Rhenium in Homogeneous Catalysis: [ReBrH(NO)(labile ligand)(large-bite-angle-diphosphine)] Complexes as Highly Active Catalysts in Olefin Hydrogenations - Supporting information

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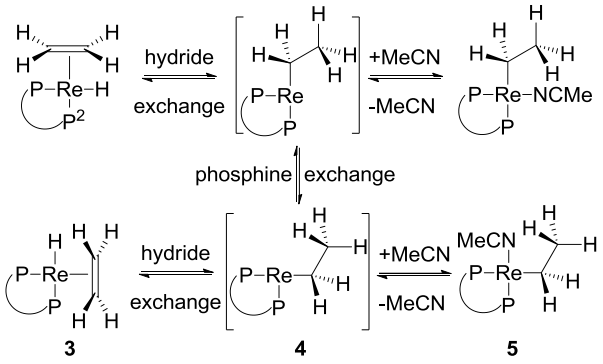
Spectroscopic features of 3a, 3b and 3d

The IR spectra of **3a, 3b** and **3d** provided evidence for the presence of the hydride and the NO ligands revealing distinct ν(ReH) (**3a** 1960 cm^{-1}; **3b** 1974 cm^{-1}; **3d** 2009 cm^{-1}) and ν(NO) (**3a** 1685 cm^{-1}; **3b** 1678 cm^{-1}; **3d** 1673 cm^{-1}) bands.

The $^{31}P\{^{1}H\}$ NMR spectra of **3a** and **3b** displayed each a set of two sharp doublets In accordance with the proposed structure. Hence, in contrast to **1a** and **1b**[1], **3a** and **3b** did not undergo exchange of the phosphine sides according to Scheme 1. This contrasts **3d**, for which the $^{31}P\ \{^{1}H\}$NMR spectrum at 300 K in benzene consisted of one extremely broad phosphorus resonance originating from the coalescing signals of the two chemically different phosphorus nuclei. This is explained by a virtual diphosphine side exchange according to Scheme 1, which is not observed for **3a-c**.

Scheme 1: Schematic mechanisms for the hydride and the phosphine exchange. The earlier is observed for **3a**, **3b**, **3c** and **3d**. The phosphine exchange is solely observed for **3d**.



The ^{1}H NMR spectra of **3a, 3b** and **3d** showed exchange of the H(Re) atom with two of the ethylene protons at room temperature. For further insight into the exchange process $^{1}H\{^{31}P\}$ VT NMR spectra of **3a** were recorded in a temperature range from 220 to 300 K in 10 K intervals (Figure 1).

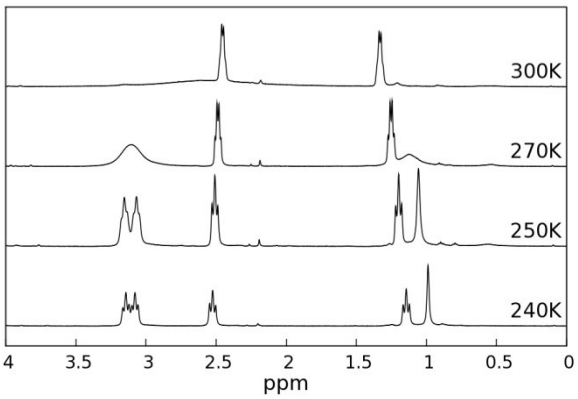


Figure 1: $^{1}H\{^{31}P\}$ spectra of **3a** in the ethylene hydride region at various temperatures (CD_2Cl_2, 500 MHz).

At 240 K the signals of the four ethylene protons and the H(Re) are no longer in exchange. By aid of a HSQC experiment the different sets of ethylene protons could be attributed to the respective C(ethylene) nuclei. The two protons at 3.03 and 2.98 ppm, which are involved in the exchange, showed correlation with the C(ethylene) nucleus at 36.7 ppm, while the two other ethylene protons at 2.49 and 1.21 ppm showed correlation with the C(ethylene) nucleus at 40.0 ppm. Warming the NMR sample up caused first broadening of the ethylene protons signals at 3.03 and 2.98 ppm and the H(Re) signal at 0.88 ppm. At approx. 300 K these signals reached coalescence. The signals of the two other ethylene protons at 2.49 and 1.21 ppm remained sharp and were apparently not affected by the exchange (Figure 1). This suggests the presence of a rotamer of **3a** with the C=C vector pointing towards the H(Re) atom. Consequently only the exchange of the H(Re) with the near-by CH_2(ethylene) is feasible. Furthermore the rotation of the ethylene ligand is hindered by a rotational barrier - at least on the NMR time scale - since otherwise all protons of the ethylene ligand would get involved in the exchange process. The exchange was modeled according to the mechanism denoted as "hydride exchange" in Scheme 1 with aid of the gNMR program package, which allowed to extract the exchange rate at temperatures ranging from 230 to 300 K. The process denoted as phosphine exchange in Scheme 1 is not observed for **3a-c**, but it is observed in solutions of **3e**. The activation parameters were determined according to the transition state theory[2] amounting to $\Delta H^{\ddagger} = 62$ kJmol^{-1} and $\Delta S^{\ddagger} = 31$ Jmol^{-1}K^{-1}.

The ^{1}H spectrum of **3d** in benzene consists apart from the signals originating from the homoxantphos ligand only of a set of broad signals at 3.01 and 2.32 ppm in a 3:2 ratio. Heating the sample to 320 K focuses the signals and a COSY experiment revealed an A_2B_3 spin system with a ^{3}J(HH) = 7 Hz. Unlike in the case of **3a-c** the methylene protons of **3d** give rise to only one signal via the equilibration process according to the windshield wiper movement of the ethyl moiety in the intermediate **4e** (Scheme 1). As in the case of **3c** *(vide infra)* the found ^{1}J(CH) coupling of the observed CH_3(ethyl) group protons to the α-carbon nucleus (^{1}J(CH) = 97 Hz) is significantly lower than the characteristic value (120-130 Hz) for a methyl group[3]. Therefore it seems likely that the observed spectrum results again from averaging of signals via fast exchange of the H(Re) atom with the adjacent CH_2(ethylene) protons by the transient formation of the unsaturated complex **4d**.

Spectroscopic observation of up/down isomerism: The NMR and IR spectroscopic data of **3a** and **3b** do not provide evidence for the presence of more than one conformational isomers, but their existence cannot be excluded. The diphosphine side exchange of **3d** according Scheme 1 can be slowed by the addition of excess of acetonitrile via formation of **5d**. The affinity of **4d** to acetonitrile is lower than the affinity of **4c** to this ligand. Shifting the **3d**/**5d** equilibrium towards **5d** by addition of acetonitrile leads to two sharp singlets for **5d(down)** at 18.1 and -5.1 ppm accounting for approx. 85 % of the overall intensity and a set of two slightly shifted signals for **5d(up)** at 20.0 and 1.5 ppm accounting for the residual 15 % of the signal intensities. This ratio for **5d(up)** and **5d(down)** reflects the isomer ratio observed in the structural analysis of **3d(up)** and **3d(down)**. As this ratio of the isomers did not change during the VT-NMR study between 285 K and 320 K it was concluded that the isomers of **5d** are kinetically stable.

Spectroscopic features of the 3c/5c equilibrium

The IR spectrum of 3c/5c: The solid state IR spectrum of **5c** displays a characteristic ν(NO) band at 1653 cm^{-1} but no ν(ReH) band. This is in accordance with the expectations since **5c** is isolated analytically pure. However in solution the described **5c** ⇆ **3c** + MeCN equilibrium is observed. Therefore the IR spectrum of **3c**/**5c** was also recorded in benzene solution. As expected the ν(NO) band of **5c** was observed at 1653 cm^{-1}, which is the only visible ν(NO) band in the solid state IR spectrum, but in solution two ν(NO) bands at 1704 cm^{-1} and 1683 cm^{-1} and two distinct ν(ReH) bands at 2014 cm^{-1} and 1954 cm^{-1} could be attributed to the two isomeric forms of **3c**. The addition of acetonitrile to the solution led to a drastic increase of the ν(NO) band of **5c** at 1653 cm^{-1}, while the other ν(NO) and ν(ReH) bands disappeared.

The $^{31}P\{^{1}H\}$ NMR spectrum of **3c**/**5c** consist of set of doublets at 1.6 and -12.7 ppm (assigned to **3c)** and two sharp singlets at 6.0 and -9.0 ppm (assigned to **5c)**. This assignment was further substantiated by addition of MeCN to the sample, which led to an increase of the signals for **5c**. The absence of the ^{2}J(PP) was interpreted in terms of the exchange of the ligands *trans* to the diphosphine unit according to a mechanism depicted in Scheme 1. The relative intensities of the ^{31}P NMR signals revealed a **3c**/**5c** ratio of approximately 1:3 at room temperature in $CDCl_3$.

The ^{1}H NMR spectrum of 3c/5c: In benzene the methyl group of the acetonitrile ligand gave rise to two resonances for the bound (0.56 ppm) and the free (0.53 ppm) molecules, also in an approximate 1:3 ratio. Signals at 2.30, 2.73 and 3.65 ppm in 3:1:1 ratio were assigned to the ethyl moiety of **5c**. A COSY experiment revealed them to constitute an A_3BC spin system. A similar spin system was observed at 3.64, 2.42 and 2.15 ppm in a 3:1:1 ratio assigned complex **3c**. The signal assignment was further substantiated by DEPT 135 and the HSQC experiments, which revealed an extraordinary low ^{1}J(CH) coupling constant of 98 Hz of the apparent methyl protons[3] at 3.64 ppm. This clearly indicates that these protons constitute not a CH_3 group but rather a CH_2 moiety which is in fast exchange with the Re-H.

Since a VT-NMR study of the exchange process by cooling the sample was not possible due to either an inappropriate melting point of the solvent or an unfavorable signal overlap and a drastic shift of the **3c**/**5c** equilibrium towards **3c** at low temperatures, no VT NMR series could be acquired.

Spectroscopic features of the ortho-metallated species 8e(up/down)

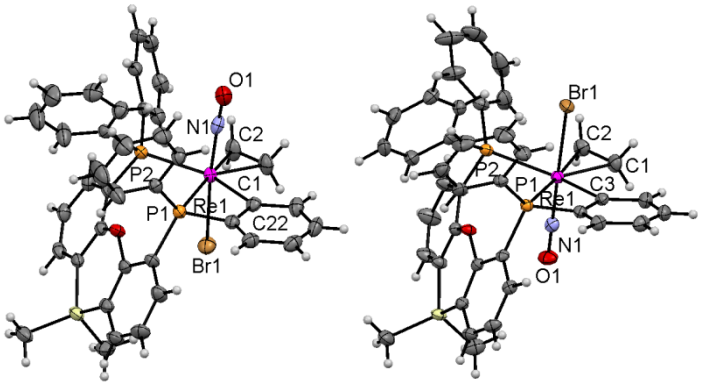


Figure 2: ORTEP diagrams of **8e(down)** and **8e(up)** drawn at 50% probability.

Selected bond lengths of **8e(down)** [Å]: Br1-Re1 2.5816(3), C1-Re1 2.195(3), C2-Re1 2.225(3), C1-C2 1.400(5), C22-Re1 2.165(3), N1-Re1 1.819(3), N1-O1 1.074(3), P1-Re1 2.5039(8), P2-Re1 2.5605(8). Selected bond angels [°]: Br1-Re1-N1 174.46(8), C1-Re1-C2 36.94(12), C1-Re1-C22 81.65(12), C2-Re1-P2 82.18(9), C22-Re1-P1 64.60(8), O1-N1-Br1 177.0(3), P1-Re1-P2 94.41(2).

Selected bond lengths of **8e(up)** [Å]: Br1-Re1 2.5912(2), C1-Re1 2.200(2), C2-Re1 2.235(2), C1-C2 1.412(3), C3-Re1 2.177(2), N1-Re1 1.7472(18), N1-O1 1.198(2), P1-Re1 2.5017(5), P2-Re1 2.5741(5). Selected bond anels [°]: Br1-Re1-N1 179.01(6), C1-Re1-C2 37.12(8), C1-Re1-C3 81.25(8), C2-Re1-P2 84.88(6), C3-Re1-P1 64.67(6), P1-Re1-P2 91.729(17).

In the IR spectra strong ν(NO) bands were found at 1680 cm^{-1} for **8(down)** and at 1686 cm^{-1} for **8e(up)**.

In the $^{31}P\{^{1}H\}$ spectra of the separated compounds distinct sets of doublets (**8e(down)** : -12.7 and -69.4 ppm; **8e(up)** -22.8 and -76.2 ppm) are observed.

In the ^{1}H spectra of the separated **8(up/down)** three signals for the four ethylene protons were visible apart from the Sixantphos proton signals (**8e(down)** 3.13 (2 H), 2.72 (1 H), 1.76 (1 H)ppm.

8e(up) 3.03 (2 H), 2.66 (1 H), 1.99 (1 H) ppm.). In contrast to **3a-c** dynamic behavior of **8e(up/down)** could not be traced in the NMR.

Experimental Part

General: All manipulations were performed under an atmosphere of dry nitrogen using either standard Schlenk techniques or a M-Braun glove box. All solvents were dried, distilled and degassed according to standard lab procedures. The diphosphine ligands, $[ReBr_5(NO)][NEt_4]_2$ and $[ReBr_2(MeCN)_3(NO)]$ were prepared according to published methods[4,5,6]. 1-hexene, styrene, α-methylstyrene and cyclohexene were purchased from Sigma Aldrich and were dried, distilled and degassed according to standard laboratory procedures. Hydrogen and Deuterium were purchased from Pan Gas. NMR spectra were recorded on a Bruker AV-2 500 spectrometer. Chemical shifts are expressed in parts per million (ppm) and referenced to the solvent's residual signals[7] or in case of $^{31}P\{^1H\}$ NMR to the external standard 85% H_3PO_4 at δ = 0.0 ppm. NMR spectra simulations were performed with the gNMR program package. IR spectra were recorded on a Bio Rad Excalibur spectrometer. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zürich.

Computational methods: The model calculations were carried out analogously to the investigations on the related *trans*-phosphine system $[ReH_2(\eta^2\text{-}C_2H_4)(NO)(PMe_3)_2]$ investigated by Liu et al. [8] using the B3LYP fuctional[9] in combination with a G6-31*+ basis[10] for the elements H-P and a Hay and Wadt ECP basis[11] with f polarization functions for Re and Br. The gamess[12] program package was employed for these calculations. Solvent effects were neglected. The character of the stationary points was verified by a normal mode analysis. The free energy was calculated at 298.15 K.

Kinetic measurements/catalysis: Kinetic measurements were monitored via the gas consumption by means of a Büchi press gas flow controller attached to a 45 mL steel autoclave with a resolution of 0.045 mmol. The temperature was controlled with a oil or water bath. The products were identified by NMR spectroscopy.

[ReBrH(η^2-C_2H_4)(dppfc)(NO)] (3a): 1a · 2 THF (0.800 g, 0.72 mmol), triethylsilane (1 mL, 6.26 mmol) and dichloromethane (5 mL) were placed in a 50 mL Young Schlenk tube. The Young Schlenk tube was then charged with 2 bar ethylene. The yellow suspension was stirred at 60°C for 24 h. The solvent was reduced *in vacuo* to ca. 3 mL and a layer of 3 mL hexane was added. After 3 h the precipitate was separated from the supernatant, washed with pentane (3×2 mL) and dried *in vacuo* to yield **3a** (0.440g, 0.50 mmol, 70%) as a yellow powder.

IR (KBr pellet, cm^{-1}): 1960 (m, ν(ReH)), 1685 (s, ν(NO)). ^1H NMR (500 MHz, $CDCl_3$, 28°C): δ = 7.90 (m, 2 Phenyl H), 7.74 (m, 2 Phenyl H), 7.67 (m, 2 Phenyl H), 7.47-7.24 (m, 14 Phenyl H), 5.38 (s, 1 Cp H), 4.65 (s, 1 Cp H), 4.51 (s, 1 Cp H), 4.37 (s, 2 Cp H), 4.24 (s, 2 Cp H), 4.09 (s, 1 Cp H), 2.59 (s, ReH, 2 H η^2-C_2H_4 coalescent), 2.42 (m, 1 H η^2-C_2H_4), 1.21 (m, 1 H η^2-C_2H_4). $^{31}P\{^1H\}$ NMR (125 MHz, $CDCl_3$, 28°C): δ = 10.8 (d, $^2J_{PP}$ = 34Hz), 6.49 (d, $^2J_{PP}$ = 34Hz). Anal. Calcd for $C_{36}H_{33}BrFeNOP_2Re$ (879.56). C, 49.16; H, 3.78; N, 1.59. Found: C, 49.08; H, 3.93; N, 1.56.

[ReBrH(η^2-C_2H_4)(diprpfc)(NO)] (3b): A suspension of [{ReBr(μ^2-Br)(NO)(diprpfc)}$_2$] (0.70 g, 0.88 mmol) in dichloromethane (20 mL) and $HSiEt_3$ (1 mL, 6.3 mmol) was placed in a Young Schlenk tube equipped with a magnetic stirring bar. The Young Schlenk tube was then charged with ethylene (2 bar). The suspension was then stirred 24 h at 40°C. The resulting dark brown solution was filtered through a short plug of celite. The solvent was reduced *in vacuo* to 3 mL. A layer of hexane (3 mL) was then placed on the concentrated solution. After 16 h **3b** (0.39 g, 0.54 mmol, 61%) was obtained as a microcrystalline pale orange solid.

IR (KBr pellet, cm^{-1}): 1974 (m, ν(ReH)), 1678 (s, ν(NO)). ^1H NMR (400 MHz, C_6D_6, 28°C): δ = 4.636 (s, 1 H, cp – H), 4.548 (s, 1 H, cp – H), 4.363 (s, 1 H, cp – H), 4.119 (s, 1 H, cp – H), 4.008 (s, 4 H, cp – H), 3.1-2.4 (overlapping multiplets, 9 H, 4 ethylene H, 1 Re–H, 4 *i*Pr CH), 1.961 (dd, $^2J_{PH}$ = 15.7, $^3J_{HH}$ = 6.7 Hz, 3 H, *i*Pr CH_3), 1.740 (dd, $^2J_{PH}$ = 14.4, $^3J_{HH}$ = 7.5 Hz, 3 H, *i*Pr CH_3), 1.539 (dd, $^2J_{PH}$ = 13.8, $^3J_{HH}$ = 7.4 Hz, 3 H, *i*Pr CH_3), 1.439 (s broad, 3 H, *i*Pr CH_3), 1.403 (dd, $^2J_{PH}$ = 13.9, $^3J_{HH}$ = 7.5 Hz, 3 H, *i*Pr CH_3), 1.10-0.98 (overlapping multiplets, 6 H, *i*Pr CH_3), 1.048 (dd, $^2J_{PH}$ = 11.5, $^3J_{HH}$ = 7.5 Hz, 3 H, *i*Pr CH_3) ppm. $^{31}P\{^1H\}$ NMR (125 MHz, THF-d8, 28°C): δ = 24.2 (d, $^2J_{pp}$ = 33Hz), -6.2 (s,

broadened by exchange). Anal. Calcd for $C_{24}H_{41}BrFeNOP_2Re$ (743.49). C, 38.77; H, 5.56; N, 1.88. Found: C, 38.73; H, 5.53; N, 1.80.

[ReBrH(η^2-C_2H_4)(NO)(homoxantphos)] (3d): 1d (0.500g, 0.51 mmol), $HSiEt_3$ (2 mL, 12.5 mmol) and toluene (4 mL) were placed in a 100 mL Young Schlenk tube. The tube was then charged with 2 bar of ethylene. The yellow suspension was stirred for 160 h at 50°C. During this time the suspended solid changed its color from bright to pale orange. The solid was then collected by means of centrifugation and washed with toluene (1 mL). After drying *in vacuo* **3d** (0.370 g, 0.42 mmol, 82%) was obtained as a pale orange solid.

IR (KBr pellet, cm^{-1}): 2009 (m, ν(ReH)),1673 (s, ν(NO)). ^1H NMR (500 MHz, C_6D_6, 28°C): δ = 7.934 (d, *J* = 7.5 Hz, 3 H, arom. H), 7.334 (d, *J* = 7.0 Hz, 3 H, arom. H), 7.13-6.75 (overlapping multiplets, 13 H, arom. H), 6.734 (d, *J* = 5 Hz, 2 H, arom. H), 6.592 (t, J = 7.5 Hz, 3 H, arom. H), 3.028 (t, $^2J_{HH}$ = 7 Hz, 3 H, ReH and η^2-CH_2CH_2 in coalescence), 2.706 (m, 4 H, homoxantphos CH_2CH_2), 2.294 (q, $^2J_{HH}$ = 7 Hz, 2 H, η^2-CH_2CH_2) ppm. $^{31}P\{^1H\}$ NMR (203 MHz, $CDCl_3$ with 5% $NCCH_3$, 28°C): δ = 20.1 (s, 0.18 P), 18.44 (s, 0.82 P), 1.36 (s, 0.18 P), -4.82 (s, 0.82 P) ppm. Anal. Calcd for $C_{40}H_{35}BrNO_2P_2Re$ (889.77). C, 53.99; H, 3.96; N, 1.57. Found: C, 53.80; H, 4.08; N, 1.80.

[ReBr(CH_2CH_3)(MeCN)(NO)(dpephos)] (5c): 1c (0.500 g, 0.52 mmol), $HSiEt_3$ (0.7 mL, 4.39 mmol) and dichloromethane (3 mL) were placed in a 100 mL Young Schlenk tube. The tube was then charged with 2 bar of ethylene. The yellow suspension was stirred for 24 h at 60°C. The yellow solid was separated by means of centrifugation, washed with pentane (2 mL) and dried *in vacuo* to yield **5c** (0.290 g, 0.32 mmol, 61 %) as a yellow powder. From the supernatant a fraction less pure **5c** (0.140 g, 0.15 mmol, 29 %) can be obtained by removing the solvent *in vacuo* followed by repeated pentane washes.

IR (KBr pellet): 1653 (s, ν(NO)). ^1H NMR (500 MHz, $CDCl_3$ with 5% $NCCD_3$, 28°C): δ = 7.676 (m, 2 H, arom. H), 7.5-6.8 (overlapping multiplets, 22 H, arom. H), 6.711 (m, 1 H, arom. H), 6.594 (m, 1 H, arom. H), 6.429 (m, 1 H, arom. H), 5.872 (m, 1 H, arom. H), 2.738 (m, 1 H, ReCH_2CH_3), 1.86 (s, 3 H,

$NCCH_3$), 1.726 (m, 1 H, $ReCH_2CH_3$), 1.197 (s, 3 H, $ReCH_2CH_3$) ppm. $^{31}P\{^1H\}$ NMR (203 MHz, $CDCl_3$ with 5% $NCCD_3$, 28°C): δ = 24.2 (d, $^2J_{pp}$ = 33Hz), -6.2 (s, broadened by exchange). Anal. Calcd for $C_{40}H_{36}BrN_2O_2P_2Re$ (904.78). C, 53.10; H, 4.01; N, 3.10. Found: C, 53.10; H, 4.01; N, 3.10.

[ReBr(η^2-C_2H_4)(NO)(η^3-Sixantphos)] (8e(up/down)): A solution of **1e** (1 g, 0.99 mmol) and triethyl silane (3 mL, 18.8 mmol) in dichloromethane (8 mL) was placed in a Young Schlenk tube. The tube was charged with 2 bar ethylene and the solution was stirred for 6 h at 70 °C. After cooling to room temperature, the volatiles were removed *in vacuo*. The obtained solid was washed with toluene (2×2 mL) and dried *in vacuo* to get a crude product. The crude product was chromatographed on silica gel with hexane/diethylether as eluent to obtain the products **8e(down)** (0.373 g,0.041 mmol , 41%) and **8e(up)** (0.145 g, 0.16 mmol, 16 %).

8e(down): IR (KBr pellet, cm^{-1}): 1680 (s, ν(NO)). ^1H NMR ($CDCl_3$, 500 MHz, 28°C): δ = 8.06-8.10 (m, 1 H, phenyl), 7.24-7.34 (m, 6 H, phenyl), 7.37-7.43 (m, 3 H, phenyl), 7.53 (t, J = 7.5 Hz,1 H, phenyl), 7.62 (d, J = 7.5 Hz, 1 H, phenyl), 7.79-7.84 (m, 1 H, phenyl), 7.72 (m, 2 H, phenyl), 7.13-7.20 (m, 5 H, phenyl), 7.05 (td, J = 7.0, J = 1.5 Hz, 3 H, phenyl), 6.78 (td, J = 7.0, J = 1.5 Hz, 2 H, phenyl), 3.13 (q, J = 9 Hz, 2 H, C_2H_4), 2.72 (m, 1 H, C_2H_4), 1.76 (q, J = 9.0 Hz, 1 H, C_2H_4), 0.59 (s, 3 H, $SiMe_2$), 0.44 (s, 3 H, $SiMe_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz, 24°C) : δ = -12.7 (d, ^2J = 29.7 Hz, 1 P), -69.4 (d, ^2J = 29.7 Hz, 1 P); Anal. Calcd. for $C_{40}H_{35}BrNO_2P_2ReSi$ (917.86): C, 52.34; H, 3.84; N, 1.53. Found: C, 52.68; H, 4.09; N, 1.53.

8e(up): IR (KBr pellet, cm^{-1}): 1686 (s, ν(NO)). ^1H NMR ($CDCl_3$, 500 MHz) : δ = 8.05 (p, J = 4.0 Hz, 1 phenyl H), 7.83 (td, J = 8.0, J = 1.5 Hz, 1 H, phenyl), 7.68-7.72, (m, 2 H, phenyl), 7.60-7.65 (m, 3 H, phenyl), 7.48-7.54 (m, 3 H, phenyl), 7.38-7.42 (td, J = 7.5, J = 2.5 Hz, 2 H, phenyl), 7.32-7.37 (m, 3 H, phenyl), 7.12-7.31 (m, 7 H, phenyl), 6.97 (tq, J = 8.5, J = 1.5 Hz, 1 H, phenyl), 6.63 (td, J = 8.5, J = 2.5 Hz, 2 H, phenyl), 2.97-3.09 (m, 2 H, C_2H_4), 2.66 (m, 1 H, C_2H_4) , 1.99 (q, 1H, J = 8.0 Hz, C_2H_4), 0.54 (s, 3 H, $SiMe_2$), 0.51 (s, 3 H, $SiMe_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz) : δ = -22.8 (d, ^2J = 29.3 Hz), -76.2 (d, ^2J = 34 Hz) ppm. Anal. Calcd. for $C_{40}H_{35}BrNO_2P_2ReSi$ (917.86): C, 52.34; H, 3.84; N, 1.53. Found: C, 52.71; H, 3.57; N, 1.51.

[(ReBr(η^2-H)(NO)(diprpfc))$_2$] (9b): In a NMR tube fitted with a Young Teflon cap **3b** (0.02 g, 0.03 mmol) was dissolved in a minimum of benzene. The tube was charged with 1 bar of H_2 and allowed to stand until **9b** had fully crystallized. **9b** was obtained as large dark red crystals bearing 2 equivalents benzene in quantitative yield.

9b: IR (KBr pellet, cm^{-1}): 1982 (s, ν(ReH)) 1672 (s, ν(NO)). Anal. Calcd. for $C_{56}H_{86}Br_2N_2O_2P_4Re_2$ (1587.10): C, 42.38; H, 5.46; N, 1.77. Found: C, 42.40; H, 5.39; N, 1.78.

[(ReBr(η^2-H)(NO)(Sixantphos))$_2$] (9e): Suitable single crystals for the X-ray diffraction study were obtained by procedure analogous to the preparation of **9b** reacting **8e** with D_2 at 80° in C_6D_6.

[ReBrH(MeCN)(NO)(dppfc)] (10a): A solution of **3a** (10 mg, 0.011 mmol) in C_6D_6 and MeCN (10 μL, 0.19 mmol) in a NMR tube fitted with a Young Teflon cap was degassed with three freeze, pump and thaw cycles. The NMR tube was charged with 2 bar H_2 and the sample was shaken vigorously. The reaction completed before an NMR spectrum could be obtained.

^{1}H NMR (500 MHz, C_6D_6, 28°C): δ = 8.468 (t, J = 9.3 Hz, 2 H, dppfc-ph), 8.197 (t, J = 7.5 Hz, 2 H, dppfc-ph), 8.058 (t, J = 7.5 Hz, 2 H, dppfc-ph), 7.596 (m, 2 H, dppfc-ph), 7.20-6.95 (overlapping multiplets, 12 H, dppfc-ph), 6.145 (s, 1 H, dppfc-cp), 4.744 (s, 2 H, dppfc-cp), 4.204 (s, 1 H, dppfc-cp), 4.002 (s, 1 H, dppfc-cp), 3.951 (s, 1 H, dppfc-cp), 3.871 (s, 2 H, dppfc-cp), 1.435 (dd, JPcisH = 23.4 Hz, JPtransH = 86.7 Hz, 1 H, ReH), 0.625 (s, 3 H, MeCN) ppm. ^{31}P{^{1}H} NMR (203 MHz, C_6D_6, 28°C): δ = 26.9 (d, $^2J_{PP}$ = 10.5 Hz), -4.8 (d, $^2J_{PP}$ = 10.5 Hz) ppm.

[ReBrH(MeCN)(NO)(diprpfc)] (10b): A solution of **3b** (10 mg, 0.011 mmol) in C_6D_6 (600 uL) and MeCN (10 μL, 0.19 mmol) in a NMR tube fitted with a Young Teflon cap was degassed with three freeze, pump and thaw cycles. The NMR tube was charged with 2 bar H_2 and the sample was shaken vigorously for 15 min.

^{1}H NMR (500 MHz, C_6D_6, 28°C): δ = 4.093 (s, 1 H, cp), 4.792 (s, 1 H, cp), 4.355 (s, 1 H, cp), 4.249 (s, 1 H, cp), 4.066 (s, 1 H, cp), 4.050-4.000 (overlapping multiplets, 3 H, cp), 2.926 (m, 1 H, *i*Pr CH), 2.839 (m, 1 H, *i*Pr CH), 2.562 (m, 2 H, *i*Pr CH), 1.972 (m, 3 H, *i*Pr CH_3), 1.746 (m, 3 H, *i*Pr CH_3), 1.599 (m, 3 H, *i*Pr CH_3), 1.560 (m, 3 H, *i*Pr CH_3), 1.361(m, 3 H, *i*Pr CH_3), 1.256 (m, 3 H, *i*Pr CH_3),

0.964 (dd, $^{2}J_{PH}$ = 88.1 Hz, $^{2}J_{PH}$ = 25.6 Hz, ReH) ppm. $^{31}P\{^{1}H\}$ NMR (203 MHz, C_6D_6, 28°C): δ = 19.5 (s), -4.4 (s) ppm.

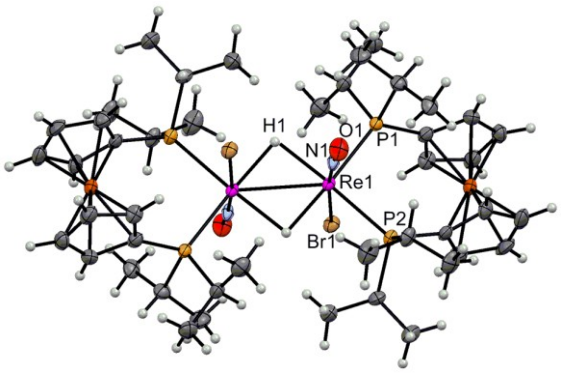
[ReBrH(MeCN)(NO)(dpephos)] (10c): A sample of **10c** was prepared analogously to **10a**.

^{1}H NMR (500 MHz, C_6D_6, 28°C): δ = 8.458 (s, 2 H, dpephos), 8.115 (s, 2 H, dpephos), 7.598 (s, 2 H, dpephos), 7.500 (s, 2 H, dpephos), 7.15-6.85 (m, 17 H), 6.465 (s, 1H, dpephos), 6.399 (s, 1 H, dpephos), 6.065 (s, 1 H, dpephos), 1.952 (dd, $^{2}J_{PH}$ = 25.5 Hz, $^{2}J_{PH}$ = 96.0 Hz, 1 H, ReH), 0.571 (s, 3 H, MeCN) ppm. $^{31}P\{^{1}H\}$ NMR (203 MHz, C_6D_6, 28°C): δ = 18.1 (s), -5.1 (s) ppm.

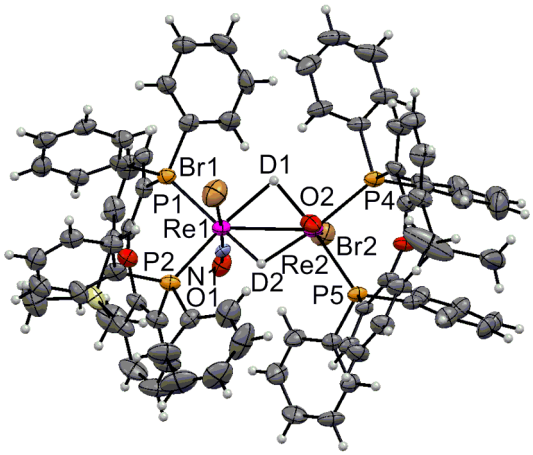
[ReBrH(MeCN)(NO)(homoxantphos)] (10d): A sample of **10d** was prepared analogously to **10a**.

^{1}H NMR (500 MHz, C_6D_6, 28°C): δ = 8.478 (s, 2 H, homoxantphos), 7.959 (m, 2 H, homoxantphos), 7.003 (s, 2 H, homoxantphos), 7.503 (s, 2 H, homoxantphos), 7.284 (s, 2 H, homoxantphos), 7.12-6.60 (m, 16 H, homoxantphos), 3.169 (m, 1 H, homoxantphos), 2.890 (m, 1 H, homoxantphos), 2.710 (m, 1 H, homoxantphos), 2.470 (m, 1 H, homoxantphos), 2.005 (dd, $^{2}J_{PH}$ = 19.5 Hz, $^{2}J_{PH}$ = 91.5 Hz, 1 H, ReH), 0.645 (s, 3 H, MeCN) ppm. $^{31}P\{^{1}H\}$ NMR (203 MHz, C_6D_6, 28°C): δ = 25.4 (s), -2.0 (s) ppm.

Crystal structure determinations



ORTEP diagram of 9b: ORTEP diagram of **9b** drawn at 50% probability. Selected bond lengths [Å]: Br1-Re1 2.6037(8), H-Re1 1.95(8), N1-Re1 1.754(6), N1-O1 1.184(8), P1-Re1 2.449(2), P2-Re1 2.430(2), Re1-Re1 2.8471(6). Selected bond angels [°]: Br1-Re1-N1 172.1(2), H-Re1-P1 170(2), O1-N1-Re 1 174.8(6), P1-Re1-P2 96.43(7).



ORTEP diagrams of 9e: Ellipsoids drawn at 50% probability, solvent molecules omitted for clarity. Selected bond lengths [Å]: Br1-Re1 2.5701(11), Br2-Re1 2.5634(12), D1-Re1 2.14, D1-Re2 2.24, D2-Re1 1.94, D2-Re2 1.74, N1-Re1 1.828(8), N2-Re1 1.823(9), N1-O1 1.053(8), N2-O2 1.059(8), P1-Re1 2.423(2), P2-Re1 2.447(2), P3-Re2 2.428(2), P4-Re2 2.455(2), Re1-Re1 2.8792(5). Selected

bond angels [°]: Br1-Re1-N1 176.1(2), Br2-Re2-N2 176.34(19), D1-Re1-P2 90, D2-Re2-P4 179, O1-N1-Re1 173.9(7), O2-N2-Re2 176.4(7) P1-Re1-P2 95.36(7), P3-Re2-P4 95.25(7).

Crystal Structure Determination.

Relevant details about the structure refinements are given in Table 1 and in the CIF. Intensity data were collected at 183(2) K an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector, and a single wavelength Enhance X-ray source with MoK_α radiation, λ = 0.71073 Å).[13] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction and analytical absorption corrections[14] were performed with the Oxford program suite *CrysAlisPro*.[15] The crystal structures were solved with SHELXS-97[16] using direct methods. The structure refinements were performed by full-matrix least-squares on F^2 with SHELXL-97. All programs used during the crystal structure determination process are included in the WINGX software[17]. The program PLATON[18] was used to check the result of the X-ray analyses.

The *trans* Br and NO groups of the hydride complex $C_{40}H_{35}BrNO_2P_2Re$ **3d** are disordered over two sets of positions with site occupancies of 0.846(1) and 0.154(1). The hydride atom was located in the difference Fourier map and freely refined.

Compounds **8e(up)** and **8e(down)** are two stereoisomers characterized by the relative positions of the Br and NO groups with respect to the ligand backbone. The two isomers could be separated by column chromatography. As expected, no Br/NO disorder exists in both crystal structures.

The dinuclear complex $C_{62}H_{92}Br_2Fe_2N_2O_2P_4Re_2$ **9b** resides on a crystallographic center of inversion. The hydride atom was located in the difference Fourier map and freely refined. No classic hydrogen bonds were found.

The asymmetric unit of **9e** contains the dinuclear complex $C_{76}H_{64}Br_2D_2N_2O_4P_4Re_2Si_2$ and many solvent molecules of dichloromethane and benzene, some of them being severely disordered. The

deuterium atoms were located in the difference Fourier map, geometrically refined and kept fixed in the final refinement cycles with U_{iso}(D) = 1.5U_{eq}(Re2) to reach convergence.

For all crystal structures, the hydrogen positions were calculated after each cycle of refinement using a riding model, with C-H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for the aromatic H atoms, with C-H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for the methylene H atoms, with C-H = 0.98 Å and U_{iso}(H) = 1.2U_{eq}(C) for the methine H atoms, and with C-H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for the methyl H atoms.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as CCDC-787673-787677. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif and are also available as Supporting Information.

Table 1. Crystallographic data for **3d**, **8e(up)**, **8e(down)**, **9b** and **9e**. The unweighted R-factor is R_1 =

	3d	**8e(up)**	**8e(down)**
CCDC deposition number	787673	787674	787675
empirical formula	$C_{40}H_{35}BrNO_2P_2Re$	$C_{40}H_{35}BrNO_2P_2ReSi$	$C_{40}H_{35}BrNO_2P_2ReSi$
formula weight (g·mol-1)	889.74	917.83	917.83
temperature (K)	183(2)	183(2)	183(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system, space group	monoclinic, $P\,2_1/c$	monoclinic, $P\,2_1/c$	monoclinic, $P\,2_1/n$
a (Å)	19.7393(3)	18.0902(1)	9.8141(1)
b (Å)	9.2862(1)	9.6663(1)	15.7671(2)
c (Å)	19.8067(3)	20.1922(2)	23.1408(3)
α (deg)	90	90	90
β (deg)	108.782(2)	93.795(1)	93.946(1)
γ (deg)	90	90	90
volume (Å3)	3437.30(9)	3523.17(5)	3572.32(7)
Z, density (calcd) (Mg·m-3)	4, 1.719	4, 1.730	4, 1.707
abs coefficient (mm-1)	4.828	4.745	4.680
F(000)	1752	1808	1808
crystal size (mm3)	0.31 x 0.17 x 0.11	0.20 x 0.12 x 0.05	0.47 x 0.28 x 0.21
θ range (deg)	2.45 to 30.51	2.57 to 30.51	2.55 to 30.51
reflections collected	34427	68012	31733
reflections unique	10489 / R_{int} = 0.030	10747 / R_{int} = 0.037	10883 / R_{int} = 0.030
completeness to θ (%)	100.0	99.9	99.9
absorption correction	analytical	analytical	analytical
max/min transmission	0.660 and 0.398	0.813 and 0.532	0.524 and 0.287
data / restraints / parameters	7811 / 3 / 438	8572 / 0 / 435	8087 / 0 / 435
goodness-of-fit on F2	0.934	0.946	0.985
final R_1 and wR_2 indices [I > 2σ(I)]	0.027, 0.0538	0.023, 0.045	0.029, 0.066
R_1 and wR_2 indices (all data)	0.043, 0.0554	0.033, 0.046	0.047, 0.069
largest diff. peak and hole ($e.A^{-3}$)	1.452, -1.529	1.905, -0.650	1.950, -0.957

	9b	**9e**
CCDC deposition number	787676	787677
empirical formula	$C_{44}H_{74}Br_2Fe_2N_2O_2P_4Re_2$, $3(C_6H_6)$	$4(C_{76}H_{64}Br_2D_2N_2O_4P_4Re_2Si_2)$, C_6H_6, $8(CH_2Cl_2)$
formula weight (g·mol-1)	1665.18	7891.89
temperature (K)	183(2)	183(2)
wavelength (Å)	0.71073	0.71073
crystal system, space group	monoclinic, $P\,2_1/c$	monoclinic, $C\,2/c$
a (Å)	12.1375(2)	50.5101(15)
b (Å)	14.8890(2)	13.0198(2)
c (Å)	17.7830(2)	30.8241(10)
α (deg)	90	90
β (deg)	98.118(1)	123.840(4)
γ (deg)	90	90
volume (Å3)	3181.46(8)	16836.9(11)
Z, density (calcd) (Mg·m-3)	2, 1.738	2, 1.557
abs coefficient (mm-1)	5.639	4.101
F(000)	1652	7764
crystal size (mm3)	0.24 x 0.24 x 0.22	0.36 x 0.10 x 0.02
θ range (deg)	2.31 to 26.37	2.46 to 26.37
reflections collected	45003	69440
reflections unique	6493 / R_{int} = 0.063	17216 / R_{int} = 0.0584
completeness to θ (%)	99.9	99.9
absorption correction	analytical	analytical
max/min transmission	0.46 and 0.30	0.906 and 0.329
data / restraints / parameters	5584 / 0 / 355	10330 / 9 / 913
goodness-of-fit on F2	1.183	0.941
final R_1 and wR_2 indices [I > 2σ(I)]	0.039, 0.117	0.049, 0.143
R_1 and wR_2 indices (all data)	0.046, 0.119	0.088, 0.152
largest diff. peak and hole (e.A^{-3})	3.562, -1.447	2.120, -2.113

$\sum$(Fo – Fc)/$\sum$Fo; I > 2 σ(I) and the weighted R-factor is $wR_2 = \{\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2\}^{1/2}$.

Coordinates of the optimized structures 2f-4f, 12f-14f and TSa-d:

2f			
	X [Å]	Y [Å]	Z [Å]
C	-1.69493422	2.143183578	1.635955662
P	-1.93729081	0.486089092	0.862045994
C	-3.59309053	0.619850651	0.058633494
RE	-0.19826102	-0.0761678	-0.55451299
N	-1.05396093	-1.51615882	-1.08752873
O	-1.57921457	-2.50816816	-1.50604082
P	1.415425543	-1.30171715	0.948451982
C	1.922882055	-0.50352367	2.539295732
C	-2.31362838	-0.60732269	2.308740606
C	0.874773035	-2.98750896	1.493014264
C	3.061171466	-1.66584328	0.177507713
H	-0.98443387	0.94936028	-1.6466441
BR	1.527331275	1.841353524	-0.46149496
H	1.674673022	-3.50710848	2.034437536
H	-0.00083497	-2.90819945	2.145338461
H	0.590803278	-3.58395318	0.619316261
H	3.70814473	-2.22713129	0.862638881
H	2.919092155	-2.25032328	-0.73790913
H	3.548631597	-0.72274929	-0.08932145
H	2.656126475	-1.11442065	3.079968107
H	2.355770193	0.476669314	2.317261164
H	1.045902946	-0.3552484	3.178136544
H	-4.36354824	0.896764786	0.788169803
H	-3.54435694	1.373149393	-0.73276349
H	-3.85595906	-0.33881669	-0.40005559
H	-3.18588245	-0.24487837	2.867099259
H	-2.51543776	-1.62411387	1.955637
H	-1.45189117	-0.64007879	2.982735808
H	-2.53950797	2.382648688	2.293286683
H	-0.76594763	2.155311762	2.212753476
H	-1.61409596	2.898087456	0.84937052

3f			
	X [Å]	Y [Å]	Z [Å]
C	1.129200196	-2.41812006	1.997533421
P	1.725266316	-0.92063756	1.104957392
C	3.301667311	-1.51079163	0.346229172
RE	0.252897406	0.186949985	-0.55387091
N	1.39648946	1.510115177	-0.69304793
O	2.166370203	2.422312597	-0.78745154
P	-1.25846953	1.271169393	1.176432128
C	-1.57013973	0.364697624	2.762533923
C	2.380994124	0.162157469	2.458497166
C	-0.64380365	2.914853334	1.769525723
C	-2.99818353	1.668208865	0.694501671
H	1.146422559	-0.92946222	-1.44124029
BR	-1.50222939	-1.82856227	-0.37035157
H	-1.3246429	3.351335459	2.510400548
H	0.34926121	2.807909337	2.217522287
H	-0.55306594	3.603814222	0.92282265
H	-3.53466799	2.124141155	1.535159259
H	-3.01214347	2.358580085	-0.15307699
H	-3.50862329	0.745436324	0.400841217
H	-2.29336102	0.907797112	3.381549649
H	-1.97296495	-0.62317553	2.518420586
H	-0.64558995	0.237012927	3.333182342
H	3.978655138	-1.91265034	1.109546102
H	3.080002165	-2.2866563	-0.39230849
H	3.789457272	-0.67853849	-0.17101587
H	3.10262409	-0.37889696	3.082288167
H	2.878840315	1.031268144	2.014584146
H	1.56865613	0.52446602	3.094907192
H	1.909304981	-2.8044246	2.663756339
H	0.232079558	-2.18301354	2.576181195
H	0.853835311	-3.17951699	1.262940255
C	-0.33822323	0.371244806	-2.71314862
C	-1.25132193	1.163027503	-1.98746528
H	-1.1524368	2.247415135	-1.99269396
H	-2.2513891	0.781753859	-1.80952836
H	-0.64495942	-0.60364006	-3.07875041
H	0.47141972	0.836389016	-3.26930349

$3f_1$			
	X [Å]	Y [Å]	Z [Å]
C	3.16815152	-1.08595318	0.86126803
P	2.26722744	0.43787517	0.34392674
C	3.38105181	1.10788846	-0.96793580
RE	-0.09114306	0.34877781	-0.46311768
N	-0.20044909	2.09088469	-0.30028574
O	-0.26417458	3.27992301	-0.16661403
P	-1.06537173	-0.24079537	1.81168602
C	0.02081168	-1.18028300	2.98166382
C	2.59667999	1.62426048	1.72908322
C	-1.55246680	1.21966544	2.84184746
C	-2.58157450	-1.29837616	1.86462762
H	0.85564120	0.36909697	-1.84795308
BR	0.10342631	-2.31843686	-0.66068930
H	-1.97910650	0.90774386	3.80281778
H	-0.67544434	1.84841548	3.02768013

H	-2.28656711	1.82740249	2.30344347
H	-2.82093526	-1.56570174	2.90040408
H	-3.43663846	-0.77611682	1.42660618
H	-2.39506137	-2.21129845	1.29047970
H	-0.53144760	-1.45075473	3.88916450
H	0.37044291	-2.09181248	2.48788693
H	0.88742228	-0.57822433	3.27312488
H	4.39939283	1.26219275	-0.58966608
H	3.40360381	0.40692293	-1.80738264
H	2.98111198	2.05897126	-1.33291597
H	3.67355343	1.74902150	1.89173641
H	2.16024644	2.59712644	1.48000704
H	2.14045272	1.27116448	2.65940537
H	4.21732206	-0.84788151	1.07225383
H	2.70847926	-1.52363240	1.75108428
H	3.10986311	-1.82731178	0.05926519
C	-1.39742448	0.24449991	-2.28918997
C	-2.26523683	0.13473610	-1.17829107
C	-3.24512756	1.24712174	-0.85096924
H	-2.59961588	-0.87093413	-0.93200761
H	-1.10923630	-0.64195273	-2.84526969
H	-1.34757902	1.17681798	-2.84831327
H	-3.51892557	1.29523087	0.21073526
H	-2.85049162	2.22842519	-1.13738749
H	-4.18021913	1.09561785	-1.41191645

$3f_2$			
C	-1.02838448	3.25031010	-0.23356102
P	-1.68612372	1.55596234	0.07509014
C	-3.13468073	1.48906903	-1.06819839
RE	-0.22809277	-0.44261414	-0.18734784
N	-1.41619802	-1.40008321	0.67702723
O	-2.23169163	-2.02917003	1.29006050
P	1.25982605	0.04859014	1.81720460
C	1.37797835	1.80028692	2.40666055
C	-2.53416272	1.72351453	1.71414726
C	0.78025501	-0.85157160	3.36342555
C	3.05685964	-0.35534091	1.67207029
H	-1.07147667	-0.35444595	-1.63883245
BR	1.54703152	1.08995246	-1.48624565
H	1.46590133	-0.61449952	4.18537252
H	-0.23976333	-0.58193132	3.65621970
H	0.80281347	-1.93093137	3.18133594
H	3.58911476	-0.04327008	2.57832594
H	3.20356290	-1.43015360	1.53066917
H	3.46885952	0.17053835	0.80550411
H	2.08852104	1.88472407	3.23768524
H	1.72229845	2.42873215	1.57915297
H	0.40337481	2.16333096	2.74709758
H	-3.81194919	2.33497440	-0.90268257

H	-2.77802534	1.49942917	-2.10269827
H	-3.67819329	0.55196388	-0.90921392
H	-3.27457618	2.53180597	1.69326374
H	-3.03865804	0.78353731	1.96188577
H	-1.80545134	1.93815256	2.50107091
H	-1.83748095	3.98775599	-0.17032689
H	-0.25671053	3.49961741	0.50038906
H	-0.57061315	3.28102506	-1.22500366
C	0.37279126	-2.15998224	-1.55991167
C	1.24336472	-2.16895535	-0.44890663
H	1.12311946	-2.93434482	0.31810378
H	2.24912967	-1.77935645	-0.56987230
H	0.74332565	-1.68460214	-2.46603662
C	-0.66712797	-3.23414200	-1.79693108
H	-1.50470953	-2.86210714	-2.39638392
H	-0.20663322	-4.06997824	-2.34563201
H	-1.06995888	-3.63354778	-0.86005948

$3f_3$	X [Å]	Y [Å]	Z [Å]
C	2.02631269	1.38513363	-2.37124346
P	2.06407336	0.76680692	-0.63437137
C	2.95605947	2.13463233	0.23089729
RE	-0.01719027	0.13618754	0.55672112
N	0.95508816	-0.48216866	1.87828721
O	1.62278395	-0.91348647	2.77536534
P	-0.29205886	-2.07317987	-0.68354075
C	0.25634631	-2.18425550	-2.44977589
C	3.39189876	-0.52650833	-0.67899880
C	0.63282104	-3.46723865	0.11324699
C	-1.99462857	-2.77728253	-0.83848095
H	0.17914770	1.75922050	0.94575278
BR	-1.43907881	1.07751935	-1.50572206
H	0.49923537	-4.41005802	-0.43117264
H	1.69928488	-3.22395787	0.15411998
H	0.28345801	-3.59614887	1.14268673
H	-1.97460740	-3.69492781	-1.43857893
H	-2.40610059	-3.01010755	0.14807487
H	-2.64646691	-2.04565637	-1.32613639
H	0.11932729	-3.20232896	-2.83269471
H	-0.33787428	-1.48573857	-3.04627243
H	1.31203725	-1.91481073	-2.55068195
H	3.94732350	2.29519245	-0.20884214
H	2.37019301	3.05563376	0.15573775
H	3.06551629	1.88685897	1.29169202
H	4.32287304	-0.11574269	-1.08747664
H	3.58149300	-0.88500105	0.33873257
H	3.08822399	-1.37989853	-1.29236393
H	3.03876569	1.66676990	-2.68370217
H	1.63215594	0.62641373	-3.05354451
H	1.36557986	2.25402299	-2.42530364
C	-1.66572690	0.75210193	2.03978937

C	-1.97709161	-0.52381397	1.52012039
H	-1.80340595	-1.41226091	2.12482343
H	-2.77926464	-0.60546985	0.79066059
C	-2.51588239	1.97406516	1.77237678
H	-1.14660842	0.78333355	2.99668731
H	-1.94026838	2.90333556	1.84727031
H	-2.98142590	1.94128979	0.78527580
H	-3.31461386	2.01390760	2.52985675

3f$_4$

	X [Å]	Y [Å]	Z [Å]
C	3.05842325	-1.91106476	-0.02069988
P	2.25930180	-0.26567197	0.24887009
C	3.41923070	0.87398318	-0.61829636
RE	-0.07520429	-0.13655373	-0.59950747
N	-0.04497801	-1.75099157	-1.28035952
O	-0.01794455	-2.86151519	-1.72892369
P	-1.13873028	-1.04551018	1.53961594
C	-0.21999084	-2.46955602	2.30095284
C	2.65988848	0.11456482	2.01381775
C	-1.39815370	0.08157668	2.97838632
C	-2.79451114	-1.86394151	1.36713565
H	0.89214242	0.55399999	-1.78892461
BR	0.05850833	2.31378848	0.48085355
H	-1.89039151	-0.44906403	3.80187572
H	-0.43844207	0.48040930	3.31916151
H	-2.00915899	0.93445936	2.66962902
H	-3.11624253	-2.28510625	2.32720859
H	-3.54927496	-1.15473357	1.02084310
H	-2.72286268	-2.67523860	0.63425167
H	-0.75426077	-2.86222472	3.17434360
H	-0.12141496	-3.26824956	1.55775016
H	0.78364444	-2.17047073	2.61376521
H	4.43364579	0.76401731	-0.21761877
H	3.42322232	0.64840031	-1.68925970
H	3.08018351	1.90541193	-0.48294294
H	3.74164293	0.05584710	2.18446955
H	2.31134315	1.12692731	2.23804699
H	2.16307207	-0.57919727	2.69827676
H	4.11242952	-1.88901835	0.28092181
H	2.54083233	-2.68737784	0.55147304
H	2.99506315	-2.17654201	-1.08073783
C	-1.37681287	0.65283547	-2.24560187
C	-2.27902758	0.25184603	-1.23336971
C	-3.14698047	1.26988242	-0.51872215
H	-2.74166523	-0.72901079	-1.35178875
H	-1.21204378	0.03898463	-3.12751277
H	-1.18902109	1.71407156	-2.39069092
H	-3.46243874	0.94343734	0.47916429
H	-2.62718036	2.22374551	-0.40288094
H	-4.06113492	1.44439863	-1.10656888

3f$_5$

	X [Å]	Y [Å]	Z [Å]
C	-3.26904275	0.28489153	1.38450829
P	-2.25076955	0.84383218	-0.04577756
C	-2.52444146	2.67141349	-0.04477433
RE	0.18636060	0.39264974	0.15950850
N	0.54600128	1.82224025	-0.78611958
O	0.77822810	2.78515056	-1.46204682
P	0.48303348	-1.26141308	-1.75059480
C	-0.98971848	-2.24240197	-2.29629431
C	-3.30504628	0.33581337	-1.48580894
C	1.02354906	-0.50200536	-3.35260925
C	1.69450078	-2.64359143	-1.53260041
H	-0.31773946	1.20087489	1.55258683
BR	-0.42165399	-1.84443300	1.51562236
H	1.10253843	-1.26099204	-4.13992820
H	0.29942202	0.25965890	-3.66039650
H	1.99415262	-0.01078804	-3.23320914
H	1.69263161	-3.28564017	-2.42115236
H	2.70897350	-2.26832529	-1.37442050
H	1.40096688	-3.23342769	-0.65873187
H	-0.69144109	-3.00408583	-3.02633864
H	-1.43663954	-2.73595193	-1.42712300
H	-1.73332726	-1.58856569	-2.75801932
H	-3.59129822	2.90816623	-0.13396718
H	-2.13909484	3.08810214	0.89101879
H	-1.98181096	3.13893859	-0.87185994
H	-4.30851441	0.76811997	-1.39146795
H	-2.85719509	0.69099962	-2.41967712
H	-3.39576378	-0.75304605	-1.52685228
H	-4.29593987	0.65834679	1.29667447
H	-3.26846098	-0.80715538	1.43492191
H	-2.81304570	0.65928355	2.30467206
C	1.92925723	0.68799383	1.60344199
C	2.43418966	-0.09302966	0.53849406
C	3.47245928	0.42835828	-0.43581530
H	2.46376531	-1.16436474	0.72113268
C	2.36127080	2.11239966	1.88870399
H	1.61573422	0.13997540	2.48975974
H	3.52488717	-0.17378821	-1.34987161
H	3.28883380	1.46387833	-0.73794950
H	4.47239109	0.39470972	0.02444666
H	1.64604901	2.61193773	2.54993895
H	3.34088808	2.10767202	2.39149288
H	2.45682695	2.71789812	0.98320177

3f$_6$

	X [Å]	Y [Å]	Z [Å]
C	3.57217784	-0.36070018	-0.77127868
P	2.24463653	0.63568420	0.04581133
C	2.64185100	2.34035065	-0.53700875

RE	-0.05789738	-0.05593012	-0.54823170
N	0.47506410	-1.28735834	-1.67346001
O	0.85091264	-2.13758155	-2.43068634
P	-0.26345282	-1.83266952	1.27911820
C	1.26143501	-2.87504483	1.47996358
C	2.82159252	0.71710473	1.80380457
C	-0.62844854	-1.31811009	3.01309978
C	-1.48944112	-3.19422618	0.99249488
H	0.29302763	1.22712577	-1.57924890
BR	-0.67221269	1.83784342	1.25402936
H	-0.63995033	-2.17936614	3.69232077
H	0.12546617	-0.59788852	3.34219292
H	-1.59535875	-0.80860413	3.04445557
H	-1.38374324	-3.96884129	1.76197826
H	-2.51538618	-2.81618381	1.01601113
H	-1.31258816	-3.64713426	0.01147258
H	1.07960922	-3.71250603	2.16454664
H	1.55718627	-3.27753032	0.50486180
H	2.09307147	-2.28265550	1.87217206
H	3.64198157	2.64323765	-0.20582823
H	2.59885424	2.35512308	-1.63002330
H	1.89393046	3.03759385	-0.14932646
H	3.85064422	1.09210738	1.84345266
H	2.16531878	1.39757393	2.35363422
H	2.78505797	-0.26558068	2.28292450
H	4.55071206	0.11230053	-0.63040217
H	3.60288025	-1.37595437	-0.36283127
H	3.36413353	-0.43716982	-1.84398697
C	-1.88168578	0.40066042	-1.87721286
C	-2.33733347	-0.48834695	-0.87632102
C	-3.38968177	-0.10719578	0.14538238
H	-2.35141135	-1.54283677	-1.14913714
C	-2.36093600	1.82970839	-2.02134568
H	-1.58409830	-0.05151017	-2.82213170
H	-3.36289584	-0.75310722	1.03042666
H	-3.29055756	0.92253040	0.49479567
H	-4.38874994	-0.21677029	-0.30508967
H	-1.69726413	2.39413957	-2.68423473
H	-3.36855566	1.83458040	-2.46604247
H	-2.40785871	2.36336399	-1.06923830

$3f_7$

	X [Å]	Y [Å]	Z [Å]
C	-2.96955888	-1.35706800	-1.23799948
P	-2.37461553	-0.07668395	-0.04924402
C	-3.39451450	-0.45956920	1.44294614
RE	0.04010837	0.16632773	0.50987695
N	-0.28412411	1.75083789	1.18216864
O	-0.52457950	2.83927189	1.62335933
P	0.71719337	0.93957126	-1.82161518
C	-0.31564130	0.41488123	-3.26955524
C	-3.19311254	1.47156658	-0.65462757
C	0.75346848	2.77892059	-2.04493582
C	2.37908205	0.42239200	-2.45014484
H	-0.59840824	-0.68787964	1.80766492
BR	0.42539716	-2.24688936	-0.62037960
H	1.13165482	3.04891988	-3.03777566
H	-0.25285321	3.19506591	-1.92298628
H	1.39268592	3.23646387	-1.28341492
H	2.53039432	0.77689476	-3.47671170
H	3.17628971	0.81965289	-1.81756929
H	2.42814708	-0.67036253	-2.42974124
H	0.11151542	0.80285827	-4.20140572
H	-0.33017157	-0.67894543	-3.30832734
H	-1.34291596	0.78017263	-3.18016322
H	-4.46287701	-0.46643862	1.19592278
H	-3.10248331	-1.43884941	1.83329304
H	-3.20278936	0.28642386	2.22047100
H	-4.27454261	1.32836263	-0.76677662
H	-3.01265440	2.28046237	0.06098198
H	-2.77944025	1.77374696	-1.62209727
H	-4.05538532	-1.27403413	-1.36528276
H	-2.47789552	-1.24307022	-2.20657107
H	-2.71868334	-2.35132388	-0.85750084
C	1.67399940	-0.25079132	2.05472324
C	2.31461476	0.29718157	0.91811676
C	2.94394553	1.67782893	0.98088195
H	2.82151660	-0.41535272	0.26701805
C	1.88816360	-1.66968397	2.53719508
H	1.47019595	0.45153772	2.86465846
H	3.04484211	2.15545720	-0.00086736
H	2.36706898	2.35483590	1.62029519
H	3.95756784	1.60692159	1.40482286
H	1.03757464	-2.02976014	3.12575392
H	2.05159549	-2.36917559	1.71427607
H	2.77847927	-1.68857639	3.18543023

$3f_8$

	X [Å]	Y [Å]	Z [Å]
C	3.04250173	1.91634823	0.56555766
P	2.31115225	0.26647231	0.16002103
C	3.24309395	-0.86042924	1.28215848
RE	-0.15156655	0.13922211	0.48063231
N	-0.27233192	1.77836952	1.08717210
O	-0.32600047	2.91507365	1.46517766
P	-0.72036415	1.01444743	-1.85839561
C	0.30524655	2.47409792	-2.37548622
C	3.08139442	-0.13132754	-1.47515637
C	-0.58912086	-0.10174270	-3.32279324
C	-2.40415759	1.76157899	-2.08807210
H	0.49437129	-0.50798745	1.89204836
BR	0.24410442	-2.32629923	-0.50170735
H	-0.75157216	0.46004015	-4.24998107
H	0.39400494	-0.57908537	-3.34371417

H	-1.33471102	-0.89970196	-3.24657938
H	-2.49042831	2.22046863	-3.07969511
H	-3.17762478	0.99864460	-1.98054923
H	-2.56932656	2.53105148	-1.32586038
H	-0.05601103	2.89341026	-3.32213393
H	0.24741287	3.24783096	-1.60208503
H	1.35382227	2.19032128	-2.49849571
H	4.32345858	-0.76853718	1.12037473
H	3.00249182	-0.61339531	2.32016474
H	2.92952682	-1.89150575	1.09242696
H	4.17520930	-0.09890192	-1.40329982
H	2.76614047	-1.13440565	-1.77566039
H	2.76430702	0.58163978	-2.24141973
H	4.13684466	1.88184220	0.51038297
H	2.67496546	2.67918416	-0.12831304
H	2.74196637	2.20859366	1.57647987
C	-1.81360239	-0.62860919	1.82470956
C	-2.43113362	-0.27991327	0.59923008
C	-3.08567906	-1.33444020	-0.27460523
H	-2.92591751	0.69326583	0.57369609
C	-2.02800197	0.15536802	3.10345124
H	-1.62504842	-1.69120724	1.97740562
H	-3.13890621	-1.05150603	-1.33259728
H	-2.54976703	-2.28444039	-0.21842337
H	-4.11797123	-1.49967936	0.06951137
H	-1.19579789	0.03456422	3.80532754
H	-2.15607872	1.22471653	2.90642556
H	-2.94240237	-0.20416189	3.60012556

TSa			
	X [Å]	Y [Å]	Z [Å]
RE	0.194218727	-0.20272905	-0.54008565
P	1.543214931	1.073993553	1.054347836
P	-1.06572327	-1.69615245	0.965599866
BR	-1.72747143	1.585122119	0.066778286
N	1.459228691	-1.37778956	-0.85282113
O	2.333797639	-2.17742692	-1.02885403
C	0.652666744	1.141272861	-2.24111971
H	0.375097984	2.179765382	-2.07695533
H	1.663727331	1.001410838	-2.62041328
C	-0.37132975	0.251021241	-2.74815849
H	-1.36105043	0.670779343	-2.92482546
H	-0.08415411	-0.50761917	-3.47550068
H	-0.94622252	-0.73535804	-1.76105404
C	-0.40360224	-3.42419641	0.976082187
C	-1.26737914	-1.37567894	2.779662585
C	-2.82743197	-1.95929375	0.466653801
C	3.229436278	0.373270494	1.353209364
C	1.933300012	2.788385942	0.483241381
H	3.813547424	1.02374443	2.014812393
H	3.151587661	-0.62114279	1.804586644
H	3.755218629	0.266860584	0.399255929

C	0.95360003	1.406102795	2.777338896
H	1.626086927	2.105810066	3.288318809
H	-0.05347858	1.830571574	2.738651858
H	0.919079312	0.473099774	3.345807963
H	2.518825402	3.326902086	1.238135257
H	2.500549548	2.746658603	-0.45164171
H	0.997866147	3.324816242	0.299062999
H	-1.93652614	-2.1155141	3.237254529
H	-0.29492164	-1.43712197	3.278993716
H	-1.68056497	-0.37487454	2.936904923
H	-0.38447299	-3.81686176	-0.04564403
H	0.622863588	-3.43325169	1.356427241
H	-1.02414715	-4.077917	1.600483524
H	-3.32459442	-2.67658667	1.130657917
H	-3.35636372	-1.00249715	0.501798391
H	-2.85884068	-2.33173546	-0.56216398

4f(ag)			
	X [Å]	Y [Å]	Z [Å]
RE	0.2302392	0.0112874	-0.5089024
P	1.6260392	0.4749312	1.337275
P	-1.2212165	-1.8064465	0.3784855
BR	-1.7361243	1.5530724	0.429576
N	1.4536899	-1.067928	-1.1605827
O	2.2871086	-1.8192041	-1.5840671
C	0.7003702	1.7001346	-1.7573138
H	0.4355658	2.6901918	-1.381561
H	1.7059008	1.7055057	-2.1846056
C	-0.3408138	1.1093867	-2.6959208
H	0.0657804	0.7531622	-3.647789
H	-0.8454748	0.1482954	-2.2731043
H	-1.2164723	1.7461572	-2.8526118
C	-1.7888384	-1.8274368	2.1413503
C	-2.8435005	-1.9618414	-0.503304
C	-0.5236889	-3.512393	0.1783986
C	1.9158832	-0.7779388	2.6750973
C	3.3632628	0.8092087	0.7968904
C	1.2041774	1.9824597	2.3090217
H	2.7215171	-0.4561968	3.3462465
H	1.0030114	-0.9160612	3.2626372
H	2.1911831	-1.7386052	2.2269658
H	1.9885888	2.180389	3.0495464
H	1.1075122	2.8381496	1.635013
H	0.2440083	1.8482262	2.8138364
H	4.0026955	1.0632337	1.6511133
H	3.7720288	-0.0743387	0.2956458
H	3.3653928	1.6379031	0.082777
H	-3.4470571	-2.7779932	-0.0891811
H	-3.3890078	-1.0184244	-0.4057629
H	-2.6680755	-2.1521374	-1.5684344
H	-2.5114393	-2.634239	2.3172913
H	-0.935936	-1.9718117	2.8124817

H	-2.2557865	-0.8660297	2.3754202
H	-1.2382211	-4.2729493	0.5146545
H	-0.2815796	-3.6882593	-0.8744557
H	0.4010084	-3.6100502	0.7563973

TSb

	X [Å]	Y [Å]	Z [Å]
RE	-0.1950225	-0.0884539	-0.4232532
P	-1.7848016	0.0816669	1.2532661
P	1.4408814	1.7381389	0.1811064
BR	1.6186549	-1.6338065	0.6454409
N	-1.1381377	0.9639881	-1.464984
O	-1.733027	1.6939559	-2.2091949
C	-1.0544083	-1.9331386	-1.2002599
H	-0.8753829	-2.7680681	-0.5104982
H	-2.1417246	-1.8662834	-1.3491012
C	-0.3894074	-2.249211	-2.556403
H	-0.7291552	-3.2159989	-2.9613552
H	-0.6220527	-1.4874563	-3.3139713
H	0.7048363	-2.3162629	-2.4723253
C	2.2238248	1.8881578	1.8528912
C	2.93451	1.6700449	-0.916944
C	0.8336307	3.4624159	-0.1214936
C	-1.7588379	1.4965567	2.450961
C	-3.5212362	0.1475538	0.6349771
C	-1.7704363	-1.3835841	2.3735871
H	-2.6117063	1.4447642	3.1387793
H	-0.8323057	1.4687981	3.0330688
H	-1.8016538	2.4427616	1.9021827
H	-2.5317403	-1.2703807	3.1550772
H	-1.9736771	-2.2884209	1.7936659
H	-0.7828529	-1.490069	2.8298911
H	-4.2339929	0.1889146	1.4670255
H	-3.6560269	1.0292394	0.0001749
H	-3.7216798	-0.7405706	0.0287587
H	3.6083848	2.517288	-0.7439767
H	3.472291	0.7340916	-0.732487
H	2.6098492	1.6775722	-1.9630002
H	2.9792184	2.6832913	1.8583429
H	1.4622865	2.1203864	2.6044359
H	2.6941324	0.9366599	2.1177446
H	1.6450958	4.1962513	-0.0410804
H	0.3889361	3.5291218	-1.119181
H	0.0597695	3.7153688	0.6117382

4f

	X [Å]	Y [Å]	Z [Å]
RE	-0.2489233	-0.118481	0.390864
P	-1.3852545	-0.6004472	-1.5692407
P	2.1161271	-0.7881121	-0.176943
BR	0.6683663	2.2894888	-0.0170688
N	-0.6558634	-1.6956445	1.0465914
O	-0.8956034	-2.7641201	1.5371489
C	-2.0056872	0.877837	1.2179231
H	-2.2655926	1.7732861	0.6356304
H	-2.8912351	0.2255934	1.205168
C	-1.7259797	1.3020518	2.6742471
H	-2.6109583	1.7667566	3.1374597
H	-0.9127138	2.0370257	2.7270487
H	-1.4483959	0.4462137	3.3062893
C	2.9684314	-0.1796501	-1.7050464
C	3.3337073	-0.2823338	1.1272047
C	2.4124232	-2.6155653	-0.25999
C	-0.612195	-1.6626771	-2.8763459
C	-2.9992101	-1.4620038	-1.3226274
C	-1.3013928	-1.8108676	-3.7169672
H	0.3029135	-1.1911103	-3.2469418
H	-0.3569092	-2.6392308	-2.4519825
H	-1.8388665	0.9213033	-2.5081973
H	-2.3758951	0.651817	-3.4254547
H	-2.4765846	1.5566352	-1.8867616
H	-0.9377864	1.487832	-2.7577599
H	-3.5125604	-1.6055457	-2.2806748
H	-2.8263797	-2.4383284	-0.8580945
H	-3.6332039	-0.8716449	-0.6558945
H	4.3436948	-0.6366417	0.8885738
H	3.3420472	0.8092939	1.2085166
H	3.0321753	-0.7002366	2.0942178
H	4.0179646	-0.4984008	-1.7205037
H	2.4725872	-0.5690664	-2.6006731
H	2.9211812	0.9128819	-1.7321386
H	3.4768447	-2.8461959	-0.3905263
H	2.0583513	-3.0825357	0.6654856
H	1.8508809	-3.0515594	-1.0920938

11f

C	1.1401266	-1.7255693	2.4742525
P	1.7597283	-0.6744832	1.0935835
C	3.1658666	-1.6783048	0.4434289
RE	0.1472772	0.0589328	-0.7455789
N	1.2489503	1.2950707	-1.3422122
O	1.9903088	2.1345654	-1.7478976
P	-1.2199295	1.5785832	0.7655083
C	-1.3226045	1.2353186	2.5779379
C	2.657234	0.6929927	1.9644554
C	-0.6970022	3.3511296	0.7062813
C	-3.0007508	1.6578425	0.3069458
H	1.0311682	-1.2427602	-1.3383264
BR	-1.5545094	-1.8215374	0.0618365
H	-1.3578713	3.9835091	1.3103877
H	0.3301985	3.4531078	1.0712288
H	-0.719348	3.6948258	-0.3326277

H	-3.5497446	2.3285891	0.9781751
H	-3.0907487	2.0138596	-0.7236749
H	-3.4278212	0.6512551	0.3584108
H	-1.9922342	1.9520104	3.0684314
H	-1.7115669	0.2229719	2.7281163
H	-0.3366602	1.3082691	3.0486145
H	3.8770778	-1.9279604	1.2400917
H	2.7747539	-2.5996562	0.0015791
H	3.6837043	-1.119859	-0.3430929
H	3.4058116	0.2967525	2.6606729
H	3.1590126	1.3230415	1.2224884
H	1.9553195	1.319739	2.5238142
H	1.9679709	-2.0259451	3.1270681
H	0.3921982	-1.1845339	3.0602976
H	0.6511104	-2.6113852	2.0589836
H	-0.1281886	-0.4999937	-2.2804218
H	-1.1721216	0.6394753	-1.6109594

10f			
RE	0.0250396	-0.3057986	-0.4389946
P	-2.3300559	0.2351535	-0.3878659
P	0.4314597	-0.5660095	2.0275026
N	-0.3496154	-1.9907235	-0.7646284
H	-0.0885848	0.2137358	-2.0458828
BR	0.6275164	2.2700818	0.0511394
N	2.061506	-0.486105	-0.8873516
O	-0.6115456	-3.1427484	-0.9694151
C	3.1613501	-0.5094121	-1.2556336
C	4.522427	-0.5053428	-1.7776842
H	4.838471	-1.5280101	-2.0110512
H	5.2161735	-0.0826355	-1.0425578
H	4.5713497	0.0950113	-2.6933748
C	0.1440771	-2.2717137	2.6968
C	-0.5514739	0.4674983	3.2063565
C	2.1541449	-0.2128736	2.6100892
C	-3.0741588	0.3804383	-2.0735841
C	-2.9174319	1.7901324	0.4158355
C	-3.4286091	-1.0411413	0.3876927
H	-4.1559816	0.5575285	-2.026994
H	-2.5889035	1.2051656	-2.6045139
H	-2.8785194	-0.5400964	-2.6321784
H	-2.637208	1.8025094	1.4726532
H	-2.4488912	2.6532757	-0.0648621
H	-4.0079347	1.8612277	0.3301386
H	-4.4864594	-0.7798145	0.2653116
H	-3.2441874	-2.0155623	-0.0763806
H	-3.2082228	-1.1249168	1.4574334
H	-0.4065951	1.5218193	2.9525872
H	-1.6154067	0.2260877	3.1074845
H	-0.2494563	0.2939752	4.2468969
H	2.8599489	-0.8882234	2.1138953
H	2.4119108	0.8156017	2.3362153

H	2.2416338	-0.3343438	3.6957802
H	0.3850029	-2.3256545	3.7652231
H	-0.9043661	-2.5528295	2.5532315
H	0.7604551	-2.9953613	2.152628

12f			
	X [Å]	Y [Å]	Z [Å]
RE	-0.25207951	-0.19325236	0.480713461
P	-1.29363514	0.061851941	-1.69868287
P	2.054191597	-1.03641997	-0.23710421
BR	0.918753402	2.187727947	0.143371511
N	-0.92546647	-1.79809512	0.711790901
O	-1.36059526	-2.90389654	0.851390484
C	-2.06073502	0.856587214	1.234648761
H	-1.85785978	1.932689939	1.163297356
H	-2.92384768	0.664511184	0.579421535
C	-2.50059857	0.508194677	2.665603111
H	-3.42113688	1.04294089	2.952023503
H	-1.73839369	0.774239978	3.41290537
H	-2.70124621	-0.56528004	2.776269985
C	2.927729923	-0.46294933	-1.76808202
C	3.364028423	-0.68576911	1.025662822
C	2.173035178	-2.87998781	-0.39173334
C	-0.29872424	-0.25536755	-3.22162417
C	-2.73321419	-1.06829157	-1.94080491
H	-0.89884912	-0.08280135	-4.12350259
H	0.567152055	0.411205345	-3.23914161
H	0.051814671	-1.29309753	-3.22856248
C	-1.99032508	1.731886685	-2.05269891
H	-2.44305735	1.74665423	-3.05013985
H	-2.7445753	1.98885722	-1.30420783
H	-1.18829201	2.472399553	-1.99439223
H	-3.1904407	-0.91367293	-2.92437685
H	-2.40589658	-2.10906414	-1.85382858
H	-3.48114686	-0.88467228	-1.16316516
H	4.337603959	-1.08709091	0.718479704
H	3.445303157	0.397502927	1.159949955
H	3.082739577	-1.13447658	1.984706928
H	3.969319091	-0.80548584	-1.76240386
H	2.440477907	-0.84921483	-2.66764929
H	2.911814048	0.631132035	-1.79842151
H	3.20723517	-3.19295213	-0.57651477
H	1.815842939	-3.34996055	0.530561507
H	1.5408707	-3.23105501	-1.21385164
H	0.785906833	-0.2388716	2.014717311
H	0.056347893	0.0935648	2.271550067

TSc			
	X [Å]	Y [Å]	Z [Å]
RE	-0.2297926	-0.2093709	0.5393103

P	-1.2645333	0.0106498	-1.779563
P	2.1002778	-0.9491839	-0.258632
BR	0.8340209	2.2191518	0.1654881
N	-0.8531911	-1.8316451	0.7840576
O	-1.2583285	-2.9439791	0.9386038
C	-2.1807079	0.7508817	1.0689469
H	-2.9392216	0.4692366	0.3256133
H	-2.0203176	1.8302363	0.9616825
C	-2.7653724	0.4524232	2.4570124
H	-2.9080741	-0.6237555	2.6163867
H	-2.1053053	0.8178701	3.2540519
H	-3.744939	0.9386822	2.5908943
C	2.9103876	-0.3257215	-1.8034993
C	3.411695	-0.5466161	0.978558
C	2.279034	-2.7846629	-0.432391
C	-0.2514488	-0.2561116	-3.3012927
C	-2.013745	1.6551255	-2.1507079
H	-2.6573346	-1.1766093	-2.0375605
H	0.5309455	0.5068357	-3.3487087
H	0.2163019	-1.2450931	-3.2928057
C	-0.8760513	-0.1711463	-4.1990369
H	-3.421426	-1.0278353	-1.2684174
H	-3.1125369	-1.0373813	-3.0245445
H	-2.294119	-2.2064195	-1.9518249
H	-2.7833756	1.8985116	-1.4145563
H	-1.2298418	2.4147411	-2.0874102
H	-2.4533068	1.6516872	-3.1541561
H	3.1602212	-1.0033838	1.9407569
H	4.3924203	-0.9108203	0.6495784
H	3.4494598	0.5390652	1.1112473
H	3.9635668	-0.6309275	-1.8154022
H	2.42651	-0.7210579	-2.7001569
H	2.8542566	0.7667963	-1.821323
H	3.321602	-3.0646169	-0.6238034
H	1.9409167	-3.2720062	0.487926
H	1.6549687	-3.1488242	-1.2552933
H	0.8156119	-0.3057149	1.872699
H	-0.2874906	0.1869653	2.1585675

13f			
	X [Å]	Y [Å]	Z [Å]
RE	0.2259424	0.2285441	0.5383162
P	1.2040259	-0.0258508	-1.8279913
P	-2.1485153	0.852404	-0.2218794
BR	-0.7383289	-2.2513476	0.2727456
N	0.7984036	1.8785786	0.7129894
O	1.1702357	3.0073377	0.8199178
C	2.2481435	-0.6426239	1.0051099
H	2.9276014	-0.5558966	0.1482164
H	2.0743106	-1.7132532	1.1589579
C	2.9851759	-0.0482557	2.2148676
H	2.4289904	-0.19662	3.1497613
H	3.9745742	-0.5151513	2.3449708
H	3.1476962	1.0317251	2.1061605
C	-2.9420498	0.2039357	-1.7635479
C	-3.4149649	0.3696399	1.0310901
C	-2.4101973	2.6782553	-0.370595
C	0.1781674	0.251716	-3.3423529
C	1.9261885	-1.6795906	-2.2159509
H	2.602055	1.1500821	-2.1148873
H	-0.2923894	1.2394786	-3.3251803
H	0.7998834	0.176319	-4.2429116
C	-0.6021697	-0.5127912	-3.3963576
H	2.2437148	2.1818366	-2.032063
H	3.3766028	1.0037459	-1.3562349
H	3.0408183	1.0009294	-3.107712
H	1.1346311	-2.4305005	-2.1434625
H	2.3509721	-1.6773443	-3.2260139
H	2.7040405	-1.9389081	-1.4940471
H	-3.3673151	-0.7130544	1.180454
H	-3.1890877	0.8582174	1.9838707
H	-4.4228359	0.6542442	0.7056192
H	-4.0087447	0.459775	-1.7638219
H	-2.4862082	0.6306358	-2.660417
H	-2.8337735	-0.8842655	-1.790349
H	-3.4658891	2.9190049	-0.5442686
H	-2.0802726	3.1662839	0.5523119
H	-1.8125443	3.0798661	-1.1955639
H	-0.82215	0.3679181	1.8452096
H	0.482048	-0.1531401	2.1230373

TSd			
	X [Å]	Y [Å]	Z [Å]
RE	-0.19676226	-0.24525014	0.506289155
P	-1.12411711	0.204945929	-1.84795826
P	2.074814963	-0.96899065	-0.26706692
BR	0.715934322	2.254333542	0.434300427
N	-0.7780959	-1.89804311	0.633498529
O	-1.16897082	-3.02476388	0.717166918
C	-2.3357655	0.611037552	1.13101648
H	-2.23258518	1.693815145	1.24403368
H	-2.90894677	0.419645119	0.221079325
C	-3.08915408	-0.0094252	2.315361858
H	-4.12288967	0.363059445	2.354930338
H	-2.61149699	0.228528979	3.27372582
H	-3.13540372	-1.10270255	2.235234479
C	2.109551308	-2.57828718	-1.18278834
C	3.129203779	0.126123434	-1.31496708
C	3.200513563	-1.31966172	1.151130578
C	-0.04480682	0.099435438	-3.35031433
C	-2.48118226	-0.97518439	-2.2902979
H	0.70682564	0.894731078	-3.32173096
H	0.464568287	-0.86782317	-3.39399821
H	-0.64217376	0.220846965	-4.26194734

C	-1.90468676	1.858738007	-2.11410125
H	-2.34564262	1.918098964	-3.11527058
H	-2.68104495	2.040607881	-1.36549722
H	-1.1356258	2.626306656	-1.99478538
H	-2.87787435	-0.771485	-3.29141838
H	-2.10943729	-2.0049872	-2.25163811
H	-3.29440863	-0.89210646	-1.562021
H	4.109659571	-0.33704251	-1.47667692
H	2.654892083	0.305442305	-2.28332621
H	3.25448359	1.090098851	-0.81417456
H	3.139276784	-2.91398813	-1.35315726
H	1.575705633	-3.34012798	-0.60506437
H	1.60923144	-2.47803515	-2.15144282
H	4.182705532	-1.66660893	0.80720684
H	3.320754496	-0.40740274	1.743689171
H	2.746806765	-2.08201726	1.791404876
H	0.714171829	-0.32636451	1.913454089
H	-0.93352836	0.259327224	1.880805034

14f(up)			
	X [Å]	Y [Å]	Z [Å]
P	1.66239805	-1.38122014	-0.04484896
C	3.00937470	-0.89876216	1.11619968
H	2.65756595	-0.99232819	2.14915960
H	3.88840397	-1.53764759	0.97482094
H	3.28428449	0.14542288	0.94083807
C	2.48388605	-1.33815507	-1.69853763
H	1.80186445	-1.73908492	-2.45564516
H	2.71828237	-0.30095067	-1.95668575
H	3.40484239	-1.93281504	-1.69658335
C	1.45264205	-3.18592387	0.27659807
H	1.03356046	-3.33219245	1.27641272
H	0.75398064	-3.61360579	-0.45012894
H	2.41224091	-3.71049187	0.20474723
RE	-0.42827376	-0.08623419	0.15846285
N	-1.41064293	-1.51098507	-0.11032809
O	-2.05762957	-2.47920901	-0.38236932
BR	1.06857695	1.98700997	-0.20875046
H	-0.27999040	-0.47430166	1.73977256
H	-3.03153639	0.61981809	-2.06550402
C	-2.20575342	1.35147183	-0.18844651
C	-2.05871245	1.10462089	1.18404475
C	-3.33558267	0.79568858	-1.02613806
H	-1.53499988	1.82406385	1.80918065
H	-2.74269449	0.44360056	1.71186266
H	-4.16094408	1.52369580	-1.05252346
H	-3.73163071	-0.14103485	-0.62126738
H	-1.74829585	2.26156247	-0.57385450

14f(down)			
	X [Å]	Y [Å]	Z [Å]
P	-2.06751021	-0.64056898	-0.06246358
C	-2.38589278	-1.99049244	1.14978808
H	-2.30636934	-1.60311576	2.17150016
H	-3.38506005	-2.41429822	0.99964931
H	-1.63076773	-2.77112908	1.02392060
C	-2.43397015	-1.43320460	-1.69087484
H	-2.42565385	-0.66947258	-2.47553591
H	-1.65825610	-2.17189911	-1.91589482
H	-3.41421698	-1.92400522	-1.68183822
C	-3.50484088	0.49186349	0.18171701
H	-3.43600358	0.96614153	1.16507742
H	-3.48963990	1.28144563	-0.57691042
H	-4.44904404	-0.05940773	0.10934526
RE	0.12144580	0.48297004	0.10293631
N	-0.58499774	2.04898937	-0.24050604
O	-1.05935188	3.10334682	-0.54527934
BR	1.09977382	-1.90788472	0.03038602
H	-0.27945340	0.63729729	1.67891818
C	2.22599674	1.40399702	-0.28667103
C	1.99444900	1.33601613	1.09384741
C	3.23450552	0.55641517	-1.03045963
H	2.45123672	0.53812795	1.67716171
H	1.69506271	2.21234622	1.66118018
H	4.14936854	1.14770682	-1.18659596
H	2.87205007	0.25273736	-2.02027762
H	2.00119424	2.35416960	-0.77437488
H	3.49663952	-0.34771098	-0.47692027

TSe(up)			
	X [Å]	Y [Å]	Z [Å]
P	-1.97639978	0.60853970	0.16159696
C	-2.70932504	-0.14330780	1.67500415
H	-2.30009009	0.34469984	2.56618554
H	-3.80082531	-0.04432547	1.67815715
H	-2.43669442	-1.20230599	1.70248063
C	-3.00967695	-0.06303683	-1.20422463
H	-2.75211216	0.44705747	-2.13740155
H	-2.79578168	-1.12863632	-1.32087168
H	-4.07388459	0.08046906	-0.98527058
C	-2.51361182	2.37249377	0.26076091
H	-2.00603059	2.87758705	1.08811068
H	-2.25623903	2.89224765	-0.66793835
H	-3.59705065	2.43093021	0.41444772
RE	0.46145659	0.31647837	-0.09651282
N	0.74688350	2.04710173	-0.21138082
O	0.88984069	3.22294814	-0.31079734
BR	-0.27180437	-2.26853443	-0.10851560
H	0.40063514	0.15087270	1.66790816
H	-0.09021072	0.25896839	-1.67946840
C	2.63268291	0.03447667	0.48843821
C	2.46298365	-0.50793603	-0.81003676
C	1.91397318	-0.39635843	1.65914438

H	2.97430989	-0.00836954	-1.62766770
H	2.26034871	-1.56386177	-0.95844962
H	2.14497013	0.12072862	2.58855759
H	1.66884367	-1.44894810	1.77200155
H	3.14460468	0.99243294	0.56703792

TSe(down)			
	X [Å]	Y [Å]	Z [Å]
P	-2.02805760	0.40895138	0.14524497
C	-2.67577056	-0.36437664	1.68742434
H	-2.27446850	0.15630294	2.56363653
H	-3.77093697	-0.31993492	1.71254899
H	-2.35128646	-1.40798153	1.72367594
C	-3.01036832	-0.39654485	-1.18432178
H	-2.79588400	0.09544614	-2.13764229
H	-2.71556962	-1.44649439	-1.26018713
H	-4.08190733	-0.32463332	-0.96631799
C	-2.72030752	2.11825110	0.20536194
H	-2.26646068	2.67864623	1.02832881
H	-2.49307033	2.64094749	-0.72963789
H	-3.80695147	2.09070662	0.34498828
RE	0.40982335	0.34531939	-0.11078099
N	0.56012034	2.09421584	-0.13124851
O	0.65262914	3.27978225	-0.14053971
BR	-0.03603500	-2.28930873	-0.09887715
H	0.41250645	0.25821053	1.66035772
H	-0.14909290	0.26264161	-1.69615980
C	2.49662876	-0.39120523	0.42918090
C	2.00209428	0.19512903	1.65298338
C	2.62785423	0.23611497	-0.82490245
H	1.99281120	-0.46985179	2.51393810
H	2.24520429	1.22840659	1.89420687
H	2.87020665	-0.39850137	-1.67105811
H	2.89553380	1.28363105	-0.92625625
H	2.51500996	-1.47702740	0.42319757

15f(up)			
	X [Å]	Y [Å]	Z [Å]
P	-1.74467738	1.15181276	-0.00347781
C	-2.79174768	0.75551936	1.45501888
H	-2.31224205	1.13797553	2.36116317
H	-3.78706342	1.20237123	1.34749958
H	-2.88253794	-0.33073240	1.54235608
C	-2.80599501	0.72905800	-1.44444380
H	-2.33722871	1.10320685	-2.35942226
H	-2.89214688	-0.35861583	-1.51702563
H	-3.80208695	1.17265035	-1.33184432
C	-1.69930444	2.99381948	-0.02709763
H	-1.10572469	3.36799248	0.81212485
H	-1.23030196	3.33731125	-0.95524251
H	-2.71132967	3.41115514	0.03616219

RE	0.51658377	0.17143448	-0.00013410
N	1.29765196	1.74862099	0.00011407
O	1.78893311	2.83027211	0.00206032
BR	-0.91261557	-2.10857000	0.00157842
H	-0.01251318	0.24694406	1.59965708
H	-0.01072111	0.24273286	-1.60132376
C	2.67531929	-0.72698168	0.00624707
C	2.08085777	-1.06540257	-1.22830650
C	2.07556335	-1.06111029	1.23940542
H	2.48544075	-0.63245078	-2.13838477
H	1.54008339	-1.99902569	-1.34687791
H	2.47628098	-0.62503841	2.14971264
H	1.53404866	-1.99416667	1.35895544
H	3.42077847	0.06782233	0.00656260

15f(down)			
	X [Å]	Y [Å]	Z [Å]
P	-2.06751021	-0.64056898	-0.06246358
C	-2.38589278	-1.99049244	1.14978808
H	-2.30636934	-1.60311576	2.17150016
H	-3.38506005	-2.41429822	0.99964931
H	-1.63076773	-2.77112908	1.02392060
C	-2.43397015	-1.43320460	-1.69087484
H	-2.42565385	-0.66947258	-2.47553591
H	-1.65825610	-2.17189911	-1.91589482
H	-3.41421698	-1.92400522	-1.68183822
C	-3.50484088	0.49186349	0.18171701
H	-3.43600358	0.96614153	1.16507742
H	-3.48963990	1.28144563	-0.57691042
H	-4.44904404	-0.05940773	0.10934526
RE	0.12144580	0.48297004	0.10293631
N	-0.58499774	2.04898937	-0.24050604
O	-1.05935188	3.10334682	-0.54527934
BR	1.09977382	-1.90788472	0.03038602
H	-0.27945340	0.63729729	1.67891818
C	2.22599674	1.40399702	-0.28667103
C	1.99444900	1.33601613	1.09384741
C	3.23450552	0.55641517	-1.03045963
H	2.45123672	0.53812795	1.67716171
H	1.69506271	2.21234622	1.66118018
H	4.14936854	1.14770682	-1.18659596
H	2.87205007	0.25273736	-2.02027762
H	2.00119424	2.35416960	-0.77437488
H	3.49663952	-0.34771098	-0.47692027

Equilibrium Data for 3a, 3b and 3c + MeCN

3a: 3a (6.4 mg, 0.0073 mmol), MeCN (10 uL, 0.1917 mmol) and C_6D_6 were placed in a NMR tube with Teflon cap. The NMR spectra of the mixture was taken at temperatures ranging from 285K - 320K. K was determined by integration of the ^{31}P NMR signals of **3a** and **5a** and the known concentration of MeCN ($MeCN_0$-**5a**).

3b: The equilibrium was measured analogously to **3a** with a solution of **3b** (10.5 mg, 0.0141 mmol), MeCN (250 µL, 4.7927 mmol) and C_6D_6 (250 µL).

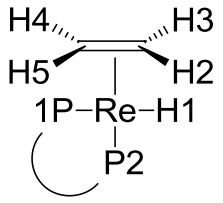
3c: The equilibrium was measured analogously to **3a** with a solution of **5c** (5.4 mg, 0.0060 mmol) in 500 uL C_6D_6.

$$K_d = \frac{[\mathbf{3}][MeCN]}{[\mathbf{5}]}$$

The following K_d values were obtained:

temperature [K]	K_d(3a/5a)	K_d(3b/5b)	K_d(3c/5c)
285	0.5957		0.01749
290	0.7059	25.87	0.02307
295	0.7612		0.02685
300	0.9097	29.81	0.03515
305	0.9711		0.04210
310	1.1018	38.52	0.04843
315	1.2713		0.05894
320	1.4133	43.01	0.07657

NMR Simulation Data



The model for the line shape analysis was defined with the following parameters:

	nucleus	count	chemical shift [ppm]	line with [Hz]	J(1) [Hz]	J(2) [Hz]	J(3) [Hz]	J(4) [Hz]
1	H	1	1.056	5.5				
2	H	1	3.067	5.5	0			
3	H	1	3.154	5.5	0	0		
4	H	1	2.508	5.5	0	10.97	10.97	
5	H	1	1.195	5.5	0	10.97	10.97	0

The exchange was defined as sum of the following exchange processes:

	Process 1	Process 2
nucleus	exchanges with	exchanges with
1	3	2
2	1	3
3	2	1
4	4	4
5	5	5

The following rates were fitted with this system:

temperature	rate
230	0
240	9
250	30
260	99
270	360
280	1200
290	3000
300	7200

These rates were fitted to:

$$k(T) = k_b*T/h*\exp(-\Delta H^{\ddagger}/(R*T))*\exp(\Delta S^{\ddagger}/R)$$

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