Supporting Information

The Metaphosphite (PO$_2^-$) Anion as a Ligand

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Materials and Methods

All experiments were carried out using Schlenk (argon atmosphere) and glovebox (argon atmosphere) techniques. All solvents were dried by passage through columns packed with activated alumina. Deuterated solvents were obtained from Euriso-Top GmbH, dried over Na/K2 channel by trap-to-trap transfer in vacuo, and degassed by three freeze–pump–thaw cycles, respectively. Silica gel 60 silanized was purchased from Merck KGaA and heated at 120°C in vacuo for 5 days prior to use. Pyridine-N-oxide (TCI) and [Fe(C8Me5)3]4 (acr) were sublimed prior to use. 18-crown-6 (Sigma Aldrich) was recrystallized prior to use. Ag[Al(O(C(CF3))2)]4 (tolite) was used as purchased. KC8 [ReI(c3-N,5-pyrazyl-2-pyrazyl-PNP)] and 1 were synthesized according to literature procedures.1 Elemental analyses were obtained from the analytical laboratories at the Georg-August University on an Elementar Vario EL 3. NMR spectra were recorded with Bruker Avance III HD 500 and a Bruker Avance Neo 400 spectrometers and were calibrated to the residual solvent proton resonance (CD3OD: 6 = 3.8 ppm, THF-d8: 6 = 3.58 ppm). Cyclic voltammograms (CVs) and electrolysis experiments were carried out with a GAMRY 1010E potentiostat using AuAg2 reference–, glassy-carbon working– and Pt wire counter electrodes. The CVs were referenced to the [Fe(C8Me5)3]/[Fe(C8Me5)3] redox couple, using [Fe(C8Me5)3] as internal reference (6E1/2 = -0.427 V).4 EPR spectra were recorded on a Bruker ELEXYSYS-II E500 CW-EPR spectrometer and simulated with EasySpin. IR spectra were measured in the solid state (neat) or KBr pellet using a BRUKER ALPHA FT-IR spectrometer with Platinum ATR module or transmission module, respectively.

Syntheses

Synthesis of 2. Complex 1 (10 mg, 14 µmol, 1.0 eq) and pyridine-N-oxide (2.6 mg, 28 µmol, 2.0 eq) are dissolved in benzene (0.5 mL) and heated to 70°C for 2 h. After cooling to room temperature, the solution is filtered off and the residue is extracted with benzene (2 x 0.5 mL). The volume is reduced to 0.5 mL and the crude product is purified by column chromatography over silanized silica (C6H6/THF). The solvent is removed and the residue is extracted with benzene. Evaporation of the solvent and subsequent lyophilization yields 2 as a red powder (8.1 mg, 10.8 µmol, 77%).

Synthesis of 2H. Complex 2 (10 mg, 13 µmol, 1.0 eq) and 18-crown-6 (3.5 mg, 13 µmol, 1.0 eq) are dissolved in THF and cooled to -80°C. KC8 (2.0 mg, 14.6 µmol, 1.1 eq) is added in one portion and the solution is slowly allowed to warm to room temperature. After stirring for 30 minutes at room temperature the solution is filtered off. The solvent is removed in vacuo and the residue is extracted with benzene (3 x 1 mL). The solvent is removed in vacuo and the product is crystallized from toluene/pentane at -80°C. The supernatant is decanted off and the residue is extracted with benzene. Lyophilization affords 2H as a red powder (8.3 mg, 7.9 µmol, 59%).

Synthesis of [Fe(C8Me5)3][Al(O(C(CF3))2)]2[Fe(C8Me5)3] (25.0 mg, 76.9 µmol, 1.0 eq) and Ag[Al(O(C(CF3))2)] (80.0 mg, 74.2 µmol, 0.97 eq) are dissolved in DCM (3 mL) at 0°C and stirred for 30 minutes. The solution is filtered, concentrated in vacuo and layered with pentane (10 mL). After crystallization at -35°C for 1 day the precipitate is filtered off, washed with pentane (3 x 1 mL) and extracted with THF (3 x 1 mL). The solvent is removed and [Fe(C8Me5)3][Al(O(C(CF3))2)]
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(78.0 mg, 59.7 µmol, 78%) is obtained as a turquoise powder. Anal. Calcd for C₃₈H₃₀AlF₃₀FeO₂: C, 33.4; H, 2.34.

**Found:** C, 33.6; H, 2.16.

**Oxidation of 2K:** Complex 2K (8.1 mg, 7.7 µmol, 1.0 eq.) and [Fe(C₅Me₅)₂][Al(O(CF₃)₃)₂] (9.9 mg, 7.7 µmol, 1.0 eq.) are placed in a J-Young NMR tube. THF-d₅ (0.5 mL) is added, the solution is shaken for 1 minute and analyzed by NMR spectroscopy. The yield of 2 was calculated from the relative ratios of 2 and [Fe(C₅Me₅)₂].

**Synthesis of 3K:** Complex 2 (7.0 mg, 9.3 µmol, 1.0 eq) and 18-crown-6 (2.5 mg, 9.3 µmol, 1.0 eq) are mixed in benzene (1 mL) and stirred for 5 min. Then KO'Bu (1.0 mg, 9.3 µmol, 1.0 eq) is added and the reaction is stirred for 20 min at RT. The red deep solution is evaporated in vacuo to dryness and the crude product is washed with pentane (3 x 1 mL) and extracted with Et₂O (4 x 0.5 mL). Removal of the solvent and lyophilization from benzene yields 3K as deep red powder (6.8 mg, 69%).

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Anal. Calcd for C₃₀H₂₉KN₃O₃P₃Re (1056.3): C, 45.48; H, 6.97; N, 5.30. Found: C, 45.78; H, 7.05; N, 5.52. NMR (THF-d₈, 25°C): ¹H (400 MHz): δ = 11.62 (d, ¹JHP = 6.2 Hz, 1H, C₅H₅), 7.86 (m, ²JHP = 16.8 Hz, 1H, N=CH₃), 3.31 (d, ²JHH = 1.9 Hz, 1H, C₅H₅), 2.19 (dd, ³JHP = 7.8 Hz, ²JHH = 1.7 Hz, 1H, C₅H₅), 6.77 (dd, ³JHP = 7.4 Hz, ²JHH = 1.4 Hz, 1H, C₅H₅), 6.40 (d, ³JHH = 1.9 Hz, 1H, C₅H₅), 6.34 (dd, ³JHH = 6.6 Hz, ²JHH = 1.8 Hz, 1H, C₅H₅), 4.09-3.89 (m, 2H, superimposed NCH₃ and CH-CH₃), 3.85-3.65 (m, 1H, NCH₂), 3.65 (s, 24H, O-CH₂), 3.03 (m, 2JHP = 9.7 Hz, 1H, CH₂-CH₂), 2.97 – 2.85 (m, 1H, PCH₂-CH₂), 2.07 – 1.96 (m, 1H, PCH₂-CH₂), 1.37 (d, ³JHP = 10.7 Hz, 6H, P(C(CH₃)₂)), 1.09 (d, ³JHP = 10.7 Hz, 6H, P(C(CH₃)₂)), 0.55 (d, br, ³JHP = 10.4 Hz, 6H, P(C(CH₃)₂)), 0.45 (d, ³JHP = 11.2 Hz, 6H, P(C(CH₃)₂)) , 12C (100.7 MHz): δ = 157.5 (s, 1C, C₄), 154.0 (s, 2C, superimposed N=CH, C₃), 138.7 (s, 1C, C₂), 138.7 (s, 1C, C₁), 126.6 (s, 1C, C₆), 117.8 (s, 1C, C₇), 117.2 (s, 1C, C₈), 102.2 (s, 1C, C₉), 71.2 (s, 12C, OCH₂), 66.7 (s, 1C, NCH₂), 42.1 (d, ¹JC₅ = 13.5 Hz, 1C, PC(CH₃)₂), 30.9 (d, ²JC₅ = 4.8 Hz, 1C, PC(CH₃)₂), 38.7 (d, ¹JC₅ = 8.7 Hz, 1C, PCH₂CH₃), 32.6 (d, ²JC₅ = 4.2 Hz, 1C, PC(CH₃)₂), 30.9 (d, ³JC₅ = 4.8 Hz, 1C, PC(CH₃)₂), 30.6 (s₆, 1C, PC(CH₃)₂), 30.3 (d, ³JC₅ = 3.3 Hz, 1C, PC(CH₃)₂), 28.5 (d, ³JC₅ = 18.9 Hz, 1C, PCH₂CH₃), 3¹P (162.0 MHz) δ = 273.2 (t, ²JHP = 27.1 Hz, 1P, PO₂), 63.8 (dd, ³JHP = 200.8, 28.4 Hz, 1P, P(C(CH₃)₂p), 48.2 (dd, ²JHP = 200.8, 25.4 Hz, 1P, P(C(CH₃)₂p)).
Spectroscopic Results

Figure S1. $^1$H NMR spectrum of complex 2 in C$_6$D$_6$ at room temperature.

Figure S2. $^{13}$C($^1$H) NMR spectrum of complex 2 in C$_6$D$_6$ at room temperature.
Figure S3. $^{31}$P($^1$H) NMR spectrum of complex 2 in C$_6$D$_6$ at room temperature.

Figure S4. $^{31}$P($^1$H) NMR spectra of the reaction of complex 1 with pyridine-N-oxide (C$_6$D$_6$, 70°C) during the reaction (top) and after full conversion (bottom). PMe$_3$ ($\delta = -61.3$ ppm) was used as internal standard in a sealed capillary.
Figure S5. $^1$H NMR spectrum of complex 2$^6$ in C$_6$D$_6$ at room temperature.

Figure S6. $^1$H NMR spectrum of complex 3$^6$ in THF-$d_8$ at room temperature.
Figure S7. $^{13}$C($^1$H) NMR spectrum of complex 3$^\text{K}$ in THF-$d_8$ at room temperature.

Figure S8. $^{31}$P($^1$H) NMR spectrum of complex 3$^\text{K}$ in THF-$d_8$ at room temperature.
Figure S9. Superimposed VT $^{31}$P($^1$H) NMR spectra of complex 2 (PO$_2^-$ signal) in toluene over the temperature range of −80 °C (left) to +100 °C (right) using PPh$_3$O as internal standard (sealed capillary, not shown); $\Delta$δ = 7.97 ppm.

Figure S10. Superimposed $^{31}$P($^1$H) NMR spectra of complex 2 (PNP signal) in toluene over the temperature range−80°C (left) to +100°C (right) using PPh$_3$O as internal standard (sealed capillary, not shown); $\Delta$δ = 5.01 ppm.
Figure S11. Concentration dependent $^{31}$P($^1$H) NMR spectra of complex 2 in C$_6$D$_6$ at room temperature.

Figure S12. $^{31}$P($^1$H) NMR spectrum of the oxidation of complex 2$^+$ with [Fe(C$_5$Me$_5$)$_2$][Al(O(CF$_3$)$_3$)$_4$] in THF at room temperature.
Figure S13. $^1$H($^31$P) NMR spectrum of the oxidation of complex 2K with [Fe(CpMe)$_2$][Al(O(C(CF$_3$)$_3))_4]$ in THF–d$_8$ at room temperature.

Figure S14. CW X-band EPR spectrum of complex 2K in THF at 300 K (black) and simulated spectrum in red (9.4169 GHz; simulation parameters: $g_{xx} = 2.046$, $A_{(90.16 Re)} = 770$ MHz).
Figure S15 Comparison of experimental (top) and DFT calculated (RI-M06L/def2-SVP, bottom) IR spectra of complexes 2 (left), 2K (middle) and 3K (right) and assignments of the asymmetric (magenta) and symmetric (blue) stretching and symmetric bending (green) modes of the PO2 ligands.

Figure S16 IR transmission spectra of a solid sample of 2/2\textsubscript{2} obtained from rapid evaporation of a benzene/THF solution (ATR, dotted line) and a sample of 2 as KBr pellet (black line) in comparison with DFT computed spectra for 2 (blue line) and 2\textsubscript{2} (red line).
Determination of the Diffusion Constant of 2

According to the Stokes-Einstein equation the hydrodynamic radius of the complex was estimated from the diffusion coefficient $D$:

$$r_D = \frac{k_B \cdot T}{6\pi \cdot \eta \cdot D}$$

$\eta_{\text{THF}, 25^\circ C} = 0.456 \text{ mPa} \cdot \text{s}$; $\eta_{\text{Benzene}, 25^\circ C} = 0.604 \text{ mPa} \cdot \text{s}$.\(^{[3]}\)\(^{[4]}\)

![Figure S17](image1.png)

Figure S17. $^{31}$P-$^1$H-DOSY NMR spectrum of complex 1 in C6D6 at room temperature ($D = 7.1 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}, r_0 = 5.1 \text{ Å}$).

![Figure S18](image2.png)

Figure S18. $^{31}$P-$^1$H-DOSY NMR spectrum of complex 2 in C6D6 at room temperature ($D = 7.3 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}, r_0 = 4.9 \text{ Å}$).
Figure S19. $^{31}$P-$^1$H-DOSY NMR spectrum of complex 2 in THF-d$_8$ at room temperature ($D = 8.1 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$, $r_0 = 5.9 \text{ Å}$).

Figure S20. $^{31}$P-$^1$H-DOSY NMR spectrum of [ReI($\text{N}^2$-N$\text{N}$-PyrPz)(PNP)] in CdD$_6$ at room temperature ($D = 8.4 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$, $r_0 = 4.3 \text{ Å}$).
Figure S21. $^1$H$^{31}$P-DOSY NMR spectra of [ReCl$_3$(HPNP')] (green) and [(µ-N$_2$)(ReCl$_2$(HPNP'))]$_2$ (red) in THF-d$_8$ at room temperature.

Figure S22. Cyclic voltammogram of complex 2 (1.0 mM, 0.2 M [NBu$_4$][PF$_6$], THF, room temperature).
Figure S23. Cyclic voltammogram of complex 2 (first reductive event; 1.0 mM, 0.2 M [NBu₄][PF₆], THF, room temperature).

Figure S24. Randles-Sevcik-plot (i_p vs. v^(1/2)) with linear fit (red line) of the first reductive event of complex 2.

The diffusion constant $D_0$ of complex 2 was derived from the Randles-Sevcik equation (at 25°C):

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C \nu^{1/2}$$
With $n$ as the number of transferred electrons ($n = 1$), $A$ as the electrode surface ($A = 0.02 \text{ cm}^2$), $C$ as the concentration of 2 ($C = 1 \text{ mM}$), $D$ as the diffusion constant and $v$ as the scan rate, $D$ was calculated from the linear fit of the experimental data ($m = 1.41 \cdot 10^{-6} \text{ A} \cdot \text{s}^{1/2} \cdot \text{V}^{-1/2}$):

\[
i_p = m \cdot v^{1/2}
\]

\[
m = 2.69 \cdot 10^5 \cdot n^{3/2} \cdot A \cdot D^{1/2} \cdot C^{1/2}
\]

\[
D = (m \cdot (2.69 \cdot 10^5 \cdot n^{3/2} \cdot A \cdot C^{-1})^{-1})^2
\]

\[
D = 6.9 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}.
\]
A 1.06 mM solution of 2 (3 mL) was electrolyzed for 16 h in THF. A small residual amount of 2 was detected via cyclic voltammetry after electrolysis and calculated to correspond to a concentration of 0.12 µM.

The number of transferred electrons per Re was calculated by:

\[ z = \frac{Q}{n \times F} \]

Q: electric charge (C), F: Faraday constant (C mol\(^{-1}\)), n: amount of substance (mol).

| \(Q / mC\) |  \
|---|---|
| Q\(_{\text{expected after 16 h and 88 % conversion}}\) | 276 |
| Q\(_{\text{measured after 16 h}}\) | 236 |

Therefore, \(z\) equals 0.86 e\(^{-}\).
Crystallographic Details

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. 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 Uiso values constrained to 1.5 Ueq of their pivot atoms for terminal sp3 carbon atoms and 1.2 times for all other atoms.

X-ray Single-Crystal Structure Analysis of 22

Table S1. Crystal data and structure refinement for 22.

| Property                              | Value                  |
|---------------------------------------|------------------------|
| CCDC                                  | 2024567                |
| Empirical formula                     | C₉₅H₁₉₀N₈O₄P₆Re₂ (+ 3 Et₂O solvent molecules) |
| Formula weight                        | 1507.65                |
| Temperature                           | 101(2) K               |
| Wavelength                            | 0.71073 Å              |
| Crystal system                        | Triclinic              |
| Space group                           | P-1                    |
| a = 15.3409(15) Å                     | α = 113.168(2)°        |
| b = 15.4611(14) Å                     | β = 91.184(3)°         |
| c = 17.6625(15) Å                     | γ = 103.670(3)°        |
| Volume                                | 3712.0(6) Å³           |
| Z                                      | 2                      |
| Density (calculated)                  | 1.349 Mg/m³            |
| Absorption coefficient                | 3.430 mm⁻¹             |
| F(000)                                | 1528                   |
| Crystal size                          | 0.296 x 0.165 x 0.150 mm³ |
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| Crystal shape and color | Block, clear intense green/brown |
|-------------------------|----------------------------------|
| Theta range for data collection | 2.193 to 25.407° |
| Index ranges | \(-18\leqslant h\leqslant 18, -18\leqslant k\leqslant 18, -20\leqslant l\leqslant 21\) |
| Reflections collected | 97135 |
| Independent reflections | \(13625 \ [R(int) = 0.1572]\) |
| Completeness to theta = 25.242° | 99.9 % |
| Refinement method | Full-matrix least-squares on \(F^2\) |
| Data / restraints / parameters | 13625 / 732 / 697 |
| Goodness-of-fit on \(F^2\) | 1.026 |
| Final R indices \([l>2\sigma(l)]\) | R1 = 0.0432, \(wR2 = 0.0907\) |
| R indices (all data) | R1 = 0.0816, \(wR2 = 0.1031\) |
| Largest diff. peak and hole | 1.852 and \(-1.154\) eÅ\(^{-3}\) |

**Table S2.** Bond lengths [Å] and angles [°] for 2. 

| Bond Lengths | Angles | 
|--------------|--------|
| Re(1)-N(1)   | 1.900(5) |
| Re(1)-N(3)   | 2.143(6) |
| Re(1)-N(2)   | 2.263(5) |
| Re(1)-P(1)   | 2.4457(19) |
| Re(1)-P(2)   | 2.4528(18) |
| Re(1)-P(3)   | 2.4564(18) |
| Re(2)-N(5)   | 1.900(5) |
| Re(2)-N(7)   | 2.143(5) |
| Re(2)-N(6)   | 2.268(6) |
| Re(2)-P(4)   | 2.4437(19) |
| Re(2)-P(5)   | 2.4521(18) |
| Re(2)-P(6)   | 2.4556(17) |
| P(1)-C(2)    | 1.824(7) |
| P(1)-C(7)    | 1.913(8) |
| P(1)-C(3)    | 1.918(7) |
| P(2)-C(12)   | 1.839(6) |
| P(2)-C(13)   | 1.908(7) |
| P(2)-C(17)   | 1.911(7) |
| P(3)-O(1)    | 1.484(5) |
| P(3)-O(2)    | 1.685(5) |
| P(3)-O(3)#1  | 1.685(5) |
| P(3)-P(3)#1  | 2.528(3) |
| P(4)-C(30)   | 1.840(7) |
| P(4)-C(31)   | 1.910(7) |
| P(4)-C(35)   | 1.917(7) |
| P(5)-C(40)   | 1.819(7) |
| P(5)-C(41)   | 1.899(7) |
| P(5)-C(45)   | 1.906(7) |
| P(6)-O(3)    | 1.485(5) |
| P(6)-O(4)    | 1.671(4) |
| P(6)-O(4)#2  | 1.679(5) |
| P(6)-P(6)#2  | 2.515(3) |
| O(2)-P(3)#1  | 1.685(5) |
| O(4)-P(6)#2  | 1.679(5) |
| N(1)-C(1)    | 1.490(8) |
| N(1)-C(11)   | 1.496(8) |
| N(2)-C(21)   | 1.362(9) |
| N(2)-C(25)   | 1.365(8) |
| N(3)-N(4)    | 1.347(8) |
| N(3)-C(26)   | 1.365(9) |
| N(4)-C(28)   | 1.352(9) |
| N(5)-C(29)   | 1.486(8) |
| N(5)-C(39)   | 1.500(8) |
| N(6)-C(53)   | 1.360(8) |
| N(6)-C(49)   | 1.363(8) |
| N(7)-C(54)   | 1.336(9) |
| N(7)-N(8)    | 1.354(8) |
| N(8)-C(56)   | 1.347(9) |

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| Bond Lengths (Å)            | Bond Angles (°)           |
|-----------------------------|---------------------------|
| C(2)-P(1)-C(7)              | 104.9(3)                  |
| C(2)-P(1)-C(3)              | 101.4(3)                  |
| C(7)-P(1)-C(3)              | 106.3(3)                  |
| C(2)-P(1)-Re(1)             | 97.6(2)                   |
| C(7)-P(1)-Re(1)             | 123.6(2)                  |
| C(3)-P(1)-Re(1)             | 118.9(2)                  |
| C(12)-P(2)-C(13)            | 100.5(3)                  |
| C(12)-P(2)-C(17)            | 105.1(3)                  |
| C(13)-P(2)-C(17)            | 106.7(3)                  |
| C(12)-P(2)-Re(1)            | 97.2(2)                   |
| C(13)-P(2)-Re(1)            | 120.7(2)                  |
| C(17)-P(2)-Re(1)            | 122.3(2)                  |
| C(1)-P(3)-O(2)              | 107.4(3)                  |
| O(1)-P(3)-O(2)#1            | 108.3(3)                  |
| O(2)-P(3)-O(2)#1            | 82.8(2)                   |
| N(1)-P(3)-Re(1)             | 119.2(2)                  |
| O(2)-P(3)-Re(1)             | 116.9(18)                 |
| O(2)-P(3)-Re(1)#1           | 116.20(17)                |
| O(2)-P(3)-P(3)#1            | 114.1(2)                  |
| Re(1)-P(3)-P(3)#1           | 134.40(16)                |
| Re(1)-P(3)-P(3)#1           | 134.40(16)                |
| C(30)-P(4)-C(31)            | 104.9(3)                  |
| C(30)-P(4)-C(35)            | 100.5(3)                  |
| C(31)-P(4)-C(35)            | 106.3(3)                  |
| C(30)-P(4)-Re(2)            | 98.1(2)                   |
| C(31)-P(4)-Re(2)            | 122.9(2)                  |
| C(35)-P(4)-Re(2)            | 119.9(2)                  |
| C(40)-P(5)-C(41)            | 105.2(3)                  |
| C(40)-P(5)-C(45)            | 101.0(3)                  |
| C(41)-P(5)-C(45)            | 106.5(3)                  |
| C(40)-P(5)-Re(2)            | 97.4(2)                   |
| C(41)-P(5)-Re(2)            | 122.9(2)                  |
| C(45)-P(5)-Re(2)            | 119.9(2)                  |
| O(3)-P(6)-O(4)              | 108.5(2)                  |
| O(3)-P(6)-O(4)#2            | 108.0(3)                  |
| O(4)-P(6)-O(4)#2            | 82.7(2)                   |
| O(3)-P(6)-Re(2)             | 117.9(2)                  |
Table S3. Torsion angles [°] for 2.

| Bond | Torsion Angle |
|------|--------------|
| N(1)-P(1)-O(2)-P(3) | -107.0(3) |
| N(1)-P(3)-O(2)-P(3) | 0.000(2) |
| Re(1)-P(3)-O(2)-P(3) | 115.7(9) |
| O(3)-P(6)-O(4)-P(6) | 106.6(3) |
| O(6)-P(5)-O(4)-P(6) | 0.000(1) |
| C(3)-N(3)-N(4)-C(28) | 0.3(8) |
| C(3)-N(3)-N(4)-C(25) | 178.1(5) |
| N(7)-Re(2)-N(5)-C(29) | -92.8(5) |
| N(4)-Re(2)-N(5)-C(29) | -7.3(5) |
| N(5)-Re(2)-N(5)-C(29) | -178.0(5) |
| N(6)-Re(2)-N(5)-C(29) | 87.1(5) |
| N(7)-Re(2)-N(5)-C(29) | 93.7(5) |
| P(4)-Re(2)-N(5)-C(29) | 179.1(5) |
| P(5)-Re(2)-N(5)-C(29) | 8.5(5) |
| P(6)-Re(2)-N(5)-C(29) | -86.4(5) |
| C(54)-N(7)-N(8)-C(56) | -0.2(8) |
| C(54)-N(7)-N(8)-C(56) | -179.6(5) |
| C(11)-N(1)-C(1)-C(2) | -164.2(6) |
| N(1)-C(1)-C(2) | 10.8(8) |
| N(1)-C(1)-C(2) | -28.0(7) |
| C(7)-P(1)-C(2)-C(1) | 156.3(5) |
| C(3)-P(1)-C(2)-C(1) | -93.2(5) |
| C(1)-N(1)-C(1)-C(2) | 28.4(5) |
| C(1)-N(1)-C(1)-C(2) | 162.3(6) |
| Re(1)-P(1)-C(2)-C(1) | 28.4(5) |
| Re(1)-P(1)-C(2)-C(1) | 156.3(5) |
| C(1)-N(1)-C(1)-C(2) | -12.8(5) |
| C(1)-N(1)-C(1)-C(2) | 162.3(6) |
| C(1)-N(1)-C(1)-C(2) | 162.3(6) |
| C(7)-P(1)-C(2)-C(1) | 156.3(5) |
| C(3)-P(1)-C(2)-C(1) | -93.2(5) |
| C(1)-N(1)-C(1)-C(2) | 28.4(5) |
| C(1)-N(1)-C(1)-C(2) | 162.3(6) |
| Re(1)-P(1)-C(2)-C(1) | 28.4(5) |
| Re(1)-P(1)-C(2)-C(1) | 156.3(5) |
| C(1)-N(1)-C(1)-C(2) | -12.8(5) |
| C(1)-N(1)-C(1)-C(2) | 162.3(6) |
| C(7)-P(1)-C(2)-C(1) | 156.3(5) |
| C(3)-P(1)-C(2)-C(1) | -93.2(5) |
| C(1)-N(1)-C(1)-C(2) | 28.4(5) |
| C(1)-N(1)-C(1)-C(2) | 162.3(6) |
| Re(1)-P(1)-C(2)-C(1) | 28.4(5) |
| Re(1)-P(1)-C(2)-C(1) | 156.3(5) |
| C(1)-N(1)-C(1)-C(2) | -12.8(5) |
| C(1)-N(1)-C(1)-C(2) | 162.3(6) |
| C(7)-P(1)-C(2)-C(1) | 156.3(5) |
| C(3)-P(1)-C(2)-C(1) | -93.2(5) |
| C(1)-N(1)-C(1)-C(2) | 28.4(5) |
| C(1)-N(1)-C(1)-C(2) | 162.3(6) |
| Re(1)-P(1)-C(2)-C(1) | 28.4(5) |
| Re(1)-P(1)-C(2)-C(1) | 156.3(5) |
| C(1)-N(1)-C(1)-C(2) | -12.8(5) |
| C(1)-N(1)-C(1)-C(2) | 162.3(6) |
| C(7)-P(1)-C(2)-C(1) | 156.3(5) |
| C(3)-P(1)-C(2)-C(1) | -93.2(5) |
| C(1)-N(1)-C(1)-C(2) | 28.4(5) |
SUPPORTING INFORMATION

C(45)-P(5)-C(41)-C(43) 50.7(6)  C(51)-C(52)-C(53)-C(54) 179.2(7)
Re(2)-P(5)-C(41)-C(43) -93.2(5) N(8)-N(7)-C(54)-C(55) 0.5(8)
C(40)-P(5)-C(41)-C(44) -84.6(5) Re(2)-N(7)-C(54)-C(55) 179.9(4)
C(45)-P(5)-C(41)-C(44) 168.8(5) N(8)-N(7)-C(54)-C(53) 179.0(6)
Re(2)-P(5)-C(41)-C(44) 25.0(6) Re(2)-N(7)-C(54)-C(53) -1.6(9)
C(40)-P(5)-C(41)-C(45) 33.9(6) N(6)-C(53)-C(54)-N(7) 1.3(9)
C(45)-P(5)-C(41)-C(45) -72.7(6) C(52)-C(53)-C(54)-N(7) -178.9(7)
Re(2)-P(5)-C(41)-C(45) 143.4(4) N(6)-C(53)-C(54)-C(55) 174.9(7)
C(53)-N(6)-C(49)-C(50) -0.4(10) C(52)-C(53)-C(54)-C(55) -0.8(13)
Re(2)-N(6)-C(49)-C(50) -179.4(6) N(7)-C(54)-C(55)-C(56) -0.5(8)
N(6)-C(49)-C(50)-C(51) 0.6(12) C(53)-C(54)-C(55)-C(56) -178.7(8)
C(49)-C(50)-C(51)-C(52) -0.9(12) N(7)-N(8)-C(56)-C(55) -0.2(8)
C(50)-C(51)-C(52)-C(53) 1.1(12) C(54)-C(55)-C(56)-N(8) 0.5(8)
C(49)-N(6)-C(53)-C(52) 0.6(10) Symmetry transformations used to generate equivalent atoms:
Re(2)-N(6)-C(53)-C(52) 179.7(6) #1 -x+2,-y+1,-z
C(49)-N(6)-C(53)-C(54) -179.6(6) #2 -x+1,-y+1,-z+1
Re(2)-N(6)-C(53)-C(54) -0.5(8)
C(51)-C(52)-C(53)-N(6) -1.0(12)

X-ray Single-Crystal Structure Analysis of 3K

Figure S27. Thermal ellipsoid plot of 3K with the anisotropic displacement parameters drawn at the 50% probability level. The asymmetric unit contains one complex molecule and a disordered THF molecule. The disordered THF molecule was set to a population of 0.5 and refined using some restraints and constraints (SADI, EADP).

Table S4. Crystal data and structure refinement for 3K.

| Property                          | Value                        |
|----------------------------------|------------------------------|
| CCDC                             | 2024610                      |
| Empirical formula                | C_{40}H_{73}K_{4}N_{4}O_{8}P_{3}Re \times 0.5 (C_{4}H_{8}O) |
| Formula weight                   | 1092.28                      |
| Temperature                      | 100(2) K                     |
| Wavelength                       | 0.71073 Å                    |
| Crystal system                   | Monoclinic                   |
| Space group                      | P2_1/c                       |
| Unit cell dimensions             |                             |
| a                                | 12.8339(4) Å                |
| b                                | 23.5174(8) Å                |
| c                                | 16.6688(5) Å                |
| α                                | 90°                          |
| β                                | 100.086(2)°                  |
| γ                                | 90°                          |
| Volume                           | 4953.2(3) Å^3               |
| Z                                | 4                            |
| Density (calculated)             | 1.465 Mg/m^3                 |
| Absorption coefficient           | 2.686 mm^-1                  |

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Table S5. Bond lengths [Å] and angles [°] for 3°.

| Bond                  | Length [Å] | Angle [°] |
|-----------------------|------------|-----------|
| Re(1)-N(1)            | 2.082(2)   |           |
| Re(1)-N(2)            | 2.141(2)   |           |
| Re(1)-N(3)            | 2.162(2)   |           |
| Re(1)-P(3)            | 2.254(7)   |           |
| Re(1)-P(1)            | 2.397(7)   |           |
| Re(1)-P(2)            | 2.433(2)   |           |
| K(1)-O(1)             | 2.730(2)   |           |
| K(1)-O(2)             | 2.731(2)   |           |
| K(1)-O(6)             | 2.806(2)   |           |
| K(1)-O(4)             | 2.866(2)   |           |
| K(1)-O(6)             | 2.893(2)   |           |
| K(1)-O(3)             | 2.949(2)   |           |
| K(1)-O(7)             | 2.979(2)   |           |
| K(1)-O(5)             | 2.980(2)   |           |
| K(1)-C(15)#1         | 3.257(3)   |           |
| K(1)-P(3)             | 3.287(9)   |           |
| K(1)-C(31)            | 3.490(3)   |           |
| P(1)-C(2)             | 1.844(3)   |           |
| P(1)-C(7)             | 1.919(3)   |           |
| P(1)-C(3)             | 1.921(3)   |           |
| P(2)-C(12)            | 1.855(3)   |           |
| P(2)-C(13)            | 1.905(3)   |           |
| P(2)-C(17)            | 1.910(3)   |           |
| P(3)-O(2)             | 1.512(2)   |           |
| P(3)-O(1)             | 1.517(2)   |           |
| O(3)-C(30)            | 1.419(4)   |           |
| O(3)-C(31)            | 1.422(4)   |           |
| O(4)-C(33)            | 1.411(4)   |           |
| O(4)-C(32)            | 1.424(4)   |           |
| O(5)-C(34)            | 1.416(4)   |           |
| O(5)-C(35)            | 1.418(4)   |           |
| O(6)-C(37)            | 1.411(4)   |           |
| O(6)-C(36)            | 1.420(4)   |           |
| O(7)-C(39)            | 1.421(4)   |           |
| O(7)-C(38)            | 1.423(4)   |           |
| O(8)-C(29)            | 1.411(4)   |           |
| O(8)-C(40)            | 1.419(4)   |           |
| N(1)-C(11)            | 1.327(4)   |           |
| N(1)-C(11)            | 1.468(4)   |           |
| N(2)-C(21)            | 1.362(4)   |           |
| N(2)-C(25)            | 1.381(3)   |           |
| N(3)-N(4)             | 1.354(3)   |           |
| N(3)-C(26)            | 1.358(4)   |           |
| N(4)-C(28)            | 1.351(4)   |           |
| C(1)-C(2)             | 1.526(4)   |           |
| C(3)-C(4)             | 1.532(4)   |           |

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| SUPPORTING INFORMATION |
|-------------------------|
| N(2)-Re(1)-P(2)        | 104.79(6)  |
| N(3)-Re(1)-P(2)        | 88.86(6)   |
| P(3)-Re(1)-P(2)        | 92.97(2)   |
| P(1)-Re(1)-P(2)        | 155.70(2)  |
| O(1)-K(1)-O(2)         | 54.14(6)   |
| O(1)-K(1)-O(8)         | 91.93(7)   |
| O(2)-K(1)-O(8)         | 81.27(6)   |
| O(1)-K(1)-O(4)         | 86.42(6)   |
| O(2)-K(1)-O(4)         | 138.01(6)  |
| O(8)-K(1)-O(4)         | 117.68(7)  |
| O(1)-K(1)-O(6)         | 125.71(7)  |
| O(2)-K(1)-O(6)         | 84.26(7)   |
| O(8)-K(1)-O(6)         | 116.92(7)  |
| O(4)-K(1)-O(6)         | 113.68(7)  |
| O(1)-K(1)-O(3)         | 84.17(6)   |
| O(2)-K(1)-O(3)         | 121.35(6)  |
| O(8)-K(1)-O(3)         | 58.64(6)   |
| O(4)-K(1)-O(3)         | 59.23(6)   |
| O(6)-K(1)-O(3)         | 149.92(7)  |
| O(1)-K(1)-O(7)         | 122.15(6)  |
| O(2)-K(1)-O(7)         | 71.59(6)   |
| O(8)-K(1)-O(7)         | 58.90(7)   |
| O(4)-K(1)-O(7)         | 150.34(6)  |
| O(6)-K(1)-O(7)         | 58.24(7)   |
| O(3)-K(1)-O(7)         | 111.77(7)  |
| O(1)-K(1)-O(5)         | 119.01(6)  |
| O(2)-K(1)-O(5)         | 126.65(7)  |
| O(8)-K(1)-O(5)         | 146.29(6)  |
| O(4)-K(1)-O(5)         | 56.70(6)   |
| O(6)-K(1)-O(5)         | 56.99(7)   |
| O(3)-K(1)-O(5)         | 108.40(6)  |
| O(7)-K(1)-O(5)         | 108.05(6)  |
| O(1)-K(1)-C(15)#1     | 156.45(9)  |
| O(2)-K(1)-C(15)#1     | 138.73(8)  |
| O(8)-K(1)-C(15)#1     | 74.51(8)   |
| O(4)-K(1)-C(15)#1     | 83.21(8)   |
| O(6)-K(1)-C(15)#1     | 77.84(9)   |
| O(3)-K(1)-C(15)#1     | 72.35(9)   |
| O(7)-K(1)-C(15)#1     | 67.33(8)   |
| O(5)-K(1)-C(15)#1     | 71.82(8)   |
| O(1)-K(1)-P(3)        | 27.30(4)   |
| O(2)-K(1)-P(3)        | 27.20(4)   |
| O(8)-K(1)-P(3)        | 89.32(5)   |
| O(4)-K(1)-P(3)        | 111.57(5)  |
| O(6)-K(1)-P(3)        | 103.71(5)  |
| O(3)-K(1)-P(3)        | 105.90(5)  |
| O(7)-K(1)-P(3)        | 98.02(5)   |
| O(5)-K(1)-P(3)        | 124.26(5)  |
| C(15)#1-K(1)-P(3)     | 162.15(7)  |
| O(1)-K(1)-C(31)       | 70.06(7)   |
| O(2)-K(1)-C(31)       | 119.58(7)  |
| O(8)-K(1)-C(31)       | 79.18(8)   |
| O(4)-K(1)-C(31)       | 42.14(7)   |
| O(6)-K(1)-C(31)       | 154.13(7)  |
| O(3)-K(1)-C(31)       | 23.67(7)   |
| O(7)-K(1)-C(31)       | 135.27(8)  |
| O(5)-K(1)-C(31)       | 98.09(7)   |
| C(15)#1-K(1)-C(31)    | 88.26(9)   |
| P(3)-K(1)-C(31)       | 96.20(6)   |
| C(2)-P(1)-C(7)        | 102.49(13) |
| C(2)-P(1)-C(3)        | 100.43(14) |
| C(7)-P(1)-C(3)        | 105.57(13) |
| C(2)-P(1)-Re(1)       | 99.48(9)   |
SUPPORTING INFORMATION

Table S6. Torsion angles [°] for 3k.

|          | C(14)-C(13)-P(2) | 107.7(2) | C(27)-C(26)-C(25) | 133.8(3) |
|----------|------------------|----------|--------------------|----------|
| C(15)-C(13)-P(2) | 114.8(2) | C(28)-C(27)-C(26) | 103.1(3) |
| C(16)-C(15)-P(2) | 110.5(2) | N(4)-C(28)-C(27) | 112.4(3) |
| C(13)-C(15)-K(1)$^2$ | 160.4(2) | O(8)-C(29)-C(30) | 107.5(3) |
| C(13)-C(15)-H(15A) | 107(2) | O(3)-C(30)-C(29) | 109.2(3) |
| K(1)#2-C(15)-H(15A) | 86(2) | O(3)-C(31)-C(32) | 108.7(3) |
| K(1)#2-C(15)-H(15B) | 106(2) | O(3)-C(31)-K(1) | 56.32(15) |
| H(15A)-C(15)-H(15B) | 55(2) | O(32)-C(31)-K(1) | 87.30(19) |
| H(15A)-C(15)-H(15C) | 111(3) | O(4)-C(32)-C(31) | 107.7(3) |
| H(15B)-C(15)-H(15C) | 112(3) | O(4)-C(33)-C(34) | 108.3(3) |
| C(19)-C(17)-C(20) | 108(3) | O(5)-C(34)-C(33) | 109.7(3) |
| C(19)-C(17)-C(18) | 108.1(3) | O(5)-C(35)-C(36) | 109.8(3) |
| C(20)-C(17)-C(18) | 105.0(2) | O(6)-C(36)-C(35) | 109.1(3) |
| C(19)-C(17)-P(2) | 111.4(2) | O(6)-C(37)-C(38) | 109.7(3) |
| C(20)-C(17)-P(2) | 114.6(2) | O(7)-C(38)-C(37) | 108.7(3) |
| C(18)-C(17)-P(2) | 108.8(2) | O(7)-C(39)-C(40) | 110.2(3) |
| N(2)-C(21)-C(26) | 123.2(3) | O(8)-C(40)-C(39) | 108.5(3) |
| C(21)-C(22)-C(23) | 120.4(3) | C(42)-C(41)-O(9) | 86.8(11) |
| C(24)-(23)-C(22) | 117.8(3) | C(44)-O(9)-C(41) | 106.2(12) |
| C(23)-(24)-C(25) | 120.6(3) | C(41)-C(42)-C(43) | 126.3(14) |
| N(2)-C(25)-C(24) | 122.1(3) | C(44)-C(43)-C(42) | 91.4(13) |
| N(2)-C(25)-C(26) | 114.6(2) | C(43)-C(44)-O(9) | 111.4(13) |
| C(24)-(25)-C(26) | 123.2(3) | C(33) | 118.7(3) |
| N(3)-C(26)-C(27) | 109.1(3) | C(34) | 116.6(2) |
| N(3)-C(26)-C(25) | 116.8(2) | C(35) | 115.3(3) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y-1/2,-z+3/2  #2 -x+1,y+1/2,-z+3/2
SUPPORTING INFORMATION

|            | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|------------|--------|----------|----------|--------|
| O(4)-C(33) - C(34)-O(5) | -61.7(3) | 177.2(3) |
| C(34)-O(5)-C(35)-C(36) | 88.6(3) | -28.6(3) |
| K(1)-O(5)-C(35)-C(36) | -58.0(3) | 67.3(3)  |
| C(37)-O(6)-C(36)-C(35) | 176.2(3) | -31.4(13) |
| O(5)-C(35)-C(36)-O(6) | -38.8(3) | 13(3)    |
| K(1)-O(6)-C(37)-C(38) | 176.2(3) | -34(2)   |
| C(39)-O(7)-C(38)-C(37) | 179.1(3) | 47.6(17) |
| K(1)-O(7)-C(38)-C(37) | 69.1(3)  |         |
| O(6)-C(37)-C(38)-O(7) | -69.1(4) |         |
| C(38)-O(7)-C(39)-C(40) | -176.4(3) |         |
| K(1)-O(7)-C(39)-C(40) | -66.2(3) |         |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y-1/2,-z+3/2  #2 -x+1,y+1/2,-z+3/2

Table S7. Hydrogen bonds for 3K [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------|--------|----------|----------|--------|
| C(15)-H(15B)...K(1)#2 | 0.98(4) | 2.81(4)  | 3.257(3) | 108(2) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y-1/2,-z+3/2  #2 -x+1,y+1/2,-z+3/2
Computational Details

Structure optimizations and single point calculations including electronic structure analyses were performed within the ORCA 4.2.1 program suite. The thermodynamics of the dimerization equilibrium \( (2 + 2) \rightleftharpoons 2_2 \) were evaluated by three methods employing different DFT functionals:

The molecular structure was either optimized using the PBE functional with the RIJ approximation to minimize computational costs and Ahlrichs' revised def2-SVP basis sets in combination with the corresponding auxiliary basis sets, which include an all electron basis for all elements except Re, for which a Stuttgart-Dresden 60 electron core potential replaces the inner shell 1s-4f orbitals. To increase numerical accuracy and facilitate optimization of the molecular structure of \( 2_2 \), tight convergence criteria in the SCF procedure and a fine integration grid (Grid6 and GridX6) were applied. Additionally, single point calculations were conducted with the same method but without RIJ or RIJCOSX approximation, using Ahlrichs' def2-TZVP basis for all atoms, again replacing the 60 core electrons of Re with the SD(60,MWB) effective core potential. The influence of the solvent (THF) was accounted for by Truhlar's SMD solvation model. Thermodynamic corrections were evaluated by means of analytical vibrational analyses at the same level of theory as the geometry optimization applying Grimme's quasi-RRHO approach which treats low energy frequencies below 35 cm\(^{-1}\) as free rotors instead of harmonic vibrations for the vibrational partition function.

In a second approach, the PBE0 functional was employed in both the optimizations and single point calculations. As PBE0 includes 25 % Hartree-Fock exchange, the RIJCOSX integral evaluation routine was used instead of RIJ. Otherwise the procedure was identical with method 1.

In a third method, Truhlar's strongly parametrized M06L density functional was used for the structure optimizations to evaluate the influence of Grimme's dispersion correction, applying the RIJ approximation and Ahlrich's def2-SVP basis. The thermodynamics are slightly biased by two low negative vibrational modes of \( 2_2 \) which could not be eliminated, even in repeated optimizations. Finally, single point energies were calculated with the M06 functional. Ahlrichs' def2-TZVP basis set and the SMD solvation model.

The free energies were corrected for the difference between ideal gas standard conditions (1 atm, 298.15 K) and standard solution conditions (1 mol/L, 298.15 K), effectively reducing the calculated \( \Delta G \) value of the equilibrium by 1.89 kcal/mol:

\[
G_{sol} = G_{gas} + RT \ln \frac{RT}{P}
\]

\[
G_{sol} = G_{gas} + RT \ln(24.47)
\]

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

NBO analyses were conducted using the D3BJ-RJJCOSX-PBE0/def2-TZVP single point calculations with the NBO 6.0 software of Landis and Weinhold. In order to ensure comparability between 2, \( 2^- \) and \( 2^{\text{NO2}} \), all analyzed structures exhibit the same backbone conformation. In case of 2, the lowest energy conformation deviates but NBO analyses of both conformers are very similar. The NBO Lewis structures of the \( \text{PO}_3/\text{NO}_2 \) groups were enforced with the CHOOSE command (see figure). The strength of \( \pi \)-backdonation was examined by investigating the interaction of the filled Re lone pairs and the P=O or N=O \( \pi^- \)-orbital by second order perturbation theory.

The structures obtained from method 2 were used to calculate the \( ^{31}P \) NMR shifts of 2 and \( 2_2 \), using the PBE0 functional, the RJJCOSX approximation and the GIAOs (Gauge Including Atomic Orbitals) approach. As in the single point calculations, the def2-TZVP basis sets in combination with the def/2 auxiliary basis were employed except for the phosphorous and oxygen atoms, for which Jensen's special pcSseg-4 basis sets were utilized which were specifically developed for nuclear magnetic shielding calculations. Very tight convergence criteria and a fine Grid (Grid6 and GridX6) were applied. The solvent (benzene) was included by means of the conductor-like polarizable continuum model (C-PCM) as implemented in ORCA. As reference, the \( ^{31}P \) NMR shift of \( \text{H}_3\text{PO}_4 \) (0 ppm) calculated in water was used. The relative chemical shifts of the two \( ^{31}P \) signals computed for 2 (\( \Delta \delta \)) are in excellent agreement with experiment but differ from the absolute values by about 70 ppm, which partially arises from the missing inclusion of relativistic effects. Therefore, \( ^{31}P \) NMR chemical shift calculations were also performed with the NMR module of the ADF program, which accounts for relativistic spin-orbit contributions to nuclear magnetic shielding constants by means of the two-component ZORA formalism implemented in ADF. The PBE0 hybrid functional was employed in combination with the TZVP Slater type orbital basis set. Solvent effects were taken into account with the COSMO model implemented in ADF. The absolute chemical shifts obtained from this method are significantly closer (about 20 ppm) to the experimental results (see below).

Molecular graphics and vibrational spectra were rendered with the programs CylView, Jmol and ChemCraft.
Computed geometries and electronic properties

Table S8. Calculated structural parameters (RI-M06L/def2-SVP; in Å and deg) of the PO₂ complexes in comparison to experiment (for atom captions see figures below).

|       | 2        | 2⁻       | 2⁺       | 2⁺ (exp) | 3⁻       | 3⁺       | 3⁺ (exp) |
|-------|----------|----------|----------|----------|----------|----------|----------|
| Re-P1 | 2.459    | 2.442    | 2.446    | 2.470    | 2.4457(19)| 2.404    | 2.422    | 2.3977(7) |
| Re-P2 | 2.463    | 2.436    | 2.453    | 2.472    | 2.4528(18)| 2.441    | 2.457    | 2.4332(7) |
| Re-P3 | 2.408    | 2.319    | 2.266    | 2.458    | 2.4564(18)| 2.300    | 2.248    | 2.2545(7) |
| Re-N1 | 1.916    | 2.052    | 2.045    | 1.912    | 1.900(5)  | 2.086    | 2.101    | 2.082(2)  |
| Re-N2 | 2.313    | 2.195    | 2.200    | 2.333    | 2.263(5)  | 2.169    | 2.171    | 2.141(2)  |
| Re-N3 | 2.140    | 2.192    | 2.178    | 2.155    | 2.143(6)  | 2.191    | 2.178    | 2.162(2)  |
| P3-O1 | 1.508    | 1.528    | 1.545    | 1.516    | 1.484(5)  | 1.529    | 1.550    | 1.517(2)  |
| P3-O2 | 1.511    | 1.524    | 1.542    | 1.714    | 1.685(5)  | 1.531    | 1.551    | 1.512(2)  |
| O1-P3-O2| 119.8 | 116.1    | 110.4    |          | 115.1    | 109.3    | 110.26(12)|
| O1,2-K|          | 2.668 / 2.726 |        |          | 2.626 / 2.713 | 2.730 / 2.731 |

Figure S28. Optimized structures (RI-M06L/def2-SVP) of complexes 2 (left) and 2⁻ (right). Hydrogen atoms are omitted for clarity.

Figure S29. Optimized structures (RI-M06L/def2-SVP) of complexes 2NO₂ (left) and 3⁻ (right). Hydrogen atoms are omitted for clarity.
Figure S30. Optimized structures (RI-M06L/def2-SVP) of complexes 2$^\ddagger$ (left) and 3$^\ddagger$ (right). Hydrogen atoms are omitted for clarity.

Figure S31. Optimized structures (RI-M06L/def2-SVP) of complex 2. Both Re fragments exhibit identical structural parameters. Hydrogen atoms are omitted for clarity.
Figure S32. Molecular orbital scheme of complex 2 (D3BJ-PBE0/def2-TZVP). For simplicity, pure pyrazolopyridine ligand base \(n\)-type orbitals (in gray) are not included and H atoms are omitted.
Figure S33. Molecular orbital scheme of complex $2^{\text{NO2}}$ (D3BJ-PBE0/def2-TZVP). For simplicity, pure pyrazolopyridine ligand base $\pi$-type orbitals (in gray) are not included and H atoms are omitted.

Figure S34. Spin density plot of $2^-$ (D3BJ-PBE0/def2-TZVP). For simplicity, H atoms are omitted.
Table S9. NLMO analyses of complexes 2, 2\textsuperscript{−} and 2\textsuperscript{2NO2}.

|       | 2          | 2\textsuperscript{−} | 2\textsuperscript{2NO2} |
|-------|------------|-----------------------|--------------------------|
| Re–P bond | Wilberg Bond Index: 0.754 | Wilberg Bond Index: 0.817 | Wilberg Bond Index: 0.598 |
| NLMO: | 36 % Re, 61 % P | 35 % Re, 62 % P | 21 % Re, 78 % N |
| Re Lone Pair 1 | NLMO: 90 % Re, 1.9 % P (2.5 % PO\textsubscript{2}) | NLMO: 82 % Re, 0.7 % P (0.9 % PO\textsubscript{2}) | NLMO: 89 % Re, (1.0 % NO\textsubscript{2}) |
| Re Lone Pair 2 | NLMO: 88 % Re, 3.0 % P (4.0 % PO\textsubscript{2}) | NLMO: 86 % Re, 5.6 % P (7.5 % PO\textsubscript{2}) | NLMO: 86 % Re, 3.8 % N (8.9 % NO\textsubscript{2}) |
| Re Lone Pair 3\textsuperscript{[b]} | NLMO: 94 % Re, 1.4 % P (1.8 % PO\textsubscript{2}) | | |

[a] Averaged values of the \( \alpha \) and \( \beta \) spin orbitals. Depicted are always the \( \alpha \) spin orbitals.

[b] Only occupied in the \( \alpha \) space.
SUPPORTING INFORMATION

Thermodynamics of the equilibrium of 2 and 2₂

The free energy of the equilibrium between 2 and 2₂ is either slightly exergonic, thermoneutral or endergonic depending on the applied density functional. The transition state of the reaction could not be located. Taking into account, that in solution the ³¹P signal of 2₂ cannot be detected, a ratio of at least 1:40 appears reasonable. This corresponds to a free energy of ∆G = +2.2 kcal·mol⁻¹, which is in good agreement with the computed value of method 3.

Table S10. Computed thermodynamics of the formation of 2₂.

| Method/ functional | ΔE (in kcal·mol⁻¹)ᵃ | ΔH (kcal·mol⁻¹) | ΔG (kcal·mol⁻¹) |
|--------------------|---------------------|-----------------|-----------------|
| Method 1: PBE      | -16.7               | -17.2           | 0.4             |
| Method 2: PBE0     | -19.8               | -21.0           | -2.1            |
| Method 3: M06L/ M06| -16.4               | -18.0           | 1.7             |

[a] SCF energies including zero-point energies.
Computed IR and NMR Data of 2, 22, 2K and 3K

**IR**

**Figure S35.** Calculated IR intensities (RI-M06L/def2-SVP) of complex 2. IR bands are highlighted according to the atom type (square mass-weighted) participating in the vibrational motion: H – light grey, C – dark grey, N – blue, O – red, P – orange.

**Figure S36.** Calculated IR intensities (RI-M06L/def2-SVP) of complex 2. IR bands are highlighted according to the atom type (square mass-weighted) participating in the vibrational motion: H – light grey, C – dark grey, N – blue, O – red, P – orange.
Figure S37. Calculated IR intensities (RI-M06L/def2-SVP) of complex 2. IR bands are highlighted according to the atom type (square mass-weighted) participating in the vibrational motion: H – light grey, C – dark grey, N – blue, O – red, P – orange.

Figure S38. Calculated IR intensities (RI-M06L/def2-SVP) of complex 3. IR bands are highlighted according to the atom type (square mass-weighted) participating in the vibrational motion: H – light grey, C – dark grey, N – blue, O – red, P – orange.
**Table S11.** Experimental (black) and calculated (RI-M06L/def2SVP, red) calculated vibrations of the Re-PO₂ moiety in 2, 2⁸, and 3⁸. Analyzed are the symmetric (\(\nu_{PO_2, \text{sym}}\)) and asymmetric (\(\nu_{PO_2, \text{asym}}\)) stretching as well as the bending mode (\(\delta_{PO_2}\)) of the PO₂ group.

| Vibration     | 2               | 2⁸              | 3⁸              |
|---------------|-----------------|-----------------|-----------------|
| \(\nu_{PO_2, \text{asym}}\) | 1245.1 / 1262.8 | ~1096 / 1110.8  | 1060.3 / 1085.4 |
| \(\nu_{PO_2, \text{sym}}\)       | 1078.8 / 1085.7 | 1017.2 / 1024.8 | 1014 or 1000 / 1005.6 |
| \(\delta_{PO_2}\)          | 506.0 / 504.7   | 538.9 / 524.3   | 536.6 / 535.0   |

**NMR**

**Table S12.** Computed \(^{31}\)P NMR chemical shifts of 2 and 2s.

|                  | Experiment (in ppm) | ORCA (in ppm) | ADF (in ppm) |
|------------------|---------------------|---------------|--------------|
| 2                | 13                  | 78[\text{[a]}] | 46           |
| \(P_{PDP}\)     | 246                 | 311           | 260[\text{[a]}] |
| \(P_{PCO_2}\)   | 187[\text{[a]}]    | 122[\text{[a]}] |

\[\text{[a]}\] Averaged values.
SUPPORTING INFORMATION

XYZ coordinates

2

E (SCF) = -2565.534491, EO = 0.733269

Re 12.4071467163910 5.18554971209281 2.35811339318412
F 12.45485237839379 3.47016854857649 0.59685796246287
P 12.97714068864732 6.77051040170241 4.13871373171513
O 13.43338471074629 6.94426304616483 0.72506075643457
Cl 11.22479791815326 7.05612807217490 0.25780814783066
Br 12.02413450562508 7.27438782182167 0.1443647488978225
N 12.88237083026072 5.24052334457618 0.24529139347422
N 11.13656429390617 5.33041391421591 2.5130923131884
N 11.77693551745203 3.75693241598587 3.79856647204255
N 12.51408050964475 2.9079483693137 4.49489122043091
C 15.00447477783222 4.46174567690991 1.0425820130909
H 15.54693350454706 3.65651459804963 1.54759972094144
H 16.26106797898457 3.88484794000172 1.74269300159467
H 16.91278100056843 3.10643689623325 0.95456975283401
H 13.72888750526865 1.27904833327097 0.6736207863443
H 14.00381811481427 1.02644895059079 0.63063792432797
H 14.23784504637545 0.83544738452632 0.61908484904841
H 13.18519602508264 0.25465477224273 0.7206928483893
H 12.09317955027412 0.5204262001900 0.4799635170037
H 12.34131797930231 5.03879416215346 -0.18157509470117
C 15.2203338011046 6.22804446619917 2.59763161509439
C 15.74185264147217 6.68425312061674 1.74437083930685
C 11.90055074505393 5.67525874996522 1.93121432237494
C 14.57537313793854 7.3324189007115 3.4155556657103
C 12.3166972738798 8.1570227085700 2.7342458128449
C 15.2731623691621 7.72697382152884 4.16877602794139
C 14.9563984769558 6.07083981714366 5.8379800465740
C 14.5785029650544 5.0213194127393 5.5544104351350
C 14.2512191063551 4.2647901918290 4.8406136832535
C 11.5053078426602 4.50004132558581 6.4975609151194
C 11.5150632040415 5.48648767663080 5.20670926843893
C 12.3106503086856 5.41450109237951 6.5548486879900
C 11.7006982969404 4.78807159874668 5.9891142534162
C 11.6513944947892 6.15898183992763 7.01830270290491
C 12.639356209838 4.707576530272 3.762769531434
C 14.106793408600 7.10952312719777 6.78057562784730
C 14.90413052723702 7.70474817690188 6.31127699804453
C 14.5589924918237 6.5767581354222 6.73381629132761
C 13.5509660546769 7.7937236981784 7.19468275103507
C 11.4947660649383 8.87278706280669 3.07881374201951
C 12.30266587578378 9.09174814419839 2.66642054133132
C 8.81225615344287 8.81225615344287 3.2308212995128
C 10.81699421577249 8.15751449738953 2.60468005095859
C 10.80030492524605 8.9051756778316 5.31461357111422
C 10.11219709962645 8.94993857871343 5.28922903067686
### Supporting Information

Table 1: Geometric Parameters (Å) for Compound H

| Atoms | x      | y      | z      |
|-------|--------|--------|--------|
| H     | 11.0784764902325 | 7.92308853928598 | 6.36337919228927 |
| C     | 10.2447844844281 | 7.2076824561030 | 4.95768523165186 |
| C     | 12.8547793896047 | 9.5197335115424 | 5.01874115973859 |
| C     | 13.7357170547723 | 9.73982194702079 | 4.39755485724909 |
| C     | 13.1925404937969 | 9.33356279525621 | 6.04260080995728 |
| C     | 12.2404284781690 | 10.43541566552392 | 5.03734619297287 |
| C     | 9.3275247277126 | 16.4911030383344 | 1.8146836882409 |
| C     | 8.1292818938318 | 6.83006725144767 | 1.11276409705286 |
| C     | 7.9484605388885 | 6.16381505296379 | 1.9658306446180 |
| C     | 7.36029774959685 | 6.85621137631882 | 1.36132587138008 |
| C     | 7.3517250964873 | 5.30173836799879 | 2.88435067931870 |
| N     | 6.2689310576076 | 5.29138037977039 | 3.02849516714441 |
| C     | 8.1709935013161 | 4.45674282406287 | 3.6175239484539 |
| C     | 7.76455123425103 | 3.7595566188854 | 3.43778228636754 |
| C     | 9.52760661147722 | 4.85919317482207 | 3.41202836405311 |
| C     | 10.46731980215805 | 3.63126551950952 | 4.17156132961861 |
| C     | 10.35296437423263 | 2.628883276089 | 5.09087560274366 |
| C     | 9.45270350459947 | 2.26233581392997 | 5.7695034468157 |
| C     | 11.67353229155988 | 2.2177804152874 | 5.2819360002053 |
| C     | 12.0619275561162 | 1.44861134081626 | 5.95245982566970 |

Table 2: Energies (E[SCF])

| Compounds | E[SCF]   |
|-----------|----------|
| C-H       | -2.31190115733757 |
**SUPPORTING INFORMATION**

| \( E \text{(SCF)} \) | \(-0.18899633206075\) | \(3.9444634677372\) |
|----------------|------------------------|--------------------------|
| \( H \) | \(-0.28540814695209\) | \(3.2846356463434\) |
| \( C \) | \(-0.28640720407241\) | \(3.3748838503322\) |
| \( H \) | \(-2.7570297361358\) | \(4.2556646827049\) |
| \( C \) | \(-3.8307031842646\) | \(2.8500423756470\) |
| \( C \) | \(-3.2972431731259\) | \(0.4984878764036\) |
| \( C \) | \(-3.8630432857293\) | \(0.8722619828007\) |
| \( C \) | \(-0.452995457042486\) | \(0.1727552554599\) |
| \( H \) | \(-4.11360476810103\) | \(1.8891175909995\) |
| \( N \) | \(-0.3017560590095\) | \(-4.49\) |
| \( O \) | \(-1.04844990519006\) | \(0.7999222925076\) |
| \( O \) | \(-2.217612536866492\) | \(-0.9303415703676\) |
| \( O \) | \(-2.57845974809894\) | \(-0.9805544269587\) |
| \( O \) | \(-1.6256609496247\) | \(-1.22426964526568\) |
| \( O \) | \(-2.78161784138994\) | \(-1.6663939000565\) |
| \( O \) | \(-1.49330113265549\) | \(1.3908458049391\) |
| \( O \) | \(-1.68312274742620\) | \(1.17936742897765\) |
| \( P \) | \(-1.04225838415205\) | \(0.262285841952\) |
| \( K \) | \(-0.24846260431682\) | \(-0.035094230337\) |
| \( N \) | \(0.9261943057647\) | \(-1.6455866247016\) |
| \( C \) | \(0.20207193589401\) | \(-1.00768102558494\) |
| \( C \) | \(2.7612396165357\) | \(-1.4737683516768\) |
| \( C \) | \(2.3015907431653\) | \(-0.0993277812456\) |
| \( C \) | \(3.6359801543799\) | \(-0.904118506024\) |
| \( C \) | \(2.38720462894254\) | \(-0.6623954612933\) |
| \( C \) | \(2.96385061954051\) | \(-3.0642546388692\) |
| \( C \) | \(0.5227841875523\) | \(-0.0278109603359\) |
| \( C \) | \(0.8868992498763\) | \(-0.4226199100926\) |
| \( N \) | \(-2.56673667600002\) | \(-3.1412194238458\) |
| \( O \) | \(-1.3539940301422\) | \(-2.6431463663408\) |
| \( P \) | \(-2.73000882923105\) | \(-4.15634197029591\) |
| \( C \) | \(-1.5980362971904\) | \(-4.3206609662376\) |
| \( C \) | \(-3.6610296975393\) | \(-4.7249413526677\) |
| \( C \) | \(-0.73430667823429\) | \(-3.3169329610368\) |
| \( C \) | \(-1.42931073597119\) | \(-5.0397980545601\) |
| \( O \) | \(1.2313592863921\) | \(0.59379366560122\) |
| \( O \) | \(2.40613004164676\) | \(1.0514697974143\) |
| \( O \) | \(-6.527298839036\) | \(1.126184829417836\) |

**E**: -4086.877797906045, **EO**: -1.1319836

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**S35**
| X     | Y     | Z     |
|-------|-------|-------|
| H     | 11.57390997970617 | 9.00809531192610 |
| C     | 4.1999141882217   | 9.58070407587343 |
| H     | 3.98661770664000  | 9.81597502319167 |
| C     | 4.93718329333510  | 8.75474007001217 |
| H     | 2.55946965024100  | 7.93102819584100 |
| C     | 3.28525417684000  | 1.74991624594709 |
| H     | 2.42524867040600  | 0.84283069735260 |
| C     | 1.23968002775940  | 0.68426245558786 |
| C     | 0.53210696994796  | 8.49444122924540 |
| H     | 0.80997781523980  | 6.7313434380031  |
| C     | 0.25391287240000  | 7.37400987866250 |
| H     | -0.23444751788367 | 6.45483371573520 |
| C     | -0.46364946763845 | 8.20928128797895 |
| H     | 0.56750311618367  | 7.19518561220630 |
| C     | 0.36051685587030  | 6.9226900261075  |
| H     | 1.27960083844883  | 6.35722736290610 |
| C     | 1.14807238115999  | 8.46484181774987 |
| H     | 1.77078498364000  | 7.64795046288438 |
| C     | 0.13062929856666  | 8.36378422928224 |
| H     | 1.73895076161909  | 9.79447364614133 |
| C     | 1.04933267220638  | 10.6086713340975 |
| H     | 1.62923859106861  | 9.94642939764892 |
| C     | 3.75612927914000  | 10.99239087922913 |
| H     | 3.83858025709792  | 11.49658292302368 |
| C     | 3.20115004534000  | 11.83549824036804 |
| H     | 5.13836026024640  | 10.93234853750738 |
| H     | 5.72868111712417  | 11.789849861331 |
| C     | 5.64675505147427  | 10.0039066008422 |
| H     | 1.91071350336667  | 16.00945054882191 |

E(SCF) = -2279.140086, E0 = 0.762415
### SUPPORTING INFORMATION

| Element | X (Å)  | Y (Å)  | Z (Å)  |
|---------|--------|--------|--------|
| C       | 13.11  | 3.1368 | 0.6084 |
| H       | 15.87  | 5.20   | 0.6084 |
| C       | 15.10  | 4.56   | 1.06   |
| N       | 12.56  | 2.97   | 0.00   |
| N       | 11.82  | 3.86   | 3.68   |
| N       | 14.34  | 5.37   | 2.02   |
| O       | 11.20  | 7.82   | 0.22   |
| P       | 12.47  | 7.10   | 0.62   |
| P       | 12.55  | 3.60   | 0.52   |
| O       | 0.82   | 1.02   | 0.43   |
| H       | 2.85   | 4.31   | 0.96   |
| C       | 2.31   | 0.06   | 0.84   |
| N       | 2.32   | 0.84   | 1.78   |
| C       | 4.80   | 1.02   | 2.75   |
| H       | 5.10   | 3.53   | 0.40   |
| C       | 5.30   | 2.20   | 3.57   |
| C       | 4.74   | 2.64   | 4.06   |
| H       | 4.93   | 4.06   | 3.75   |
| H       | 4.22   | 3.63   | 0.12   |
| C       | 11.69  | 7.04   | 1.86   |
| C       | 1.19   | 0.26   | 0.89   |
| N       | 1.98   | 0.23   | 0.84   |
| H       | 2.74   | 1.10   | 2.35   |
| C       | 3.75   | 0.34   | 0.17   |
| N       | 5.22   | 0.59   | 0.23   |
| C       | 1.06   | 0.03   | 0.19   |
| C       | 0.97   | 0.21   | 0.21   |
| C       | 1.17   | 0.10   | 0.04   |
| C       | 0.37   | 0.01   | 0.00   |
| C       | 1.09   | 1.81   | 0.16   |
| C       | 1.65   | 2.50   | 0.16   |
| C       | 0.88   | 0.88   | 0.00   |
| O       | 0.90   | 1.00   | 0.00   |

**2σ**

| E(SCF) | -513.140490 | EQ | 1.470346 |

**176**

Re: 12.4570005742991
P: 12.5448087293484
F: 12.9870204823070
D: 12.4703481017897
O: 11.1972489854091
C: 10.1179730324340
N: 10.4310826075285
N: 10.1844730157473
N: 11.8244385028604
C: 15.1029047732643
H: 0.26216214871491
O: 0.8713533389711

**S38**

**WILEY-VCH**
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 11.5365 | 4934534 | 3434    |
| H       | 10.7104 | 81116262 | 3666    |
| H       | 11.1707 | 477416976 | 6767    |
| H       | 11.7852 | 94039661 | 4343    |
| C       | 13.9963 | 223211314 | 3478    |
| H       | 14.9310 | 712156822 | 3142    |
| C       | 14.0330 | 352013402 | 4283    |
| H       | 13.4746 | 60875040974 | 4128    |
| C       | 12.2559 | 498229295 | 4343    |
| H       | 15.8101 | 209794894 | 4343    |
| C       | 12.7306 | 468233129 | 4343    |
| H       | 13.0406 | 697450291 | 4343    |
| C       | 12.2918 | 9650576400 | 4343    |
| H       | 9.5904 | 999457018 | 4343    |
| H       | 9.7267 | 8861809472 | 4343    |
| H       | 10.6053 | 7132374755 | 4343    |
| C       | 11.8008 | 7490357232 | 4343    |
| H       | 11.5329 | 742953847 | 4343    |
| H       | 10.2410 | 871819880 | 4343    |
| C       | 11.2519 | 316294426038 | 4343    |
| H       | 15.9706 | 205572377 | 4343    |
| C       | 14.6578 | 5848519940 | 4343    |
| H       | 15.4913 | 7623373840 | 4343    |
| C       | 15.3217 | 303645689 | 4343    |
| H       | 14.8628 | 666949114 | 4343    |
| H       | 15.2248 | 4161398193 | 4343    |
| C       | 12.6253 | 1165822219 | 4343    |
| H       | 15.4425 | 725574071 | 4343    |
| C       | 12.1647 | 7113400904 | 4343    |
| H       | 11.6235 | 532220873 | 4343    |
| H       | 11.4584 | 4066695738 | 4343    |
| H       | 12.5036 | 516478771 | 4343    |
| C       | 13.9360 | 4002997490 | 4343    |
| H       | 14.7593 | 7565821076 | 4343    |
| C       | 14.3367 | 6835201725 | 4343    |
| H       | 13.1573 | 7888200093 | 4343    |
| H       | 12.0663 | 309417872 | 4343    |
| C       | 13.6148 | 651218954 | 4343    |
| H       | 12.4635 | 7705940939 | 4343    |
| H       | 10.0756 | 8575936170 | 4343    |
| C       | 10.9421 | 8105345416 | 4343    |
| H       | 10.8120 | 8276216042 | 4343    |
| H       | 10.0376 | 866666665 | 4343    |
| H       | 10.2295 | 587279085 | 4343    |
| C       | 10.9301 | 2430753531 | 4343    |
| H       | 10.8320 | 6494752371 | 4343    |
| H       | 10.2445 | 061258852 | 4343    |
| C       | 12.3465 | 6283059801 | 4343    |
| H       | 9.3908 | 383387676 | 4343    |
| H       | 9.8657 | 558380662 | 4343    |
| H       | 8.0608 | 650148685 | 4343    |
| C       | 4.8676 | 7685973804 | 4343    |
| H       | 4.7960 | 858143309 | 4343    |
| H       | 6.4614 | 923571578 | 4343    |
| C       | 7.9015 | 5594960237 | 4343    |
| H       | 6.6243 | 716844403 | 4343    |
| H       | 5.5230 | 1557719953 | 4343    |
| C       | 4.1578 | 7161733762 | 4343    |
| H       | 9.5220 | 488320170 | 4343    |
| H       | 7.1395 | 568714380 | 4343    |
| C       | 5.5576 | 885045293 | 4343    |
| H       | 15.8309 | 891880816 | 4343    |
| C       | 13.3288 | 8513110816 | 4343    |
| H       | 14.75 | 714016473449 | 4343    |
| H       | 14.4740 | 7931413975 | 4343    |
| C       | 13.4995 | 544219249 | 4343    |
| H       | 11.2762 | 731458156 | 4343    |
E(SCF) = 

\[ \begin{array}{ccc}
H & 5.65384921513002 & 17.30768964173152 & 11.41594 \\
H & 4.56945324635941 & 16.66861314348361 & 10.15349041634706 \\
H & 4.61257802443275 & 18.80493784161083 & 13.34 \\
H & 1.57257280639773 & 18.75378937806662 & 11.10657968708910 \\
H & 0.74872506214218 & 16.0511767461 \\
C & & & \\
H & 14.90048434065004 & 13.5866712661722 & -5.70385018717215
\end{array} \]
|      | C      | H      | O      | N      | S      |
|------|--------|--------|--------|--------|--------|
| 1    | 4.2638 | 5.0564 | 0.3311 | 1.0438 | 3.0640 |
| 2    | 3.6787 | 15.6796 | 14.8837 | 13.7295 | 13.9494 |
| 3    | 2.9792 | 13.8267 | 14.8376 | 11.7925 | 11.9814 |
| 4    | 3.1740 | 15.1239 | 13.5045 | 12.6067 | 12.1432 |
| 5    | 4.5124 | 14.0084 | 14.8837 | 11.7925 | 11.9814 |
| 6    | 5.0646 | 14.6628 | 13.5045 | 12.6067 | 12.1432 |
| 7    | 4.4271 | 14.0253 | 14.8837 | 11.7925 | 11.9814 |
| 8    | 5.7447 | 13.9968 | 13.5045 | 12.6067 | 12.1432 |
| 9    | 5.6852 | 15.2792 | 13.8267 | 11.7925 | 11.9814 |
| 10   | 5.2081 | 16.4618 | 14.8376 | 11.7925 | 11.9814 |
| 11   | 5.7850 | 17.1042 | 14.8376 | 11.7925 | 11.9814 |
| 12   | 5.9360 | 15.8639 | 13.5045 | 12.6067 | 12.1432 |
| 13   | 4.6751 | 17.1034 | 13.5045 | 12.6067 | 12.1432 |
| 14   | 1.7409 | 13.9336 | 8.6832 | 12.1350 | 11.1930 |
| 15   | 2.3346 | 13.7213 | 9.2004 | 11.1350 | 10.1930 |
| 16   | 1.7156 | 14.6150 | 7.3087 | 11.1350 | 10.1930 |
| 17   | 2.3008 | 13.9137 | 6.7093 | 11.1350 | 10.1930 |
| 18   | 0.9456 | 15.6208 | 6.7137 | 11.1350 | 10.1930 |
| 19   | 0.8969 | 15.7302 | 6.5273 | 11.1350 | 10.1930 |
| 20   | 0.2554 | 16.4870 | 5.7457 | 11.1350 | 10.1930 |
| 21   | 0.3285 | 17.3074 | 7.1468 | 11.1350 | 10.1930 |
| 22   | -0.2706 | 17.2402 | 8.9785 | 11.1350 | 10.1930 |
| 23   | -0.9345 | 18.4740 | 9.7710 | 11.1350 | 10.1930 |
| 24   | -1.2544 | 20.0064 | 8.8705 | 11.1350 | 10.1930 |
| 25   | -1.1490 | 20.8568 | 11.1034 | 11.1350 | 10.1930 |
| 26   | -1.5750 | 19.7569 | 11.5017 | 11.1350 | 10.1930 |

SUPPORTING INFORMATION

E(ScF) = -4086.28046564; E0 = 1.12040678

Re 0.9089 15.1671 11.6704 4824385954
K 2.8288 10.0133 6.6625 5147275758
L -1.2093 13.9993 8.2886 6139057061
P 2.8297 16.4313 12.4828 6036705180
R 0.2961 13.1822 8.1977 9793760178
O 2.9466 12.6291 7.3085 4221550227
Q 1.6851 12.1076 9.0094 48626814
C 5.3004 10.4117 10.1625 5067062863
C 3.0140 9.2317 8.8805 2319768652
O 1.4280 7.6549 10.5611 2084196540
O 1.0753 8.3921 13.2367 60839995
C 1.9598 8.7906 16.6715 9210992824
C 5.0055 10.9714 12.9596 7980233968
C 0.5037 15.3363 13.7103 9561823752
C 1.0438 13.3585 9.5311 1063771789
C 0.4386 17.0367 11.1953 2378705705
C 0.5247 18.0253 9.9376 5098991164
C 3.4995 24.3051 14.4448 8305896780
C -0.9006 18.0409 13.1705 11162841281
C 0.4975 13.7261 15.0828 6448531622
C -0.1312 13.3491 6.5549 612979994
C -2.0024 13.0927 8.1284 5128126051
C -0.4370 12.4320 13.4401 0057169299
C -2.8655 14.9691 9.9601 0032149777
C -4.1051 14.1189 12.2483 01599184
C -4.3945 13.4677 12.4181 379052413
C -4.9525 14.8019 12.4316 324431939
C -3.9933 13.5013 13.1529 4668038367
C -3.1163 15.7954 10.6958 8404953422
C -3.3758 15.1739 9.8263 7222574875
C -2.2508 16.4099 12.4699 505149399
C -3.6947 16.4769 12.8747 941552275
C -2.6957 15.9224 13.1490 775117440
C -1.7710 15.6111 13.0961 5634739722
C -2.7937 15.3791 10.1409 2385656252
C -3.5337 16.4004 13.1473 3426798195
C -1.6001 12.4310 8.8096 4965061422
C -0.3022 11.7343 10.3728 9404204993
C -0.5515 10.8555 9.7515 8442855272
C 0.2750 11.3865 9.2383 8259351434
C 0.3314 12.3939 9.7728 6319053205
C -2.3865 11.3720 11.6165 1024579545

S42
SUPPORTING INFORMATION

|     |   |   |   |   |   |   |
|-----|---|---|---|---|---|---|
| C   | 0.55512814142197 | 7.20220476896732 | 12.72625237924470 |
| H  | -0.38143374026056 | 6.91885206470975 | 13.24784969997445 |
| H  | 1.27187769099866  | 6.36725454096118 | 12.85828961491527 |
| C   | 1.12350787960619 | 8.45642575304244 | 14.63676272426303 |
| H   | 1.74942765063801 | 7.63864848419813 | 15.04429683647989 |
| H  | 0.10577350088338 | 8.34595283672491 | 15.06148039232812 |
| C   | 1.70845457653792 | 9.78511508888181 | 15.02988552670585 |
| H  | 1.17865950395075 | 10.59947092303457 | 14.50312308867776 |
| H   | 1.58384655818544 | 9.93400438583616 | 16.12270598818153 |
| C   | 3.71728488947138 | 10.99583579073355 | 14.93703996076219 |
| H   | 3.78317560094243 | 11.17389370794285 | 16.03034027655141 |
| H   | 3.16045698818132 | 11.82450946101956 | 14.46772447618093 |
| C   | 5.10319272200272 | 10.93449860518837 | 14.35551331036408 |
| H   | 5.68974893071475 | 11.79972768513203 | 14.72299731450664 |
| H   | 5.61586046075013 | 10.01186610919308 | 14.69520944024939 |
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