Supporting Information for

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

J. A. Schachner,*,[†]B. Berner,[†]F. Belaj[†] and N. C. Mösch-Zanetti*,[†]

[†]Institute of Chemistry, Inorganic Chemistry, University of Graz, Schubertstraße 1, 8010 Graz.

Ligands HL1a^{1,2} and HL1b² 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 mmol, 1 equiv.) of H1c'' were mixed with 13.95 g (156.5 mmol, 5 equiv.) of 2-amino-2-methylpropanol and heated to 85 °C for 16 h under neat conditions. After cooling, the reaction mixture was dissolved and acidified with HCl to pH = 2, upon which crude H1c' precipitated. Aqueous work-up with DCM yielded H1c' (7.16 g, 90%). ¹H NMR (300 MHz, Chloroform-d) δ 13.20 (s, 1H), 8.34 (d, *J* = 2.4 Hz, 1H), 8.28 (d, *J* = 9.2 Hz, 1H), 7.06 (d, *J* = 9.2 Hz, 1H), 6.61 (s, 1H), 3.75 (s, 2H), 1.49 (s, 6H). IR (cm⁻¹): 3370, 3328 (NH), 2976 (OH), 1619 (C=O), 1341, 1289 (NO₂); EI-MS (*m/z*): 254.09 (M⁺).

Synthesis of H1c: 4.32 g (17 mmol, 1 equiv.) of H1c' were suspended in 40 mL heptane and thionyl chloride (2.5 mL, 34.1 mmol, 2 equiv.) was added. After stirring overnight at 25 °C the solid hydrochloride salt H1c·HCl was isolated by filtration and quenched/worked up with CH₂Cl₂/sat. NaHCO₃ to give H1c (3.77 g, 94%). ¹H NMR (300 MHz, Chloroform-d) δ 13.16 (s, 1H), 8.56 (d, *J* = 2.8 Hz, 1H), 8.23 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.05 (d, *J* = 9.2 Hz, 1H), 4.18 (s, 2H), 1.42 (s, 6H). ¹³C NMR (75 MHz, Chloroform-d) δ 165.21, 162.58, 139.65, 128.60, 124.74, 117.57, 110.78, 79.03, 67.65, 28.50. IR (cm⁻¹): 2976 (OH), 1645 (C=N), 1337, 1301, 1285 (NO₂); EI-MS (*m*/*z*): 236.08 (M⁺).

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-N,O]-oxidorhenium(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 (Re1-O21 2.011(8)Å, Re2-O41 2.005(8)Å) are in trans positions to the oxo groups (Re1-O1 1.690(7)Å, Re2-O2 1.699(7)Å; O1-Re1-O21 171.4(3)°, O2-Re2-O41 171.3(3)°). The Re–Cl distances of the Cl atoms (Re1–Cl2 2.377(2)Å, Re2–Cl5 2.390(3)Å) trans to the oxazolyl rings (Re1-N13 2.172(8)Å, Re2-N33 2.157(9)Å; N13-Re1-Cl2 169.7(2)°, N33-Re2-Cl5 171.0(2)°) do not differ from those trans to each other (Re-Cl 2.368(3)-2.420(3)Å; Cl1-Re1-Cl3 171.51(10)°, Cl4-Re2-Cl6 171.59(11)°). 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 (-1 0 0 / 0 - 1)0 / 0 0 - 1) was applied and a scale factor was refined (0.354(10)) between the two unequal components. The H atoms of the CH₂ 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 C–H distances of 0.99Å. 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 0.98Å. The H atoms of the phenyl rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same ring.

Table S1 Selected bond lengths [Å] and angles [°] for 2a

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

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

C(34)-N(33)-Re(2) 125.5(7) C(41)-O(41)-Re(2) 136.4(7)

Crystal structure determination of 2b. The crystal structure analysis of 2b confirmed the compound as tetra(*n*-butyl)ammonium trichlorido-[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2yl)-6-methoxyphenolato-N,O]-oxoidorhenate(V). All atoms lie on general positions. The phenolato ligand [Re1-O21 1.980(2)Å] is in *trans* position to the oxido group (Re1-O1 1.681(2)Å; O1–Re1–O21 171.18(9)°). The tetra(*n*-butyl)ammonium cation shows a rather flat all-trans conformation with the centre oriented towards the OCl₂ 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 C–C–C angles at C–H distances of 0.95Å and a common isotropic displacement parameter was refined. The H atoms of the CH₂ groups were refined with common isotropic displacement parameters for the H atoms of equivalent groups and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. 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 X-C bond, and C-H distances of 0.98Å.

 Table S2 Selected bond lengths [Å] and angles [°] for 2b.

Re(1)-O(1)	1.6801(16)
Re(1)-O(21)	1.9800(16)
Re(1)-N(13)	2.1386(16)
$\operatorname{Re}(1)$ - $\operatorname{Cl}(1)$	2.3909(4)
Re(1)-Cl(2)	2.3717(4)
Re(1)-Cl(3)	2.3891(4)
C(12)-N(13)	1.298(3)
N(13)-C(14)	1.511(3)
Re(1)-Cl(3) C(12)-N(13) N(13)-C(14)	2.3891(4) 1.298(3) 1.511(3)

N(13)-Re(1)-Cl(2)	171.40(4)
O(1)-Re(1)-O(21)	171.14(6)
Cl(3)-Re(1)-Cl(1)	169.71(2)
C(12)-N(13)-C(14)	107.62(17)
C(12)-N(13)-Re(1)	126.22(14)
C(14)-N(13)-Re(1)	125.83(12)
C(26)-O(26)-C(27)	114.04(17)

	2a	2b	
Empirical formula	$C_{16}H_{36}N^+C_{11}H_{12}Cl_3NO_3Re^-$	$C_{16}H_{36}N^+C_{12}H_{14}Cl_3NO_4Re^-$	
Formula weight	741.22	771.25	
Crystal description	needle, yellow-green	block, green	
Crystal size	0.27 x 0.11 x 0.06mm	0.23 x 0.13 x 0.10mm	
Crystal system, space group	monoclinic, P 2 ₁	orthorhombic, P c a 2_1	
Unit cell dimensions: a	10.3673(17)Å	22.2603(7)Å	
b	17.062(3)Å	9.1943(3)Å	
с	17.831(3)Å	16.4089(5)Å	
β	91.518(8)°	-	
Volume	3153.0(9)Å ³	3358.37(18)Å ³	
Ζ	4	4	
Calculated density	1.561Mg/m ³	1.525Mg/m ³	
F(000)	1496	1560	
Linear absorption coefficient µ	4.137mm ⁻¹	3.890mm ⁻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 100K	9479 reflections used at 100K	
Temperature	100K	100K	
Diffractometer	Bruker APEX-II CCD		
Radiation source	Incoatec microfocus sealed tube		
Radiation and wavelength	$MoK_{\alpha}, 0$	0.71073Å	
Monochromator	multilayer monochromator graphite		
Scan type	ϕ and ω scans		
Θ range for data collection	1.65 to 26.00°	2.21 to 30.00°	
Reflections collected / unique	32901 / 12182	45438 / 9765	
Significant unique reflections	10180 with I > $2\sigma(I)$	9073 with I > $2\sigma(I)$	
R(int), R(sigma)	0.0446, 0.0561	0.0298, 0.0317	
Completeness to $\Theta =$	99.9% (26°)	100.0% (30°)	
Refinement method	Full-matrix least-squares on F ²		
Data / parameters / restraints	12182 / 660 / 1	9765 / 362 / 1	
Goodness-of-fit on F ²	1.040	1.021	
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0464, WR2 = 0.1169	R1 = 0.0154, WR2 = 0.0354	
R indices (all data)	R1 = 0.0549, WR2 = 0.1203	R1 = 0.0177, wR2 = 0.0361	
Absolute structure parameter	0.354(10)	-0.001(2)	
Extinction expression	none	none	
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_o^2)/3$		
Weighting scheme param. a, b	0.0717.0.0000 0.0117.0.0000		
Largest Λ/σ in last cycle	0.001	0.002	
Largest difference peak and hole	1.641 and -1.613e/Å ³	1.227 and -0.773e/Å ³	
Structure Solution Program	SHELXS-97 ⁵		
Structure Refinement Program	SHELXL-2014/66		
CCDC no.	1895410	1850856	

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

Crystal structure determination of 3a. The crystal structure analysis of 3a confirmed the chlorido-bis[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-phenolato-N,O]compound as oxidorhenium(V). All atoms lie on general positions. The asymmetric unit consists of two N,Ntrans-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 β and the γ angles of the unit cell are close to 90°, the crystal suffered from twinning. Therefore an appropriate twin matrix $(1 \ 0 \ 0 \ -1 \ 0 \ / \ 0 \ -1)$ 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(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 CH₂ groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. 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 C-H distances of 0.98Å. The H atoms of the phenyl rings were put at the external bisectors of the C-C-C angles at C-H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same ring. Table S4 Selected bond lengths [Å] and angles [°] for 3a

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

Crystal structure determination of 3b. The crystal structure analysis of 3b confirmed the chlorido-bis[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-6compound as 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 (N-Re-N angles of 165.4(3)° and 164.2(3)°). 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 (SHELXL-2014/6).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 (-1 0 0 / 0 - 1 0 / 0 0 - 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 cischlorido-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 CH₂ groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the phenyl rings were put at the external bisectors of the C-C-C angles at C-H distances of 0.95Å 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 X–C bond, and C–H distances of 0.98Å. The structure is only approximately centrosymmetric: A refinement in the centrosymmetric space group $P2_1/n$ (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 6.73eÅ⁻³ (instead of 1.78eÅ⁻³ in the non-centrosymmetric space group P n) caused by the inequalities in the cis-chlorido-oxidorhenium(V) groups of the two molecules of the asymmetric unit. For 671 parameters final R indices of R1 = 0.0233 and $wR^2 = 0.0487$ (GOF = 1.042) were obtained. The largest peak in a difference Fourier map was 1.781eÅ⁻³.

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

Table S5 Selected bond lengths [Å] and angles [°] for 3b.

Crystal structure determination of 3c. The crystal structure analysis of 3c confirmed the compound as chlorido-bis[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-4-nitrophenolato-N,O]-oxidorhenium(V). All atoms lie on general positions. The central Cl-Re=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 N,N-trans-complexes there are disordered solvent molecules in tubes parallel to the c-axis causing rather large displacement parameters of the nitro group N44. The cis-chlorido-oxido-rhenium(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 CH₂ groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. 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 C-H distances of 0.98Å. The H atoms of the phenyl rings were put at the external bisectors of the C-C-C angles at C-H distances of 0.95Å 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 program⁷. 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 427Å^3 each with electron counts of approx. 38 per void. For 350 parameters final *R* indices of R1 = 0.0356 and wR² = 0.1026 (GOF = 1.087) were obtained. The largest peaks in a final difference Fourier map (1.40 - 2.33eÅ⁻³) were in the vicinity (0.70 - 0.77Å) of the Re atom.

 Table S6 Selected bond lengths [Å] and angles [°] for 3c.

Re(1)-O(1)	1.719(4)	O(41)-Re(1)-Cl(1)	166.62(10)
Re(1)-Cl(1)	2.4087(18)	C(12)-N(13)-C(14)	108.7(3)
Re(1)-N(13)	2.205(3)	C(12)-N(13)-Re(1)	126.0(2)
Re(1)-O(21)	2.033(3)	C(14)-N(13)-Re(1)	125.0(2)
Re(1)-N(33)	2.037(3)	C(21)-O(21)-Re(1)	133.0(2)
Re(1)-O(41)	1.962(3)	C(32)-N(33)-C(34)	108.7(3)
		C(32)-N(33)-Re(1)	123.0(3)
O(1)-Re(1)-O(21) 172.91(17)	C(34)-N(33)-Re(1)	128.0(2)
N(13)-Re(1)-N	1(33) 168.63(13)	C(41)-O(41)-Re(1)	129.6(2)

Crystal data	3 a	3 b	3c	
Empirical formula	C ₂₂ H ₂₄ ClN ₂ O ₅ Re	C ₂₄ H ₂₈ ClN ₂ O ₇ Re	C ₂₂ H ₂₂ ClN ₄ O ₉ Re	
Formula weight	618.08	678.13	708.08	
Crystal description	block, green	block, green	block, green	
Crystal size [mm]	0.31x0.28x0.20	0.20x0.15x0.14	0.22x0.20x0.15	
Space group	triclinic, P -1	monoclinic, P n	orthorhombic, P c c n	
Unit cell dimensions: a	10.714(5)Å	9.9571(3)Å	21.9023(14)Å	
b	11.548(5)Å	11.4206(4)Å	10.7081(7)Å	
с	18.589(9)Å	21.6403(6)Å	23.4319(16)Å	
α	84.351(7)°	-	-	
β	89.354(6)°	91.0099(11)°	-	
γ	89.921(5)°	-	-	
Volume	2288.6(18)Å ³	2460.47(13)Å ³	5495.5(6)Å ³	
Z	4	4	8	
Calculated density	$1.794 Mg/m^{3}$	1.831Mg/m ³	$1.712 Mg/m^3$	
F(000)	1208	1336	2768	
Linear abs. coefficient u	5.461mm ⁻¹	5.095mm ⁻¹	4.573mm ⁻¹	
Absorption correction	sem	i-empirical from ed	uivalents	
Max. and min. transmission	0.745 and 0.301	0.604 and 0.453	1.000 and 0.823	
Unit cell determination	2 60°<Θ<27 41°	2.59°<Θ<28.48°	2 54°<Θ<28 55°	
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	MoK 0 71073Å			
Monochromator	multilaver monochromator			
Scan type	d and ω scans			
Θ range for data collection	1.10 to 26.00°	2.59 to 28.00°	1.74 to 28.00°	
Refl collected / unique	22403 / 8987	27783 / 11405	62498 / 6636	
Sign, unique reflections	7711 with I >	10924 with I >	5514 with $I > 2\sigma(I)$	
	$2\sigma(I)$	$2\sigma(I)$		
R(int), R(sigma)	0.0518.0.0733	0.0231.0.0279	0.0767. 0.0370	
Completeness to $\Theta = 0$	99.9% (26°)	99.8% (28°)	100.0% (28°)	
Refinement method	Fu	ll-matrix least-squa	res on F^2	
Data/parameters/restraints	8987 / 604 / 76	11405 / 671 / 2	6636 / 350 / 2	
$Goodness-of-fit on F^2$	1 106	1 042	1 087	
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0487.	$R_1 = 0.0233$.	$R_1 = 0.0356$, wR2 =	
	wR2 = 0.1159	wR2 = 0.0477	0.1001	
R indices (all data)	R1 = 0.0561,	R1 = 0.0253,	R1 = 0.0426, WR2 =	
	wR2 = 0.1195	wR2 = 0.0487	0.1026	
Extinction expression	none	none	none	
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_o^2)/3$			
Weighting scheme	0.0354, 1.7439	0.0000, 4.7806	0.0586, 2.1120	
parameters a, b	· ·			
Largest Δ/σ in last cycle	0.001	0.002	0.000	
Largest diff. peak and hole	1.997 and -	1.781 and -	2.332 and -1.197e/Å ³	
	1.921e/Å ³	2.026e/Å ³		
Structure Solution Program	SHELXS-97 ⁵			
Structure Refinement Prog.	SHELXL-2014/66			
CCDC no.	1562677	1562678	1562679	

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

- 1. J. A. Schachner, B. Terfassa, L. M. Peschel, N. Zwettler, F. Belaj, P. Cias, G. Gescheidt and N. C. Mösch-Zanetti, *Inorg. Chem.*, 2014, **53**, 12918–12928.
- 2. Helen C. Aspinall, Oliver Beckingham, Michael D. Farrar, Nicholas Greeves and Christopher D. Thomas, *Tetrahedron Lett.*, 2011, **52**, 5120–5123.
- 3. J. T. Roland and Z. Guan, J. Am. Chem. Soc., 2004, 126, 14328–14329.
- 4. M. Hoogenraad, K. Ramkisoensing, S. Gorter, W. L. Driessen, E. Bouwman, J. G. Haasnoot, J. Reedijk, T. Mahabiersing and F. Hartl, *Eur. J. Inorg. Chem.*, 2002, 377–387.
- 5. G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112–122.
- 6. G. M. Sheldrick, Acta Crystallogr., Sect. C: Cryst. Struct. Chem., 2015, 71, 3–8.
- 7. A. L. Spek, Acta Crystallogr., Sect. D: Biol. Crystallogr., 2009, 65, 148–155.