

Supporting Information for

Isomers in chlorido and alkoxido-substituted oxidorhenium(V) complexes: effects on catalytic epoxidation activity

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NMR spectra of complexes *trans*-2a, *cis*-2b and 4b

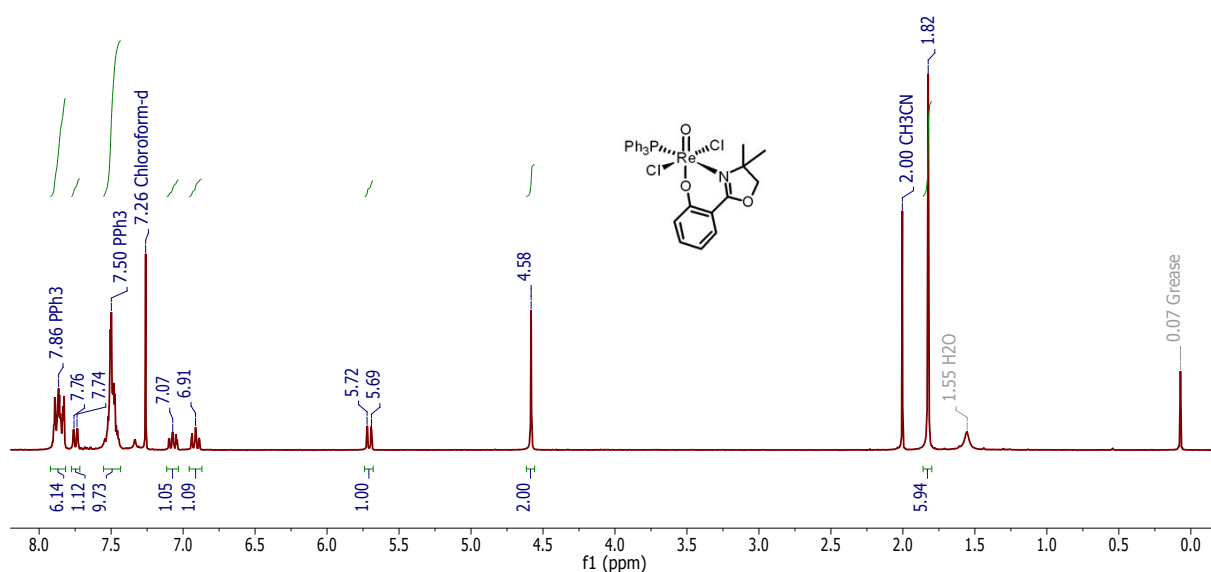


Figure S1. ¹H NMR spectrum of *trans*-[ReOCl₂(PPh₃)(L1a)]·CH₃CN (*trans*-2a) in CDCl₃.

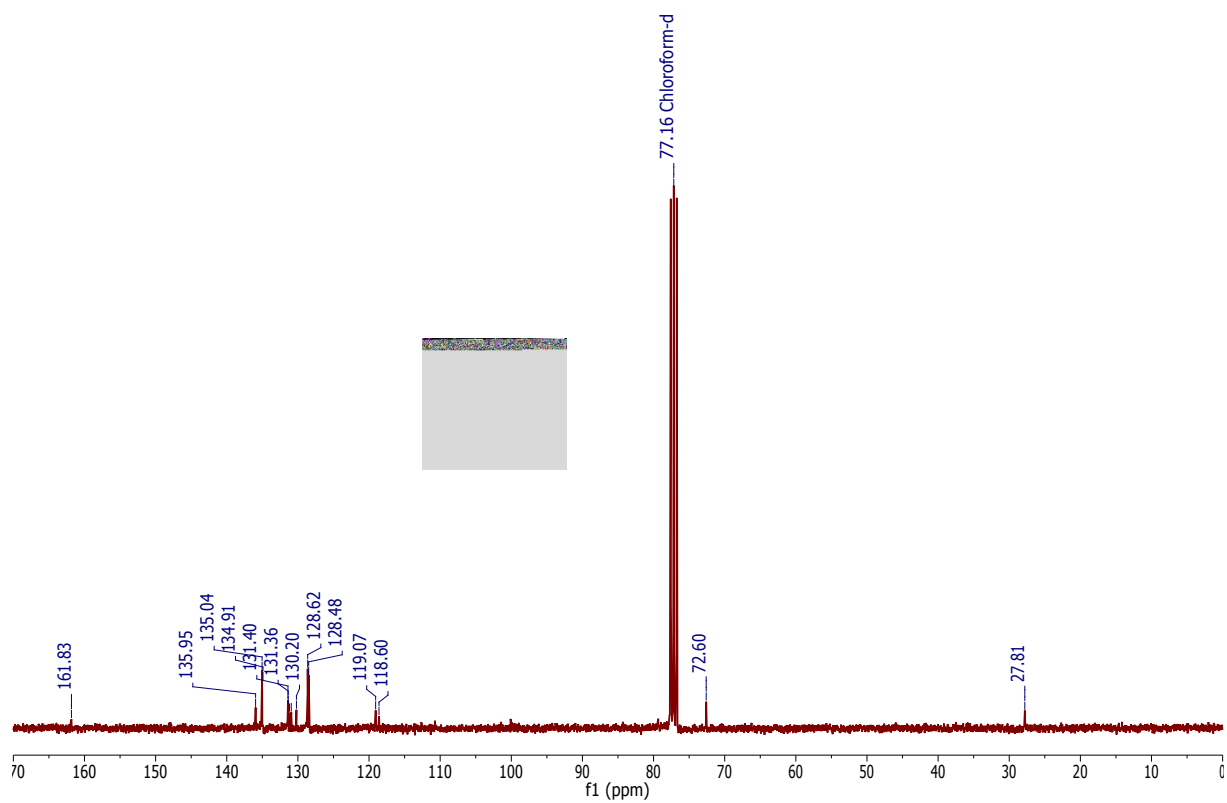


Figure S2. ^{13}C NMR spectrum of *trans*-[ReOCl₂(PPh₃)(L1a)] (*trans*-2a) in CDCl₃.

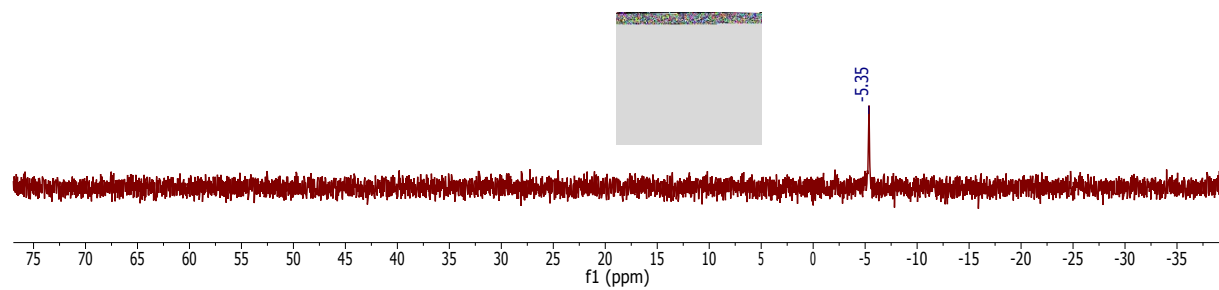


Figure S3. ^{31}P NMR spectrum of *trans*-[ReOCl₂(PPh₃)(L1a)] (*trans*-2a) in CDCl₃.

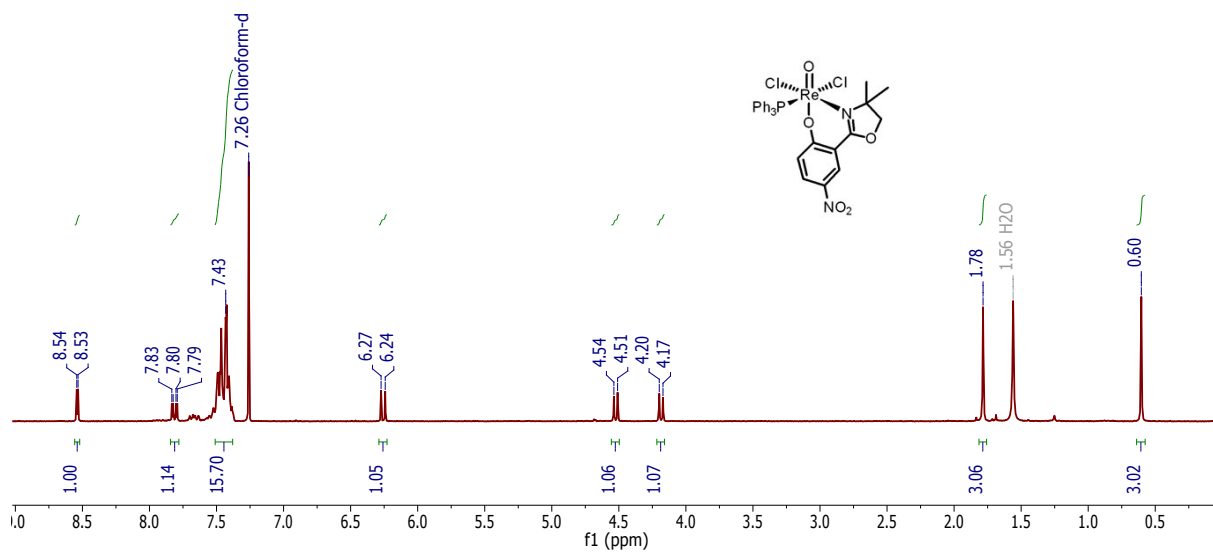


Figure S4. ^1H NMR spectrum of $[\text{ReOCl}_2(\text{PPh}_3)(\text{L1b})]$ (*cis*-**2b**) in CDCl_3 .

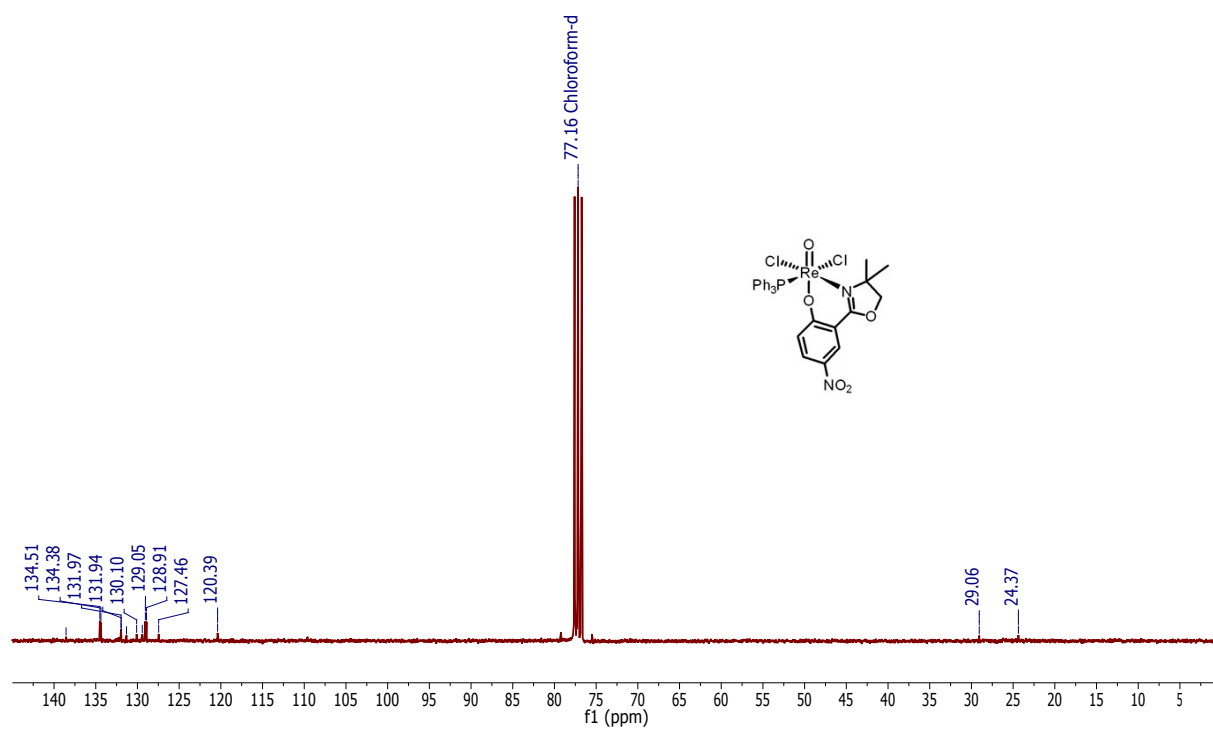


Figure S5. ^{13}C NMR spectrum of $[\text{ReOCl}_2(\text{PPh}_3)(\text{L1b})]$ (*cis*-**2b**) in CDCl_3 .

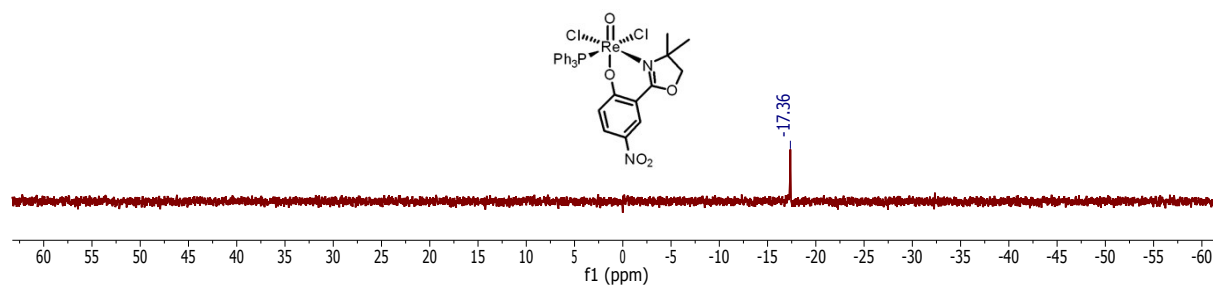


Figure S6. ^{31}P NMR spectrum of $[\text{ReOCl}_2(\text{PPh}_3)(\text{L1b})]$ (*cis*-**2b**) in CDCl_3 .

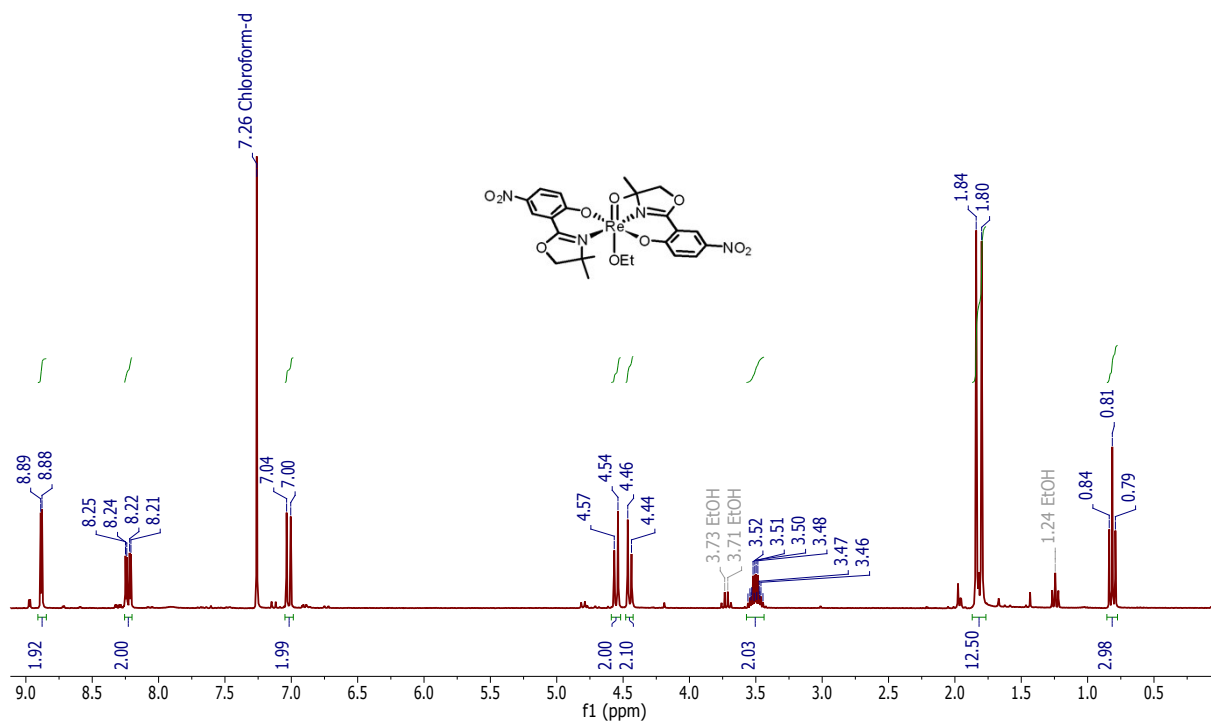


Figure S7. ^1H NMR spectrum of $[\text{ReO}(\text{OEt})(\text{L1b})_2]$ (**4b**) in CDCl_3 .

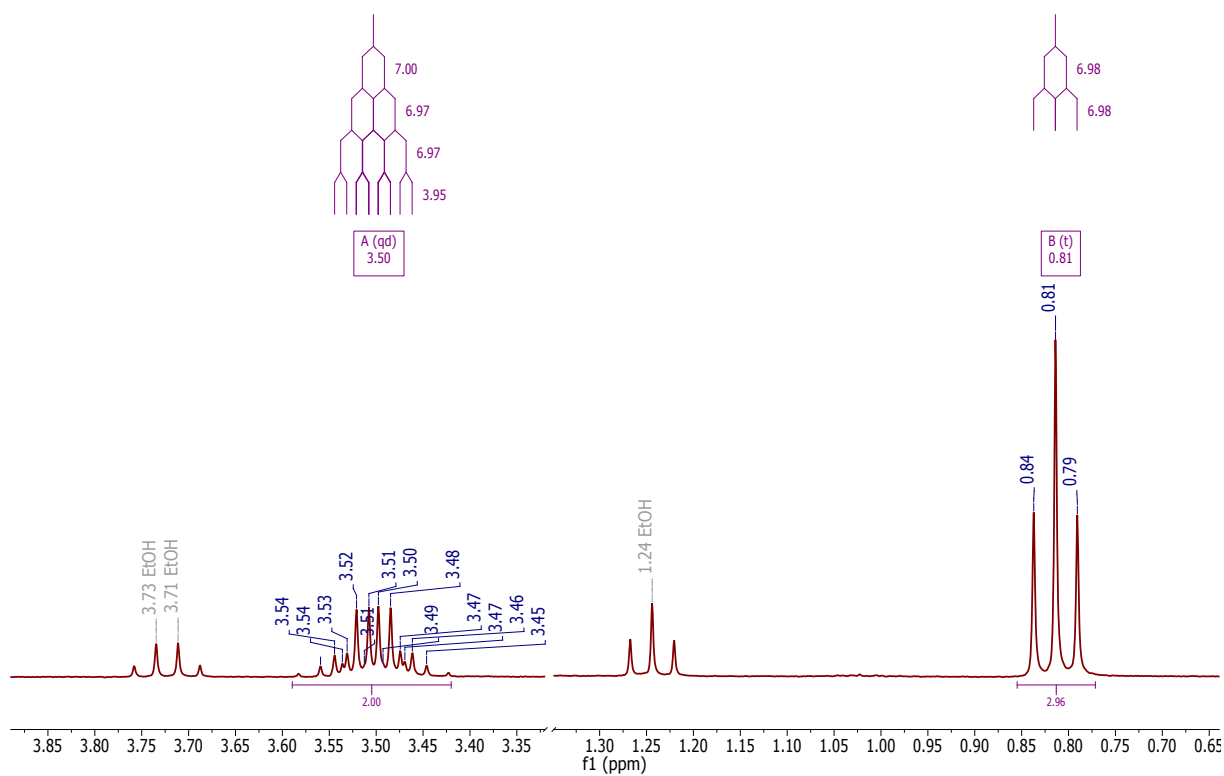


Figure S8. ^1H NMR spectrum of complex $[\text{ReOCl}(\text{OEt})(\text{L1b})_2]$ showing the qd and t peaks of the ethoxido ligand (**4b**); peaks for residual EtOH solvent (3.73 and 1.24 ppm) showing the expected q and t peaks are labelled in grey.

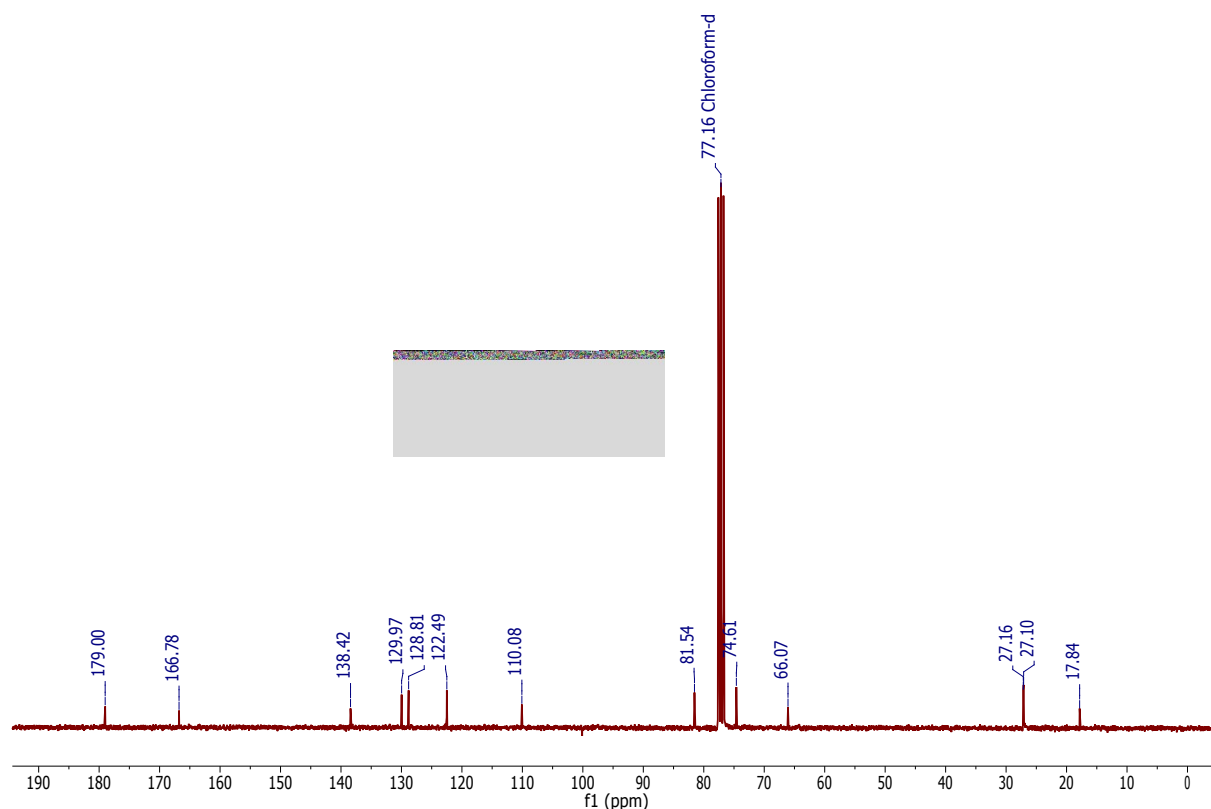


Figure S9. ^{13}C NMR spectrum of $[\text{ReO}(\text{OEt})(\text{L1b})_2]$ (**4b**) in CDCl_3 .

Cyclovoltammetry

To analyze the electronic situation of the rhenium center directly, complexes *cis-2a*, *trans-2a*, *cis-2b*, **4a** and **4b** were subjected to electrochemical measurements via cyclovoltammetry (CV). Electrochemical data for **3a/b** has been previously published.¹ Solvent used for all measurements was dry acetonitrile (stored over molecular sieves, analyte concentration was 1 mM), with $(\text{NBu}_4)\text{PF}_6$ (0.1 M) as the supporting electrolyte. All measurements were performed in a glove box under inert N_2 atmosphere, with a three electrode set-up (working: Pt; supporting: Pt-wire; reference: $\text{Ag}/0.01\text{M AgNO}_3$ in acetonitrile, 0.1 M $(\text{NBu}_4)\text{PF}_6$). As previously observed for other mono-ligated oxorhenium(V) complexes,² all three complexes *cis/trans-2a* and *cis-2b* only showed several irreversible faradaic processes. The same behavior was observed for alkoxido complexes **4a** and **4b**. For **4a**, after the CV measurements, a slow de-coloration (over four hours) of the initially blue-green analyte solution to yellow was observed, indicating decomposition to unknown products. Measurements of complex **4b** were plagued by incomplete dissolution in CH_3CN . Even addition of 10 vol% of dry CH_2Cl_2 to the electrochemical cell did not allow to obtain meaningful voltammograms of **4b**. The observed instability of **4a** was somewhat surprising as the complex is stable over 24 h

when dissolved in CD_3CN . Potentially the addition of the 100-fold excess of the electrolyte $(\text{NBu}_4)\text{PF}_6$ caused the decomposition under CV conditions.

Crystal structure determinations

The single crystal measurements were performed on a Bruker APEX-II CCD diffractometer at 100 K using Mo K α radiation with a wavelength of 0.71073 Å from an Incoatec microfocus sealed tube equipped with a multilayer monochromator. Absorption corrections were made semi-empirically from equivalents. The structures were solved by direct methods (SHELXS-97)³ and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/6)⁴. A weighting scheme of $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ was used where $P = (F_o^2 + 2F_c^2)/3$. The non-hydrogen atoms of the metal complexes were refined with anisotropic displacement parameters without any constraints. The acetonitrile molecule of *trans*-**2a** lying around a center of symmetry and disordered over two orientations was refined with site occupation factors of 0.5 as a rigid body. The H atoms of the aromatic rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same ring. The H atoms of the CH₂ groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with approx. tetrahedral angles and C–H distances of 0.99 Å. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bonds, and C–H distances of 0.98 Å. The largest peaks in final difference Fourier maps (1.29–2.73 eÅ⁻³) were in the vicinities (0.65–1.26 Å) of the Re atoms. Crystal data, data collection parameters and structure refinement details are listed in Table S1. Further refinement information, structure and bonding parameters, SHELXL .res and .hkl files are given in the deposited CIF file which is available free of charge from The Cambridge Crystallographic Data Centre (CCDC 1854788–1854789, 2011198).

Table S1. Crystal data and structure refinement for *trans-2a* and *cis-2a*.

Crystal data	<i>trans-2a</i>	<i>cis-2a</i>
CIF data code	JS31	JS31A
Empirical formula	$2C_{29}H_{27}Cl_2NO_3PRe \cdot C_2H_3N$	$C_{29}H_{27}Cl_2NO_3PRe$
Formula weight	1492.22	725.58
Crystal description	block, green	plate, green
Crystal size	0.15 x 0.12 x 0.12mm	0.21 x 0.10 x 0.05mm
Temperature	100K	100K
Crystal system	triclinic	triclinic
Space group	P -1	P -1
a	10.1415(4)Å	9.945(2)Å
b	11.3165(5)Å	10.196(2)Å
c	14.1899(6)Å	14.358(3)Å
α	81.0109(14)°	79.637(3)°
β	70.7506(13)°	79.537(2)°
γ	64.3553(12)°	69.695(2)°
Volume	1385.85(10)Å ³	1331.8(5)Å ³
Z	1	2
Calc. density	1.788Mg/m ³	1.809Mg/m ³
F(000)	734	712
Linear absorption coefficient μ	4.669mm ⁻¹	4.856mm ⁻¹
Max. and min. transmission	0.837 and 0.719	1.000 and 0.545
Unit cell determination	$2.38^\circ < \Theta < 30.97^\circ$	$2.44^\circ < \Theta < 30.42^\circ$
Reflections used	9876	9524
Data collection		
Θ range for data collection	2.00 to 30.00°	2.20 to 30.00°
Reflections collected/ unique	41467 / 8052	25679 / 7766
Significant unique reflections	7792 with $I > 2\sigma(I)$	6840 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0245, 0.0159	0.0549, 0.0548
Completeness to Θ_{max}	99.7%	99.9%
Refinement		
Data/ parameters/ restraints	8052 / 360 / 0	7766 / 343 / 0
Goodness-of-fit on F ²	1.093	1.045
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0167, wR2 = 0.0443	R1 = 0.0343, wR2 = 0.0809
R indices (all data)	R1 = 0.0175, wR2 = 0.0448	R1 = 0.0431, wR2 = 0.0853
Weighting scheme param. a, b	0.0208, 1.6254	0.0278, 4.2745
Largest Δ/σ in last cycle	0.002	0.001
Largest diff. peak and hole	2.199 and -0.947e/Å ³	1.845 and -1.996e/Å ³
CCDC no.	1854788	1854789

Table S2. Crystal data and structure refinement for *cis-2b*.

Crystal data	<i>cis-2b</i>
CIF data code	JS90
Empirical formula	C ₂₉ H ₂₆ Cl ₂ N ₂ O ₅ Pre
Formula weight	770.59
Crystal description	block, green
Crystal size	0.33 x 0.26 x 0.23mm
Temperature	100K
Crystal system	triclinic
Space group	P -1
a	10.7088(4)Å
b	10.7534(4)Å
c	12.8027(5)Å
α	77.6402(17)°
β	87.6176(18)°
γ	82.1537(18)°
Volume	1426.54(9)Å ³
Z	2
Calc. density	1.794Mg/m ³
F(000)	756
Linear absorption coefficient μ	4.545mm ⁻¹
Max. and min. transmission	0.746 and 0.426
Unit cell determination	2.27° < Θ < 30.03°
Reflections used	9993
Data collection	
Θ range for data collection	1.92 to 30.00°
Reflections collected/ unique	55063 / 8300
Significant unique reflections	7645 with I > 2 σ (I)
R(int), R(sigma)	0.0783, 0.0529
Completeness to Θ_{\max}	99.9%
Refinement	
Data/ parameters/ restraints	8300 / 370 / 0
Goodness-of-fit on F ²	1.083
Final R indices [I > 2 σ (I)]	R1 = 0.0297, wR2 = 0.0627
R indices (all data)	R1 = 0.0327, wR2 = 0.0636
Weighting scheme param. a, b	0.0190, 0.4664
Largest Δ/σ in last cycle	0.002
Largest diff. peak and hole	2.735 and -2.273e/Å ³
CCDC no.	2011198

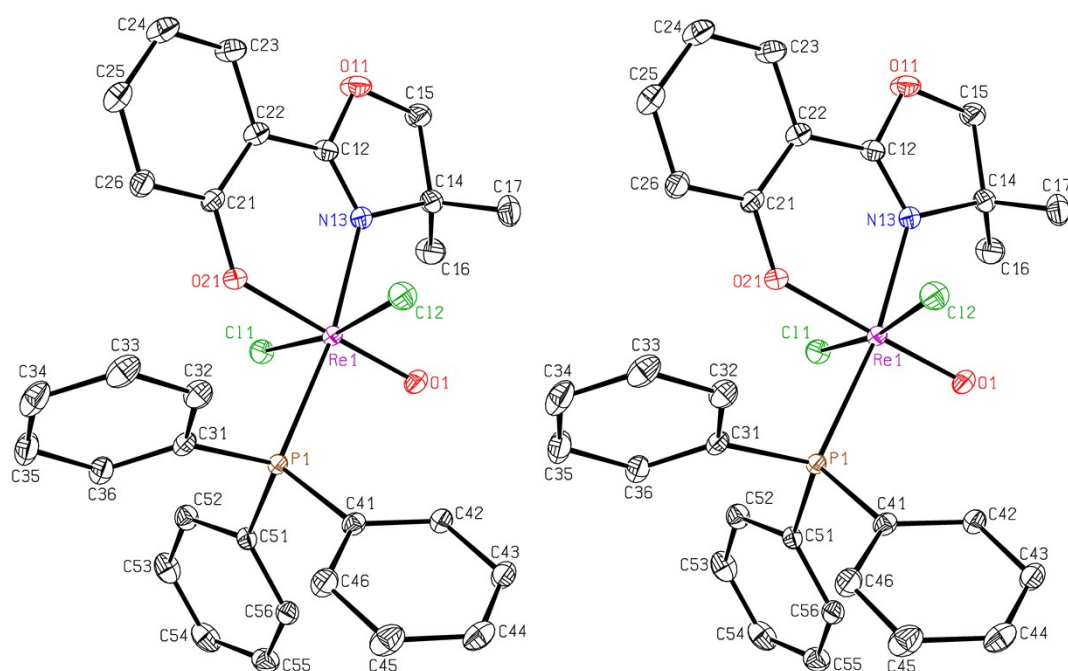


Figure S10. Stereoscopic ORTEP⁵ plot of *trans*-**2a** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms and the disordered acetonitrile solvent molecule were omitted for clarity.

Table S3. Selected bond lengths [Å] and angles [°] for *trans*-**2a**.

O1-Re1	1.6917(13)	O1-Re1-P1	93.67(5)
Re1-O21	1.9481(13)	O21-Re1-Cl1	87.57(4)
Re1-N13	2.1423(16)	O21-Re1-Cl2	85.62(4)
Re1-Cl1	2.3981(5)	O21-Re1-N13	82.30(6)
Re1-Cl2	2.4026(5)	O21-Re1-P1	86.81(4)
Re1-P1	2.4723(5)	C12-N13-C14	108.53(16)
C12-N13	1.291(2)	C12-N13-Re1	127.05(13)
N13-C14	1.508(2)	C14-N13-Re1	124.05(12)
O21-C21	1.331(2)	C21-O21-Re1	137.74(12)
P1-C31	1.8182(18)		
P1-C41	1.8204(18)	O11-C12-N13-Re1	178.35(13)
P1-C51	1.8147(18)	C22-C12-N13-Re1	0.7(3)
		O1-Re1-N13-C12	-167.98(16)
O1-Re1-O21	177.71(6)	O1-Re1-N13-C14	4.32(15)
Cl1-Re1-Cl2	171.181(16)	Re1-N13-C14-C15	176.71(12)
N13-Re1-P1	168.60(4)	P1-Re1-O21-C21	152.74(18)
O1-Re1-Cl1	94.60(5)	N13-Re1-O21-C21	-23.88(20)
O1-Re1-Cl2	92.14(5)	Re1-O21-C21-C26	-156.12(15)
O1-Re1-N13	97.08(6)	Re1-O21-C21-C22	24.4(3)

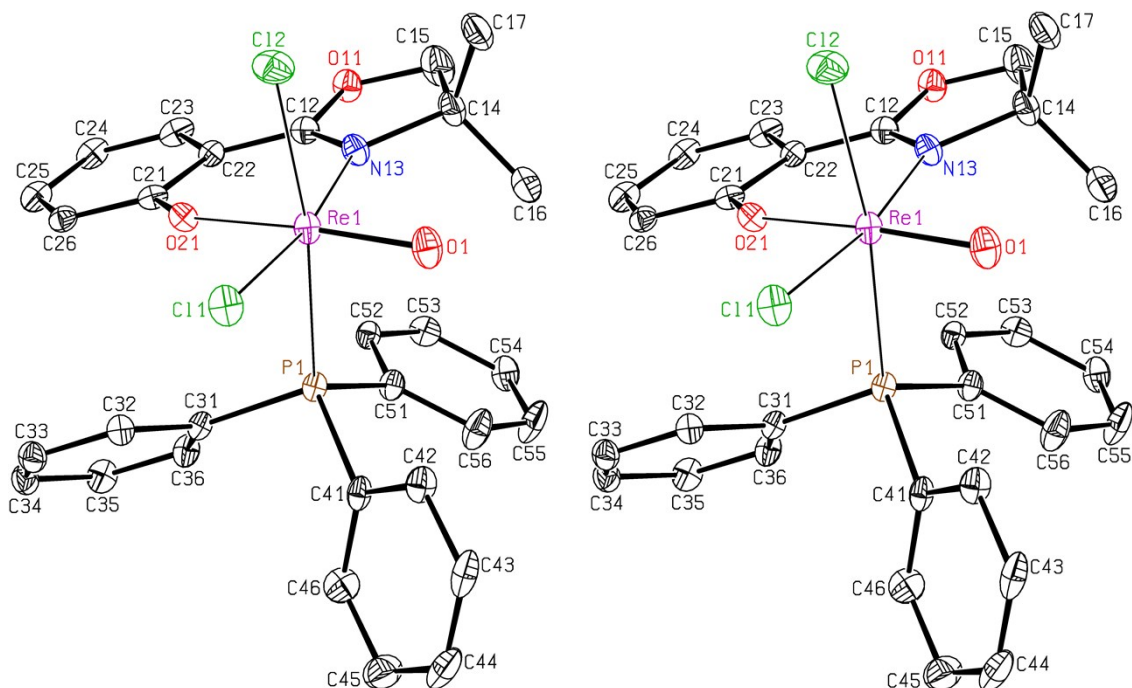


Figure S11. Stereoscopic ORTEP⁵ plot of *cis-2a* showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity.

Table S4. Selected bond lengths [Å] and angles [°] for *cis-2a*.

Re1-O1	1.684(3)	O1-Re1-N13	90.29(14)
Re1-O21	1.947(3)	O1-Re1-P1	87.26(11)
Re1-N13	2.166(3)	O21-Re1-C11	90.63(8)
Re1-C11	2.3747(11)	O21-Re1-C12	88.23(9)
Re1-C12	2.4019(12)	O21-Re1-N13	82.54(12)
Re1-P1	2.4961(11)	O21-Re1-P1	83.94(8)
C12-N13	1.304(5)	C12-N13-C14	108.8(3)
N13-C14	1.511(5)	C12-N13-Re1	126.1(3)
O21-C21	1.339(4)	C14-N13-Re1	125.0(3)
P1-C31	1.824(4)	C21-O21-Re1	139.5(3)
P1-C41	1.832(4)		
P1-C51	1.827(4)	O11-C12-N13-Re1	179.4(3)
		C22-C12-N13-Re1	-2.5(6)
O1-Re1-O21	168.16(13)	O1-Re1-N13-C12	165.0(4)
C11-Re1-N13	171.03(10)	O1-Re1-N13-C14	-18.5(3)
C12-Re1-P1	171.54(4)	Re1-N13-C14-C15	-177.9(3)
C11-Re1-C12	86.39(4)	Re1-P1-C31-C32	-48.3(2)
N13-Re1-P1	94.54(10)	Re1-P1-C41-C42	-8.0(3)
O1-Re1-C11	97.37(11)	Re1-P1-C51-C52	-76.0(2)
O1-Re1-C12	100.93(11)	Re1-P1-C51-C56	100.1(2)

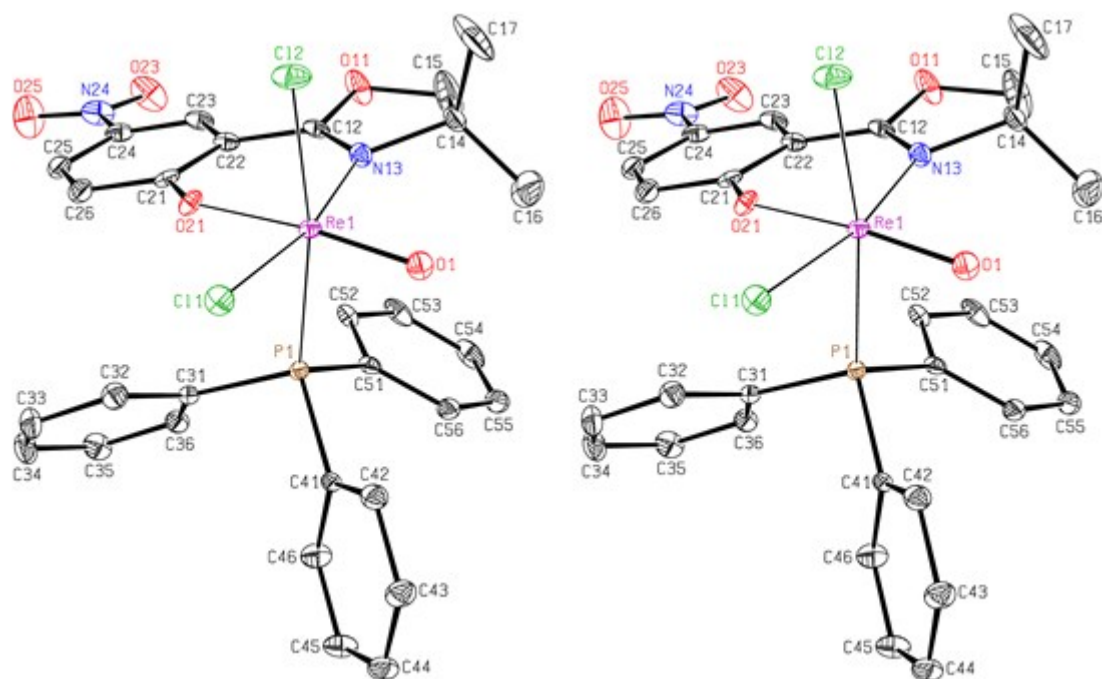


Figure S12. Stereoscopic ORTEP⁵ plot of *cis*-**2b** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity.

Table S5. Selected bond lengths [Å] and angles [°] for *cis*-**2b**.

Re1-O1	1.6775(19)	O21-Re1-P1	82.83(6)
Re1-O21	1.9969(18)	N13-Re1-P1	93.07(7)
Re1-N13	2.155(2)	Cl1-Re1-P1	91.46(2)
Re1-Cl1	2.3632(7)	Cl2-Re1-P1	169.80(3)
Re1-C12	2.3766(7)	O1-Re1-Cl2	103.84(7)
Re1-P1	2.4749(7)	O21-Re1-Cl2	87.16(6)
C12-N13	1.290(3)	N13-Re1-Cl2	87.50(7)
N13-C14	1.527(4)	Cl1-Re1-Cl2	86.27(3)
O21-C21	1.320(3)	C12-O11-C15	106.1(2)
P1-C31	1.821(3)	N13-C12-O11	117.0(3)
P1-C41	1.827(3)		
P1-C51	1.815(3)		
O1-Re1-O21	167.51(8)	O11-C12-N13-Re1	177.73(19)
O1-Re1-N13	92.02(9)	C22-C12-N13-Re1	-3.1(4)
O21-Re1-N13	82.42(8)	Re1-N13-C14-C17	-70.5(3)
O1-Re1-Cl1	98.31(7)	Re1-N13-C14-C16	54.6(3)
O21-Re1-Cl1	88.17(6)	Re1-N13-C14-C15	170.5(2)
N13-Re1-Cl1	168.96(6)	Re1-P1-C31-C32	-48.3(2)
O1-Re1-P1	86.32(7)	N13-Re1-O21-C21	16.5(4)
		Re1-O21-C21-C26	164.7(3)
		Re1-O21-C21-C22	-17.0(6)

References and notes

1. J. A. Schachner, B. Berner, F. Belaj and N. C. Mösch-Zanetti, *Dalton Trans.*, 2019, **48**, 8106-8115.
2. N. Zwettler, J. A. Schachner, F. Belaj and N. C. Mösch-Zanetti, *Inorg. Chem.*, 2014, **53**, 12832–12840.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112–122.
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