

## **Supporting Information**

The C–C Bond Forming Reaction Through Aldol-Type Addition Mediated  
by  $[\text{Ru}_2(\text{CO})_4]^{2+}$  Core

**Sanjib K. Patra and Jitendra K. Bera\***

Department of Chemistry  
*Indian Institute of Technology Kanpur 208016, INDIA*

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\* To whom correspondence should be addressed. E-mail: [jbera@iitk.ac.in](mailto:jbera@iitk.ac.in)

**Table S1.** Selected Bond Distances (Å) and Bond Angles (°) in [Ru<sub>2</sub>(CO)<sub>4</sub>(L1)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (2)•(CH<sub>3</sub>)<sub>2</sub>CO.

<b>Bond Distances</b>			
Ru1-Ru1	2.6103(17)	Ru1-N2	2.131(8)
Ru1-O3	22.244(6)	Ru1-C1	1.867(12)
Ru1-N1	2.189(8)	Ru1-C2	1.856(11)

<b>Bond Angles</b>			
O3-Ru1-Ru1	165.67(18)	C2-Ru1-N2	93.2(4)
N1-Ru1-Ru1	82.3(2)	C1-Ru1-N2	175.3(4)
N2-Ru1-Ru1	82.3(2)	C2-Ru1-N1	175.4(4)
N1-Ru1-N2	89.6(3)	C2-Ru1-C1	87.8(4)
N1-Ru1-O3	88.7(3)	C1-Ru1-O3	97.9(3)
N2-Ru1-O3	86.5(3)	C2-Ru1-O3	95.1(3)
C1-Ru1-N1	89.1(4)		

**Table S2.** Selected Bond Distances (Å) and Bond Angles (°) in [Ru<sub>2</sub>(CO)<sub>4</sub>(L1)<sub>2</sub>][OTf]<sub>2</sub> (2a)•(CH<sub>3</sub>)<sub>2</sub>CO.

<b>Bond Distances</b>			
Ru1-Ru1	2.6343(7)	Ru1-N2	2.159(3)
Ru1-O3	2.241(3)	Ru1-C1	1.859(4)
Ru1-N1	2.190(4)	Ru1-C2	1.848(5)
<b>Bond Angles</b>			
O3-Ru1-Ru1	165.12(9)	C2-Ru1-N2	95.11(16)
N1-Ru1-Ru1	81.56(9)	C1-Ru1-N2	177.47(16)
N2-Ru1-Ru1	85.68(9)	C2-Ru1-N1	173.09(16)
N1-Ru1-N2	87.20(13)	C2-Ru1-C1	87.25(18)
N1-Ru1-O3	87.46(13)	C1-Ru1-O3	96.76(16)
N2-Ru1-O3	83.77(13)	C2-Ru1-O3	99.26(16)
C1-Ru1-N1	90.35(16)		

**Table S3.** Selected Bond Distances (Å) and Bond Angles (°) in [Ru<sub>2</sub>(CO)<sub>4</sub>(L2)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (3).

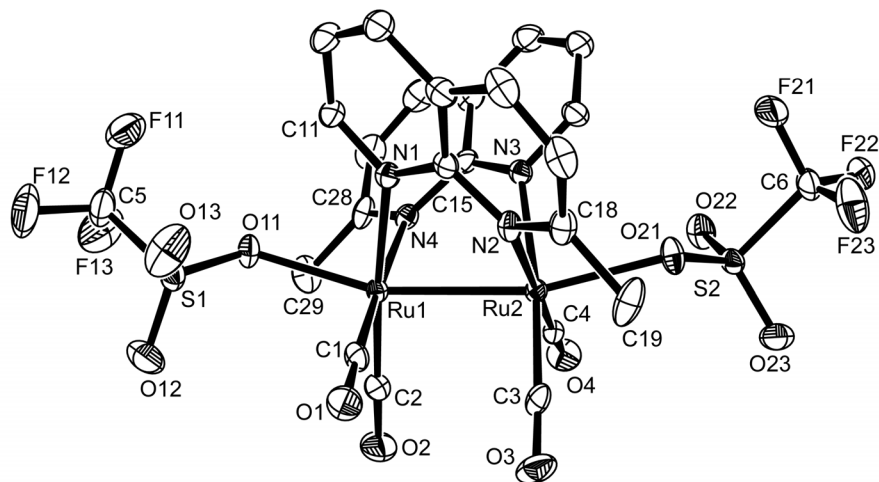
<b>Bond Distances</b>			
Ru1-Ru2	2.6096(10)	Ru2-O6	2.233(6)
Ru1-O5	2.230(6)	Ru2-N2	2.171(7)
Ru1-N1	2.193(7)	Ru2-N4	2.172(6)
Ru1-N3	2.175(7)	Ru2-C3	1.841(9)
Ru1-C1	1.854(10)	Ru2-C4	1.853(9)
Ru1-C2	1.857(9)		

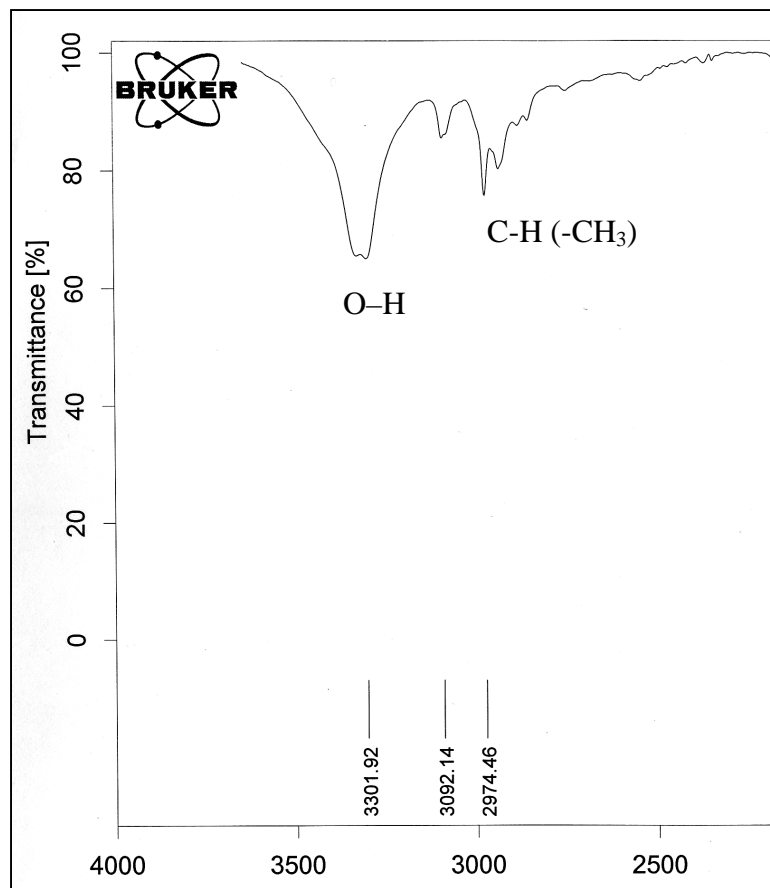
<b>Bond Angles</b>			
O5-Ru1-Ru2	163.01(15)	O6-Ru2-Ru1	165.65(15)
N1-Ru1-Ru2	81.81(18)	N2-Ru2-Ru1	85.61(18)
N3-Ru1-Ru2	85.87(19)	N4-Ru2-Ru1	82.00(19)
N1-Ru1-N3	84.6(2)	N2-Ru2-N4	84.7(3)
N1-Ru1-O5	86.5(2)	N2-Ru2-O6	83.4(3)
N3-Ru1-O5	80.8(2)	N4-Ru2-O6	87.8(2)
C1-Ru1-N1	173.2(3)	C3-Ru2-N2	171.9(3)
C1-Ru1-N3	98.3(3)	C3-Ru2-N4	87.4(3)
C2-Ru1-N1	90.2(3)	C4-Ru2-N2	100.1(3)
C2-Ru1-N3	174.8(3)	C4-Ru2-N4	172.9(3)
C1-Ru1-C2	86.7(4)	C3-Ru2-C4	87.5(4)
C1-Ru1-O5	100.0(3)	C3-Ru2-O6	98.4(3)
C2-Ru1-O5	99.8(3)	C4-Ru2-O6	97.8(3)

**Table S4.** Selected Bond Distances (Å) and Bond Angles (°) in [Ru<sub>2</sub>(CO)<sub>4</sub>(L3)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (4).

<b>Bond Distances</b>			
Ru1-Ru1	2.6128(12)	Ru1-N2	2.189(6)
Ru1-O3	2.224(5)	Ru1-C1	1.858(8)
Ru1-N1	2.157(6)	Ru1-C2	1.856(7)
<b>Bond Angles</b>			
O3-Ru1-Ru1	166.43(13)	C2-Ru1-N2	174.5(3)
N1-Ru1-Ru1	81.81(15)	C1-Ru1-N2	89.4(2)
N2-Ru1-Ru1	82.73(14)	C2-Ru1-N1	94.8(3)
N1-Ru1-N2	87.7(2)	C2-Ru1-C1	87.8(3)
N1-Ru1-O3	87.3(2)	C1-Ru1-O3	96.0(3)
N2-Ru1-O3	88.84(19)	C2-Ru1-O3	96.1(3)
C1-Ru1-N1	175.6(3)		



**Figure S1.** ORTEP diagram (50% probability thermal ellipsoids) of the molecular structure of  $[\text{Ru}_2(\text{CO})_4(2\text{-MeNP})_2(\text{OTf})_2]$  (**1a**) with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Crystal data: formula  $\text{C}_{24}\text{H}_{16}\text{F}_6\text{N}_4\text{O}_{10}\text{Ru}_2\text{S}_2$ , crystal system orthorhombic, space group  $Pbca$ ,  $a = 13.3005(10)$  Å,  $b = 14.1940(11)$  Å,  $c = 33.341(2)$  Å,  $V = 6294.4(8)$  Å<sup>3</sup>,  $R1 = 0.0528$ ,  $wR1 = 0.1039$ , goodness-of-fit 1.222. Important bond lengths (Å) and angles (°). Ru1-Ru2 2.5994(4), Ru1-O11 2.240(3), Ru2-O21 2.285(3), Ru1-Ru2-O21 165.35(8), Ru2-Ru1-O11 163.21(8), N1-Ru1-Ru2 80.76(8), N3-Ru1-Ru2 84.45(8), N2-Ru2-Ru1 84.51(8), N4-Ru2-Ru1 80.79(9).



**Figure S2.** IR spectrum showing band at  $3302\text{ cm}^{-1}$  corresponding to the stretching frequency of hydroxyl group (-OH) in compound **3**.

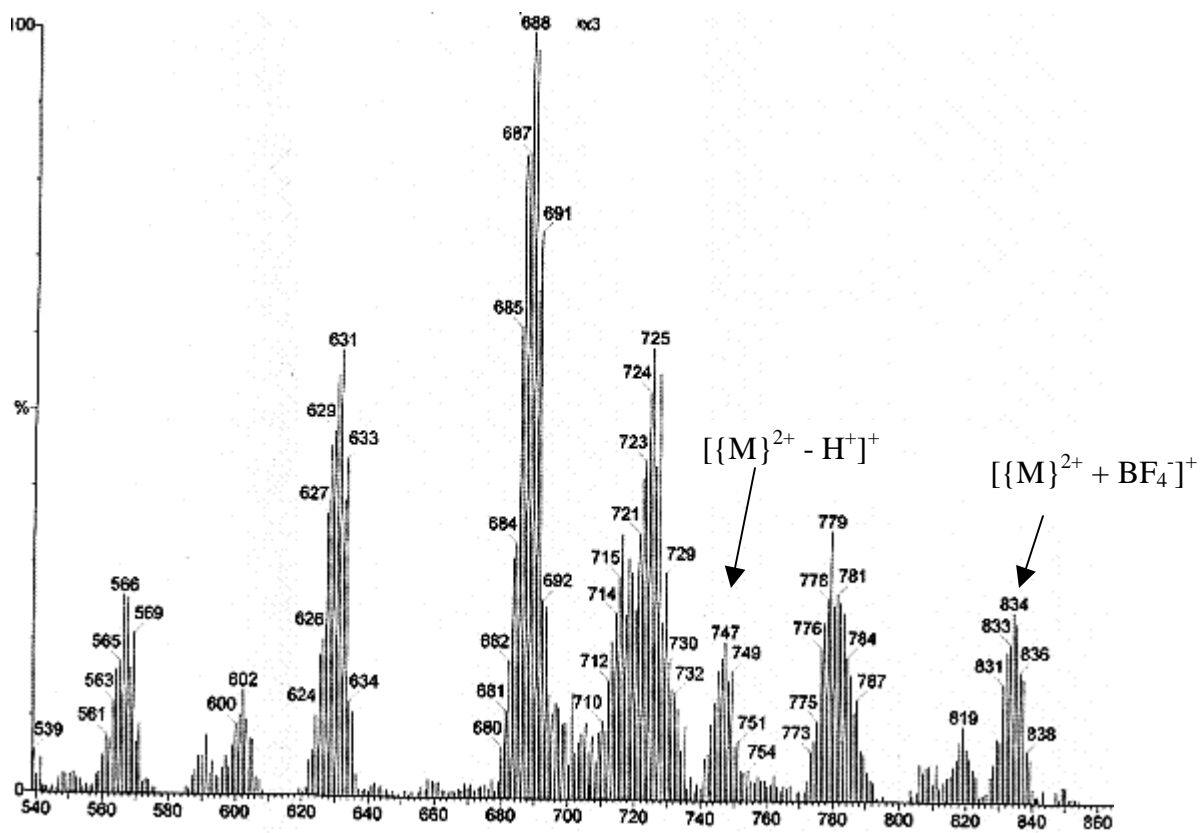


Figure S3. ESI-MS spectrum of compound 3 in CH<sub>3</sub>CN.