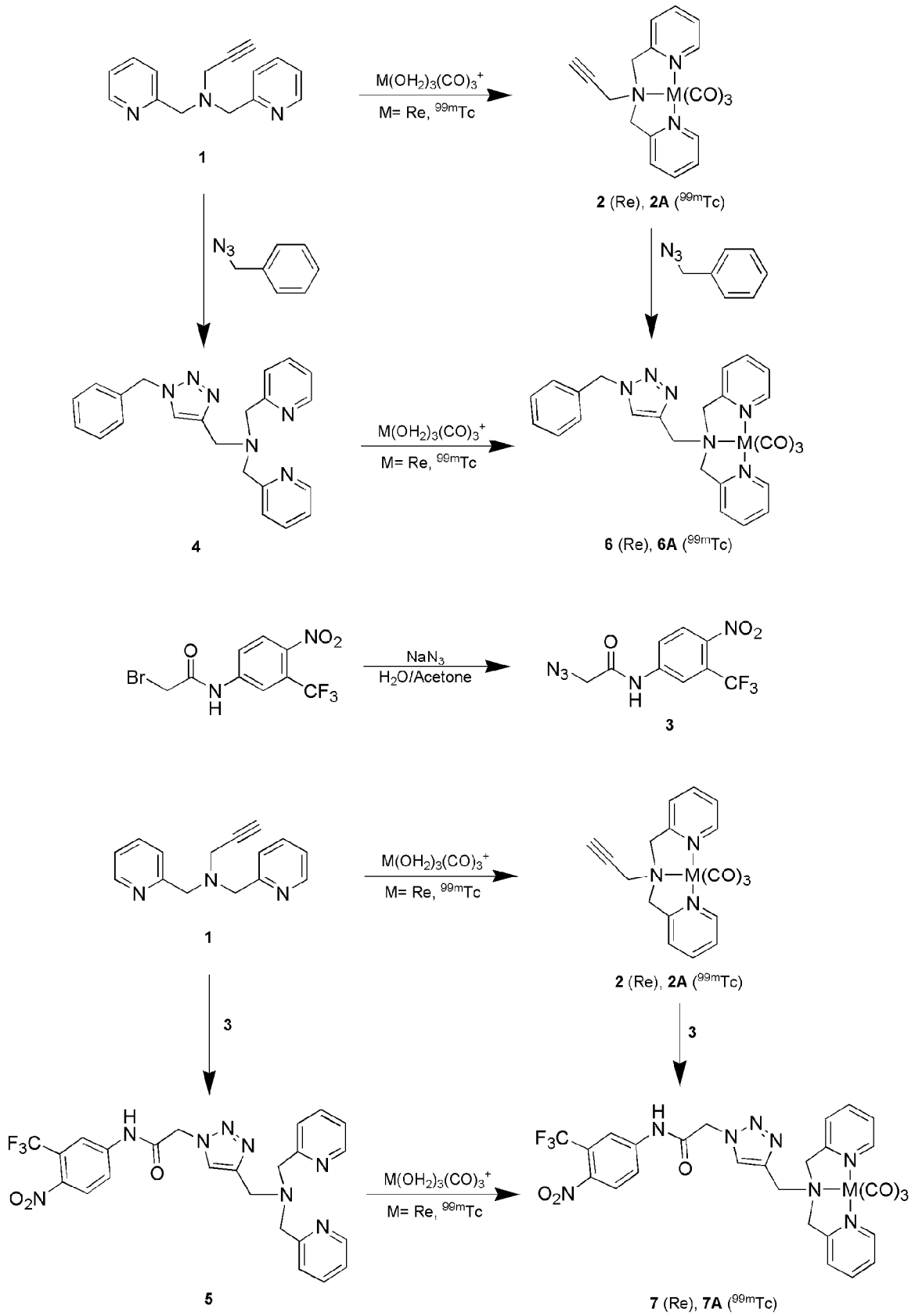
Electronic Supplementary Information for Dalton Transactions

"Click" Labeling Strategy for $M(CO)_3$ (M= Re, ^{99m}Tc) Prostate Cancer Targeted Flutamide Agents

Adam L. Moore [a], Dejan-Krešimir Bučar[b], Leonard R. MacGillivray[b], and Paul D. Benny*[a]

[a]*Department of Chemistry, Washington State University, PO Box 644630, Pullman, WA 99164, USA.*

[b]*Department of Chemistry, University of Iowa, Iowa City, IA 52242-1294, USA*



Experimental

All reagents and organic solvents of reagent grade or better were used as purchased from Aldrich, Acros, or Fluka without further purification. Rhenium starting materials $[Re(CO)_5][Br]$, and *fac*-$[Re(CO)_3(H_2O)_3][SO_3CF_3]$, were prepared by literature methods from $Re_2(CO)_{10}$ purchased from Strem.[1] The preparations of *N,N*-bis(pyridine-2-ylmethyl)prop-2-yn-1-amine, (**1**) and 1-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-*N,N*-bis(pyridine-2-ylmethyl)methanamine (**4**) were prepared as previously reported.[2] UV-Vis spectra were obtained using a Varian Carry 50 spectrophotometer (1 cm path-length). ^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz instrument at 25 ºC in deuterated methanol. Elemental analyses were performed by Quantitative Technologies, Inc., NJ. Separation and identification of compounds were conducted on a Perkin Elmer Series 200 High Pressure Liquid Chromatograph (HPLC) equipped with a UV/VIS Series 200 detector and a Radiomatic 610TR detector. Utilizing an Agilent Zorbex 5μm particle and 30 cm SB-C18 column, the compounds were separated with a reverse phase gradient system beginning with 0.1% trifluoroacetic acid (TFA) aqueous eluent gradually shifting to methanol according to the following method, 0-3.0 min (100% TFA), 3.0-9.0 min (75% TFA, 25% MeOH), 9.0-20.0 min (25% to 100% MeOH linear gradient), 20.0-25.0 min (100% MeOH) at a flow rate of 1.0 mL/min or 5.0 mL/min for separation. FT-IR spectra were obtained on a Thermo Nicolet 6700 FT-IR with an ATR cell and analyzed with OMNIC 7.1a software. Mass spectra data were collected using a Q3 scans on an API4000 triple quadrapole (Applied Biosystems). Sample concentrations of ~0.1 μg/μL in methanol were infused at 10 μL/min, with orifice heating on, declustering potential 20 V, and entrance potential 10 V.

[*fac*-Re(CO)$_3$(1)]OTf, 2.

To a methanolic solution of **1** (277 mg, 1.16 mmol), in a sealable 25 cm^3 vial, was added 0.1 M [Re(CO)$_3$(OH$_2$)$_3$]OTf$_{(aq)}$ (11.6 mL, 1.16 mmol). The vial was sealed, and stirred at room temperature for 12 hr. which produced a light brown precipitate that was collected by vacuum filtration. Recrystallization of **2** with CH_3OH/Et_2O yielded clean product. X-ray quality crystals were grown by slow diffusion of CH_3OH/Et_2O (280 mg, 37%). δ_H(299.8 MHz, CD_3OD) 8.52 (2 H, d), 7.60 (2 H, t), 7.48 (2 H, m), 7.11 (2 H, m), 3.89 (4 H, s), 3.39 (2 H, d), 2.26 (1 H, t); δ_C(75.5 MHz, CD_3OD) 195.5, 195.0, 160.3, 152.1, 140.5, 125.8, 125.7, 68.1, 65.7, 57.9; λ_{max}(CH_2Cl_2)/nm: 261 (ε/dm^3 mol^{-1} cm^{-1} 24 000); υ_{max}/cm^{-1}: 2360 (C≡C); 2030 and 1926 (CO); m/z 505.3 (M$^+$, 100%), 503.3 (58), 506.3 (31); Found: C, 33.50; H, 2.29; N, 6.19. Calc. for $C_{19}H_{15}N_3O_6ReSF_3 \bullet OH_2$: C, 33.81; H, 2.54; N, 6.23.

2-azido-*N*-(4-nitro-3-(trifluoromethyl)phenyl)acetamide, 3.

The product was prepared under conditions developed for compounds in a previous report, (2-bromo-*N*-(4-nitro-3-(trifluoromethyl)phenyl)acetamide).[3] 2-bromo-*N*-(4-nitro-3-(trifluoromethyl)phenyl)acetamide (300 mg, 0.92 mmol) followed by the addition of NaN_3 (126 mg, 1.94 mmol) was added to a vigorously stirred acetone/water solution (4:1, 10 cm^3/2.5). The solution was stirred for 3 hours at room temperature at which time complete conversion of the starting material into **3** was observed by thin layer chromatography (Rf = 0.15 CH_2Cl_2/Hexane 3:1). The reaction mixture was dried under vacuum and the residue was redissolved in CH_2Cl_2 and filtered. Purification was achieved by silica gel chromatography with (CH_2Cl_2:Hexane 3:1) (250.3 mg, 94.1%).

δ_H(299.8 MHz, CD_3OD) 8.22 (1 H, s,), 8.04 (2 H, s), 4.08 (2 H, s); δ_C(75.5 MHz, CD_3OD) 168.1, 143.0, 142.9, 127.0, 124.3 (dd, J_{CF} 34), 122.6, 121.2, (dd, J_{CF} 272), 118.1, (dd, J_{CF} 6), 52.0; $\lambda_{max}(CH_2Cl_2)$/nm: 230 (ε/dm^3 mol^{-1} cm^{-1} 1 900), 285 (1 500); υ_{max}/cm^{-1}: 1713 (CO); 2101 (N_3^-); 3349 (NH); m/z 235.6; Found: C, 37.47; H, 1.95; N, 24.00. Calc. for $C_9H_6N_5O_3F_3$: C, 37.36; H, 2.09; N, 24.22.

2-4-((bis(pyridine-2-ylmehtyl)amino)methyl)-1*H*-1,2,3-triazol-1-yl)-*N*-(4-nitro-3-(trifluoromethyl)phenyl)acetamide, 5.

A 25 cm^3 scintillation vial was charged with *N,N*-bis(pyridine-2-ylmethyl)prop-2-yn-1-amine, (**1)** (0.100 g, 0.420 mmol) and **3 (**0.121 g, 0.420 mmol) and dissolved in CH_3OH (4 cm^3). To the mixture was added sodium ascorbate (0.166 g, 0.840 mmol) in water (2 cm^3) followed by of $Cu^{II}(OAc)_2$ (0.076 g, 0.420 mmol) in water (2 cm^3). The solution was stirred at room temperature for 12 hrs. An additional 30 minutes of stirring was needed after the addition of excess EDTA. The pH was then raised to 11 through the addition of KOH pellets. The mixture was extracted 3 times with CH_2Cl_2 (20 cm^3). The organic portions were combined and dried over Na_2SO_4. The volume was reduced (ca. 5 cm^3) and precipitated with Et_2O to yield an off white precipitate which was collected by vacuum filtration (0.178 g, 81.0%). δ_H(299.8 MHz, CD_3OD) 8.87 (2 H, dd), 8.44 (1 H, s), 8.32 (1 H, m), 7.82-7.78 (4 H, m), 7.26 (4 H, m), 5.55 (2 H, s), 5.09 (2 H, s), 4.81 (4 H, dd, J_{AB} 12); δ_C(75.5 MHz, CD_3OD) 216.3, 165.5, 144.2, 143.1, 142.9 (dd, J_{CF} 1347), 142.8, 126.0, 124.5 (dd, J_{CF} 36), 123.7, 123.3, 122.7, 122.6, 121.2, 117.9 (dd, J_{CF} 6), 66.7, 59.1, 52.8; $\lambda_{max}(CH_2Cl_2)$/nm: 265 (ε/dm^3 mol^{-1} cm^{-1} 12 000), 235 (16 000);

υ_{max}/cm^{-1}: 1710 (CO); 2100 (N_3^-); m/z 448; Found: C, 53.96; H, 4.04; N, 20.57. Calc. for $C_{24}H_{21}N_8O_3F_3 \bullet 0.5OH_2$: C, 53.81; H, 4.14; N, 20.93.

[*fac*-Re(CO)$_3$(4)]OTf, 6.

Method A: A 25 cm^3 scintillation vial was charged with $[Re^I(CO)_3(\mathbf{1})]^+$, **2**, (0.050 g, 0.076 mmol), benzylazide **(**0.010 g, 0.076 mmol) and dissolved in *tert*-butyl alcohol (4 cm^3). To the mixture was added sodium ascorbate (0.003 g, 0.0015 mmol) in water (2 cm^3) followed by $Cu^{II}(OAc)_2$ (0.002 g, 0.0076 mmol) in water (2 cm^3). This mixture was stirred at room temperature for 90 minutes. The mixture was neutralized and extracted 3 times with CH_2Cl_2 (20 cm^3). The organic portions were combined and dried over Na_2SO_4 and the volume was reduced to ca. 5 cm^3. The product was precipitated with Et_2O to yield an light brown precipitate which was collected by vacuum filtration. (41 mg, 84.1%)

Method B: Ligand **4** (0.035 g, 0.066 mmol) was dissolved in CH_3OH (5 cm^3) and added dropwise to 0.1 M $[Re^I(CO)_3(OH_2)_3]OTf_{(aq)}$ (0.664 mL, 0.066 mmol) stirring in a 10 cm^3 scintiliation vial. The vial was sealed, and stirred at room temperature for 12 hr. which produced a light brown precipitate that was collected by vacuum filtration. Complex **6** was recrystallized as an off-white solid by slow addition of Et_2O to a saturated solution in CH_3OH (0.035 g, 74%). δ_H(299.8 MHz, CD_3OD) 8.84 (2 H, dd), 8.32 (1 H, s), 7.89 (2 H, m), 7.48 (2 H, m), 7.41-7.32 (7 H, m), 5.68 (2 H, s), 4.98 (2 H, s), 4.84 (4 H, dd, J_{AB} 12); δ_C(75.5 MHz, CD_3OD) 195.7, 195.1, 160.5, 152.0, 140.4, 135.2, 128.9, 128.6, 128.3, 127.8, 126.8, 125.7, 123.5, 122.7, 68.1, 62.9, 54.0; $\lambda_{max}(CH_2Cl_2)$/nm: 261 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 29 000), 295 (19 000); υ_{max}/cm^{-1}: 2342 (N_3), 2028 and 1908 (CO); m/z 641.4 (M^+,

100%), 639.4 (58), 642.4 (31); Found: C, 38.16; H, 2.57; N, 10.28 Calc. for $C_{25}H_{22}N_6O_3Re(CO_3SF_3)_{0.75}Br_{0.25}\bullet CH_2Cl_2$: C, 38.05; H, 2.83; N, 10.05.

[*fac*-Re(CO)$_3$(4)]OTf, 7.

Complex **7** was prepared in a similar manner to that of **6**, except **1, 3,** and **5** were used instead of **4** and **Bz, Method A**:(50 mg, 81.0 %), **Method B**: (33 mg, 52%). δ_H(299.8 MHz, CD_3OD) 8.89 (dd, 2H), 8.44 (1 H, s), 8.30 (2 H, dt), 8.08 (2 H, m), 7.92-7.36 (5 H, m), 5.55 (2 H, s), 5.08 (2 H, s), 4.84 (4 H, dd, J_{AB} 12); δ_C(75.5 MHz, CD_3OD) 195.7, 195.1, 160.5, 152.0, 142.9 (dd, J_{CF} 1247), 140.4, 135.2, 128.9, 128.6, 128.3**,** 127.1, 126.8, 125.7 (dd, J_{CF} 34), 123.5, 122.7, 118.8 (dd, J_{CF} 6), 68.1, 62.9, 54.0 ; $\lambda_{max}(CH_2Cl_2)$/nm: 270 (ε/dm^3 mol^{-1} cm^{-1} 49 000); υ_{max}/cm^{-1}: 2030 and 1926 (CO), 2360 (N_3); m/z 797.2 (M^+, 100%), 795.2 (58), 798.2 (31); Found: C, 33.33; H, 2.33; N, 10.42 Calc. for $C_{27}H_{21}N_8O_6ReF_3\bullet(OH_2)_2\bullet(CH_2Cl_2)_2$: C, 33.54; H, 2.82; N, 10.80.

General ^{99m}Tc(H$_2$O)$_3$(CO)$_3^+$ radiolabeling procedure

The ligand (100 μm^3, 10^{-4}, 10^{-5} or 10^{-6} M) and phosphate buffer (800 μL, 0.1 M) at pH 7.4 was added to a sealable labeling vial (5.0 cm^3). The vial was sealed and degassed with nitrogen for ~10 min. The ^{99m}Tc(H$_2$O)$_3$(CO)$_3^+$ precursor solution (100 μm^3) was prepared according to the Isolink® kit following Tyco specifications. The solution was added to a degassed vial and the vial heated for 60 min. at 70° C. The reaction mixture was then carefully allowed to cool on an ice bath prior to injection and analysis by radio-HPLC.

Table 1. $^{99m}Tc^{I}(CO)_3$(Ligand) complex labeling efficiency by direct reaction of $[^{99m}Tc^{I}(CO)_3(OH_2)_3]^+$ with ligands (**1**, **4**, **5**) at 60 min. at 70° C.

[Ligand] (M)	2A	6A	7A
10^{-5}	100	97	100
10^{-6}	88	78	82
10^{-7}	77	42	36

General method for click reactions with 2A.

Complex **6A** was formed through subsequent addition of PBS (700μm^3), benzylazide (100 μm^3) and Sodium L-Ascorbate (100 μm^3) to a 5 cm^3 sealable vial. The vial was degassed with N_2 for ~ 10 min. and **2A** (100 μm^3) was added followed by copper (II) acetate (100 μm^3). The mixture was then stirred at the appropriate temperature for 15 min.

Table 2. Labeling efficiency of the conversion of **2A** to **6A** with a reaction time of 15 minutes while varying the concentration of benzylazide (10^{-4} – 10^{-6} M) and the temperature of the reaction (70º-25º C).

Temperature (°C)	10^{-3}	10^{-4}	10^{-5} (M)
70	100	100	75
50	100	100	61
37	100	100	23
25	100	93	23

Flutamide derivative click reactions with 2A.

Complex **7A** was formed through subsequent addition of PBS (700μm^3), **3** (100 μm^3) and Sodium L-Ascorbate (100 μm^3) to a 5 cm^3 sealable vial. The vial was degassed with N_2 for ~ 10 min. and **2A** (100 μm^3) was added followed by copper (II) acetate (100 μm^3). The mixture was then stirred at the 50 ºC for 15 min. producing quantitative yields at molar concentrations of 10^{-3} - 10^{-4} M.

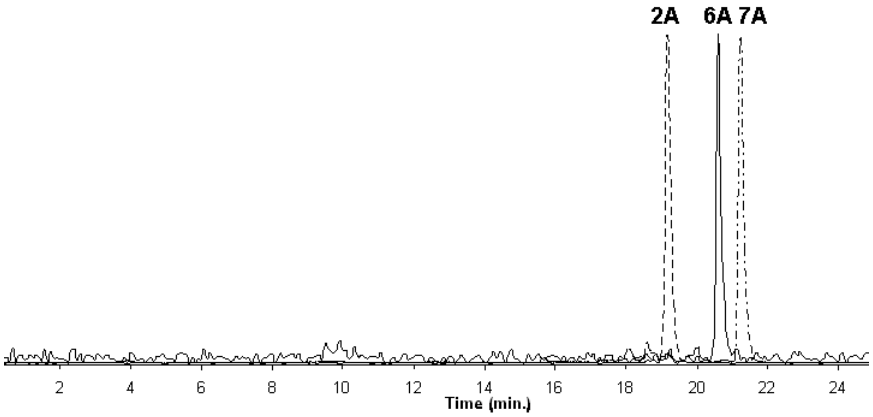


Figure 1. Normalized Radio HPLC traces of **2A**, **6A**, and **7A**. All plots were HPLC purified before reinjection.

X-ray experimental

Crystals of compounds **2**, **6**, and **7** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and placed in the low-temperature nitrogen stream.[4] Data (**2** and **7**) were collected at low temperatures using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data for **6** were collected on a Kappa CCD (Mo Kα radiation, λ = 0.71073 Å) using phi and omega scans. Data for **2** and **7** were measured using omega scans of 0.3 ° per frame for various exposures, and a full sphere of data was collected in each case. A total of 2400 frames were collected with final resolutions of 0.77 Å. Cell parameters were retrieved using SMART[5] software and refined using SAINTPlus[6] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[7] Data for **6** were collected at low temperature on a Nonius Kappa CCD (Mo Kα radiation, λ = 0.71073 Å) using phi and omega scans. A total of 532 frames were collected with 120 seconds per frame exposure time. 2994 reflections were used for unit cell refinement. The final resolution of the structure was 0.76 Å. Absorption corrections were preformed using HKL Scalepack. Structures of **2**, **6**, and **7** were solved by direct methods and refined by least squares method on F^2 using the SHELXTL[8] program package. Each structure was solved by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically (riding model). No decomposition of crystals was observed during data collection. Details of the data collection and refinement are given in Tables 1, 3 and 5.

Table 3. Crystal data and structure refinement for **2**.

Formula	$Re(C_{15}H_{15}N_3)(CO)_3][CF_3SO_3]\cdot 1.5CH_2Cl_2$
Formula weight	1567.98 $gmol^{-1}$
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	*C* 2/*m*
Unit cell dimensions	*a* = 29.647(3) Å *b* = 10.4289(11) Å *c* = 8.1706(9) Å α = 90°. β = 100.620(5)°. γ = 90°.
Volume	2483.0(5) $Å^3$
Z	2
Density (calculated)	2.097 Mg/m^3
Absorption coefficient	5.368 mm^{-1}
F(000)	1516
Crystal size	0.20 × 0.03 × 0.02 mm^3
Theta range for data collection	3.11 to 24.99°.
Index ranges	-35<=h<=35, -12<=k<=12, -9<=l<=9
Reflections collected	8477
Independent reflections	2318 [R(*int*) = 0.0349]
Completeness to theta = 24.99°	99.7 %
Max. and min. transmission	0.9002 and 0.4132
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2318 / 68 / 158
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R_1 = 0.0454, wR_2 = 0.1239
R indices (all data)	R_1 = 0.0517, wR_2 = 0.1283
Extinction coefficient	0.0012(3)
Largest diff. peak and hole	2.438 and -2.021 e$Å^{-3}$

Table 4. Bond lengths [Å] and angles [°] for **2**.

S(1A)-O(4A)#1	1.400(9)
S(1A)-O(4A)	1.400(9)
S(1A)-O(3A)	1.428(13)
S(1A)-C(12A)	1.820(16)
C(12A)-F(1A)	1.330(5)
C(12A)-F(2A)	1.332(5)
C(12A)-F(2A)#1	1.332(5)
S(1B)-O(4B)#1	1.400(9)
S(1B)-O(4B)	1.400(9)
S(1B)-O(3B)	1.429(13)
S(1B)-C(12B)	1.796(15)
C(12B)-F(2B)	1.331(5)
C(12B)-F(1B)	1.333(5)
C(12B)-F(1B)#1	1.333(5)
Re(1)-C(2)	1.909(12)
Re(1)-C(1)	1.942(10)
Re(1)-C(1)#2	1.942(10)
Re(1)-N(1)	2.171(7)
Re(1)-N(1)#2	2.171(7)
Re(1)-N(2)	2.223(8)
N(2)-C(8)#2	1.485(10)
N(2)-C(8)	1.485(10)
N(2)-C(9)	1.510(15)
C(2)-O(2)	1.158(14)
N(1)-C(3)	1.346(11)
N(1)-C(7)	1.356(9)
C(1)-O(1)	1.135(10)
C(7)-C(6)	1.373(12)
C(7)-C(8)	1.486(11)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.487(17)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(3)-C(4)	1.356(13)
C(3)-H(3)	0.9300
C(6)-C(5)	1.381(14)
C(6)-H(6)	0.9300
C(4)-C(5)	1.402(14)
C(4)-H(4)	0.9300
C(10)-C(11)	1.145(19)
C(5)-H(5)	0.9300
C(11)-H(11)	0.9300
O(4A)#1-S(1A)-O(4A)	118.2(13)
O(4A)#1-S(1A)-O(3A)	112.4(7)
O(4A)-S(1A)-O(3A)	112.4(7)
O(4A)#1-S(1A)-C(12A)	104.9(6)
O(4A)-S(1A)-C(12A)	104.9(6)
O(3A)-S(1A)-C(12A)	102.1(8)
F(1A)-C(12A)-F(2A)	109.4(9)
F(1A)-C(12A)-F(2A)#1	109.4(9)
F(2A)-C(12A)-F(2A)#1	109.4(13)
F(1A)-C(12A)-S(1A)	109.1(9)
F(2A)-C(12A)-S(1A)	109.7(7)
F(2A)#1-C(12A)-S(1A)	109.7(7)
O(4B)#1-S(1B)-O(4B)	118.2(12)
O(4B)#1-S(1B)-O(3B)	110.6(8)
O(4B)-S(1B)-O(3B)	110.6(8)
O(4B)#1-S(1B)-C(12B)	106.3(6)
O(4B)-S(1B)-C(12B)	106.3(6)
O(3B)-S(1B)-C(12B)	103.7(8)
F(2B)-C(12B)-F(1B)	109.2(9)
F(2B)-C(12B)-F(1B)#1	109.2(9)
F(1B)-C(12B)-F(1B)#1	102.6(12)
F(2B)-C(12B)-S(1B)	110.9(9)
F(1B)-C(12B)-S(1B)	112.3(7)
F(1B)#1-C(12B)-S(1B)	112.3(7)
C(2)-Re(1)-C(1)	88.4(3)
C(2)-Re(1)-C(1)#2	88.4(3)
C(1)-Re(1)-C(1)#2	90.1(5)
C(2)-Re(1)-N(1)	98.0(3)
C(1)-Re(1)-N(1)	94.8(3)
C(1)#2-Re(1)-N(1)	172.1(3)
C(2)-Re(1)-N(1)#2	98.0(3)
C(1)-Re(1)-N(1)#2	172.1(3)
C(1)#2-Re(1)-N(1)#2	94.8(3)
N(1)-Re(1)-N(1)#2	79.7(3)
C(2)-Re(1)-N(2)	174.1(4)
C(1)-Re(1)-N(2)	95.8(3)
C(1)#2-Re(1)-N(2)	95.8(3)
N(1)-Re(1)-N(2)	77.5(2)
N(1)#2-Re(1)-N(2)	77.5(2)
C(8)#2-N(2)-C(8)	109.4(9)
C(8)#2-N(2)-C(9)	109.0(6)
C(8)-N(2)-C(9)	109.0(6)
C(8)#2-N(2)-Re(1)	109.1(5)
C(8)-N(2)-Re(1)	109.1(5)
C(9)-N(2)-Re(1)	111.2(7)
O(2)-C(2)-Re(1)	179.5(9)
C(3)-N(1)-C(7)	118.7(7)
C(3)-N(1)-Re(1)	125.3(5)
C(7)-N(1)-Re(1)	115.3(5)
O(1)-C(1)-Re(1)	179.1(8)
N(1)-C(7)-C(6)	121.1(8)
N(1)-C(7)-C(8)	116.7(7)
C(6)-C(7)-C(8)	122.1(7)
N(2)-C(8)-C(7)	111.8(7)
N(2)-C(8)-H(8A)	109.3
C(7)-C(8)-H(8A)	109.3
N(2)-C(8)-H(8B)	109.3
C(7)-C(8)-H(8B)	109.3
H(8A)-C(8)-H(8B)	107.9
C(10)-C(9)-N(2)	113.8(11)
C(10)-C(9)-H(9A)	108.8
N(2)-C(9)-H(9A)	108.8
C(10)-C(9)-H(9B)	108.8
N(2)-C(9)-H(9B)	108.8

H(9A)-C(9)-H(9B)	107.7
N(1)-C(3)-C(4)	122.9(8)
N(1)-C(3)-H(3)	118.6
C(4)-C(3)-H(3)	118.6
C(7)-C(6)-C(5)	120.0(8)
C(7)-C(6)-H(6)	120.0
C(5)-C(6)-H(6)	120.0
C(3)-C(4)-C(5)	118.8(9)
C(3)-C(4)-H(4)	120.6
C(5)-C(4)-H(4)	120.6
C(11)-C(10)-C(9)	174.1(17)
C(6)-C(5)-C(4)	118.4(9)
C(6)-C(5)-H(5)	120.8
C(4)-C(5)-H(5)	120.8
C(10)-C(11)-H(11)	180.0

Symmetry transformations used to generate equivalent atoms: #1: x,-y+1,z #2 x,-y+2,z

Table 5. Crystal data and structure refinement for **6**.

Formula	$[Re(C_{22}H_{22}N_6)(CO)_3][CF_3SO_3]_{1.27}[Br]_{0.73}$
Formula weight	1527.64 $gmol^{-1}$
Temperature	210(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P\,2_1/c$
Unit cell dimensions	a = 10.2803(11) Å b = 18.7456(19) Å c = 30.539(4) Å α = 90°. β = 99.339(5)°. γ = 90°.
Volume	5807.2(11) $Å^3$
Z	4
Density (calculated)	1.747 Mg/m^3
Absorption coefficient	4.803 mm^{-1}
F(000)	2974
Crystal size	0.22 × 0.05 × 0.04 mm^3
Theta range for data collection	2.01 to 25.00°.
Index ranges	-12<=h<=12, -22<=k<=22, -36<=l<=36
Reflections collected	35711
Independent reflections	10203 [R(*int*) = 0.0655]
Completeness to theta = 25.00°	99.8 %
Max. and min. transmission	0.8311 and 0.4180
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10203 / 101 / 738
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R_1 = 0.0475, wR_2 = 0.1247
R indices (all data)	R_1 = 0.0760, wR_2 = 0.1375
Largest diff. peak and hole	2.037 and -1.607 $eÅ^{-3}$

Table 6. Bond lengths [Å] and angles [°] for **6**.

C(44A)-C(45A)	1.443(14)
C(44A)-N(12)	1.513(12)
C(44A)-H(44A)	0.9800
C(44A)-H(44B)	0.9800
C(45A)-C(46A)	1.3900
C(45A)-C(50A)	1.3900
C(46A)-C(47A)	1.3900
C(46A)-H(46A)	0.9400
C(47A)-C(48A)	1.3900
C(47A)-H(47A)	0.9400
C(48A)-C(49A)	1.3900
C(48A)-H(48A)	0.9400
C(49A)-C(50A)	1.3900
C(49A)-H(49A)	0.9400
C(50A)-H(50A)	0.9400
C(45B)-C(46B)	1.3900
C(45B)-C(50B)	1.3900
C(46B)-C(47B)	1.3900
C(46B)-H(46B)	0.9400
C(47B)-C(48B)	1.3900
C(47B)-H(47B)	0.9400
C(48B)-C(49B)	1.3900
C(48B)-H(48B)	0.9400
C(49B)-C(50B)	1.3900
C(49B)-H(49B)	0.9400
C(50B)-H(50B)	0.9400
S(1)-O(9)	1.434(9)
S(1)-O(7)	1.435(9)
S(1)-O(8)	1.454(9)
S(1)-C(51)	1.783(13)
C(51)-F(1)	1.301(11)
C(51)-F(3)	1.308(10)
C(51)-F(2)	1.323(11)
S(2)-O(12)	1.402(12)
S(2)-O(10)	1.469(12)
S(2)-O(11)	1.487(11)
S(2)-C(52)	1.751(15)
C(52)-F(6)	1.283(14)
C(52)-F(4)	1.315(14)
C(52)-F(5)	1.363(13)
Re(2)-C(26)	1.917(9)
Re(2)-C(27)	1.925(9)
Re(2)-C(28)	1.926(9)
Re(2)-N(7)	2.175(6)
Re(2)-N(9)	2.182(6)
Re(2)-N(8)	2.237(6)
C(27)-O(5)	1.135(10)
C(26)-O(4)	1.157(10)
C(28)-O(6)	1.153(9)
Re(1)-C(2)	1.894(9)
Re(1)-C(1)	1.928(10)
Re(1)-C(3)	1.934(9)
Re(1)-N(3)	2.169(7)
Re(1)-N(1)	2.179(7)
Re(1)-N(2)	2.230(6)
C(3)-O(3)	1.132(9)
C(2)-O(2)	1.165(10)
C(1)-O(1)	1.141(10)
C(10)-N(2)	1.511(10)
C(10)-C(11)	1.523(12)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(29)-N(7)	1.337(10)
C(29)-C(30)	1.343(12)
C(29)-H(29)	0.9400
C(18)-N(6)	1.360(11)
C(18)-C(17)	1.384(12)
C(18)-H(18)	0.9400
C(32)-C(33)	1.363(12)
C(32)-C(31)	1.381(13)
C(32)-H(32)	0.9400
C(4)-N(1)	1.342(11)
C(4)-C(5)	1.386(13)
C(4)-H(4)	0.9400
N(1)-C(8)	1.347(10)
C(34)-C(33)	1.479(11)
C(34)-N(8)	1.507(9)
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
N(8)-C(35)	1.477(10)
N(8)-C(41)	1.512(9)
C(7)-C(8)	1.373(11)
C(7)-C(6)	1.379(14)
C(7)-H(7)	0.9400
C(37)-C(38)	1.366(14)
C(37)-C(36)	1.384(11)
C(37)-H(37)	0.9400
N(7)-C(33)	1.352(10)
N(3)-C(11)	1.350(11)
N(3)-C(15)	1.359(11)
C(38)-C(39)	1.346(14)
C(38)-H(38)	0.9400
N(6)-N(5)	1.320(10)
N(6)-C(19)	1.455(11)
C(36)-N(9)	1.365(10)
C(36)-C(35)	1.473(11)
C(41)-C(42)	1.500(11)
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(25)-C(20)	1.379(15)
C(25)-C(24)	1.425(18)
C(25)-H(25)	0.9400
C(19)-C(20)	1.508(13)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(40)-N(9)	1.336(10)
C(40)-C(39)	1.391(12)
C(40)-H(40)	0.9400
N(12)-N(11)	1.327(10)

N(12)-C(43)	1.348(11)
C(42)-C(43)	1.352(11)
C(42)-N(10)	1.380(10)
N(11)-N(10)	1.318(10)
C(20)-C(21)	1.352(17)
C(43)-H(43)	0.9400
N(4)-N(5)	1.318(10)
N(4)-C(17)	1.376(10)
C(17)-C(16)	1.477(11)
C(9)-C(8)	1.465(12)
C(9)-N(2)	1.475(10)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(16)-N(2)	1.512(10)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(21)-C(22)	1.422(17)
C(21)-H(21)	0.9400
C(39)-H(39)	0.9400
C(24)-C(23)	1.310(19)
C(24)-H(24)	0.9400
C(14)-C(13)	1.345(16)
C(14)-C(15)	1.367(13)
C(14)-H(14)	0.9400
C(22)-C(23)	1.37(2)
C(22)-H(22)	0.9400
C(15)-H(15)	0.9400
C(30)-C(31)	1.389(14)
C(30)-H(30)	0.9400
C(31)-H(31)	0.9400
C(5)-C(6)	1.371(14)
C(5)-H(5)	0.9400
C(23)-H(23)	0.9400
C(11)-C(12)	1.372(12)
C(6)-H(6)	0.9400
C(13)-C(12)	1.417(15)
C(13)-H(13)	0.9400
C(12)-H(12)	0.9400

C(45A)-C(44A)-N(12)	110.9(9)
C(45A)-C(44A)-H(44A)	109.5
N(12)-C(44A)-H(44A)	109.5
C(45A)-C(44A)-H(44B)	109.5
N(12)-C(44A)-H(44B)	109.5
H(44A)-C(44A)-H(44B)	108.0
C(46A)-C(45A)-C(50A)	120.0
C(46A)-C(45A)-C(44A)	120.1(7)
C(50A)-C(45A)-C(44A)	119.8(6)
C(45A)-C(46A)-C(47A)	120.0
C(45A)-C(46A)-H(46A)	120.0
C(47A)-C(46A)-H(46A)	120.0
C(48A)-C(47A)-C(46A)	120.0
C(48A)-C(47A)-H(47A)	120.0
C(46A)-C(47A)-H(47A)	120.0
C(47A)-C(48A)-C(49A)	120.0
C(47A)-C(48A)-H(48A)	120.0
C(49A)-C(48A)-H(48A)	120.0
C(48A)-C(49A)-C(50A)	120.0
C(48A)-C(49A)-H(49A)	120.0
C(50A)-C(49A)-H(49A)	120.0
C(49A)-C(50A)-C(45A)	120.0
C(49A)-C(50A)-H(50A)	120.0
C(45A)-C(50A)-H(50A)	120.0
C(46B)-C(45B)-C(50B)	120.0
C(47B)-C(46B)-C(45B)	120.0
C(47B)-C(46B)-H(46B)	120.0
C(45B)-C(46B)-H(46B)	120.0
C(46B)-C(47B)-C(48B)	120.0
C(46B)-C(47B)-H(47B)	120.0
C(48B)-C(47B)-H(47B)	120.0
C(49B)-C(48B)-C(47B)	120.0
C(49B)-C(48B)-H(48B)	120.0
C(47B)-C(48B)-H(48B)	120.0
C(48B)-C(49B)-C(50B)	120.0
C(48B)-C(49B)-H(49B)	120.0
C(50B)-C(49B)-H(49B)	120.0
C(49B)-C(50B)-C(45B)	120.0
C(49B)-C(50B)-H(50B)	120.0
C(45B)-C(50B)-H(50B)	120.0
O(9)-S(1)-O(7)	117.2(7)
O(9)-S(1)-O(8)	114.3(7)
O(7)-S(1)-O(8)	114.7(6)
O(9)-S(1)-C(51)	103.8(5)
O(7)-S(1)-C(51)	101.9(6)
O(8)-S(1)-C(51)	102.1(6)
F(1)-C(51)-F(3)	106.0(10)
F(1)-C(51)-F(2)	102.4(10)
F(3)-C(51)-F(2)	107.9(10)
F(1)-C(51)-S(1)	113.5(9)
F(3)-C(51)-S(1)	112.8(8)
F(2)-C(51)-S(1)	113.5(8)
O(12)-S(2)-O(10)	118.8(11)
O(12)-S(2)-O(11)	115.0(10)
O(10)-S(2)-O(11)	108.6(9)
O(12)-S(2)-C(52)	104.3(9)
O(10)-S(2)-C(52)	102.2(9)
O(11)-S(2)-C(52)	106.3(8)
F(6)-C(52)-F(4)	108.3(19)
F(6)-C(52)-F(5)	105.0(15)
F(4)-C(52)-F(5)	110.9(15)
F(6)-C(52)-S(2)	111.6(11)
F(4)-C(52)-S(2)	112.9(11)
F(5)-C(52)-S(2)	107.8(11)
C(26)-Re(2)-C(27)	86.4(3)
C(26)-Re(2)-C(28)	90.8(3)
C(27)-Re(2)-C(28)	88.5(3)
C(26)-Re(2)-N(7)	174.5(3)
C(27)-Re(2)-N(7)	95.9(3)
C(28)-Re(2)-N(7)	94.2(3)
C(26)-Re(2)-N(9)	95.6(3)

C(27)-Re(2)-N(9)	98.2(3)	C(35)-N(8)-C(34)	110.8(6)
C(28)-Re(2)-N(9)	170.9(3)	C(35)-N(8)-C(41)	110.1(6)
N(7)-Re(2)-N(9)	79.2(2)	C(34)-N(8)-C(41)	109.5(6)
C(26)-Re(2)-N(8)	98.2(3)	C(35)-N(8)-Re(2)	105.2(4)
C(27)-Re(2)-N(8)	173.2(3)	C(34)-N(8)-Re(2)	108.7(5)
C(28)-Re(2)-N(8)	96.3(3)	C(41)-N(8)-Re(2)	112.4(4)
N(7)-Re(2)-N(8)	79.1(2)	C(8)-C(7)-C(6)	119.6(9)
N(9)-Re(2)-N(8)	76.5(2)	C(8)-C(7)-H(7)	120.2
O(5)-C(27)-Re(2)	178.7(8)	C(6)-C(7)-H(7)	120.2
O(4)-C(26)-Re(2)	176.7(7)	C(38)-C(37)-C(36)	119.9(10)
O(6)-C(28)-Re(2)	178.7(7)	C(38)-C(37)-H(37)	120.1
C(2)-Re(1)-C(1)	85.2(4)	C(36)-C(37)-H(37)	120.1
C(2)-Re(1)-C(3)	88.0(3)	C(29)-N(7)-C(33)	118.6(7)
C(1)-Re(1)-C(3)	91.1(4)	C(29)-N(7)-Re(2)	125.5(6)
C(2)-Re(1)-N(3)	98.0(3)	C(33)-N(7)-Re(2)	115.5(5)
C(1)-Re(1)-N(3)	94.1(3)	C(11)-N(3)-C(15)	117.5(8)
C(3)-Re(1)-N(3)	172.3(3)	C(11)-N(3)-Re(1)	116.5(6)
C(2)-Re(1)-N(1)	97.4(3)	C(15)-N(3)-Re(1)	125.5(7)
C(1)-Re(1)-N(1)	174.1(3)	C(39)-C(38)-C(37)	120.6(9)
C(3)-Re(1)-N(1)	94.3(3)	C(39)-C(38)-H(38)	119.7
N(3)-Re(1)-N(1)	80.2(3)	C(37)-C(38)-H(38)	119.7
C(2)-Re(1)-N(2)	173.8(3)	N(5)-N(6)-C(18)	110.4(7)
C(1)-Re(1)-N(2)	98.5(3)	N(5)-N(6)-C(19)	121.2(8)
C(3)-Re(1)-N(2)	96.9(3)	C(18)-N(6)-C(19)	128.3(8)
N(3)-Re(1)-N(2)	76.8(3)	N(9)-C(36)-C(37)	119.9(8)
N(1)-Re(1)-N(2)	78.5(2)	N(9)-C(36)-C(35)	115.4(7)
O(3)-C(3)-Re(1)	177.6(8)	C(37)-C(36)-C(35)	124.6(8)
O(2)-C(2)-Re(1)	177.8(8)	C(42)-C(41)-N(8)	113.2(6)
O(1)-C(1)-Re(1)	175.5(8)	C(42)-C(41)-H(41A)	108.9
N(2)-C(10)-C(11)	109.6(7)	N(8)-C(41)-H(41A)	108.9
N(2)-C(10)-H(10A)	109.7	C(42)-C(41)-H(41B)	108.9
C(11)-C(10)-H(10A)	109.7	N(8)-C(41)-H(41B)	108.9
N(2)-C(10)-H(10B)	109.7	H(41A)-C(41)-H(41B)	107.7
C(11)-C(10)-H(10B)	109.7	C(20)-C(25)-C(24)	119.4(13)
H(10A)-C(10)-H(10B)	108.2	C(20)-C(25)-H(25)	120.3
N(7)-C(29)-C(30)	124.0(9)	C(24)-C(25)-H(25)	120.3
N(7)-C(29)-H(29)	118.0	N(6)-C(19)-C(20)	112.1(8)
C(30)-C(29)-H(29)	118.0	N(6)-C(19)-H(19A)	109.2
N(6)-C(18)-C(17)	105.8(8)	C(20)-C(19)-H(19A)	109.2
N(6)-C(18)-H(18)	127.1	N(6)-C(19)-H(19B)	109.2
C(17)-C(18)-H(18)	127.1	C(20)-C(19)-H(19B)	109.2
C(33)-C(32)-C(31)	120.9(9)	H(19A)-C(19)-H(19B)	107.9
C(33)-C(32)-H(32)	119.6	N(9)-C(40)-C(39)	122.5(9)
C(31)-C(32)-H(32)	119.6	N(9)-C(40)-H(40)	118.7
N(1)-C(4)-C(5)	123.1(9)	C(39)-C(40)-H(40)	118.7
N(1)-C(4)-H(4)	118.5	N(7)-C(33)-C(32)	120.1(8)
C(5)-C(4)-H(4)	118.5	N(7)-C(33)-C(34)	118.0(7)
C(4)-N(1)-C(8)	120.0(8)	C(32)-C(33)-C(34)	121.8(8)
C(4)-N(1)-Re(1)	123.9(6)	N(11)-N(12)-C(43)	111.5(7)
C(8)-N(1)-Re(1)	115.4(6)	N(11)-N(12)-C(44A)	119.7(8)
C(33)-C(34)-N(8)	115.8(7)	C(43)-N(12)-C(44A)	128.7(8)
C(33)-C(34)-H(34A)	108.3	C(43)-C(42)-N(10)	106.7(7)
N(8)-C(34)-H(34A)	108.3	C(43)-C(42)-C(41)	131.2(8)
C(33)-C(34)-H(34B)	108.3	N(10)-C(42)-C(41)	122.1(7)
N(8)-C(34)-H(34B)	108.3	N(10)-N(11)-N(12)	106.4(7)
H(34A)-C(34)-H(34B)	107.4	C(21)-C(20)-C(25)	119.0(11)

C(21)-C(20)-C(19)	118.9(11)
C(25)-C(20)-C(19)	122.1(11)
N(11)-N(10)-C(42)	109.6(7)
N(12)-C(43)-C(42)	105.8(8)
N(12)-C(43)-H(43)	127.1
C(42)-C(43)-H(43)	127.1
C(40)-N(9)-C(36)	118.8(7)
C(40)-N(9)-Re(2)	126.0(6)
C(36)-N(9)-Re(2)	114.5(5)
N(5)-N(4)-C(17)	109.4(7)
N(4)-C(17)-C(18)	106.2(8)
N(4)-C(17)-C(16)	122.9(7)
C(18)-C(17)-C(16)	130.9(8)
N(4)-N(5)-N(6)	108.2(7)
C(8)-C(9)-N(2)	117.0(7)
C(8)-C(9)-H(9A)	108.0
N(2)-C(9)-H(9A)	108.0
C(8)-C(9)-H(9B)	108.0
N(2)-C(9)-H(9B)	108.0
H(9A)-C(9)-H(9B)	107.3
C(36)-C(35)-N(8)	111.4(7)
C(36)-C(35)-H(35A)	109.3
N(8)-C(35)-H(35A)	109.3
C(36)-C(35)-H(35B)	109.3
N(8)-C(35)-H(35B)	109.3
H(35A)-C(35)-H(35B)	108.0
C(17)-C(16)-N(2)	113.6(6)
C(17)-C(16)-H(16A)	108.8
N(2)-C(16)-H(16A)	108.8
C(17)-C(16)-H(16B)	108.8
N(2)-C(16)-H(16B)	108.8
H(16A)-C(16)-H(16B)	107.7
C(9)-N(2)-C(10)	111.0(6)
C(9)-N(2)-C(16)	110.1(6)
C(10)-N(2)-C(16)	108.1(6)
C(9)-N(2)-Re(1)	108.8(5)
C(10)-N(2)-Re(1)	106.5(5)
C(16)-N(2)-Re(1)	112.3(5)
C(20)-C(21)-C(22)	120.2(13)
C(20)-C(21)-H(21)	119.9
C(22)-C(21)-H(21)	119.9
N(1)-C(8)-C(7)	119.7(9)
N(1)-C(8)-C(9)	117.1(7)
C(7)-C(8)-C(9)	123.1(8)
C(38)-C(39)-C(40)	118.2(9)
C(38)-C(39)-H(39)	120.9
C(40)-C(39)-H(39)	120.9
C(23)-C(24)-C(25)	121.8(14)
C(23)-C(24)-H(24)	119.1
C(25)-C(24)-H(24)	119.1
C(13)-C(14)-C(15)	119.8(11)
C(13)-C(14)-H(14)	120.1
C(15)-C(14)-H(14)	120.1
C(23)-C(22)-C(21)	120.2(14)
C(23)-C(22)-H(22)	119.9
C(21)-C(22)-H(22)	119.9
N(3)-C(15)-C(14)	122.4(10)
N(3)-C(15)-H(15)	118.8
C(14)-C(15)-H(15)	118.8
C(29)-C(30)-C(31)	118.2(9)
C(29)-C(30)-H(30)	120.9
C(31)-C(30)-H(30)	120.9
C(32)-C(31)-C(30)	118.1(9)
C(32)-C(31)-H(31)	120.9
C(30)-C(31)-H(31)	120.9
C(6)-C(5)-C(4)	115.9(9)
C(6)-C(5)-H(5)	122.0
C(4)-C(5)-H(5)	122.0
C(24)-C(23)-C(22)	119.4(14)
C(24)-C(23)-H(23)	120.3
C(22)-C(23)-H(23)	120.3
N(3)-C(11)-C(12)	123.0(9)
N(3)-C(11)-C(10)	115.2(7)
C(12)-C(11)-C(10)	121.7(9)
C(5)-C(6)-C(7)	121.3(9)
C(5)-C(6)-H(6)	119.4
C(7)-C(6)-H(6)	119.4
C(14)-C(13)-C(12)	119.6(10)
C(14)-C(13)-H(13)	120.2
C(12)-C(13)-H(13)	120.2
C(11)-C(12)-C(13)	117.5(10)
C(11)-C(12)-H(12)	121.2
C(13)-C(12)-H(12)	121.2

Table 7. Crystal data and structure refinement for **7**.

Formula	$[Re(C_{24}H_{21}F_3N_8O_3)(CO)_3][Cl]$
Formula weight	832.17 $gmol^{-1}$
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	*C* 2/*c*
Unit cell dimensions	*a* = 31.824(4) Å
	b = 11.2317(12) Å
	c = 16.0096(17) Å
	α = 90°.
	β = 90.604(5)°.
	γ = 90°
Volume	5722.1(11) $Å^3$
Z	8
Density (calculated)	1.932 Mg/m^3
Absorption coefficient	4.419 mm^{-1}
F(000)	3248
Crystal size	0.10 × 0.05 × 0.035 mm^3
Theta range for data collection	2.31 to 25.00°.
Index ranges	-37<=h<=37, -13<=k<=13, -18<=l<=18
Reflections collected	17938
Independent reflections	5011 [R(int) = 0.1160]
Completeness to theta = 25.00°	99.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5011 / 0 / 415
Goodness-of-fit on F^2	0.923
Final R indices [I>2sigma(I)]	R_1 = 0.0435, wR_2 = 0.0704
R indices (all data)	R_1 = 0.0935, wR_2 = 0.0806
Largest diff. peak and hole	1.332 and -0.797 e$Å^{-3}$

Table 8. Bond lengths [Å] and angles [°] for **7**.

Re(1)-C(2)	1.900(7)	C(19)-H(19A)	0.9700
Re(1)-C(1)	1.921(8)	C(19)-H(19B)	0.9700
Re(1)-C(3)	1.922(8)	C(9)-H(9A)	0.9700
Re(1)-N(1)	2.171(6)	C(9)-H(9B)	0.9700
Re(1)-N(3)	2.174(5)	C(13)-C(14)	1.372(9)
Re(1)-N(2)	2.222(5)	C(13)-C(12)	1.382(10)
F(1)-C(27)	1.347(9)	C(13)-H(13)	0.9300
C(3)-O(3)	1.150(7)	C(25)-C(26)	1.397(9)
N(3)-C(11)	1.346(7)	C(25)-C(27)	1.518(11)
N(3)-C(15)	1.348(8)	C(5)-H(5)	0.9300
N(2)-C(10)	1.491(8)	C(26)-H(26)	0.9300
N(2)-C(9)	1.514(8)	C(15)-C(14)	1.367(9)
N(2)-C(16)	1.519(8)	C(15)-H(15)	0.9300
C(2)-O(2)	1.161(7)	C(12)-H(12)	0.9300
N(1)-C(4)	1.356(8)	C(10)-H(10A)	0.9700
N(1)-C(8)	1.371(8)	C(10)-H(10B)	0.9700
N(5)-N(4)	1.331(7)	C(23)-H(23)	0.9300
N(5)-N(6)	1.337(7)	C(14)-H(14)	0.9300
O(4)-C(20)	1.218(8)		
N(4)-C(17)	1.351(8)	C(2)-Re(1)-C(1)	88.4(3)
C(11)-C(12)	1.377(9)	C(2)-Re(1)-C(3)	89.4(3)
C(11)-C(10)	1.484(9)	C(1)-Re(1)-C(3)	89.9(3)
C(7)-C(6)	1.365(9)	C(2)-Re(1)-N(1)	93.9(3)
C(7)-C(8)	1.374(10)	C(1)-Re(1)-N(1)	172.0(2)
C(7)-H(7)	0.9300	C(3)-Re(1)-N(1)	97.8(3)
F(3)-C(27)	1.312(9)	C(2)-Re(1)-N(3)	97.6(2)
O(1)-C(1)	1.145(8)	C(1)-Re(1)-N(3)	91.0(2)
O(6)-N(8)	1.222(7)	C(3)-Re(1)-N(3)	172.9(2)
C(6)-C(5)	1.359(9)	N(1)-Re(1)-N(3)	81.05(19)
C(6)-H(6)	0.9300	C(2)-Re(1)-N(2)	171.3(3)
C(22)-C(23)	1.378(9)	C(1)-Re(1)-N(2)	98.6(2)
C(22)-C(21)	1.389(9)	C(3)-Re(1)-N(2)	95.8(2)
C(22)-H(22)	0.9300	N(1)-Re(1)-N(2)	78.51(18)
C(21)-C(26)	1.383(9)	N(3)-Re(1)-N(2)	77.08(19)
C(21)-N(7)	1.421(8)	O(3)-C(3)-Re(1)	177.9(7)
C(17)-C(18)	1.384(9)	C(11)-N(3)-C(15)	118.8(6)
C(17)-C(16)	1.494(9)	C(11)-N(3)-Re(1)	115.8(4)
C(16)-H(16A)	0.9700	C(15)-N(3)-Re(1)	125.4(4)
C(16)-H(16B)	0.9700	C(10)-N(2)-C(9)	109.8(5)
C(8)-C(9)	1.497(9)	C(10)-N(2)-C(16)	109.1(5)
C(24)-C(23)	1.369(9)	C(9)-N(2)-C(16)	104.0(5)
C(24)-C(25)	1.391(10)	C(10)-N(2)-Re(1)	107.0(4)
C(24)-N(8)	1.454(9)	C(9)-N(2)-Re(1)	109.9(3)
C(4)-C(5)	1.364(10)	C(16)-N(2)-Re(1)	116.9(4)
C(4)-H(4)	0.9300	O(2)-C(2)-Re(1)	178.7(6)
N(7)-C(20)	1.345(9)	C(4)-N(1)-C(8)	116.8(6)
N(7)-H(7A)	0.8600	C(4)-N(1)-Re(1)	125.7(5)
O(5)-N(8)	1.219(8)	C(8)-N(1)-Re(1)	117.3(4)
C(18)-N(6)	1.331(8)	N(4)-N(5)-N(6)	107.0(6)
C(18)-H(18)	0.9300	N(5)-N(4)-C(17)	108.7(5)
F(2)-C(27)	1.334(9)	N(3)-C(11)-C(12)	120.9(6)
C(19)-N(6)	1.448(8)	N(3)-C(11)-C(10)	115.9(5)
C(19)-C(20)	1.517(9)	C(12)-C(11)-C(10)	123.1(5)

C(6)-C(7)-C(8)	118.4(7)
C(6)-C(7)-H(7)	120.8
C(8)-C(7)-H(7)	120.8
C(5)-C(6)-C(7)	120.9(7)
C(5)-C(6)-H(6)	119.6
C(7)-C(6)-H(6)	119.6
C(23)-C(22)-C(21)	119.5(7)
C(23)-C(22)-H(22)	120.2
C(21)-C(22)-H(22)	120.2
C(26)-C(21)-C(22)	120.5(6)
C(26)-C(21)-N(7)	122.8(7)
C(22)-C(21)-N(7)	116.6(6)
N(4)-C(17)-C(18)	108.0(6)
N(4)-C(17)-C(16)	124.1(6)
C(18)-C(17)-C(16)	127.7(6)
C(17)-C(16)-N(2)	116.1(6)
C(17)-C(16)-H(16A)	108.3
N(2)-C(16)-H(16A)	108.3
C(17)-C(16)-H(16B)	108.3
N(2)-C(16)-H(16B)	108.3
H(16A)-C(16)-H(16B)	107.4
N(1)-C(8)-C(7)	122.2(6)
N(1)-C(8)-C(9)	116.0(6)
C(7)-C(8)-C(9)	121.7(6)
O(1)-C(1)-Re(1)	174.2(6)
C(23)-C(24)-C(25)	120.0(7)
C(23)-C(24)-N(8)	117.3(7)
C(25)-C(24)-N(8)	122.6(7)
N(1)-C(4)-C(5)	123.0(7)
N(1)-C(4)-H(4)	118.5
C(5)-C(4)-H(4)	118.5
C(20)-N(7)-C(21)	128.5(6)
C(20)-N(7)-H(7A)	115.7
C(21)-N(7)-H(7A)	115.7
N(6)-C(18)-C(17)	105.0(6)
N(6)-C(18)-H(18)	127.5
C(17)-C(18)-H(18)	127.5
N(6)-C(19)-C(20)	111.8(6)
N(6)-C(19)-H(19A)	109.2
C(20)-C(19)-H(19A)	109.2
N(6)-C(19)-H(19B)	109.2
C(20)-C(19)-H(19B)	109.2
H(19A)-C(19)-H(19B)	107.9
C(8)-C(9)-N(2)	115.3(5)
C(8)-C(9)-H(9A)	108.4
N(2)-C(9)-H(9A)	108.4
C(8)-C(9)-H(9B)	108.4
N(2)-C(9)-H(9B)	108.4
H(9A)-C(9)-H(9B)	107.5
N(5)-N(6)-C(18)	111.4(6)
N(5)-N(6)-C(19)	119.8(6)
C(18)-N(6)-C(19)	128.7(6)
O(4)-C(20)-N(7)	124.3(6)
O(4)-C(20)-C(19)	122.6(7)
N(7)-C(20)-C(19)	113.1(6)
C(14)-C(13)-C(12)	119.1(7)
C(14)-C(13)-H(13)	120.4
C(12)-C(13)-H(13)	120.4
C(24)-C(25)-C(26)	119.9(6)
C(24)-C(25)-C(27)	123.0(7)
C(26)-C(25)-C(27)	117.0(7)
C(6)-C(5)-C(4)	118.6(7)
C(6)-C(5)-H(5)	120.7
C(4)-C(5)-H(5)	120.7
C(21)-C(26)-C(25)	119.2(7)
C(21)-C(26)-H(26)	120.4
C(25)-C(26)-H(26)	120.4
O(6)-N(8)-O(5)	123.7(7)
O(6)-N(8)-C(24)	117.9(7)
O(5)-N(8)-C(24)	118.0(7)
N(3)-C(15)-C(14)	122.7(6)
N(3)-C(15)-H(15)	118.7
C(14)-C(15)-H(15)	118.7
C(11)-C(12)-C(13)	119.7(7)
C(11)-C(12)-H(12)	120.1
C(13)-C(12)-H(12)	120.1
C(11)-C(10)-N(2)	112.4(5)
C(11)-C(10)-H(10A)	109.1
N(2)-C(10)-H(10A)	109.1
C(11)-C(10)-H(10B)	109.1
N(2)-C(10)-H(10B)	109.1
H(10A)-C(10)-H(10B)	107.9
C(24)-C(23)-C(22)	120.8(7)
C(24)-C(23)-H(23)	119.6
C(22)-C(23)-H(23)	119.6
F(3)-C(27)-F(2)	109.2(7)
F(3)-C(27)-F(1)	106.1(7)
F(2)-C(27)-F(1)	105.1(7)
F(3)-C(27)-C(25)	113.6(7)
F(2)-C(27)-C(25)	111.9(7)
F(1)-C(27)-C(25)	110.3(7)
C(15)-C(14)-C(13)	118.7(7)
C(15)-C(14)-H(14)	120.6
C(13)-C(14)-H(14)	120.6

References

1. C. P. Casey, M. W. Meszaros, S. M. Neumann, I. G. Cesa and K. J. Haller, *Organometallics*, 1985, 4, 143-149.
2. S. Huang, R. J. Clark and L. Zhu, *Org. Lett.*, 2007, 9, 4999-5002.
3. M. M. Sa, M. D. Ramos and L. Fernandes, *Tetrahedron*, 2006, 62, 11652-11656.
4. H. Hope, *Progress in Inorganic Chemistry, Vol 41*, 1994, 41, 1-19.
5. SMART., 2001.
6. SAINTPlus:, 2003/2004.
7. SADABS:, 2004.
8. SHELXTL:, 2004.