Electronic Supplementary Information

Formation of organorhodium complexes via C-H bond activation of 1,3-di(phenylazo)benzene. Structural diversity and catalytic potential

Paramita Majumder,[†] Suparna Baksi,[†] Sarmistha Halder,[†] Haregewine Tadesse,[‡] Alexander J. Blake,[‡] Michael G. B. Drew ,[§] and Samaresh Bhattacharya*,[†]

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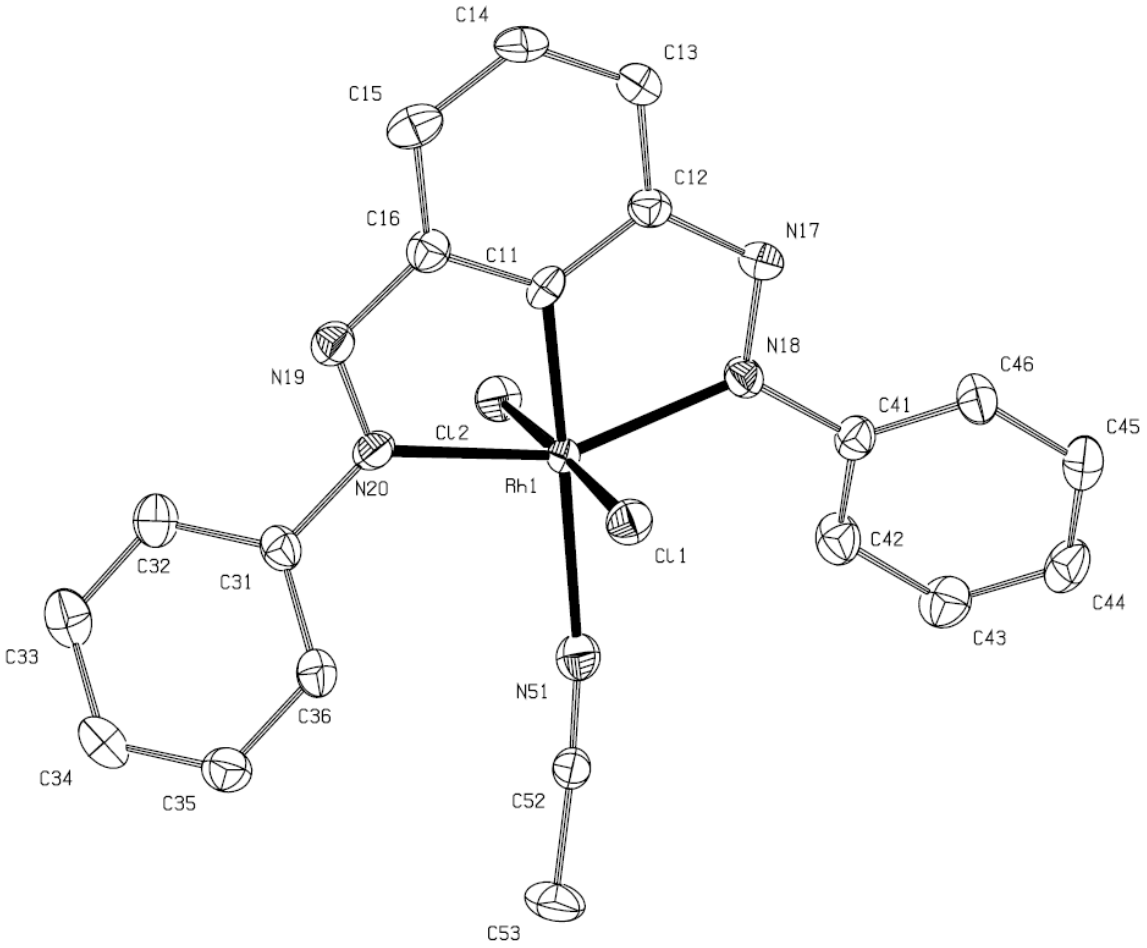
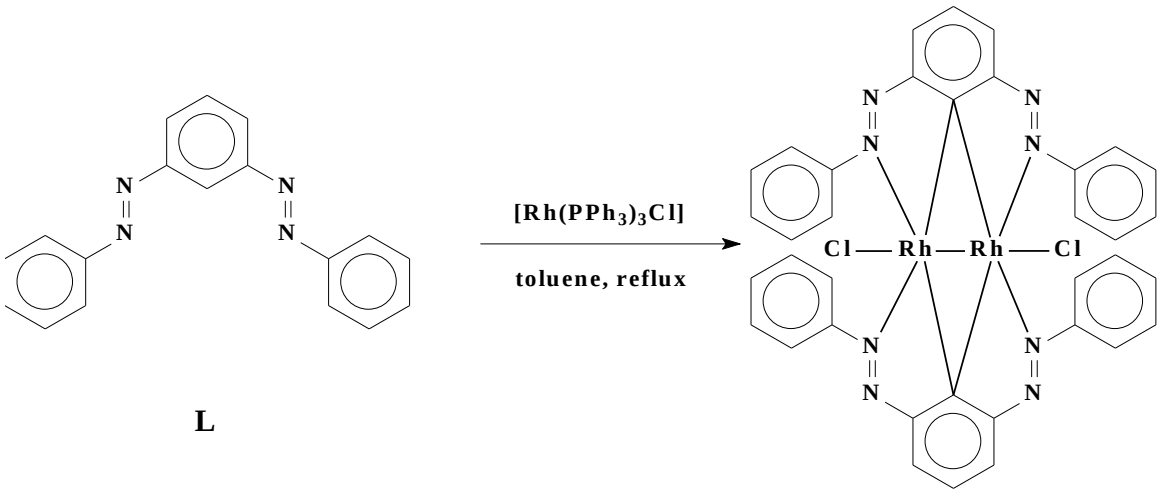
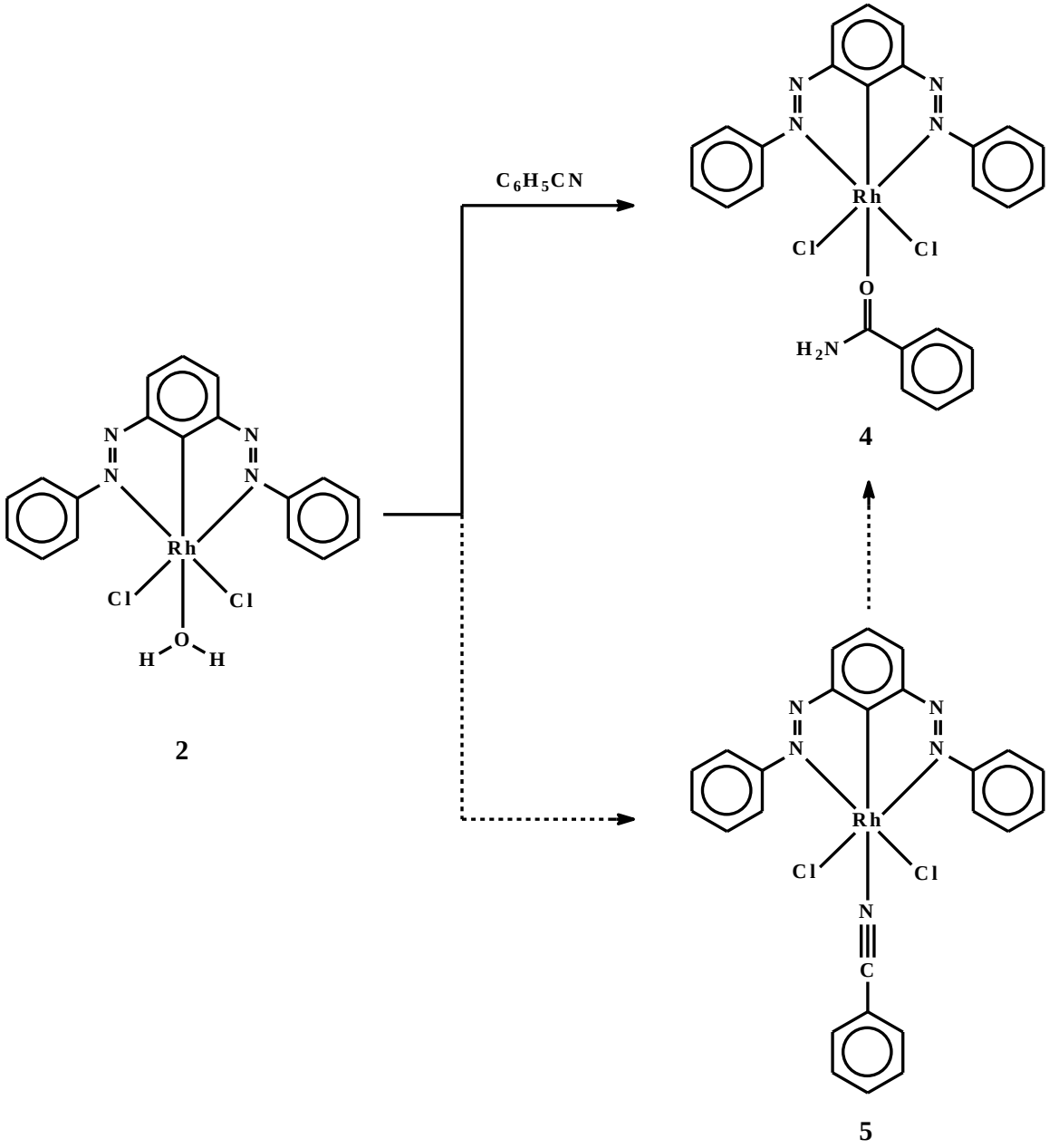


Fig. S1. Molecular structure of complex **3**. Hydrogen atoms bound to carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1-Cl1, 2.3437(15); Rh1-Cl2, 2.3395(15); Rh1-N18, 2.092(5); Rh1-N20, 2.089(5); Rh1-N51, 2.210(5); Rh1-C11, 1.877(6); N17-N18, 1.282(7); N19-N20, 1.290(7); Cl1-Rh1-Cl2, 177.54(5); N18-Rh1-N20, 154.30(19); N18-Rh1-N51, 105.25(19); N18-Rh1-C11, 76.9(2); N20-Rh1-N51, 100.45(19); N20-Rh1-C11, 77.4(2).



L **1**

Scheme S1. Formation of complex **1**.



Scheme S2. Formation of complex **4** and complex **5**.

Method of preparation

1,3-di(plenylazo)benzene: 1,3-phenylenediamine (4 g, 0.04 mol) and NaOH (3 g, 0.08 mol) were grinded well, nitrobenzene (10 g, 0.08 mol) was added to the mixture and made a paste. The paste was heated gently till orange gas evolved vigorously. The mass became solid. It was cooled and extracted with benzene. The solvent was then evaporated to give a solid mass, which was subjected to purification by thin layer chromatography on a silica plate with 1:10 benzene-hexane as the eluant. Orange band separated, which was extracted with acetonitrile. Upon slow evaporation of the orange extract 1,3-di(plenylazo)benzene was obtained. Yield: 7 g (70%). Anal. Calcd for $C_{18}H_{14}N_4$: C, 75.52; H, 4.89; N, 19.58. Found: C, 75.25; H, 4.37; N, 19.79. Mass spectral data (positive ion ES): m/z 287(M+H). ^{1}H NMR ($CDCl_3$, 25º C): δ 8.45 (s, 1H, C1), 8.05 (d, *J* = 6.6 Hz, 2H, C3, C5), 7.97 (d, *J* = 7.3 Hz, 4H, C8, C12, C14, C18), 7.68 (t, *J* = 7.8 Hz, 1H, C4), 7.48-7.57* (6H) (* overlapping signal).

Complex **1**: To a solution of 1,3-di(phenylazo)benzene (31 mg, 0.11 mmol) in toluene (40 ml) was added $[Rh(PPh_3)_3Cl]$ (100 mg, 0.11 mmol). The resulting mixture was then heated at reflux for 3 h under a dinitrogen atmosphere to yield a dark brown solution. The solvent was then evaporated to give a solid mass, which was subjected to purification by thin layer chromatography on a silica plate. With benzene as the eluant, an olive green band separated, which was extracted with acetonitrile. Evaporation of this extract gave complex **1** as a dark crystalline solid. Yield: 30 mg (30%). Anal. Calcd for $C_{36}H_{26}N_8Cl_2Rh_2$: C, 51.00; H, 3.07; N, 13.22. Found: C, 51.17; H, 2.95; N, 13.04. Mass spectral data (positive ion ES): *m/z* 774 (M-2Cl). ^{1}H NMR ($CDCl_3$, 25º C): δ 7.53 (d, *J* = 7.7 Hz, 4H, C3, C5, C3′ and C5′), 7.49 (d, *J* = 7.9 Hz, 8H, C12, C8, C18, C14, C12′, C8′, C14′ and C18′), 7.39 (t, *J* = 7.4 Hz, 4H, C10, C16, C10′, C16′), 7.17 (t, *J* = 7.9 Hz, 8H, C9, C11, C17, C15, C9′, C11′, C17′, C15′), 6.95 (t, *J* = 7.6 Hz, 2H, C4, C4′)(the carbon atoms of the second azo-ligand are marked with ′). ^{13}C NMR ($CDCl_3$, 25º C): δ 160.65, 153.24, 133.61, 131.55, 128.12, 124.62, 124.37, 117.83. IR (KBr, *ν*/cm^{-1}): 1740, 1645, 1580, 1458, 1412, 1383, 1327, 1306, 1259, 1167, 1080, 1029, 920, 797, 764, 717, 689, 596, 575, 530, 451.

Complex **2**: To a solution of 1,3-di(phenylazo)benzene (109 mg, 0.40 mmol) in ethanol (40 ml) was added $RhCl_3 \cdot 3H_2O$ (100 mg, 0.38 mmol). The resulting mixture was then heated at reflux for 3 h to yield a red solution. The solvent was then evaporated to give a solid mass, which was subjected to purification by recrystallization from dichloromethane-ethanol solution affording complex **2** as a crystalline orange solid. Yield: 110 mg (60%). Anal. Calcd for $C_{18}H_{15}N_4O_1Cl_2Rh$: C, 45.30; H, 3.10; N; 11.70. Found: C, 47.38; H, 3.06; N, 11.94. ^{1}H NMR ($CDCl_3$, 25º C): δ 8.39 (d, *J* = 7.9 Hz, 2H, C3, C5), 8.06 (d, *J* = 7.8 Hz, 4H, C8, C12, C14, C18), 7.70 (t, *J* = 7.9 Hz, 2H, C10, C16), 7.43-7.57* (5H). ^{13}C NMR ($CDCl_3$, 25º C): δ 160.49, 152.45, 131.88, 130.29, 129.12, 128.98, 125.72, 123.93. IR (KBr, *v*/cm^{-1}): 1576, 1493, 1457, 1326, 1306, 1260, 1155, 1023, 794, 762, 716, 689, 600, 574, 526, 458.

Complex **3**: This complex was obtained as an orange crystalline solid upon evaporation of solvent (takes about 2 h under ambient condition) from a solution of complex **2** (10 mg) in acetonitrile (20 ml). Yield: Quantitative. Anal. Calcd for $C_{20}H_{16}N_5Cl_2Rh$: C, 48.00; H, 3.20; N; 14.00. Found: C, 47.85; H, 3.36; N, 13.94. ^{1}H NMR ($CDCl_3$, 25º C): δ 8.39 (d, *J* = 7.9 Hz, 2H, C3, C5), 8.09 (d, *J* = 7.5 Hz, 4H, C8, C12, C14, C18), 7.67 (t, *J* = 7.9 Hz, 2H, C10, C16), 7.46-7.57* (5H), 2.19 (s, 3H, CH_3CN). ^{13}C NMR ($CDCl_3$, 25º C): δ 160.51, 152.48, 131.91, 130.35, 129.01, 128.84, 125.75, 123.94, 118.32, 2.83. IR (KBr, *v*/cm^{-1}): 2361, 1580, 1458, 1327, 1306, 1259, 1167, 1080, 1030, 920, 797, 764, 717, 687, 575, 528, 455.

Complex **4**: This complex was obtained as an orange crystalline solid upon evaporation (takes about 7 days under ambient condition) of solvent from a solution of complex **2** (10 mg) in benzonitrile (20 ml). Yield: Quantitative. Anal. Calcd for $C_{25}H_{20}N_5O_1Cl_2Rh$: C, 51.70; H, 3.40; N; 12.10. Found: C, 51.85; H, 3.36; N, 12.94. ^{1}H NMR ($CDCl_3$, 25º C): δ 8.39 (d, *J* = 7.7 Hz, 2H, C3, C5), 8.16 (d, *J* = 8.5 Hz, 4H, C8, C12, C14, C18), 7.87 (d, *J* = 7.0 Hz, 2H, *ortho*-phenyl of benzamide), 7.46-7.70* (10H), 6.27 (s, 2H, amide NH_2 of benzamide). ^{13}C NMR ($CDCl_3$, 25º C): δ 160.45, 152.44, 133.60, 132.78, 132.42, 131.79, 130.19, 129.30, 128.94, 128.88, 127.62, 125.60, 123.82. IR (KBr, *v*/cm^{-1}): 1647, 1579, 1481, 1458, 1327, 1306, 1254, 1171, 1080, 1032, 802, 764, 721, 689, 600, 575, 525, 452.

Complex **5**: This complex was obtained as an orange crystalline solid upon evaporation (takes about a day under ambient condition) of solvents from a solution of complex **2** (10 mg) in 19:1 acetone-benzonitrile (20 mL). Yield: Quantitative. Anal. Calcd for $C_{25}H_{18}N_5Cl_2Rh$: C, 53.40; H, 3.20; N; 12.50. Found: C, 53.51; H, 3.67; N, 12.94. ^{1}H NMR ($CDCl_3$, 25º C): δ 8.40 (d, *J* = 7.9 Hz, 2H, C3, C5), 8.14 (d, *J* = 7.0 Hz, 4H, C8, C12, C14, C18), 7.65-7.70* (4H), 7.46-7.57* (8H). ^{13}C NMR ($CDCl_3$, 25º C): δ 160.32, 152.31, 132.67, 131.93, 131.81, 130.25, 129.41, 128.89, 128.77, 127.66, 125.67, 123.78, 117.34. IR (KBr, ν/cm^{-1}): 2337, 1561, 1458, 1327, 1306, 1257, 1173, 1080, 1031, 800, 764, 719, 689, 576, 526, 451.

Selected crystallographic data, for complex **4**: $C_{25}H_{20}Cl_2N_5ORh$, M_r = 580.27, monoclinic, space group $P2_1/c$, a = 12.1868(2) Å, b = 12.0880(2) Å, c = 15.7543(2) Å, β = 92.597(6)°, V = 2318.5(2) Å^3, Z = 4, μ = 0.997 mm^{-1}, T = 150 K, λ = 0.71073 Å, R_1 = 0.0543, wR_2 = 0.1530, GOF = 0.80

Selected bond lengths (A°) and angles (deg) of complex **4**: Rh1-Cl1, 2.3292(13); Rh1-Cl2, 2.3335(12); Rh1-N1, 2.102(4); Rh1-N4, 2.062(4); Rh1-O1, 2.225(4); Rh1-C21, 1.878(5); N1-N2, 1.277(5); N3-N4, 1.277(5); O1-C4, 1.207(7); N5-C4, 1.402(9); Cl1-Rh1-Cl2, 175.76(5); N1-Rh1-N4, 153.99(14); N1-Rh1-O1, 105.04(13); N1-Rh1-C21, 77.08(18); O1-Rh1-C21, 175.52(18); N4-Rh1-C1, 76.70(14).

Selected crystallographic data, for complex **5** $C_{25}H_{18}Cl_2N_5Rh$, M_r = 562.25, monoclinic, space group $P2_1/c$, a = 11.2704(2) Å, b = 13.3655(2) Å, c = 15.7056(2) Å, β = 89.900(1)°, V = 2365.80(6) Å^3, Z = 4, μ = 0.971 mm^{-1}, T = 296 K, λ = 0.71073 Å, R_1 = 0.0300, wR_2 = 0.1615, GOF = 0.65

Selected bond lengths (A°) and angles (deg) of complex **5**: Rh1-Cl1, 2.3385(8); Rh1-Cl2, 2.3284(10); Rh1-N2, 2.106(3); Rh1-N4, 2.075(3); Rh1-N5, 2.212(3); Rh1-C1, 1.877(3); N1-N2, 1.285(4); N3-N4, 1.269(3); N5-C19, 1.142(4); Cl1-Rh1-Cl2, 177.23(3); N2-Rh1-N4, 153.54(11); N2-Rh1-N5, 104.51(11); N2-Rh1-C1, 76.86(15); N4-Rh1-N5, 101.94(10); N4-Rh1-C1, 76.70(14).