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Reactivity of the Oxime/Oximato Group in Ruthenium(II) Complexes

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Oxime targeted reactions of the complexes *trans*-[(κ^3-dapdOH)Ru(CO)(PPh_3)$_2$]PF_6 (**1**) (dapdOH = diacetylpyridinedioxime) and *trans*-[(κ^3-dapmOH)RuCl(PPh_3)$_2$]PF_6 (**2**) (dapmOH = diacetylpyridinemonooxime) with $SOCl_2$, $NaBH_4$, or HCHO led into conversion of oxime to oximato, imino, or hydroxymethylimino groups. The reaction products have been characterized by analytical and spectral studies. Molecular structures of the representative homo/heteroleptic oxime/oximato complexes *trans*-[(κ^3-dapdOH)Ru(CO)(PPh_3)$_2$]PF_6 (**1**), *trans*-[(κ^3-dapdO)Ru(CO)(PPh_3)$_2$] (**11**) and oximato/imino complex *trans*-[(κ^3-dapd-NH)Ru(CO)(PPh_3)$_2$]PF_6 (**13**) have been authenticated by single-crystal X-ray diffraction analyses. Structural studies revealed the presence of various oxime/oximato/imino based O−H···O, C−H···O, and N−H···F interactions in the complexes **1**, **11**, and **13**.

Introduction

Justification of the role of metal complexes in organic reactions has attracted sustained interest among the scientific community over many decades. In this regard, application of a purely organic approach in inorganic molecules has been the subject of investigation by many research groups.[1] Further, analogous to Schiff bases, oxime ligands have played a significant role in the development of coordination chemistry[2] because a ligand oxime moiety is potentially ambidentate and can coordinate with metal ions either through nitrogen or oxygen atoms.[3] It may coordinate with one metal ion through nitrogen and another through the oxygen atom forming an oximato bridge.[4] In the majority of complexes, oxime generally coordinates via nitrogen, and the oxygen atom does not participate in coordination to the metal center. In contrast, O-binding occurs in multinuclear assemblies incorporating two-atom bridging modes, wherein the nitrogen atom is also involved in bonding.[5] Among the oxime ligands, the chelating properties of 2,6-diacetylpyridinedioxime (dapdOH_2) and 2,6-diacetylpyridinemonooxime (dapmOH) have been investigated, and various coordination modes have been discovered.[6] Further, dapdOH_2 has been recently employed in the construction of high-nuclearity clusters.[7] Although, synthetic and structural chemistries of metal−oxime complexes have been extensively studied,[8−10] reactivity of the coordinated oxime group has received little attention.[11−16]

Metal mediated or catalyzed Beckmann rearrangement has been an established approach in isomerization of aldoxime to amide, and depending upon the nature of reacting oxime

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moieties, reaction conditions have been modified considerably.[17] In contrast to aldoximes, metal-mediated isomerization of ketoximes is a rare reaction.[18] In this direction, we have dedicated our efforts to examine the influence of metal ion on reactivity of the metal coordinated ketoxime group of the ligands $dapdOH_2$ and dapmOH in ruthenium complexes *trans*-[(κ^3-dapdOH)Ru(CO)(PPh_3)$_2$]PF_6 (**1**) and *trans*-[(κ^3-dapmOH)RuCl(PPh_3)$_2$]PF_6 (**2**). In this paper, we describe the reactivity of the oxime moiety of dapmOH and $dapdOH_2$ with various species, $SOCl_2$, $NaBH_4$, and HCHO, in complexes **1** and **2** leading to the oximato, imino, or hydroxymethylimino groups. We also present herein structural support for the formation of heteroleptic oxime/oximato complex *trans*-[(κ^3-dapdOH)Ru(CO)(PPh_3)$_2$]PF_6 (**1**) and its transformed products homoleptic oximato/oximato complex *trans*-[(κ^3-dapdO)Ru(CO)(PPh_3)$_2$] (**11**) and heteroleptic oximato/imino complex *trans*-[(κ^3-dapd-NH)Ru(CO)(PPh_3)$_2$]PF_6 (**13**).

Results and Discussion

Synthesis and Characterization of Cationic *trans*-[(κ^3-dapdOH)Ru(CO)(PPh_3)$_2$]PF_6 (1) and *trans*-[(κ^3-dapmOH)RuCl(PPh_3)$_2$]PF_6 (2). The parent cationic complex *trans*-[(κ^3-dapdOH)Ru(CO)(PPh_3)$_2$]PF_6 (**1**) was prepared by reaction of a methanolic solution of $dapdOH_2$ with $RuH(CO)Cl(PPh_3)_3$ under refluxing conditions, and *trans*-[(κ^3-dapmOH)RuCl(PPh_3)$_2$]PF_6 (**2**) was prepared following our earlier procedure.[19] The infrared spectrum of **1** displayed a marked shift in position of the bands associated with $\nu_{C=N}$ and oxime ν_{N-O} toward higher frequency by 30 and 85 cm^{-1}, respectively, compared with that in free ligand. Further, it exhibited an additional band at 1093 cm^{-1} corresponding to ν_{N-O}. The presence of a band associated with ν_{N-O} in the high-energy side suggested deprotonation of one of the oxime N−OH groups. Bands at 1601 and 1625 cm^{-1} may be assigned to $\nu_{C=N}$ of the oximato and $\nu_{C=N}$ of the oxime group, respectively. Coordinated carbonyl group ($\nu_{C\equiv O}$) vibrated as a sharp band at 1987 cm^{-1}. In the ^1H NMR spectrum of **1**, a singlet corresponding to the N−OH proton was observed at δ 10.94 ppm. Further, the protons associated with dapdOH and triphenylphosphine ligands appeared at their usual positions (see Experimental Section).[14,19] The position and integrated intensity of various peaks supported proposed formulation of the complex. It was further authenticated crystallographically. An ORTEP view of the complex cation of **1** is shown in Figure 1. Important crystallographic data

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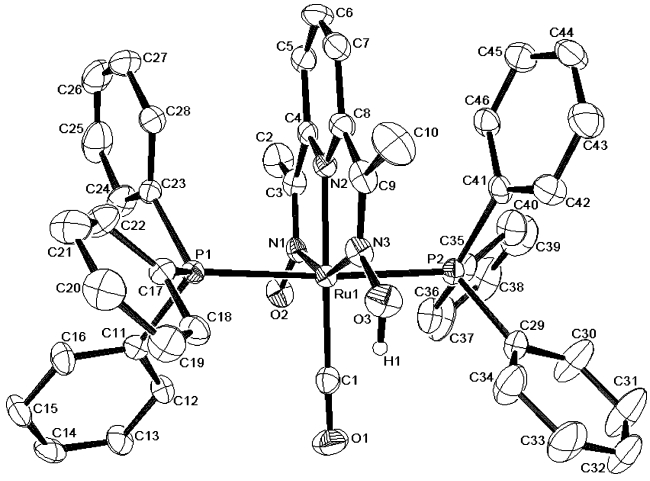

Figure 1. ORTEP view of complex cation of **1** (hydrogen atoms omitted for clarity).

Table 1. Crystallographic Data for **1**, **11**, and **13**

	1	**11**	**13**
formula	$C_{92}H_{80}F_{12}N_6O_8P_6Ru_2$	$C_{46}H_{39}N_3O_3P_2Ru$	$C_{46}H_{40}F_6N_3O_5P_3Ru$
fw	2013.58	844.81	1022.79
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$	$P2_1/c$
a, Å	15.919(2)	9.837(2)	9.924(2)
b, Å	24.2481(16)	23.636(5)	20.904(4)
c, Å	24.8093(16)	17.079(3)	22.941(5)
β, deg	106.15	90.48(3)	91.03(3)
V, Å^3	9198.7(15)	3970.7(14)	4758.2(17)
Z	4	4	4
ρ(calcd), g cm^{-3}	1.454	1.413	1.428
μ, mm^{-1}	0.515	0.521	0.501
no. reflns collected	16740	51079	42955
no. unique reflns	16099	7117	8340
R_{int}	0.0444	0.0972	0.1730
$R_1[I > 2\sigma(I)]$	0.0560	0.0635	0.0963
$wR_2[I > 2\sigma(I)]$	0.1441	0.2449	0.2137
R_1 (all data)	0.1557	0.0700	0.1207
wR_2 (all data)	0.1747	0.2549	0.2300
GOF	1.017	1.139	1.082

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **1**, **11**, and **13**

	1	**11**	**13**
Ru−N2$_{py}$	2.010(5)	2.019(5)	2.021(6)
Ru−N1$_{oximato}$	2.063(5)	2.114(5)	2.059(6)
Ru−N3$_{oxime/oximato/imino}$	2.117(5)	2.099(4)	2.121(6)
Ru−C1$_{carbonyl}$	1.898(8)	1.868(6)	1.871(8)
Ru−P1	2.4317(17)	2.3932(14)	2.4222(18)
Ru−P2	2.4225(18)	2.4016(13)	2.3910(18)
N1−O2$_{oximato}$	1.294(6)	1.320(6)	1.280(9)
N3−O3$_{oxime/oximato}$	1.377(6)	1.302(6)	
C1−O1$_{carbonyl}$	1.145(8)	1.151(8)	1.133(9)
C3−N1$_{oximato}$	1.329(8)	1.329(9)	1.354(10)
C9−N3$_{oxime/oximato/imino}$	1.296(8)	1.352(8)	1.283(9)
P1−Ru1−P2	175.74(6)	175.57(4)	176.38(6)
N1−Ru1−N3	154.4(2)	153.9(2)	152.8(3)
C1−Ru1−N2	177.9(3)	177.90(18)	178.0(3)

and selected geometrical parameters are summarized in Tables 1 and 2, respectively.

Orange red crystals of the heteroleptic complex **1** crystallize in the $P2_1/a$ space group with two crystallographically independent molecules in the asymmetric unit. Coordination geometry about each Ru(II) center (Ru1 and Ru2) can be best described as a distorted octahedron with CN_3P_2 donor groups. In each unit (Ru1,C1,N1,N2,N3,P1,P2 and Ru2,C2,N4,N5,N6,P3,P4), equatorial positions about the ruthenium center are occupied by the central pyridyl nitrogen (avg Ru−N 2.013 Å), the oximato (avg Ru−N 2.075 Å) and oxime nitrogens (avg Ru−N 2.115 Å) of dapdOH, and the carbonyl group (avg Ru−C 1.897 Å), which is *trans* to the central pyridyl nitrogen (avg C−Ru−N 178.35°). The apical positions are occupied by triphenylphosphine groups (avg Ru−P 2.4272 Å, avg P−Ru−P 176.98°). It is noteworthy that the Ru−N$_{oximato}$ distances (avg 2.075 Å) are shorter than the Ru−N$_{oxime}$ distance (avg 2.115 Å), indicating better donor ability of the oximato group.[12a] Furthermore, deprotonation of the N−OH group leads to shortening of the N−O and lengthening of the C═N bond lengths. As indicated, the C═N$_{oximato}$ bond lengths (C3−N1 1.328 Å; C49−N4 1.318 Å; avg 1.323 Å) are longer than the C═N$_{oxime}$ bond distances (C9−N3 1.297 Å; C55−N6 1.302 Å; avg 1.300 Å). The N−O$_{oximato}$ bond lengths (N(3)−O(2) 1.295(6) Å; N(6)−O(5) 1.300 Å; avg 1.298 Å) are well below the N−O$_{oxime}$ bond distances (N(1)−O(1) 1.371(7) Å; N(4)−O(4) 1.363(6) Å; avg 1.367 Å).

Although coordination geometry about the metal center in the crystallographically independent molecular units of **1** are equivalent, overall arrangements of the phenyl rings of triphenylphosphine are quite different (see Supporting Information, Figure S1). It is interesting to see that the phenyl rings of triphenylphosphine in the molecule associated with Ru2 are in eclipsed conformation with a dihedral angle of 0.75°, on the other hand a highly stable staggered arrangement (dihedral angle 60.69°) has been observed in the other unit with Ru1 as the metal center. The eclipsed conformation of the phosphines leaves ∼50% of dapdOH ligand uncovered, with involvement of direct $\pi_{ph}/\pi_{py}/\pi_{ph}$ interactions ($\pi_{ph}-\pi_{py}$ 3.546 Å, $\pi_{py}-\pi_{ph}$ 3.387 Å); however in the staggered arrangement, the whole of the dapdOH is covered and, as expected, no direct $\pi/\pi/\pi$ interactions have been observed (average parameter for π/π interactions, $\pi_{ph}-\pi_{py}$ 3.412 Å).[20] The molecular units of **1** are interconnected via the intermediacy of a bridging water molecule (bridging angle = 123.31(23)°) as shown in Figure 2. The oxime and oximato oxygen atoms are involved in an intermolecular hydrogen-bonding interaction. The O$_{oxime}$···O$_{water}$ distances are 2.691(13) and 2.716(13) Å for O3···O2w and O6···O1w, respectively. The corresponding O5···O2w distance for oximato oxygen is 2.726(11) Å.[21]

Complexes **1** and **2** reacted with various species under varying reaction conditions to afford complexes **3**−**14**. Analytical and spectral data along with the reaction details are recorded in the Experimental Section. Substitution of the chloro group in complex **2** by CN^- and Br^- easily afforded the complexes *trans*-[(κ^3-dapmOH)RuCN(PPh$_3$)$_2$]PF$_6$ (**3**) and

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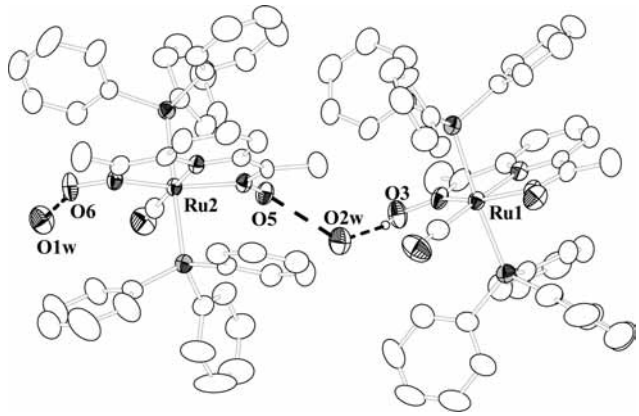
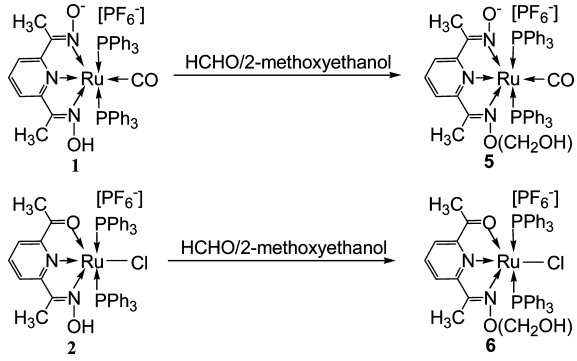


Figure 2. Diagram showing hydrogen-bonding interactions between two crystallographically independent molecular units of **1**.

Scheme 1

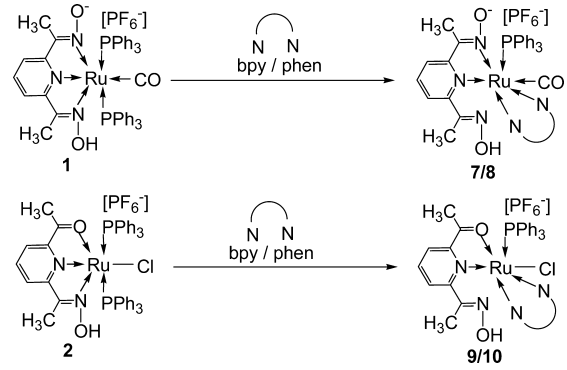


trans-[(κ^3-(dapmOH)RuBr(PPh_3)$_2$]PF_6 (**4**). The presence of characteristic bands corresponding to coordinated CN at 2070 cm^{-1} in the infrared spectrum of **3** indicated the feasibility of the substitution processes.

Synthesis of *trans*-[(κ^3-dapd-OCH_2OH)Ru(CO)(PPh_3)$_2$]PF_6 (5) and *trans*-[(κ^3-dapm-OCH_2OH)RuCl(PPh_3)$_2$]PF_6 (6). Alkylation, acylation, and arylation of oximes have been extensively studied in organic chemistry;[22] however, involvement of metal complexes in these processes have scarcely been explored.[12a,23] Reactions of **1** with formaldehyde in 2-methoxyethanol transformed the oxime OH to OCH_2OH and afforded complex **5**. In a similar manner, complex **2** afforded [(κ^3-dapm-OCH_2OH)RuCl-(PPh_3)$_2$]PF_6 (**6**) as shown in Scheme 1. ^{1}H NMR spectra of **5** and **6** in $CDCl_3$ displayed resonances associated with methylene protons as singlets at 2.75 and 3.24 ppm, respectively. The hydroxyl proton in these complexes appeared at 12.300 (**5**) and 11.669 ppm (**6**). Pyridyl and PPh_3 protons resonated at their usual positions.[14]

Synthesis of [(κ^2-dapdOH)Ru(CO)(L)(PPh_3)]PF_6 (L = bpy (7), phen (8)) and [(κ^2-dapmOH)RuCl(L)-(PPh_3)]PF_6 (L = bpy (9), phen (10)). Treatment of **1** and **2** with 2,2-bipyridine (bpy) and 1,10-phenanthroline (phen) in dichloromethane at room temperature afforded complexes

Scheme 2



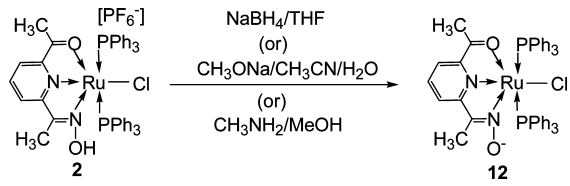
7−**10** in appreciably good yields (Scheme 2). All the complexes have been characterized by analytical and spectral studies (see Experimental Section). It was observed that the reactions of bis-chelating ligands bpy or phen forced the coordinated κ^3-dapdOH to κ^2 mode providing a site for coordination of the entrant group.[25] Spectral data of **7** and **8** supported octahedral coordination geometry about the metal center, wherein ruthenium is bonded to a bidentate ligand bpy or phen, triphenylphosphine, carbonyl group, and dapdOH bonded in a κ^2 mode. Further, being a strong donor, oximato nitrogen is expected to remain intact with the metal center in complexes **7** and **8**. Analytical and spectral data supported an analogous arrangement of the various groups about the metal center with pendant oxime nitrogen in **9** and **10**. The central pyridyl nitrogen of dapdOH or dapmOH is *trans* to carbonyl and chloro groups in **7** and **8** and **9** and **10**, respectively.

Further, it was observed that in each case an excess of bis-chelating ligand is required to afford the final products. In the formation of **8** and **10**, use of 1.5−2.0-fold excess of phenanthroline afforded the complexes in good yield. Further, reaction of complex **2** with a large excess of phenanthroline led to the formation of $[Ru(phen)_3]^{2+}$ as one of the side products.

Synthesis of *trans*-[(κ^3-dapdO)Ru(CO)(PPh_3)$_2$] (11) and *trans*-[(κ^3-dapmO)RuCl (PPh_3)$_2$] (12). Metal-assisted deoxygenation reactions of oximes are expected to undergo reduction with intermediacy of an oximato−metal intermediate complex, which is formed by cleavage of the oxime OH bond;[24,25] however decarboxylation is also considered in some cases.[26] The organic imines formed by deoxygenation are easily hydrolyzed to ketone, whereas coordination of the oxime with the metal center provides enough stability and rigidity to coordinated nitrogen to diminish the chances of facile hydrolysis of imine to ketone. Reaction of an equimolar mixture of **1** in dry methanol and $NaBH_4$ rapidly afforded a dark-red precipitate, which was characterized as **11** (Scheme

(22) Metzger, H. In *Houben-Weyl's Methoden der organischen Chemie*, 4th ed.; Müller, E., Ed.; G. Thieme Verlag: Stuttgart, Germany, 1968; Stickstoffverbindungen I, Teil 4, Vol. *10:4*, p 217.
(23) (a) Kazankov, G. M.; Dyachenko, O. G.; Nemukhin, A. V.; Ryabov, A. D. *Mendeleev Commun.* **1997**, 159. (b) Zerbib, V.; Robert, F.; Gouzerh, P. *J. Chem. Soc., Chem. Commun.* **1993**, 2179.
(24) (a) Alper, H.; Edward, J. T. *Can. J. Chem.* **1970**, *48*, 1543. (b) Charalambous, J.; Haines, L. I. B.; Morgan, J. S.; Peat, D. S.; Campbell, M. J. M.; Bailey, J. *Polyhedron* **1987**, *6*, 1027.
(25) Akazome, M.; Tsuji, Y.; Watanabe, Y. *Chem. Lett.* **1990**, 635.
(26) Langenbahn, M.; Stoeckli-Evans, H.; Suss-Fink, G. *Helv. Chim. Acta* **1991**, *74*, 549.

Scheme 3



3). Contrary to other reports, a single product was obtained.[27] Furthermore, conversion of the carbonyl group to a formyl group was not observed as reported for related carbonyl complexes.[27] This may be attributed to the ability of a softer client for the oxime N−OH bond than the carbonyl group. An easier dissociation of the oxime proton leads to delocalization of electron density over C═N−O$^-$ bond. Although use of dry methanol as a solvent facilitated reaction by effective precipitation and purification of the final product, acetonitrile−water (1:1 v/v) mixture also afforded the same product in quantitative yield.[28] An analogous product with the formulation *trans*-[(κ^3-dapmO)Ru(PPh$_3$)$_2$Cl] (**12**) was obtained from reactions of **2** under analogous conditions. Treatment of **1** and **2** with other mild bases such as methyl amine or methoxide afforded neutral products, which corresponded to **11** and **12**, respectively (Scheme 3). All the complexes have been characterized by elemental analyses and spectral data. The coordinated CO group in the infrared spectrum of **11** vibrated at 1959 cm^{-1}. Deprotonation of the oxime causes lengthening of the C═N bond distance, which is supported by presence of a band at 1582 cm^{-1}. Similarly, in the infrared spectrum of **12**, the band at 1582 cm^{-1} may be attributed to $\nu_{C=N}$ oximato, and the $\nu_{C=O}$ band appears at 1627 cm^{-1}.

It is noteworthy that the treatment of dapdOH$_2$ with RuH(CO)Cl(PPh$_3$)$_3$ in benzene also afforded **11** in high yield, which has been characterized by spectral data (Scheme 3). The molecular structure of **11** has been determined crystallographically. ORTEP depiction of **11** is shown in Figure 3.

Crystallographic data and selected bond parameters for **11** are summarized in the Tables 1 and 2, respectively. Complex **11** exhibits a distorted octahedral geometry about the ruthenium center analogous to that observed in complex **1**, with a dianionic κ^3-dapdO, two *trans* disposed triphenylphosphines, and a carbonyl group *trans* to central pyridyl nitrogen. A significant distortion is evidenced from the N1−Ru1−N3 bond angle, which is 153.9°. The P1−Ru1−P2 angle of 175.57° shows that the triphenylphosphine ligands are disposed *trans* to each other. The chelate bite angles involving N1−Ru1−N2 and N2−Ru1−N3 are 77.0° and 76.9°, respectively, which also reflects observed deviation

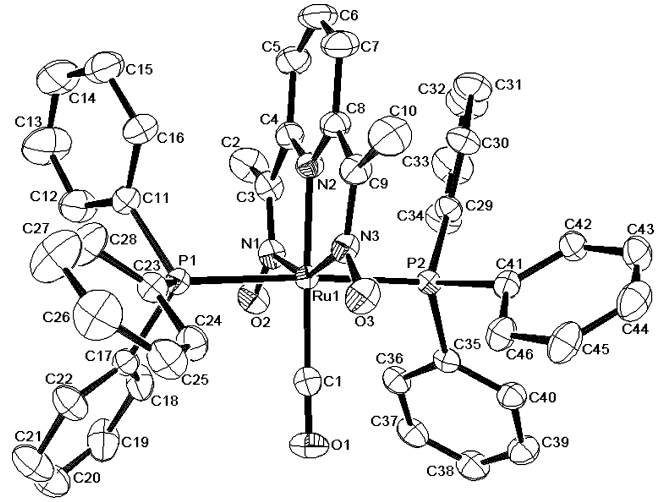


Figure 3. ORTEP plot for complex **11** with 30% ellipsoid probability.

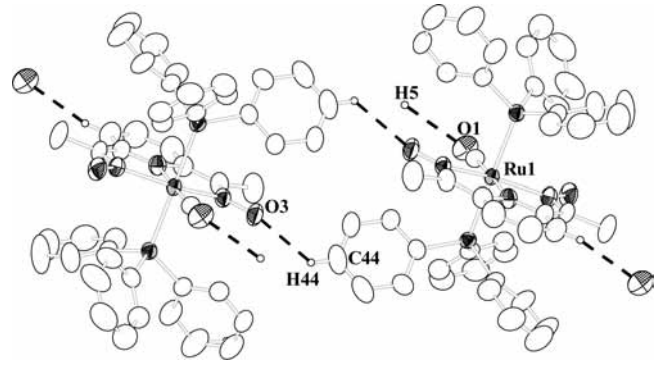


Figure 4. Diagram showing hydrogen bonding between two adjacent molecular units in **11**.

from the octahedral geometry. The C1−Ru1−N2 bond angle of 177.90° suggested that the carbonyl group is *trans* to the central pyridyl nitrogen. Both the N−O bond distances are similar with an average distance of ca. 1.311 Å,[12a] and the C−O bond distance is 1.151(8) Å. Figure 4 shows the involvement of oximato and carbonyl oxygen atoms in intermolecular C−H···O hydrogen bonding interactions with phenyl and pyridyl protons, respectively. The matrices for these interactions are as follows: $C44_{Ph}$−H44···$O3_{oximato}$, H44···O3 2.612(35) Å, C44···O3 3.319(48) Å, ∠C44−H44···O3 133.27(35)°; $C5_{py}$−H5···$O1_{CO}$, H5···O1 2.550(34) Å, C5···O1 3.465(47) Å, ∠C5−H5···O1 167.68(34)°.

Synthesis of *trans*-[(κ^3-dapd-NH)Ru(CO)(PPh$_3$)$_2$]PF$_6$ (13) and *trans*-[(κ^3-dapm-NH)Ru(CO)(PPh$_3$)$_2$]PF$_6$ (14). An attempt has been made to examine isomerization of the metal coordinated ketoxime ligand in **1** and **2** under the conditions employed for Beckmann rearrangement. Treatment of cationic parent complexes **1** and **2** with thionyl chloride in tetrahydrofuran followed by vigorous boiling of resultant solid product in distilled water afforded complex **13** and **14**, respectively. Interestingly, in contrast to expected amido group, the oxime group is efficiently transformed to imine as shown in Scheme 4.

Both the complexes were characterized by elemental analyses, spectral data, and X-ray crystallography. A sharp band at ca. 3500 cm^{-1} in the infrared spectra reflects

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(28) (a) Gibson, D. H.; Owens, K.; Richardson, J. F. *Organometallics* **1987**, *6*, 2624. (b) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (c) Gibson, D. H.; Owens, K.; Mandal, S. K.; Franco, J. O.; Sattich, W. E. *Organometallics* **1989**, *8*, 498.

Scheme 4

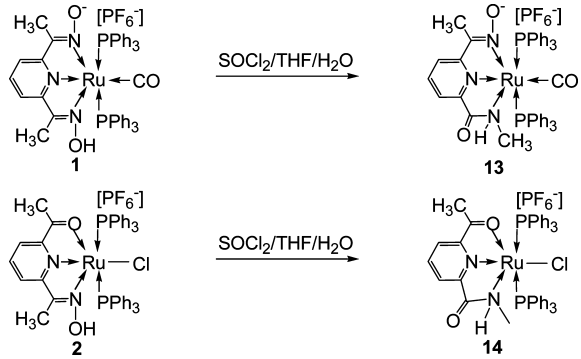
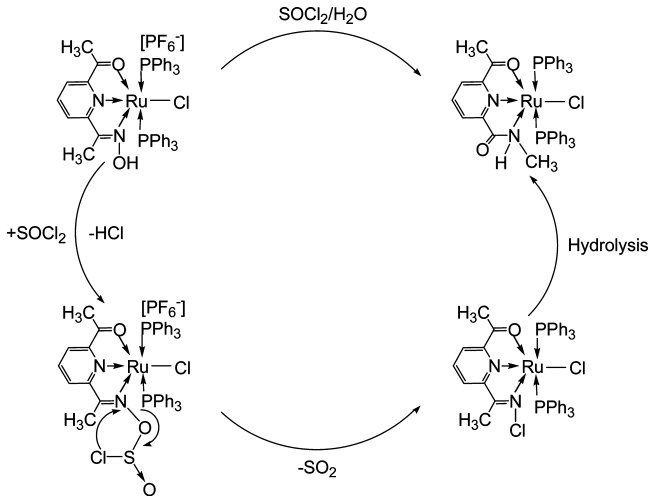


Chart 1



reduction of the N−OH to N−H. Following the conventional mechanistic pathway for Beckmann rearrangement in organic molecules, a proposed mechanism is illustrated in Chart 1. However in our case the oxime to imino transformation process favors a "water-assisted reduction pathway", because it has been observed that under the reaction conditions water may act as a dehalogenating agent.[17e,f]

ORTEP views of **13** and **14** are shown in Figures 5 and 6, respectively. Crystallographic data and important bond

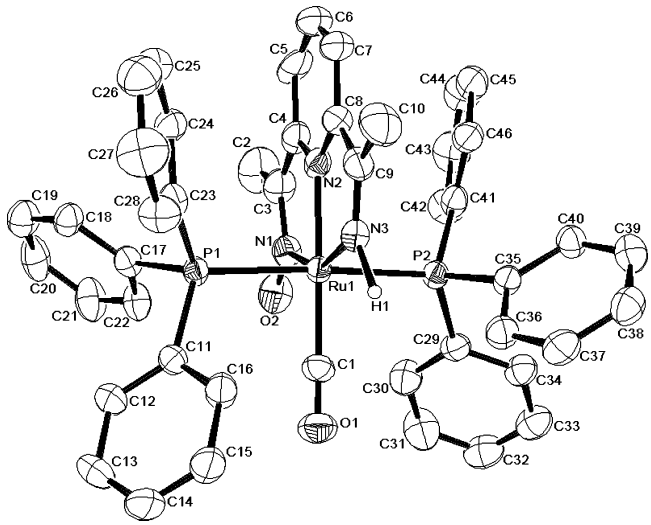


Figure 5. ORTEP view of complex **13** with 30% ellipsoid probability.

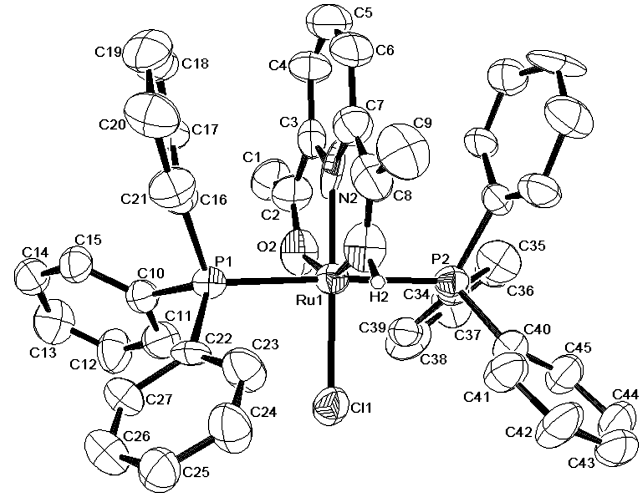


Figure 6. ORTEP view of complex **14** with 30% ellipsoid probability.

parameters of **13** are summarized in Tables 1 and 2. (We could not get satisfactory data on complex **14**, and structural refinement of this complex is not sufficiently good for reporting; however, available data supports our viewpoint.) The molecular identity and overall coordination geometry about the ruthenium center in **13** and **14** is similar to that in the respective parent complexes **1** and **2**. In *trans*-[(κ^3-dapd-NH)Ru(CO)(PPh_3)$_2$]PF_6 (**13**), the Ru−N_{imine} bond is 2.099(4) Å. The chelate bite angles involving N1−Ru1−N2 and N2−Ru1−N3 are 77.0(2)° and 76.9(2)°, respectively, which reflects observed deviation from the octahedral geometry. Further, the tridentate mode of dapd−NH reflects the distortion as evidenced by the N1−Ru1−N3 bond angle of 152.8(3)°. The phosphine ligands are essentially *trans* disposed (P1−Ru1−P2 176.38(6)°); however, the relative orientation of the phenyl rings force it to a staggered arrangement when viewed along P1−Ru1−P2 axis. The *trans* position of the carbonyl group to the central pyridyl nitrogen is reflected by the C1−Ru1−N2 bond angle of 178.0(3)°. The imino nitrogen is involved in an intermolecular N−H···F interaction with a fluoride atom of the counteranion PF_6^-. The matrices for these interactions are as follows: N3−H1···F1, H1···F1 1.819 Å, N3···F1 3.013 Å, ∠N3−H1···F1 147.21°.

Conclusions

In this work an effort has been made to apply an organic approach to inorganic molecules and to efficiently transform metal-coordinated oxime to oximato/imino/hydroxyimino complexes. Application of conventional Beckmann rearrangement on **1** and **2** shows that the coordination of heteroatoms to the metal center additionally stabilizes the organic moiety, thus effectively influencing the traditional mechanistic pathways and final products.

Experimental Section

General Considerations. Elemental analyses on complexes were performed by the Microanalytical Section of the Sophisticated Analytical Instrumentation Centre, Central Drug Research Institute, Lucknow. Infrared spectra in KBr discs were obtained on a Varian

spectrometer. NMR spectra were recorded on a Bruker DRX-300 NMR spectrometer. ^{1}H and ^{31}P and chemical shifts are reported relative to TMS and PCl_3 ($\delta = 220$), respectively. FAB mass spectra were acquired on a JEOL SX 102/DA 6000 mass spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. Accelerating voltage was 10 kV, and the spectra were recorded at room temperature with *m*-nitrobenzyl alcohol as matrix.

Materials. All the synthetic manipulations were performed using deaerated AR grade solvents, which were purified rigorously by standard procedures prior to their use.[29] Ammonium hexafluorophosphate, 2,6-diacetylpyridine, and ruthenium(III) chloride hydrate (all Aldrich) were used as received without further purification. The complexes $RuH(CO)Cl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ and the ligands 2,6-diacetylpyridinedioxime ($dapdOH_2$) were synthesized following the literature procedures.[30,31] The precursor complex *trans*-[(κ^3-dapmOH)$RuCl(PPh_3)_2$]PF_6 (**2**) was synthesized using our procedure reported elsewhere.[19]

Synthesis and Characterization of *trans*-[(κ^3-dapdOH)-$Ru(CO)(PPh_3)_2$]PF_6 (1). To a methanolic solution (15 mL) of $dapdOH_2$ (1.0 mmol, 0.192 g), $RuH(CO)Cl(PPh_3)_3$ (0.955 g, 1.0 mmol) was added, and the reaction mixture was refluxed for 14 h. The resulting orange-red solution was filtered and concentrated to approximately (4 mL). A saturated solution of ammonium hexafluorophosphate dissolved in methanol (10 mL) was added to it and left undisturbed to concentrate slowly by evaporation at room temperature. It separated as an orange red microcrystalline complex, which was separated by filtration, washed twice with methanol and diethyl ether, and dried under vacuum; the yield was 0.605 g (~61%). Anal. Calcd for $C_{46}H_{40}N_3OP_3F_6Ru$ (992): C, 55.65; H, 4.03; N, 4.23%. Found: C, 55.79; H, 4.42; N, 3.92%. Selected IR data (KBr, cm^{-1}): 1987 $\nu_{C\equiv O}$, 1625, 1601, 1483, 1435, 1294, 1093, 999, 854, 775, 748, 698, 519. ^{1}H NMR (300 MHz, acetone-d_6): δ 10.94 (s, 1H, N-OH), 7.79 (t, $J = 7.8$ Hz, 1H), 7.50 (d, $J = 7.2$ Hz, 1H), 7.38−7.44 (m, 30H, PPh_3), 6.64 (d, $J = 7.8$ Hz, 1H), 1.85 (s, br.). ^{31}P NMR (120 MHz, acetone-d_6): δ 29.45 (s, *P*Ph_3), −142.81 (septet, *P*F_6). UV−vis.(acetone, λ_{max} nm): 450 (12300), 355 (46220), 273 (48900); Emission (acetone, λ_{em} (λ_{ex}) nm): 675 (450).

Synthesis and Characterization of *trans*-[(κ^3-dapmOH)-$RuCN(PPh_3)_2$]PF_6 (3). To a suspension of complex **2** (0.985 g, 1.0 mmol) in methanol (25 mL), NaCN (0.049 g, 1.0 mmol) was added and refluxed for 8 h. Resulting solution was evaporated to dryness and washed a couple of times with diethyl ether and dried in air to afford a light brown compound. It was recrystallized from $CHCl_3$ and petroleum ether (60−80 °C); the yield was 0.771 g (79%). Anal. Calcd for $C_{46}H_{40}N_3O_2P_3F_6Ru$ (976): C, 56.56; H, 4.16; N, 4.30%. Found: C, 56.48; H, 4.52; N, 4.12%. Selected IR data (KBr, cm^{-1}): 2070 ($\nu_{C\equiv N}$), 842 (ν_{P-F}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.41 (s, 1H, N-OH), 7.60 (t, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 7.2$ Hz, 1H), 7.26−7.21 (m, 30H, PPh_3), 6.81 (d, $J = 5.0$ Hz, 1H), 1.85 (s, 6H). ^{31}P NMR (120 MHz, $CDCl_3$): δ 30.11 (s, *P*Ph_3), −141.79 (septet, *P*F_6).

Synthesis and Characterization of *trans*-[(κ^3-dapmOH)-$RuBr(PPh_3)_2$]PF_6 (4). Complex **4** was prepared by reaction of complex **2** (0.985 g, 1.0 mmol) with a large excess of KBr (~20 mmol) in an ethanol−water mixture (25 mL, 3:1 v/v) under refluxing over 8 h. Resulting solution was cooled to room temperature and evaporated to dryness to afford a dark brown residue. The residue was washed with water, redissolved in methanol, and evaporated to dryness. The solid product thus obtained was washed with diethyl ether and dried in air; the yield was 0.742 g (72%). Anal. Calcd for $C_{45}H_{40}N_2O_2BrP_3F_6Ru$ (1030): C, 52.43; H, 3.88; N, 2.72%. Found: C, 52.78; H, 3.72; N, 2.92. IR (KBr, cm^{-1}): ν_{P-F} 842. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.41 (s, 1H, N-OH), 7.60 (t, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 7.2$ Hz, 1H), 7.26−7.21 (m, 30H, PPh_3), 6.81 (d, $J = 5.0$ Hz, 1H), 1.85 (s, 6H). ^{31}P NMR (120 MHz, $CDCl_3$): δ 29.97 (s, *P*Ph_3), −141.21 (septet, *P*F_6).

Synthesis and Characterization of *trans*-[(κ^3-dapd-OCH_2-OH)$Ru(CO)(PPh_3)_2$]PF_6 (5). To a suspension of complex **1** (0.992 g, 1.0 mmol) in 2-methoxyethanol (60 mL), formaldehyde (37−41% 20 mL) was added, and the reaction mixture was refluxed for 4 h. The resulting solution was filtered to remove any solid impurities and filtrate was precipitated by addition of diethyl ether. The orange-brown product thus precipitated was separated by filtration, repeatedly washed with petroleum spirit, and dried in air; the yield was 0.634 g (62%). Anal. Calcd for $C_{46}H_{42}N_3O_4P_3F_6Ru$ (1022): C, 55.19; H, 4.11; N, 4.11%. Found: C, 54.98; H, 4.32; N, 3.92%. Selected IR data (KBr, cm^{-1}): 2001 ($\nu_{C\equiv O}$), 1654($\nu_{C=N}$), 842 (ν_{P-F}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (t, $J = 7.7$ Hz, 1H), 7.48 (d, $J = 7.2$ Hz, 1H), 7.36−7.25 (m, 30H, PPh_3), 6.69 (d, $J = 5.0$ Hz, 1H), 4.12 (br, s, 1H, OH), 2.75 (s, CH_2, 2H), 1.85 (br. s, 6H, CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ 45.84 (s, *P*Ph_3), −141.23 (septet, *P*F_6).

Synthesis and Characterization of *trans*-[(κ^3-dapm-OCH_2-OH)$RuCl(PPh_3)_2$]PF_6 (6). Complex **6** was prepared following the above procedure adopted for **5**, except that complex **2** was used in place of **1**. After filtration, the solution was allowed to cool at ~ 4 °C over several days. It gave a microcrystalline dark brown compound, which was washed with diethyl ether and air-dried; the yield was 0.620 g, (~61%). Anal. Calcd for $C_{46}H_{42}N_2O_3ClP_3F_6Ru$ (1016): C, 54.33; H, 4.13; N, 2.76%. Found: C, 54.48; H, 4.02; N, 2.98%. Selected IR data (KBr, cm^{-1}): 1627 ($\nu_{C=N}$), 840 (ν_{P-F}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (m, 1H), 7.51−7.12 (m, 30H, PPh_3), 6.82 (d, $J = 7.1$ Hz, 1H), 4.12 (br, s, 1H, OH), 3.24 (s, CH_2, 2H), 2.01 (br. s, 6H, CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ 32.24 (s, *P*Ph_3), −141.01 (septet, *P*F_6).

Synthesis and Characterization of [(κ^2-dapdOH)$Ru(CO)$-(κ^2-bpy)(PPh_3)]PF_6 (7). Complex **1** (0.099 g, 0.1 mmol) was treated with a large excess of 2,2′-bipyridine (~1.5 mmol) in dichloromethane (80 mL) and stirred for 8 h. The solution was evaporated to dryness and extracted with dichloromethane and filtered. The filtrate was treated with diethyl ether to afford a light orange compound. The product was separated by filtration, washed with diethyl ether, and dried under vacuum; the yield was 0.050 g (56%). Anal. Calcd for $C_{38}H_{33}N_5O_3P_2F_6Ru$ (885): C, 51.53; H, 3.73; N, 7.91%. Found: C, 51.90; H, 3.62; N, 8.02%. Selected IR data (KBr, cm^{-1}): 1998 ($\nu_{C\equiv O}$), 1601 ($\nu_{C=N}$), 843 (ν_{P-F}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.01 (s, 1H, N−O*H*), 8.92 (m, 2H), 8.68 (d, $J = 7.9$ Hz, 2H), 8.35 (d, $J = 7.9$ Hz, 2H), 7.78−7.62 (m, 3H), 7.50−7.36 (m, 15H), 6.24 (d, $J = 7.7$ Hz, 2H), 1.26 (br. s, 6H, CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ 30.64 (s, *P*Ph_3), −142.11 (septet, *P*F_6).

Synthesis and Characterization of [(κ^2-dapdoH)$Ru(CO)$-(κ^2-phen)(PPh_3)]PF_6 (8). Complex **8** was prepared following the above procedure for **7** except that a small excess of 1,10-phenenthroline (0.040 g, 0.2 mmol) was used in place of 2,2′-bipyridine. Complex **8** was obtained as red-orange solid; the yield was 0.049 g, (54%). Anal. Calcd for $C_{40}H_{33}N_5O_3P_2F_6Ru$ (909): C, 52.81; H, 3.63; N, 7.70%. Found: C, 52.47; H, 3.77; N, 7.91%.

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Selected IR data (KBr, cm^{-1}): 1965 ($\nu_{C\equiv O}$), 1654 ($\nu_{C=N}$), 844 (ν_{P-F}). ^1H NMR (300 MHz, $CDCl_3$): δ 10.95 (s, 1H, N−O*H*), 9.20 (d, J = 3.9 Hz, 2H), 8.26 (d, J = 6.9 Hz, 2H), 7.81−7.65 (m, 5H), 7.45−7.29 (m, 15H), 6.18 (d, J = 7.8 Hz, 2H), 1.25 (br. s, 6H, CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ 30.52 (s, *P*Ph_3), −143.21 (septet, *P*F_6).

Synthesis and Characterization of [(κ^2-dapmOH)RuCl(κ^2-bpy)(PPh_3)]PF_6 (9). Complex **2** (0.099 g, 0.1 mmol) was dissolved in dichloromethane (35 mL), and bpy (0.020 g, 0.15 mmol) was added to it. The resulting dark brown-orange solution was stirred for 24 h and then completely evaporated to dryness. The solid residue was extracted with dichloromethane and precipitated with diethyl ether. Resulting solid was washed with diethyl ether and dried in air; the yield was 0.053 g (60%). Anal. Calcd for $C_{37}H_{33}N_4O_2ClP_2F_6Ru$ (879): C, 50.51; H, 3.75; N, 6.37%. Found: C, 50.79; H, 3.79; N, 6.62%. Selected IR data (KBr, cm^{-1}): 1602 ($\nu_{C=N}$), 840 (ν_{P-F}). ^1H NMR (300 MHz, $CDCl_3$): δ 10.06 (s, 1H, N−O*H*), 9.61 (m, 2H), 8.69 (d, J = 7.9 Hz, 2H), 8.39 (d, J = 8.1 Hz, 2H), 7.83−7.66 (m, 3H), 7.52−7.23 (m, 15H), 6.96 (d, J = 7.5 Hz, 2H), 1.98 (br. s, 6H, CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ 28.51 (s, *P*Ph_3), −142.71 (septet, *P*F_6).

Synthesis and Characterization of [(κ^2-dapdoH)RuCl(κ^2-phen)(PPh_3)]PF_6 (10). Complex **10** was prepared from the reaction of complex **2** (0.099 g, 0.1 mmol) with 1,10-phenanthroline (0.030 g, 0.15 mmol) in dichloromethane (30 mL) and worked up as complex **9**. Complex **10** was obtained as orange-brown solid; the yield was 0.054 g (∼61%). Anal. Calcd for $C_{39}H_{33}N_4O_2ClP_2F_6Ru$ (903): C, 51.83; H, 3.65; N, 6.20%. Found: C, 52.01; H, 3.72; N, 6.02%. Selected IR data (KBr, cm^{-1}): 1602 ($\nu_{C=N}$), 840 (ν_{P-F}) ^1H NMR (300 MHz, $CDCl_3$): δ 10.06 (s, 1H, N−O*H*), 9.59 (m, 2H), 9.19 (d, J = 7.9 Hz, 2H), 8.25 (d, J = 8.1 Hz, 2H), 7.81−7.60 (m, 3H), 7.52−7.23 (m, 15H), 6.96 (d, J = 7.5 Hz, 2H), 1.99 (s, 6H, CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ 28.63 (s, *P*Ph_3), −143.01 (septet, *P*F_6).

Synthesis and Characterization of *trans*-[(κ^3-dapdO)Ru(CO)(PPh_3)$_2$] (11). Complex **1** (0.099 g, 1.0 mmol) was stirred with $NaBH_4$ (0.019 g in 1 mL of diglyme) in dry methanol (10 mL) for 15 min, whereupon a dark red precipitate separated out. The resulting precipitate was filtered through a sintered crucible, washed with acetonitrile and diethyl ether, and dried under vacuum; the yield was 0.060 g (70%). Anal. Calcd for $C_{46}H_{39}N_3O_3P_2Ru$ (846): C, 65.25; H, 4.61; N, 4.96%. Found: C, 65.60; H, 4.32; N, 4.82%. Selected IR data (KBr, cm^{-1}): $\nu_{C\equiv O}$ 1959, $\nu_{C=N}$ 1586. ^1H NMR (300 MHz, $CDCl_3$): δ 7.43 (t, J = 5.7 Hz, 1H), 7.31−7.21 (m, 30H), 6.12 (d, J = 7.1 Hz, 2H), 1.12 (s, 6H, CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ 29.43 (s, *P*Ph_3).

Synthesis and Characterization of *trans*-[(κ^3-dapmO)RuCl(PPh_3)$_2$] (12). Complex **2** (0.099 g, 0.1 mmol) was stirred with $NaBH_4$ (0.019 g in 1 mL of diglyme) in an acetonitrile−water mixture (6 mL, 1:1 v/v) for 30 min. A brown precipitate separated, which was filtered, washed with diethyl ether, and air-dried; the yield was 0.058 g (69%). Anal. Calcd for $C_{45}H_{39}N_2O_2ClP_2Ru$ (840): C, 64.29; H, 4.64; N, 3.33%. Found: C, 64.66; H, 4.97; N, 3.45%. Selected IR data (KBr, cm^{-1}): 1584 ($\nu_{C=N}$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.43 (t, J = 5.7 Hz, 1H), 7.31−7.21 (m, 30H), 6.12 (d, J = 7.1 Hz, 2H), 1.12 (s, 6H, CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ 31.02 (s, *P*Ph_3).

Synthesis and Characterization of *trans*-[(κ^3-dapd-NH)Ru(CO)(PPh_3)$_2$]PF_6 (13). Complex **1** (0.099 g, 0.1 mmol) was dissolved in acetone (2 mL), and THF (25 mL) was added to it. The resulting solution was concentrated to a final volume of 10 mL in a water bath, cooled to room temperature, and filtered. To the filtrate, freshly distilled thionyl chloride (3 mL) was added, and the reaction mixture was stirred for 1 h. The dark red solution rapidly turns to an orange-brown solution. It was allowed to stir for an additional 1 h to afford a brown-orange precipitate. The reaction mixture along with the precipitate was concentrated to dryness and vigorously boiled with distilled water (25 mL) for several hours. Resulting residue was filtered and washed with diethyl ether to afford an orange-brown solid; the yield was 0.064 g (66%). Anal. Calcd for $C_{46}H_{40}N_3O_2P_3F_6Ru$ (976): C, 56.56; H, 4.10; N, 4.30%. Found: C, 56.78; H, 4.42; N, 3.98%. Selected IR data (KBr, cm^{-1}): 1959 ($\nu_{C\equiv O}$), 1584 ($\nu_{C=N}$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.43 (t, J = 5.7 Hz, 1H), 7.41−7.26 (m, 30H), 6.65 (d, J = 7.1 Hz, 2H), 1.92 (s, 6H, CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ 33.19 (s, *P*Ph_3), −141.41 (sep., *P*F_6).

Synthesis and Characterization of *trans*-[(κ^3-dapm-NH)RuCl(PPh_3)$_2$]PF_6 (14). A solution of complex **2** (0.099 g, 0.1 mmol) in THF (20 mL) was treated with freshly distilled thionyl chloride (2.5 mL) and stirred for 1 h, affording a dark brown precipitate. The solution along with the precipitate was concentrated, and the residue thus obtained was vigorously boiled in distilled water (25 mL) for several hours. The residue was extracted with ethanol, which upon evaporation gave the desired complex; the yield was 0.066 g (68%). Anal. Calcd for $C_{45}H_{40}N_2OClP_3F_6Ru$ (970): C, 55.67; H, 4.12; N, 2.89. Found: C, 55.98; H, 4.42; N, 2.90%. Selected IR data (KBr, cm^{-1}): 1590, 839 (ν_{P-F}). ^1H NMR (300 MHz, $CDCl_3$): δ 7.89 (t, J = 8.1 Hz, 1H), 7.45−7.30 (m, 30H), 6.71 (d, J = 7.8 Hz, 2H), 2.00 (s, 6H, CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ 28.24 (s, *P*Ph_3), −141.63 (sep., *P*F_6).

Crystal Structure Determinations. Crystals suitable for single-crystal X-ray diffraction analyses for complexes **1**, **11**, **13**, and **14** were obtained by a liquid−liquid diffusion technique at room temperature. Intensity data for **1** were collected at 293(2) K on Enraf-Nonius CAD 4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Intensities of these reflections were measured periodically to monitor crystal decay. Single-crystal X-ray diffraction data for complexes **11**, **13**, and **14** were collected on an R-AXIS RAPID II diffractometer at room temperature with Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (SHELX-97).[32] All non-hydrogen atoms were refined anisotropically. The contributions due to H-atoms attached to carbon atoms were included as fixed contributions. Details about data collection, structure solution, and refinement are recorded in Table 1, and selected geometrical parameters are presented in Table 2.

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Supporting Information Available: Crystallographic data (cif format) of the complexes **1**, **11**, and **13** and figures showing the relative arrangement of phenyl rings of the triphenylphosphine in complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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