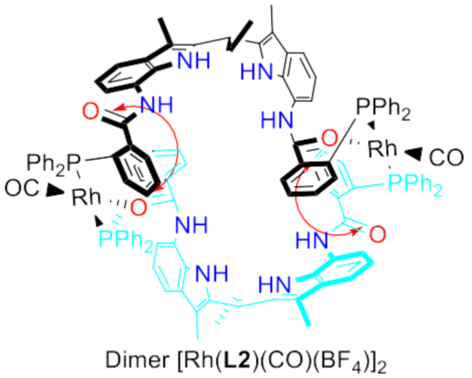


Fig S9. The carbonyl-O association and dissociation under fast exchanging are indicated by double red arrows. This feature is further confirmed by VT NMR experiments shown in Fig S10.

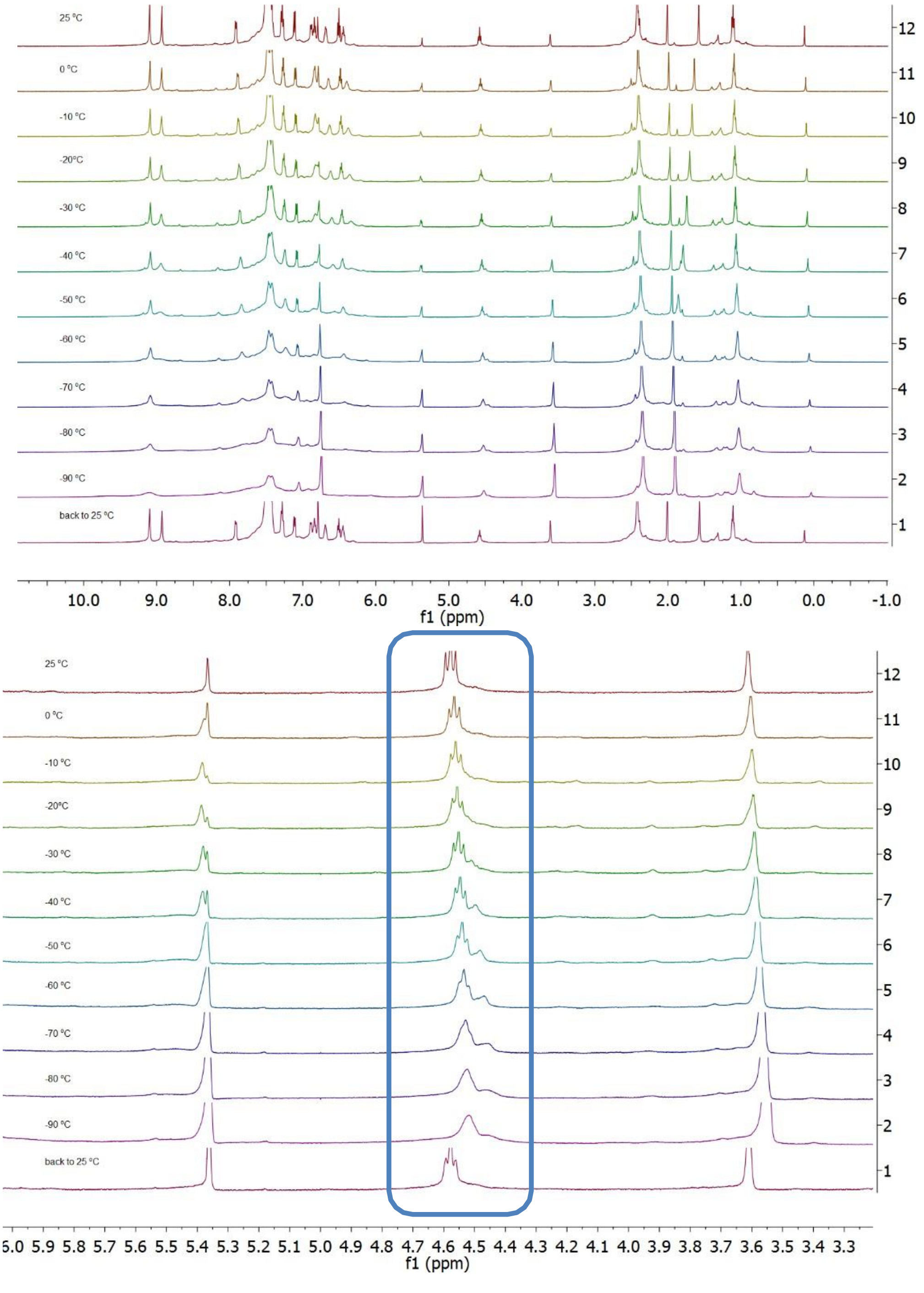


Fig S10. Variable-temperature (VT) ^{1}H NMR spectra of the dimeric Rh-complex [Rh(**L2**)(CO)(BF$_4$)]$_2$. The CH$_3$CH$_2$CH-proton of the OrthoDIMphos ligand of the rhdium complexes (shown in the blue box).

VT NMR show that various complexes fast exchange at NMR time scale at RT, resulting in one single species observed. When the temperature was lowered from room temperature to minus 90 degrees, these fast exchanging process are slowed down and the distinguishable signals of various complexes were observed. The fast equilibrium between different states of dimeric complexes is via the dynamic association and dissociation of the carbonyl-O of the ligand as indicated before in Fig. S9.

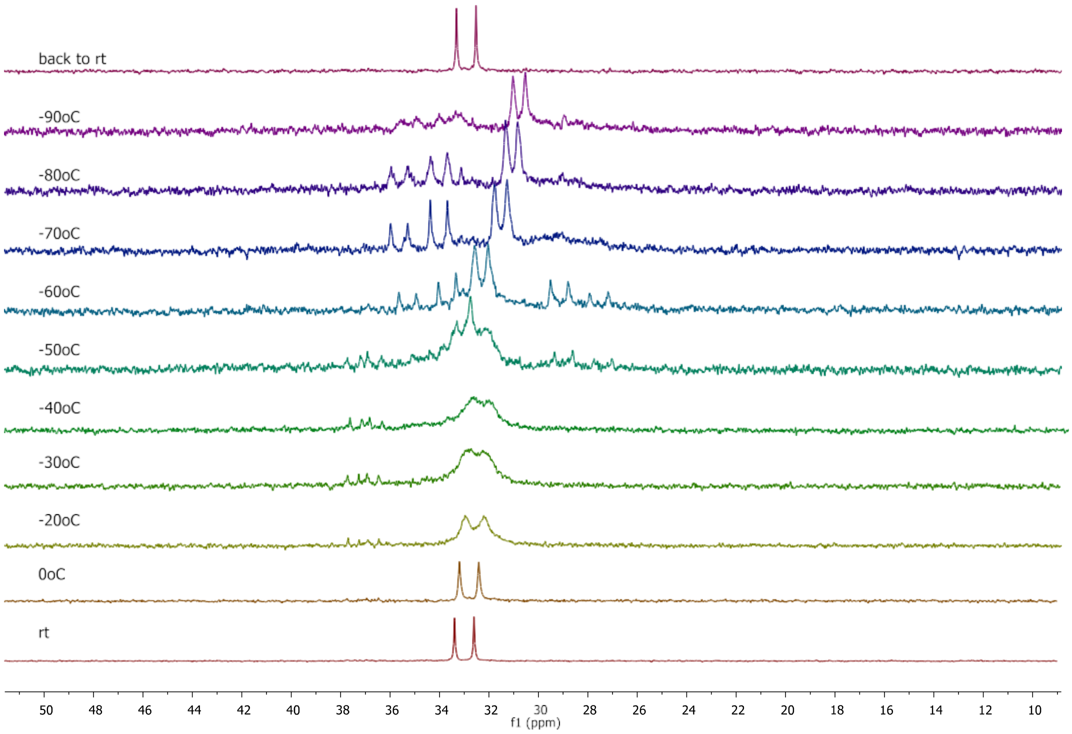


Fig S11. Variable-temperature (VT) ^{31}P NMR spectra of the Rh-dimeric complex [Rh(**L2**)(CO)(BF$_4$)]$_2$.

The phosphorus chemical shifts of the complexes formed are in fast exchange at NMR time scale at RT, resulting in one single species observed. When the temperature was lowered from room temperature to minus 90 degrees, these fast exchange process are slowed down and the phosphorus signals of various complexes were observed. These results further suggest that the dimeric complex with fast equilibrium between different states via the dynamic association and dissociation of the carbonyl-O of the ligands within the dimeric complex.

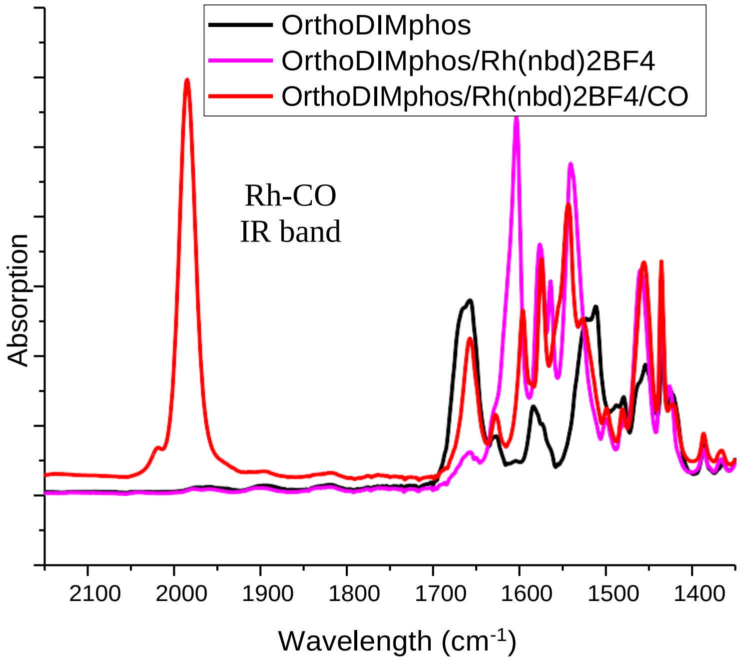


Fig S12. FT-IR spectra of the ligand OrthoDIMPhos **L2**, dimeric complexes [Rh(**L2**)(nbd/dcm)(BF_4)]$_2$ and [Rh(**L2**)(CO)(BF_4)]$_2$.

The Rh-CO IR absorption signal at 1986 cm^{-1} clearly shows that the dimeric complex [Rh(**L2**)(CO)(BF_4)]$_2$ with one CO coordination to rhodium atom in contrast to the dimeric complex formed without CO.

Binding studies of the square planar dimer [Rh(**L2**)(CO)(BF_4)]$_2$ with effector

NMR titration studies with the square planar dimeric Rh-complex: A flamed-dried 5 mL Schlenk flask equipped with a Teflon stirring bar was charged with OrthoDIMPhos **L2** (4.000 mg, 4.40*10^{-3} mmol, 1 eq.) and [Rh(nbd)$_2$BF$_4$] (1.647 mg, 4.40*10^{-3} mmol, 1 eq.) followed by the addition of 2.0 mL dried and degassed CD_2Cl_2 via syringe through septum under nitrogen atmosphere to obtain 2.20*10^{-3} M concentration solution in terms of the DIM-receptor. After stirring for 2 hours, the yellow solution was bubbled with CO over 5 minutes under -70 ^{o}C using dried ice-ethanol bath to reduce the evaporation of CD_2Cl_2 and the formation of dimeric complex [Rh(**L2**)(CO)BF$_4$]$_2$ was confirmed by ^{1}H NMR. Another flamed-dried 5 mL Schlenk flask equipped with a Teflon stirring bar was charged with tetrabutylammonium benzoate salt (as received from Fluka anyalytical, 4.803 mg, $13.2*10^{-3}$ mmol) followed by transferring 1 mL previous prepared $2.20*10^{-3}$ M DIM-receptor of dimeric complex solution to dissolve the guest in the Glove-Box. Under inert atmosphere (Glove-Box), aliquots (500 uL) of the dimer-solution were transferred to NMR tubes, followed by the addition of aliquots (0-500 uL) of tetrabutylammonium benzoate in the dimeric complex solution. For the evaluation of the binding constant of the benzoate in the DIM-receptor as the direct evidence of the carboxylate binding strength, the chemical shifts of the DIM-receptor upon the addition of varying amounts of the benzoate were observed. As expected, both pyrrole-NH and amide-NH protons shift downfield because of hydrogen bonding interaction between the carboxylate group and the DIM-receptor. Due to slow carboxylate/receptor association/dissociation on the NMR timescale, there are two sets of NH proton signals observed between 0 and 1 equivalent of benzoate with corresponding to the DIM-receptor. And the same phenomena were confirmed by phosphorus NMR titrations. When slightly more than one equivalent of benzoate is added (1.03 eq.), all the signals of the DIM-receptor moved to the downfield at the same chemical shift, indicating that the DIM-receptor was saturated by the benzoate guest. Moreover, further addition of benzoate up to 3.00 equivalents made no changes compared with 1.03 equivalents addition. And as such, we assumed that at the point of 1.03 equivalents addition of benzoate, the DIM-receptor is saturated because of the extremely high binding strength of the DIM-receptor with carboxylate. Taking into account the total DIM-receptor concentration ($C_{DIM\text{-}receptor} = 2.20*10^{-3}$ M), the binding constant can be estimated: $K_{binding} = [G\text{-}H]/([G]*[H])$, with [G-H] = the concentration of DIM-receptor-benzoate complex, [H] = the concentration of unbinded DIM-receptor, [G] = the concentration of free benzoate. Based on analysis of the spectra at 1.03 equivalents of anion: $[G\text{-}H]>>0.97*C_{DIM\text{-}receptor}$, $[H]<<0.03*C_{DIM\text{-}receptor}$, $[G]\sim0.03*C_{DIM\text{-}receptor}$. After calculation, $K_a>>10^5$ M^{-1}.

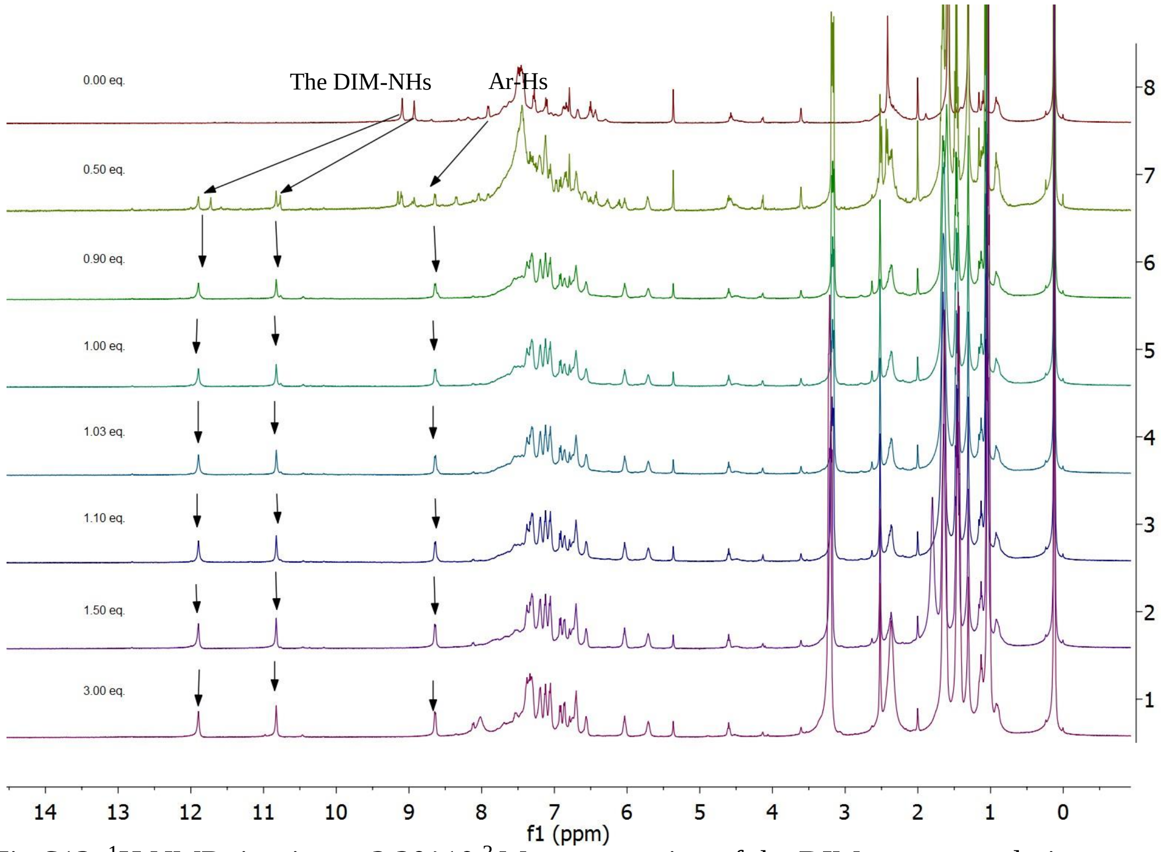


Fig S13. ^{1}H NMR titration at 2.20*10^{-3} M concentration of the DIM-receptor solution.

The pyrrole-NH and amide-NH protons of the DIM-receptors shift down field (Δδ 1.93-2.86 ppm), indicating the binding of the carboxylate containing effector to the DIM-receptor via hydrogen bonds. Also, due to the binding of the benzoate effector to the DIM-receptor in this case, some Ar-H protons are shielded by the aromatic ring of the effector, and as such these Ar-H protons also shift down field.

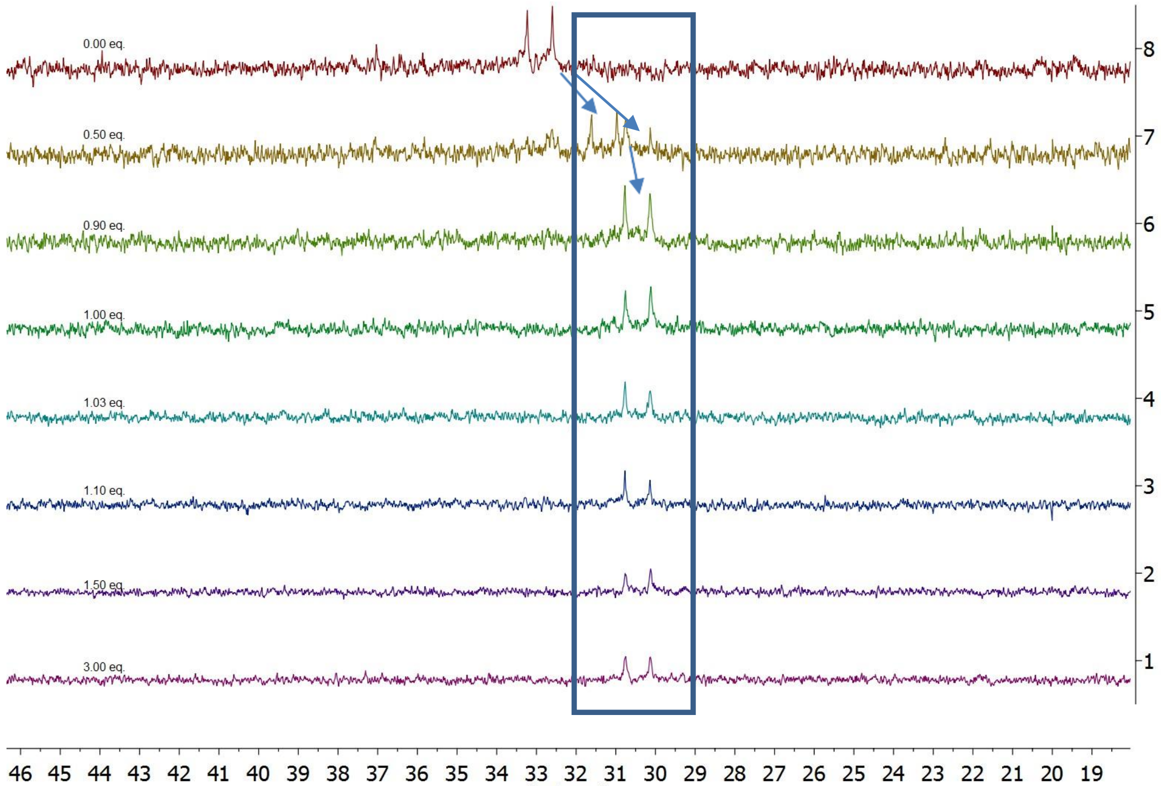


Fig S14. $^{31}P\{^{1}H\}$ NMR titration at $2.20*10^{-3}$ M concentration of the DIM-receptor solution.

When benzoate effector binding to the DIM-receptor, both the electronic properties and the chemical environment around the phosphorus atoms are changed slightly. These effects lead to the up field shifts of the phosphorus signals ($\Delta\delta$ ca. 2.5 ppm) of the dimeric complex.

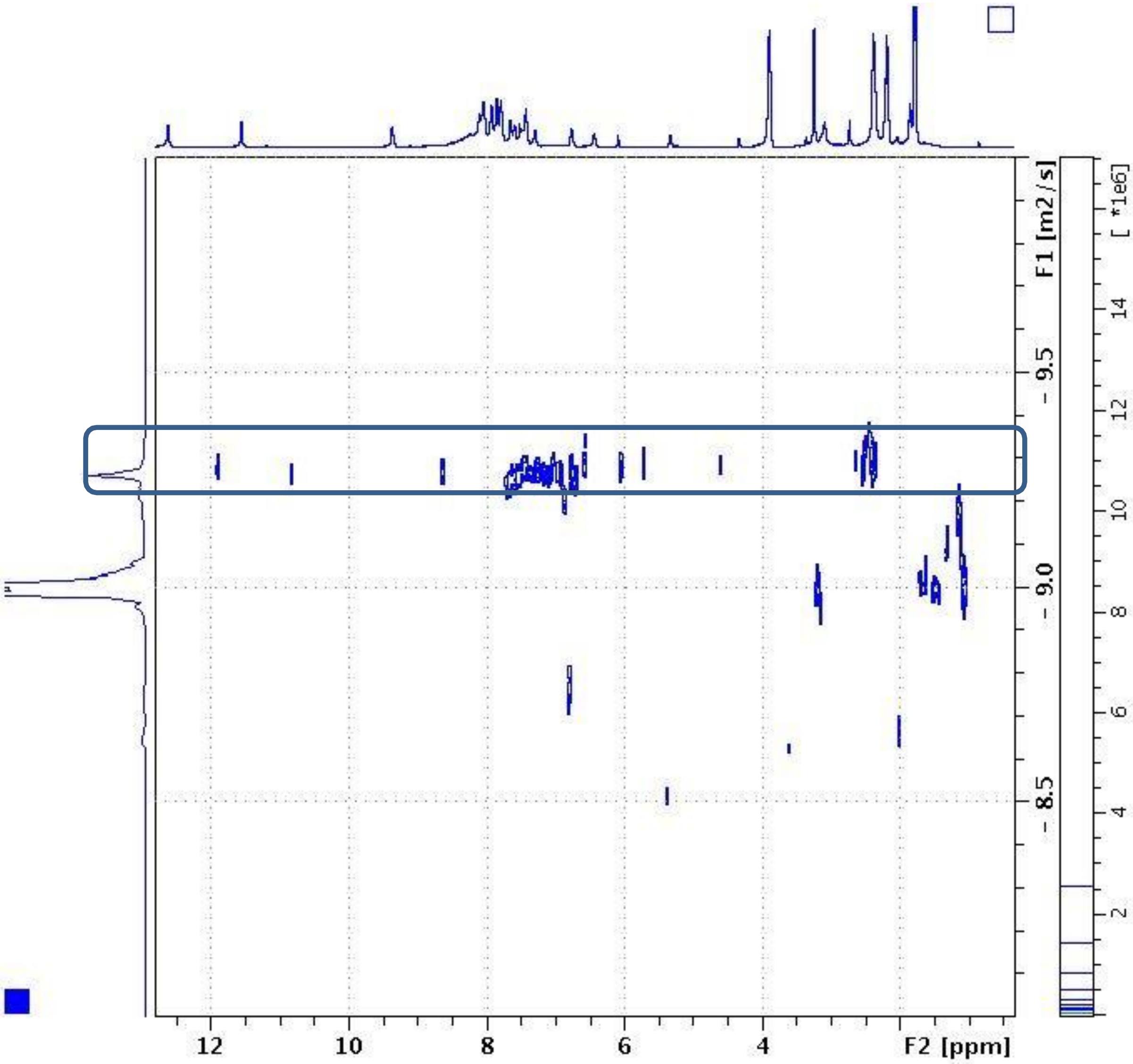


Fig S15. ^{1}H DOSY NMR spectra of the dimeric complex [Rh(Benzoate□**L2**)(CO)(BF_4)]$_2$.

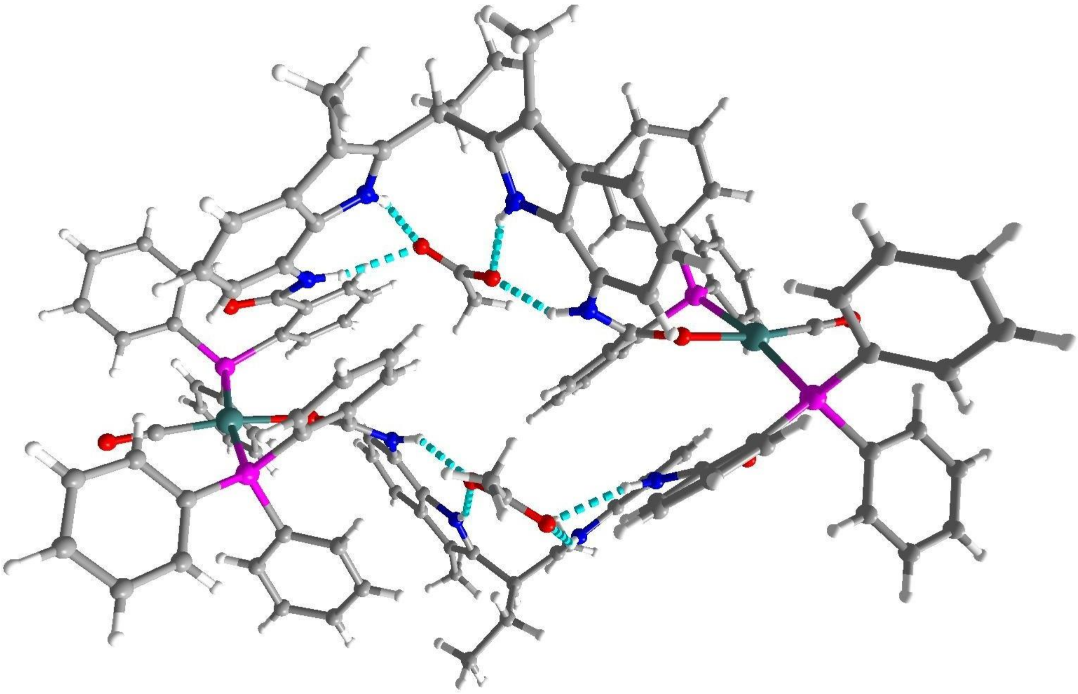
DOSY spectroscopy reveals the formation of one single species with a large size (log D=-9.30 m^2/s, r_H=1.08 nm; log D=-9.00 m^2/s of TBA counterion) that is identical to the guest free dimeric complex. These comparable diffusion constants (log D=-9.30 vs. -9.27 m^2/s) reveal that the DIM-receptors of the square planar dimeric complex are free to bind carboxylate effectors and are not partaken in dimer species formation. Instead of the DIM-receptors, the ditopic P,O coordination of each ligand to the Rh center contribute to the dimerization process. Thus, the binding of effector to the square planar dimeric complex will not destroy the dimeric structure and result in the formation of a monomeric complex.

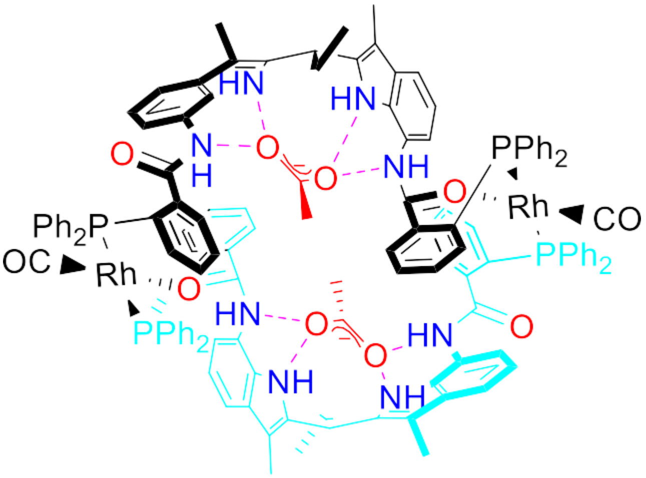
Stoke-Einstein equation: rH=k.T/(D.6π.η)

(K = the Boltzmann constant, T=the absolute temperature, η=the fluid viscosity, rH=the hydrodynamic radius, D=diffusion constant)

X-ray crystal structure determination of square planar dimeric complex with acetate effector binding [Rh(OAc⊂**L2**)(CO)]$_2$

$[C_{120}H_{100}N_8O_6P_4Rh_2](C_2H_3O_2)_2 \cdot 5.4CH_2Cl_2$, FW = 2656.46, yellow block, 0.24 × 0.18 × 0.12 mm^3, triclinic, $P\overline{1}$ (no. 2), a = 12.8064(2), b = 15.7601(3), c = 17.3674(2) Å, α = 70.329(1), β = 75.142(1), γ = 70.305(1) °, V = 3066.94(9) Å^3, Z = 1, d_{calc} = 1.438 g/cm^3, μ = 0.62 mm^{-1}. The crystal appeared to be cracked into two fragments. Consequently, two orientation matrices were used for the integration with the Eval15 software.[3] 47177 Reflections were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. Absorption correction and scaling were performed with Twinabs[4]. (0.67-0.75 correction range). 14043 Reflections were unique (R_{int} = 0.034) of which 11254 were observed [I>2σ(I)]. The structure was solved with Direct Methods using the program SIR-97. [7] Structure refinement was done with SHELXL-2018.[5] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. The co-crystallized CH_2Cl_2 solvent molecules were refined with partial occupancy and a disorder model. 762 Parameters were refined with 69 restraints (concerning distances, angles and displacement parameters in the disordered CH_2Cl_2). R1/wR2 [I>2σ(I)] = 0.0529/0.1329. R1/wR2 [all refl.] = 0.0717/0.1457. S = 1.025. BASF = 0.228(7). Residual electron density between -1.22 and 2.34 e/Å^3. Structure calculations and checking for higher symmetry were performed with PLATON.[6] For detials check CCDC 1877078.





Dimer [Rh(acetate⊂**L2**)(CO)(BF$_4$)]$_2$

Fig S16. X-ray crystal structure of the dimeric complex [Rh(OAc□**L2**)(CO)]$_2$ with acetate binding to the DIM-receptors (dissolved solvent molecules are omitted for clarity; acetate binds to the DIM-receptor via four hydrogen bonds, and the N-O distances of 2.775-3.051 Å).

X-ray structure of the dimeric complex with acetates as effector binding to the DIM-receptors suggest that the DIM-receptors doesn't partake in the formation of the square planar dimeric complex. Instead, the carbonyl-O coordinates to the Rh center for dimerization. Thus, the effectors binding to the DIM-receptors of this dimeric complex will not influence the whole structure. The chemdraw structure is shown in the bottom (the hydrogen bonds are indicated by purple dots in chemdraw structure and green dots in X-ray structure).

Characterization of the trigonal bipyramidal dimeric Rh-active species $[Rh(L2)(CO)_2H]_2$ under hydroformylation conditions

In situ high-pressure (HP) NMR spectroscopic experiments without effectors: A flame dried 5 mL Schlenk flask equipped with a Teflon stirring bar was charged with OrthoDIMPhos **L2**) (8.000 mg, $8.81*10^{-3}$ mmol, 1 eq.) and $[Rh(acac)(CO)_2]$ (2.273 mg, $8.81*10^{-3}$ mmol, 1 eq.) under nitrogen atmosphere followed by the addition of dried and degassed CD_2Cl_2 (0.6 mL) to prepared [Rh] 14.7 mM complex solution. After stirring under nitrogen for 30 minutes, the yellow solution was transferred to high-pressure (HP) NMR tube under inert conditions. The tube was then purged three times with 7 bar of syngas and subsequently pressurized under 7 bar of syngas. After well mixing, the sample was taken to perform a series of ((VT) ^1H, $^1H\{^{31}P\}$, $^1H\{sel^{31}P\}$, (VT) ^{31}P, DOSY) NMR experiments.

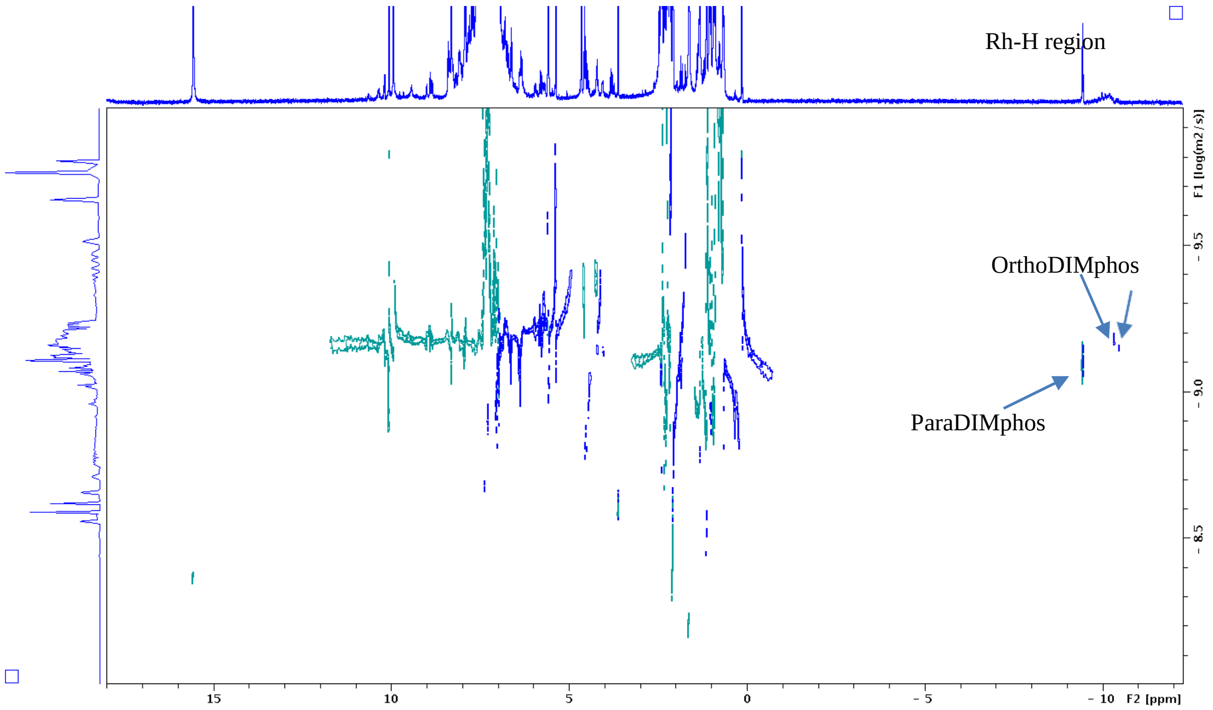


Fig S17. ^{1}H DOSY NMR spectra of the monomeric ParaDIMphos-Rh active species [Rh(**L1**)$(CO)_2$H] and the dimeric and monomeric OrthoDIMphos-Rh active species [Rh(**L2**)$(CO)_2$H$]_2$ and [Rh(**L2**)$(CO)_2$H] under 7 bar syngas at 25 °C.

The comparable diffusion constant of these monomeric species suggests that the monomeric ParaDIMphos-Rh active species and the monomeric OrthoDIMphos-Rh active species involve similar structure (log D of -9.10 vs.-9.13 m^2/s)

Stoke-Einstein equation: rH=k.T/(D.6π.η)

(k=the Boltzmann constant, T=the absolute temperature, η=the fluid viscosity, rH=the hydrodynamic radius, D=diffusion constant.)

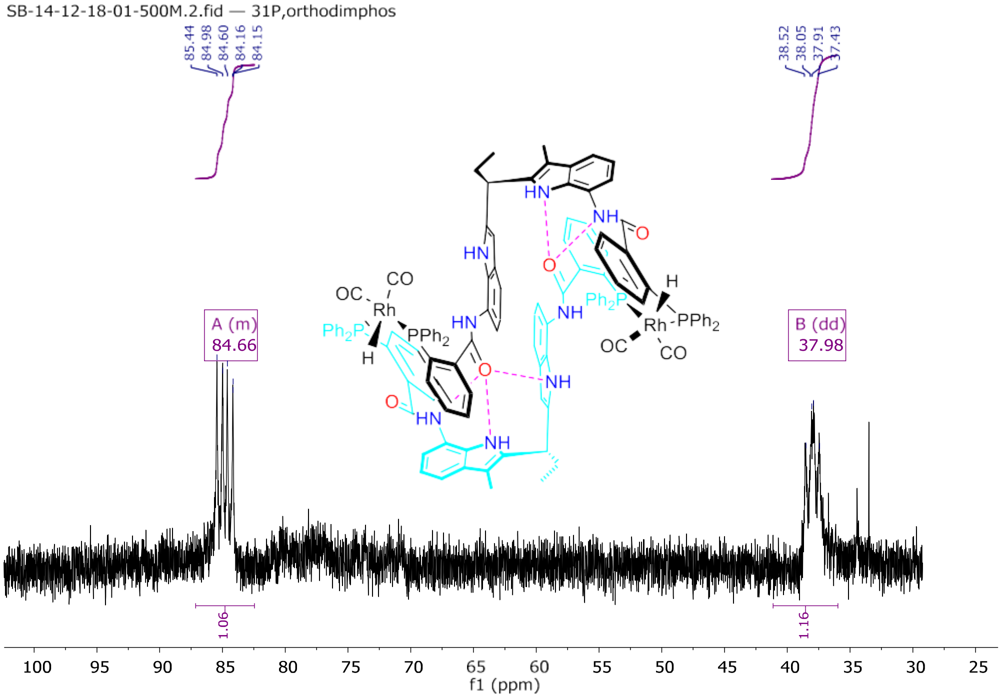


Fig S18. HP $^{31}P\{^{1}H\}$ NMR spectra of the dimeric Rh-active species [Rh(**L2**)$(CO)_2H]_2$ (the ee-ee isomer is shown by chemdraw structure in the figure) formed under 7 bar syngas.

Two doublets of doublets phosphorus signals (^{31}P NMR (202 MHz, CD_2Cl_2) δ 84.79 (dd, *J* = 167.8, 90.9 Hz), 37.98 (dd, *J* = 124.4, 93.5 Hz)) reveal the formation of an asymmetric dimeric species from symmetric OrthoDIMphos ligand **L2**. Compared with one doublet signals observed for monomeric Rh-active species [Rh(**L1**)$(CO)_2H$] formed from ParaDIMphos **L1** (shown in the next figure Fig S19), these results suggest the formation of a dimeric species.

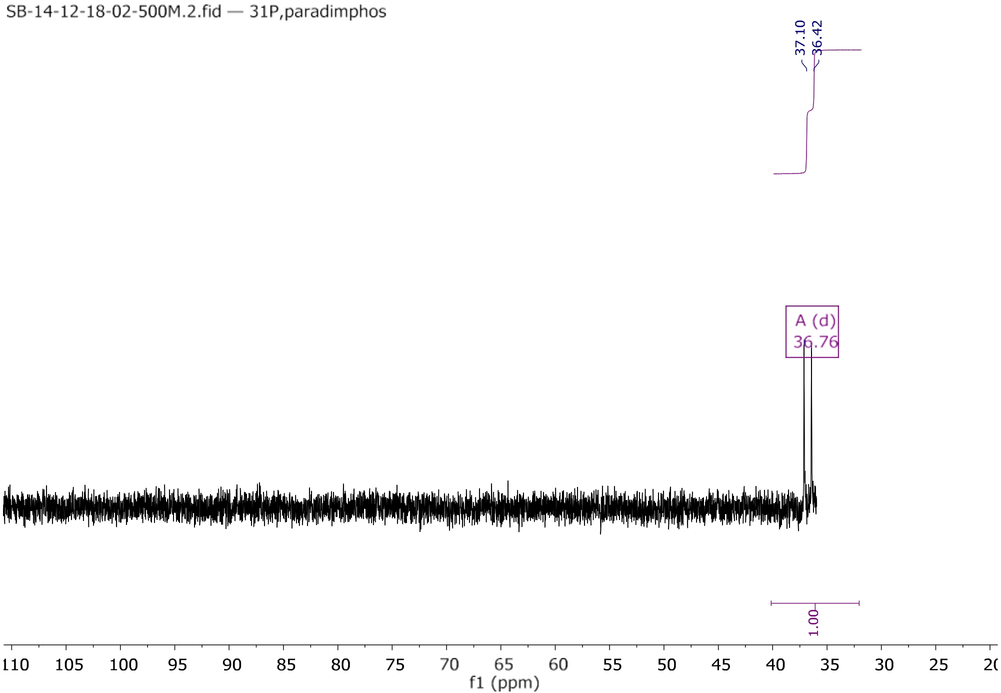


Fig S19. HP $^{31}P\{^{1}H\}$ NMR spectra of the monomeric Rh-active species [Rh(**L1**)$(CO)_2H$] formed under 7 bar syngas.

One doublet phosphorus signals (^{31}P NMR (202 MHz, CD_2Cl_2) δ 36.76 (d, *J* = 137.6 Hz)) reveal the formation of a symmetric monomeric species from symmetric ParaDIMphos ligand **L1**, in line with previous findings.

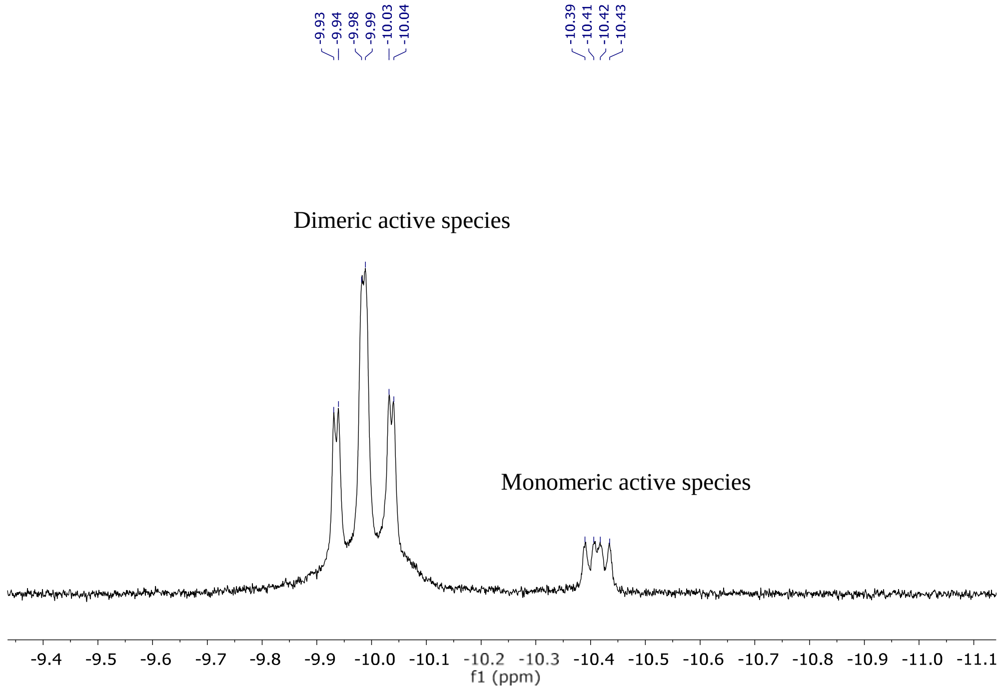
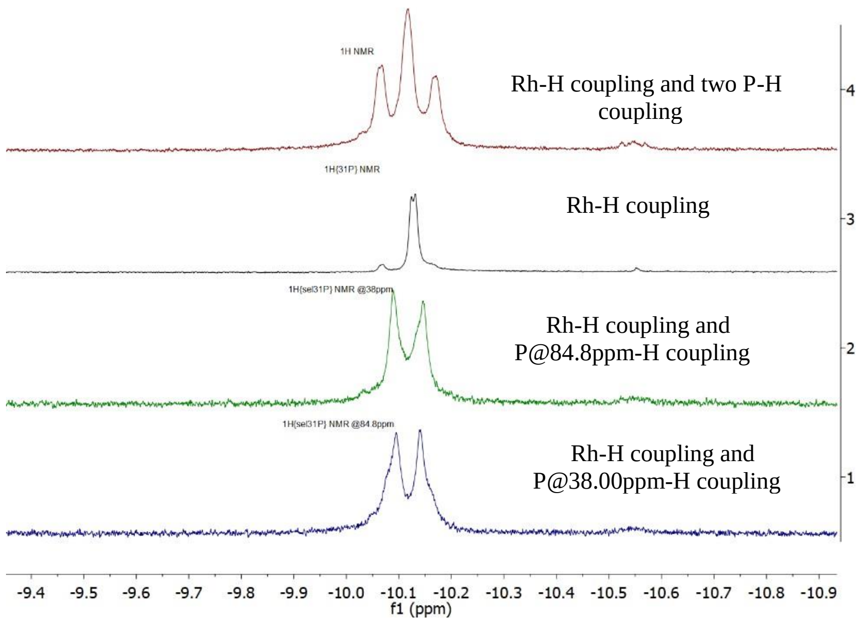


Fig S20. HP ^{1}H NMR spectra of the Rh-active species formed at 40 °C under 7 bar syngas showing the major dimeric species [Rh(**L2**)$(CO)_2$H]$_2$ (at -9.99 ppm) and the minor monomeric species [Rh(**L2**)$(CO)_2$H] (-10.42 ppm).

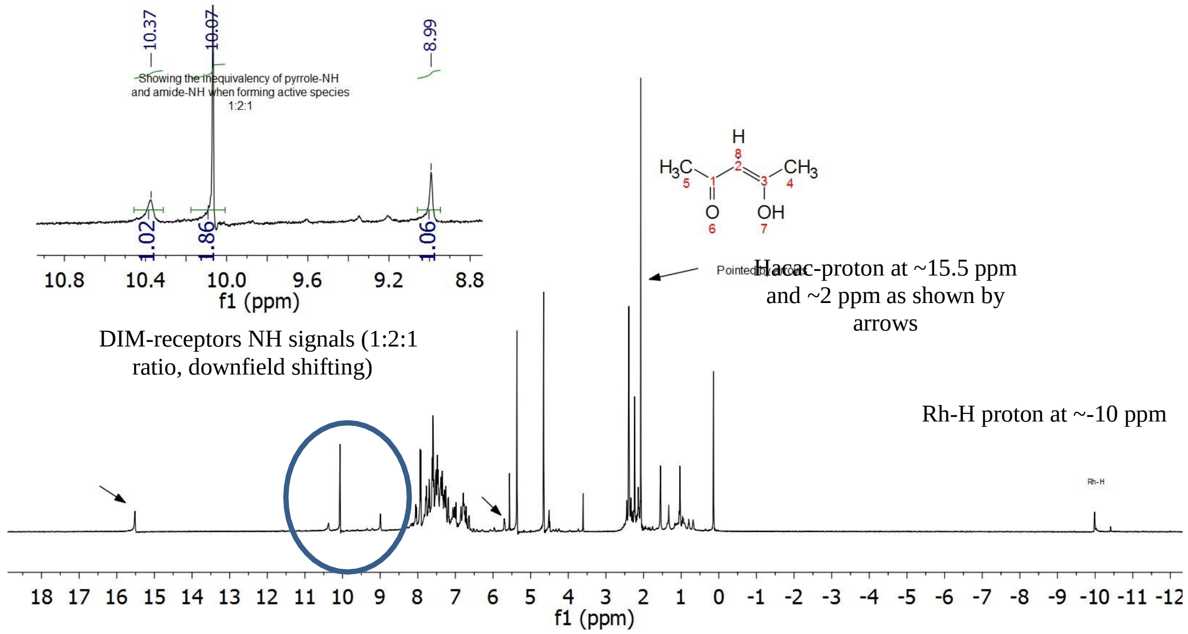

Rh-H coupling and two P-H coupling

Rh-H coupling

Rh-H coupling and P@84.8ppm-H coupling

Rh-H coupling and P@38.00ppm-H coupling

Fig S21. HP ^{1}H, $^{1}H\{^{31}P\}$, and $^{1}H\{sel^{31}P\}$ NMR spectra of the dimeric species [Rh(**L2**)(CO)$_2$H]$_2$ under 7 bar syngas showing both phosphorus atoms at 84.8 ppm and 38.00 ppm directly connecting to the same rhodium atom, further confirming the asymmetric structure of the dimeric active species


Showing the inequivalency of pyrrole-NH and amide-NH when forming active species 1:2:1

DIM-receptors NH signals (1:2:1 ratio, downfield shifting)

Hacac-proton at ~15.5 ppm and ~2 ppm as shown by arrows

Rh-H proton at ~-10 ppm

Fig S22. $^{1}H\{^{31}P\}$ NMR spectra of the dimeric active species [Rh(**L2**)(CO)$_2$H]$_2$ formed with OrthoDIMphos **L2** under 7 bar syngas. The free Hacac protons are indicated by arrows.

The amide-NH and indole-NH protons of the DIM-receptor of the active species shift down field and the shifts are not equivalents for the amide-NHs or the indole-NHs (around 1:2:1 ratio for these protons at 10.37, 10.07 and 8.99 ppm), indicating that internal hydrogen bonds are formed with the DIM-receptors. Importantly, compared with the square planar dimeric complex, these results suggest that the DIM-receptors contribute to the dimerization process. Furthermore, a minor quantity of the monomeric active species was observed by DOSY and proton NMR experiments. These results suggest that effector binding to the DIM-receptor can result in the formation of the monomeric species via converting the dimer species to monomeric species. Also, it is expected that effector binding to the DIM-receptor would form more favorable hydrogen bonds than the internal hydrogen bonds formed within the twisted dimeric structure.

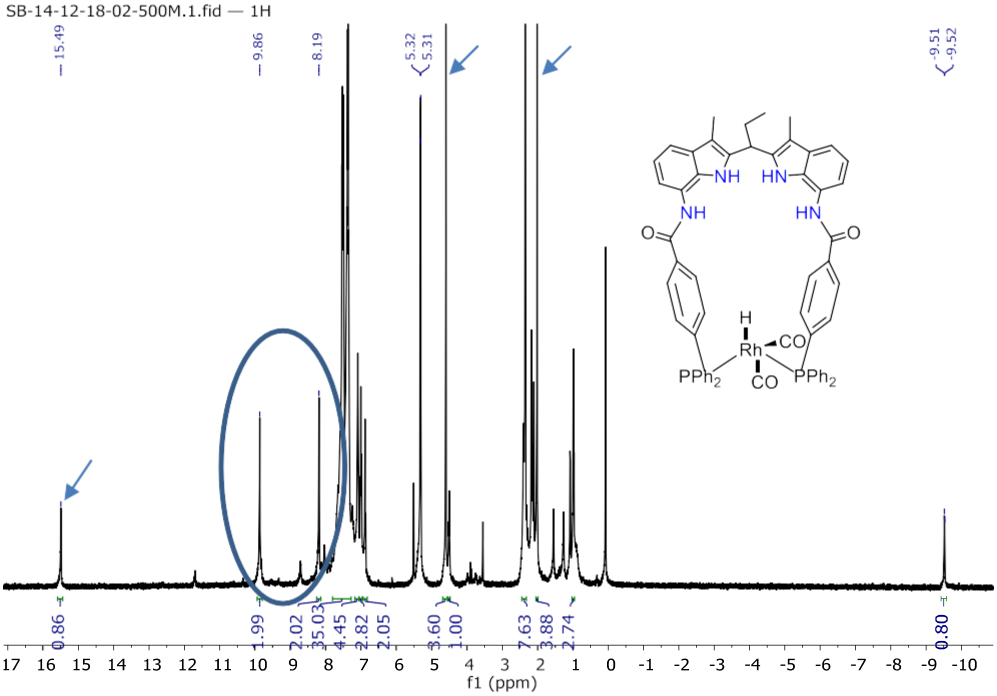


Fig S23. ^{1}H{^{31}P} NMR spectra of the monomeric active species [Rh(**L1**)(CO)$_2$H] (the ee isomer shown by chemdraw structure) formed with ParaDIMphos ligand **L1** under 7 bar syngas. The free Hacac protons are indicated by arrows.

The amide-NH and indole-NH protons of the DIM-receptor of the monomeric species are at 9.86 and 8.19 ppm with 2:2 ratio (shown by blue cycle), suggesting that the DIM-receptor doesn't partake in the formation of the monomeric active species [Rh(**L1**)(CO)$_2$H] via hydrogen binding interactions.

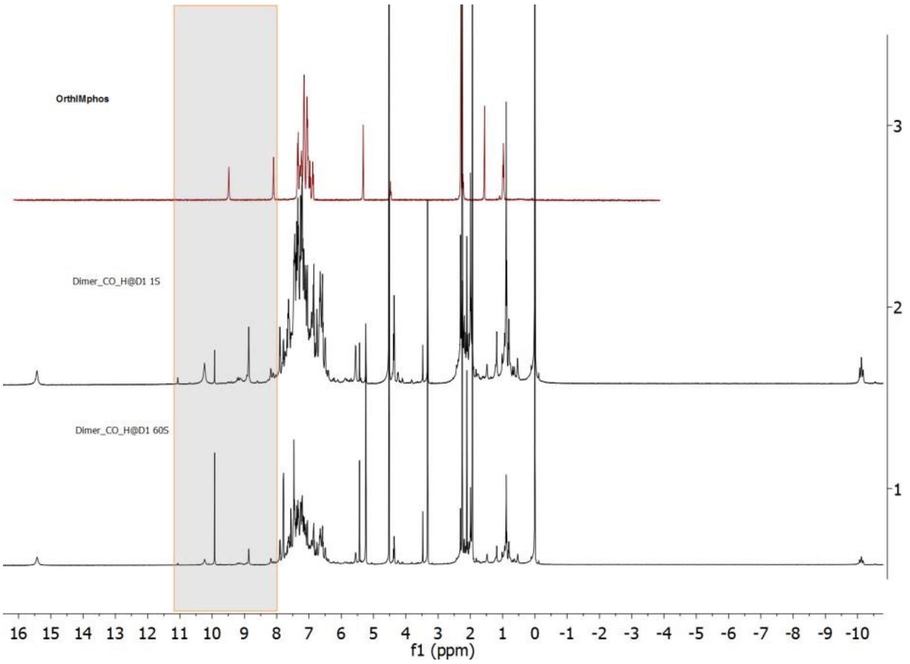
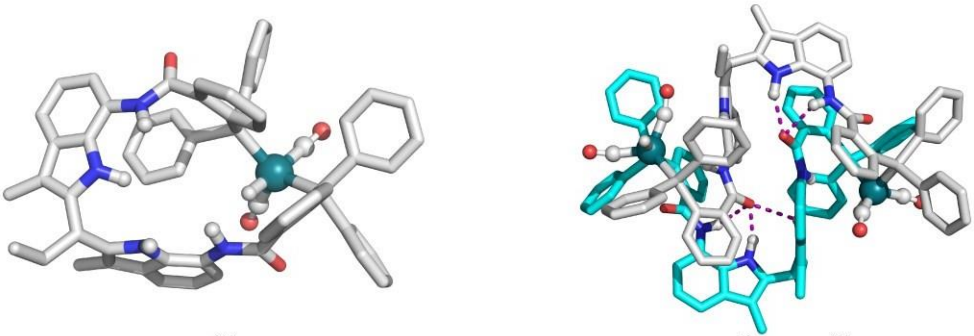
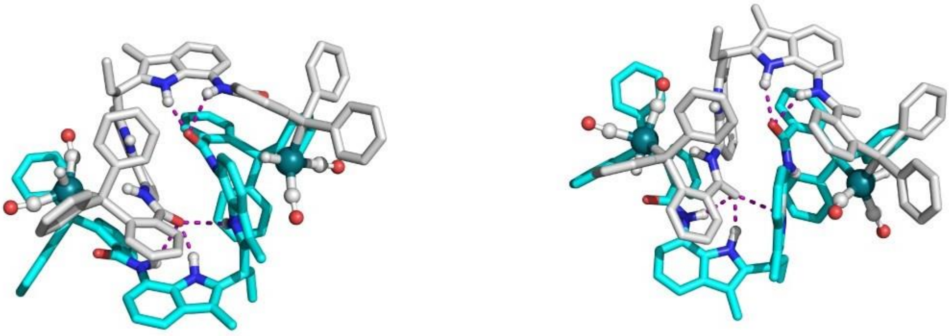


Fig S24. ^{1}H NMR spectra of OrthoDIMPhos ligand **L2** and the dimeric active species [Rh(**L2**)$(CO)_2$H]$_2$ under 7 bar syngas at different relaxation time (1.0 and 60 seconds).

The down field shifts of the protons of the DIM-receptors suggest the partaken of the DIM-receptors in the formation of the dimeric species via hydrogen bonds. Also the integration of amide-NH and indole-NH signals is 1:2:1 ratio instead of 2:2 ratio for four protons, suggesting the asymmetric structure, of which the DIM-receptor is partially involved in the internal hydrogen bonding interactions. Furthermore, the integration of theses proton signals was influenced by the relaxation time used for acquisition, further confirming that the DIM-receptors partake in internal hydrogen bonding interactions.

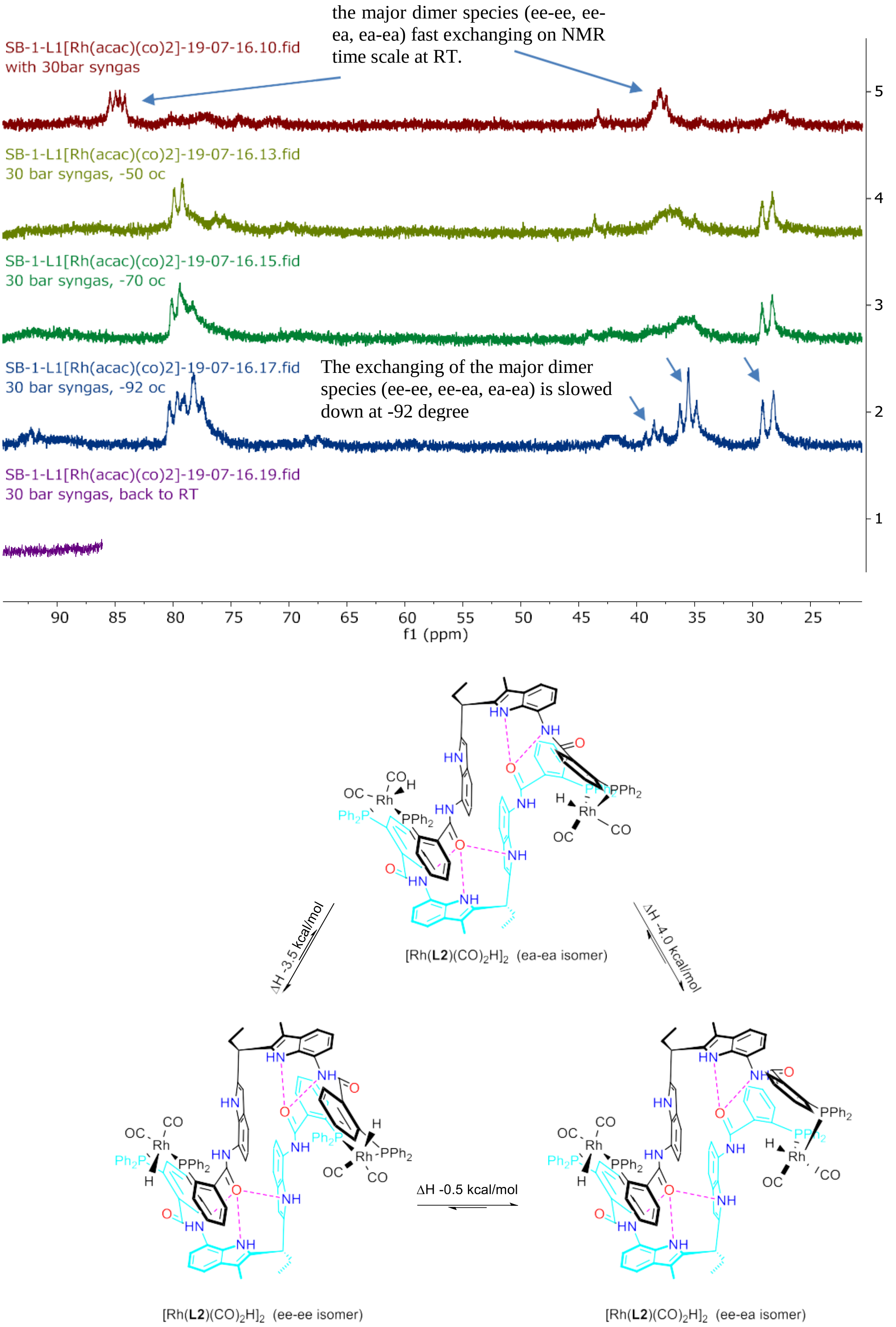


monomer-ee (**A**) dimer-ea-ea (**B**)



dimer-ee-ea (**C**) dimer-ee-ee (**D**)

Fig S25. DFT calculated stable monomeric and dimeric active species. DFT calculated structures indicate the partaken of internal hydrogen bonding interactions with the DIM-receptors in the dimeric structures.



the major dimer species (ee-ee, ee-ea, ea-ea) fast exchanging on NMR time scale at RT.

The exchanging of the major dimer species (ee-ee, ee-ea, ea-ea) is slowed down at -92 degree

Fig S26. HP VT $^{31}P\{^{1}H\}$ NMR spectra of the dimeric Rh-active species [Rh(**L2**)$(CO)_2H]_2$ formed under 30 bar syngas showing the geometrical isomers as shown by the assignments.

The dimeric species are under fast equilibrium at room temperature and as such the phosphorus signals corresponding to one species was observed. When temperature lowered to minus 90 degrees, approximately three species were observed by phosphorus NMR, in line with dimeric species with ee-ea, ee-ee and ea-ea conformation. Also, based on the integrations at minus 90 degrees, these three major dimeric species have ratio of cat. 2:2:1, assigned to be ee-ea, ee-ee, and ea-ea conformations, respectively. In line with experimental observations, DFT modelling corroborates that the dimeric active species with ee-ee and ee-ea conformation are more stable than dimer of ea-ea structure (vide supra, calculated enthalpy at 298 k, BP86-D3/SVP //B3LYP-D3/TZVP/COMSMO(DCM), details see the DFT section). For all the DFT optimized structures, including the monomeric complexes, and their energies, see the DFT calculation section. Hydrogen bonds are shown in purple dots.

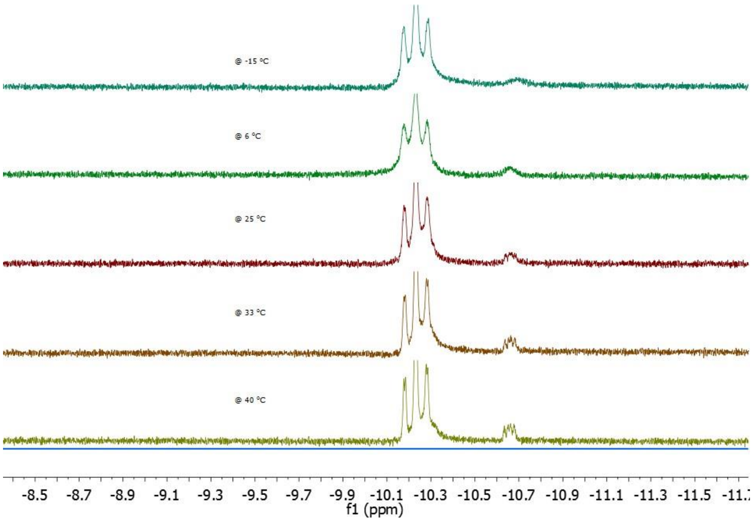


Fig S27. Variable-temperature (VT) ^{1}H NMR spectra of the active species [Rh(**L2**)$(CO)_2$H]$_2$ and [Rh(**L2**)$(CO)_2$H] under 7 bar syngas.

The ratio of the dimer and monomer species is related to the temperature as monitored by NMR experiments. Noted that the hydrogen bonding interaction is weaker at higher temperatures. Indeed, slightly more monomeric species is observed when the temperature increases from -15 degree to 40 degree (9% vs. 13% of the monomer), further confirming that the internal hydrogen bonding interactions with the DIM-receptors contribute to the self-dimerization. Thus, replacing the internal hydrogen bonds by effectors binding to the DIM-receptors should induce the structural changes of this supramolecular catalytic system.

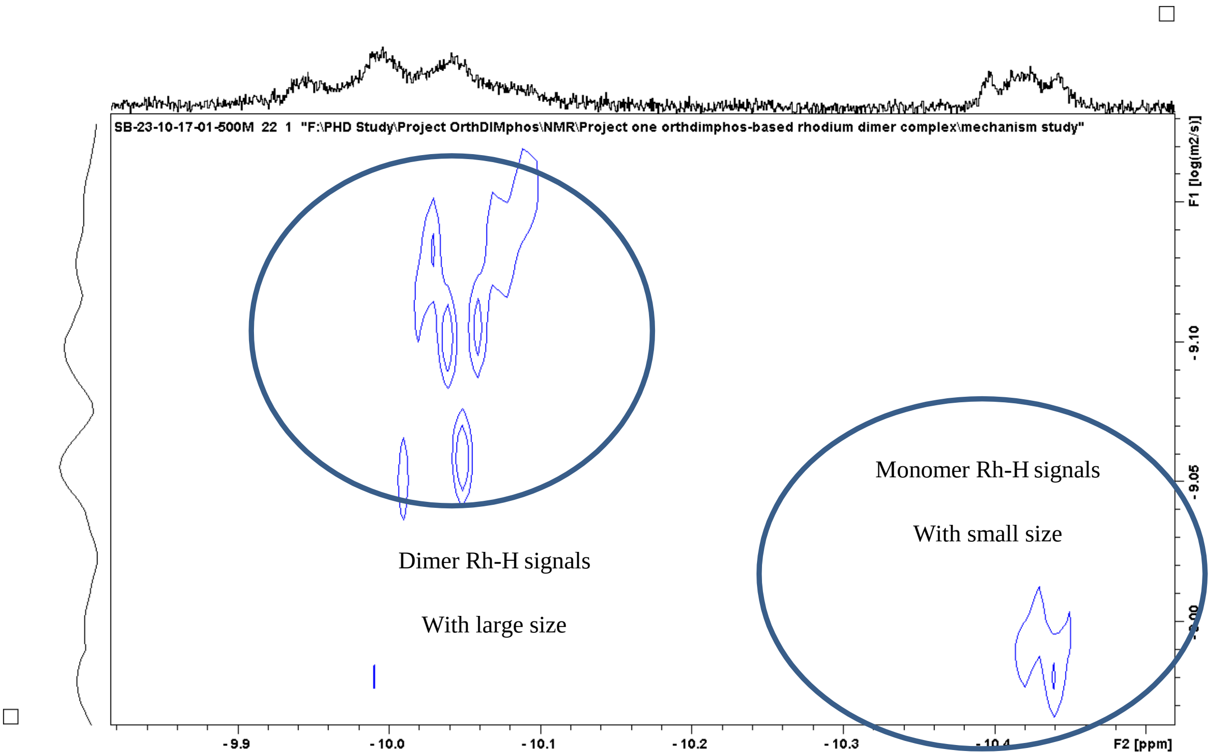


Fig S28. ^{1}H DOSY NMR spectra of the major dimeric species and the minor monomeric species under 7 bar syngas at 40 ^{o}C.

The difference of the diffusion constants of these species, corresponding to the relative hydrodynamic radius (rH$_{dimer}$=8.1 Å vs. rH$_{monomer}$=5.5 Å), further confirms the formation of the major dimeric species along with the minor monomeric active species.

Stoke-Einstein equation: $rH=k.T/(D.6\pi.\eta)$

(k=the Boltzmann constant, T=the absolute temperature, η=the fluid viscosity, rH=the hydrodynamic radius, D=diffusion constant.)

Table S1: DFT calculated infrared spectra of the dimeric species **B**-**D** [a]

species	**C** (ee-ea isomer)/cm^{-1}	**D** (ee-ee isomer) /cm^{-1}	**B** (ea-ea isomer)/cm^{-1}
Rh-CO (ee part)	1961, 1989	1952, 1961, 1994, 2006, 2054, 2062	
Rh-CO (ea part)	1959, 1993		1958, 1963, 1991, 1993
Rh-H	1961, 1989, 2060, 2086	1952, 1961, 1994, 2006, 2054, 2062	2021, 2061

[a] Rh-H, Rh-CO@axial coupled IR bands colored red (BP86-D3/SV(P)). Experimentally observed bands: 2062, 2040, 2012, 1982, 1966 cm^{-1}. Calculated CO bonds: 2062, 2054, 2006, (1994, 1993, 1991, 1989,) (1963, 1961, 1959, 1958) cm^{-1}.

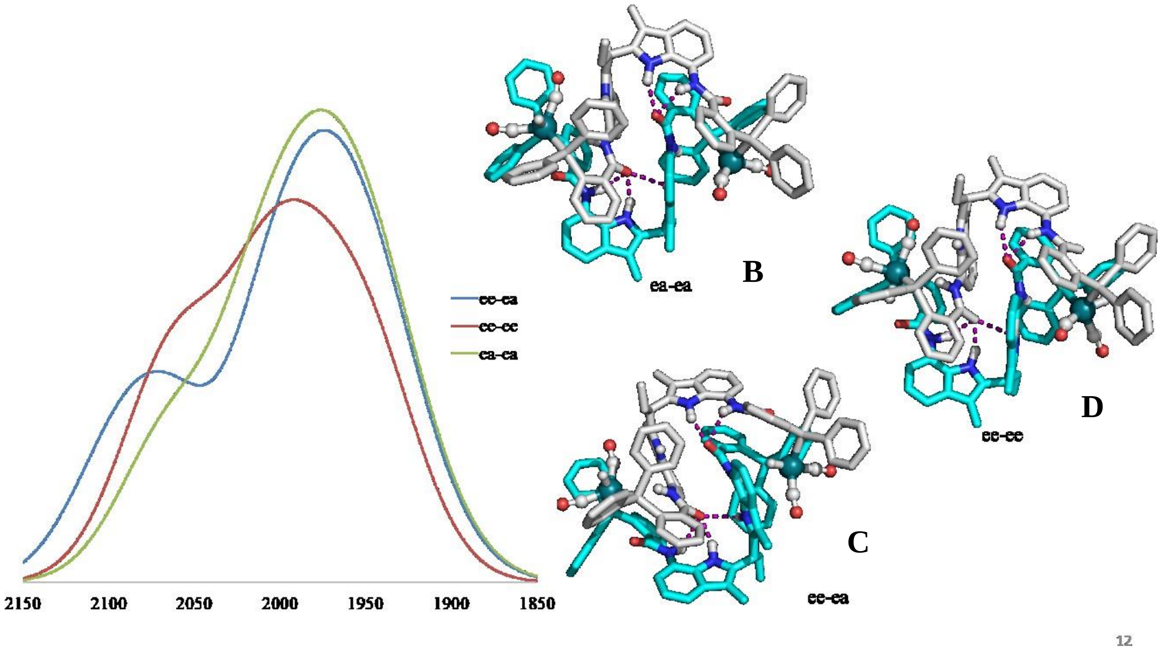


Fig S29. DFT calculated IR spectra of the DFT optimized active dimeric Rh-species [Rh(**L2**)(CO)$_2$H]$_2$ with ee-ea, ea-ea, and ee-ee geometries.

The combination of the DFT calculated IR spectra is in line with experimentally observed HP IR spectra of the dimeric active species [Rh(**L2**)(CO)$_2$H]$_2$.

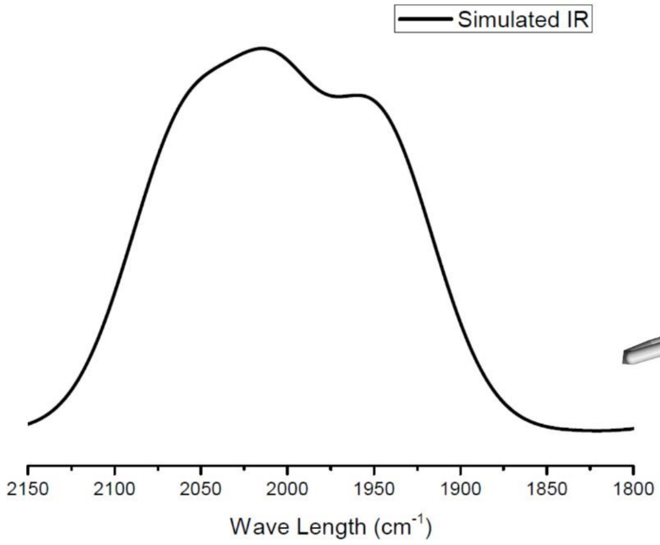
In situ high-pressure infrared (HP IR) spectroscopic experiments under hydroformylation conditions: These experiments were performed in a stainless steel (SS 316) 50 mL autoclave equipped with IRTRAN windows (ZnS, transparent up to 700 cm^{-1}, 10 mm i.d., optical path length 0.4 mm), a mechanical stirrer, a temperature controller, and a pressure transducer. The autoclave is equipped with a separately pressurized reservoir which allows for the addition of liquid to the main chamber, while it is pressurized. If not stated otherwise, the HP IR experiments were performed at room temperature. All manipulations were conducted under nitrogen atmosphere.

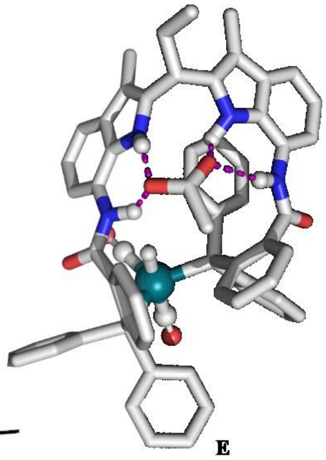
Sample preparation: A flame dried 25 mL Schlenk flask equipped with a Teflon stirring bar was charged with OrthoDIMPhos **L2** (13.000 mg, 14.3*10^{-3} mmol, 1 eq.) under nitrogen atmosphere followed by the addition of dried and degassed DCM (10 mL) to prepare ligand solution. Another flame dried 5 mL Schlenk flask equipped with a Teflon stirring bar was charged with [Rh(acac)(CO)$_2$] (3.354mg, 14.3*10^{-3} mmol, 1 eq.) followed by the addition of dried and degassed DCM (2 mL) under nitrogen atmosphere to prepare rhodium precursor solution. After stirring under nitrogen for 30 minutes, the ligand solution was transferred to the main autoclave chamber under nitrogen atmosphere, which was then purged with 20 bar of syngas and then pressurized under 20 bar of syngas. After full equilibration (30 minutes), a background spectrum was collected. Then the rhodium precursor solution was added from the reservoir under nitrogen atmosphere and the autoclave was subsequently purged three times with 20 bar of syngas and then pressurized under 20 bar of syngas followed by a series of measurements.

Characterization of the trigonal bipyramidal monomeric Rh-active species [Rh(effector□L2)(CO)$_2$H] with effector binding to the DIM-receptor under hydroformylation conditions

In situ high-pressure infrared (HP IR) spectroscopy experiments under hydroformylation conditions: These experiments were performed in a stainless steel (SS 316) 50 mL autoclave equipped with IRTRAN windows (ZnS, transparent up to 700 cm^{-1}, 10 mm i.d., optical path length 0.4 mm), a mechanical stirrer, a temperature controller, and a pressure transducer. The autoclave is equipped with a separately pressurized reservoir, which allows for the addition of liquid to the main chamber, while it is pressurized. If not stated otherwise, the HP IR experiments were performed at room temperature. All manipulations were conducted under nitrogen atmosphere.

In situ formation of the monomeric active species with effector binding to the DIM-receptor: A flame dried 25 mL Schlenk flask equipped with a Teflon stirring bar was charged with OrthoDIMPhos **L2** (13.000 mg, $14.3*10^{-3}$ mmol, 1 eq.), acetic acid (or benzoic acid, 2-vinyl benzoic acid, 3-butenoic acid) and triethylamine (1:1 ratio, 200-300 eq. to the DIM-receptor) under nitrogen atmosphere followed by the addition of dried and degassed DCM (10 mL) to prepare ligand-effectors solution. Another flame dried 5 mL Schlenk flask equipped with a Teflon stirring bar was charged with [Rh(acac)(CO)$_2$] (3.354mg, $14.3*10^{-3}$ mmol, 1 eq.) followed by the addition of dried and degassed DCM (2 mL) under nitrogen atmosphere to prepare rhodium precursor solution. After stirring under nitrogen for 30 minutes, the ligand-effectors solution was transferred to the main autoclave chamber under nitrogen atmosphere, which was then purged with 20 bar of syngas and then pressurized under 20 bar of syngas. After full equilibration (30 minutes), a background spectrum was collected. Then the rhodium precursor solution was added from the reservoir under nitrogen atmosphere and the autoclave was subsequently purged three times with 20 bar of syngas and then pressurized under 20 bar of syngas followed by a series of measurements.





E
monomer-ee-cofactor

Fig S30. DFT calculated IR spectra of the DFT optimized monomeric active species **E** [Rh(acetate**L2**)(CO)$_2$H]. DFT calculations show two CO absorption bands and one Rh-H absorption band merged at 2035 cm^{-1}.

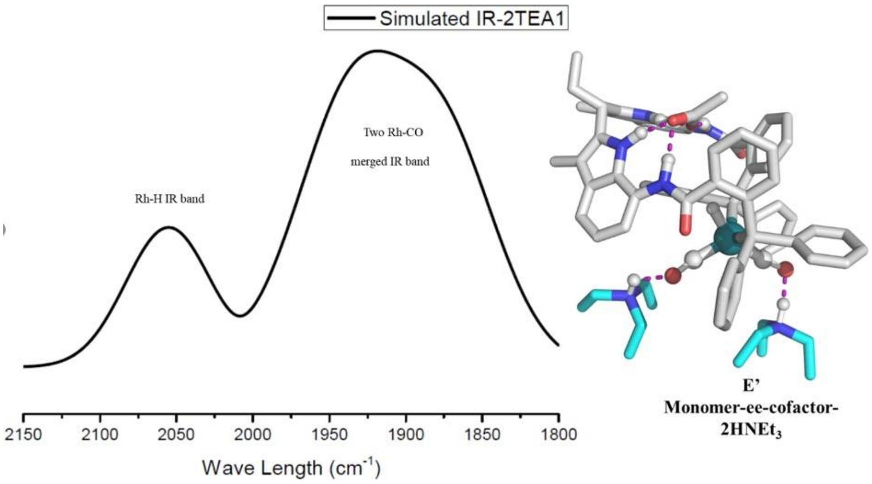


Fig S31. DFT calculated IR spectra of the DFT optimized monomeric active species **E'** [Rh(acetate**L2**)(CO)$_2$H]·(HNEt$_3^+$)$_2$.

DFT calculations show that the two CO absorption bands are merged at 1900 cm^{-1} and the Rh-H absorption band is at 2030 cm^{-1}. Importantly, DFT calculations demonstrate that, due to the surrounded triethylammonium that can form hydrogen bonding interactions with the carbonyl-O, the two merged CO absorption bands shift to the low frequency region (1900 vs. 2035 cm^{-1}). Noted that hydrogen bonding interactions are known to result in the red shift of the infrared absorption. Additionally, the band at 1900 cm^{-1} was also observed in our previous work.[8]

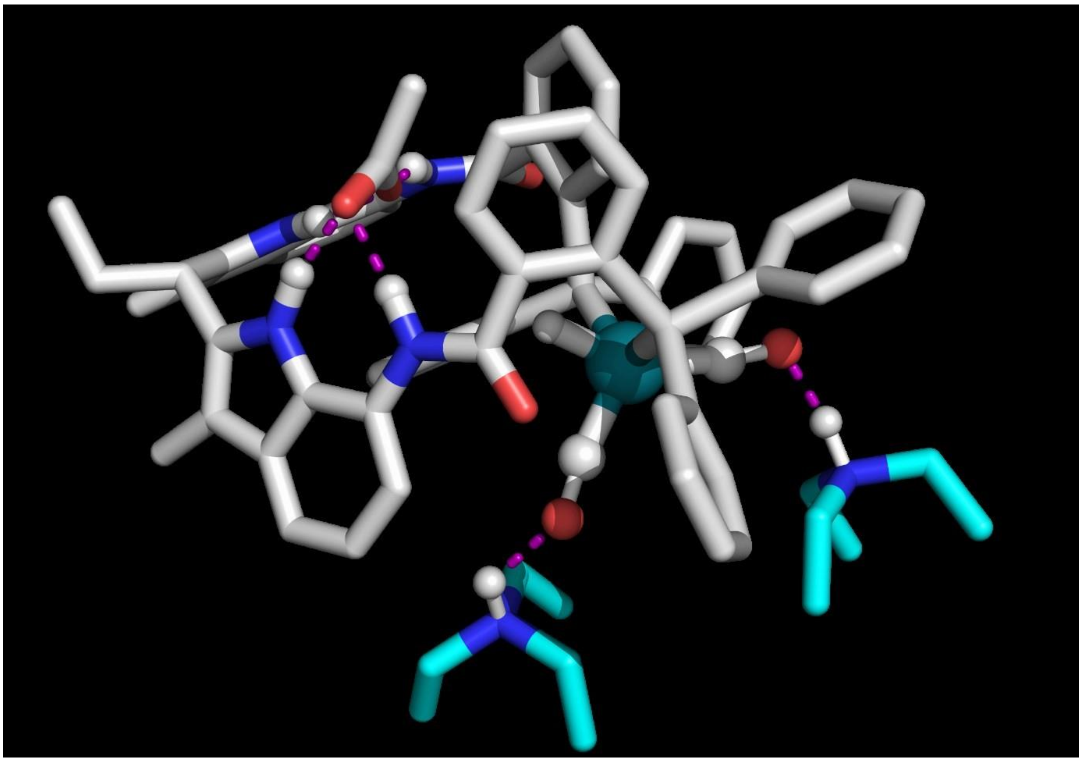


Fig S32. DFT model of the monomeric active species [Rh(acetate□**L2**)$(CO)_2H$] with effector binding in the presence of 2 molecules of triethylammonium.

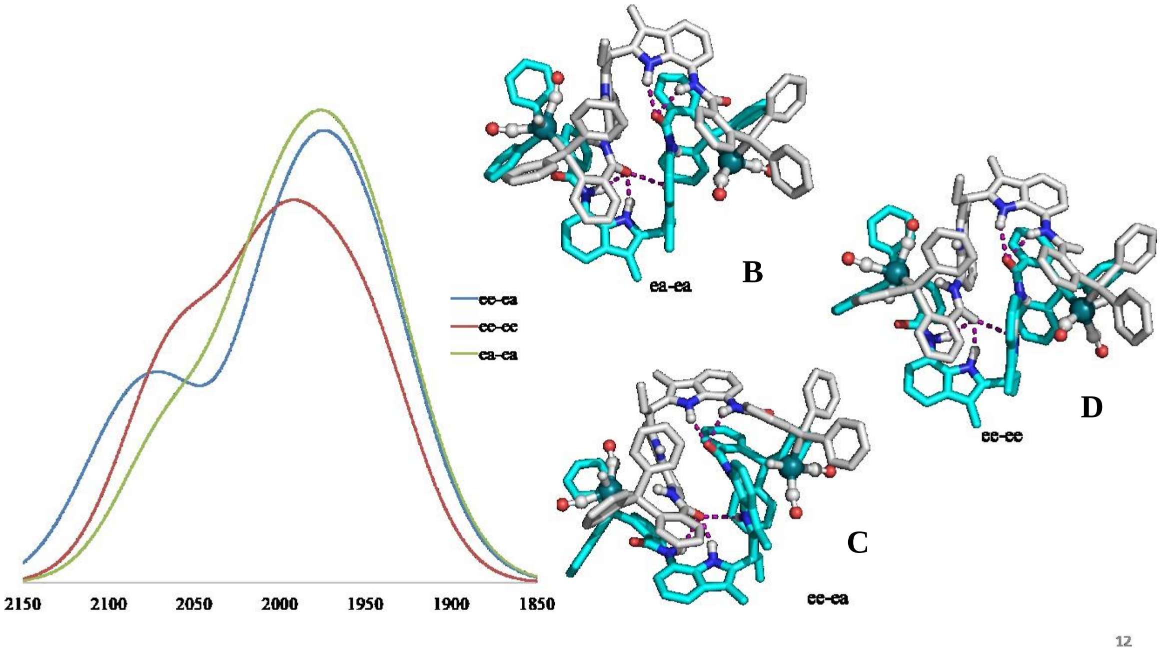


Fig S33. DFT calculated IR spectra of the DFT optimized active dimeric Rh-species [Rh(**L2**)$(CO)_2H]_2$ with ee-ea, ea-ea, and ee-ee geometries.

The combination of the DFT calculated IR spectra is in line with experimentally observed HP IR spectra of the dimeric active species [Rh(**L2**)(CO)$_2$H]$_2$.

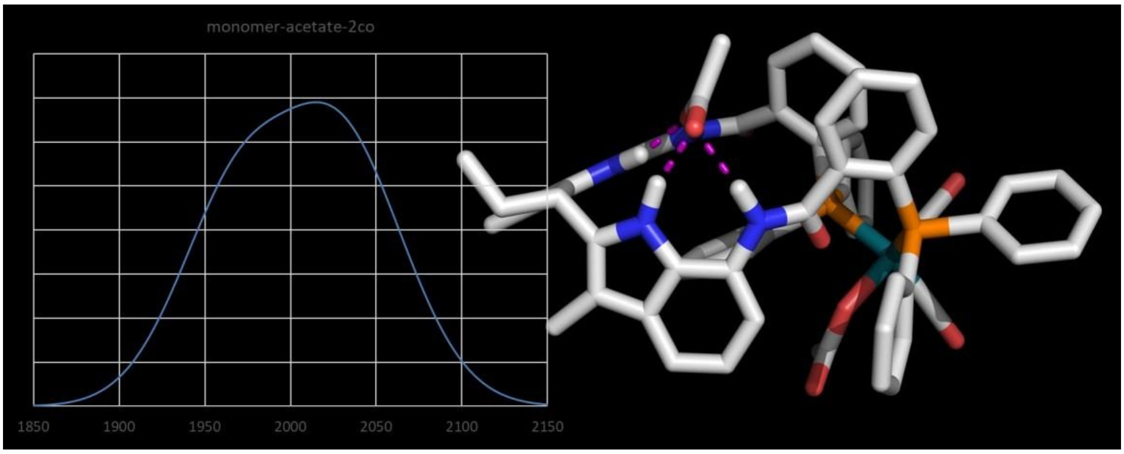


Fig S34. DFT calculated IR spectra of the DFT optimized restingstate monomeric Rh-species [Rh(acetate□**L2**)(CO)$_2$(acetate)] with effector binding to the DIM-receptor and also to the rhodium center.

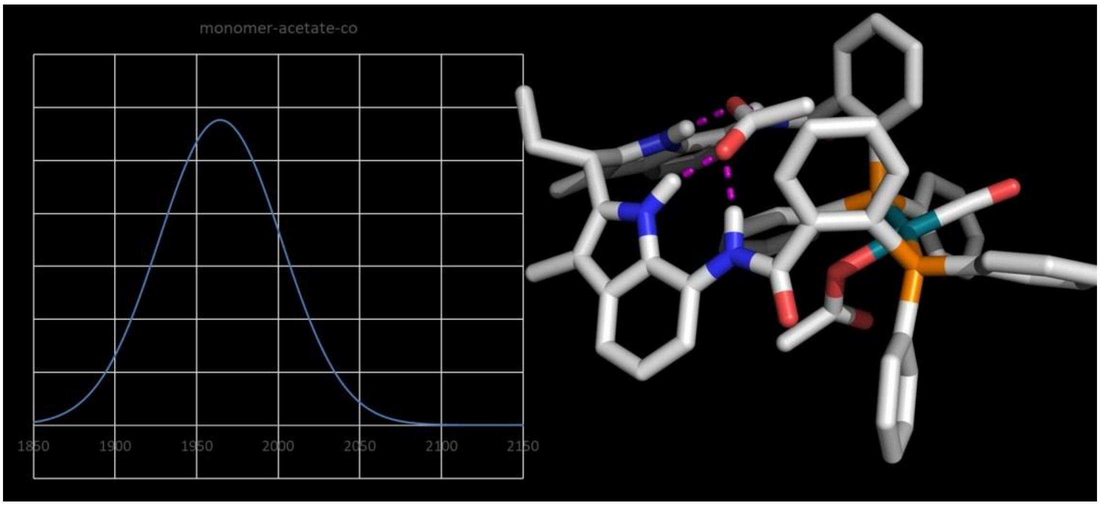


Fig S35. DFT calculated IR spectra of the DFT optimized restingstate monomeric Rh-species [Rh(acetate□**L2**)(CO)(acetate)] with effector binding to the DIM-receptor and also to the rhodium center.

In situ high-pressure (HP) NMR spectroscopic experiments with 200 equivalents of acetate as effectors: A flame dried 5 mL Schlenk flask equipped with a Teflon stirring bar was charged with OrthoDIMPhos **L2** (3.450 mg, 1.3 eq.) and [Rh(acac)(CO)$_2$] (0.774 mg, 1.0 eq.) under nitrogen atmosphere followed by the addition of dried and degassed CD_2Cl_2 (3.0 mL) to prepared [Rh] 1.0 mM complex solution. After stirring under nitrogen for 30 minutes, the yellow solution was transferred to high-pressure (HP) sapphire NMR tube under inert conditions. The tube was then purged three times with 20 bar of syngas and subsequently pressurized under 20 bar of syngas. After well mixing, the sample was taken to perform 3 days of $^{31}P\{^1H\}$ NMR experiments and 1 day of ^1H NMR experiments.

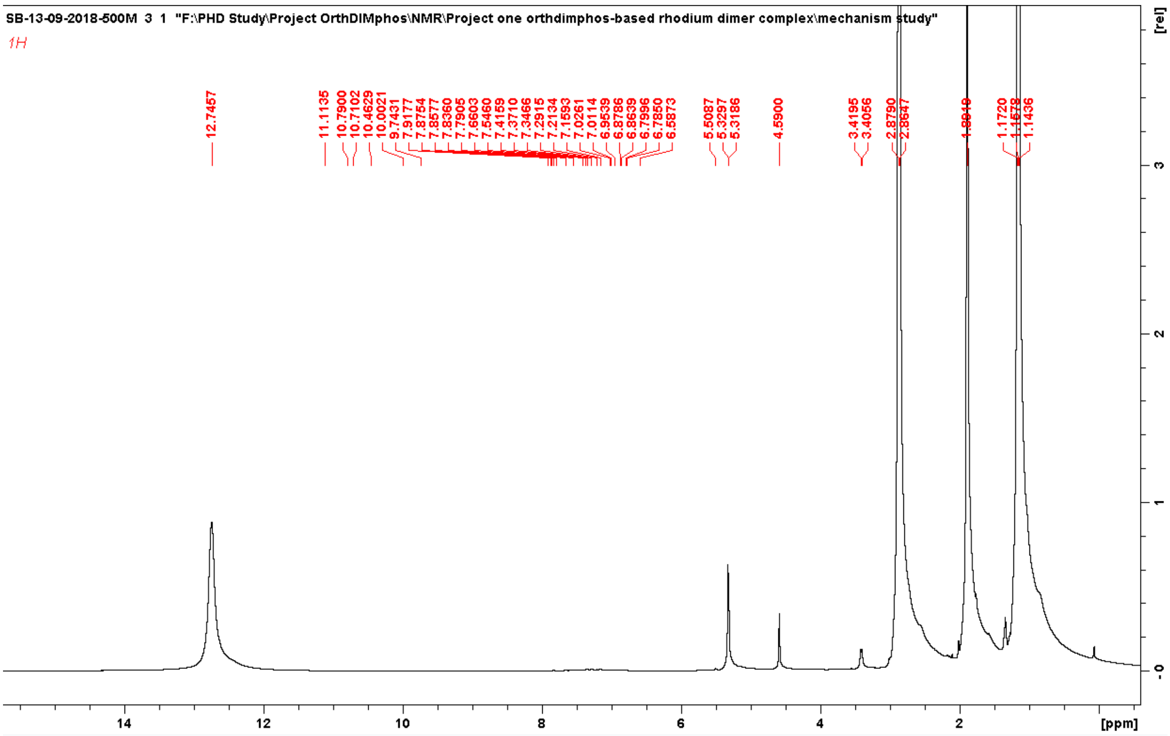
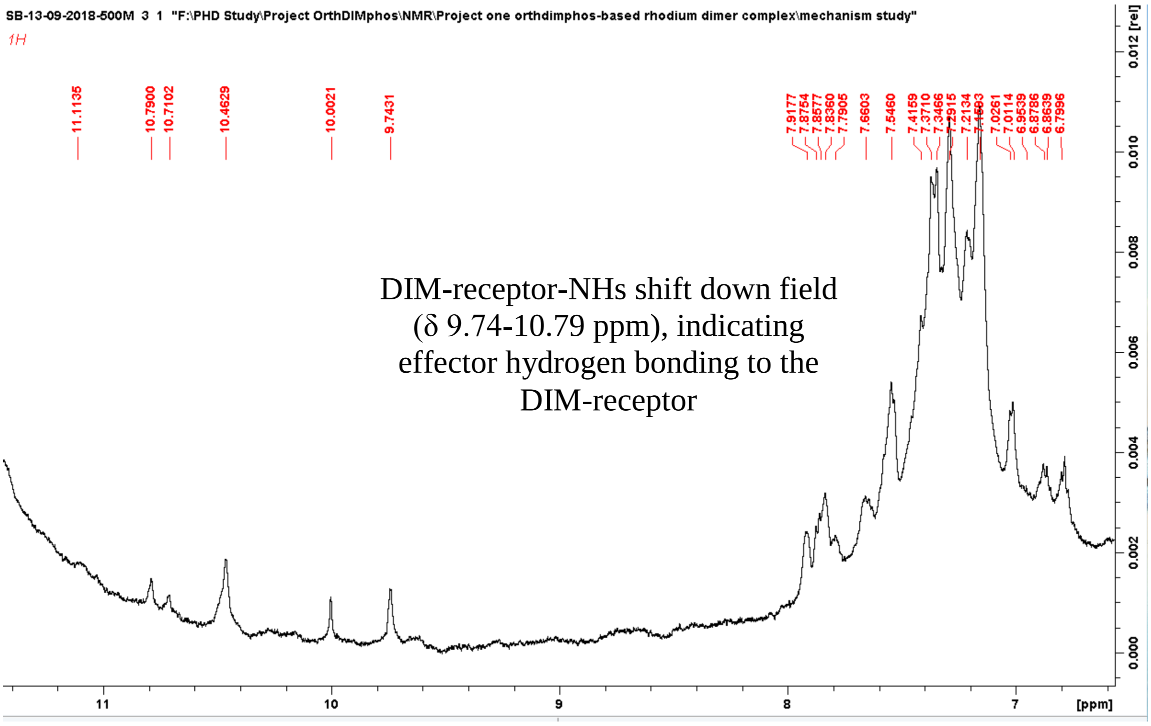


Fig S36. ^1H NMR full spectra of the monomeric active species [Rh(acetate□**L2**)(CO)$_2$H] with acetate as the effector binding to the DIM-receptor (200 equivalents of acetic acid and triethylamine were added, and without zoning in the peaks of the active species are not visible)



DIM-receptor-NHs shift down field (δ 9.74-10.79 ppm), indicating effector hydrogen bonding to the DIM-receptor

Fig S37. ^{1}H NMR spectra of the DIM-receptor region of the monomeric active species [Rh(acetate□**L2**)(CO)$_2$H] with acetate as the effector binding to the DIM-receptor (200 equivalents of acetic acid and triethylamine were added). DIM-receptor-NHs signals shift down field (δ 9.74-10.79 ppm), indicating effector hydrogen bonding to the DIM-receptor

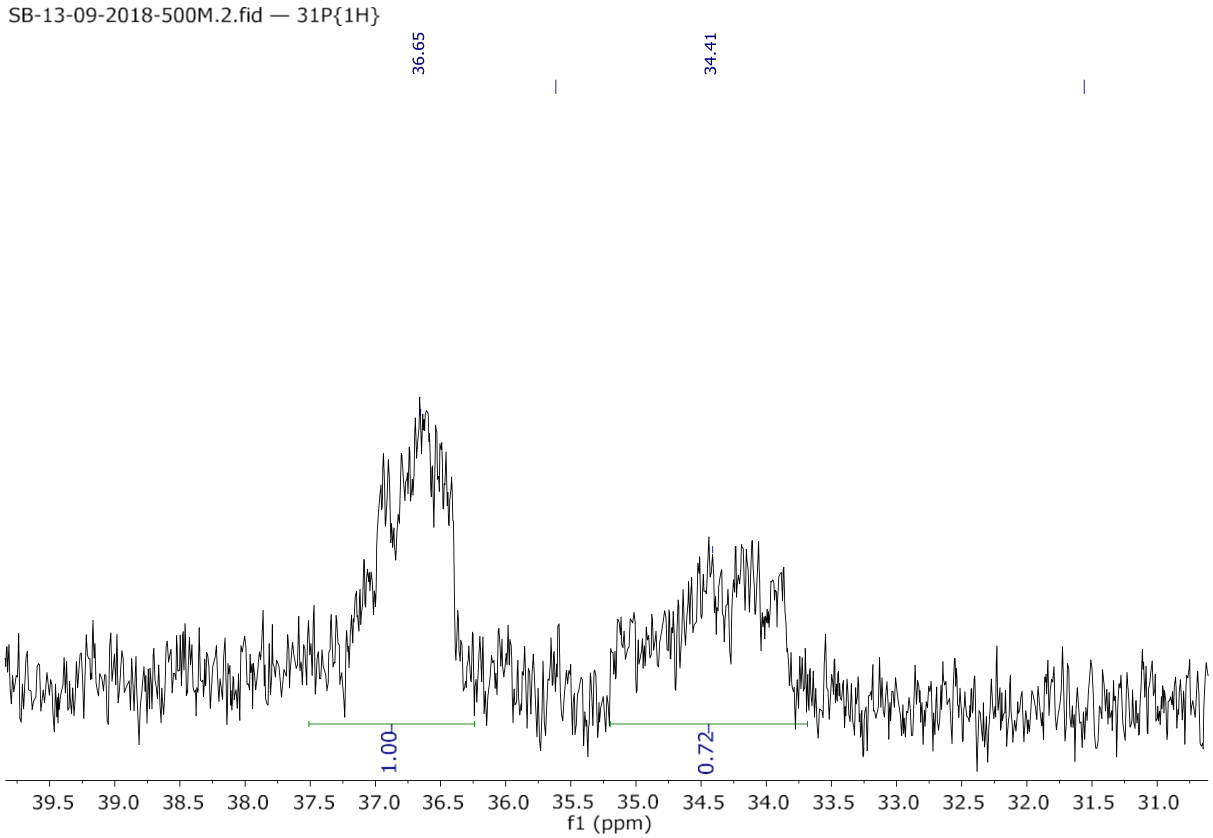


Fig S38. ^{31}P{^{1}H} NMR spectra of the monomeric active species [Rh(acetate□**L2**)(CO)$_2$H] with acetate as effector binding to the DIM-receptor (200 equivalents of acetic acid and triethylamine were added).

NMR spectra suggests that the two phosphorus atoms of the monomer species ([Rh(acetate□**L2**)(CO)$_2$H]) are with distinct chemical environment. In line with NMR experiment, DFT calculations corroborate that the two phosphorus atoms coordinate slightly different to the Rh center and experience different chemical environment. Furthermore, due to the different chemical environment, the relaxation time for each phosphorus is also slightly different, resulting in 1:0.72 ratio instead of 1:1 ratio.

In order to assign and understand the phosphorus spectra of the monomeric species, we performed DFT calculations (BP86/DZP) using ADF program[9]. The calculated data, including the chemicals shifts and coupling constants, are further inputted into gNMR software to simulate the phosphorus spectra. The computed ^{31}P NMR spectrum of the monomeric rhodium complex in the ee coordination mode **(E)** shows two phosphorus signals separated by 7 ppm, with calculated P-Rh and P-P coupling constants of 99.2, 100 and 71.8 Hz, respectively, in line with the experimental spectra. In comparison, the monomeric rhodium complex **(G)** in the ea coordination mode, which was calculated to be less stable, shows two phosphorus signals separated by 17 ppm. The computed ^{31}P NMR spectrum of the dimeric Rh-species show the phosphorus signals separated by 45.6, 21.4 and 43.5 ppm for the dimeric species with the rhodium complexes in ee-ee, ee-ea and ea-ea coordination fashion, respectively, which are very different from the experimental spectra taken in the presence of cofactors. These results further confirm the formation of the monomeric rhodium complexes in the presence of cofactor that bind to the DIM-receptor. For details see the Figures S39-43.

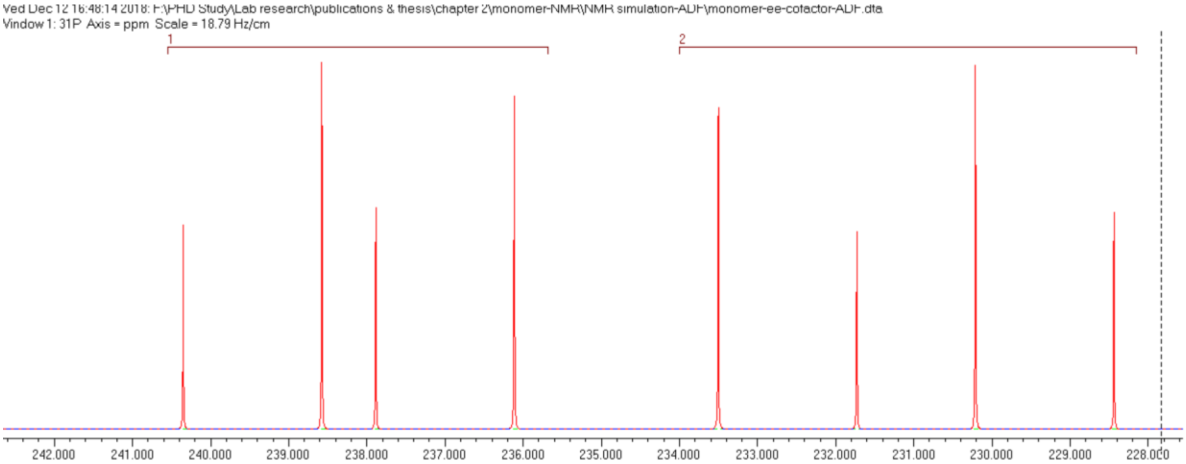


Fig S39. DFT calculated ^{31}P{^{1}H} NMR spectra of the monomeric active species [Rh(acetate⊂**L2**)(CO)$_2$H] of ee coordination fashion with acetate as the effector binding to the DIM-receptor.

DFT calculated phosphorus NMR shows that the two phosphorus atoms are with different chemical shifts that is 7.04 ppm apart, and that the P-P, P$_{\text{@down-field}}$-Rh and P$_{\text{@up-field}}$-Rh coupling constant are 71.8 Hz, 100 Hz and 99.2 Hz, respectively, in line with experimental spectra. Importantly, compared with the experimental spectra, both the difference of the chemicals shifts and the width of the signals match the experimental data.

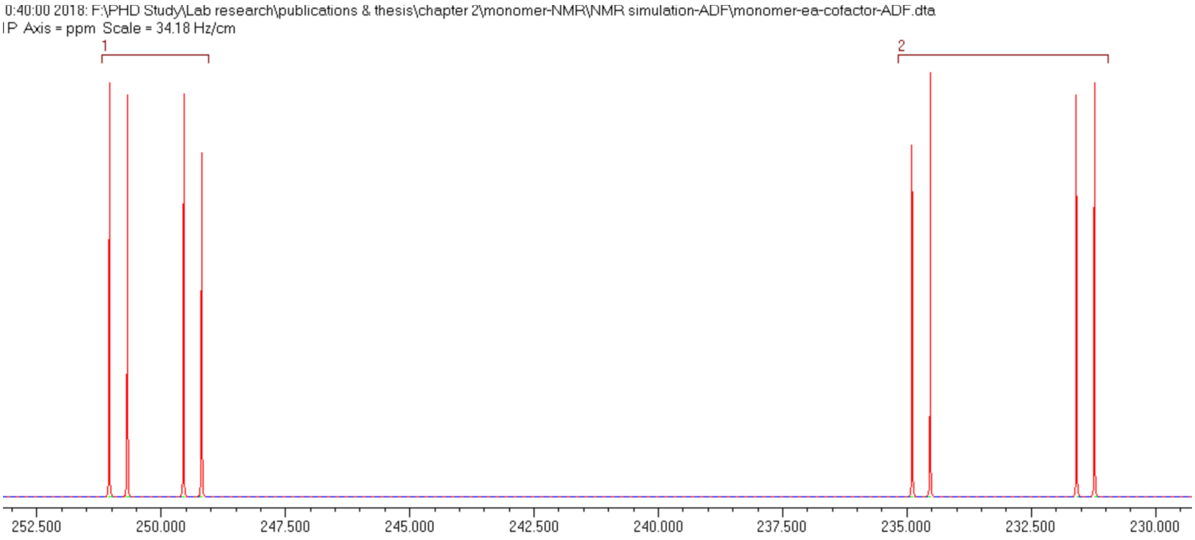


Fig S40. DFT calculated $^{31}P\{^{1}H\}$ NMR spectra of the monomeric active species [Rh(acetate□**L2**)$(CO)_2H$] of ea coordination fashion with acetate as the effector binding to the DIM-receptor.

DFT calculated phosphorus NMR shows that the two phosphorus atoms are with different chemical shifts that is 17.05 ppm apart, and P-P, $P_{@down\text{-}field}$-Rh and $P_{@up\text{-}field}$-Rh coupling constants are 14.7 Hz, 72.5 Hz and 60.5 Hz, respectively. Compared with the experimental spectra, both the difference of the chemicals shifts and the width of the signals doesn’t match the experimental data.

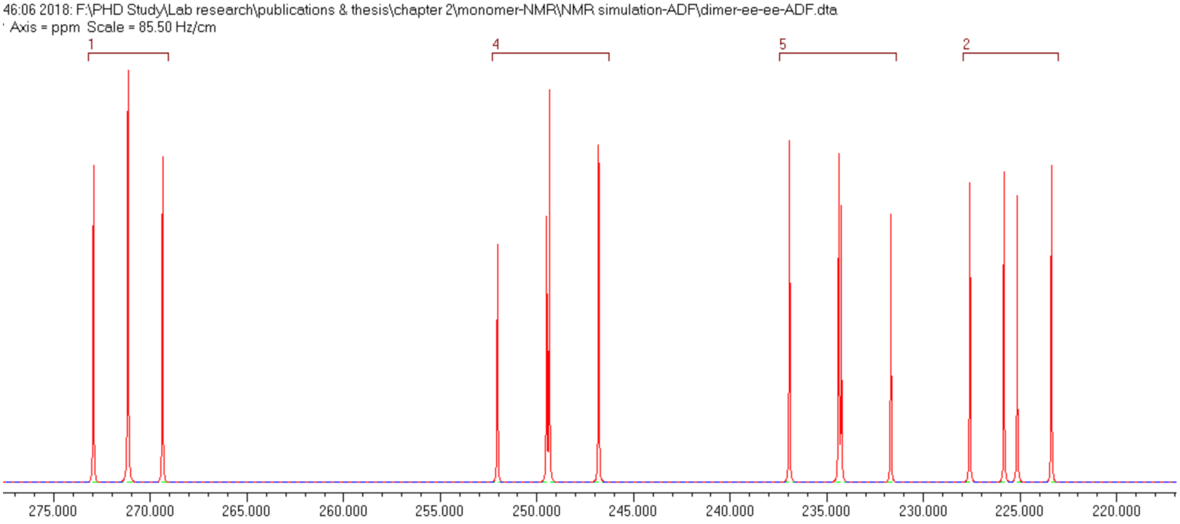


Fig S41. DFT calculated $^{31}P\{^{1}H\}$ NMR spectra of the dimeric active species $[Rh(\mathbf{L2})(CO)_2H]_2$ of ee-ee coordination fashion.

DFT calculated phosphorus NMR shows that the two boundary phosphorus atoms are with different chemical shifts that is 45.64 ppm apart.

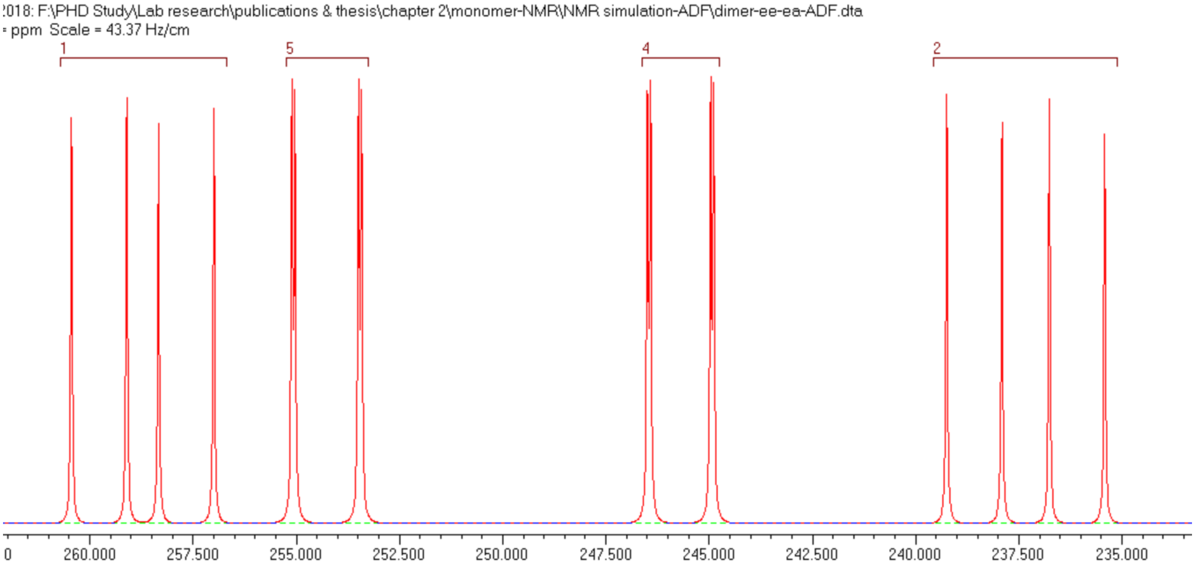


Fig S42. DFT calculated ^{31}P{^{1}H} NMR spectra of the dimeric active species [Rh(**L2**)(CO)$_2$H]$_2$ of ee-ea coordination fashion.

DFT calculated phosphorus NMR shows that the two boundary phosphorus atoms are with different chemical shifts that is 21.35 ppm apart.

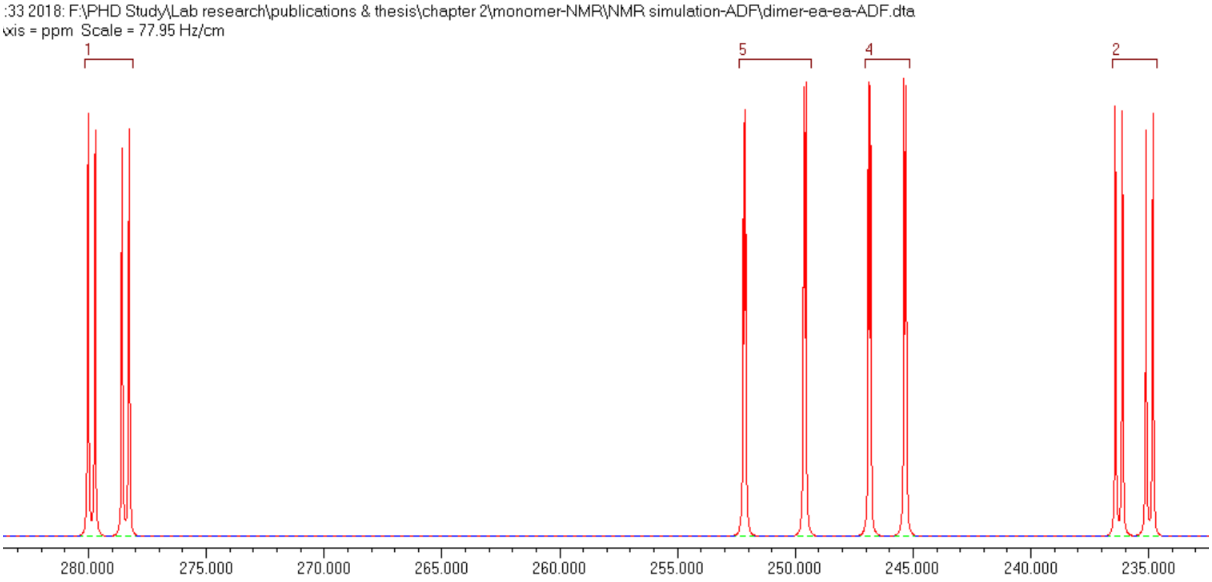


Fig S43. DFT calculated ^{31}P{^{1}H} NMR spectra of the dimeric active species [Rh(**L2**)(CO)$_2$H]$_2$ of ea-ea coordination fashion.

DFT calculated phosphorus NMR shows that the two boundary phosphorus atoms are with different chemical shifts that is 43.53 ppm apart. Noted that the combination of the DFT calculated spectra of the dimeric active species match well with the experimentally observed HP NMR spectra of the dimeric species regarding the big difference of the chemical shifts observed (46 ppm apart of the two phosphorus signals). This match further corroborates that the dimeric active species are formed as the major species in the absence of effectors. Importantly, the monomeric active species is formed when effector binding to the DIM-receptor.

In situ HP IR titration experiments using acetate as the effector: A flame dried 25 mL Schlenk flask equipped with a Teflon stirring bar was charged with OrthoDIMPhos **L2** (13.000 mg, 14.3*10^{-3} mmol, 1 eq.) under nitrogen atmosphere followed by the addition of dried and degassed DCM (10 mL) to prepare ligand solution. Another flame dried 5 mL Schlenk flask equipped with a Teflon stirring bar was charged with [Rh(acac)(CO)$_2$] (3.354mg, 14.3*10^{-3} mmol, 1 eq.) followed by the addition of dried and degassed DCM (2 mL) under nitrogen atmosphere to prepare rhodium precursor solution. Another flame dried 5 mL Schlenk flask equipped with a Teflon stirring bar was charged with acetic acid and triethylamine (1:1 ratio, 30-360 eq. corresponding to the DIM-receptor) under nitrogen atmosphere to prepare the effectors solution. After stirring under nitrogen for 30 minutes, the ligand solution was transferred to the main autoclave chamber under nitrogen atmosphere, which was then purged with 20 bar of syngas and then pressurized under 20 bar of syngas. After full equilibration (30 minutes), a background spectrum was collected. Then the rhodium precursor solution was added from the reservoir under nitrogen atmosphere and the autoclave was subsequently purged three times with 20 bar of syngas and then pressurized under 20 bar of syngas to form the active dimeric active species, followed by a series of titration experiments with varying amounts of effectors.

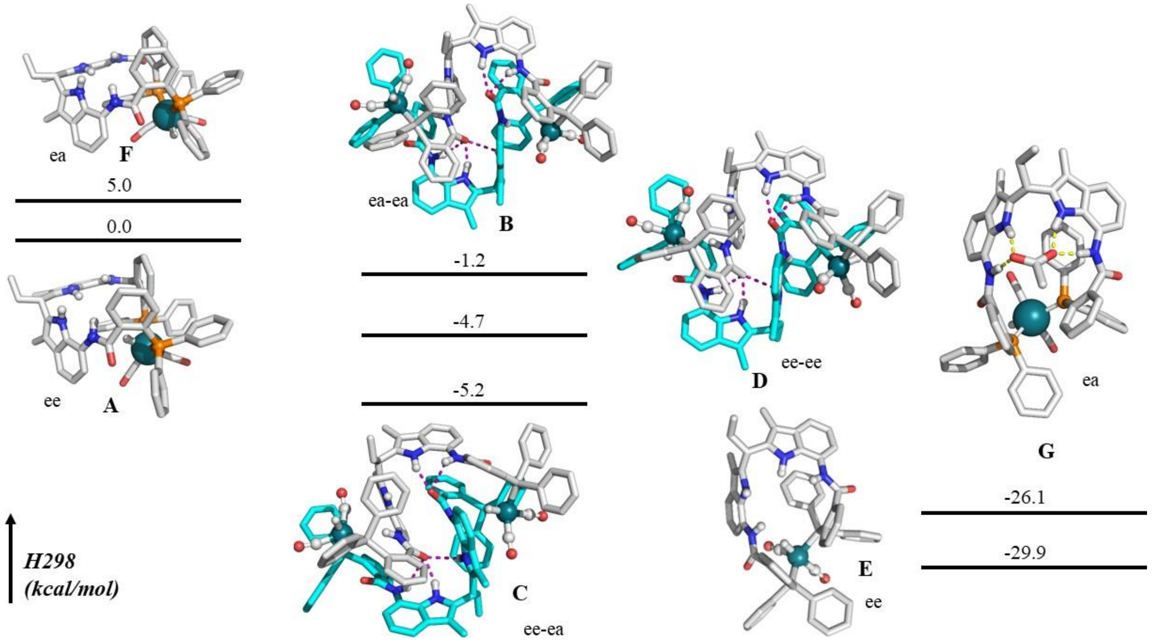


Fig S44. Molecular modelling studies of the dimer-monomer species equilibrium controlled by effectors (BP86-D3/def2-SV(P)//B3LYP-D3/def2-TZVP/COSMO(DCM)). Enthalpy energies of all the structures are shown with reference to complex **A** at 298 K.

General procedures for hydroformylation experiments

A stock solution of the catalyst was prepared by charging a flame-dried Schlenk flask with Rh(acac)$(CO)_2$, ligand and dried and degassed dichloromethane with standard Schlenk technique. A stock solution of the effectors was prepared by charging a flame-dried Schlenk flask with acetic acid, *N*,*N*-diisopropylethylamine (DIPEA) or triethylamine (TEA), and dried and degassed dichloromethane with standard Schlenk technique. The solution was stirred for 30 minutes and then 1.5 mL reaction vials (pre-dried in oven overnight) equipped with mini Teflon stir bars were charged with proper amount of substrates solution and internal standard (1-dodecane), followed by the addition of a proper amount of catalyst stock solution and effector stock solution in the Glove-Box. The vials were placed in a stainless steel autoclave (250 mL) charged with an insert suitable for 8 reaction vials for conducting parallel reactions. The autoclave was closed properly and then purged three times with 30 bar syngas followed by pressurized at 20 bar of syngas. The reaction mixtures were stirred at the appropriate temperature for the required reaction time, after which the pressure was released and the yield and regioselectivity were determined by ^{1}H NMR and GC analysis. For NMR analysis, usually 100 uL reaction mixture was transferred to NMR tubes followed by adding proper amount of $CDCl_3$. Analysis of characteristic signals in the aliphatic and aldehyde regions were in agreement in all cases. For GC analysis, usually 50 uL reaction mixture was dilute to 1 mL with dichloromethane and injected to GC for measurements with RTX-1 column. Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 3 min. Retention time: t (S) = 4.978 min, t (branched) = 9.103 min and t (linear) = 9.708 min, t (1-dodecane) = 11.432 min.[2] After catalysis, we have checked the reaction mixture by ^{1}H NMR and GC. The conversion is determined from GC analysis using 1-dodecane as the internal standard. Both NMR and GC analysis didn’t show the isomerization products or the hydrogenation products. Thus, substrate conversion is identical to aldehyde yield.

Reaction kinetics experiments

The gas-uptake experiments under constant pressure have been performed in the parallel autoclave system AMTEC SPR16, equipped with pressure sensors and a mass-flow controller suitable for monitoring and recording gas-uptake curves throughout the reactions. Prior to hydroformylation reactions, the stainless steel autoclaves (15 mL) of the AMTEC SPR16 were flushed with 5 times argon to remove traces of water and oxygen (3 times 20 bars of argon at T =110°C, 2 times 10 bar argon at room temperature).

Separately, a flame-dried Schlenk was charged with the appropriate amounts of [Rh(acac)(CO)$_2$], OrthoDIMPhos **L2** or ParaDIMphos **L1** or Xantphos and dried and degassed dichloromethane to prepare the catalyst stock solutions. The mixture was stirred until a clear solution was obtained to ensure complex formation followed by adding 1-octene and internal standard (1-dodecane) into the catalyst solution. Another flame-dried Schlenk was charged with appropriate amounts of acetic acid and triethylamine (1:1 ratio) and dried and degassed dichloromethane to prepare the effectors stock solution. Then, each of the 16 AMTEC reactors was charged under a positive argon flow with catalyst and substrate solution (4 mL), effectors (0.0 mL – 4.0 mL) and dichloromethane to a total of 8 mL. The reactors were warmed up to 25 °C under 20 bars of syngas pressure. After a reaction time of 48 hours, the autoclaves were cooled to room temperature, depressurized and the atmosphere was exchanged for argon. Conversions and selectivity were determined by ^{1}H NMR and GC analysis of the final reaction mixtures. Initially, the measured data of the gas consumption in time, attributed quantitatively to the conversion in time, were fitted, with the Igor Pro 6.5. To avoid artefacts, the correctness of the model used was evaluated and confirmed by the analysis of regular residuals of the fitting. The fitted data was used to for the reaction progress kinetic analysis and obtain the reaction order.

Table S2: Gas up take experiments of the hydroformylation of 1-octene[a]

Reactor	[Rh/L]/mM	acetic acid-DIPEA/mM	Sub/M	Total volume/mL
1	1	0	0.6	8
2	1	100	0.6	8
3	1	200	0.6	8
4	1	400	0.6	8
5	1	0	0.6	8
6	1	100	0.6	8
7	1	200	0.6	8
8	1	400	0.6	8
9	1	0	0.6	8
10	1	100	0.6	8
11	1	200	0.6	8
12	1	400	0.6	8

[a] Conditions: L/Rh 1.1, 48 hours of catalysis, 1-octene as the substrate, gas-uptake, 20 bar of syngas, 25 ^{o}C.

Table S3: The results of the hydroformylation of 1-octene in gas-uptake experiments[a]

Reactor	effector/eq.	Catalyst	conversion/%	branched/%	l/b
1	0	OrthoDIMphos	33	19	4.2
2	100	OrthoDIMphos	8	31	2.3
3	200	OrthoDIMphos	9	35	1.9
4	400	OrthoDIMphos	3	36	1.8
5	0	ParaDIMphos	5	12	7.3
6	100	ParaDIMphos	5	9	9.7
7	200	ParaDIMphos	9	8	11.0
8	400	ParaDIMphos	7	9	10.3
9	0	Xantphos	3	2	57.5
10	100	Xantphos	3	1	71.4
11	200	Xantphos	3	1	67.2
12	400	Xantphos	3	2	62.5

[a] Conditions: L/Rh 1.1, 48 hours of catalysis, 1-octene as the substrate, gas-uptake, 20 bar of syngas, 25 °C.

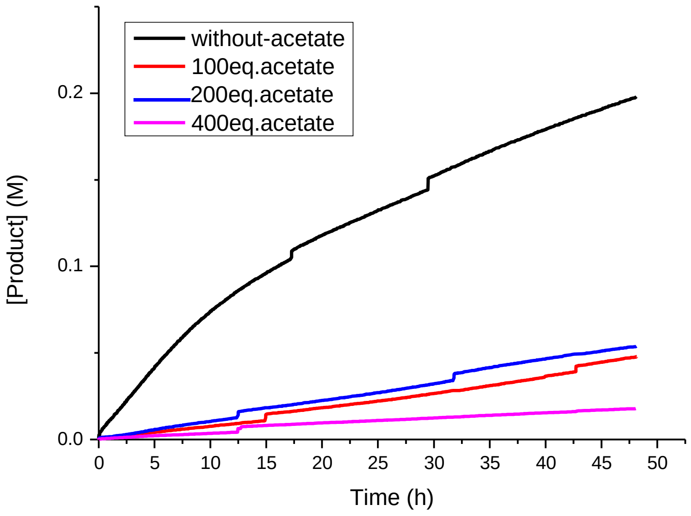


Fig S45. Product formation vs. time showing OrthoDIMphos-Rh catalytic system displays distinct activity in the hydroformylation of 1-octene with different amount of effectors. Reaction conditions: [1-octene] = 0.6 M, [Rh] = 1 mM, effector concentration (0.0 mM to 400 mM), solvent dichloromethane, total volume 8 mL, pressure 20 bar, reaction temperature 25 °C, stirring speed 800 rpm.

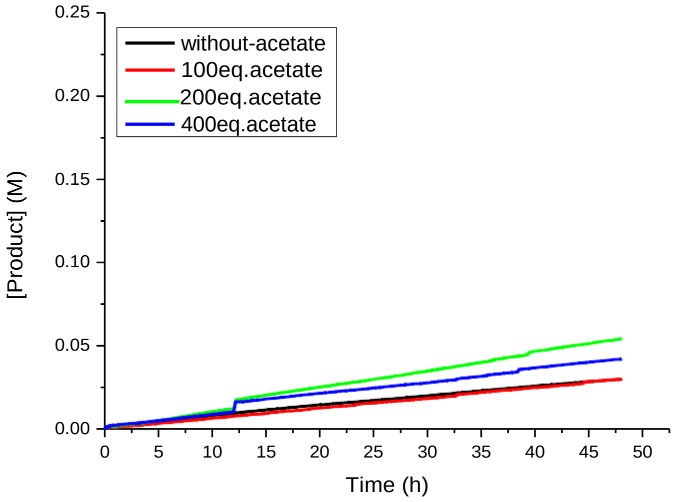


Fig S46. Product formation vs. time showing ParaDIMphos-Rh catalytic system displays similar activity in the hydroformylation of 1-octene with different amount of effectors as only monomeric active species are formed, which is not influenced by anionic effectors. Reaction conditions: [1-octene] = 0.6 M, [Rh] = 1 mM, effector concentration (0.0 mM to 400 mM), solvent dichloromethane, total volume 8 mL, pressure 20 bar, reaction temperature 25 °C, stirring speed 800 rpm.

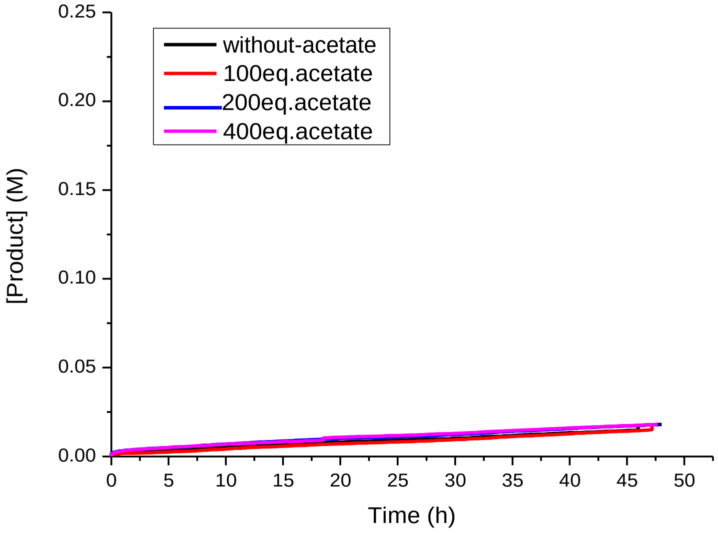


Fig S47. Product formation vs. time showing Xantphos-Rh catalytic system displays similar activity in the hydroformylation of 1-octene with different amount of effectors as only monomeric active species are formed, which is not influenced by anionic effectors. Reaction conditions: [1-octene] = 0.6 M, [Rh] = 1 mM, effector concentration (0.0 mM to 400 mM), solvent dichloromethane, total volume 8 mL, pressure 20 bar, reaction temperature 25 °C, stirring speed 800 rpm.

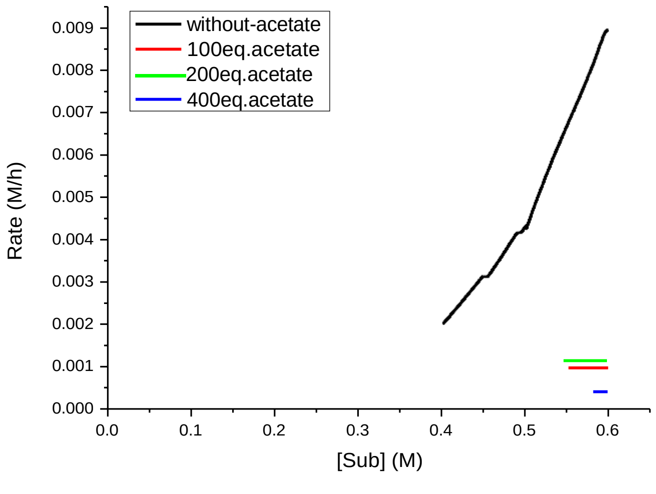


Fig S48. Reaction Progress Kinetic Analysis curves constructed from the recorded gas-uptake curves of OrthoDIMphos-Rh catalytic system. The RPKA plot displays the rate instead of the often used TOF (turnover frequency). OrthoDIMphos-rhodium catalytic system displays distinct activity in the hydroformylation of 1-octene with different amount of effectors because effectors regulate the dimer-monomer equilibrium and that the dimeric active species are more active than the monomeric active species. Reaction conditions: [1-octene] = 0.6 M, [Rh] = 1 mM, effector concentration (0.0 mM to 400 mM), solvent dichloromethane, total volume 8 mL, pressure 20 bar, reaction temperature 25 °C, stirring speed 800 rpm.

Computational methods, results and coordinates

Turbomole program[10] coupled to the PQS Baker optimizer[11] via the BOpt package[12] was used for all DFT geometry optimizations. Geometries were fully optimized as minima using the BP86 functional[13-14] and the resolution-of-identity (ri) method[15] using the Turbomole def2-SVP basis[16] for all atoms. On the optimized geometries, single-point energy calculations were carried out using the B3LYP[17-19] functional in conjunction with a triple-zeta quality def2-TZVP basis set to obtain more accurate reaction energies. Grimme's dispersion corrections (D3 version, implemented with the keyword disp3 in Turbomole)[16] were applied in all calculations. Solvents effects (COSMO) was considered for all the calculation. All minima (no imaginary frequencies) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. The relative (gibbs free or enthalpy) energies obtained from these calculations are reported in the main text of this paper.

Table S4. Gas phase thermochemical data (BP86-D3/def2-SV(P)//B3LYP-D3/def2-TZVP/COSMO) [a]

Species	SCF	ZPE	H_{corr}	G_{corr}	SCF+ZPE	H	G
acetate	-228.5986	0.0461	0.0507	0.0201	-228.5525	-228.5479	-228.5785
CO	-113.3105	0.0049	0.0082	-0.0142	-113.3056	-113.3023	-113.3248
A	-3667.9494	0.9434	1.0110	0.8391	-3667.0060	-3666.9384	-3667.1103
B	-7335.9042	1.8917	2.0256	1.7177	-7334.0125	-7333.8786	-7334.1864
C	-7335.9107	1.8917	2.0257	1.7158	-7334.0191	-7333.8850	-7334.1949
D	-7335.9095	1.8912	2.0253	1.7157	-7334.0184	-7333.8842	-7334.1938
E	-3896.5995	0.9939	1.0655	0.8870	-3895.6055	-3895.5340	-3895.7125
F	-3667.9415	0.9438	1.0111	0.8413	-3666.9978	-3666.9304	-3667.1003
G	-3896.5933	0.99386	1.0654	0.88719	-3895.5994	-3895.5279	-3895.7061

SCF = self-consistent field energy of the stationary point geometry (atomic units)

ZPE = Zero-point energy (atomic units)
H_{corr} and **G_{corr}** = correction to enthalpy and Gibb's free energy respectively at 298 K (atomic units)
H and ***G*** = enthalpy and Gibb's free energy (atomic units)
Unit kcal/mol

XYZ coordinates

A (Monomer-CO-H-ee)

123

C	-6.8321690	-3.3959425	0.7002398
C	-6.9825713	-4.7166956	4.1402941
C	-6.2723378	-5.8368474	4.5946304
C	-5.4580760	-6.6167128	3.7376026
C	-5.3322787	-6.2652110	2.3837125
C	-7.3795633	-3.2453801	1.9746666
N	-6.0304399	-4.5468774	0.6750967
C	-6.8524252	-4.3366948	2.7830559
C	-6.0125468	-5.1122321	1.9403634
C	-6.8639770	-2.5965515	-0.5928205
C	-3.3519051	-1.9430726	-1.5929477
C	-1.0519415	-7.7171866	-5.5476793
C	-2.1122350	-6.8085517	-5.6640135
C	-2.0391331	-5.5804684	-4.9870081
P	1.5366935	-5.8715146	-2.8357616
N	-4.5752814	-6.9636699	1.4260622
C	-3.5111098	-7.8271455	1.5818251
C	-2.9375514	-8.1980172	0.2273193
C	-3.6839421	-9.1134214	-0.5447337
C	-3.2505740	-9.5061942	-1.8206716
C	-2.0698413	-8.9596779	-2.3428495
C	-1.3353212	-8.0375501	-1.5829427
C	-1.7365552	-7.6454327	-0.2910833
O	0.1752464	-3.1674450	-3.7992714
N	-1.9562630	-3.4292596	-2.9357164
C	-0.8236117	-3.8573642	-3.6158416
C	-0.9230451	-5.2508086	-4.1921098
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P	-0.5872799	-6.4678128	0.6044469
C	0.1460849	-6.1816635	-4.0486663
C	0.0572453	-7.4071168	-4.7413300
C	-5.4981108	-1.9794362	-0.8174788
C	-2.4604052	0.0611426	-0.4908323
C	-1.2367568	-0.2063559	-1.1103342
C	-1.0508109	-1.3277368	-1.9492187
C	-2.1008141	-2.2352592	-2.1893996
C	-4.8998128	-0.8679904	-0.2422048
N	-4.5479873	-2.6612470	-1.5996822
C	-3.5396576	-0.8145946	-0.7402033
C	-2.3159272	-4.2672344	0.9371599
C	-1.7089959	-5.3648289	1.5898174
C	-1.9246864	-5.5432486	2.9724043
C	-3.1417473	-3.3855753	1.6495307
C	-2.7433613	-4.6493710	3.6828462

C	-3.3584019	-3.5743826	3.0254476
C	0.1890628	-7.5626922	1.8724708
C	-0.0248031	-8.9541230	1.9303440
C	0.6660422	-9.7350177	2.8724487
C	1.5596776	-9.1356996	3.7738874
C	1.7666102	-7.7451475	3.7291512
C	1.0940010	-6.9650607	2.7790203
C	2.4784807	-7.4796831	-2.9123388
C	3.3971381	-7.7662310	-3.9470540
C	4.0765723	-8.9949315	-3.9747312
C	3.8498479	-9.9526876	-2.9710780
C	2.9456500	-9.6719603	-1.9332845
C	2.2697302	-8.4420985	-1.9005789
C	2.6774502	-4.7518876	-3.7648085
C	2.6097055	-4.5904062	-5.1634362
C	3.5323391	-3.7631962	-5.8224517
C	4.5291593	-3.0935518	-5.0918325
C	4.5950322	-3.2482777	-3.6966712
C	3.6685602	-4.0690765	-3.0340372
Rh	0.9481537	-5.2027347	-0.6503958
C	1.1274734	-3.3555748	-0.1962536
O	1.2587202	-2.2392449	0.1057191
H	5.2491686	-2.4415848	-5.6101309
H	3.4666020	-3.6338200	-6.9139367
H	5.3654085	-2.7173975	-3.1167020
H	4.7942853	-9.2015187	-4.7838004
H	3.6991271	-4.1689228	-1.9379764
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H	1.8213913	-5.1002488	-5.7373859
H	-2.9861576	-7.0435259	-6.2901729
H	-2.8462416	-4.8402322	-5.1067613
H	2.7720108	-10.4065744	-1.1322148
H	1.5845794	-8.2171998	-1.0687549
H	-0.4225338	-7.5927713	-1.9963668
H	-1.7168472	-9.2337196	-3.3470695
H	-3.8398936	-10.2300215	-2.4043278
H	-4.6152881	-9.5270846	-0.1262133
H	-7.6173994	-4.1410133	4.8306038
H	-6.3525099	-6.1338003	5.6514960
H	-2.9215168	-4.8155740	4.7554185
H	-4.0207416	-2.8914824	3.5774486
H	-3.6089897	-2.5376392	1.1313952
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H	-7.0023597	-3.3500499	-1.4052575
H	-4.7753306	-6.7254972	0.4533972

H	-4.9044449	-7.4862903	4.1114470
H	-1.4847923	-6.4055114	3.4905067
H	-0.7420932	-9.4338344	1.2504833
H	0.4914438	-10.8213600	2.9072788
H	2.0953300	-9.7504853	4.5133988
H	2.4644937	-7.2654439	4.4321461
H	1.2696911	-5.8787309	2.7337514
H	0.8647428	-8.1460449	-4.6379144
H	-1.0826346	-8.6795561	-6.0814716
H	4.3877818	-10.9130611	-2.9920036
H	3.5880380	-7.0209598	-4.7337622
H	-4.8311097	-3.2728212	-2.3675457
C	-8.0325200	-1.5994644	-0.7353950
H	-7.8264355	-0.9608369	-1.6197020
C	-8.3261744	-2.2013764	2.5028787
H	-7.8444539	-1.2066015	2.6148721
H	-9.2175336	-2.0612306	1.8603933
H	-8.6961143	-2.4893823	3.5059985
C	-5.4845228	0.0603517	0.7811897
H	-6.0010257	0.9294979	0.3208633
H	-6.2143507	-0.4630990	1.4280224
H	-4.6911510	0.4636652	1.4417058
H	-8.0483155	-0.9100881	0.1307043
C	-9.3871673	-2.2977338	-0.8943528
H	-9.5760194	-3.0094027	-0.0648019
H	-10.2207747	-1.5676764	-0.9161948
H	-9.4265486	-2.8814355	-1.8379440
H	-0.4444625	-4.7613063	-1.3192731
C	2.5652622	-5.8754494	0.1418619
O	3.5395173	-6.3062372	0.6072477

B (Dimer-ea-ea)

246

Rh	1.4485116	3.2775583	4.7310105
P	-0.9443162	3.4382565	5.1998274
P	-2.0466464	-1.4581567	-3.8417093
O	-0.7737994	0.7098444	5.7353231
O	1.3116958	0.7280931	-1.4854585
O	2.1140748	4.5165499	7.4294359
N	-1.9154478	-0.9696634	4.6484407
N	-2.0811084	-3.5211902	3.2177313
N	-0.0038108	-1.1532129	-1.4336834
N	-0.9197502	-3.5991819	0.0515254
C	-2.1457831	-5.3241036	1.4612860
C	-3.4764371	-4.8774605	0.8255996
C	-4.7046741	-5.4686716	1.5173913
C	-1.4478297	-7.0864104	4.1758113
C	-1.6042408	-5.6032994	4.0289448
C	-1.9941101	-4.8845382	2.9024174

C	-1.6441522	-3.3533486	4.5238244
C	-1.3489266	-4.6316092	5.0752365
C	-0.8159374	-4.7084719	6.3822826
C	-0.5562143	-3.5128349	7.0675552
C	-0.8605335	-2.2453120	6.5162765
C	-1.4480796	-2.1538786	5.2418850
C	-1.7097074	0.3415416	5.0135746
C	-2.7485704	1.2948412	4.4966199
C	-4.0291424	0.8115492	4.1384679
C	-5.0403630	1.6693416	3.6915047
C	-4.7760085	3.0415293	3.5997005
C	-3.5222797	3.5407176	3.9810732
C	-2.4951226	2.6936862	4.4490599
C	-1.1925778	5.2525744	4.8607457
C	-1.1365212	6.2205677	5.8835586
C	-1.1587370	7.5901621	5.5649493
C	-1.2406208	8.0091411	4.2272790
C	-1.2881485	7.0479263	3.2019055
C	-1.2566711	5.6832523	3.5156402
C	-1.4510483	3.2842892	6.9826019
C	-2.6879025	3.8144615	7.4088020
C	-3.0874335	3.6962912	8.7491116
C	-2.2605245	3.0363522	9.6744372
C	-1.0372547	2.4907032	9.2506477
C	-0.6361440	2.6093490	7.9108987
C	0.8374391	-6.5681843	1.4621869
C	0.3812109	-5.3034227	0.8018578
C	-0.9244035	-4.8228634	0.7209358
C	0.3790124	-3.2514858	-0.2612641
C	1.2298116	-4.3071802	0.1984068
C	2.6274040	-4.1965570	0.0371841
C	3.1352714	-3.0571196	-0.5924924
C	2.2854677	-2.0382131	-1.0763644
C	0.8927919	-2.1114690	-0.9173185
C	0.2390883	0.1484557	-1.7718164
C	-0.8416765	0.8832910	-2.5243851
C	-0.8788993	2.2627978	-2.2411625
C	-1.6941160	3.1560837	-2.9356144
C	-2.4884756	2.6682452	-3.9773807
C	-2.5084914	1.2928685	-4.2465816
C	-1.7232589	0.3661697	-3.5236121
C	-3.1234284	-1.3360112	-5.3509987
C	-2.4437325	-1.1806762	-6.5798277
C	-3.1632347	-1.0841888	-7.7783386
C	-4.5677394	-1.1598626	-7.7710828
C	-5.2471363	-1.3125834	-6.5519959
C	-4.5314160	-1.3899122	-5.3436549
C	-3.2898395	-1.7384089	-2.4664126
C	-3.4472217	-0.8679817	-1.3627443

C	-4.3989267	-1.1452211	-0.3629606
C	-5.2336584	-2.2673017	-0.4650237
C	-5.0825213	-3.1424216	-1.5564984
C	-4.1065943	-2.8960318	-2.5311300
C	1.7964388	3.9428689	6.4629313
H	-2.5260863	-1.1090878	3.8417699
H	-2.1056030	-6.4330201	1.4549092
H	-1.8986430	-2.7813879	2.5157871
H	-3.5448480	-3.7690723	0.8590938
H	-3.4655007	-5.1415283	-0.2524800
H	-0.9475150	-1.5041218	-1.6157818
H	-4.7044385	-6.5772528	1.4627502
H	-5.6416078	-5.1083181	1.0465748
H	-4.7299555	-5.1887719	2.5905275
H	-1.7286238	-2.9847510	-0.0495589
H	-1.6893552	-7.6270892	3.2402944
H	-2.1126640	-7.4865259	4.9711774
H	-0.4092489	-7.3601077	4.4601611
H	-0.5766366	-5.6821598	6.8356657
H	-0.1072224	-3.5502223	8.0718787
H	-0.6487280	-1.3234177	7.0710919
H	-4.2574771	-0.2587368	4.2496229
H	-6.0301079	1.2667471	3.4288173
H	-5.5498350	3.7384273	3.2441540
H	-3.3546955	4.6237183	3.9295495
H	-1.0571566	5.9101845	6.9355057
H	-1.1060494	8.3341942	6.3747268
H	-1.2555041	9.0824069	3.9830868
H	-1.3300181	7.3550644	2.1459221
H	-1.2620705	4.9479079	2.6969396
H	-3.3441419	4.3274201	6.6890228
H	-4.0516418	4.1196055	9.0701777
H	-2.5740006	2.9414190	10.7255476
H	-0.3903807	1.9608007	9.9664238
H	0.3032368	2.1551903	7.5686971
H	1.1289539	-6.4053116	2.5231818
H	-1.2529481	6.1577584	-1.8031400
H	1.7178958	-6.9943202	0.9400088
H	-2.0383298	6.5763843	-0.2505161
H	0.0454664	-7.3426391	1.4659263
H	-0.3639560	7.1068092	-0.5880485
H	3.2957691	-4.9919406	0.3979476
H	4.2195845	-2.9430540	-0.7372125
H	2.7016920	-1.1799772	-1.6082382
H	-0.2194094	2.6341334	-1.4567648
H	-1.6702979	4.2225135	-2.6773392
H	-3.1064131	3.3489412	-4.5815526
H	-3.1668121	0.9318681	-5.0459266
H	-1.3476179	-1.1126175	-6.5870575

H	-2.6133705	-0.9598401	-8.7235339
H	-5.1316521	-1.0973217	-8.7145388
H	-6.3468427	-1.3653124	-6.5344386
H	-5.0811654	-1.4797383	-4.3959735
H	-2.8445478	0.0474333	-1.2653363
H	-4.4941062	-0.4552654	0.4891510
H	-5.9898855	-2.4715633	0.3081268
H	-5.7209563	-4.0351188	-1.6412763
H	-3.9876893	-3.5993787	-3.3682880
Rh	-0.7582361	-3.5733534	-4.1773352
P	1.0296617	-3.1931059	-5.7472087
P	2.4281934	1.1060830	4.1713508
O	0.5842932	-0.4345513	-5.5896755
O	-1.0783027	-1.1415509	1.7301201
O	-2.6503177	-5.0447543	-6.0729926
N	1.7128011	1.1476222	-4.3667743
N	1.8489855	3.5448329	-2.6648615
N	-0.0316999	0.8527774	2.0761544
N	0.7948203	3.3320704	0.6150222
C	1.9564330	5.1559019	-0.7337687
C	3.3126384	4.6379914	-0.2205893
C	4.5048346	5.2678488	-0.9408309
C	1.0814460	7.1627665	-3.2309695
C	1.2510644	5.6734914	-3.2271211
C	1.7388372	4.8632423	-2.2048249
C	1.3281128	3.4837930	-3.9481045
C	0.9468431	4.7982296	-4.3423352
C	0.3235287	4.9862294	-5.5969957
C	0.0684611	3.8584020	-6.3903905
C	0.4671550	2.5578944	-6.0020487
C	1.1434277	2.3593493	-4.7840087
C	1.5454643	-0.1173760	-4.8743617
C	2.6341132	-1.0907268	-4.5266180
C	3.8145555	-0.6563012	-3.8741970
C	4.8064866	-1.5550303	-3.4694797
C	4.6304657	-2.9235992	-3.7201776
C	3.5046870	-3.3643035	-4.4275461
C	2.5083170	-2.4670458	-4.8758829
C	1.7262073	-4.8314525	-6.3354729
C	2.8176747	-4.8427020	-7.2360146
C	3.3403554	-6.0531683	-7.7102545
C	2.7712849	-7.2744948	-7.3039306
C	1.6806340	-7.2723390	-6.4217383
C	1.1611850	-6.0580297	-5.9376940
C	0.9005066	-2.4430288	-7.4334518
C	1.8423360	-1.5385487	-7.9620787
C	1.7099050	-1.0738432	-9.2794549
C	0.6392593	-1.5096219	-10.0804210
C	-0.2967074	-2.4169707	-9.5571117

C	-0.1684469	-2.8824439	-8.2379373
C	-1.0776185	6.2686949	-0.7106115
C	-0.5677845	5.0062367	-0.0873384
C	0.7568601	4.5758118	-0.0105854
C	-0.4920687	2.9223428	0.9064214
C	-1.3835027	3.9411007	0.4401521
C	-2.7726280	3.6834230	0.4062865
C	-3.2225313	2.4201853	0.8017498
C	-2.3414165	1.4447314	1.3200675
C	-0.9636368	1.7024031	1.4376668
C	-0.1298714	-0.5018616	2.2394040
C	0.9015593	-1.2100556	3.0861062
C	0.8288253	-2.6139349	2.9616252
C	1.4799621	-3.4950609	3.8240041
C	2.1987546	-2.9632850	4.8973835
C	2.3761086	-1.5755397	4.9839747
C	1.8134905	-0.6692216	4.0541678
C	3.8796851	0.8527840	5.3241569
C	3.7748827	1.2389783	6.6739864
C	4.8401108	1.0195608	7.5637081
C	6.0246655	0.4163966	7.1103951
C	6.1341429	0.0212978	5.7651813
C	5.0680390	0.2315629	4.8780133
C	3.3834153	1.2971245	2.5637660
C	3.1881918	0.5282138	1.3972282
C	3.9944640	0.7428690	0.2614407
C	5.0217481	1.6950983	0.2812947
C	5.2203415	2.4712947	1.4377624
C	4.3966679	2.2897884	2.5538614
C	-1.9483508	-4.4164462	-5.3828602
H	2.2887202	1.2069763	-3.5250006
H	1.9212686	6.2575414	-0.6045904
H	1.8273619	2.7236845	-2.0393048
H	3.3551476	3.5364148	-0.3538027
H	3.3776271	4.8148808	0.8706691
H	0.6914275	1.3616315	2.6092599
H	4.5320103	6.3671351	-0.7904601
H	5.4609272	4.8525126	-0.5638087
H	4.4574455	5.0815635	-2.0333145
H	1.6379772	2.7828245	0.7964993
H	1.3619911	7.6172019	-2.2609939
H	1.7148099	7.6351374	-4.0127107
H	0.0334067	7.4595674	-3.4495155
H	0.0167587	5.9902392	-5.9268824
H	-0.4510354	3.9786407	-7.3533087
H	0.2586085	1.6922753	-6.6417665
H	3.9749125	0.4145453	-3.6834210
H	5.7048176	-1.1870038	-2.9519556
H	5.3782051	-3.6558486	-3.3813000

H	3.3968333	-4.4375197	-4.6316116
H	3.2636295	-3.8932525	-7.5696950
H	4.1924483	-6.0438545	-8.4074179
H	3.1779550	-8.2257795	-7.6806947
H	1.2248442	-8.2219445	-6.1020346
H	0.3073472	-6.0602334	-5.2450165
H	2.6783774	-1.1873373	-7.3390436
H	2.4471292	-0.3619875	-9.6816841
H	0.5364112	-1.1417708	-11.1127673
H	-1.1373909	-2.7665789	-10.1757604
H	-0.9120305	-3.5846953	-7.8313117
H	-3.4719632	4.4380058	0.0174404
H	-4.2926772	2.1760986	0.7366365
H	-2.7225087	0.4778822	1.6574560
H	0.1912657	-3.0160576	2.1754040
H	1.3610422	-4.5772531	3.6824786
H	2.6475518	-3.6170576	5.6595446
H	2.9969307	-1.1925349	5.8018592
H	2.8500606	1.7172297	7.0269710
H	4.7428445	1.3311629	8.6149944
H	6.8637562	0.2531168	7.8042605
H	7.0566048	-0.4581611	5.4023475
H	5.1564047	-0.0991745	3.8327927
H	2.4295745	-0.2648863	1.3466159
H	3.8039630	0.1435832	-0.6375581
H	5.6552906	1.8491829	-0.6055059
H	6.0125804	3.2345655	1.4668248
H	4.5603027	2.9087746	3.4488194
C	0.5449877	-4.4395037	-3.1158106
O	1.2981543	-5.1905262	-2.6330506
C	1.5242333	4.5162520	3.2949946
O	1.8045357	5.4363836	2.6316788
H	-1.7264936	-4.0687115	-3.0162383
H	3.0111330	3.4841101	4.6288032

C (Dimer-CO-H-ea-ee)

246

Rh	1.4134010	3.2049741	4.7789405
P	-0.9697053	3.4641620	5.2238770
P	-2.0154417	-1.2623167	-3.9469197
O	-0.8700529	0.7366880	5.8052364
O	1.3206836	0.7942832	-1.4680916
O	2.1410523	4.3864011	7.4857056
N	-2.0137512	-0.9276191	4.6973509
N	-2.2009647	-3.4490663	3.2384602
N	-0.1136062	-0.9916045	-1.3690052
N	-1.0613576	-3.4711855	0.0567581
C	-2.2855359	-5.2129301	1.4439325
C	-3.6225236	-4.7437760	0.8371046

C	-4.8468187	-5.3325392	1.5372868
C	-1.5053560	-7.0263370	4.0995909
C	-1.6963281	-5.5437134	3.9957002
C	-2.1036919	-4.8027053	2.8897637
C	-1.7543547	-3.3075197	4.5434460
C	-1.4461467	-4.5948974	5.0645136
C	-0.9082964	-4.6940618	6.3682834
C	-0.6561569	-3.5107341	7.0778074
C	-0.9648255	-2.2332427	6.5517137
C	-1.5531870	-2.1200856	5.2794540
C	-1.7929607	0.3807788	5.0606539
C	-2.7993949	1.3490824	4.5055997
C	-4.0773755	0.8862161	4.1121976
C	-5.0608448	1.7587039	3.6325853
C	-4.7724082	3.1263694	3.5449695
C	-3.5208111	3.6055963	3.9569213
C	-2.5205760	2.7430552	4.4540142
C	-1.1638952	5.2786572	4.8537199
C	-1.0976638	6.2607548	5.8625088
C	-1.0792591	7.6253362	5.5227661
C	-1.1298019	8.0253463	4.1777250
C	-1.1864889	7.0497929	3.1664844
C	-1.1956340	5.6898891	3.5015665
C	-1.5156629	3.3536042	6.9984020
C	-2.7449326	3.9270291	7.3896439
C	-3.1759674	3.8433670	8.7226751
C	-2.3886397	3.1755874	9.6765026
C	-1.1735768	2.5872314	9.2880497
C	-0.7416067	2.6711658	7.9552809
C	0.6202596	-6.6203165	1.1296926
C	0.1864139	-5.2904600	0.5948990
C	-1.0829823	-4.7240829	0.6690920
C	0.2240175	-3.1853888	-0.3612173
C	1.0366518	-4.3237053	-0.0532623
C	2.4179835	-4.2948364	-0.3449739
C	2.9500415	-3.1388385	-0.9231202
C	2.1387218	-2.0259964	-1.2361270
C	0.7588031	-2.0275179	-0.9665713
C	0.2158548	0.2767344	-1.7546359
C	-0.7893719	1.0447844	-2.5725641
C	-0.7810100	2.4298770	-2.3178589
C	-1.5127457	3.3439800	-3.0760132
C	-2.2581442	2.8702220	-4.1592348
C	-2.3161411	1.4920614	-4.4102803
C	-1.6217410	0.5449779	-3.6234541
C	-3.0727454	-1.1155565	-5.4649566
C	-2.3775858	-1.0124693	-6.6925233
C	-3.0874007	-0.9497632	-7.8987673
C	-4.4934104	-1.0071501	-7.8983991

C	-5.1853245	-1.1089815	-6.6808197
C	-4.4805051	-1.1530039	-5.4641974
C	-3.2712587	-1.5139423	-2.5771520
C	-3.5117960	-0.5840220	-1.5393174
C	-4.4627731	-0.8617422	-0.5383222
C	-5.2224923	-2.0389831	-0.5858619
C	-4.9981213	-2.9656422	-1.6219640
C	-4.0122142	-2.7216177	-2.5855972
C	1.7915364	3.8402359	6.5145435
H	-2.6118209	-1.0563980	3.8795168
H	-2.2597846	-6.3215451	1.4160027
H	-2.0294651	-2.6900412	2.5536342
H	-3.6790961	-3.6349384	0.8834153
H	-3.6202123	-4.9967723	-0.2428947
H	-1.0893911	-1.2703052	-1.5078926
H	-4.8567525	-6.4403095	1.4683193
H	-5.7870851	-4.9588426	1.0830536
H	-4.8567894	-5.0662467	2.6141267
H	-1.8182183	-2.7878044	0.0974625
H	-1.7945826	-7.5515948	3.1689103
H	-2.1114498	-7.4561733	4.9254903
H	-0.4457998	-7.2856176	4.3124105
H	-0.6591383	-5.6746614	6.8010818
H	-0.2062299	-3.5661690	8.0809644
H	-0.7533684	-1.3210744	7.1225572
H	-4.3286597	-0.1790522	4.2220283
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H	-2.9347105	1.1460333	-5.2471920
H	-1.2781164	-0.9766537	-6.6917484
H	-2.5298936	-0.8711560	-8.8446090
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H	-5.9791522	-2.2456193	0.1863976
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H	-3.8136521	-3.4705373	-3.3669051
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D (Dimer-ee-ee)

246

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H	4.3290986	6.5145492	-0.8289976
H	5.3272558	5.0425600	-0.6194454
H	4.2896768	5.2268548	-2.0710419
H	1.5728556	2.7995445	0.8280662
H	1.1475513	7.6419933	-2.2474673

H	1.5295977	7.6789239	-3.9921638
H	-0.1556208	7.4539282	-3.4592090
H	-0.0597722	6.0139319	-5.9524116
H	-0.4250413	4.0073312	-7.4170025
H	0.3134779	1.7323686	-6.7036442
H	3.9231878	0.5056800	-3.6158592
H	5.6466111	-1.0576204	-2.7834121
H	5.3936957	-3.5345491	-3.2194507
H	3.4993161	-4.3600720	-4.5714418
H	3.4818330	-3.8670469	-7.5508473
H	4.4814592	-6.0219591	-8.2908505
H	3.4929633	-8.2020238	-7.5265817
H	1.4874659	-8.1943384	-6.0138065
H	0.4863605	-6.0205992	-5.2710823
H	2.9510836	-1.2878936	-7.3474856
H	2.8049928	-0.3955792	-9.6715932
H	0.8481778	-0.9860199	-11.1314231
H	-0.9552764	-2.4950319	-10.2415368
H	-0.8101624	-3.3816813	-7.9106272
H	-3.5757956	4.3169159	0.0288891
H	-4.3497594	2.0570620	0.8054313
H	-2.7472177	0.4129406	1.7511668
H	0.0637848	-3.0503796	2.3085930
H	1.2485161	-4.6185026	3.7876184
H	2.7433729	-3.6728127	5.6201775
H	3.2063522	-1.2638355	5.6634527
H	3.1175736	1.4559962	6.9878872
H	5.1304417	1.0577913	8.4079465
H	7.2330323	0.1387001	7.3829283
H	7.2847659	-0.4014220	4.9300765
H	5.2686521	-0.0256142	3.5208984
H	2.4787669	-0.3037794	1.2798346
H	3.8252090	0.1798925	-0.7262780
H	5.5683145	1.9914665	-0.7019743
H	5.8376323	3.4222490	1.3487420
H	4.4106892	3.0132788	3.3507092
H	-1.4573902	-3.3485383	-5.8793427
C	0.4556017	-4.2357446	-3.1142482
O	1.2607040	-4.9175654	-2.6226079
H	0.9558001	1.6306491	5.9489365
C	1.6665129	4.1402402	3.5670212
O	1.9768352	4.9855732	2.8307673

E (monomer-ee-acetate)

130

C	-6.737000	-3.385000	0.683000
C	-6.864000	-4.759000	4.077000
C	-6.246000	-5.941000	4.478000

C	-5.506000	-6.742000	3.583000
C	-5.366000	-6.371000	2.240000
C	-7.201000	-3.219000	1.985000
N	-6.039000	-4.578000	0.603000
C	-6.749000	-4.368000	2.730000
C	-6.016000	-5.189000	1.830000
C	-6.783000	-2.572000	-0.598000
C	-3.350000	-1.774000	-1.626000
C	-1.192000	-7.492000	-5.601000
C	-2.135000	-6.487000	-5.803000
C	-2.014000	-5.284000	-5.107000
P	1.417000	-5.861000	-2.816000
N	-4.590000	-7.070000	1.297000
C	-3.605000	-7.986000	1.523000
C	-2.913000	-8.401000	0.241000
C	-3.466000	-9.496000	-0.435000
C	-2.894000	-9.987000	-1.610000
C	-1.775000	-9.349000	-2.143000
C	-1.228000	-8.253000	-1.478000
C	-1.754000	-7.777000	-0.268000
O	0.273000	-3.122000	-3.585000
N	-1.959000	-3.225000	-2.990000
C	-0.813000	-3.708000	-3.565000
C	-0.950000	-5.059000	-4.224000
O	-3.300000	-8.498000	2.604000
P	-0.723000	-6.494000	0.597000
C	0.033000	-6.067000	-4.037000
C	-0.125000	-7.280000	-4.725000
C	-5.452000	-1.891000	-0.825000
C	-2.507000	0.268000	-0.576000
C	-1.289000	0.017000	-1.196000
C	-1.079000	-1.111000	-2.014000
C	-2.104000	-2.039000	-2.239000
C	-4.902000	-0.740000	-0.274000
N	-4.516000	-2.502000	-1.639000
C	-3.562000	-0.640000	-0.786000
C	-2.419000	-4.286000	0.867000
C	-1.859000	-5.391000	1.532000
C	-2.113000	-5.564000	2.902000
C	-3.208000	-3.372000	1.561000
C	-2.896000	-4.638000	3.595000
C	-3.440000	-3.540000	2.929000
C	0.077000	-7.507000	1.913000
C	-0.048000	-8.899000	2.005000
C	0.654000	-9.608000	2.985000
C	1.475000	-8.937000	3.892000
C	1.597000	-7.545000	3.813000
C	0.911000	-6.839000	2.828000
C	2.326000	-7.482000	-2.966000

C	3.125000	-7.790000	-4.082000
C	3.795000	-9.012000	-4.165000
C	3.681000	-9.949000	-3.132000
C	2.898000	-9.650000	-2.015000
C	2.231000	-8.426000	-1.933000
C	2.627000	-4.786000	-3.701000
C	2.560000	-4.536000	-5.078000
C	3.535000	-3.757000	-5.701000
C	4.591000	-3.222000	-4.956000
C	4.658000	-3.463000	-3.581000
C	3.677000	-4.236000	-2.956000
Rh	0.842000	-5.253000	-0.635000
C	0.997000	-3.398000	-0.183000
O	1.130000	-2.287000	0.114000
H	5.349000	-2.606000	-5.443000
H	3.464000	-3.556000	-6.772000
H	5.468000	-3.036000	-2.988000
H	4.415000	-9.229000	-5.037000
H	3.710000	-4.397000	-1.877000
H	-2.788000	-3.840000	-3.039000
H	-0.451000	0.697000	-1.037000
H	-0.104000	-1.292000	-2.454000
H	-2.640000	1.139000	0.068000
H	1.726000	-4.932000	-5.658000
H	-2.978000	-6.640000	-6.478000
H	-2.771000	-4.511000	-5.234000
H	2.810000	-10.365000	-1.196000
H	1.638000	-8.192000	-1.047000
H	-0.369000	-7.737000	-1.899000
H	-1.333000	-9.682000	-3.083000
H	-3.341000	-10.843000	-2.118000
H	-4.362000	-9.964000	-0.023000
H	-7.413000	-4.144000	4.793000
H	-6.318000	-6.261000	5.519000
H	-3.111000	-4.801000	4.651000
H	-4.075000	-2.833000	3.464000
H	-3.645000	-2.526000	1.033000
H	-2.229000	-4.132000	-0.195000
H	-5.462000	-4.876000	-0.208000
H	-6.878000	-3.319000	-1.409000
H	-4.614000	-6.727000	0.319000
H	-4.998000	-7.636000	3.934000
H	-1.729000	-6.439000	3.424000
H	-0.708000	-9.437000	1.326000
H	0.542000	-10.693000	3.044000
H	2.017000	-9.493000	4.659000
H	2.235000	-7.008000	4.516000
H	1.021000	-5.755000	2.755000
H	0.596000	-8.082000	-4.572000

H	-1.282000	-8.448000	-6.120000
H	4.209000	-10.902000	-3.195000
H	3.230000	-7.065000	-4.889000
H	-4.635000	-3.398000	-2.163000
C	-7.983000	-1.622000	-0.764000
H	-7.861000	-1.112000	-1.733000
C	-8.005000	-2.117000	2.604000
H	-7.422000	-1.580000	3.373000
H	-8.345000	-1.373000	1.875000
H	-8.899000	-2.517000	3.110000
C	-5.518000	0.184000	0.732000
H	-6.135000	0.973000	0.268000
H	-6.153000	-0.362000	1.442000
H	-4.735000	0.688000	1.317000
H	-7.950000	-0.827000	-0.007000
C	-9.330000	-2.347000	-0.718000
H	-9.466000	-2.872000	0.237000
H	-10.166000	-1.643000	-0.847000
H	-9.395000	-3.100000	-1.519000
H	-0.546000	-4.826000	-1.322000
C	2.449000	-5.916000	0.175000
O	3.423000	-6.333000	0.649000
C	-4.432000	-5.841000	-2.491000
O	-4.406000	-4.776000	-3.189000
O	-4.519000	-5.860000	-1.227000
C	-4.320000	-7.169000	-3.220000
H	-3.254000	-7.391000	-3.366000
H	-4.786000	-7.107000	-4.211000
H	-4.753000	-7.982000	-2.628000

F (Monomer-CO-H-ea)

123

C	-6.8896131	-3.4406161	0.7089471
C	-6.9303769	-4.7478262	4.1568765
C	-6.1722823	-5.8396246	4.6024560
C	-5.3451699	-6.5934221	3.7344595
C	-5.2573944	-6.2454251	2.3764100
C	-7.4153956	-3.3001246	1.9930144
N	-6.0519416	-4.5655069	0.6723866
C	-6.8384723	-4.3702592	2.7958972
C	-5.9894414	-5.1217411	1.9406018
C	-6.9796908	-2.6504479	-0.5867044
C	-3.5064126	-1.8471557	-1.6114358
C	-1.1298666	-7.5714896	-5.4902479
C	-2.1813742	-6.6458194	-5.5355996
C	-2.0753802	-5.4591809	-4.7961097
P	1.5770051	-5.8854412	-2.7756780
N	-4.4895726	-6.9187617	1.4090600
C	-3.3956494	-7.7446678	1.5585770

C	-2.8167260	-8.1198269	0.2074759
C	-3.5708904	-9.0203967	-0.5743987
C	-3.1076853	-9.4589055	-1.8249966
C	-1.8851050	-8.9767278	-2.3117659
C	-1.1468173	-8.0612215	-1.5472678
C	-1.5807989	-7.6193633	-0.2843342
O	0.2485394	-3.2261519	-3.3221239
N	-1.9996124	-3.3536385	-2.7947402
C	-0.8166782	-3.8401503	-3.3340681
C	-0.9390105	-5.1848909	-4.0038460
O	-2.9573471	-8.1577253	2.6281750
P	-0.4424831	-6.4439440	0.6243415
C	0.1310418	-6.1255160	-3.9486478
C	0.0035950	-7.3123498	-4.7031193
C	-5.6525334	-1.9633154	-0.8387865
C	-2.7596645	0.2979568	-0.6824137
C	-1.5214788	0.0692983	-1.2879502
C	-1.2482185	-1.1105306	-2.0148865
C	-2.2293058	-2.1093566	-2.1655423
C	-5.1273962	-0.7793610	-0.3425965
N	-4.6570102	-2.6382190	-1.5707733
C	-3.7728426	-0.6719128	-0.8485509
C	-2.2700994	-4.3141322	0.8000912
C	-1.6114103	-5.3263772	1.5344507
C	-1.8238014	-5.4123358	2.9253126
C	-3.1166642	-3.4034569	1.4492115
C	-2.6787352	-4.5020613	3.5685753
C	-3.3246015	-3.4964681	2.8356848
C	0.2603519	-7.5375095	1.9406403
C	0.0354602	-8.9270246	1.9848013
C	0.6641183	-9.7120517	2.9659742
C	1.5041922	-9.1170538	3.9201178
C	1.7221565	-7.7282692	3.8877656
C	1.1134400	-6.9440602	2.8982520
C	2.4432144	-7.5387754	-2.9247687
C	3.2278012	-7.8633678	-4.0559452
C	3.8682939	-9.1091899	-4.1473405
C	3.7375435	-10.0494747	-3.1100390
C	2.9702671	-9.7321839	-1.9773549
C	2.3347338	-8.4833370	-1.8825225
C	2.7588673	-4.8628403	-3.7672087
C	2.4577945	-4.3541519	-5.0448616
C	3.4199574	-3.6194991	-5.7572995
C	4.6905992	-3.3903126	-5.2038275
C	4.9964031	-3.9000831	-3.9298943
C	4.0358614	-4.6301155	-3.2137214
Rh	1.3222413	-5.1950080	-0.4736463
C	0.5756303	-3.4897342	-0.0943494
O	0.2967675	-2.4026307	0.2201176

H	5.4420482	-2.8124892	-5.7636472
H	3.1705423	-3.2198145	-6.7524793
H	5.9891012	-3.7262532	-3.4869742
H	4.4797037	-9.3436079	-5.0326238
H	4.2825502	-5.0291530	-2.2175596
H	-2.7466655	-4.0445802	-2.7153435
H	-0.7136165	0.8074555	-1.1760020
H	-0.2515751	-1.2903808	-2.4289036
H	-2.9429579	1.2055839	-0.0886516
H	1.4629767	-4.5201293	-5.4817080
H	-3.0700100	-6.8340569	-6.1565652
H	-2.8722419	-4.7023907	-4.8724924
H	2.8748579	-10.4521893	-1.1502522
H	1.7659215	-8.2325367	-0.9747115
H	-0.2019765	-7.6694971	-1.9375856
H	-1.5018994	-9.2965825	-3.2907467
H	-3.7030779	-10.1736770	-2.4135216
H	-4.5291680	-9.3940317	-0.1796616
H	-7.5721855	-4.1915685	4.8565239
H	-6.2225178	-6.1344388	5.6617455
H	-2.8563882	-4.5983031	4.6497278
H	-4.0066888	-2.7940829	3.3366648
H	-3.6051357	-2.6033436	0.8789617
H	-2.0861455	-4.2122425	-0.2804810
H	-5.2328909	-4.5522878	0.0553980
H	-7.0900961	-3.4160503	-1.3926842
H	-4.7032330	-6.6833858	0.4387336
H	-4.7532934	-7.4396728	4.1027704
H	-1.3533513	-6.2175785	3.5044470
H	-0.6398127	-9.4035841	1.2611218
H	0.4836486	-10.7977096	2.9884017
H	1.9910679	-9.7348077	4.6902673
H	2.3810713	-7.2524189	4.6298152
H	1.3066850	-5.8609175	2.8568165
H	0.8047925	-8.0632670	-4.6674049
H	-1.1846065	-8.5046169	-6.0720613
H	4.2450640	-11.0239452	-3.1799137
H	3.3423728	-7.1308831	-4.8696649
H	-4.9065397	-3.3083323	-2.3004329
C	-8.2043868	-1.7217838	-0.7176194
H	-8.0504128	-1.0814151	-1.6112922
C	-8.3836475	-2.2814663	2.5313406
H	-7.9498162	-1.2597992	2.5685508
H	-9.3175838	-2.2179780	1.9378857
H	-8.6785847	-2.5393220	3.5667711
C	-5.7763226	0.1876221	0.6043974
H	-6.3973282	0.9448096	0.0798968
H	-6.4270508	-0.3359688	1.3311858
H	-5.0114401	0.7381282	1.1871523

H	-8.2458989	-1.0263880	0.1422094
C	-9.5197234	-2.4971711	-0.8438819
H	-9.6536484	-3.2060829	-0.0013356
H	-10.3932398	-1.8151893	-0.8602389
H	-9.5426442	-3.0955563	-1.7788027
H	2.4906115	-4.2209469	-0.9126166
C	2.7606089	-6.0976403	0.3817861
O	3.7202519	-6.5428207	0.8719788

G (monomer-ea-acetate)
130

C	-6.801000	-3.424000	0.739000
C	-6.736000	-4.754000	4.175000
C	-6.057000	-5.915000	4.561000
C	-5.338000	-6.714000	3.636000
C	-5.285000	-6.361000	2.275000
C	-7.220000	-3.242000	2.066000
N	-6.077000	-4.598000	0.650000
C	-6.706000	-4.374000	2.811000
C	-5.991000	-5.195000	1.882000
C	-6.926000	-2.608000	-0.540000
C	-3.525000	-1.771000	-1.675000
C	-1.132000	-7.546000	-5.549000
C	-2.123000	-6.567000	-5.704000
C	-2.052000	-5.391000	-4.947000
P	1.481000	-5.882000	-2.733000
N	-4.539000	-7.055000	1.301000
C	-3.483000	-7.899000	1.499000
C	-2.823000	-8.314000	0.193000
C	-3.439000	-9.353000	-0.532000
C	-2.859000	-9.870000	-1.700000
C	-1.664000	-9.316000	-2.182000
C	-1.061000	-8.265000	-1.477000
C	-1.602000	-7.763000	-0.278000
O	0.228000	-3.342000	-3.121000
N	-2.078000	-3.295000	-2.914000
C	-0.887000	-3.849000	-3.314000
C	-0.986000	-5.160000	-4.051000
O	-3.082000	-8.348000	2.578000
P	-0.562000	-6.510000	0.635000
C	0.056000	-6.128000	-3.927000
C	-0.062000	-7.326000	-4.668000
C	-5.621000	-1.893000	-0.843000
C	-2.742000	0.396000	-0.818000
C	-1.514000	0.134000	-1.431000
C	-1.266000	-1.067000	-2.138000
C	-2.263000	-2.052000	-2.266000

C	-5.105000	-0.674000	-0.391000
N	-4.668000	-2.538000	-1.616000
C	-3.768000	-0.571000	-0.930000
C	-2.403000	-4.391000	0.710000
C	-1.767000	-5.390000	1.481000
C	-2.001000	-5.446000	2.871000
C	-3.225000	-3.443000	1.333000
C	-2.835000	-4.498000	3.485000
C	-3.436000	-3.488000	2.721000
C	0.128000	-7.548000	2.010000
C	-0.065000	-8.940000	2.101000
C	0.554000	-9.674000	3.127000
C	1.352000	-9.027000	4.083000
C	1.537000	-7.635000	4.006000
C	0.938000	-6.903000	2.972000
C	2.402000	-7.511000	-2.941000
C	3.146000	-7.795000	-4.111000
C	3.835000	-9.011000	-4.248000
C	3.794000	-9.967000	-3.217000
C	3.067000	-9.693000	-2.048000
C	2.384000	-8.472000	-1.910000
C	2.670000	-4.834000	-3.700000
C	2.368000	-4.279000	-4.958000
C	3.334000	-3.532000	-5.653000
C	4.611000	-3.333000	-5.101000
C	4.917000	-3.887000	-3.845000
C	3.952000	-4.631000	-3.149000
Rh	1.255000	-5.275000	-0.403000
C	0.479000	-3.564000	-0.068000
O	0.181000	-2.476000	0.216000
H	5.365000	-2.744000	-5.646000
H	3.081000	-3.097000	-6.633000
H	5.913000	-3.736000	-3.400000
H	4.411000	-9.210000	-5.166000
H	4.197000	-5.065000	-2.167000
H	-2.929000	-3.886000	-3.027000
H	-0.694000	0.865000	-1.347000
H	-0.275000	-1.267000	-2.558000
H	-2.903000	1.325000	-0.248000
H	1.368000	-4.420000	-5.391000
H	-2.964000	-6.724000	-6.397000
H	-2.854000	-4.645000	-5.033000
H	3.037000	-10.425000	-1.226000
H	1.843000	-8.255000	-0.977000
H	-0.140000	-7.814000	-1.860000
H	-1.205000	-9.677000	-3.114000
H	-3.356000	-10.687000	-2.246000
H	-4.392000	-9.761000	-0.160000
H	-7.271000	-4.144000	4.920000

H	-6.064000	-6.221000	5.620000
H	-3.039000	-4.572000	4.563000
H	-4.104000	-2.754000	3.194000
H	-3.708000	-2.660000	0.738000
H	-2.244000	-4.338000	-0.378000
H	-5.561000	-4.935000	-0.199000
H	-7.048000	-3.357000	-1.356000
H	-4.656000	-6.757000	0.308000
H	-4.773000	-7.592000	3.970000
H	-1.567000	-6.257000	3.471000
H	-0.713000	-9.457000	1.380000
H	0.395000	-10.763000	3.184000
H	1.831000	-9.606000	4.888000
H	2.162000	-7.116000	4.749000
H	1.105000	-5.817000	2.895000
H	0.702000	-8.108000	-4.560000
H	-1.180000	-8.487000	-6.119000
H	4.338000	-10.919000	-3.323000
H	3.187000	-7.053000	-4.923000
H	-4.769000	-3.460000	-2.117000
C	-8.169000	-1.697000	-0.608000
H	-8.089000	-1.081000	-1.528000
C	-8.036000	-2.132000	2.671000
H	-7.564000	-1.134000	2.550000
H	-9.059000	-2.058000	2.241000
H	-8.159000	-2.294000	3.761000
C	-5.750000	0.329000	0.522000
H	-6.463000	1.003000	-0.004000
H	-6.308000	-0.165000	1.342000
H	-4.983000	0.974000	0.997000
H	-8.162000	-0.978000	0.234000
C	-9.481000	-2.489000	-0.612000
H	-9.548000	-3.152000	0.276000
H	-10.365000	-1.818000	-0.609000
H	-9.551000	-3.140000	-1.509000
H	2.448000	-4.307000	-0.797000
C	2.657000	-6.195000	0.473000
O	3.606000	-6.650000	0.984000
C	-4.558000	-5.895000	-2.481000
O	-4.486000	-4.799000	-3.129000
O	-4.766000	-5.968000	-1.232000
C	-4.358000	-7.195000	-3.247000
H	-3.280000	-7.451000	-3.226000
H	-4.658000	-7.077000	-4.304000
H	-4.908000	-8.024000	-2.765000

Spectra

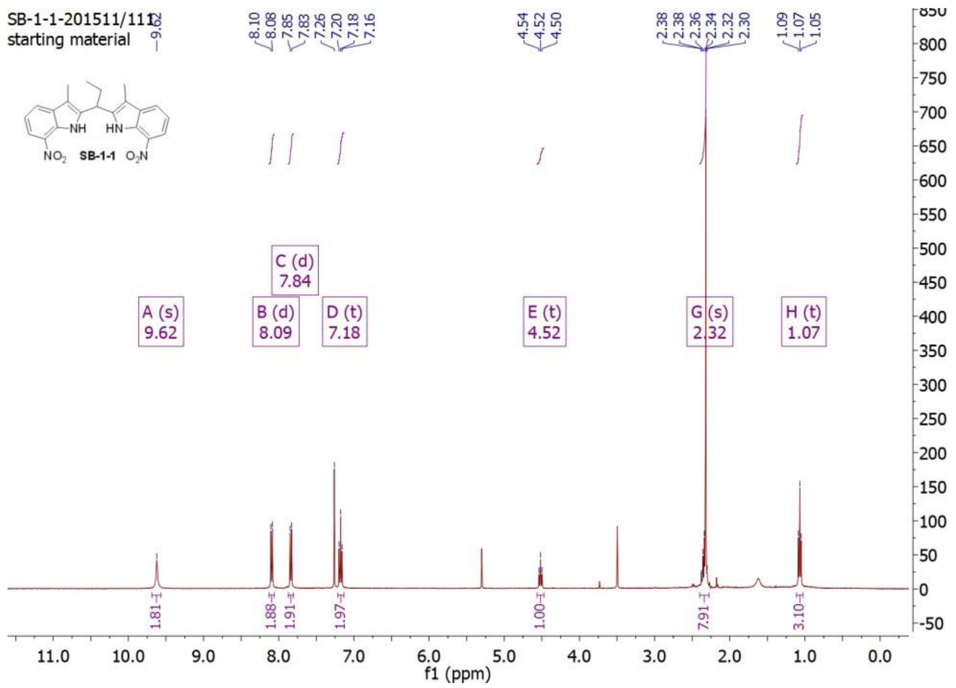

Fig S49. ^{1}H NMR spectra of 1,1-bis-(3-methyl-7-nitro-1H-indol-2-yl)-propane (**SB-1-1**)

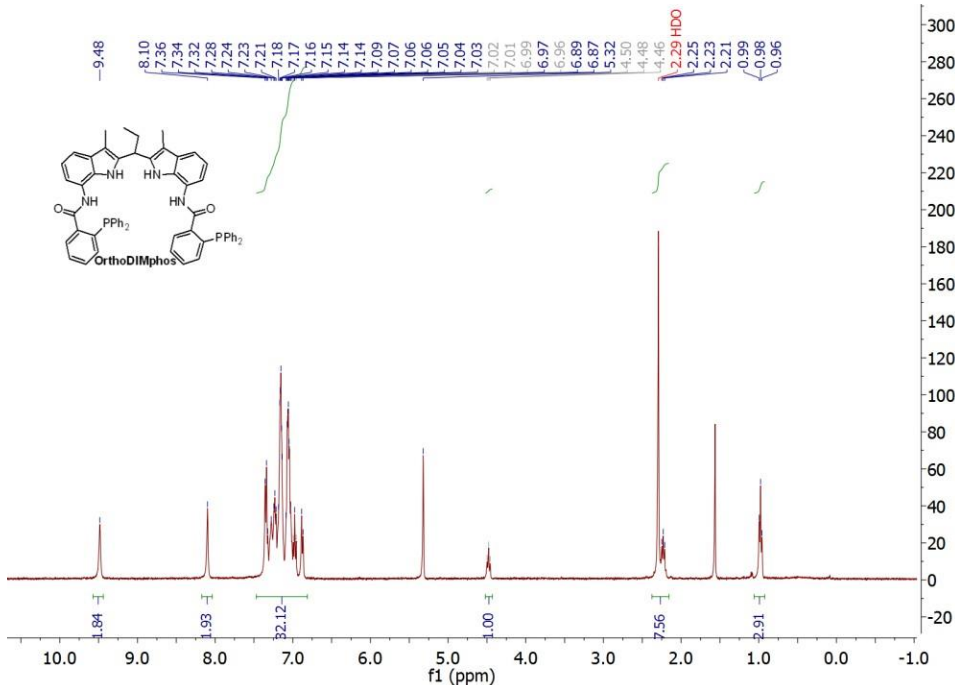

Fig S50. ^{1}H NMR spectra of 2,2'-(propane-1,1-diyl)bis(*N*-(2-(diphenylphosphaneyl)phenyl)-3-methyl-1H-indol-7-amine) (OrthoDIMPhos **L2**)

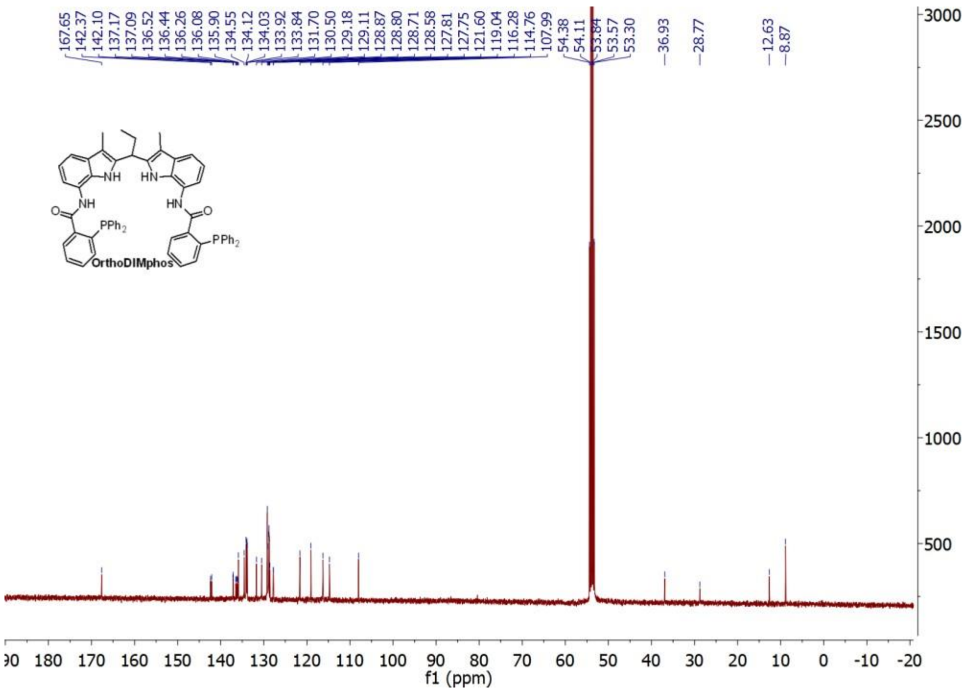

Fig S51. ^{13}C NMR spectra of 2,2'-(propane-1,1-diyl)bis(*N*-(2-(diphenylphosphaneyl)phenyl)-3-methyl-1H-indol-7-amine) (OrthoDIMPhos **L2**)

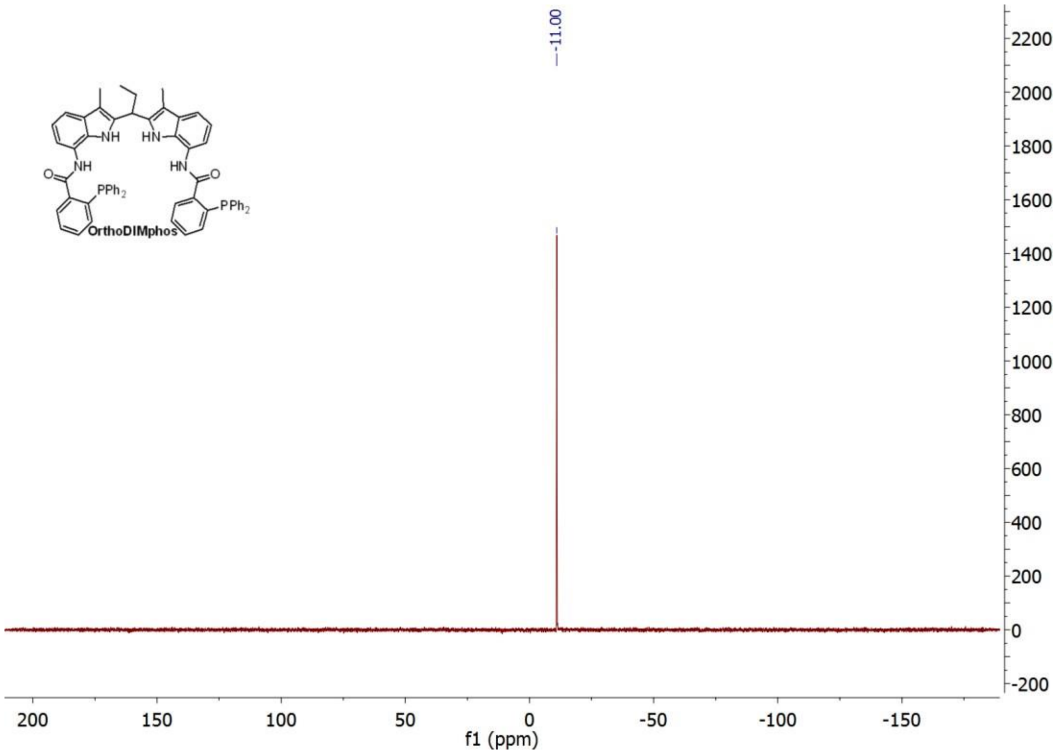

Fig S52. ^{31}P NMR spectra of 2,2'-(propane-1,1-diyl)bis(*N*-(2-(diphenylphosphaneyl)phenyl)-3-methyl-1H-indol-7-amine) (OrthoDIMPhos **L2**)

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