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**ACCESSORY PUBLICATION**

# Contrasting Reactivity of 2-Mesityl-1,8-Naphthyridine (Mes-NP) with Singly-Bonded [$Rh^{II}$–$Rh^{II}$] and [$Ru^{I}$–$Ru^{I}$] Compounds

Biswajit Saha, S. M. Wahidur Rahaman, Arup Sinha and Jitendra K. Bera*[,†]

[†]*Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India.*

* To whom correspondence should be addressed. E-mail: jbera@iitk.ac.in

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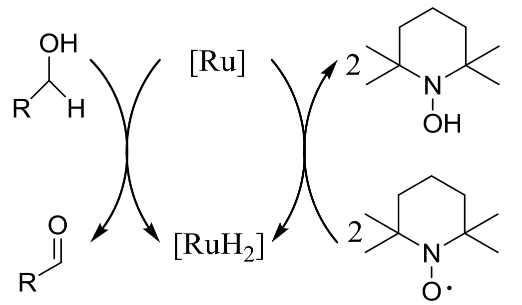


$[Ru] = [Ru(NP\text{-}Mes)_2(CH_3CN)_2](BF_4)_2$

Scheme S1: Oxidation of alcohol to aldehyde by catalyst **2** in presence of tempo.

**Oxidation of alcohol to aldehyde:** Catalyst **2** (0.01 mmol, 9 mg) was dissolved in 1 mL dichloroethane solution and 3 mL toluene was added to it. Then alcohol (1 mmol) and tempo (2 mmol, 292 mg) were added. The reaction mixture was heated to 80°C for 6 h. The progress of the reaction was monitored by GC. After the reaction was over, the resulting mixture was cooled to room temperature, then it was extracted with diethyl ether (3 × 20 mL). The ethereal solution was washed with brine (3 × 10 mL) and dried over $MgSO_4$ and filtered. After removing the solvent under vacuum, the product was purified by chromatography on a silica gel column using a mixture hexane/EtOAc as eluent.

**Aldehyde-olefination reaction:** 3 mL toluene solution of EDA (1.5 mmol, 0.14 mL) was added drop-wise to the mixture of triphenylphosphine (1.2 mmol, 314 mg), aldehyde (1 mmol) and catalyst **2** (0.01 mmol, 9 mg) in toluene and dichloroethane solution mixture over a period of 30 min under nitrogen atmosphere. Then the solution was heated for 6 h at 80°C. The progress of the reaction was monitored by GC. After the reaction was over, the resulting mixture was cooled to room temperature, then it was extracted with diethyl ether (3 × 20 mL). The ethereal solution was washed with brine (3 × 10 mL) and dried over $MgSO_4$ and filtered. After removing the solvent under vacuum, the product was purified by chromatography on a silica gel column using a mixture hexane/EtOAc as eluent.

**One pot synthesis of α,β-unsaturated ester from alcohol:** Catalyst **2** (0.02 mmol, 18 mg) was dissolved in 1 mL dichloroethane solution and the 3 mL toluene was added to it. Then alcohol (1 mmol) and tempo (2 mmol, 292 mg) were added. The reaction mixture was heated to 80°C for 6 h. After 6 h reaction mixture is cooled to room temperature and then triphenylphosphine (1.2 mmol, 314 mg) was directly added in the same reaction mixture and 3 mL toluene solution of

EDA (1.5 mmol, 0.14 mL) was added drop wise over it. Then the solution was heated for 6 h at 80°C. The progress of the reaction was monitored by GC. After the reaction was over, the resulting mixture was cooled to room temperature, then it was extracted with diethyl ether (3 × 20 mL). The ethereal solution was washed with brine (3 × 10 mL) and dried over $MgSO_4$ and filtered. After removing the solvent under vacuum, the product was purified by chromatography on a silica gel column using a mixture hexane/EtOAc as eluent.

**Table S1**. Selected Bond Lengths (Å) and Bond Angles (deg) and Dihedral Angles (deg) for **1.** [a]

| | | | |
|---|---|---|---|
| | Bond Lengths (Å) | | |
| Rh1-N1 | 2.001(3) | C12-C13 | 1.367(5) |
| Rh1-O2 | 2.016(2) | C12-C11 | 1.402(5) |
| Rh1-O1 | 2.028(2) | C19-C26 | 1.401(5) |
| Rh1-N2 | 2.044(3) | C19-C20 | 1.411(5) |
| Rh1-Rh1 | 2.3866(5) | C26-C25 | 1.395(5) |
| F3-B1 | 1.394(5) | C26-C27 | 1.514(5) |
| F4-B1 | 1.383(5) | C20-C22 | 1.391(5) |
| F2-B1 | 1.392(5) | C20-C21 | 1.502(5) |
| N1-C18 | 1.334(4) | C22-C23 | 1.396(5) |
| N1-C15 | 1.361(4) | C25-C23 | 1.383(5) |
| C14-C15 | 1.407(4) | C23-C24 | 1.509(5) |
| C14-C13 | 1.411(5) | O1-C1 | 1.277(4) |
| C14-C16 | 1.418(5) | F1-B1 | 1.395(5) |
| C18-C17 | 1.413(5) | C1-O2 | 1.276(4) |
| C18-C19 | 1.491(5) | C1-C2 | 1.496(5) |
| C16-C17 | 1.363(5) | O2-Rh1 | 2.016(2) |
| C15-N2 | 1.371(4) | Cl1-C1S | 1.767(4) |
| N2-C11 | 1.325(5) | C1S-Cl1 | 1.767(4) |
| N2-Rh1 | 2.044(3) | | |
| | Bond Angles (deg) | | |
| N1-Rh1-O2 | 88.31(10) | C12-C13-C14 | 119.4(3) |
| N1-Rh1-O1 | 92.78(10) | N2-C11-C12 | 123.2(3) |
| O2-Rh1-O1 | 176.22(9) | C26-C19-C20 | 120.6(3) |
| N1-Rh1-N2 | 177.81(11) | C26-C19-C18 | 120.1(3) |
| O2-Rh1-N2 | 90.45(10) | C20-C19-C18 | 119.3(3) |
| O1-Rh1-N2 | 88.34(10) | C25-C26-C19 | 118.7(3) |
| N1-Rh1-Rh1 | 88.99(8) | C25-C26-C27 | 119.4(3) |
| O2-Rh1-Rh1 | 88.61(7) | C19-C26-C27 | 121.9(3) |
| O1-Rh1-Rh1 | 87.79(7) | C22-C20-C19 | 118.1(3) |
| N2-Rh1-Rh1 | 89.17(8) | C22-C20-C21 | 119.7(3) |
| C18-N1-C15 | 120.4(3) | C19-C20-C21 | 122.2(3) |
| C18-N1-Rh1 | 115.6(2) | C20-C22-C23 | 122.2(4) |
| C15-N1-Rh1 | 123.9(2) | C23-C25-C26 | 121.9(3) |
| C15-C14-C13 | 117.6(3) | C25-C23-C22 | 118.2(4) |
| C15-C14-C16 | 117.7(3) | C25-C23-C24 | 120.5(4) |
| C13-C14- C16 | 124.6(3) | C22-C23-C24 | 121.2(4) |

| | | | |
|---|---|---|---|
| N1-C18-C17 | 121.3(3) | C1-O1-Rh1 | 119.6(2) |
| N1-C18-C19 | 113.6(3) | F4-B1-F2 | 109.8(3) |
| C17-C18-C19 | 125.2(3) | F4-B1-F3 | 109.8(3) |
| C17-C16-C14 | 120.0(3) | F2-B1-F3 | 109.1(4) |
| N1-C15-N2 | 116.4(3) | F4-B1-F1 | 109.6(4) |
| N1-C15-C14 | 121.2(3) | F2-B1-F1 | 109.3(3) |
| N2-C15-C14 | 122.4(3) | F3-B1-F1 | 109.2(3) |
| C16-C17-C18 | 119.3(3) | O2-C1-O1 | 124.6(3) |
| C11-N2-C15 | 117.9(3) | O2-C1-C2 | 118.4(3) |
| C11-N2-Rh1 | 120.8(2) | O1-C1-C2 | 117.0(3) |
| C15-N2-Rh1 | 121.3(2) | C1-O2-Rh1 | 119.4(2) |
| C13-C12-C11 | 119.2(3) | Cl1-C1S-Cl1 | 111.3(4) |
| Dihedral Angles (deg) | | | |
| Ru1–N1–C15-N2 | 2.4(3) | Ru1–N2–C18–C19 | 7.3(7) |
| N3–Ru1–N2–C18 | 88.3(5) | | |

[a] Symmetry transformation used to generate equivalent atoms: 1/2-X, 3/2-Y, 2-Z.

**Table S2**. Selected Bond Lengths (Å) and Bond Angles (deg) and Dihedral Angles (deg) for **2.** [a]

| | | | |
|---|---|---|---|
| Bond Lengths (Å) | | | |
| Ru1-N3 | 2.018(3) | C15-C14 | 1.388(5) |
| Ru1-N3 | 2.018(3) | C21-C22 | 1.386(6) |
| Ru1-N2 | 2.086(3) | C14-C13 | 1.408(5) |
| Ru1-N2 | 2.086(3) | C14-C16 | 1.415(6) |
| Ru1-N1 | 2.100(3) | C11-C12 | 1.406(6) |
| Ru1-N1 | 2.100(3) | C18-C17 | 1.421(5) |
| N2-C18 | 1.319(5) | C23-C22 | 1.400(6) |
| N2-C15 | 1.362(4) | C12-C13 | 1.369(6) |
| N1-C11 | 1.322(5) | C16-C17 | 1.372(5) |
| N1-C15 | 1.358(5) | C22-C27 | 1.505(5) |
| C24-C23 | 1.389(5) | C1-C2 | 1.454(6) |
| C24-C19 | 1.411(5) | Cl1S-C1S | 1.739(5) |
| C24-C25 | 1.507(5) | C1S-Cl1S | 1.739(5) |
| C19-C20 | 1.397(5) | F1-B1 | 1.367(6) |
| C19-C18 | 1.494(5) | F3-B1 | 1.364(6) |
| N3-C1 | 1.128(5) | F4-B1 | 1.364(6) |
| C20-C21 | 1.392(5) | F2-B1 | 1.355(5) |
| C20-C26 | 1.514(6) | | |
| Bond Angles (deg) | | | |
| N3-Ru1-N3 | 180.0(2) | C21-C20-C26 | 120.1(4) |
| N3-Ru1-N2 | 88.48(12) | C19-C20-C26 | 121.6(4) |
| N3-Ru1-N2 | 91.52(12) | N1-C15-N2 | 108.3(3) |
| N3-Ru1-N2 | 91.52(12) | N1-C15-C14 | 125.7(3) |
| N3-Ru1-N2 | 88.48(12) | N2-C15-C14 | 125.9(3) |
| N2-Ru1-N2 | 180.00(12) | C22-C21-C20 | 122.1(4) |
| N3-Ru1-N1 | 90.75(12) | C15-C14-C13 | 115.6(4) |
| N3-Ru1-N1 | 89.25(12) | C15-C14-C16 | 114.9(3) |
| N2-Ru1-N1 | 63.58(12) | C13-C14-C16 | 129.4(4) |
| N2-Ru1-N1 | 116.42(12) | N1-C11-C12 | 121.0(4) |
| N3-Ru1-N1 | 89.25(12) | N2-C18-C17 | 120.1(3) |
| N3-Ru1-N1 | 90.75(12) | N2-C18-C19 | 116.3(3) |

| | | | |
|---|---|---|---|
| N2-Ru1-N1 | 116.42(12) | C17-C18-C19 | 123.5(3) |
| N2-Ru1-N1 | 63.58(12) | C24-C23-C22 | 121.4(4) |
| N1-Ru1-N1 | 180.0(3) | C13-C12-C11 | 121.1(4) |
| C18-N2-C15 | 118.3(3) | C17-C16-C14 | 119.6(4) |
| C18-N2-Ru1 | 147.4(3) | C21-C22-C23 | 118.6(4) |
| C15-N2-Ru1 | 94.2(2) | C21-C22-C27 | 121.1(4) |
| C11-N1-C15 | 117.5(3) | C23-C22-C27 | 120.3(4) |
| C11-N1-Ru1 | 148.7(3) | C12-C13-C14 | 119.0(4) |
| C15-N1-Ru1 | 93.8(2) | C16-C17-C18 | 121.0(4) |
| C23-C24-C19 | 118.4(3) | N3-C1-C2 | 178.7(5) |
| C23-C24-C25 | 120.1(3) | Cl-1S-C1S-Cl1S | 114.1(5) |
| C19-C24-C25 | 121.5(3) | F2-B1-F3 | 111.0(5) |
| C20-C19-C24 | 121.2(3) | F2-B1-F4 | 112.0(4) |
| C20-C19-C18 | 118.8(3) | F3-B1-F4 | 108.8(4) |
| C24-C19-C18 | 120.0(3) | F2-B1-F1 | 107.7(4) |
| C1-N3-Ru1 | 179.1(3) | F3-B1-F1 | 107.6(4) |
| C21-C20-C19 | 118.3(4) | F4-B1-F1 | 109.7(4) |
| Dihedral Angles (deg) | | | |
| Rh1–N1–C15–N2 | 4.8(4) | Rh1–O2–C1–O1 | 1.7(3) |
| Rh1–N1–C18–C19 | 6.9(3) | Rh1–O2–C1–C2 | 179.1(3) |

[a] Symmetry transformation used to generate equivalent atoms: 1/2-X,1/2-y,-z.