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

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The reaction of rhenium α-dimine (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 yield, 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)₃(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 weak π-acids like pyridine. Attempts of direct nitrosylation of α-dimine fac-[Re(CO)₃]⁺ complexes bearing π-basic OR-type ligands gave the [Re(CO)₃(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)₃(NO)(N-N)]⁺ 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,⁴ 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(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 phosphatidylycerol 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(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(CO)3]⁺ core. The latter possibility is more challenging, but there are options. In particular our attention turned to the N-N ligands. The resulting compounds are structurally nearly tricarbonyl complexes widely applicable to different supporting 1).28 Nothing is known about the chemistry of the compound or its substitution chemistry aiming at the realization of the dicationic species just mentioned above.

A compound of formula fac-[Re(CO)3(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(μ3-O)(CO)3(NO)]₄ clusters and, under inert conditions, from the [Re(μ-Cl)(CO)3(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 equivalent but there are options. In particular our attention turned to the fac-[Re(CO)3(NO)(bpy)Cl]⁺ core.24-26

In this contribution, we describe our synthetic efforts and we present an efficient direct nitrosylation of α-diimine 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(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)3(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 4,7-derivatives 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(CO)3]⁺ species.

In this contribution, we describe our synthetic efforts and we present an efficient direct nitrosylation of α-diimine rhenium dicarbonyl 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, the substitution chemistry of metal ion in fac-[Re(CO)3(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)3(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)3(NO)(N-N)X]⁺ species

The chemistry of the fac-[Re(CO)3(NO)]⁺24 core is essentially dominated by cyclopentadienyl (Cp) species of general formula [CpRe(CO)3(NO)]⁺. These compounds are most often prepared by reaction of the corresponding [CpRe(CO)3] with either NO2PF6,29 NOHSO4,30 or NOBF₄.31,32 The last two reagents were successfully used in the preparation of fac-[Re(CO)3(NO)X]⁺,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, the consequence of this behaviour is that, while similar complexes are reported as rhenium(I) dicarbonyl-nitrosyl fac-[Re(CO)3(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 4,7-derivatives 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(CO)3]⁺ species.

Results and discussion

Synthesis of fac-[Re(CO)3(NO)(N-N)X]⁺ species

The chemistry of the fac-[Re(CO)3(NO)]⁺²⁴ core is essentially dominated by cyclopentadienyl (Cp) species of general formula [CpRe(CO)₃(NO)]⁺. These compounds are most often prepared by reaction of the corresponding [CpRe(CO)₃] with either NO₂PF₆,²⁹ NOH₂SO₄,³⁰ or NOBF₄.³¹,³² The last two reagents were successfully used in the preparation of fac-[Re(CO)₃(NO)X]⁺,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(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)₃(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 4,7-derivatives 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(CO)₃]⁺ species.
to higher wavenumbers, which is unusual for carbonyls bound to the low valent metal.\textsuperscript{33, 34} In fact, the vCO’s are found in the region where rhenium(III) dicarbonyl complexes\textsuperscript{35} (e.g. \([\text{Re}^{III}(\text{CO})_2(\text{Br}_2)]\)\textsuperscript{36} are observed, and much higher than corresponding rhenium(II) species.\textsuperscript{37} The symmetric vCO mode of the molecules is actually not far from that of CO gas (2143 cm\textsuperscript{-1}). The evidence points to a significant reduction of Re-CO π-backbonding in favour of the stronger π-acceptor NO\textsuperscript{+}. The stretching vibration of the NO\textsuperscript{+} ion usually occurs in the 2300-2350 cm\textsuperscript{-1} frequency range, e.g. 2340 cm\textsuperscript{-1} in NOBF\textsubscript{4},\textsuperscript{38} 2326 cm\textsuperscript{-1} in NOAuF\textsubscript{6},\textsuperscript{39} and 2298 cm\textsuperscript{-1} in sulfuric acid solutions.\textsuperscript{40} Its vibrational frequency in the complexes is found in the 1800 cm\textsuperscript{-1} region, closer to that of a N=O double bond than that of the initial triple bond. This indicates that the π\*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 π\*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 \textit{(vide infra)} and their lack of photoluminescence \textit{(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 π → π\* 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)\textsubscript{2}(NO)(N-N)X]\textsuperscript{+} 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)\textsubscript{2}(NO)(N-N)]\textsuperscript{I+} species**

Having established a sufficiently high-yielding procedure for fac-[Re(CO)\textsubscript{2}(NO)(N-N)Br]\textsuperscript{+} ions, we moved to explore the substitution of Br\textsuperscript{-} for neutral pyridine (py) ligands. Typically for the corresponding tricarbonyl complexes, bromide 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 AgCF\textsubscript{3}SO\textsubscript{3} to fac-[Re(CO)\textsubscript{2}(NO)(bpy)Br]\textsuperscript{+} (1) in coordinating wet solvents like CH\textsubscript{3}OH or CH\textsubscript{3}CN. 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

| Complex | v(CO) [cm\textsuperscript{-1}] | v(NO) [cm\textsuperscript{-1}] | λ\textsubscript{max} [nm (M\textsuperscript{-1}cm\textsuperscript{-1})] |
|---------|----------------|----------------|-----------------|
| 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        |
| 7       | 2114, 2050  | 1796          | 322, 332        |
| 8       | 2127, 2069  | 1820          | 320, 330        |
| 9       | 2114, 2050  | 1796          | 322, 332        |

\textsuperscript{3}Solid state. \textsuperscript{4}in DMF

**Table 1. Physical properties of fac-[Re(CO)\textsubscript{2}(NO)(N-N)]\textsuperscript{I+} complexes.**

The higher apparent formal oxidation state of the metal ion, implies depletion of electron density from the same, and affinity for π-basic ligands rather than donors. We reasoned, therefore, that electron-donating substituents on N-N might help stabilize the rhenium ion towards the same reaction. NR\textsubscript{2} groups (where R = aliphatic chain) are amongst the most effective electron donating groups.\textsuperscript{42} However, when the N\textsuperscript{4},N\textsuperscript{4},N\textsuperscript{5},N\textsuperscript{5}-tetraethyl-\textsuperscript{[2,\textsuperscript{4}′-bipyridine]-4,4′-di-amine (Et\textsubscript{2}N-bpy)} complex 3 was used the corresponding fac-[Re(CO)\textsubscript{2}(NO)(Et\textsubscript{2}N-bpy)]\textsuperscript{+} \textsuperscript{6} (7) also formed as the only product. Compound \textsuperscript{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-dimine rhenium(I) dicarbonyl complexes of formula \([\text{Re(CO)}\textsubscript{2}(\text{N-N})\text{Br}(\text{py})]\) capable of exchanging the halide for other ligands.\textsuperscript{37} Therefore, we next tried the reaction of the corresponding \([\text{Re(CO)}\textsubscript{2}(\text{N-N})\text{Br}(\text{py})]\) complex (8) with NOBF\textsubscript{4}. Under reaction conditions similar to those applied for the synthesis of 1-5, complex 8 reacted by substituting py for NO\textsuperscript{+} giving 1 (Fig. 4). We only found trace...
It should be noted here that Rattat reported that whereas the imidazole (Im) complexes [ReCl3(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)]₃, isolation of the [Re(Im)2(CO)2(NO)]⁺ was not successful. 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. 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(CO)3(N-N)(py)]⁺ complexes with nitrosation 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 (Me2N-py). 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(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.

Reactivity of fac-[Re(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(CO)3(N-N)] complexes with monodentate π-basic ligands (OR). Given the apparent affinity of the fac-[Re(CO)3(NO)]²⁺ core for π-donors, we reasoned that fac-[Re(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)3(NO)(N-N)L]²⁺ compounds. Therefore, we decided to test the reaction of fac-[Re(CO)3(N-N)OR], where OR = OH⁻, benzoate (10), 2-(4-bromophenyl)acetate (11).
To our surprise, irrespective of the OR ligand, nitrosylation of \( \text{fac-}[\text{ReI(CO)}_3(\text{N-N})\text{OR}] \) 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 \( \nu_{\text{CO}} \) 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 \( \text{OH}^- \) base. Kurz and Alberto showed that the reactivity \( \mu\text{-oxo} \) bridged teranuclear \([\text{Re}({\mu_3-}\text{O})(\text{CO})_2(\text{NO})]_4\) clusters towards neutral bidentate ligands is possible by disassembly of the same in \( \text{HBF}_4 \) and proceeds “presumably [via] Re-bound labile \( \text{BF}_4^- \) anion”.\(^{27} \)

We managed to crystallize the nitrosylated product obtained from \( \text{fac-}[\text{Re(CO)}_3(\text{N-N})\text{OR}] \) and we confirmed that the reaction gives \( \text{fac-}[\text{Re(CO)}_3(\text{NO})(\text{N-N})(\text{BF}_4^-)]\text{BF}_4^- \) (12) as the only product in good yield (Fig. 6). To our knowledge, 12 is only the fourth structurally characterized Re-\( \text{BF}_4^- \) complex, and the very first one of its kind.\(^{47-49} \) The Re-\( \text{BF}_4^- \) bond is persistent in solution, and in CH\(_3\)CN only a small fraction of the molecules (ca. 5-7\%) substitute the anion for CH\(_3\)CN. We were also able to selectively crystallize out the \( \text{fac-}[\text{Re(CO)}_3(\text{NO})(\text{N-N})(\text{CH}_3\text{CN})]^+ \) complex (13) as a \([\text{Na(BF}_4^-)]_2^+ \) 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 \( \text{fac-}[\text{Re(CO)}_3(\text{NO})]^+ \) 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 related \( \text{fac-}[\text{Re(CO)}_3]^+ \) species, revealed the following general characteristics. Within 3\( \sigma \), the Re-CO and the C≡O bonds are respectively longer and shortened 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 \( \text{fac-}[\text{Re(CO)}_3(\text{NO})]^+ \) 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 \( \text{fac-}[\text{Re(CO)}_3(\text{NO})(\text{N-N})X]^+ \) 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)\(_3\) 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 \( d^4 \) complexes.\(^{52} \)
CO Releasing Properties

In the initial phases of our investigation, we also probed the direct nitrosylation of tricarbonyl complexes with ortho-substituted α-dimines. 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 perrennate ion appeared (Fig. 8).

This observation indicated to us either that steric hindrance at the ortho position of the α-dimine ligand can destabilize fac-[Re(CO)2(NO)]3+ 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)Br]3− 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. 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. 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.

To our knowledge, fac-[Re(CO)2(NO)(N-N)Br]3+ complexes represent a new class of Re photoCORMs. Spontaneous and light-induced CO release of 16- and 17-electron rhenium complexes,56-57 and 18-electron fac-[Re(CO)3(N-N)PR3]+ (where PR3 = phosphine or phosphite) is well known.68-69 In the last five years several examples of diimine complexes bearing either σ- or π-donating ancillary ligands active towards CO photo-substitution 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 1MLCT 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 1MLCT 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→CO 3MLCT transition. Thus, excitation by high-energy light of fac-[Re(CO)3(N-N)L]3+ species (were L = π-base or α-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-diamine 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(CO)2(NO)(N-N)X]+ 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, this was not confirmed by the corresponding 1H chemical shifts, which were reported relative to the center. ESI-MS (MeOH): m/z, 507.7 [Re(CO)2(NO)(C2H4N2)Br]+, [M]+. IR (solid, cm⁻¹): νCO: 2112, 2050, νNO: 1795. 1H-NMR (400 MHz, CD3CN, ppm): 7.69 (s, 1 H) 7.73 (m, 10 H) 8.14 (d, J=5.50 Hz, 2 H) 8.26 (s, 2 H) 9.69 (d, J=8.31, 1.22 Hz, 2 H). UV-Vis (CH3CN, λ nm): 342, 357. Crystals suitable for X-ray diffraction were obtained from slow evaporation of a dichloromethane solution.

Experimental Section

Reagents and chemicals

All reagents and solvents were purchased from standard sources and used without further purification. Compound [Re(CO)3Br] was purchased from Sigma Aldrich, while complexes of formula fac-[Re(CO)3(N-N)Br]19, [Et2N][Re(NO)(Et2N-bpy)Br]68, fac-[Re(CO)3(N-N)(py)Br]17, fac-[Re(CO)3(bpy)OH]68 and fac-[Re(CO)3(bpy)(Me2N-py)][(CF3SO3)4]66 were synthesized according to published procedures. Unless otherwise noted, solvents used in the preparation of all molecules were dry and O2-free.

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 (CuKα1 (λ = 1.5406 Å)) equipped with a cryocooler Oxford Cryosystems. The structures were solved using the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. 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] 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)(C2H4N2)Br]+, [M]+. IR (solid, cm⁻¹): νCO: 2112, 2050, νNO: 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)(C6H4N2)Br]+, [M]+. IR (solid, cm⁻¹): νCO: 2104, 2040, νNO: 1770. 1H-NMR (400 MHz, CD3CN, ppm): 1.22 - 1.28 (m, 12 H) 3.64 (br. s., 8 H) 6.79 (m, 4 H) 6.89 (m, 2 H) 9.89 (m, 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)F][BF4] (3). Et2N-bpy = N4,N4,N4',N4'-tetraethyl-[2,2'-bipyridine]-4,4'-diamine. Yellow solid, yield 87%. ESI+-MS (MeOH): m/z, 649.8 [Re(CO)2(NO)(C24H16N2)Br]+, [M]+. IR (solid, cm⁻¹): νCO: 2104, 2040, νNO: 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)2(NO)(Bu-bpy)Br][BF4] (4). Bu-bpy = 4,4’-di-tert-butyl-2,2’-bipyridine. Yellow solid, yield 69%. ESI+-MS (MeOH): m/z, 619.7 [Re(CO)2(NO)(C12H18N2)Br]+, [M]+. IR (solid, cm⁻¹): νCO: 2114, 2053, νNO: 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)2(NO)(phen)][BF4] (5). phen = 4,4'-diphenyl-1,10-phenanthroline. Yellow solid, yield 61%. ESI+-MS (MeOH): m/z, 683.7 [Re(CO)2(NO)(C24H18N2)Br]+, [M]+. IR (solid, cm⁻¹): νCO: 2114, 2052, νNO: 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)(Et2N-bpy)][BF4] (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 overnight 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
[Re(CO)2(NO)(C11H10N2)Br] (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); νCO: 2129, 2069, 1781. 1H-NMR (400 MHz, DMSO-d6, ppm): 3.13 (s, 4 H), 2.47 (s, 2 H), 1.96 (s, 2 H), 1.10 (s, 6 H). Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetone 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. 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 assessed by measuring the absorption 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. 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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Figure S33. UV-Vis spectrum of $[\text{Re(CO)}_2\text{NO}(\text{bpy})\text{BF}_4][\text{BF}_4]$ (12) in DMF

Figure S34. UV-Vis spectrum of $[\text{Re(CO)}_2\text{NO}(\text{bpy})(\text{Me}_2\text{N-py})][\text{BF}_4]_2$ (9) in acetonitrile
Fig. S35. Emission spectra of selected nitrosyl Re complexes. Top: $\lambda_{ex} = 318$; bottom $\lambda_{ex} = 350$. 
Suitable crystal were selected and mounted on loop with oil on a Stoehr 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.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.
checkCIF/PLATON report

Structure factors have been supplied for datablock(s) renobipy_e_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: renobipy_e_pl**

| Bond precision: | C-C = 0.0076 A | Wavelength=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 | P n m a | 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 |
| Dx, g cm-3 | 2.383 | 2.383 |
| Z | 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 |
| Tmin, Tmax | 0.072,0.242 | 0.044,0.176 |
| Tmin' | 0.012 | |

Correction method=#  
Reported T Limits: Tmin=0.044 Tmax=0.176  
AbsCorr = MULTI-SCAN

Data completeness= 0.995  
Theta(max)= 67.672

R(reflections)= 0.0248( 1569)  
wR2(reflections)= 0.0700( 1573)

S = 1.192  
Npar= 129

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**

CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier.

greenish

PLAT218_ALERT_3_C Constrained U(ij) Components(s) for F2 . 2 Check
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
PLAT244_ALERT_4_C Low ‘Solvent’ Ueq as Compared to Neighbors of B1 Check
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resid. # 1 Note
   C12 H8 Br N3 O3 Re
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 9 Report

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**Alert level G**

PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 1 Report
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F2A --B1 . 7.5 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F3 --B1 . 9.5 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F3A --B1 . 6.8 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F4 --B1 . 6.3 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F6 --B1 . 8.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Re1 --Br1 . 9.8 s.u.
PLAT100_ALERT_4_G Atom Site Occupancy of F2 Constrained at 0.25 Check
PLAT100_ALERT_4_G Atom Site Occupancy of F2A Constrained at 0.25 Check
PLAT100_ALERT_4_G Atom Site Occupancy of F3 Constrained at 0.25 Check
PLAT100_ALERT_4_G Atom Site Occupancy of F3A Constrained at 0.25 Check
PLAT100_ALERT_4_G Atom Site Occupancy of F4 Constrained at 0.25 Check
PLAT100_ALERT_4_G Atom Site Occupancy of F5 Constrained at 0.25 Check
PLAT100_ALERT_4_G Atom Site Occupancy of F6 Constrained at 0.25 Check
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resid 2) 64% Note
PLAT432_ALERT_2_G Short Int X...Y Contact F1 ..C6 2.94 Ang.
   x,1/2-y,-1+z = 8_564 Check
PLAT432_ALERT_2_G Short Int X...Y Contact F1 ..C6 2.94 Ang.
   x,y,-1+z = 1_554 Check
PLAT432_ALERT_2_G Short Int X...Y Contact F3 ..C5 2.95 Ang.
   x,y,z = 1_555 Check
PLAT432_ALERT_2_G Short Int 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
   F5 --B1 --F2 1.555 1.555 1.555 32.90 Deg.
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group # 3 Check
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resid. # 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

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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
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
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**

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**Publication of your CIF in other journals**

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

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

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-phen

Bond precision:  C-C = 0.0053 Å  Wavelength=1.54186

Cell:

| Calculated | Reported |
|------------|----------|
| 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 |
| Dx, g cm^-3 2.432 | 2.432 |
| Z 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 |
| Tmin,Tmax 0.234,0.418 | 0.028,0.197 |
| Tmin' 0.049 | |

Correction method= # Reported T Limits: Tmin=0.028 Tmax=0.197
AbsCorr = MULTI-SCAN

Data completeness= 0.959  Theta(max)= 68.025
R(reflections)= 0.0260( 2854)  wr2(reflections)= 0.0745( 2947)
S = 1.061  Npar= 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 Tmin & STh/L= 0.600 115 Report

Alert level G
PLAT230_ALERT_2_G Hirshfeld Test Diff for O2 --C13 . 8.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Rel --N3 . 8.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Rel --C13 . 8.5 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Rel --C14 . 7.0 s.u.
PLAT244_ALERT_4_G Low ‘Solvent’ Ueq as Compared to Neighbors of B1 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact F3 ..C14 2.90 Ang. 1+x,y,z = 1_655 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact F4 ..C13 2.93 Ang. 1+x,y,z = 1_655 Check
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 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

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
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.

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

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

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No syntax errors found. CIF dictionary Interpreting this report

**Datablock: ks188-1**

| Bond precision: | C-C = 0.0088 Å | Wavelength=1.54186 |
|-----------------|----------------|---------------------|
| Cell:           | a=10.0421(2)   | b=7.8180(2)         |
|                 | c=20.2281(4)   |                     |
|                 | alpha=90       | beta=98.026(1)      |
| Temperature:    | 250 K          |                     |
| Volume          | Calculated     | Reported            |
|                 | 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              |
| Dx, g cm-3      | 2.257          | 2.256               |
| Z               | 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                |
| Tmin, Tmax      | 0.155, 0.387   | 0.108, 0.495        |
| Tmin’           | 0.054          |                     |

Correction method= # Reported T Limits: Tmin=0.108 Tmax=0.495
AbsCorr = MULTI-SCAN

Data completeness= 0.990                Theta(max)= 67.536

R(reflections)= 0.0289 ( 2782)          wr2(reflections)= 0.0647 ( 2801)

S = 1.290                    Npar= 226

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**

| Alert Code | Description                                                                 | Value     |
|------------|-----------------------------------------------------------------------------|-----------|
| PLAT342_ALERT_3_C | Low Bond Precision on C-C Bonds                                             | 0.00878 Ang. |
| PLAT431_ALERT_2_C | Short Inter HLA Contact F2                                                   | 2.83 Ang.  |
|             | x,y,z = 1_555 Check                                                         | x,y,z = 1_555 Check |
| PLAT431_ALERT_2_C | Short Inter HLA Contact F2                                                   | 2.83 Ang.  |
|             | x,y,z = 1_555 Check                                                         | 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 Rel                                   | -1.52 eA-3 |

**Alert level G**

| Alert Code | Description                                                                 | Value     |
|------------|-----------------------------------------------------------------------------|-----------|
| PLAT083_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 B1 | Check     |
| PLAT909_ALERT_3_G | Percentage of I>2sig(I) Data at Theta(Max) Still            | 98% Note  |
| PLAT910_ALERT_3_G | Missing # of FCF Reflection(s) Below Theta(Min).    | 1 Note    |
| PLAT955_ALERT_1_G | Reported (CIF) and Actual (FCF) Lmax Differ by         | 1 Units   |
| PLAT978_ALERT_2_G | Number C-C Bonds with Positive Residual Density.       | 0 Info    |

**Alert level A** = Most likely a serious problem - resolve or explain

**Alert level B** = A potentially serious problem, consider carefully

**Alert level C** = Check. Ensure it is not caused by an omission or oversight

**Alert level G** = General information/check it is not something unexpected

1 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
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
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**Publication of your CIF in other journals**

Please refer to the [Notes for Authors](notes) of the relevant journal for any special instructions relating to CIF submission.

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

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

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: reno-h2o

Bond precision: C-C = 0.0077 A Wavelength=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
Dx, g cm-3 1.770 1.770
Z 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
Tmin,Tmax 0.392,0.671 0.072,0.296
Tmin’ 0.131

Correction method= # Reported T Limits: Tmin=0.072 Tmax=0.296
AbsCorr = MULTI-SCAN

Data completeness= 0.965 Theta(max)= 68.405
R(reflections)= 0.0309( 4031) wr2(reflections)= 0.0888( 4497)
S = 1.109 Npar= 321

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.  0.978 Why?
PLAT220_ALERT_2_C  NonSolvent Resd 1 C  Ueq(max)/Ueq(min) Range 3.1 Ratio
PLAT230_ALERT_2_C  Hirshfeld Test Diff for N4 --C15 .  5.8 s.u.
PLAT360_ALERT_2_C  Short C(sp3)-C(sp3) Bond C15 - C16 .  1.41 Ang.
PLAT431_ALERT_2_C  Short Inter HL..A Contact F5 ..O3 .  2.88 Ang.
               x,y,z =  1_555 Check
PLAT911_ALERT_3_C  Missing FCF Refl Between Thmin & STh/L=  0.600  88 Report

Alert level G

PLAT230_ALERT_2_G  Hirshfeld Test Diff for O4 --C20 .  7.7 s.u.
PLAT232_ALERT_2_G  Hirshfeld Test Diff (M-X) Rel --N5 .  8.0 s.u.
PLAT232_ALERT_2_G  Hirshfeld Test Diff (M-X) Rel --C20 .  8.3 s.u.
PLAT244_ALERT_4_G  Low ‘Solvent’ Ueq as Compared to Neighbors of B1 Check
PLAT432_ALERT_2_G  Short Inter X...Y Contact F5 ..C19  2.85 Ang.
               x,y,z =  1_555 Check
PLAT912_ALERT_4_G  Missing # of FCF Reflections Above STh/L=  0.600  56 Note
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
6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
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**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**
checkCIF/PLATON report

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

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: yc-38-f1-p

| Bond precision: | C-C = 0.0143 Å | Wavelength=1.54186 |
|-----------------|----------------|---------------------|
| Cell:           | a=16.1750(2)   | b=8.3545(1)         | c=25.8524(3) |
|                 | alpha=90       | beta=90             | gamma=90     |
| Temperature:    | 200 K          |                     |
| Volume          | Calculated     | Reported             |
|                 | 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              |
| Dx, g cm⁻³      | 2.120          | 2.120                |
| Z               | 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             |
| Nref            | 6327{ 3239}    | 4908                 |
| Tmin,Tmax       | 0.040,0.269    | 0.084,0.234          |
| 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 = 1.101                             Npar= 434

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

**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) Re1 --Br1 . 6.8 s.u.

**PLAT232_ALERT_2_G**
Hirshfeld Test Diff (M-X) Re2 --Br2 . 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_3_G**
Missing # of FCF Reflections Above STh/L= 0.600 8 Note

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
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**Publication of your CIF in other journals**

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

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 Å Wavelength=1.54186

Cell:
\[ a=20.1830(6) \quad b=10.7028(2) \quad c=9.4252(3) \]
\[ \alpha=90 \quad \beta=97.923(2) \quad \gamma=90 \]

Temperature: 200 K

\[
\begin{array}{ll}
\text{Calculated} & \text{Reported} \\
\text{Volume} & 2016.55(10) & 2016.55(10) \\
\text{Space group} & P \ 21/c & P \ 21/c \ 1 \\
\text{Hall group} & -P \ 2ybc & -P \ 2ybc \\
\text{Moiety formula} & C_{21} \ H_{14} \ Br \ N_{2} \ O_{5} \ Re & C_{21} \ H_{14} \ Br \ N_{2} \ O_{5} \ Re \\
\text{Sum formula} & C_{21} \ H_{14} \ Br \ N_{2} \ O_{5} \ Re & C_{21} \ H_{14} \ Br \ N_{2} \ O_{5} \ Re \\
\text{Mr} & 640.45 & 640.45 \\
\text{Dx, g cm}^{-3} & 2.110 & 2.110 \\
\text{Z} & 4 & 4 \\
\text{Mu (mm}^{-1}) & 14.433 & 14.433 \\
\text{F000} & 1216.0 & 1216.0 \\
\text{F000'} & 1195.25 & \\
\text{h,k,l max} & 24,12,11 & 23,12,10 \\
\text{Nref} & 3656 & 3542 \\
\text{Tmin,Tmax} & 0.233,0.649 & 0.057,0.211 \\
\text{Tmin'} & 0.039 & \\
\end{array}
\]

Correction method= # Reported T Limits: Tmin=0.057 Tmax=0.211
AbsCorr = MULTI-SCAN

Data completeness= 0.969 Theta(max)= 67.818

R(reflections)= 0.0686(3379) wR2(reflections)= 0.1795(3542)

S = 1.167 Npar= 273

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 B

| Alert number | Description |
|--------------|-------------|
| PLAT342_ALERT_3_B | Low Bond Precision on C-C Bonds | 0.02647 Ang. |

### Alert level C

| Alert number | Description |
|--------------|-------------|
| PLAT029_ALERT_3_C | _differn.measured_fraction_theta_full value Low | 0.973 Why? |
| PLAT234_ALERT_4_C | Large Hirshfeld Difference O1 --C11 | 0.17 Ang. |
| PLAT906_ALERT_3_C | Large K Value in the Analysis of Variance | 7.025 Check |
| 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

| Alert number | Description |
|--------------|-------------|
| 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 |

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

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

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: r18-thf-pentane

Bond precision:  C-C = 0.0088 Å  Wavelength=1.54186

Cell:  
\[ \begin{align*} 
  a &= 8.4295(4) \\
  b &= 9.4918(4) \\
  c &= 12.7023(6) \\
  \alpha &= 106.704(3) \\
  \beta &= 92.147(4) \\
  \gamma &= 112.452(3) 
\end{align*} \]

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         |
| Dx, g cm\(^{-3}\)    | 2.050            | 2.050          |
| Z                    | 2                | 2              |
| Mu (mm\(^{-1}\))     | 13.724           | 13.724         |
| F000                 | 524.0            | 524.0          |
| F000'                | 514.92           |                 |
| h,k,l\(\max\)       | 9,11,14          | 9,11,14        |
| Nref                 | 3009             | 2904           |
| Tmin\(\), Tmax\(\)  | 0.067,0.253      | 0.024,0.228    |
| Tmin'                | 0.003            |                 |

Correction method= # Reported T Limits: Tmin=0.024 Tmax=0.228
AbsCorr = MULTI-SCAN

Data completeness= 0.965  Theta(max)= 64.909

R(reflections)= 0.0312( 2903)  wR\(^2\)(reflections)= 0.0793( 2904)

S = 1.123  Npar= 253

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 |
|----------------|
| THETM01_ALERT_3_C | The value of \( \sin(\theta_{\text{max}})/\text{wavelength} \) is less than 0.590 |
| Calculated \( \sin(\theta_{\text{max}})/\text{wavelength} \) = 0.5874 |
| PLAT029_ALERT_3_C | _diffrrn_measured_fraction_theta_full value Low . 0.965 Why? |
| PLAT342_ALERT_3_C | Low Bond Precision on C-C Bonds ................. 0.00875 Ang. |
| PLAT911_ALERT_3_C | Missing FCF Ref1 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 Rel -1.96 eA-3 |
| PLAT974_ALERT_2_C | Check Calcd Negative Resid. Density on Rel -1.09 eA-3 |

| Alert level G |
|----------------|
| PLAT232_ALERT_2_G | Hirshfeld Test Diff (M-X) Rel --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 |

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6 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
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8 ALERT type 3 Indicator that the structure quality may be low
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1 ALERT type 5 Informative message, check
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PLATON version of 22/03/2021; check.def file version of 19/03/2021
checkCIF/PLATON report

Structure factors have been supplied for datablock(s) reohno

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: reohno

Bond precision:  C-C = 0.0112 Å  Wavelength=1.54186

Cell:  

| Parameter          | Calculated          | Reported          |
|--------------------|---------------------|-------------------|
| a                  | 7.4804(2)           | 7.4804(2)         |
| b                  | 24.3398(7)          | 24.3398(7)        |
| c                  | 11.1812(2)          | 11.1812(2)        |
| alpha              | 90                  | 90                |
| beta               | 109.070(2)          | 109.070(2)        |
| gamma              | 90                  | 90                |
| Temperature        | 250 K               | 250 K             |

Volume 1924.05(9) 1924.05(9)

Space group P 21/n P 1 21/n 1

Hall group -P 2yn -P 2yn

Moiety formula

| Formula | Calculated | Reported |
|---------|------------|----------|
| C12 H8 B F4 N3 O3 Re, B | C12 H8 B F4 N3 O3 Re, B |
| F4, H2 O | F4, H2 O |
| C12 H10 B2 F8 N3 O4 Re | C12 H10 B2 F8 N3 O4 Re |

Mr 620.06 620.05

Dx, g cm⁻³ 2.141 2.141

Z 4 4

Mu (mm⁻¹) 13.323 13.323

F000 1168.0 1168.0

F000’ 1151.56

h,k,lmax 8,29,13 8,27,12

Nref 3494 3229

Tmin,Tmax 0.152,0.587 0.103,0.285

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 = 1.082  Npar= 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 F6A --B2 | . | 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 O4 | 0.107 Check |
| PLAT342_ALERT_3_C | Low Bond Precision on C-C Bonds | 0.01122 Ang. |
| PLAT431_ALERT_2_C | Short Inter HL..A Contact F7 ..O1 | 2.86 Ang. |
| PLAT790_ALERT_4_C | Centre of Gravity not Within Unit Cell: Resd. # | 1 Note |
| PLAT906_ALERT_3_C | Large K Value in the Analysis of Variance | 7.491 Check |
| PLAT910_ALERT_3_C | Large K Value in the Analysis of Variance | 2.558 Check |
| PLAT910_ALERT_3_C | Missing # of FCF Reflection(s) Below Theta(Min). | 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 | SHEXLS Second Parameter in WGHT Unusually Large | 8.15 Why ? |
| PLAT169_ALERT_4_G | The CIF-Embedded .res File Contains AFIX 1 Recds | 1 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) F5A --B2 | 10.3 s.u. |
| PLAT231_ALERT_4_G | Hirshfeld Test (Solvent) F8A --B2 | 9.3 s.u. |
| PLAT231_ALERT_4_G | Hirshfeld Test (Solvent) F5 --B2 | 6.5 s.u. |
| PLAT231_ALERT_4_G | Hirshfeld Test (Solvent) F6 --B2 | 10.0 s.u. |
| PLAT231_ALERT_4_G | Hirshfeld Test (Solvent) F8 --B2 | 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 X...Y Contact F4 ..C5 | 2.83 Ang. |
| PLAT432_ALERT_2_G | Short Inter X...Y Contact F4 ..C6 | 2.93 Ang. |
| PLAT432_ALERT_2_G | Short Inter X...Y Contact F7 ..C11 | 2.85 Ang. |
| PLAT790_ALERT_4_G | Centre of Gravity not Within Unit Cell: Resd. | 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 |
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.

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

Structure factors have been supplied for datablock(s) r27

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No syntax errors found.  CIF dictionary  Interpreting this report

**Datablock: r27**

| Bond precision: C-C = 0.0111 Å | Wavelength=1.54186 |
|-------------------------------|---------------------|
| Cell:                         |                     |
| a=8.6774(3)                  | b=10.8057(4)        |
| alpha=75.144(3)              | beta=73.474(3)      |
| c=13.1764(4)                 | gamma=89.797(3)     |
| Temperature: 200 K           |                     |
| Volume                        |                     |
| Calculated 1141.65(7)         | Reported 1141.65(7)  |
| Space group                   |                     |
| P -1                          | P -1                |
| Hall group                    |                     |
| -P 1                          | -P 1                |
| Moiety formula                |                     |
| B6 F24 Na2, 2(C14 H11 N4 O3 Re) | C14 H11 N4 O3 Re, B3 F12 Na |
| Sum formula                   |                     |
| C28 H22 B6 F24 N8 Na2 O6 Re2  | C14 H11 B3 F12 N4 Na O3 Re |
| Mr 1505.80                    | 752.89              |
| Dx,g cm⁻³ 2.190              | 2.190               |
| Z 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                      |                     |
| Nref 4118                     | 3817                |
| Tmin,Tmax                     | 0.322,0.438         |
| 0.184,0.486                   |                     |
| Tmin’ 0.211                   |                     |

Correction method= # Reported T Limits: Tmin=0.184 Tmax=0.486 AbsCorr = MULTI-SCAN

Data completeness= 0.927  Theta(max)= 67.533

R(reflections)= 0.0406( 3815)  wR2(reflections)= 0.1022( 3817)

S = 1.102  Npar= 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

| ALERT | Description                                                                 | Alert Level | Why? |
|-------|-----------------------------------------------------------------------------|-------------|------|
| PLAT029_ALERT_3_A | _dиффр measured_fraction_theta_full value Low. 0.927 | Alert Level A |  |

**Author Response:** low diffraction intensities in high angles.

### Alert level B

| ALERT | Description                                                                 | Alert Level | Why? |
|-------|-----------------------------------------------------------------------------|-------------|------|
| PLAT241_ALERT_2_B | High ‘MainMol’ Ueq as Compared to Neighbors of F5 | Alert Level B | F5 Check |
| PLAT911_ALERT_3_B | Missing FCF Refl Between Thmin & STh/L= 0.599 301 | Alert Level B | 0.599 301 Report |

### Alert level C

| ALERT | Description                                                                 | Alert Level | Why? |
|-------|-----------------------------------------------------------------------------|-------------|------|
| PLAT220_ALERT_2_C | NonSolvent Resd 1 F Ueq(max)/Ueq(min) Range 3.1 Ratio | Alert Level C |  |
| PLAT234_ALERT_4_C | Large Hirshfeld Difference F5 --B2 . 0.21 Ang. | Alert Level C |  |
| PLAT234_ALERT_4_C | Large Hirshfeld Difference F8 --B2 . 0.17 Ang. | Alert Level C |  |
| PLAT234_ALERT_4_C | Large Hirshfeld Difference O2 --C11 . 0.16 Ang. | Alert Level C |  |
| PLAT241_ALERT_2_C | High ‘MainMol’ Ueq as Compared to Neighbors of F1 Check | Alert Level C |  |
| PLAT241_ALERT_2_C | High ‘MainMol’ Ueq as Compared to Neighbors of F6 Check | Alert Level C |  |
| PLAT242_ALERT_2_C | Low ‘MainMol’ Ueq as Compared to Neighbors of Na1 Check | Alert Level C |  |
| PLAT242_ALERT_2_C | Low ‘MainMol’ Ueq as Compared to Neighbors of B3 Check | Alert Level C |  |
| PLAT342_ALERT_3_C | Low Bond Precision on C-C Bonds 0.0111 Ang. | Alert Level C |  |
| PLAT971_ALERT_2_C | Check Calcd Resid. Dens. 0.91A From Rel 1.94 eA-3 | Alert Level C |  |
| PLAT971_ALERT_2_C | Check Calcd Resid. Dens. 0.86A From Rel 1.90 eA-3 | Alert Level C |  |

### Alert level G

| ALERT | Description                                                                 | Alert Level | Why? |
|-------|-----------------------------------------------------------------------------|-------------|------|
| PLAT042_ALERT_1_G | Calc. and Reported Moiety Formula Strings Differ | Alert Level G | Please Check |
| PLAT045_ALERT_1_G | Calculated and Reported Z Differ by a Factor ... 0.50 Check | Alert Level G |  |
| PLAT083_ALERT_2_G | SHELXL Second Parameter in WGHT Unusually Large 9.42 Why? | Alert Level G |  |
| PLAT154_ALERT_1_G | The s.u.’s on the Cell Angles are Equal ..(Note) 0.003 Degree | Alert Level G |  |
| PLAT171_ALERT_4_G | The CIF-Embedded .res File Contains EADP Records 1 Report | Alert Level G |  |
| PLAT230_ALERT_2_G | Hirshfeld Test Diff for F9 --B3 . 8.4 s.u. | Alert Level G |  |
| PLAT230.Alert_4.G | Hirshfeld Test Diff for F11 --B3 . 6.4 s.u. | Alert Level G |  |
| PLAT230_ALERT_2_G | Hirshfeld Test Diff for F12 --B3 . 6.0 s.u. | Alert Level G |  |
| PLAT230_ALERT_2_G | Hirshfeld Test Diff for F9A --B3 . 5.6 s.u. | Alert Level G |  |
| PLAT230_ALERT_2_G | Hirshfeld Test Diff for F11A --B3 . 9.3 s.u. | Alert Level G |  |
| PLAT230_ALERT_2_G | Hirshfeld Test Diff for F12A --B3 . 5.6 s.u. | Alert Level G |  |
| PLAT232_ALERT_2_G | Hirshfeld Test Diff (M-X) Rel --C11 . 5.7 s.u. | Alert Level G |  |
| PLAT242_ALERT_2_G | Low ‘MainMol’ Ueq as Compared to Neighbors of B1 Check | Alert Level G |  |
| PLAT242_ALERT_2_G | Low ‘MainMol’ Ueq as Compared to Neighbors of B2 Check | Alert Level G |  |
| PLAT301_ALERT_3_G | Main Residue Disorder ............(Resd 1 ) 19% Note | Alert Level G |  |
| PLAT432_ALERT_2_G | Short Inter X...Y Contact F7 ..C11 2.91 Ang. | Alert Level G |  |
| PLAT909_ALERT_3_G | Percentage of I>2sig(I) Data at Theta(Max) Still 100% Note | Alert Level G |  |
| PLAT933_ALERT_2_G | Number of OMIT Records in Embedded .res File ... 1 Note | Alert Level G |  |
| PLAT936_ALERT_5_G | Dataset Contains no Negative Intensities ...... Please Check | Alert Level G |  |
| PLAT978_ALERT_2_G | Number C-C Bonds with Positive Residual Density. 0 Info | Alert Level G |  |

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
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.

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

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 Å  Wavelength=1.54186

Cell:  a=7.0101(4)  b=10.9539(4)  c=11.3985(7)
      alpha=84.168(3)  beta=77.822(5)  gamma=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   |
| Dx,g cm⁻³            | 2.385      | 2.385    |
| Z                    | 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     |
| Tmin,Tmax            | 0.059,0.420| 0.076,0.661 |
| Tmin'                | 0.003      |          |

Correction method= # Reported T Limits: Tmin=0.076 Tmax=0.661
AbsCorr = MULTI-SCAN

Data completeness= 0.958  Theta(max)= 64.785

R(reflections)= 0.0234( 2749)  wR2(reflections)= 0.0626( 2750)

S = 1.149  Npar= 237

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 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 Rel -1.52 eA-3

**Alert level G**

PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Rel --Br1 . 5.7 s.u.

PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Rel --N3 . 5.2 s.u.

PLAT244_ALERT_4_G Low ‘Solvent’ Ueq as Compared to Neighbors of B1 Check

PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still 100% Note

PLAT961_ALERT_5_G Dataset Contains no Negative Intensities ....... Please Check

PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual 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
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.

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

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 A  Wavelength=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      | P n m a       | P n m a       |
| 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        |
| Dx,g cm-3        | 2.382         | 2.382         |
| Z                | 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       |
| Nref             | 1152          | 1082          |
| Tmin,Tmax        | 0.177,0.443   | 0.019,0.108   |
| Tmin’            | 0.021         |               |

Correction method= #  Reported T Limits: Tmin=0.019  Tmax=0.108
AbsCorr = MULTI-SCAN

Data completeness= 0.939  Theta(max)= 67.413

R(reflections)= 0.0346(1042)  wr2(reflections)= 0.1019(1082)

S = 1.085  Npar= 108

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. 0.939 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 Rel1 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 Rel1 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
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 X...Y Contact 01 ..C11 2.96 Ang.
x,y,z = 1_555 Check
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_1_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 ALERT level A = Most likely a serious problem - resolve or explain
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**Validation response form**

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

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

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