Supplementary Information

Synthesis and characterization of propylene and butylene bridged \textit{fac}\textendash \textit{tri}carbonyl\textit{rhenium(\textit{i})} \textit{biscarbene complexes}

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Single Crystal X-Ray Structure Determinations of Compound 6a, 6c, 6d, 7a and 7d

**General:**

Crystallographic details for compounds 6c and 7a are summarised in Table S1. The data were collected on an X-ray diffractometer equipped with a CCD detector (APEX II, \(\kappa\)-CCD), a rotating anode (Bruker AXS, FR591) with MoK\(\alpha\) radiation (\(\lambda = 0.71073\ \text{Å}\)), and a graphite monochromator by using the SMART software package. [1] The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on the top of a glass fiber and transferred to the diffractometer. Crystals from 6c, 6d and 7d were frozen under a stream of cold nitrogen. 6c and 7a were measured at rt. A matrix scan using at least 20 centered reflections was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT 4.15. [2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS. [2] Space group assignments were based upon systematic absences, \(E\) statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX [7] based on SIR-92. [3] Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogen atoms). If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing \(\Sigma w(F_o^2-F_c^2)^2\) with SHELXL-97 [5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from \textit{International Tables for Crystallography}. [4] Images of the crystal structures were generated by PLATON [6].

Single Crystal X-Ray Structure Determination of Compound 6a
**Figure F1** – Ortep drawing of compound 6a with 50% ellipsoids. [6]

**Operator:** *** Herdtweck *** 

**Molecular Formula:** C$_{14}$ H$_{16}$ Br N$_4$ O$_3$ Re 

**Crystal Color / Shape:** Colorless plate 

**Crystal Size:** Approximate size of crystal fragment used for data collection: 0.05 × 0.10 × 0.13 mm 

**Molecular Weight:** 554.42 a.m.u. 

**F$_{000}$:** 1048 

**Space Group:** Monoclinic $P\bar{2}1$ (I.T.-No.: 14) 

**Cell Constants:** 
- $a = 885.04(3)$ pm 
- $b = 1563.50(4)$ pm 
- $c = 1252.68(4)$ pm 
- $\alpha = 90.065(3)^\circ$ 
- $\beta = 94.065(3)^\circ$ 
- $\gamma = 90.000(3)^\circ$ 
- $V = 1729.05(9) \times 10^6$ pm$^3$; $Z = 4$; $D_{calc} = 2.130$ g cm$^{-3}$; Mos. = 0.71 

**Diffractometer:** IPDS 2T; Imaging Plate Diffraction System (STOE & CIE.); rotating anode, graphite monochromator; 50 kV; 40 mA; $\lambda = 71.073$ pm; Mo(K$\alpha$) 

**Temperature:** (20±1) °C; (293±1) K 

**Measurement Range:** $3.77^\circ < \theta < 26.13^\circ$; h, -10/10, k: -18/18, l: -15/15 

**Measurement Time:** 60 s per frame 

**Measurement Mode:** Rotation/oscillation; dx = 80.0 mm 

- **Run1:** $\varphi = 0.0^\circ$; Start: $\omega = 0.0^\circ$; End: $\omega = 180.0^\circ$; Increment: $\Delta\omega = 1.0^\circ$ 
- **Run2:** $\varphi = 45.0^\circ$; Start: $\omega = 0.0^\circ$; End: $\omega = 180.0^\circ$; Increment: $\Delta\omega = 1.0^\circ$ 
- **Run3:** $\varphi = 90.0^\circ$; Start: $\omega = 0.0^\circ$; End: $\omega = 91.0^\circ$; Increment: $\Delta\omega = 1.0^\circ$ 

**LP - Correction:** Yes [2a] 

**Intensity Correction:** No 

**Absorption Corrections:** Mathematical absorption correction; DELABS [6]; $\mu = 9.357$ mm$^{-1}$ 

**Correction Factors:** $T_{\text{min}} = 0.160$; $T_{\text{max}} = 0.633$ 

**Reflection Data:** 26327 reflections were integrated 
- 609 reflections systematic absent and rejected 
- 25718 reflections to be merged
3223 independent reflections
0.073 $R_{int}$: (basis $F_o^2$)
3223 independent reflections (all) were used in refinements
2940 independent reflections with $I_o > 2\sigma(I_o)$
98.8 % completeness of the data set
210 parameter full-matrix refinement
15.3 reflections per parameter

Solution:
Direct Methods [3]; Difference Fourier syntheses

Refinement Parameters:
In the asymmetric unit:
23 Non-hydrogen atoms with anisotropic displacement parameters

Hydrogen Atoms:
In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions ($d_{C-H} = 93, 96, 97$ pm). Isotropic displacement parameters were calculated from the parent carbon atom ($U_H = 1.2/1.5 U_C$). The hydrogen atoms were included in the structure factor calculations but not refined.

Atomic Form Factors: For neutral atoms and anomalous dispersion [4]

Extinction Correction: no

Weighting Scheme:
$$w^{-1} = \sigma^2(F_o^2) + (a*P)^2 + b*P$$
with $a$: 0.0397; $b$: 2.5105; $P$: [Maximum(0 or $F_o^2$) + $2*F_c^2$]/3

Shift/Err:
Less than 0.001 in the last cycle of refinement:

Resid. Electron Density:
$+0.76 e_0^-/\AA^3; -0.89 e_0^-/\AA^3$

R1:
$$\frac{\sum[w(F_o^2 - F_c^2)]}{\sum[w(F_o^2)]} = 0.0293$$

$[F_o > 4\sigma(F_o)];$ N=2940;
[all reflcts; N=3223]: $= 0.0344$

wR2:
$$\frac{[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}}{\sum[w(F_o^2)]} = 0.0712$$

$[F_o > 4\sigma(F_o)];$ N=2940;
[all reflcts; N=3223]: $= 0.0737$

Goodness of fit:
$$\frac{[\sum[w(F_o^2 - F_c^2)^2]/(NO-NV)]^{1/2}}{\sum[w(F_o^2)]} = 1.082$$

Remarks:
Refinement expression $\sum[w(F_o^2 - F_c^2)^2$ "TWIN" [1a] integration

Single Crystal X-Ray Structure Determination of Compound 6d
Figure F2 – Ortep drawing of compound 6d with 50% ellipsoids. [6]

Operator: *** Herdtweck ***
Molecular Formula: C_{30} H_{32} Br N_{4} O_{3} Re
Crystal Color / Shape: Colourless fragment
Crystal Size: Approximate size of crystal fragment used for data collection: 0.13 × 0.36 × 0.43 mm
Molecular Weight: 762.71 a.m.u.
F_{000}: 748
Systematic Absences: none
Space Group: Triclinic P\textsuperscript{1} (I.T.-No.: 2)
Cell Constants: Least-squares refinement of 9477 reflections with the programs “APEX suite” and “SAINT” [1,2]; theta range 2.36° < \( \theta < 25.37\); Mo(K\textsubscript{a}). \( \lambda = 71.073 \) pm

\begin{align*}
a &= 821.15(4) \text{ pm} & \alpha &= 95.6508(17)^\circ \\
b &= 938.79(4) \text{ pm} & \beta &= 91.4818(17)^\circ \\
c &= 1978.63(8) \text{ pm} & \gamma &= 102.1270(18)^\circ \\
V &= 1482.32(11) \cdot 10^6 \text{ pm} \ ^3 & Z &= 2; D_{\text{calc}} = 1.709 \text{ g cm}^{-3}; \text{ Mos.} = 0.70
\end{align*}

Diffraetometer: Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; \( \lambda = 71.073 \) pm; Mo(K\textsubscript{a})
Temperature: (-100±1) °C; (173±1) K
Measurement Range: 2.36° < \( \theta < 25.37\); h: -9/9, k: -11/11, l: -23/23
Measurement Time: 2 × 5 s per film
Measurement Mode: measured: 7 runs; 3293 films / scaled: 7 runs; 3293 films
\( \phi \)- and \( \omega \)-movement; Increment: \( \Delta \phi \Delta \omega = 0.50^\circ \); dx = 35.0 mm
LP - Correction: Yes [2]
Intensity Correction: No/Yes; during scaling [2]
Absorption Correction: Multi-scan; during scaling; \( \mu = 5.483 \text{ mm}^{-1} \) [2]
Correction Factors: \( T_{\text{min}} = 0.4187 \) \( T_{\text{max}} = 0.7452 \)
Reflection Data: 52639 reflections were integrated and scaled
2 obvious wrong intensity and rejected
52637 reflections to be merged
5271 independent reflections
0.056 \( R_{\text{int}} \): (basis \( F_o^2 \))
5271 independent reflections (all) were used in refinements
5214 independent reflections with $I_o > 2\sigma(I_o)$
96.7% completeness of the data set
358 parameter full-matrix refinement
14.7 reflections per parameter

Solution: Direct Methods [3]; Difference Fourier syntheses

Refinement Parameters: In the asymmetric unit:
39 Non-hydrogen atoms with anisotropic displacement parameters

Hydrogen Atoms:
In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions (d_C-H = 95, 98, 99 pm). Isotropic displacement parameters were calculated from the parent carbon atom (U_H = 1.2/1.5 U_C). The hydrogen atoms were included in the structure factor calculations but not refined.

Atomic Form Factors: For neutral atoms and anomalous dispersion [4]

Extinction Correction: no

Weighting Scheme:
$$w^{-1} = \sigma^2(F_o^2)+a*P+b*P$$
with a: 0.0201; b: 4.1600; P: [Maximum(0 or $F_o^2$)+2*$F_c^2$]/3

Shift/Err:
Less than 0.002 in the last cycle of refinement:

Resid. Electron Density: +0.91 e_0/Å$^3$; -1.17 e_0/Å$^3$

R1:
$$\frac{\sum|F_o|-|F_c|}{\sum|F_o|} = 0.0221$$

wr2:
$$\frac{\sum w(F_o^2-F_c^2)^2}{\sum w(F_o^2)^2} = 0.0571$$

Goodness of fit:
$$\frac{\sum w(F_o^2-F_c^2)^2/(NO-NV)^{1/2}}{1.065}$$

Remarks:
Refinement expression $\sum w(F_o^2-F_c^2)$

Single Crystal X-Ray Structure Determination of Compound 7d

Figure F3 – Ortep drawing compound 7d with 50% ellipsoids. [6]

Operator: *** Herdtweck ***
Molecular Formula: \( \text{C}_{31} \text{H}_{34} \text{Br N}_{4} \text{O}_{3} \)

Crystal Color / Shape: Colorless column

Crystal Size: Approximate size of crystal fragment used for data collection:
\( 0.25 \times 0.30 \times 0.61 \, \text{mm} \)

Molecular Weight: 776.73 a.m.u.

\( F_{000} \): 3056

Systematic Absences: \( hkl: h+k=2n; \ h0l: l=2n \)

Space Group: Monoclinic \( C2/c \) (I.T.-No.: 15)

Cell Constants: Least-squares refinement of 9753 reflections with the programs “APEX suite” and “SAINT” [1,2]; theta range 1.67° < \( \theta < 25.41^\circ \); Mo(K\( \alpha \) \( \lambda = 71.073 \, \text{pm} \)); \( a = \ 1517.96(10) \, \text{pm} \)
\( b = \ 2232.92(14) \, \text{pm} \)
\( \beta = \ 106.295(3)^\circ \)
\( c = \ 1862.33(12) \, \text{pm} \)
\( V = 6058.8(7) \, \text{pm}^3 \); \( Z = 8 \); \( D_{\text{calc}} = 1.703 \, \text{g cm}^{-3} \); Mos. = 0.74

Diffractometer: Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; \( \lambda = 71.073 \, \text{pm} \); Mos. = 0.74

Temperature: \((-100\pm1) \, \text{°C}; \ (173\pm1) \, \text{K})\)

Measurement Range: \( 1.67° < \theta < 25.41^\circ \); \( h: -18/18 \), \( k: -26/26 \), \( l: -22/22 \)

Measurement Time: \( 2 \times 5 \, \text{s per film} \)

Measurement Mode: measured: 6 runs; 3743 films / scaled: 6 runs; 3743 films

\( \varphi - \) and \( \omega - \) movement; Increment: \( \Delta \varphi / \Delta \omega = 0.50^\circ \); \( dx = 35.0 \, \text{mm} \)

LP - Correction: Yes [2]

Intensity Correction No/Yes; during scaling [2]

Absorption Correction: Multi-scan; during scaling; \( \mu = 5.368 \, \text{mm}^{-1} \) [2]

Correction Factors: \( T_{\text{min}} = 0.1986 \quad T_{\text{max}} = 0.7452 \)

Reflection Data:
102421 reflections were integrated and scaled
1971 reflections systematic absent and rejected
100450 reflections to be merged
5558 independent reflections

5558 independent reflections (all) were used in refinements
99.4% completeness of the data set
367 parameter full-matrix refinement
15.1 reflections per parameter

Solution: Direct Methods [3]; Difference Fourier syntheses

Refinement Parameters: In the asymmetric unit:
40 Non-hydrogen atoms with anisotropic displacement parameters

Hydrogen Atoms: In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions \( d_{\text{C-H}} = 95, 98, 99 \, \text{pm} \). Isotropic displacement parameters were calculated from the parent carbon atom (\( U_{\text{H}} = 1.2/1.5 \, U_{\text{C}} \)). The hydrogen atoms were included in the structure factor calculations but not refined.

Atomic Form Factors: For neutral atoms and anomalous dispersion [4]

Extinction Correction: no

Weighting Scheme: \( w^{-1} = \sigma(F_o^2) + (a*P)^2 + b*P \)
with \( a: 0.0086 \); \( b: 199.6573 \); \( P: \text{[Maximum}(0 \ or \ F_o^2)+2*F_c^2)/3 \)

Shift/Err: Less than 0.001 in the last cycle of refinement:

Resid. Electron Density: +2.32 e^\text{\( \text{e}^3/\text{Å}^3 \)}; -1.53 e^\text{\( \text{e}^3/\text{Å}^3 \)}

R1:
\[ |F_o| > 4\sigma(F_o); \ N=5269 \]
\[ \text{all reflcts; N}=5558 \]
\[ wR2: \]
\[ [F_o > 4\sigma(F_o); \ N=5269 ]; \]
\[ [\text{all reflcts; N}=5558 ]; \]

Goodness of fit: \[ \Sigma (|F_o|^2 - |F_c|^2)^2 / (\Sigma |F_o|^2)^{1/2} \]

Remarks: Refinement expression \( \Sigma w(F_o^2 - F_c^2)^2 \)
References:


Remarks on the refinement of compounds 6c, and 7a:

The refinements were aborted due to a disorder of the bromine ligand and one CO ligand.

Figure F4 – Ortep drawing of compound 6c with 50% ellipsoids. [6]
Figure F5 – Ortep drawing of compound 7a with 50% ellipsoids. [6]
Table S1. Crystallographic details of compounds 6c, and 7a.

<table>
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<th>Compound Name</th>
<th>6c</th>
<th>7a</th>
</tr>
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<tbody>
<tr>
<td>Sum formula</td>
<td>C_{24}H_{32}BrN_{4}O_{3}Re</td>
<td>C_{15}H_{18}BrN_{4}O_{3}Re</td>
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<td>M_r (g/mol)</td>
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<td>Crystal description</td>
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<td>Colorless fragment</td>
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<td>293(2)</td>
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<td>b (Å)</td>
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<td>15.3216(8)</td>
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<td>11.2687(6)</td>
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<td>γ (°)</td>
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<td>90</td>
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<td>V (Å³)</td>
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<td>μ (mm⁻¹)</td>
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<td>±10, -15/16, ±11</td>
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<td>0.051</td>
</tr>
<tr>
<td>Unique reflections [I₀ 2 σ(I₀)]</td>
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<td>Remarks</td>
<td>Refinements aborted</td>
<td>Measurements and refinements aborted</td>
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