Supporting Information 1

Air-stable Catalysts for Highly Efficient and Enantioselective Hydrogenation of Aromatic Ketones

Jing Wu, Hua Chen, Waihim Kwok, Rongwei Guo, Zhongyuan Zhou,

Chihung Yeung,^{*} Albert S. C. Chan^{*}

*Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis and
Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong*

Crystallographic Procedures. Orange crystals of *trans*-[RuCl₂{(R)-Tol-P-Phos}{(R,R)-DPEN}][*(R,RR)*-**2b**] were grown by diffusion of hexane to a toluene solution of the complex at ambient temperature. A single crystal with dimensions of 0.30 × 0.26 × 0.26 mm³ was mounted on a Bruker CCD area detector diffractometer using MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) from generator operating at 50 kV, 30 mA condition. The intensity data of compound (*R,RR*)-**2b** were collected in range of $2\theta = 3$ to 55 degree, oscillation frames of ϕ and ω in the range of 0 to 180 degree. Frames of 1321 were taken in 4 shell. An empirical absorption correction of SADABS (Sheldrick, 1996) program based on Fourier coefficient fitting was applied. The crystal system is monoclinic. Space group is *C*2 (No. 5) with cell parameters: $a = 25.073(3)$, $b = 17.012(3)$, $c = 13.935(2) \text{ \AA}$, $V = 5942.6(16) \text{ \AA}^3$, $\beta = 91.307(4)^\circ$, $Z = 4$, $\rho(\text{calcd}) = 1.213 \text{ Mg m}^{-3}$, $\mu = 0.451 \text{ mm}^{-1}$, $FW = 1084.97$, $F(000) = 2248$.

The crystal structure of compound (*R,RR*)-**2b** was determined by the direct method (or Patterson function) which yielded the positions of part of non-hydrogen atoms and subsequent Difference Fourier Syntheses were employed to locate all of the remaining non-hydrogen atoms which did not show up in the initial structure. Hydrogen atoms were located basing on Difference Fourier Syntheses connecting geometrical analysis. All of non-hydrogen atoms were refined

anisotropically with weight function $W = 1/[\sigma^2(F_o^2) + 0.1000p]^2 + 0.0000p]$, where $p = (F_o^2 + 2F_c^2)/3$ were refined. And all of hydrogen atoms were refined with fixed individual displacement parameters. All experiment and computation were performed on a Bruker CCD Area Detector Diffractometer and PC computer with program of Bruker Smart and Bruker SHELXTL packages.

Figure S1 ORTEP drawing of the complex (*R,RR*)-**2b** with numbering schemes. All hydrogen atoms except for the amino and methine protons of DPEN have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru (1) – Cl (1) = 2.406 (9), Ru (1) – Cl (2) = 2.429 (8), Ru (1) – P (1) = 2.267 (8), Ru (1) – P (2) = 2.277 (8), Ru (1) – N (1) = 2.141 (3), Ru (1) – N (2) = 2.179 (3), Cl (1) – Ru (1) – Cl (2) = 166.06 (3), P (1) – Ru (1) – P (2) = 94.36 (3), N (1) – Ru (1) – N (2) = 77.82 (10)

The molecular structure of complex (*R,RR*)-**2b** (Figure S1) was unambiguously determined as a distorted octahedral geometry around the ruthenium center. The dihedral angle of 3.2° between the P(1)/Ru(1)/P(2) and N(1)/Ru(1)/N(2) planes revealed this slight distortion. The metal center was ligated by two neutral phosphorus atoms and two neutral nitrogen atoms on the equatorial plane. Both Tol-P-Phos and DPEN chelate ligands coordinated to Ru adopting a distorted skew boat conformation of λ helicity. A dihedral angle θ of 70.1° between the least-squares planes of the two pyridyl planes was observed.