C−C Bond Forming Reaction through Aldol-Type Addition Mediated by a $[Ru_2(CO)_4]^{2+}$ Core

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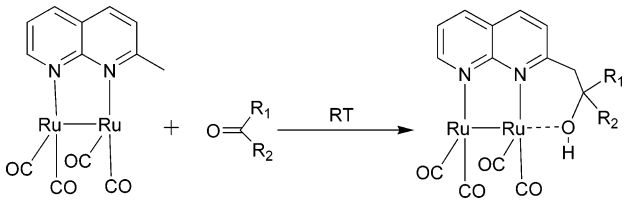
Received February 12, 2007

An aldol-like addition of acetone to 2-methyl-1,8-naphthyridine and 2,3-dimethyl-1,8-naphthyridine mediated by a $[Ru_2(CO)_4]^{2+}$ core at room temperature affords the C−C-coupled compounds 2-methyl-1-(1,8-naphthyridin-2-yl)propan-2-ol (L1) and 2-methyl-1-(3-methyl-1,8-naphthyridin-2-yl)propan-2-ol (L2). A similar reaction with methyl ethyl ketone and 2-methyl-1,8-naphthyridine affords 2-methyl-1-(1,8-naphthyridin-2-yl)butan-2-ol (L3). The syntheses and structures of $[Ru_2(CO)_4(L1)_2][X]_2$ (**2**, X = BF_4; **2a**, X = OTf), $[Ru_2(CO)_4(L2)_2][BF_4]_2$ (**3**), and $[Ru_2(CO)_4(L3)_2][BF_4]_2$ (**4**) are reported here.

Introduction

Transition-metal-assisted organic transformations are useful tools in organic synthesis.[1] Di- and polynuclear metal complexes are of particular interest, since the presence of bridging ligands and cooperation among closely spaced metal centers present scopes for novel chemical reactions.[2] We have initiated a program that is geared toward the utilization of metal−metal singly bonded $[Ru-Ru]^{2+}$ compounds in organometallic chemistry.[3] A recent study on the $[Ru_2(CO)_4]^{2+}$ core reveals a close approach of axial ligands, causing destabilization of the Ru−Ru σ orbital.[4] The aryl C−H bond placed at the axial site of the $[Ru_2(CO)_4]^{2+}$ core results in room-temperature cleavage, yielding Ru−C-bonded organometallic compounds.[5] 1,8-Naphthyridine (NP)-based ligands have been used, as they are efficient bridges for dimetal units, providing access to compounds with remarkable electronic and electrochemical properties.[6] The present work describes the aldol-type addition of 2-methyl-1,8-naphthyridine (2-MeNP) with ketone at the axial site of the $[Ru_2(CO)_4]^{2+}$ core (Scheme 1). The C−C bond formation reactions assisted by the $[Ru_2(CO)_4]^{2+}$ core, leading to 1,8-naphthyridine derivatives, are described herein.

Scheme 1



Results and Discussion

The addition of acetone to $[Ru_2(CO)_4(2\text{-MeNP})_2(MeCN)_2][BF_4]_2$ (**1**) at room temperature in dichloromethane yields the C−C-coupled compound $[Ru_2(CO)_4(L1)_2][BF_4]_2$ (**2**; L1 = 2-methyl-1-(1,8-naphthyridin-2-yl)propan-2-ol). The X-ray structure of compound **2** (Figure 1) reveals the formation of the 1,8-naphthyridine derivative L1 through C−C bond formation between the coordinated 2-MeNP and acetone. The tridentate L1 binds to $[Ru_2(CO)_4]$ core in a cis arrangement, forming a nonplanar $[RuNC_3O]$ six-membered chelate ring which adopts a twisted-boat conformation. The Ru−Ru distance is 2.6103(17) Å, and axial sites are occupied by weakly bound OH groups with an Ru−O distance of 2.244(6) Å.

The ^{1}H NMR spectrum of **2** displays multiple resonances amounting to ten aromatic protons of two ligands in the range 7.50−8.87 ppm. Interestingly, two sets of resonances were observed for the methyl, methylene, and hydroxyl protons. Although the resonances at 1.78 and 1.50 ppm could be attributed to inequivalent methyl groups of the chelate ring, the OH signals at 6.61 and 6.50 ppm and the methylene signals at 3.41 and 3.75 ppm strongly indicate the presence of two conformers in solution (vide infra). The conformational behavior

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Publication on Web 03/31/2007

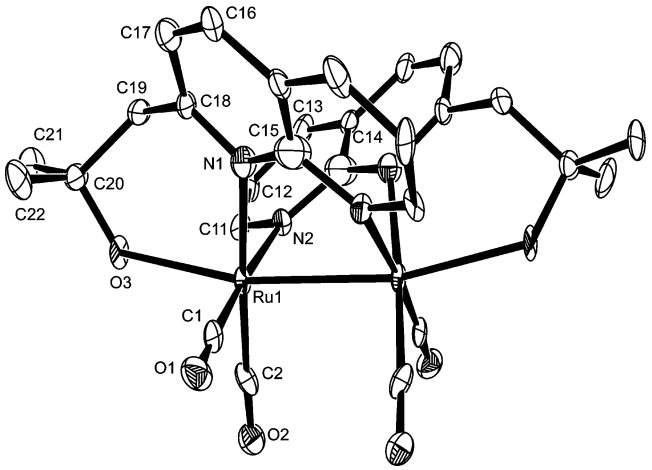

Figure 1. ORTEP diagram (50% probability thermal ellipsoids) of the cationic unit $[Ru_2(CO)_4(L1)_2]^{2+}$ in compound **2** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Important bond lengths (Å) and angles (deg): Ru1−Ru1 = 2.6103(17), Ru1−O3 = 2.244(6), Ru1−N1 = 2.189(8), Ru1−N2 = 2.131(8); Ru1−Ru1−O3 = 165.67(18), Ru1−Ru1−N1 = 82.3(2), Ru1−Ru1−N2 = 82.3(2).

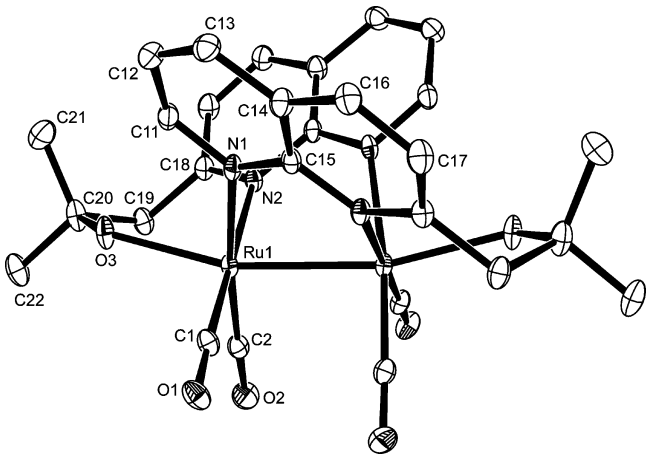

Figure 2. ORTEP diagram (50% probability thermal ellipsoids) of the cationic unit $[Ru_2(CO)_4(L1)_2]^{2+}$ in compound **2a** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Important bond lengths (Å) and angles (deg): Ru1−Ru1 = 2.6343(7), Ru1−O3 = 2.241(3), Ru1−N1 = 2.190(4), Ru1−N2 = 2.159(3); Ru1−Ru1−O3 = 165.12(9), Ru1−Ru1−N1 = 81.56(9), Ru1−Ru1−N2 = 85.68(9).

of a chelate with more than five atoms in the ring is well established.[7] A particular conformer of a metallacycle may well be preferred in the solid state while exhibiting several conformers of similar energy in solution.[8] With the intent of stabilizing the identical molecule with different $[RuNC_3O]$ ring conformers, the structure determination of the $[Ru_2(CO)_4(L1)_2]^{2+}$ unit was carried out with triflates as counteranions (**2a**). The only notable difference was the conformation of the six-membered chelate ring involving the Ru atom (Figure 2). Though the conformations of six-membered chelate rings are best described as twisted boat for both the compounds, the obvious difference was manifested in C20−O3−Ru1−N2 torsional angles that are 6.41(3) and 39.07(1)° in compounds **2** and **2a**, respectively. The NMR spectrum of **2a** is similar to that of **2**.

The C−C coupled product $[Ru_2(CO)_4(L2)_2][BF_4]_2$ (**3**; L2 = 2-methyl-1-(3-methyl-1,8-naphthyridin-2-yl)propan-2-ol) was obtained from the reaction of acetone and $[Ru_2(CO)_4(2,3\text{-}Me_2NP)_2(MeCN)_2][BF_4]_2$ (2,3-Me_2NP = 2,3-dimethyl-1,8-naphthyridine). The X-ray structure (Figure 3) reveals that the chelate ring adopts the twisted-boat conformation similar to **2a** with C21−O6−Ru2−N2 and C41−O5−Ru1−N3 torsional angles of 50.20(1) and 56.54(1)°, respectively. The Ru1−Ru2, Ru1−O5, and Ru2−O6 distances are 2.6096(10), 2.230(6), and 2.233(6) Å. The prochiral reagent methyl ethyl ketone was employed with **1**, affording $[Ru_2(CO)_4(L3)_2][BF_4]_2$ (**4**; L3 = 2-methyl-1-(1,8-naphthyridin-2-yl)butan-2-ol). C−C bond formation was noted, with Ru1−Ru1 and Ru−O3 distances of 2.6128(12) and 2.224(5) Å, respectively (Figure 4). Interestingly, the conformation of the $[RuNC_3O]$ ring in **4** was similar to that observed for compound **2** with an C20−O3−Ru1−N2 torsional angle of 0.75(3)°. Compound **4** displays multiple resonances in the aromatic region 7.50−8.86 ppm, as well as two signals for the

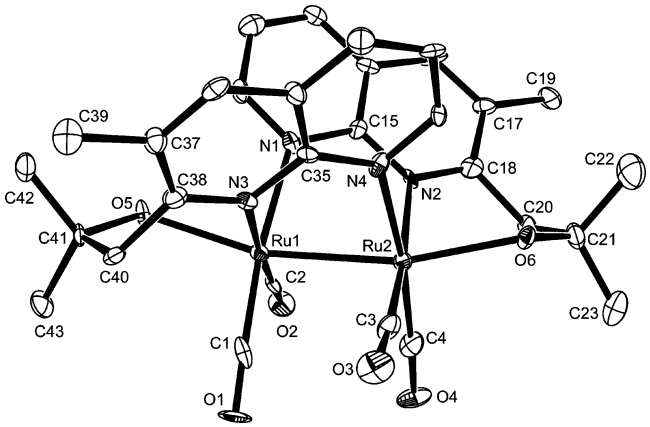

Figure 3. ORTEP diagram (50% probability thermal ellipsoids) of the cationic unit $[Ru_2(CO)_4(L2)_2]^{2+}$ in compound **3** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Important bond lengths (Å) and angles (deg): Ru1−Ru2 = 2.6096(10), Ru1−O5 = 2.230(6), Ru2−O6 = 2.233(6), Ru1−N1 = 2.193(7), Ru1−N3 = 2.175(7), Ru2−N2 = 2.171(7), Ru2−N4 = 2.172(6); Ru1−Ru2−O6 = 165.65(15), Ru2−Ru1−O5 = 163.01(15), Ru2−Ru1−N1 = 81.81(18), Ru2−Ru1−N3 = 85.87(19), Ru1−Ru2−N2 = 85.61(18), Ru1−Ru2−N4 = 82.00(19).

coordinated OH at 6.41 and 6.17 ppm in ^{1}H NMR. The signal for the methylene protons of the ethyl group appears at 1.52 ppm, whereas the methyl protons appear as a multiplet centered at 1.18 ppm. The other methyl protons display a broad singlet at 1.71 ppm, including a multiplet at 3.74 ppm corresponding to the ring methylene protons.

The assignment of the dicationic core involving neutral ligands in compounds **2**, **2a**, **3**, and **4** is based on the ^{1}H NMR, IR, and ESI-MS data. For instance, the ESI-MS of **3** reveals an ion at a mass-to-charge ratio (*m*/*z*) of 747, which corresponds to $[\{M\}^{2+} - H^+]^+$. It does not, however, exclude the possibility of an alternate neutral compound M′ of formulation $[Ru_2(CO)_4(L2')_2]$, where L2′ is [L2-H$^+$]. The signal at *m*/*z* 834 could be attributed to $[\{M\}^{2+} + BF_4^-]^+$ on the basis of the mass and isotopic distribution pattern (see the Supporting Information). It is less likely that the neutral compound M′ is the origin of this peak, corresponding to a mass of the formulation [{M′} +

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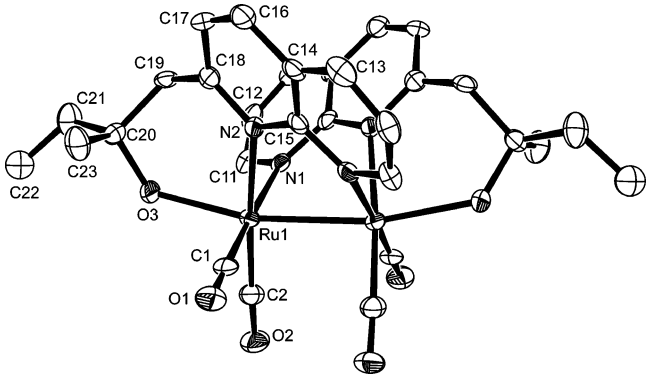


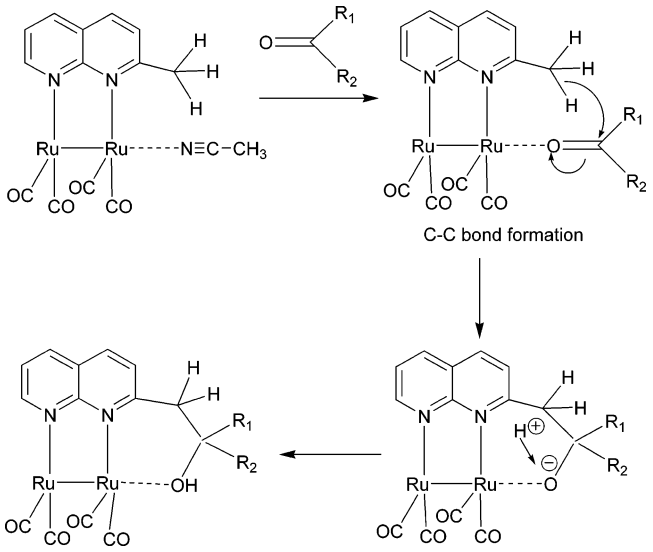
Figure 4. ORTEP diagram (50% probability thermal ellipsoids) of the cationic unit $[Ru_2(CO)_4(L3)_2]^{2+}$ in compound **4** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Important bond lengths (Å) and angles (deg): Ru1−Ru1 = 2.6128(12), Ru1−O3 = 2.224(5), Ru1−N1 = 2.157(6), Ru1−N2 = 2.189(6); Ru1−Ru1−O3 = 166.43(13), Ru1−Ru1−N1 = 81.81(15), Ru1−Ru1−N2 = 82.73(14).

$2H^+ + BF_4^-]^+$. The dicationic core in compound **3** is confirmed from the ^{1}H NMR spectrum, which shows a distinct signal for the hydroxyl proton of the neutral ligand L2 at 6.34 ppm. The IR spectrum recorded under a dry nitrogen atmosphere shows a band at 3302 cm^{-1} corresponding to the stretching frequency of the hydroxyl groups.

The ^{1}H NMR spectra of the compounds reveal interesting features of their solution structures. The ring methylene proton signals of compounds are plotted along with solid-state conformers of the $[RuNC_3O]$ chelate ring of the corresponding compounds obtained from X-ray structures in Figure 5. For compounds **2** and **2a**, the methylene signals exhibit two "AB quartets" (centered at 3.41 and 3.75 ppm for **2** and 3.31 and 3.74 ppm for **2a**) with a $^2J_{HH}$ value of 14−15 Hz for two conformers. It is our assertion that these two conformers correspond to two ring structures exhibited in the solid-state structures (Figure 5d). The appearance of the AB pattern is due to a comparable chemical shift difference and the coupling constant.[9,10a] The environments of a particular proton of the chelate ring differ in two conformers, which are reflected in the ^{1}H NMR, showing two different signals. Interestingly, only one form of the $[RuNC_3O]$ ring conformer of **3** is present in solution, as reflected in the ^{1}H NMR spectrum, exhibiting only two doublets at 3.60 and 3.96 ppm with $^2J_{HH}$ values of 14.8 and 14.4 Hz, corresponding to the two inequivalent methylene protons of the chelate ring. It is likely that the methyl group at the 3-position of NP leads to conformational locking by favoring one particular conformer (Figure 3). The methylene protons of the chelate ring in **4** appear as a multiplet centered at 3.74 ppm, and the pattern is more complex, presumably due to the neighboring chiral center and/or the presence of more than one conformer of the chelate ring in solution.

Scheme 2 shows a proposed reaction pathway for the formation of the C−C-coupled product. In the initial step, ketone coordinates to the $[Ru_2(CO)_4]$ unit axially, replacing the acetonitrile. Elimination of hydrogen from the methyl group of coordinated 2-MeNP and C−C bond formation between the methyl group and ketone take place through a concerted six-membered intermediate. Finally, the proton migrates to the negatively charged alkoxy oxygen.[10] Thus, a new six-membered $[RuNC_3O]$ chelate ring is formed. Notably, the C−C bond formation and the transfer of proton occurs without adding any external base or heating, which are often prerequisite for aldol-type addition reactions. The activation of the methyl proton is the key for this reaction. A possible pathway is certainly the C−H bond activation by the metal ion.[11] However, the methyl at the 2-position of the NP unit is unlikely to have a strong interaction with Ru, an inference that is primarily based on geometric considerations.[12] A more logical rationale is the increased acidity of the 2-methyl proton due to coordination of the NP ligand to the $[Ru_2(CO)_4]^{2+}$ unit.[13] It is well documented that the alkyl group at the 2-position of pyridine is more reactive compared to the alkyl group attached in benzene, and the former undergoes a base-catalyzed aldol-type condensation with carbonyl compounds.[14]

Scheme 2



The axial coordination of ketone is essential for this reaction. The use of coordinated solvents such as acetonitrile drastically reduces the efficiency. The identity of the anions in the precursor molecule also plays an influential role. $[Ru_2(CO)_4(2\text{-MeNP})_2(OTf)_2]$ (**1a**) exhibits a sluggish reaction compared to its tetrafluroborate analogue **1**. A simple explanation is that the triflate anions compete with acetone for axial coordination, thereby reducing the rate of the reaction. This is confirmed from the solid-state structure of $[Ru_2(CO)_4(2\text{-MeNP})_2(OTf)_2]$. The structure reveals the axial coordination of triflates (Figure S1 in the Supporting Information).

To our best knowledge, the 1,8-naphthyridine-based ligands L1−L3 have been synthesized for the first time through metal-mediated aldol-type addition. Owing to the scarce chemical literature on the subject, the derivatization of 1,8-naphthyridine is of special interest to synthetic organic chemists. Further, these compounds constitute an important class of compounds because of their possible biological and pharmacological applications.[15] A literature study revealed that the pyridine analogue 2-methyl-

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(12) The Ru−H29C distance in **1a** is calculated to be 2.830 Å, which is longer than the M−H distances observed in typical *agostic* complexes.

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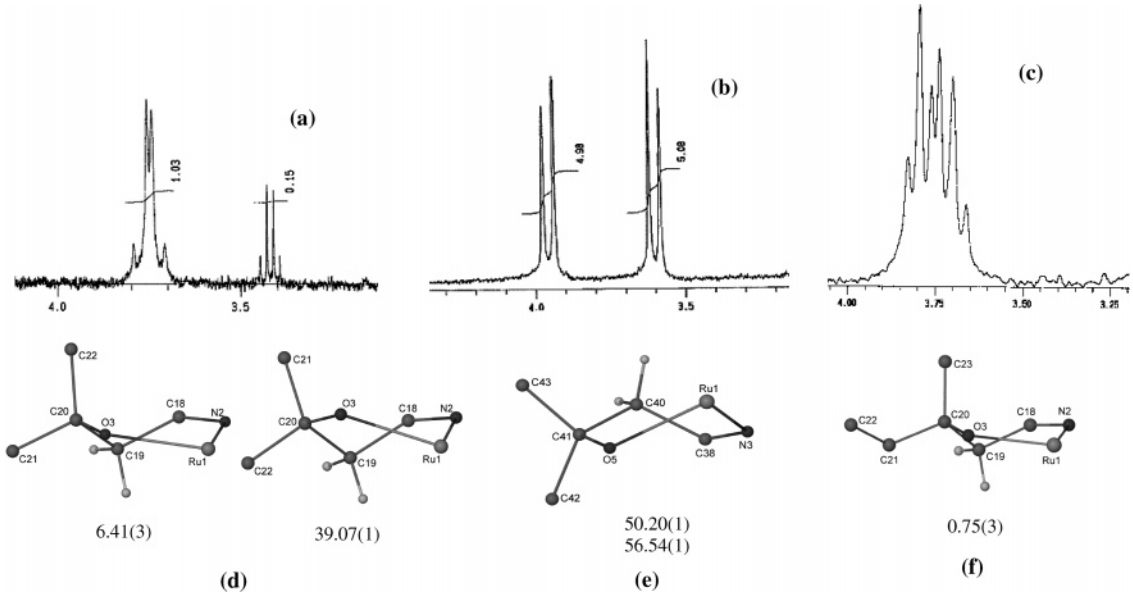

Figure 5. Plots of methylene proton signals in ^{1}H NMR for compounds **2** (a), **3** (b), and **4** (c) in CD_3CN at room temperature and conformers of the $[RuNC_3O]$ chelate ring present in compounds **2** and **2a** (d), **3** (e), and **4** (f) with the corresponding C−O−Ru−N torsional angles (deg).

1-(pyridin-2-yl)propan-2-ol was synthesized from 2-methylpyridine with 1 equiv of *n*-BuLi, followed by the addition of an excess of acetone.[16] This work illustrates a similar derivatization of the NP ring assisted by the $[Ru_2(CO)_4]^{2+}$ core under very mild conditions, thereby avoiding side reactions.[17]

Conclusion

A new type of C−C bond formation reaction between 2-methyl-1,8-naphthyridine and acetone/methyl ethyl ketone mediated by $[Ru_2(CO)_4]^{2+}$ has been reported. Reactions of this type proceed at room temperature and under mild conditions, providing access to a variety of naphthyridine derivatives. Further work is being undertaken to examine the reactions with carbonyl compounds such as aldehydes or carboxylic acid derivatives to synthesize important 1,8-naphthyridine derivatives.

Experimental Section

General Procedures. All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk-vessel and vacuum-line techniques. Infrared spectra were recorded in the range 4000−400 cm^{-1} on a Bruker Vertex 70 spectrophotometer with KBr pellets. ^{1}H NMR spectra were obtained on a JEOL JNM-LA 400 MHz spectrometer. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. Electronic absorptions were measured on a Lambda-20 Perkin-Elmer spectrophotometer. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. ESI-MS spectra were recorded on a MICROMASS QUATTRO II triple-quadrupole mass spectrometer.

Materials. Solvents were dried by conventional methods, distilled over nitrogen, and deoxygenated prior to use.[18] $RuCl_3 \cdot nH_2O$ (39% Ru) was purchased from Arora Matthey, Calcutta, India. The compound $[Ru_2(CO)_4(CH_3CN)_6][BF_4]_2$ was synthesized by following a procedure similar to the synthesis of $[Ru_2(CO)_4(CH_3CN)_6][PF_6]_2$.[19] The ligands 2-MeNP and 2,3-Me_2NP were prepared by the Friedlander condensation of 2-aminonicotinaldehyde with corresponding acyl derivatives.[20]

Syntheses. $[Ru_2(CO)_4(2\text{-MeNP})_2(MeCN)_2][BF_4]_2$ (1) and $[Ru_2(CO)_4(2\text{-MeNP})_2(OTf)_2]$ (1a). 2-MeNP (31 mg, 0.21 mmol) was added to an acetonitrile solution (15 mL) of $[Ru_2(CO)_4(MeCN)_6][BF_4]_2$ (68 mg, 0.093 mmol), and the mixture was stirred for 8 h at room temperature. The resulting orange solution was concentrated under vacuum, and 15 mL of diethyl ether was added with stirring to induce precipitation. The solid residue obtained was washed with ether (3 × 5 mL) and dried under vacuum to give $[Ru_2(CO)_4(2\text{-MeNP})_2(MeCN)_2][BF_4]_2$ (**1**). This product was dissolved in dichloromethane and recrystallized by layering petroleum ether on it. Yield: 74 mg (93%). IR (KBr; cm^{-1}): ν(CO) 2043, 2028, 1945; $\nu(BF_4^-)$ 1058. ^{1}H NMR (CD_3CN; δ, ppm): 8.60 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, H(NP)), 8.47 (dd, 2H), 8.06 (m, 2H), 7.96 (d, 2H, 8.2 Hz, H(NP)), 7.26 (m, 2H), 3.43 (s, 6H, CH_3). UV−vis (CH_3CN; λ_{max}, nm (ϵ, $dm^3\ mol^{-1}\ cm^{-1}$)): 258 (sh), 301 (3.25×10^3). X-ray-quality crystals of $[Ru_2(CO)_4(2\text{-MeNP})_2(OTf)_2]$ (**1a**) were obtained in quantitative yield by layering a saturated benzene solution of [n-Bu_4N][OTf] onto a dichloromethane solution of **1**. IR (KBr; cm^{-1}): ν(CO) 2045, 2025, 1948; $\nu(OTf^-)$ 1262. Anal. Calcd for $C_{24}H_{16}N_4O_{10}S_2F_6Ru_2$: C, 32.00; H, 1.79; N, 6.22; S, 7.12. Found: C, 32.12; H, 1.96; N, 6.36; S, 6.95.

$[Ru_2(CO)_4(L1)_2][BF_4]_2$ (2). A 1 mL portion of acetone was added to a dichloromethane solution (10 mL) of $[Ru_2(CO)_4(2\text{-MeNP})_2(MeCN)_2][BF_4]_2$ (45 mg, 0.052 mmol), and the solution was stirred for 12 h at room temperature. The yellow solution was

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Table 1. Crystallographic Data and Refinement Parameters for Compounds 2·$(CH_3)_2CO$, 2a·$(CH_3)_2CO$, 3, and 4

	2·$(CH_3)_2CO$	2a·$(CH_3)_2CO$	3	4
empirical formula	$C_{31}H_{32}B_2F_8N_4O_7Ru_2$	$C_{33}H_{32}F_6N_4O_{13}Ru_2S_2$	$C_{30}H_{30}B_2F_8N_4O_6Ru_2$	$C_{30}H_{14}B_2F_8N_4O_6Ru_2$
formula wt	948.37	1072.89	918.34	902.21
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*2/*c*	*C*2/*c*	$P2_1$	*C*2/*c*
a, Å	12.590(5)	23.639(3)	9.4518(10)	25.612(5)
b, Å	8.383(3)	12.3280(14)	15.8721(17)	8.737(5)
c, Å	20.993(6)	17.635(2)	11.5989(12)	18.469(5)
β, deg	123.243(16)	127.424(2)	94.025(2)	121.375(5)
V, Å^3	1853.1(11)	4081.3(8)	1735.8(3)	3529(2)
Z	2	4	2	4
ρ_{calcd}, g cm^{-3}	1.700	1.746	1.757	1.698
μ, mm^{-1}	0.905	0.936	0.961	0.945
F(000)	944	2144	912	1760
no. of rflns				
collected	8774	11 615	10 276	8764
indep	3140	4149	5591	2996
obsd ($I > 2\sigma(I)$)	2079	3478	4618	2234
no. of variables	237	268	475	227
goodness of fit	0.982	1.046	0.990	1.041
final *R* indices ($I > 2\sigma(I)$)[a]				
R1	0.0833	0.0498	0.0570	0.0575
wR2	0.1955	0.1230	0.0987	0.1416
R indices (all data)[a]				
R1	0.1183	0.0603	0.0732	0.0815
wR2	0.2143	0.1290	0.1053	0.1552

[a] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. wR2 = $[\sum w(|F_o^2| - |F_c^2|)^2/\sum|F_o^2|^2]^{1/2}$.

concentrated under vacuum, and 15 mL of diethyl ether was added with stirring to induce precipitation. The solid residue obtained was washed with ether and redissolved in acetone, and petroleum ether was layered on this solution to give $[Ru_2(CO)_4(L1)_2][BF_4]_2$ as yellow crystals suitable for X-ray analysis. Yield: 39 mg (83%). ^{1}H NMR (CD_3CN; δ, ppm): 8.87 (d, $^3J_{H-H}$ = 7.9 Hz, H(NP)), 8.74 (d, $^3J_{H-H}$ = 8.1 Hz, H(NP)), 8.63 (d, $^3J_{H-H}$ = 8.1 Hz, H(NP)), 8.56 (d, $^3J_{H-H}$ = 8.0 Hz, H(NP)), 8.20 (m, H(NP)), 8.09 (m, H(NP)), 8.02 (d, $^3J_{H-H}$ = 8.1 Hz, H(NP)), 7.51 (d, $^3J_{H-H}$ = 8.1 Hz, H(NP)), 7.45 (m, H(NP)), 6.61 and 6.50 (s, 2H, OH), 3.75 and 3.41 (AB system, 4H, $^2J_{H-H}$ = 14.5 and 14.2 Hz, CH_2), 1.78 (s, 6H, CH_3), 1.50 (s, 6H, CH_3). IR (KBr; cm^{-1}): ν(CO) 2047, 2010, 1962; ν(OH) 3302; $\nu(BF_4^-)$ 1061. ESI-MS: *m*/*z* 719 $[\{M\}^{2+} - H^+]^+$, 806 $[\{M\}^{2+} + BF_4^-]^+$. Anal. Calcd for $C_{28}H_{28}N_4O_6B_2F_8Ru_2$: C, 37.69; H, 3.16; N, 6.28. Found: C, 37.43; H, 3.08; N, 6.37. UV−vis (CH_3CN; λ_{max}, nm (ϵ, dm^3 mol^{-1} cm^{-1})): 262 (sh), 302 (7.65 × 10^3).

$[Ru_2(CO)_4(L1)_2][OTf]_2$ (2a). X-ray-quality crystals of $[Ru_2(CO)_4(L1)_2][OTf]_2$ (**2a**) were obtained in quantitative yield by layering a saturated benzene solution of [*n*-Bu_4N][OTf] onto an acetone solution of **2**. ^{1}H NMR (CD_3CN; δ, ppm): 8.89 (d, $^3J_{H-H}$ = 7.8 Hz, H(NP)), 8.74 (d, $^3J_{H-H}$ = 8.1 Hz, H(NP)), 8.63 (d, $^3J_{H-H}$ = 8.1 Hz, H(NP)), 8.56 (d, $^3J_{H-H}$ = 8.0 Hz, H(NP)), 8.19 (d), 8.09 (m, H(NP)), 8.01 (d, $^3J_{H-H}$ = 8.1 Hz, H(NP)), 7.49 (d, $^3J_{H-H}$ = 8.1 Hz, H(NP)), 7.45 (m, H(NP)), 6.51 (s, 2H, OH), 3.74 and 3.31 (AB system, 4H, $^2J_{H-H}$ = 15.2 and 14.9 Hz, CH_2), 1.77 (s, 6H, CH_3), 1.48 (s, 6H, CH_3). IR (KBr; cm^{-1}): ν(CO) 2041, 2009, 1962; ν(OH) 3303; $\nu(OTf^-)$ 1262. Anal. Calcd for $C_{30}H_{28}N_4O_{12}S_2F_6Ru_2$: C, 35.44; H, 2.78; N, 5.51; S, 6.31. Found: C, 35.27; H, 2.71; N, 5.63; S, 6.21. UV−vis (CH_3CN; λ_{max}, nm (ϵ, dm^3 mol^{-1} cm^{-1})): 264 (sh), 303 (7.87 × 10^3).

$[Ru_2(2,3\text{-}Me_2NP)_2(CO)_4(MeCN)_2][BF_4]_2$. The reaction of $[Ru_2(CO)_4(MeCN)_6][BF_4]_2$ (42 mg, 0.057 mmol) and 2,3-Me_2NP (21 mg, 0.13 mmol) was carried out by following a procedure similar to that described in the synthesis of compound **1**. Yield: 46 mg (91%). ^{1}H NMR (CD_3CN; δ, ppm): (CD_3CN, δ): 8.37 (d, 2H, $^3J_{H-H}$ = 7.9 Hz, H(NP)), 8.32 (m, 2H), 7.97 (m, 2H), 7.15 (m, 2H), 3.34 (s, 6H, CH_3), 2.65 (s, 6H, CH_3). IR (KBr; cm^{-1}): ν(CO) 2042, 2027, 1946; $\nu(BF_4^-)$ 1061. Anal. Calcd for $C_{28}H_{26}N_6O_4B_2F_8Ru_2$: C, 37.94; H, 2.96; N, 9.48. Found: C, 37.82; H, 3.01; N, 9.39. UV−vis (CH_3CN; λ_{max}, nm (ϵ, dm^3 mol^{-1} cm^{-1})): 264 (sh), 308 (3.84 × 10^3).

$[Ru_2(CO)_4(L2)_2][BF_4]_2$ (3). The reaction of $[Ru_2(2,3\text{-}Me_2NP)_2(CO)_4(MeCN)_2][BF_4]_2$ (35 mg, 0.039 mmol) and acetone was carried out by following a procedure similar to that described in the synthesis of compound **2**. The product, **3**, was crystallized by layering petroleum ether on the dichloromethane solution of the compound. Yield: 30 mg (83%). ^{1}H NMR (CD_3CN; δ, ppm): 8.57 (s, 2H, H(NP)), 8.46 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, H(NP)), 8.12 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, H(NP)), 7.37 (m, 2H, H(NP)), 6.34 (s, 2H, OH), 3.96 (d, 2H, $^2J_{H-H}$ = 14.4 Hz, CH_2), 3.60 (d, 2H, $^2J_{H-H}$ = 14.8 Hz, CH_2), 2.72 (s, 6H, CH_3(NP)), 1.79 (s, 6H, CH_3), 1.52 (s, 6H, CH_3). IR (KBr; cm^{-1}): ν(CO) 2045, 2010, 1964; ν(OH) 3302; $\nu(BF_4^-)$ 1060. ESI-MS: *m*/*z* 747 $[\{M\}^{2+} - H^+]^+$, 834 $[\{M\}^{2+} + BF_4^-]^+$. Anal. Calcd for $C_{30}H_{32}N_4O_6B_2F_8Ru_2$: C, 39.15; H, 3.50; N, 6.09. Found: C, 39.06; H, 3.58; N, 6.18. UV−vis (CH_3CN; λ_{max}, nm (ϵ, dm^3 mol^{-1} cm^{-1})): 263 (sh), 304 (6.34 × 10^3).

$[Ru_2(CO)_4(L3)_2][BF_4]_2$ (4). The reaction of **1** (42 mg, 0.049 mmol) and methyl ethyl ketone was carried out by following a procedure similar to that described in the synthesis of compound **2**. The product, **4**, was crystallized by layering petroleum ether on a dichloromethane solution of the compound. Yield: 38 mg (84%). ^{1}H NMR (CD_3CN; δ, ppm): 8.86 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, H(NP)), 8.73 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, H(NP)), 8.60 (m, 2H, H(NP)), 8.06 (m, 2H, H(NP)), 7.50 (m, 2H, H(NP)), 6.41 and 6.17 (s, 2H, OH), 3.74 (m, 4H, CH_2), 1.71 (s, 6H, CH_3), 1.52 (m, 4H, CH_2(Et)), 1.23−1.10 (m, 6H, CH_3(Et)). IR (KBr; cm^{-1}): ν(CO) 2042, 2007, 1962; ν(OH) 3301; $\nu(BF_4^-)$ 1058. ESI-MS: *m*/*z* 747 $[\{M\}^{2+} - H^+]^+$, 834 $[\{M\}^{2+} + BF_4^-]^+$. Anal. Calcd for $C_{30}H_{32}N_4O_6B_2F_8Ru_2$: C, 39.15; H, 3.50; N, 6.09. Found: C, 39.02; H, 3.58; N, 6.21. UV−vis (CH_3CN; λ_{max}, nm (ϵ, dm^3 mol^{-1} cm^{-1})): 267 (sh), 304 (5.48 × 10^3).

X-ray Data Collection and Refinement. Single-crystal X-ray structural studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.710 73 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software package,[21] and the data were corrected for absorption using the SADABS program.[22] The structures were solved and refined

(21) SAINT+ Software for CCD Diffractometers; Bruker AXS, Madison, WI, 2000.

using the SHELX suite of programs,[23] while additional crystallographic calculations were performed by the program PLATON.[24] Figures were drawn using ORTEP32.[25] The hydrogen atoms were included at geometrically calculated positions in the final stages of the refinement and were refined according to the "riding model". The alcoholic H atoms of compounds **2**, **2a**, **3**, and **4** were not assigned in the structures. All non-hydrogen atoms were refined with anisotropic thermal parameters, with the exception of C and O atoms of acetone solvent molecules in **2** and **2a**, C15 in **2**, and C22, C22a, and C23 in **4**. The O atom of the acetone solvent molecule in **2a** and the F atoms of the tetrafluoroborate anion in **4** were found to be disordered and were modeled satisfactorily. The methyl and ethyl groups of **4** were found to be positionally disordered and were modeled in a satisfactory manner. No hydrogens were generated for the carbons C21, C22, C22a, and C23 in the structure of **4**. Pertinent crystallographic data for compounds **2**, **2a**, **3**, and **4** are summarized in Table 1.

Acknowledgment. We thank the anonymous reviewers for their valuable comments and insights. We thank the Department of Science and Technology, New Delhi, India, for financial support of this work.

Supporting Information Available: Tables giving details of the crystal data and CIF files giving crystal data for the compounds **2**, **2a**, **3**, and **4** and figures giving IR and ESI-MS spectra of compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070139J

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