Electronic Supplementary Material (ESI) for RSC Advances.

[Re(CO)$_3$Cl(C$_5$H$_4$ClP)$_2$] and [Re(CO)$_2$Cl(C$_5$H$_4$ClP)$_3$]: Synthesis and Characterization of Two Novel Rhenium(I) Phosphinine Complexes

Manuela Hollering,[a,b] Richard O. Reithmeier,[a] Simon Meister,[a] Eberhardt Herdtweck,[b] Fritz E. Kühn,[b,*] Bernhard Rieger[a,*]

[a] WACKER-Chair of Macromolecular Chemistry, [b] Chair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Straße 1, 85748 Garching b. München.

* E-Mail for B.R.: rieger@tum.de, Fax: (+49)-89-289-13562;
E-Mail for F.E.K.: fritz.kuehn@ch.tum.de, Fax: (+49)-89-289-13473.

Supporting Information

Contents

1. Analytical Data 2
2. Crystallographic Details 8
3. DFT Computed Data 17

1. Analytical Data

cis-[Re(CO)$_3$Cl(η^1-C$_5$H$_4$ClP)$_2$] (**1**)

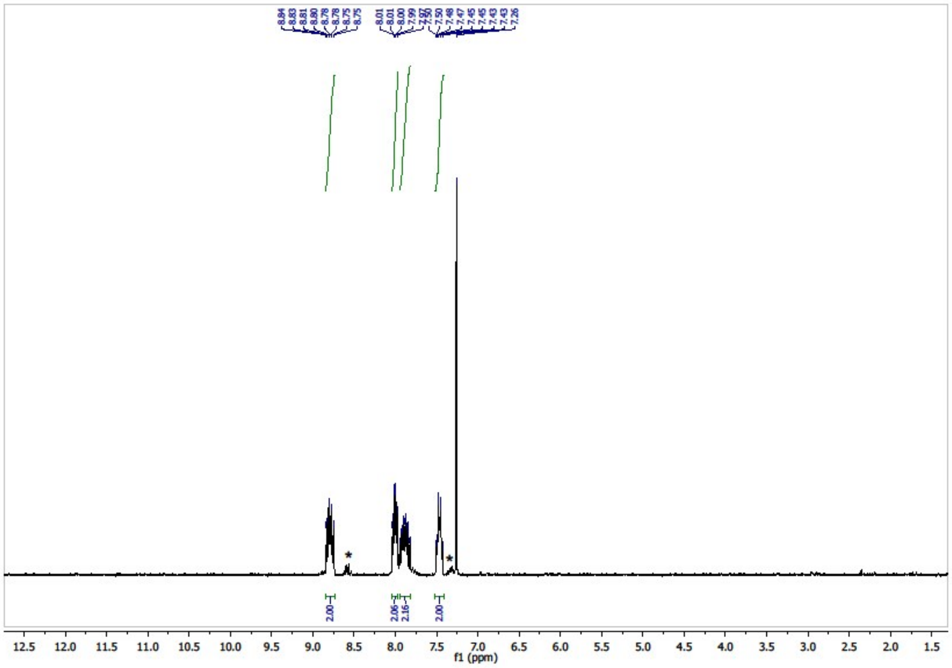

Figure S1. ^{1}H NMR of compound **1** (360 MHz, CDCl$_3$): δ = 8.79 (ddd, $^2J_{H6\text{-}P}$ = 20.5 Hz, $^3J_{H6\text{-}H5}$ = 10.2 Hz, $^4J_{H6\text{-}H4}$ = 1.3 Hz, 2H), 8.00 (ddt, $^3J_{H3\text{-}H4}$ = 8.9 Hz, $^3J_{H3\text{-}P}$ = 13.6 Hz, $^3J_{H3\text{-}H6}$ = 1.0 Hz, 2H), 7.89 (dddd, $^3J_{H5\text{-}P}$ = 24.9 Hz, $^3J_{H5\text{-}H6}$ = 10.3 Hz, $^3J_{H5\text{-}H4}$ = 8.1 Hz, $^4J_{H5\text{-}H3}$ = 1.0 Hz, 2H), 7.47 (dd, $^3J_{H4\text{-}H5}$ = 7.9 Hz, $^4J_{H4\text{-}H6}$ = 1.3 Hz, 2H). * Trace impurity of complex **2**.

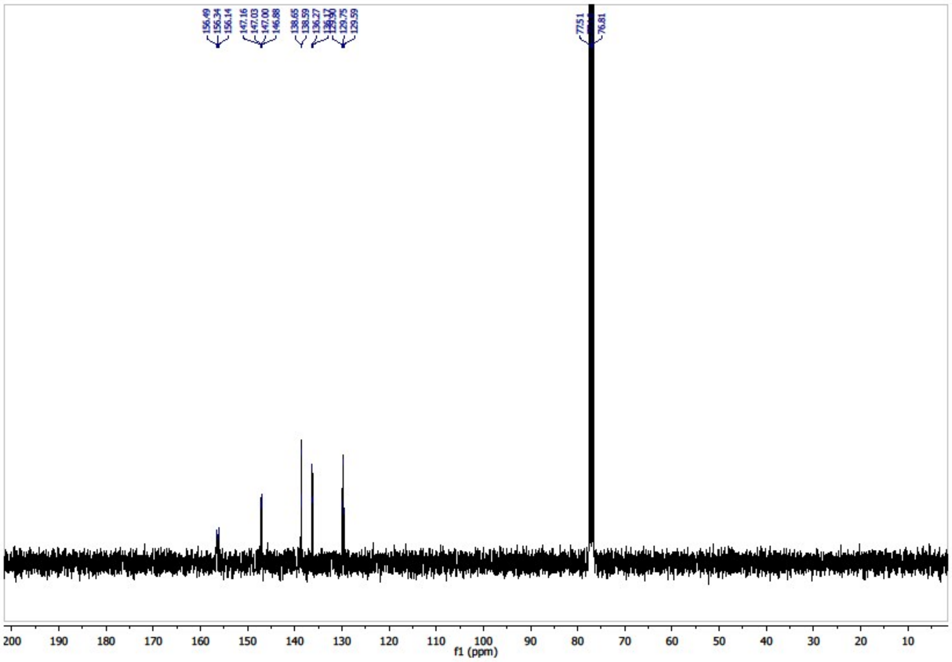

Figure S2. ^{13}C NMR of compound **1** (90.6 MHz, $CDCl_3$): δ = 156.21 (dd, $^1J_{C\text{-}P}$ = 18.9 Hz, $^3J_{C\text{-}P}$ = 13.0 Hz, C_2), 146.93 (dd, $^1J_{C\text{-}P}$ = 15.0 Hz, $^3J_{C\text{-}P}$ = 10.5 Hz, C_6), 138.58 (t, $^3J_{C\text{-}P}$ = 5.3 Hz, C_4), 136.28 (d, $^2J_{C\text{-}P}$ = 9.5 Hz, C_5 or C_3), 129.78 (t, $^2J_{C\text{-}P}$ = 13.9 Hz, C_3 or C_5).

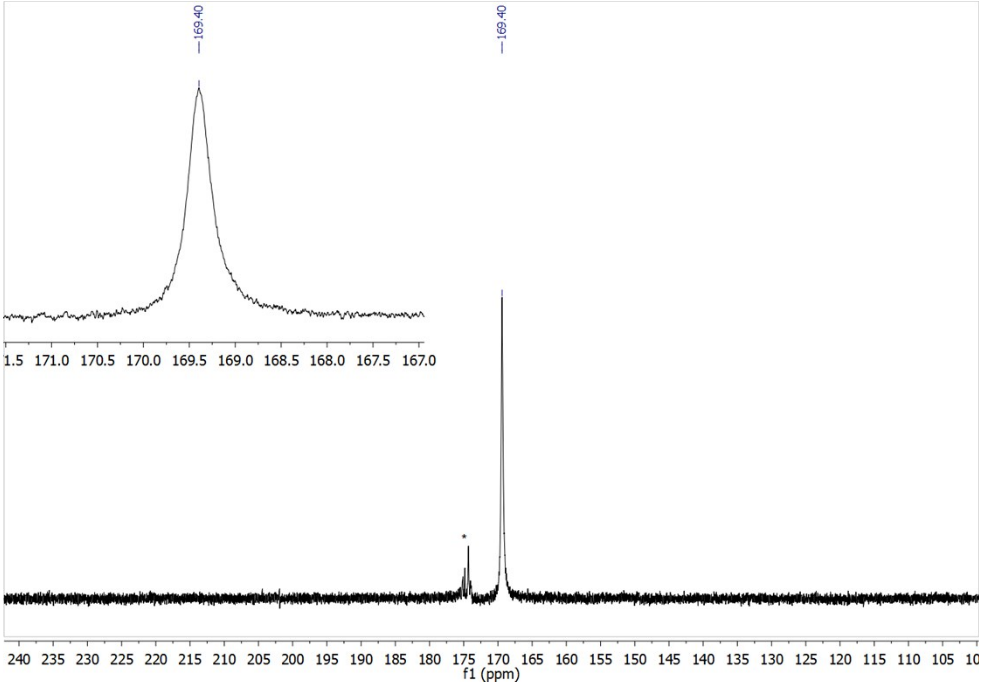

Figure S3. ^{31}P NMR of compound **1** (145.8 MHz, $CDCl_3$): δ = 169.4. * Trace impurity of complex **2.**

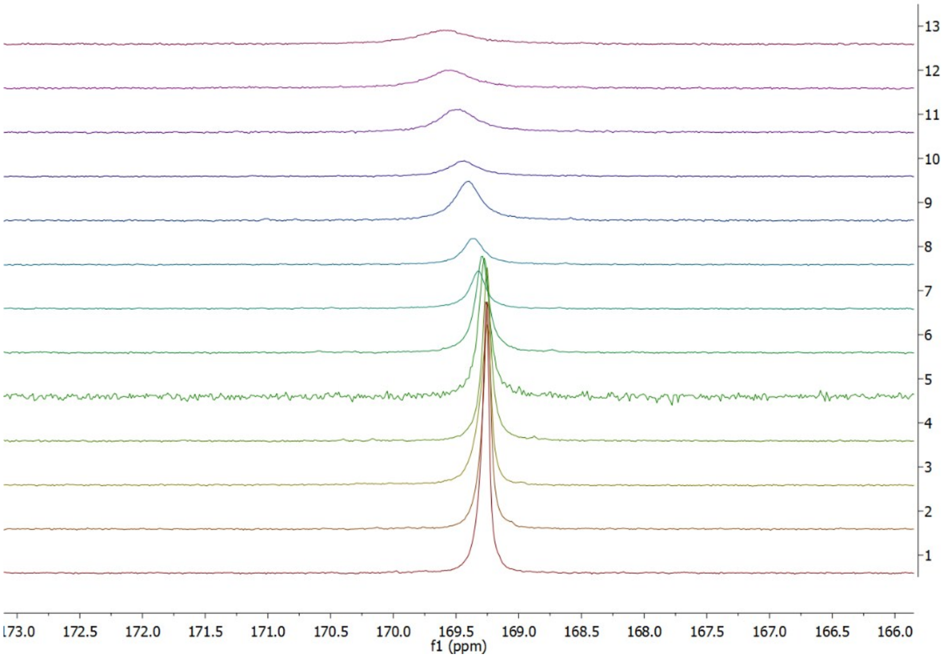

Figure S4. VT-NMR study of ^{31}P NMR of compound **1** (145.8 MHz, $CDCl_3$) from -60 °C to 60 °C in steps of 10 °C. Spectrum 1 corresponds to the measurement at -60 °C, spectrum 7 corresponds to 0 °C, spectrum 9 corresponds to 20 °C and spectrum 13 corresponds to 60 °C. The signal broadens significantly at elevated temperatures, while the signal sharpens at lower temperatures. Decoalescence is not observed in this temperature range.

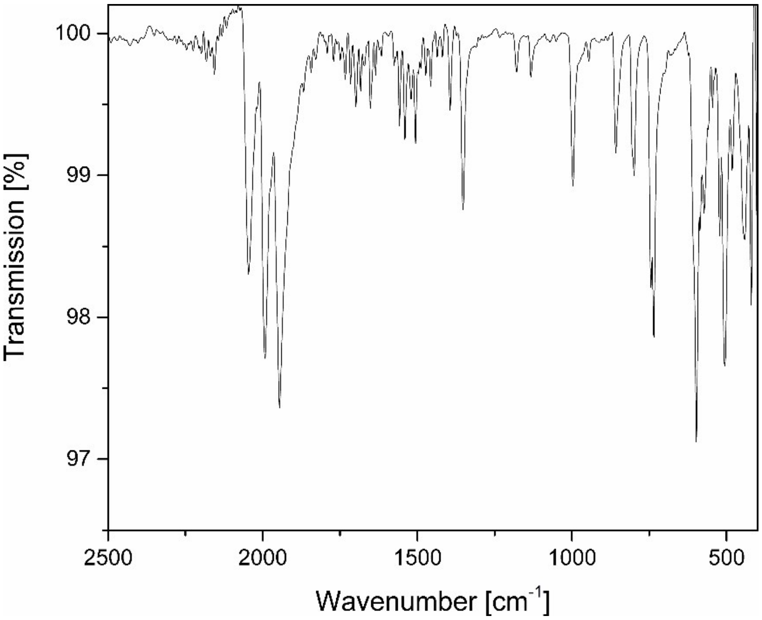

Figure S5. IR spectrum of compound **1**, with the carbonyl vibrations ν_{CO} = 2046, 1992, 1945 cm^{-1}.

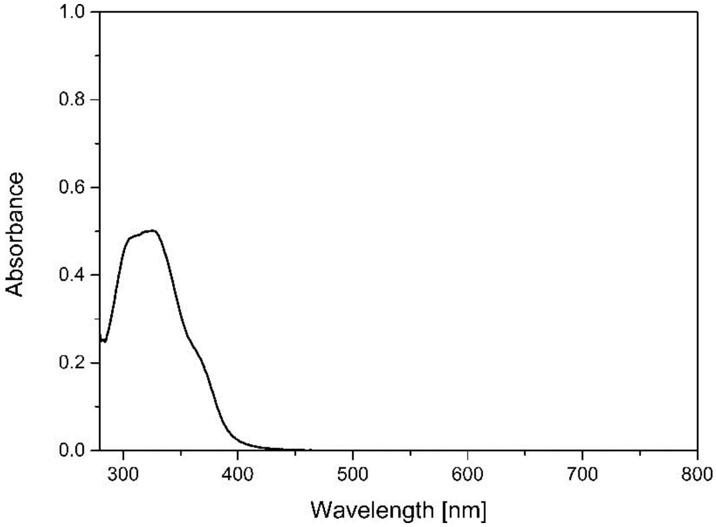

Figure S6. UV/Vis of compound **1** (CH_2Cl_2): λ_{max} [nm] ($\varepsilon \cdot 10^3$ [L mol^{-1} cm^{-1}]) = 310 (6.3).

mer-[Re(CO)$_2$Cl(η^1-C$_5$H$_4$ClP)$_3$] (**2**)

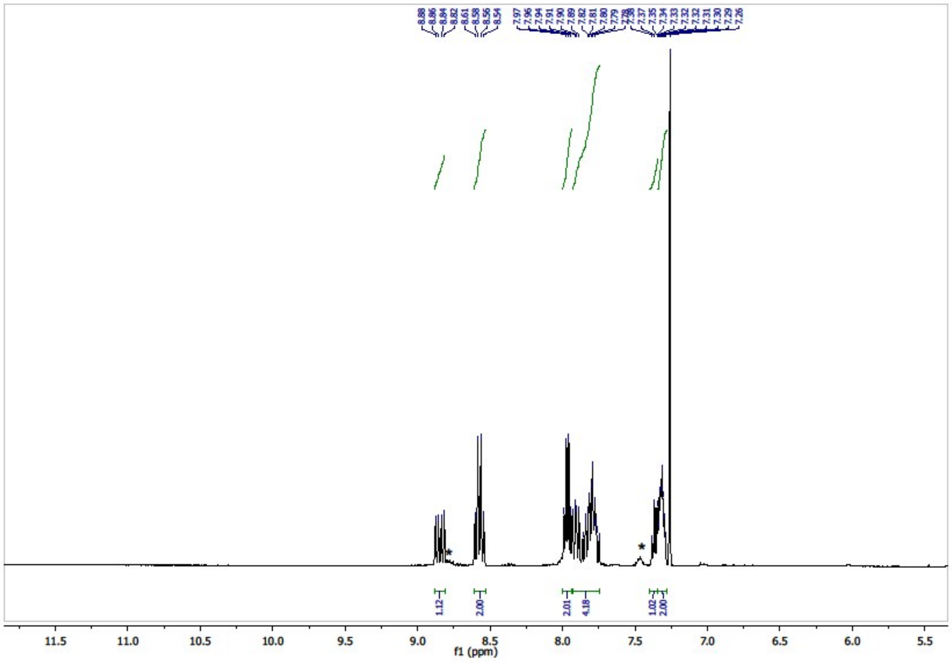

Figure S7. ^{1}H NMR of compound **2** (500 MHz, CDCl$_3$): δ = 8.85 (dd, $^2J_{H6'-P}$ = 20.4 Hz, $^3J_{H6'-H5'}$ = 10.2 Hz, 1H), 8.57 (qd, $^3J_{H6-H5}$ = 10.1 Hz, $^4J_{H6-H4}$ = 1.3 Hz, 2H), 7.97 (q, $^3J_{H3-P}$ = 7.9 Hz, 2H), 7.84 (m, 4H), 7.37 (t, $^3J_{H4'-H5'}$ = 8.2 Hz, 1H), 7.31 (dt, $^3J_{H4-H5}$ = 7.4 Hz, $^4J_{H4-H6}$ = 3.5 Hz, 2H). *Trace impurity of complex **1**.

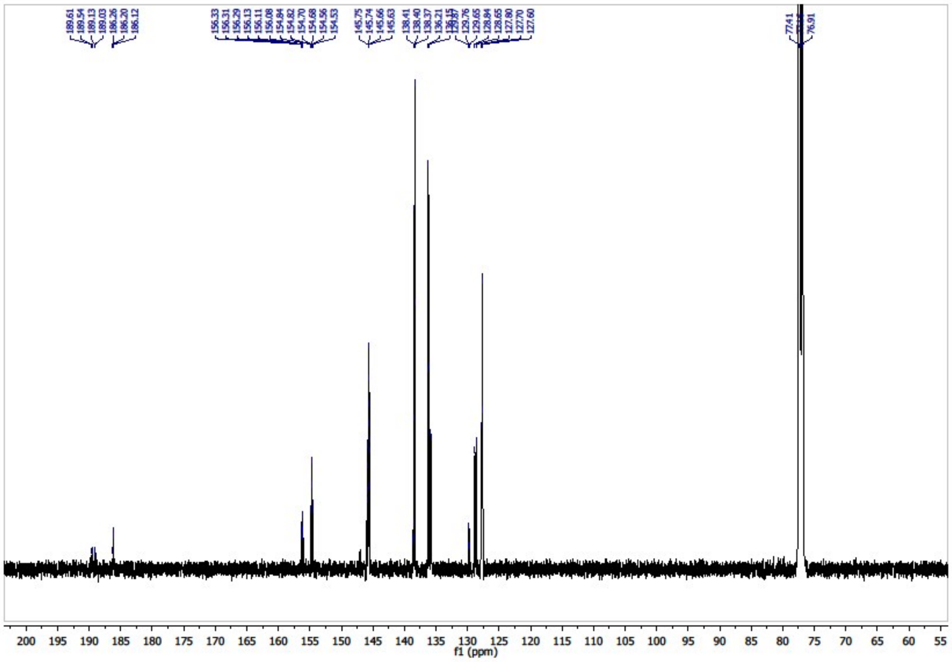

Figure S8. ^{13}C NMR of compound **2** (125.8 MHz, CDCl$_3$): δ = 189.33 (dd, $^2J_{C-P}$ = 75 Hz, $^2J_{C-P}$ = 11 Hz, CO), 186.19 (m, CO), 156.21 (dt, $^1J_{C-P}$ = 26.2 Hz, J_{C-P} = 2.72 Hz, C$_{ar}$), 154.69 (td, $^1J_{C-P}$ = 18.3 Hz, J_{C-P} = 3.1 Hz, C$_{ar}$), 145.73 (m, C$_{ar}$), 138.39 (m, C$_{ar}$), 136.21 (t, J_{C-P} = 7.6 Hz, C$_{ar}$), 135.8 (d, $^1J_{C-P}$ = 16.9 Hz, C$_{ar}$), 128.74 (t, J_{C-P} = 24.3 Hz, C$_{ar}$), 127.7 (d, J_{C-P} = 12.7 Hz, C$_{ar}$).

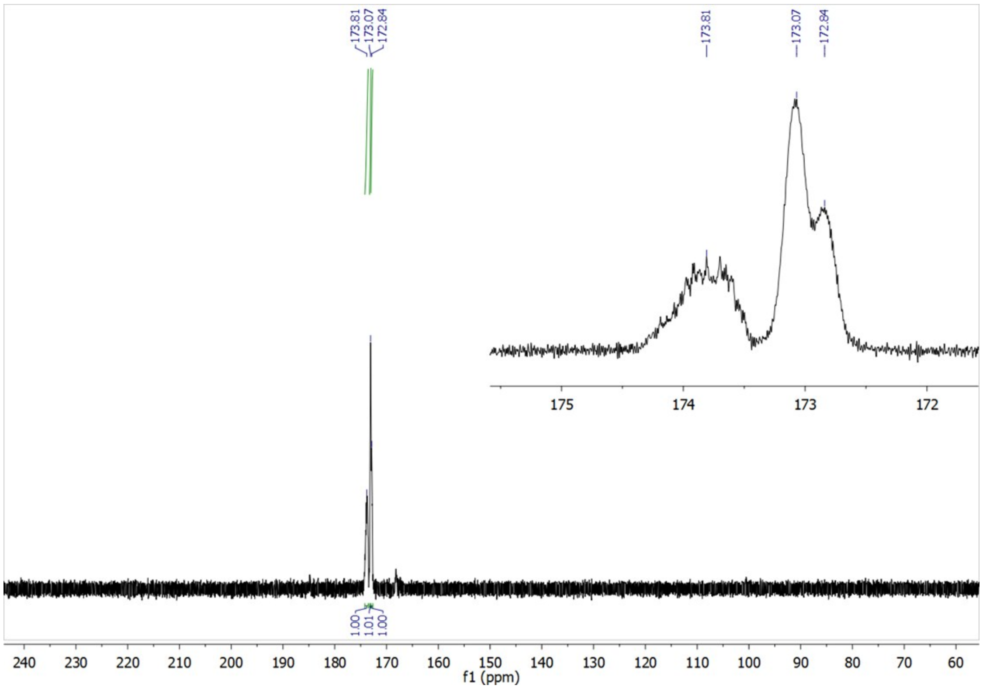

Figure S9. ^{31}P NMR of compound **2** (202.6 MHz, CDCl$_3$): δ = 173.1 (ps, 1P), 173.3 (pd, $^{2}J_{\text{P-P tans}}$ = 190 Hz, 2P).

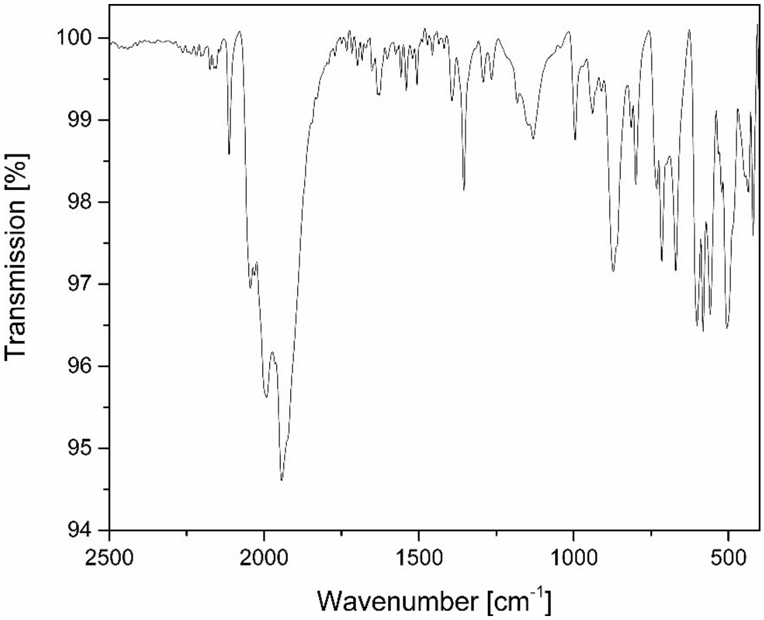

Figure S10. IR spectrum of a mixture of compound **1** and compound **2**, with the carbonyl vibrations ν_{CO} = 1965, 1924 cm^{-1}. The IR spectrum could only be obtained as a mixture due to the formation of compound **2** besides compound **1**.

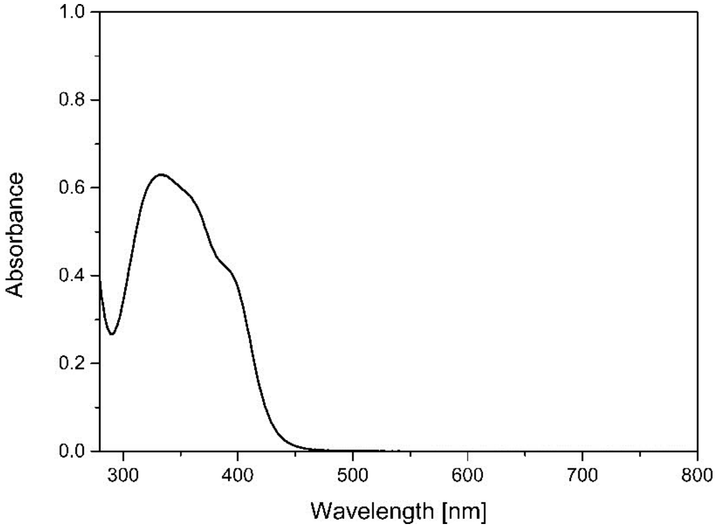

Figure S11. UV/Vis of compound **2** (CH_2Cl_2): λ_{max} [nm] ($\varepsilon \cdot 10^3$ [L mol^{-1} cm^{-1}]) = 394 (8.3), 335 (12.7).

2. Crystallographic Details

Single Crystal X-Ray Structure Determination of Compound **1** and **2**

General:

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (Bruker APEX II, κ-CCD), a rotating anode (Bruker AXS, FR591) with MoK_α radiation (λ = 0.71073 Å), and a Montel mirror optic by using the SMART software package.[1] The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on the top of a glass fiber (**1**) or of a cactus prickle (Opuntia ficus-india) (**2**) and transferred to the diffractometer. The crystals were frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[2] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX[7] based on SIR-92[3] in conjunction with SHELXL-97[5]. Unless otherwise noticed, methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene C–H distances of 0.99 Å, and $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $Sw(F_o^2-F_c^2)^2$ with SHELXL-97[5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. [4] Images of the crystal structures were generated by PLATON.[6]

HOLB 6345-123 Compound 1 CCDC 1005247

Operator:	*** Herdtweck ***
Molecular Formula:	$C_{13}H_8Cl_3O_3P_2Re$

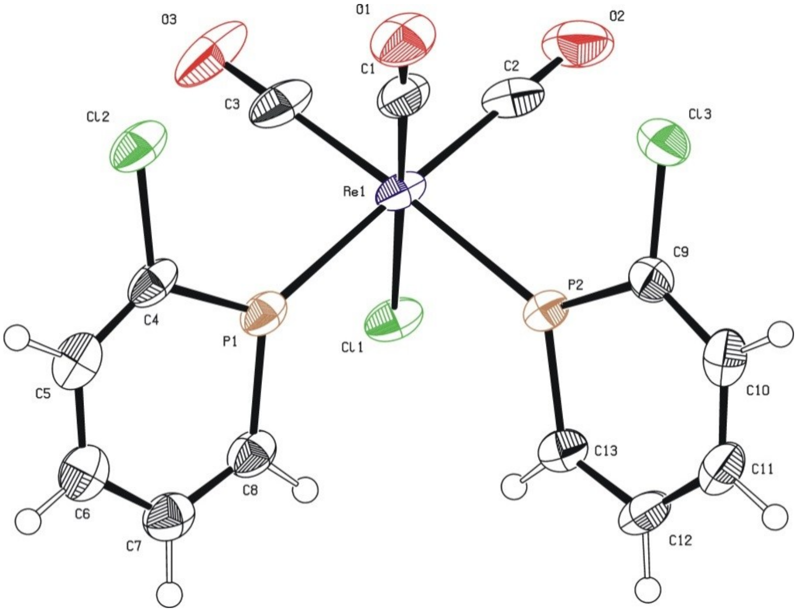

Figure S12. ORTEP style drawing of **1** with 50% ellipsoids.

Crystal Color / Shape	Colorless plate
Crystal Size	Approximate size of crystal fragment used for data collection: $0.03 \times 0.15 \times 0.28$ mm
Molecular Weight:	566.69 a.m.u.
F_{000}:	2128
Systematic Absences:	hkl: h+k≠2n; h0l: l≠2n
Space Group:	Monoclinic *C* 2/*c* (I.T.-No.: 15)
Cell Constants:	Least-squares refinement of 9878 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 1.92° < θ < 25.39°; Mo(K$\overline{\alpha}$); l = 71.073 pm a = 2499.9(3) pm b = 978.2(1) pm b = 121.979(4)° c = 1674.2(2) pm $V = 3472.8(7) \cdot 10^6$ pm^3; $Z = 8$; $D_{calc} = 2.168$ g cm^{-3}; Mos. = 0.79

Diffractometer: Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; l = 71.073 pm; Mo(K$\overline{\alpha}$)

Temperature: (-150±1) °C; (123±1) K

Measurement Range: 1.92° < θ< 25.39°; h: -30/30, k: -11/11, l: -20/20

Measurement Time: 2 × 5 s per film

Measurement Mode: measured: 10 runs; 6126 films / scaled: 10 runs; 6126 films
j- and *w*-movement; Increment: *Dj*/*Dw* = 0.50°; dx = 50.0 mm

LP - Correction: Yes [2]

Intensity Correction No/Yes; during scaling [2]

Absorption Correction: Multi-scan; during scaling; *m* = 7.649 mm^{-1} [2]
Correction Factors: T_{min} = 0.4585 T_{max} = 0.7452

Reflection Data:

50625	reflections were integrated and scaled
1766	reflections systematic absent and rejected
48859	reflections to be merged
3191	independent reflections
0.049	R_{int}: (basis F_o^2)
3191	independent reflections (all) were used in refinements
2874	independent reflections with $I_o > 2s(I_o)$
99.8 %	completeness of the data set
199	parameter full-matrix refinement
16.0	reflections per parameter

Solution: Direct Methods [3]; Difference Fourier syntheses

Refinement Parameters: In the asymmetric unit:

22	Non-hydrogen atoms with anisotropic displacement parameters

Hydrogen Atoms: In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions ($d_{C\text{-}H}$ = 95 pm). Isotropic displacement parameters were calculated from the parent carbon atom ($U_H = 1.2\ U_C$). The hydrogen atoms were included in the structure factor calculations but not refined.

Atomic Form Factors: For neutral atoms and anomalous dispersion [4]

Extinction Correction: no

Weighting Scheme: $w^{-1} = s^2(F_o^2)+(a*P)^2+b*P$
with a: 0.0143; b: 20.3696; P: [Maximum(0 or F_o^2)+2*F_c^2]/3

Shift/Err: Less than 0.001 in the last cycle of refinement:

Resid. Electron Density: +1.30 e**Error!**/Å^3; -0.80 e**Error!**/Å^3

R1: $S(||F_o|-|F_c||)/S|F_o|$
[$F_o > 4s(F_o)$; N=2874]: = 0.0211
[all reflctns; N=3191]: = 0.0264

wR2: $[Sw(F_o^2-F_c^2)^2/Sw(F_o^2)^2]^{1/2}$
[$F_o > 4s(F_o)$; N=2874]: = 0.0474
[all reflctns; N=3191]: = 0.0512

Goodness of fit: $[Sw(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$ = 1.101

Flack's Parameter : $x = 0.1(6)$

Remarks: Refinement expression $Sw(F_o^2-F_c^2)^2$

References:

Measurements and Data Reduction

[1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[2] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

Solution

[3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli M. "**SIR92**", *J. Appl. Cryst.* **1994**, *27*, 435-436.

Refinement

[4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.

[5] Sheldrick, G. M. "**SHELXL-97**", University of Göttingen, Göttingen, Germany, (1998).

Graphics

[6] Spek, A. L. "**PLATON**", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2010).

Miscellaneous

[7] L. J. Farrugia, "**WinGX** (Version 1.70.01 January 2005) ", *J. Appl. Cryst.* **1999**, *32*, 837-838.

HOLA 6344-123 Compound 2 CCDC 1005248

Operator: *** Herdtweck ***

Molecular Formula: $C_{17} H_{12} Cl_4 O_2 P_3 Re$

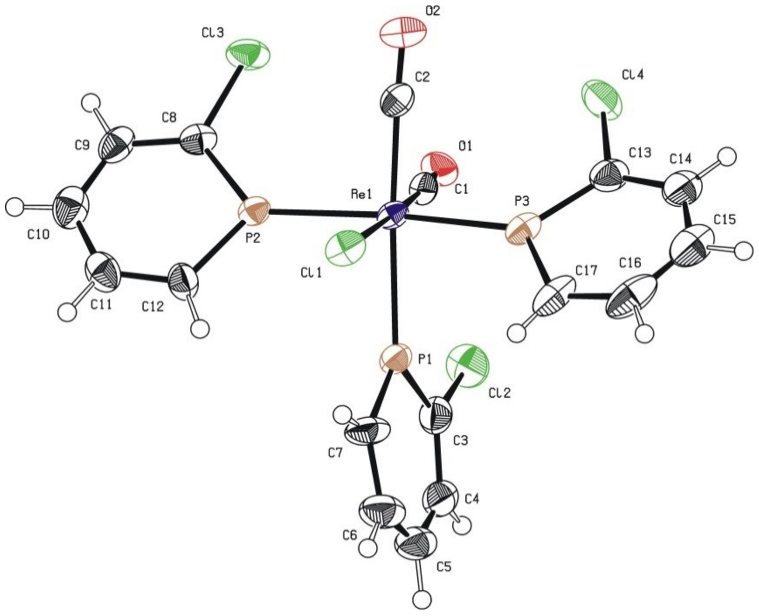

Figure S13. ORTEP style drawing of **2** with 50% ellipsoids.

Crystal Color / Shape Yellow fragment

Crystal Size Approximate size of crystal fragment used for data collection:
0.05 × 0.10 × 0.25 mm

Molecular Weight: 669.19 a.m.u.

F_{000}: 1272

Systematic Absences: 0kl: k+l≠2n; h0l: h≠2n; 00l: l≠2n

Space Group: Orthorhombic $P\,na2_1$ (I.T.-No.: 33)

Cell Constants: Least-squares refinement of 9423 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 1.99° < θ< 25.38°; Mo(K$\overline{\alpha}$); *l* = 71.073 pm

a = 1619.81(6) pm
b = 1323.31(5) pm
c = 987.39(4) pm

$V = 2116.48(14) \cdot 10^6$ pm^3; $Z = 4$; $D_{\mathrm{calc}} = 2.100$ g cm^{-3}; Mos. = 0.64

Diffractometer: Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; l = 71.073 pm; Mo(K$\overline{\alpha}$)

Temperature: (-150±1) °C; (123±1) K

Measurement Range: 1.99° < θ< 25.38°; h: -19/19, k: -15/15, l: -11/11

Measurement Time: 2 × 5 s per film

Measurement Mode: measured: 10 runs; 3748 films / scaled: 10 runs; 3748 films
j- and *w*-movement; Increment: *Dj*/*Dw* = 0.50°; dx = 40.0 mm

LP - Correction: Yes [2]

Intensity Correction No/Yes; during scaling [2]

Absorption Correction: Multi-scan; during scaling; m = 6.484 mm^{-1} [2]

Correction Factors: T_{min} = 0.4929 T_{max} = 0.7452

Reflection Data:

60767	reflections were integrated and scaled
3192	reflections systematic absent and rejected
57575	reflections to be merged
3871	independent reflections
0.052	R_{int}: (basis F_o^2)
3871	independent reflections (all) were used in refinements
3785	independent reflections with $I_o > 2s(I_o)$
99.9 %	completeness of the data set
244	parameter full-matrix refinement
15.9	reflections per parameter

Solution: Direct Methods [3]; Difference Fourier syntheses

Refinement Parameters: In the asymmetric unit:

27 Non-hydrogen atoms with anisotropic displacement parameters

Hydrogen Atoms: In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions ($d_{C\text{-}H}$ = 95 pm). Isotropic displacement parameters were calculated from the parent carbon atom ($U_H = 1.2\ U_C$). The hydrogen atoms were included in the structure factor calculations but not refined.

Atomic Form Factors: For neutral atoms and anomalous dispersion [4]

Extinction Correction: no

Weighting Scheme: $w^{-1} = s^2(F_o^2)+(a*P)^2+b*P$

with a: 0.0157; b: 4.1046; P: [Maximum(0 or F_o^2)+2*F_c^2]/3

Shift/Err: Less than 0.001 in the last cycle of refinement:

Resid. Electron Density: +1.22 e**Error!**/Å^3; -0.66 e**Error!**/Å^3

R1: $S(||F_o|-|F_c||)/\mathrm{S}|F_o|$
$[F_o > 4s(F_o)$; N=3785]: = 0.0194
[all reflctns; N=3871]: = 0.0199

wR2: $[Sw(F_o^2-F_c^2)^2/Sw(F_o^2)^2]^{1/2}$
$[F_o > 4s(F_o)$; N=3785]: = 0.0469
[all reflctns; N=3871]: = 0.0471

Goodness of fit: $[Sw(F_o^2-F_c^2)^2/(\mathrm{NO-NV})]^{1/2}$ = 1.077

Flack's Parameter : $x = 0.038(6)$

Remarks: Refinement expression $Sw(F_o^2-F_c^2)^2$

The correct enantiomere is proved by Flack's Parameter.

References:

Measurements and Data Reduction

[1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[2] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

Solution

[3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli M. "**SIR92**", *J. Appl. Cryst.* **1994**, *27*, 435-436.

Refinement

[4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.

[5] Sheldrick, G. M. "**SHELXL-97**", University of Göttingen, Göttingen, Germany, (1998).

Graphics

[6] Spek, A. L. "**PLATON**", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2010).

Miscellaneous

[7] L. J. Farrugia, "**WinGX** (Version 1.70.01 January 2005) ", *J. Appl. Cryst.* **1999**, *32*, 837-838.

3. DFT Computed Data

All DFT calculations have been performed by Gaussian09 D.01,[1] optimizations and frequency/thermochemistry determinations have been conducted using the density functional B3LYP[2-4] together with the basis set 6-31+G**[5-8] for all atoms except Re and the Stuttgart 1997 ECP for rhenium,[9] downloaded from the Basis Set Exchange.[10] All obtained geometries have been identified via the numbers of negative frequencies as minima (NImag = 0). All reported energies are unscaled and reported in kJ mol^{-1} or eV relatively to a defined zero point. Free energy differences have been calculated for the gas phase in 298.15 K and 1.0 atm. Calculated IR spectra are unscaled and therefore slightly overestimated, the trend, however, corresponds well to observed shifts. A text file of all computed molecule Cartesian coordinates in a format for convenient visualization is included. Calculated bond lengths and angles correspond well to data obtained from the crystal structure. Deviations result from influences in the solid state in single-crystals versus calculations in the gas phase. NBO analysis was carried out in order to discuss the composition of metal – ligand orbitals.[11-17]

References

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NBO analysis

The relevant compositions of the orbitals are listed in Table S1 – S3 for the precursor [Re((CO)$_5$Cl], **1** and **2**, respectively and illustrate the contribution of both bonding partners in Re–L (L = CO, phosphinine, Cl) to the metal-ligand bond in percent. A (hypothetical) 100% localization corresponds to complete localization of the bonding electrons to the respective atom or group.

Table S1. Relevant compositions of the orbitals of the NBO analysis for ReCO$_5$Cl.

Re–X bond		Contribution to the chemical bond	s-character	p-character	d-character
Re1–C2	Re1	32.73%	18.72%	46.73%	34.55%
	C2	67.27%	65.78	34.22%	0.00%
Re1–C4	Re1	30.11%	17.24%	49.80%	32.96%
	C4	69.89%	66.80%	33.20%	0.00%
Re1–C6	Re1	30.11%	17.24%	49.80%	32.96%
	C6	69.89%	66.80%	33.20%	0.00%
Re1–C8	Re1	30.11%	17.24%	49.80%	32.96%
	C8	69.89%	66.80%	33.20%	0.00%
Re1–C11	Re1	30.11%	17.24%	49.80%	32.96%
	C11	69.89%	66.80%	33.20%	0.00%
Re1–Cl10	Re1	25.48%	12.85%	52.11%	35.03%
	Cl10	74.52%	19.92%	79.97%	0.11%

Table S2. Relevant compositions of the orbitals of the NBO analysis for complex **1**.

Re–X bond		Contribution to the chemical bond	s-character	p-character	d-character
Re11–P12	R11	28.30%	16.05%	55.83%	28.12%
	P12	71.70%	46.06%	53.87%	0.07%
Re11–P23	R11	28.44%	15.90%	55.70%	28.41%
	P23	71.56%	46.13%	53.80%	0.07%
Re11–C24	R11	32.64%	19.17%	43.65%	37.18%
	C24	67.36%	65.91%	34.09%	0.00%
Re11–C26	R11	32.73%	18.99%	43.55%	37.47%
	C26	67.27%	65.92%	34.08%	0.00%
Re11–C28	R11	33.48%	18.50%	45.03%	36.47%
	C28	66.52%	65.83%	34.17%	0.00%
Re11–Cl30	R11	23.20%	12.20%	53.66%	34.14%
	Cl30	76.80%	23.63%	76.30%	0.08%

Table S3. Relevant compositions of the orbitals of the NBO analysis for complex **2**.

Re–X bond		Contribution to the chemical bond	s-character	p-character	d-character
Re11–P12	R11	31.68%	18.77%	49.96%	31.27%
	P12	68.32%	46.37%	53.54%	0.09%
Re11–P23	R11	28.67%	15.38%	56.18%	28.44%
	P23	71.33%	47.30%	52.63%	0.07%
Re11–P39	R11	31.79%	18.54%	49.90%	31.56%
	P39	68.21%	46.51%	53.40%	0.09%
Re11–C24	R11	33.15%	18.47%	43.24%	38.30%
	C24	66.85%	66.08%	33.92%	0.00%
Re11–C26	R11	34.20%	18.20%	44.15%	37.65%
	C26	65.80%	65.95%	34.05%	0.00%
Re11–Cl28	R11	22.72%	11.22%	54.47%	34.31%
	Cl28	77.28%	25.02%	74.91%	0.06%

Optimized Geometries and HOMO/LUMO pictures of Computed Compounds

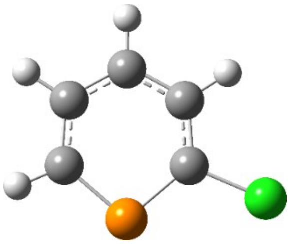

Figure S14. Optimized geometry of 2-chlorphosphinine.

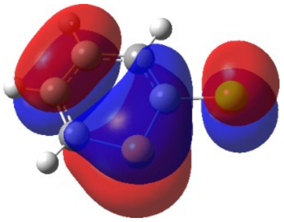

Figure S15. Computed HOMO of 2-chlorphosphinine.

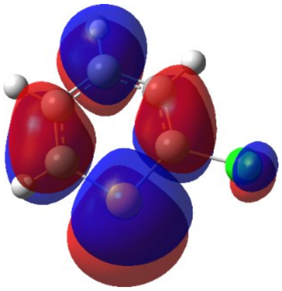

Figure S16. Computed LUMO of 2-chlorphosphinine.

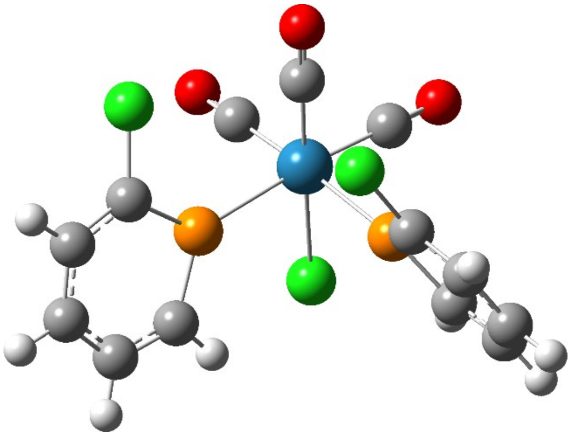

Figure S17. Optimized geometry of **1**.

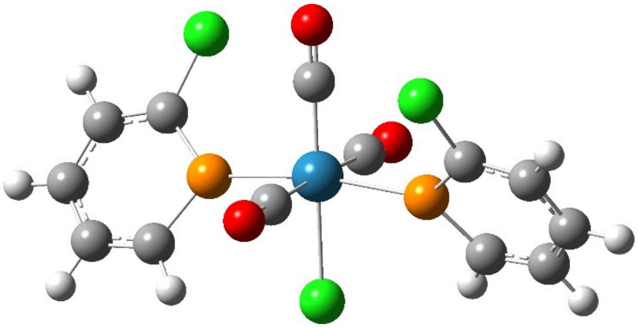

Figure S18. Optimized geometry of computed complex *trans*-[Re(CO)$_3$Cl(C$_5$H$_4$ClP)$_2$] (**1a**) featuring *trans*-coordinated 2-chlorphosphinine ligands.

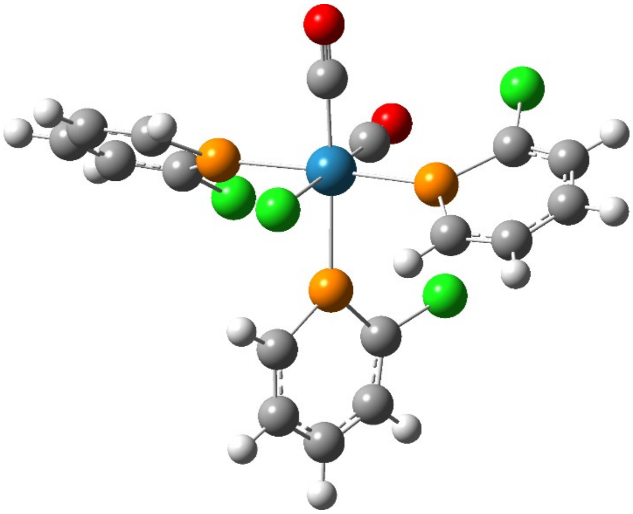

Figure S19. Optimized geometry of **2**.

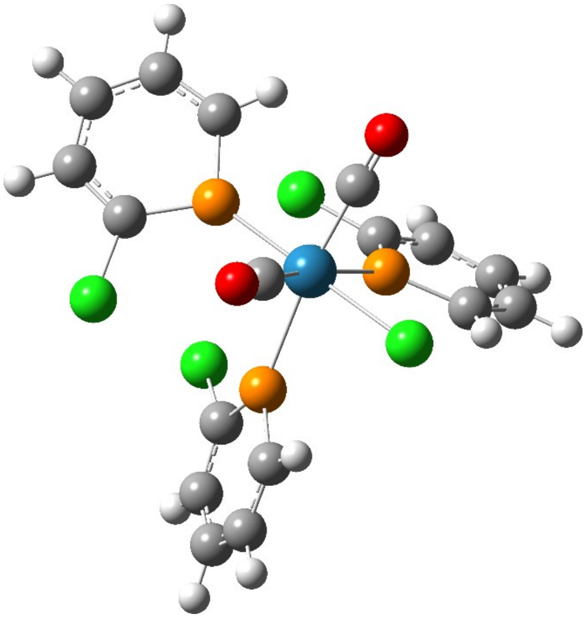

Figure S20. Optimized geometry of computed complex *fac*-[Re(CO)$_2$Cl(C$_5$H$_4$ClP)$_3$] (**2a**) featuring *facial*-coordinated 2-chlorphosphinine ligands.