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Dichroic, Dinuclear μ_2-(η^2-*NO*)-Nitrosoaniline-Bridged Complexes of Rhenium of the Type $[\{(CO)_3Re(\mu\text{-}X)\}_2ONC_6H_4NR_2]$ (X = Cl, Br, I; R = Me, Et)

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Abstract: A series of unusual dinuclear μ_2-(η^2-*NO*)-nitrosoaniline-bridged complexes $[\{(CO)_3Re(\mu\text{-}X)\}_2ONC_6H_4NR_2]$ (X = Cl, Br, I; R = Me, Et) with dichroic properties have been synthesised by reaction of pentacarbonylhalogenorhenium(I) $[(CO)_5ReX]$ (X = Cl, Br, I) with the corresponding nitrosoaniline derivatives $R_2NC_6H_4NO$ (R = Me, Et). The deeply coloured solutions in CH_2Cl_2 show broad UV/Vis absorptions from 595 to 620 nm depending on the halogen bridges and N substituents. Single crystals of all six compounds exhibit a pronounced linear dichroism. The molecular structures have been determined by single-crystal X-ray analyses. All the compounds contain two face-shared octahedra, with two halogens and one NO ligand as bridges. The NO ligand coordinates in a non-symmetrical η^2-like fashion with N or O coordination to each Re centre. Therefore, the *C*-nitroso group and the planar NC_2 moiety of NR_2 both lie almost exactly within the symmetry plane of the dinuclear complexes. These complexes belong to the novel and simple class of neutral dinuclear *C*-nitroso complexes that include the rare, non-assisted μ_2-(η^2-*NO*) ligand function and have only single halogen atoms in bridging positions.

Keywords: bridging ligands · dichroism · N,O ligands · nitrosoaniline · rhenium

Introduction

We recently reported the synthesis and molecular structure of the first neutral dinuclear *C*-nitroso-bridged complexes of rhenium of the type $[\{(CO)_3ReCl\}_2ONC_6H_4R]$ (R = H, NMe_2), which exhibit dichroic properties.[1] They were obtained by reactions of the μ_2-*O*-aminophenoxy complex $[(CO)_3Re(\mu_2\text{-}O{\frown}NH_2)]_2$[2] with *C*-nitroso compounds in the presence of stoichiometric amounts of $AlCl_3$, which occurred instead of the desired condensation reactions which would have given N=N bonds and hence the directed synthesis of azo dyes in the coordination sphere of a transition metal. The coordination chemistry of organic nitroso compounds RNO has been investigated extensively.[3]. There are three terminal and four bridging ligand functions of the RNO group (Scheme 1). In the first series, the η^2-*N,O* coordination mode (type I)[4] predominates over those with N (η^1-*N*; type II)[5 6] or O coordination (η^1-*O*; type III),[7] respectively. In the second series, the RNO ligand bridges two metal centres mainly (μ-η^1-*N*, type IV;[6] μ-η^1:η^2-*N,O*, type V;[8] μ-η^1:η^1-*N,O*, type VIa;[6,9,10] μ_2-η^2:η^2-*N,O*, type VII[8c,11]). However, bridging as many as four metals (μ_4-η^2:η^2-*NO*, type VIII[12]) is also possible. The non-assisted μ-η^1:η^1-*N,O* ligand function (type VIa) as a simple bridging ligand is less common. In most known examples, further secondary coordination by another donor system (for example, amido or carbonyl groups) forming a five-membered (type VIb)[13] or six-membered ring (type VIc)[14] is observed. To our knowledge, apart from a special case,[6] type VIa is observed only in cationic dinuclear complexes of Rh with two further μ_2-thiolato bridges.[9]

The complexes we reported recently[1] are the first simple, neutral and dinuclear *C*-nitroso complexes which have the rare, non-assisted μ-η^1:η^1-*N,O* ligand function (type VIa) and only single atoms as additional bridges. Moreover, they have been synthesised directly from nitroso compounds as starting materials. It is noteworthy that many nitroso complexes have been synthesised by reduction of organic nitro com-

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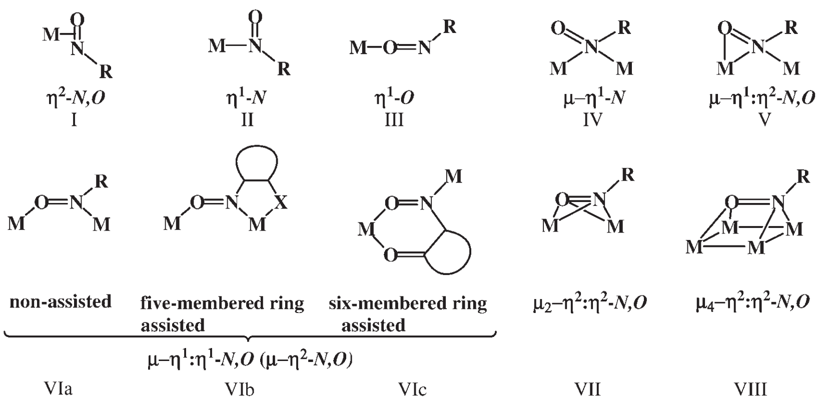
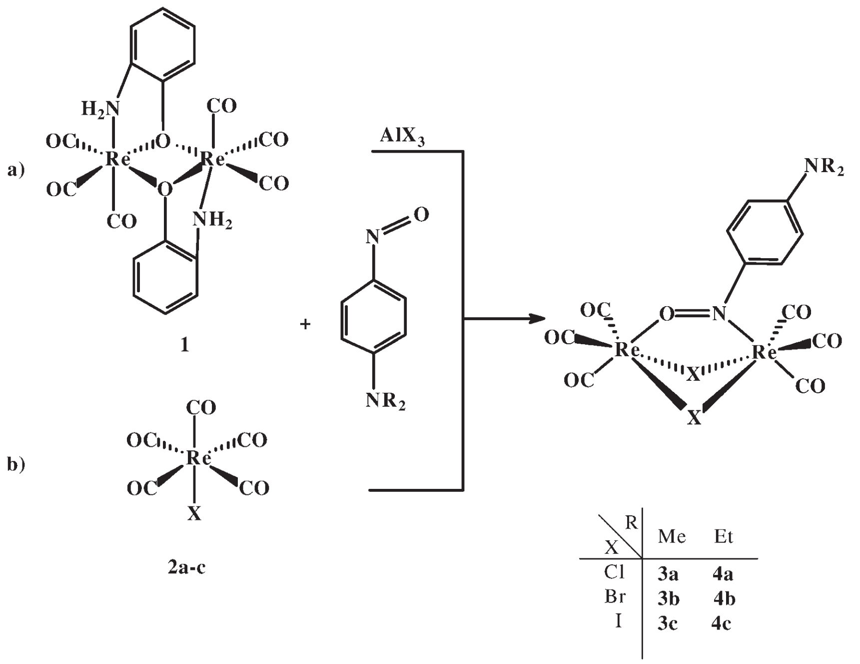


Scheme 1. Ligand functions of nitrosophenyl derivatives.

pounds. This reaction may proceed through an intermediate nitroso compound,[3] or by nitrosyl migration.[3] We have already described our first attempts using AlX_3 (X = Br, I) instead of $AlCl_3$.[1]. These have now resulted in the formation of the corresponding bromo- and iodo-bridged complexes. In addition, we proposed that monomeric $[Re(CO)_5X]$ (X = Cl, Br, I) could also be used as a starting material instead of the μ_2-*O*-aminophenoxy-bridged dimer $[(CO)_3Re(\mu_2\text{-}O^{\cap}NH_2)]_2$. Here we report our results using both synthetic routes leading to new dichroic complexes of the type $[\{(CO)_3ReX\}_2ONC_6H_4NR_2]$ (X = Cl, Br, I; R = Me, Et).



Scheme 2. Synthesis of the complexes **3a–c** and **4a–c** by routes a) and b).

Results and Discussion

The reaction of the dimeric μ_2-*O*-aminophenoxy complex **1**[2] with *N,N*-dimethyl-4-nitrosoaniline in the presence of stoichiometric amounts of $AlCl_3$[1] was repeated following the same procedure *but* using stoichiometric amounts of AlX_3 (X = Br, I). As in the case of $AlCl_3$, the halogen X was indeed incorporated into the products. The bis-μ_2-halogeno-bridged dinuclear complexes **3a–c** were obtained by a substitution reaction. In the analogous reaction using *N,N*-diethyl-4-nitrosoaniline, the corresponding complexes **4a–c** were obtained instead (Scheme 2a).

Moreover, when we used $Re(CO)_5X$ (X = Cl, Br, I) (**2a–c**) instead of **1** as simple but suitable starting materials for the reaction with the same *C*-nitroso compounds, we observed CO elimination and formation of the same products **3a–c** and **4a–c** (Scheme 2b). Almost all the reactions were carried out in boiling toluene; only in the case of **3b** was $CHCl_3$ used as a solvent. The yields increased from approximately 10–60% to over 80% when route b (Scheme 2) was used.

Compounds **3a–c** and **4a–c** are golden, gleaming, microcrystalline solids, which are stable in air for some days. They are soluble in THF, acetone, $CHCl_3$, CH_2Cl_2 and even toluene, but insoluble in nonpolar solvents such as pentane or hexane. The deep blue solutions formed in these solvents can be kept in air for some days without decomposition. In acetone, however, they appear to decompose and the solutions change to purple. In the UV/Vis spectra ($CHCl_3$) one very intensive broad absorption at λ = 599–653 nm due to a ligand-to-metal CT band ([NO-Re^I]) is observed. It is shifted to lower frequencies than the corresponding electronic transition (π-π^*NO) of the free ligands (R = Me: λ = 419 nm; (R = Et: 424 nm) and is solvochromic (**3a**: λ = 617 nm (in $CHCl_3$), 540 nm (in CH_3CN)). The spectral position of this absorption depends on the halogen, and its energy increases in the sequence $I < Br < Cl$ in parallel with the ionisation energies and ligand field parameters of the halide ions (16010 (**4c**), 16450 (**4b**), 16695 cm^{-1} (**4a**)). For a given metal ion (here Re^I with d^6), ligand-to-metal charge transfer energies decrease as the ligand becomes more readily oxidisable.[15]

Light reflected from crystalline powders of the substances shines in different colours. We have previously observed linear dichroism in crystals of similar compounds, so we also investigated the polarisation-dependent absorption properties of the compounds **3a–c** and **4a–c**. In all cases, only crystallites with diameters in the micrometre range were obtained. Visual inspection of these crystallites with polarised excitation light under a microscope clearly showed that absorption by all the compounds is polarisation-dependent. However, only for **4b** sufficiently large individual crystals suitable for spectroscopic measurements were obtained; complex **4b** had a pronounced linear dichroism with a maximum at 660 nm (Figure 1).

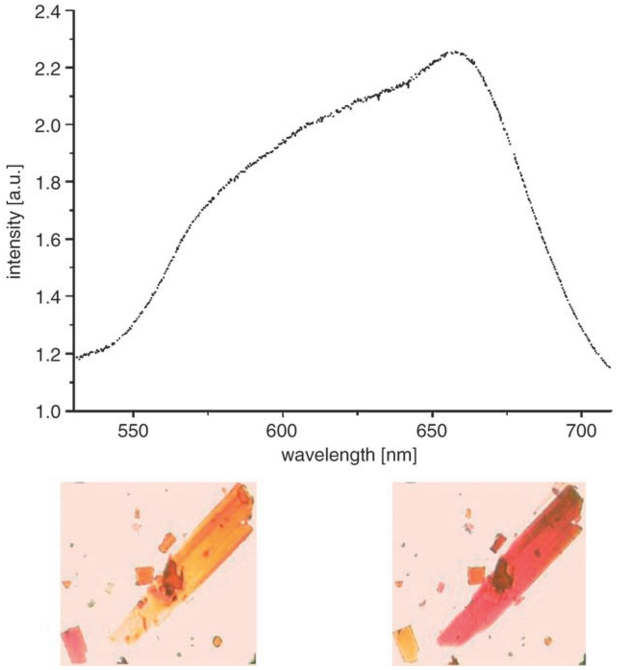


Figure 1. Top: linear dichroism spectrum of crystals of **4b**. This is a plot of the $I_{\perp}/I_{\parallel}$ ratio of the absorptions with mutually orthogonally polarised excitation light. The respective absorption values were obtained by normalising the observed transmitted light to the measured light intensity without a sample. Visual inspection of crystals from all the compounds investigated revealed a pronounced linear dichroism, but only **4b** yielded large enough single crystals for the recording of spectra. Bottom: **4b** crystals illuminated with two orthogonal polarisations.

The IR spectra of **3a–c** and **4a–c** in CH_2Cl_2 show four ν(CO) absorptions. As the NO group is bonded by N and O to different Re centres, the electronic situation at the two Re centres is different. This results in two different *facial*-$Re(CO)_3$ fragments, each with local C_{3v} symmetry. Therefore, we observed two separate ν(CO) patterns with A_1 and E symmetry. For electronic reasons the N-bonded $Re(CO)_3$ moiety should be more electron-rich and act as the better σ donor than the O-bonded one. Therefore, we assign the two absorptions at higher wavenumbers to the $\{(CO)_3Re{-}O\}$ fragment ($\tilde{\nu}$ = 2037–2047 cm^{-1} (A_1), 1941–1947 cm^{-1} (E)), and the two absorptions at lower wavenumbers ($\tilde{\nu}$ = 2021–2024 cm^{-1} (A_1), 1916–1919 cm^{-1} (E)) to the $\{(CO)_3Re{-}N\}$ fragment. Because several bonds lie too close together it is not possible to draw any conclusions about the substituents R or the bridging ligands X (X = Cl, Br, I), respectively. The corresponding IR spectra in KBr exhibit in some cases only three absorptions (**3a–c**), or even just two (**4c**), instead of the four observed in CH_2Cl_2. The NO groups of **3a–c** and **4a–c** are found to absorb at lower wavenumbers than that previously mentioned for **3a**.[1] On the basis of this series of complexes, we have now determined that ν(NO) lies in the 1392–1421 cm^{-1} region. This is a shift of approximately 130 cm^{-1} to lower frequencies with respect to the free *C*-nitroso ligand and is comparable with that of other RNO complexes.[3,16]

The ^1H NMR spectra (at room temperature) of **3a** (THF) and **3b** (CD_2Cl_2) show two singlets at δ = 3.39–3.55 ppm for the *N*-methyl protons (**3c** shows only one broad signal at δ = 3.31 ppm). Complex **3a** has four doublets of doublets for the different phenyl protons at δ = 6.95–8.53 ppm, whereas **3b** exhibits only four simple doublets in the same region. It is noteworthy that **3c** merely shows three broad signals in the aromatic region (δ = 6.99–8.67 ppm) with intensity ratio 1:1:2. However, at −80 °C, four doublets of doublets appear again, as in the case of **3a** (Figure 2). This observation can be explained by considering two mesomeric forms for the bridging *C*-nitroso ligand, depending on the additional halogen bridges (Scheme 3). In the case of the more electronegative chloro bridges the quinoid structure seems to be preferred, whereas in the case of iodo bridges the benzenoid form dominates. This allows the rotation

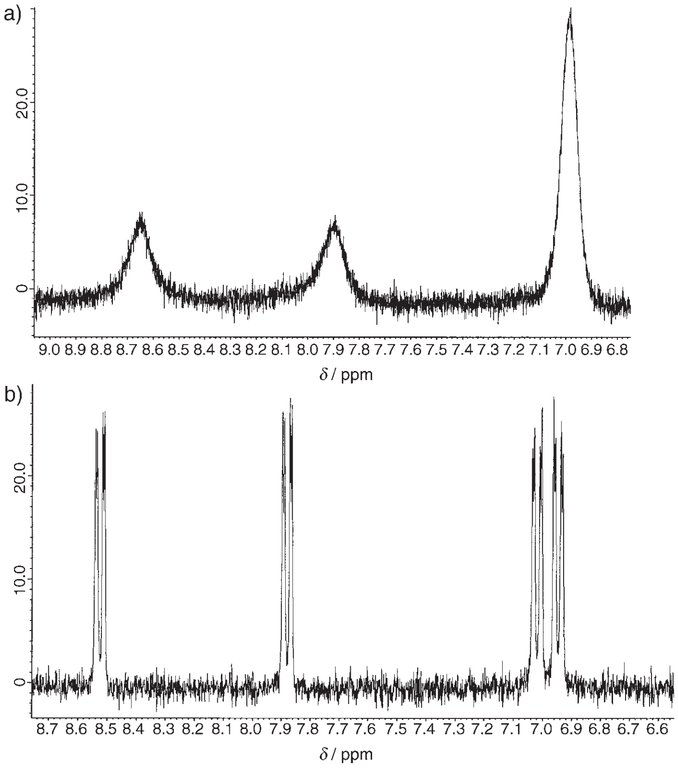
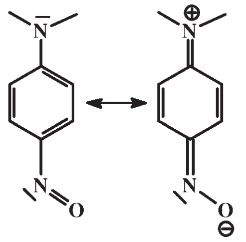


Figure 2. ^1H NMR spectra of **3c** at a) 25 °C and b) −80 °C.



Scheme 3. Two mesomeric forms of *N,N*-dimethylnitrosoaniline.

around the N–C_{Ph} axis, resulting in three broad signals. At −80 °C, however, this rotation is hindered and four doublets of doublets are observed.

Compounds **4a** and **4b** show two triplets for the CH_3 protons ($\delta \approx 1.4$ ppm) as well as two quartets (**4a**) or only one quartet (**4b**), at $\delta = 3.7$ ppm for the CH_2 protons with the exact integrals and usual coupling constants. **4c** exhibits only one singlet at $\delta = 1.53$ ppm (Me) and one quartet at $\delta = 3.66$ ppm (CH_2). The phenyl protons of **4a–c** show peaks in the range $\delta = 6.92$–8.63 ppm (four doublets of doublets for **4a** and **4b** and three broad signals for **4c** at room temperature).

In the ^{13}C NMR spectra of **3a–c**, each C atom of the NMe_2 group (**3b** is an exception with only one signal) and phenyl ring is found as a separate signal between $\delta = 30$–43 (Me) and $\delta = 117$–162 ppm (Ph). For the ethyl derivatives **4a–c**, only singlets at $\delta = 29.7$ (Me) and 48.2 ppm (CH_2), as well as the typical signals for the phenyl ring at $\delta = 114$–163 ppm, are observed. The signals for the CO ligands appear at $\delta = 187$–198 ppm as one (**4b**), two (**3b**, **4a**, **4c**), and four signals (**3a**, **4c**).

In the mass spectra (DEI-MS) of **3a–c** and **4a–c** the parent peaks as well as peaks corresponding to fragments resulting from the successive loss of up to six CO ligands are observed.

The compositions and structures of complexes **3a–c** and **4a–c** were confirmed by X-ray structure analysis. In all cases, single crystals were obtained by diffusion of pentane into solutions of **3a–c** and **4a–c** in $CHCl_3$. The molecular structures and selected bond lengths and angles are given in Figures 3–8.[17] They show two face-joined octahedra with two halogens and the NO group as bridging ligands. The N1−O1 distances are about 1.30 Å and clearly longer than the N−O distances in the two free *C*-nitroso compounds (≈1.21 Å[18]). The N−O distances do not depend on the halogen bridges. In all cases, the Re−O bonds (≈2.13 Å) are significantly shorter than the Re−N ones (≈2.20 Å), whereas all the Re−X bonds in the bridges of each compound are exactly (**3a**, **3b**) or nearly of the same length (**3c**, **4a–c**) (Tables 1 and 2).

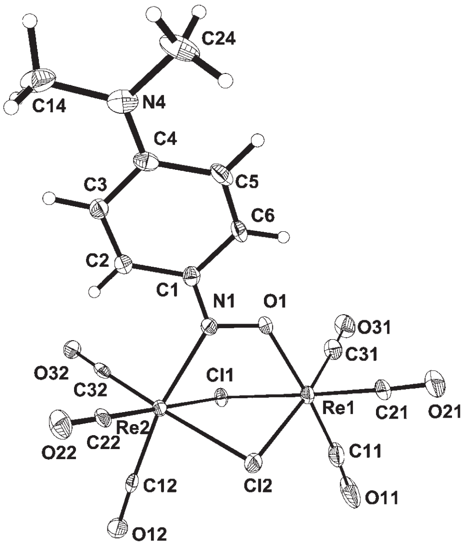


Figure 3. Molecular structure of **3a**. Selected bond lengths [Å] and angles [°]: Re1−C11 1.882(11), Re1−C21 1.887(10), Re1−C31 1.913(11), Re1−O1 2.131(6), Re1−Cl2 2.492(2), Re1−Cl1 2.497(2), C11−O11 1.175(13), C21−O21 1.161(11), C31−O31 1.132(11), Re2−C22 1.889(9), Re2−C32 1.891(9), Re2−C12 1.922(10), Re2−N1 2.208(7), Re2−Cl2 2.490(2), Re2−Cl1 2.493(2), N1-C1 1.347(11), C12−O12 1.145(10), C22−O22 1.170(10), C32−O32 1.169(10), O1−N1 1.319(8); C21-Re1-Cl2 95.6(3), Cl2-Re1-Cl1 80.69(7), O1-N1-C1 113.4(7), Re2-Cl1-Re1 90.36(7), Re2-Cl2-Re1 90.53(6).

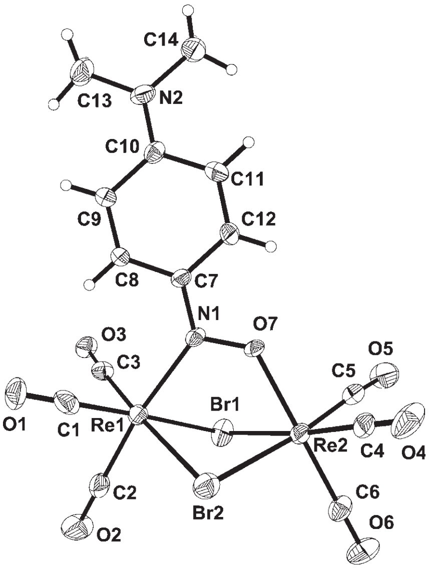


Figure 4. Molecular structure of **3b**. Selected bond lengths [Å] and angles [°]: Re1−C1 1.87(2), Re1−C2 1.910(16), Re1−C3 1.963(18), Re1−N1 2.218(12), Re1−Br2 2.6243(19), Re1−Br1 2.627(2), Re2−C4 1.89(2), Re2−C6 1.898(17), Re2−C5 1.91(2), Re2−O7 2.115(9), Re2−Br2 2.613(2), Re2−Br1 2.624(2), O3−C3 1.094(19), N1−O7 1.309(15), N1−C7 1.335(17), O1−C1 1.18(2), O2−C2 1.12(2), O4−C4 1.16(2), O5−C5 1.15(3), O6−C6 1.12(2); Br2-Re1-Br1 82.44(6), C3-Re1-Br2 176.4(5), Re1-N1-O7 130.4(8), O7-N1-C7 114.5(11), Re2-Br2-Re1 87.07(6), Re2-Br1-Re1 86.77(6).

With the exception of **3a** alone, the dihedral angles Re1-N1-O7/O1-Re2 and O7/O1-N1-C7-C8 are less than 5° and 3°, respectively. For **3a** they are much larger (6.5° and 10.1°, respectively). So far we have no explanation for this finding. As would be expected, for **3b** and **3c** and **4a–c** the NO group and the phenyl ring lie almost within the symmetry plane of the molecule. In **3a**, by contrast, the phenyl ring is slightly more twisted out of the plane. The observed crystal dichroism correlates with the arrangement of the molecules **3a–4c** in their unit cells, with alignment of the RNO units along a crystal plane. It is also noteworthy that both nitrogen atoms are exactly trigonal planar in geometry (sum of angles: for N1, ≈359.87°–360°; for N2/N4, ≈358.19°–360°), consistently with their sp^2 nature. No Re–Re interaction is

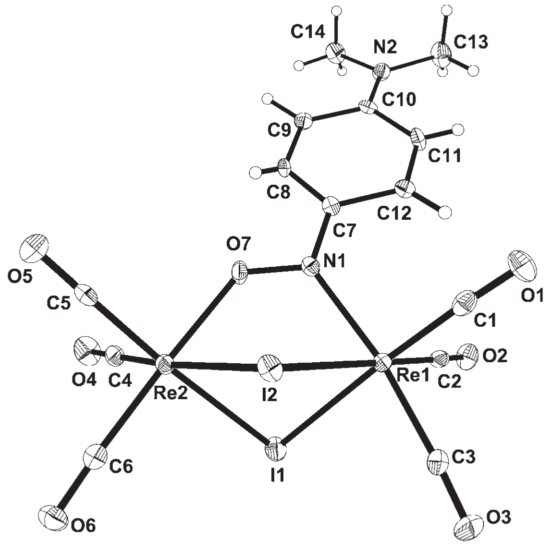


Figure 5. Molecular structure of **3c**. Selected bond lengths [Å] and angles [°]: Re1−C1 1.884(9), Re1−C2 1.909(10), Re1−C3 1.929(9), Re1−N1 2.205(6), Re1−I2 2.7999(10), Re1−I1 2.8219(8), Re2−C5 1.901(10), Re2−C6 1.911(9), Re2−C4 1.923(10), Re2−O7 2.134(5), Re2−I2 2.7984(10), Re2−I1 2.8039(9), O7−N1 1.280(8), N1−C7 1.377(10), O2−C2 1.155(11), O4−C4 1.131(11), O1−C1 1.178(11), O5−C5 1.162(12), O6−C6 1.154(10), O3−C3 1.149(11); I2-Re1-I1 85.02(2), O7-N1-C7 111.8(6), I2-Re2-I1 85.39(2), C5-Re2-I2 92.5(3), Re1-N1-O7 118.3(5), Re2-O7-N1 130.1(5), Re2-I2-Re1 83.08(2), Re2-I1-Re1 82.59(2).

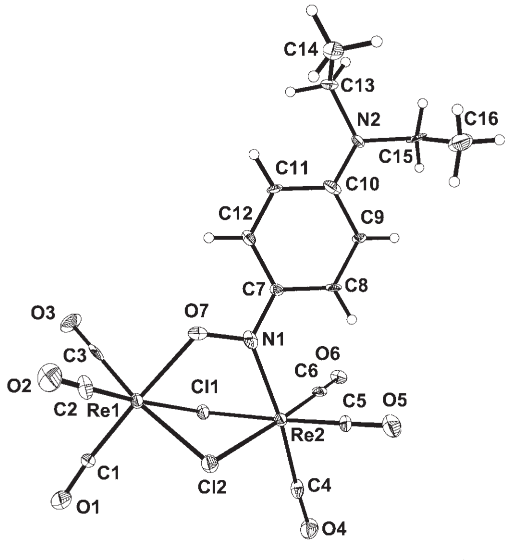


Figure 6. Molecular structure of **4a**. Selected bond lengths [Å] and angles [°]: Re1−C3 1.86(3), Re1−C1 1.88(2), Re1−C2 1.90(3), Re1−O7 2.165(15), Re1−Cl2 2.491(5), Re1−Cl1 2.510(5), Re2−C5 1.86(2), Re2−C6 1.88(2), Re2−C4 1.91(2), Re2−N1 2.174(19), Re2−Cl2 2.490(5), Re2−Cl1 2.503(5), O1−C1 1.18(2), O2−C2 1.15(3), O3−C3 1.20(3), O4−C4 1.19(3), O5−C5 1.17(2), O6−C6 1.17(2), O7−N1 1.28(2), N1−C7 1.37(3); C5-Re2-Cl2 91.4(6), Cl2-Re1-Cl1 81.31(17), Cl2-Re2-Cl1 81.47(6), O7-N1-C7 109.5(18), Re2-Cl1-Re1 89.67(17), Re2-Cl2-Re1 90.43(16).

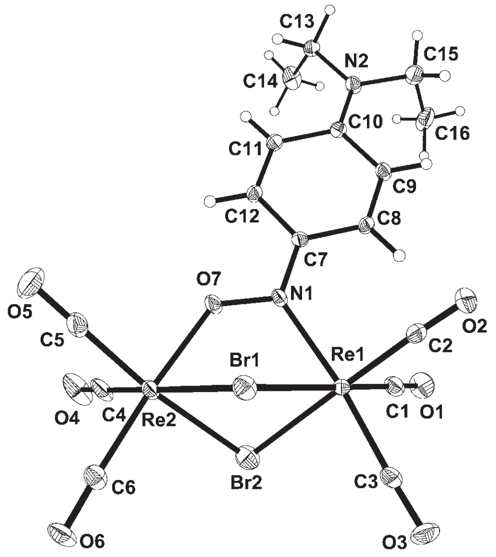


Figure 7. Molecular structure of **4b**. Selected bond lengths [Å] and angles [°]: Re1−C2 1.902(8), Re1−C1 1.907(8), Re1−C3 1.929(8), Re1−N1 2.199(6), Re1−Br2 2.5954(9), Re1−Br1 2.6097(9), Re2−O7 2.126(5), Re2−C5 1.906(10), Re2−C6 1.911(8), Re2−Br2 2.5852(10), Re2−Br1 2.6097(9), Re2−C4 1.908(10), O1−C1 1.141(10), O2−C2 1.149(10), O3−C3 1.155(10), O4−C4 1.142(10), O5−C5 1.139(12), O6−C6 1.152(10), O7−N1 1.308(8), N1−C7 1.360(9); C5-Re2-Br1 96.1(3), O7-N1-C7 113.2(6), Br2-Re1-Br1 82.86(3), Br2-Re2-Br1 83.28(3), Re2-Br1-Re1 86.57(2), Re2-Br2-Re1 87.62(3).

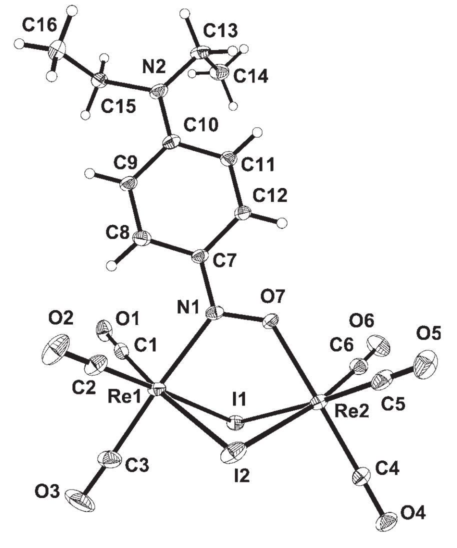


Figure 8. Molecular structure of **4c**. Selected bond lengths [Å] and angles [°]: Re1−C1 1.902(5), Re1−C2 1.908(5), Re1−C3 1.926(6), Re1−N1 2.196(4), Re1−I2 2.8075(4), Re1−I1 2.8232(4), Re2−C6 1.909(6), Re2−C4 1.910(5), Re2−C5 1.913(6), Re2−O7 2.139(3), Re2−I2 2.7998(4), Re2−I1 2.8094(4), O1−C1 1.145(6), O2−C2 1.143(6), O3−C3 1.139(7), O4−C4 1.145(6), O5−C5 1.141(7), O6−C6 1.147(7), O7−N1 1.297(5), N1−C7 1.354(6); C5-Re2-I2 94.04(18), I2-Re1-I1 83.512(11), O7-N1-C7 113.0(4), I2-Re2-I1 83.906(12), Re2-I1-Re1 82.372(10).

seen in any of the compounds (Re1−Re2 ≈ 3.50 Å (**3a**, **4a**), 3.60 Å (**3b**, **4b**), 3.70 Å (**3c**, **4c**)). Having discovered the prototype for novel dichroic compounds two years ago, we undertook specific investigations and succeeded in synthesising a series of neutral and dinuclear *N*,*N*-methyl and -ethyl substituted nitrosoaniline complexes. They contain the non-

Table 1. Crystallographic data for **3a–c** and **4a–c**.[17]

	3a	**3b**	**3c**	**4a**	**4b**	**4c**
empirical formula	$C_{14}H_{10}Cl_2N_2O_7Re_2$	$C_{14}H_{10}Br_2N_2O_7Re_2$	$C_{14}H_{10}I_2N_2O_7Re_2$	$C_{16}H_{14}Cl_2N_2O_7Re_2$	$C_{16}H_{14}Br_2N_2O_7Re_2$	$C_{16}H_{14}I_2N_2O_7Re_2$
formula weight [g mol^{-1}]	761.54	850.46	944.44	789.59	878.51	972.52
crystal size [mm^3]	0.10 × 0.05 × 0.004	0.2 × 0.2 × 0.05	0.30 × 0.17 × 0.10	0.01 × 0.03 × 0.15	0.04 × 0.14 × 0.20	0.02 × 0.03 × 0.22
crystal colour and habit	red plate	yellow plate	blue plate	blue plate	blue plate	golden plate
crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P1-$	$P1-$	$P2_1/n$
a [Å]	6.4246(2)	15.770(3)	15.610(3)	9.8381(6)	9.84620(10)	6.60280(10)
b [Å]	9.5409(3)	9.517(3)	9.466(2)	10.1253(6)	10.1865(2)	31.6970(3)
c [Å]	16.6048(4)	13.584(3)	14.113	12.0653(9)	12.1324(2)	10.75220(10)
α [°]	83.7500(13)	90.00	90.00	88.0029(18)	87.2574(7)	90.00
β [°]	83.0888(13)	92.55(3)	91.14(3)	74.913(2)	75.5512(8)	95.3841(4)
γ [°]	70.9047(12)	90.00	90.00	64.779(3)	66.0564(8)	90.00
volume [Å^3]	952.20(5)	2036.6(7)	2084.9(7)	1045.83(12)	1075.00(3)	2240.39(4)
Z	2	4	4	2	2	4
ρ_{calcd} [g cm^{-3}]	2.65620(14)	2.774	3.009	2.507	2.714	2.883
μ [mm^{-1}]	13.020	15.837	14.599	11.860	15.006	13.590
$F(000)$	696	1536	1680	728	800	1744
index ranges	$-7 \leq h \leq 7$, $-11 \leq k \leq 11$, $-19 \leq l \leq 19$	$-17 \leq h \leq 17$, $-10 \leq k \leq 8$, $-10 \leq l \leq 15$	$-18 \leq h \leq 18$, $-11 \leq k \leq 11$, $-16 \leq l \leq 16$	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-13 \leq l \leq 13$	$-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-15 \leq l \leq 15$	$-8 \leq h \leq 8$, $-41 \leq k \leq 40$, $-13 \leq l \leq 13$
θ range [°]	3.41–25.00	6.92–23.25	3.14–25.12	3.27–23.00	3.25–27.51	3.16–27.49
reflections collected	14429	6851	29711	9806	18922	32241
independent reflections	3364	2678	3690	2900	4823	5116
observed reflections	2737	2191	3311	2160	4130	4485
parameter/restraints	246/0	245/0	261/0	262/19	263/0	281/0
R_1/wR_2 (all data)	0.0471/0.0731	0.0697/0.1754	0.0413/0.1012	0.0808/0.1339	0.0445/0.0962	0.0348/0.0528
R_1/wR_2 (final)	0.0331/0.0694	0.0598/0.1620	0.0362/0.0983	0.0555/0.1274	0.0360/0.0914	0.0267/0.0503
goodness of fit	1.112	0.987	1.095	1.144	1065	1.083
min./max. ρ_e [e Å^3]	−1.125/1.321	−1.883/3.281	−1.966/2.240	−1.704/2.772	−2.266/1930	−1.715/0.915
temperature [K]	200(2)	193(2)	293(2)	200(2)	200(2)	200(2)
diffractometer used	Nonius Kappa CCD	Siemens CCD	Siemens CCD	Nonius Kappa CCD	Nonius Kappa CCD	Nonius Kappa CCD
scan type	area detection	area detection	area detection	area detection	area detection	area detection
solution	SHELXS-97	SHELXS-97	SHELXS-97	SHELXS-97	SHELXS-97	SHELXS-97
refinement	SHELXL-97	SHELXS-97	SHELXS-97	SHELXS-97	SHELXS-97	SHELXS-97

assisted μ_2-(η^2-*N*,*O*) bridge (type VIa, Scheme 1) and only single atoms (here X = Cl, Br, I) as additional bridges. In addition, they have been synthesised directly using nitroso compounds and their substitution reaction with two different starting materials (Scheme 2).

The hypothesis we proposed previously[1] to explain the observed dichroism has been proven by the synthesis of the new complexes reported here. It is now safe to assume that this dichroism originates from the special ligand function of the nitroso compound, and its placement within the plane of symmetry. In a very similar structure for dinuclear dialkylnitrosoamine complexes (with an *N*-nitroso ligand) of Cu^{II} with the same μ_2-(η^2-*N*,*O*) ligand function[19], however, the NO group does not lie parallel to the Cu–Cu axis, and therefore the single crystals do not exhibit any dichroism in the visible region. We plan to synthesise similar compounds of Re^I with one or two bulky substituents in both positions *ortho* to the N$-$C$_{Ph}$ bond. We believe that the phenyl plane will be orthogonally inclined to the Re–Re axis, resulting in the loss of dichroism.

Table 2. Comparison of bond lengths [Å] and angles [°] of compounds **3a–c** and **4a–c**.

	3a	**3b**	**3c**	**4a**	**4b**	**4c**
Re−X_{av}	2.491	2.617	2.810	2.500	2.602	2.815
Re−O	2.131(6)	2.115(9)	2.134(5)	2.165(15)	2.126(5)	2.139(3)
Re−N	2.208(7)	2.218(12)	2.205(6)	2.174(19)	2.199(6)	2.196(4)
N−O	1.319(8)	1.309(15)	1.280(8)	1.280(2)	1.308(8)	1.297(5)
N−C_{Ph}	1.347(11)	1.335(17)	1.377(10)	1.37(3)	1.360(9)	1.354(6)
Re-X-Re_{av}	90.45	86.92	82.83	90.05	87.12	84.71
Re-N-O	116.9(5)	116.1(8)	118.3(5)	119.4(13)	116.8(4)	118.7(3)
Re-O-N	124.6(5)	128.2(7)	130.1(5)	123.0(13)	126.8(4)	129.1(3)
Re-O-N-C	6.54	0.30	0.08	4.13	5.31	1.48

Experimental Section

All operations were carried out under Ar in dry solvents.[20] $[Re(CO)_5X]$ (X = Cl, Br, I) was prepared according to the literature procedure.[21,22] 4-Nitroso-*N*,*N*-dimethylaniline and 4-nitroso-*N*,*N*-diethylaniline were used as purchased from Alfa Aesar and Lancaster. NMR spectra were recorded on a JEOL Ex 400 spectrometer (^{1}H: 399.78 MHz; ^{13}C: 100.54 MHz) in $[D_8]$THF and CD_2Cl_2 (25 °C, TMS). Mass spectra were obtained on a JEOL MStation JMS-700. IR and UV/Vis spectra were measured on a Perkin Elmer Spectrum One FT-IR or Perkin Elmer Lambda 16 spectrometer, respectively. Elemental analyses were performed on a Heraeus Elementar Vario EL. Linear dichroism measurements of microcrystallites were made using a high numerical aperture objective (100× oil immersion, NA 1.4) on an inverted microscope (Zeiss Axiovert 200) equipped with a spectrograph and a CCD camera (Acton Research SP-150 and Pixel Vision SpectraVideo). The crystallites were illuminated with the light from a standard halogen lamp which was passed through a Glen-Taylor polariser.

Compounds **3a–c** and **4a–c** can be prepared by reaction of the corresponding nitrosoaniline derivative with the Re dimer **1** (route a, Scheme 2) or with the halogenorhenium carbonyls **2a–c** (route b, Scheme 2). Route b is more convenient as it results in higher yields (almost 90 %), and requires simple monomeric starting materials which can be purchased easily. Compound **1** was prepared according to the literature.[2] Therefore, the procedures given here in detail follow route b, and route a as described without any repetition of spectroscopic data.

Synthesis of 3a–c and 4a–c from 2a–c

General procedure: $[Re(CO)_5X]$ (**2a–c**) and $R_2NC_6H_4NO$ (R = Me, Et) were dissolved in toluene (20 mL) and heated at 100 °C for 2 h, whereupon the solution turned deep blue. The solvent was evaporated, and the blue residue was purified by column chromatography (CH_2Cl_2).

Complex 3a: Complex **2a** (143.1 mg, 0.396 mmol), R = Me (29.7 mg, 0.198 mmol). Yield: 145.4 mg (0.190 mmol, 96 %), blue-red dichroic crystals. M.p. 205–207 °C; ^{1}H NMR ($[D_8]$THF, 399.78 MHz): δ = 3.54 (s, 3H; CH_3), 3.55 (s, 3H; CH_3), 7.24 (dd, ^{3}J = 10.16 Hz, ^{4}J = 2.64 Hz, 1H; $CH_{arom.}$), 7.41 (dd, ^{3}J = 10.27 Hz, ^{4}J = 2.75 Hz, 1H; $CH_{arom.}$), 8.02 (dd, ^{3}J = 10.22 Hz, ^{4}J = 2.64 Hz, 1H; $CH_{arom.}$), 8.51 ppm (dd, ^{3}J = 10.22 Hz, ^{4}J = 2.64 Hz, 1H; $CH_{arom.}$); ^{13}C NMR ($[D_8]$THF, 100.53 MHz): δ = 30.61 (N−CH_3), 43.08 (N−CH_3), 117.98 ($CH_{arom.}$), 119.23 ($CH_{arom.}$), 128.22 ($CH_{arom.}$), 139.44 ($CH_{arom.}$), 160.90 (N−C_q), 161.60 (ON−C_q), 191.84 (CO), 192.01 (CO), 195.26 (CO), 198.40 ppm (CO); IR (KBr): $\tilde{\nu}$ = 3099 (w), 2938 (w), 2857 (w), 2733 (w), 2040 (vs, CO, A_1), 2021 (vs, CO, A_1), 1904 (vs, CO, *E*), 1605 (w), 1392 (s, NO), 1394 (s), 1331 (s), 1171 (vs), 1130 (m), 931 (w), 879 (w), 834 (m), 741 (s), 644 (w), 566 (w), 518 (w), 494 (w), 466 (w), 399 cm^{-1} (w); IR (CH_2Cl_2): $\tilde{\nu}$ = 2041 (s, CO, A_1), 2024 (vs, CO, A_1), 1946 (m, CO, *E*), 1917 cm^{-1} (s, CO, *E*); UV/Vis ($CHCl_3$): λ_{max} (ε) = 265 (10638), 364 (3449), 617 nm (32570 $mol^{-1} m^3 cm^{-1}$); elemental analysis (%) calcd for $C_{14}H_{10}Cl_2N_2O_7Re_2$ (761.54): C 22.08, H 1.32, N 3.68; found: C 22.85, H 1.49, N 3.63; MS (DEI, 70 eV): *m*/*z* (%): 762.5 (56) [M^+], 678.4 (9) [M^+−3CO), 650.4 (62) [M^+−4CO], 622.4 (35) [M^+−5CO], 594.4 (29) [M^+−6CO].

Complex 3b: Complex **2b** (136.9 mg, 0.337 mmol), R = Me (25.4 mg, 0.169 mmol). Yield: 87.7 mg (0.103 mmol, 61 %), blue-golden dichroic crystals. M.p. 208–210 °C; ^{1}H NMR (CD_2Cl_2, 399.78 MHz): δ = 3.39 (s, 3H; CH_3), 3.41 (s, 3H; N−CH_3), 6.96 (d, ^{3}J = 9.87 Hz, 1H; $CH_{arom.}$), 7.04 (d, ^{3}J = 10.11 Hz, 1H; *o*-$CH_{Arom.}$), 8.01 (d, ^{3}J = 9.91 Hz, 1H; $CH_{arom.}$), 8.63 ppm (d, ^{3}J = 10.31 Hz, 1H; $CH_{arom.}$); ^{13}C NMR (CD_2Cl_2, 100.53 MHz): δ = 42.71 (N−CH_3), 115.37 ($CH_{arom.}$), 117.30 ($CH_{arom.}$), 127.72 ($CH_{arom.}$), 139.46 ($CH_{arom.}$), 159.51 (N−C_q), 162.35 (ON−C_q), 190.05 (CO), 194.14 ppm (CO); IR (KBr): $\tilde{\nu}$ = 2960 (s), 2923 (s), 2857 (s), 2038 (m, CO, A_1), 2022 (vs, CO, A_1), 1907 (vs, CO, *E*), 1604 (w), 1458 (m), 1393 (m, NO), 1327 (m), 1308 (m), 1296 (m), 1263 (m), 1172 (vs), 1131 (m), 1104 (m), 1060 (w), 1024 (w), 932 (w), 878 (w), 832 (m), 804 (m), 740 (m), 628 (m), 564 (m), 515 (m), 493 (m), 464 (m), 398 (m), 326 (m), 302 cm^{-1} (m); IR (CH_2Cl_2): $\tilde{\nu}$ = 2041 (s, CO, A_1), 2023 (vs, CO, A_1), 1947 (m, CO, *E*), 1917 cm^{-1} (s, CO, *E*); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 269 (9674), 359 (2527), 610 nm (30195 $mol^{-1} m^3 cm^{-1}$); elemental analysis (%) calcd for $C_{14}H_{10}Br_2N_2O_7Re_2$ (850.46): C 19.77, H 1.85, N 3.29; found: C 20.31, H 1.24, N 3.18; MS (DEI, 70 eV): *m*/*z* (%): 849.8 (10) [M^+], 765.7 (5) [M^+−3CO], 737.8 (11) [M^+−4CO], 709.8 (7) [M^+−5CO], 681.8 (7) [M^+−6CO].

Complex 3c: Complex **2c** (123.1 mg, 0.272 mmol), R = Me (20.4 mg, 0.136 mmol). Yield: 99.5 mg (0.105 mmol, 78 %), blue-golden dichroic crystals. M.p. 210–212 °C; ^{1}H NMR (CD_2Cl_2, 399.78 MHz, 25 °C): δ = 6.99 (br, 2H; $CH_{arom.}$), 7.90 (br, 1H; $CH_{arom.}$), 7.67 ppm, (br, 1H; $CH_{arom.}$); ^{1}H NMR (CD_2Cl_2, 399.78 MHz, −80 °C): δ = 3.31 (s, 6H; CH_3), 6.95 (dd, ^{3}J = 10.44 Hz, ^{4}J = 2.75 Hz, 1H; $CH_{arom.}$), 7.02 (dd, ^{3}J = 10.11 Hz, ^{4}J = 2.42 Hz, 1H; $CH_{arom.}$), 7.90 (dd, ^{3}J = 10.41 Hz, ^{4}J = 2.73 Hz, 1H; $CH_{arom.}$), 8.53 ppm (dd, ^{3}J = 10.11 Hz, ^{4}J = 2.31 Hz, 1H; $CH_{arom.}$); ^{13}C NMR (CD_2Cl_2, 100.53 MHz): δ = 42.69 (N−CH_3), 42.76 (N−CH_3), 114.55 ($CH_{arom.}$), 116.41 ($CH_{arom.}$), 126.95 ($CH_{arom.}$), 138.41 ($CH_{arom.}$), 157.98 (N−C_q), 161.29 (ON−C_q), 187.60 (CO), 188.48 (CO), 192.59 (CO), 197.50 ppm (CO); IR (KBr): $\tilde{\nu}$ = 2925 (w), 2859 (w), 2034 (s, CO, A_1), 2020 (vs, CO, A_1), 1907 (vs, CO, *E*), 1602 (m), 1558 (w), 1454 (w), 1393 (m, NO), 1319 (w), 1295 (w), 1170 (m), 1132 (w), 927 (w), 872 (w), 831 (w), 741 (w), 631 (w), 559 (w), 513 (w), 488 cm^{-1} (w); IR (CH_2Cl_2): $\tilde{\nu}$ = 2037 (m, CO, A_1), 2021 (vs, CO, A_1), 1947 (m, CO, *E*), 1919 cm^{-1} (s, CO, *E*); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 274 (11562), 297 (10930), 362 (4082), 624 (35553), 653 nm(34036 $mol^{-1} m^3 cm^{-1}$); elemental analysis (%) calcd for $C_{14}H_{10}I_2N_2O_7Re_2$ (944.46): C 17.80, H 1.07, N 2.97; found: C 17.91, H 1.06, N 2.91; MS (DEI, 70 eV): *m*/*z* (%): 944.0 (100) [M^+], 860.0 (26) [M^+−3CO], 804.0 (73) [M^+−5CO], 778.0 (45) [M^+−6CO].

Complex 4a: Complex **2a** (140.8 mg, 0.389 mmol), R = Et (34.7 mg, 0.195 mmol). Yield: 102.0 mg (0.130 mmol, 64 %) blue-golden dichroic crystals. M.p. 190 °C ; ^{1}H NMR (CD_2Cl_2, 399.78 MHz): δ = 1.42 (t, ^{3}J = 7.28 Hz, 3H; CH_3), 1.44 (t, ^{3}J = 7.28 Hz, 3H; CH_3), 3.73 (q, ^{3}J = 7.24 Hz, 2H; CH_2), 3.74 (q, ^{3}J = 7.24 Hz, 2H; CH_2), 6.94 (dd, ^{3}J = 10.11 Hz, ^{4}J = 2.84 Hz, 1H; $CH_{arom.}$), 7.02 (dd, ^{3}J = 10.11 Hz, ^{4}J = 2.84 Hz, 1H; $CH_{arom.}$), 8.03 (dd, ^{3}J = 10.11 Hz, ^{4}J = 2.64 Hz, 1H; $CH_{arom.}$), 8.57 ppm (dd, ^{3}J = 10.11 Hz, ^{4}J = 2.64 Hz, 1H; $CH_{arom.}$); ^{13}C NMR (CD_2Cl_2, 100.53 MHz): δ = 29.76 (CH_3), 48.27 (CH_2), 115.62 ($CH_{arom.}$), 117.60 ($CH_{arom.}$), 128.07 ($CH_{arom.}$), 139.78 ($CH_{arom.}$), 158.39 (N−C_q), 161.22 (ON−C_q), 187.18 (CO), 190.87 ppm (CO); IR (KBr): $\tilde{\nu}$ = 3091 (w), 2963 (w), 2924 (m), 2853 (m), 2044 (s, CO, A_1), 2019 (vs, CO, A_1), 1939 (vs, CO, *E*), 1908 (vs, CO, *E*), 1607 (m), 1551 (w), 1498 (w), 1462 (w), 1421 (m, NO), 1380 (w), 1330 (s), 1309 (m), 1184 (s), 1163 (s), 1130 (m), 1089 (m), 1005 (w), 877 (w), 832 (m), 740 (w), 724 (m), 650 (w), 571 (w), 517 (w), 509 cm^{-1} (w); IR (CH_2Cl_2): $\tilde{\nu}$ = 2041 (s, CO, A_1), 2024 (vs, CO, A_1), 1946 (m, CO, *E*), 1916 cm^{-1} (s, CO, *E*); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 265 (10104), 317 (6418), 360 (3297), 599 nm (32898 $mol^{-1} m^3 cm^{-1}$); elemental analysis (%) calcd for

$C_{16}H_{14}Cl_2N_2O_7Re_2$ (789.61): C 24.34, H 1.79, N 3.55; found: C 24.21, H 1.80, N 3.49; MS (DEI, 70 eV): m/z (%): 789.7 (31) $[M^+]$, 677.8 (38) $[M^+-4\,CO]$, 647.8 (12) $[M^+-5\,CO]$, 619.8 (14) $[M^+-6\,CO]$.

Complex 4b: Complex **2b** (132.4 mg, 0.326 mmol), R = Et (29.1 mg, 0.163 mmol). Yield: 140.2 mg (0.159 mmol, 97 %), blue-golden crystals. M.p. 180 °C; ^1H NMR (CD_2Cl_2, 399.78 MHz): $\delta = 1.41$ (t, $^3J = 7.25$ Hz, 3H; CH_3), 1.44 (t, $^3J = 7.25$ Hz, 3H; CH_3), 3.71 (q, $^3J = 7.24$ Hz, 4H; CH_2), 6.93 (dd, $^3J = 10.11$ Hz, $^4J = 2.63$ Hz, 1H; $CH_{arom.}$), 7.01 (dd, $^3J = 10.11$ Hz, $^4J = 2.63$ Hz, 1H; $CH_{arom.}$), 7.99 (dd, $^3J = 10.11$ Hz, $^4J = 2.63$ Hz, 1H; $CH_{arom.}$), 8.61 ppm (dd, $^3J = 9.91$ Hz, $^4J = 2.84$ Hz, 1H; $CH_{arom.}$); ^{13}C NMR (CD_2Cl_2, 100.53 MHz): $\delta = 29.75$ (CH_3), 48.24 (CH_2), 115.25 ($CH_{arom.}$), 117.31 ($CH_{arom.}$), 128.00 ($CH_{arom.}$), 139.68 ($CH_{arom.}$), 158.05 ($N-C_q$), 161.98 ($ON-C_q$), 189.92 ppm (CO); IR (KBr): $\tilde{\nu} = 2924$ (m), 2854 (w), 2036 (s, CO, A_1), 2024 (vs, CO, A_1), 1926 (vs, CO, E), 1906 (vs, CO, E), 1714 (w), 1606 (m), 1547 (s), 1491 (w), 1454 (w), 1420 (m, NO), 1385 (w), 1327 (m), 1309 (m), 1278 (w), 1183 (s), 1159 (m), 1086 (w), 1074 (w), 1006 (w), 879 (w), 834 (w), 800 (w), 724 (w), 689 (w), 557 (w), 511 cm^{-1} (w); IR (CH_2Cl_2): $\tilde{\nu} = 2040$ (s, CO, A_1), 2023 (vs, CO, A_1), 1946 (m, CO, E), 1917 cm^{-1} (s, CO, E); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 268 (10003), 317 (5934), 608 nm (31401 $mol^{-1}\,m^3\,cm^{-1}$); elemental analysis (%) calcd for $C_{16}H_{14}Br_2N_2O_7Re_2$ (878.59): C 21.88, H 1.60, N 3.18; found: C 22.83, H 1.86, N 3.18; MS (DEI, 70 eV): m/z (%): 878.7 (49) $[M^+]$, 794.7 (26) $[M^+-3\,CO]$, 765.7 (64) $[M^+-4\,CO]$, 737.7 (31) $[M^+-5\,CO]$, 709.7 (34) $[M^+-6\,CO]$.

Complex 4c: Complex **2c** (146.8 mg, 0.324 mmol), R = Et (28.9 mg, 0.162 mmol). Yield: 95.5 mg (0.099 mmol, 61 %) blue-golden dichroic crystals. M.p. 170 °C; ^1H NMR (CD_2Cl_2, 399.78 MHz): $\delta = 1.53$ (s, 6H; CH_3), 3.66 (q, $^3J = 7.24$ Hz, 4H; CH_2), 6.92 (br, 1H; $CH_{arom.}$), 7.01 (br, 1H; $CH_{arom.}$), 7.90 (br, 1H; $CH_{arom.}$), 8.63 ppm (br, 1H; $CH_{arom.}$); ^{13}C NMR (CD_2Cl_2, 100.53 MHz): $\delta = 29.63$ (CH_3), 48.14 (CH_2), 114.68 ($CH_{arom.}$), 116.71 ($CH_{arom.}$), 127.79 ($CH_{arom.}$), 139.53 ($CH_{arom.}$), 157.88 ($N-C_q$), 162.74 ($ON-C_q$), 188.27 (CO), 192.95 ppm (CO); IR (KBr): $\tilde{\nu} = 2924$ (w), 2854 (w), 2729 (w), 2415 (w), 2338 (w), 2021 (vs, CO, A_1), 1909 (vs, CO, E), 1604 (m), 1546 (w), 1493 (w), 1448 (w), 1420 (m, NO), 1384 (w), 1350 (w), 1318 (m), 1277 (w), 1183 (s), 1158 (m), 1074 (w), 1002 (w), 876 (w), 832 (w), 724 (w), 622 (w), 557 (w), 513 cm^{-1} (w); IR (CH_2Cl_2): $\tilde{\nu} = 2037$ (m, CO, A_1), 2021 (vs, CO, A_1), 1946 (m, CO, E), 1918 cm^{-1} (s, CO, E); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 273 (10739), 363 (3845), 621 nm (32786 $mol^{-1}\,m^3\,cm^{-1}$); elemental analysis (%) calcd for $C_{16}H_{14}I_2N_2O_7Re_2$ (972.51): C 19.76, H 1.45, N 2.88; found: C 19.66, H 1.39, N 2.79; MS (DEI, 70 eV): m/z (%): 971.3 (100) $[M^+]$, 887.3 (45) $[M^+-3\,CO]$, 859.3 (52) $[M^+-4\,CO]$, 831.4 (98) $[M^+-5\,CO]$, 803.3 (58) $[M^+-6\,CO]$.

Synthesis of 3a–c and 4a–c from 1

Procedure for 3a: Compound **1** (388.2 mg, 0.513 mmol),[2] $(CH_3)_2NC_6H_4NO$ (118.2 mg, 0.787 mmol) and $AlCl_3$ (173.2 mg, 1.035 mmol) were dissolved in toluene (100 mL) and refluxed for 10 min, whereupon the solution turned deep blue. The solvent was evaporated and the shiny blue, almost black residue was dissolved in CH_2Cl_2 and purified by column chromatography. Yield: 258 mg (0.338 mmol, 66 %).

General procedure for 3b, 3c and 4a–c: The dimer **1**,[2] the corresponding *N*,*N*-dialkyl-4-nitrosoaniline $R_2NC_6H_4NO$ (R = Me or Et) and AlX_3 (X = Cl, Br, I) were dissolved in toluene (20 mL) and stirred for 16 h at ambient temperature, whereupon the solution turned deep blue. The solvent was evaporated and the shiny blue residue was dissolved in CH_2Cl_2, and purified by column chromatography.

Complex 3b: Complex **1** (121.7 mg, 0.161 mmol), R = Me (48.3 mg, 0.322 mmol), X = Br (85.8 mg, 0.322 mmol). Yield: 28.7 mg (0.035 mmol, 22 %).

Complex 3c: Complex **1** (100.0 mg, 0.132 mmol), R = Me (39.8 mg, 0.265 mmol), X = I (107.8 mg, 0.265 mmol). Yield: 37.4 mg (0.039 mmol, 29 %).

Complex 4a: Complex **1** (141.5 mg, 0.187 mmol), R = Et (66.7 mg, 0.374 mmol), X = Cl (49.9 mg, 0.374 mmol). Yield: 54.7 mg (0.069 mmol, 35 %).

Complex 4b: Complex **1** (138.3 mg, 0.183 mmol), R = Et (65.2 mg, 0.366 mmol), X = Br (97.5 mg, 0.366 mmol). Yield: 59.6 mg (0.068 mmol, 37 %).

Complex 4c: Complex **1** (127.9 mg, 0.169 mmol), R = Et (60.1 mg, 0.338 mmol), X = I (137.7 mg, 0.338 mmol). Yield: 17.8 mg (0.018 mmol, 11 %).

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