Supporting Information for

An Anionic Rhodium η^4 -Quinonoid Complex as a Multifunctional Catalyst for the Phenylation of Aldehydes with Phenylboronic Acid

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Synthetic Procedure and Characterization of the New Materials

General : All reactions were carried out under N₂ in flame-dried glassware. HPLC grade THF and Diethyl Ether solvents were used as received. [Rh(COD)Cl]₂ was provided by Strem Chemicals. The ¹H NMR spectra were recorded by Bruker(300MHz) spectrometers. Elementary analyses were performed by Quantitative Technologies Inc.

Synthesis of 1⁺BF₄⁻ : After flame drying the glassware, [Rh(COD)Cl]₂ (0.20g, 0.41mmol) and AgBF₄(0.19g, 0.97 mmol) were mixed for 1h at room temperature in a mixed solution of methylene chloride(4mL) and acetone(1mL). While stirring, a white precipitate formed on the bottom of the glassware. 1,4-hydroquinone (0.18g , 1.63 mmol) was dissolved in acetone(2mL) and added to the reaction mixture. After stirring for 2h at r.t., the solvent was removed via rotary evaporation. The residue was taken up in methylene chloride(3mL) and slowly added dropwise to ether through a glass filter. The yellow precipitate was filtered and washed three times with 10 mL aliquots of diethyl ether. The isolated yield was 72% (0.24g, 0.59 mmol). **To get the single crystals :** 1(25mg) was dissolved in a mixture of acetone(0.1mL) and methylene chloride(1.5mL) in 5mL-vial. Diethyl ether (3mL) was carefully added to the upper layer. The solution was placed in a refrigerator for 3 days. Yellow crystals were formed on the wall of vial.

¹H NMR(CD₂Cl₂) : δ 7.64(brs, OH, 2H), 6.53(s, protons in hydroquinone ring, 4H), 4.41(br, protons in double bond in COD, 4H), 2.40(m, protons in COD, 4H), 2.12(m, protons in COD, 4H) ppm Elemental Anal. Calcd for C₁₄O₂H₁₈Rh₁B₁F₄: C, 41.21; H, 4.45. Found: C, 41.44; H, 4.31.

Synthesis of 2 : 1(0.1g, 0.24mmol) was dissolved in THF (5mL) in a 20mL-one neck Schlenk flask and the solution was mixed with 1 eq. K^tBuO (0.027g, 0.25mmol) and stirred at r.t. for 2h. While, stirring the solution became turbid and a yellow precipitate formed. The precipitate was filtered under N₂ and the collected solid was washed three times with THF and dried in vacuum. The isolated yield was 83%(0.065g, 0.20mmol)

¹H NMR(DMSO-d₆) : δ 5.94(d, J = 6.3Hz, protons in arene ring, 2H), 5.51 (br, OH, 1H) 5.20 (d, J = 6.3 Hz, protons in arene ring, 2H), 3.83(br, protons in double bond in COD,

4H), 2.20 (m, protons in COD, 4H), 1.97 (m, protons in COD, 4H) ppm. Elemental Anal. Calcd for $C_{14}O_2H_{17}Rh_1$: C, 52.52; H, 5.35. Found: C, 50.82; H, 5.33.

Synthesis of K^+3^- : **1** (0.1g, 0.24mmol) was dissolved in THF (5mL) in 20mL-one neck Schlenk flask and the solution was mixed with 3 eq. K^tBuO (0.082g, 0.74mmol) and stirred at r.t. for 2h. While stirring, the solution became turbid and a yellow precipitate formed. The precipitate was filtered under N_2 and the collected solid was washed five times with THF and dried in vacuum. The isolated yield was 50%(0.074g, 0.12mmol).

1H NMR(DMSO- d_6) : δ 4.89(s, protons in benzoquinone ring, 4H), 3.47 (br, protons in double bond in COD, 4H), 2.18 (m, protons in COD, 4H), 1.96 (m, protons in COD, 4H) ppm. 1H NMR(D_2O) : δ 5.67(s, protons in benzoquinone ring, 4H), 4.01(br, protons in double bond in COD, 4H), 2.35 (m, protons in COD, 4H), 2.13 (m, protons in COD, 4H) ppm. Elemental Anal. Calcd for $C_{14}O_2H_{16}Rh_1K_3B_2F_8$: C, 27.56; H, 2.64. Found; C, 27.20; H, 2.59.

Synthesis of $K(18-crown-6)^+3^-$: 18-crown-6 (0.19g, 0.74mmol) was dissolved in THF(5mL) in 20mL-one neck Schlenk flask and K^tBuO solution (0.082g, 0.74mmol) in 5mL was added to this solution. The solution was stirred for 30 minutes. To this solution, a THF(5mL) solution of **1**(0.1g, 0.24mmol) was added. The solution was stirred for 5 hours at room temperature. Compared to the synthetic procedure of **3**(K^+), no precipitate formed. The solvent was evaporated and the resulting yellow solid was washed five times with diethyl ether(15mL, five times). After drying in vacuum, the solid was dissolved in THF and diethyl ether was added carefully on the layer of THF. After a few days yellow crystals were collected and the isolated yield was 79%(0.20g, 0.19mmol).

1H NMR(DMSO- d_6) : δ 4.88(s, protons in benzoquinone ring, 4H), 3.54(s, protons in crown ether, 48H), 3.47 (br, protons in double bond in COD, 4H), 2.19 (m, protons in COD, 4H), 1.96 (m, protons in COD, 4H) ppm. 1H NMR(CD_2Cl_2) : δ 5.24(s, protons in benzoquinone ring, 4H), 3.69(br, protons in double bond in COD, 4H), 3.60(s, protons in crown ether, 48H), 2.26(m, protons in COD, 4H), 2.03 (m, protons in COD, 4H) ppm. 1H NMR(D_2O) : δ 5.68(s, protons in benzoquinone ring, 4H), 4.02(br, protons in double bond in COD, 4H), 3.72(s, protons in crown ether, 48H), 2.35 (m, protons in COD, 4H), 2.14 (m, protons in COD, 4H) ppm. Elemental Anal. Calcd. for $C_{38}O_{15}H_{66}Rh_1K_2B_1F_4$: C, 44.28; H, 6.45. Found; C, 44.48; H, 6.61.

Synthesis of Li^+3^- : **1**(0.1g, 0.24mmol) was dissolved in THF (5mL) in 20mL-one neck Schlenk flask and the solution was mixed with 3 eq. Li^tBuO (0.060g, 0.75mmol) and stirred at r.t. for 5h. The solvent was evaporated and the resulting yellow solid was washed five times with mixture of THF and diethyl ether(v/v = 1:5, 15mL, five times). The precipitate was filtered under N_2 and the collected solid was washed five times with THF and dried in vacuum. The isolated yield was 56%(0.057g, 0.14mmol)

1H NMR(DMSO- d_6) : δ 4.96(s, protons in benzoquinone ring, 4H), 3.51(br, protons in

double bond in COD, 4H), 2.20 (m, protons in COD, 4H), 1.98 (m, protons in COD, 4H) ppm. Elemental Anal. Calcd. for $C_{14}O_2H_{16}Rh_1Li_2B_1F_4$: C, 40.05; H, 3.84. Found; C, 40.04; H, 4.17.

Synthesis of $n\text{-Bu}_4\text{N}^+\mathbf{3}^-$: **1**(0.1g, 0.24mmol) and $\text{Bu}_4\text{N}^+\text{BF}_4^-$ (0.21g, 0.75mmol) were dissolved in THF (5mL) in 20mL-one neck Schlenk flask and the solution was mixed with 3 eq. K^tBuO (0.082g, 0.74mmol) and stirred at r.t. for 4h. After reaction, compared to the synthetic procedure of **3**(K^+), there was no precipitate. The solvent was evaporated and the resulting yellow solid was washed five times with diethyl ether(15mL, five times). After drying in vacuum, the solid was dissolved in THF and the diethyl ether was added carefully on the layer of THF. After a few days yellow crystals were collected and the isolated yield was 61%(0.23g, 0.15mmol).

^1H NMR(DMSO-d^6) : δ 4.90(s, protons in benzoquinone ring, 4H), 3.48(br, protons in double bond in COD, 4H), 3.17(t, $J = 7.8\text{Hz}$, protons in Bu, 32H), 2.19 (m, protons in COD, 4H), 1.97 (m, protons in COD, 4H), 1.57(brm, protons in Bu, 32H), 1.32 (m, protons in Bu, 32H), 0.94 (t, $J = 7.2\text{Hz}$, protons in Bu, 48H) ppm Elemental Anal. Calcd. for $C_{78}H_{160}O_2N_4Rh_1B_3F_{12}$: C, 60.46; H, 10.41; N, 3.62. Found; C, 59.23; H, 10.52; N, 3.52.

Crystallography. X-ray data collection was carried out using a Bruker single-crystal diffractometer equipped with an APEX CCD area detector and controlled by SMART version 5.0. Collection was done either at room temperature or 100 K. Data reduction was performed by SAINT version 6.0 and absorption corrections were applied by SADABS version 2.0. The structures were typically determined by direct methods and refined on F^2 by use of programs in SHELXTL version 5.0. Most hydrogen atoms appeared in a difference map, or they were generally inserted in ideal positions, riding on the atoms to which they are attached.

General Procedure of Catalytic Reaction. (entry 8)

Distilled water(2mL) was added to the elongated 15mL-Schlenk flask. The water was bubbled for 5 minutes with nitrogen gas. After bubbling, the catalyst $\text{K}^+\mathbf{3}^-$ (15mg, 0.024mmol), phenylboronic acid(0.15g, 1.23mmol) and benzaldehyde (0.1ml, 0.98mmol) were added. The mixture solution was heated at 75°C for 3hours. After reaction, the solution was cooled to room temperature and CDCl_3 (3.5mL) was added. The solution was shaken for 1 minute and the CDCl_3 part was directly analyzed by ^1H NMR. The yield was calculated by the comparison of peak area of aldehyde of reactant and benzyl proton of product.

Figure S1. Typical ^1H NMR (Entry 8) showing formation of diaryl methanol

Table S1. ¹H NMR data of Diaryl methanols

product	benzylproton (ppm)	other(ppm)	arene(ppm)	ref.
5.85(1H)	2.20(OH, 1H)	7.48–7.05(10H)	1
5.73(1H)	3.74(Ome, 3H) 2.51(OH, 1H)	7.30(5H) 7.22(2H), 6.82(2H)	1
6.32(1H)	2.52(OH, 1H) 2.28(3H) 2.23(6H)	7.27–7.15(5H) 6.85(2H)	2
5.85(1H)	2.56(OH, 1H) 2.40(Me, 3H)	7.47–7.18(9H)	1
5.60(1H)	2.56(OH, 1H)	7.40–7.12(9H)	1
5.73(1H)	2.42(OH, 1H)	7.39–7.10(14H)	2
5.85(1H)	2.66(OH, 1H)	8.00(2H), 7.59(2H) 7.40(5H)	3

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2. Rudolf, J.; Schmidt, F.; Bolm, C. *Adv. Synth. Catal.* **2004**, *346*, 867.
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Figure S2. ^1H NMR of PhB(OH)_2 with (top) and without (bottom) $\text{K}^+\text{3}^-$ in D_2O .

Figure S3. Diagram of 1^+BF_4^- (jrssrhcod)

NOTES on X-ray structure 1^+BF_4^- (jrssrhcod)

A novel rhodium complex was prepared and crystallized. The solved structure contained two independent complexes of rhodium with hydroquinone (HQ) and (COD) ligands, a BF_4 counterion and a diethyl ether molecule filling the void. Each HQ-Rh-COD complex is positioned on a two-fold axis, Rh(1) along an axis parallel to b, Rh(2) along one parallel to a (the asymmetric unit is charge-balanced, +1 for the two half complexes, and -1 for the BF_4). Strange features remained, particularly a “ghost” atom, and the R value remained high – around 13%.

Rechecking by different methods:

Orthorhombic symmetry (mmm) produced R(int) and R(symm) convincingly below 5%. Cell_now ranked the original cell first (C-centered). The space group was uniquely determined to be C222(1) by the systematic absences. Solving by use of the Patterson method yielded the same solution for the heavy atoms as found earlier. However, the original difficulties were highlighted: three independent heavy atoms found, with estimated atomic numbers 48, 39, and 24 – in spite of the fact that the only heavy atom is rhodium.

The third heavy atom had been tentatively treated as carbon, but it clearly was something bigger, and its position mirrored the second rhodium atom on the other side of the HQ ligand. This suggested that the mystery atom might be a fractional part of a disordered rhodium atom. When its identification as Rh(3) was tested, the R values dropped and the bonds to the expected ligands became apparent. Rh(3) occupied a position between the HQ coordinated to Rh(2) and the COD coordinated to the Rh(2) in the adjacent cell. Since neither ligand can bond to two rhodium atoms, disorder of the whole Rh(2) complex must be present. The HQ ligand on Rh(2) is approximately overlapped by another on Rh(3), and the COD on the adjacent Rh(2) is approximately overlapped by another on Rh(3). This “whole molecule disorder” is very difficult to model accurately, so an approximate model was constructed by restraining the ligands on Rh(2) and Rh(3) to be similar to the better-defined ligands on Rh(1), by treating all atoms except rhodium in the Rh(3) complex as isotropic, and by ignoring the likely disorder in the diethyl ether. With this model, the occupancy of the Rh(2) complex was about 68%, the Rh(3) complex about 32%; hence the electron counts on the three rhodium atoms are roughly consistent with the Patterson results.

That is not the end of the disorder besetting this crystal; it is also a racemic twin, with enantiomers in a 55:45 ratio.

The complications in the analysis preclude placing much weight on bond lengths and angles, but the connectivity is determined beyond a reasonable doubt.

Figure S4. Diagram of $n\text{-Bu}_4\text{N}^+3^-$ (jrssrhn)