# FULL PAPER

# Reactivity of 1-Nitroso-2-naphthol Towards the Carbonyl Complexes XRe(CO)$_5$ (X = Cl, Br, I): Molecular Structures of *cis*-[η²-{*N,O*-C$_{10}$H$_6$ON(O)}Re(CO)$_4$] and *fac*-[η²-{*N,O*-C$_{10}$H$_6$ON(H)}Re(CO)$_3$X]

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The halogeno complexes (CO)$_5$ReX (**1a–c**) (X = Cl, Br, I) react with 1-nitroso-2-naphthol C$_{10}$H$_6$N(O)OH (**2**) in refluxing CH$_2$Cl$_2$ to give the substitution product *cis*-(CO)$_4$-Re{C$_{10}$H$_6$ON(O)} (**3**) via HX and CO elimination in good yield. Compound **3** is coordinated to the Re centre by the bidentate chelate ligand via the N-atom of the nitroso and O-atom of the naptholato groups. The same reaction in refluxing toluene, however, gave no HX elimination but instead, the *fac*-(CO)$_3$XRe{C$_{10}$H$_6$ON(H)} (**4–6**) complexes are formed, which contain the rare, *N,O*-chelating ligand 1,2-naphthaquinone-2-imine. The nitroso function of **2** has been reduced to the imine function by an intermolecular redox process, which was confirmed by the detection of CO$_2$ generated during the reaction. The new compounds **3–6** have been characterised by their IR, $^1$H and $^{13}$C NMR, UV/Vis and mass spectra, as well as by X-ray structure analyses. The Re$^I$ centres show a distorted octahedral coordination of the CO and X (in **4–6**) ligands and the almost planar aromatic (**3**) or quinoid (**4–6**) *N,O* chelating ligands.

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## Introduction

Metal complexes with *C*-nitroso ligands have attracted great attention for several reasons. The *C*-nitroso group is isoelectronic with dioxygen and like dioxygen can form adducts with metalloproteins[1–6] and metalloporphyrins.[6] Some metal complexes with *C*-nitroso compounds have also been proposed as reaction intermediates,[6–9] for example in the cytochrome-P450-dependent oxidative metabolism of amphetamines and other amino derivatives.[10]

Recently, we reported the synthesis of the dinuclear μ$_2$-(η²-*NO*)-nitrosoaniline complexes of rhenium(I) of the type [{(CO)$_3$ReX}$_2$ONC$_6$H$_4$NR$_2$] (X = Cl, Br, I; R = Me, Et).[11,12] The single crystals of all six compounds exhibit a pronounced linear dichroism. This surprising property may be due to the *C*-nitroso group which lies together with the planar phenyl- and NC$_2$-moieties (of NR$_2$) almost exactly within the symmetry plane of the dinuclear complexes.[11,12] Therefore, we tried to synthesise analogous complexes of XRe(CO)$_5$ (X = Cl, Br, I) with the sterically more demanding 1-nitroso-2-naphthol. Instead of the desired analogous dinu-

clear complexes mentioned above, we obtained new monomeric complexes of the type [Re(CO)$_3$X{C$_{10}$H$_6$ON(H)}] (X = Cl, Br, I), whereby the nitroso group of the naphthol-derivative has been reduced to an imino-function by a CO-ligand, resulting in the new bidentate ligand 1,2-naphthaquinone-2-imine. Using milder reaction conditions we were also successful in isolating and characterising the intermediate product [Re(CO)$_4${C$_{10}$H$_6$ON(O)}], where the *C*-nitroso group remains intact.

Metal complexes which contain 1,2-naphthoquinone-monoimines are of interest because they are widely used for analytical purposes.[13,14] Metal complexes derived from 1,2-naphthoquinone-monoimines can also be employed as starting reagents in the synthesis of a wide variety of organic compounds.[15–17]

It is well known that nitro and nitroso compounds can be reduced to give products via the formation of imido intermediates. In 1975 Saarinen et al. published the X-ray structure of a copper complex with the 1-nitroso-2-naphthol ligand, which was followed by a report by Charalambous et al. in 1983.[18–20] Recently, Wong et al. prepared complexes with 1-nitroso-2-naphthol ligands and characterised a ruthenium complex as a by-product, where the nitroso group had been reduced to an imino function in very low yields.[21,22] N–O bond cleavage reactions of oximes have been recently documented by their oxidative addition reactions with suitable Re complexes to give the corresponding imine complexes.[23–25] Whereas Pombeiro et al.[23] report

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oxygen transfer only to the metal, Zubieta et al.[24] and Chakravorty et al.[25] observe its transfer to both metal and oxophilic co-ligands like phosphanes. In this work we present the first report on the formation of the 1,2-nitrosonaphtholato-*O,N* complex **3** which appears to be an intermediate in the reaction of XRe(CO)$_5$ (X = Cl, Br, I) with 1-nitroso-2-naphthol, because complexes **4**–**6** which are obtained by the same reaction in refluxing toluene, possess the 1,2-naphthochinone-2-imine-*N,O* ligand, which is generated by an intramolecular redox process.

## Results and Discussion

The addition of one equivalent of 1-nitroso-2-naphthol to XRe(CO)$_5$ (X = Cl, Br, I) in CH$_2$Cl$_2$ or toluene followed by heating of this solution to 40 °C for 30 min leads to a colour change from yellow to orange. After 40 h, the orange product [Re(CO)$_4$\{C$_{10}$H$_6$ON(O)\}] (**3**) was isolated by column chromatography (CH$_2$Cl$_2$, Scheme 1). When the same reaction was repeated in toluene with XRe(CO)$_5$ (X = Cl, Br, I) at 100 °C the colour changed initially to orange, then to green and finally to blue. After purifying the blue product by column chromatography (3 cm column, CH$_2$Cl$_2$), blue crystals of the compounds [Re(CO)$_3$X\{C$_{10}$H$_6$ON(H)\}] (X = Cl, Br, I) (**4**–**6**) could be isolated. In compounds **4**–**6** no nitroso function was observed as it had been reduced to an imine function. Our first assumption that the overall redox reaction can only occur when a CO ligand is oxidised to CO$_2$ has been proven experimentally, as a white precipitate of BaCO$_3$ formed when the gas atmosphere in the reaction tube was connected with a solution of Ba(OH)$_2$ in H$_2$O (Scheme 1).
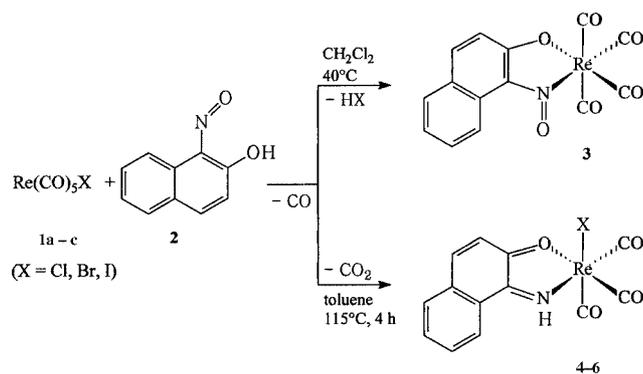


Scheme 1. Synthesis of **3**–**6**.

Compounds **3**–**6** are stable in air for some days, and are soluble in THF, acetone, CHCl$_3$, CH$_2$Cl$_2$ and even toluene, but nearly insoluble in nonpolar solvents like pentane or hexane. The orange (**3**) and blue solutions (**4**–**6**) can be stored in air for some days without decomposition. In the UV/Vis spectrum (CHCl$_3$) of **3** two broad absorptions at $\lambda_1$ = 260–315 nm and $\lambda_2$ = 360–440 nm due to ligand-to-metal CT bands ([NO–Re$^I$] and [O–Re$^I$]) are observed. For **4**–**6** two absorptions were also observed at lower frequencies in comparison to those observed for **3** at 380–395 and 570–670 nm (**4**), 380–420 and 570–670 nm (**5**), 450–500 and 590–690 nm (**6**) corresponding to

[NH–Re$^I$] and [O–Re$^I$]. The position of these absorptions depends on the halogen and increases from X = Cl to X = I. In comparison with the corresponding electronic transition ($\pi$-$\pi$* NO) of the free ligand **2**, the absorption bands of the complexes **3**–**6** are shifted to lower frequencies.

The IR spectra (in CH$_2$Cl$_2$ and KBr) of the tetracarbonyl derivative **3** show four $\nu$(CO)-absorptions at 2113 ($A_1$), 2017 ($A_1$), 2002 ($B_2$) and 1957 cm$^{-1}$ ($B_2$) due to the pseudo-$C_{2v}$ symmetry. The IR spectra of the facial tricarbonyl derivatives **4**–**6** in CH$_2$Cl$_2$ show three absorptions due to their lower symmetry ($C_1$) at 2031–2032 (*A*), 1923–1925 (*A*) and 1945–1951 cm$^{-1}$ (*A*). The corresponding IR spectra (in KBr) show only two broad absorptions instead of the three observed in CH$_2$Cl$_2$ for compounds **4** and **5**. The NO group of **3** is found to absorb at 1380 cm$^{-1}$, indicating that the absorption of the NO bond of 1-nitroso-2-naphthol is shifted to lower wavenumbers on complexation. Depending on the halogen present, the $\nu$(NH) absorptions of **4**–**6** are found at 3162 (**4**), 3175(**5**) and 3192 cm$^{-1}$ (**6**).

The $^1$H NMR spectrum of **3** shows three doublets for each proton at $\delta$ = 7.04, 7.82, 9.26 ppm and a triplet at $\delta$ = 7.49 ppm. The other three aromatic protons were only observed as a multiplet between 7.62–7.65 ppm. The $^1$H NMR spectra of compounds **4**–**6** are very similar and display a double-doublet at $\delta$ = 7.05 (**4**), 7.10 (**5**) and 7.16 ppm (**6**). A further aromatic proton of **4**–**6** is detected at $\delta$ = 8.05 ppm, in addition to two multiplets at $\delta$ = 7.70–7.78 and 8.28–8.49 ppm. Only **5** shows an additional signal for the NH-group at $\delta$ = 14.47. All of the signals of **4**–**6** are generally shifted to a lower field in comparison to **3**.

In the $^{13}$C NMR spectra of **3**–**6** the aromatic carbon atoms can be found between $\delta$ = 123.0–134.4 ppm, and the *N*-bonded carbon atom at $\delta$ = 156.3 (**3**), 160.1 (**4**), 166.4 (**5**) and 165.0 ppm (**6**). Compounds **4** and **6** show an additional signal for a quaternary carbon-atom at $\delta$ = 150.4 (**4**) and 148.0 ppm (**6**). The signals for the CO ligands and carbonyl groups appear between $\delta$ = 181.2–183.4 ppm. In comparison with the starting material **2**, all of the signals of complexes **4**–**6** are shifted to a lower field.

In the mass spectra (DEI-MS) of **3**–**6** the parent peaks are observed, as well as peaks corresponding to fragments resulting from the successive loss of up to three (**4**–**6**) and four CO ligands (**3**).

The stoichiometry and structures of complexes **3**–**6** were confirmed by X-ray structure analyses (Table 1).[26] In all cases, single crystals were obtained by the diffusion of pentane into solutions of **3**–**6** in CHCl$_3$. The molecular structures and selected bond lengths and angles are given in Figures 1, 2, 3 and 4.

All four compounds show the same distorted octahedral arrangement of the Re$^I$ centre with O–Re–N angles between 73 and 75° [75.20 (**3**), 73.33 (**4**), 73.70 (**5**) and 73.07° (**6**)]. The O–Re–X and N–Re–X angles of **4**–**6** increase within the series **4** < **5** < **6** (84.65, 86.96 < 86.09, 87.40 < 88.20, 88.24°) depending on the size of the halogen atom. The Re–N bonds of **3** and **6** are approximately 2.115 Å and are significantly shorter than the corresponding Re–O bonds [2.155 (**3**) and 2.129 Å (**6**)]. However, in compounds **4** and **5**, the Re–O dis-

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Table 1. X-ray structure analysis of compounds **3**–**6**.[26]

| | 3 | 4 | 5 | 6 |
|---|---|---|---|---|
| Empirical formula | $C_{14}H_6NO_6Re$ | $C_{13}H_7ClNO_4Re$ | $C_{13}H_7BrNO_4Re$ | $C_{13}H_7INO_4Re$ |
| Formula mass [g mol⁻¹] | 470.40 | 462.85 | 507.31 | 554.31 |
| Crystal size [mm] | $0.20 \times 0.06 \times 0.03$ | $0.23 \times 0.27 \times 0.27$ | $0.18 \times 0.06 \times 0.04$ | $0.150 \times 0.07 \times 0.05$ |
| Crystal colour, habit | orange, plate | black, platelet | black, platelet | black, platelet |
| Crystal system | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $C2/c$ | $C2/c$ | $C2/c$ |
| $a$ [Å] | 7.1437(14) | 10.222(2) | 10.4446(7) | 10.925(2) |
| $b$ [Å] | 8.9999(18) | 22.302(5) | 22.0422(15) | 21.687(4) |
| $c$ [Å] | 11.475(2) | 12.480(9) | 12.4732(9) | 12.809(3) |
| $\alpha$ [°] | 75.17(3) | 90 | 90 | 90 |
| $\beta$ [°] | 78.76(3) | 107.03(3) | 106.768(8) | 107.45(3) |
| $\gamma$ [°] | 68.91(3) | 90 | 90 | 90 |
| Volume [Å³] | 661.1(2) | 2720.4(9) | 2749.5(3) | 2895.3(10) |
| $Z$ | 2 | 8 | 8 | 8 |
| Density, calcd. [g cm⁻³] | 2.363 | 2.260 | 2.451 | 2.543 |
| Absorption coefficient [mm⁻¹] | 9.221 | 9.140 | 11.756 | 10.537 |
| $F(000)$ | 440 | 1728 | 1872 | 2016 |
| Index ranges | $-8 \leq h \leq 8$ | $-11 \leq h \leq 0$ | $-13 \leq h \leq 13$ | $-13 \leq h \leq 13$ |
| | $-12 \leq k \leq 11$ | $-25 \leq k \leq 0$ | $-28 \leq k \leq 29$ | $-28 \leq k \leq 29$ |
| | $-7 \leq l \leq 15$ | $-13 \leq l \leq 14$ | $-16 \leq l \leq 16$ | $-16 \leq l \leq 16$ |
| $\theta$ range [°] | 2.48–29.04 | 2.45–23.96 | 2.24–27.97 | 3.33–25.01 |
| Reflections collected | 3408 | 2260 | 11836 | 18221 |
| Independent reflections | 2585 | 2131 | 3301 | 2554 |
| Observed reflections | 2424 | 1848 | 2444 | 2238 |
| Parameter/restrains | 200/0 | 182/0 | 185/0 | 182/0 |
| $R_1/wR_2$ (all data) | 0.0526/0.1314 | 0.0246/0.0416 | 0.0656/0.1165 | 0.0424/0.0924 |
| $R_1/wR_2$ (final) | 0.0546/0.1340 | 0.0168/0.0390 | 0.0468/0.1112 | 0.0349/0.0878 |
| Goodness of fit | 1.074 | 1.077 | 0.953 | 1.061 |
| Min./max. $\rho_e$ (e Å³) | –4.492/5.558 | –0.451/0.466 | –5.939/2.138 | –2.356/1.247 |
| Temperature [K] | 200 | 293 | 200 | 200 |
| Diffractometer used | Siemens CCD Area-Detector | Nonius Mach 3 | Nonius Kappa CCD | Nonius Kappa CCD |
| Scan type | area detection | area detection | area detection | area detection |
| Solution, software | SHELXS-97 | SHELXS-97 | SHELXS-97 | SHELXS-97 |
| Refinement, software | SHELXS-97 | SHELXS-97 | SHELXS-97 | SHELXS-97 |
| CCDC number | 259837 | 258934 | 258935 | 258936 |
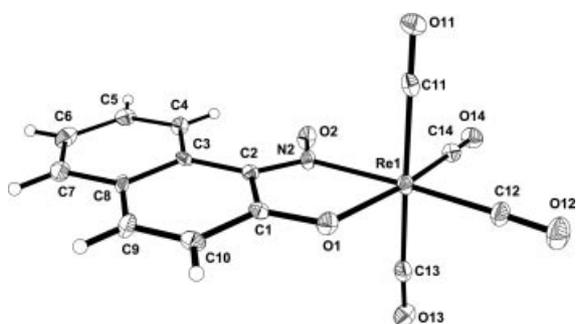


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Re(1)–N(2) 2.155(7), Re(1)–O(1) 2.117(6), N(2)–O(2) 1.246(11), Re(1)–C(11) 2.015(10), Re(1)–C(12) 1.972(9), Re(1)–C(13) 1.983(11), Re(1)–C(14) 1.931(8), O(1)–C(1) 1.297(9), N(2)–C(2) 1.358(10); O(1)–Re(1)–N(2) 75.2(2), C(13)–Re(1)–N(2) 91.6(3), C(11)–Re(1)–N(2) 89.5(3), C(11)–Re(1)–O(1) 90.1(3), C(13)–Re(1)–C(11) 178.3(2), C(2)–N(2)–Re(1) 116.1(5), C(1)–O(1)–Re(1) 115.7(5).
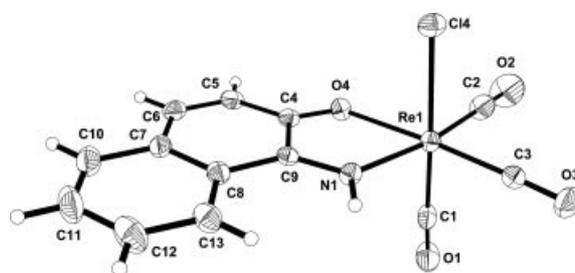


Figure 2. Molecular structure of **4**. Selected bond lengths [Å] and angles [°]: Re(1)–N(1) 2.109(3), Re(1)–O(4) 2.152(3), Re(1)–Cl(4) 2.4807(12), Re(1)–C(1) 1.916(5), Re(1)–C(2) 1.926(5), Re(1)–C(3) 1.903(5), O(4)–C(4) 1.245(5), N(1)–C(9) 1.290(5); N(1)–Re(1)–O(4) 73.33(12), N(1)–Re(1)–Cl(4) 86.96(9), O(4)–Re(1)–Cl(4) 84.65(8), C(1)–Re(1)–N(1) 94.27(16), C(1)–Re(1)–O(4) 93.57(16), C(1)–Re(1)–Cl(1) 177.46(15), C(4)–O(4)–Re(1) 117.8(3), C(9)–N(1)–Re(1) 119.8(3).

tances [2.152 (**4**), 2.149 Å (**5**)] are longer than the Re–N bonds [2.109 (**4**), 2.105 Å (**5**)]. The C(4)/C(9)–O(4) bond lengths increase from **4** to **6** [1.245 (**4**), 1.267 (**5**), 1.301 Å (**6**)] and C(1)–O(1) in compound **3** is approximately 1.297 Å, therefore they all lie between normal C–O (1.43 Å) and C=O

(1.19 Å) bonds. In the case of **3**, this observation can be rationalised by considering two mesomeric forms of 1-nitroso-2-naphthol (Scheme 2).

The short C–N bond lengths of **4**–**6** can be explained as a result of the reduction due to CO forming the quinoid sys-
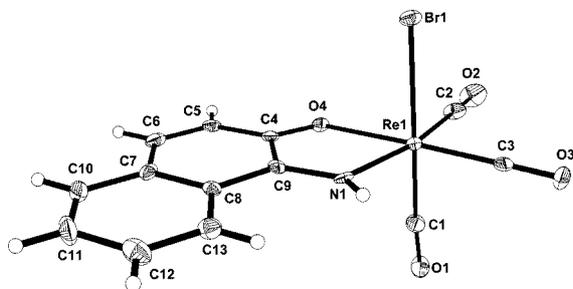
Figure 3. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: Re(1)–N(1) 2.105(8), Re–O(4) 2.149(6), Re–Br 2.6118(10), Re–C(1) 1.921(10), Re–C(2) 1.908(10), Re–C(3) 1.908(18), O(4)–C(4) 1.267(11), N–C(9) 1.311(12); N–Re–O(4) 73.7(3), N–Re–Br 87.40(18), O(4)–Re–Br 86.09(16), C(1)–Re–N 94.4(4), C(1)–Re–O(4) 93.0(4), C(1)–Re–Br 177.7(3), C(4)–O(4)–Re 117.5(6), C(9)–N–Re 119.0(6).
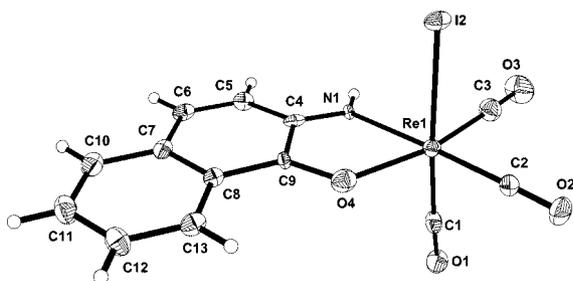


Figure 4. Molecular structure of **6**. Selected bond lengths [Å] and angles [°]: Re(1)–N(1) 2.129(4), Re(1)–O(4) 2.113(5), Re(1)–I(2) 2.7940(9), Re(1)–C(1) 1.912(8), Re(1)–C(2) 1.902(8), Re(1)–C(3) 1.939(8), O(4)–C(9) 1.301(9), N(1)–C(4) 1.238(8), N(1)–Re(1)–O(4) 73.07(18), N(1)–Re(1)–I(2) 88.24(12), C(1)–Re(1)–N(1) 95.2(2), C(1)–Re(1)–O(4) 95.2(2), C(1)–Re(1)–I(2) 175.7(2), C(9)–O(4)–Re(1) 120.1(4), C(4)–N(1)–Re(1) 119.2(4).

tem. In addition **4** and **5** have significantly shorter C–O bonds than **3**.

The N–O distance of the nitroso group in **3** is 1.246 Å, which is within the range of most metal complexes with *N*-bonded nitroso groups, for example in [Cu{η²-N(O)C₁₀H₆O}[PPh₃]₂] (1.287 Å)[17] and *cis*-[Ru{η²-N(O)C₁₀H₆O}₂(CO)₂] (1.258 Å).[21] The dihedral angles N(1)–C(9)–C(4)–O(4) and N(1)–C(9)–C(8)–C(13) (for **4** and **5**) as well as N(1)–C(4)–C(9)–O(4) and N(1)–C(4)–C(5)–C(6) (for **6**) are less than 1.3°, which means that the quinone-imine in **4**–**6** is planar. In contrast to **4**–**6**, the 1-nitroso-naphthol ligand of **3** is slightly twisted out of the Re–O plane [N(2)–C(2)–C(1)–O(1) = 5.42°, N(2)–C(2)–C(3)–C(4) = 8.47°].
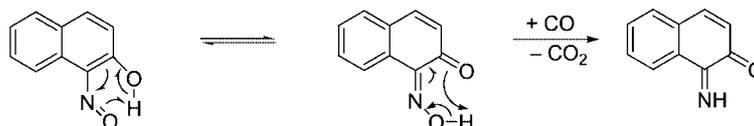
## Experimental Section

All operations were carried out in an oxygen free atmosphere under Ar in dry and Ar-saturated solvents.[27] Re(CO)₅X (X = Cl, Br, I) was prepared according to the literature procedure.[28] 1-Nitroso-2-naphthol was used as purchased from Alfa Aesar. NMR spectra were recorded with a Jeol EX 400 spectrometer (¹H: 399.78 MHz and ¹³C: 100.54 MHz) and with a Jeol 270 spectrometer (¹H: 270.17 MHz, ¹³C: 67.93 MHz) in [D₈]THF or CD₂Cl₂. 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 and a Perkin–Elmer UV Lambda 16 spectrometer, respectively. Elemental analyses were performed with a Heraeus Elementar Vario EL.

**Tetracarbonyl-1-nitroso-napholato-*N,O*-rhenium(I) (3):** Compounds **1b** (99.7 mg, 0.246 mmol) and **2** (46.9 mg, 0.271 mmol) were dissolved in CH₂Cl₂ (20 mL) and heated under reflux for 40 h, whereby the solution turned deep orange. The solvent was evaporated, and the orange residue was purified by column chromatography (CH₂Cl₂). The same product was obtained in similar yields when the appropriate quantities of **1a** or **1c** are used instead of **1b**. Yield: orange crystals (97.6 mg, 0.207 mmol, 72%), m.p. 184 °C (dec.). ¹H NMR (399.78 MHz, CDCl₃): $\delta$ = 7.04 (d, 1 H, ³*J* = 9.40 Hz, CH$_{arom.}$), 7.49 (t, 1 H, ³*J* = 7.86 Hz, CH$_{arom.}$), 7.62–7.65 (m, 2 H, CH$_{arom.}$), 7.82 (d, 1 H, ³*J* = 9.40 Hz, CH$_{arom.}$), 9.26 (d, 1 H, ³*J* = 8.35 Hz, CH$_{arom.}$) ppm. ¹³C NMR (100.53 MHz, CDCl₃): $\delta$ = 123.0 (CH$_{arom.}$), 124.1 (CH$_{arom.}$), 125.0 (CH$_{arom.}$), 127.1 (CH$_{arom.}$), 128.0 (CH$_{arom.}$), 129.1 (CH$_{arom.}$), 133.4 (CH$_{arom.}$), 144.9 (CH$_{arom.}$), 156.3 (C$_{q,arom.}$), 183.4 (C$_{q,arom.}$), 190.9 (C$_{q,carbonyl}$) ppm. IR (KBr) : $\tilde{\nu}$ = 3121 (w), 3065 (w), 2962 (m), 2926 (m), 2854 (w), 2753 (w), 2687 (w), 2644 (w), 2584 (w), 2456 (w), 2421 (w), 2338 (w), 2114 (vs), 2017 (vs), 1994 (vs), 1958 (vs), 1820 (w), 1790 (w), 1726 (w), 1647 (m), 1619 (m), 1608 (s), 1599 (s), 1554 (s), 1517 (vs), 1482 (m), 1454 (w), 1422 (w), 1380 (s), 1357 (vs), 1323 (s), 1311 (s), 1266 (s), 1214 (s), 1139 (m), 1024 (m), 970 (w), 878 (w), 832 (w), 821 (s), 803 (m), 755 (s), 739 (m), 712 (w), 683 (w), 664 (m), 625 (s), 590 (w), 565 (m) cm⁻¹. IR (CH₂Cl₂): $\tilde{\nu}$ = 2113 (vs), 2017 (vs), 2002 (vs), 1957 (vs) cm⁻¹. UV/Vis (CHCl₃) $\lambda_{max}$ (log ε): 299 (13705), 323 (5836), 419 (13612) nm. C₁₄H₆NO₅Re (470.40): calcd. C 35.63, H 1.50, N 2.97; found C 35.27, H 1.20, N 2.67. MS (DEI): *m/z* (%) = 470.7 (60) [M]⁺, 442.8 (22) [M – CO]⁺, 414.8 (7) [M – 2 CO]⁺, 386.8 (35) [M – 3 CO]⁺, 358.9 (100) [M – 4 CO]⁺, 328.9 (47) [M – 4 CO, – NO]⁺.

**Synthesis of 4–6. General Procedure:** Re(CO)₅X (**1a**–**c**) and 1-nitroso-2-naphthol (**2**) were dissolved in toluene (20 mL) and heated to 115 °C for 4 h, whereby the solution turned deep blue. The solvent was evaporated, and the blue residue was purified by column chromatography (CH₂Cl₂, 3 cm column).

**Tricarbonyl-chloro-(1-imino-*1H*-naphthalene-2-one)rhenium(I) (4):** Complex **1a** (143 mg, 0.397 mmol) and **2** (68.4 mg, 0.397 mmol). Yield: blue crystals (104 mg, 0.225 mmol, 57%), m.p. 234 °C (dec.). ¹H NMR (270.16 MHz, [D₈]THF): $\delta$ = 7.05 (dd, 1 H, ³*J* = 9.80, ⁴*J* = 1.34 Hz, CH$_{arom.}$), 7.70–7.76 (m, 3 H, CH$_{arom.}$), 8.05 (d, 1 H, ³*J* = 9.94 Hz, CH$_{arom.}$), 8.47–8.49 (m, 1 H, CH$_{arom.}$) ppm. ¹³C NMR (67.94 MHz, [D₈]THF): $\delta$ = 125.4 (CH$_{arom.}$), 127.7 (CH$_{arom.}$), 128.7 (CH$_{arom.}$), 132.3 (CH$_{arom.}$), 132.3 (CH$_{arom.}$), 132.5 (CH$_{arom.}$), 134.2



Scheme 2. Tautomerisation of 1-nitroso-2-naphthol and its reduction to form 1,2-naphtaquinone-2-imine.

($CH_{arom.}$), 150.4 ($C_{q,arom.}$), 160.1 ($C_{q,arom.}$), 182.4 ($C_{q,arom.}$), 195.7 ($C_{q,carbonyl}$) ppm. IR (KBr): $\tilde{v}$ = 3162 (w), 2026 (vs), 1937 (vs), 1911 (vs), 1605 (m), 1555 (w), 1517 (w), 1409 (w), 1463 (w), 1409 (m), 1381 (w), 1356 (w), 1314 (w), 1288 (w), 1275 (w), 1213 (w), 1169 (w), 1139 (w), 1094 (w), 1023 (w), 959 (w), 907 (w), 846 (w), 755 (w), 692 (w), 637 (w), 604 (w), 582 (w), 547 (w) cm$^{-1}$. IR (CH$_2$Cl$_2$): $\tilde{v}$ = 2031 (vs), 1945 (s), 1932 (vs) cm$^{-1}$. UV/Vis (CHCl$_3$) $\lambda_{max}$ (log $\varepsilon$): 307 (5002), 388 (2040), 630 (8209) nm. C$_{13}$H$_7$ClNO$_4$Re (462.85): calcd. C 33.70, H 1.51, N 3.02; found C 33.51, H 1.90, N 2.76. MS (DEI): $m/z$ (%): 463.0 (8) [M]$^+$, 435.1 (17) [M – CO]$^+$, 407.1.1 (12) [M – 2 CO]$^+$, 379.1 (88) [M – 3 CO]$^+$.

**Bromo-tricarbonyl-(1-imino-1*H*-naphthalene-2-one)rhenium(I)** **(5):** Complex **1b** (242 mg, 0.596 mmol) and **2** (104 mg, 0.596 mmol). Yield: blue crystals (197 mg, 0.387 mmol, 65%), m.p. 242 °C (dec.). $^1$H NMR (399.78 MHz, [D$_8$]THF): $\delta$ = 7.10 (dd, 1 H, $^3J$ = 9.67, $^4J$ = 1.32 Hz, CH$_{arom.}$), 7.72–7.76 (m, 3 H, CH$_{arom.}$), 8.07 (d, 1 H, $^3J$ = 10.11 Hz, CH$_{arom.}$), 8.47–8.48 (m, 1 H, CH$_{arom.}$), 14.47 (s, 1 H, NH) ppm. $^{13}$C NMR (100.53 MHz, [D$_8$]THF): $\delta$ = 125.5 (CH$_{arom.}$), 127.6 (CH$_{arom.}$), 128.6 (CH$_{arom.}$), 132.3 (CH$_{arom.}$), 132.5 (CH$_{arom.}$), 132.6 (CH$_{arom.}$), 134.1 (CH$_{arom.}$), 166.4 (C$_{q,arom.}$), 181.7 (C$_{q,arom.}$), 194.9 (C$_{q,carbonyl}$), 197.9 (C$_{q,carbonyl}$) ppm. IR (KBr): $\tilde{v}$ = 3175 (m), 3053 (w), 2924 (w), 2853 (w), 2028 (vs), 1930 (vs), 1914 (vs), 1736 (w), 1604 (s), 1559 (w), 1480 (m), 1461 (m), 1408 (s), 1380 (w), 1315 (w), 1229 (w), 1169 (w), 1141 (w), 1092 (w), 1020 (w), 974 (w), 902 (w), 844 (w), 804 (w), 755 (w), 717 (w), 653 (w), 581 (w), 547 (w) cm$^{-1}$. IR (CH$_2$Cl$_2$): $\tilde{v}$ = 2032 (vs), 1951 (s), 1925 (s) cm$^{-1}$. UV/Vis (CHCl$_3$) $\lambda_{max}$ (log $\varepsilon$): 300 (5021), 407 (2741), 637 (10960) nm. C$_{13}$H$_7$BrNO$_4$Re (507.31): calcd. C 30.75, H 1.38, N 2.76; found C 30.83, H 1.35, N 2.74. MS (DEI): $m/z$ (%): 506.7 (17) [M]$^+$, 478.7 (33) [M – CO]$^+$, 450.7 (16) [M – 2 CO]$^+$, 422.7 (66) [M – 3 CO]$^+$, 342.8 (17) [M – 3 CO, – Br]$^+$.

**Tricarbonyl-iodo-(1-imino-*1H*-naphthalene-2-one)rhenium(I)** **(6):** Complex **1c** (102 mg, 0.225 mmol) and **2** (42.0 mg, 0.247 mmol). Yield: blue crystals (81.1 mg, 0.146 mmol, 65%), m.p. 247 °C (dec.). $^1$H NMR (399.78 MHz, [D$_8$]THF): $\delta$ = 7.16 (dd, 1 H, $^3J$ = 9.65, $^4J$ = 1.34 Hz, CH$_{arom.}$), 7.74–7.78 (m, 3 H, CH$_{arom.}$), 8.03 (d, 1 H, $^3J$ = 9.65 Hz, CH$_{arom.}$), 8.28 (m, 1 H, CH$_{arom.}$) ppm. $^{13}$C NMR (100.53 MHz, [D$_8$]THF): $\delta$ = 124.4 (CH$_{arom.}$), 127.4 (CH$_{arom.}$), 128.3 (CH$_{arom.}$), 132.0 (CH$_{arom.}$), 132.3 (CH$_{arom.}$), 133.7 (CH$_{arom.}$), 134.4 (CH$_{arom.}$), 148.0 (CH$_{arom.}$), 165.0 (C$_{q,arom.}$), 181.2 (C$_{q,arom.}$), 193.2 (C$_{q,carbonyl}$), 196.9 (C$_{q,carbonyl}$) ppm. IR (KBr): $\tilde{v}$ = 3192 (m), 2148 (w), 2025 (vs), 1935 (vs), 1919 (vs), 1626 (w), 1603 (m), 1533 (w), 1480 (w), 1454 (w), 1406 (m), 1315 (m), 1289 (w), 1271 (w), 1231 (w), 1168 (w), 1108 (w), 1022 (w), 887 (w), 838 (w), 805 (w), 754 (w), 692 (w), 632 (w), 581 (w) cm$^{-1}$. IR (CH$_2$Cl$_2$): $\tilde{v}$ = 2032 (vs), 1955 (s), 1931 (s) cm$^{-1}$. UV/Vis (CHCl$_3$) $\lambda_{max}$ (log $\varepsilon$): 483 (3856), 638 (6337) nm. C$_{13}$H$_7$INO$_4$Re (554.31): calcd. C 28.14, H 1.26, N 2.53; found C 27.78, H 1.53, N 2.41. MS (DEI): $m/z$ (%): 554.6 (19) [M]$^+$, 526.7 (26) [M – CO]$^+$, 498.7 (12) [M – 2 CO]$^+$, 470.7 (46) [M – 3 CO]$^+$, 343.9 (15) [M – 3 CO, – I]$^+$.

CCDC-259837 (for **3**), -258934 (for **4**), -258935 (for **5**) and -258936 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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