Supplementary Information

Synthesis and characterization of propylene and butylene bridged <it>fac</it>-tricarbonylrhenium(<scp>i</scp>) 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, κ–CCD), a rotating anode (Bruker AXS, FR591) with MoK_α radiation (λ = 0.71073 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 *International Tables for Crystallography*. [4] Images of the crystal structures were generated by PLATON [6].

Single Crystal X-Ray Structure Determination of Compound 6a

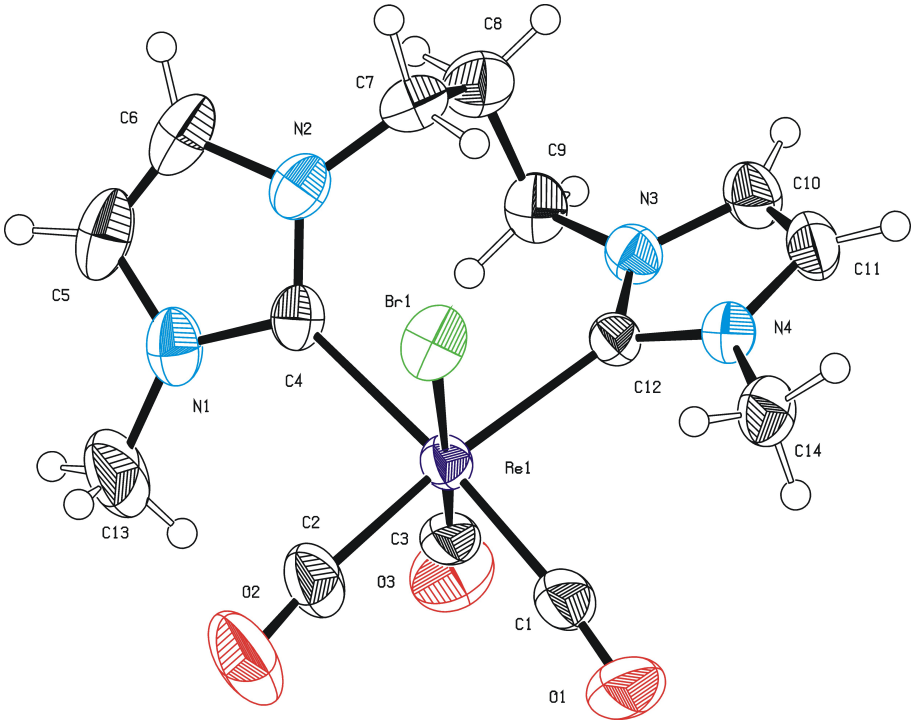

Figure F1 – Ortep drawing drawing of compound **6a** with 50% ellipsoids. [6]

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
Systematic Absences:	h0l: h+l≠2n; 0k0: k≠2n
Space Group:	Monoclinic $P\,2_1/n$ (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 30355 reflections with the program "X-AREA" [1a]; theta range 3.77° < θ < 26.13°; Mo(K $\overline{\alpha}$); λ = 71.073 pm a = 885.04(3) pm b = 1563.50(4) pm β = 94.065(3)° c = 1252.68(4) pm V = 1729.05(9)· 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; λ = 71.073 pm; Mo(K $\overline{\alpha}$)
Temperature:	(20±1) °C; (293±1) K
Measurement Range:	3.77° < θ < 25.63°; h: -10/10, k: -18/18, l: -15/15
Measurement Time:	60 s per frame
Measurement Mode:	Rotation/oscillation; dx = 80.0 mm Run1: φ = 0.0°; Start: ω = 0.0° End: ω = 180.0°; Increment: $\Delta\omega$ = 1.0° Run2: φ =45.0°; Start: ω = 0.0° End: ω = 180.0°; Increment: $\Delta\omega$ = 1.0° Run3: φ =90.0°;Start: ω = 0.0° End: ω = 91.0°; Increment: $\Delta\omega$ = 1.0°
LP - Correction:	Yes [2a]
Intensity Correction	No
Absorption Corrections:	Mathematical absorption correction; DELABS [6]; μ = 9.357 mm^{-1} Correction Factors: T_{min} = 0.160 T_{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 $e_{0;}^-$/Å^3; -0.89 $e_{0;}^-$/Å^3	
R1:	$\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$	
[$F_o > 4\sigma(F_o)$; N=2940]:		= 0.0293
[all reflctns; N=3223]:		= 0.0344
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$	
[$F_o > 4\sigma(F_o)$; N=2940]:		= 0.0712
[all reflctns; N=3223]:		= 0.0737
Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$	= 1.082
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)^2$ "TWIN" [1a] integration	

Single Crystal X-Ray Structure Determination of Compound 6d

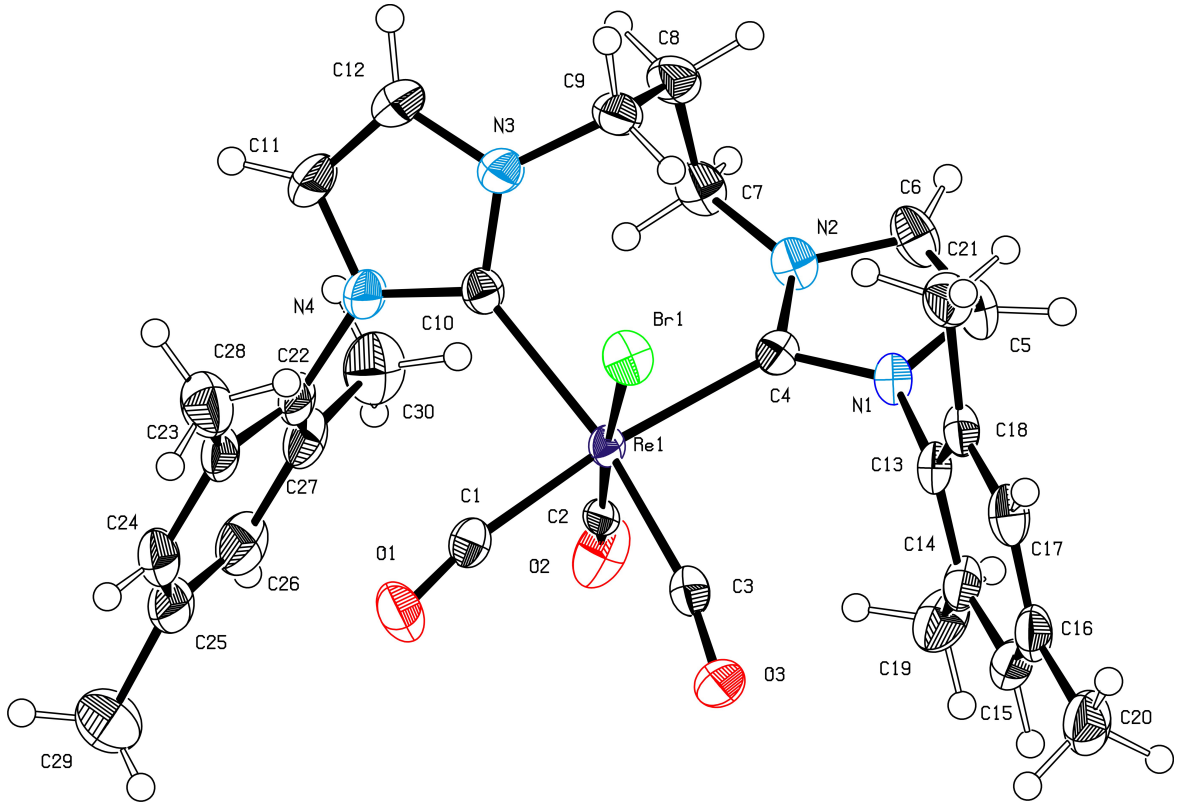

Figure F2 – Ortep drawing of compound **6d** with 50% ellipsoids. [6]

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 $P\bar{1}$ (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° < θ < 25.37°; Mo(K$\bar{\alpha}$); λ = 71.073 pm
	a = 821.15(4) pm α = 95.6508(17)°
	b = 938.79(4) pm β = 91.4818(17)°
	c = 1978.63(8) pm γ = 102.1270(18)°
	V = 1482.32(11)· 10^6 pm^3; Z = 2; D_{calc} = 1.709 g cm^{-3}; Mos. = 0.70
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; λ = 71.073 pm; Mo(K$\bar{\alpha}$)
Temperature:	(-100±1) °C; (173±1) K
Measurement Range:	2.36° < θ < 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
	φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 0.50°; dx = 35.0 mm
LP - Correction:	Yes [2]
Intensity Correction	No/Yes; during scaling [2]
Absorption Correction:	Multi-scan; during scaling; μ = 5.483 mm^{-1} [2]
	Correction Factors: T_{min} = 0.4187 T_{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_{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 ($d_{C\text{-}H}$ = 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:	$w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$	
	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:	$\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$	
[$F_o > 4\sigma(F_o)$; N=5214]:		= 0.0221
[all reflctns; N=5271]:		= 0.0223
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$	
[$F_o > 4\sigma(F_o)$; N=5214]:		= 0.0571
[all reflctns; N=5271]:		= 0.0573
Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$	= 1.065
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)^2$	

Single Crystal X-Ray Structure Determination of Compound 7d

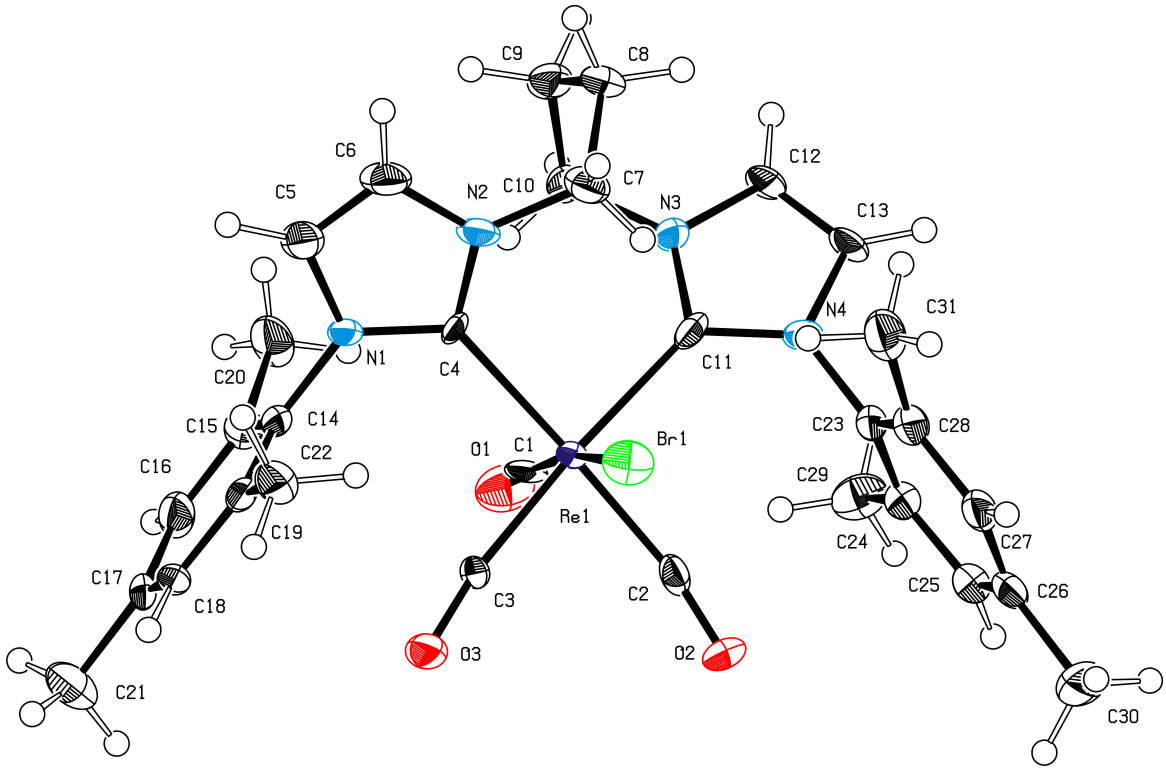

Figure F3 – Ortep drawing compound **7d** with 50% ellipsoids. [6]

Operator: *** Herdtweck ***

Molecular Formula:	C_{31} H_{34} Br N_4 O_3 Re
Crystal Color / Shape	Colorless column
Crystal Size	Approximate size of crystal fragment used for data collection: 0.25 × 0.30 × 0.61 mm
Molecular Weight:	776.73 a.m.u.
F_{000}:	3056
Systematic Absences:	hkl: h+k≠2n; h0l: l≠2n
Space Group:	Monoclinic *C* 2/*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° < θ < 25.41°; Mo(K $\overline{\alpha}$); λ = 71.073 pm *a* = 1517.96(10) pm *b* = 2232.92(14) pm β = 106.295(3)° *c* = 1862.33(12) pm *V* = 6058.8(7)· 10^6 pm^3; *Z* = 8; D_{calc} = 1.703 g cm^{-3}; Mos. = 0.74
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; λ = 71.073 pm; Mo(K $\overline{\alpha}$)
Temperature:	(-100±1) °C; (173±1) K
Measurement Range:	1.67° < θ < 25.41°; h: -18/18, k: -26/26, l: -22/22
Measurement Time:	2 × 5 s per film
Measurement Mode:	measured: 6 runs; 3743 films / scaled: 6 runs; 3743 films φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 0.50°; dx = 35.0 mm
LP - Correction:	Yes [2]
Intensity Correction	No/Yes; during scaling [2]
Absorption Correction:	Multi-scan; during scaling; μ = 5.368 mm^{-1} [2] Correction Factors: T_{min} = 0.1986 T_{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 0.072 R_{int}: (basis F_o^2) 5558 independent reflections (all) were used in refinements 5269 independent reflections with $I_o > 2\sigma(I_o)$ 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_{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:	$w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$ with a: 0.0086; b: 199.6573; 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:	+2.32 $e_{0;}^-$ /Å^3; -1.53 $e_{0;}^-$ /Å^3
R1:	$\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$
[$F_o > 4\sigma(F_o)$; N=5269]:	= 0.0433
[all reflctns; N=5558]:	= 0.0462
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$
[$F_o > 4\sigma(F_o)$; N=5269]:	= 0.0978
[all reflctns; N=5558]:	= 0.0996
Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$ = 1.117
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)^2$

References:

[1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[1a] Data Collection Software and Data Processing Software for Stoe IPDS 2T diffractometer, X-ARERA, Version 1.26, Stoe & Cie, Darmstadt, Germany, 2004.

[2] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[2a] Data Processing Software for Stoe IPDS 2T diffractometer, XRED, XSHAPE, Version 1.26, Stoe & Cie, Darmstadt, Germany, 2004.

[3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, Moliterni A. G. G.; A.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R. "**SIR97**", A New Tool for Crystal Structure Determination and Refinement; *J. Appl. Crystallogr.* **1999**, *32*, 115-119.

[4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.

[5] Sheldrick, G. M. "**SHELXL-97**", University of Göttingen, Göttingen, Germany, (1998).

[6] Spek, A. L. "**PLATON**", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2010).

[7] L. J. Farrugia, "**WinGX** (Version 1.70.01 January 2005) ", *J. Appl. Cryst.* **1999**, *32*, 837-838.

***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.

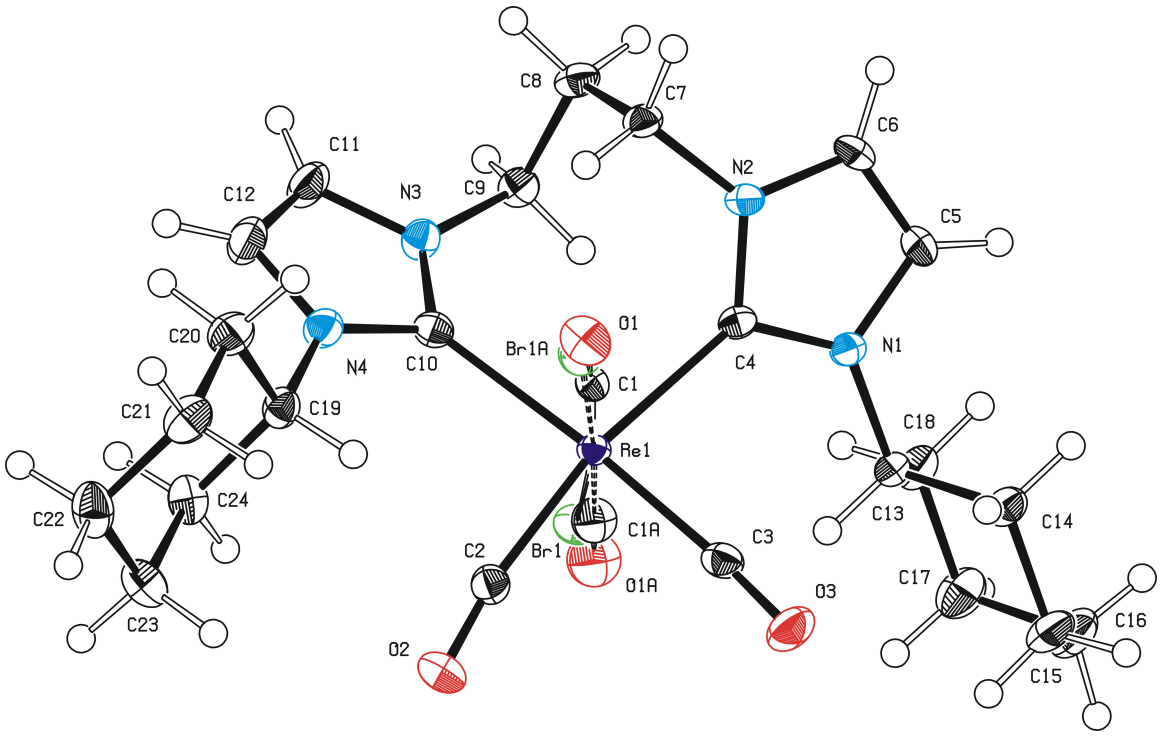

Figure F4 – Ortep drawing of compound **6c** with 50% ellipsoids. [6]

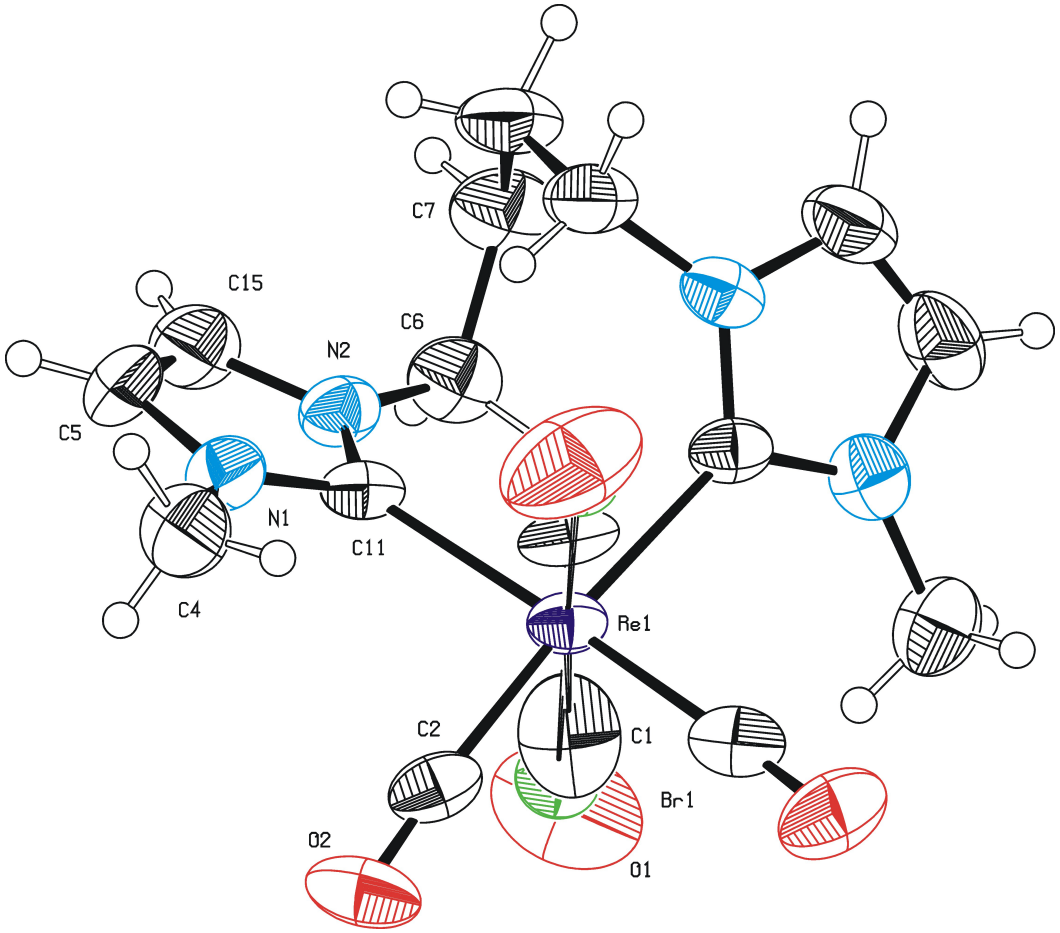

Figure F5 – Ortep drawing of compound **7a** with 50% ellipsoids. [6]

Table S1. Crystallographic details of compounds **6c**, and **7a**.

Compound Name	**6c**	**7a**
Sum formula	$C_{24}H_{32}BrN_4O_3Re$	$C_{15}H_{18}BrN_4O_3Re$
M_r (g/mol)	690.65	568.44
Crystal description	Colorless fragment	Colorless fragment
T (K)	123(1)	293(2)
crystal system, space group	Orthorhombic, *Pbca* (I.T.-No.: 61)	Monoclinic, *C*2/*c* (I.T.-No.: 15)
a (Å)	15.3641(5)	10.2853(5)
b (Å)	15.2250(5)	15.3216(8)
c (Å)	21.4626(6)	11.2687(6)
α(°)	90	90
β (°)	90	94.081(2)
γ(°)	90	90
V (Å^3)	5020.5(3)	1771.30(16)
Z	8	4
D_{calc} (g/cm^3)	1.827	2.132
F_{000}	2704	1080
μ (mm^{-1})	6.465	9.137
Index ranges (h,k,l)	±18, ±18, ±24	±10, -15/16, ±11
Θ-ranges (°)	1.90-25.31	2.39-22.01
Collected reflections	55582	13838
Unique reflections [all data]	4537	1084
R_{int}	0.051	0.051
Unique reflections [I_0 2 $\sigma(I_0)$]	4234	987
Data/Restraints/Parameter	4537/0/311	1084/0/124
GoF (on F^2)	1.152	1.144
R_1/wR_2 [I_0 2 $\sigma(I_0)$]	0.0178/0.0437	0.0381/0.0924
R_1/wR_2 [all data]	0.0202/0.0452	0.0446/0.0990
Max./Min. residual electron density	1.09/-0.66	1.69/-0.96
Remarks	Refinements aborted	Measurements and refinements aborted