



## Supporting Information

for

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## Efficient Asymmetry Generation in the Synthesis of Oxo-Rhenium(V) Complex $cis$ -[ReOCl<sub>2</sub>{OCMe<sub>2</sub>CMe<sub>2</sub>OP(OCMe<sub>2</sub>CMe<sub>2</sub>O)}py]

W. K. Rybak,\* A. Skarżyńska, T. Głowiak, in *Angew. Chem.*

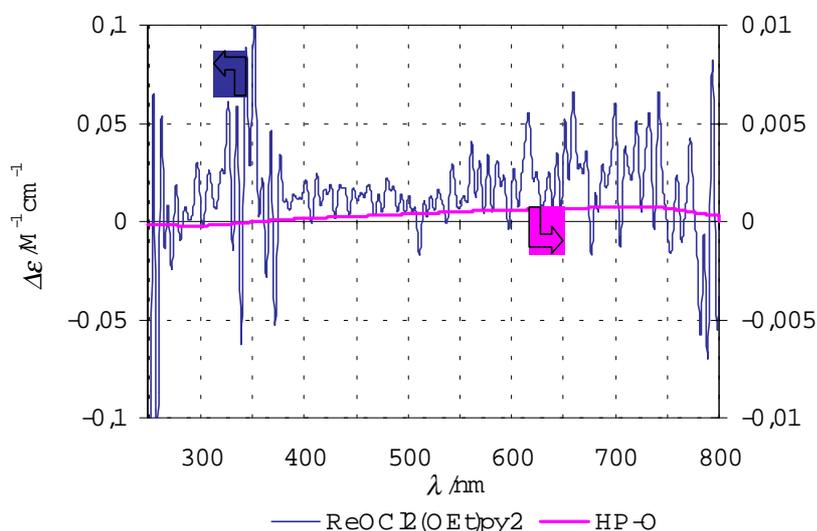


Fig. 1. Silent CD spectra of the starting substrates,  $trans$ -[ReOCl<sub>2</sub>(OEt)py<sub>2</sub>] ( $8.36 \times 10^{-4}$ M) and spirophosphorane HP(OCMe<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub> (HP-O;  $1.02 \times 10^{-3}$ M) in acetonitrile solution (20 °C, 0.5 cm cell), used for asymmetric synthesis of  $cis$ -[ReOCl<sub>2</sub>{OCMe<sub>2</sub>CMe<sub>2</sub>OP(OCMe<sub>2</sub>CMe<sub>2</sub>O)}py].

### *Cis-trans isomerization (racemization) reaction:*

$cis$ -C-[ReOCl<sub>2</sub>{OCMe<sub>2</sub>CMe<sub>2</sub>OP(OCMe<sub>2</sub>CMe<sub>2</sub>O)}py] (0.203 g, 0.33 mmol), finely ground polycrystalline dextrorotatory sample (+99% ee), was added to toluene (25 cm<sup>3</sup>). The mixture was boiled and vigorously stirred for 5 h. After cooling to room temperature, the remaining solid was filtered and washed with toluene and ethyl ether affording the starting  $cis$ -C-complex (0.181 g, 89.3% with ee +99%).

*Anal.* Calc. for C<sub>17</sub>H<sub>29</sub>O<sub>5</sub>Cl<sub>2</sub>NPRe: C, 33.17; H, 4.75; N, 2.27; Cl, 11.51; Found: C, 33.7; H, 4.55; N, 2.3; Cl, 11.8; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, δ) 0.88, 1.00, 1.21, 1.34, 1.46, 1.47, 1.54, 1.57 (s's, 24H, CH<sub>3</sub>); 7.59 (t, 7 Hz, 2H, aryl), 7.87 (t, 8 Hz, 1H, aryl), 8.92 (d, 5 Hz, 2H, aryl); <sup>31</sup>P{H} NMR 91.01 (s).

The mother liquor was evaporated to dryness, the solid washed with hexane to get pure  $trans$ -[ReOCl<sub>2</sub>{OCMe<sub>2</sub>CMe<sub>2</sub>OP(OCMe<sub>2</sub>CMe<sub>2</sub>O)}py] (0.0214 g, 10.5%).

*Anal.* Found: C, 33.5; H, 4.65; N, 2.52; Cl, 11.9; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, δ) 1.14, 1.41, 1.52, 1.60, (s's, 24H, CH<sub>3</sub>); 7.66 (t, 7 Hz, 2H, aryl), 7.98 (t, 8 Hz, 1H, aryl), 8.84 (m, 2H, aryl); <sup>31</sup>P{H} NMR 93.06 (s).

The same reaction conditions applied for the starting  $cis$ -*rac*-complex affording  $cis$ -*rac*- (0.167 g, 82.2% with ee 0%) and  $trans$ -complex (0.0355 g, 17.5%).

No further conversions were observed for either  $cis$ -C- or  $cis$ -*rac*- complexes after prolonged reaction time (20 h).

Similar conditions were applied for reverse isomerization except for the reaction time. *trans*-[ReOCl<sub>2</sub>{OCMe<sub>2</sub>CMe<sub>2</sub>OP(OCMe<sub>2</sub>CMe<sub>2</sub>O)}py] (0.203 g, 0.33 mmol), was vigorously stirred in boiling toluene (25 cm<sup>3</sup>) for 2 h. After cooling to room temperature, the obtained solid was filtered and washed with toluene and ethyl ether affording the *cis-rac*-complex (0.147 g, 72.7%, with *ee* 0%). The seeded experiments were conducted under the same reaction conditions, save for addition at the beginning the finely grounded *cis-C*-complex (2%, *ee* +99%) as seeds, providing *cis-C*-complex (0.164 g, 80.7%, with *ee* +48%). No further conversions were observed after prolonged reaction time (5 h) and reaction seemed to be completed during 1h.

The evolution of the *trans*-complex from the decay of *cis-C*-complex can be also graphically depicted in Figure 2. The observed closely related rates of the optical activity (*ee*) decay and growth of the *trans*-complex concentration in reaction mixture reinforce the conclusion about *cis-trans* racemization mechanism operating in the system.

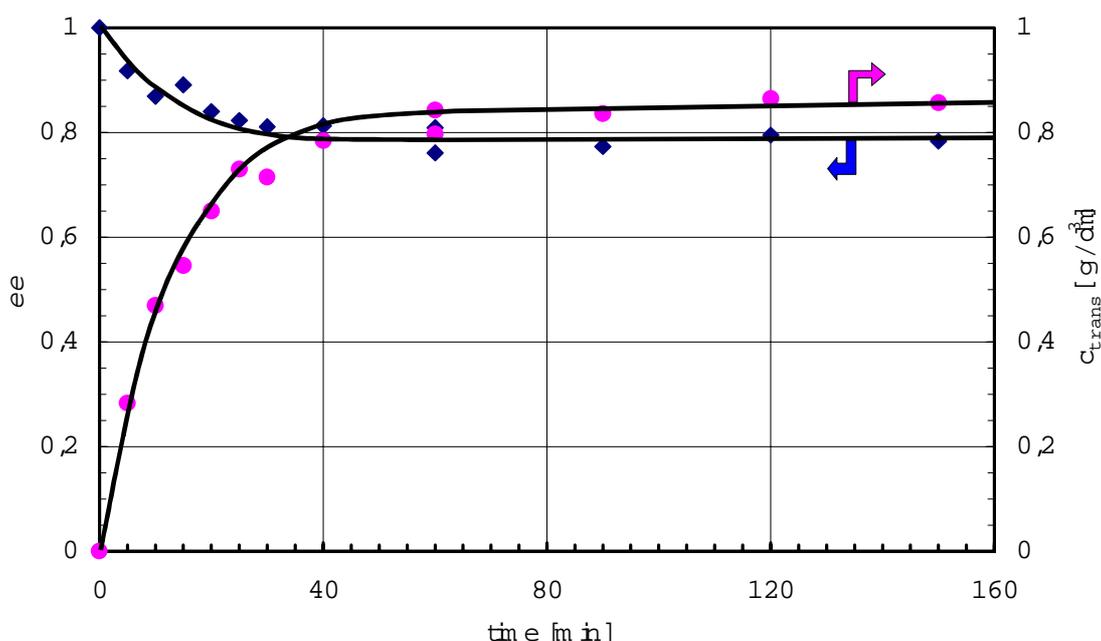


Fig. 2. Isomerization of *cis-C*-[ReOCl<sub>2</sub>{OCMe<sub>2</sub>CMe<sub>2</sub>OP(OCMe<sub>2</sub>CMe<sub>2</sub>O)}py] (0.004 g, 0.0066 mmol, *ee* +99%) in toluene (1 cm<sup>3</sup>) at 110 °C. Time dependence of optical activity *ee* (blue) of the sample and concentration of the *trans*-complex (red) in toluene solution. The ultimate concentration 0.86 g/dm<sup>3</sup> of the *trans*-complex corresponds to 0.788 *ee* of the entire sample.