Supplementary material

A hardwon dirhodium paddlewheel with guanidinate type (hpp) bridging ligands

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Synthesis and Characterization of $[Rh_2(hpp)(O_2CCH_3)_3]\{(O_2CCH_3)(H_2hpp)\}_2$, 2. Compound **2** was prepared in several reactions but the yield was not optimized. Two methods follow.

Method A. 100 mg of $Rh_2(OAc)_4(MeOH)_2$, 120 mg of Hhpp, 120 μL of NEt_3, and 220 μL of a 1 M solution of I_2 in Et_2O were heated in 12 mL of THF for 15 h. The initially brown-purple mix became green and a dark brown gummy substance separated. After filtration, the green filtrate was layered with hexanes, and it became blue as a grey amorphous solid settled to the bottom of the flask. The dark brown gummy substance was washed with benzene and dissolved in CH_2Cl_2. The mixture was filtered, and the filtrate layered with hexanes resulting in the deposition of a sticky brown oil. From the two tubes with the filtrate, a small amount of blue crystals of **2**·$2H_2O$ grew.

IR (KBr, cm^{-1}): 3221 w, 3146 w, 2963 m, 2865 m, 2757 w, 1663 s, 1589 s, 1561 m, 1526 m, 1476 w, 1413 s, 1342 w, 1322 m, 1290 w, 1262 m, 1205 m, 1097 m, 1074 m, 1022 m, 918 w, 802 m, 698 m, 661 w, 625 w, 477 w. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm.): 11.04 br, s (4H, NH), 3.3–3.2 m (16H, CH_2), 3.057 t (J = 6 Hz, 4H, CH_2), 2.125 s (6H, CH_3), 2.062 s (3H, CH_3), 1.966 q (J = 5.6 Hz, 8H, CH_2), 1.79–1.74 m (10H, CH_2 + CH_3). ESI+ Mass spectrum: 800 $[Rh_2(hpp)(OAc)_3(Hhpp)_2]^+$, 721 $[Rh_2(hpp)(OAc)_3\{(H_2hpp)(OAc)\}]^+$, 661 $[Rh_2(hpp)(OAc)_3(Hhpp)]^+$, 582 $[Rh_2(hpp)(OAc)_3(OAc)]^+$, 522 $[Rh_2(hpp)(OAc)_3]^+$. Elemental analysis, Calcd. for $C_{31}H_{58}N_9O_{12}Rh_2$, **2**: C, 39.00; H, 6.12; N, 13.20%. Found: C, 39.49; H 6.16; N, 12.65%.

Crystal Data for **2**·H_2O: Triclinic, $P\bar{1}$, a = 11.272(3), b = 11.400(3), c = 15.856(4) Å, α = 80.768(5), β = 78.128(5), γ = 87.688(5) deg., V = 1968.3(9) $Å^3$, Z = 2, d = 1.582 g cm^{-3}, R1 ($I > 2\sigma(I)$): 0.0413, wR2 ($I > 2\sigma(I)$): 0.0951, R1 (all data): 0.0650, wR2 (all data): 0.1069.

Method B. In 30 mL of THF and a small volume of CH_2Cl_2, 200 mg of $Rh_2(OAc)_4(MeOH)_2$ and 241 mg of Hhpp were heated to reflux overnight giving a blue solution which was filtered from a brown precipitate and layered with hexanes. Three types of crystals that formed were crystallographically characterized. The compounds were: $[Rh_2(hpp)(O_2CCH_3)_3]\{(O_2CCH_3)(H_2hpp)\}_2 \cdot 2H_2O$, **2**·$H_2O$, $[Rh_2(O_2CCH_3)_4]\{(O_2CCH_3)(H_2hpp)\}_2 \cdot 3CH_2Cl_2$, **4**·$3CH_2Cl_2$, and $[H_2hpp](OAc)$.

Crystal Data for **4**·$3CH_2Cl_2$: Monoclinic, *C*2/*c*, $a = 17.368(8)$, $b = 14.227(6)$, $c = 20.933(9)$ Å, $\beta = 107.792(7)$ deg., $V = 4925(4)$ Å^3, $Z = 4$, $d = 1.477$ g cm^{-3}, $\mu = 1.049$ mm^{-1}, R1 ($I > 2\sigma(I)$): 0.0669, *w*R2 ($I > 2\sigma(I)$): 0.1901, R1 (all data): 0.0807, *w*R2 (all data): 0.2021. The structure of the rhodium acetate adduct $[Rh_2(O_2CCH_3)_4]\{(O_2CCH_3)(H_2hpp)\}_2 \cdot$in **4**·$3CH_2Cl_2$ is shown in Figure S2.

Synthesis of $[Rh_2(hpp)(O_2CCH_3)_3(Hhpp)_2]$, 3. Crystals were obtained either from method B, vide supra, or by briefly exposing to air a CH_2Cl_2 solution of **2**. The blue solution became purple and crystals of **3** grew from this solution after some solvent evaporated.

Crystal Data **3**·$2CH_2Cl_2$:: Monoclinic, *C*2/*c*, $a = 20.952(3)$ Å, $b = 13.2172(19)$ Å, $c = 14.875(2)$ Å, $\beta = 108.844(2)$ deg., $V = 3898.5(10)$ Å^3, $Z = 4$, $d = 1.652$ g cm^{-3}, $\mu = 1.173$ mm^{-1}, R1 ($I > 2\sigma(I)$): 0.0281, *w*R2 ($I > 2\sigma(I)$): 0.0692, R1 (all data): 0.0353, *w*R2 (all data): 0.0747. A drawing of the molecule of $[Rh_2(hpp)(O_2CCH_3)_3(Hhpp)_2]$ in **3**·$2CH_2Cl_2$ is shown in Figure S1.

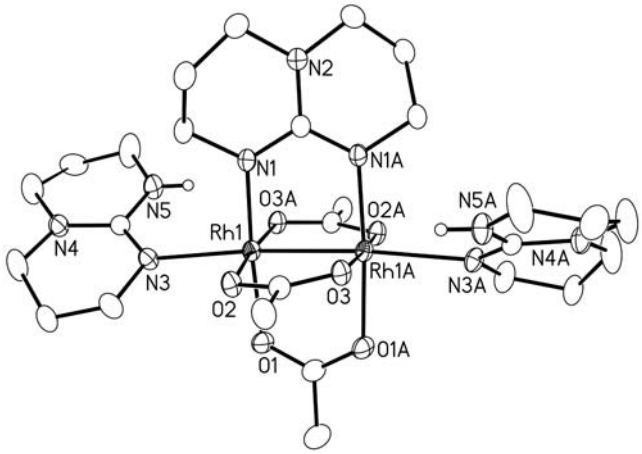

Fig S1 The structure of $[Rh_2(hpp)(O_2CCH_3)_3(Hhpp)_2]$ in **3**·$2CH_2Cl_2$. The Rh−Rh distance is 2.4262(5) Å.

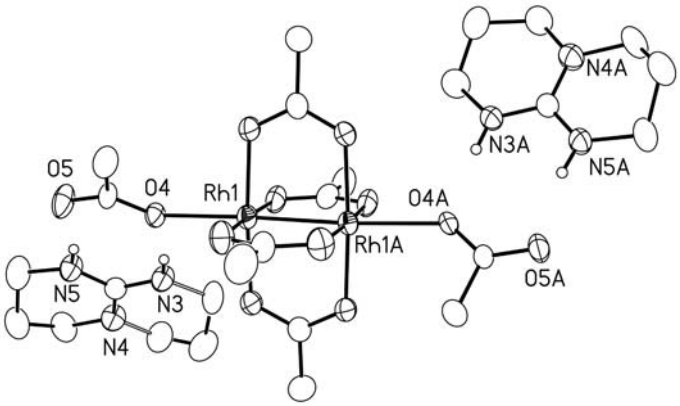

Fig S2 The structure of the rhodium acetate adduct $[Rh_2(O_2CCH_3)_4]\{(O_2CCH_3)(H_2hpp)\}_2$·in **4**·$3CH_2Cl_2$,