4234 *Organometallics* **2010,** *29,* 4234–4238
DOI: 10.1021/om100674x

ORGANOMETALLICS
Article

Bidentate Oxazoline−Imine Ruthenium(II) Complexes: Intermediates in the Methanolysis/Hydration of Nitrile Groups

Hamed Ben Ammar,[†,‡] Xiaowei Miao,[‡] Cédric Fischmeister,[‡] Loic Toupet,[§] and Pierre H. Dixneuf*[,‡]

[†]*Laboratoire de Chimie Organique Appliquée, Faculté des Sciences de Gabès, 6072, Tunisia,* [‡]*Laboratoire Catalyse et Organométalliques, Institut Sciences Chimiques de Rennes, UMR 6226, CNRS−Université de Rennes, Campus de Beaulieu, 35042 Rennes, France, and* [§]*Institut de Physique de Rennes, UMR 6251 CNRS−Université de Rennes 1, 35042 Rennes, France*

Received July 13, 2010

The reaction of $[RuCl_2(p\text{-cymene})]_2$ with benzoxazoleacetonitriles and $NH_4^+BF_4^-$ in methanol leads to bidentate *N,N′*-benzoxazole-methoxyimine-ruthenium(II) complexes **7**, corresponding to the addition of methanol to the ruthenium(II)-activated nitrile triple bond. The X-ray structure of a complex **7** shows equivalent Ru−N and slightly different C═N bond distances. The catalytic hydration of benzoxazolacetonitriles with $[RuCl_2(p\text{-cymene})]_2$ in methanol/water leads to quantitative formation of corresponding amides under mild conditions.

Introduction

The hydration of nitrile derivatives constitutes a straightforward way to generate amides, a useful functionality in synthesis,[1] that easily leads to their carboxylic acid derivatives. The amide formation slow step can be accelerated by enzymes,[2] and several metal-containing catalytic systems have recently been shown to perform this selective transformation under mild conditions.[3]

The molecular ruthenium catalyst $RuH_2(PPh_3)_4$ was first used by Murahashi et al.[4] to transform nitriles into amides and subsequently into ene-lactames in water/DME media. Then, Lin and Lau showed that the ruthenium hydride precursor $RuH(C_9H_7)(Ph_2PCH_2PPh_2)$ (C_9H_7: indenyl) promoted the nitrile to amide transformation, and B3LYP calculations[5] led to proposing a mechanism based on initial interaction of water with the (Ru−H) hydride, before its addition to the η^1-N-coordinated nitrile group. Recently, it was demonstrated that $Ru(acac)_2(Ph_2P\text{-}Py)_2$ allowed the catalytic hydration of nitrile with high turnover frequency in DME/water media.[6]

Platinum(II) complexes containing $R_2P(O)H$ ligands have allowed the selective catalytic hydration of nitriles in alcohol/water media at temperatures as low as 80 °C.[7,8] Recently, the $[Rh(\mu\text{-OMe})(COD)]/PCy_3$ catalytic system was used to perform the hydration of nitriles at room temperature,[9] and $Cu(OTf)_2$ allowed the hydration of carbonyl-ene-nitrile compounds into the reactive corresponding amide group.[10] The hydration of acetonitrile into acetamide in water under basic conditions has already been performed at 80 °C using $[Rh(\mu\text{-OMe})(COD)]_2$/TPPTS (TPPTS = tris(3-sulfonatophenyl) phosphine sodium salt.[11] Recently, Cadierno and Gimeno[12] succeeded in performing the nitrile hydration in water at only 100 °C, using an ionic ruthenium catalyst, $RuCl_2(L^+)(C_6Me_6)$, containing a water-solubilizing cationic tertiary phosphine derivative L^+, whereas Kaneda et al. reported that supported silver nanoparticles promote the hydration of nitriles in water at 140 °C but allow the recycling of the catalyst.[13]

Functional oxazoline derivatives have already been shown as potential bidentate ligands in ruthenium catalysis.[14] One

*To whom correspondence should be addressed. E-mail: pierre.dixneuf@univ-rennes1.fr.

(1) (a) *The Amide Linkage: Structural Significance in Chemistry, Biochemistry and Materials Science*; Greenberg, A.; Breneman, C. M.; Liebman, J. F., Ed.; Wiley: New York, 2000. (b) *The Chemistry of Amides*; Zabicky, J., Ed.; Wiley-Interscience: New York, 1970.

(2) (a) Kobayashi, M.; Shimizu, S. *Curr. Opin. Chem. Biol.* **2000**, *4*, 95–102. (b) Endo, I.; Nojori, M.; Tsujimura, M.; Nakasako, M.; Nagashima, S.; Yohda, M.; Odaka, M. *J. Inorg. Biochem.* **2001**, *83*, 247–253. (c) Dadd, M. R.; et al. *J. Microbiol. Methods* **2000**, *41*, 69–75.

(3) For reviews see: (a) Kukushkin, V. Yu.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **2005**, *358*, 1–21. (b) Kukushkin, V. Yu.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771–1802.

(4) (a) Murahashi, S.-I.; Sasao, S.; Saito, E.; Naota, T. J. *Org. Chem.* **1992**, *57*, 2521–2523. (b) Murahashi, S.-I.; Sasao, S.; Saito, E.; Naota, T. *Tetrahedron* **1993**, *49*, 8805–8826. (c) Murahashi, S.-I.; Takaya, H. *Acc. Chem. Res.* **2000**, *33*, 225–233.

(5) (a) Fung, W. K.; Huang, X.; Man, M. L.; Ng, S. M.; Hung, M. Y.; Lin, Z.; Lau, C. P. *J. Am. Chem. Soc.* **2003**, *125*, 11539–11544. (b) Leung, C. W.; Zheng, W.; Wang, D.; Ng, S. M.; Yeung, C. H.; Zhou, Z.; Lin, Z.; Lau, C. P. *Organometallics* **2007**, *26*, 1924–1933. (c) Leung, C. W.; Zheng, W.; Zhou, Z.; Lin, Z.; Lau, C. P. *Organometallics* **2008**, *27*, 4957–4969.

(6) Oshiki, T.; Yamashita, H.; Sawada, K.; Utsunomiya, M.; Takahashi, K.; Takai, K. *Organometallics* **2005**, *24*, 6287–6290.

(7) (a) Ghaffar, T.; Parkins, A. W *Tetrahedron Lett.* **1995**, *36*, 8657–8660. (b) Akisanya, J.; Parkins, A. W.; Steed, J. W. *Org. Process Res. Dev.* **1998**, *2*, 274–276. (c) Ghaffar, T.; Parkins, A. W. *J. Mol. Catal. A* **2000**, *160*, 249–261.

(8) Jiang, X.-B.; Minnaard, A. J.; Feringa, B. L.; de Vries, J. G. *J. Org. Chem.* **2004**, *69*, 2327–2331.

(9) Goto, A.; Endo, K.; Saito, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 3607–3609.

(10) Murai, M.; Miki, K.; Ohe, K. *J. Org. Chem.* **2008**, *73*, 9174–9176.

(11) Djoman, M. C. K.-B.; Ajjou, A. N. *Tetrahedron Lett.* **2000**, *41*, 4845–4849.

(12) Cadierno, V.; Francos, J.; Gimeno, J. *Chem.—Eur. J.* **2008**, *14*, 6601–6605.

(13) Mitsudome, T.; Mikami, Y.; Mori, H.; Arita, S.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Chem. Commun.* **2009**, 3258–3260.

(14) (a) Ben Ammar, H.; Le Notre, J.; Salem, M.; Kaddachi, M. T.; Dixneuf, P. H. *J. Organomet. Chem.* **2002**, *662*, 63–69. (b) Ben Ammar, H.; Le Notre, J.; Salem, M.; Kaddachi, M. T.; Toupet, L.; Renaud, J. L.; Bruneau, C.; Dixneuf, P. H. *Eur. J. Inorg. Chem.* **2003**, 4055–4064.

 Published on Web 09/02/2010

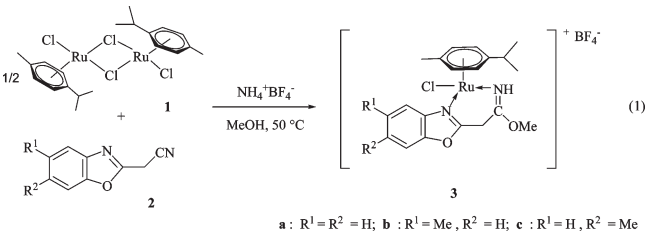
oxazoline family contains the nitrile functionality: the oxazol-2-yl and benzoxazol-2-yl acetonitrile derivatives, which are easy to prepare[15,16] and are potential precursors of functional oxazoline by simple modifications of the nitrile group. We have thus studied the interaction of potentially coordinating benzoxazol-2-yl acetonitriles with arene-ruthenium(II) derivatives by ruthenium(II) sites as an attempt to better understand the activation of the nitrile group.

It is noteworthy that the activation of the acetonitrile ligand by an iridium(III) center has allowed the nucleophilic addition of water, alcohol, and amine to the M−NCR nitrile group to generate amido, imino-ether, and amidine complexes.[17] By contrast, the activation by copper(II) salts in alcohol of nitrile groups attached to polydentate ligands has led to polydentate copper(II) complexes containing the nitrogen-coordinated imino-ether ligands.[18]

We now report (i) the (arene)ruthenium(II) activation of the nitrile group of benzoxazol-2-yl acetonitriles and analogues toward the addition of methanol to generate new mixed *N,N′*-bidentate oxazoline-methoxyimine ruthenium(II) complexes, as models showing the first step of nitrile methanolysis or hydration, and (ii) the catalytic hydration of these functional nitriles into amides with the $[RuCl_2(p\text{-cymene})]_2$ precursor under mild conditions in methanol/water medium.

Results and Discussion

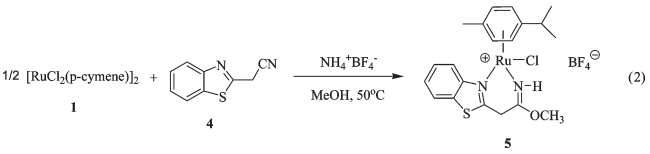
Preparation of *N,N′*-Bidentate Ruthenium(II)−Arene Complexes. The arene-ruthenium(II) complex $[RuCl_2(p\text{-cymene})]_2$ (**1**), the ideal precursor of [arene-RuCl]$^+$ and $[RuCl_2]$ moieties,[19] reacted with the benzoxazolylacetonitrile **2a**,[16] in various solvents (toluene, THF, dichloromethane), but no stable or defined complex of type $RuCl_2(L)(p\text{-cymene})$ was obtained, illustrating the weak coordinating ability of the benzoxazole ring nitrogen atom. However, when the same substrate **2a** was reacted with $[RuCl_2(p\text{-cymene})]_2$ (**1**) but in the presence of 1 equiv of $NH_4^+BF_4^-$ per ruthenium atom in dry methanol, conditions favoring the substitution of chloride by a noncoordinating BF_4^- anion and the coordination of a four-electron bidentate ligand, a yellow complex formed rapidly. The reaction was completed after heating at 50 °C for 4 h. The ionic yellow complex **3a** was obtained in good yield (98%) (eq 1). The same reaction performed with benzoxazolylacetonitrile derivatives **2b** and **2c** led to the formation of analogous complexes **3b** (94%) and **3c** (97%).



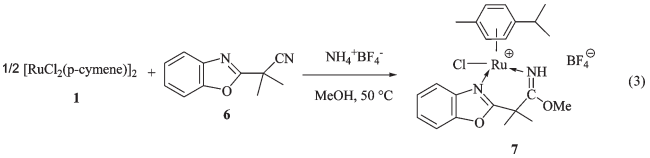
The NMR of complexes **3** showed the incorporation of the bidentate ligand, that the nitrile functionality was no longer present, but that one molecule of methanol was added, and the data were consistent with *N,N′*-bidentate benzoxazole-methoxyimine-ruthenium complex **3**, as shown in eq 1.

The ^{1}H NMR reveals the chirality of the complex **3** by the nonequivalency of the isopropyl methyl groups and of the four *p*-cymene arene CH protons. Especially the bridging methylene protons of the bidentate ligand are nonequivalent [**3a** ^{1}H NMR: δ ppm CH_2: 4.18 and 4.69 (AB), $^2J_{HAHB}$ = 19.5 Hz].

The reaction of the sulfur-containing analogous molecule, the benzothiazolylacetonitrile **4**, with the ruthenium precursor **1**, in methanol at 50 °C, afforded the yellow complex **5**, which was isolated in 96% yield (eq 2).



The above complexes **3** and **5** did not afford suitable crystals for X-ray diffraction. Thus in order to reach a more rigid complex, the benzoxazole **6** was prepared from **2a**, simply on reaction with 3 equiv of methyl iodide with an excess of K_2CO_3 in acetone at reflux. The reaction of ligand **6** with the ruthenium precursor **1** in methanol at 50 °C, but at least for 16 h to reach transformation completion, led to the formation of the yellow complex **7**, which was isolated in 96% yield (eq 3). Its recrystallization in a dicloromethane/diethyl ether mixture afforded suitable crystals for X-ray diffraction study.



The X-ray structure of complex **7** (Figure 1)[23] shows that methanol was added to the coordinated CN bond to afford a methoxy imino ligand. Thus the ruthenium is bonded to two different imino nitrogen atoms, with two different Ru−N(R)=C moieties: the oxazoline moiety (Ru1−N1 = 2.098(9), N1−C7 = 1.286(14) Å) and the methoxy imine moiety (Ru1−N2 = 2.071(9), N2−C9 = 1.316(13) Å). Thus the Ru−NH distance is

(15) Youssef, C.; Ben Ammar, H.; Ben Salem, R.; Bruneau, C.; Dixneuf, P. H. *J. Soc. Chim. Tunisie* **2009**, *11*, 9–13.
(16) Ben Ammar, H.; Kaddachi, M. T.; Khan, P. H. *J. Phys. Chem. News* **2003**, *9*, 137.
(17) Chin, C. S.; Chong, D.; Lee, B.; Jeong, H.; Won, G.; Do, Y.; Park, Y. J. *Organometallics* **2000**, *19*, 638–648.
(18) (a) Blake, A. J.; Hubberstey, P.; Suksangpanya, U.; Wilson, C. L. *J. Chem. Soc., Dalton Trans.* **2000**, 3873–3880. (b) Tei, L.; Blake, A. J.; Lippolis, V.; Wilson, C.; Schröder, M. *Dalton Trans.* **2003**, 304–310.
(19) (a) Organometallic Chemistry of Arene-Ruthenium and Osmium Complexes. Le Bozec, H.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *29*, 163–247. (b) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809–817. (c) Fürstner, A.; Liebl, M.; Lehmann, C. W.; Picquet, M.; Kunz, R.; Bruneau, C.; Touchard, D.; Dixneuf, P. H. *Chem.—Eur. J.* **2000**, *6*, 1847–1857. (d) Özdemir, I.; Demir, S.; Gürbüz, N.; Çetinkaya, B.; Toupet, L.; Bruneau, C.; Dixneuf, P. H. *Eur. J. Inorg. Chem.* **2009**, 1942–1949. (e) Govindaswamy, A.; Süss-Fink, G.; Therrien, B. *Organometallics* **2007**, *26*, 915–924.
(20) CCDC 780359 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
(21) Thallaj, N. K.; Przybilla, J.; Welter, R.; Mandon, D. *J. Am. Chem. Soc.* **2008**, *130*, 2414–2415.
(22) Garcia-Fidalgo, E.; Plasseraud, L.; Süss-Fink, G. *J. Mol. Catal. A: Chem.* **1998**, *132*, 5–12.
(23) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1998**, *31*, 74–77.

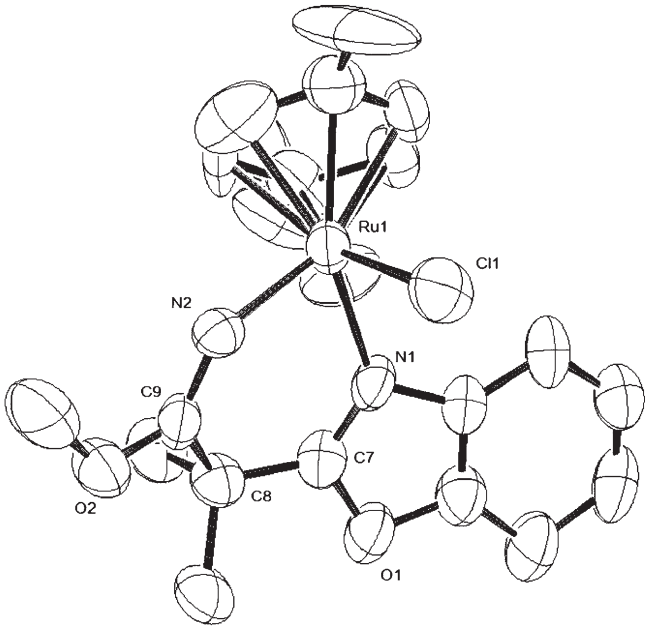


Figure 1. Molecular structure of complex **7** at 50% thermal ellipsoid probability. H atoms, BF_4 anion, and crystallization solvent (CH_2Cl_2) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−N1 = 2.098(9), Ru1−N2 = 2.071(9), Ru1−Cl1 = 2.389(3), N1−C7 = 1.286(14), N2−C9 = 1.316(13), N2Ru1N1 = 82.6(4)°, C7C8C9 = 112.6(9)°.

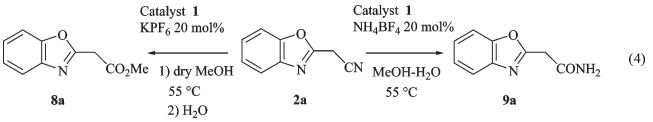
longer than the Ru−N(oxazoline) but associated with a shorter N═C bond distance. It is noteworthy that the N−Ru−N angle is rather small, 82.6(4)°.

The above results show that the nitriles containing as a neighbor a coordinating group, the benzoazole nitrogen atom, are activated by ruthenium(II) centers in an (η^2-CN)Ru fashion, rather than by the Lewis-type interaction Ru←N≡CR. This lateral coordination favors nucleophilic addition of methanol to give the methoxyimine function, leading to isolable complexes **3**, **5**, and **7**. The coordinating group likely favors bidentate coordination, which prevents the Lewis-type interaction of the nitrile nitrogen atom. An analogous side-on activation of a nitrile group attached to a polypyridine ligand by an iron(II) complex has also been observed,[21] and the activation by Cu(II) salts of nitrile groups incorporated into nitrogen-containing polydentate ligands also leads to imino-ether ligands, likely via lateral coordination of the nitrile group.[18]

Catalytic Hydratation and Methanolysis of Benzoxazol-2-ylacetonitrile, 2. The catalytic methanolysis of the functional nitrile **2a** was attempted in dry methanol only with 5 mol % $[RuCl_2(p\text{-cymene})]_2$ (**1**) and 20 mol % KPF_6 at 55 °C for 19 h. Then hydrolysis of the mixture was performed, and products were extracted. The TLC, mass spectra, and ^1H NMR analysis revealed that 70% of remaining nitrile **2a** was present with 30% of the newly formed methyl ester **8a** (eq 4). The partial formation of methyl ester suggested that the stability of the intermediate complex of type **3** prevented complete transformation.

The catalytic hydration of the functional nitrile **2a** was then attempted directly in water using $[RuCl_2(p\text{-cymene})]_2$ (**1**) as a catalyst precursor since analogous arene-ruthenium(II) complexes were shown by Süss-Fink et al.[22] to generate new catalysts in water. The derivative **2a** was only slightly soluble in water; thus 1 mmol of **2a** and 5 mol % complex **1** were dissolved in 1 mL of methanol, and 20 mol % $NH_4^+BF_4^-$, 2 equiv per ruthenium atom, were introduced. Then 1.5 mL of distilled water was added. The mixture was heated at 55 °C for 3 h in order to get complete transformation of **2a**. The white amide **9a** was isolated in 75% yield (eq 4).

The hydration of the benzoxazolylacetonitrile **2c** under similar conditions led to complete transformation and after chromatography to the isolation of 62% amide **9c**.



(4)

The positive role of the salt NH_4BF_4 was shown. When the same transformation of **2a** into **9a** was performed without NH_4BF_4 salt after 3 h of reaction at 55 °C, the conversion of **2a** into amide reached only 80%, whereas it reached 100% in its presence. It is likely that NH_4BF_4 has the role of solubilizing the catalyst **1** in the $MeOH/H_2O$ medium and dissociating a Ru−Cl bond in order to coordinate the CN function in an η^2-fashion, which means a ruthenium(II) activation step of the nitrile toward the addition of water.

Conclusion

The above results show a straightforward access to new *N, N′*-bidentate mixed diimine-ruthenium(II) complexes directly from benzoxazolylacetonitriles on reaction with the complex $[RuCl_2(p\text{-cymene})]_2$ and demonstrate the initial addition of methanol to the coordinated nitrile group. The mild catalytic conditions of the hydration of these nitriles into their amides take place in neutral methanol/water solution at only 55 °C without addition of base or water-soluble ligand to the simple, commercially available catalyst $[RuCl_2(p\text{-cymene})]_2$.

Experimental Section

Instrumentation. All reactions were carried out with exclusion of air using Schlenk tube techniques. Organic solvents were dried by standard procedures and distilled under argon prior to use. ^1H NMR spectra were recorded at 200 and 300 MHz. ^{13}C NMR spectra were recorded at 50.3 and 75.5 MHz. The reactions were monitored using a Shimadzu 2014 gas chromatograph equipped with an Equity-1 fused silica capillary column. Pure products were obtained by column chromatography on silica gel using mixtures of petroleum ether and diethyl ether or a mixture of petroleum ether and ethyl acetate as the eluent. Transmittance FT-IR spectra were recorded using a Bruker IFS 28 spectrometer. The high-resolution mass spectra (HR-MS) were recorded using a Varian Mat 311 equipped with a magnetic field, an electric field (geometry BE), and a room of collisions. Elemental analysis data were obtained on a micro-analyzer (Flash EA1112 CHNS/O, Thermo Electron). Products were further analyzed by GC-MS on a Shimadzu QP2010S apparatus.

General Procedure for the Preparation of Complexes 3. In a Schlenk tube equipped with a stirring bar under inert atmosphere (nitrogen) were successively introduced $[RuCl_2(p\text{-cymene})]_2$ (**1**; 100 mg, 0.163 mmol), the benzoxazolacetonitrile **2**[15,16] (56 mg, 0.358 mmol), $NH_4^+BF_4^-$ (35 mg, 0.326 mmol), and 10 mL of methanol. The mixture was heated at 50 °C under stirring for 4 h. The solvent was evaporated under vacuum, and the formed yellow product was then dissolved in 10 mL of dichloromethane. This solution was filtrated with the help of a canula equipped with a paper filter, and the solvent was evaporated.

The product was washed twice with 20 mL of diethyl ether and dried under vacuum. The complex **3** was then obtained as a yellow powder.

Preparation of Complex 3a. Benzoxazol-2-ylacetonitrile (**2a**; 61 mg, 0.358 mmol). Complex **3a** was isolated as a yellow-green powder (88 mg, 98%). Anal. Calcd for $C_{20}H_{24}BClF_4N_2O_2Ru$: C, 43.86; H, 4.42. Found: C, 43.21; H, 4.47. HRMS: *m*/*z* calcd for $[C_{20}H_{24}N_2O_2ClRu]^+$ 461.0570; found 461.0584. ^{1}H NMR (300.132 MHz, CD_2Cl_2) δ ppm: 1.29 (d, 3H, J = 6.9 Hz, $CH(CH_3)_2$); 1.36 (d, 3H, J = 6.9 Hz, $CH(CH_3)_2$); 2.12 (s, 3H, CH_3); 2.90 (sept, 1 H, J = 6.9 Hz, $CH(CH_3)_2$); 4.11 (s, 3H, OCH_3); 4.18 (d, 1 H, J = 19.5 Hz, CH_2); 4.69 (d, 1H, J = 19.5 Hz, CH_2); 5.76 (d, 1H, J = 6.0 Hz, CH); 5.91 (d, 1H, J = 6.0 Hz, CH); 5.95 (d, 1H, 6.0 Hz, CH); 6.04 (d, 1 H, J = 6.0 Hz, CH); 7.60−7.65 (m, 2H, CH), 7.69−7.75 (m, 1H, CH), 7.82 (br s, 1H, NH), 7.85−7.90 (m, 1H, CH). ^{13}C NMR (75.48 MHz, CD_2Cl_2) δ ppm: 18.4 (CH_3); 21.7 (CH_3); 22.5 (CH_3); 31.1 (CH); 32.6 (CH_2); 55.7 (OCH_3); 82.4 (CH); 82.6 (CH); 83.0 (CH); 84.7 (CH); 100.0 (C); 105.8 (C); 112.0 (CH); 119.6 (CH). IR (cm^{-1}): 1152 (ν P−F), 1550 (ν C═C), 1640 (ν C═N), 1609 (ν C═N).

Preparation of Complex 3b. 5-Methylbenzoxazol-2-ylacetonitrile (**2b**; 62 mg, 0.358 mmol). Complex **3b** was isolated as a light yellow powder (88 mg, 96%). Anal. Calcd for $C_{21}H_{26}BClF_4N_2O_2Ru$: C, 44.90; H, 4.66. Found: C, 44.87; H, 4.78. HRMS: *m*/*z* calcd for $[C_{21}H_{26}N_2O_2ClRu]^+$ 475.0726; found 475.0727; calcd for $[C-HCl]^+$ 439.0959; found 439.0957. ^{1}H NMR: (300.132 MHz, CD_2Cl_2) δ ppm: 1.28 (d, 3H, J=6.9 Hz, $CH(CH_3)_2$); 1.35 (d, 3H, J=6.9 Hz, $CH(CH_3)_2$); 2.14 (s, 3H, CH_3); 2.58 (s, 3H, CH_3); 2.89 (sept, 1H, J = 6.9 Hz, $CH(CH_3)_2$); 4.08 (s, 3H, OCH_3) 4.12 (d, 1H, J = 19.7 Hz, CH_2); 4.63 (d, 1H, J = 19.7 Hz, CH_2); 5.75 (d, 1H, J = 6.0 Hz, CH_2); 5.88 (d, 1H, J = 6.0 Hz, CH); 5.93 (d, 1H, 6.0 Hz, CH); 6.01 (d, 1H, J = 6.0 Hz, CH) ; 7.42 (d, 1H, J = 8.3 Hz, CH); 7.56−7.62 (m, 2H, CH); 7.99 (br s, 1H, NH). ^{13}C NMR (75.48 MHz, CD_2Cl_2) δ ppm: 18.5 (CH_3); 21.5 (CH_3) ; 21.7 (CH_3); 22.7 (CH_3); 31.2 (CH); 32.7 (CH_2); 55.7 (OCH_3); 82.5 (CH); 82.6 (CH); 83.0 (CH); 84.9 (CH); 100.0 (C); 105.8 (C); 111.4 (CH); 119.1 (CH); 128.4 (CH); 137.0 (C); 139.2 (C); 148.5 (C); 159.8 (C═N); 165.8 (C═N). IR (cm^{-1}): 1156 (ν P−F), 1555 (ν C═C), 1630 (ν C═N), 1619 (ν C═N).

Preparation of Complex 3c. 6-Methylbenzoxazol-2-ylacetonitrile (**2c**; 61 mg, 0.358 mmol). Complex **3c** was isolated as a yellow powder (89 mg, 97%). HRMS: *m*/*z* calcd for $[C_{21}H_{26}N_2O_2ClRu]^+$ 475.0726; found 475.0729; calcd for $[C-HCl]^+$ calcd 439.0959; found 439.0955. ^{1}H NMR (300.132 MHz, CD_2Cl_2) δ ppm: 1.27 (d, 3H, J = 6.9 Hz, $CH(CH_3)_2$); 1.34 (d, 3H, J = 6.9 Hz, $CH(CH_3)_2$); 2.14 (s, 3H, CH_3); 2.57 (s, 3H, CH_3); 2.89 (sept, 1 H, J = 6.9 Hz, $CH(CH_3)_2$); 4,09 (s, 3H, OCH_3), 4.12 (d, 1H, J = 19.7 Hz, CH_2); 4.64 (d, 1H, J = 19.7 Hz, CH_2); 5.75 (d, 1H, J = 6.0 Hz, CH_2); 5.88 (d, 1H, J= 6.0 Hz, CH); 5.93 (d, 1H, 6.0 Hz, CH); 6.01 (d, 1H, J = 6.0 Hz, CH); 7.42 (d, 1H, J = 8.3 Hz, CH); 7.51 (br s, 1H, CH); 7.71 (d, 1H, J = 8.3 Hz, CH); 7.95 (br, 1H, NH). ^{13}C NMR (75.48 MHz, CD_2Cl_2) δ ppm: 18.5 (CH_3); 21.5 (CH_3); 21.7 (CH_3); 22.6 (CH_3); 31.2 (CH); 32.6 (CH_2); 55.7 (OCH_3); 82.4 (CH); 82.5 (CH); 83.0 (CH); 85.1 (CH); 100.1 (C); 105.6 (C); 111.9 (CH); 118.8 (CH); 127.7 (CH); 136.9 (C); 138.8 (C); 150.4 (C); 159.1 (C═N); 165.9 (C═N). IR (cm^{-1}): 1159 (ν P−F), 1559 (ν C═C), 1647 (ν C═N), 1619 (ν C═N).

Preparation of Complex 5. Benzothiazol-2-ylacetonitrile (**4**; 62 mg, 0.358 mmol). Complex **5** was isolated as a yellow-green powder (90 mg, 98%). ^{1}H NMR (300.132 MHz, CD_2Cl_2) δ ppm: 1.24 (d, 3H, J = 6.9 Hz, $CH(CH_3)_2$); 1.34 (d, 3H, J = 6.9 Hz, $CH(CH_3)_2$); 1.95 (s, 3H, CH_3); 2.90 (sept, 1H, J = 6.9 Hz, $CH(CH_3)_2$); 4.07 (s, 3H, OCH_3); 4.18 (d, 1H, J = 19.5 Hz, CH_2); 4.69 (d, 1H, J = 19.5 Hz, CH_2); 5.76 (d, 1H, J = 6.0 Hz, CH); 5.91 (d, 1H, J = 6.0 Hz, CH); 5.95 (d, 1H, 6.0 Hz, CH); 6.04 (d, 1H, J = 6.0 Hz, CH); 7.40 (br s, 1H, NH); 7.63−7.66 (m, 1H, CH); 7.72−7.75 (m, 1H, CH); 8.00 (d, 1H, J = 8.0 Hz, CH); 8.54 (d, 1H, J = 8.4 Hz, CH). ^{13}C NMR (75.48 MHz, CD_2Cl_2) δ ppm: 18.4 (CH_3); 21.2 (CH_3); 23.0 (CH_3); 31.2 (CH); 38.2 (CH_2); 55.5 (OCH_3); 82.9 (CH); 83.2 (CH); 83.3 (CH); 86.5 (CH); 99.9 (C); 105.0 (C); 122.6 (CH); 124.7(CH); 127.4 (CH); 127.7 (CH); 132.3 (C); 151.5 (C); 164.3 (C═N); 166.6 (C═N).

Table 1. Crystal Data and Structure Refinement for Compound 7

empirical formula	$C_{44.50}H_{57}B_2Cl_3F_8N_4O_4Ru_2$
fw	1194.05
temp (K)	233(2)
wavelength (Å)	0.71073
cryst syst, space group	triclinic, $P\bar{1}$
a, b, c (Å)	9.9246(6), 13.6773(8), 21.3290(10)
α, β, γ (deg)	106.784(5), 90.482(5), 110.924(6)
V (Å^3)	2568.9(2)
Z	2
density (Mg/m^3)	1.544
absorp coeff (mm^{-1})	0.817
F(000)	1210
cryst size (mm)	0.30 × 0.15 × 0.15
θ range for data collection	2.80 to 27.00
reflns collected/unique	19 880/10 912
goodness-of-fit on F^2	0.929
data/restraints/params	10 912/4/594
final R indices [$I > 2\sigma(I)$]	R1 = 0.0966, wR2 = 0.2678
R indices (all data)	R1 = 0.1995, wR2 = 0.2978

Preparation of Complex 7. In a Schlenk tube equipped with a stirring bar under inert atmosphere were successively introduced $[RuCl_2(p\text{-cymene})]_2$ (**1**; 100 mg, 0.163 mmol), the nitrile oxazoline **6** (91 mg, 0.489 mmol), $NH_4^+BF_4^-$ (35 mg, 0.33 mmol), and 10 mL of methanol. The mixture was heated at 50 °C under stirring for 16 h. The solvent was then evaporated under vacuum, and the formed product was dissolved in 10 mL of dichloromethane. This solution was filtrated, and the solvent was evaporated. The product was dissolved with 5 mL of dichloromethane, the solution was filtered, and diethyl ether was added to the solution to precipitate the complex **7**, which was then obtained as a yellow powder, 92 mg (96% yield). Some part was recrystallized from dichloromethane and diethyl ether to afford crystals for X-ray diffraction. ^{1}H NMR (500.13 MHz, CD_2Cl_2) δ ppm: 1.22 and 1.33 (each d, J = 7.0 Hz, $CHMe_2$); 1.81 and 1.89 (s, CMe_2); 2.14 (s, Me); 2.90 (sept, J = 7.0 Hz, $CHMe_2$); 4.18 (s, OMe), 5.86 (d, J = 6.2 Hz, CH); 5.88 (d, J = 6.2 Hz, CH); 6.06 (d, J = 6.0 Hz, CH); 6.11 (d, J = 6.0 Hz, CH); 7.63 (m, 2H); 7.73 (m, 1H); 7.87 (m, 1H); 8.43 (br s, NH). ^{13}C NMR (75,48 MHz, CD_2Cl_2) δ ppm: 18.5 (CH_3); 20.9 (CH_3) ; 23.1 (CH_3); 23.4 (CH_3); 27.6 (CH_3); 31.3 (CH); 43.4 ($C(CH_3)_2$); 55.6 (OCH_3); 82.5 (CH); 82.6 (CH); 83.4 (CH); 86.6 (CH); 100.7 (C); 105.7 (C); 112.0 (CH); 120.0 (CH); 126.5 (CH); 127.8 (CH); 139.9 (C); 149.5 (C); 165,7 (C═N); 170.8 (C═N).

Catalytic Hydrolysis of Nitrile Derivatives 2. Preparation of Amide 9a. In a Schlenk tube under argon were introduced successively 1 mmol (158 mg) of **2a**, $[RuCl_2(p\text{-cymene})]_2$ (**1**; 5 mol %, 30.6 mg), 1 mL of methanol, a slight excess of 2 equiv per Ru atom of $NH_4^+BF_4^-$ (20 mol %), and 1.5 mL of distilled water. The mixture was stirred at 55 °C for 3 h. After cooling, water was added and the mixture was extracted with dichloromethane and dried with Na_2SO_4. The solution was chromatographed on a short pad of silica to eliminate the catalyst residue. The white product **9a** was obtained in 75% yield (132 mg). HRMS: $[M + Na]^+$ ($C_9H_8N_2O_2Na$) *m*/*z* calcd 199.04835; found 199.0483; $[M + K]^+$ ($C_9H_8N_2O_2K$) *m*/*z* calcd 215.02229; found 215.0222. ^{1}H NMR (200 MHz, dmso-d_6) δ ppm: 3.98 (s, 2H, CH_2); 6.74−7.06 (m, 3H, CH); 7.80 (d, 1H, J = 7.8 Hz, CH), 9.53 and 9.90 (s, NH). ^{13}C NMR (75,48 MHz, dmso-d_6) δ ppm: 26.7(CH_2); 115.6, 116.6, 119.3, 122.6 (CH arom), 125.4, 125.8 (C arom), 148.3 (C═N), 161.5 ($CONH_2$).

Preparation of Amide 9c. The hydration of **2c** (186 mg, 1.074 mmol) was performed analogously with $[RuCl_2(p\text{-cymene})]_2$ (32.8 mg, 0.0537 mmol, 5 mol %) and NH_4BF_4 (22.6 mg, 0.2145 mmol) in a mixture of MeOH (0.5 mL)/H_2O (1.5 mL) at 55 °C for 3 h. The mixture was then extracted with dichloromethane, washed with distilled water, and finally dried over Na_2SO_4. Solvent was evaporated, and the product was purified

by short column chromatography on silica gel (1.5 cm ×5 cm) using a mixture of petroleum ether/ethyl acetate (7:3) as eluent to give 120 mg of greenish solid **9c** (62% isolated yield). ^{1}H NMR (300.13 MHz, $(CD_3)_2CO$) δ ppm: 2.24 (s, 3H, $C\underline{H}_3$); 3.96 (s, 2H, $C\underline{H}_2$); 6.81 (s, 2H, H arom); 7.73 (s, 1H, H arom); 8.65 (s, 1H, $N\underline{H}_2$); 9.02 (s, 1H, $N\underline{H}_2$).

Catalytic Methanolysis of Derivative 2a. In a Schlenk tube under argon were introduced successively 1 mmol (158 mg) of **2a**, $[RuCl_2(p\text{-cymene})]_2$ (**1**; 5 mol %, 30.6 mg), 5 mL of dry methanol, and 2 equiv per Ru atom of $K^+PF_6^-$ (20 mol %). The mixture is stirred at 55 °C for 19 h. After cooling, water was added and the mixture was extracted with dichloromethane and dried with Na_2SO_4. The ^{1}H NMR and mass spectra of the resulting greenish oily mixture revealed that it contains 70% of starting nitrile **2a** and only 30% of the methyl ester **8a**. The ratio is based on the ^{1}H NMR CH_2 signal intensity of the derivatives **2a** and **8a**. ^{1}H NMR (200 MHz, acetone-d_6) δ ppm: 3.75 (s, 3H, OMe); 4.14 (s, 2H, CH_2CO); 7.38−7.76 (m, 4H, C_6H_4).

Experimental Crystallographic Data for Complex 7. The sample was studied on a CCD Saphire 3 Xcalibur with graphite-monochromatized Mo Kα radiation. The structure was solved with SIR-97,[23] which revealed the non-hydrogen atoms of the molecule. The whole structure was refined with SHELXL97.[24] The level A alert in the checkcif is due to the large thermal motion of some atoms. It must be noticed that we have unsuccessfully investigated the possibility of mononclinic *C* symmetry (space group C_2).

Full details of the crystal structure analyses in CIF format for complex **7** including crystal data and structure refinement, atomic coordinates, bond lengths and angles, hydrogen coordinates, and the data for X-ray diffraction analysis of complex **7** can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment. The authors are grateful to the bilateral France−Tunisia CMCU and French Embassy programs for support to H.B.A. and the Institut Universitaire de France for support to P.H.D.

(24) Sheldrick, G. M. *SHELX97: Program for the Refinement of Crystal Structures*; Univ. of Göttingen: Germany, 1997.