

*Electronic Supplementary Information for*  
**Organometallic crystal engineering of [(1,4- and 1,3-hydroquinone)Rh(P(OPh)<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>  
by charge assisted hydrogen bonding**

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**Synthetic Procedure and Characterization of the New Materials**

**General :** All reactions were carried out under N<sub>2</sub> in flame-dried glassware. HPLC grade THF and Diethyl Ether solvents were used as received. [Rh(COD)Cl]<sub>2</sub> was provided by Strem Chemicals. The <sup>1</sup>H NMR spectra were recorded by Bruker(300MHz) spectrometers. X-ray data were collected by Bruker APEX. Elementary analyses were performed by Quantitative Technologies Inc.(QTI in New Jersey )

**1. Synthesis of  $\eta^6$ -1,4-hydroquinone Rh[bis(triphenylphosphite)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> :** After flame drying the glassware, [Rh(P(OPh)<sub>3</sub>)<sub>2</sub>Cl]<sub>2</sub> (0.36g, 0.24mmol) and AgBF<sub>4</sub> (0.11g, 0.56mmol) were mixed for 1h at room temperature in methylene chloride(5mL). While stirring, a white precipitate was formed on the bottom of the glassware. 1,4-hydroquinone (0.10g, 0.91mmol) was added to the reaction mixture. After stirring for 2h at r.t., the solvent was removed using rotary evaporator. The residue was dissolved in methylene chloride(3mL) and slowly dropped to ethereal solution through the Celite pad. The formed yellow solid in ether was collected by filter and washed with diethyl ether (10mL, three times). The isolated yield was 71% (0.31g, 0.34mmol). **To get the crystals :**  $\eta^6$ -1,4-hydroquinone Rh[bis(triphenylphosphite)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (30mg) was dissolved in methylene chloride(1.0mL) in 5mL-vial. Diethyl ether (3mL) was carefully added to upper layer. The solution stands in refrigerator for 3 days. The reddish-yellow crystals were formed on the wall of vial.

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) :  $\delta$  7.36( t, J = 7.8Hz, protons in OPh, 12H) 7.26 ( t, J = 7.6Hz, protons in OPh, 6H), 7.02 (d, J= 8.0Hz, protons in OPh, 12H), 6.56 ( brs, OH, 2H), 5.63 (s, protons in hydroquinone ring, 4H) ppm Elemental Anal. Calcd for  $\text{C}_{42}\text{O}_8\text{H}_{36}\text{P}_2\text{Rh}_1\text{B}_1\text{F}_4$ : C, 54.81; H, 3.94. Found: C, 54.66; H, 3.86%.

**2. Synthesis of  $\eta^6$ -1,3-hydroquinone  $\text{Rh}[\text{bis}(\text{triphenylphosphite})]^+\text{BF}_4^-$**  : Same procedure using resorcinol instead of hydroquinone. The isolated yield was 89%. **To get the crystals:**  $\eta^6$ -1,3-hydroquinone  $\text{Rh}[\text{bis}(\text{triphenylphosphite})]^+\text{BF}_4^-$  (25mg) was dissolved in methylene chloride(0.7mL) in 5mL-vial. Toluene (3mL) was carefully added to upper layer. The solution stands in refrigerator for 3 days. The orange crystals were formed on the wall of vial.

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) :  $\delta$  8.41 (brs, OH, 2H), 7.35 ( t, J = 7.8Hz, protons in OPh, 12H), 7.25 ( t, J = 7.6Hz, protons in OPh, 6H), 7.02 (t, J =7.00, protons in resorcinol, 1H), 7.00 (d, J= 7.8Hz, protons in OPh, 12H), 6.31 (s, protons in resorcinol, 1H), 4.88(d, J= 7.8Hz, protons in resorcinol, 2H) ppm Elemental Anal. Calcd for  $\text{C}_{42}\text{O}_8\text{H}_{36}\text{P}_2\text{Rh}_1\text{B}_1\text{F}_4$ : C, 54.81; H, 3.94. Found: C, 54.55; H, 4.10%.