# Stereoisomers and functional groups in oxidorhenium(V) complexes: effects on catalytic activity 

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Ligands HL1a ${ }^{1,2}$ and HL1b ${ }^{2}$ were synthesized according to previously published procedures.
Ligand HL1c was synthesized based on a published procedure. ${ }^{3,4}$


Scheme S1 Synthesis of ligand HL1c
Compound HL1c" was synthesized based on a published procedure. ${ }^{3}$
Synthesis of H1c': 6.18 g ( $31.3 \mathrm{mmol}, 1$ equiv.) of H1c" were mixed with $13.95 \mathrm{~g}(156.5 \mathrm{mmol}$, 5 equiv.) of 2-amino-2-methylpropanol and heated to $85^{\circ} \mathrm{C}$ for 16 h under neat conditions. After cooling, the reaction mixture was dissolved and acidified with HCl to $\mathrm{pH}=2$, upon which crude H1c' precipitated. Aqueous work-up with DCM yielded H1c' ${ }^{\prime}(7.16 \mathrm{~g}, 90 \%) .{ }^{1} \mathrm{H}$ NMR ( 300 MHz, Chloroform-d) $\delta 13.20(\mathrm{~s}, 1 \mathrm{H}$ ), $8.34(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.28(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.06(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.61(\mathrm{~s}, 1 \mathrm{H}), 3.75(\mathrm{~s}, 2 \mathrm{H}), 1.49(\mathrm{~s}, 6 \mathrm{H}) . \mathrm{IR}\left(\mathrm{cm}^{-1}\right): 3370,3328(\mathrm{NH})$, $2976(\mathrm{OH}), 1619(\mathrm{C}=\mathrm{O}), 1341,1289\left(\mathrm{NO}_{2}\right) ;$ EI-MS $(\mathrm{m} / \mathrm{z}): 254.09\left(\mathrm{M}^{+}\right)$.

Synthesis of H1c: $4.32 \mathrm{~g}\left(17 \mathrm{mmol}\right.$, 1 equiv.) of $\mathrm{H} 1 \mathbf{c}^{\prime}$ were suspended in 40 mL heptane and thionyl chloride ( $2.5 \mathrm{~mL}, 34.1 \mathrm{mmol}, 2$ equiv.) was added. After stirring overnight at $25^{\circ} \mathrm{C}$ the solid hydrochloride salt $\mathrm{H} \mathbf{c} \cdot \mathrm{HCl}$ was isolated by filtration and quenched/worked up with $\mathrm{CH}_{2} \mathrm{Cl}_{2} /$ sat. $\mathrm{NaHCO}_{3}$ to give $\mathrm{H} 1 \mathrm{c}(3.77 \mathrm{~g}, 94 \%) .{ }^{1} \mathrm{H}$ NMR ( 300 MHz , Chloroform-d) $\delta 13.16$ $(\mathrm{s}, 1 \mathrm{H}), 8.56(\mathrm{~d}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 8.23(\mathrm{dd}, J=9.2,2.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.05(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.18$ (s, 2H), $1.42(\mathrm{~s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 MHz , Chloroform-d) $\delta$ 165.21, 162.58, 139.65, 128.60, 124.74, 117.57, 110.78, 79.03, 67.65, 28.50. IR ( $\mathrm{cm}^{-1}$ ): $2976(\mathrm{OH}), 1645(\mathrm{C}=\mathrm{N}), 1337,1301$, $1285\left(\mathrm{NO}_{2}\right)$; EI-MS $(m / z): 236.08\left(\mathrm{M}^{+}\right)$.

Crystal structure determination of 2a. The crystal structure analysis of 2a confirmed the compound as tetrabutylammonium trichlorido-[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-phenolato- $\mathrm{N}, \mathrm{O}$-oxidorhenium $(\mathrm{V})$. All atoms lie on general positions. The asymmetric unit consists of two formula units. As observed for the 6-methoxyphenolato compound 2b the phenolato ligands ( $\operatorname{Re} 1-\mathrm{O} 212.011(8) \AA, \operatorname{Re} 2-\mathrm{O} 412.005(8) \AA$ ) are in trans positions to the oxo groups (Re1-O1 1.690(7) $\AA, \mathrm{Re} 2-\mathrm{O} 21.699(7) \AA$; O1-Re1-O21 171.4(3) ${ }^{\circ}$, O2-Re2-O41 $\left.171.3(3)^{\circ}\right)$. The $\mathrm{Re}-\mathrm{Cl}$ distances of the Cl atoms ( $\mathrm{Re} 1-\mathrm{Cl} 22.377(2) \AA, \mathrm{Re} 2-\mathrm{Cl} 52.390(3) \AA$ ) trans to the oxazolyl rings (Re1-N13 2.172(8) $\AA$, Re2-N33 2.157(9) $\AA$; N13-Re1-Cl2 169.7(2) ${ }^{\circ}$, N33-Re2-Cl5 171.0(2) ${ }^{\circ}$ ) do not differ from those trans to each other (Re-Cl $2.368(3)-2.420(3) \AA$; $\left.\mathrm{Cl} 1-\mathrm{Re} 1-\mathrm{Cl} 3171.51(10)^{\circ}, \mathrm{Cl} 4-\mathrm{Re} 2-\mathrm{Cl} 6171.59(11)^{\circ}\right)$. The nonhydrogen atoms were refined with anisotropic displacement parameters without any constraints. The absolute configuration was established by anomalous dispersion effects in the diffraction measurements on the crystal. Since racemic twinning was detected a twin matrix ( $-100 / 0-1$ $0 / 00-1$ ) was applied and a scale factor was refined ( $0.354(10)$ ) between the two unequal components. The H atoms of the $\mathrm{CH}_{2}$ groups were refined with common isotropic displacement parameters for the H atoms of the same metal complex or for the cations, resp., and idealized geometries with approximately tetrahedral angles and $\mathrm{C}-\mathrm{H}$ distances of $0.99 \AA$. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same metal complex or for the cations, resp., and idealized geometries with tetrahedral angles, staggered conformations, and C-H distances of $0.98 \AA$. The H atoms of the phenyl rings were put at the external bisectors of the $\mathrm{C}-\mathrm{C}-\mathrm{C}$ angles at $\mathrm{C}-\mathrm{H}$ distances of $0.95 \AA$ and common isotropic displacement parameters were refined for the H atoms of the same ring.

Table S1 Selected bond lengths $\left[\AA\right.$ ] and angles [ ${ }^{\circ}$ ] for 2a

| $\operatorname{Re}(1)-\mathrm{O}(1)$ | $1.690(7)$ |
| :--- | :--- |
| $\operatorname{Re}(1)-\mathrm{Cl}(1)$ | $2.381(3)$ |
| $\operatorname{Re}(1)-\mathrm{Cl}(2)$ | $2.377(2)$ |
| $\operatorname{Re}(1)-\mathrm{Cl}(3)$ | $2.420(3)$ |
| $\operatorname{Re}(1)-\mathrm{N}(13)$ | $2.172(8)$ |
| $\operatorname{Re}(1)-\mathrm{O}(21)$ | $2.011(8)$ |
| $\mathrm{O}(21)-\mathrm{C}(21)$ | $1.325(13)$ |
| $\operatorname{Re}(2)-\mathrm{O}(2)$ | $1.699(7)$ |
| $\operatorname{Re}(2)-\mathrm{Cl}(4)$ | $2.419(3)$ |
| $\operatorname{Re}(2)-\mathrm{Cl}(5)$ | $2.390(3)$ |
| $\operatorname{Re}(2)-\mathrm{Cl}(6)$ | $2.368(3)$ |
| $\operatorname{Re}(2)-\mathrm{N}(33)$ | $2.157(9)$ |
| $\operatorname{Re}(2)-\mathrm{O}(41)$ | $2.005(8)$ |
| $\mathrm{O}(41)-\mathrm{C}(41)$ | $1.296(13)$ |


| $\mathrm{O}(1)-\mathrm{Re}(1)-\mathrm{O}(21)$ | $171.4(3)$ |
| :--- | :--- |
| $\mathrm{N}(13)-\mathrm{Re}(1)-\mathrm{Cl}(2)$ | $169.7(2)$ |
| $\mathrm{Cl}(1)-\mathrm{Re}(1)-\mathrm{Cl}(3)$ | $171.51(10)$ |
| $\mathrm{C}(12)-\mathrm{N}(13)-\mathrm{C}(14)$ | $109.0(8)$ |
| $\mathrm{C}(12)-\mathrm{N}(13)-\operatorname{Re}(1)$ | $125.3(6)$ |
| $\mathrm{C}(14)-\mathrm{N}(13)-\operatorname{Re}(1)$ | $124.4(6)$ |
| $\mathrm{C}(21)-\mathrm{O}(21)-\operatorname{Re}(1)$ | $132.9(7)$ |
| $\mathrm{O}(2)-\operatorname{Re}(2)-\mathrm{O}(41)$ | $171.3(3)$ |
| $\mathrm{N}(33)-\operatorname{Re}(2)-\mathrm{Cl}(5)$ | $171.0(2)$ |
| $\mathrm{Cl}(4)-\operatorname{Re}(2)-\mathrm{Cl}(6)$ | $171.59(11)$ |
| $\mathrm{C}(32) \mathrm{N}(33)-\mathrm{C}(34)$ | $109.1(9)$ |
| $\mathrm{C}(32)-\mathrm{N}(33)-\operatorname{Re}(2)$ | $123.9(7)$ |

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C(34)-N(33)-Re(2) 125.5(7)
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$\mathrm{C}(41)-\mathrm{O}(41)-\operatorname{Re}(2) \quad 136.4(7)$

Crystal structure determination of 2b. The crystal structure analysis of $\mathbf{2 b}$ confirmed the compound as tetra( $n$-butyl)ammonium trichlorido-[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-6-methoxyphenolato-N,O]-oxoidorhenate(V). All atoms lie on general positions. The phenolato ligand [ $\operatorname{Re} 1-\mathrm{O} 211.980(2) \AA$ ] is in trans position to the oxido group ( $\mathrm{Re} 1-\mathrm{O} 1$ $1.681(2) \AA$; O1-Re1-O21 171.18(9) ${ }^{\circ}$ ). The tetra( $n$-butyl)ammonium cation shows a rather flat all-trans conformation with the centre oriented towards the $\mathrm{OCl}_{2}$ face of the octahedron around the Re atom. The absolute configuration was established by anomalous dispersion effects in the diffraction measurements on the crystal. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the phenyl ring were put at the external bisectors of the $\mathrm{C}-\mathrm{C}-\mathrm{C}$ angles at $\mathrm{C}-\mathrm{H}$ distances of $0.95 \AA$ and a common isotropic displacement parameter was refined. The H atoms of the $\mathrm{CH}_{2}$ groups were refined with common isotropic displacement parameters for the H atoms of equivalent groups and idealized geometry with approximately tetrahedral angles and $\mathrm{C}-\mathrm{H}$ distances of $0.99 \AA$. 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 $\mathrm{X}-\mathrm{C}$ bond, and C-H distances of $0.98 \AA$.

Table S2 Selected bond lengths $\left[\AA\right.$ ] and angles $\left[{ }^{\circ}\right]$ for $\mathbf{2 b}$.

| $\operatorname{Re}(1)-\mathrm{O}(1)$ | $1.6801(16)$ | $\mathrm{N}(13)-\mathrm{Re}(1)-\mathrm{Cl}(2)$ | $171.40(4)$ |
| :--- | :--- | :--- | :--- |
| $\operatorname{Re}(1)-\mathrm{O}(21)$ | $1.9800(16)$ | $\mathrm{O}(1)-\mathrm{Re}(1)-\mathrm{O}(21)$ | $171.14(6)$ |
| $\operatorname{Re}(1)-\mathrm{N}(13)$ | $2.1386(16)$ | $\mathrm{Cl}(3)-\mathrm{Re}(1)-\mathrm{Cl}(1)$ | $169.71(2)$ |
| $\operatorname{Re}(1)-\mathrm{Cl}(1)$ | $2.3909(4)$ | $\mathrm{C}(12)-\mathrm{N}(13)-\mathrm{C}(14)$ | $107.62(17)$ |
| $\operatorname{Re}(1)-\mathrm{Cl}(2)$ | $2.3717(4)$ | $\mathrm{C}(12)-\mathrm{N}(13)-\mathrm{Re}(1)$ | $126.22(14)$ |
| $\operatorname{Re}(1)-\mathrm{Cl}(3)$ | $2.3891(4)$ | $\mathrm{C}(14)-\mathrm{N}(13)-\mathrm{Re}(1)$ | $125.83(12)$ |
| $\mathrm{C}(12)-\mathrm{N}(13)$ | $1.298(3)$ | $\mathrm{C}(26)-\mathrm{O}(26)-\mathrm{C}(27)$ | $114.04(17)$ |
| $\mathrm{N}(13)-\mathrm{C}(14)$ | $1.511(3)$ |  |  |

Table S3 Crystal data and structure refinement for 2a-b.

|  | 2 a | 2b |
| :---: | :---: | :---: |
| Empirical formula | $\mathrm{C}_{16} \mathrm{H}_{36} \mathrm{~N}^{+} \mathrm{C}_{11} \mathrm{H}_{12} \mathrm{Cl}_{3} \mathrm{NO}_{3} \mathrm{Re}^{-}$ | $\mathrm{C}_{16} \mathrm{H}_{36} \mathrm{~N}^{+} \mathrm{C}_{12} \mathrm{H}_{14} \mathrm{Cl}_{3} \mathrm{NO}_{4} \mathrm{Re}^{-}$ |
| Formula weight | 741.22 | 771.25 |
| Crystal description | needle, yellow-green | block, green |
| Crystal size | $0.27 \times 0.11 \times 0.06 \mathrm{~mm}$ | $0.23 \times 0.13 \times 0.10 \mathrm{~mm}$ |
| Crystal system, space group | monoclinic, P $2_{1}$ | orthorhombic, P c a 21 |
| Unit cell dimensions: a | 10.3673(17) $\AA$ | 22.2603(7) $\AA$ |
| b | 17.062(3) $\AA$ | 9.1943(3) $\AA$ |
| c | 17.831(3) $\AA$ | 16.4089(5) |
| $\beta$ | $91.518(8)^{\circ}$ | - |
| Volume | $3153.0(9) \AA^{3}$ | 3358.37(18) $\AA^{3}$ |
| Z | 4 | 4 |
| Calculated density | $1.561 \mathrm{Mg} / \mathrm{m}^{3}$ | $1.525 \mathrm{Mg} / \mathrm{m}^{3}$ |
| $\mathrm{F}(000)$ | 1496 | 1560 |
| Linear absorption coefficient $\mu$ | $4.137 \mathrm{~mm}^{-1}$ | $3.890 \mathrm{~mm}^{-1}$ |
| Absorption correction | semi-empirical from equivalents |  |
| Max. and min. transmission | 1.000 and 0.337 | 1.0000 and 0.7682 |
| Unit cell determination | $3.21^{\circ}<\Theta<24.48^{\circ}$ | $2.70^{\circ}<\Theta<31.04^{\circ}$ |
|  | 1198 reflections used at 100 K | 9479 reflections used at 100 K |
| Temperature | 100K | 100K |
| Diffractometer | Bruker APEX-II CCD |  |
| Radiation source | Incoatec microfocus sealed tube |  |
| Radiation and wavelength | $\mathrm{MoK}_{\alpha}, 0.71073 \AA$ |  |
| Monochromator | multilayer monochromator | graphite |
| Scan type | $\phi$ and $\omega$ scans |  |
| $\Theta$ range for data collection | 1.65 to $26.00^{\circ}$ | 2.21 to $30.00^{\circ}$ |
| Reflections collected / unique | $32901 / 12182$ | 45438 / 9765 |
| Significant unique reflections | 10180 with $\mathrm{I}>2 \sigma(\mathrm{I})$ | 9073 with $\mathrm{I}>2 \sigma(\mathrm{I})$ |
| R (int), R(sigma) | 0.0446, 0.0561 | 0.0298, 0.0317 |
| Completeness to $\Theta=$ | 99.9\% ( $26^{\circ}$ ) | 100.0\% (30 ${ }^{\circ}$ ) |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |  |
| Data / parameters / restraints | 12182 / 660 / 1 | 9765 / 362 / 1 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.040 | 1.021 |
| Final R indices [ $\mathrm{I}>2 \sigma(\mathrm{I})$ ] | $\mathrm{R} 1=0.0464, \mathrm{wR} 2=0.1169$ | $\mathrm{R} 1=0.0154, \mathrm{wR} 2=0.0354$ |
| R indices (all data) | $\mathrm{R} 1=0.0549, \mathrm{wR} 2=0.1203$ | $\mathrm{R} 1=0.0177, \mathrm{wR} 2=0.0361$ |
| Absolute structure parameter | 0.354(10) | -0.001(2) |
| Extinction expression | none | none |
| Weighting scheme | $\mathrm{w}=1 /\left[\mathrm{\sigma}^{2}\left(\mathrm{~F}_{\mathrm{o}}{ }^{2}\right)+(\mathrm{aP})^{2}+\mathrm{bP}\right]$ where $\mathrm{P}=\left(\mathrm{F}_{0}{ }^{2}+2 \mathrm{~F}_{\mathrm{c}}{ }^{2}\right) / 3$ |  |
| Weighting scheme param. $\mathrm{a}, \mathrm{b}$ | 0.0717, 0.0000 | 0.0117, 0.0000 |
| Largest $\Delta / \sigma$ in last cycle | 0.001 | 0.002 |
| Largest difference peak and hole | 1.641 and $-1.613 \mathrm{e} / \AA^{3}$ | 1.227 and $-0.773 \mathrm{e} / \AA^{3}$ |
| Structure Solution Program | SHELXS-97 ${ }^{5}$ |  |
| Structure Refinement Program | SHELXL-2014/6 ${ }^{6}$ |  |
| CCDC no. | 1895410 | 1850856 |

Crystal structure determination of 3a. The crystal structure analysis of 3a confirmed the compound as chlorido-bis[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-phenolato-N,O]oxidorhenium(V). All atoms lie on general positions. The asymmetric unit consists of two $\mathrm{N}, \mathrm{N}-$ trans-complexes in which the oxido and chlorido ligands are interchanged (site occupation factors of $0.795(3) / 0.205(3)$ and $0.582(2) / 0.418(2)$, resp.). Presumably due to the fact that the $\beta$ and the $\gamma$ angles of the unit cell are close to $90^{\circ}$, the crystal suffered from twinning. Therefore an appropriate twin matrix ( $100 / 0-10 / 00-1$ ) was applied and a scale factor was refined $(0.1651(12))$ between the two unequal components. The asymmetric unit consists of two complexes related by a pseudo-twofold screw axes parallel to the b-axis. The cis-chloridooxidorhenium $(\mathrm{V})$ groups are disordered over two orientations (site occupation factors of $0.795(3) / 0.205(3)$ and $0.582(2) / 0.418(2)$, resp.). In these disordered fragments the same anisotropic displacement parameters were used for atoms whose positions are close together and the equivalent bonds were restrained to have the same lengths. The other non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the $\mathrm{CH}_{2}$ groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and $\mathrm{C}-\mathrm{H}$ distances of $0.99 \AA$. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same ligand and idealized geometry with tetrahedral angles, staggered conformation, and $\mathrm{C}-\mathrm{H}$ distances of $0.98 \AA$. The H atoms of the phenyl rings were put at the external bisectors of the $\mathrm{C}-\mathrm{C}-\mathrm{C}$ angles at $\mathrm{C}-\mathrm{H}$ distances of $0.95 \AA$ and common isotropic displacement parameters were refined for the H atoms of the same ring.
Table S4 Selected bond lengths $\left[\AA\right.$ ] and angles [ ${ }^{\circ}$ ] for 3a

| $\mathrm{Re}(1) \mathrm{O}(1)$ | 1.682(6) | $\mathrm{C}(14)-\mathrm{N}(13)-\mathrm{Re}(1)$ | 121.8(5) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Re}(1)-\mathrm{Cl}(1)$ | 2.440(2) | $\mathrm{C}(21)-\mathrm{O}(21)-\mathrm{Re}(1)$ | 131.1(6) |
| $\operatorname{Re}(1)-\mathrm{N}(13)$ | $2.203(5)$ | $\mathrm{C}(32)$-N(33)-C(34) | 106.5(6) |
| $\operatorname{Re}(1)-\mathrm{O}(21)$ | 2.056 (7) | $\mathrm{C}(32)-\mathrm{N}(33)-\mathrm{Re}(1)$ | 124.0(5) |
| $\operatorname{Re}(1)-\mathrm{N}(33)$ | 2.058(5) | $\mathrm{C}(34)-\mathrm{N}(33)-\mathrm{Re}(1)$ | 129.5(5) |
| $\operatorname{Re}(1)-\mathrm{O}(41)$ | 1.944(7) | $\mathrm{C}(41)-\mathrm{O}(41)-\mathrm{Re}(1)$ | 127.5(6) |
| $\mathrm{Re}(2)-\mathrm{O}(2)$ | 1.683(6) | $\mathrm{O}(2)-\mathrm{Re}(2)-\mathrm{O}(61)$ | 168.8(15) |
| $\mathrm{Re}(2)-\mathrm{Cl}(2)$ | 2.438(2) | $\mathrm{N}(53)-\mathrm{Re}(2)-\mathrm{N}(73)$ | 166.4(2) |
| $\operatorname{Re}(2)-\mathrm{N}(53)$ | 2.231(5) | $\mathrm{O}(81)-\mathrm{Re}(2)-\mathrm{Cl}(2)$ | 161.3(10) |
| $\operatorname{Re}(2)-\mathrm{O}(61)$ | 2.057(8) | $\mathrm{C}(52)$-N(53)-C(54) | 109.4(6) |
| $\operatorname{Re}(2)-\mathrm{N}(73)$ | 2.037(5) | $\mathrm{C}(52)-\mathrm{N}(53)-\mathrm{Re}(2)$ | 126.8(5) |
| $\mathrm{Re}(2)-\mathrm{O}(81)$ | 1.942(8) | $\mathrm{C}(54)-\mathrm{N}(53)-\mathrm{Re}(2)$ | 123.8(5) |
|  |  | $\mathrm{C}(61)-\mathrm{O}(61)-\mathrm{Re}(2)$ | 137.2(9) |
| $\mathrm{O}(1)-\mathrm{Re}(1)-\mathrm{O}(21)$ | 173.2(3) | $\mathrm{C}(72)$ - N (73)-C(74) | 107.6(7) |
| $\mathrm{N}(13)-\mathrm{Re}(1)-\mathrm{N}(33)$ | 165.9(2) | $\mathrm{C}(72)-\mathrm{N}(73)-\operatorname{Re}(2)$ | 121.8(6) |
| $\mathrm{O}(41)-\mathrm{Re}(1)-\mathrm{Cl}(1)$ | 163.8(6) | $\mathrm{C}(74)-\mathrm{N}(73)-\mathrm{Re}(2)$ | 130.6(5) |
| $\mathrm{C}(12)-\mathrm{N}(13)-\mathrm{C}(14)$ | 111.8(7) | $\mathrm{C}(81)-\mathrm{O}(81)-\mathrm{Re}(2)$ | 120.8(8) |
| $\mathrm{C}(12)-\mathrm{N}(13)-\mathrm{Re}(1)$ | 126.3(5) |  |  |

Crystal structure determination of $\mathbf{3 b}$. The crystal structure analysis of $\mathbf{3 b}$ confirmed the compound
as chlorido-bis[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-6-methoxyphenolato]-oxidorhenium( V ). All atoms lie on general positions. The asymmetric unit consists of two molecules. The structure is only approx. centrosymmetric: whereas in one molecule the cis-chlorido-oxidorhenium( V ) group is disordered over two orientations (site occupation factors of $0.590(6)$ and $0.410(6)$, resp.), in the other molecule no disorder is detectable. In both molecules the Re atoms are octahedrally coordinated, with the N atoms of the 1,3-oxazolyl ligands in trans positions ( $\mathrm{N}-\mathrm{Re}-\mathrm{N}$ angles of $165.4(3)^{\circ}$ and $\left.164.2(3)^{\circ}\right)$. The structure was solved by interpretation of the patterson map and subsequent structure expansion (SHELXS-97), ${ }^{5}$ and refined by full-matrix least-squares techniques against $F^{2}$ (SHELXL2014/6). ${ }^{6}$ The absolute configuration was established by anomalous dispersion effects in the diffraction measurements on the crystal. Since racemic twinning was detected a twin matrix ($100 / 0-10 / 00-1$ ) was applied and a scale factor was refined ( $0.416(10)$ ) between the two unequal components. The asymmetric unit consists of two molecules. In one molecule the cis-chlorido-oxido-rhenium(V) group was disordered over two orientations and refined with site occupation factors of $0.590(6)$ and $0.410(6)$, respectively. In this fragment the same anisotropic displacement parameters were used for atoms whose positions are close together. The other non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the $\mathrm{CH}_{2}$ groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and $\mathrm{C}-\mathrm{H}$ distances of $0.99 \AA$. The H atoms of the phenyl rings were put at the external bisectors of the $\mathrm{C}-\mathrm{C}-\mathrm{C}$ angles at $\mathrm{C}-\mathrm{H}$ distances of $0.95 \AA$ and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. 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 $\mathrm{X}-\mathrm{C}$ bond, and $\mathrm{C}-\mathrm{H}$ distances of $0.98 \AA$. The structure is only approximately centrosymmetric: A refinement in the centrosymmetric space group $\mathrm{P} 2_{1} / \mathrm{n}(\mathrm{Z}=4$, only one molecule in the asymmetric unit) resulted in an R value R1 of $8.16 \%$ (instead of $2.33 \%$ ) and much higher difference peaks of up to $6.73 \mathrm{e} \AA^{-3}$ (instead of $1.78 \mathrm{e}^{-3}{ }^{-3}$ in the non-centrosymmetric space group $\mathrm{P} n$ ) caused by the inequalities in the cis-chlorido-oxidorhenium $(\mathrm{V})$ groups of the two molecules of the asymmetric unit. For 671 parameters final $R$ indices of $R 1=0.0233$ and $\mathrm{wR}^{2}=0.0487(\mathrm{GOF}=1.042)$ were obtained. The largest peak in a difference Fourier map was $1.781 \mathrm{e}^{\AA} \AA^{-3}$.

Table S5 Selected bond lengths $\left[\AA\right.$ ] and angles $\left[{ }^{\circ}\right]$ for $\mathbf{3 b}$.

| $\operatorname{Re}(1)-\mathrm{O}(1)$ | $1.753(6)$ | $\operatorname{Re}(2)-\mathrm{N}(73)$ | $2.095(6)$ |
| :--- | :--- | :--- | :--- |
| $\operatorname{Re}(1)-\mathrm{O}(21)$ | $1.986(5)$ | $\operatorname{Re}(2)-\mathrm{Cl}(2)$ | $2.354(5)$ |
| $\operatorname{Re}(1)-\mathrm{O}(41)$ | $1.999(6)$ | $\operatorname{Re}(2)-\mathrm{Cl}(3)$ | $2.295(4)$ |
| $\operatorname{Re}(1)-\mathrm{N}(13)$ | $2.118(6)$ | $\mathrm{O}(1)-\mathrm{Re}(1)-\mathrm{O}(21)$ | $177.3(3)$ |
| $\operatorname{Re}(1)-\mathrm{N}(33)$ | $2.096(6)$ | $\mathrm{N}(13)-\mathrm{Re}(1)-\mathrm{N}(33)$ | $165.4(3)$ |
| $\operatorname{Re}(1)-\mathrm{Cl}(1)$ | $2.401(3)$ | $\mathrm{O}(41)-\mathrm{Re}(1)-\mathrm{Cl}(1)$ | $168.07(18)$ |
| $\mathrm{C}(12)-\mathrm{N}(13)$ | $1.305(11)$ | $\mathrm{C}(12)-\mathrm{N}(13)-\mathrm{C}(14)$ | $110.4(7)$ |
| $\mathrm{O}(21)-\mathrm{C}(21)$ | $1.312(8)$ | $\mathrm{C}(12)-\mathrm{N}(13)-\operatorname{Re}(1)$ | $125.9(5)$ |
| $\mathrm{C}(32)-\mathrm{N}(33)$ | $1.301(10)$ | $\mathrm{C}(14)-\mathrm{N}(13)-\operatorname{Re}(1)$ | $123.4(6)$ |
| $\mathrm{O}(41)-\mathrm{C}(41)$ | $1.305(13)$ | $\mathrm{C}(21)-\mathrm{O}(21)-\operatorname{Re}(1)$ | $136.9(5)$ |
| $\operatorname{Re}(2)-\mathrm{O}(2)$ | $1.719(11)$ | $\mathrm{C}(32)-\mathrm{N}(33)-\mathrm{C}(34)$ | $108.7(6)$ |
| $\operatorname{Re}(2)-\mathrm{O}(3)$ | $1.712(13)$ | $\mathrm{C}(32)-\mathrm{N}(33)-\operatorname{Re}(1)$ | $123.7(5)$ |
| $\operatorname{Re}(2)-\mathrm{O}(61)$ | $1.996(6)$ | $\mathrm{C}(34)-\mathrm{N}(33)-\operatorname{Re}(1)$ | $127.4(5)$ |
| $\operatorname{Re}(2)-\mathrm{O}(81)$ | $1.990(6)$ | $\mathrm{C}(41)-\mathrm{O}(41)-\operatorname{Re}(1)$ | $129.9(5)$ |
| $\operatorname{Re}(2)-\mathrm{N}(53)$ | $2.088(6)$ |  |  |
|  |  |  |  |

Crystal structure determination of 3c. The crystal structure analysis of $\mathbf{3 c}$ confirmed the compound as chlorido-bis[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-4-nitrophenolato$\mathrm{N}, \mathrm{O}]$-oxidorhenium $(\mathrm{V})$. All atoms lie on general positions. The central $\mathrm{Cl}-\mathrm{Re}=\mathrm{O}$ fragment is disordered over two orientations. The refinement resulted in two different site occupation factors ( 0.647 (2) and $0.353(2)$ ). Besides the $\mathrm{N}, \mathrm{N}$-trans-complexes there are disordered solvent molecules in tubes parallel to the c-axis causing rather large displacement parameters of the nitro group N 44 . The cis-chlorido-oxido-rhenium $(\mathrm{V})$ groups are disordered over two orientations with site occupation factors of $0.647(2)$ and $0.353(2)$. In this fragment the same anisotropic displacement parameters were used for atoms whose positions are close together and the equivalent bonds were restrained to have the same lengths. The other non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the $\mathrm{CH}_{2}$ groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and $\mathrm{C}-\mathrm{H}$ distances of $0.99 \AA$. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same ligand and idealized geometry with tetrahedral angles, staggered conformation, and $\mathrm{C}-\mathrm{H}$ distances of $0.98 \AA$. The H atoms of the phenyl rings were put at the external bisectors of the $\mathrm{C}-\mathrm{C}-\mathrm{C}$ angles at $\mathrm{C}-\mathrm{H}$ distances of $0.95 \AA$ and common isotropic displacement parameters were refined for the H atoms of the same ring. Besides the described complex there are disordered solvent molecules in tubes parallel to the c -axis. Since it was not possible to describe the peaks of residual electron density as partially occupied individual solvent molecules, the diffuse electron density in these regions was
removed by the SQUEEZE routine of the PLATON program ${ }^{7}$. The solvent contribution to the calculated structure factors for each reflection hkl is included in the FAB file. The SQUEEZE routine computed two large void volumes of $427 \AA^{3}$ each with electron counts of approx. 38 per void. For 350 parameters final $R$ indices of $\mathrm{R} 1=0.0356$ and $\mathrm{wR}^{2}=0.1026(\mathrm{GOF}=1.087)$ were obtained. The largest peaks in a final difference Fourier map $\left(1.40-2.33 \mathrm{e} \AA^{-3}\right)$ were in the vicinity ( $0.70-0.77 \AA$ ) of the Re atom.

Table S6 Selected bond lengths $\left[\AA\right.$ ] and angles $\left[{ }^{\circ}\right]$ for 3c.

| $\operatorname{Re}(1)-\mathrm{O}(1)$ | $1.719(4)$ | $\mathrm{O}(41)-\mathrm{Re}(1)-\mathrm{Cl}(1)$ | $166.62(10)$ |
| :--- | :--- | :--- | :--- |
| $\operatorname{Re}(1)-\mathrm{Cl}(1)$ | $2.4087(18)$ | $\mathrm{C}(12)-\mathrm{N}(13)-\mathrm{C}(14)$ | $108.7(3)$ |
| $\operatorname{Re}(1)-\mathrm{N}(13)$ | $2.205(3)$ | $\mathrm{C}(12)-\mathrm{N}(13)-\operatorname{Re}(1)$ | $126.0(2)$ |
| $\operatorname{Re}(1)-\mathrm{O}(21)$ | $2.033(3)$ | $\mathrm{C}(14)-\mathrm{N}(13)-\operatorname{Re}(1)$ | $125.0(2)$ |
| $\operatorname{Re}(1)-\mathrm{N}(33)$ | $2.037(3)$ | $\mathrm{C}(21)-\mathrm{O}(21)-\operatorname{Re}(1)$ | $133.0(2)$ |
| $\operatorname{Re}(1)-\mathrm{O}(41)$ | $1.962(3)$ | $\mathrm{C}(32)-\mathrm{N}(33)-\mathrm{C}(34)$ | $108.7(3)$ |
| $\mathrm{O}(1)-\operatorname{Re}(1)-\mathrm{O}(21)$ | $172.91(17)$ | $\mathrm{C}(32)-\mathrm{N}(33)-\mathrm{Re}(1)$ | $123.0(3)$ |
| $\mathrm{N}(13)-\operatorname{Re}(1)-\mathrm{N}(33)$ | $168.63(13)$ | $\mathrm{C}(44)-\mathrm{N}(33)-\mathrm{-e}(1)$ | $128.0(1)$ |
|  |  |  |  |

Table S7 Crystal data and structure refinement for 3a-c.

| Crystal data | 3a | 3b | 3c |
| :---: | :---: | :---: | :---: |
| Empirical formula | $\mathrm{C}_{22} \mathrm{H}_{24} \mathrm{ClN}_{2} \mathrm{O}_{5} \mathrm{Re}$ | $\mathrm{C}_{24} \mathrm{H}_{28} \mathrm{ClN}_{2} \mathrm{O}_{7} \mathrm{Re}$ | $\mathrm{C}_{22} \mathrm{H}_{22} \mathrm{ClN}_{4} \mathrm{O}_{9} \mathrm{Re}$ |
| Formula weight | 618.08 | 678.13 | 708.08 |
| Crystal description | block, green | block, green | block, green |
| Crystal size [mm] | 0.31 x 0.28 x 0.20 | $0.20 \times 0.15 \times 0.14$ | $0.22 \times 0.20 \mathrm{x} 0.15$ |
| Space group | triclinic, P -1 | monoclinic, P n | orthorhombic, P c c n |
| Unit cell dimensions: a | 10.714(5) $\AA$ | 9.9571(3) $\AA$ | 21.9023(14) $\AA$ |
| b | 11.548(5) $\AA$ | 11.4206(4) ${ }^{\text {a }}$ | 10.7081(7) ${ }^{\text {a }}$ |
| c | 18.589(9) $\AA$ | 21.6403(6) $\AA$ | 23.4319(16) |
| $\alpha$ | $84.351(7)^{\circ}$ | - | - |
| $\beta$ | 89.354(6) ${ }^{\circ}$ | 91.0099(11) ${ }^{\circ}$ | - |
| $\chi$ | 89.921(5) ${ }^{\circ}$ | - | - |
| Volume | 2288.6(18) $\AA^{3}$ | 2460.47(13) $\AA^{3}$ | $5495.5(6) \AA^{3}$ |
| Z | 4 | 4 | 8 |
| Calculated density | $1.794 \mathrm{Mg} / \mathrm{m}^{3}$ | $1.831 \mathrm{Mg} / \mathrm{m}^{3}$ | $1.712 \mathrm{Mg} / \mathrm{m}^{3}$ |
| F(000) | 1208 | 1336 | 2768 |
| Linear abs. coefficient $\mu$ | $5.461 \mathrm{~mm}^{-1}$ | $5.095 \mathrm{~mm}^{-1}$ | $4.573 \mathrm{~mm}^{-1}$ |
| Absorption correction | semi-empirical from equivalents |  |  |
| Max. and min. transmission | 0.745 and 0.301 | 0.604 and 0.453 | 1.000 and 0.823 |
| Unit cell determination | $2.60^{\circ}<\Theta<27.41^{\circ}$ | $2.59^{\circ}<\Theta<28.48^{\circ}$ | $2.54{ }^{\circ}<\Theta<28.55^{\circ}$ |
| Reflections used (100K) | 9882 | 9888 | 9940 |
| Temperature [K] | 100 | 100 | 100 |
| Diffractometer | Bruker APEX-II CCD |  |  |
| Radiation source | fine-focus sealed tube |  |  |
| Radiation and wavelength | $\mathrm{MoK}_{\alpha}, 0.71073 \AA$ |  |  |
| Monochromator | multilayer monochromator |  |  |
| Scan type | $\phi$ and $\omega$ scans |  |  |
| $\Theta$ range for data collection | 1.10 to $26.00^{\circ}$ | 2.59 to $28.00^{\circ}$ | 1.74 to $28.00^{\circ}$ |
| Refl. collected / unique | 22403 / 8987 | 27783 / 11405 | 62498 / 6636 |
| Sign. unique reflections | $\begin{aligned} & \hline 7711 \text { with } \mathrm{I}> \\ & 2 \sigma(\mathrm{I}) \\ & \hline \end{aligned}$ | $\begin{aligned} & 10924 \text { with I > } \\ & 2 \sigma(\mathrm{I}) \end{aligned}$ | 5514 with $\mathrm{I}>2 \sigma(\mathrm{I})$ |
| R (int), R (sigma) | 0.0518, 0.0733 | 0.0231, 0.0279 | 0.0767, 0.0370 |
| Completeness to $\Theta=()$ | 99.9\% ( $26^{\circ}$ ) | 99.8\% ( $28^{\circ}$ ) | 100.0\% ( $28^{\circ}$ ) |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |  |  |
| Data/parameters/restraints | 8987 / 604 / 76 | 11405 / 671 / 2 | 6636 / 350 / 2 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.106 | 1.042 | 1.087 |
| Final R indices [ $\mathrm{I}>2 \sigma(\mathrm{I})$ ] | $\begin{aligned} & \mathrm{R} 1=0.0487, \\ & \mathrm{wR} 2=0.1159 \end{aligned}$ | $\begin{aligned} & \hline \mathrm{R} 1=0.0233, \\ & \mathrm{wR} 2=0.0477 \\ & \hline \end{aligned}$ | $\begin{aligned} & \mathrm{R} 1=0.0356, \mathrm{wR} 2= \\ & 0.1001 \end{aligned}$ |
| R indices (all data) | $\begin{aligned} & \mathrm{R} 1=0.0561, \\ & \mathrm{wR} 2=0.1195 \end{aligned}$ | $\begin{aligned} & \mathrm{R} 1=0.0253, \\ & \mathrm{wR} 2=0.0487 \end{aligned}$ | $\begin{aligned} & \mathrm{R} 1=0.0426, \mathrm{wR} 2= \\ & 0.1026 \end{aligned}$ |
| Extinction expression | none | none | none |
| Weighting scheme | $\mathrm{w}=1 /\left[\sigma^{2}\left(\mathrm{~F}_{\mathrm{o}}{ }^{2}\right)+(\mathrm{aP})^{2}+\mathrm{bP}\right]$ where $\mathrm{P}=\left(\mathrm{F}_{0}{ }^{2}+2 \mathrm{~F}_{\mathrm{c}}{ }^{2}\right) / 3$ |  |  |
| Weighting scheme parameters $\mathrm{a}, \mathrm{b}$ | 0.0354, 1.7439 | 0.0000, 4.7806 | 0.0586, 2.1120 |
| Largest $\Delta / \sigma$ in last cycle | 0.001 | 0.002 | 0.000 |
| Largest diff. peak and hole | $\begin{aligned} & \hline 1.997 \text { and - } \\ & 1.921 \mathrm{e} / \AA^{3} \\ & \hline \end{aligned}$ | $\begin{aligned} & \hline 1.781 \mathrm{and}- \\ & 2.026 \mathrm{e} / \AA^{3} \\ & \hline \end{aligned}$ | 2.332 and -1.197e/ $\AA^{3}$ |
| Structure Solution Program | SHELXS-975 |  |  |
| Structure Refinement Prog. | SHELXL-2014/6 ${ }^{6}$ |  |  |
| CCDC no. | 1562677 | 1562678 | 1562679 |

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