ELECTRONIC SUPPLEMENTARY INFORMATION

pH-Driven dynamic stereoinduction: Epimerization upon dimerization in rhenium(I) complexes

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Materials and Methods.

^1H NMR spectra were recorded at 400.13 or 300.13 MHz, ^{13}C NMR spectra were recorded at 100.61 or 75.78 MHz, and ^{31}P NMR at 161.98 MHz. Chemical shifts are reported in ppm and referenced to the solvent peak and to a H_3PO_4 aqueous solution (85%) for ^{31}P NMR experiments. The temperature of the NMR was calibrated with methanol and ethylene glycol standards. All solvents were purified by standard techniques.[1] Reactions were performed under nitrogen in Schlenk flasks. All filtrations were performed through Celite under nitrogen.

Experimental details for the preparation of compounds 1, 2, 3, 6 and 7.

- **Synthesis of *fac*-[ReBr(CO)$_3$(pyC(H)=O)], (3)**

Pyridine-2-carboxaldehyde (0.268 g, 2.50 mmol) is solved in 50 ml of hexane and then [ReBr(CO)$_5$] (1 g, 2.46 mmol) is added. The reaction mixture was refluxed for 10 hours. A brownish precipitate is formed, filtered, washed with hexane (3 x 15 ml), and dried under high vacuum. Yield: 1.090 g (95%).

IR (CH_2Cl_2, cm^{-1}): 2033, 1933, 1911 (CO), 1617 (C=O).

IR (Nujol, cm^{-1}): 1617 (C=O).

^1H NMR (298K, 300.13 MHz, Me_2CO-d_6): 10.75 [1H, s, pyC(*H*)=O], 9.23 [1H, d(*J*=5 Hz), py*H6*], 8.88 [1H,d(*J*=8 Hz), py*H3*], 8.55 [1H, td(*J*=8, 1 Hz), py*H4*], 8.12 [1H, m, py*H5*].

Elemental Analysis: Found: C, 23.82; H, 1.02; N, 3.09; Calc. for $C_9H_5BrNO_4Re$: C, 23.64; H, 1.10; N, 3.06.

Crystalization conditions: CH_2Cl_2/ hexane at -20ºC.

- **Synthesis of *fac*-[Re(CO)$_3$κ$_3$(N,O,O')-{py-CH(OH)CH$_2$COCH$_3$}][OTf], (1)**

To a solution of *fac*-[ReBr(CO)$_3$(pyC(H)=O)] (**3**) (0.300 g, 0.656 mmol) in 30 ml of acetone, AgOTf (0.169 g, 0.656 mmol) was added. The resulting suspension was stirred for 2h in the dark. Then solvent was removed and the solid extracted with CH_2Cl_2.Hexane is added and a white precipitate is formed, which is subsequently filtered. Yield: 0.337 g (88%).

IR (Me_2CO, cm^{-1}): 2039, 1929, 1918 (CO).

IR (CH_2Cl_2, cm^{-1}): 2045, 1944, 1921 (CO), 1663 (C=O).

^1H NMR (298K, 400.13 MHz, CD_2Cl_2): 8.87 [1H, d(*J*=5 Hz), py*H6*], 8.10 [1H, td(*J*=8, 2 Hz), py*H4*], 7.71 [1H, d(*J*=8 Hz), py*H3*], 7.52 [1H, m, py*H5*], 5.83 [1H, dd(*J*=6, 2 Hz), C*H*], 3.95 [1H, dd(*J*=21, 6 Hz), C*H*2], 3.32 [1H, dd(*J*=21, 2 Hz), C*H*2], 2.32 [3H, s , C*H*3], 1.90 [1H, br, O*H*].

^1H NMR (323K, 400.13 MHz, Me_2CO-d_6): Isomer ratio **1**/**4**/**5**=60/20/20. Major isomer (**1**): 11.34 [1H, br, O*H*], 9.05 [1H, d(*J*=5 Hz), py*H6*], 8.29 [1H, td(*J*=8, 2 Hz), py*H4*], 8.03 [1H,

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[1] Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, 1996.

d(*J*=7 Hz), py*H3*], 7.73 [1H, m, py*H5*], 6.08 [1H, d(*J*=5 Hz), C*H*], 4.12 [1H, dd(*J*=21, 5 Hz), C*H*2], 3.89 [1H, d(*J*=21 Hz), C*H*2], 2.43 [3H, s, C*H*3].

Minor isomers (**4**, **5**): 10.04 (**4**+**5**) [2H, br, O*H*], 8.95 (**4**+**5**) [2H, m, py*H6*], 8.22 (**4**+**5**) [2H, m, py*H4*], 7.85 (**4**+**5**) [2H, m, py*H3*], 7.66 (**4**+**5**) [2H, m, py*H5*], 6.28 (**4**) [1H, m, C*H*], 6.12 (**5**) [1H, m, C*H*], 3.51-3.41 (**4**+**5**) [3H, m, C*H*2], 3.28 (**4**) [1H, dd (19, 3 Hz), C*H*2], 2.23 (**4**) [3H, s, C*H*3], 2.19 (**5**) [3H, s, C*H*3].

^{13}C NMR (298K, 75.78 MHz, Me_2CO-d_6): 224.81 [C=O], 225.93 [C=O], 195.81-194.90 [m, 6CO], 163.26 [pyC2], 162.52 [pyC2], 162.12 [pyC2], 153.82 [pyC6], 153.42 [pyC6], 153.13 [pyC6], 142.86 [pyC4], 141.95 [pyC4], 141.73 [pyC4], 127.13 [pyC5], 127.03 [pyC5], 126.75 [pyC5], 124.08 [pyC3], 123.95 [pyC3], 123.08 [pyC3], 78.12 [CH], 77.83 [CH], 76.56 [CH], 50.06 [CH2], 49.70 [CH2], 48.03 [CH2], 32.23 [m, CH3].

Elemental Analysis: Found: C, 26.98; H, 1.77; N, 2.35. Calc. for $C_{13}H_{11}F_3NO_8ReS$: C, 26.71; H, 1.90; N, 2.40.

Crystalization conditions: CH_2Cl_2/ hexane at -20ºC.

- **Synthesis of *fac*-$[Re(CO)_3\mu(O)\kappa_2(N,O)\text{-}(pyCH(O)CH_2COCH_3]_2$ (2)**

To a solution of *fac*-$[Re(CO)_3\kappa_3(N,O,O')\text{-}\{py\text{-}CH(OH)CH_2COCH_3\}][OTf]$ (**1**) (0.200 g, 0.342 mmol) in 30 ml of acetone, an excess of K_2CO_3 (0.500 g, 3.618 mmol) is added. The solution was stirred for 2 h at room temperature. Then solvent was removed and solid was solved in CH_2Cl_2. Hexane was added to the transparent solution and solvent was evaporated to obtain compound **2** as a white solid. Yield: 0.126 g (85%).

IR (CH_2Cl_2, cm^{-1}): 2030, 2013, 1924, 1891 (CO), 1720 (C=O).

^{1}H NMR (298K, 400.13 MHz, Me_2CO-d_6): 8.85 [2H, d(*J*=5 Hz), py*H6*], 7.73 [2H, td(*J*=8, 2 Hz), py*H4*], 7.41 [2H, m, py*H5*], 7.13 [2H, d(*J*=8 Hz), py*H3*], 5.73 [2H, dd(*J*=10, 4 Hz), C*H*], 2.77 [2H, dd(*J*=15, 10 Hz), C*H*2], 2.39 [2H, dd (*J*=15, 4 Hz), C*H*2], 2.26 [6H, s, C*H*3].

^{13}C{1H} NMR (298K, 100.61 MHz, Me_2CO-d_6): 203.78 [C=O], 198.16 [CO], 197.96 [CO], 197.38 [CO], 167.51 [pyC2], 151.15 [pyC6], 139.90 [pyC4], 124.85 [pyC5], 120.33 [pyC3], 84.71 [CH], 50.67 [CH_2], 30.35 [CH_3].

Elemental Analysis: Found: C, 33.21; H, 2.44; N, 3.07; Calc. for $C_{24}H_{20}N_2O_{10}Re_2$: C, 33.18; H, 2.32; N, 3.22.

Crystalization conditions: CH_2Cl_2/ hexane at -20ºC.

- **Synthesis of *fac*-[Re(PPh3)(CO)3(pyCH(OH)-CH2COCH3[OTf], (6a and 7a)**

To a solution of *fac*-[Re(CO)3κ3(N,O,O')-{py-CH(OH)CH2COCH3}][OTf] (**1**) (0.100 g, 0.171 mmol) in 25 mL of CH_2Cl_2, PPh_3 (0.045 g, 0.171 mmol) is added. The solution is stirred at room temperature for 30 minutes. Then hexane is added and the solvent slowly evaporated. A mixture of compounds **6a** and **7a** is obtained as a white solid. Yield: 0.132 g (91%).

IR (CH_2Cl_2, cm^{-1}): 2042, 1954, 1918 (CO), 1723 (C=O).

^{1}H NMR (298K, 400.13 MHz, CD_2Cl_2): Isomer **6a**, 8.39 [1H, d(*J*=6 Hz), py*H6*], 7.72 [1H, t(*J*=8), py*H4*], 7.45-7.01 [17H, m, PPh3, py*H3*, py*H5*], 5.05 [1H, t(*J*=5 Hz), C*H*], 3.33 [1H, dd(*J*=19, 4 Hz), C*H*2], 3.16 [1H, dd(*J*=19, 6 Hz), C*H*2], 2.17[3H, s, C*H*3]. Isomer **7a**, 7.94 [1H, d(*J*=5 Hz), py*H6*], 7.70 [1H, t(*J*=8 Hz), py*H4*], 7.45-7.01 [17H, m, PPh3, py*H3*, py*H5*], 5.45 [1H, m, C*H*], 2.89 [2H, d(*J*=4 Hz), C*H*2], 1.90 [3H, s, C*H*3].

^{1}H NMR (298K, 400.13 MHz, Me2CO-*d6*): Isomer **6a**, 9.56 [1H, br, O*H*], 8.59 [1H, d(*J*=6 Hz), py*H6*], 7.96 [1H, td(*J*=8, 1 Hz), py*H4*], 7.71-7.21 17H, [m, PPh3, py*H3*, py*H5*], 5.15 [1H, t(*J*=5 Hz), C*H*], 3.49 [2H, dd(*J*=19, 5 Hz), C*H*2], 2.12[3H, s, C*H*3]. Isomer **7a**, 10.04 [1H, br, O*H*], 8.21 [1H, d(*J*=6 Hz), py*H6*], 8.05 [1H, td(*J*=8, 1 Hz), py*H4*], 7.71-7.21 [17H, m, PPh3, py*H3*, py*H5*], 5.83 [1H, m, C*H*], 3.20 [1H, dd(*J*=19, 4 Hz), C*H*2], 2.64 [1H, dd(*J*=19, 7 Hz), C*H*2], 1.91 [3H, s, C*H*3].

^{13}C NMR (298K, 100.61 MHz, Me2CO-*d6*): Isomer **6a**, 202.98 [C=O], 194.00 [d(8), CO], 193.58 [d(6) CO] 189.66 [d(17), CO], 161.12 [pyC2], 152.28 [pyC6], 139.96 [pyC4], 133.8-129.2 [m, C6H5], 125.68 [pyC5]121.92 [pyC3], 77.66 [CH], 47.10 [CH2], 28.77 [CH3]. Isomer **7a**, 203.56 [C=O], 193.78 [d(8), CO], 193.51 [d(6), CO], 188.96 [d(16), CO], 160.05 [pyC2], 152.09 [pyC6], 139.91 [pyC4], 133.8-129.2 [m, C6H5], 126.04 [pyC5], 122.71 [pyC3], 78.46 [CH], 47.98 [CH2], 28.90 [CH3].

^{31}P NMR (298K, 161.98 MHz, CD_2Cl_2): Isomer **6a**, 20.40 (s). Isomer **7a**, 23.23 (s).

^{31}P NMR (298K, 161.98 MHz, Me_2CO-d_6): Isomer **6a**, 20.01 (s). Isomer **7a**, 23.37(s).

Elemental Analysis: Found: C, 44.12; H, 3.37; N, 1.69; Calc. for $C_{31}H_{26}F_3NO_8PReS$: C, 43.97; H, 3.09; N, 1.65.

Crystalization conditions: CH_2Cl_2/ hexane at -20ºC.

- **Synthesis of *fac*-[Re(CO)$_3$(CNXyl)(pyCH(OH)-CH$_2$COCH$_3$][OTf], (6b and 7b)**

To a solution of *fac*-[Re(CO)$_3$κ$_3$(N,O,O')-{py-CH(OH)CH$_2$COCH$_3$}][OTf] (**2**) (0.100 g, 0.171 mmol) in 25 ml of CH_2Cl_2, 2,6-dimethylphenylisocyanide (0.022 g, 0.171 mmol) was added. The solution was stirred at room temperature for 30 minutes. Then hexane is added, solvent is removed and a white solid is obtained. Yield: 0.104 g (85%).

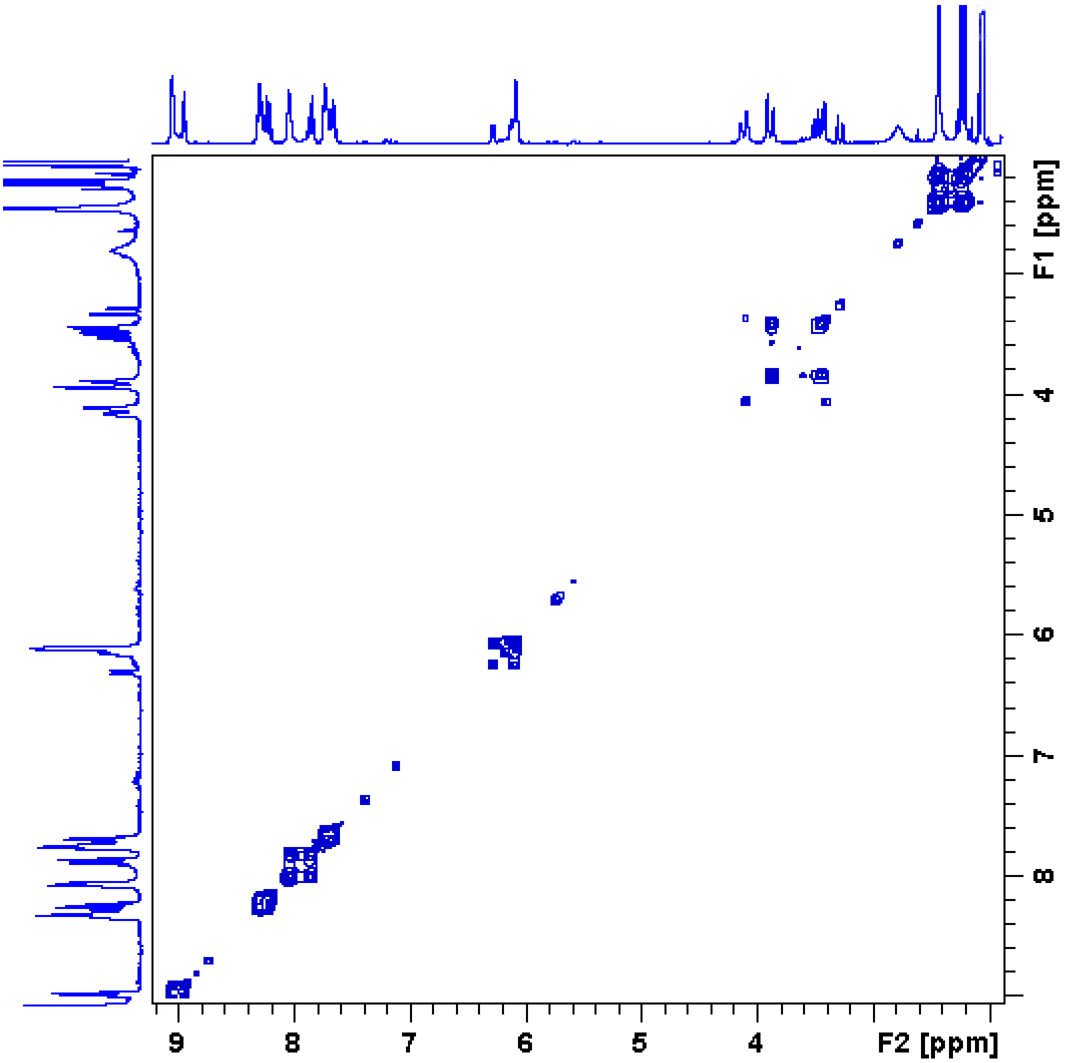
IR (CH_2Cl_2, cm^{-1}): 2173 (CN), 2043, 1971, 1931 (CO), 1719 (C=O).

^{1}H NMR (298K, 300.13 MHz, Me_2CO-d_6): Isomer **6b**, 10.13 [1H, br, O*H*], 9.08 [1H, d(*J*=5 Hz), py*H6*], 8.24[1H, td(*J*=8, 1 Hz), py*H4*], 7.88 [1H, d(*J*=8 Hz), py*H3*], 7.71 [1H, t(*J*=7 Hz), py*H5*], 7.32 [1H, m, C6*H*3], 7.21 [2H, m, C6*H*3], 6.12 [1H, m, C*H*], 3.53 [2H, m, C*H*2], 2.26 [6H, s, 2C*H*3], 2.21 [3H, s, COC*H*3]. Isomer **7b**, 10.15 [1H, br, O*H*], 9.08 [1H, d(*J*=5 Hz), py*H6*], 8.23 [1H, td(*J*=8, 1 Hz), py*H4*], 7.85 [1H, d(*J*=8 Hz), py*H3*], 7.71 [1H, t(*J*=7 Hz), py*H5*], 7.32 [1H, m, C6*H*3], 7.24 [2H, m, C6*H*3], 5.98 [1H, t(*J*=5 Hz), C*H*], 3.61 [2H, m, C*H*2], 2.37 [6H, s, 2C*H*3], 2.16 [3H, s, COC*H*3].

Elemental Analysis: Found: C, 36.63; H, 2.71; N 3.81; Calc. for $C_{22}H_{20}F_3N_2O_8ReS$: C, 36.9; H, 2.82; N, 3.91.

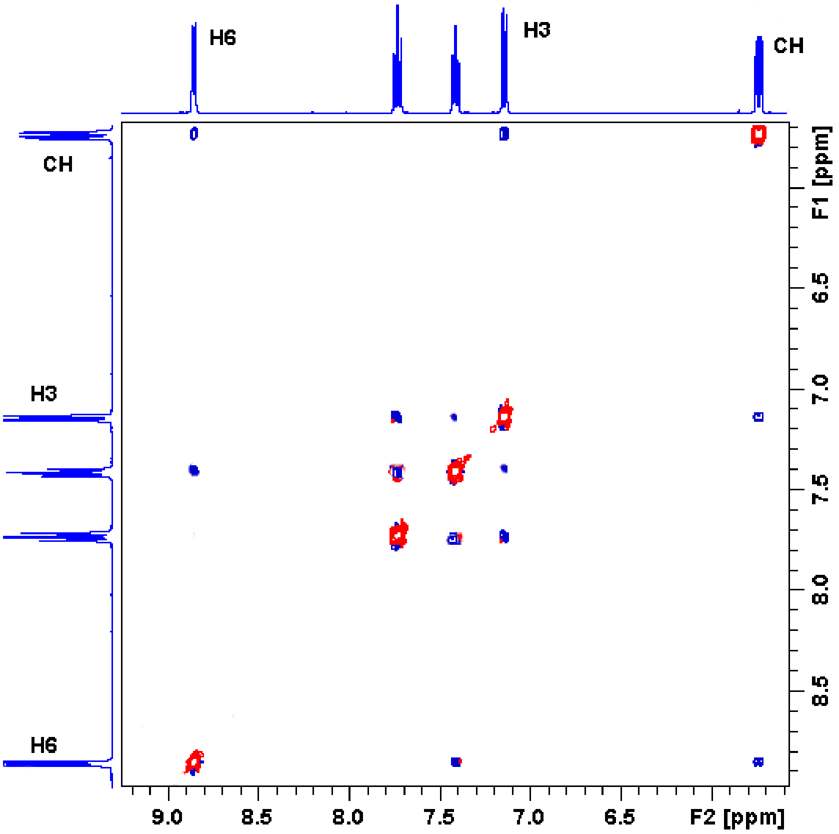
Crystalization conditions: CH_2Cl_2/ hexane at -20ºC.

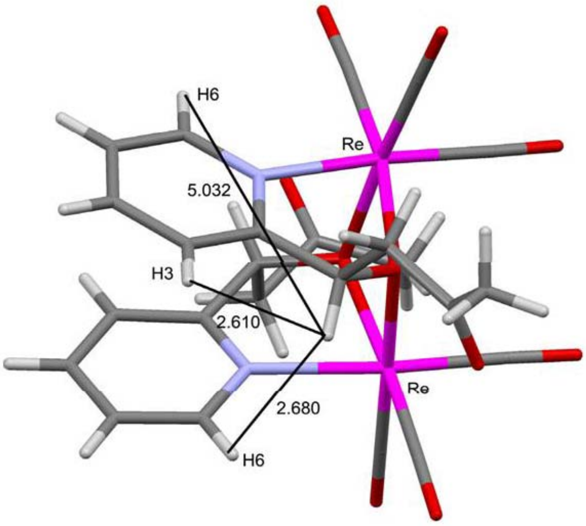
2D EXSY of compound 1 in Me$_2$CO-d_6



2D NOESY of compound 2 in Me_2CO-d_6

Although molecule **2** is completely symmetrical and therefore the same ^{1}H NMR peaks are observed for both ligand molecules of the dimer, there are NOE cross peaks between CH and H6 and H3 which is impossible within the same ligand molecule and therefore confirms the *cisoid* configuration in solution.





Crytallographic data of compounds 1, 2, 6a, 7a, and 7b

Intensity measurement was made with a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo Kα X-radiation and a CCD area detector. Raw frame data were integrated with the SAINT program.[2] A semi-empirical absorption correction was applied with the program SADABS.[3] The structures were solved by direct methods with SIR2002,[4] under WINGX,[5] and refined against F^2 with SHELXTL.[6] All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. Calculations were made with SHELXTL and PARST,[7] and graphics were made with SHELXTL and MERCURY.[8]

Compound 1: $C_{13}H_{11}F_3NO_8ReS$, M = 584.49, monoclinic, a = 10.239(3) Å, b = 13.250(3) Å, c = 13.777(4) Å, α = 90.00°, β = 98.535(6)°, γ = 90.00°, V = 1848.3(8) Å^3, T = 293(2) K, space group $P2_1/n$, Z = 4, μ(MoKα) = 6.757 mm^{-1}, 10273 reflections measured, 3375 independent reflections (R_{int} = 0.0304). Final residues R_1 = 0.0202 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.0493 (all data). G.O.F (on F^2) = 1.023.

Compound 2: $C_{25}H_{22}Cl_2N_2O_{10}Re_2$, M = 953.75, triclinic, a = 9.771(4) Å, b = 10.788(5) Å, c = 16.627(7) Å, α = 76.752(7)°, β = 76.379(7)°, γ = 64.443(7)°, V = 1520.3(11) Å^3, T = 298(2) K, space group $P\bar{1}$, Z = 2, μ(MoKα) = 8.186 mm^{-1}, 15221 reflections measured, 7427 independent reflections (R_{int} = 0.0562). Final residues R_1 = 0.0391 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.0976 (all data). G.O.F (on F^2) = 0.982.

Compound 6a: $C_{31}H_{26}F_3NO_8PReS$, M = 846.76, triclinic, a = 10.435(5) Å, b = 10.745(5) Å, c = 17.496(9) Å, α = 72.785(8)°, β = 89.968(8)°, γ = 63.120(7)°, V = 1650.6(14) Å^3, T = 298(2) K, space group $P\bar{1}$, Z = 2, μ(MoKα) = 3.859 mm^{-1}, 13346 reflections measured, 5998 independent reflections (R_{int} = 0.0251). Final residues R_1 = 0.0240 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.0682 (all data). G.O.F (on F^2) = 1.061.

Compound 7a: $C_{32}H_{28}Cl_2F_3NO_8PReS$, M = 931.68, monoclinic, a = 16.0976(19) Å, b = 11.2626(14) Å, c = 19.588(2) Å, α = 90.00°, β = 96.309(2)°, γ = 90.00°, V = 3529.7(7) Å^3, T = 298(2) K, space group $P2_1/c$, Z = 4, μ(MoKα) = 3.764 mm^{-1}, 29542 reflections measured, 6948 independent reflections (R_{int} = 0.0932). Final residues R_1 = 0.0476 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.1499 (all data). G.O.F (on F^2) = 1.027.

Compound 7b: $C_{22.50}H_{21}ClF_3N_2O_8ReS$, M = 758.12, monoclinic, a = 21.040(13) Å, b = 19.262(12) Å, c = 14.903(9) Å, α = 90.00°, β = 109.330(8)°, γ = 90.00°, V = 5699(6) Å^3, T = 298(2) K, space group $C2/c$, Z = 8, μ(MoKα) = 4.497 mm^{-1}, 27620 reflections measured, 6995 independent reflections (R_{int} = 0.0480). Final residues R_1 = 0.0341 ($I > 2\sigma(I)$). $wR(F^2)$= 0.0983 (all data). G.O.F (on F^2) = 1.063.

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[2] SAINT+. SAX area detector integration program. Version 6.02. Bruker AXS, Inc. Madison, WI, 1999.

[3] G. M. Sheldrick, SADABS, Empirical Absorption Correction Program. University of Göttingen: Göttingen, Germany, 1997.

[4] M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidory and R. Spagna, SIR2002, A program for automatic solution and refinement of crystal structures. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115-119.

[5] L.J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837-838.

[6] G. M Sheldrick *Acta Cryst.* 2008, **A64**, 112-122. G. M. Sheldrick, SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data. Version 5.1. Bruker AXS, Inc. Madison, WI, 1998.

[7] *(a)* M. Nardelli, *Comput. Chem.*, 1983, **7**, 95-97. *(b)* M. Nardelli, *J. Appl. Crystallogr.*, 1995, **28**, 659.

[8] MERCURY: a) I. J. Bruno, J. C. Cole, P. R. Edgington, M. K. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr.*, 2002, **B58**, 389-397. b) C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457.

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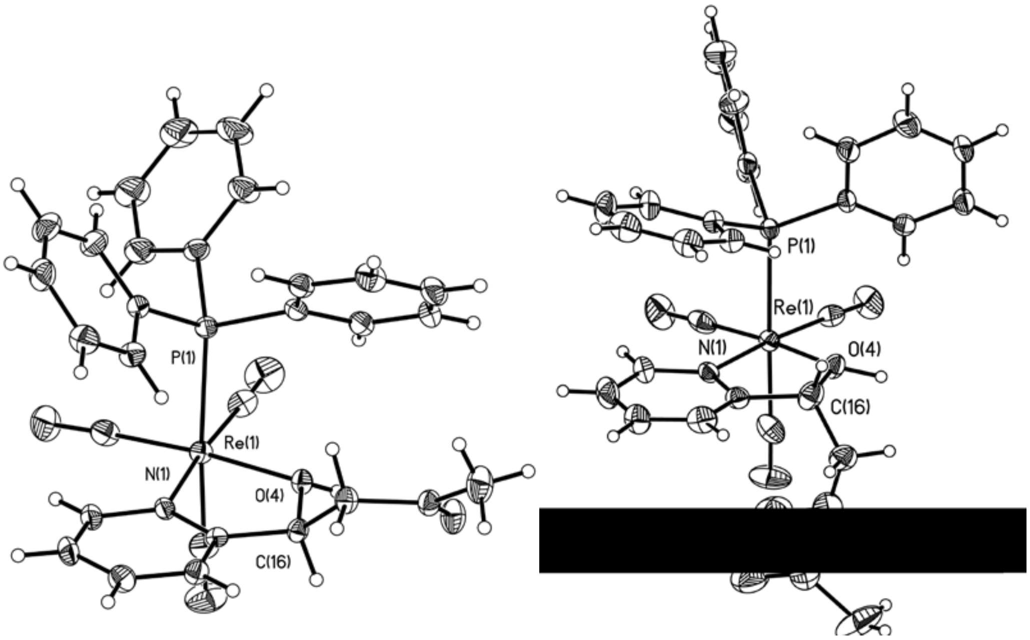
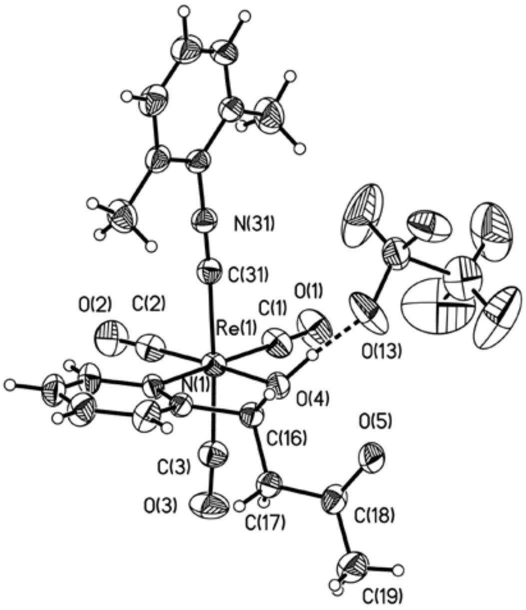


[redacted]

Perspective view of the two diastereomers **6a** (left) and **7a** (right) of the triphenylphosphine complex. It can be seen that they have the same configuration at the metal, and opposite configuration at C(16). The triflate anions in both structures, and a molecule of solvent CH_2Cl_2 in the structure of **7a** have been omitted for clarity.



Perspective view of the isocyanide complex **7b**, showing the H-bonding of the triflate anion to the cation. Solvent CH_2Cl_2 (one-half molecule) has been omitted for clarity.