Crystal and molecular structures of fac-[Re(Bid)-(PPh₃)(CO)₃] [Bid is tropolone (TropH) and tribromotropolone (TropBr₃H)]

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Two rhenium complexes, namely, fac-tricarbonyl(triphenylphosphane-κP)(tropolonato-κ²O,O’)rhenium(I), [Re(C₇H₅O₂)(C₁₈H₁₅P)(CO)₃] or fac-[Re(Trop)-(PPh₃)(CO)₃] (1), and fac-tricarbonyl(3,5,7-tribromotropolonato-κ²O,O’)rhenium(I), [Re(C₇H₂Br₃O₂)(C₁₈H₁₅P)(CO)₃] or fac-[Re(TropBr₃)(PPh₃)(CO)₃] (2) (TropH is tropolone and TropBr₃H is tribromotropolone), were synthesized and their crystal and molecular structures confirmed by single-crystal X-ray diffraction. Both crystallized in the space group P1 and display an array of inter- and intramolecular interactions which were confirmed by solid-state ¹³C NMR spectroscopy using cross polarization magic angle spinning (CPMAS) techniques, as well as Hirshfeld surface analysis. The slightly longer Re–P distance of 1 [2.4987 (5) Å versus 2.4799 (11) Å for 1 and 2, respectively] suggests stronger back donation from the carbonyl groups in the former case, possibly due to the stronger electron-donating ability of the unsubstituted tropolonate ring system. However, this is not supported in the Re–CO bond distances of 1 and 2.

1. Introduction

Rhenium(I) tricarbonyl complexes not only have application as models for similar technetium(I) complexes in radiopharmacy, but their anticancer and antimicrobial properties have recently been investigated by several research groups, including ours (Gantsho et al., 2020; Collery et al., 2019; Li et al., 2012; Otero et al., 2019; Leonidova & Gasser, 2014; Brink et al., 2018; Sovari et al., 2020, 2021; Varma et al., 2020). Similarly, the bidentate ligand tropolone and its derivatives have shown anticancer and antiviral properties on their own (Ishihara et al., 2010; Borowski et al., 2007; Dittes et al., 1995a) and when combined with metal complexes (Ishihara et al., 2010; Borowski et al., 2007; Dittes et al., 1995a,b; Trust, 1975). Kinetic studies have shown that tropolone and other O,O’-bidentate ligands like 3-hydroxyflavone increase the rate of substitution of water or methanol in fac-[Re(Bid).X(CO)₃]ⁿ⁻ (Bid = bidentate ligand, X = H₂O or methanol, and n = 0 or 1+) type complexes by up to 20000 times (Gantsho et al., 2020; Schutte et al., 2012; Schutte-Smith et al., 2019b; Schutte et al., 2011; Manicum et al., 2020; Schutte-Smith & Visser, 2015). This kind of mechanistic information is extremely important when designing molecules for anticancer, antibacterial and antiviral applications, as well as in radiopharmacy (Collery et al., 2019; Schutte-Smith et al., 2019b). Recently, we showed that kinetic data can be correlated with cytotoxicity and cell availability (Schutte-Smith et al., 2020).

Our focus is to try to understand the basic chemistry (mechanism of action, structure–activity relationships and
stability) of these organometallic compounds to aid in the design of new bioactive pharmaceuticals. This also includes the characterization by means of solid- and solution-state multinuclear NMR spectroscopy, single-crystal X-ray diffraction and other spectroscopic methods. The application of solid-state NMR spectroscopy to study hydrogen-bond and other intra- and intermolecular interactions is growing rapidly, with many research groups involved in the development of new techniques to study crystalline and even amorphous phases, making it a useful tool for our purposes as well (Chierotti & Gobetto, 2008; Traer et al., 2007; Zhao et al., 2022). Coupling constants (J) are reported in Hz. The solid-state NMR spectra were collected on a 400 MHz Bruker Avance III spectrometer equipped with a 4 mm VTN multinuclear double resonance magic angle spinning probe, operating at 25.0 °C. The 13C NMR spectra were recorded at 100.6 MHz, using the cross polarization magic angle spinning (CP/MAS) technique. A rotating speed of 10000 Hz was used with a contact time of 2 ms, a recycle delay of 5 s and an acquisition time of 33.9 ms. All the spectra were recorded with 3k scans. The samples were packed in 4 mm zirconia rotors.

2. Experimental

2.1. Materials and methods

All reagents employed in the preparation and characterization of the title compounds were of analytical grade, were purchased from Sigma–Aldrich or Merck (South Africa) and were used without any further purification; all experiments were performed aerobically. The IR spectra were recorded at room temperature on a PerkinElmer BX II IR spectrometer in the range 4000–370 cm⁻¹.

The liquid-state ¹H, ¹³C and ³¹P NMR spectra were recorded at 25.0 °C on a 300 MHz Bruker Fourier NMR spectrometer, a 400 MHz Avance III NMR spectrometer and a 600 MHz Avance II Bruker spectrometer, respectively, and methanol-d₄, toluene-d₈ and acetone-d₆ were used as solvents. The chemical shifts (δ) are reported in parts per million (ppm); for methanol-d₄ and acetone-d₆, the spectra were referenced relative to the solvent peak (3.31 ppm for ¹H and 49.15 ppm for ¹³C, and 2.05 for ¹H and 29.92 for ¹³C, respectively). Coupling constants (J) are reported in Hz. The solid-state NMR spectra were collected on a 400 MHz Bruker Avance III spectrometer equipped with a 4 mm VTN multinuclear double resonance magic angle spinning probe, operating at 25.0 °C. The ¹³C NMR spectra were recorded at 100.6 MHz, using the cross polarization magic angle spinning (CP/MAS) technique. A rotating speed of 10000 Hz was used with a contact time of 2 ms, a recycle delay of 5 s and an acquisition time of 33.9 ms. All the spectra were recorded with 3k scans. The samples were packed in 4 mm zirconia rotors.

2.2. Synthesis and crystallization

2.2.1. fac-[Re(Trop)(PPh₃)(CO)₃] (1). fac-[Re(Trop)(CO)₃(H₂O)] (50 mg, 0.122 mmol), synthesized according to a previously reported procedure (Schutte et al., 2012), was dissolved in acetone (30 ml) and triphenylphosphane (32 mg, 0.122 mmol) was added to the solution. The mixture was stirred overnight at room temperature and left to crystallize from the acetone solution (yield: 69 mg, 87%).

IR (KBr, cm⁻¹): ν(CO) = 1096, 1387. ¹H NMR (400.13 MHz, acetone-d₆): δ = 7.42 (m, 15H), 7.23 (t, 2H, J = 10.6 Hz), 6.91 (d, 2H, J = 10.8 Hz), 6.84 (t, 1H, J = 9.6 Hz), ¹³C NMR (100.61 MHz, acetone-d₆): δ = 184 (Trop), 138 (Trop), 134...
(PPh₃), 131 (PPh₃), 129 (PPh₃), 127 (Trop). ¹³C CP/MAS NMR (100.61 MHz): δ 183, 182, 136, 135, 133, 132, 129, 128, 127, 126. ³¹P (161.97 MHz, acetone-d₆): δ 18.2. Analysis calculated (%): C 51.45, H 3.08, P 4.74; found: C 51.43, H 3.11, P 1.76.

2.2.2. fac-[Re(TropBr₃)(PPh₃)(CO)₃](1), fac-[Re(TropBr₃)-(CO)₃(H₂O)] (50 mg, 0.077 mmol), synthesized according to a previously reported procedure (Schutte et al., 2008), was dissolved in acetone (30 ml) and triphenylphosphane (20 mg, 0.0077 mmol) was added to the solution. The mixture was stirred overnight at room temperature and left to crystallize from the acetone solution (yield: 62.5 mg, 91%). IR (KBr, cm⁻¹): ν₁ (CO) = 2018, 1922, 1889. ¹HN M R (400.13 MHz, acetone-d₆): δ 8.15 (s, 2H), 7.42 (m, 15H). ¹³C NMR (150.95 MHz, acetone-d₆): δ 176 (Trop), 143 (Trop), 134 (PPh₃), 132 (Trop), 129 (Trop). ¹³C CP/MAS NMR (100.61 MHz): δ 135, 133, 131, 129. ³¹P (161.97 MHz, acetone-d₆): δ 19.6. Analysis calculated (%): C 37.77, H 1.92, P 3.48; found: C 37.81, H 1.90, P 3.45.

2.3. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 1. All aromatic H atoms were placed in geometrically idealized positions (C—H = 0.95 Å) and constrained to ride on their parent atoms, with Uiso(H) = 1.2Ueq(C).

3. Results and discussion
3.1. Synthesis
fac-[Re(Trop)(PPh₃)(CO)₃] and fac-[Re(TropBr₃)(PPh₃)-(CO)₃] (2) were synthesized from the respective aqua complexes, which were synthesized according to previously reported procedures (Gantsho et al., 2020; Schutte et al., 2008, 2012). The synthesis of 1 was described previously, but crystals suitable for single-crystal X-ray diffraction could not be obtained at the time (Gantsho et al., 2020). Compounds 1 and 2 were synthesized in good yield from acetone solutions, after stirring the respective aqua complexes with one equivalent of triphenylphosphane overnight.

In the ¹H NMR spectra, a significant downfield shift is observed from 1 (7.23, 6.91 and 6.84 ppm) to 2 (8.15 ppm) for the tropolonate and tribromotropolonate H atoms, respectively, which is expected due to the electron-withdrawing Br atoms in 2 causing deshielding of the nuclei. This is confirmed in the ³¹P NMR spectra with a slight downfield shift in the phosphorus peak of 1 at 18.2 ppm and 2 at 19.6 ppm. The IR carbonyl stretching frequencies of 1 (2010, 1934 and 1887 cm⁻¹) are lower than 2 (2018, 1922 and 1889 cm⁻¹), which is expected since the tropolonate ligand in 1 is more electron donating than the tribromotropolonate ligand in 2, therefore implying stronger backbonding from the carbonyl ligands to the metal centre and resulting in lower CO stretching frequencies. This, in turn, labilizes the phosphane ligand in the sixth position and is confirmed in the solid-state structures, with the Re—P bond lengths reported as 2.4987 (5) Å for 1 and 2.4799 (11) Å for 2.

3.2. X-ray crystallography
A summary of the crystal data for 1 and 2 is given in Table 1. fac-[Re(Trop)(PPh₃)(CO)₃], 1, crystallized in the triclinic space group P̅1 with one molecule in the asymmetric unit. The molecular diagram and selected bond lengths and angles are given in Fig. 1 and Table 2, respectively. Three intermolecular

Table 2
Selected geometric parameters (Å, °) for 1.

| Bond                  | Length (Å) | Angle (°) |
|-----------------------|------------|-----------|
| Re1—Cl1               | 1.900 (2)  | Re1—O12   | 2.1322 (13)  |
| Re1—C2               | 1.912 (2)  | Re1—O11   | 2.1345 (13)  |
| Re1—C3               | 1.944 (2)  | Re1—P1    | 2.4987 (5)   |
| O12—Re1—O11          | 73.99 (5)  | O12—Re1—P1| 88.10 (4)    |
| C3—Re1—P1            | 177.15 (6) | O11—Re1—P1| 86.59 (4)    |

Figure 1
The molecular structures of (a) fac-[Re(Trop)(PPh₃)(CO)₃] (1) and (b) fac-[Re(TropBr₃)(PPh₃)(CO)₃] (2), showing the atom-numbering schemes. H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.
and one intramolecular hydrogen-bonding interaction (C—H···O) are observed in the structure, as well as two intermolecular C—O···π and one intramolecular π·π interaction (Figs. S1 and S2 in the supporting information). A summary of the geometric parameters of these interactions is given in Tables S1 and S2 in the supporting information. Interestingly, the hydrogen-bond interactions involve the tropolonate ligand and the C atoms of the C41-ring as C—H donor atoms, and the O atoms of the tropolonate ring and the O atom of a carbonyl ligand as acceptor atoms. The π-interactions, on the other hand, involve interactions between the carbonyl O2 and O3 atoms and the centroids of the five-membered Re/O11/C11/C12/O12 ring, as well as the arene rings of the phosphane ligand (C21–C26 and C31–C36).

fac-\([\text{Re(TropBr}_3](\text{PPh}_3)(\text{CO}))_3]\), 2, also crystallized in the triclinic space group \(P\overline{1}\) with one molecule in the asymmetric unit. The molecular diagram is given in Fig. 1 and selected bond lengths and angles are provided in Table 3. Four intermolecular hydrogen-bond interactions (three C—H···O and one C—H···Br) and one intramolecular hydrogen-bond interaction (C—H···O) are observed in the structure of 2 (Fig. S3 in the supporting information). A short contact of 3.250 \((\text{Å})\) is observed between Br2 and O3\((-x+1,-y+1,-z+1)\) (Fig. S4). Two intermolecular contacts form an infinite one-dimensional chain with base vector [110] between Br1 and Br3\((x-1,y-1,z)\), and between Br3 and Br1\((x+1,y+1,z)\), both with a distance of 3.4809 \((\text{Å})\) (Fig. S5). A range of π-interactions are observed: one \(X—H···\pi\), two \(\pi·\pi\) and three \(Y—X···\pi\) interactions ranging between 3.438 (4) and 3.865 (2) \((\text{Å})\) (Fig. S4). A summary of the geometric parameters of these interactions is given in Tables S3 and S4 in the supporting information. All three Br atoms are involved in short contacts, while Br2 is additionally involved in a π-interaction and Br3 is involved as an acceptor in a hydrogen-bond interaction. All five of the ring systems, i.e. the three arene rings of the \(\text{PPh}_3\) ligand, the tropolonate ring and the Re1/O11/C11/C12/O12 five-membered ring, are involved in the π-interactions.

The bond lengths and angles of 1 and 2 compare well with each other and also with similar structures in the literature (Gantsho et al., 2020; Schutte-Smith et al., 2019b; Schutte et al., 2007, 2008; Manicum et al., 2020; Bochkova et al., 1987; Kydonaki et al., 2016). The Re—P1 bond length of 1 is slightly longer than in 2, possibly due to the electron-withdrawing effect of the three Br atoms on the backbone of 2. The tropolonate ligand in 1 donates more electron density to the rhenium metal centre, initiating more backbonding from the...
carbonyl ligands, labilizing the Re—P bond. Although this is
what we expect, it is not observed in the Re—CO bond lengths
of 1 and 2, which do not differ significantly. Considering the
angles around the Re5 metal core, a good correlation between
1 and 2 is found. The small bite angles of 73.99 (5) and
73.05 (10)° for 1 and 2, respectively, indicate the degree of
distortion of the octahedral geometry, which is normal and
within the range of other similar structures where a five-
membered O,O'-chelate ring is formed with the metal centre
(Gantsho et al., 2020; Schutte et al., 2007, 2008; Schutte-Smith
et al., 2019b; Bochkova et al., 1987). In the case of a six-
membered O,O'-chelate ring (with PPh3 in the sixth position),
the bite angle is slightly larger, with values ranging between
82.2 and 84.7° (Manicum et al., 2020; Kydonaki et al., 2016).

The tropolone and tribromotropolonate ligands bend
slightly towards the triphenylphosphane ligand in 1 and 2, with
dihedral angles between the plane through the Re(CO)5 entity
and the ligand (the plane through Re/C1/O1/C2/O2 and the
plane through O11/O12/C11–C17) of 8.85 (8) and 12.43 (14)°,
respectively (illustrated in Fig. S6 in the supporting informa-
tion). In 2, the Br atoms are slightly ‘out of plane’ with respect
to the tropolone ring (C11–C17) at −0.1463 (4), 0.1760 (5)
and −0.2114 (5) Å for Br1, Br2 and Br3, respectively. This
could be due to the different interactions observed: the
intermolecular contacts between Br1 and Br3 and the C–
H—Br3 hydrogen-bond interaction, and the Br2—Br3 short
contact and C15—Br2—Cg1(−x + 1, −y + 1, −z + 1)
π-interaction for Br2 (Cg1 is the centroid of the Re/C1/O1/C2/
O2 ring).

The Hirshfeld surfaces of 1 and 2 are illustrated in Fig. 2
(Spackman & Jayatilaka, 2009). The molecular diagram of the
compound is given at the top of the figure to illustrate the
orientation of each compound in the curvedness (middle) and
shape index (bottom) plots below it. In 1, the blue concave
regions around O2 and O3 correspond to the C2—O2—
Br3 (−x + 2, −y, −z + 1) (Cg3 is the centroid of the C31–C36 ring)
and C3—O3—Cg1(−x + 2, −y, −z) Y—X···π interactions as
given in Table S2 (see supporting information), while a red
convex region around O1 corresponds to the C17—H17···O1-
(−x + 2, −y + 1, −z) hydrogen-bond interaction (Table S1).
The large red convex area above the rhenium five-membered
ring and atoms O11 and O12 correlates with the three
hydrogen-bond interactions C44—H44···O12(x, y + 1, z),
C45—H45···O11(−x + 2, −y + 1, −z) and C46—H46···O11,
and the π-interaction C3—O3···Cg1(−x + 2, −y, −z) (Table
S1 and Table S2).

In 2, the blue and red adjacent triangles above the tri-
bromotropolonate ring system correlate with the π···π inter-
actions given in Table S4 (Seth et al., 2011). Blue convex
regions are observed around the donor atoms Br1, Br2 and
Br3 [C15—Br2···Cg1(−x + 1, −y + 1, −z + 1), Br1···Br3-
(x − 1, y − 1, z), Br3···Br1(x + 1, y + 1, z) and Br2···O3-
(−x + 1, −y + 1, −z + 1)], as well as red concave regions above

| Table 4
| Comparison of bond lengths (Å) of fac-[Re(Trop)(PPh3)(CO)2] (1) and [Re(Trop)(PPh3)(CO)2] (3). |
| Bond | 1 | 3 |
| Re1—C1 | 1.900 (2) | 1.883 (3) |
| Re1—C2 | 1.912 (2) | 1.887 (3) |
| Re1—O11 | 2.1345 (13) | 2.1578 (19) |
| Re1—O12 | 2.1322 (13) | 2.1548 (18) |
| Re1—P1 | 2.4987 (5) | 2.4302 (8) |
| Re1—P2 | 2.4987 (5) | 2.4302 (8) |

Figure 4
Fingerprint plots of 2: (a) full plot with the total Hirshfeld surface area of the molecules. Fingerprint plots of 2 resolved into (b) C···H/H···C (16%), (c) Br···H/H···Br (15.2%), (d) Br···Br (5.1%), (e) H···H (25%) and (f) O···H/H···O (23.7%).
the five-membered rhenium ring system [C15—Br2···Cg1-(x + 1, -y + 1, -z + 1) and C36—H36···O11] and atom O3 [Br2···O3(-x + 1, -y + 1, -z + 1) and C46—H46···O3(x + 1, y, z)] which correlates with the data given in Tables S3 and S4 in the supporting information.

Overall, the curvedness of 1 has less ‘flat’ regions compared to 2, and compares well with the increased number of π-interactions observed in 2 compared to 1.

Figs. 3 and 4 show the fingerprint plots of 1 and 2, respectively. Fingerprint plots can be decomposed to separate the contributions from different types of interactions that overlap in the full fingerprint. In 1, the proportion of O···H/H···O interactions comprise 28.1%, H···H comprise 38.1% and H···C/C···H comprise 26.5% of the total Hirshfeld surfaces for each molecule. In 2, the distribution is slightly different; the C···H/H···C interactions comprise 16%, the Br···H/ H···Br interactions comprise 15.2%, the Br···Br interactions comprise 5.1%, the H···H interactions comprise 25% and the O···H/H···O interactions comprise 23.7% of the total Hirshfeld surfaces.

When dnorm (as defined and explained by Spackman & Jayatilaka, 2009) is mapped on a Hirshfeld surface, intermolecular contacts appear as red spots, contacts shorter than van der Waal separations, on a largely blue surface. It has been proven to be useful as an unbiased method to identify close intermolecular contacts, even in complex crystal structures.

dnorm Hirshfeld plots of 1 and 2 are presented in Fig. 5, indicating the red spots associated with close contacts. Not all interactions are shown for conciseness because all the interactions are not visible from one orientation. All the interactions reported in Tables S1–S4 correlate with these plots.

By comparing 1 and the previously reported bis(triphenylphosphane) complex [Re(Trop)(PPh3)2(CO)2] (3) (Gantsho et al., 2020), it is clear that most of the bond lengths around the metal centre change when the axial carbonyl ligand is substituted by a second PPh3 ligand (Table 4). When the carbonyl ligand is substituted by a PPh3 ligand, more electron density is donated to the Re(I) metal centre, shortening the equatorial Re—CO bond lengths from 1.900 (2) and 1.912 (2) Å to 1.883 (3) and 1.887 (3) Å. PPh3 also has a weaker trans effect than CO, which is evident in the shortening of the Re1—P1 bond(s).

Interestingly, the trans effect is clearly observed in the axial Re—CO distances in the solid-state crystal structures of fac-[Re(Trop)(CO)3(H2O)] (Schutte et al., 2012), fac-[Re(Trop)-

Figure 5
The Hirshfeld surfaces for 1 and 2 mapped with dnorm over the range from −0.2 to 1.4.

Figure 6
The atom-numbering schemes of 1 and 2.

Figure 7
Solid-state versus liquid-state 13C NMR spectra of 1.
(Py)(CO)₃] (Schutte et al., 2012) and fac-[Re(Trop)(PPh₃)-(CO)₃] [increasing from 1.890 (7) to 1.919 (4) to 1.944 (2) Å], and also in fac-[Re(TropBr₃)(CO)₃(H₂O)] (Schutte et al., 2008), fac-[Re(TropBr₃)(Br)(CO)₃] (Schutte et al., 2007) and fac-[Re(TropBr₃)(PPh₃)(CO)₃] [increasing from 1.882 (7) to 1.897 (3) to 1.950 (5) Å] as the trans effect increases according to the following trend: H₂O < Py < Br < P₃R = tertiary phosphane).

3.3. Solid-state NMR

In solid-state ¹³C NMR spectroscopy, the cross polarization magic angle spinning (CP/MAS) technique is often used to enhance the polarization of the low-abundance ¹³C nuclei via its interaction with ¹H nuclei. The effectiveness of the CP/MAS technique depends on the magnitude of ¹H–¹³C dipolar coupling (Freitas et al., 2016; Conte et al., 2004; Smernik et al., 2002). It is expected that the observed hydrogen-bond interactions, as well as other short contacts and π-interactions in the solid state, will deshield the C atoms and cause a downfield shift in the solid-state ¹³C NMR spectra (Patterson-Elenbaum et al., 2006). In the liquid state, the intra- and intermolecular interactions are disrupted because of the motion of the molecules within the solution; thus, we only observe the dynamic average of the motion. The degree of interactions present in the solid-state can be determined by the difference in chemical shift values (Δδ) of the specific C atoms in the liquid- versus solid-state NMR spectra (Patterson-Elenbaum et al., 2006). A larger difference in chemical shift is normally indicative of a stronger interaction, which is determined by the specific bond length and angle (Siskos et al., 2017).

It is known that broad peaks (or no peaks) are observed when there are not many C atoms that are directly bound to H atoms (Freitas et al., 2016), which is the case in 2. Nevertheless, we aimed to correlate the change in chemical shift from the ¹³C liquid-state NMR to the solid-state ¹³C NMR to the interactions observed in the crystal structures.

Fig. 6 provides the numbering scheme of atoms in 1 and 2. The solid-state ¹³C NMR data of 1 did not shift much from the solution state to the solid state, with not more than a 1 ppm change (Δδ) in the chemical shift at most, which is basically negligible (Fig. 7). Four hydrogen-bond interactions and three π-interactions are observed in 1 (Tables S1 and S2 in the supporting information), two of the π-interactions being very weak (distance > 3.8 Å). The five interactions that are considered to be stronger with shorter distances involve the P₃R ligand, the O atoms of the tropolonate ligand, the carbonyl ligands and the centroid of the five-membered Re₁/O₁₁/C₁₁/C₁₂/O₁₂ ring system. The carbonyl ligands are not visible on the liquid- and solid-state ¹³C NMR spectra due to the economic and time implications involved to observe it. IR spectroscopy are used to confirm the presence of the carbonyl ligands in this type of complex.

In the solution-state ¹³C NMR spectra, the peak at 184 ppm is assigned to C₁₁ and C₁₂, and seeing that these atoms are bound to O₁₁ and O₁₂ (involved in three interactions) and are part of the five-membered ring system (Re₁/O₁₁/C₁₁/C₁₂/O₁₂), a downfield shift is expected because of the effect of the
deshielding of these interactions. However, it shifted slightly upfield to 183 and 182 ppm, and yielded two peaks in the solid state compared to a single peak in the solution state. This is due to the fact that C11 and C12 are not equivalent in the solid state because of the interactions observed in the crystal structure: C17—H17···O1(−x + 2, −y + 1, −z), C45—H45···O11(−x + 2, −y + 1, −z) and C46—H46···O11 all indirectly involve C11, while C44—H44···O12(x + 1, z) is the only interaction that indirectly involves C12; thus, the splitting of the single peak in the solid state.

The single peak for C13, C14, C16 and C17 at 138 ppm, the peaks for the PPh3 ligand at 134, 131 and 129 ppm, and the single peak for C15 at 127 ppm in the solution state are not as well defined in the solid state and yield a broad peak from 138 to 126 ppm, similar to the range found in the solution state; we expected a downfield shift because of the interactions involving the tropolonate ring system and one arene ring of the PPh3 ligand. We could, however, see some significant splitting of the peaks; compared to the five single peaks at 138, 134, 131, 129 and 127 ppm in the solution state, splitting of the peaks (although it is a broad peak) is seen in the solid state, indicating that many of the C atoms are not equivalent anymore because of the interactions observed in the crystal structure [C17—H17···O1(−x + 2, −y + 1, −z), meaning C13, C14, C16 and C17 are not equivalent anymore; C44—H44···O12(x + 1, z), C45—H45···O11(−x + 2, −y + 1, −z) and C46—H46···O11, meaning the C41–C46 arene ring in PPh3 is not equivalent to the C21–C26 and C31–C36 arene rings].

In the case of 2, the fact that the tribromotropolonate ring system only has two H atoms directly bound to C atoms had an impact on the solid-state 13C NMR spectra and we only observe the PPh3 ligand, and the seven C atoms in the tribromotropolonate ligand are not observed (Fig. 8) (Freitas et al., 2016). In the solution-state spectra, the PPh3 ligand has a single peak at 134 ppm which split up into four peaks at 135, 132, 131 and 129 ppm in the solid-state spectra. Again, this is because the C atoms are not equivalent in the solid state.

4. Conclusion
Two new crystal structures of rhenium(I) tricarbonyl complexes with either a tropolonate or a tribromotropolonate bidentate ligand are reported and correspond well with similar known structures. The solid-state NMR data indicated the presence of inter- and intramolecular interactions, as seen by the splitting of some signals, but unfortunately, due to the fact that both 1 and 2 contain only a few C—H units each, credible chemical shifts could not be obtained and correlated with the crystal data. The intermolecular interactions obtained from PLATON (Spek, 2020) correlate with the Hirshfeld surfaces generated with CrystalExplorer (Spackman et al., 2021).

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References
Bochkova, R. I., Zakharov, L. N., Patrikeev, N. V., Shal’nova, K. G., Abakumov, G. A. & Cherkasov, V. K. (1987). Koord. Khim. 13, 702.
Borowski, P., Lang, M., Haag, A. & Baier, A. (2007). Antivir. Chem. Chemother. 18, 103–109.
Brandenburg, K. & Putz, H. (2019). DIAMOND. Crystal Impact GbR, Bonn, Germany.
Brink, A., Kroon, R. E., Visser, H. G., van Rensburg, C. E. J. & Roodt, A. (2018). New J. Chem. 42, 5193–5203.
Bruker (2012). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Chierotti, M. R. & Gobetto, R. (2008). Chem. Commun. pp. 1621–1634.
Collery, P., DesmaeLe, D. & Vijaykumar, V. (2019). Curr. Pharm. Des. 25, 3306–3322.
Conte, P., Spaccini, R. & Piccolo, A. (2004). Prog. Nucl. Magn. Reson. Spectrosc. 44, 215–223.
Dittes, U., Diemer, R. & Kepper, B. K. (1995a). J. Cancer Res. Clin. Oncol. 121, A50.
Dit tes, U., Diemer, R., Lenz, O. & Kepper, B. K. (1995b). J. Inorg. Biochem. 59, 215.
Farrugia, L. J. (2012). J. Appl. Cryst. 45, 849–854.
Freitas, J. C. C., Cipriano, D. F., Zuconello, C. G., Cunha, A. G. & Emmerich, F. G. (2016). J. Spectrosc. 2016, 1543273.
Gantsho, V. L., Doto u, M., Jakubashev, M., Goud, B., Gasser, G., Visser, H. G. & Schutte-Smith, M. (2020). Dalton Trans. 49, 35–46.
Ishihara, M., Wakabayashi, H., Motohashi, N. & Sakagami, H. (2010). Anticancer Res. 30, 129–133.
Kydona ki, T. E., Tsoukas, E., Mendes, F., Hatzidimitriou, A. G., Paulo, A., Papadopoulo u, L. C., Papagiannopou lo, D. & Psomas, G. (2016). J. Inorg. Biochem. 160, 94–105.
Leonidova, A. & Gasser, G. (2014). ACS Chem. Biol. 9, 2180–2193.
Li, M., Liu, X., Nie, M., Wu, Z., Yi, C., Chen, G. & Yam, V. W. (2012). Organometallics 31, 4459–4466.
Manic u, A.-L., Alexander, O., Schutte-Smith, M. & Visser, H. G. (2020). J. Mol. Struct. 1209, 127953.
Otero, C., Carreñ o, A., Polanco, R., Llancalahuen, F. M., Arratia-Pérez, R., Gacitúa, M. & Fuentes, J. A. (2019). Front. Chem. 7, 454.
Patterson-Elenbaum, S., Stanley, J. T., Dillner, D. K., Lin, S. & Traficante, D. (2006). Magn. Reson. Chem. 44, 797–806.
Sch utte, M., Kemp, G., Visser, H. G. & Roodt, A. (2011). Inorg. Chem. 50, 12486–12498.
Schutte, M., Roodt, A. & Visser, H. G. (2012). Inorg. Chem. 51, 11996–12006.
Schutte, M., Visser, H. G. & Roodt, A. (2008). Acta Cryst. E64, m1610–m1611.
Schutte, M., Visser, H. G. & Steyl, G. (2007). Acta Cryst. E63, m3195–m3196.
Schutte-Smith, M., Marker, S. C., Wilson, J. J. & Visser, H. G. (2020). Inorg. Chem. 59, 15888–15897.
Schutte-Smith, M., Roodt, A., Alberto, R., Twigg, L., Visser, H. G., Kirsten, L. & Koen, R. (2019a). Acta Cryst. C75, 378–387.
Schutte-Smith, M., Roodt, A. & Visser, H. G. (2019b). Dalton Trans. 48, 9984–9997.
Schutte-Smith, M. & Visser, H. G. (2015). *Polyhedron*, **89**, 122–128.
Seth, S. K., Mandal, P. C., Kar, T. & Mukhopadhyay, S. (2011). *J. Mol. Struct.* **994**, 109–116.
Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
Siskos, M. G., Choudhary, M. I. & Gerothanassis, I. P. (2017). *Molecules*, **22**, 415.
Smernik, R. J., Balduck, J. A. & Oades, J. M. (2002). *Solid State Nucl. Magn. Reson.* **22**, 71–82.
Sovari, S. N., Radakovic, N., Roch, P., Crochet, A., Pavic, A. & Zobi, F. (2021). *Eur. J. Med. Chem.* **226**, 113858.
Sovari, S. N., Vojnovic, S., Bogojevic, S. S., Crochet, A., Pavic, A., Nikodinovic-Runic, J. & Zobi, F. (2020). *Eur. J. Med. Chem.* **205**, 112533.

Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K. & Spackman, M. A. (2021). *CrystalExplorer*. Version 21.5. University of Western Australia. https://crystalexplorer.scb.uwa.edu.au/.
Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
Traer, J. W., Britten, J. F. & Goward, G. R. (2007). *J. Phys. Chem. B*, **111**, 5602–5609.
Trust, T. J. (1975). *Antimicrob. Agents Chemother.* **7**, 500–506.
Varma, R. R., Purswani, B. H., Suresh, E., Bhatt, B. S. & Patel, M. N. (2020). *J. Mol. Struct.* **1200**, 127068.
Wilhelm, A., Bonnet, S., Twigge, L., Rarova, L., Stenclova, T., Visser, H. G. & Schutte-Smith, M. (2022). *J. Mol. Struct.* **1251**, 132001.
Zhao, X., Edén, M. & Levitt, M. A. (2001). *Chem. Phys. Lett.* **342**, 353–361.
Crystal and molecular structures of \textit{fac-}[Re(Bid)(PPh\textsubscript{3})(CO)\textsubscript{3}] [Bid is tropolone (TropH) and tribromotropolone (TropBr\textsubscript{3}H)]

Marietjie Schutte-Smith and Hendrik Gideon Visser

Computing details

For both structures, data collection: \textit{APEX2} (Bruker, 2012); cell refinement: \textit{SAINT-Plus} (Bruker, 2012); data reduction: \textit{SAINT-Plus} (Bruker, 2012); program(s) used to solve structure: \textit{SHELXT} (Sheldrick, 2015\textit{a}); program(s) used to refine structure: \textit{SHELXL2018} (Sheldrick, 2015\textit{b}); molecular graphics: \textit{DIAMOND} (Brandenburg & Putz, 2019); software used to prepare material for publication: \textit{WinGX} (Farrugia, 2012) and \textit{DIAMOND} (Brandenburg & Putz, 2019).

\textit{fac-Tricarbonyl(triphenylphosphane-κP)(tropolonato-κ\textsubscript{2}O,O\textquotesingle)rhenium(I)} (1)

\textbf{Crystal data}

$[\text{Re}(\text{C}_7\text{H}_5\text{O}_2)(\text{C}_{13}\text{H}_{15}\text{P})(\text{CO})_3]$  
$M_r = 653.61$  
Triclinic, $P\bar{1}$  
\begin{align*}
a &= 9.9301 (11) \text{ Å} \\
b &= 10.1686 (10) \text{ Å} \\
c &= 12.7882 (14) \text{ Å} \\
\alpha &= 80.948 (3) ^\circ \\
\beta &= 71.899 (3) ^\circ \\
\gamma &= 88.682 (3) ^\circ \\
V &= 1211.6 (2) \text{ Å}^3 \\
Z &= 2 \\
F(000) &= 636 \\
D_x &= 1.792 \text{ Mg m}^{-3} \\
\text{Mo } K\alpha \text{ radiation, } \lambda = 0.71073 \text{ Å} \\
\text{Cell parameters from } 9782 \text{ reflections} \\
\theta &= 2.9\text{--}28.3\text{°} \\
\mu &= 5.12 \text{ mm}^{-1} \\
T &= 100 \text{ K} \\
\text{Cuboid, orange} \\
0.27 \times 0.17 \times 0.13 \text{ mm} $

\textbf{Data collection}

Bruker APEXII CCD  
\begin{align*}
\varphi \text{ and } \omega \text{ scans} \\
\text{Absorption correction: multi-scan} \\
(\text{SADABS}; \text{Bruker, 2012}) \\
T_{\text{min}} &= 0.357, T_{\text{max}} = 0.511 \\
25538 \text{ measured reflections} \\
5820 \text{ independent reflections} \\
5726 \text{ reflections with } I > 2\sigma(I) \\
R_{\text{int}} &= 0.037 \\
\theta_{\text{max}} &= 28.0\text{°}, \theta_{\text{min}} = 2.9\text{°} \\
h &= -13\rightarrow 13 \\
k &= -13\rightarrow 13 \\
l &= -16\rightarrow 16 \\
\end{align*}

\textbf{Refinement}

Refinement on $F^2$  
Least-squares matrix: full  
$R[F^2 > 2\sigma(F^2)] = 0.015$  
w$R(F^2) = 0.038$  
$S = 1.08$  
5820 reflections  
316 parameters  
0 restraints  
Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained  
$w = 1/[\sigma^2(F_o^2) + 0.7798P]$  
where $P = (F_o^2 + 2F_c^2)/3$  
$\Delta\rho_{\text{max}} = 0.46 \text{ e Å}^{-3}$  
$\Delta\rho_{\text{min}} = -0.60 \text{ e Å}^{-3}$

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Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The reflection data of \textit{fac-}[\textit{Re(Trop)(PPh$_3$)}(CO)$_3$] and \textit{fac-}[\textit{Re(TropBr$_3$)(PPh$_3$)}(CO)$_3$] were collected at 100 (2) K on a Bruker D8 Quest Eco Chi Photon II CPAD diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and at 104 (2) K on a Bruker D8 Venture 4K Kappa Photon III C28 diffractometer also using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), respectively. The unit-cell parameters were refined by \textit{SAINT-Plus} (Bruker, 2012), while \textit{SADABS} (Bruker, 2012) was used for absorption corrections. The structures were solved by direct methods and refined on $F^2$ using anisotropic displacement parameters for all non-H atoms. \textit{SHELXL97} (Sheldrick, 1997, 2008) and \textit{WinGX} (Farrugia, 2012) were used for structure solutions and refinements, respectively. The molecular graphics were prepared with \textit{DIAMOND} (Brandenburg & Putz, 2019).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)

| Atom | x   | y   | z   | $U_{iso}$/$U_{eq}$ |
|------|-----|-----|-----|-------------------|
| Re1  | 0.90667 (2) | 0.18057 (2) | 0.20344 (2) | 0.01253 (3) |
| P1   | 0.75009 (5)  | 0.32233 (5)  | 0.33175 (4) | 0.01302 (9)  |
| O12  | 0.72021 (14) | 0.08360 (13) | 0.20023 (11) | 0.0173 (3) |
| O11  | 0.84257 (15) | 0.29691 (14) | 0.07383 (11) | 0.0185 (3) |
| O2   | 0.95372 (19) | −0.00475 (16) | 0.40161 (13) | 0.0331 (4) |
| O3   | 1.11659 (16) | 0.00229 (16) | 0.05887 (13) | 0.0266 (3) |
| C2   | 0.9374 (2)  | 0.0666 (2)  | 0.32747 (17) | 0.2014 (4) |
| O1   | 1.2871 (16) | 0.2912 (2)  | 0.2058 (16) | 0.0173 (3) |
| C3   | 1.0415 (2)  | 0.0959 (2)  | 0.0710 (16) | 0.0182 (4) |
| C1   | 1.0657 (2)  | 0.2090 (2)  | 0.18974 (16) | 0.0185 (4) |
| C21  | 0.56224 (19) | 0.28800 (18) | 0.35765 (15) | 0.0149 (3) |
| C11  | 0.6555 (2)  | 0.1414 (2)  | 0.13322 (16) | 0.0187 (4) |
| C22  | 0.4701 (2)  | 0.3853 (2)  | 0.33403 (16) | 0.0196 (4) |
| H22  | 0.503393   | 0.474971   | 0.307256   | 0.024* |
| C41  | 0.77452 (19) | 0.50141 (18) | 0.28609 (15) | 0.0152 (3) |
| C46  | 0.8520 (2)  | 0.5519 (2)  | 0.17672 (17) | 0.0221 (4) |
| H46  | 0.893136   | 0.492594   | 0.125721   | 0.027* |
| C23  | 0.3293 (2)  | 0.3515 (2)  | 0.34958 (18) | 0.0250 (4) |
| H23  | 0.266556   | 0.418322   | 0.334279   | 0.030* |
| C31  | 0.7728 (2)  | 0.30410 (18) | 0.46994 (15) | 0.0159 (3) |
| C24  | 0.2805 (2)  | 0.2210 (2)  | 0.38720 (17) | 0.0242 (4) |
| H24  | 0.184097   | 0.198099   | 0.396922   | 0.029* |
| C26  | 0.5115 (2)  | 0.15676 (19) | 0.39609 (15) | 0.0180 (4) |
| H26  | 0.573467   | 0.089675   | 0.412313   | 0.022* |
| C25  | 0.3717 (2)  | 0.1234 (2)  | 0.41080 (17) | 0.0211 (4) |
| H25  | 0.338152   | 0.033770   | 0.437030   | 0.025* |
| C44  | 0.8087 (2)  | 0.7755 (2)  | 0.21524 (19) | 0.0251 (4) |
| H44  | 0.818632   | 0.868908   | 0.190649   | 0.030* |
| C15  | 0.4437 (3)  | 0.2377 (3)  | −0.0044 (2) | 0.0457 (7) |
| H15  | 0.367881   | 0.248628   | −0.035242  | 0.055* |
| C43  | 0.7332 (2)  | 0.7260 (2)  | 0.32494 (18) | 0.0229 (4) |
### Atomic displacement parameters (Å²)

| Atom | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|------|-----|-----|-----|-----|-----|-----|
| Re1  | 0.01235 (4) | 0.01212 (4) | 0.01298 (4) | 0.00146 (3) | −0.00321 (3) | −0.00325 (3) |
| P1   | 0.0130 (2) | 0.0131 (2) | 0.0120 (2) | 0.00118 (16) | −0.00242 (17) | −0.00256 (16) |
| O12  | 0.0152 (6) | 0.0153 (6) | 0.0218 (7) | 0.00003 (5) | −0.0050 (5) | −0.0055 (5) |
| O11  | 0.0215 (7) | 0.0217 (7) | 0.0165 (6) | 0.00116 (5) | −0.0067 (5) | −0.0019 (5) |
| O2   | 0.0441 (10) | 0.0296 (9) | 0.0276 (8) | 0.0072 (7) | −0.0174 (7) | 0.0020 (6) |
| C2   | 0.0206 (7) | 0.0297 (8) | 0.0321 (8) | 0.0082 (6) | −0.0063 (6) | −0.0176 (7) |
| C10  | 0.0219 (9) | 0.0188 (9) | 0.0227 (10) | 0.0024 (7) | −0.0059 (8) | −0.0058 (7) |
| C11  | 0.0219 (7) | 0.0300 (8) | 0.0325 (8) | −0.0079 (6) | −0.0079 (6) | −0.0050 (6) |
| C3   | 0.0185 (9) | 0.0177 (9) | 0.0203 (9) | −0.0001 (7) | −0.0076 (7) | −0.0050 (7) |
| C1   | 0.0191 (9) | 0.0189 (9) | 0.0165 (9) | 0.0026 (7) | −0.0033 (7) | −0.0047 (7) |
| C21  | 0.0143 (8) | 0.0173 (9) | 0.0130 (8) | 0.0012 (7) | −0.0032 (7) | −0.0039 (6) |
| C11  | 0.0202 (9) | 0.0240 (10) | 0.0175 (9) | 0.0082 (8) | −0.0073 (7) | −0.0111 (7) |
| C12  | 0.0174 (9) | 0.0215 (9) | 0.0204 (9) | 0.0061 (7) | −0.0061 (7) | −0.0129 (7) |
| C22  | 0.0205 (9) | 0.0180 (9) | 0.0222 (9) | 0.0013 (7) | −0.0085 (8) | −0.0047 (7) |
| C1   | 0.0148 (8) | 0.0125 (8) | 0.0184 (9) | 0.0003 (6) | −0.0052 (7) | −0.0029 (6) |
| C46  | 0.0266 (10) | 0.0167 (9) | 0.0206 (9) | 0.0046 (8) | −0.0028 (8) | −0.0053 (7) |
| C23  | 0.0200 (10) | 0.0263 (11) | 0.0328 (11) | 0.0062 (8) | −0.0131 (9) | −0.0077 (8) |
| C31  | 0.0186 (9) | 0.0154 (8) | 0.0142 (8) | 0.0036 (7) | −0.0054 (7) | −0.0035 (6) |
| C24  | 0.0154 (9) | 0.0322 (11) | 0.0264 (10) | −0.0004 (8) | −0.0068 (8) | −0.0080 (8) |
| C26  | 0.0179 (9) | 0.0195 (9) | 0.0152 (8) | 0.0012 (7) | −0.0035 (7) | −0.0020 (7) |
| C25  | 0.0203 (10) | 0.0220 (10) | 0.0194 (9) | −0.0035 (8) | −0.0040 (8) | −0.0026 (7) |
C44 0.0259 (10) 0.0128 (9) 0.0342 (11) −0.0003 (8) −0.0062 (9) −0.0031 (8)
C15 0.0330 (13) 0.079 (2) 0.0416 (15) 0.0235 (14) −0.0252 (12) −0.0320 (15)
C43 0.0214 (9) 0.0176 (9) 0.0306 (11) 0.0029 (7) −0.0055 (8) −0.0120 (8)
C45 0.0325 (11) 0.0169 (10) 0.0235 (10) 0.0014 (8) 0.0032 (9) 0.0015 (8)
C42 0.0206 (9) 0.0186 (9) 0.0185 (9) 0.0017 (7) −0.0062 (9) −0.0031 (8)
C13 0.0203 (10) 0.0375 (13) 0.0336 (12) −0.0001 (9) −0.0076 (9) −0.0182 (10)
C32 0.0186 (9) 0.0343 (12) 0.0212 (10) 0.0051 (8) −0.0066 (8) −0.0080 (8)
C34 0.0470 (14) 0.0296 (12) 0.0222 (10) 0.0077 (10) −0.0191 (10) −0.0069 (8)
C36 0.0243 (10) 0.0240 (10) 0.0175 (9) −0.0036 (8) −0.0029 (8) −0.0045 (7)
C35 0.0425 (13) 0.0304 (12) 0.0143 (9) −0.0047 (10) −0.0055 (9) −0.0019 (8)
C14 0.0220 (11) 0.0669 (19) 0.0447 (15) 0.0060 (11) −0.0151 (11) −0.0310 (13)
C17 0.0371 (12) 0.0344 (12) 0.0222 (10) 0.0126 (10) −0.0142 (9) −0.0078 (9)
C33 0.0277 (11) 0.0392 (13) 0.0299 (11) 0.0082 (9) −0.0163 (9) −0.0127 (9)
C16 0.0462 (15) 0.0579 (17) 0.0298 (12) 0.0290 (13) −0.0248 (11) −0.0200 (11)

Geometric parameters (Å, º)

| Bond                               | Distance (Å) | Angle (º) |
|------------------------------------|--------------|-----------|
| Re1—C1                             | 1.900 (2)    | C24—H24  | 0.9500 |
| Re1—C2                             | 1.912 (2)    | C26—C25  | 1.384 (3) |
| Re1—C3                             | 1.944 (2)    | C26—H26  | 0.9500 |
| Re1—O12                            | 2.1322 (13)  | C25—H25  | 0.9500 |
| Re1—O11                            | 2.1345 (13)  | C44—C45  | 1.383 (3) |
| Re1—P1                             | 2.4987 (5)   | C44—C43  | 1.387 (3) |
| P1—C41                             | 1.8203 (19)  | C44—H44  | 0.9500 |
| P1—C21                             | 1.8224 (19)  | C15—C14  | 1.379 (4) |
| P1—C31                             | 1.8305 (18)  | C15—C16  | 1.380 (4) |
| O12—C12                            | 1.288 (2)    | C15—H15  | 0.9500 |
| O11—C11                            | 1.293 (2)    | C43—C42  | 1.386 (3) |
| O2—C2                              | 1.151 (3)    | C43—H43  | 0.9500 |
| O3—C3                              | 1.148 (2)    | C45—H45  | 0.9500 |
| O1—C1                              | 1.159 (2)    | C42—H42  | 0.9500 |
| C21—C22                            | 1.395 (3)    | C13—C14  | 1.386 (3) |
| C21—C26                            | 1.395 (3)    | C13—H13  | 0.9500 |
| C11—C17                            | 1.403 (3)    | C32—C33  | 1.388 (3) |
| C11—C12                            | 1.459 (3)    | C32—H32  | 0.9500 |
| C12—C13                            | 1.404 (3)    | C34—C35  | 1.375 (3) |
| C22—C23                            | 1.393 (3)    | C34—C33  | 1.388 (3) |
| C22—H22                            | 0.9500       | C34—H34  | 0.9500 |
| C41—C46                            | 1.391 (3)    | C36—C35  | 1.394 (3) |
| C41—C42                            | 1.397 (3)    | C36—H36  | 0.9500 |
| C46—C45                            | 1.389 (3)    | C35—H35  | 0.9500 |
| C46—H46                            | 0.9500       | C14—H14  | 0.9500 |
| C23—C24                            | 1.382 (3)    | C17—C16  | 1.390 (3) |
| C23—H23                            | 0.9500       | C17—H17  | 0.9500 |
| C31—C32                            | 1.392 (3)    | C33—H33  | 0.9500 |
| C31—C36                            | 1.394 (3)    | C16—H16  | 0.9500 |
| C24—C25                            | 1.390 (3)    |           |         |
| Bond/Unit         | Distance (Å) | Angle  (°) |
|------------------|--------------|-----------|
| C1—Re1—C2       | 90.76 (8)    |           |
| C1—Re1—C3       | 88.64 (8)    |           |
| C2—Re1—C3       | 87.11 (8)    |           |
| C1—Re1—O12      | 170.57 (7)   |           |
| C2—Re1—O12      | 98.46 (7)    |           |
| C3—Re1—O12      | 93.75 (7)    |           |
| C1—Re1—O11      | 96.70 (7)    |           |
| C2—Re1—O11      | 171.97 (7)   |           |
| C3—Re1—O11      | 96.00 (7)    |           |
| O12—Re1—O11     | 73.99 (5)    |           |
| C1—Re1—P1       | 89.87 (6)    |           |
| C2—Re1—P1       | 90.48 (6)    |           |
| C3—Re1—P1       | 177.15 (6)   |           |
| O12—Re1—P1      | 88.10 (4)    |           |
| O11—Re1—P1      | 86.59 (4)    |           |
| C41—P1—C21      | 105.23 (8)   |           |
| C41—P1—C31      | 101.97 (8)   |           |
| C21—P1—C31      | 105.15 (8)   |           |
| C41—P1—Rel      | 115.75 (6)   |           |
| C21—P1—Rel      | 112.81 (6)   |           |
| C31—P1—Rel      | 114.69 (6)   |           |
| C12—O12—Rel     | 117.43 (12)  |           |
| C11—O11—Rel     | 117.33 (12)  |           |
| O2—C2—Rel       | 178.07 (18)  |           |
| O3—C3—Rel       | 173.87 (17)  |           |
| C1—C1—Rel       | 176.74 (18)  |           |
| C22—C21—C26     | 119.03 (17)  |           |
| C22—C21—P1      | 122.77 (14)  |           |
| C26—C21—P1      | 118.07 (14)  |           |
| O11—C11—C17     | 118.1 (2)    |           |
| O11—C11—C12     | 115.25 (17)  |           |
| C17—C11—C12     | 126.62 (19)  |           |
| O12—C12—C13     | 118.46 (19)  |           |
| O12—C12—C11     | 115.62 (16)  |           |
| C13—C12—C11     | 125.92 (19)  |           |
| C23—C22—C21     | 120.16 (18)  |           |
| C23—C22—H22     | 119.9        |           |
| C21—C22—H22     | 119.9        |           |
| C46—C41—C42     | 119.24 (17)  |           |
| C46—C41—P1      | 120.36 (14)  |           |
| C42—C41—P1      | 120.40 (14)  |           |
| C45—C46—C41     | 120.27 (18)  |           |
| C45—C46—H46     | 119.9        |           |
| C41—C46—H46     | 119.9        |           |
| C24—C23—C22     | 120.24 (19)  |           |
| C24—C23—H23     | 119.9        |           |
| C22—C23—H23     | 119.9        |           |
| C32—C31—C36     | 118.81 (18)  |           |
C32—C31—P1 117.76 (15) C15—C16—H16 115.0  
C36—C31—P1 123.42 (15) C17—C16—H16 115.0  
C23—C24—C25 119.95 (18)  

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| C17—H17···O1i | 0.95 | 2.54 | 3.471 (3) | 166 |
| C44—H44···O12ii | 0.95 | 2.38 | 3.227 (2) | 149 |
| C45—H45···O11i | 0.95 | 2.49 | 3.286 (3) | 142 |
| C46—H46···O11 | 0.95 | 2.31 | 3.102 (2) | 141 |

Symmetry codes: (i) −x+2, −y+1, −z; (ii) x, y+1, z.

fac-Tricarbonyl(3,5,7-tribromotropolonato-κ²O,O’)(triphenylphosphate-κP)rhenium(I) (2)

Crystal data

[Re(C7H2Br3O2)(C18H15P)(CO)3]

Z = 2  
F(000) = 840  
Dc = 2.138 Mg m−3  
Mo Kα radiation, λ = 0.71073 Å  
Cell parameters from 9973 reflections  
θ = 2.6–28.3°  
µ = 8.82 mm−1  
T = 104 K  
V = 1383.3 (3) Å³  

Data collection

Bruker APEXII CCD  
diffractometer  
5913 reflections with I > 2σ(I)  
5918 independent reflections  
6818 measured reflections  

Refinement

Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.029  
wR(F²) = 0.062  
S = 1.06  
6818 reflections  
343 parameters  
0 restraints  

Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained  
w = 1/[σ²(Fo²) + 2.6793P]  
where P = (Fo² + 2Fe²)/3  
(Δ/σ)max = 0.001  
Δρmax = 0.93 e Å⁻³  
Δρmin = −1.48 e Å⁻³  

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x         | y         | z         | Uiso*/Ueq |
|---|-----------|-----------|-----------|-----------|
| Re1 | 0.34371 (2) | 0.51462 (2) | 0.23619 (2) | 0.01495 (5) |
| Br1 | 0.20138 (5) | 0.09101 (5) | 0.37277 (2) | 0.02757 (11) |
| Br3 | 0.84257 (5) | 0.83501 (6) | 0.41990 (2) | 0.02938 (11) |
| Br2 | 0.78047 (5) | 0.33967 (6) | 0.54936 (2) | 0.03099 (11) |
| P1  | 0.54024 (11) | 0.39220 (13) | 0.18066 (5) | 0.0151 (2) |
| O12 | 0.3101 (3) | 0.3526 (3) | 0.30298 (14) | 0.0173 (6) |
| O11 | 0.5457 (3) | 0.6347 (3) | 0.32020 (13) | 0.0168 (6) |
| O1  | 0.4042 (4) | 0.7481 (4) | 0.14031 (15) | 0.0252 (7) |
| O2  | 0.0536 (3) | 0.2717 (4) | 0.12850 (16) | 0.0286 (7) |
| O3  | 0.1118 (4) | 0.6938 (4) | 0.29969 (16) | 0.0263 (7) |
| C1  | 0.3838 (4) | 0.6630 (5) | 0.1768 (2) | 0.0166 (8) |
| C31 | 0.7272 (4) | 0.5482 (5) | 0.1641 (2) | 0.0177 (8) |
| C12 | 0.4222 (5) | 0.3904 (5) | 0.3542 (2) | 0.0171 (8) |
| C16 | 0.7463 (5) | 0.5456 (5) | 0.4653 (2) | 0.0207 (9) |
| H16 | 0.850648 | 0.611307 | 0.493127 | 0.025* |
| C13 | 0.4042 (5) | 0.2776 (5) | 0.3969 (2) | 0.0192 (8) |
| C11 | 0.5588 (4) | 0.5511 (5) | 0.36368 (19) | 0.0155 (7) |
| C14 | 0.5107 (5) | 0.2750 (5) | 0.4502 (2) | 0.0207 (8) |
| H14 | 0.473096 | 0.180912 | 0.469142 | 0.025* |
| C2  | 0.1619 (5) | 0.3673 (5) | 0.1684 (2) | 0.0196 (8) |
| C15 | 0.6653 (5) | 0.3928 (6) | 0.4791 (2) | 0.0216 (9) |
| C36 | 0.7773 (5) | 0.7145 (5) | 0.1999 (2) | 0.0195 (8) |
| H36 | 0.713497 | 0.747856 | 0.232854 | 0.023* |
| C3  | 0.1976 (5) | 0.6252 (5) | 0.2784 (2) | 0.0195 (8) |
| C41 | 0.6223 (5) | 0.2739 (5) | 0.22865 (19) | 0.0164 (8) |
| C17 | 0.6966 (5) | 0.6162 (5) | 0.4167 (2) | 0.0188 (8) |
| C21 | 0.4454 (5) | 0.2534 (5) | 0.0969 (2) | 0.0182 (8) |
| C35 | 0.9204 (5) | 0.8337 (6) | 0.1882 (2) | 0.0248 (9) |
| H35 | 0.953631 | 0.948010 | 0.212415 | 0.030* |
| C33 | 0.9654 (5) | 0.6163 (6) | 0.1050 (2) | 0.0271 (10) |
| H33 | 1.030558 | 0.582921 | 0.072702 | 0.033* |
| C32 | 0.8217 (5) | 0.4985 (5) | 0.1167 (2) | 0.0212 (8) |
| H32 | 0.788150 | 0.384355 | 0.092208 | 0.025* |
| C42 | 0.5127 (5) | 0.1357 (5) | 0.2467 (2) | 0.0209 (8) |
| H42 | 0.395756 | 0.099066 | 0.231562 | 0.025* |
| C34 | 1.0131 (5) | 0.7830 (6) | 0.1408 (2) | 0.0252 (10) |
| H34 | 1.110932 | 0.863403 | 0.132541 | 0.030* |
| C26 | 0.3990 (5) | 0.0804 (5) | 0.0832 (2) | 0.0254 (9) |
| H26 | 0.427315 | 0.029290 | 0.116835 | 0.031* |
| C22 | 0.4046 (5) | 0.3266 (5) | 0.0467 (2) | 0.0231 (9) |
| H22 | 0.435001 | 0.445147 | 0.055876 | 0.028* |
| C45 | 0.8523 (6) | 0.2426 (7) | 0.2927 (3) | 0.0348 (11) |
| H45 | 0.968798 | 0.279725 | 0.308745 | 0.042* |
| C43 | 0.5751 (6) | 0.0525 (5) | 0.2867 (2) | 0.0261 (9) |
| H43 | 0.500071 | −0.042640 | 0.298282 | 0.031* |
| Atomic displacement parameters (Å²) | U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|-----------------------------------|----|----|----|----|----|----|
| Re1                              | 0.01419 (7) | 0.01332 (8) | 0.01797 (8) | 0.00483 (5) | 0.00064 (5) | 0.00571 (6) |
| Br1                              | 0.00246 (2) | 0.00223 (2) | 0.00326 (2) | −0.00051 (16) | 0.00127 (17) | 0.01517 (19) |
| Br3                              | 0.00263 (2) | 0.00235 (2) | 0.00297 (2) | −0.00378 (17) | −0.00761 (17) | 0.01230 (19) |
| Br2                              | 0.00310 (2) | 0.00401 (3) | 0.00291 (2) | 0.01602 (19) | 0.00000 (18) | 0.0194 (2) |
| P1                               | 0.00150 (4) | 0.00134 (5) | 0.00177 (5) | 0.00494 (4) | 0.0009 (4) | 0.0062 (4) |
| O12                              | 0.00146 (12) | 0.00169 (14) | 0.00208 (14) | 0.00442 (10) | 0.0014 (10) | 0.0080 (12) |
| O11                              | 0.00169 (12) | 0.00159 (14) | 0.00154 (13) | 0.00228 (10) | −0.0015 (10) | 0.0047 (11) |
| O1                               | 0.00290 (15) | 0.00218 (16) | 0.00288 (16) | 0.0095 (12) | 0.0039 (12) | 0.0143 (14) |
| O2                               | 0.00214 (14) | 0.00255 (17) | 0.00299 (17) | 0.00535 (12) | −0.0087 (13) | −0.0036 (14) |
| O3                               | 0.00257 (15) | 0.00262 (17) | 0.00289 (17) | 0.00143 (13) | 0.0026 (13) | 0.0035 (14) |
| C1                               | 0.00159 (17) | 0.00114 (18) | 0.00194 (19) | 0.00505 (14) | −0.0008 (14) | −0.0020 (15) |
| C31                              | 0.00162 (17) | 0.0019 (2) | 0.00200 (19) | 0.00662 (15) | 0.0001 (15) | 0.0089 (16) |
| C12                              | 0.00185 (17) | 0.00178 (19) | 0.00171 (19) | 0.0072 (15) | 0.0048 (15) | 0.0071 (16) |
| C16                              | 0.00164 (17) | 0.0027 (2) | 0.00183 (19) | 0.00646 (16) | 0.0005 (15) | 0.0061 (17) |
| C13                              | 0.00172 (17) | 0.00157 (19) | 0.0025 (2) | 0.0033 (15) | 0.0046 (15) | 0.0084 (17) |
| C11                              | 0.00168 (17) | 0.00148 (19) | 0.00174 (18) | 0.0076 (14) | 0.0043 (14) | 0.0055 (15) |
| C14                              | 0.0027 (2) | 0.0019 (2) | 0.0021 (2) | 0.00117 (16) | 0.0075 (16) | 0.0091 (17) |
| C2                               | 0.00187 (18) | 0.0019 (2) | 0.0026 (2) | 0.00107 (15) | 0.0068 (16) | 0.0082 (17) |
| C15                              | 0.00244 (19) | 0.0029 (2) | 0.0018 (2) | 0.00148 (17) | 0.0027 (16) | 0.0107 (18) |
| C36                              | 0.00175 (18) | 0.0020 (2) | 0.0023 (2) | 0.0069 (15) | 0.0027 (15) | 0.0081 (17) |
| C3                               | 0.00177 (18) | 0.00146 (19) | 0.0021 (2) | 0.0005 (15) | −0.0049 (15) | 0.0050 (16) |
| C41                              | 0.00205 (18) | 0.00139 (18) | 0.00164 (18) | 0.0080 (14) | 0.0016 (15) | 0.0047 (15) |
| C17                              | 0.00175 (17) | 0.0020 (2) | 0.00189 (19) | 0.0042 (15) | 0.0043 (15) | 0.0084 (16) |
| C21                              | 0.00196 (18) | 0.00157 (19) | 0.00176 (19) | 0.0059 (15) | 0.0022 (15) | 0.0015 (16) |
| C35                              | 0.00216 (19) | 0.0020 (2) | 0.0028 (2) | 0.0008 (16) | −0.0025 (17) | 0.0091 (18) |
| C33                              | 0.0023 (2) | 0.0033 (3) | 0.0028 (2) | 0.0016 (18) | 0.0082 (17) | 0.011 (2) |
| C32                              | 0.00190 (18) | 0.0021 (2) | 0.0026 (2) | 0.0090 (15) | 0.0033 (16) | 0.0075 (18) |
| C42                              | 0.0025 (2) | 0.0017 (2) | 0.0020 (2) | 0.0060 (16) | 0.0034 (16) | 0.0052 (16) |
| C34                              | 0.00167 (18) | 0.0027 (2) | 0.0033 (2) | 0.0028 (16) | 0.0049 (17) | 0.016 (2) |
| C26                              | 0.0032 (2) | 0.0016 (2) | 0.0023 (2) | 0.0014 (17) | 0.0023 (17) | 0.0064 (17) |
| C22                              | 0.0026 (2) | 0.0018 (2) | 0.0023 (2) | 0.0070 (16) | −0.0014 (17) | 0.0052 (17) |
| C45                              | 0.0027 (2) | 0.0042 (3) | 0.0043 (3) | 0.0018 (2) | 0.001 (2) | 0.018 (2) |
| C43                              | 0.0037 (2) | 0.0017 (2) | 0.0027 (2) | 0.0014 (18) | 0.0091 (19) | 0.0071 (18) |
| C23                              | 0.0029 (2) | 0.0037 (3) | 0.0020 (2) | 0.0013 (2) | −0.0032 (17) | 0.007 (2) |
| Atom | Uxx  | Uyy  | Uzz  | Uxy  | Uxz  | Uyz  |
|------|------|------|------|------|------|------|
| C24  | 0.030 (2) | 0.036 (3) | 0.023 (2) | -0.003 (2) | -0.0041 (18) | 0.002 (2) |
| C46  | 0.0215 (19) | 0.028 (2) | 0.030 (2) | 0.0097 (17) | 0.0002 (17) | 0.0144 (19) |
| C44  | 0.040 (2) | 0.034 (3) | 0.030 (2) | 0.024 (2) | 0.003 (2) | 0.017 (2) |
| C25  | 0.049 (3) | 0.018 (2) | 0.032 (3) | 0.001 (2) | 0.007 (2) | 0.004 (2) |

**Geometric parameters (Å, °)**

| Bond/Distance | Value   |
|---------------|---------|
| Re1—C2       | 1.903 (4) |
| Re1—C1       | 1.917 (4) |
| Re1—C3       | 1.950 (5) |
| Re1—O12      | 2.127 (3) |
| Re1—O11      | 2.159 (2) |
| Re1—P1       | 2.4799 (11) |
| Br1—C13      | 1.893 (4) |
| Br3—C17      | 1.889 (4) |
| Br2—C15      | 1.902 (4) |
| P1—C41       | 1.820 (4) |
| P1—C21       | 1.824 (4) |
| P1—C31       | 1.831 (4) |
| O12—C12      | 1.276 (4) |
| O11—C11      | 1.280 (4) |
| O1—C1        | 1.139 (5) |
| O2—C2        | 1.148 (5) |
| O3—C3        | 1.140 (5) |
| C31—C36      | 1.384 (6) |
| C31—C32      | 1.390 (6) |
| C12—C13      | 1.423 (5) |
| C12—C11      | 1.464 (5) |
| C16—C15      | 1.381 (6) |
| C16—C17      | 1.383 (5) |
| C13—C14      | 1.376 (5) |
| C11—C17      | 1.415 (5) |
| C14—C15      | 1.377 (6) |
| C14—H14      | 0.9500  |
| C36—C35      | 1.393 (5) |
| C36—H36      | 0.9500  |

| Bond/Angle   | Value   |
|---------------|---------|
| C2—Re1—C1    | 86.27 (16) |
| C2—Re1—C3    | 90.47 (17) |
| C1—Re1—C3    | 88.72 (17) |
| C2—Re1—O12   | 95.53 (14) |
| C1—Re1—O12   | 177.62 (13) |
| C3—Re1—O12   | 92.81 (14) |
| C2—Re1—O11   | 167.93 (14) |
| C1—Re1—O11   | 105.04 (13) |
| C3—Re1—O11   | 93.90 (13) |
| O12—Re1—O11  | 73.05 (10) |
C2—Re1—P1 91.16 (13)  
C1—Re1—P1 87.84 (12)  
C3—Re1—P1 176.09 (11)  
O12—Re1—P1 90.57 (8)  
O11—Re1—P1 85.20 (8)  
C41—P1—C21 107.08 (19)  
C41—P1—C31 104.34 (17)  
C21—P1—C31 103.82 (18)  
C41—P1—Re1 114.79 (13)  
C21—P1—Re1 112.03 (14)  
C31—P1—Re1 113.84 (15)  
C12—O12—Re1 118.7 (2)  
C11—O11—Re1 117.4 (2)  
O1—C1—Re1 178.2 (3)  
C36—C31—C32 119.8 (4)  
C36—C31—P1 120.4 (3)  
C32—C31—P1 119.8 (3)  
O12—C12—C13 118.8 (3)  
O12—C12—C11 115.3 (3)  
C13—C12—C11 126.0 (3)  
C15—C16—C17 128.9 (4)  
C15—C16—H16 115.5  
C17—C16—H16 115.5  
C14—C13—C12 131.7 (3)  
C14—C13—Br1 114.4 (3)  
C12—C13—Br1 113.8 (3)  
O11—C11—C17 124.5 (3)  
O11—C11—C12 115.1 (3)  
C17—C11—C12 124.5 (3)  
C13—C14—C15 127.6 (4)  
C13—C14—H14 116.2  
C15—C14—H14 116.2  
O2—C2—Re1 176.5 (4)  
C14—C15—C16 129.0 (4)  
C14—C15—Br2 115.3 (3)  
C16—C15—Br2 115.7 (3)  
C31—C36—C35 120.8 (4)  
C31—C36—H36 119.6  
C35—C36—H36 119.6  
O3—C3—Re1 175.8 (3)  
C46—C41—C42 118.8 (4)

Hydrogen-bond geometry (Å, º)

| D—H····A       | D—H | H····A | D····A | D—H····A |
|---------------|------|--------|--------|---------|
| C24—H24····O2i | 0.95 | 2.58   | 3.390 (5) | 144 |
| C26—H26····O1i | 0.95 | 2.54   | 3.350 (5) | 143 |
| C36—H36····O11 | 0.95 | 2.52   | 3.299 (5) | 139 |

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C44—H44···Br3

|        |        |         |         |     |
|--------|--------|---------|---------|-----|
| C44—H44 | 0.95   | 2.88    | 3.819 (4) | 168 |
| C46—H46 | 0.95   | 2.58    | 3.354 (5) | 138 |

Symmetry codes: (i) −x, −y, −z; (ii) x, y−1, z; (iii) x+1, y, z.