Efficient direct nitrosylation of α -diimine rhenium tricarbonyl complexes to structurally nearly identical higher charge congeners activable towards photo-CO release

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The reaction of rhenium α -diimine (N-N) tricarbonyl complexes with nitrosonium tetrafluoroborate yields the corresponding dicarbonyl-nitrosyl [Re(CO)₂(NO)(N-N)X]⁺ species (where X = halide). The complexes, accessible in a single step in good yied, are structurally nearly identical higher charge congeners of the tricarbonyl molecules. Substitution chemistry aimed at the realization of equivalent dicationic species (intended for applications as potential antimicrobial agents), revealed that the reactivity of metal ion in [Re(CO)₂(NO)(N-N)X]⁺ is closer to that of a harder Re(III) acid, probably due to the stronger π -acceptor properties of NO⁺ as compared to those of CO. The metal ion thus shows great affinity for π -basic ligands, which are consequently difficult to replace by e.g. σ -donor or week π -acids like pyridine. Attempts of direct nitrosylation of α -diimine *fac*-[Re(CO)₃]⁺ complexes bearing π -basic OR-type ligands gave the [Re(CO)₂(NO)(N-N)(BF₄)][BF₄] salt, as the only product in good yield, featuring a stable Re-F-BF₃ bond. The solid state crystal structure of nearly all molecules presented could be elucidated. A fundamental consequence of the chemistry of [Re(CO)₂(NO)(N-N)X]⁺ complexes, it that the same can be photo-activated towards CO release and represent an entirely new class of photoCORMs.

Introduction

The growing trend of antimicrobial resistance (AMR) poses a serious threat to the public's health, making it more and more difficult to prevent and treat related diseases. Thousands of deaths have been attributed to AMR infections according to WHO findings published in 2018,¹ with an estimated death toll in millions of cases per year by 2050 if appropriate measures are not taken.² With the increasing difficulty of major pharmaceutical companies to meet the demand of new antibiotics discovery and production, universities are contributing to the finding of new classes of active compounds. Pathogens, however, are likely to adapt rapidly and become resistant to new drugs if conventional medicinal chemistry approaches remain based exclusively on organic molecules, also in light of the fact that the majority of drugs in clinical development are modified versions of already-approved antibiotics.³

There is increasing awareness in academia of the potential of metal complexes to act as the new class of molecules for the purpose. Indeed, the unique chemistry and larger variety of 3D geometries of metal compounds can address targets and modes of action unavailable to organic molecules. In the last decade, complexes of virtually all transition metals have been evaluated,^{3, 4} with rhenium, among others,^{5, 6} showing promising potential for new antibiotic development.⁷⁻¹⁰

Our group has been interested in the development of the chemistry of tri- and dicarbonyl rhenium complexes for applications in different medicinal fields,¹¹⁻¹⁸ including their use

as antibacterial agents. We recently reported studies on the antimicrobial properties of families of rhenium diimine (N-N) complexes and found several complexes of general formula fac- $[Re^{I}(CO)_{3}(N-N)L]^{+}$ (L = pyridine, py, type-ligand), showing low to no toxicity in vivo and potent in vitro and in vivo activity against infection of clinically relevant bacteria (MRSA) and fungi (Candida species).^{19, 20} Unlike similar complexes tested against cancers, where the overall charge of the compound does not seem to be a critical factor, a survey of the literature, and our own data,²⁰ indicates that positively charged rhenium complexes are most effective against the microbes. The mechanism of action these agents remains largely unknown, but we hypothesize that the positive charge of the complexes is important for their interaction with phosphatidylglycerol and cardiolipin anionic lipids. All bacterial membranes contain at least 15% anionic lipid. Exposure to these lipids confers selectivity to cationic antimicrobial agents for toxicity against bacteria but not against mammalian cells.^{21, 22} Among the steps involved in the mechanism of action of the highly effective trimetallic complexes of Metzler-Nolte and Bandow, e.g., is the targeting of the cytoplasmic membrane, where the complexes affect membrane architecture and disrupt essential cellular functions, such as respiration and cell wall formation and integrity.7

Given the data currently available on rhenium species, it is possible that by increasing the overall complex charge and by modulating molecules' lipophylicity, binding to fungal and bacterial cell walls, as well as cell membrane (and/or intracellular) accumulation might be enhanced; thereby potentially enhancing the overall antimicrobial efficacy of this class of molecules. To test this hypothesis, the new species should be structurally very close (if not identical) to the active fac-[Re^I(CO)₃(N-N)L]⁺ complexes, but with a higher charge. Charge modulation may be archived by the appropriate choice of a cationic N-N derivative or the monodentate ligand L in the drug sphere of the complexes,²³ or by chemically modifying the fac-[Re^I(CO)₃]⁺ core. The latter possibility is more challenging, but there are options. In particular our attention turned to the equivalent fac-[Re^I(CO)₂(NO)]²⁺ core.²⁴⁻²⁶

A compound of formula *fac*-[Re^I(CO)₂(NO)(bpy)Cl]⁺ (where *fac* refers here to the arrangement of the CO and NO ligands) was prepared previously by the groups of Alberto and Berke *via* a multi-step synthesis from cubic μ -oxo bridged teranuclear [Re(μ_3 -O)(CO)₂(NO)]₄ clusters²⁷ and, under inert conditions, from the [ReCl(μ -Cl)(CO)₂(NO)]₂ dimer respectively (scheme 1).²⁸ Nothing is known about the chemistry of the compound or if the same could be used as a synthon for *fac*-[Re^I(CO)₂(NO)(N-N)L]²⁺ species. We, therefore, set out to first establish a convenient synthetic procedure to *fac*-[Re^I(CO)₂(NO)(N-N)X]⁺ complexes (where X = halide) and then to study their substitution chemistry aiming at the realization of the dicationic species just mentioned above.



Scheme 1. Known synthetic procedures to fac-[Re^I(CO)₂(NO)(N-N)(X)]⁺ type-complexes. The % yields refer to those of the last step only.

In this contribution, we describe our synthetic efforts and we present an efficient direct nitrosylation of α -diimine rhenium tricarbonyl complexes widely applicable to different supporting N-N ligands. The resulting compounds are structurally nearly identical higher charge congeners of tricarbonyls. We found that, while similar complexes are reported as rhenium(I) dicarbonyl-nitrosyl species,²⁴⁻²⁸ the substitution chemistry of metal ion in *fac*-[Re(CO)₂(NO)(N-N)X]⁺ is closer to that of a harder Re(III) acid, probably due to the stronger π -acceptor properties of NO⁺ as compared to those of CO. A fundamental consequence of this behaviour is that *fac*-[Re(CO)₂(NO)(N-N)X]⁺ complexes can be photo-activated towards CO release and represent an entirely new class of photoCORMs.

Results and discussion

Synthesis of fac-[Re(CO)2(NO)(N-N)X]⁺ species

The chemistry of the fac- $[Re(CO)_2(NO)]^{2+}$ core is essentially dominated by cyclopentadienyl (Cp) species of general formula $[CpRe(CO)_2(NO)]^+$. These compounds are most often prepared by reaction of the corresponding $[CpRe(CO)_3]$ with either NO_2PF_{6} ,²⁹ NOHSO₄,³⁰ or NOBF₄.^{31, 32} The last two reagents were successfully used in the preparation of fac-[Re¹(CO)₂(NO)X₃]^{-,24}, ²⁷ and of the two, the latter appeared to us the most convenient as the procedure involves simple addition of the nitrosonium tetrafluoroborate salt in a CH₂Cl₂ (DCM) solution of the rhenium tricarbonyl complex.³² The reaction has also the advantage of producing an ion pair from the initially introduced components with, theoretically, no side products.

Thus, we first attempted reaction of *fac*-[Re^I(CO)₃(bpy)Br] with an excess (2.5-5 eq.) of NOBF₄ in DCM. During the course of the reaction, the colour of the solution changed from a dark to a pale yellow and the same lost its photoluminescence properties. The corresponding dicarbonyl-nitrosyl fac- $[Re(CO)_2(NO)(bpy)Br]^+$ species (1) was isolated as a BF₄- salt in 70% yield (Fig. 1), following crystallisation by vapour diffusion with pentane or by slow evaporation of DMC, after excess NOBF₄ was filtered off. In its crystalline form, 1 is slightly hygroscopic, and it decomposes if purification is attempted on a solid phase (silica or alumina). The same reaction was also attempted with phenanthroline (phen) and 4,4'- or 4,7derivatives of bpy and phen respectively, giving similar results (complexes 2-5, Fig. 1, in 60-70% yield). In comparison, to the synthetic procedures of Alberto and Berke, our route appears straightforward, overall higher yielding and generally applicable to widely accessible α -diimine *fac*-[Re^I(CO)₃]⁺ species.



Fig. 1. General synthetic approach to *fac*-[Re(CO)₂(NO)(N-N)Br]⁺ complexes **1-5** (top) and crystal structures of compounds **1** (left) and **2**. Thermal ellipsoids are at 30% probability. Hydrogen atoms and BF₄⁻ counter ion omitted for clarity. Selected bond lengths (Å): **1**, Re-N1 2.140(4), Re-N2 1.782(6), Re-Br 2.5372(7), Re-C0 1.990(5), C-O 1.123(6), N-O 1.164(7); **2**, Re-N1 2.154(3), Re-N2 2.153(3), Re-N3 1.801(4), Re-Br 2.5425(5), Re-CO 2.002(4) and 2.009(4), C-O 1.118(5) and 1.120(5), N-O 1.143(5).

Spectroscopic properties of fac-[Re(CO)₂(NO)(N-N)X]⁺ species

Physical properties of the fac- $[Re(CO)_2(NO)]^{2+}$ complexes prepared in this study are summarized in Table 1. The IR spectra of the compounds show the pattern expected for the dicarbonyl-nitrosyl species. Consistent with what reported before, the CO stretching (vCO's) frequencies of *fac*- $[Re(CO)_2(NO)(N-N)Br]^+$ complexes **1-5** are substantially shifted to higher wavenumbers, which is unusual for carbonyls bound to the low valent metal. $^{\rm 33,\,34}$ In fact, the vCO's are found in the region where rhenium(III) dicarbonyl complexes³⁵ (e.g. [Re^{III}(CO)₂Br₄]⁻)³⁶ are observed, and much higher than corresponding rhenium(II) species.³⁷ The symmetric vCO mode of the molecules is actually not far from that of CO gas (2143 cm⁻¹). The evidence points to a significant reduction of Re-CO πbackbonding in favour of the stronger π -acceptor NO⁺. The stretching vibration of the NO⁺ ion usually occurs in the 2300-2350 cm⁻¹ frequency range, e.g. 2340 cm⁻¹ in NOBF₄,³⁸ 2326 cm⁻ ¹ in NOAuF₆,³⁹ and 2298 cm⁻¹ in sulfuric acid solutions.⁴⁰ Its vibrational frequency in the complexes is found in the 1800 cm⁻ ¹ region, closer to that of a N=O double bond than that of the initial triple bond. This indicates that the $\pi^*p(NO)$ -orbitals accept electron density to a great degree, depleting the metal ion of the same. Theoretically, a N=O double implies full occupation of a $\pi^* p(NO)$ -orbital, which would formally result in a metal centre of oxidation state Re(III). Indeed this formalism could account for the reactivity of the species (vide infra) and their lack of photoluminescence (see ESI).

The UV-Vis spectra of the compounds are characterized by a main absorption with two closely spaced maxima in 300-340 nm region (Table 1 and ESI). Only complexes **2** and **5** (phenanthroline derivatives) show a single relatively broad peak for the same absorption, with two additional lower-lying small peaks at 340 and 375 nm respectively. We did not perform a TDDFT analysis, but we suggest that the high-energy transitions are likely associated with $\pi \rightarrow \pi^*$ intra-ligand transitions attributed to the diimine-system. In solution, all dicarbonyl-nitrosyl species show sharp signals in their NMR spectra, consistent with the diamagnetic nature of the molecules. With respect to the corresponding tricarbonyl complexes, *fac*-[Re(CO)₂(NO)(N-N)X]⁺ show consistently a downfield shift of the N-N signals (Fig. 2 and ESI). This evidence further supports the assignment of a higher oxidation state of the Re atom.

Attempted synthesis of fac-[Re(CO)₂(NO)(N-N)L]²⁺ species

Having established a sufficiently high-yielding procedure for fac-[Re(CO)₂(NO)(N-N)Br]⁺ ions, we moved to explore the substitution of Br⁻ for neutral pyridine (py) ligands. Typically for corresponding tricarbonyl complexes, bromide the replacement is archived either by treatment with trifluoromethanesulfonic acid or by addition of a silver salt. We first monitored by ¹H-NMR the addition of AgCF₃SO₃ to fac-[Re(CO)₂(NO)(bpy)Br]⁺ (1) in coordinating wet solvents like CH₃OH or CH₃CN. The spectrum revealed no change in the frequency of the proton signals over a period of 3 days. In a parallel reaction, the same conditions were used, but pyridine was added to the mixture. Overnight new signals appeared in the NMR spectrum, but the set of frequencies attributable to free py remained unchanged. We initially hypothesized that the hydroxide

Table 1. Physical properties of fac-[Re^I(CO)₂(NO)(N-N)X]⁺ complexes.

Complex	v(CO) [cm ⁻¹]ª	v(NO) [cm ⁻¹] ^a	λ _{max} [nm (M ⁻¹ cm ⁻¹)] ^b
1	2112, 2050	1801	312, 321
2	2118, 2057	1790	304, 339, 375
3	2104, 2040	1770	342, 357
4	2114, 2053	1797	309, 318
5	2114, 2052	1795	297, 336, 375
6	2106, 2033	1784	342, 352
6	2114, 2050	1796	323, 332
11	2127, 2069	1820	320, 330
13	2114, 2050	1796	323, 332

^aSolid state. ^bin DMF



Fig. 2. Aromatic regions of the ¹H-NMR spectra of fac-[Re(CO)₂(NO)(bpy)Br]⁺ (**1**, top) and fac-[Reⁱ(CO)₃(bpy)Br]⁺. Both spectra recorded in CD₃CN.

fac-[Re(CO)₂(NO)(bpy)(OH)]⁺ had formed, but later found that py, as a base, promoted BF₄⁻ hydrolysis to [BF₃(OH)]⁻ and F^{-,41} and the latter substituted Br⁻ to give fac-[Re(CO)₂(NO)(bpy)F]⁺ (**6**, Fig. 3). As mentioned above, this type of reactivity of the metal ion is more consistent with a harder Re(III) acid and fully congruous with the spectroscopic data discussed above.

The higher apparent formal oxidation state of the metal ion, implies depletion of electron density from the same, and affinity for π -basic ligands rater σ -donors. We reasoned, therefore, that electron-donating substituents on N-N might help stabilizing the rhenium ion towards the same reaction. NR₂ groups (where R = aliphatic chain) are amongst the most effective electron donating groups.⁴² However, when the $N^4, N^4, N^4', N^{4'}$ -tetraethyl-[2,2'-bipyridine]-4,4'-diamine (Et₂N-bpy) complex **3** was used the corresponding *fac*-[Re^I(CO)₂(NO)(Et₂N-bpy)F]⁺ (**7**) also formed as the only product. Compound (**7**) was isolated in 30% yield and was recrystallized from methanol. Its X-ray structure is also shown in Fig. 3.

We recently published synthetic procedures to aerobically stable and substitutionally labile α -diimine rhenium(I) dicarbonyl complexes of formula [Re^I(CO)₂(N-N)Br(py)] capable of exchanging the halide for other ligands.³⁷ Therefore, we next tried the reaction of the corresponding [Re^I(CO)₂(bpy)Br(py)] complex (**8**) with NOBF₄. Under reaction conditions similar to those applied for the synthesis of **1-5**, complex **8** reacted by substituting py for NO⁺ giving **1** (Fig. 4). We only found trace evidence in the MS spectrum of the desired *fac*-[Re(CO)₂(NO)(bpy)py]²⁺ species.



Fig. 3. Reaction scheme of attempted synthesis fac- $[Re(CO)_2(NO)(N-N)py]^{2+}$ species from corresponding dicarbonyl-nitrosyl species in the presence of Ag⁺ and py (top) and crystal structure of compound **6** (left) and **7**. Thermal ellipsoids are at 30% probability. Hydrogen atoms and BF_a⁺ counter ion omitted for clarity. Selected bond lengths (Å): **6**, Re-N1 2.138(4), Re-N2 2.145(4), Re-N3 1.773(6), Re-F 1.970(3), Re-CO 2.020(6) and 1.999(6), C-O 1.108(7) and 1.115(7), N-O 1.159(7); **7**, Re-N1 2.121(3), Re-N2 2.123(4), Re-N5 1.763(4), Re-F 1.984(3), Re-CO 2.017(5) and 1.991(6), C-O 1.123(6) and 1.129(6), N-O 1.185(5).



Fig. 4. Reaction scheme of attempted synthesis fac-[Re(CO)₂(NO)(N-N)py]²⁺ species from corresponding [Re^I(CO)₂(N-N)(py)Br] complex **8** and crystal structure of the same. Thermal ellipsoids are at 30% probability. Hydrogen atoms are omitted for clarity.

It should be noted here that Rattat reported that whereas the imidazole (Im) complexes [ReCl₂(Im)(CO)₂(NO)] and [ReCl(Im)₂(CO)₂(NO)]⁺ can be synthesized in high yields from [NEt₄][ReCl₃(CO)₂(NO)] or [ReCl(μ -Cl)(CO)₂(NO)]₂, isolation of the [Re(Im)₃(CO)₂(NO)]²⁺ was not successful.⁴³ The authors argued that this is due to the behaviour of the *fac*-[Re(CO)₂(NO)]²⁺ fragment in water (the reaction solvent), where the core initially binds three water molecules, one of which is deprotonated, and the resulting hydroxy group cannot be substituted by the σ -donor Im.⁴⁴ However, the trace evidence

of the desired fac-[Re(CO)₂(NO)(bpy)py]²⁺ species we detected by mass spectrometry, encouraged us to pursue our attempts. Therefore, we probed directly the reactivity of fac-[Re^I(CO)₃(N-N)(py)]⁺ complexes with nitrosonium tetrafluoroborate. Following the logic above, we probed the reaction of fac-[Re(CO)₃]⁺complexes with combinations of bpy and Et₂N-bpy (as N-N ligands) with py and N,N-dimethylpyridin-4-amine (Me₂Npy).^{45, 46} What guided our choice, was again consideration that electron-donating substituents (EDS) on N-N or py might be needed to stabilize the rhenium ion in the particular ligand arrangement. We envisioned two cases as shown in Fig 5. In case A we considered the possibility of EDS on the bidentate N-N ligand cis to NO, in case B EDS on the monodentate ligand trans to NO. As illustrated in Fig. 5, we found no evidence of reaction with NO⁺ when the *fac*-[Re^I(CO)₃(Et₂N-bpy)(py)]⁺ complex A was tested. However, complex B gave the corresponding fac-[Re(CO)₂(NO)(bpy)(Me₂N-py)]²⁺ (9) species as the kinetic, but not as the thermodynamically stable, product. The dicationic species could be isolated as it precipitated immediately from DCM following CO replacement by NO⁺. Evidence for the product came from both NMR and IR, which show, respectively, the expected downfield shift of all protons and the dicarbonyl-nitrosyl pattern (ESI). The complex, however, is not pure and purification or crystallization attempts invariably lead to its decomposition.



Fig. 5. Molecular possibilities (A and B) envisioned to stabilize the *fac*- $[Re(CO)_2(NO)]^{2+}$ core *via* EDS on N-N and monodentate py ligand and reactions of corresponding tricabonyl complexes with NO⁺.

Reactivity of fac-[Re¹(CO)₃(N-N)OR] species (OR = π -base) with NO⁺

While studying the reactions above, and in order to better understand the chemistry of the NO⁺ species, we also decided to explore nitrosylation of *fac*-[Re^I(CO)₃(N-N)] complexes with monodante π -basic ligands (OR). Given the apparent affinity of the *fac*-[Re(CO)₂(NO)]²⁺ core for π -donors, we reasoned that *fac*-[Re^I(CO)₃(N-N)OR] species might offer us a different chemical approach for the design of an efficient synthetic strategy to *fac*-[Re(CO)₂(NO)(N-N)L]²⁺ compounds. Therefore, we decided to test the reaction of *fac*-[Re^I(CO)₃(N-N)OR], where OR = OH⁻, benzoate (**10**), 2-(4-bromophenyl)acetate (**11**).



Fig. 6. Top: crystal structures of carboxylato compounds **10** (left) and **11**. Middle: scheme of the reaction of *fac*-[Reⁱ(CO)₃(N-N)(OR)] (OR = OH⁻, benzoate, 2-(4-bromophenyl)acetate) with NOBF₄. Bottom: Bottom: crystal structures of **12** (left) and the *fac*-[Re(CO)₂(NO)(N-N)(CH₃CN)]²⁺ ion (**13**). Thermal ellipsoids are at 30% probability. Selected bond lengths (Å) for **12**: Re-F1 2.082(4), Re-N1 2.137(6), Re-N2 2.132(5), Re-N3 1.794(7), Re-CO 1.999(9) and 1.985(9), C-O 1.123(10) and 1.125(10), N-O 1.139(8); for **13**: Re-N1 2.145(5), Re-N2 2.139(6), Re-N3 1.791(5), Re-N4 2.079(6), Re-CO 1.991(7) and 1.997(8), C-O 1.118(9) and 1.123(9), N-O 1.151(7).

To our surprise, irrespective of the OR ligand, nitrosylation of fac-[Re^I(CO)₃(N-N)OR] gave always the same dicarbonyl-nitrosyl product (i.e. with the identical spectroscopic signature). In the case of OR = benzoate or 2-(4-bromophenyl)acetate, the NMR evidence clearly indicated that OR was no longer coordinated to the rhenium ion. However, it was initially difficult to reconcile the spectroscopic fingerprints of the product with those of the same obtained from the hydroxo complex (i.e. when OR = OH⁻), also in light of the fact that we used dry solvents in the manipulations. The relatively high vCO frequencies of the product (2127 and 2069 cm⁻¹) were also surprising and, on the basis of what we have shown before,^{33, 34} they could not correspond to the electronic contribution of a coordinated OH⁻ base. Kurz and Alberto showed that the reactivity μ -oxo bridged teranuclear $[Re(\mu_3-O)(CO)_2(NO)]_4$ clusters towards neutral bidentate ligands is possible by disassembly of the same in HBF₄ and proceeds "presumably [via] Re-bound labile BF4⁻ anion".²⁷ We managed to crystallize the nitrosylated product obtained from fac-[Re^I(CO)₃(N-N)OR] and we confirmed that the reaction gives fac-[Re(CO)₂(NO)(N-N)(BF₄)][BF₄] (12) as the only product in good yield (Fig. 6). To our knowledge, 12 is only the fourth

structurally characterized Re-FBF₃ complex, and the very first one of its kind.⁴⁷⁻⁴⁹ The Re-FBF₃ bond is persistent in solution, and in CH₃CN only a small fraction of the molecules (ca. 5-7%) substitute the anion for CH₃CN. We were also able to selectively crystallize out the *fac*-[Re(CO)₂(NO)(N-N)(CH₃CN)]²⁺ complex (**13**) as a [Na(BF₄)₃]²⁻ salt (Fig. 6), but we did not study it further.

X-ray Crystallography

Crystallographic details of all complexes reported here are in ESI, while selected bond lengths of fac-[Re(CO)₂(NO)]²⁺ species are given in figure captions. All rhenium dicarbonyl-nitrosyl complexes show a distorted octahedral geometry around the Re ion. Structural analysis of the species and comparison to related fac-[Re(CO)₃]⁺ species, revealed the following general characteristics. Within 3σ , the Re-CO and the C=O bonds are respectively longer and shorted than the corresponding tricarbonyl complexes. There is no significant statistical difference in the Re-Br bond, while the Re-N(diamine) is slightly shorter in fac-[Re(CO)₂(NO)]²⁺ species. In these, overall, crystal parameters are consistent with a rhenium ion in a higher oxidation state than +1, and are in agreement with the spectroscopic data. The shorter C≡O distances, e.g., are clearly reflected in the higher frequency of vibration of the bond in the IR spectrum. Likewise, the longer N-O distance (by ca. 0.1 Å in comparison to the free ion^{50, 51}) of Re-bound NO is observed in a lower frequency vibration of the same. Perhaps the most striking feature in fac-[Re(CO)₂(NO)(N-N)X]⁺ species (where X = halide, 1-5) is represented by the bending (ca. 17°, but up to 25° for complex 7) of the diamine ligand away from the bound NO (the diimine and the $Re(CO)_2$ planes define the angle). In comparison, the same angle measures 4-6° in corresponding tricarbonyl molecules, and ca. 11° for 12 and 13. Similarly, in nitrosyl complexes 1-5, the two COs are also slightly bent towards the same direction (Fig. 7). Overall, the molecules appear as moving towards a trigonal distortion observed in octahedral d⁴ complexes.⁵²



Fig. 7. Main structural differences between related diimine fac-[Re(CO)₂(NO)]²⁺ and fac-[Re(CO)₃]⁺ species. At the bottom we compare the structures of **2** and a tricarbonyl phen derivative.⁵³

CO Releasing Properties

In the initial phases of our investigation, we also probed the direct nitrosylation of tricarbonyl complexes with *ortho*-substituted α -diimines. The reaction is generally lower yielding with these ligands, but it works as well. In synthetic terms, nitrosylation of the complex bearing 6-methyl-2,2'-bipyridine (6Me-bpy) gave the best results (67% yield). We found, however, that when CH₃CN solutions of *fac*-[Re(CO)₂(NO)(6Me-bpy)Br]BF₄ (**14**) were left exposed to ambient light, over time, crystals of the fully oxidized perrhenate ion appeared (Fig. 8).



Fig. 8. Crystal structures of compounds 14 (left) and its fully oxidized product. Thermal ellipsoids are at 30% probability. Hydrogen atoms and BF₄ counter ion omitted for clarity. Selected bond lengths for 14 (Å): Re-N1 2.135(4), Re-N2 2.188(4), Re-N3 1.784(4), Re-Br 2.5358(5), Re-CO 2.006(5) and 1.975(5), C-O 1.120(6) and 1.135(6), N-O 1.161(5).

This observation indicated to us either that steric hindrance at the *ortho* position of the α -diimine ligand can destabilize *fac*-[Re(CO)₂(NO)]²⁺ species which can then be oxidized by O₂ to ReO₄⁻, or that the complexes are photo-labile towards CO (and/or NO) release, i.e. acting as photoCORMs. Marti has shown that, unlike the tricarbonyl congener, the *fac*-[Re(CO)₂(NO)Br₃]⁻ ion reacts with tetradentate chelating ligands giving monocarbonyl-mononitrosyl species, indicative of a tendency of the rhenium dicarbonyl-nitrosyl complexes to liberate CO if specific conditions are satisfied.²⁵ Consequently we probed the CO-releasing properties of the *fac*-[Re(CO)₂(NO)(N-N)X]⁺ molecules under conditions of the standard myoglobin (Mb) assay in the presence and absence of light.

Spectrophotometric measurements of the CO release from complexes 1-5 and 14, as a function of the conversion of deoxy-Mb to MbCO, revealed that dicarbonyl-mononitrosyl complexes only released the gas if exposed to a cold light source of 275-375 nm radiation. In the dark, the complexes are stable and do not elicit any change in the deoxy-Mb spectrum. A typical spectrum of the conversion of the deoxy-Mb spectrum under photolysis of 1-5 and 14 is given in Fig. 9. The equivalents of CO released by the molecules were calculated by measuring the change of absorbance at 540 nm (ϵ_{540} =15.4 mmol L⁻¹ cm⁻¹), as a direct measure of the concentration of MbCO. The amount of the formed MbCO is dependent on the concentration of the complex, but analysis of the saturation curve of MbCO showed, that for all tested complexes approximately 0.6-0.7 moles CO are released per mole of complex. In Fig. 9, the peak at 620 nm is attributable to the formation of metmyoglobin (MetMb) after

prolonged exposure to the light source.⁵⁴ The loss of CO was verified by MS experiments, whereby solutions of the complexes were irradiated under similar conditions in CH₃CN solutions. The spectra consistently revealed that only CO is released by the species during the irradiation process and that a solvent molecule replaces the ligand.



Fig. 9 Typical UV-visible spectrum of conversion of deoxy-myoglobin (deoxy-Mb) to carbon monoxide myoglobin (MbCO) by *fac*-[Re^I(CO)₂(NO)(N-N)Br]BF₄ complexes **1-5** and **14**. Solutions (20 μ M Mb and photoCORM, 25 °C, 0.05 M phosphate buffer at pH 6.8) were exposed to a 275 nm light source (intervals of 10 min) before the conversion reached a plateau after 120 min. Prolonged exposure to the light source eventually favoured formation of metmyoglobin (MetMb), as evidenced by the peak at 620 nm. In the reaction scheme above the spectra, S = solvent molecule.

To our knowledge, fac-[Re(CO)₂(NO)(N-N)Br]⁺ complexes represent a new class of Re photoCORMs. Spontaneous and light-induced CO release of 16- and 17-electron rhenium complexes,⁵⁵⁻⁵⁷ and 18-electron *fac*-[Re^I(CO)₃(N-N)PR₃]⁺ (where PR_3 = phosphine or phosphite) is well known.⁵⁸⁻⁶⁰ In the last five years several examples of diimine complexes bearing either oor π-donating ancillary ligands active towards CO photosubstitution have also been described.⁶¹⁻⁶⁵ For PR₃ species, the strong *trans*-labilizing ability of the phosphorus donor of π -acid ligands is crucial for activating Re tricarbonyl species towards photochemical substitution of CO, and works in conjunction with the internal conversion between the ³MLCT and thermally accessible higher energy photoexcited ³LF state that is productive in terms of CO dissociation.⁶⁶ For tricarbonyl rhenium diimine complexes with π -basic ligands, mechanistic studies and picosecond time-resolved IR measurements indicate that only irradiation with higher energy photons can induce photochemical ligand substitution reactions via higher energy vibrational states rather than the lowest-lying ³MLCT excited or thermally accessible ³LF states. These higher vibrational levels are those of the ¹MLCT state and/or higher electronic excited state(s) including the Re \rightarrow CO 1 MLCT transition. Thus, excitation by high-energy light of fac- $[Re(CO)_3(N-N)(L)]^n$ species (were L = π -base or σ -donor ligand), leads to vibrationally hot photoproducts, which relax within 50-100 ps, while CO ligand dissociation occurs with subpicosecond rates after excitation.⁶⁷ A similar mechanism is likely to be at play here.

Conclusions

In this contribution, we have described an efficient direct nitrosylation of α -diimine rhenium tricarbonyl complexes widely applicable to different supporting N-N ligands, and studied the substitution chemistry of the resulting species. We showed that fac-[Re^I(CO)₃(N-N)Br] complexes react efficiently with NOBF₄ to yield the corresponding dicarbonyl-mononitrosyl species. The resulting compounds are structurally nearly identical higher charge congeners of tricarbonyls. Although the rhenium ion is formally described as having oxidation state +1, we found that the substitution chemistry of metal ion in fac- $[Re(CO)_2(NO)(N-N)X]^+$ is closer to that of a harder Re(III) acid, probably due to the stronger π -acceptor properties of NO⁺ as compared to those of CO. In comparison to tricarbonyl species, the higher apparent formal oxidation state of the metal ion in dicarbonyl-mononitrosyl complexes, implies greater depletion of electron density from the same and, consequently, lower π back Re-CO bonding. A fundamental consequence is that fac- $[Re(CO)_2(NO)(N-N)X]^+$ complexes can be photo-activated towards CO release and represent a new class of photoCORMs, releasing ca. 1 equivalent of CO when photo-irradiated with UV light.

Experimental Section

Reagents and chemicals

All reagent and solvents were purchased from standard sources and used without further purification. Compound $[Re(CO)_5Br]$ was purchased from Sigma Aldrich, while complexes of formula fac- $[Re^{I}(CO)_{3}(N-N)Br]^{19}$, $(Et_4N)[Re^{II}(CO)_2Br_4]^{36}$, fac- $[Re^{I}(CO)_2(N-N)(py)Br]^{37}$, fac- $[Re(CO)_{3}(bpy)OH]^{68}$ and fac- $[Re(CO)_{3}(bpy)(Me_2N-py)](CF_3SO_3)^{46}$ were synthesized according to published procedures. Unless otherwise noted, solvents used in the preparation of all molecules were dry and O_2 -free.

Instruments and analysis

NMR spectra were measured on a Bruker Advance III 400 MHz. The corresponding ¹H chemical shifts are reported relative to residual solvent protons. Mass analyses were performed using a Bruker FTMS 4.7-T Apex II in positive mode. UV-Vis spectra were measured on a Jasco V730 spectrophotometer. IR spectra were recorded on a Bruker TENSOR II with the following parameters: 16 scans for background, 32 scans for sample with a resolution of 4 cm⁻¹ in the 4000-600 cm⁻¹ region. Single crystal diffraction data collection was performed on a Stoe IPDS2 diffractometer (CuK α 1 (λ = 1.5406 Å)) equipped with a cryostat from Oxford Cryosystems. The structure were solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.^{69, 70} All crystal structures are deposited at the Cambridge Crystallographic Data Centre. CCDC numbers 2093631-2093640 and 2094070 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/structures.

Synthetic procedures

The following general procedure was followed for the synthesis of $[Re(CO)_2(NO)(N-N)Br]BF_4$ complexes. In a glove box the corresponding *fac*- $[Re(CO)_3(N-N)Br]$ (typically 0.2 mmol ca. 100 mg) was dissolved in CH₂Cl₂ (100 ml, dry). To the resulting yellow solution, NOBF₄ (84-115 mg, 0.5-1 mmol, 2.5-5 eq.) was added in the solid form. The reaction was stirred at room temperature for 2 days. A light off-white precipitate was filtered off and the filtrate either allowed to evaporate or layered with pentane to afford light yellow crystals, which were collected by filtration.

[Re(CO)₂(NO)(bpy)Br](BF₄) (1). Yellow solid, yield 70%. ESI⁺-MS (MeOH): m/z, 507.7 [Re(CO)₂(NO)(C₁₀H₈N₂)Br]⁺, [M]⁺. IR (solid, cm⁻¹); vCO: 2112, 2050, vNO: 1801. ¹H-NMR (400 MHz, CD₃CN, ppm): 7.87 (ddd, J=7.70, 5.62, 1.34 Hz, 2 H) 8.48 (td, J=7.98, 1.53 Hz, 2 H) 8.64 (d, J=8.19 Hz, 2 H) 9.22 - 9.30 (m, 2 H). UV-Vis (CH₃CN, λ nm): 312, 321. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution.

[Re(CO)₂(NO)(phen)Br](BF₄) (2). Yellow solid, yield 55%. ESI⁺-MS (MeOH): m/z, 531.6 [Re(CO)₂(NO)(C₁₂H₈N₂)Br]⁺, [M]⁺. IR (solid, cm⁻¹); vCO: 2118, 2057, vNO: 1790. ¹H-NMR (400 MHz, DMSO-d6, ppm): 8.34 (dd, J=8.31, 5.26 Hz, 2 H) 8.49 (s, 2 H) 9.25 (dd, J=8.31, 1.22 Hz, 2 H) 9.89 (dd, J=5.26, 1.22 Hz, 2 H). UV-Vis (CH₃CN, λ nm): 304, 339, 375. Crystals suitable for X-ray diffraction were obtained from layering a solution of acetonitrile with ether/hexane (1:1).

[Re(CO)₂(NO)(Et₂N-bpy)Br](BF₄) (3). Et₂N-bpy = N⁴, N⁴, N^{4'}, N^{4'}, tetraethyl-[2,2'-bipyridine]-4,4'-diamine. Yellow solid, yield 87%. ESI⁺-MS (MeOH): m/z, 649.8 [Re(CO)₂(NO)(C₁₈H₂₆N₄)Br]⁺, [M]⁺. IR (solid, cm⁻¹); vCO: 2104, 2040, vNO: 1770. ¹H-NMR (400 MHz, CD₃CN, ppm): 1.22 - 1.28 (m, 12 H) 3.64 (br. s., 8 H) 6.79 (dd, J=7.03, 2.87 Hz, 2 H) 7.37 (d, J=2.93 Hz, 2 H) 8.51 (d, J=7.09 Hz, 2 H). UV-Vis (CH₃CN, λ nm): 342, 357.

[Re(CO)₂NO('Bu-bpy)Br](BF₄) (4). ^tBu-bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine. Yellow solid, yield 69%. ESI⁺-MS (MeOH): m/z, 619.7 [Re(CO)₂(NO)(C₁₈H₂₄N₂)Br]⁺, [M]⁺. IR (solid, cm⁻¹); vCO: 2114, 2053, vNO: 1797. ¹H NMR (400 MHz, CD₃CN, ppm): 1.42 - 1.54 (m, 18 H) 7.84 (dd, J=6.05, 2.02 Hz, 2 H) 8.58 - 8.61 (m, 2 H) 9.09 - 9.14 (m, 2 H). UV-Vis (CH₃CN, λ nm): 309, 318.

[Re(CO)₂NO(φ-phen)Br](BF₄) (5). φ-phen = 4,7-diphenyl-1,10phenanthroline. Yellow solid, yield 61%. ESI⁺-MS (MeOH): m/z, 683.7 [Re(CO)₂(NO)(C₂₄H₁₆N₂)Br]⁺, [M]⁺. IR (solid, cm⁻¹); vCO: 2114, 2052, vNO: 1795. ¹H-NMR (400 MHz, CD₃CN, ppm): 7.69 - 7.73 (m, 10 H) 8.14 (d, J=5.50 Hz, 2 H) 8.26 (s, 2 H) 9.69 (d, J=5.62 Hz, 2 H). UV-Vis (CH₃CN, λ nm): 297, 336, 375.

 $[Re(CO)_2(NO)(Et_2N-bpy)F](BF_4)$ (7). Complex 3 (80.0 mg) was dissolved in 5 mL of methanol. The solution was then heated to 55°C and pyridine (25.8 mg, 3 eq.) was added followed by the addition of silver triflate (41.8 mg, 1.5 eq.) in the dark. The reaction mixture was stirred over night at 55°C, filtered and the solvent evaporated. The crude product was then dissolved in a minimal amount of methanol and precipitated with cold ether to give **6** as a white/beige solid (21.0 mg, ca. 29%) which contained traces of pyridine. ESI⁺-MS (MeOH): m/z, 589.67 $[\text{Re}(\text{CO})_2(\text{NO})(\text{C}_{18}\text{H}_{26}\text{N}_4)\text{F}]^+, [M]^+. \text{ IR (solid, cm}^{-1}): v\text{CO}: 2106, 2033, v\text{NO}: 1784. {}^{1}\text{H}-\text{NMR} (400 \text{ MHz, CD}_3\text{CN, ppm}): 1.25 (t, J=7.15 \text{ Hz}, 12 \text{ H}) 3.63 (d, J=7.09 \text{ Hz}, 8 \text{ H}) 6.77 (dd, J=7.09, 2.93 \text{ Hz}, 2 \text{ H}) 7.35 (d, J=2.81 \text{ Hz}, 2 \text{ H}) 7.99 (t, J=7.09 \text{ Hz}, 2 \text{ H}) 8.46 \text{ -} 8.60 (m, 3 \text{ H}) 8.69 (d, J=5.26 \text{ Hz}, 2 \text{ H}). UV-Vis (DMF, nm): 342, 352. Crystals suitable for X-ray diffraction were obtained by layering ether on a methanol solution of the compound.$

[Re(CO)₂(py)(bpy)Br] (8). This complex was prepared by following a previously published procedure for similar species.³⁷ Brown solid, yield 80%. IR (solid, cm⁻¹); vCO: 1864, 1781. ¹H-NMR (400 MHz, CD₂Cl₂, ppm): 6.83 (dd, J=7.52, 6.66 Hz, 2 H) 7.37 - 7.49 (m, 3 H) 7.89 (td, J=7.89, 1.47 Hz, 2 H) 8.09 (d, J=8.07 Hz, 2 H) 8.37 (dd, J=6.60, 1.47 Hz, 2 H) 9.16 (d, J=5.38 Hz, 2 H). UV-Vis (DMF, λ nm): 393, 308. Crystals suitable for X-ray diffraction were obtained by layering pentane on a DCM solution of the compound.

[Re(CO)₂NO(bpy)(Me₂N-py)](BF₄)₂ (9). In a glove box *fac*-[Re(CO)₃(bpy)(Me₂N-py)](CF₃SO₃)⁴⁶ (30 mg, 0.043 mmol, where Me₂N-py = *N*,*N*-dimethylpyridin-4-amine) was dissolved in CH₂Cl₂ (30 ml, dry) and to the resulting yellow solution, NOBF₄ (10 mg, 2 eq.) was added in the solid form. The reaction was stirred at room temperature for 2 days. A light yellow solid appeared. It was filtered off, washed with cold CH₂Cl₂ and dried in vacuo. Attempts to purify the salt lead to the decomposition of the product. Yield 62%. IR (solid, vCO cm⁻¹): 2129, 2070, vNO: 1830. ¹H NMR (400 MHz, CD₃CN, ppm): 9.24 - 9.31 (m, 2H), 8.67 - 8.73 (m, 2H), 8.52 - 8.61 (m, 2H), 7.98 - 8.02 (m, 2H), 7.91 - 7.97 (m, 2H), 6.87 (d, J = 6.85 Hz, 2H), 3.19 - 3.22 (m, 6H).

The *fac*-[Re(CO)₃(bpy)] carboxylato complexes were prepared by adaptation of a published procedure.⁷¹ Briefly, *fac*-[Re(CO)₃(bpy)Br] (100 mg, 0.2 mmol) and the appropriate carboxylic acid ligand were dissolved in anhydrous degassed tetrahydrofuran (30 mL). The reaction mixture was stirred for 5 min, then trimethylamine (33 μ L, 24 mg, 0.24 mmol) and AgCF₃SO₃(50 mg, 0.2 mmol) were added and the mixture stirred at 70 °C for 18 h. The mixture was filtered, solvent evaporated to dryness and the residue purified by column chromatography on deactivated alumina with DCM as the eluent. Analytically pure products were obtained after recrystallization from dichloromethane/n-hexane mixtures.

[Re(CO)₃(bpy)(O₂CBz)] (10). O₂CBz = benzoate. Yellow solid, yield 59%. ESI⁺-MS (MeOH): m/z, 571 [Re(CO)₃(C₁₀H₈N₂)(C₇H₅O₂)] + Na⁺, [M+Na]⁺. IR (solid, cm⁻¹); vCO: 2012, 1904, 1866. ¹H-NMR (400 MHz, CD₃CN, ppm): 9.08 - 9.15 (m, 2 H) 8.41 (d, J=8.19 Hz, 2 H) 8.20 (td, J=7.92, 1.53 Hz, 2 H) 7.58 - 7.67 (m, 2 H) 7.38 (dd, J=8.01, 1.28 Hz, 2 H) 7.21 - 7.29 (m, 1 H) 7.08 - 7.17 (m, 2 H). UV-Vis (DMF, λ nm): 369, 317, 293. Crystals suitable for X-ray diffraction were obtained from layering a solution of tetrahydrofuran with pentane.

 319, 293. Crystals suitable for X-ray diffraction were obtained from layering a solution of tetrahydrofuran with pentane.

[Re(CO)₂NO(bpy)BF₄](BF₄) (12). Compound 10 or 11 (20-25 mg) was dissolved in dry DCM (20 ml). NOBF₄ (1.5 eq.) was added in solid form to the resulting solution. The reaction mixture was stirred for 24h at room temperature in dark. A white solid appeared, and then the solvent was decanted from the mixture. The residue was dissolved in DCM and water (1:1). The two phases were separated and the aqueous phase was washed with DCM. The aqueous phase was concentrated under vacuum. The crude product was crystalized by slow evaporation of a CHCl₃ : acetone (1:1) solution to yield crystals of the pure product 12. White solid, yield 55%. ESI+-MS (MeOH): m/z, 515.5 [Re(CO)₂(NO)(C₁₀H₈N₂)BF₄]⁺. IR (solid, cm⁻¹); vCO: 2127, 2069, vNO: 1820. ¹H NMR (400 MHz, CD₃CN, ppm): 9.24 - 9.27 (dd, 2H), 8.62 - 8.65 (dd, 2H), 8.45 - 8.50 (t, 2H), 7.85 - 7.89 (td, 2H). Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetone solution.

[Re(CO)2NO(6Me-bpy)Br](BF₄) (14). Prepared according to general procedure for 1-5. 6Me-bpy = 6-methyl-2,2'-bipyridine. Yellow solid, yield 67%. ESI⁺-MS (MeOH): m/z, 521.6 [Re(CO)₂(NO)(C₁₁H₁₀N₂)Br]⁺, [M]⁺. IR (solid, cm⁻¹); vCO: 2114, 2050, vNO: 1796. ¹H-NMR (400 MHz, DMSO-d6, ppm): 3.13 (s, 3 H) 7.98 (ddd, J=7.40, 5.87, 1.16 Hz, 1 H) 8.02 - 8.07 (m, 1 H) 8.47 (t, J=7.95 Hz, 1 H) 8.59 (td, J=7.95, 1.47 Hz, 1 H) 8.82 (d, J=7.58 Hz, 1 H) 8.94 (d, J=8.31 Hz, 1 H) 9.50 (dd, J=5.69, 0.92 Hz, 1 H). UV-Vis (CH₃CN, λ nm): 323, 332. Crystals suitable for X-ray diffraction were obtained by vapour diffusion of pentane into a dichloromethane solution.

Detection of CO release using the myoglobin assay

The photorelease of CO from 1-5 and 14 was assessed spectrophotometrically by measuring the conversion of deoxymyoglobin (Mb) to carbonmonoxy myoglobin (MbCO) as previously reported.⁷² A small aliquot of a freshly prepared solution of the selected complex (in DMSO) was added to 1 mL of the Mb solution in phosphate buffer (0.05M) prepared at pH 6.8. Final concentrations: 20 µM for Re complex and Mb. Mb spectra were recorded after each photoirradiation (5-10 min) at 375nm at 25 °C. The methanol or DMSO content of the solution never exceeded 0.5%. The amount of MbCO formed was determined by measuring the absorbance at 540 nm (extinction coefficient ϵ = 15.4 M cm⁻¹). The MbCO concentration was plotted over time and directly related to the equivalents of CO released from the compounds. Control experiments were run under identical conditions but without light or addition of the metal complexes.

Author contributions

S.N.S. and I.K. investigation, formal analysis, data curation, methodology, writing – original draft; Y.C., K.S. and S.-C.L. investigation, formal analysis; A.C. crystallography; A.P. conceptualization. F.Z. writing – original draft, review & editing, conceptualization, supervision, validation, acquisition, resources, project administration.

Conflicts of interest

There are no conflicts to declare.

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SUPPORTING INFORMATION FOR

Efficient direct nitrosylation of α -diimine rhenium tricarbonyl complexes to structurally nearly identical higher charge congeners activable towards photo-CO release

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Emission spectra of selected nitrosyl Re complexes - Figures S35 - page 16

Table S1 Crystal data and structure refinement for complexes - page 17

NMR spectra



Figure S1. 400 MHz ¹H-NMR of [Re(CO)₂(NO)(bpy)Br](BF₄) (1) (in Acetonitrile, ***** = solvent residual peak).



Figure S2. 400 MHz ¹H NMR spectrum of the $[Re(CO)_2(NO)(phen)Br](BF_4)$ (2) (in DMSO-d₆, * = solvent residual peak).



Figure S3. 400 MHz ¹H NMR spectrum of the $[Re(CO)_2(NO)(Et_2N-bpy)Br](BF_4)$ (**3**) (in Acetonitrile, ***** = solvent residual peak).



Figure S4. 400 MHz ¹H NMR spectrum of $[Re(CO)_2NO(tBu-bpy)Br](BF_4)$ (4) (in Acetonitrile, ***** = solvent residual peak).



Figure S5. 400 MHz ¹H NMR spectrum of $[Re(CO)_2NO(\varphi-phen)Br](BF_4)$ (5) (in Acetobitrile, ***** = solvent residual peak).



Figure S6. 400 MHz ¹H NMR spectrum of [[Re(CO)₂(NO)(Et₂N-bpy)F](BF₄) (7) (in Acetonitrile, * = solvent residual peak).



Figure S7. 400 MHz ¹H-NMR of [Re(CO)₃(bpy)(O₂CBz)] (10) (in Acetonitrile).



Figure S8. 400 MHz ¹H-NMR of [Re(CO)₃(bpy)(O₂CPh)] (11) (in Acetonitrile).



Figure S9. 400 MHz ¹H NMR spectrum of [Re(CO)₂NO(bpy)BF₄](BF₄) **(12)** (in Acetonitrile).



Figure S10. 400 MHz ¹H-NMR of [Re(CO)₂NO(6-Me-bpy)Br](BF₄) (**14**) (in Acetonitrile, ***** = solvent residual peak).



Figure S11. 400 MHz ¹H NMR spectrum of [Re(CO)₂NO(bpy)(Me2N-py)](BF₄)₂ (9) (in Acetonitrile).



Figure S12. Comparison of the ¹H NMR spectra (400 MHz) of (top to bottom) *N*,*N*-dimethylpyridin-4-amine (Me2N-py), *fac*-[Re(CO)₃(bpy)(Me2N-py)](CF₃SO₃) (**B**) and [Re(CO)₂NO(bpy)(Me2N-py)](BF₄)₂ (**9**) (in Acetonitrile).





Figure S13. IR spectrum of $[Re(CO)_2(NO)(bpy)Br](BF_4)$ (1)



Figure S14. IR spectrum of [Re(CO)₂NO(phen)Br](BF₄) (2)



Figure S15. IR spectrum of [Re(CO)₂NO(Et₂N-bpy)Br](BF₄) (3)



Figure S16. IR spectrum of [Re(CO)₂NO(tBu-bpy)Br](BF₄) (4)



Figure S17. IR spectrum of $[Re(CO)_2NO(\phi-phen)Br](BF_4)$ (5)



Figure S18. IR spectrum of [Re(CO)₂NO(Et₂N-bpy)F](BF₄) (7)



Figure S19. IR spectrum of [Re(CO)₂NO(bpy)(Me2N-py)](BF₄)₂ (9)



Figure S20. IR spectrum of [Re(CO)₃(bpy)(O₂CBz)] (10)



Figure S21. IR spectrum of [Re(CO)₃(bpy)(O₂CPh)] (11)



Figure S22. IR spectrum of [Re(CO)₂NO(bpy)BF₄](BF₄) (12)



Figure S23. IR spectrum of [Re(CO)₂NO(6-Me-bpy)Br](BF₄) (14)

UV-Vis spectra



FigureS24.UV-Visspectrumof[Re(CO)_2NO(bpy)Br](BF_4) (1) in acetonitrile



FigureS25.UV-Visspectrumof[Re(CO)_2NO(phen)Br](BF4) (2) in DMF



Figure S26. UV-Vis spectrum of [Re(CO)₂NO(Et₂N-bpy)Br](BF₄) **(3**) in acetonitrile



Figure S27. UV-Vis spectrum of [Re(CO)₂NO(tBubpy)Br](BF₄) (**4**) in DMF



Figure S28. UV-Vis spectrum of $[Re(CO)_2NO(\phi-phen)Br](BF_4)$ (5) in acetonitrile



Figure S29. UV-Vis spectrum of [Re(CO)₂NO(6-Me-bpy)Br](BF₄) (**14**) in acetonitrile



Figure S30. UV-Vis spectrum of [Re(CO)₂(NO)(Et₂N-bpy)F](BF₄) (7) in acetonitrile



FigureS31.UV-Visspectrumof $[Re(CO)_3(bpy)(O_2CBz)]$ (10) in DMF



 $[Re(CO)_3(bpy)(O_2CPh)]$ (**11**) in DMF



 Figure
 S33.
 UV-Vis
 spectrum
 of

 [Re(CO)₂NO(bpy)BF₄](BF₄) (12) in DMF



FigureS34.UV-Visspectrumof[Re(CO)_2NO(bpy)(Me2N-py)](BF_4)_2(9)inacetonitrile



Fig. S35. Emission spectra of selected nitrosyl Re complexes. Top: λ_{ex} = 318; bottom λ_{ex} = 350.

Identification code	1	2	6	7	8	10	11	12	13	14	ox'd 14
CSD number	2093631	2093632	2094070	2093633	2093634	2093635	2093636	2093637	2093638	2093639	2093640
Empirical formula	$C_{12}H_8BBrF_4N_3O_3Re$	$C_{14}H_8BBrF_4N_3O_3Re$	$C_{12}H_8BF_5N_3O_3Re$	$C_{20}H_{26}BF_5N_5O_3Re$	$C_{34}H_{26}Br_2N_6O_4Re_2$	$C_{21}H_{14}BrN_2O_5Re$	C ₂₀ H ₁₃ N ₂ O ₅ Re	$C_{12}H_{10}B_2F_8N_3O_4Re$	$C_{14}H_{11}B_3F_{12}N_4NaO_3\mathit{R}e$	$C_{13}H_{10}BBrF_4N_3O_3Re$	C ₁₁ H ₁₁ N ₂ O ₄ <i>R</i> e
Formula weight	595.13	619.15	534.22	676.47	1114.83	640.45	547.52	620.05	752.89	609.16	421.42
Temperature/K	200(2)	200(2)	250(2)	200(2)	200(2)	200(2)	200(2)	250(2)	200(2)	200(2)	200(2)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	triclinic	triclinic	orthorhombic
Space group	<i>P</i> nma	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /n	Pna2 ₁	P21/c	P-1	<i>P</i> 2 ₁ /n	P-1	<i>P</i> -1	<i>P</i> nma
a/Å	17.0900(4)	10.6603(3)	10.0421(2)	9.26150(10)	16.1750(2)	20.1830(6)	8.4295(4)	7.4804(2)	8.6774(3)	7.0101(4)	9.5298(4)
b/Å	12.1181(2)	12.4496(3)	7.8180(2)	23.2899(3)	8.35450(10)	10.7028(2)	9.4918(4)	24.3398(7)	10.8057(4)	10.9539(4)	6.6170(3)
c/Å	8.01100(10)	13.2172(4)	20.2281(4)	12.5774(2)	25.8524(3)	9.4252(3)	12.7023(6)	11.1812(2)	13.1764(4)	11.3985(7)	18.6332(11)
α/°	90	90	90	90	90	90	106.704(3)	90	75.144(3)	84.168(3)	90
в/°	90	105.443(2)	98.0260(10)	110.6400(10)	90	97.923(2)	92.147(4)	109.070(2)	73.474(3)	77.822(5)	90
γ/°	90	90	90	90	90	90	112.452(3)	90	89.797(3)	84.140(4)	90
Volume/Å ³	1659.06(5)	1690.81(8)	1572.54(6)	2538.80(6)	3493.54(7)	2016.55(10)	887.12(7)	1924.05(9)	1141.65(7)	848.21(8)	1174.99(10)
Ζ	4	4	4	4	4	4	2	4	2	2	4
$\rho_{calc}g/cm^3$	2.383	2.432	2.256	1.770	2.120	2.110	2.050	2.141	2.190	2.385	2.382
µ/mm⁻¹	17.733	17.442	15.833	9.977	16.411	14.433	13.724	13.323	11.792	17.364	20.343
F(000)	1104.0	1152.0	1000.0	1320.0	2096.0	1216.0	524.0	1168.0	712.0	568.0	792.0
20 range for data collection/°	10.352 to 135.344	8.606 to 136.05	9.362 to 135.072	7.592 to 136.81	10.94 to 135.768	8.848 to 135.636	10.67 to 129.818	13.102 to 135.856	7.26 to 135.066	13.778 to 129.57	10.426 to 134.826
Reflections collected	20797	17444	41477	38156	34006	3542	21038	18854	36017	15094	4916
Independent reflections	1573 [<i>R</i> _{int} = 0.0336, <i>R</i> _{sigma} = 0.0124]	2947 [R _{int} = 0.0386, R _{sigma} = 0.0170]	$2801 [R_{int} = 0.0280, R_{sigma} = 0.0082]$	4497 [R _{int} = 0.0343, R _{sigma} = 0.0159]	4908 [R _{int} = 0.0294, R _{sigma} = 0.0127]	3542 [R _{int} = ?, R _{sigma} = 0.0151]	2904 [<i>R</i> _{int} = 0.0509, <i>R</i> _{sigma} = 0.0238]	3229 [R _{int} = 0.0529, R _{sigma} = 0.0237]	3817 [<i>R</i> _{int} = 0.0677, <i>R</i> _{sigma} = 0.0229]	2750 [<i>R</i> _{int} = 0.0278, <i>R</i> _{sigma} = 0.0129]	1082 [<i>R</i> _{int} = 0.0236, <i>R</i> _{sigma} = 0.0121]
Data/restraints/parameters	1573/0/129	2947/0/245	2801/0/226	4497/0/321	4908/1/434	3542/110/273	2904/0/253	3229/36/299	3817/0/343	2750/0/237	1082/1/108
Goodness-of-fit on F ²	1.192	1.061	1.290	1.109	1.101	1.167	1.123	1.082	1.102	1.149	1.085
Final R indexes [I>=2o (I)]	R ₁ = 0.0248, wR ₂ = 0.0700	$R_1 = 0.0260, wR_2 = 0.0738$	R ₁ = 0.0289, wR ₂ = 0.0647	$R_1 = 0.0309, wR_2 = 0.0873$	$R_1 = 0.0250, wR_2 = 0.0654$	$R_1 = 0.0686,$ w $R_2 = 0.1786$	$R_1 = 0.0312,$ w $R_2 = 0.0793$	R ₁ = 0.0439, wR ₂ = 0.1020	$R_1 = 0.0406, wR_2 = 0.1022$	$R_1 = 0.0234, wR_2 = 0.0626$	$R_1 = 0.0346$, w $R_2 = 0.1014$
Final R indexes [all data]	$R_1 = 0.0249, wR_2 = 0.0700$	$R_1 = 0.0267, wR_2 = 0.0745$	$R_1 = 0.0290, wR_2 = 0.0647$	$R_1 = 0.0334, wR_2 = 0.0888$	$R_1 = 0.0252, wR_2 = 0.0656$	$R_1 = 0.0703,$ w $R_2 = 0.1795$	$R_1 = 0.0312,$ w $R_2 = 0.0793$	R ₁ = 0.0473, wR ₂ = 0.1041	$R_1 = 0.0406, wR_2 = 0.1022$	$R_1 = 0.0234, wR_2 = 0.0626$	$R_1 = 0.0352$, w $R_2 = 0.1019$
Largest diff. peak/hole / e Å-3	0.95/-0.71	1.46/-1.02	1.25/-1.54	0.72/-1.00	0.81/-0.76	2.58/-2.83	0.72/-1.96	0.95/-0.93	2.04/-1.64	1.31/-1.55	1.55/-0.83
Flack parameter					0.429(14)						

Table S1. Crystal data and structure refinement for 1, 2, 6-8, 10-14, and fully oxidized complex 14

Suitable crystal were selected and mounted on loop with oil on a Stoe StadiVari diffractometer. The crystal were kept at 200(2) K during data collection, excepted for **6** and **12** (250(2) K). Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimization.

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3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) renobipy_e_pl

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Datablock: renobipy_e_pl

Bond precision: C-C = 0.0076 AWavelength=1.54186 Cell: a=17.0900(4) b=12.1181(2) c=8.0110(1)alpha=90 beta=90 gamma=90 Temperature: 200 K Calculated Reported Volume 1659.07(5) 1659.06(5)Space group Рпта P n m a Hall group -P 2ac 2n -P 2ac 2n Moiety formula C12 H8 Br N3 O3 Re, B F4 C12 H8 Br N3 O3 Re, B F4 Sum formula C12 H8 B Br F4 N3 O3 Re C12 H8 B Br F4 N3 O3 Re Mr 595.13 595.13 2.383 2.383 Dx,g cm-3 Ζ 4 4 Mu (mm-1) 17.732 17.733 F000 1104.0 1104.0 F000′ 1083.57 h,k,lmax 20,14,9 20,14,9 Nref 1581 1573 0.072,0.242 0.044,0.176 Tmin,Tmax Tmin' 0.012 Correction method= # Reported T Limits: Tmin=0.044 Tmax=0.176 AbsCorr = MULTI-SCAN Data completeness= 0.995 Theta(max) = 67.672R(reflections) = 0.0248(1569) wR2(reflections) = 0.0700(1573) S = 1.192Npar= 129

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🏓 Alert level C CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier. greenish 2 Check PLAT218_ALERT_3_C Constrained U(ij) Components(s) for F2 . PLAT218_ALERT_3_C Constrained U(ij) Components(s) for F3A 2 Check . PLAT218_ALERT_3_C Constrained U(ij) Components(s) for F4 2 Check PLAT218_ALERT_3_C Constrained U(ij) Components(s) for F6 2 Check PLAT218_ALERT_3_C Constrained U(ij) Components(s) for F5 2 Check B1 Check PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1 Note C12 H8 Br N3 O3 Re PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 9 Report Alert level G PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 1 Report 7.5 s.u. PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F2A --B1 . PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F3 --B1 9.5 s.u. . --B1 PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F3A 6.8 s.u. . PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F4 --B1 6.3 s.u. . --B1 . --Br1 . PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F6 8.0 s.u. • PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Re1 9.8 s.u. 0.25 Check Constrained at Constrained at Constrained at PLAT300_ALERT_4_G Atom Site Occupancy of F2 PLAT300_ALERT_4_G Atom Site Occupancy of F2A 0.25 Check PLAT300_ALERT_4_G Atom Site Occupancy of F3 0.25 Check 0.25 Check PLAT300_ALERT_4_G Atom Site Occupancy of F3A Constrained at PLAT300_ALERT_4_G Atom Site Occupancy of F4 Constrained at 0.25 Check 0.25 Check PLAT300_ALERT_4_G Atom Site Occupancy of F5 Constrained at PLAT300_ALERT_4_G Atom Site Occupancy of F6 Constrained at 0.25 Check PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 2) 64% Note PLAT432_ALERT_2_G Short Inter X...Y Contact F1 2.94 Ang. ..C6 8_564 Check x, 1/2-y, -1+z =PLAT432_ALERT_2_G Short Inter X...Y Contact F1 2.94 Ang. ..C6 x,y,-1+z = 1_554 Check PLAT432_ALERT_2_G Short Inter X...Y Contact F3 2.95 Ang. ..C5 1_555 Check x,y,z = PLAT432_ALERT_2_G Short Inter X...Y Contact F3 ..C5 2.95 Ang. x, 1/2 - y, z =8 565 Check PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) . 1.13 Ratio PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle(s) in CIF . # 55 Check F3 -B1 -F6 1.555 1.555 1.555 33.80 Deg. PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle(s) in CIF . # 60 Check F4 -B1 -F2 1.555 1.555 8.565 25.00 Deg. PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle(s) in CIF . # 66 Check F6 -B1 -F3A 1.555 1.555 8.565 20.30 Deg. PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle(s) in CIF . # 68 Check 32.90 Deg. F5 -B1 -F2 1.555 1.555 1.555 PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group # 3 Check PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 2 Note B F4 PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do ! PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still 98% Note PLAT961_ALERT_5_G Dataset Contains no Negative Intensities Please Check PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 2 Info

0 ALERT level A = Most likely a serious problem - resolve or explain 0 ALERT level B = A potentially serious problem, consider carefully 9 ALERT level C = Check. Ensure it is not caused by an omission or oversight 30 ALERT level G = General information/check it is not something unexpected

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2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6 ALERT type 2 Indicator that the structure model may be wrong or deficient
7 ALERT type 3 Indicator that the structure quality may be low
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No syntax errors found. CIF dictionary Interpreting this report

Datablock: reno-phen

Bond precision: C-C = 0.0053 A Wavelength=1.54186 Cell: a=10.6603(3) b=12.4496(3) c=13.2172(4)alpha=90 beta=105.443(2) gamma=90 Temperature: 200 K Calculated Reported Volume 1690.81(8) 1690.81(8) Space group P 21/c P 1 21/c 1 Hall group -P 2ybc -P 2ybc Moiety formula C14 H8 Br N3 O3 Re, B F4 C14 H8 Br N3 O3 Re, B F4 Sum formula C14 H8 B Br F4 N3 O3 Re C14 H8 B Br F4 N3 O3 Re Mr 619.15 619.15 2.432 2.432 Dx,g cm-3 Ζ 4 4 Mu (mm-1) 17.442 17.442 F000 1152.0 1152.0 F000′ 1131.70 h,k,lmax 12,14,15 12,14,15 Nref 3073 2947 0.234,0.418 0.028,0.197 Tmin,Tmax Tmin' 0.049 Correction method= # Reported T Limits: Tmin=0.028 Tmax=0.197 AbsCorr = MULTI-SCAN Data completeness= 0.959 Theta(max) = 68.025R(reflections) = 0.0260(2854) wR2(reflections) = 0.0745(2947) S = 1.061Npar= 245

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level C		
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low .	0.962	Why?
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600	115	Report
Alert level G		
PLAT230_ALERT_2_G Hirshfeld Test Diff for 02C13 .	8.0	s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Re1N3 .	8.0	s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Re1C13 .	8.5	s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Re1C14 .	7.0	s.u.
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of	B1	Check
PLAT432_ALERT_2_G Short Inter XY Contact F3C14	2.90	Ang.
1+x,y,z =	1_655 Chec	ck
PLAT432_ALERT_2_G Short Inter XY Contact F4C13	2.93	Ang.
1+x,y,z =	1_655 Chec	ck
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. #	2	Note
B F4		
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still	95%	Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600	11	Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF	2	Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File	2	Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.	1	Info
(ALERT Level A = Most likely a serious problem - resolve or evo	lain	
0 ALERT level B = A potentially serious problem, consider carefu	llv	

2 ALERT level C = Check. Ensure it is not caused by an omission or oversight 13 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data 8 ALERT type 2 Indicator that the structure model may be wrong or deficient 4 ALERT type 3 Indicator that the structure quality may be low 3 ALERT type 4 Improvement, methodology, query or suggestion 0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/12/2020; check.def file version of 05/12/2020


Structure factors have been supplied for datablock(s) ks188-1

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: ks188-1

Bond precision: C-C = 0.0088 A Wavelength=1.54186 Cell: a=10.0421(2) b=7.8180(2) c=20.2281(4) alpha=90 beta=98.026(1) gamma=90 Temperature: 250 K Calculated Reported Volume 1572.54(6) 1572.54(6)Space group P 21/n P 1 21/n 1 Hall group -P 2yn -P 2yn Moiety formula C12 H8 F N3 O3 Re, B F4 C12 H8 F N3 O3 Re, B F4 Sum formula C12 H8 B F5 N3 O3 Re C12 H8 B F5 N3 O3 Re Mr 534.23 534.22 2.257 2.256 Dx,g cm-3 Ζ 4 4 Mu (mm-1) 15.833 15.833 F000 1000.0 1000.0 F000′ 982.50 h,k,lmax 12,9,24 11,9,24 Nref 2830 2801 0.155,0.387 0.108,0.495 Tmin,Tmax Tmin' 0.054 Correction method= # Reported T Limits: Tmin=0.108 Tmax=0.495 AbsCorr = MULTI-SCAN Data completeness= 0.990 Theta(max) = 67.536R(reflections) = 0.0289(2782) wR2(reflections) = 0.0647(2801) S = 1.290Npar= 226

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Alert level C	
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds	0.00878 Ang.
PLAT431_ALERT_2_C Short Inter HLA Contact F203 .	2.83 Ang.
x,y,z =	1_555 Check
PLAT431_ALERT_2_C Short Inter HLA Contact F2N3 .	2.83 Ang.
x,y,z =	1_555 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance	3.442 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.599	23 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .	1 Check
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.77A From Re1	-1.52 eA-3
Alert level G	
PLATU83_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large	7.14 Why ?
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of	BI Check
PLAT909_ALERT_3_G Percentage of 1>2sig(1) Data at Theta(Max) Still	98% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).	1 Note
PLA1955_ALERI_I_G Reported (CIF) and Actual (FCF) Lmax Diller by .	
PLAT9/8_ALERT_2_G Number C-C Bonds With Positive Residual Density.	0 Into
0 ALERT level A = Most likely a serious problem - resolve or exp	lain
U ALERT level B = A potentially serious problem, consider carefu	.11y
ALERT level C = Check. Ensure it is not caused by an omission	or oversignt
6 ALERT LEVEL G = General information/check it is not something	unexpected
1 ALERT type 1 CIF construction/syntax error, inconsistent or mi	ssing data
5 ALERT type 2 Indicator that the structure model may be wrong o	r deficient
6 ALERT type 3 Indicator that the structure quality may be low	
1 ALERT type 4 Improvement, methodology, query or suggestion	
0 ALERT type 5 Informative message, check	

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 03/06/2021; check.def file version of 02/06/2021



Structure factors have been supplied for datablock(s) reno-h2o

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: reno-h2o

Bond precision: C-C = 0.0077 AWavelength=1.54186 Cell: a=9.2615(1) b=23.2899(3) c=12.5774(2) alpha=90 beta=110.640(1) gamma=90 Temperature: 200 K Calculated Reported Volume 2538.80(6) 2538.80(6) Space group P 21/n P 1 21/n 1 Hall group -P 2yn -P 2yn Moiety formula C20 H26 F N5 O3 Re, B F4 C20 H26 F N5 O3 Re, B F4 Sum formula C20 H26 B F5 N5 O3 Re C20 H26 B F5 N5 O3 Re Mr 676.48 676.47 1.770 1.770 Dx,g cm-3 Ζ 4 4 Mu (mm-1) 9.977 9.977 F000 1320.0 1320.0 F000′ 1303.18 h,k,lmax 11,28,15 10,27,15 Nref 4661 4497 0.392,0.671 0.072,0.296 Tmin,Tmax Tmin' 0.131 Correction method= # Reported T Limits: Tmin=0.072 Tmax=0.296 AbsCorr = MULTI-SCAN Data completeness= 0.965 Theta(max) = 68.405R(reflections) = 0.0309(4031) wR2(reflections) = 0.0888(4497) S = 1.109Npar= 321

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Alert level (C						
PLAT029_ALERT_3_C	_diffrn_measured	_fraction	_theta_f	ull value	Low .	0.978	Why?
PLAT220_ALERT_2_C	NonSolvent Reso	d 1 C	Ueq(max)	/Ueq(min)	Range	3.1	Ratio
PLAT230_ALERT_2_C	Hirshfeld Test D:	iff for	N4	C15		5.8	s.u.
PLAT360_ALERT_2_C	Short C(sp3)-C(s	sp3) Bond	l C15	- C16		1.41	Ang.
PLAT431_ALERT_2_C	Short Inter HL	A Contact	F5	03	•	2.88	Ang.
				x,y,z	=	1_555 Chec	:k
PLAT911_ALERT_3_C	Missing FCF Refl	Between	Thmin & :	STh/L=	0.600	88	Report

Alert level G

PLAT230_ALERT_2_G	Hirshfeld Test I	Diff for	04 -	-C20	. 7.7	s.u.
PLAT232_ALERT_2_G	Hirshfeld Test I	Diff (M-X)	Rel -	-N5	. 8.0	s.u.
PLAT232_ALERT_2_G	Hirshfeld Test I	Diff (M-X)	Rel -	-C20	. 8.3	s.u.
PLAT244_ALERT_4_G	Low 'Solvent'	' Ueq as Com	pared to N	Neighbors c	f B1	Check
PLAT432_ALERT_2_G	Short Inter X	.Y Contact	F5 .	.C19	2.85	Ang.
			х	x,y,z =	1_555 Cheo	ck
PLAT912_ALERT_4_G	Missing # of FCF	F Reflection	s Above ST	Ch/L= 0.60	0 56	Note
PLAT978_ALERT_2_G	Number C-C Bonds	s with Posit	ive Residu	al Density	. 0	Info

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0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
7 ALERT level G = General information/check it is not something unexpected
0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
9 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check
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Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 22/03/2021; check.def file version of 19/03/2021



Structure factors have been supplied for datablock(s) yc-38-f1-p

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: yc-38-f1-p

Bond precision: C-C = 0.0143 AWavelength=1.54186 Cell: a=16.1750(2) b=8.3545(1) c = 25.8524(3)alpha=90 beta=90 gamma=90 Temperature: 200 K Calculated Reported Volume 3493.54(7) 3493.54(7)Space group P n a 21 P n a 21 Hall group P 2c -2n P 2c -2n Moiety formula C17 H13 Br N3 O2 Re 2(C17 H13 Br N3 O2 Re) Sum formula C17 H13 Br N3 O2 Re C34 H26 Br2 N6 O4 Re2 Mr 557.41 1114.83 2.120 2.120 Dx,g cm-3 Ζ 8 4 Mu (mm-1) 16.411 16.411 F000 2096.0 2096.0 F000′ 2053.09 h,k,lmax 19,10,31 19,10,30 6327[3239] Nref 4908 0.040,0.269 0.084,0.234 Tmin,Tmax Tmin' 0.001 Correction method= # Reported T Limits: Tmin=0.084 Tmax=0.234 AbsCorr = MULTI-SCAN Data completeness= 1.52/0.78 Theta(max)= 67.884 R(reflections) = 0.0250(4873) wR2(reflections) = 0.0656(4908) S = 1.101Npar= 434

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Alert level C		
STRVA01_ALERT_4_C Flack test results are ambiguous.		
From the CIF: _refine_ls_abs_structure_Flack 0.429		
From the CIF: _refine_ls_abs_structure_Flack_su 0.014		
PLAT090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18)	7.39	Note
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds	0.01435	Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600	23	Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .	3	Check

Alert level G

PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ	Please	Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor	2.00	Check
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Re1Br1 .	6.8	s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Re2Br2 .	6.8	s.u.
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed	!	Info
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still	99%	Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).	1	Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600	8	Note

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0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
8 ALERT level G = General information/check it is not something unexpected
2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check
```

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/12/2020; check.def file version of 05/12/2020



Structure factors have been supplied for datablock(s) r14-thf-hexane_tw

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: r14-thf-hexane_tw

Bond precision: C-C = 0.0265 AWavelength=1.54186 Cell: a=20.1830(6) b=10.7028(2) c=9.4252(3) alpha=90 beta=97.923(2) gamma=90 Temperature: 200 K Calculated Reported Volume 2016.55(10) 2016.55(10)Space group P 21/c P 1 21/c 1 Hall group -P 2ybc -P 2ybc C21 H14 Br N2 O5 Re Moiety formula C21 H14 Br N2 O5 Re Sum formula C21 H14 Br N2 O5 Re C21 H14 Br N2 O5 Re Mr 640.45 640.45 2.110 2.110 Dx,g cm-3 Ζ 4 4 Mu (mm-1) 14.433 14.433 F000 1216.0 1216.0 F000′ 1195.25 h,k,lmax 24,12,11 23,12,10 Nref 3656 3542 0.233,0.649 0.057,0.211 Tmin,Tmax Tmin' 0.039 Correction method= # Reported T Limits: Tmin=0.057 Tmax=0.211 AbsCorr = MULTI-SCAN Data completeness= 0.969 Theta(max) = 67.818R(reflections) = 0.0686(3379) wR2(reflections) = 0.1795(3542) S = 1.167Npar= 273

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Alert level B PLAT342_ALERT_3_B Low Bond Precision on C-C Bonds 0.02647 Ang.

🤪 Alert level C

PLAT029 ALERT 3 C diffrm measured fraction theta full value Low	0.973	Whv?
DIAT234 ALEPT 4 C Large Hirshfeld Difference 01	0 17	Ang
FLAT234_ADERT_1_C Darge in the interference of	7 0.17	all-
PLAT906_ALERT_3_C Large K value in the Analysis of Variance	/.025	Спеск
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600	78	Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .	1	Check
PLAT939_ALERT_3_C Large Value of Not (SHELXL) Weight Optimized S .	12.03	Check

Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms	16	Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large	90.58	Why ?
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records	3	Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records	3	Report
PLAT860_ALERT_3_G Number of Least-Squares Restraints	110	Note
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed	!	Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .	Please	Do !
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still	91%	Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).	1	Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600	9	Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File	15	Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity	1.0	Low

0 ALERT level A = Most likely a serious problem - resolve or explain 1 ALERT level B = A potentially serious problem, consider carefully 6 ALERT level C = Check. Ensure it is not caused by an omission or oversight 12 ALERT level G = General information/check it is not something unexpected 1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data 3 ALERT type 2 Indicator that the structure model may be wrong or deficient 10 ALERT type 3 Indicator that the structure quality may be low 5 ALERT type 4 Improvement, methodology, query or suggestion 0 ALERT type 5 Informative message, check

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 22/03/2021; check.def file version of 19/03/2021



Structure factors have been supplied for datablock(s) r18-thf-pentane

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: r18-thf-pentane

Bond precision: C-C = 0.0088 A Wavelength=1.54186 Cell: a=8.4295(4) b=9.4918(4) c=12.7023(6)alpha=106.704(3) beta=92.147(4) gamma=112.452(3) Temperature: 200 K Calculated Reported Volume 887.12(8) 887.12(7)Space group P -1 P -1 Hall group -P 1 -P 1 Moiety formula C20 H13 N2 O5 Re C20 H13 N2 O5 Re Sum formula C20 H13 N2 O5 Re C20 H13 N2 O5 Re Mr 547.53 547.52 2.050 2.050 Dx,g cm-3 Ζ 2 2 Mu (mm-1) 13.724 13.724 F000 524.0 524.0 F000′ 514.92 h,k,lmax 9,11,14 9,11,14 Nref 3009 2904 0.067,0.253 0.024,0.228 Tmin,Tmax Tmin' 0.003 Correction method= # Reported T Limits: Tmin=0.024 Tmax=0.228 AbsCorr = MULTI-SCAN Data completeness= 0.965 Theta(max) = 64.909R(reflections) = 0.0312(2903) wR2(reflections) = 0.0793(2904) S = 1.123Npar= 253

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

🏓 Alert level C THETM01 ALERT 3 C The value of sine(theta max)/wavelength is less than 0.590 Calculated sin(theta_max)/wavelength = 0.5874 PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low . 0.965 Whv? PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds 0.00875 Ang. PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.587 104 Report PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) . 5 Check PLAT939_ALERT_3_C Large Value of Not (SHELXL) Weight Optimized S . 10.92 Check PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.95A From Re1 -1.96 eA-3 -1.09 eA-3 PLAT974_ALERT_2_C Check Calcd Negative Resid. Density on Rel Alert level G PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Re1 --C19 6.0 s.u. . PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still 100% Note PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 1 Note PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 4 Note PLAT961_ALERT_5_G Dataset Contains no Negative Intensities Please Check PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 0 Info 0 ALERT level A = Most likely a serious problem - resolve or explain 0 ALERT level B = A potentially serious problem, consider carefully 8 ALERT level C = Check. Ensure it is not caused by an omission or oversight 6 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data 5 ALERT type 2 Indicator that the structure model may be wrong or deficient 8 ALERT type 3 Indicator that the structure quality may be low 0 ALERT type 4 Improvement, methodology, query or suggestion 1 ALERT type 5 Informative message, check

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

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PLATON version of 22/03/2021; check.def file version of 19/03/2021



Structure factors have been supplied for datablock(s) reohno

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: reohno

Bond precision: C-C = 0.0112 A Wavelength=1.54186 Cell: a=7.4804(2) b=24.3398(7) c=11.1812(2) alpha=90 beta=109.070(2) gamma=90 Temperature: 250 K Calculated Reported Volume 1924.05(9) 1924.05(9)P 21/n P 1 21/n 1 Space group Hall group -P 2yn -P 2yn C12 H8 B F4 N3 O3 Re, B C12 H8 B F4 N3 O3 Re, B Moiety formula F4, H2 O F4, H2 O Sum formula C12 H10 B2 F8 N3 O4 Re C12 H10 B2 F8 N3 O4 Re 620.06 Mr 620.05 Dx,g cm-3 2.141 2.141 Ζ 4 4 Mu (mm-1) 13.323 13.323 F000 1168.0 1168.0 F000′ 1151.56 h,k,lmax 8,27,12 8,29,13 Nref 3494 3229 Tmin,Tmax 0.152,0.587 0.103,0.285 Tmin' 0.009 Correction method= # Reported T Limits: Tmin=0.103 Tmax=0.285 AbsCorr = MULTI-SCAN Data completeness= 0.924 Theta(max)= 67.928 R(reflections) = 0.0439(2967) wR2(reflections) = 0.1041(3229) S = 1.082Npar= 299

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

🗳 Alert level A

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.926 Why?

Author Response: low intensities in high angles.

🔍 Alert level B

PLAT911_ALERT_3_B Missing FCF Refl Between Thmin & STh/L= 0.600 210 Report

Alert level C

PLAT234_ALERT_4_C Large Hirshfeld Difference F6AB2 .	0.17 Ang.
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of	F1 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of	B2 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including F5A	0.111 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including 04	0.107 Check
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds	0.01122 Ang.
PLAT431_ALERT_2_C Short Inter HLA Contact F701 .	2.86 Ang.
-1-x,1-y,-z =	3_465 Check
<pre>PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. #</pre>	1 Note
C12 H8 B F4 N3 O3 Re	
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance	7.491 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance	2.558 Check
<pre>PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).</pre>	5 Note

Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms	6 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms	3 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large	8.15 Why ?
PLAT169_ALERT_4_G The CIF-Embedded .res File Contains AFIX 1 Recds	3 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records	1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records	1 Report
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F5AB2 .	10.3 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F8AB2 .	9.3 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F5B2 .	6.5 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F6B2 .	10.0 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F8B2 .	8.0 s.u.
PLAT242_ALERT_2_G Low 'MainMol' Ueq as Compared to Neighbors of	B1 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4B Constrained at	0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4C Constrained at	0.5 Check
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 2)	60% Note
PLAT432_ALERT_2_G Short Inter XY Contact F4C5	2.83 Ang.
1+x,y,z =	1_655 Check
PLAT432_ALERT_2_G Short Inter XY Contact F4C6	2.93 Ang.
1+x,y,z =	1_655 Check
PLAT432_ALERT_2_G Short Inter XY Contact F7C11	2.85 Ang.
-1-x,1-y,-z =	3_465 Check
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # H2 O	3 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints	36 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still	87% Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600	9 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File	2 Note

PLAT951_ALERT_5_G Calculated (ThMax) and CIF-Reported Kmax Differ	2	Units
PLAT957_ALERT_1_G Calculated (ThMax) and Actual (FCF) Kmax Differ	2	Units
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.	0	Info

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1 ALERT level A = Most likely a serious problem - resolve or explain
1 ALERT level B = A potentially serious problem, consider carefully
11 ALERT level C = Check. Ensure it is not caused by an omission or oversight
26 ALERT level G = General information/check it is not something unexpected
1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
12 ALERT type 2 Indicator that the structure model may be wrong or deficient
8 ALERT type 3 Indicator that the structure quality may be low
16 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check
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Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 16/05/2021; check.def file version of 13/05/2021



Structure factors have been supplied for datablock(s) r27

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: r27

Bond precision: C-C = 0.0111 A Wavelength=1.54186 Cell: a=8.6774(3) b=10.8057(4) c=13.1764(4)alpha=75.144(3) beta=73.474(3) gamma=89.797(3) Temperature: 200 K Calculated Reported Volume 1141.65(7) 1141.65(7)P -1 Space group P -1 Hall group -P 1 -P 1 B6 F24 Na2, 2(C14 H11 N4 C14 H11 N4 O3 Re, B3 F12 Moiety formula 03 Re) Na C28 H22 B6 F24 N8 Na2 O6 Sum formula C14 H11 B3 F12 N4 Na O3 Re Re2 Mr 1505.80 752.89 2.190 2.190 Dx,q cm-3 Ζ 1 2 Mu (mm-1) 11.792 11.792 F000 712.0 712.0 F000′ 704.63 h,k,lmax 10,12,15 10,12,15 4118 3817 Nref 0.322,0.438 0.184,0.486 Tmin,Tmax Tmin′ 0.211 Correction method= # Reported T Limits: Tmin=0.184 Tmax=0.486 AbsCorr = MULTI-SCAN Data completeness= 0.927 Theta(max) = 67.533R(reflections) = 0.0406(3815) wR2(reflections) = 0.1022(3817) S = 1.102Npar= 343

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

🗳 Alert level A

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.927 Why?

Author Response: low diffraction intensities in high angles.

🎈 Alert level B					
PLAT241_ALERT_2_B High	'MainMol'	Ueq as Compared	to Neighbors of	F5	Check
PLAT911_ALERT_3_B Missing	g FCF Refl	Between Thmin &	STh/L= 0.599	301	Report

➔ Alert level C

PLAT220_ALERT_2_C	NonSolvent Resd 1 F Ueq(max)/Ueq(min) Range	3.1	Ratio
PLAT234_ALERT_4_C	Large Hirshfeld Difference F5B2 .	0.21	Ang.
PLAT234_ALERT_4_C	Large Hirshfeld Difference F8B2 .	0.17	Ang.
PLAT234_ALERT_4_C	Large Hirshfeld Difference 02C11 .	0.16	Ang.
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of	F1	Check
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of	Fб	Check
PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	Nal	Check
PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	В3	Check
PLAT342_ALERT_3_C	Low Bond Precision on C-C Bonds	0.0111	Ang.
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 0.91A From Rel	1.94	eA-3
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 0.86A From Rel	1.90	eA-3

Alert level G

PLAT042_ALERT_1_G (Calc. and Reported Moiety F	'ormula St	rings Diff	er	Please	Check
PLAT045_ALERT_1_G (Calculated and Reported Z D	Differ by	a Factor .	••	0.50	Check
PLAT083_ALERT_2_G \$	SHELXL Second Parameter in	WGHT Unu	sually Lar	ge	9.42	Why ?
PLAT154_ALERT_1_G	The s.u.'s on the Cell Angl	es are Eq	ual(Not	e)	0.003	Degree
PLAT171_ALERT_4_G	The CIF-Embedded .res File	Contains	EADP Recor	ds	1	Report
PLAT230_ALERT_2_G H	Hirshfeld Test Diff for	F9	B3	•	8.4	s.u.
PLAT230_ALERT_2_G H	Hirshfeld Test Diff for	F11	B3	•	6.4	s.u.
PLAT230_ALERT_2_G H	Hirshfeld Test Diff for	F12	B3	•	6.0	s.u.
PLAT230_ALERT_2_G H	Hirshfeld Test Diff for	F9A	B3		5.6	s.u.
PLAT230_ALERT_2_G H	Hirshfeld Test Diff for	F11A	B3	•	9.3	s.u.
PLAT230_ALERT_2_G H	Hirshfeld Test Diff for	F12A	B3	•	5.6	s.u.
PLAT232_ALERT_2_G H	Hirshfeld Test Diff (M-X)	Rel	C11	•	5.7	s.u.
PLAT242_ALERT_2_G]	Low 'MainMol' Ueq as Com	npared to	Neighbors	of	B1	Check
PLAT242_ALERT_2_G]	Low 'MainMol' Ueq as Com	npared to	Neighbors	of	В2	Check
PLAT301_ALERT_3_G N	Main Residue Disorder		.(Resd 1)	19%	Note
PLAT432_ALERT_2_G	Short Inter XY Contact	F7	C11		2.91	Ang.
		1-x,1	-y,-z =	2_6	565 Cheo	ck
PLAT909_ALERT_3_G 1	Percentage of I>2sig(I) Dat	a at Thet	a(Max) Sti	11	100%	Note
PLAT933_ALERT_2_G 1	Number of OMIT Records in E	Imbedded .	res File .	••	1	Note
PLAT961_ALERT_5_G Dataset Contains no Negative Intensities			••	Please	Check	
PLAT978_ALERT_2_G N	Number C-C Bonds with Posit	ive Resid	lual Densit	у٠	0	Info

1 ALERT level A = Most likely a serious problem - resolve or explain
2 ALERT level B = A potentially serious problem, consider carefully
11 ALERT level C = Check. Ensure it is not caused by an omission or oversight
20 ALERT level G = General information/check it is not something unexpected

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3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
21 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check
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Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 22/03/2021; check.def file version of 19/03/2021



Structure factors have been supplied for datablock(s) reno-me_pl

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: reno-me_pl

Bond precision: C-C = 0.0076 AWavelength=1.54186 Cell: a=7.0101(4) b=10.9539(4) c=11.3985(7)alpha=84.168(3) beta=77.822(5) qamma = 84.140(4)Temperature: 200 K Calculated Reported Volume 848.21(8) 848.21(8) Space group P -1 P -1 Hall group -P 1 -P 1 Moiety formula C13 H10 Br N3 O3 Re, B F4 C13 H10 Br N3 O3 Re, B F4 Sum formula C13 H10 B Br F4 N3 O3 Re C13 H10 B Br F4 N3 O3 Re Mr 609.16 609.16 2.385 2.385 Dx,g cm-3 Ζ 2 2 Mu (mm-1) 17.364 17.364 F000 568.0 568.0 F000′ 557.82 h,k,lmax 8,12,13 8,12,13 Nref 2870 2750 0.059,0.420 0.076,0.661 Tmin,Tmax Tmin' 0.003 Correction method= # Reported T Limits: Tmin=0.076 Tmax=0.661 AbsCorr = MULTI-SCAN Data completeness= 0.958 Theta(max) = 64.785R(reflections) = 0.0234(2749) wR2(reflections) = 0.0626(2750) S = 1.149Npar= 237

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full value Low . 0.958 Why?

Alert level C THETM01_ALERT_3_C The value of sine(theta_max)/wavelength is less than 0.590 Calculated sin(theta_max)/wavelength = 0.5868 PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min). 5 Note PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.587 116 Report PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.97A From Re1 -1.52 eA-3

Alert level G

PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Re1 -	-Brl	. 5.7	s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Re1 -	N3	. 5.2	s.u.
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to N	Neighbors o	f B1	Check
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta	a(Max) Stil	1 100%	Note
PLAT961_ALERT_5_G Dataset Contains no Negative Intensit	ies	. Please	Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residu	al Density	. 1	Info

0 ALERT level A = Most likely a serious problem - resolve or explain
1 ALERT level B = A potentially serious problem, consider carefully
4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
6 ALERT level G = General information/check it is not something unexpected
0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/12/2020; check.def file version of 05/12/2020



Structure factors have been supplied for datablock(s) remeno

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: remeno

Bond precision: C-C = 0.0113 AWavelength=1.54186 Cell: a=9.5298(4) b=6.6170(3) c=18.6332(11) alpha=90 beta=90 gamma=90 Temperature: 200 K Calculated Reported Volume 1174.99(10) 1174.99(10)Space group Рпта Рпта Hall group -P 2ac 2n -P 2ac 2n Moiety formula C11 H11 N2, O4 Re O4 Re, 0.5(C22 H22 N4) Sum formula C11 H11 N2 O4 Re C11 H11 N2 O4 Re Mr 421.43 421.42 2.382 2.382 Dx,g cm-3 Ζ 4 4 Mu (mm-1) 20.343 20.343 F000 792.0 792.0 F000′ 773.11 h,k,lmax 11,7,22 11,7,21 1082 Nref 1152 0.177,0.443 0.019,0.108 Tmin,Tmax Tmin' 0.021 Correction method= # Reported T Limits: Tmin=0.019 Tmax=0.108 AbsCorr = MULTI-SCAN Data completeness= 0.939 Theta(max) = 67.413R(reflections) = 0.0346(1042) wR2(reflections) = 0.1019(1082) S = 1.085Npar= 108

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Alert level A PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low .	0.939	Why?
Alert level B PLAT911_ALERT_3_B Missing FCF Refl Between Thmin & STh/L= 0.599	66	Report
Alert level C		
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of	Rel	Check
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds	0.0113	Ang.
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .	1	Check
PLAT971_ALERT_2_C Check Calcd Resid. Dens. 0.86A From Re1	1.54	eA-3
PLAT975_ALERT_2_C Check Calcd Resid. Dens. 0.80A From O2	0.47	eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H1	-0.47	eA-3
Alert level G		
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite	2	Note
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ	Please	Check
PLAT073_ALERT_1_G H-atoms ref, but _hydrogen_treatment Reported as	constr	Check
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records	1	Report
PLAT300_ALERT_4_G Atom Site Occupancy of H11A Constrained at	0.5	Check
PLAT300_ALERT_4_G Atom Site Occupancy of H11B Constrained at	0.5	Check
PLAT300_ALERT_4_G Atom Site Occupancy of H11C Constrained at	0.5	Check
PLAT367_ALERT_2_G Long? C(sp?)-C(sp?) Bond C10 - C11 .	1.50	Ang.
PLAT432_ALERT_2_G Short Inter XY Contact 01C11	2.96	Ang.
x,y,z =	1_555 Chec	ck
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group #	3	Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints	1	Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still	95%	Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).	1	Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF	1	Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File	2	Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity	4.5	Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.	3	Info
	1 - /	

1 ALERT level A = Most likely a serious problem - resolve or explain 1 ALERT level B = A potentially serious problem, consider carefully 6 ALERT level C = Check. Ensure it is not caused by an omission or oversight 17 ALERT level G = General information/check it is not something unexpected 2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data 9 ALERT type 2 Indicator that the structure model may be wrong or deficient 9 ALERT type 3 Indicator that the structure quality may be low 5 ALERT type 4 Improvement, methodology, query or suggestion 0 ALERT type 5 Informative message, check

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT029_remeno
;
PROBLEM: _diffrn_measured_fraction_theta_full value Low . 0.939 Why?
RESPONSE: ...
;
# end Validation Reply Form
```

PLATON version of 05/12/2020; check.def file version of 05/12/2020

