Supporting Information for

Mechanism of Chemical and Electrochemical N_2 Splitting by a Rhenium Pincer Complex

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1. Experimental Details

1.1. Materials and synthetic methods

All experiments were carried out under inert conditions using standard Schlenk and glove-box techniques (argon or nitrogen atmosphere). All solvents were purchased in HPLC quality (Sigma Aldrich/Merck), and dried using an MBRAUN Solvent Purification System. THF was additionally dried over Na/K. THF-d_8 was bought from Euriso-Top GmbH and dried over Na/K. $^{15}N_2$, $Co(Cp^*)_2$, hexamethylbenzene, $P(OSi(CH_3)_3)_3$, PPh_3 were used as purchased. Na/Hg (1M) was prepared from elemental Na and Hg. $Fe(Cp)_2$ and $Fe(Cp^*)_2$ were sublimed at 40 °C/0.020 mbar or 105 °C/0.020 mbar respectively, $[^nBu_4N][PF_6]$ and $[^nBu_4N]Cl$ were dried at 50 °C/0.020 mbar and 85 °C/0.020 mbar respectively, before use. The abbreviation (PNP) is used for the $N(CH_2CH_2P\textit{t}Bu_2)_2^-$ ligand. $[ReCl_2(PNP)]$ was prepared according to published procedures.[1]

1.2. Analytical methods

NMR spectra were recorded on a Bruker Avance III 300, Avance III 400, and Avance 500 spectrometer with a Prodigy broadband cryoprobe and were calibrated to the residual solvent signals (THF-d_8: δ ^1H = 3.58 ppm, δ ^{13}C = 67.6 ppm). ^{31}P NMR and ^{15}N NMR chemical shifts are reported relative to external phosphoric acid and nitromethane standard (δ ^{31}P = 0.0 ppm, δ ^{15}N = 0.0 ppm), respectively. Signal multiplicities are abbreviated as: s (singlet), d (doublet), m (multiplet). UV-vis absorption spectra were measured on a CARY300 Scan Varian spectrometer using inert sealed cuvettes. Infrared spectroscopy was carried out with a Thermo Scientific Nicolet iS5 FT-IR equipped with an iD1 Transmission Accessory (Thermo Scientific) for solution measurements in a demountable liquid cell (0.05 mm) with CaF_2 windows (Pike Technologies Inc.). Electrochemistry was measured on a Pine WaveDriver Bipotentiostat using Aftermath software or on a GAMRY 600 reference potentiostat, using the GAMRY software. Cyclic voltammetry (CV) was measured using a glassy carbon (3 mm diameter) working electrode, besides the high-pressure reactions, which were measured using a glassy carbon (1.6 mm diameter) working electrode. A Pt wire counter electrode was used and a Ag wire pseudo-reference electrode in a fritted sample holder separate compartment, and referencing was performed against the $[Fe(Cp)_2]^{+/0}$ couple. Controlled Potential Electrolysis was performed using reticulated vitreous carbon as working electrode, Pt-wire as counter electrode in a compartment separated by fritted sample holder with $Fe(Cp^*)_2$ as sacrificial reductant and a Ag-wire as pseudo-reference electrode in a fritted sample holder separate compartment. For all electrochemical experiments, a 0.2 M $[^nBu_4N][PF_6]$ solution in THF was used as electrolyte, with appropriate iR compensation.

1.3. Syntheses

[{ReCl(PNP)}$_2$(μ-N$_2$)] (3)

Degassed THF (0.5 mL) was vacuum transferred to a mixture of ReCl$_2$(PNP) (5,4 mg; 8,7 μmol) and Na/Hg (1M, 130 mg, 1.1 eq.), and placed under a N$_2$-atmosphere at −30 °C. The mixture was shaken vigorously for 3-5 minutes, resulting in a color change from violet to deep red, indicating formation of the title compound. This species was not isolable and was further characterized *in situ* with a maximum yield of 74 % by ^{1}H NMR spectroscopy. For kinetic analysis, full conversion of the starting material was secured by ^{1}H NMR where the main side-product in the mixture was Re(N)Cl(*PNP*). For the ^{15}N labeled dimer complex, the same procedure was carried out under a $^{15}N_2$ atmosphere. Crystals suitable for X-ray were obtained by layering a solution of in THF with pentane at −80 °C. NMR (THF-d_8, ppm) at −20 °C: ^{1}H (400 MHz), δ −16.48 to −16.53 (m, 2H's, 2 XCH*H*), −12.46 to −12.56 (m, 2H's, 2 XCH*H*), 0.38 to 0.50 (m, 2H's, XCH*H*), 0.50 to 0.90 (broad, 18 H's, 2 PC(C*H*)$_3$)$_3$), 3.25 to 3.43 (m, 36 H's, 2x2 PC(C*H*)$_3$)$_3$), 3.59 (m, 2H's, XCH*H*, overlapping with THF-d_8), 3.72 to 3.94 (m, 18 H's, 2 PC(C*H*)$_3$)$_3$), 4.06 to 4.16 (m, 2H's, XCH*H*), 8.60 to 8.71 (m, 2H's, XCH*H*), 10.49 to 10.62 (m, 2H's, XCH*H*). ^{31}P{^{1}H} (161 MHz): δ 16.98 (d, *J* = 235.8 Hz), −120.20 (d, *J* = 234.5 Hz). UV-vis (λ, THF, −30 °C): 375 nm, 533 nm.

*1.4. NMR kinetic measurement for N_2 splitting of **3***

[(μ-N$_2$){ReCl(PNP)}$_2$] (**3**) was prepared as described in section 1.3 with addition of a capillary containing P(OSi(CH$_3$)$_3$)$_3$ as internal standard. For kinetic analysis, full conversion of the starting material was secured by ^{1}H NMR spectroscopy at −30 °C. The main side-product in the mixture was Re(N)Cl(PNP) (**2**). Conversion of **3** was followed at −15 °C, −10 °C, −5 °C, −2.5 °C, 0 °C, 2.5 °C, 5 °C, and 7.5 °C, respectively, by ^{1}H NMR over more than two half-lives. Each run was repeated at least twice. A typical kinetic profile at 0 °C is given in Figure S1. The Eyring analysis is presented in Figure 1 in the main text.

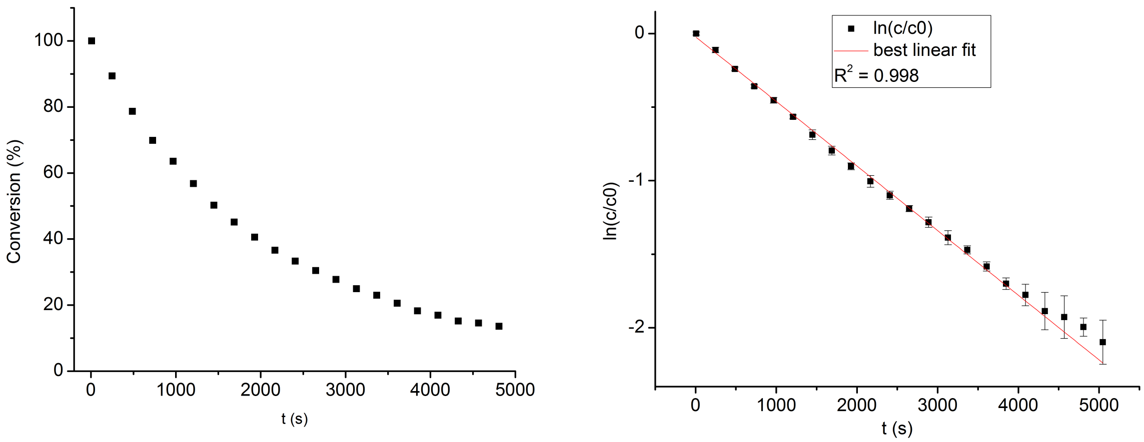


Figure S1. Plot of **3** versus time at 0 °C (left) and plot of ln(**3**/**3$_0$**) versus time at 0 °C (right).

1.5. Controlled Potential Electrolysis (CPE) Experiments

CPE of 1

[$ReCl_2$(PNP)] (10.6 mg, 17.2 µmol) and 4 mL 0.2 M [$^nBu_4N$][PF_6] electrolyte solution in THF were added to the working electrode compartment of the electrolysis cell. The solution was electrolyzed for 2 h at the peak potential of the first reduction feature obtained by CV, resulting in a color change from purple to brown to yellow. Integration of the current versus time plot gave a charge corresponding to 1.2 mol e^- per mol Re. The electrolysis solution was dried to a pale yellow solid, which was triturated with pentane (2 × 5 mL), dried, and dissolved in 0.6 mL THF-d_8. PPh_3 (9.0 mg, 34 µmol) was added as an internal standard and the solution was analyzed by ^1H and $^{31}P\{^1H\}$ NMR. Re(N)Cl(*PNP*) (**2**) was obtained in 58 % yield by $^{31}P\{^1H\}$ NMR integration and 66 % yield by ^1H NMR, see Figures S18 and S19.

1.6. VT UV-visible spectroscopic and spectroelectrochemical characterization

Temperature Dependent UV-vis Spectroscopy of 1.

Under N_2, THF (10 mL) was added to a Schlenk tube equipped with a UV-visible dip probe septum feedthrough. The background UV-visible spectrum of the solvent was recorded. A solution of **1** (10 mg, 16 µmol) in 2 mL THF was added to the flask, the solution was stirred for one minute and the UV-visible spectrum recorded. The flask was cooled to 0 °C with an ice-water bath and the solution was stirred for 10 min before the UV-visible spectrum was recorded. The flask was then cooled to −78 °C with a dry ice-acetone bath and the solution was stirred for 20 min before the UV-visible spectrum was recorded. While the absorbance changed very slightly, no new features were observed as the solution was cooled, see Figure S27.

UV-visible Spectroelectrochemistry of 1.

A 2.0 mM solution of **1** in THF with 0.2 M [$^nBu_4N$][PF_6] was added to a short path (0.2 cm) cuvette. The cuvette was equipped with a Au honeycomb working electrode, Au counter electrode, and a Ag wire pseudoreference electrode. A CV was recorded to determine the potential of the first reduction feature. The solution was replaced with a fresh solution of **1** and the determined potential was applied for 10 min, with collection of the UV-vis spectrum every 5 seconds over that period, see Figure 4 and S28. Kinetics were derived from the absorbance after 100 seconds, when the passed current had strongly decreased indicating no further electrochemical reduction. The kinetics were derived from the decay of the band of **3** at 540 nm from 100 until 160 seconds. The half-life of **3** form the UV-vis spectroelectrochemical experiment was derived from a plot of ln[(A_f-A_t/A_0-A_f)] versus time (Figure S2), where A_t is the absorbance at time t, A_f the final absorbance after the UV-vis stabilizes and A_0 an 'initial' absorbance of **3** at 100 seconds.

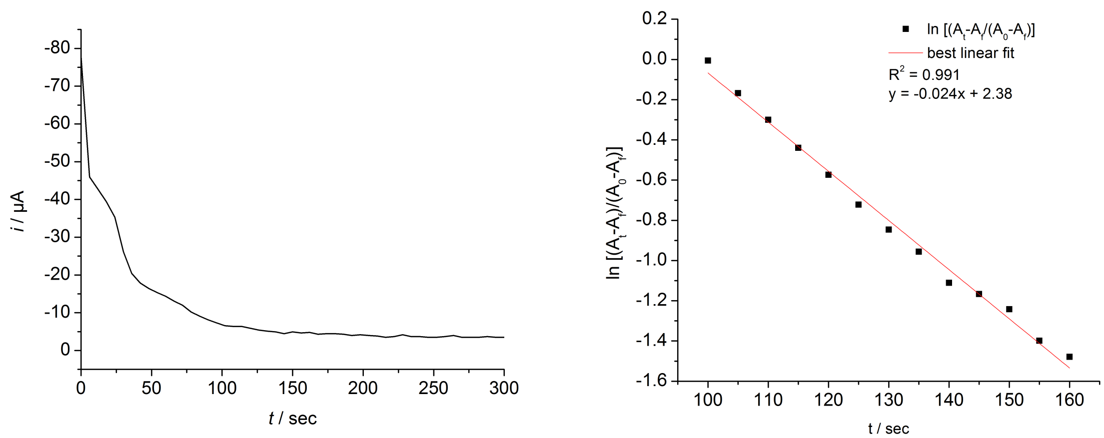


Figure S2. Current vs. time plot of the UV-vis spectroelectrochemical reduction of **1** at 25 °C under N_2. Kinetic analysis of ln[(A_f-A_t/A_0-A_f)] vs time at 540 nm (right) was started after *t* = 100 seconds, when minimal current was passing (left).

*1.7. NMR experiments of **1** at high pressures and with added chloride*

NMR spectroscopy of 1 at increased pressure.

Complex **1** (3.9 mg, 6.5 µmol) was dissolved in THF-*d*$_8$ (0.3 mL) in a high pressure NMR tube and degassed via 3 freeze-pump-thaw cycles. 5 bars of N_2 or Ar, respectively, were applied via a pressure regulator valve and NMR spectra were measured between +25 °C and −95 °C, see Figures S20-S22.

NMR Stability tests for 1

1 (5.0 mg, 8.1 µmol) was dissolved in THF-d_8 (0.5 mL) in a J-Young tube and measured under Ar. The samples were degassed via 3 freeze-pump-thaw cycles and backfilled with N_2. The stability under N_2 was monitored NMR spectroscopically over time. To examine the stability against chloride, [^{n}Bu$_4$N]Cl (11.0 mg; 40.5 µmol; 5 eq.) was added to form a suspension and NMR spectroscopy was measured in regular time distances. See Figures S23-S24.

*1.8. Further electrochemical experiments for **1***

Chloride Concentration Dependence under N_2 and Ar.

1 (3.9 mg, 6.3 µmol) was dissolved in a 0.2 M solution of [^{n}Bu$_4$N][PF$_6$] in THF (8 mL) and a small amount of Fe(Cp*)$_2$ was added as an internal potential reference. 2 mL of the solution was added to a vial containing [^{n}Bu$_4$N]Cl (35.3 mg, 1.27×10^{-4} mol). Aliquots of the resultant [^{n}Bu$_4$N]Cl solution were added to the 6 mL solution of **1**. After each chloride addition, CVs for the first reduction feature under N_2 (as well as the first two reduction features for Ar) were recorded at 0.05, 0.1, 0.25, 0.5, 0.75, and 1 Vs^{-1}, respectively, see Figures 4 and S32. S33, S35.

N_2 Pressure Dependence.

A Parr reactor with a Teflon inset comprising a glass inlet (Figure S3) was charged with **1** (3.0 mg, 4.9 µmol), 0.2 M [^{n}Bu$_4$N][PF$_6$] in THF (5 mL), and a pipette tip of Fe(Cp)$_2$ under a N_2 atmosphere. The reactor was sealed and an initial 1 atm N_2 CV at a scan rate of 0.1 Vs^{-1} was recorded. The pressure of the reactor was increased to 2 atm, the solution was stirred for 10 minutes, and a CV at a scan rate of 0.1 Vs^{-1} was recorded. The process was repeated for total N_2 pressures of 4, 6, 8, and 10 atm. The pressure was then reduced to 8, 6, 4, 2, and 1 atm by releasing pressure through the vent valve on the Parr reactor, with stirring. CVs were recorded at each of these pressures as before. See Figures S37 and S38.

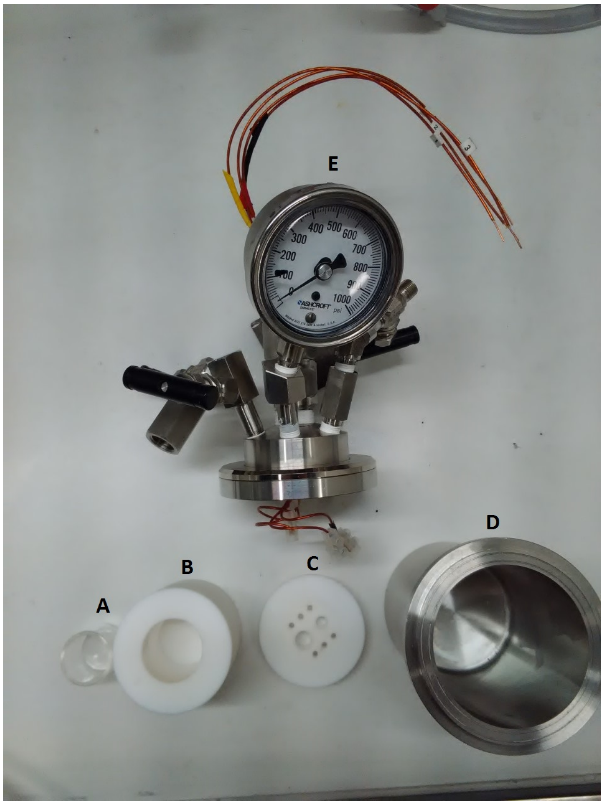


Figure S3. Parr reactor electrochemistry setup with A: glass inlet, B: Teflon inlet, C: Teflon inlet cap, D: Parr Reactor bottom part, E: Parr Reactor top part with electrochemical feedthrough

Rhenium Concentration Dependence under N_2 and Ar.

A stock solution of **1** was prepared by dissolving **1** (14.7 mg, 23.8 µmol) in a 1.0 mL solution of 0.2 M [^{n}Bu$_4$N][PF$_6$] in THF. Aliquots of this stock solution were added to a 5 mL solution of 0.2 M [^{n}Bu$_4$N][PF$_6$] in THF, with a spatula tip of Fe(Cp)$_2$ as an electrochemical reference, to afford solutions of 0.5, 1.0, 2.0, and 4.0 mM **1**. CVs for both the first reduction feature (as well as the first 2 reduction features under Ar) were recorded at 0.05, 0.1, 0.25, 0.5, 0.75, and 1 Vs^{-1}, see Figures S34 and S36.

2 Spectroscopic Results

*2.1. [(μ-N_2){ReCl(PNP)$_2$}$_2$](**3**)*

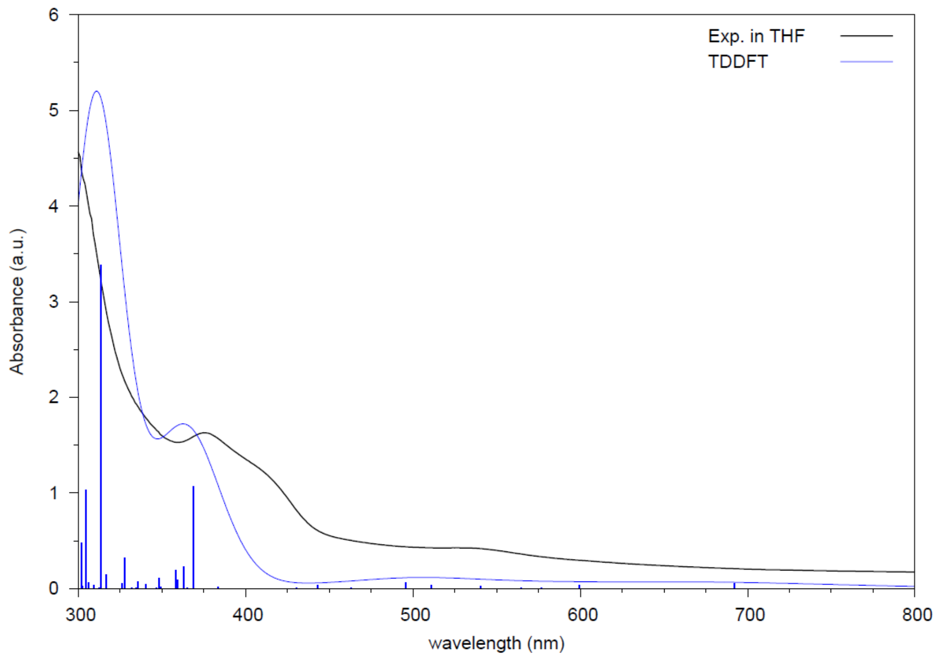


Figure S4. UV-vis spectrum of **3** measured in THF at −30 °C (black) and the TD-DFT calculated UV-vis spectrum in THF (blue).

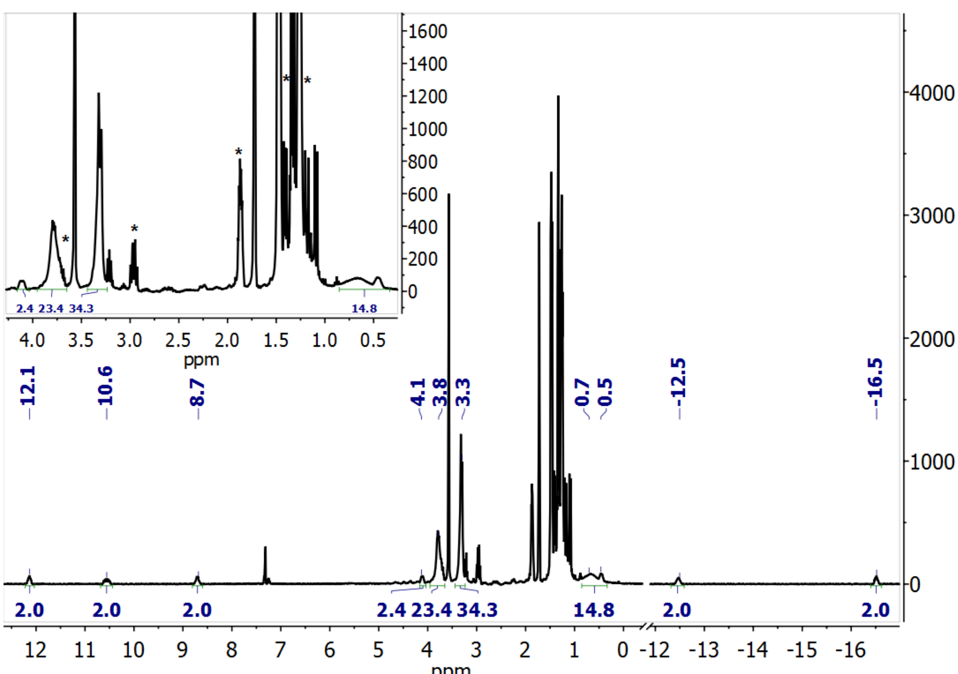


Figure S5. ^{1}H NMR spectrum of **3** at −20 °C in THF-d_8. **1** is fully consumed and **2** (marked with the asterisk) is the main side product. This sample represents a typical sample as used from determining kinetics of the decay of **3**.

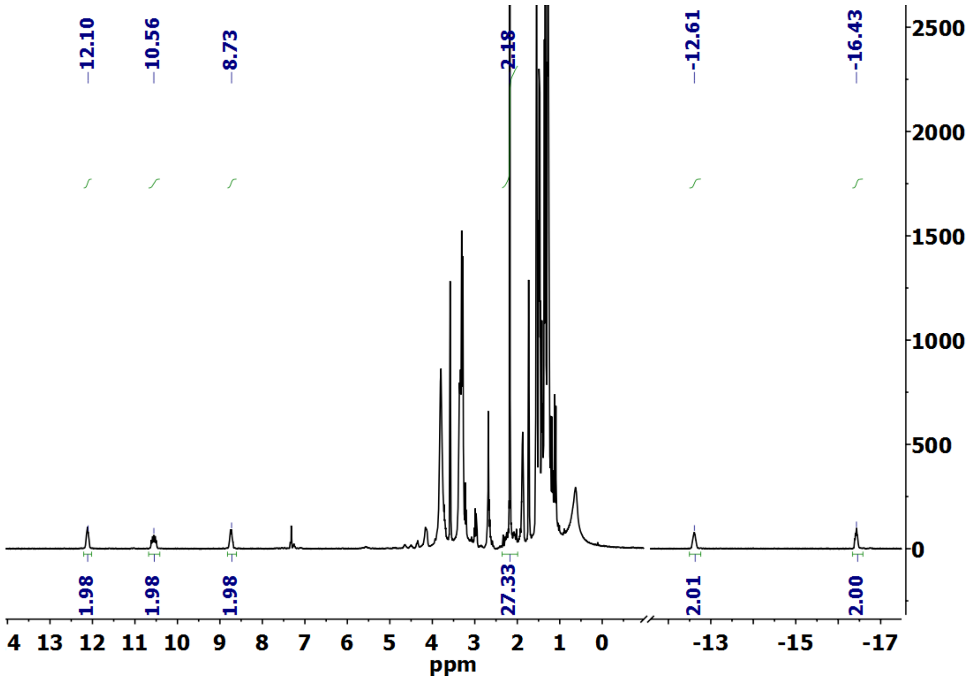


Figure S6. [1]H NMR spectrum of **3** at −15 °C with addition of 4.6 µmol hexamethylbenzene as internal standard (peak at 2.1 ppm), to determine the yield of **3** (3.0 µmol, 74 %).

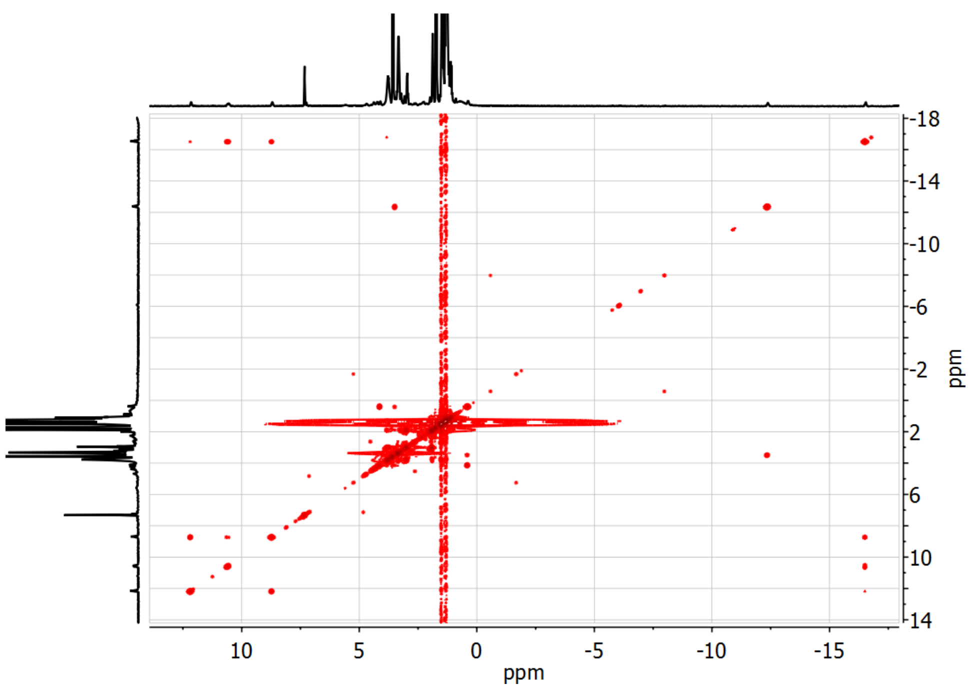


Figure S7. [1]H COSY NMR spectrum of **3** at −20 °C in THF-d_8.

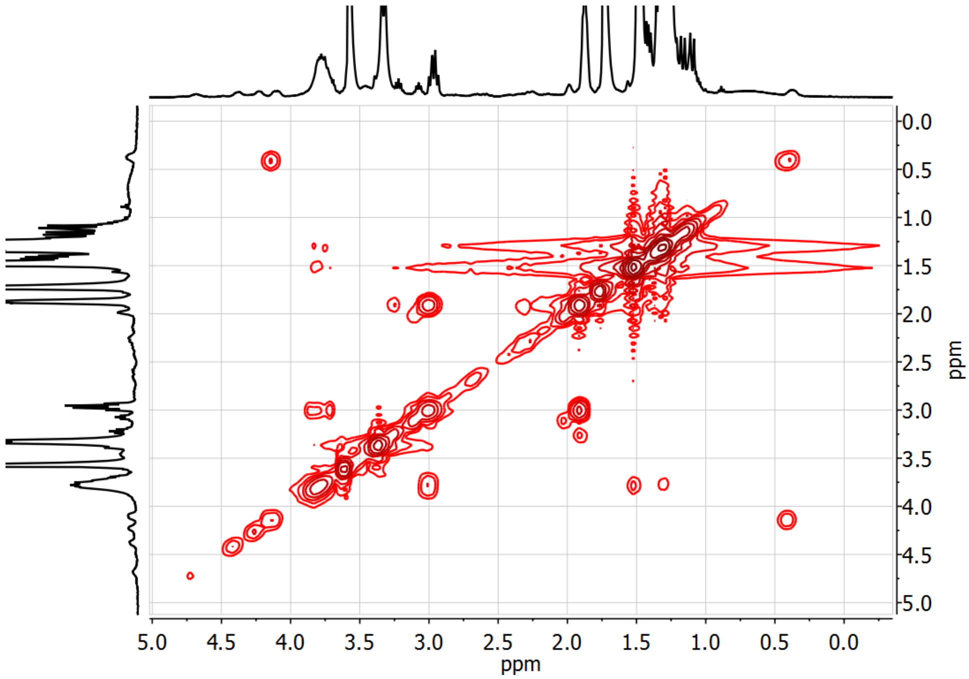


Figure S8. Expansions of the [1]H COSY NMR spectrum of **3** at −20 °C in THF-d_8.

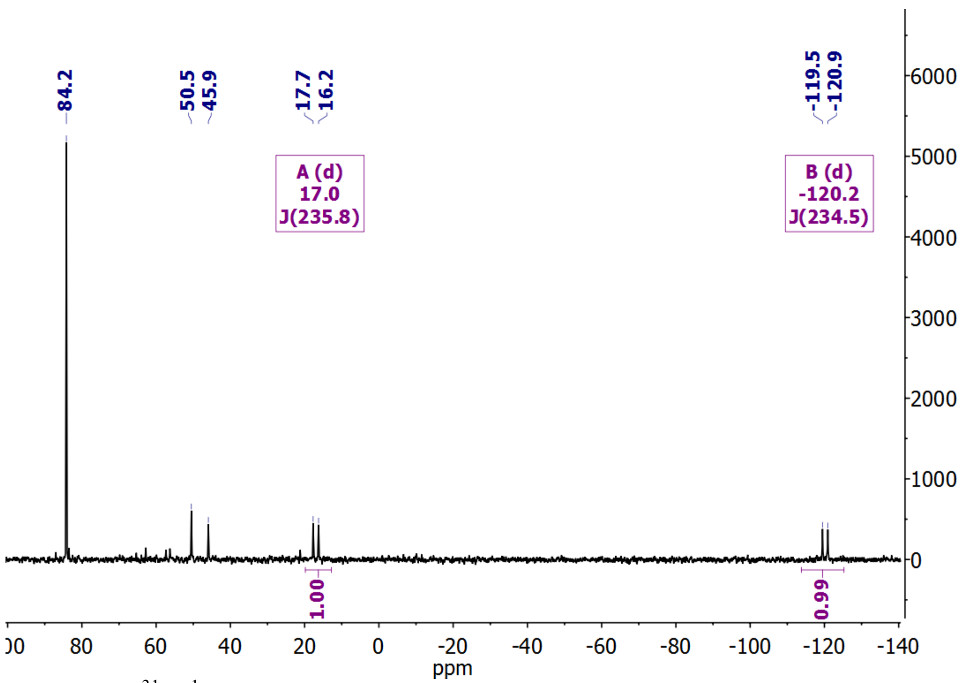


Figure S9. $^{31}P\{^1H\}$ NMR spectrum of **3** at −20 °C.

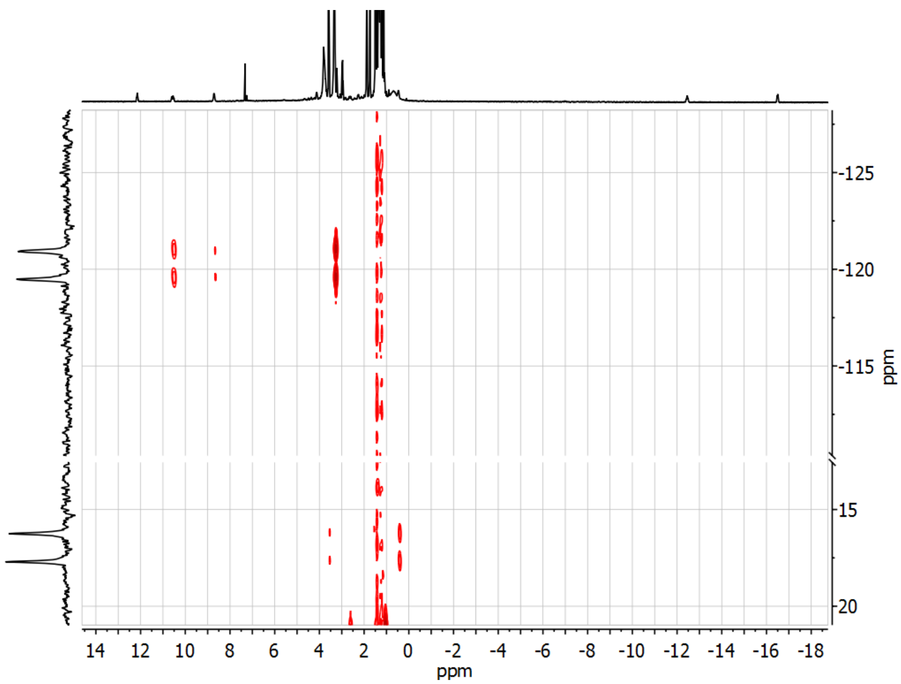


Figure S10. ^{1}H-^{31}P HMBC NMR spectrum of **3** at −20 °C.

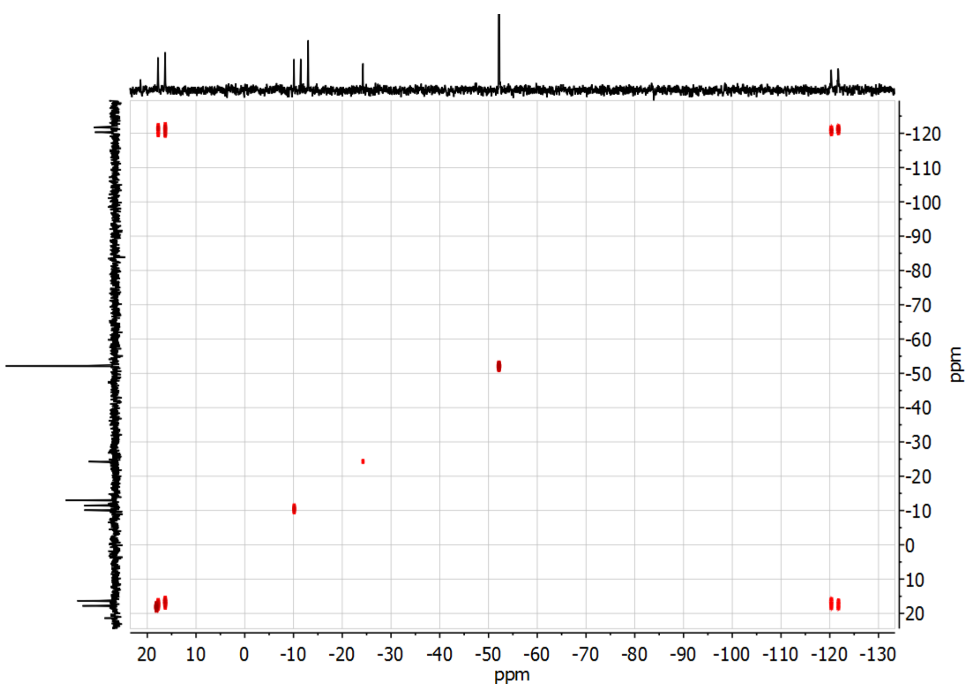


Figure S11. $^{31}P\{^{1}H\}$-$^{31}P\{^{1}H\}$ COSY NMR spectrum of **3** at −20 °C.

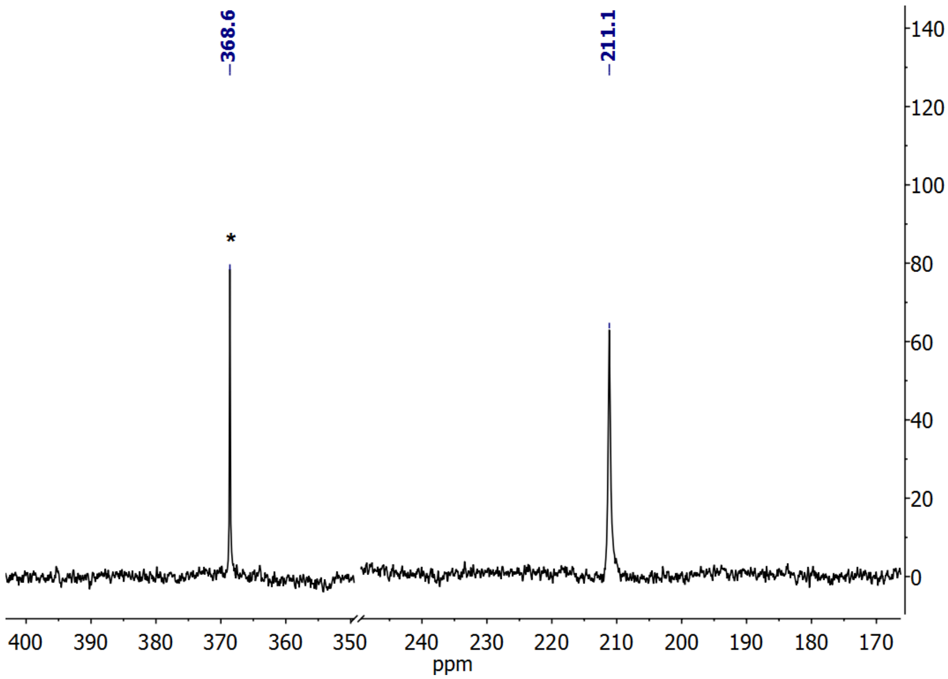


Figure S12. $^{15}N\{^1H\}$ NMR spectrum of **3** at −30 °C. Nitride **2** (indicated with an asterisk) is the main side product.

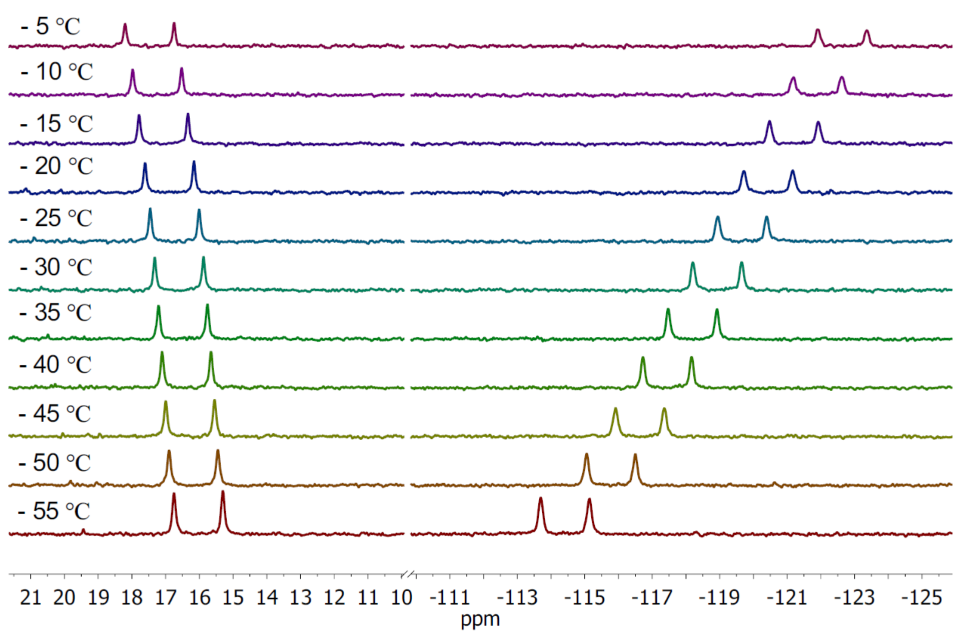


Figure S13. Temperature dependent $^{31}P\{^1H\}$ NMR spectra between −55 °C and −5°C.

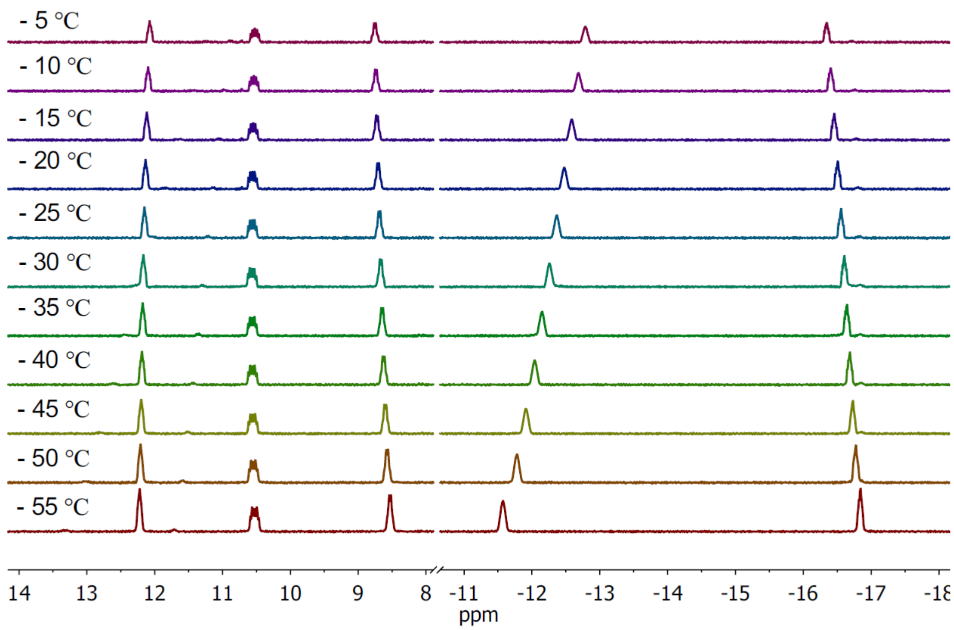


Figure S14. Expansions of the temperature dependent [1]H NMR spectra of **3** between −55 °C and −5°C.

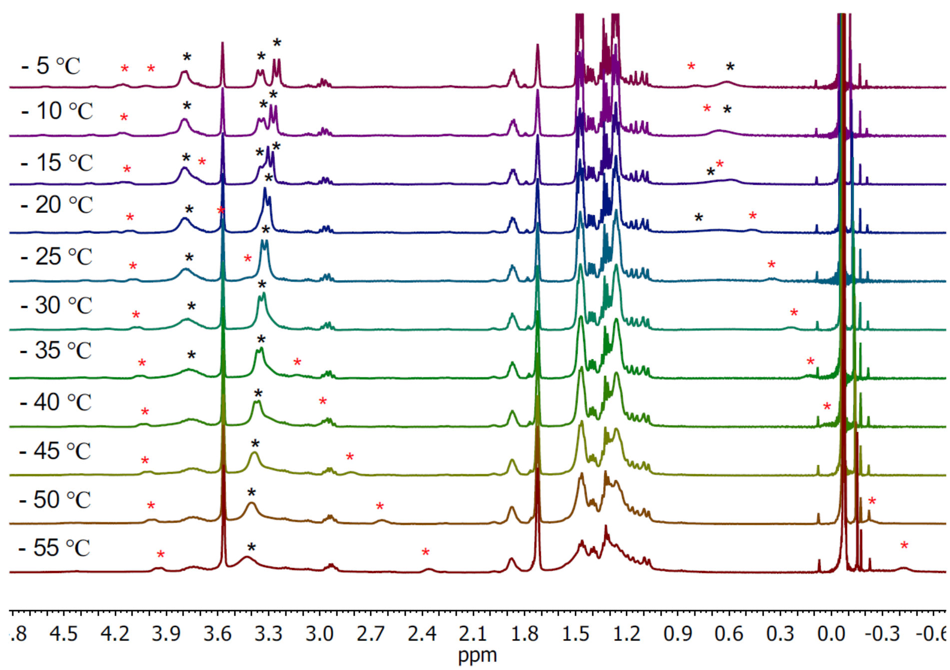


Figure S15. Expansions of temperature dependent [1]H NMR spectra of **3** between −55 °C and −5°C. Red asterisks indicate backbone protons and black asterisks indicate the ^{t}Bu moieties.

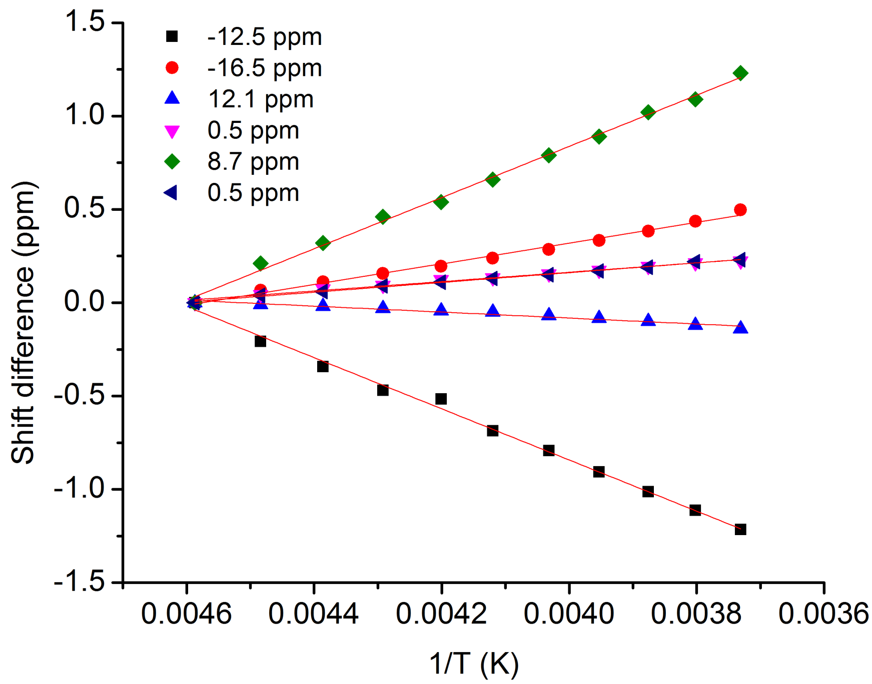


Figure S16. Plot of the backbone [1]H NMR signals shifting from −55 °C to −5°C against T^{-1}, where the peaks are labeled with the chemical shift at −20 °C (Figure S5). A positive shift indicates an upfield shift.

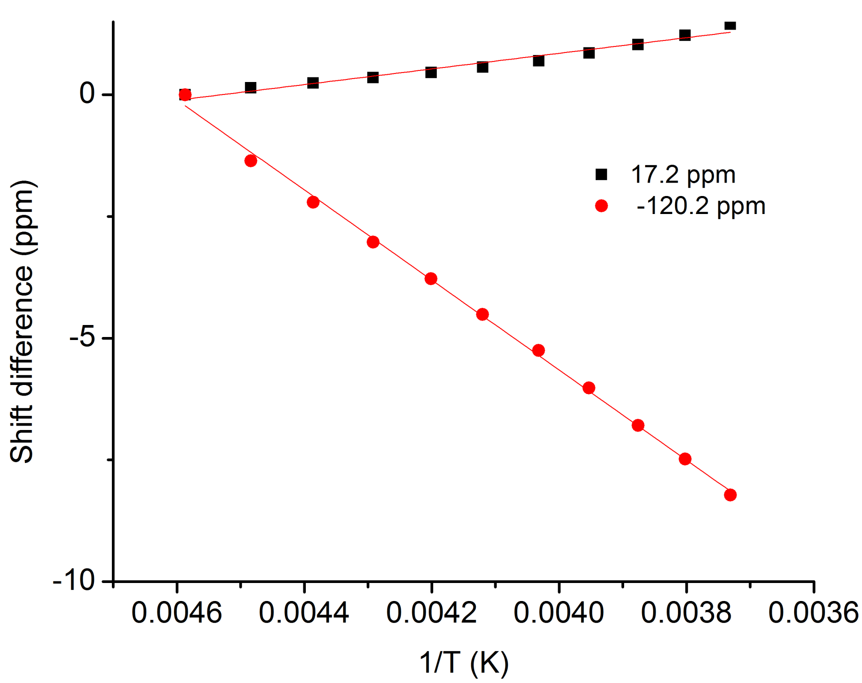


Figure S17. Plot of both [31]P NMR signals shifting from −55 °C to −5°C against T^{-1}, where the peaks are labeled with the chemical shift at −20 °C (Figure S9). A positive shift indicates an upfield shift.

*2.2. Re(N)Cl(PNP) (**2**)*

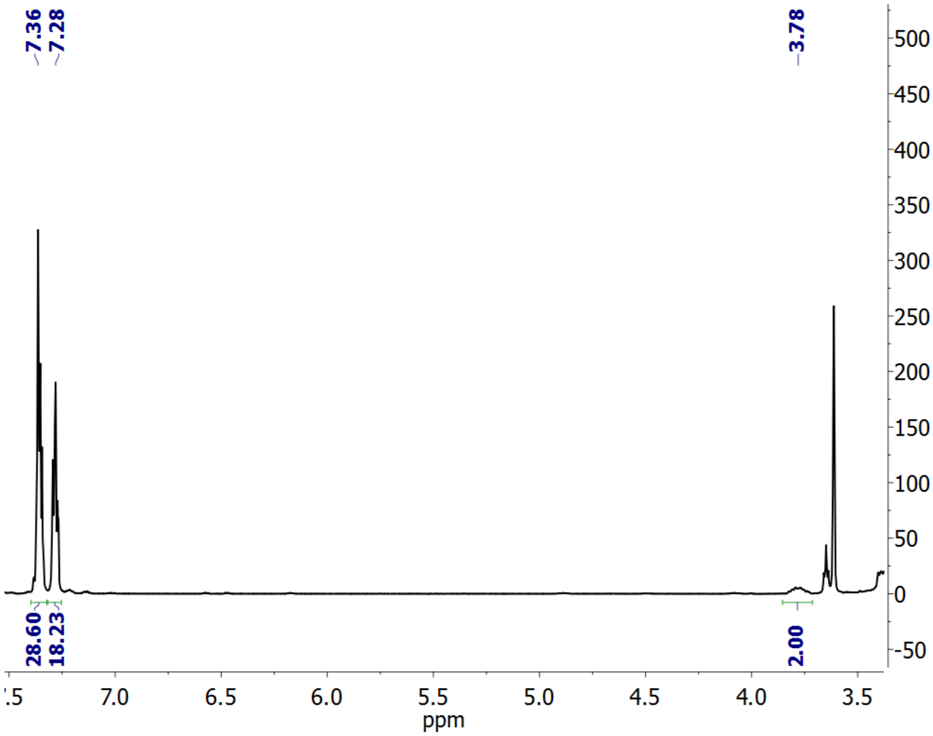


Figure S18. ^{1}H NMR spectrum in THF-d_8 after controlled potential electrolysis of **1** with addition of 34 µmol of PPh_3 as internal standard (signal at 7.36 and 7.28 ppm) used for yield determination (66% yield).

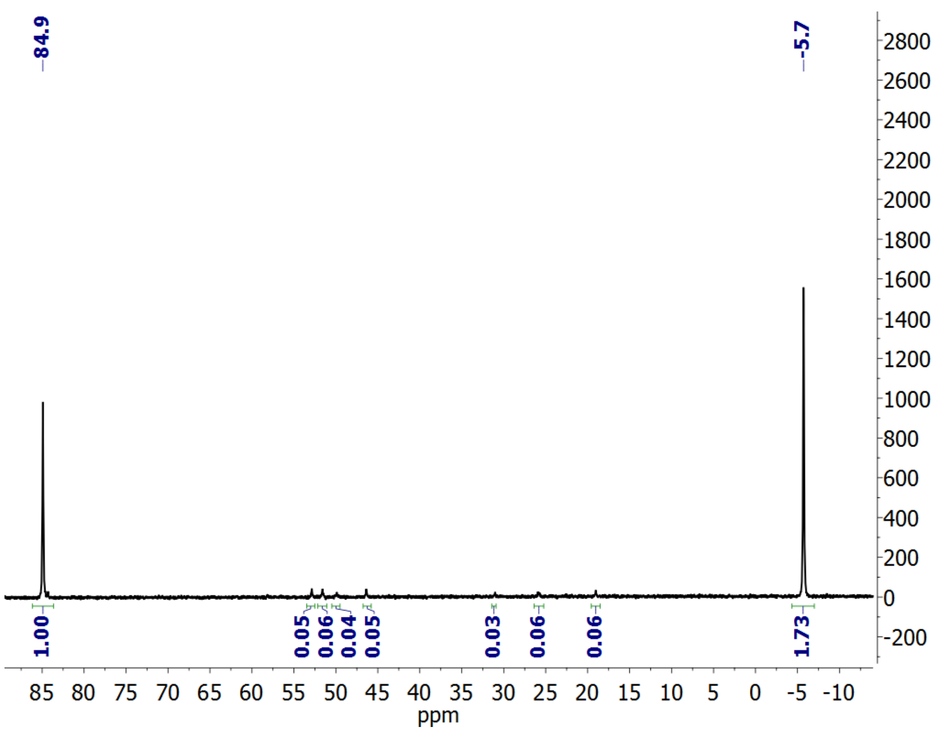


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum in THF-d_8 after controlled potential electrolysis of **1** with addition of 34 µmol of PPh_3 as internal standard (signal at −5.7 ppm) used for yield determination (58% yield).

*2.3. Pressure and chloride dependence of NMR spectra of **1**.*

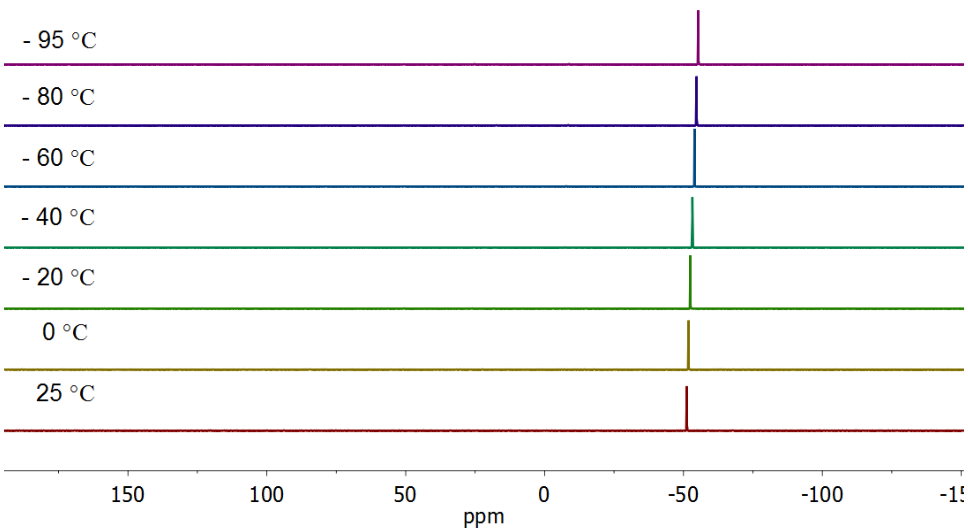


Figure S20. $^{31}P\{^1H\}$ NMR spectrum of **1** in THF-d_8 under N_2-pressure (5 atm).

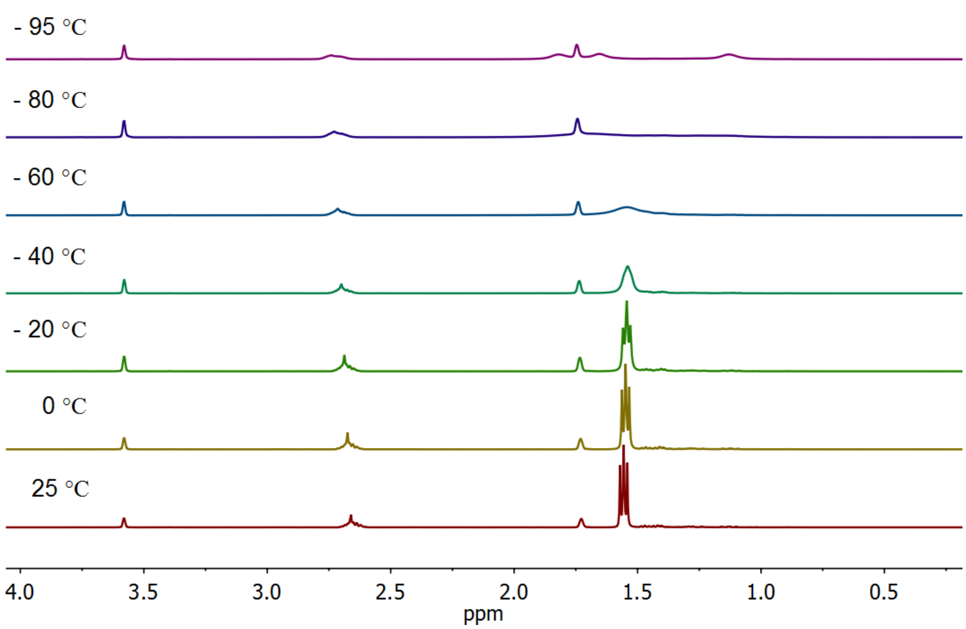


Figure S21. ^1H NMR spectrum of **1** in THF-d_8 under N_2-pressure (5 atm). We attribute the broadening of the ^{t}Bu-groups to freezing out of the rotation.

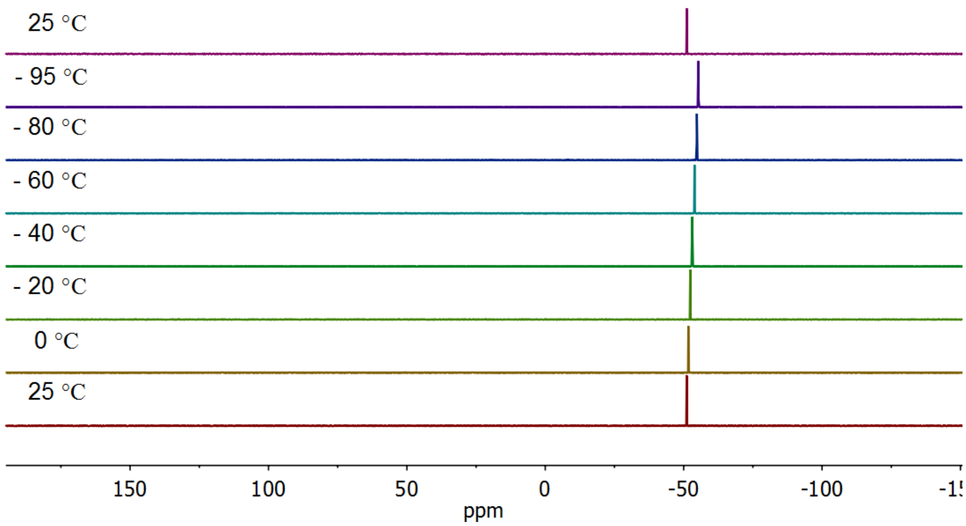


Figure S22. $^{31}P\{^1H\}$ NMR spectrum of **1** in THF-d_8 under Ar-pressure (5 atm).

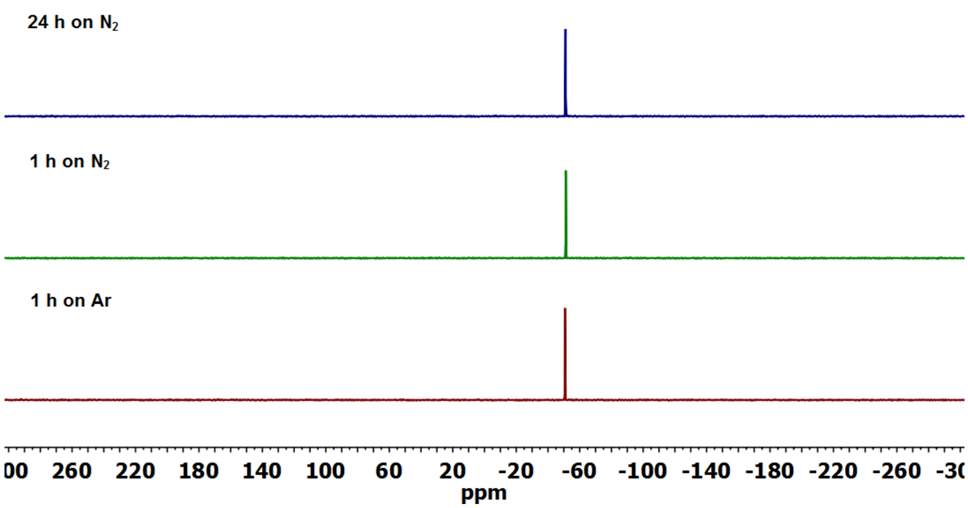


Figure S23. Stability of **1** under N_2 as examined by $^{31}P\{^1H\}$ NMR spectroscopy in THF-d_8.

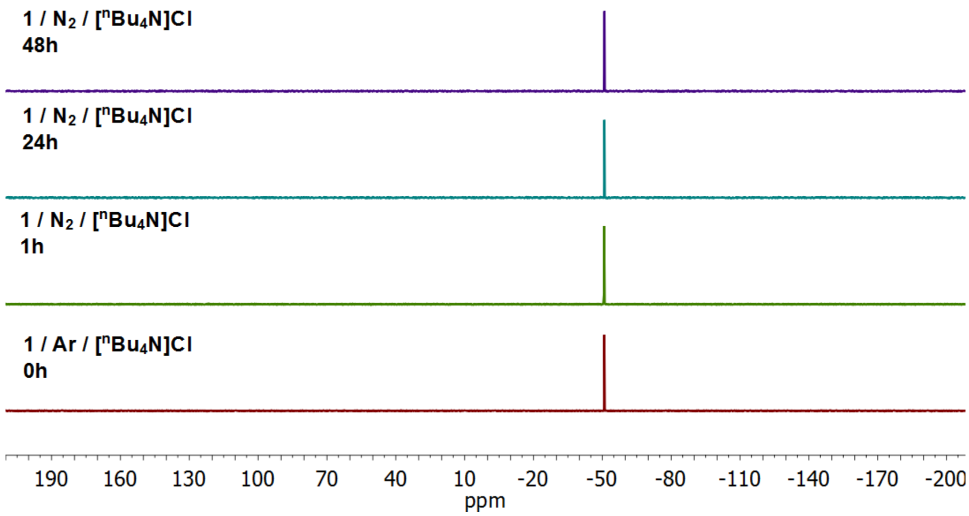


Figure S24. Stability of **1** under N_2 in presence of a slight excess of [^{n}Bu_4N]Cl, by $^{31}P\{^1H\}$ NMR in THF-d_8.

*2.4. Infrared and UV-visible spectroscopy of **1** and **2***

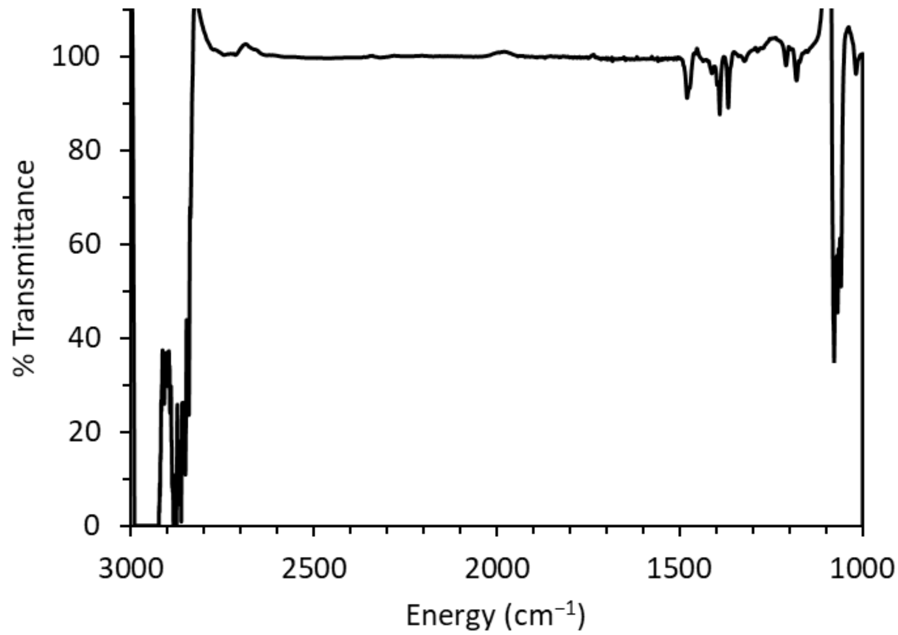


Figure S25. IR spectrum of **1** in THF under N_2. No evidence for a metal-bound N_2 vibration was observed.

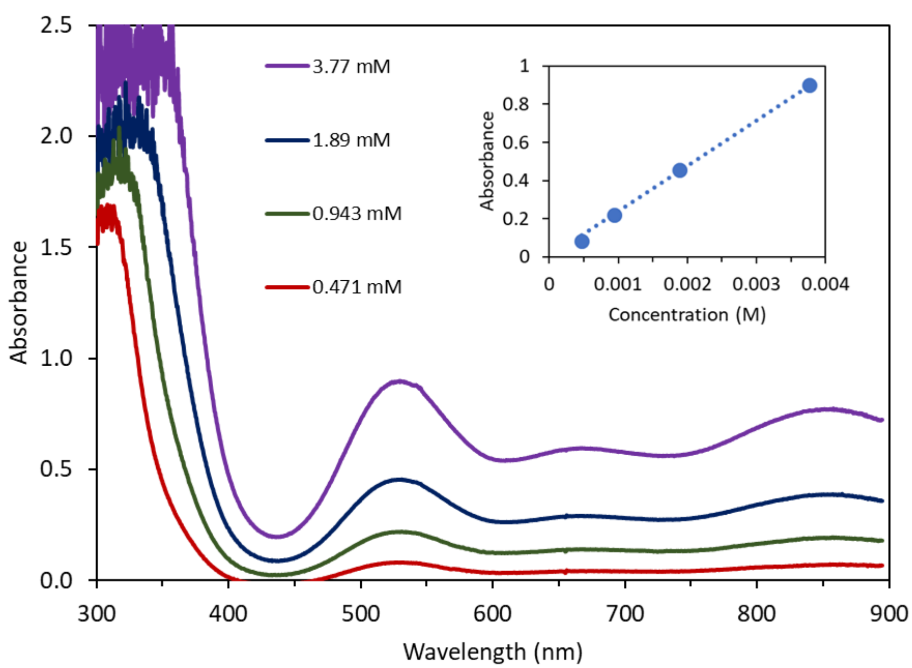


Figure S26. UV-vis spectrum of 0.471, 0.943, 1.89, and 3.77 mM **1** in THF under argon. Inset: Molar absorptivity determined to be 283 $M^{-1}cm^{-1}$ ($R^2 = 0.997$).

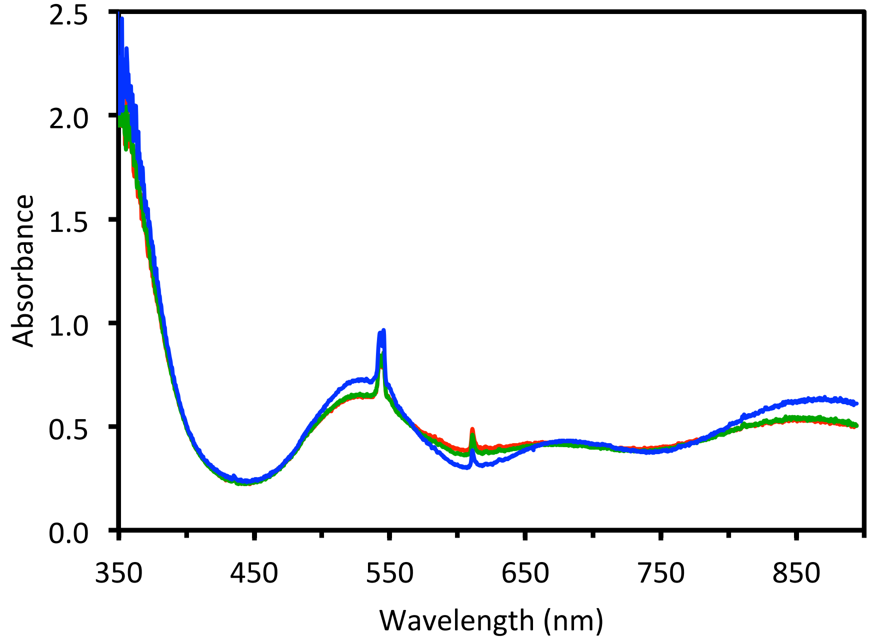


Figure S27. UV-visible spectrum of **1** at N_2 in THF at 23 °C (red), 0 °C (green), and −78 °C (blue).

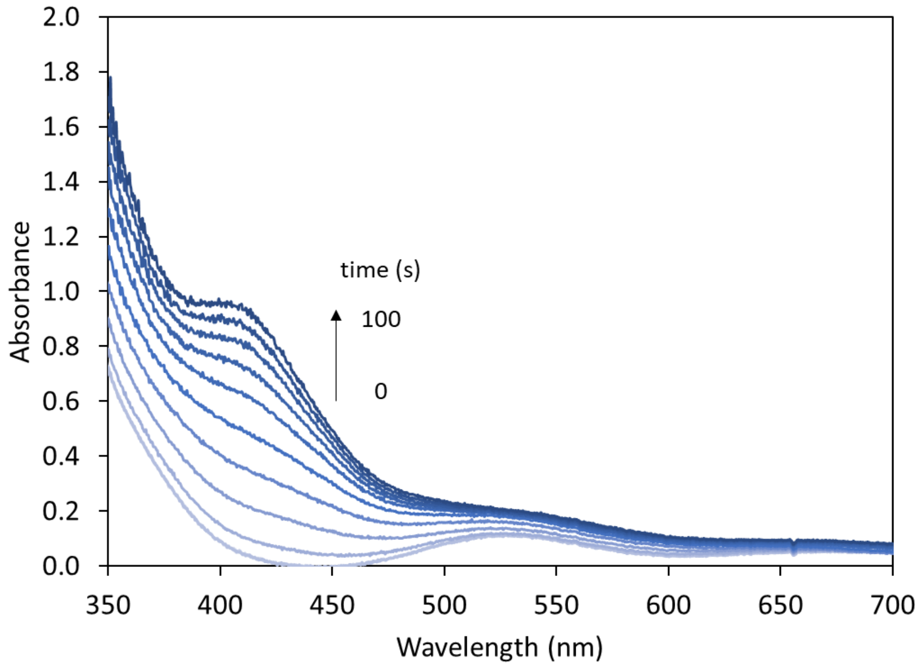


Figure S28. UV-visible spectrum of **1** in THF during electrolysis under Ar.

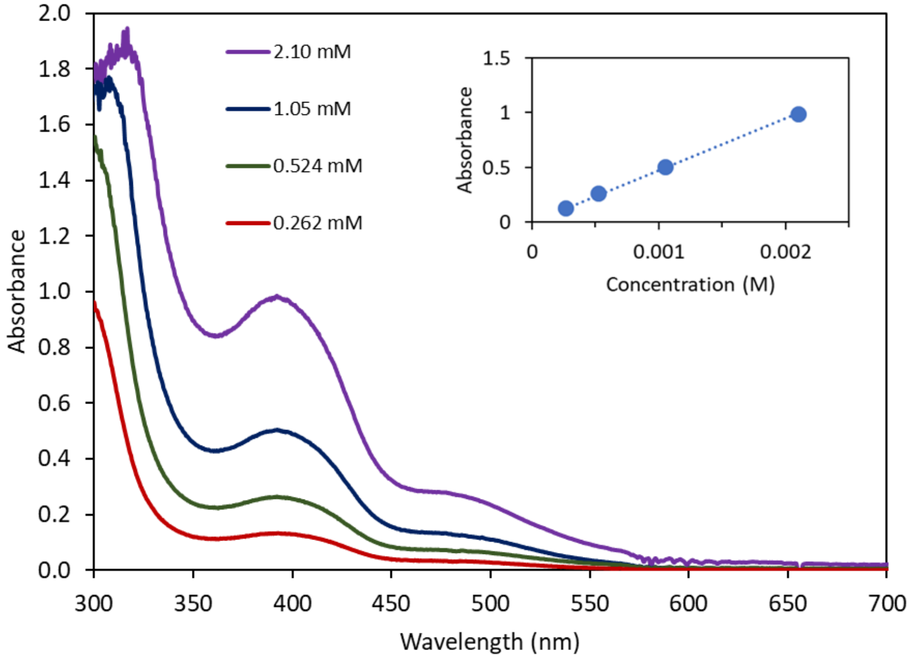


Figure S29. UV-vis spectrum of 0.262, 0.524, 1.04, and 2.10 mM **2** in THF. Inset: Molar absorptivity determined to be 474 $M^{-1}cm^{-1}$ ($R^2 = 0.999$).

3. Cyclic Voltammetry (CV) Data

*3.1. ReCl$_2$(PNP) (**1**)*

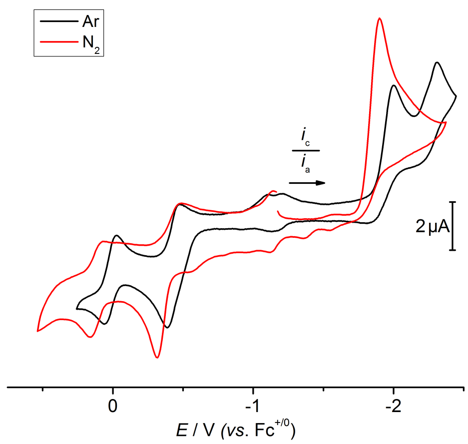


Figure S30. CV of 0.8 mM **1** in 0.2 M [^{n}Bu$_4$N][PF$_6$] in THF under N_2 (red) and under Ar (black) (v = 0.1 Vs^{-1})

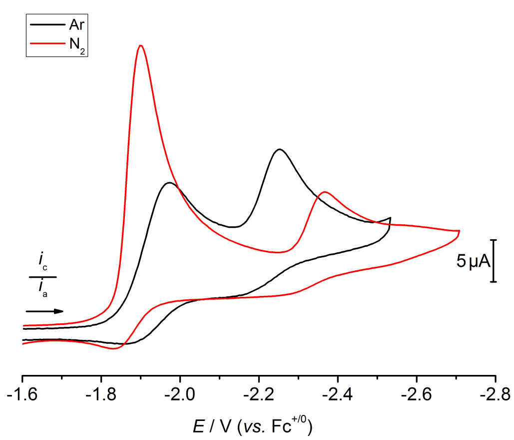


Figure S31. CV of the reductive area 0.8 mM **1** in 0.2 M [^{n}Bu$_4$N][PF$_6$] in THF under N_2 (red) and under Ar (black) (v =0.1 Vs^{-1}).

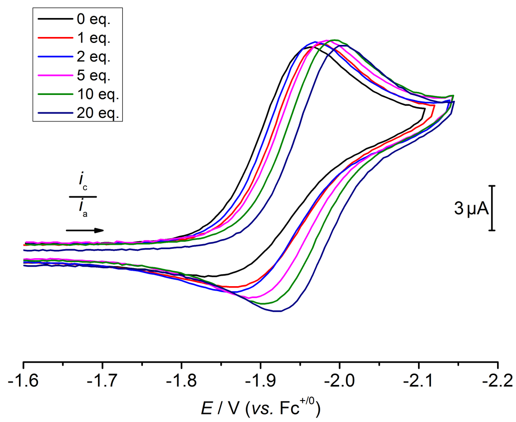


Figure S32. CV of 0.79 mM $ReCl_2$(PNP) (**1**) in THF with 0.2 M [^{n}Bu$_4$N][PF_6] with 0-20 equiv [^{n}Bu$_4$N]Cl under Ar (v =0.1 Vs^{-1}), first reduction feature.

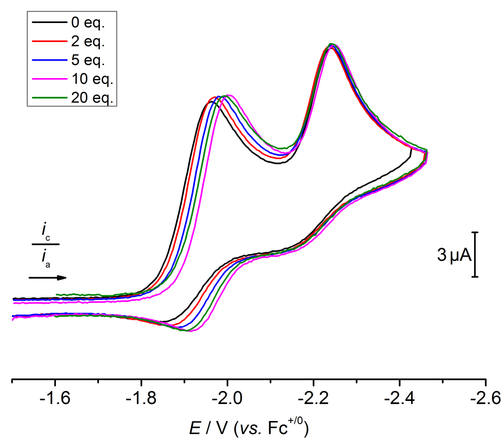


Figure S33. CV of 0.79 mM $ReCl_2$(PNP) (**1**) in THF with 0.2 M [^{n}Bu$_4$N][PF_6] with 0-20 equiv [^{n}Bu$_4$N]Cl under Ar (v = 0.1 Vs^{-1}), both reduction features.

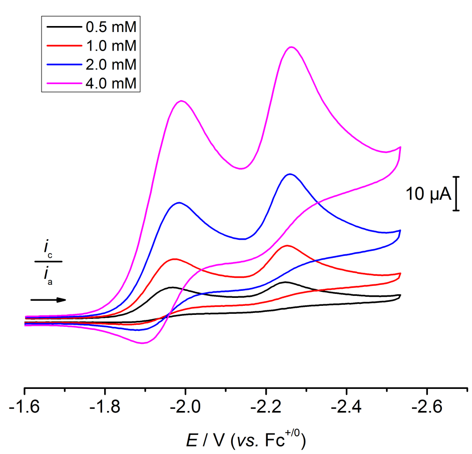


Figure S34. CV of 0.5-4.0 mM $ReCl_2$(PNP) (**1**) in THF with 0.2 M [^{n}Bu$_4$N][PF_6] under Ar (v = 0.1 Vs^{-1}).

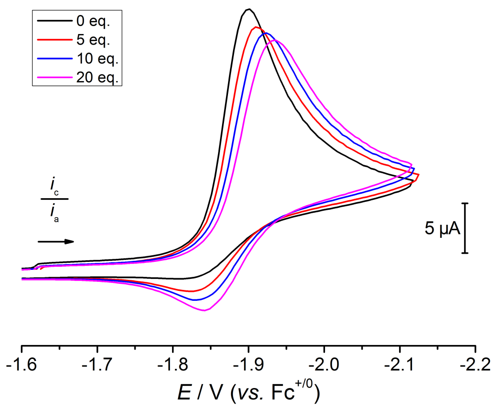


Figure S35. CV of 0.79 mM $ReCl_2$(PNP) (**1**) in THF with 0.2 M [$^nBu_4N$][PF_6] with 0-20 equiv [$^nBu_4N$]Cl under N_2 (v = 0.1 Vs^{-1}).

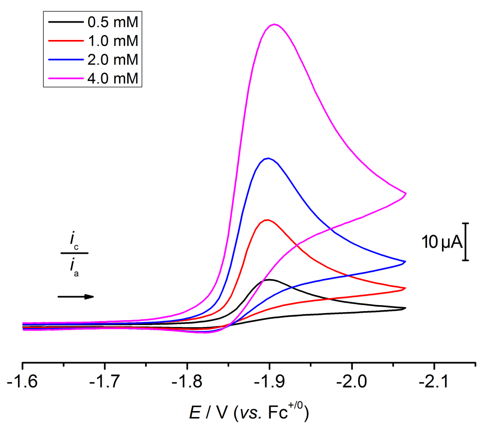


Figure S36. CV of 0.5-4.0 mM $ReCl_2$(PNP) (**1**) in THF with 0.2 M [$^nBu_4N$][PF_6] under N_2 (v = 0.1 Vs^{-1}).

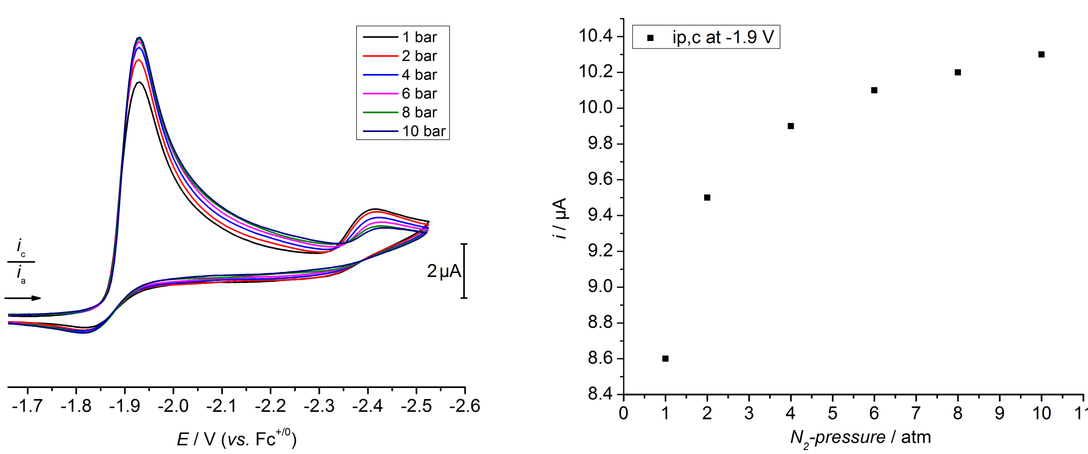


Figure S37. CV of circa 1 mM $ReCl_2$(PNP) (**1**) in THF with 0.2 M [$^nBu_4N$][PF_6] under varying increasing N_2 pressures (1-10 bar) (v = 0.1 Vs^{-1}) (left) and plot of peak current at -1.9 V vs N_2-pressure, showing the peak current reaches a plateau (right).

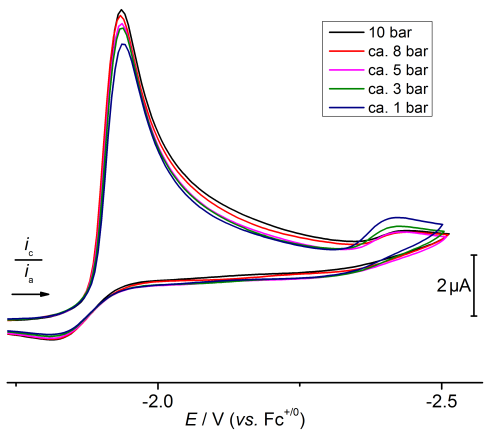


Figure S38. CV of circa 1 mM $ReCl_2$(PNP) (**1**) in THF with 0.2 M [$^nBu_4N$][PF_6] under varying decreasing N_2 pressures (10-1 bar) (v = 0.1 Vs^{-1}).

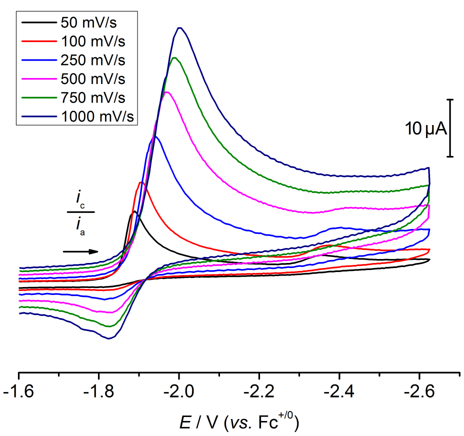


Figure S39. Scan rate dependence of 0.5 mM **1** in THF with 0.2 M [$^nBu_4N$]PF_6 under N_2.

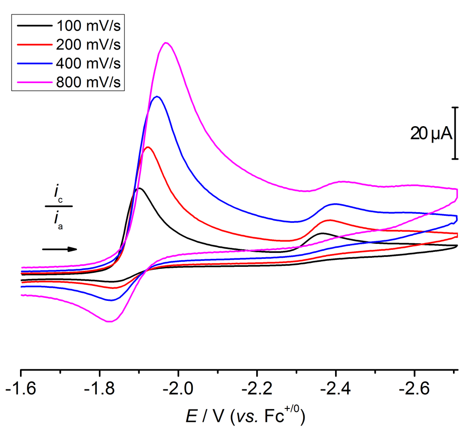


Figure S40. Scan rate dependence of 1.0 mM **1** in THF with 0.2 M [$^nBu_4N$]PF_6 under N_2.

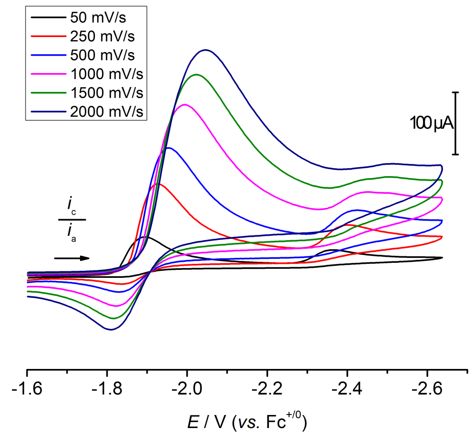


Figure S41. Scan rate dependence of 4.0 mM **1** in THF with 0.2 M [^{n}Bu$_4$N]PF$_6$ under N_2.

4. Simulated CV Data

Simulation under Argon

The diffusion coefficient *D* of **1** was determined to be $9.1 \cdot 10^{-6}$ cm²s^{-1} by DOSY-NMR spectroscopy. The diffusion coefficient of all Re species was set to this value as reduction or chloride loss should not have a large impact on *D*. The diffusion coefficient *D* of chloride ions was set to $5 \cdot 10^{-5}$ cm²s^{-1}.

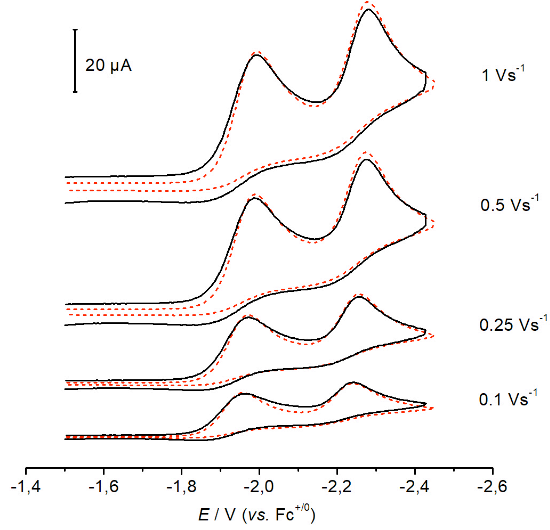


Figure S42. CV data of 1 mM **1** at rt under Ar (*I* = 0.2 M [^{n}Bu$_4$N][PF$_6$]). Black lines: experimental data; red dashed lines: simulation according to Scheme 6 with the parameter values of Table 1.

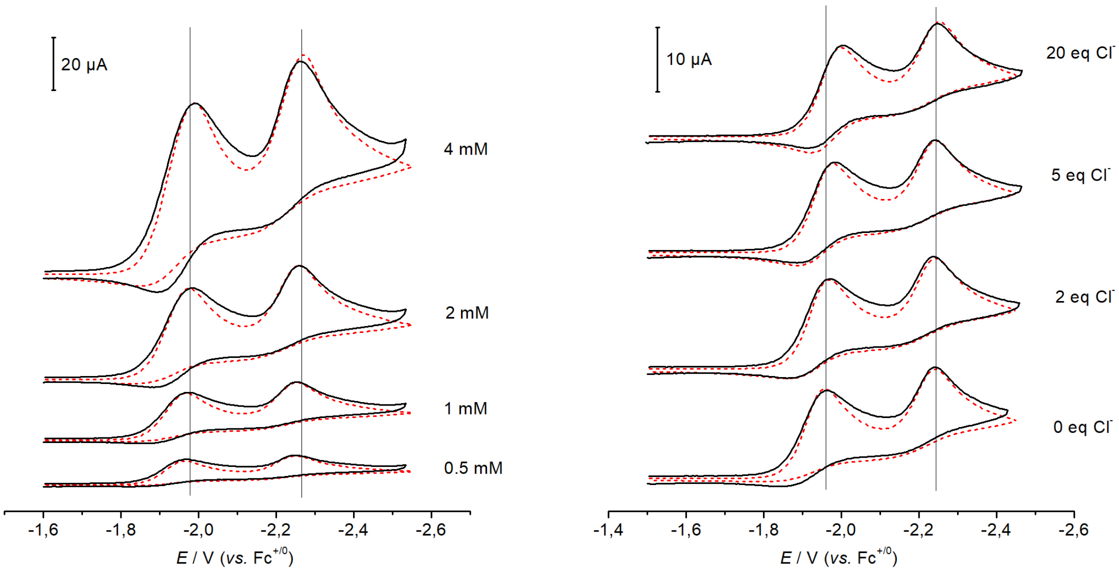


Figure S43. Left: Concentration dependent CV data of **1** at rt under Ar (I = 0.2 M [^{n}Bu$_4$N][PF$_6$], v = 0.1 Vs^{-1}). Right: CV data of **1** at different chloride ion concentrations (I = 0.2 M [^{n}Bu$_4$N][PF$_6$], v = 0.1 Vs^{-1}). Black lines: experimental data; red dashed lines: simulation according to Scheme 6 with the parameter values of Table 1.

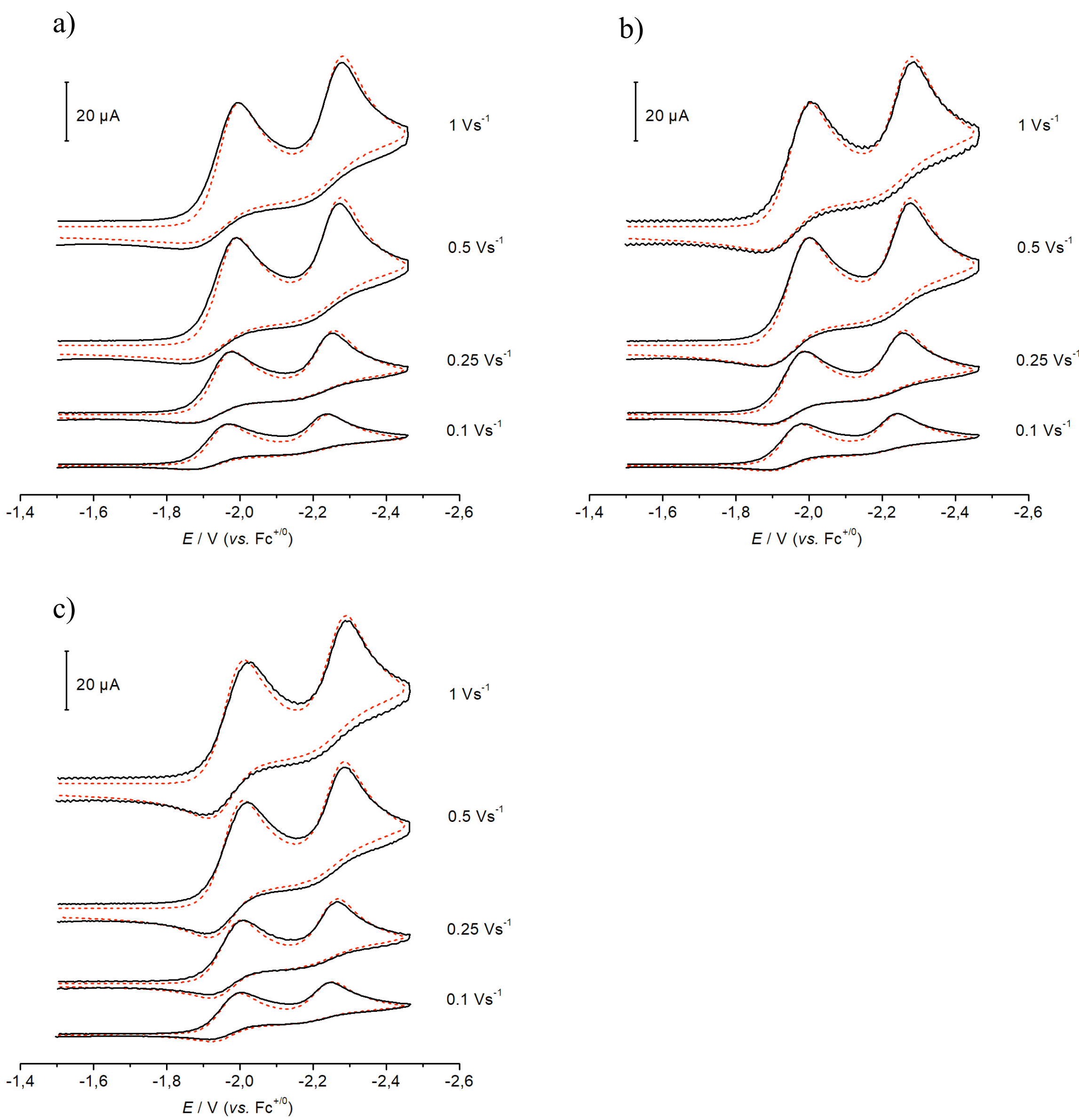
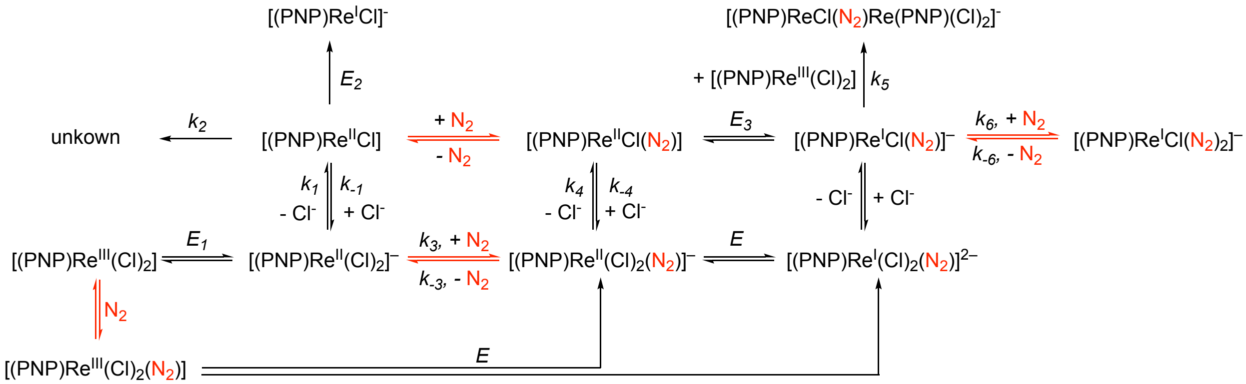


Figure S44. CV data of **1** at different chloride ion concentrations under Ar (I = 0.2 M [^{n}Bu$_4$N][PF$_6$]), a) 2 eq. [^{n}Bu$_4$N]Cl, b) 5 eq. of [^{n}Bu$_4$N]Cl, c) 20 eq. [^{n}Bu$_4$N]Cl. Black lines: experimental data; red dashed lines: simulation according to Scheme 6 with the parameter values of Table 1.

Simulation under N_2



Scheme S1. Possible N_2 activation pathways that were considered to model the formation of the dimer.

We evaluated each model with respect to the several experimental observations, which we determined out of series of nine experiment under otherwise identical conditions:

- The first reduction is a multi-electron step.
- The peak potential is at 1.905 V, $v = 0.1$ Vs^{-1}, 20 mV experimental error.
- The peak potential shifts by 95 mV between scan rates of 0.1 and 1 Vs^{-1} in the absence of Cl$^-$ ions, 3-fold standard deviation as experimental error (Table S2).
- The peak potential shifts by 37 mV upon adding 20 eq. Cl$^-$ ions, $v = 0.1$ Vs^{-1}, 3-fold standard deviation as experimental error (Table S2).
- Peak potential shifts by 21 mV upon adding 20 eq. Cl$^-$ ions, $v = 1$ Vs^{-1}, 3-fold standard deviation as experimental error (Table S2).
- Peak currents under various experimental conditions as denoted in Table S1 with 3-fold standard deviations as experimental errors.
- The peak potential holds constant, when the concentration of **1** is doubled, experimental error of 10 mV.
- The reduction of [Re^{II}Cl(PNP)] vanishes under N_2.
- The reverse peak gets slightly more pronounced with increasing chloride ion concentrations.
- The peak potential holds constant, when the N_2 pressure is increased to 10 bar (experimental error of 10 mV).

The simulation parameters were chosen to maximize conserved parameters from the Ar data, and to minimize the number of variables in the simulation.

The diffusion coefficient D of dissolved N_2 was set to $1\cdot10^{-5}$ cm²s^{-1} and the N_2 concentration to 6.4 mM at 1 bar and 64 mM at 10 bar.[2]

Table S1. Average values and standard deviations of the concentration normalized peak currents ($i_p \cdot c^{-1}$) under various conditions.

	0 eq. Cl^-		5 eq. Cl^-		10 eq. Cl^-		20 eq. Cl^-	
	0.1 Vs^{-1}	1 Vs^{-1}	0.1 Vs^{-1}	1 Vs^{-1}	0.1 Vs^{-1}	1 Vs^{-1}	0.1 Vs^{-1}	1 Vs^{-1}
Ø $i_p \cdot c^{-1}$ /μA·mM^{-1}	31	85	30	80	29	81	29	79
σ /μA·mM^{-1}	2	10	2	10	2	6	3	9

Table S2. Average values and standard deviations of the peak potential shifts (V) under various conditions.

	0 eq. Cl^- and 20 eq. Cl^-		0.1 Vs^{-1} and 1 Vs^{-1}, 0 eq. Cl^-
	0.1 Vs^{-1}	1 Vs^{-1}	
Ø $\Delta E_{p,c}$ /V	37	21	95
σ /V	4	8	6

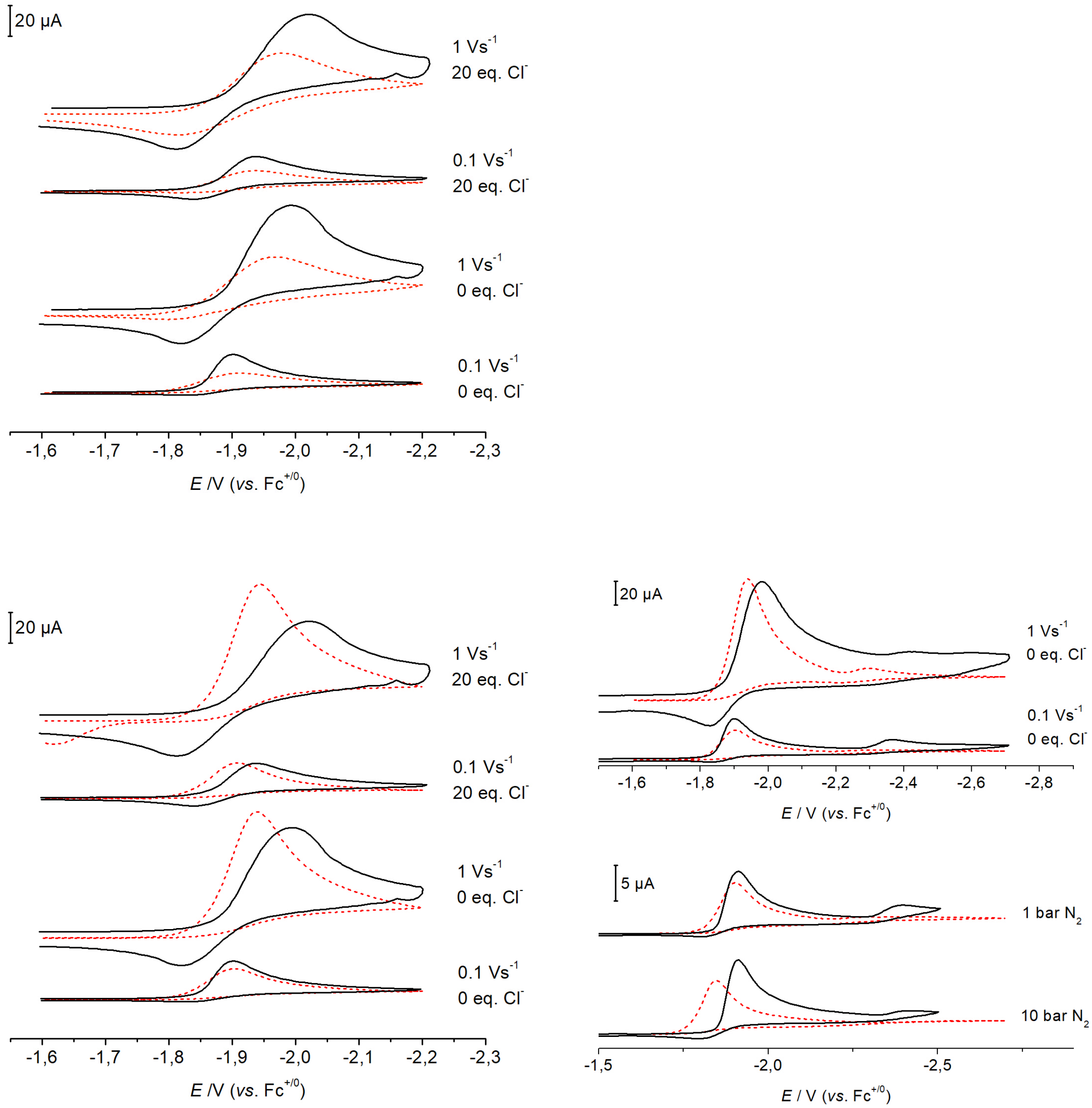


Figure S45. Representative CV data of **1** under different experimental conditions and scan rates under N_2 (I = 0.2 M [^{n}Bu$_4$N][PF$_6$]). Black lines: experimental data; red dashed lines: simulation applying the $EC^{N2}C^{Cl}C^{dim}E$ model (Top) and $C^{N2}E^{2e}C^{Cl}C^{dim}$ model (Bottom) for N_2 activation and dimer formation, respectively (Scheme S1).

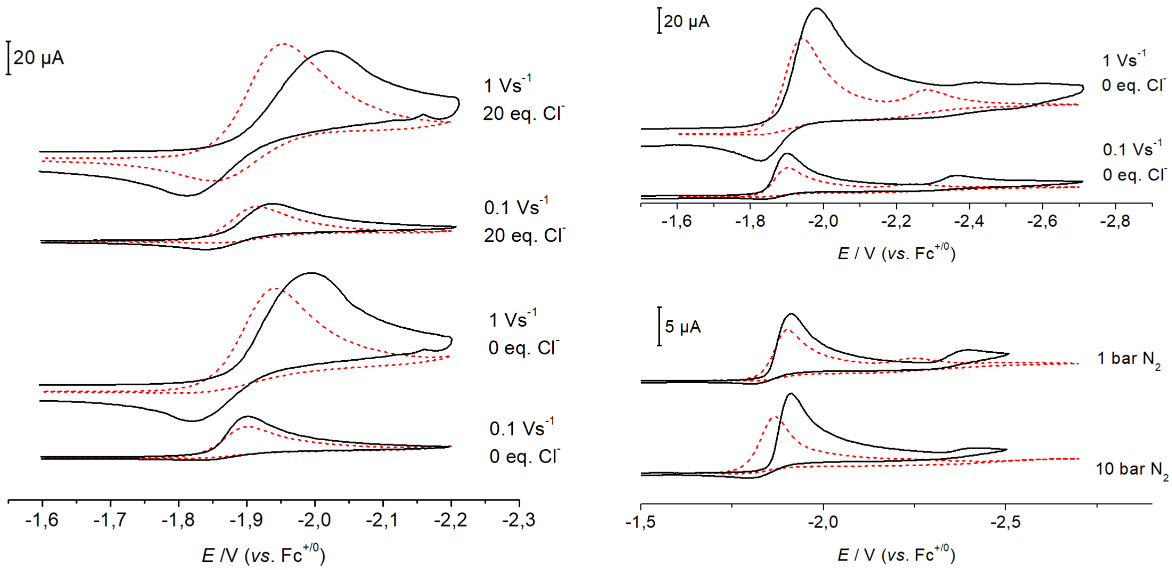


Figure S46. Representative CV data of **1** under different experimental conditions and scan rates under N_2 (I = 0.2 M [^{n}Bu$_4$N][PF$_6$]). Black lines: experimental data; red dashed lines: simulation applying a $C^{N2}EEC^{Cl}C^{dim}$ model for N_2 activation and dimer formation (Scheme S1).

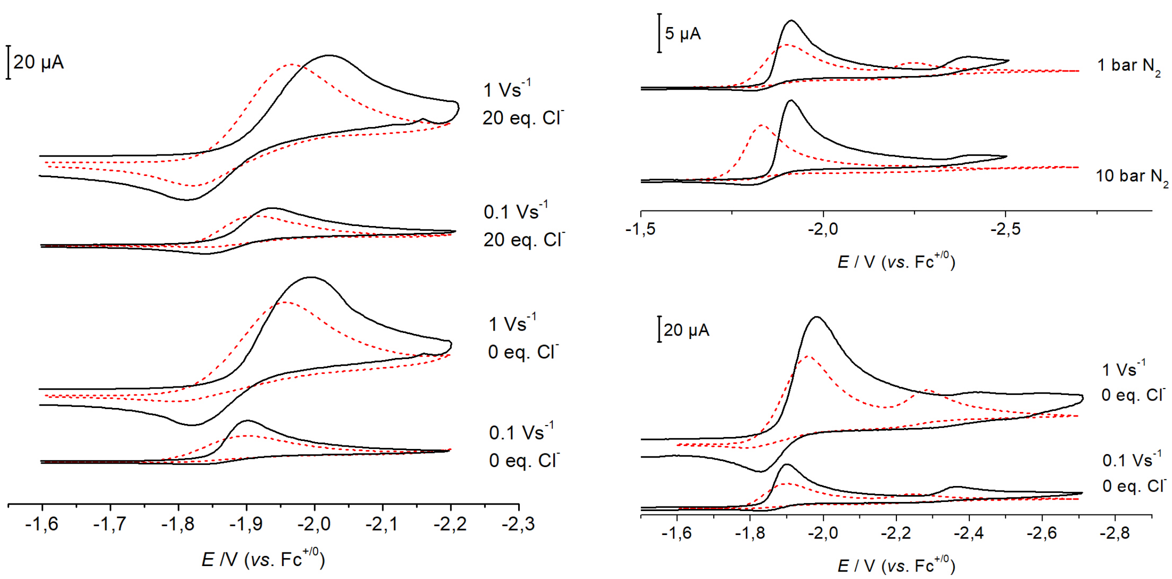


Figure S47. Representative CV data of **1** under different experimental conditions and scan rates under N_2 (I = 0.2 M [^{n}Bu$_4$N][PF$_6$]). Black lines: experimental data; red dashed lines: simulation applying a $C^{N2}EC^{Cl}EC^{dim}$ model for N_2 activation and dimer formation (Scheme S1).

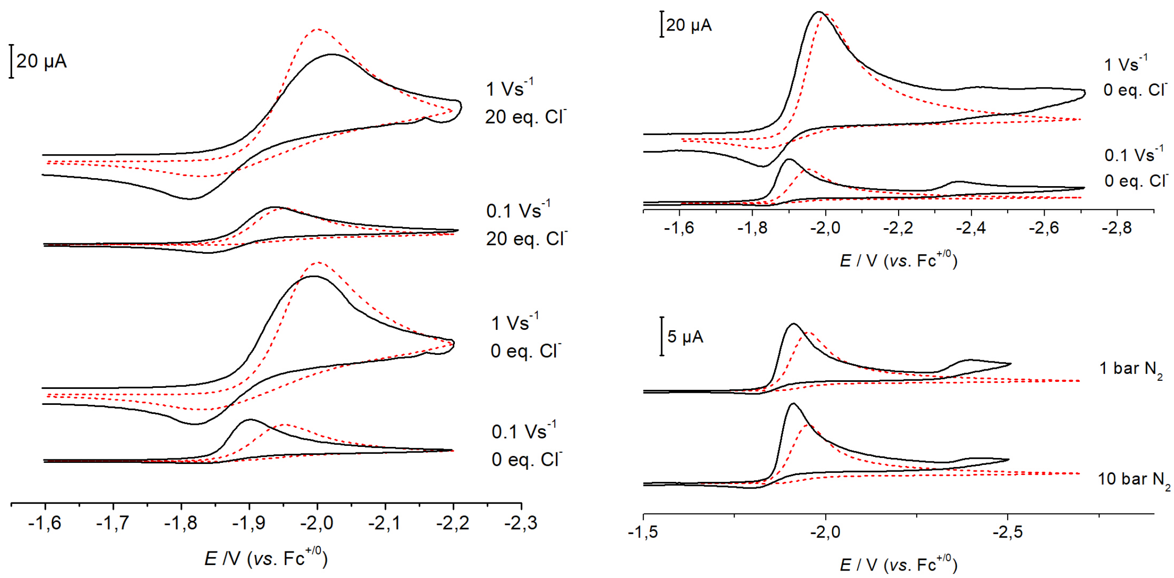


Figure S48. Representative CV data of **1** under different experimental conditions and scan rates under N_2 (I = 0.2 M [^{n}Bu$_4$N][PF$_6$]). Black lines: experimental data; red dashed lines: simulation applying a EC^{Cl}C^{N2}EC^{dim} model for N_2 activation and dimer formation (Scheme S1).

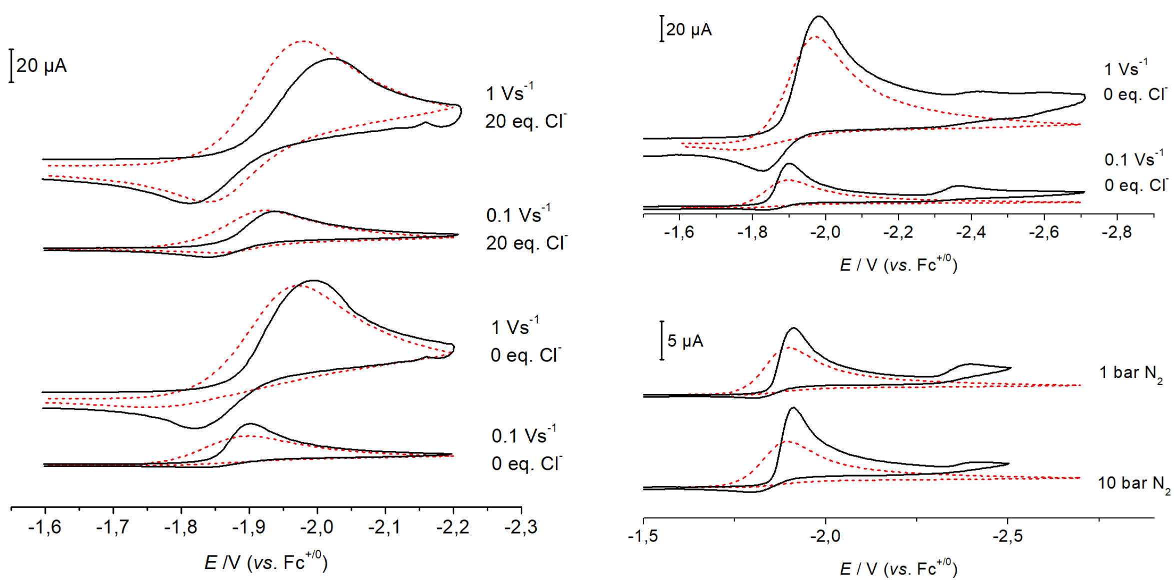


Figure S49. Representative CV data of **1** under different experimental conditions and scan rates under N_2 (I = 0.2 M [^{n}Bu$_4$N][PF$_6$]). Black lines: experimental data; red dashed lines: simulation applying a EC^{N2}EC^{Cl}C^{dim} model for N_2 activation and dimer formation (Scheme S1).

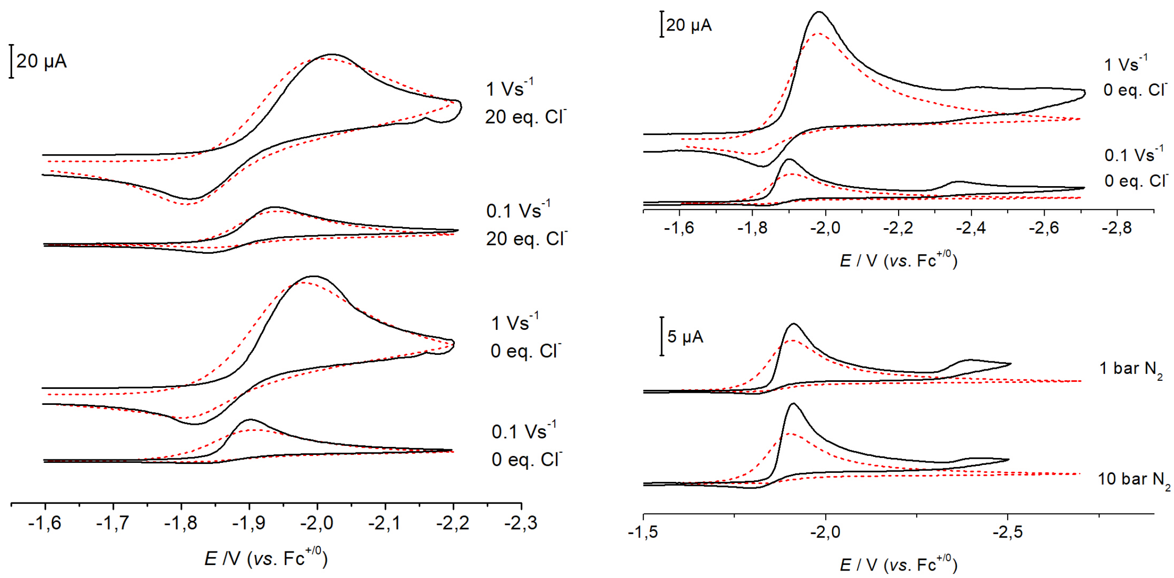


Figure S50. Representative CV data of **1** under different experimental conditions and scan rates under N_2 (I = 0.2 M [^{n}Bu$_4$N][PF$_6$]). Black lines: experimental data; red dashed lines: simulation applying a $EC^{N2}C^{Cl}EC^{dim}$ model for N_2 activation and dimer formation (Scheme S1, parameter values of Tables 1 and 2).

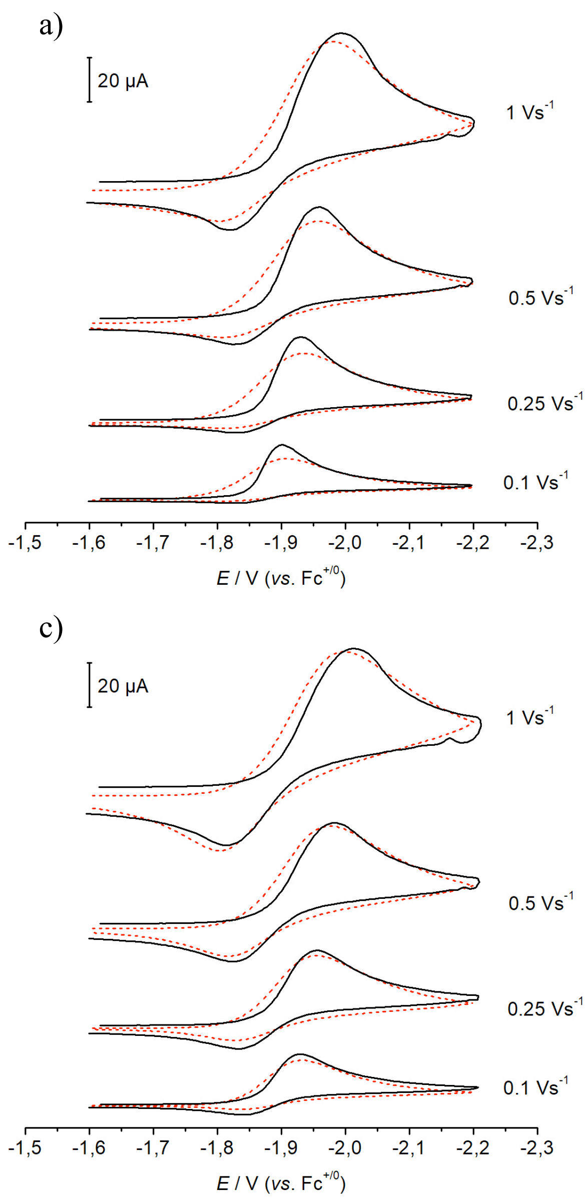


Figure S51. CV data of **1** at different chloride ion concentrations under N_2 (I = 0.2 M [^{n}Bu$_4$N][PF$_6$]), a) 0 eq. [^{n}Bu$_4$N]Cl, b) 5 eq. of [^{n}Bu$_4$N]Cl, c) 10 eq. of [^{n}Bu$_4$N]Cl, d) 20 eq. [^{n}Bu$_4$N]Cl. Black lines: experimental data; red dashed lines: simulation according to Scheme S1 with the parameter values of Tables 1 and 2.

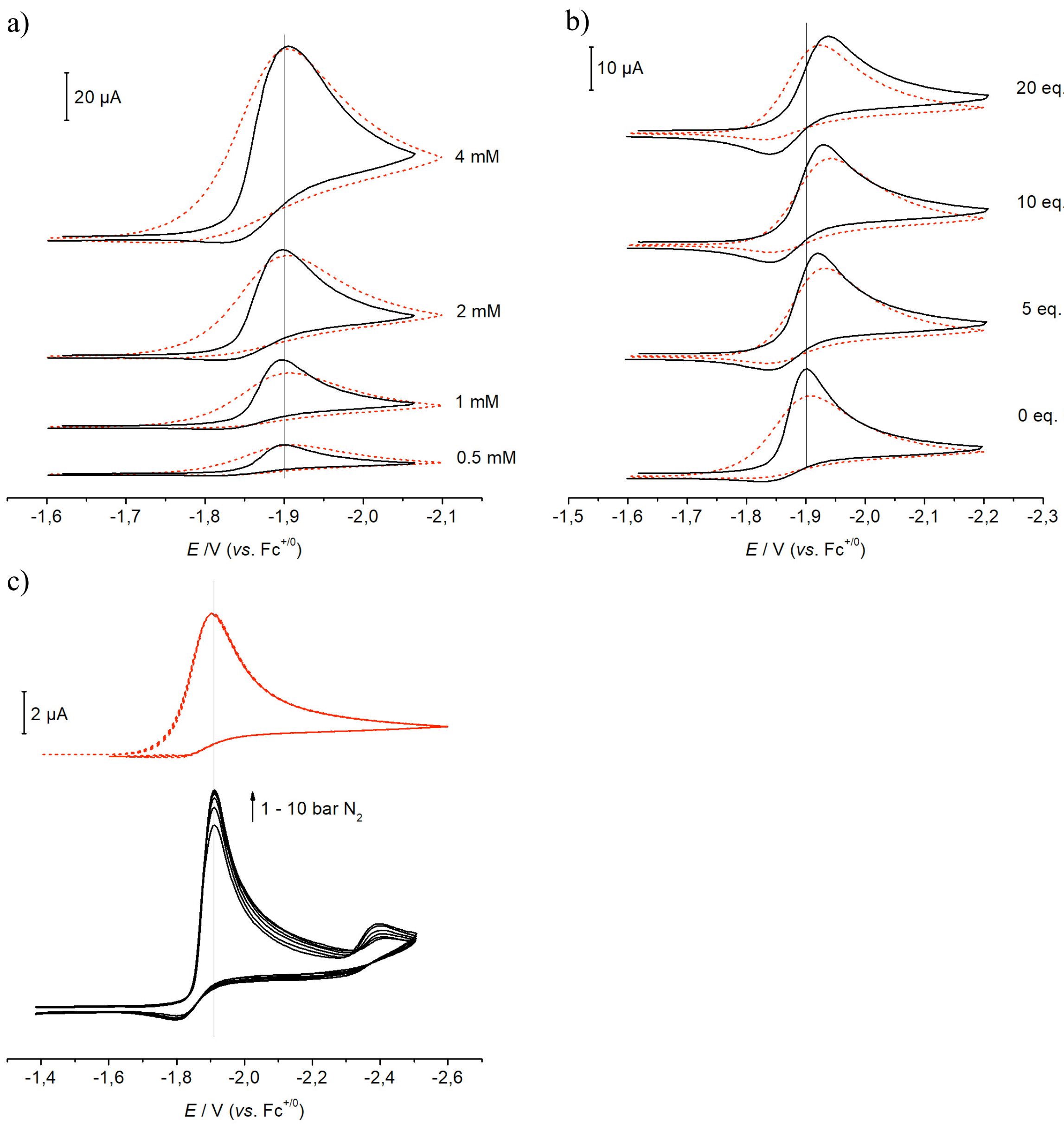


Figure S52. a) Concentration dependent CV data of **1** at rt under N_2 (I = 0.2 M [^{n}Bu$_4$N][PF$_6$], v = 0.1 Vs^{-1}). b) CV data of **1** at different chloride ion concentrations (I = 0.2 M [^{n}Bu$_4$N][PF$_6$], v = 0.1 Vs^{-1}). c) N_2-pressure dependent data of **1** at rt (I = 0.2 M [^{n}Bu$_4$N][PF$_6$], v = 0.1 Vs^{-1}). Black lines: experimental data; red dashed lines: simulation according to Scheme S1 with the parameter values of Tables 1 and 2.

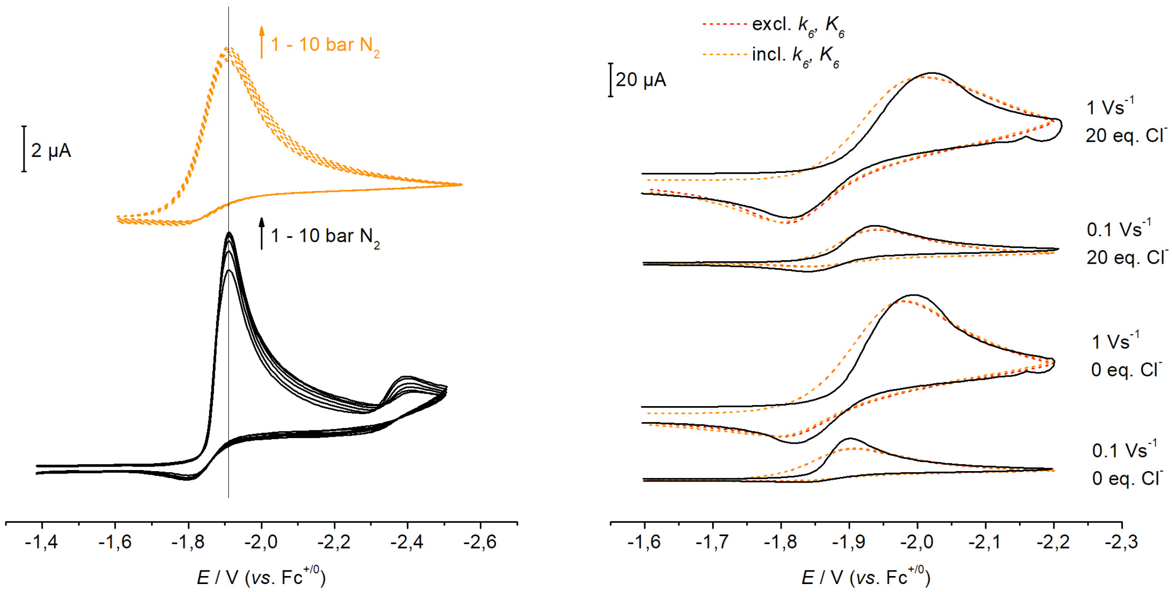


Figure S53. Left: N_2-pressure dependent data of **1** at rt (I = 0.2 M [^{n}Bu$_4$N][PF$_6$], v = 0.1 Vs^{-1}). Right: Representative CV data of **1** under different experimental conditions and scan rates (I = 0.2 M [^{n}Bu$_4$N][PF$_6$]). Black lines: experimental data; orange dashed lines: simulation applying an EC^{N2}C^{Cl}EC^{dim} model for N_2 activation and a further N_2 equilibrium denoted as k_6 and K_6 in Scheme S1 with the parameter values of Tables 1 and 2, k_6 ~ 1000 M^{-1}s^{-1}, and K_6 ~50 M^{-1}; red dashed lines: simulation according to Scheme S1 with the parameter values of Tables 1 and 2.

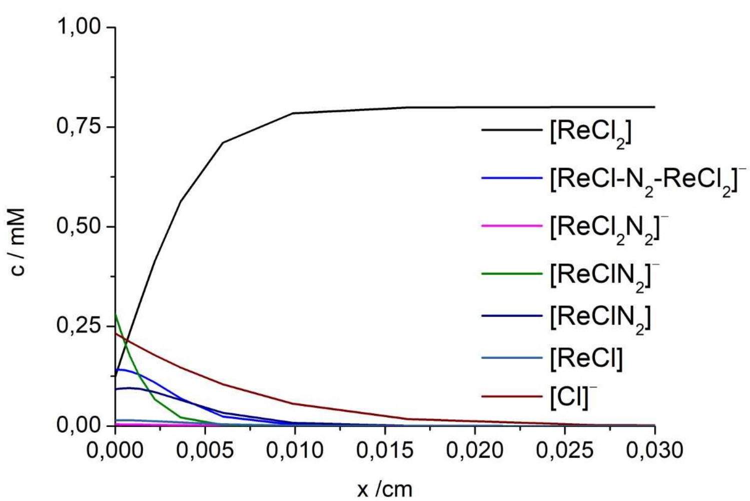


Figure S54. Simulated concentration profile at −1.93 V during a CV of **1** (v = 0.1 Vs^{-1}) under N_2 atmosphere applying the EC^{N2}C^{Cl}EC^{dim} model for N_2 activation (Scheme 5) with the parameters values of Tables 1 and 2.

5. Equilibrium Constant Calculation

The possibility of N_2 coordination to **1** was examined by NMR spectroscopy under 5 bars of N_2 pressure. With no evidence for coordination of N_2, this experiment provides an estimate of the upper limit for the equilibrium constant of N_2 binding to **1** using the expression below. A detection limit of approx. 0.5 mM of $ReCl_2(PNP)(N_2)$ was estimated assuming a signal-to-noise ratio of 3:1.

$$ReCl_2(\mathit{PNP}) + N_2 \xrightleftharpoons{K_{eq}} ReCl_2(\mathit{PNP})(N_2)$$

$$K_{eq} = \frac{[ReCl_2(PNP)(N_2)]}{[ReCl_2(PNP)] * [N_2]}$$

$[ReCl_2(\mathit{PNP})]_{starting} = 21$ mM

$[N_2]_{starting} = 5 * 6.4$ mM = 32 mM [3]

$[ReCl_2(\mathit{PNP})]_{Upper\ limit} \sim 20.5$ mM

$[N_2]_{Upper\ limit} \sim 31.5$ mM

$[ReCl_2(N_2)(\mathit{PNP})]_{Upper\ limit} \sim 0.5$ mM

$$K_{eq} < 7.7 * 10^{-1}\, M^{-1}$$

From this calculation K_{eq} was assumed to be approx. below 1 M^{-1}.

6. Crystallographic Details

6.1. General crystallographic experimental details

CCDC-1832925 (**3**•0.5**1**•0.5**2**•0.5C_5H_{12}) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ products/csd/request/ (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Suitable single crystals for X-ray structure determination were selected from the mother liquor under an inert gas atmosphere and transferred in protective perfluoro polyether oil on a microscope slide. The selected and mounted crystals were transferred to the cold gas stream on the diffractometer. The diffraction data were obtained at 100 K on a Bruker D8 three-circle diffractometer, equipped with a PHOTON 100 CMOS detector and an INCOATEC microfocus source with Quazar mirror optics (Mo-Kα radiation, λ= 0.71073 Å). The data obtained were integrated with SAINT and a semi-empirical absorption correction from equivalents with SADABS was applied. The structure was solved and refined using the Bruker SHELX 2014 software package.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. All C-H hydrogen atoms were refined isotropically on calculated positions by using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp3 carbon atoms and 1.2 times for all other carbon atoms.

*6.2. Crystallographic details of **3***

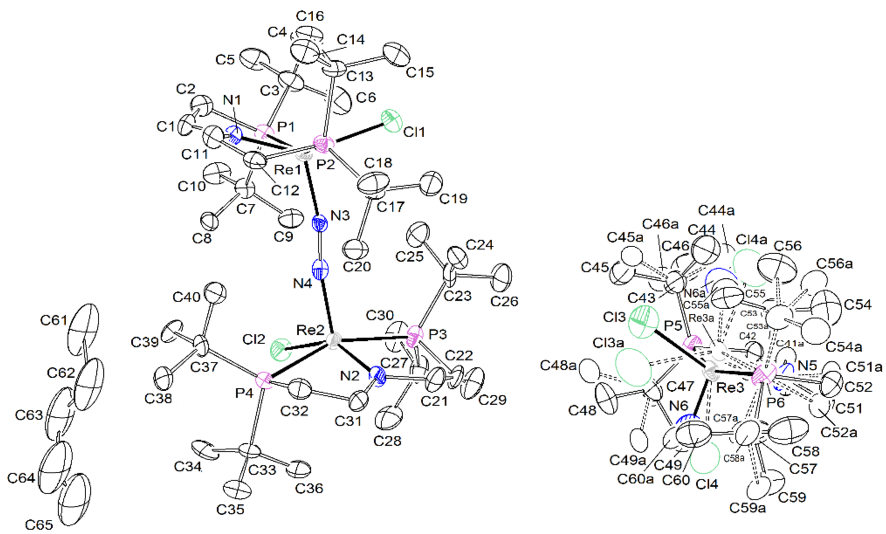


Figure S55. Thermal ellipsoid plot of **3** with the anisotropic displacement parameters drawn at the 50% probability level. The asymmetric unit contains one dimeric species, a monomeric species and a half pentane solvent molecule. The mononuclear species was refined as superimposed [$ReCl_2$(PNP)] (**1**) and [Re(N)Cl(PNP)] (**2**) (with occupation factors of 0.5 for both complexes) using some restraints and constraints (SADI, RIGU, EADP). The pentane solvent molecule was refined using some restraints and constraints (SADI, RIGU, DFIX).

Table S3. Crystal data and structure refinement for **3**•0.5**1**•0.5**2**•0.5C_5H_{12}.

CCDC nr.	1832925	
Empirical formula	$C_{40}H_{88}Cl_2N_4P_4Re$ (100%)	
	$C_{20}H_{44}Cl_2NP_2Re$ (50%)	
	$C_{20}H_{44}ClN_2P_2Re$ (50%)	
	C_5H_{12} (50%)	
Formula weight	1835.27	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.4165(8) Å	α = 90°
	b = 33.602(2) Å	β= 101.313(2)°
	c = 19.7243(14) Å	γ = 90°

Volume	8069.5(9) Å^3	
Z	4	
Density (calculated)	1.511 Mg/m^3	
Absorption coefficient	4.761 mm^{-1}	
F(000)	3704	
Crystal size	0.217 x 0.085 x 0.064 mm^3	
Crystal shape and color	Plate,	clear dark brown
Theta range for data collection	2.228 to 26.451°	
Index ranges	-15<=h<=15, -39<=k<=42, -24<=l<=24	
Reflections collected	143213	
Independent reflections	16610 [R(int) = 0.1745]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16610 / 469 / 963	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0639,	wR2 = 0.1178
R indices (all data)	R1 = 0.1113,	wR2 = 0.1328
Largest diff. peak and hole	2.340 and -1.787 eÅ^{-3}	

Table S4. Bond lengths [Å] and angles [°] for **3**.

Re(1)-N(3)	1.861(8)	P(3)-C(22)	1.845(11)
Re(1)-N(1)	1.937(7)	P(3)-C(23)	1.878(11)
Re(1)-P(2)	2.405(3)	P(3)-C(27)	1.898(11)
Re(1)-P(1)	2.406(3)	P(4)-C(32)	1.817(11)
Re(1)-Cl(1)	2.463(3)	P(4)-C(37)	1.871(10)
Re(2)-N(4)	1.886(8)	P(4)-C(33)	1.910(10)
Re(2)-N(2)	1.949(8)	N(1)-C(1)	1.469(12)
Re(2)-P(4)	2.406(3)	N(1)-C(11)	1.486(11)
Re(2)-P(3)	2.409(3)	N(2)-C(21)	1.469(12)
Re(2)-Cl(2)	2.455(3)	N(2)-C(31)	1.482(13)
P(1)-C(2)	1.851(11)	N(3)-N(4)	1.202(10)
P(1)-C(3)	1.888(11)	N(5)-C(51A)	1.432(18)
P(1)-C(7)	1.895(10)	N(5)-C(41)	1.441(12)
P(2)-C(12)	1.831(10)	N(5)-C(51)	1.449(12)
P(2)-C(17)	1.892(10)	N(5)-C(41A)	1.451(18)
P(2)-C(13)	1.915(10)	N(5)-Re(3A)	2.041(9)

N(5)-Re(3)	2.106(9)	C(57)-P(6)	1.875(12)
C(1)-C(2)	1.516(14)	C(42)-P(5)	1.854(10)
C(3)-C(6)	1.546(16)	C(51)-C(52)	1.499(14)
C(3)-C(4)	1.547(15)	C(50)-C(47)	1.49(2)
C(3)-C(5)	1.551(15)	C(49)-C(47)	1.57(2)
C(7)-C(9)	1.531(14)	C(48)-C(47)	1.490(18)
C(7)-C(10)	1.537(13)	C(46)-C(43)	1.519(14)
C(7)-C(8)	1.546(14)	C(45)-C(43)	1.510(13)
C(11)-C(12)	1.496(14)	C(44)-C(43)	1.554(14)
C(13)-C(16)	1.525(14)	C(52)-P(6)	1.857(11)
C(13)-C(15)	1.538(14)	C(53)-C(55)	1.517(14)
C(13)-C(14)	1.542(14)	C(53)-C(56)	1.521(15)
C(17)-C(20)	1.525(13)	C(53)-C(54)	1.524(14)
C(17)-C(18)	1.526(14)	C(53)-P(6)	1.88(2)
C(17)-C(19)	1.541(15)	Re(3A)-Cl(3A)	2.351(14)
C(21)-C(22)	1.513(14)	Re(3A)-P(5)	2.401(4)
C(23)-C(24)	1.525(15)	Re(3A)-P(6)	2.426(4)
C(23)-C(26)	1.530(14)	C(41A)-C(42A)	1.50(2)
C(23)-C(25)	1.536(15)	C(42A)-P(5)	1.859(17)
C(27)-C(30)	1.520(16)	C(51A)-C(52A)	1.50(2)
C(27)-C(28)	1.547(17)	C(50A)-C(47)	1.65(6)
C(27)-C(29)	1.549(15)	C(49A)-C(47)	1.49(5)
C(31)-C(32)	1.507(14)	C(48A)-C(47)	1.78(6)
C(33)-C(34)	1.523(17)	C(46A)-C(43)	1.537(18)
C(33)-C(35)	1.526(17)	C(45A)-C(43)	1.514(18)
C(33)-C(36)	1.531(16)	C(44A)-C(43)	1.524(18)
C(37)-C(39)	1.518(16)	C(52A)-P(6)	1.862(17)
C(37)-C(40)	1.529(15)	C(53A)-C(56A)	1.518(18)
C(37)-C(38)	1.539(15)	C(53A)-C(55A)	1.520(18)
Re(3)-Cl(3)	2.374(5)	C(53A)-C(54A)	1.524(18)
Re(3)-P(6)	2.434(3)	C(53A)-P(6)	1.91(8)
Re(3)-P(5)	2.449(3)	C(58A)-C(57A)	1.56(10)
C(41)-C(42)	1.493(14)	C(57A)-C(59A)	1.50(12)
C(60)-C(57)	1.52(3)	C(57A)-C(60A)	1.67(9)
C(59)-C(57)	1.51(4)	C(57A)-P(6)	1.868(17)
C(58)-C(57)	1.51(3)	P(5)-C(47)	1.864(12)

P(5)-C(43)	1.868(12)	C(17)-P(2)-Re(1)	123.8(3)
C(61)-C(62)	1.462(14)	C(13)-P(2)-Re(1)	112.0(3)
C(62)-C(63)	1.435(18)	C(22)-P(3)-C(23)	102.9(5)
C(63)-C(64)	1.469(19)	C(22)-P(3)-C(27)	101.8(5)
C(64)-C(65)	1.43(2)	C(23)-P(3)-C(27)	110.9(5)
		C(22)-P(3)-Re(2)	100.5(3)
N(3)-Re(1)-N(1)	118.0(3)	C(23)-P(3)-Re(2)	118.4(3)
N(3)-Re(1)-P(2)	101.5(2)	C(27)-P(3)-Re(2)	118.6(4)
N(1)-Re(1)-P(2)	80.8(2)	C(32)-P(4)-C(37)	104.1(5)
N(3)-Re(1)-P(1)	99.3(2)	C(32)-P(4)-C(33)	104.6(5)
N(1)-Re(1)-P(1)	81.6(2)	C(37)-P(4)-C(33)	109.7(5)
P(2)-Re(1)-P(1)	157.38(9)	C(32)-P(4)-Re(2)	99.5(4)
N(3)-Re(1)-Cl(1)	95.5(2)	C(37)-P(4)-Re(2)	123.7(3)
N(1)-Re(1)-Cl(1)	146.3(2)	C(33)-P(4)-Re(2)	112.6(4)
P(2)-Re(1)-Cl(1)	89.39(9)	C(1)-N(1)-C(11)	107.3(7)
P(1)-Re(1)-Cl(1)	97.45(9)	C(1)-N(1)-Re(1)	126.9(6)
N(4)-Re(2)-N(2)	119.3(3)	C(11)-N(1)-Re(1)	125.3(6)
N(4)-Re(2)-P(4)	102.8(2)	C(21)-N(2)-C(31)	107.1(8)
N(2)-Re(2)-P(4)	80.5(2)	C(21)-N(2)-Re(2)	126.9(6)
N(4)-Re(2)-P(3)	99.3(2)	C(31)-N(2)-Re(2)	125.6(6)
N(2)-Re(2)-P(3)	81.3(2)	N(4)-N(3)-Re(1)	167.9(7)
P(4)-Re(2)-P(3)	156.28(9)	N(3)-N(4)-Re(2)	168.4(7)
N(4)-Re(2)-Cl(2)	94.0(2)	C(41)-N(5)-C(51)	113.5(9)
N(2)-Re(2)-Cl(2)	146.6(3)	C(51A)-N(5)-C(41A)	115(3)
P(4)-Re(2)-Cl(2)	90.23(10)	C(51A)-N(5)-Re(3A)	119(2)
P(3)-Re(2)-Cl(2)	96.76(9)	C(41A)-N(5)-Re(3A)	109(2)
C(2)-P(1)-C(3)	101.2(5)	C(41)-N(5)-Re(3)	120.1(7)
C(2)-P(1)-C(7)	103.0(5)	C(51)-N(5)-Re(3)	118.1(8)
C(3)-P(1)-C(7)	111.2(5)	N(1)-C(1)-C(2)	113.2(8)
C(2)-P(1)-Re(1)	100.8(3)	C(1)-C(2)-P(1)	109.4(7)
C(3)-P(1)-Re(1)	119.1(4)	C(6)-C(3)-C(4)	107.7(10)
C(7)-P(1)-Re(1)	117.7(3)	C(6)-C(3)-C(5)	108.8(9)
C(12)-P(2)-C(17)	105.2(5)	C(4)-C(3)-C(5)	108.4(9)
C(12)-P(2)-C(13)	103.9(5)	C(6)-C(3)-P(1)	109.3(8)
C(17)-P(2)-C(13)	110.8(4)	C(4)-C(3)-P(1)	106.9(7)
C(12)-P(2)-Re(1)	98.0(3)	C(5)-C(3)-P(1)	115.5(8)

C(9)-C(7)-C(10)	108.6(8)	C(34)-C(33)-C(35)	110.7(10)
C(9)-C(7)-C(8)	109.6(8)	C(34)-C(33)-C(36)	107.1(11)
C(10)-C(7)-C(8)	108.3(9)	C(35)-C(33)-C(36)	108.4(10)
C(9)-C(7)-P(1)	110.1(7)	C(34)-C(33)-P(4)	110.9(8)
C(10)-C(7)-P(1)	115.1(7)	C(35)-C(33)-P(4)	112.6(9)
C(8)-C(7)-P(1)	105.0(6)	C(36)-C(33)-P(4)	106.9(7)
N(1)-C(11)-C(12)	113.7(8)	C(39)-C(37)-C(40)	106.4(9)
C(11)-C(12)-P(2)	109.0(7)	C(39)-C(37)-C(38)	111.0(10)
C(16)-C(13)-C(15)	107.6(9)	C(40)-C(37)-C(38)	107.6(10)
C(16)-C(13)-C(14)	107.6(8)	C(39)-C(37)-P(4)	110.5(8)
C(15)-C(13)-C(14)	109.7(8)	C(40)-C(37)-P(4)	107.8(7)
C(16)-C(13)-P(2)	108.0(6)	C(38)-C(37)-P(4)	113.2(8)
C(15)-C(13)-P(2)	111.3(7)	N(5)-Re(3)-Cl(3)	151.0(3)
C(14)-C(13)-P(2)	112.4(7)	N(5)-Re(3)-P(6)	80.3(2)
C(20)-C(17)-C(18)	107.8(9)	Cl(3)-Re(3)-P(6)	94.13(13)
C(20)-C(17)-C(19)	107.0(9)	N(5)-Re(3)-P(5)	79.9(2)
C(18)-C(17)-C(19)	111.4(9)	Cl(3)-Re(3)-P(5)	96.01(12)
C(20)-C(17)-P(2)	107.2(7)	P(6)-Re(3)-P(5)	155.26(10)
C(18)-C(17)-P(2)	113.4(7)	N(5)-C(41)-C(42)	112.5(10)
C(19)-C(17)-P(2)	109.7(7)	C(59)-C(57)-C(58)	109.6(19)
N(2)-C(21)-C(22)	111.7(8)	C(59)-C(57)-C(60)	108(2)
C(21)-C(22)-P(3)	110.4(7)	C(58)-C(57)-C(60)	111(2)
C(24)-C(23)-C(26)	108.2(9)	C(59)-C(57)-P(6)	107.7(16)
C(24)-C(23)-C(25)	107.9(9)	C(58)-C(57)-P(6)	113.5(15)
C(26)-C(23)-C(25)	108.8(9)	C(60)-C(57)-P(6)	107.1(13)
C(24)-C(23)-P(3)	105.7(7)	C(41)-C(42)-P(5)	110.7(9)
C(26)-C(23)-P(3)	114.7(8)	N(5)-C(51)-C(52)	115.9(11)
C(25)-C(23)-P(3)	111.1(7)	C(51)-C(52)-P(6)	108.8(9)
C(30)-C(27)-C(28)	110.5(10)	C(55)-C(53)-C(56)	107.2(16)
C(30)-C(27)-C(29)	109.9(10)	C(55)-C(53)-C(54)	105.7(17)
C(28)-C(27)-C(29)	107.8(10)	C(56)-C(53)-C(54)	109.5(16)
C(30)-C(27)-P(3)	108.9(8)	C(55)-C(53)-P(6)	111.8(14)
C(28)-C(27)-P(3)	106.4(8)	C(56)-C(53)-P(6)	106.5(13)
C(29)-C(27)-P(3)	113.4(8)	C(54)-C(53)-P(6)	115.8(13)
N(2)-C(31)-C(32)	114.1(8)	N(5)-Re(3A)-Cl(3A)	148.2(7)
C(31)-C(32)-P(4)	108.7(8)	N(5)-Re(3A)-P(5)	82.3(3)

Cl(3A)-Re(3A)-P(5)	91.4(6)	C(52A)-P(6)-C(53A)	119(2)
N(5)-Re(3A)-P(6)	81.8(3)	C(57A)-P(6)-C(53A)	107(4)
Cl(3A)-Re(3A)-P(6)	98.1(6)	C(52A)-P(6)-Re(3A)	93.9(16)
P(5)-Re(3A)-P(6)	162.38(17)	C(57A)-P(6)-Re(3A)	122(3)
N(5)-C(41A)-C(42A)	120(3)	C(53A)-P(6)-Re(3A)	114.6(15)
C(41A)-C(42A)-P(5)	98(3)	C(52)-P(6)-Re(3)	102.5(4)
N(5)-C(51A)-C(52A)	102(3)	C(57)-P(6)-Re(3)	117.9(8)
C(51A)-C(52A)-P(6)	111(3)	C(53)-P(6)-Re(3)	117.6(5)
C(56A)-C(53A)-C(55A)	111(6)	C(45)-C(43)-C(46)	113.1(15)
C(56A)-C(53A)-C(54A)	105(5)	C(45A)-C(43)-C(44A)	117(4)
C(55A)-C(53A)-C(54A)	117(6)	C(45A)-C(43)-C(46A)	100(5)
C(56A)-C(53A)-P(6)	102(4)	C(44A)-C(43)-C(46A)	103(4)
C(55A)-C(53A)-P(6)	106(5)	C(45)-C(43)-C(44)	103.0(13)
C(54A)-C(53A)-P(6)	115(5)	C(46)-C(43)-C(44)	109.3(14)
C(59A)-C(57A)-C(58A)	99(4)	C(45)-C(43)-P(5)	110.4(10)
C(59A)-C(57A)-C(60A)	102(6)	C(45A)-C(43)-P(5)	122(3)
C(58A)-C(57A)-C(60A)	96(5)	C(46)-C(43)-P(5)	115.2(10)
C(59A)-C(57A)-P(6)	122(6)	C(44A)-C(43)-P(5)	103(2)
C(58A)-C(57A)-P(6)	122(5)	C(46A)-C(43)-P(5)	110(3)
C(60A)-C(57A)-P(6)	111(4)	C(44)-C(43)-P(5)	104.7(10)
C(42)-P(5)-C(47)	108.1(6)	C(48)-C(47)-C(50)	114.0(13)
C(42A)-P(5)-C(47)	91.0(14)	C(48)-C(47)-C(49)	105.3(12)
C(42)-P(5)-C(43)	101.7(5)	C(50)-C(47)-C(49)	108.3(12)
C(42A)-P(5)-C(43)	116.3(18)	C(49A)-C(47)-C(50A)	100(3)
C(47)-P(5)-C(43)	110.1(6)	C(49A)-C(47)-C(48A)	91(3)
C(42A)-P(5)-Re(3A)	102.8(14)	C(50A)-C(47)-C(48A)	99(3)
C(47)-P(5)-Re(3A)	128.1(4)	C(48)-C(47)-P(5)	108.4(9)
C(43)-P(5)-Re(3A)	107.7(4)	C(49A)-C(47)-P(5)	126(2)
C(42)-P(5)-Re(3)	100.8(4)	C(50)-C(47)-P(5)	115.5(10)
C(47)-P(5)-Re(3)	114.9(4)	C(49)-C(47)-P(5)	104.4(9)
C(43)-P(5)-Re(3)	119.3(4)	C(50A)-C(47)-P(5)	123(3)
C(52A)-P(6)-C(57A)	101(4)	C(48A)-C(47)-P(5)	109(2)
C(52)-P(6)-C(57)	105.6(10)	C(63)-C(62)-C(61)	118.2(19)
C(52)-P(6)-C(53)	99.6(7)	C(62)-C(63)-C(64)	116(2)
C(57)-P(6)-C(53)	110.6(11)	C(65)-C(64)-C(63)	116(2)

Table S5. Torsion angles [°] for **3**.

N(1)-Re(1)-N(3)-N(4)	10(3)
P(2)-Re(1)-N(3)-N(4)	96(3)
P(1)-Re(1)-N(3)-N(4)	-75(3)
Cl(1)-Re(1)-N(3)-N(4)	-174(3)
Re(1)-N(3)-N(4)-Re(2)	-140(3)
N(2)-Re(2)-N(4)-N(3)	25(4)
P(4)-Re(2)-N(4)-N(3)	112(3)
P(3)-Re(2)-N(4)-N(3)	-60(3)
Cl(2)-Re(2)-N(4)-N(3)	-157(3)
C(11)-N(1)-C(1)-C(2)	161.1(8)
Re(1)-N(1)-C(1)-C(2)	-25.7(12)
N(1)-C(1)-C(2)-P(1)	31.1(10)
C(3)-P(1)-C(2)-C(1)	-146.8(7)
C(7)-P(1)-C(2)-C(1)	98.1(7)
Re(1)-P(1)-C(2)-C(1)	-24.0(7)
C(2)-P(1)-C(3)-C(6)	-171.1(8)
C(7)-P(1)-C(3)-C(6)	-62.3(9)
Re(1)-P(1)-C(3)-C(6)	79.6(8)
C(2)-P(1)-C(3)-C(4)	72.7(9)
C(7)-P(1)-C(3)-C(4)	-178.5(8)
Re(1)-P(1)-C(3)-C(4)	-36.6(9)
C(2)-P(1)-C(3)-C(5)	-48.0(9)
C(7)-P(1)-C(3)-C(5)	60.8(10)
Re(1)-P(1)-C(3)-C(5)	-157.3(7)
C(2)-P(1)-C(7)-C(9)	-173.4(7)
C(3)-P(1)-C(7)-C(9)	78.9(8)
Re(1)-P(1)-C(7)-C(9)	-63.6(8)
C(2)-P(1)-C(7)-C(10)	63.5(9)
C(3)-P(1)-C(7)-C(10)	-44.2(9)
Re(1)-P(1)-C(7)-C(10)	173.3(7)
C(2)-P(1)-C(7)-C(8)	-55.5(7)
C(3)-P(1)-C(7)-C(8)	-163.2(7)
Re(1)-P(1)-C(7)-C(8)	54.3(7)
C(1)-N(1)-C(11)-C(12)	167.2(8)
Re(1)-N(1)-C(11)-C(12)	-6.1(12)

N(1)-C(11)-C(12)-P(2)	31.3(10)
C(17)-P(2)-C(12)-C(11)	-165.0(7)
C(13)-P(2)-C(12)-C(11)	78.5(7)
Re(1)-P(2)-C(12)-C(11)	-36.6(7)
C(12)-P(2)-C(17)-C(20)	59.3(8)
C(13)-P(2)-C(17)-C(20)	170.9(7)
Re(1)-P(2)-C(17)-C(20)	-51.5(8)
C(12)-P(2)-C(17)-C(18)	-59.5(8)
C(13)-P(2)-C(17)-C(18)	52.1(9)
Re(1)-P(2)-C(17)-C(18)	-170.3(6)
C(12)-P(2)-C(17)-C(19)	175.2(7)
C(13)-P(2)-C(17)-C(19)	-73.2(8)
Re(1)-P(2)-C(17)-C(19)	64.4(7)
C(31)-N(2)-C(21)-C(22)	157.0(9)
Re(2)-N(2)-C(21)-C(22)	-29.8(13)
N(2)-C(21)-C(22)-P(3)	33.1(11)
C(23)-P(3)-C(22)-C(21)	98.7(8)
C(27)-P(3)-C(22)-C(21)	-146.4(8)
Re(2)-P(3)-C(22)-C(21)	-24.0(8)
C(22)-P(3)-C(23)-C(24)	-55.4(8)
C(27)-P(3)-C(23)-C(24)	-163.6(7)
Re(2)-P(3)-C(23)-C(24)	54.4(7)
C(22)-P(3)-C(23)-C(26)	63.8(9)
C(27)-P(3)-C(23)-C(26)	-44.4(9)
Re(2)-P(3)-C(23)-C(26)	173.6(7)
C(22)-P(3)-C(23)-C(25)	-172.2(8)
C(27)-P(3)-C(23)-C(25)	79.6(8)
Re(2)-P(3)-C(23)-C(25)	-62.5(8)
C(22)-P(3)-C(27)-C(30)	-168.7(8)
C(23)-P(3)-C(27)-C(30)	-59.8(9)
Re(2)-P(3)-C(27)-C(30)	82.2(9)
C(22)-P(3)-C(27)-C(28)	72.2(8)
C(23)-P(3)-C(27)-C(28)	-178.9(7)
Re(2)-P(3)-C(27)-C(28)	-36.8(9)
C(22)-P(3)-C(27)-C(29)	-46.1(10)
C(23)-P(3)-C(27)-C(29)	62.8(10)

Re(2)-P(3)-C(27)-C(29)	-155.2(8)
C(21)-N(2)-C(31)-C(32)	165.3(9)
Re(2)-N(2)-C(31)-C(32)	-8.0(13)
N(2)-C(31)-C(32)-P(4)	30.5(11)
C(37)-P(4)-C(32)-C(31)	-163.0(7)
C(33)-P(4)-C(32)-C(31)	81.9(8)
Re(2)-P(4)-C(32)-C(31)	-34.6(8)
C(32)-P(4)-C(37)-C(39)	173.4(8)
C(33)-P(4)-C(37)-C(39)	-75.1(9)
Re(2)-P(4)-C(37)-C(39)	61.7(9)
C(32)-P(4)-C(37)-C(40)	57.6(9)
C(33)-P(4)-C(37)-C(40)	169.0(8)
Re(2)-P(4)-C(37)-C(40)	-54.2(9)
C(32)-P(4)-C(37)-C(38)	-61.4(10)
C(33)-P(4)-C(37)-C(38)	50.1(11)
Re(2)-P(4)-C(37)-C(38)	-173.1(8)
C(51)-N(5)-C(41)-C(42)	-166.7(12)
Re(3)-N(5)-C(41)-C(42)	45.8(15)
N(5)-C(41)-C(42)-P(5)	-41.8(15)
C(41)-N(5)-C(51)-C(52)	166.2(13)
Re(3)-N(5)-C(51)-C(52)	-45.5(17)
N(5)-C(51)-C(52)-P(6)	38.1(17)
C(51A)-N(5)-C(41A)-C(42A)	162(5)
Re(3A)-N(5)-C(41A)-C(42A)	-61(5)
N(5)-C(41A)-C(42A)-P(5)	57(5)
C(41A)-N(5)-C(51A)-C(52A)	-170(4)
Re(3A)-N(5)-C(51A)-C(52A)	57(5)
N(5)-C(51A)-C(52A)-P(6)	-60(5)
C(41)-C(42)-P(5)-C(47)	-99.3(11)
C(41)-C(42)-P(5)-C(43)	144.9(10)
C(41)-C(42)-P(5)-Re(3)	21.7(11)
C(41A)-C(42A)-P(5)-C(47)	-156(3)
C(41A)-C(42A)-P(5)-C(43)	91(3)
C(41A)-C(42A)-P(5)-Re(3A)	-26(3)
C(51)-C(52)-P(6)-C(57)	107.8(14)
C(51)-C(52)-P(6)-C(53)	-137.5(12)

C(51)-C(52)-P(6)-Re(3)	-16.2(12)
C(51A)-C(52A)-P(6)-C(57A)	161(4)
C(51A)-C(52A)-P(6)-C(53A)	-83(4)
C(51A)-C(52A)-P(6)-Re(3A)	38(4)
C(59A)-C(57A)-P(6)-C(52A)	-14(8)
C(58A)-C(57A)-P(6)-C(52A)	113(6)
C(60A)-C(57A)-P(6)-C(52A)	-135(6)
C(59A)-C(57A)-P(6)-C(53A)	-139(7)
C(58A)-C(57A)-P(6)-C(53A)	-12(7)
C(60A)-C(57A)-P(6)-C(53A)	100(6)
C(59A)-C(57A)-P(6)-Re(3A)	87(7)
C(58A)-C(57A)-P(6)-Re(3A)	-146(5)
C(60A)-C(57A)-P(6)-Re(3A)	-34(7)
C(59)-C(57)-P(6)-C(52)	-51.3(19)
C(58)-C(57)-P(6)-C(52)	70(2)
C(60)-C(57)-P(6)-C(52)	-166.8(15)
C(59)-C(57)-P(6)-C(53)	-158.2(17)
C(58)-C(57)-P(6)-C(53)	-37(2)
C(60)-C(57)-P(6)-C(53)	86.3(17)
C(59)-C(57)-P(6)-Re(3)	62.4(19)
C(58)-C(57)-P(6)-Re(3)	-176.0(14)
C(60)-C(57)-P(6)-Re(3)	-53(2)
C(55)-C(53)-P(6)-C(52)	-168.5(12)
C(56)-C(53)-P(6)-C(52)	74.7(13)
C(54)-C(53)-P(6)-C(52)	-47.4(13)
C(55)-C(53)-P(6)-C(57)	-57.7(14)
C(56)-C(53)-P(6)-C(57)	-174.5(14)
C(54)-C(53)-P(6)-C(57)	63.4(15)
C(55)-C(53)-P(6)-Re(3)	81.8(12)
C(56)-C(53)-P(6)-Re(3)	-35.0(14)
C(54)-C(53)-P(6)-Re(3)	-157.1(11)
C(42)-P(5)-C(43)-C(45)	174.1(12)
C(47)-P(5)-C(43)-C(45)	59.7(12)
Re(3)-P(5)-C(43)-C(45)	-76.3(12)
C(42A)-P(5)-C(43)-C(45A)	-179(4)
C(47)-P(5)-C(43)-C(45A)	80(4)

Re(3A)-P(5)-C(43)-C(45A)	-64(4)
C(42)-P(5)-C(43)-C(46)	44.4(13)
C(47)-P(5)-C(43)-C(46)	-70.0(13)
Re(3)-P(5)-C(43)-C(46)	154.0(11)
C(42A)-P(5)-C(43)-C(44A)	-45(3)
C(47)-P(5)-C(43)-C(44A)	-147(2)
Re(3A)-P(5)-C(43)-C(44A)	69(2)
C(42A)-P(5)-C(43)-C(46A)	64(3)
C(47)-P(5)-C(43)-C(46A)	-38(3)
Re(3A)-P(5)-C(43)-C(46A)	178(3)
C(42)-P(5)-C(43)-C(44)	-75.7(10)
C(47)-P(5)-C(43)-C(44)	169.9(9)
Re(3)-P(5)-C(43)-C(44)	33.9(10)
C(42)-P(5)-C(47)-C(48)	162.1(10)
C(43)-P(5)-C(47)-C(48)	-87.6(11)
Re(3)-P(5)-C(47)-C(48)	50.4(11)
C(42A)-P(5)-C(47)-C(49A)	86(3)
C(43)-P(5)-C(47)-C(49A)	-155(3)
Re(3A)-P(5)-C(47)-C(49A)	-21(3)
C(42)-P(5)-C(47)-C(50)	-68.5(13)
C(43)-P(5)-C(47)-C(50)	41.7(12)
Re(3)-P(5)-C(47)-C(50)	179.8(10)
C(42)-P(5)-C(47)-C(49)	50.2(9)
C(43)-P(5)-C(47)-C(49)	160.5(8)
Re(3)-P(5)-C(47)-C(49)	-61.4(9)
C(42A)-P(5)-C(47)-C(50A)	-51(3)
C(43)-P(5)-C(47)-C(50A)	67(3)
Re(3A)-P(5)-C(47)-C(50A)	-158(3)
C(42A)-P(5)-C(47)-C(48A)	-167(3)
C(43)-P(5)-C(47)-C(48A)	-48(2)
Re(3A)-P(5)-C(47)-C(48A)	86(2)
C(61)-C(62)-C(63)-C(64)	-162(3)
C(62)-C(63)-C(64)-C(65)	-122(4)

7. DFT Calculations

7.1. Computational details

All calculations were performed within the ORCA program package.[4] The optimization of the molecular structures was carried out using the PBE[5] functional, Grimme's dispersion correction with Becke-Johnson damping (D3(BJ))[6] and the Resolution of Identity (RI-*J*)[7] approach to minimize computational costs. Ahlrichs' revised def2-SVP basis set and the corresponding auxiliary basis set were used with an all electron basis for all elements but Re for which a Stuttgart-Dresden 60 electron core potential replaced the inner shell 1s-4f orbitals.[8] Tight convergence criteria in the SCF procedure and optimization and a fine integration grid (Grid 5) were applied in all calculations. No symmetry restrains were imposed and the optimized (gas phase) structures were defined as minima (no negative eigenvalue) or transition states (one negative eigenvalue) by vibrational analyses at the D3(BJ)-RI-*J*-PBE/def2-SVP level of theory. Transition states were verified by distortion of the structures along the reaction mode followed by full optimizations.

The free energies were calculated according to established procedures for redox potentials applying thermodynamic cycles to estimate the free energies in solution (G_{sol}):[9]

$$G_{sol} = G_{gas}^{g} + \Delta G_{corr} + E_{sol}^{s} - E_{gas}^{g}$$

E_{gas}^{g} and G_{gas}^{g} are the electronic and the gas phase free energy, respectively, that were obtained for the gas-phase geometries at the D3(BJ)-RI-*J*-PBE/def2-SVP level. In this respect, Grimme's quasi-RRHO approach which treats low energy frequencies below 35 cm^{-1} as free rotors instead of harmonic vibrations was applied for the vibrational partition function.[10] The (translational) free energy of the chloride anion has been calculated (1 atm, 298.15 K) by:

$$G_{trans} = -RTln\left(\frac{k_B T}{p}\left(\frac{2\pi M k_B T}{1000 * N_A h^2}\right)^{3/2}\right)$$

$$G_{trans} = -9.44 \text{ kcal/mol}$$

E_{sol}^{s} is the electronic energy in solution. Possible structural changes of the solute induced by the solvent shell have been accounted for by optimizations at the D3(BJ)-RI-*J*-PBE/def2-SVP level applying Truhlar's SMD solvation model.[11] Finally, the energy was obtained by single point calculations applying the M06 functional[12] and Ahlrichs' def2-TZVP basis which again replaces the inner shell 1s-4f orbitals of Re by an ECP. In this approach, only the influence of the solvent on the molecular vibrations of the solute is neglected. Beside M06 and SMD, several DFT functionals and the conductor-like screening model (COSMO)[13] (ε = 7.25 for THF) were evaluated by calibration to experiment and DLPNO-CCSD(T) calculations (see below) where M06 in combination with SMD showed the best overall performance.

Finally, ΔG_{corr} corrects the free energies for the difference between ideal gas standard conditions (1atm, 298.15 K) and standard solution conditions (1 mol/L, 298.15 K):

$$G_{sol} = G_{gas} + RTln\frac{RT}{p}$$

$$G_{sol} = G_{gas} + RTln(24.47)$$

$$G_{sol} = G_{gas} + 1.89 \text{ kcal/mol}$$

Explicit chemical interactions with the solvent were evaluated by calculating the THF adducts of [(PNP)ReCl$_2$], [(PNP)ReCl$_2$]$^-$, [(PNP)ReCl] and [(PNP)ReCl]$^-$, respectively. However, coordination of THF was always endergonic and thus further neglected. The free energy of the THF molecule has been corrected by applying the actual concentration in the pure solvent, i.e (ρ = 0.889 g/ml (25°C), c = 12.3 mol/L):

$$G'_{sol} = G_{sol} + RTlnc$$

$$G'_{sol} = G_{sol} + 1.49 \text{ kcal/mol}$$

The potentials of the redox processes in THF have been calculated from the free energy differences of the redox couples according to:

$$E_{abs} = \frac{G(Ox) - G(Red)}{F}$$

giving the absolute potential which is not known from experiment. To circumvent any possible problems that could arise by comparison with a reference such as ferrocene,[14] we decided to calculate the actual potentials by calibration to the [Re^{V}(N)Cl(PNP)]/[Re^{VI}(N)Cl(PNP)]$^+$ redox couple that exhibits a fully reversible wave at -0.086 V:[15]

$$E(Red/Ox) = E_{abs}^{DFT}(Red/Ox) - E_{abs}^{DFT}(Re^{V}/Re^{VI}) + (-0.086\ V)$$

NBO analyses have been undertaken at the M06/def2-TZVP-SMD(THF)-level using NBO6.0.[16]

7.2. Experimental benchmarking

Several density functionals were evaluated upon comparison to the experimental values E_1, E_2, E_3, K_1, K_4 and K_5. In general, the redox potentials are well reproduced, partially by error cancelation: the TPSS functional in combination with the COSMO solvation model reproduces the redox potentials very well while PBE0, TPSSh and M06 produce better results with the SMD model. For none of the evaluated functionals, chloride loss of $[ReCl_2(N_2)(PNP)]^-$ (K_5) is endergonic, i.e. in disagreement with experiment. However, the same reaction for $[ReCl_2(PNP)]^-$ is well reproduced. N_2 binding is overestimated by TPSS and TPSSh. That was also demonstrated by DLPNO-CCSD(T) calculations (see next chapter).

Table S6. Calculated and experimental redox potentials and reaction free energies in comparison.

				COSMO[a]				SMD			
		unit	**Exp.**	**PBE0[b]**	**TPSS[b]**	**TPSSh[b]**	**M06**	**PBE0[b]**	**TPSS[b]**	**TPSSh[b]**	**M06**
1	$\boldsymbol{E_1}$	V	**-2.00**	-2.18	-2.03	-2.09	-2.18	-2.05	-1.89	-1.95	-2.08
2	$\boldsymbol{E_2}$	V	**-2.29**	-2.68	-2.36	-2.51	-2.63	-2.40	-2.08	-2.23	-2.39
3	$\Delta\boldsymbol{E}$ ($E_2 - E_1$)	V	**-0.29**	-0.50	-0.33	-0.42	-0.45	-0.35	-0.19	-0.28	-0.31
4	$\boldsymbol{E_3}$	V	**-1.84 – -1.88**	-2.19	-1.92	-2.05	-2.23	-1.98	-1.72	-1.84	-2.02
5	$\Delta\boldsymbol{G_1} = -RT\cdot\ln\boldsymbol{K_1}$	$kcal\cdot mol^{-1}$	**1.8**	3.3	5.2	4.4	4.8	5.5	7.5	6.6	5.8
6	$\Delta\boldsymbol{G_4} = -RT\cdot\ln\boldsymbol{K_4}$	$kcal\cdot mol^{-1}$	**-5.1 – -6.4**	-0.4	-7.8	-4.5	2.5	-3.0	-10.4	-7.1	-0.8
7	$\Delta\boldsymbol{G_5} = -RT\cdot\ln\boldsymbol{K_5}$	$kcal\cdot mol^{-1}$	**2.3 – 3.7**	-5.5	-2.8	-4.1	-2.8	-3.7	-0.9	-2.1	-0.8

a) Including outlying charge correction; b) Including Grimme's dispersion correction with Becke-Johnson damping.

7.3. DLNPO-CCSD(T) benchmarking

To assess the quality of the DFT calculations domain-based local pair natural orbital based coupled cluster (DLPNO-CCSD(T)) single point calculations[17] have been performed for selected molecules employing a truncated model system in which the *tert*-butyl groups of the pincer ligand were replaced by methyl groups. The model complexes were fully optimized on the D3(BJ)-RI-*J*-PBE/def2-TZVP level. In the DLPNO-CCSD(T) calculations we used the correlation consistent cc-pVTZ and cc-pVQZ basis sets for C and H, the augmented correlation consistent aug-cc-pVTZ and aug-cc-pVQZ basis sets for N, P and Cl[18] and the augmented correlation consistent aug-cc-pVTZ-PP and aug-cc-pVQZ-PP basis sets for Re in which the inner shell 1s-4f orbitals are replaced by an ECP,[19] in combination with the corresponding density fitting basis sets,[20] tight SCF convergence criteria and tight DLPNO thresholds. The complete basis set (CBS) limit has been estimated for the Hartree-Fock energy from the SCF energy of the cc-pVQZ basis (E_{SCF}^{QZ}) by:[21]

$$E_{SCF}^{CBS} = E_{SCF}^{QZ} - Ae^{-\alpha\sqrt{4}}$$

where α is 5.79[22] and A has been extrapolated from the SCF energies obtained with the cc-pVTZ (E_{SCF}^{TZ}) and cc-pVQZ bases:

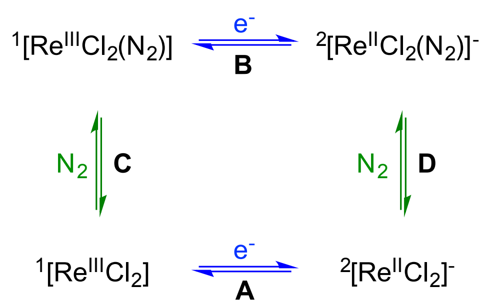
$$A = \frac{E_{SCF}^{QZ} - E_{SCF}^{TZ}}{e^{-\alpha\sqrt{4}} - e^{-\alpha\sqrt{3}}}$$

3 and 4 represent the cardinal numbers of the basis sets cc-pVTZ and cc-pVQZ, respectively. The correlation energy has been extrapolated to the complete basis set limit by:[23]

$$E_{corr}^{CBS} = \frac{4^{\beta} E_{corr}^{QZ} - 3^{\beta} E_{corr}^{TZ}}{4^{\beta} - 3^{\beta}}$$

applying a value of 3.05 for the exponent β.[22]

The energy differences of the following reactions have been investigated (Table S7), including two electron transfer steps (**A** and **B**) and two N_2 binding steps (**C** and **D**):



All DFT functionals deliver for the reduction steps **A** and **B** almost identical values within an energy range of 2-3 kcal·mol^{-1} (Table S8). Accordingly, the calculated reduction potentials are in very good agreement with experiment (see above). In contrast, only M06 and slightly less PBE0 reproduce N_2 binding energies from the DLPNO-CCSD(T) calculations sufficiently well. PBE, TPSS and TPSSh severely overestimate N_2 binding.

Table S7. SCF and correlation energies of the DLNPO-CCSD(T) calculations, the CBS extrapolation values and the resulting reaction energies **A-D**.

	E_{SCF} (H)	E_{corr} (H)	ΔE (kcal/mol)
N_2			
cc-pVTZ	-108.9836091	-0.3963775	
cc-pVQZ	-108.9904282	-0.4158839	
CBS	-108.9922622	-0.4297702	
^{1}[(PNP)ReCl$_2$]			
cc-pVTZ	-2047.7039097	-3.1489602	
cc-pVQZ	-2047.7446500	-3.3525984	
CBS	-2047.7556070	-3.4975662	
^{2}[(PNP)ReCl$_2$]$^-$			**A: -10.24**
cc-pVTZ	-2047.7011591	-3.1658369	
cc-pVQZ	-2047.7417549	-3.3708618	
CBS	-2047.7526731	-3.5168169	
^{1}[(PNP)ReCl$_2$(N$_2$)]			**C: +0.37**
cc-pVTZ	-2156.6508398	-3.5877455	
cc-pVQZ	-2156.6972234	-3.8080679	
CBS	-2156.7096982	-3.9649132	
^{2}[(PNP)ReCl$_2$(N$_2$)]$^-$			**B: -28.81**
cc-pVTZ	-2156.6637842	-3.6182461	**D: -18.19**
cc-pVQZ	-2156.7100810	-3.8400707	
CBS	-2156.7225324	-3.9979853	

Table S8. Deviation of the at DFT level calculated energy differences from the corresponding DLNPO-CCSD(T) values (ΔE^{DFT} - $\Delta E^{CCSD(T)}$) in kcal/mol. All DFT energies were obtained with Ahlrich's def2-TZVP basis without solvent correction.

	PBE[a]	PBE0[a]	TPSS[a]	TPSSh[a]	M06L	M06	M06-2X
A	-2.41	-2.01	-2.45	-2.33	-2.51	-5.22	-5.08
B	-5.10	-4.83	-4.51	-4.51	-4.84	-5.98	-5.13
C	-10.48	-3.89	-11.05	-8.22	-7.90	-2.99	6.45
D	-13.18	-6.72	-13.11	-10.40	-10.23	-3.75	6.39

a) Including Grimme's dispersion correction with Becke-Johnson damping.

*7.4. TD-DFT calculation of the UV-vis-spectrum of **3***

The UV-vis spectrum of **3** was calculated employing the M06 functional within the time-dependent DFT framework as implemented in ORCA. Relativistic effects were treated at the all-electron level with the ZORA method[24] in conjunction with the corresponding re-contracted ZORA-def2-TZVPP basis sets for N, P, Cl, Re and the 8 C atoms of the pincer backbones while the remaining C and H atoms were covered by the smaller ZORA-def2-SVP basis set.[25] "Picture change effects"[26] were also included as a correction within the scalar relativistic framework. The density-fitting procedure was used within the RIJCOSX approximation in conjunction with the corresponding def2/J and SARC/J fitting basis sets.[27] Given the increased demands on numerical accuracy for the evaluation of two-electron integrals posed by use of the ZORA Hamiltonian, we employed large integration grids (Grid6 and GridX6 in ORCA convention) and an improved radial integration accuracy around heavy atoms (P, Cl, Re; SpecialGridIntAcc 7). Finally, solvation was included by means of the C-PCM solvation model[28] applying the dielectric constant and refraction index of THF (ε_0 = 7.25, n_D = 1.407). The computed UV-vis spectrum is shown in comparison to the experimental spectrum in Figure S4.

7.5. Electronic structure of [$Re^{I}Cl(N_2)(PNP)]^{-}$

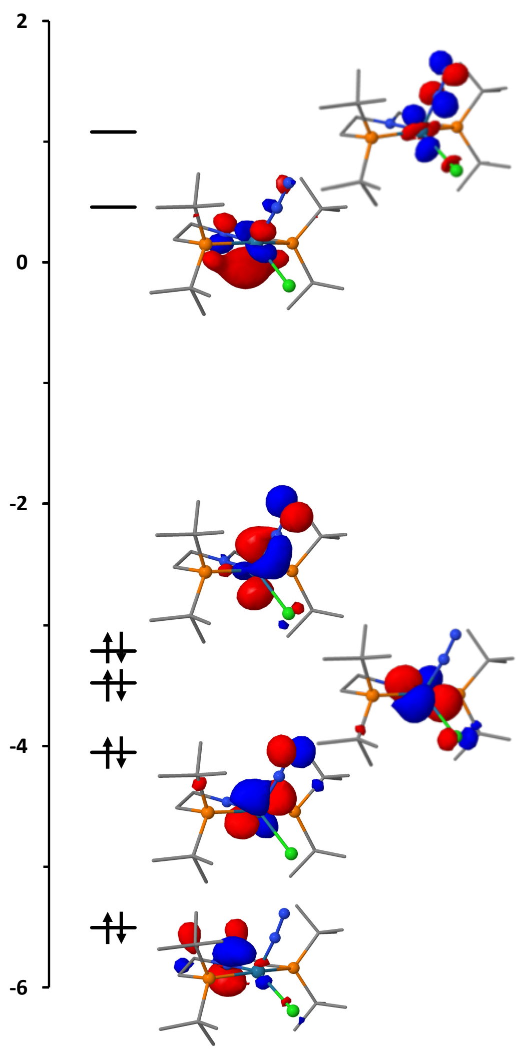


Figure S56. Molecular Orbitals of [$Re^{I}Cl(N_2)(PNP)]^{-}$ (M06/def2-TZVP (SMD(THF)).

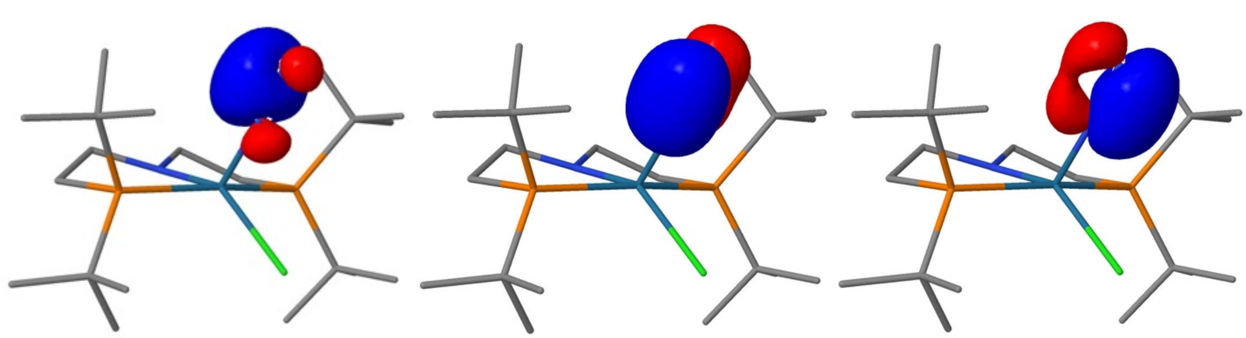


Figure S57. N-N Natural Bonding Orbitals (NBOs) of [$Re^{I}Cl(N_2)(PNP)]^{-}$ (M06/def2-TZVP (SMD(THF)).

7.6. Electronic structure and geometry of the transition state of N_2 splitting

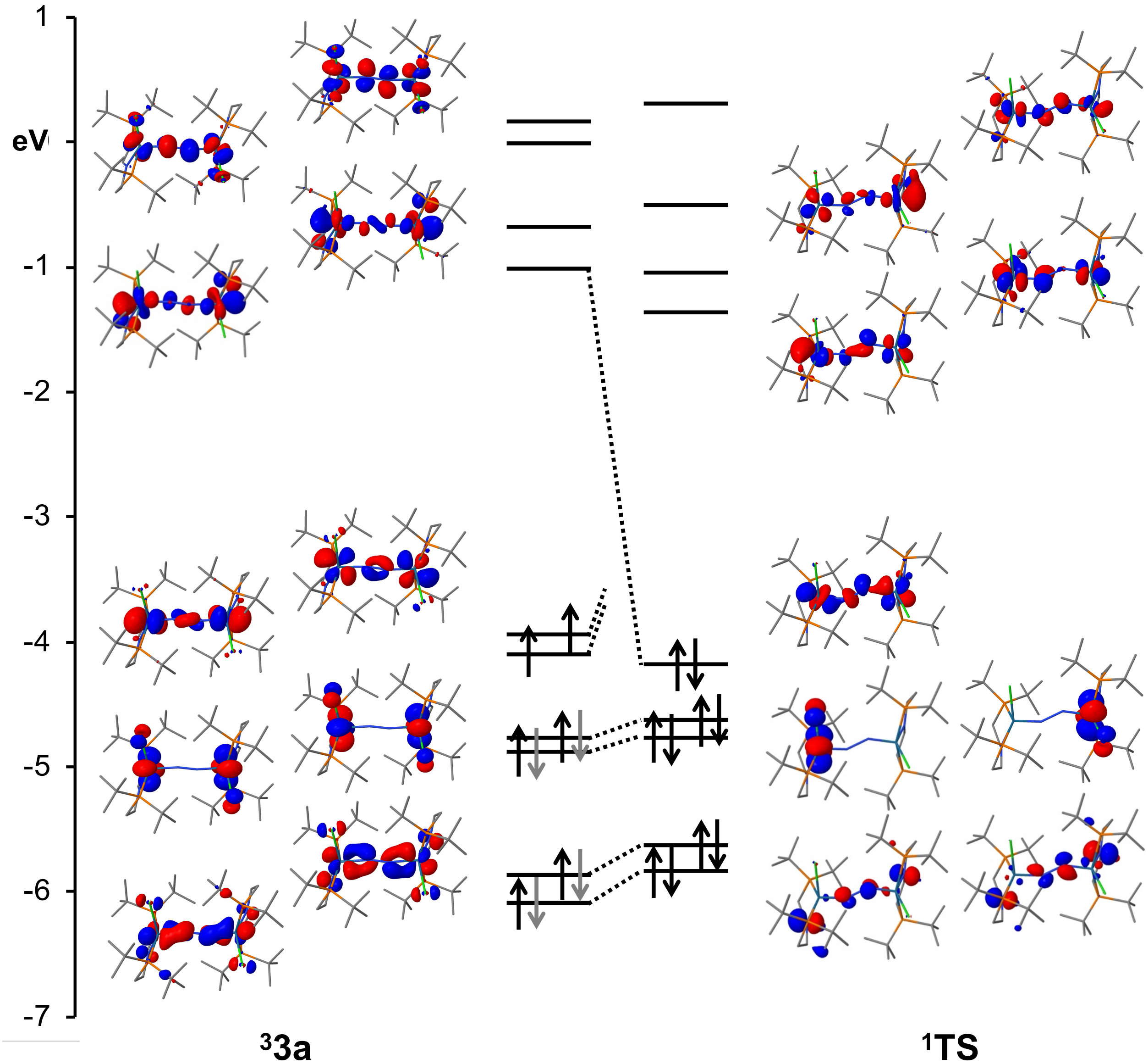
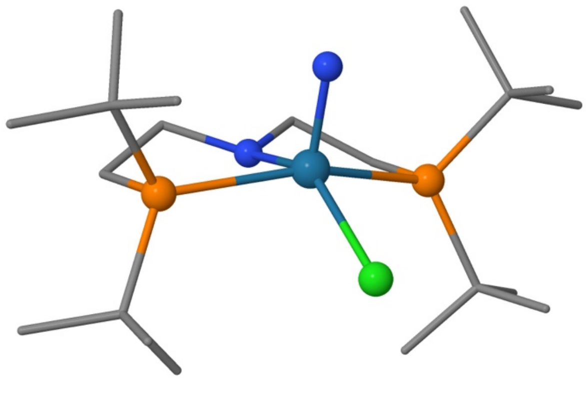


Figure S59. Molecular Orbitals of ^{3}**3** (a space) in Comparison to the Transition State (^{1}**TS**) of N_2 Splitting (M06/def2-TZVP (SMD(THF)).

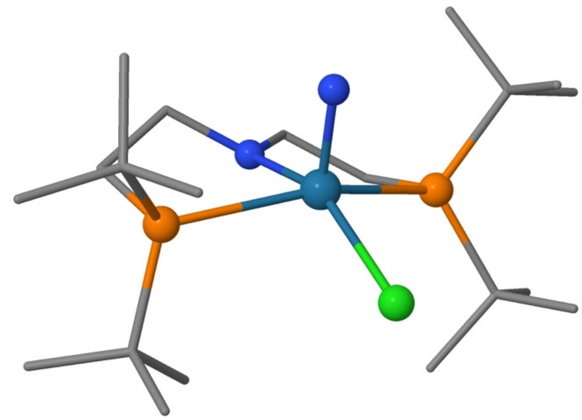
Table S9. Calculated structural parameters (in Å and deg) for **3**, **TS**, and **2**.

	3 (exp)	3 (calc)	TS	2
Re1-N1	1.937(7)	1.975	1.994	2.031
Re2-N2	1.949(8)		2.025	
Re1-N3	1.861(8)	1.875	1.768	1.675
Re2-N4	1.886(8)		1.738	
N3-N4	1.202(10)	1.200	1.589	—
Re1-Cl1	2.463(3)	2.504	2.466	2.475
Re2-Cl2	2.455(3)		2.484	
Re1-N3-N4	167.9(7)	169.5	139.0	—
Re2-N4-N3	168.4(7)		144.2	
N1-Re1-Cl1	146.3(2)	147.2	145.2	145.8
N2-Re2-Cl2	146.6(3)		151.6	
N1-Re1-N3	118.0(3)	119.5	106.5	105.8
N2-Re2-N4	119.3(3)		111.6	
N3-Re1-Cl1	95.5(2)	93.2	108.3	108.4
N4-Re2-Cl2	94.0(2)		96.8	
P-Re1-P	157.38(10)	157.4	153.6	155.9
P-Re2-P	156.28(9)		149.5	
Re-N-N-Re	-	-	173.5	—
N1-Re1-N3-N4	-	-	91.1	—
N2-Re2-N4-N3	-	-	-169.8	—

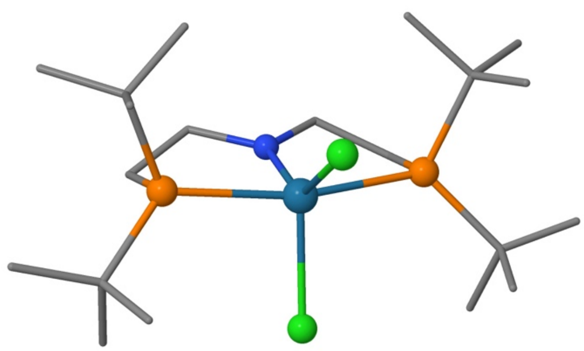
7.7 Structures



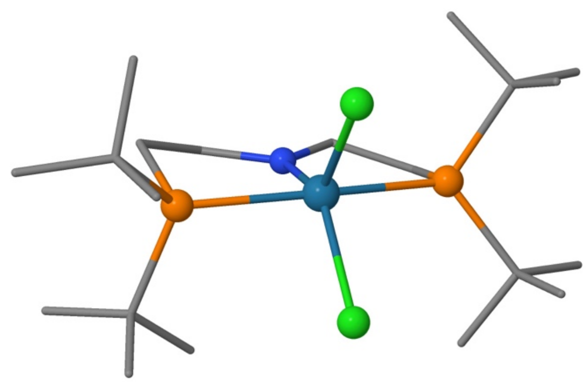
[Re(N)Cl(PNP)]



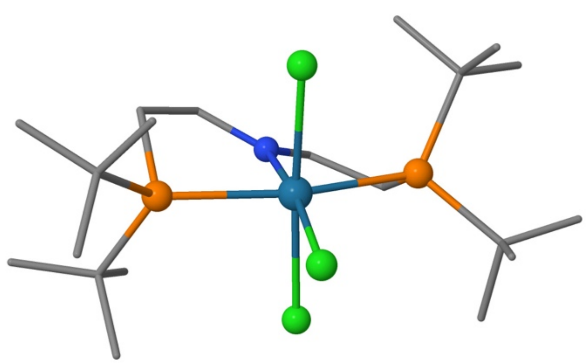
$[Re(N)Cl(PNP)]^{+}$



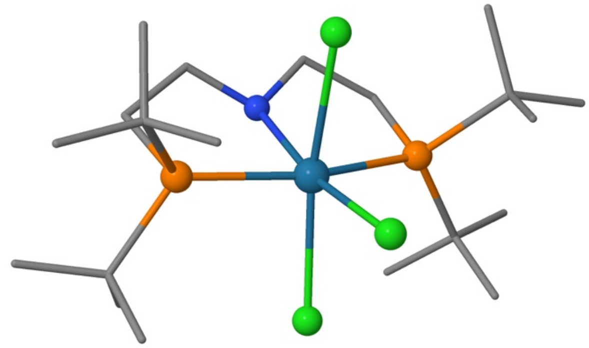
$[ReCl_2(PNP)]$



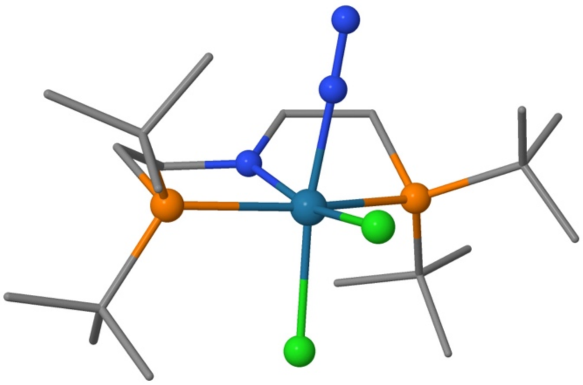
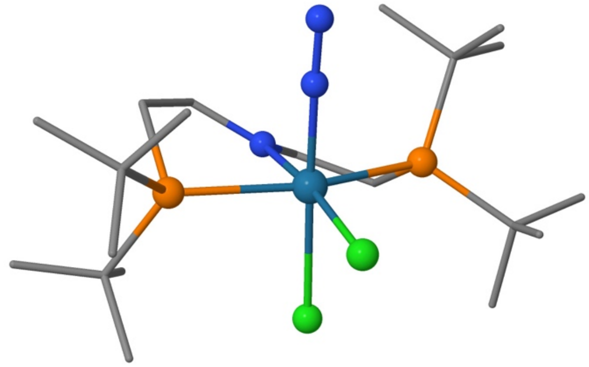
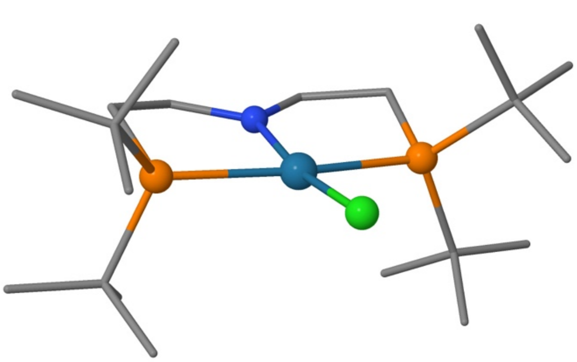
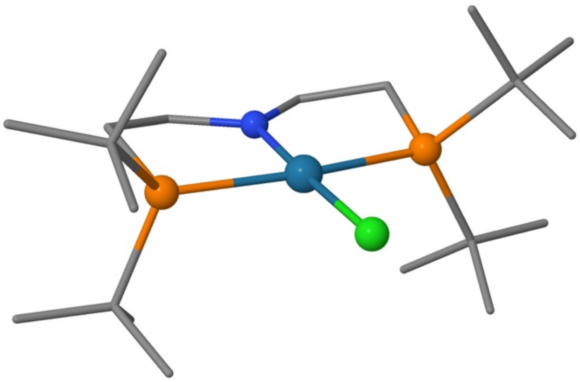
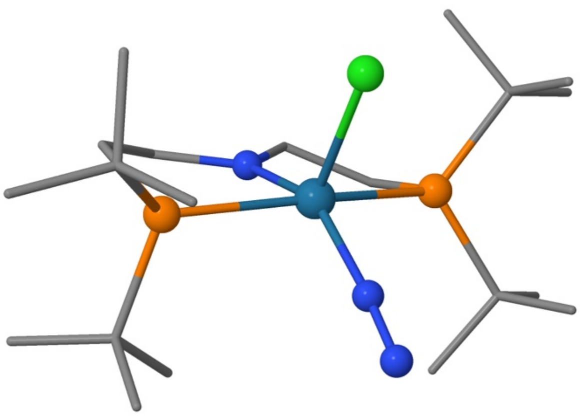
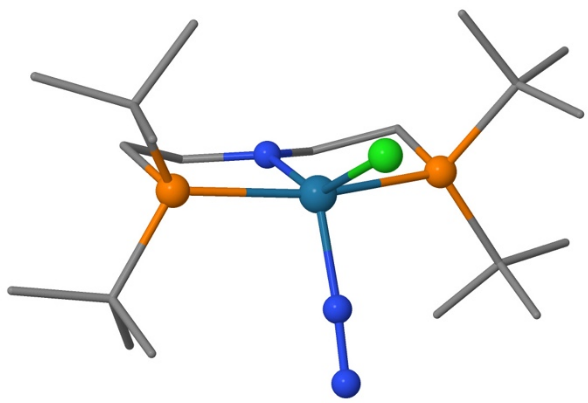
$[ReCl_2(PNP)]^{-}$

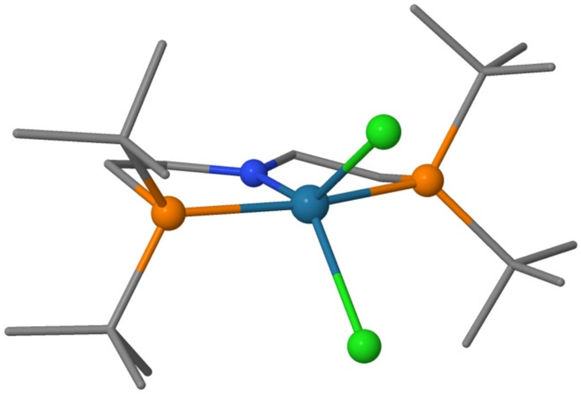
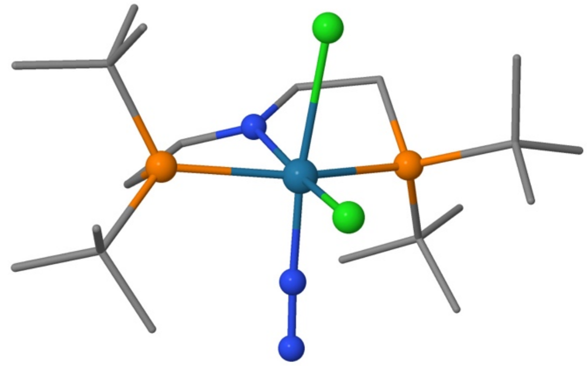
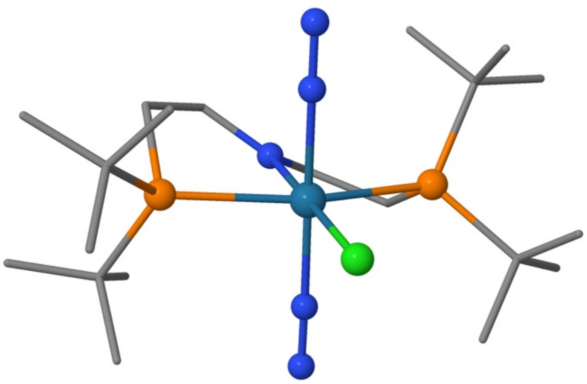
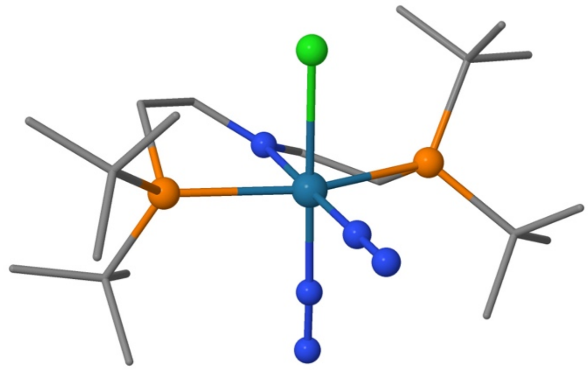
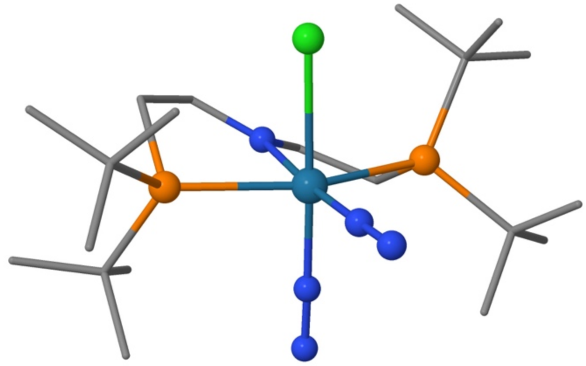


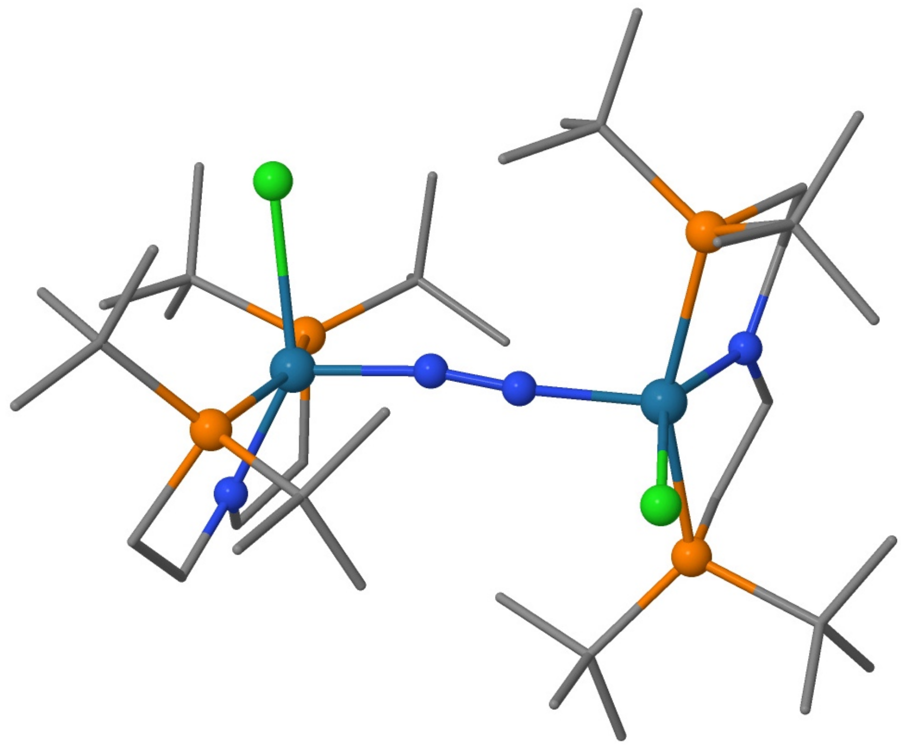
$[ReCl_3(PNP)]^{-}$



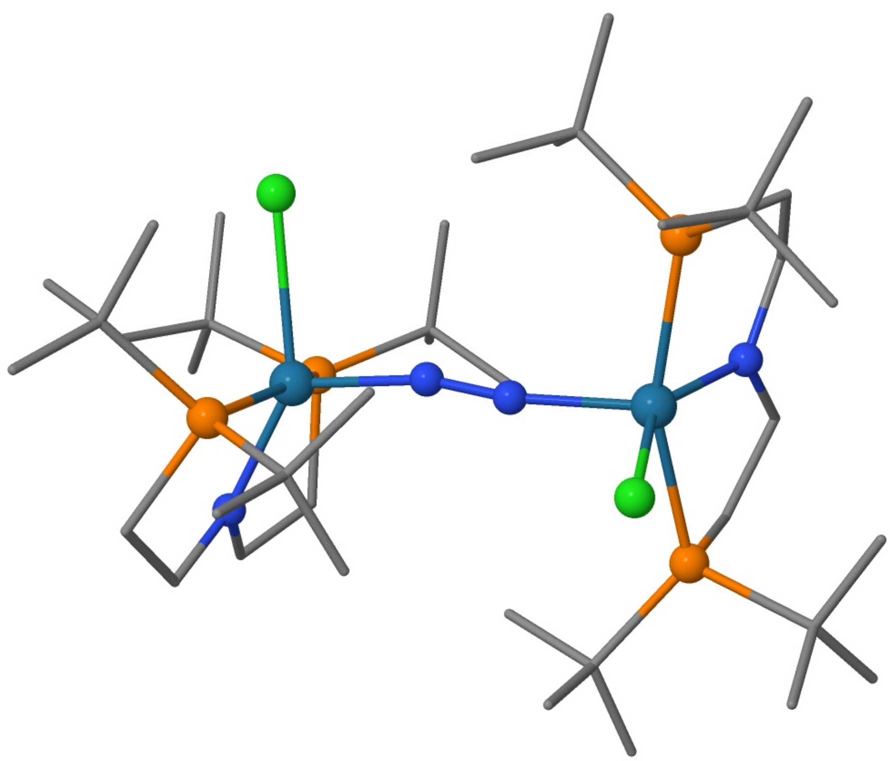
$[ReCl_3(PNP)]^{2-}$

	
[Re(PNP)Cl$_2$(N$_2$)]	**[Re(PNP)Cl$_2$(N$_2$)]$^{-}$**
	
[Re(PNP)Cl]	**[Re(PNP)Cl]$^{-}$**
	
[Re(PNP)Cl(N$_2$)]	**[Re(PNP)Cl(N$_2$)]$^{-}$**

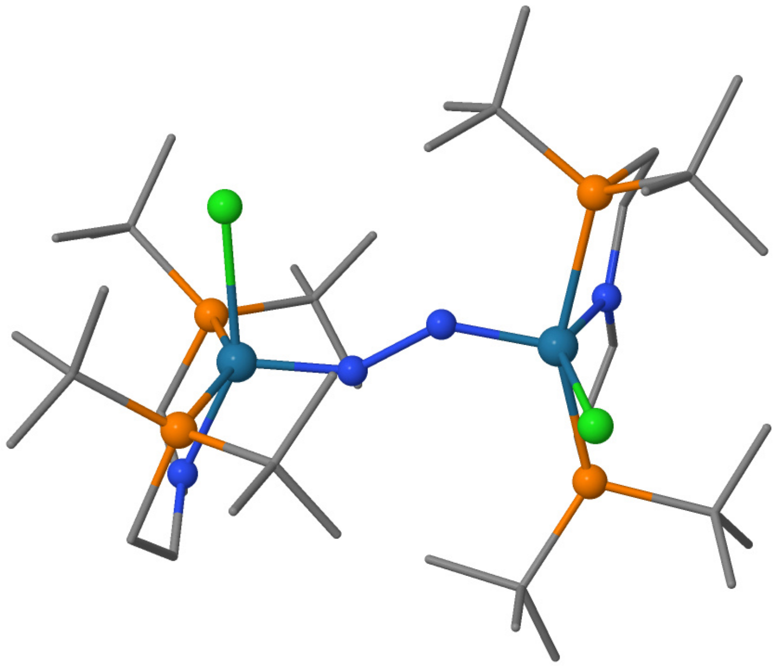
	
$[Re(PNP)Cl_2]^{2-}$	**$[Re(PNP)Cl_2(N_2)]^{2-}$**
	
***trans*-$[Re(PNP)Cl(N_2)_2]$**	***cis*-$[Re(PNP)Cl(N_2)_2]$**
	
***trans*-$[Re(PNP)Cl(N_2)_2]^{-}$**	***cis*-$[Re(PNP)Cl(N_2)_2]^{-}$**



[{Re(PNP)Cl}(μ-N_2){Re(PNP)Cl}] PNP



[{Re(PNP)Cl}(μ-N_2){Re(PNP)Cl}]$^{-}$



TS: [{Re(PNP)Cl}(μ-N_2) {Re(PNP)Cl}] Nitrogen splitting

7.8. XYZ-Coordinates

N_2

N	-0.06685	0.12854	1.30664
N	-0.09181	0.00007	2.41055

THF

C	-4.22261	0.84443	0.11925
O	-2.80458	0.85913	-0.05295
C	-2.34403	2.20390	-0.19155
C	-3.51226	3.10384	0.22712
C	-4.71283	2.25785	-0.21708
H	-4.66332	0.06309	-0.53761
H	-4.47634	0.57640	1.17428
H	-1.43722	2.34555	0.43577
H	-2.05135	2.40182	-1.25218
H	-3.52330	3.23822	1.32943
H	-3.47685	4.10869	-0.23789
H	-5.65998	2.52329	0.29249
H	-4.87348	2.36338	-1.31084

[(PNP)Re(N)Cl]

Re	-0.00001	-0.17116	-0.23533
C	3.14796	0.38435	1.73886
P	2.39366	0.29056	-0.01741
N	0.00001	1.78212	-0.78997
P	-2.39366	0.29060	-0.01742
C	-3.14797	0.38443	1.73884
Cl	-0.00003	-1.75914	1.66223
C	3.47819	-0.71770	-1.22463
C	-3.47821	-0.71765	-1.22464
N	-0.00001	-1.05114	-1.66110
C	-2.46137	2.06285	-0.59500
H	-2.48472	2.69138	0.31715
H	-3.38629	2.27654	-1.16771
C	-1.19617	2.37732	-1.39225
H	-1.07555	3.48671	-1.44432
H	-1.31622	2.03781	-2.45274
C	1.19622	2.37730	-1.39223
H	1.31628	2.03779	-2.45272
H	1.07562	3.48670	-1.44430

C	2.46140	2.06281	-0.59497
H	3.38634	2.27649	-1.16767
H	2.48475	2.69133	0.31718
C	-3.44748	-1.03204	2.25757
H	-3.73075	-0.96892	3.33010
H	-2.55300	-1.68211	2.17783
H	-4.29451	-1.50403	1.72221
C	-4.40865	1.26382	1.81137
H	-4.73557	1.32235	2.87164
H	-5.25357	0.85621	1.22826
H	-4.22321	2.30226	1.47293
C	-2.04482	1.01296	2.61603
H	-2.44152	1.16262	3.64279
H	-1.71011	2.00178	2.24098
H	-1.16739	0.34118	2.68272
C	2.04461	1.01239	2.61616
H	2.44127	1.16201	3.64294
H	1.16740	0.34031	2.68275
H	1.70958	2.00116	2.24128
C	3.44794	-1.03210	2.25736
H	3.73120	-0.96905	3.32990
H	4.29512	-1.50373	1.72193
H	2.55367	-1.68245	2.17753
C	4.40836	1.26415	1.81152
H	4.73525	1.32263	2.87179
H	4.22257	2.30257	1.47322
H	5.25340	0.85690	1.22835
C	-4.97661	-0.42812	-1.04519
H	-5.54014	-0.95772	-1.84255
H	-5.21330	0.65127	-1.13758
H	-5.36315	-0.79197	-0.07416
C	-3.18746	-2.21409	-1.00919
H	-3.77606	-2.80355	-1.74397
H	-3.46680	-2.55814	0.00373
H	-2.11414	-2.43606	-1.16297
C	-3.05873	-0.32845	-2.65479
H	-3.61489	-0.97059	-3.37018
H	-1.97625	-0.49241	-2.82108
H	-3.30602	0.72463	-2.89583
C	3.05888	-0.32830	-2.65478
H	3.61504	-0.97044	-3.37019

H	3.30632	0.72477	-2.89569
H	1.97640	-0.49212	-2.82118
C	4.97661	-0.42837	-1.04503
H	5.54014	-0.95795	-1.84240
H	5.36302	-0.79237	-0.07400
H	5.21344	0.65100	-1.13728
C	3.18724	-2.21413	-1.00936
H	3.77585	-2.80359	-1.74415
H	2.11392	-2.43595	-1.16326
H	3.46646	-2.55831	0.00354

$[(PNP)Re(N)Cl]^{+}$

Re	0.02043	-0.25049	-0.28474
C	3.04340	0.66320	1.61988
P	2.46462	0.28255	-0.15498
N	-0.00720	1.67520	-0.87380
P	-2.41211	0.29160	0.08341
C	-3.12652	0.10121	1.84493
Cl	0.06787	-1.90446	1.40208
C	3.58220	-0.90939	-1.12631
C	-3.48569	-0.48109	-1.28942
N	0.07680	-1.08124	-1.73216
C	-2.35762	2.12684	-0.17062
H	-2.22904	2.56174	0.84043
H	-3.32122	2.50443	-0.56696
C	-1.18786	2.52230	-1.06351
H	-0.91859	3.58475	-0.86264
H	-1.49462	2.48525	-2.13579
C	1.10210	2.09068	-1.74449
H	1.08799	1.50576	-2.69528
H	0.97506	3.15845	-2.02674
C	2.44831	1.91827	-1.03053
H	3.30674	2.00671	-1.72481
H	2.56357	2.70484	-0.25976
C	-3.46963	-1.37165	2.12030
H	-3.74691	-1.47687	3.18952
H	-2.60826	-2.04147	1.93205
H	-4.33417	-1.71899	1.52364
C	-4.36944	0.99164	2.03691
H	-4.71394	0.87610	3.08560
H	-5.21191	0.70877	1.38250

H	-4.15361	2.06753	1.88818
C	-2.02529	0.56566	2.81977
H	-2.43962	0.55417	3.84896
H	-1.68252	1.60207	2.62353
H	-1.15299	-0.11376	2.80432
C	1.85774	1.38650	2.29156
H	2.15555	1.68629	3.31758
H	0.97579	0.72240	2.39015
H	1.54930	2.30422	1.75221
C	3.34402	-0.64041	2.37785
H	3.53896	-0.39220	3.44163
H	4.24640	-1.15062	1.99147
H	2.49216	-1.34709	2.34956
C	4.27839	1.58229	1.62950
H	4.53194	1.80966	2.68586
H	4.09877	2.55265	1.12694
H	5.16659	1.11147	1.17227
C	-4.97637	-0.16504	-1.07941
H	-5.53589	-0.52898	-1.96583
H	-5.17702	0.92150	-0.99188
H	-5.39955	-0.67827	-0.19589
C	-3.25309	-2.00295	-1.31126
H	-3.86125	-2.43887	-2.13040
H	-3.55932	-2.49609	-0.37083
H	-2.19390	-2.25560	-1.51056
C	-3.02343	0.12634	-2.62723
H	-3.57446	-0.38163	-3.44527
H	-1.94319	-0.03219	-2.81236
H	-3.25469	1.20695	-2.70267
C	3.23107	-0.75713	-2.61817
H	3.81920	-1.50621	-3.18716
H	3.49912	0.23911	-3.02146
H	2.16076	-0.95603	-2.82105
C	5.06672	-0.56791	-0.91020
H	5.67473	-1.21262	-1.57799
H	5.40014	-0.76579	0.12587
H	5.30436	0.48407	-1.16642
C	3.27821	-2.35044	-0.67659
H	3.91904	-3.04347	-1.25947
H	2.22286	-2.62469	-0.86697
H	3.49216	-2.51914	0.39454

[(PNP)ReCl$_2$]

Re	2.71353	6.08031	10.43351
P	4.49047	4.45714	10.50485
N	3.11701	6.26870	12.30394
Cl	1.00101	4.50692	10.21336
C	4.14218	5.48999	13.04546
H	3.73550	5.26628	14.05719
H	5.03751	6.13186	13.21977
Cl	3.49252	7.00944	8.37866
P	1.24354	7.93994	10.85241
C	4.52191	4.18671	12.34976
H	3.73423	3.43471	12.54702
H	5.47900	3.78504	12.73666
C	4.33529	2.69584	9.73923
C	3.81100	2.90610	8.30467
H	3.67023	1.91854	7.81503
H	4.50607	3.49844	7.68038
H	2.83515	3.42921	8.31660
C	-1.33105	9.30622	10.46981
H	-0.90704	10.13200	9.86893
H	-1.34951	9.61768	11.53363
H	-2.38778	9.17873	10.14893
C	-0.59473	7.97224	10.27428
C	1.84119	10.10332	9.09188
H	2.22152	9.32075	8.40630
H	2.42098	11.03263	8.90228
H	0.78604	10.32017	8.83977
C	3.27610	1.91360	10.54135
H	3.65043	1.60735	11.53866
H	3.03283	0.98213	9.98634
H	2.33822	2.48785	10.66265
C	7.38096	4.44512	10.88967
H	7.28226	4.56968	11.98659
H	8.35283	4.90151	10.60227
H	7.44749	3.36545	10.66985
C	6.26241	6.64220	10.55193
H	6.04580	6.77877	11.62904
H	5.54059	7.23898	9.96680
H	7.27442	7.06258	10.36656
C	6.25462	5.15973	10.12298

C	5.62374	1.85940	9.72882
H	6.02773	1.70769	10.75004
H	6.42085	2.29191	9.09600
H	5.39087	0.85314	9.31744
C	1.16910	7.80240	12.71094
H	0.88829	8.74146	13.22702
H	0.38012	7.05404	12.91605
C	2.50218	7.26368	13.22033
H	3.22739	8.09020	13.40693
H	2.35143	6.77240	14.20770
C	6.51858	5.10819	8.60667
H	7.46991	5.63970	8.38717
H	5.70938	5.61457	8.04477
H	6.62725	4.07496	8.22641
C	1.47861	10.77156	11.50506
H	0.38750	10.91583	11.42193
H	1.96061	11.74091	11.25321
H	1.71987	10.56151	12.56633
C	3.54419	9.56148	10.82599
H	4.00974	10.56418	10.71204
H	4.02844	8.88406	10.10067
H	3.77470	9.20919	11.84996
C	2.02866	9.68673	10.56251
C	-1.36803	6.89326	11.05880
H	-1.54372	7.18980	12.11223
H	-0.85662	5.91248	11.03527
H	-2.36635	6.76499	10.58784
C	-0.57115	7.57816	8.78374
H	-0.12808	6.57212	8.65155
H	0.00865	8.28906	8.16544
H	-1.61066	7.55475	8.39162

[(PNP)ReCl$_2$(N$_2$)]

P	4.58311	4.45129	10.39409
N	3.41697	6.46978	12.11513
Cl	1.49081	5.69397	8.29862
C	3.94377	5.39525	12.97816
H	3.16891	5.14190	13.74199
H	4.80097	5.81466	13.55121
Cl	4.30021	7.60735	9.00880
P	1.34115	8.12404	10.79092

C	4.37109	4.12474	12.22711
H	3.57383	3.35872	12.28872
H	5.27729	3.68141	12.68490
C	4.33023	2.72372	9.57858
C	4.89231	2.76604	8.14699
H	4.54606	1.86334	7.60085
H	5.99821	2.75937	8.12286
H	4.52736	3.65322	7.59120
C	-1.31562	8.74143	11.79517
H	-1.18163	9.82949	11.67757
H	-1.01668	8.46438	12.82563
H	-2.40338	8.53098	11.71022
C	-0.57686	7.90442	10.73432
C	1.80405	9.87086	8.61294
H	2.52163	9.11660	8.24249
H	2.12915	10.86908	8.24837
H	0.81449	9.65972	8.17010
C	2.81420	2.47394	9.48037
H	2.34237	2.34831	10.47269
H	2.65651	1.52556	8.92389
H	2.28949	3.28548	8.93771
C	7.39756	3.84342	10.72093
H	7.15006	3.43919	11.72317
H	8.42510	4.26171	10.78222
H	7.43370	3.00312	10.00253
C	6.63119	6.17337	11.19780
H	6.49710	5.90767	12.26471
H	5.94755	7.00207	10.93519
H	7.67254	6.54272	11.08528
C	6.44318	4.95915	10.26394
C	4.95969	1.56777	10.37559
H	4.54835	1.49835	11.40204
H	6.05978	1.62846	10.44637
H	4.71261	0.61187	9.86579
C	1.71317	8.20223	12.62373
H	1.55714	9.21512	13.04670
H	0.99433	7.51848	13.12099
C	3.13997	7.70141	12.87971
H	3.88463	8.47119	12.58430
H	3.27983	7.51600	13.96713
C	6.81885	5.37753	8.82839

H	7.83002	5.83784	8.85062
H	6.11298	6.12446	8.42350
H	6.86742	4.51816	8.13737
C	0.77254	10.97705	10.62162
H	-0.23436	10.86057	10.18057
H	1.15943	11.96503	10.29156
H	0.67468	11.01973	11.72526
C	3.15064	10.28956	10.70051
H	3.44252	11.25881	10.24258
H	3.92871	9.55004	10.43893
H	3.13553	10.44427	11.79831
C	1.76265	9.89715	10.15343
C	-0.88433	6.42369	11.00821
H	-0.50705	6.08111	11.99117
H	-0.46941	5.77308	10.21695
H	-1.98726	6.29175	11.01815
C	-1.08711	8.22906	9.31854
H	-0.51936	7.66118	8.55427
H	-1.03838	9.30777	9.07894
H	-2.15315	7.92489	9.24632
Re	2.84345	6.19592	10.28149
N	1.69376	4.83624	11.12197
N	1.09740	4.05073	11.69612

[(PNP)ReCl$_3$]$^-$

Re	3.03085	6.42917	10.15529
P	4.80809	4.81915	10.24008
N	3.14000	6.27449	12.08057
Cl	1.26677	4.66974	10.11048
C	4.34437	5.84213	12.80678
H	4.08107	5.03087	13.52660
H	4.68034	6.70281	13.43740
Cl	4.67955	8.24277	10.02056
P	1.28829	7.99127	10.78990
C	5.49279	5.40088	11.88711
H	6.15134	4.66646	12.39750
H	6.10233	6.28541	11.61067
C	4.42066	2.93573	10.58834
C	3.60455	2.35148	9.41888
H	3.27790	1.32153	9.68896
H	4.18580	2.28066	8.48289

H	2.70018	2.96321	9.23454
C	-1.26027	9.38270	10.07625
H	-0.79623	10.37448	9.91680
H	-1.63319	9.32542	11.11809
H	-2.14740	9.33026	9.40560
C	-0.32304	8.22006	9.71589
C	2.18976	10.64403	10.33200
H	3.02679	10.16991	9.78194
H	2.53831	11.62750	10.72109
H	1.35896	10.84233	9.62563
C	3.54768	2.87542	11.85843
H	4.12343	3.13531	12.76890
H	3.18812	1.83020	11.98819
H	2.65827	3.52891	11.77211
C	7.67485	4.45387	9.78057
H	7.91173	5.17845	10.58506
H	8.51027	4.50290	9.04603
H	7.67834	3.43999	10.21860
C	6.52776	6.23081	8.47401
H	6.73684	6.99443	9.24431
H	5.61077	6.54890	7.94071
H	7.37885	6.20763	7.75547
C	6.36331	4.82138	9.06485
C	5.65595	2.05969	10.85066
H	6.28923	2.45767	11.67052
H	6.29029	1.92359	9.95440
H	5.31466	1.04713	11.16412
C	0.77712	7.09284	12.35304
H	0.19389	7.70818	13.06934
H	0.13898	6.26402	11.99225
C	2.02984	6.50262	13.01896
H	2.37607	7.14727	13.86230
H	1.77583	5.51640	13.48189
C	6.09801	3.88397	7.87331
H	6.89993	4.03455	7.11690
H	5.13023	4.13617	7.39375
H	6.09978	2.81158	8.14462
C	0.64006	10.45058	12.31719
H	-0.15803	10.88800	11.69557
H	1.09954	11.28566	12.89161
H	0.16914	9.77266	13.05841

C	2.93302	9.57257	12.48005
H	3.32002	10.58221	12.74445
H	3.76253	8.99779	12.02932
H	2.61068	9.09320	13.42548
C	1.74934	9.75189	11.50519
C	-1.15764	6.92980	9.78108
H	-1.64874	6.80812	10.76930
H	-0.54695	6.02770	9.58427
H	-1.96428	6.99308	9.01678
C	0.19005	8.41483	8.27642
H	0.84728	7.58138	7.95211
H	0.77830	9.34873	8.17221
H	-0.67891	8.48364	7.58367
Cl	2.94007	6.35137	7.67558

$[(PNP)ReCl_2]^-$

Re	2.91407	6.26957	10.33436
P	4.69820	4.73469	10.41161
N	3.10777	6.23092	12.28260
Cl	1.46392	4.90951	8.84372
C	4.06423	5.41104	13.05788
H	3.50283	4.58326	13.56008
H	4.48078	6.03019	13.89109
Cl	3.65918	7.51888	8.28387
P	1.31609	7.92477	10.83088
C	5.21193	4.84633	12.22637
H	5.56134	3.87593	12.63445
H	6.07472	5.53995	12.25868
C	4.33773	2.82827	10.23546
C	3.96596	2.50447	8.77811
H	3.54970	1.47232	8.72744
H	4.84601	2.53604	8.10700
H	3.19309	3.20593	8.40281
C	-1.36845	9.10045	10.55004
H	-1.01017	10.08831	10.19990
H	-1.46094	9.13625	11.65576
H	-2.39419	8.96023	10.13823
C	-0.46951	7.94791	10.08182
C	1.85572	10.39886	9.48400
H	2.30962	9.74115	8.71371
H	2.40528	11.36767	9.47843

H	0.80489	10.61696	9.20884
C	3.08572	2.61220	11.11053
H	3.28053	2.82345	12.18192
H	2.76536	1.54831	11.03292
H	2.25326	3.25646	10.76343
C	7.58673	4.31623	10.01750
H	7.68897	4.30247	11.12216
H	8.52471	4.75379	9.60590
H	7.53761	3.26829	9.66702
C	6.65528	6.63760	9.85349
H	6.77160	6.84047	10.93786
H	5.83537	7.26953	9.45753
H	7.60563	6.93842	9.35685
C	6.38585	5.15010	9.54619
C	5.44573	1.87467	10.70558
H	5.82922	2.12073	11.71715
H	6.30567	1.85483	10.00979
H	5.04175	0.83763	10.75235
C	1.00713	7.55622	12.64518
H	0.61636	8.40894	13.23758
H	0.23419	6.76402	12.64666
C	2.29213	6.99636	13.24938
H	2.91056	7.82028	13.68910
H	2.03389	6.33354	14.11244
C	6.20284	5.01758	8.02457
H	7.09927	5.42920	7.50771
H	5.31720	5.59622	7.68979
H	6.09319	3.96307	7.70677
C	1.32188	10.65090	11.93846
H	0.22629	10.73927	11.81581
H	1.74850	11.67744	11.86914
H	1.52333	10.28848	12.96698
C	3.48538	9.64319	11.19914
H	3.92684	10.66534	11.24188
H	4.00641	9.06106	10.41367
H	3.67151	9.15195	12.17438
C	1.98157	9.75682	10.87638
C	-1.13165	6.60994	10.46825
H	-1.40502	6.56578	11.54226
H	-0.47232	5.75448	10.21391
H	-2.07460	6.49913	9.88734

C	-0.31385	7.96027	8.54847
H	0.29254	7.09212	8.21999
H	0.16833	8.88127	8.17401
H	-1.32131	7.88672	8.07951

$[(PNP)ReCl_2(N_2)]^-$

Re	3.05728	6.49783	10.04852
P	4.85036	4.87412	10.21751
N	3.18931	6.32154	12.06948
Cl	1.27268	4.70392	10.07636
C	4.42656	6.00678	12.76164
H	4.24313	5.21038	13.52727
H	4.77695	6.89407	13.35712
Cl	2.89603	6.45959	7.55997
P	1.30762	8.01731	10.79569
C	5.55912	5.55539	11.81763
H	6.25444	4.85842	12.33217
H	6.15205	6.43387	11.48871
C	4.47513	3.01778	10.63943
C	3.65853	2.38601	9.49544
H	3.34101	1.36512	9.80603
H	4.23851	2.28439	8.56113
H	2.74842	2.98468	9.29272
C	-1.23762	9.45046	10.20894
H	-0.77646	10.44685	10.06812
H	-1.56505	9.35491	11.26358
H	-2.15324	9.42753	9.57611
C	-0.31968	8.30076	9.76731
C	2.27700	10.63214	10.33148
H	3.05361	10.15198	9.70639
H	2.69672	11.58694	10.71940
H	1.41312	10.88699	9.68621
C	3.60781	3.00610	11.91431
H	4.18441	3.31158	12.80977
H	3.25660	1.96483	12.08917
H	2.71715	3.65428	11.80067
C	7.70663	4.53502	9.68247
H	7.95412	5.25136	10.49118
H	8.52021	4.60751	8.92612
H	7.73657	3.51481	10.10489
C	6.48348	6.30608	8.42883

H	6.72277	7.06602	9.19532
H	5.54485	6.60930	7.92312
H	7.30901	6.31096	7.68204
C	6.36858	4.88680	9.00949
C	5.72583	2.16947	10.91790
H	6.37062	2.61029	11.70623
H	6.34283	2.00298	10.01400
H	5.40308	1.16792	11.28105
C	0.81397	7.06688	12.32885
H	0.21358	7.65735	13.05220
H	0.19091	6.24207	11.93426
C	2.07283	6.46804	12.98835
H	2.37971	7.10208	13.86138
H	1.80854	5.47322	13.43749
C	6.07942	3.94675	7.82639
H	6.85287	4.10877	7.04341
H	5.09159	4.17967	7.37865
H	6.10964	2.87541	8.10247
C	0.82306	10.44738	12.38842
H	-0.00817	10.88686	11.81344
H	1.32357	11.28041	12.92998
H	0.39439	9.77362	13.15823
C	3.09706	9.50567	12.42172
H	3.52338	10.49976	12.68115
H	3.89014	8.91063	11.94495
H	2.81090	9.01377	13.37172
C	1.87068	9.73246	11.51205
C	-1.15123	7.00639	9.80192
H	-1.62448	6.84839	10.79330
H	-0.54071	6.11309	9.56320
H	-1.96991	7.09485	9.05344
C	0.15362	8.54662	8.32193
H	0.79792	7.72160	7.95155
H	0.73995	9.48284	8.23152
H	-0.73461	8.64014	7.65746
N	4.36913	7.85765	9.94499
N	5.14670	8.71980	9.89532

$[(PNP)ReCl_3]^{2-}$

Re	3.05554	6.41379	10.26773
P	4.61894	4.62497	10.47447

N	3.07065	6.22454	12.37728
Cl	1.34101	4.91628	9.13782
C	4.24152	5.64844	13.02245
H	4.01280	5.42194	14.10225
H	5.08449	6.39494	13.04998
Cl	3.45756	7.03054	7.76527
P	1.40841	8.05089	10.80849
C	4.72552	4.37022	12.34071
H	4.03835	3.53633	12.58653
H	5.74026	4.07996	12.68517
C	4.16559	2.76952	9.96089
C	4.02377	2.76566	8.43124
H	3.68316	1.76308	8.07727
H	4.98644	2.99187	7.92719
H	3.27746	3.52552	8.11954
C	-1.50260	8.73549	11.12102
H	-1.56462	9.71768	10.62271
H	-1.25937	8.90510	12.19124
H	-2.52561	8.29046	11.08821
C	-0.51555	7.75817	10.45341
C	2.41280	10.00388	9.04455
H	3.32616	9.37767	9.02241
H	2.67777	11.05596	8.77880
H	1.74995	9.59839	8.25384
C	2.80397	2.42939	10.60106
H	2.88997	2.28175	11.69764
H	2.44508	1.46385	10.17082
H	2.04310	3.20575	10.39147
C	7.39188	3.64686	9.69564
H	7.49368	3.00796	10.59638
H	8.41934	3.98855	9.42090
H	7.02703	3.02237	8.85618
C	7.22095	5.71654	11.02985
H	7.37486	5.13436	11.96275
H	6.65064	6.64096	11.25568
H	8.23075	6.01636	10.65888
C	6.52181	4.88661	9.93900
C	5.13069	1.66323	10.42965
H	5.41301	1.78435	11.49686
H	6.05688	1.59531	9.83433
H	4.61579	0.67699	10.34098

C	1.34731	7.98794	12.69266
H	1.16881	8.98069	13.15646
H	0.49321	7.33537	12.96193
C	2.64803	7.35833	13.18703
H	3.45275	8.14573	13.21401
H	2.51354	7.03635	14.25833
C	6.46484	5.70605	8.64031
H	7.50392	5.93149	8.29783
H	5.91100	6.65461	8.78139
H	5.93694	5.16582	7.82893
C	0.55008	10.94162	10.41359
H	-0.18265	10.71008	9.61514
H	0.93246	11.97161	10.21140
H	0.01733	10.97884	11.38546
C	2.73539	10.51170	11.47659
H	3.06228	11.53518	11.17197
H	3.63700	9.86816	11.53752
H	2.27230	10.60195	12.48175
C	1.74400	9.97871	10.42740
C	-0.87977	6.36183	10.99818
H	-0.90603	6.34590	12.10761
H	-0.18205	5.58289	10.63459
H	-1.90660	6.10349	10.64478
C	-0.68076	7.76712	8.92619
H	-0.01183	7.00810	8.47014
H	-0.43527	8.75800	8.49077
H	-1.73549	7.52672	8.64998
Cl	4.95737	8.14058	10.77102

[(PNP)ReCl]

Re	2.87958	6.22525	10.48237
P	4.55125	4.56852	10.54449
N	3.21033	6.34430	12.38070
C	4.22480	5.56089	13.13632
H	3.79154	5.26392	14.11897
H	5.06889	6.24783	13.37763
Cl	2.12517	5.74692	8.22959
P	1.36356	7.98113	10.88681
C	4.72914	4.32258	12.39651
H	4.08378	3.45609	12.64326
H	5.76079	4.05648	12.70445

C	4.19415	2.78827	9.92304
C	4.32978	2.75974	8.39084
H	3.93701	1.79401	8.00529
H	5.38516	2.83671	8.06291
H	3.74448	3.57849	7.92435
C	-1.44681	8.65868	11.27152
H	-1.28770	9.74373	11.13463
H	-1.36552	8.43391	12.35385
H	-2.49492	8.43816	10.97302
C	-0.49010	7.80589	10.42329
C	2.41074	9.68807	8.93232
H	3.08729	8.83376	8.72269
H	2.93719	10.62748	8.65758
H	1.53428	9.58180	8.26707
C	2.71460	2.54475	10.28396
H	2.53022	2.59975	11.37682
H	2.41642	1.52803	9.94813
H	2.05787	3.28422	9.78443
C	7.39662	4.11360	10.02950
H	7.48855	3.66431	11.03942
H	8.37336	4.58807	9.79005
H	7.24412	3.29563	9.29942
C	6.64331	6.34795	10.88169
H	6.85951	6.02556	11.91959
H	5.82485	7.09898	10.91165
H	7.55405	6.85307	10.49465
C	6.28228	5.16485	9.96220
C	5.06186	1.69512	10.56646
H	4.96708	1.67646	11.67067
H	6.13348	1.79729	10.31629
H	4.72995	0.70055	10.19636
C	1.31426	7.97486	12.76270
H	1.15914	8.98334	13.19712
H	0.42876	7.36646	13.03439
C	2.57693	7.31433	13.31451
H	3.34328	8.08132	13.57344
H	2.34315	6.79240	14.27081
C	6.12754	5.70519	8.52878
H	7.07255	6.19461	8.20855
H	5.31029	6.45388	8.47429
H	5.89149	4.91014	7.79776

C	1.06585	10.88952	10.70634
H	0.16827	10.86071	10.05916
H	1.58175	11.85442	10.50795
H	0.73148	10.90782	11.76389
C	3.31198	9.91541	11.24464
H	3.83829	10.83195	10.90189
H	4.00413	9.05671	11.11127
H	3.10908	10.03633	12.32730
C	2.02292	9.72551	10.42164
C	-0.80126	6.31151	10.64605
H	-0.63777	5.99557	11.69715
H	-0.17230	5.67558	9.99221
H	-1.86831	6.11740	10.40292
C	-0.66514	8.11657	8.92666
H	0.05578	7.53914	8.31237
H	-0.54652	9.19542	8.70477
H	-1.69139	7.82900	8.61092

[(PNP)ReCl(N_2)]

Re	2.83130	6.21272	10.32603
P	4.69309	4.67499	10.42318
N	3.01823	6.16373	12.28772
Cl	1.24468	4.71205	9.33552
C	3.96117	5.31809	13.04953
H	3.39790	4.44809	13.46222
H	4.32888	5.88815	13.93465
P	1.24357	7.93062	10.85079
C	5.15566	4.84515	12.22906
H	5.58616	3.91026	12.64105
H	5.95361	5.61276	12.26591
C	4.41819	2.78464	10.20181
C	3.89794	2.51180	8.77868
H	3.61033	1.44090	8.69982
H	4.66559	2.70420	8.00632
H	3.00233	3.12286	8.55527
C	-1.29198	9.31329	10.43298
H	-0.83644	10.24264	10.04178
H	-1.41417	9.41722	11.53031
H	-2.31144	9.24174	9.99562
C	-0.50118	8.05108	10.05772
C	2.01746	10.32230	9.49484

H	2.44860	9.66169	8.71769
H	2.61774	11.25754	9.50596
H	0.99055	10.59759	9.18932
C	3.30473	2.43671	11.21190
H	3.64884	2.52257	12.26222
H	2.99487	1.38143	11.05409
H	2.41167	3.07564	11.06603
C	7.59052	4.58532	10.13860
H	7.69836	4.75672	11.22811
H	8.48049	5.03771	9.65032
H	7.63449	3.49783	9.95593
C	6.42742	6.76183	9.77704
H	6.41529	7.04482	10.84907
H	5.61638	7.31156	9.26850
H	7.39103	7.11753	9.35331
C	6.32168	5.23751	9.56223
C	5.64473	1.90610	10.48577
H	6.13036	2.13994	11.45498
H	6.40754	1.97937	9.68711
H	5.32388	0.84264	10.52862
C	0.93146	7.51402	12.63730
H	0.53764	8.35929	13.23593
H	0.15125	6.72977	12.60970
C	2.20228	6.93103	13.24950
H	2.82880	7.73630	13.70479
H	1.92415	6.26139	14.09687
C	6.22243	4.95571	8.05355
H	7.05441	5.46919	7.52586
H	5.27178	5.32818	7.62490
H	6.30792	3.87532	7.82879
C	1.45405	10.62043	11.93905
H	0.37778	10.80723	11.77425
H	1.97235	11.60265	11.89376
H	1.58390	10.23551	12.97012
C	3.55328	9.45653	11.25224
H	4.07338	10.43872	11.26915
H	4.06707	8.81571	10.50825
H	3.68583	8.99044	12.24719
C	2.06954	9.67771	10.89197
C	-1.30558	6.81717	10.51544
H	-1.62177	6.89044	11.57510

H	-0.73976	5.87738	10.36099
H	-2.23137	6.75684	9.90423
C	-0.30160	7.95592	8.53164
H	0.19393	7.00240	8.26367
H	0.30075	8.78898	8.12428
H	-1.29383	7.98286	8.03228
N	3.27784	7.02136	8.59069
N	3.58941	7.57678	7.63269

***trans*-[(PNP)ReCl(N_2)$_2$]**

Re	3.03025	6.40151	10.09644
P	4.84418	4.75527	10.34371
N	3.16641	6.29408	12.12972
C	4.40756	6.01947	12.83830
H	4.20819	5.28592	13.65648
H	4.77386	6.93973	13.36404
Cl	2.86763	6.52051	7.63859
P	1.28084	8.00065	10.75598
C	5.53213	5.47581	11.92980
H	6.17575	4.75707	12.47665
H	6.19125	6.30107	11.59221
C	4.34941	2.95031	10.79465
C	3.54922	2.33211	9.62959
H	3.03540	1.41534	9.98849
H	4.20098	2.03739	8.78868
H	2.77856	3.01370	9.23099
C	-1.57616	8.49405	10.66495
H	-1.49271	9.46138	11.19058
H	-1.75284	7.70278	11.42013
H	-2.48554	8.54005	10.02793
C	-0.36573	8.17417	9.77014
C	2.49445	10.49559	10.14943
H	3.18621	9.86165	9.56844
H	3.07481	11.35919	10.53738
H	1.73865	10.89333	9.45004
C	3.46266	3.01676	12.05498
H	4.05236	3.28450	12.95322
H	3.02852	2.01105	12.23557
H	2.63016	3.73450	11.96115
C	7.66128	4.30205	9.82814
H	7.93756	5.01012	10.63438

H	8.47976	4.33389	9.07721
H	7.64348	3.28311	10.25299
C	6.52207	6.11554	8.54673
H	6.82542	6.85968	9.30637
H	5.59965	6.46738	8.04356
H	7.33483	6.07388	7.79062
C	6.34631	4.70594	9.13815
C	5.54975	2.04699	11.12328
H	6.18925	2.46639	11.92605
H	6.18301	1.84265	10.23997
H	5.16954	1.06796	11.48612
C	0.79981	7.10778	12.33061
H	0.23651	7.75797	13.03043
H	0.09941	6.31670	11.99417
C	2.03033	6.47864	13.02044
H	2.33899	7.11973	13.88135
H	1.73048	5.50328	13.48536
C	6.02017	3.75960	7.96932
H	6.80089	3.87881	7.18858
H	5.04476	4.01325	7.50735
H	6.01490	2.69390	8.26512
C	0.71111	10.60172	11.91787
H	-0.02946	10.90321	11.15409
H	1.14566	11.53460	12.33696
H	0.17816	10.09035	12.74480
C	2.89331	9.54794	12.45232
H	3.34843	10.53252	12.68921
H	3.70594	8.85785	12.16913
H	2.42679	9.17145	13.38328
C	1.84892	9.74734	11.33445
C	-0.62861	6.83717	9.05528
H	-0.83958	6.01273	9.76129
H	0.21864	6.54683	8.40271
H	-1.53087	6.95774	8.41864
C	-0.18812	9.24616	8.68000
H	0.71958	9.05693	8.07232
H	-0.14330	10.27334	9.08779
H	-1.06243	9.20396	7.99662
N	1.61402	5.03851	10.10733
N	0.80279	4.23652	10.14425
N	5.24868	8.57611	10.06024

N	4.43969	7.77101	10.05338

***cis*-[(PNP)ReCl(N_2)$_2$]**

Re	3.02408	6.39553	10.09730
P	4.84925	4.74346	10.30764
N	3.17173	6.28295	12.11036
C	4.41084	5.97285	12.81059
H	4.19892	5.24173	13.62615
H	4.77039	6.89653	13.32912
Cl	4.78706	8.13633	10.09485
P	1.30665	8.05258	10.75803
C	5.53231	5.44330	11.89762
H	6.18285	4.72416	12.43482
H	6.15727	6.29203	11.55627
C	4.34445	2.93570	10.76138
C	3.53719	2.31072	9.60639
H	3.16646	1.31438	9.92928
H	4.14431	2.15711	8.69768
H	2.65485	2.91566	9.33546
C	-1.56604	8.46980	10.69009
H	-1.49679	9.42399	11.23987
H	-1.72329	7.65568	11.42448
H	-2.47986	8.51520	10.05950
C	-0.35419	8.19501	9.78064
C	2.46465	10.59811	10.20191
H	3.31364	10.03591	9.76942
H	2.85889	11.55648	10.60324
H	1.74792	10.84769	9.40025
C	3.45293	2.99801	12.01859
H	4.03903	3.25502	12.92207
H	3.01344	1.99278	12.18900
H	2.62035	3.71586	11.92243
C	7.67184	4.31779	9.86651
H	7.93301	5.09613	10.60955
H	8.50433	4.28114	9.13148
H	7.64204	3.34146	10.38148
C	6.55544	6.03203	8.44442
H	6.75394	6.84212	9.16781
H	5.66437	6.33182	7.86244
H	7.41741	5.95939	7.74680
C	6.37109	4.66135	9.11745

C	5.54258	2.03126	11.09928
H	6.17423	2.45159	11.90762
H	6.18636	1.82239	10.22511
H	5.15772	1.05398	11.46184
C	0.82928	7.15131	12.32853
H	0.26047	7.79372	13.03082
H	0.14300	6.34813	11.99181
C	2.06192	6.53885	13.01827
H	2.40948	7.20466	13.84234
H	1.76754	5.58395	13.52353
C	6.10487	3.64083	7.99599
H	6.91456	3.72897	7.24120
H	5.14738	3.84638	7.47670
H	6.09919	2.59257	8.34742
C	0.63972	10.62242	11.93604
H	-0.09413	10.92686	11.16642
H	1.04518	11.55534	12.38313
H	0.10349	10.08284	12.74302
C	2.85464	9.63202	12.48286
H	3.26500	10.63152	12.74037
H	3.69936	8.99427	12.16075
H	2.39880	9.22272	13.40553
C	1.81403	9.81474	11.35881
C	-0.60841	6.86593	9.04963
H	-0.77798	6.02152	9.74197
H	0.22264	6.59617	8.37166
H	-1.52660	6.97741	8.43468
C	-0.22230	9.29162	8.70868
H	0.68201	9.14674	8.08391
H	-0.19524	10.31124	9.13540
H	-1.10442	9.23990	8.03605
N	1.63064	5.06471	10.11363
N	0.80573	4.26653	10.18478
N	2.89181	6.60133	6.97047
N	2.93786	6.52734	8.10760

[(PNP)ReCl]$^{-}$

Re	2.87119	6.21860	10.46628
P	4.52232	4.60028	10.54152
N	3.19839	6.33215	12.37928
C	4.22687	5.57562	13.12893

H	3.80693	5.27526	14.12159
H	5.07732	6.26210	13.36543
Cl	2.36229	5.98313	8.07250
P	1.39253	7.94946	10.87917
C	4.73673	4.33411	12.39478
H	4.09777	3.46418	12.64822
H	5.77574	4.07947	12.69503
C	4.18809	2.78746	9.92597
C	4.28554	2.78227	8.39156
H	3.87275	1.82826	7.99091
H	5.33487	2.85776	8.04127
H	3.70431	3.62396	7.95725
C	-1.45838	8.67251	11.24421
H	-1.32786	9.75373	11.05299
H	-1.34913	8.50424	12.33528
H	-2.51019	8.41552	10.97904
C	-0.49170	7.80100	10.42877
C	2.37500	9.73453	8.94069
H	3.02567	8.86033	8.72689
H	2.92290	10.66921	8.68225
H	1.49324	9.66179	8.27602
C	2.72026	2.52548	10.31398
H	2.58156	2.48597	11.41426
H	2.39074	1.54703	9.89391
H	2.06722	3.33946	9.93602
C	7.39810	4.06119	10.05414
H	7.46035	3.61099	11.06715
H	8.39168	4.51621	9.83458
H	7.24834	3.24299	9.32179
C	6.67121	6.32010	10.86591
H	6.87704	6.00778	11.91038
H	5.83476	7.05488	10.87302
H	7.58951	6.81579	10.47673
C	6.30288	5.12853	9.96208
C	5.06914	1.68578	10.53320
H	5.03453	1.69034	11.64206
H	6.12854	1.76481	10.22604
H	4.70348	0.68668	10.20035
C	1.32650	7.97830	12.76193
H	1.17809	8.99242	13.19087
H	0.44164	7.37059	13.03937

C	2.59380	7.31631	13.30571
H	3.35923	8.09188	13.55687
H	2.36186	6.80854	14.27542
C	6.17453	5.65676	8.52329
H	7.11528	6.17202	8.22321
H	5.32984	6.37468	8.45754
H	5.98085	4.84946	7.79149
C	1.01418	10.88989	10.72946
H	0.11891	10.85784	10.07712
H	1.51229	11.87100	10.55100
H	0.67343	10.88328	11.78625
C	3.28090	9.95056	11.24386
H	3.79853	10.87532	10.90112
H	3.95671	9.07912	11.09466
H	3.08102	10.06279	12.32933
C	1.98989	9.74726	10.42953
C	-0.82046	6.31694	10.68158
H	-0.75339	6.05274	11.75726
H	-0.10188	5.66335	10.14495
H	-1.85954	6.10060	10.34116
C	-0.64600	8.07324	8.92323
H	0.10014	7.49250	8.33954
H	-0.52844	9.14834	8.67836
H	-1.66423	7.76926	8.58879

$[(PNP)ReCl_2]^{2-}$

Re	2.99619	6.33669	10.37014
P	4.69187	4.76936	10.43480
N	3.15367	6.24744	12.31907
Cl	1.69246	5.15282	8.44020
C	4.10155	5.42636	13.09010
H	3.53344	4.62634	13.64110
H	4.56307	6.06004	13.89637
Cl	3.87624	7.69071	8.30572
P	1.41093	7.95280	10.85008
C	5.21876	4.79125	12.25797
H	5.49070	3.79075	12.66252
H	6.13032	5.42013	12.30857
C	4.26628	2.84954	10.21246
C	3.99106	2.54943	8.73072
H	3.50817	1.54596	8.64023

H	4.92313	2.51626	8.13076
H	3.29751	3.30834	8.30461
C	-1.41995	8.85259	10.73869
H	-1.21285	9.88745	10.39764
H	-1.41968	8.85104	11.84983
H	-2.45790	8.60290	10.40596
C	-0.42384	7.84238	10.15685
C	1.84237	10.39610	9.37755
H	2.34677	9.69639	8.67514
H	2.36241	11.38289	9.31917
H	0.79369	10.56173	9.05580
C	2.93356	2.70439	10.97291
H	3.04779	2.90660	12.05817
H	2.55228	1.65809	10.85654
H	2.19349	3.42886	10.56987
C	7.56141	4.16708	9.97638
H	7.66894	4.08822	11.07907
H	8.53082	4.55276	9.57573
H	7.42995	3.14329	9.57341
C	6.78484	6.55531	9.92893
H	6.93088	6.70238	11.01878
H	5.98277	7.24251	9.58394
H	7.74491	6.82181	9.42006
C	6.41704	5.10316	9.56589
C	5.27085	1.82898	10.76524
H	5.54681	2.02878	11.82222
H	6.20600	1.78520	10.17257
H	4.81924	0.80679	10.73513
C	1.11582	7.67979	12.69898
H	0.84007	8.58943	13.27782
H	0.26062	6.97801	12.75854
C	2.35942	7.01369	13.29154
H	3.01292	7.78876	13.77996
H	2.04209	6.33265	14.12911
C	6.20698	5.06358	8.04267
H	7.13281	5.42186	7.53133
H	5.37047	5.73917	7.75840
H	5.99597	4.04242	7.67127
C	1.17594	10.79577	11.76823
H	0.09541	10.87294	11.53816
H	1.60442	11.82508	11.69340

H	1.27674	10.48264	12.82852
C	3.41984	9.84665	11.21514
H	3.82323	10.89039	11.16461
H	3.98588	9.17897	10.53160
H	3.56837	9.46794	12.24682
C	1.93245	9.85915	10.81468
C	-0.90175	6.40990	10.46471
H	-1.03516	6.22455	11.55062
H	-0.17674	5.67369	10.05391
H	-1.89495	6.24901	9.97776
C	-0.35920	7.96216	8.62340
H	0.34969	7.20834	8.21548
H	-0.04868	8.96752	8.28370
H	-1.37123	7.75867	8.19684

[(PNP)ReCl(N_2)]$^-$

Re	3.11290	6.45647	10.36986
P	4.64476	4.65426	10.50993
N	3.21860	6.35555	12.37557
C	4.27046	5.63082	13.09797
H	3.90158	5.35104	14.11877
H	5.14680	6.30655	13.27729
Cl	2.01004	5.64224	8.19707
P	1.44985	8.07408	10.85218
C	4.72375	4.36568	12.37171
H	4.01171	3.54450	12.59055
H	5.72571	4.03067	12.71302
C	4.09069	2.89255	9.90958
C	4.24509	2.80071	8.38271
H	3.73493	1.88098	8.01704
H	5.30693	2.73035	8.07256
H	3.76735	3.67378	7.89027
C	-1.45114	8.41311	11.24848
H	-1.46145	9.50757	11.09184
H	-1.31421	8.22469	12.33262
H	-2.46201	8.03227	10.97738
C	-0.39737	7.69414	10.39077
C	2.04500	10.14469	9.01093
H	2.81561	9.46269	8.60839
H	2.39032	11.18856	8.83617
H	1.11455	9.99860	8.43181

C	2.58512	2.83020	10.23819
H	2.38011	2.96563	11.32018
H	2.18980	1.83204	9.94144
H	2.03828	3.61411	9.67431
C	7.43193	3.77515	10.31561
H	7.34638	3.40433	11.35777
H	8.48545	4.10344	10.16672
H	7.25705	2.92332	9.62966
C	6.93332	6.17249	10.85456
H	6.96385	5.95122	11.94055
H	6.26119	7.03579	10.68645
H	7.96081	6.46693	10.54394
C	6.48736	4.95051	10.02649
C	4.80148	1.71131	10.59004
H	4.70888	1.74159	11.69450
H	5.87677	1.65186	10.33986
H	4.33117	0.76043	10.25098
C	1.35401	7.97510	12.73236
H	1.12925	8.95484	13.20364
H	0.50857	7.29686	12.96588
C	2.64801	7.36820	13.27163
H	3.40090	8.17590	13.46593
H	2.44377	6.91076	14.27435
C	6.56526	5.31856	8.53311
H	7.61411	5.59694	8.28407
H	5.92077	6.18223	8.28933
H	6.27829	4.47491	7.87889
C	0.76761	10.91810	11.03293
H	-0.16515	10.86979	10.43804
H	1.15616	11.95809	10.94802
H	0.50853	10.74902	12.09857
C	3.16202	10.21359	11.24761
H	3.49325	11.25002	11.01308
H	3.95355	9.51501	10.91560
H	3.05921	10.13797	12.34902
C	1.83031	9.93519	10.52129
C	-0.53855	6.17157	10.59310
H	-0.33284	5.86105	11.63807
H	0.15690	5.63006	9.91896
H	-1.58252	5.86844	10.35061
C	-0.62279	7.99470	8.90032

H	0.15837	7.50245	8.28313
H	-0.63589	9.08268	8.68938
H	-1.61168	7.58814	8.58923
N	4.20051	7.57562	9.32683
N	4.93906	8.31813	8.80437

***cis*-[(PNP)ReCl$_2$(N$_2$)]$^{2-}$**

Re	3.00205	6.37998	10.00653
P	4.45150	4.53750	10.33578
N	2.93308	6.11317	12.13594
Cl	1.03574	4.65703	9.92935
C	3.24930	4.88840	12.80721
H	2.39156	4.53474	13.46127
H	4.10041	5.00992	13.55768
Cl	2.59983	6.65892	7.49322
P	1.57432	8.15328	10.70170
C	3.61342	3.75943	11.82388
H	2.67418	3.35147	11.39880
H	4.18490	2.94210	12.31616
C	4.61634	3.06719	9.02188
C	4.77584	3.78448	7.66805
H	4.74814	3.03288	6.84307
H	5.74024	4.32658	7.59716
H	3.97095	4.53636	7.50595
C	-1.03027	9.05573	11.77737
H	-1.21746	9.83960	11.01636
H	-0.48801	9.51810	12.62895
H	-2.02694	8.73033	12.16094
C	-0.29075	7.83597	11.20823
C	0.56752	9.91877	8.69048
H	0.71104	9.02384	8.04837
H	0.73187	10.82345	8.05909
H	-0.48208	9.94997	9.04461
C	3.27911	2.30874	9.01493
H	3.17043	1.66437	9.91317
H	3.24461	1.64284	8.11985
H	2.40997	3.00058	8.98687
C	6.86623	3.68450	11.76352
H	6.26440	3.43916	12.66274
H	7.88527	3.96486	12.12040
H	6.96920	2.76724	11.15843

C	6.24174	6.06026	11.98724
H	5.62829	5.84624	12.88183
H	5.88294	6.99310	11.52161
H	7.29042	6.23051	12.33063
C	6.26014	4.87549	10.99788
C	5.73305	2.02708	9.19461
H	5.65330	1.48084	10.15790
H	6.74995	2.46182	9.12307
H	5.64901	1.26513	8.38166
C	2.38359	8.52085	12.36088
H	3.28873	9.09865	12.07737
H	1.77266	9.16083	13.03807
C	2.79528	7.20140	13.05075
H	3.75165	7.39097	13.64294
H	2.03944	6.96981	13.86348
C	7.15507	5.26937	9.80886
H	8.16961	5.54082	10.18546
H	6.74096	6.15642	9.28886
H	7.28217	4.44675	9.07744
C	1.38423	11.10790	10.77562
H	0.39452	11.11552	11.26877
H	1.47410	12.05608	10.19290
H	2.16096	11.13910	11.56630
C	2.97787	10.04184	9.18276
H	3.02948	11.01993	8.64708
H	3.14922	9.22219	8.45621
H	3.80951	10.00682	9.91157
C	1.59342	9.90973	9.83549
C	-0.27144	6.74446	12.29559
H	0.10264	7.13541	13.26392
H	0.35758	5.88646	11.98288
H	-1.31469	6.38466	12.45850
C	-1.05324	7.28645	9.98892
H	-0.54496	6.37726	9.60442
H	-1.14152	8.02342	9.16962
H	-2.08628	7.00561	10.30523
N	4.47038	7.51003	9.84347
N	5.41729	8.19336	9.69111

***cis*-[(PNP)ReCl(N_2)$_2$]$^-$**

Re	3.02431	6.41389	10.02387

P	4.80902	4.77409	10.30095
N	3.18854	6.30256	12.13750
C	4.39467	5.94372	12.83139
H	4.19721	5.14600	13.60421
H	4.80110	6.80715	13.43630
Cl	4.86131	8.18452	10.14713
P	1.34136	8.01553	10.75352
C	5.51674	5.45450	11.89089
H	6.19805	4.74163	12.40081
H	6.10577	6.32820	11.54417
C	4.31604	2.95807	10.76472
C	3.52252	2.30765	9.61433
H	3.20100	1.29183	9.93630
H	4.11886	2.18830	8.69311
H	2.60919	2.87929	9.37281
C	-1.55239	8.43230	10.70995
H	-1.48475	9.37344	11.28389
H	-1.69520	7.60050	11.42750
H	-2.47316	8.48619	10.08671
C	-0.34070	8.18395	9.79372
C	2.48666	10.56927	10.20045
H	3.35414	10.00608	9.80235
H	2.85776	11.54270	10.59280
H	1.78484	10.78993	9.37635
C	3.40410	3.03465	12.00643
H	3.98586	3.25512	12.92247
H	2.91146	2.04829	12.14909
H	2.62274	3.80840	11.90728
C	7.65981	4.37603	9.87420
H	7.89763	5.19085	10.58521
H	8.49814	4.32339	9.14370
H	7.64644	3.42313	10.43483
C	6.48806	6.00323	8.38676
H	6.60779	6.85601	9.07978
H	5.59242	6.22566	7.77604
H	7.37153	5.94970	7.71122
C	6.35019	4.65595	9.11636
C	5.51623	2.06660	11.12977
H	6.13920	2.51252	11.93167
H	6.17008	1.84226	10.26546
H	5.13632	1.09358	11.51369

C	0.85179	7.11907	12.32239
H	0.23617	7.74345	13.00380
H	0.21266	6.28488	11.96367
C	2.09901	6.55784	13.03737
H	2.39989	7.27592	13.85145
H	1.79039	5.62908	13.60732
C	6.12670	3.58990	8.02982
H	6.94027	3.67542	7.27617
H	5.16687	3.75239	7.49983
H	6.14529	2.55330	8.41605
C	0.65460	10.60315	11.92822
H	-0.08151	10.90482	11.15815
H	1.05782	11.53881	12.37598
H	0.11923	10.06112	12.73475
C	2.86646	9.61453	12.48295
H	3.30492	10.61045	12.71465
H	3.68423	8.93458	12.17478
H	2.40001	9.23266	13.41227
C	1.82850	9.79172	11.35633
C	-0.58556	6.86696	9.03851
H	-0.71130	6.00035	9.71310
H	0.24504	6.63121	8.34716
H	-1.51902	6.97076	8.44170
C	-0.22887	9.29380	8.73422
H	0.66925	9.15255	8.09963
H	-0.19509	10.30982	9.17084
H	-1.12000	9.24853	8.07001
N	1.68625	5.07699	9.99647
N	0.86575	4.25768	10.05359
N	2.90479	6.80395	6.94788
N	2.94777	6.64724	8.08948

^{3}[{Re(PNP)Cl}(μ-N_2){Re(PNP)Cl}]

Re	0.02632	2.45895	-0.07942
C	2.03013	4.68822	1.93986
P	1.98719	2.88357	1.25494
N	1.19744	3.22741	-1.47139
P	-1.68993	2.88822	-1.74314
C	-3.09126	4.13473	-1.31959
Cl	-1.42650	2.88057	1.91578
C	2.63871	1.66081	2.57528

C	-2.37044	1.40081	-2.74438
N	-0.15642	0.59777	0.05083
C	-0.69170	3.85860	-2.99572
H	-0.85678	4.92919	-2.76163
H	-1.05464	3.69226	-4.03005
C	0.79191	3.53416	-2.85963
H	1.38747	4.40072	-3.23196
H	1.06985	2.67239	-3.51234
C	2.65466	3.45175	-1.36155
H	3.15788	3.00151	-2.25042
H	2.86260	4.54815	-1.43127
C	3.27463	2.87660	-0.08949
H	3.51234	1.80805	-0.24846
H	4.21682	3.39645	0.17337
C	-4.15409	3.42053	-0.46736
H	-4.86132	4.17448	-0.05931
H	-3.68630	2.89567	0.39007
H	-4.74925	2.69872	-1.05961
C	-3.73723	4.79403	-2.55033
H	-4.45361	5.56908	-2.20190
H	-4.30355	4.08269	-3.17617
H	-2.99645	5.30759	-3.19543
C	-2.43802	5.23601	-0.46020
H	-3.20019	6.01304	-0.23579
H	-1.59681	5.74210	-0.97688
H	-2.07398	4.82354	0.50051
C	1.14170	5.53448	1.00578
H	1.13139	6.58391	1.37179
H	0.09772	5.16428	1.00902
H	1.50321	5.54381	-0.03988
C	1.40741	4.74161	3.34582
H	1.25987	5.80599	3.62945
H	2.06115	4.28819	4.11512
H	0.41831	4.24152	3.36378
C	3.44536	5.28814	1.95632
H	3.40007	6.30457	2.40353
H	3.86164	5.40299	0.93568
H	4.16113	4.69512	2.55581
C	-3.32837	1.78268	-3.88171
H	-3.50863	0.88341	-4.50897
H	-2.91894	2.57069	-4.54584

H	-4.31336	2.11790	-3.50496
C	-3.06586	0.41570	-1.79225
H	-3.34976	-0.49689	-2.35569
H	-3.97778	0.84081	-1.33474
H	-2.39126	0.08580	-0.98601
C	-1.12827	0.71728	-3.34444
H	-1.41802	-0.27777	-3.74005
H	-0.34804	0.54848	-2.57942
H	-0.68770	1.30309	-4.17590
C	2.80305	0.30593	1.86279
H	3.06646	-0.46406	2.61870
H	3.62083	0.32184	1.11618
H	1.87543	-0.02395	1.35913
C	3.98641	2.07202	3.18584
H	4.34071	1.26663	3.86532
H	3.91088	2.99675	3.78928
H	4.76913	2.22030	2.41407
C	1.56081	1.50387	3.66534
H	1.72566	0.55121	4.21171
H	0.54408	1.48727	3.22804
H	1.59224	2.32125	4.40690
Re	0.02629	-2.45893	0.07947
C	2.03007	-4.68804	-1.94004
P	1.98714	-2.88347	-1.25493
N	1.19737	-3.22760	1.47135
P	-1.68998	-2.88832	1.74317
C	-3.09131	-4.13479	1.31953
Cl	-1.42644	-2.88043	-1.91581
C	2.63866	-1.66061	-2.57517
C	-2.37048	-1.40099	2.74455
N	-0.15634	-0.59774	-0.05067
C	-0.69177	-3.85880	2.99568
H	-0.85694	-4.92937	2.76159
H	-1.05468	-3.69246	4.03003
C	0.79186	-3.53446	2.85958
H	1.38736	-4.40110	3.23179
H	1.06988	-2.67278	3.51236
C	2.65458	-3.45196	1.36149
H	3.15782	-3.00186	2.25042
H	2.86250	-4.54837	1.43105
C	3.27457	-2.87664	0.08951

H	3.51225	-1.80811	0.24862
H	4.21678	-3.39644	-0.17340
C	-4.15414	-3.42053	0.46734
H	-4.86136	-4.17444	0.05923
H	-3.68633	-2.89561	-0.39005
H	-4.74930	-2.69876	1.05963
C	-3.73730	-4.79416	2.55023
H	-4.45362	-5.56923	2.20175
H	-4.30369	-4.08285	3.17606
H	-2.99653	-5.30768	3.19535
C	-2.43808	-5.23603	0.46008
H	-3.20026	-6.01303	0.23563
H	-1.59687	-5.74215	0.97672
H	-2.07405	-4.82350	-0.50061
C	1.14167	-5.53444	-1.00606
H	1.13146	-6.58384	-1.37214
H	0.09766	-5.16432	-1.00934
H	1.50311	-5.54380	0.03962
C	1.40735	-4.74128	-3.34601
H	1.25981	-5.80563	-3.62976
H	2.06106	-4.28777	-4.11527
H	0.41823	-4.24121	-3.36390
C	3.44532	-5.28793	-1.95659
H	3.40008	-6.30426	-2.40406
H	3.86156	-5.40302	-0.93596
H	4.16111	-4.69474	-2.55590
C	-3.32841	-1.78295	3.88185
H	-3.50860	-0.88374	4.50922
H	-2.91902	-2.57106	4.54587
H	-4.31342	-2.11806	3.50507
C	-3.06588	-0.41577	1.79252
H	-3.34981	0.49675	2.35606
H	-3.97778	-0.84084	1.33494
H	-2.39126	-0.08575	0.98635
C	-1.12828	-0.71753	3.34467
H	-1.41802	0.27750	3.74035
H	-0.34804	-0.54872	2.57966
H	-0.68775	-1.30342	4.17610
C	2.80268	-0.30570	-1.86266
H	3.06622	0.46429	-2.61853
H	3.62024	-0.32151	-1.11582

H	1.87487	0.02410	-1.35928
C	3.98652	-2.07163	-3.18552
H	4.34078	-1.26621	-3.86499
H	3.91124	-2.99640	-3.78890
H	4.76916	-2.21973	-2.41361
C	1.56091	-1.50384	-3.66541
H	1.72567	-0.55112	-4.21170
H	0.54410	-1.48746	-3.22828
H	1.59264	-2.32117	-4.40701

[{Re(PNP)Cl}(μ-N_2){Re(PNP)Cl}]$^-$

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C	2.07490	4.70719	1.88200
P	2.02238	2.90129	1.16829
N	1.13934	3.30258	-1.51237
P	-1.71750	2.82655	-1.64879
C	-3.17835	4.00789	-1.18657
Cl	-1.36057	2.87342	2.01839
C	2.75332	1.69797	2.47948
C	-2.37713	1.34284	-2.69868
N	-0.12055	0.59064	0.07990
C	-0.82748	3.86153	-2.94863
H	-1.03308	4.92117	-2.69548
H	-1.22332	3.68423	-3.97015
C	0.67569	3.60793	-2.87815
H	1.21607	4.51102	-3.25633
H	0.96717	2.77545	-3.56558
C	2.59791	3.52614	-1.46057
H	3.06804	3.07263	-2.36872
H	2.81175	4.62345	-1.54191
C	3.27863	2.95407	-0.21234
H	3.54299	1.89478	-0.38989
H	4.21574	3.50010	0.02101
C	-4.16862	3.23972	-0.29566
H	-4.90797	3.95139	0.13503
H	-3.63614	2.75080	0.54577
H	-4.73629	2.47636	-0.86283
C	-3.90686	4.63462	-2.38710
H	-4.63882	5.38516	-2.01310
H	-4.47105	3.89627	-2.98407
H	-3.21443	5.16940	-3.06853

C	-2.55860	5.14180	-0.34564
H	-3.35978	5.86520	-0.07282
H	-1.77860	5.70444	-0.89873
H	-2.11570	4.74006	0.58748
C	1.15320	5.55390	0.98143
H	1.12345	6.59663	1.37001
H	0.12072	5.15024	0.98650
H	1.49678	5.58815	-0.06973
C	1.48204	4.73850	3.30080
H	1.32686	5.79848	3.60237
H	2.15608	4.28186	4.05120
H	0.49918	4.22392	3.32687
C	3.47924	5.33140	1.87537
H	3.43045	6.34560	2.33110
H	3.87188	5.45738	0.84626
H	4.21676	4.74332	2.45389
C	-3.36042	1.70736	-3.81957
H	-3.50175	0.81942	-4.47487
H	-2.99900	2.53739	-4.46099
H	-4.35885	1.98006	-3.42558
C	-3.02592	0.30409	-1.77211
H	-3.30605	-0.59185	-2.36491
H	-3.93277	0.68979	-1.27055
H	-2.32078	-0.04885	-1.00249
C	-1.11622	0.71558	-3.32400
H	-1.36536	-0.29232	-3.71782
H	-0.31931	0.57980	-2.56850
H	-0.71350	1.32803	-4.15635
C	2.92368	0.34919	1.75976
H	3.21257	-0.42312	2.50516
H	3.72423	0.38376	0.99560
H	1.98900	0.01224	1.27171
C	4.10575	2.12716	3.06440
H	4.49651	1.32202	3.72629
H	4.02732	3.04472	3.67963
H	4.86525	2.30119	2.27400
C	1.70148	1.50702	3.59034
H	1.89361	0.54962	4.12088
H	0.67627	1.47668	3.17084
H	1.72990	2.31662	4.34153
Re	0.04352	-2.48779	0.07729

C	2.07502	-4.70714	-1.88234
P	2.02254	-2.90134	-1.16835
N	1.13949	-3.30280	1.51231
P	-1.71731	-2.82666	1.64883
C	-3.17840	-4.00764	1.18651
Cl	-1.36043	-2.87365	-2.01842
C	2.75356	-1.69784	-2.47933
C	-2.37652	-1.34298	2.69902
N	-0.12061	-0.59077	-0.07990
C	-0.82736	-3.86196	2.94847
H	-1.03307	-4.92155	2.69517
H	-1.22317	-3.68477	3.97002
C	0.67582	-3.60845	2.87802
H	1.21615	-4.51167	3.25597
H	0.96736	-2.77616	3.56566
C	2.59803	-3.52649	1.46046
H	3.06822	-3.07312	2.36864
H	2.81176	-4.62383	1.54167
C	3.27879	-2.95437	0.21227
H	3.54323	-1.89512	0.38993
H	4.21585	-3.50045	-0.02113
C	-4.16843	-3.23923	0.29555
H	-4.90795	-3.95072	-0.13515
H	-3.63578	-2.75047	-0.54588
H	-4.73592	-2.47570	0.86267
C	-3.90714	-4.63419	2.38701
H	-4.63919	-5.38463	2.01298
H	-4.47128	-3.89569	2.98385
H	-3.21488	-5.16902	3.06856
C	-2.55887	-5.14169	0.34561
H	-3.36021	-5.86487	0.07270
H	-1.77905	-5.70455	0.89874
H	-2.11580	-4.74003	-0.58746
C	1.15331	-5.55399	-0.98192
H	1.12357	-6.59665	-1.37066
H	0.12083	-5.15032	-0.98695
H	1.49686	-5.58839	0.06924
C	1.48217	-4.73822	-3.30115
H	1.32696	-5.79816	-3.60287
H	2.15620	-4.28148	-4.05148
H	0.49931	-4.22363	-3.32713

C	3.47936	-5.33136	-1.87579
H	3.43058	-6.34545	-2.33177
H	3.87193	-5.45759	-0.84669
H	4.21691	-4.74314	-2.45413
C	-3.35947	-1.70751	3.82020
H	-3.50051	-0.81961	4.47563
H	-2.99791	-2.53762	4.46144
H	-4.35805	-1.98010	3.42652
C	-3.02552	-0.30413	1.77271
H	-3.30508	0.59195	2.36557
H	-3.93275	-0.68966	1.27170
H	-2.32072	0.04853	1.00266
C	-1.11534	-0.71589	3.32397
H	-1.36427	0.29199	3.71799
H	-0.31867	-0.58011	2.56823
H	-0.71240	-1.32847	4.15612
C	2.92402	-0.34920	-1.75936
H	3.21306	0.42320	-2.50460
H	3.72451	-0.38399	-0.99514
H	1.98935	-0.01223	-1.27132
C	4.10596	-2.12701	-3.06433
H	4.49676	-1.32180	-3.72610
H	4.02747	-3.04447	-3.67971
H	4.86546	-2.30121	-2.27397
C	1.70175	-1.50658	-3.59016
H	1.89405	-0.54915	-4.12059
H	0.67655	-1.47613	-3.17065
H	1.73002	-2.31609	-4.34145

TS$_{3a\text{->}2a}$

Re	-0.01515	2.39948	-0.03900
C	2.57199	4.59687	1.16676
P	2.23646	2.72450	0.81042
N	0.91660	2.97365	-1.70625
P	-1.99835	3.06135	-1.33960
C	-3.07819	4.53069	-0.72070
Cl	-0.91644	3.13748	2.13427
C	3.10730	1.66842	2.15128
C	-3.10306	1.66280	-2.05407
N	-0.35784	0.67464	-0.22428
C	-1.15572	3.81470	-2.82701

H	-1.08018	4.90158	-2.62172
H	-1.76073	3.69600	-3.74863
C	0.24619	3.23263	-2.98893
H	0.85860	3.95015	-3.58686
H	0.21033	2.29231	-3.59172
C	2.36944	2.94731	-1.93213
H	2.59283	2.33664	-2.84201
H	2.73272	3.97820	-2.17916
C	3.16648	2.38133	-0.75703
H	3.18587	1.27881	-0.82382
H	4.21435	2.74187	-0.75961
C	-4.03555	4.02241	0.37053
H	-4.53628	4.89089	0.85029
H	-3.48310	3.47134	1.15802
H	-4.82968	3.37045	-0.04190
C	-3.85990	5.24369	-1.83893
H	-4.36401	6.13351	-1.40372
H	-4.64255	4.61342	-2.29378
H	-3.19890	5.61277	-2.64840
C	-2.11415	5.55259	-0.08780
H	-2.69896	6.43924	0.23865
H	-1.34581	5.91339	-0.80142
H	-1.61191	5.12921	0.80234
C	1.55539	5.42333	0.35647
H	1.74018	6.50281	0.54556
H	0.52030	5.20299	0.67851
H	1.62128	5.24632	-0.73244
C	2.33079	4.90982	2.65390
H	2.35304	6.01205	2.79357
H	3.11205	4.48342	3.31071
H	1.33835	4.54339	2.98410
C	3.99102	5.01878	0.75015
H	4.14478	6.08366	1.02885
H	4.13863	4.94626	-0.34562
H	4.78476	4.42975	1.24555
C	-4.27798	2.16470	-2.90606
H	-4.75053	1.28743	-3.39753
H	-3.96262	2.86053	-3.70979
H	-5.06122	2.65632	-2.29820
C	-3.62351	0.81081	-0.88731
H	-4.16975	-0.06672	-1.29114

H	-4.30770	1.37328	-0.22512
H	-2.78406	0.41632	-0.29071
C	-2.18322	0.79841	-2.93519
H	-2.73661	-0.11420	-3.23980
H	-1.29739	0.45816	-2.37090
H	-1.86357	1.32873	-3.85491
C	3.08102	0.22247	1.62196
H	3.36623	-0.46930	2.44323
H	3.81138	0.07053	0.80333
H	2.08136	-0.08352	1.25363
C	4.56549	2.06394	2.42770
H	5.01006	1.32737	3.13203
H	4.65532	3.06069	2.90016
H	5.18492	2.05244	1.50791
C	2.27041	1.74430	3.44412
H	2.51573	0.87651	4.09216
H	1.18548	1.72783	3.22945
H	2.47984	2.66059	4.02349
Re	0.07554	-2.44542	0.09429
C	0.56394	-4.53049	-3.00417
P	1.34573	-3.23231	-1.83128
N	1.56592	-3.41649	1.06226
P	-1.05088	-2.92056	2.21043
C	-2.44737	-4.23363	2.22376
Cl	-2.06933	-2.42974	-1.15898
C	2.20286	-1.83705	-2.82213
C	-1.54196	-1.36924	3.20578
N	0.32072	-0.72516	0.10207
C	0.31606	-3.74953	3.17487
H	0.14202	-4.84159	3.10569
H	0.28145	-3.47517	4.24862
C	1.65976	-3.41341	2.52664
H	2.41293	-4.16857	2.85635
H	2.03388	-2.42943	2.90195
C	2.86931	-3.68321	0.44528
H	3.52565	-2.77855	0.47930
H	3.40840	-4.46400	1.03414
C	2.72115	-4.17856	-0.99520
H	3.67109	-4.12218	-1.56508
H	2.40497	-5.24105	-0.98364
C	-3.77487	-3.59983	1.77448

H	-4.52162	-4.40778	1.61818
H	-3.65157	-3.05513	0.81677
H	-4.19075	-2.91161	2.53542
C	-2.61446	-4.92132	3.59031
H	-3.40715	-5.69479	3.49983
H	-2.92233	-4.22494	4.39038
H	-1.69357	-5.44139	3.92002
C	-2.02673	-5.28402	1.17868
H	-2.75348	-6.12434	1.19301
H	-1.01968	-5.70614	1.37506
H	-2.02904	-4.84112	0.16552
C	-0.29535	-5.43043	-2.09522
H	-0.71213	-6.26462	-2.69918
H	-1.13816	-4.85265	-1.67144
H	0.28367	-5.87721	-1.26100
C	-0.36455	-3.82922	-4.01055
H	-0.93287	-4.60125	-4.57244
H	0.19343	-3.22747	-4.75384
H	-1.09548	-3.18078	-3.48590
C	1.60390	-5.39991	-3.73203
H	1.06434	-6.16387	-4.33200
H	2.26274	-5.94848	-3.03022
H	2.24120	-4.82606	-4.42775
C	-2.24462	-1.70492	4.53003
H	-2.38777	-0.76221	5.09948
H	-1.64791	-2.38816	5.16840
H	-3.24618	-2.14967	4.37673
C	-2.43124	-0.47961	2.32233
H	-2.63229	0.47420	2.85243
H	-3.39758	-0.95201	2.07054
H	-1.91283	-0.22110	1.38148
C	-0.24240	-0.60573	3.50510
H	-0.50499	0.35756	3.98770
H	0.30316	-0.36474	2.57478
H	0.43213	-1.15648	4.19080
C	3.21206	-1.17686	-1.87003
H	3.63757	-0.28087	-2.36969
H	4.05825	-1.84442	-1.61442
H	2.71602	-0.85103	-0.93734
C	2.95464	-2.35429	-4.05794
H	3.52285	-1.51003	-4.50389

H	2.27389	-2.73885	-4.84040
H	3.68802	-3.14678	-3.80613
C	1.15243	-0.78754	-3.22203
H	1.65073	0.01380	-3.80928
H	0.69725	-0.32037	-2.32885
H	0.33933	-1.20680	-3.84194

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