Absence of Dichroism in Dinuclear Rhenium Complexes with Sterically Hindered μ2-(η2-*N,O*)-Nitrosobenzene Ligands

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The substitution reactions of [Re(CO)$_5$X] (X = Cl, Br) with 2,6-dihalo-substituted nitrosobenzene derivatives C$_6$H$_2$YZ$_2$NO (Y = H, Cl, Br; Z = Cl, Br) leads to the formation of dinuclear μ$_2$-η^2-*N,O*-nitrosobenzene-bridged complexes of the type [{(CO)$_3$Re(μ-X)}$_2$ONC$_6$H$_2$YZ$_2$] (**6a,b**, **7a,b**, **8a,b**, **9a**). The turquoise coloured solutions of the complexes in CH$_2$Cl$_2$ show only one UV/Vis absorption of medium intensity in the region 670–710 nm, depending on the halogen bridges X and substituents Z. Single crystals of the complexes do not exhibit any dichroic properties. This may be due to the almost perpendicular orientation of the phenyl ring towards the Re–O–N–Re plane. The molecular structures of six compounds, as determined by single-crystal X-ray analyses, show two face-joined octahedra with Re centres that are bridged by two halogens X and one NO group. NO coordinates in a nonsymmetrical η^2-like fashion with N- or O-linkage to each Re centre. The phenyl rings do not lie within the symmetry plane containing the atoms Re, N and O, but are almost perpendicular to this (torsion angle O–N–C–C = 83.5–85.4°) because of the 2,6-dihalogen substituents Z.

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Introduction

The coordination chemistry of organic RNO nitroso compounds has been extensively investigated,[1] and their many different coordination modes have been summarised in schemes in previous accounts of our work, as well as by others.[2,3] The dominant bonding mode bridging two metal centres is of the type μ-η^1-*N*, μ-η^1:η^2-*N,O*, μ-η^1:η^1-*N,O* or μ-η^2:η^2-*N,O* (Scheme 1), although the unassisted ligand function μ-η^1:η^1-*N,O* (type I) with a simple bridging coordination mode is less common. Co-assisted ligand functions, that is those with additional coordination by a further donor system (e.g. amido or carbonyl groups), have been verified in most examples and form additional five- (type Ia)[4] or six-membered rings (type Ib).[5] Furthermore, type I has been only observed in a unique neutral complex of platinum[6] and in a dinuclear rhodium cation with thiolato bridges.[7]

We have recently published a series of complexes[2,3] that are the first simple, neutral and dinuclear *C*-nitroso complexes to exhibit this rare, unassisted μ-η^1:η^1-*N,O* ligand function (type I), and contain only single atoms, X, as additional bridges (X = Cl, Br, I). All of these complexes show dichroic properties and form deep-blue solutions. In the UV/Vis spectra, one very intense broad absorption is found at λ = 600–650 nm (log ε > 30000), which is due to a sol-
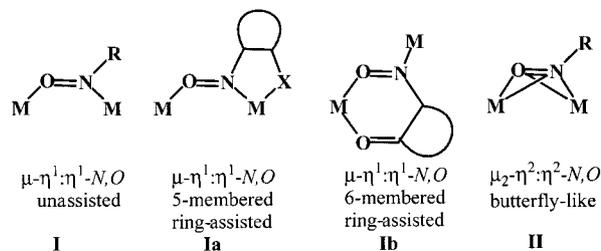
Scheme 1. Bonding modes of *C*-nitroso compounds bridging two metals (μ-η^2-*N,O*).

vochromic ligand-to-metal CT band ([NO–Re^I]). Light reflected from microcrystalline powders of the substances shines with different colours (like shells). Visual inspection of suitable crystals with polarized light under a microscope clearly showed a polarisation-dependent absorption. In the case of [{(CO)$_3$Re(μ-Br)}$_2$ONC$_6$H$_4$NEt$_2$] sufficiently large single crystals showed a pronounced linear dichroism.[3] We were able to correlate this dichroism with the arrangement of the molecules in the unit cells, which show alignment of the RNO units along a crystal plane. It is worthwhile to note that the dihedral angles Re–O–N–Re and O–N–C–C (phenyl ring) are less than 5° and 3°, respectively. This means that the NO group and the phenyl ring (together with the NR$_2$ substituent)[2,3] lie almost within the symmetry plane of the dinuclear complexes. To prove this correlation, we decided to synthesise analogous complexes with nitrosobenzene ligands that are sterically hindered in both *ortho* positions. Our aim was, therefore, to twist the phenyl

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ring out of the plane and to observe the effect this had on the dichroism. We undertook the reaction of 2,6-dihalo-substituted nitrosobenzenes with $[Re(CO)_5X]$ (X = Cl, Br), and obtained the corresponding dinuclear complexes $[\{(CO)_3Re(\mu-X)\}_2ONC_6H_2YZ_2]$, which exhibit the same nitroso ligand function μ_2-η^1:η^1-O, but with a perpendicular orientation of the phenyl ring towards the plane formed by the atoms Re, O, N and Re. As a consequence of this, the dichroism is lost.

Results and Discussion

The reaction of $[Re(CO)_5X]$ (X = Cl, Br) (**1a,b**) with the sterically hindered *C*-nitroso compounds 4-Y-2,6-$Z_2C_6H_2NO$ [Y = H, Z = Cl (**2**), Br (**3**); Y = Cl, Z = Br (**4**); Y = Br, Z = Cl (**5**)] leads to the dinuclear complexes **6a,b**–**8a,b** and **9a** (Scheme 2). All reactions were carried out in boiling CH_2Cl_2. Whereas **9a** was obtained in good yield (65%), **9b** could not be isolated under the same reaction conditions. It is interesting to note that using boiling toluene as solvent resulted in the dimeric halo complexes $[(CO)_4ReX]_2$ (X = Cl, Br); no reaction occurred when $[Re(CO)_5I]$ was used as the starting material.
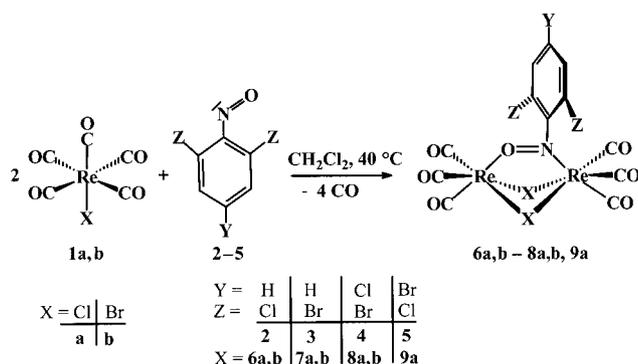
Scheme 2. Synthesis of sterically hindered μ_2-(η^2-*N*,O)-nitrosobenzene complexes **6**–**9**.

Compounds **6a,b**–**8a,b** and **9a** were obtained as dark-green crystals that are stable in air for some days. The complexes are soluble in THF, acetone, $CHCl_3$, CH_2Cl_2, and even in toluene, but nearly insoluble in pentane or hexane. The turquoise solutions formed in these solvents can be kept in air for several days without decomposition. In the UV/Vis spectra (CH_2Cl_2) two broad absorptions are observed, one lies consistently at about $\lambda_1 = 375$–380 nm, whereas the second, which originates from a ligand-to-metal CT (NO–Re^I), is observed over a larger range at $\lambda_2 = 670$–710 nm. It is shifted to lower frequency with respect to the corresponding π–π^*-NO electronic transition of the free ligands. It is noteworthy that they are also observed at lower frequencies and with smaller intensities than those of the corresponding nitrosoaniline complexes published previously,[2,3] where the NO group, phenyl ring and the NR_2 substituent lie exactly within the symmetry plane of the di-

nuclear complexes. In spite of the frequency range of λ_2, there is no dependence of its spectral position on either the halogen bridges or substituents.

The X-ray structure analyses of **6a,b**–**8a,b** show that the phenyl ring with both halo substituents in the *ortho* positions is orientated perpendicular to the symmetry plane. As is therefore expected, the light reflected from crystalline powders of these complexes does not shine in different colours and neither does it show any polarisation-dependent absorption of the type mentioned above.[2,3] Therefore, they do not exhibit any significant dichroic properties.

The IR spectra of **6a,b**–**8a,b** and **9a** show five ν(CO) absorptions. As the NO group is bonded by N and O to different Re centres, the electronic situation at both Re centres is different. This normally results in two different *fac*-$Re(CO)_3$ fragments, each with local C_{3v} symmetry. However, because of the bulky substituents in the *ortho* position of the nitrosobenzenes, the local symmetry of the $Re(CO)_3$ fragment at N is reduced to C_s. Therefore, three bands of the type 2A′ + A′′ are detected. Due to electronic reasons the *N*-bonded $Re(CO)_3$ moiety should be more electron rich and act as a better π-donor for the CO ligands than the O-bonded one. Therefore, the absorptions at higher wavenumbers with varying intensities have been assigned to the $\{(CO)_3Re$–O$\}$ fragment [$\tilde{\nu} = 2086$–2091 (A_1), 2006–2012 cm^{-1} (E)] and the three absorptions at lower wavenumbers and similar intensities to the $\{(CO)_3Re$–N$\}$ fragment [$\tilde{\nu} = 2024$–2058 (A′), 1961–1970 (A′), 1913–1949 cm^{-1} (A′′)]. Because several bands lie very close together it is not possible to draw any conclusions about the halogens as substituents or bridges. The ν(NO) band of the complexes is found at 1329–1350 cm^{-1}, which is a shift to lower frequency of about 115 cm^{-1} with respect to the free *C*-nitroso ligand and of about 50 cm^{-1} compared with other complexes.[2,3]

The ^{1}H NMR spectrum of **6a** shows three separate doublets at $\delta = 7.40$, 7.42 and 7.44 ppm. In the case of **6b**, only a multiplet between $\delta = 7.38$–7.44 ppm can be detected. In the spectra of **7a** two doublets for the ring protons in the 3,5-positions are detected at $\delta = 7.26$ and 7.37 ppm, and one triplet for the proton in the 4-position at $\delta = 7.67$ ppm. Complex **7b** exhibits a triplet at $\delta = 7.27$ ppm, a doublet at $\delta = 7.38$ ppm and a multiplet at $\delta = 7.61$–7.64 ppm, whereas **8a** only shows one broad signal at $\delta = 7.66$ ppm, and **8b** and **9a** exhibit singlets at $\delta = 7.64$ and 7.60 ppm, respectively. It is noteworthy that in spite of the mirror symmetry in the Re_2NO plane compounds **6a,b** and **7a,b** with the benzene ring substituted in 2,6-positions exhibit different signals for the three protons in the 3,4- and 5-positions. Compounds **8a,b**, and **9a**, however, show only one resonance for the 3,5-protons.

In the ^{13}C NMR spectra of **6a,b**–**8a,b** and **9a** the signals for the phenyl groups are detected at $\delta = 124.1$–140.9 ppm. Here, we observe three signals for the three different types of C-atoms in the 2,6-, 3,5- and 4-positions. The *N*-bonded quaternary carbon is observed at $\delta = 160.2$–164.5 ppm and the signals corresponding to the CO ligands at the Re centres appear at $\delta = 181$–192 ppm.

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The parent peaks as well as peaks corresponding to fragments resulting from the successive loss of up to six CO ligands are observed in the mass spectra (DEI-MS) of **6a**,**b**–**8a**,**b** and **9a**.

The compositions and structures of complexes **6a**,**b**–**8a**,**b** were confirmed by X-ray structure analysis (see Table 2). Single crystals of complexes **6a**,**b**–**8a**,**b** were obtained by the diffusion of pentane into solutions of the complexes in CHCl$_3$. The molecular structures and selected bond lengths and angles are given in Figures 1 (**6a**), 2 (**6b**), 3 (**7a**), 4 (**7b**), 5 (**8a**) and 6 (**8b**). They show two face-joined octahedra with two halogens and the NO group as bridging ligands. The N–O distances are approximately 1.299 Å, similar to the values for analogous complexes,[1–3] but significantly longer than the average N–O distances of free *C*-nitroso compounds (1.21 Å).[8] There is no significant dependence of the NO lengths upon varying the halo bridges. In all cases, and in contrast to the recently published analogous complexes,[2,3] the Re–O bonds (approx. 2.10 Å) are significantly longer than the Re–N bonds (approx. 1.99 Å), whereas all the bridging Re–X bonds in the complexes are similar in length. For better comparison, the most important structural parameters of all complexes are summarised in Table 1.
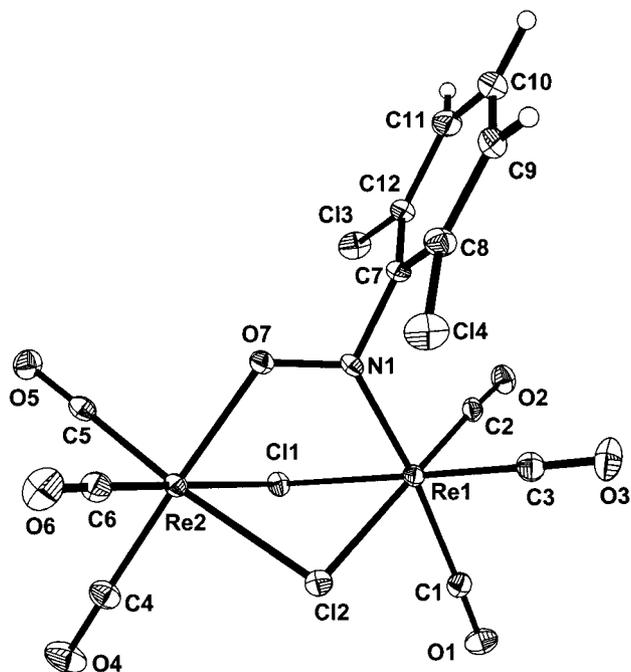
Figure 1. Molecular structure of **6a**. Selected bond lengths [Å] and angles [°]: Re(1)–N(1) 1.994(4), Re(2)–O(7) 2.124(4), Re(1)–Cl(1) 2.4914(14), Re(1)–Cl(2) 2.4726(14), Re(2)–Cl(1) 2.5024(14), Re(2)–Cl(2) 2.5056(14), O(7)–N(1) 1.282(6), N(1)–C(7) 1.457(6), Re(1)–C(1) 2.031(6), Re(1)–C(2) 1.952(6), Re(1)–C(3) 1.917(7), Re(2)–C(4) 1.928(6), Re(2)–C(5) 1.902(6), Re(2)–C(6) 1.908(6); N(1)–O(7)–Re(2) 120.2(3), O(7)–N(1)–Re(1) 123.9(3), O(7)–Re(2)–Cl(2) 82.82, O(7)–Re(2)–Cl(1) 82.82(11), N(1)–Re(1)–Cl(1) 84.52(13), N(1)–Re(1)–Cl(2) 85.96(13), Cl(2)–Re(1)–Cl(1) 80.83(5), Cl(1)–Re(2)–Cl(2) 79.98(5), O(7)–N(1)–C(7) 110.3(4), O(7)–N(1)–C(7)–C(8) 84.74.
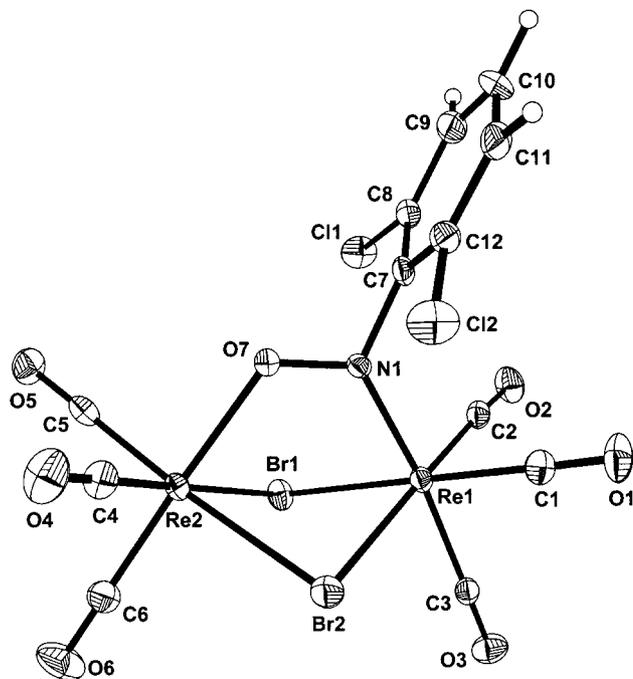
Figure 2. Molecular structure of **6b**. Selected bond lengths [Å] and angles [°]: Re(1)–N(1) 1.990(6), Re(2)–O(7) 2.116(5), Re(1)–Br(1) 2.6115(13), Re(1)–Br(2) 2.5965(11), Re(2)–Br(1) 2.6199(10), Re(2)–Br(2) 2.6305(12), O(7)–N(1) 1.299(8), N(1)–C(7) 1.451(9), Re(1)–C(1) 1.923(9), Re(1)–C(2) 1.936(9), Re(1)–C(3) 2.020(9), Re(2)–C(4) 1.902(8), Re(2)–C(5) 1.891(9), Re(2)–C(6) 1.907(9); N(1)–O(7)–Re(2) 121.8(4), O(7)–N(1)–Re(1) 126.5(5), O(7)–Re(2)–Br(2) 84.25(14), O(7)–Re(2)–Br(1) 83.58(4), N(1)–Re(1)–Br(1) 85.84(17), N(1)–Re(1)–Br(2) 86.73(17), Br(2)–Re(1)–Br(1) 82.89(4), Br(1)–Re(2)–Br(2) 82.07(4), O(7)–N(1)–C(7) 109.7(5), O(7)–N(1)–C(7)–C(12) 85.44.

The dihedral angles Re–O–N–C$_{Ph}$ of all complexes are smaller than 1.4°. The main difference between these complexes compared to those recently published[2,3] is that the dihedral angles O(7)–N(1)–C(7)–C(8/12) lie between 83.5–85.4°. This means that there is a near perpendicular orientation of the phenyl ring towards the plane formed by the atoms Re, O, N and Re. The consequence of this is the loss of dichroism. No Re–Re interaction is observed in any of the compounds, although the Re–Re distance varies with the size of the halogen bridges [Re(1)–Re(2) ≈ 3.47 (**6a**, **7a**, **8a**) and 3.54 Å (**6b**, **7b**, **8b**)].

It is worthwhile to emphasise that the orientation of the molecules described in this paper within the lattice is similar to that reported earlier[3] for the dichroic molecules. The triclinic crystal system is observed in both cases, although the packing of the dichroic molecules is closer, in particular with respect to the parallel phenyl rings of adjacent molecules, and the π-delocalisation is more widespread. Both effects lead to the significant anisotropy that is necessary for dichroism. Such close contact between the phenyl rings of the present molecules is not possible and the π-delocalisation is less. Therefore, it can be concluded that the absence of dichroism in **6a**,**b**–**8a**,**b** and **9a** is a result of the nonplanar arrangement of the phenyl rings with respect to the
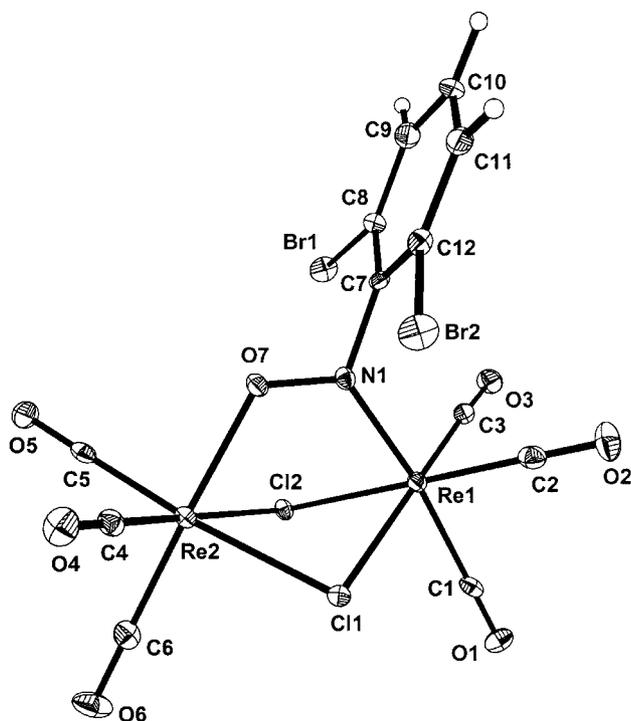
Figure 3. Molecular structure of **7a**. Selected bond lengths [Å] and angles [°]: Re(1)–N(1) 1.991(4), Re(2)–O(7) 2.126(4), Re(1)–Cl(1) 2.4801(12), Re(1)–Cl(2) 2.5000(12), Re(2)–Cl(1) 2.5117(12), Re(2)–Cl(2) 2.5144(11), O(7)–N(1) 1.282(5), N(1)–C(7) 1.460(7), Re(1)–C(1) 2.030(6), Re(1)–C(2) 1.923(6), Re(1)–C(3) 1.930(6), Re(2)–C(4) 1.903(5), Re(2)–C(5) 1.914(6), Re(2)–C(6) 1.920(6); N(1)–O(7)–Re(2) 120.3(3), O(7)–N(1)–Re(1) 126.2(3), O(7)–Re(2)–Cl(2) 82.82(9), O(7)–Re(2)–Cl(1) 83.78(11), N(1)–Re(1)–Cl(1) 86.47(12), N(1)–Re(1)–Cl(2) 84.65(12), Cl(2)–Re(1)–Cl(1) 80.87(4), Cl(1)–Re(2)–Cl(2) 79.98(5), O(7)–N(1)–C(7) 109.9(4), O(7)–N(1)–C(7)–C(12) 85.28.

Re$_2$NO plane. In addition, it is interesting to note that this is the only structural parameter that changes in comparison with the dichroic complexes.[3]

In summary, we have synthesised a novel series of analogous[2,3] neutral and dinuclear Re complexes with *C*-nitroso ligands. They also contain an unassisted μ_2-η^1:η^1-*N*,O bridge (type I, Scheme 1) and only single atoms (X = Cl, Br) as additional bridges. However, the complexes do not possess any dichroic properties. This is a result of the different orientation of the *C*-nitroso ligand, which is almost perpendicular to the Re–O–N–Re symmetry plane. This is caused by the two substituents (Z) in the two *ortho* positions of the phenyl ring. A considerably different reaction pathway has been found for the reaction of [Re(CO)$_5$X] (X = Cl, Br, I) with more sterically demanding *C*-nitroso ligands (e.g. 1-nitroso-2-naphthol), whereby HX or CO$_2$ elimination has been observed, and quite different mononuclear products have been obtained.[9]

Experimental Section

All operations were carried out under argon in dry solvents.[10] [Re(CO)$_5$X] (X = Cl, Br),[11] 2,6-dibromonitrosobenzene, 2,6-
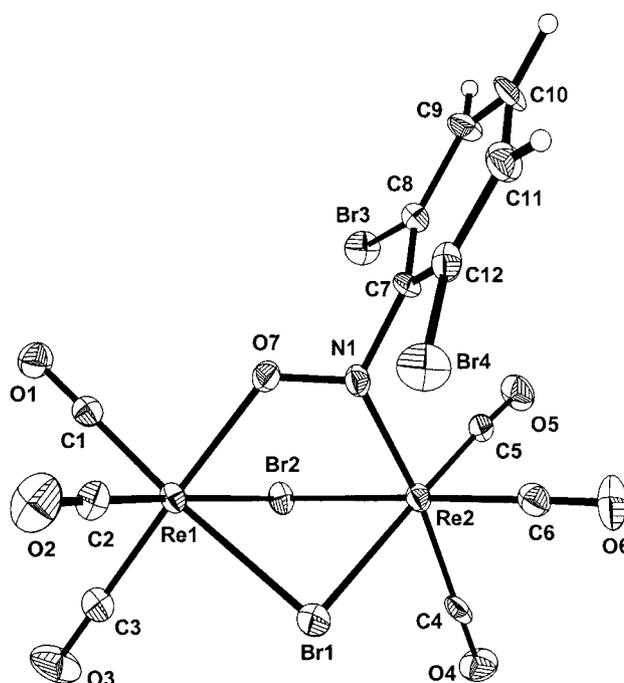
Figure 4. Molecular structure of **7b**. Selected bond lengths [Å] and angles [°]: Re(2)–N(1) 2.012(8), Re(1)–O(7) 2.123(7), Re(1)–Br(1) 2.6364(10), Re(1)–Br(2) 2.6292(10), Re(2)–Br(1) 2.6057(10), Re(2)–Br(2) 2.6182(10), O(7)–N(1) 1.279(9), N(1)–C(7) 1.453(12), Re(1)–C(1) 1.874(11), Re(1)–C(2) 1.902(10), Re(1)–C(3) 1.936(12), Re(2)–C(4) 2.043(12), Re(2)–C(5) 1.920(11), Re(2)–C(6) 1.908(11); N(1)–O(7)–Re(1) 123.4(6), O(7)–Re(1)–Br(2) 83.53(16), O(7)–Re(1)–Br(1) 84.39(16), N(1)–Re(2)–Br(1) 87.1(2), N(1)–Re(2)–Br(2) 85.6(2), Br(1)–Re(1)–Br(2) 82.51(3), Br(2)–Re(2)–Br(1) 81.72(3), O(7)–N(1)–C(7) 110.9(7), O(7)–N(1)–C(7)–C(12) 84.91.

dichloronitrosobenzene, 2,6-dibromo-4-chloronitrosobenzene and, 4-bromo-2,6-dichloronitrosobenzene were prepared according to a literature procedure.[12] NMR spectra were recorded with a Jeol Ex 400 (^{1}H: 399.78 MHz; ^{13}C: 100.54 MHz) or a Jeol Eclipse 270 MHz spectrometer (^{1}H: 270.17 MHz; ^{13}C: 67.94 MHz) in CDCl$_3$. Mass spectra were obtained with a Jeol Mstation JMS 700. IR and UV/ Vis spectra were measured with a Perkin–Elmer Spectrum One FT-IR or Perkin–Elmer Lambda 16 spectrometer. Elemental analyses were performed with a Heraeus Elementar Vario EL. For X-ray data see Table 2.

Synthesis of 6–9 from 1a,b. General Procedure: [Re(CO)$_5$X] (X = Cl, Br) (**1a,b**) and 4-Y-2,6-Z$_2$C$_6$H$_2$NO [Y = H, Z = Cl (**2**), Z = Br (**3**); Y = Cl, Z = Br (**4**); Y = Br, Z = Cl (**5**)] were dissolved in 20 mL of dichloromethane and heated for 40 h under reflux, whereby the solution turned green. The solvent was then evaporated and the green residue was purified by column chromatography (CH$_2$Cl$_2$).

μ_2-(η^2-*N*,O-2,6-Dichloronitrosobenzene)bis[μ-chlorotricarbonylrhenium(I)] (6a): Synthesised from 116 mg (0.321 mmol) of **1a** and 42.4 mg (0.240 mmol) of **3**. Yield: 51.7 mg (0.066 mmol, 41%) green crystals, m.p. 145 °C (dec.). ^{1}H NMR (399.78 MHz, CDCl$_3$): δ = 7.40 (d, ^3J = 6.54 Hz, 1 H, CH$_{arom.}$), 7.42 (d, ^4J = 0.66 Hz, 1 H, CH$_{arom.}$), 7.44 (d, ^4J = 2.04 Hz, 1 H, CH$_{arom.}$) ppm. ^{13}C NMR (100.53 MHz, CDCl$_3$): δ = 124.1 (CH$_{arom.}$), 129.2 (CH$_{arom.}$), 131.5 (CH$_{arom.}$), 161.3 (ON-C$_q$), 185.1 (CO), 192.2 (CO) ppm. IR (KBr): $\tilde{v}$ = 2965 cm^{-1} (w), 2405 (w), 2338 (w) 2098 (m), 2037 (vs), 2012 (vs), 1970 (s), 1949 (s), 1931 (vs), 1618 (m), 1566 (m), 1437 (m), 1350 (m), 1319 (m), 1293 (w), 1263 (w), 1207 (w), 1192 (s), 1154
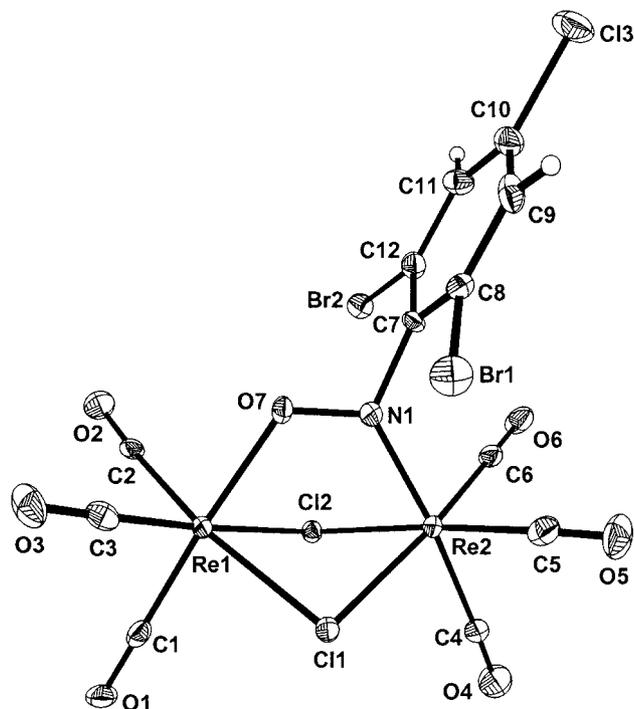
Figure 5. Molecular structure of **8a**. Selected bond lengths [Å] and angles [°]: Re(2)–N(1) 2.007(8), Re(1)–O(7) 2.099(6), Re(1)–Cl(2) 2.497(3), Re(1)–Cl(1) 2.500(2), Re(2)–Cl(2) 2.474(2), Re(2)–Cl(1) 2.482(2), O(7)–N(1) 1.297(10), N(1)–C(7) 1.440(11), Re(1)–C(1) 1.920(11), Re(1)–C(2) 1.927(10), Re(2)–C(3) 1.899(11), Re(2)–C(5) 2.018(10), Re(2)–C(5) 1.934(12), Re(2)–C(6) 1.941(11); N(1)–O(7)–Re(1) 120.8(5), O(7)–N(1)–Re(2) 123.3(6), O(7)–Re(1)–Cl(1) 83.50(18), O(7)–Re(1)–Cl(2) 83.67(18), N(1)–Re(2)–Cl(2) 85.4(2), N(1)–Re(2)–Cl(1) 85.0(2), Cl(2)–Re(1)–Cl(1) 79.27(8), Cl(2)–Re(2)–Cl(1) 80.06(8), O(7)–N(1)–C(7) 110.9(7), O(7)–N(1)–C(7)–C(12) 84.84.

Figure 6. Molecular structure of **8b**. Selected bond lengths [Å] and angles [°]: Re(1)–N(1) 2.001(12), Re(2)–O(7) 2.127(11), Re(1)–Br(3) 2.578(2), Re(1)–Br(4) 2.611(2), Re(2)–Br(3) 2.589(2), Re(2)–Br(4) 2.637(2), O(7)–N(1) 1.257(15), N(1)–C(7) 1.458(19), Re(2)–C(1) 1.963(19), Re(2)–C(2) 1.95(2), Re(2)–C(3) 1.903(17), Re(1)–C(4) 2.08(2), Re(1)–C(5) 1.908(19), Re(1)–C(6) 1.99(2); N(1)–O(7)–Re(2) 123.7(9), O(7)–N(1)–Re(1) 123.3(10), O(7)–Re(2)–Br(3) 83.5(3), O(7)–Re(2)–Br(4) 83.5(3), N(1)–Re(1)–Br(3) 86.6(3), N(1)–Re(1)–Br(4) 86.4(4), Br(3)–Re(1)–Br(4) 81.10(7), Br(3)–Re(2)–Br(4) 80.40(7), O(7)–N(1)–C(7) 109.9(11), O(7)–N(1)–C(7)–C(12) 83.49.

Table 1. Comparison of bond lengths [Å] and angles [°] of compounds **6a,b–8a,b**.

	6a	6b	7a	7b	8a	8b
Re–X$_{av}$	2.488	2.608	2.496	2.633	2.499	2.595
Re–O	2.124	2.116	2.126	2.123	2.099	2.127
Re–N	1.994	1.990	1.991	2.012	2.007	2.001
N–O	1.282	1.299	1.282	1.279	1.297	1.257
N–C$_{Ph}$	1.457	1.451	1.460	1.453	1.440	1.458
Re–X–Re$_{av}$	80.41	82.48	80.43	82.12	79.67	80.75
Re–N–O	123.9	126.5	126.2	123.4	123.3	123.3
Re–O–N	120.2	121.8	120.3	122.7	120.8	123.7
Re–O–N–C$_{Ph}$	1.03	0.53	1.34	0.78	0.27	0.82
O–N–C–C(8/12)	84.74	85.44	85.28	84.91	84.84	83.49

(w), 1101 (w), 1067 (w), 946 (w), 929 (w), 895 (w), 929 (w), 895 (w), 854 (w), 799 (m), 786 (s), 743 (w), 726 (w), 681 (w), 643 (w), 617 (m), 529 (w). IR (CH$_2$Cl$_2$): ṽ = 2090 cm^{-1} (m), 2033 (s), 2011 (vs), 1962 (s), 1941 (s). UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 376 nm (4685), 670 (7892). C$_{12}$H$_3$Cl$_4$NO$_7$Re$_2$ (787.30): calcd. C 18.30, H 0.38, N 1.78; found C 18.39, H 0.41, N 1.76. MS (DEI): m/z (%) = 786.3 (50) [M$^+$], 702.4 (38) [M$^+$ – 3 CO], 674.4 (36) [M$^+$ – 4 CO], 646.5 (92) [M$^+$ – 5 CO], 618.5 (100) [M$^+$ – 6 CO].

μ$_2$-(η^2-N,O-2,6-Dichloronitrosobenzene)bis[μ-bromotricarbonylrhenium(ɪ)] (6b): Synthesised from 152 mg (0.419 mmol) of **1b** and 43.4 mg (0.247 mmol) of **2**. Yield: 112 mg (0.128 mmol, 60%) green crystals; m.p. 147 °C (dec.). ^{1}H NMR (399.78 MHz, CDCl$_3$): δ = 7.38–7.44 (m, 3 H, CH$_{arom.}$) ppm. ^{13}C NMR (100.53 MHz, CDCl$_3$): δ = 126.3 (CH$_{arom.}$), 129.2 (CH$_{arom.}$), 130.8 (CH$_{arom.}$), 161.8 (ON-C$_q$), 184.8 (CO), 191.5 (CO) ppm. IR (KBr): ṽ = 3080 cm^{-1} (m), 2997 (w), 2094 (m), 2024 (vs), 2007 (vs), 1970 (s), 1930 (vs), 1614 (m), 1577 (s), 1475 (s), 1438 (vs), 1333 (s), 1290 (m), 1206 (s), 1161 (w), 1132 (w), 1100 (m), 1069 (w), 970 (w), 904 (m), 896 (w), 853 (w), 804 (m), 794 (s), 782 (vs), 732 (m), 640 (w), 617 (w), 581 (w), 550 (w), 522 (w). IR (CH$_2$Cl$_2$): ṽ = 2086 cm^{-1} (m), 2031 (s), 2011 (vs), 1962 (s), 1941 (s). UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 371 nm (4405), 702 (6409). C$_{12}$H$_3$Br$_2$Cl$_2$NO$_7$Re$_2$ (876.27): calcd. C 16.43, H 0.34, N 1.60; found C 16.34, H 0.39, N 1.62. MS (DEI): m/z (%) = 876.2 (18) [M$^+$], 848.2 (5) [M$^+$ – CO], 792.3 (13) [M$^+$ – 3 CO], 764.3 (10) [M$^+$ – 4 CO], 736.4 (21) [M$^+$ – 5 CO], 708.3 (24) [M$^+$ – 6 CO].

μ$_2$-(η^2-N,O-2,6-Dibromonitrosobenzene)bis[μ-chlorotricarbonylrhenium(ɪ)] (7a): Synthesised from 154 mg (0.427 mmol) of **1a** and 75.5 mg (0.285 mmol) of **3**. Yield: 106 mg (0.121 mmol, 57%) green crystals; m.p. 140 °C (dec.). ^{1}H NMR (399.78 MHz, CDCl$_3$): δ = 7.26 (d, ^3J = 8.35 Hz, 1 H, CH$_{arom.}$), 7.37 (d, ^3J = 7.91 Hz, 1 H, CH$_{arom.}$), 7.67 (t, ^3J = 8.13 Hz, 1 H, CH$_{arom.}$) ppm. ^{13}C NMR (100.53 MHz, CDCl$_3$): δ = 131.8 (CH$_{arom.}$), 132.3 (CH$_{arom.}$), 133.1 (CH$_{arom.}$), 163.7 (ON-C$_q$), 185.6 (CO), 192.1 (CO) ppm. IR (KBr): ṽ = 2953 cm^{-1} (m), 2924 (s), 2854 (m), 2337 (w), 2097 (m), 2059 (s), 2029 (vs), 2007 (s), 1966 (s), 1913 (vs), 1624 (m), 1566 (w), 1466 (w), 1432 (m), 1416 (m), 1376 (w), 1341 (w) 1316 (w), 1262 (w), 1199 (w), 1149 (w), 1100 (w), 923 (w), 893 (w), 861 (w), 774 (w), 731 (w), 688 (w), 660 (w), 662 (w). IR (CH$_2$Cl$_2$): ṽ = 2089 cm^{-1}

Table 2. Summary of crystallographic data for complexes **6a**,**b**–**8a**,**b**.[13,14]

	6a	**6b**	**7a**
Empirical formula	$C_{12}H_3Cl_4NO_7Re_2$	$C_{12}H_3Br_2Cl_2NO_7Re_2$	$C_{12}H_3Br_2Cl_2NO_7Re_2$
Formula weight [g mol^{-1}]	787.30	876.27	876.27
Crystal size [mm]	$0.38\times0.10\times0.009$	$0.02\times0.10\times0.20$	$0.02\times0.10\times0.20$
Crystal colour, habit	black block	black plate	black plate
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	8.7459(2)	8.8974(18)	8.8423(2)
b [Å]	10.2474(2)	10.310(2)	10.2035(2)
c [Å]	11.6216(3)	11.722(2)	11.8154(3)
α [°]	81.0843(11)	80.82(3)	81.5702(10)
β [°]	84.2984(11)	84.79(3)	83.8498(10)
γ [°]	65.4287(12)	66.31(3)	65.5635(8)
Volume [Å^3]	935.09(4)	971.7(3)	958.76(4)
Z	2	2	2
Density calcd. [g cm^{-3}]	2.740	2.995	3.035
Absorption coefficient [mm^{-1}]	13.532	16.865	17.094
$F(000)$	696	784	784
Index ranges	$-11 \le h \le 11$	$-10 \le h \le 9$	$-11 \le h \le 11$
	$-13 \le k \le 13$	$-11 \le k \le 0$	$-13 \le k \le 13$
	$-15 \le l \le 15$	$-13 \le l \le 13$	$-15 \le l \le 15$
θ Range [°]	3.17–27.48	2.18–23.97	3.15–27.49
Reflections collected	13095	3238	13564
Independent reflections	4208	3043	4342
Observed reflections	3753	2757	3715
Parameter/restrains	236/0	235/0	235/0
$R1/wR2$ (all data)	0.0404/0.886	0.0316/0.0736	0.0387/0.0658
$R1/wR2$ (final)	0.0341/0.0847	0.0268/0.0712	0.0295/0.0623
Goodness of fit	1.076	1.156	1.061
Min./max. ρ_e [e Å^3]	$-2.597/1.573$	$-1.450/0.591$	$-2.113/1.154$
Temperature [K]	200(2)	293(2)	200(2)
Diffractometer used	Nonius Kappa CCD	Nonius Mach 3	Nonius Kappa CCD
Scan type	area detection	area detection	area detection
Solution	SHELXS-97	SHELXS-97	SHELXS-97
Refinement	SHELXL-97	SHELXS-97	SHELXS-97

	7b	**8a**	**8b**
Empirical formula	$C_{12}H_3Br_4NO_7Re_2$	$C_{12}H_2Br_2Cl_3NO_7Re_2$	$C_{12}H_2Br_4ClNO_7Re_2$
Formula weight [g mol^{-1}]	965.18	910.72	999.64
Crystal size [mm]	$0.02\times0.11\times0.20$	$0.18\times0.11\times0.07$	$0.10\times0.08\times0.06$
Crystal colour, habit	black plate	black block	black plate
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	8.9736(2)	8.6204(17)	15.473(3)
b [Å]	10.2985(3)	9.1558(18)	39.231(8)
c [Å]	11.9402(5)	15.059(3)	14.732(3)
α [°]	81.6543(19)	75.97(3)	90
β [°]	84.3852(19)	74.55(3)	111.52(3)
γ [°]	66.3718(17)	64.54(3)	90
Volume [Å^3]	999.28(6)	1023.1(4)	8319(3)
Z	2	2	8
Density calcd. [g cm^{-3}]	3.208	2.956	3.192
Absorption coefficient [mm^{-1}]	20.132	16.150	19.476
$F(000)$	856	816	7104
Index ranges	$-10 \le h \le 10$	$-10 \le h \le 10$	$-18 \le h \le 18$
	$-12 \le k \le 12$	$-10 \le k \le 10$	$-46 \le k \le 45$
	$-14 \le l \le 14$	$-17 \le l \le 17$	$-17 \le l \le 11$
θ Range [°]	3.30–25.03	3.24–25.05	3.15–25.09
Reflections collected	11093	10395	49979
Independent reflections	3513	3559	7365
Observed reflections	2767	3218	5029
Parameter/restrains	235/0	245/0	487/0
$R1/wR2$ (all data)	0.0562/0.0924	0.0654/0.1584	0.0936/0.1590
$R1/wR2$ (final)	0.0385/0.0837	0.0613/0.1535	0.0543/0.1397
Goodness of fit	1.023	1.048	1.060
Min./max. ρ_e [e Å^3]	$-1.583/1.351$	$-4.346/3.900$	$-2.971/1.404$
Temperature [K]	200(2)	200(2)	200(2)
Diffractometer used	Nonius Kappa CCD	Nonius Kappa CCD	Nonius Kappa CCD
Scan type	area detection	area detection	area detection
Solution	SHELXS-97	SHELXS-97	SHELXS-97
Refinement	SHELXL-97	SHELXS-97	SHELXS-97

(m), 2033 (s), 2010 (vs), 1962 (m), 1940 (m). UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 260 nm (6266), 376 (2551), 699 (3973). C$_{12}$H$_3$Br$_2$Cl$_2$NO$_7$Re$_2$ (876.28): calcd. C 16.43, H 0.34, N 1.60; found C 16.26, H 0.37, N 1.54. MS (DEI): m/z (%) = 876.2 (62) [M$^+$], 848.2 (17) [M$^+$ – CO], 820.2 (4) [M$^+$ – 2 CO], 792.3 (45) [M$^+$ – 4 CO], 764.3 (23) [M$^+$ – 5 CO], 736.3 (23) [M$^+$ – 6 CO].

μ$_2$-(η^2-*N*,*O*-2,6-Dibromonitrosobenzene)bis[μ-bromotricarbonylrhenium(ɪ)] (7b): Synthesised from 425 mg (1.050 mmol) of **1b** and 139 mg (0.524 mmol) of **3**. Yield: 70.0 mg (0.073 mmol, 14%) green crystals; m.p. 144 °C (dec.). ^{1}H NMR (399.78 MHz, CDCl$_3$): δ = 7.27 (t, ^3J = 8.13 Hz, 1 H, CH$_{arom.}$), 7.38 (d, ^3J = 8.13 Hz, 1 H, CH$_{arom.}$), 7.61–7.64 (m, 1 H, CH$_{arom.}$) ppm. ^{13}C NMR (67.93 MHz, CDCl$_3$): δ = 132.9 (CH$_{arom.}$), 133.0 (CH$_{arom.}$), 133.6 (CH$_{arom.}$), 164.5 (ON-C$_q$), 185.2 (CO), 191.4 (CO) ppm. IR (KBr): $\tilde{v}$ = 3070 cm^{-1} (w), 2963 (m), 2925 (m), 2096 (m), 2058 (m), 2006 (vs), 1966 (s), 1929 (vs), 1611 (w), 1563 (s), 1571 (m), 1458 (m), 1437 (vs), 1420 (s), 1372 (w), 1343 (w), 1283 (vs), 1263 (vs), 1200 (s), 1154 (w), 1097 (s), 1060 (s), 1023 (s), 923 (w), 862 (m), 847 (s), 803 (vs), 803 (vs), 733 (s), 633 (m), 577 (w). IR (CH$_2$Cl$_2$): $\tilde{v}$ = 2088 cm^{-1} (m), 2032 (s), 2010 (vs), 1961 (m), 1943 (m). UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 260 nm (12896), 376 (5319), 699 (8244). C$_{12}$H$_3$Br$_4$NO$_7$Re$_2$ (965.18): calcd. C 14.93, H 0.31, N 1.45; found C 16.03, H 0.89, N 1.47. MS (DEI): m/z (%) = 964.1 (56) [M$^+$], 936.1 (28) [M$^+$ – CO], 880.1 (40) [M$^+$ – 3 CO], 852.2 (18) [M$^+$ – 4 CO], 824.2 (72) [M$^+$ – 5 CO], 796.2 (89) [M$^+$ – 6 CO].

μ$_2$-(η^2-*N*,*O*-2,6-Dibromo-4-chloronitrosobenzene)bis[μ-chlorotricarbonylrhenium(ɪ)] (8a): Synthesised from 132 mg (0.366 mmol) of **1a** and 73.0 mg (0.244 mmol) of **4**. Yield: 112 mg (0.123 mmol, 67%) green crystals; m.p. 129 °C (dec.). ^{1}H NMR (399.78 MHz, CDCl$_3$): δ = 7.66 (s, 2 H, CH$_{arom.}$) ppm. ^{13}C NMR (100.53 MHz, CDCl$_3$): δ = 131.2 (CH$_{arom.}$), 132.7 (CH$_{arom.}$), 133.9 (CH$_{arom.}$), 162.3 (ON-C$_q$), 187.5 (CO), 191.8 (CO) ppm. IR (KBr): $\tilde{v}$ = 3074 cm^{-1} (w), 2963 (w), 2089 (vs), 2031 (vs), 2000 (vs), 1949 (vs), 1922 (vs), 1614 (m), 1562 (m), 1538 (w), 1506 (w), 1407 (w), 1447 (w), 1419 (m), 1371 (m), 1337 (m), 1294 (w), 1195 (m), 1127 (m), 1059 (w), 925 (w), 897 (m), 862 (m), 806 (w), 747 (w), 735 (w), 642 (w), 580 (w), 562 (w). IR (CH$_2$Cl$_2$): $\tilde{v}$ = 2090 cm^{-1} (vs), 2034 (vs), 2010 (vs), 1962 (vs), 1941 (vs). UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 375 nm (4615), 707 (6304). C$_{12}$H$_2$Br$_2$Cl$_3$NO$_7$Re$_2$ (910.72): calcd. C 15.81, H 0.20, N 1.72; found C 16.21, H 0.21, N 1.63. MS (DEI): m/z (%) = 910.7 (15) [M$^+$], 826.7 (13) [M$^+$ – 3 CO], 798.7 (7) [M$^+$ – 4 CO], 770.7 (28) [M$^+$ – 5 CO], 742.8 (26) [M$^+$ – 6 CO].

μ$_2$-(η^2-*N*,*O*-2,6-Dibromo-4-chloronitrosobenzene)-bis[μ-bromotricarbonylrhenium(ɪ)] (8b): Synthesised from 137 mg (0.339 mmol) of **1b** and 73.0 mg (0.203 mmol) of **4**. Yield: 45.0 mg (0.045 mmol, 26%) green crystals; m.p. 135 °C (dec.). ^{1}H NMR (399.78 MHz, CDCl$_3$): δ = 7.64 (s, 2 H, CH$_{arom.}$) ppm. ^{13}C NMR (100.53 MHz, CDCl$_3$): δ = 131.2 (CH$_{arom.}$), 132.5 (CH$_{arom.}$), 133.9 (CH$_{arom.}$), 164.3 (ON-C$_q$), 186.3 (CO) ppm. IR (KBr): $\tilde{v}$ = 3073 cm^{-1} (w), 2963 (w), 2086 (s), 2034 (vs), 1999 (vs), 1954 (vs), 1923 (vs), 1615 (w), 1563 (m), 1507 (w), 1481 (w), 1461 (w), 1420 (w), 1373 (w), 1353 (w), 1329 (w), 1297 (w), 1126 (w), 1105 (w), 1054 (w), 1030 (w), 924 (m), 862 (m), 807 (m), 807 (m), 747 (m), 687 (w), 637 (w), 609 (w), 576 (w), 539 (w). IR (CH$_2$Cl$_2$): $\tilde{v}$ = 2086 cm^{-1} (vs), 2034 (vs), 2010 (vs), 1962 (vs), 1941 (vs). UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 373 nm (3476), 704 (3117). C$_{12}$H$_2$Br$_4$ClNO$_7$Re$_2$ (999.63): calcd. C 14.43, H 0.20, N 1.40; found C 15.87, H 0.39, N 1.66. MS (DEI): m/z (%) = 998.1 (1) [M$^+$], 914.2 (1) [M$^+$ – 3 CO], 858.1 (1) [M$^+$ – 5 CO], 830.3 (28) [M$^+$ – 6 CO].

μ$_2$-(η^2-*N*,*O*-2,6-Dichloro-4-bromonitrosobenzene)bis[μ-chlorotricarbonylrhenium(ɪ)] (9a): Synthesised from 139 mg (0.384 mmol) of **1a** and 65.3 mg (0.256 mmol) of **5**. Yield: 65.5 mg (0.076 mmol, 37%) green powder; m.p. 123 °C (dec.). ^{1}H NMR (270.16 MHz, CDCl$_3$): δ = 7.60 (s, 2 H, CH$_{arom.}$) ppm. ^{13}C NMR (100.53 MHz, CDCl$_3$): δ = 124.8 (CH$_{arom.}$), 130.3 (CH$_{arom.}$), 131.6 (CH$_{arom.}$), 160.2 (ON-C$_q$), 187.6 (CO), 191.9 (CO) ppm. IR (KBr): $\tilde{v}$ = 3116 cm^{-1} (m), 3082 (m), 2088 (vs), 2022 (vs), 1950 (vs), 1925 (vs), 1726 (w), 1615 (s), 1560 (s), 1548 (s), 1469 (s), 1429 (w),1390 (w), 1378 (m), 1365 (w), 1333 (w), 1297 (m), 1280 (w), 1263 (w), 1182 (s), 1077 (m), 927 (m), 898 (w), 858 (s), 812 (m), 787 (m), 752 (w), 659 (w), 615 (m), 590 (w), 534 (w), 540 (w). IR (CH$_2$Cl$_2$): $\tilde{v}$ = 2091 cm^{-1} (s), 2034 (vs), 2011 (vs), 1963 (vs), 1941 (vs). UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 385 nm (2952), 491 (1906). C$_{12}$H$_2$BrCl$_4$NO$_7$Re$_2$ (866.28): calcd. C 16.63, H 0.23, N 1.62; found C 17.28, H 1.38, N 1.55. MS (DEI): m/z (%) = 866.6 (52) [M$^+$], 782.6 (49) [M$^+$ – 3 CO], 754.6 (48) [M$^+$ – 4 CO], 726.7 (100) [M$^+$ – 5 CO], 698.6 (98) [M$^+$ – 6 CO].

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