Stereoselective Cyclometalation of Planar Pro-chiral (η^6-Arene)tricarbonylchromium Complexes with *OC*-6-$[Ru(CO)_2Cl_2]_n$

Akram Hijazi, Jean-Pierre Djukic,* Lionel Allouche, André de Cian, and Michel Pfeffer

Institut de Chimie, CNRS UMR 7177, Université Louis Pasteur, 4 Rue Blaise Pascal, F-67000 Strasbourg, France

Xavier-Frédéric Le Goff and Louis Ricard†

Laboratoire Hétéro-éléments et Coordination, CNRS UMR 7653, Ecole Polytechnique, Route de Saclay, F-91128 Palaiseau Cedex, France

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Ortho-metalation of ligand-appended and planar pro-chiral (η^6-arene)tricarbonylchromium complexes has been attempted with octahedral $[Ru(CO)_2Cl_2]_n$. While amino- and oxazolyl-appended substrates displayed no reactivity, 2-[tricarbonyl(η^6-phenyl)chromium]pyridine was readily converted into the corresponding cycloruthenated product consisting of a mixture of chloro-bridged heterotetranuclear dimers, which was analyzed by CPMAS ^{13}C NMR and 2D-DOSY ^1H NMR techniques in the solid state and in solution, respectively. The main side-products of this cyclometalation reaction were identified as novel dimers containing a chloro and a hydroxo bridge, according to spectroscopic and X-ray diffraction structural determination. The relative configuration of the produced tetranuclear chloro-bridged (Cr,Ru) dimers was assessed by chemical derivatization into (Cr,Ru) monomers, of which the structures were established by X-ray diffraction analysis. Consistent results as to the stereoselectivity of the cycloruthenation reaction were obtained with 2-ferrocenylpyridine. Further reactivity studies of racemic planar-chiral (Cr,Ru) and (Fe,Ru) dimeric ruthenacycles toward anionic bidentate ligands indicated that chelation of the Ru center was rather stereoselective although probably subject to polytopal rearrangements. It was established that the chelation of the ruthenium(II) center by anionic homobidentate ligands was sensitive to steric hindrance, which favors the coordination of the anionic bidentate ligand at the Ru center in an *anti* fashion with respect to both $Cr(CO)_3$ and FeCp. This property was applied to the synthesis of the first examples of scalemic ruthenacycles possessing ruthenium-centered and planar chiralities. This study is supported by 12 X-ray diffraction structures of relevant new complexes, among which are two unprecedented examples of chloro,hydroxo-bridged dicarbonylruthenium(II) [C,N] chelates.

Introduction

According to existing literature, four synthetic routes toward nonracemic planar-chiral metallacycles have been investigated and developed so far, which differ mostly by the means used to create planar chirality at the chelate with reasonable enantiomeric excess. These routes consist of (1) the enantioselective[1] or diastereoselective metalation of planar pro-chiral substrates or nonracemic substrates[2] by C−H bond activation, (2) the oxidative addition of an electron-rich metal center to a nonracemic halogenated substrate,[3] (3) the transmetalation of a racemic or nonracemic ortho-metalated or cyclometalated substrate,[4] and (4) the optical resolution of planar-chiral cyclometalated substrates from a mixture of diastereomers.[5] The pioneering works of V. I. Sokolov on the enantioselective cyclopalladation of planar pro-chiral ferrocenyl ligands[6] have been followed by a host of applications in metal-mediated organic synthesis. Quite recently, several authors have emphasized the potential of Lewis acidic nonracemic planar-chiral metallacycles (essentially *SP*-4 palladacycles) as promoters of Claisen-type rearrangements,[7] thus reviving the search for more efficient metallacyclic catalysts and highly stereoselective metalation procedures. From this point of view, we deemed essential addressing the stereochemical aspects of the metalation of planar pro-chiral substrates by asymmetric tetrahedral (*T*-4) or octahedral (*OC*-6) metal centers. Because cyclometalation of a planar-chiral or planar pro-chiral ligand by an asymmetric *T*-4 or *OC*-6 metal center creates two different elements of chirality within the same molecule (eq 1), viz., planar chirality at the chelating ligand and metal-centered chirality at the chelated metal, diastereoselectivity becomes a serious issue that

* Corresponding author. Phone: +33(0)390241523. Fax: +33(0)-390245001. E-mail: djukic@chimie.u-strasbg.fr.

† To whom requests pertaining to the X-ray structural determination of **3c**, **5**, [PPN]**8**, **9a**, **10a**, **12**, **14a**, **14b**, and **15a** should be addressed. E-mail: louis.ricard@polytechnique.fr.

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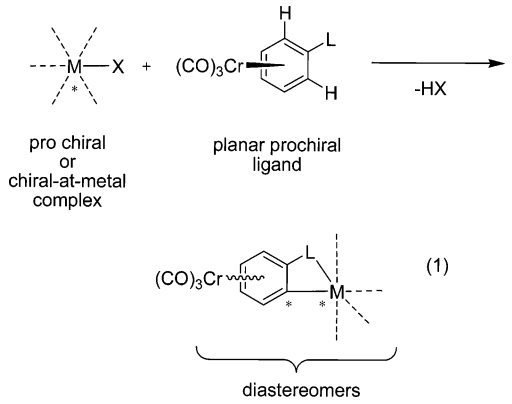
must be handled with circumspection since chiral metal centers may be subject to configurational unstability: numerous cases of configurationally labile *T*-4 complexes have been reported in the literature.[8] In previous reports we have demonstrated that enantiopure *SP*-4 palladacyclic and nonracemic pseudo-*T*-4 ruthenacyclic (η^6-arene)tricarbonylchromium complexes could be efficiently and diastereoselectively prepared by transmetalation from racemic chloromercurated substrates.



In this report, we address the direct cycloruthenation[9] of planar pro-chiral (η^6-arene)tricarbonylchromium complexes containing a pendant ancillary ligand with an octahedral (*OC*-6) metal center originating from $[Ru(CO)_2Cl_2]_n$.[10] Even though the propensity of $[Ru(CO)_2Cl_2]_n$ to cyclometalate aromatic ligands is long known,[11] underlying mechanistic aspects of the metalation reaction have not been investigated so far; neither has the reactivity of the related metallacycles been scrutinized in all its aspects.[12] The field was therefore wide open for further investigation of the direct ruthenation of pro-chiral (η^6-arene)-tricarbonylchromium complexes with this ruthenium(II) polymer. We show that in spite of the electron-withdrawing effect of the $Cr(CO)_3$ moiety, which should inhibit the metalation by the presumed "electrophilic" $[Ru(CO)_2Cl_2]_n$ polymer, cyclometalation takes place with a 2-phenylpyridine complex in an effective and diastereoselective manner.

Results and Discussion

Cyclometalation reactions involving $[Ru(CO)_2Cl_2]_n$ generally require a base in order to trap the hydrochloric acid that is formally released in the course of the reaction. Of course, the

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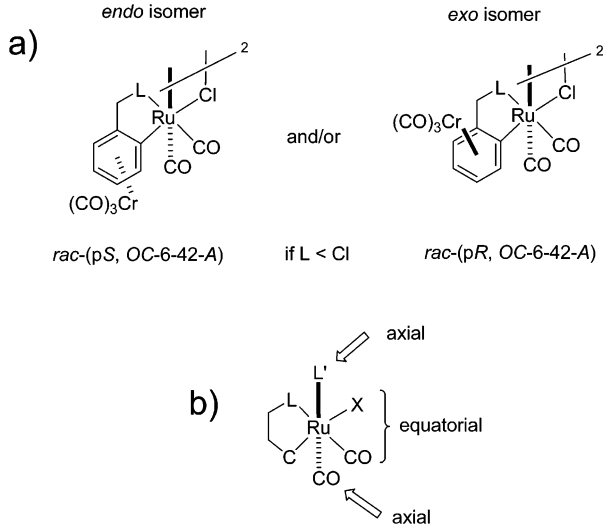
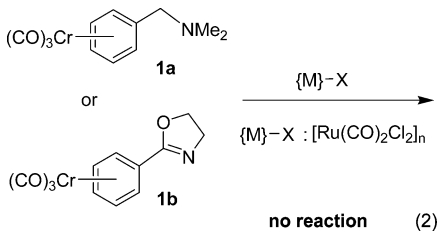


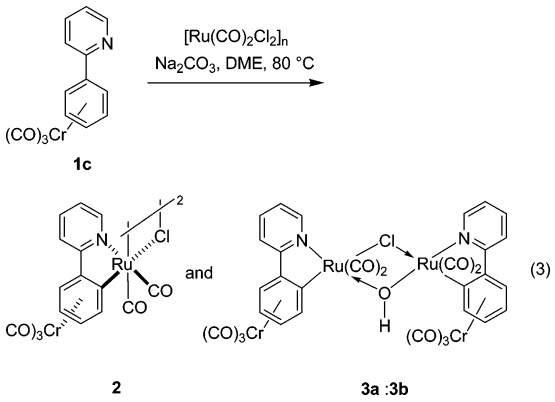
Figure 1. (a) Expected diastereoisomerism for planar-chiral ruthenacycles: the *endo* isomer differs from its *exo* counterpart by the position of the axial CO ligand; in the *endo* geometry the axial Ru-bound CO sits nearby the $Cr(CO)_3$ moiety. (b) Positional terminology defining, in this article, "axial" and "equatorial" positions for ligands.

aromatic substrate itself may play the role of the base. This is however somewhat inconvenient, as protonation of the substrate may limit the overall efficiency of the reaction. In this study, we have used a noncoordinating external base such as sodium carbonate, which *a priori* should neutralize the acidity released by the reaction without interacting either with the starting $[Ru(CO)_2Cl_2]_n$ polymer or with the expected ruthenacyclic product. We also anticipated the reaction of (η^6-arene)tricarbonylchromium complexes with $[Ru(CO)_2Cl_2]_n$ to be quite stereochemically unselective. Taking into account all the possible orientations of the octahedral $Ru(CO)_2Cl$ fragment relative to the $Cr(CO)_3$ moiety (Figure 1) added to the stereoisomerism introduced by the μ-chloro bridging of two metallacyclic units, difficulties in separating and characterizing diastereomers were seemingly lying ahead (see Supporting Information for a graphical representation of all the possible combinations).

Preliminary Investigation of the "Electrophilic" Cyclometalation of Oxazolyl- and *N*,*N*-Dimethylaminomethyl-Appended (η^6-Arene)tricarbonylchromium Complexes. A first series of experiments was carried out in order to evaluate the reactivity of a set of prototypical complexes bearing ancillary ligands of various nature, viz., **1a**−**c**, versus $[Ru(CO)_2Cl_2]_n$. Cycloruthenation reactions were carried out in refluxing 1,2-dimethoxyethane with sodium carbonate as base.



In our hands, all experiments conducted with substrates **1a** and **1b** in refluxing 1,2-dimethoxyethane in the presence of Na_2CO_3 failed to produce any cyclometalated compound: starting material was fully recovered in all cases (eq 2). Contrasting results were obtained with **1c**, as described in the following.



Direct Ortho-ruthenation of 1c with $[Ru(CO)_2Cl_2]_n$. Practically, the main product of the reaction of **1c** with $[Ru(CO)_2Cl_2]_n$ was found to be compound **2**, which precipitated out of a red-colored solution and was recovered in 83% yield upon filtration (eq 3): this yellow powder, which displayed good stability to air and moisture, was found to be partly soluble in *N*,*N*-dimethylformamide, acetone, chloroform, and dimethylsulfoxide and sparingly soluble in tetrahydrofuran and dichloromethane. The spectroscopic characterization of **2** in solution and in the solid state was undertaken by conventional techniques including IR and NMR spectroscopy in order to assess chemical purity and evaluate the number of formed diastereomers.

The IR spectrum of a KBr pellet of **2** displayed the combined typical features arising from the *fac*-$Cr(CO)_3$ and *cis*-$Ru(CO)_2$ moieties, which consisted of four carbonyl ligand stretching bands showing up between 2049 and 1878 cm^{-1}.

Solution NMR analysis of **2** led to somewhat different spectra depending on the coordinative ability of the chosen solvent. In perdeuterated dimethylsulfoxide, which most likely cleaves the μ-chloro bridges and binds the ruthenium center, both ^1H and ^{13}C NMR spectra suggested the presence of a single species, putatively the "axial" d_6-dmso adduct (Figure 1b). In perdeuterated *N*,*N*-dimethylformamide, the situation was less clear as to the exact fate of the μ-chloro-bridged complexes in this coordinating solvent: three species were formally detected by ^1H and ^{13}C NMR spectroscopy in a 14:3:1 ratio, their respective spectra being obviously different. Each compound displayed two sets of four signals in the 5−6 ppm region and in the 6−9 ppm region, respectively.

Subsequent diffusion-ordered 2D proton NMR[13] experiments (DOSY) carried out with a solution of **2** in d_7-*N*,*N*-dimethylformamide clearly revealed that a symmetric dimeric species was the major component. This conclusion was based on the measured values of the diffusion coefficients, which allowed the calculation of the corresponding dimensions of the main two components of the solution, assuming a spherical shape for a solvated dinuclear (Cr,Ru) species and an oblate ellipsoid shape ($a = b > c$) for a solvated tetranuclear chloro-bridged dimer. The major component, which displayed a diffusion coefficient of 430 $\mu m^2/s$ (cf. Supporting Information), was first subjected to a spherical-model treatment, yielding a hydrodynamic radius of 6.3 Å. By applying an ellipsoid-model treatment an equatorial length a of 14 Å and a polar length c of 12 Å were obtained, which was deemed consistent with the expected dimensions of solvated dimer **2**. Similar conclusions could be drawn for the second most abundant species, which displayed a diffusion coefficient of 500 $\mu m^2/s$. More important, no signals

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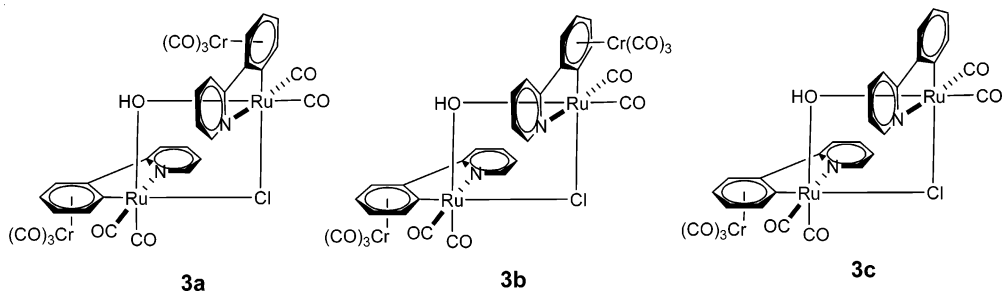

Figure 2. Structure and relative stereochemistry proposed for chloro,hydroxo-bridged dimers **3a**−**c**.

pertaining to a coordinated *N,N*-dimethylformamide moiety were found at these values of the diffusion coefficient. This suggests that the two most abundant species detected in a 14:3 ratio were essentially stereoisomers of dimer **2** and not d_7-*N,N*-dimethylformamide adducts. For comparison purposes, we carried out a ^{1}H 2D-DOSY experiment in $CDCl_3$ with a well-characterized dinuclear (Cr,Ru) complex (compound **9a**, *vide infra*): it displayed a significantly higher diffusion coefficient of 780 μm^2/s, which corresponds to a calculated radius of 3.5 Å assuming the shape of the molecule to be a sphere (cf. Supporting Information).

Solid-state CP-MAS ^{13}C NMR (cf. Supporting Information) was used in order to obtain complementary information on the chemical purity of **2**: 11 sharp signals in the 80−170 ppm region were assigned to the chelating ligand backbone carbon atoms, and two narrow singlets detected at δ 191.9 and 195.5 ppm were readily assigned to the $Ru(CO)_2$ moiety. Two signals arising at δ 235.6 and 237.7 ppm in a roughly 1:2 intensity ratio were assigned to the $Cr(CO)_3$ moiety assuming this split of resonances to be a consequence of the magnetic anisotropy of the carbonyl ligands in a nearly static tricarbonylmetal rotor, as suggested by Hanson et al. and Oprunenko, Günther, et al.[14]

Besides compound **2**, two side-products, **3a** and **3b**, were obtained in minute amounts in a roughly 4.5:1 molar ratio and were identified as the main components of the red-colored reaction's supernatant (eq 3). These two compounds were subsequently separated by conventional low-temperature flash chromatography on silica gel. Their ^{1}H NMR spectra contained sharp singlets at δ −2.92 ppm for **3a** and −3.30 ppm for **3b**, which were assigned to a hydroxo ligand bridging two ruthenacyclic units:[15] this rather upfield position of the signal contrasts notably with the NMR data reported for most μ-hydroxo-bridged bis-ruthenium(II) complexes, which assume for this ligand a downfield resonance far above 0 ppm.[16] An upfield resonance of the hydroxo ligand is generally encountered with mononuclear hydroxo-Ru(II) species.[17] In the region spanning from 5 to 9 ppm, the major compound, i.e., **3a**, displayed eight doublets and eight triplets, a clear sign of asymmetry for this hetero-tetranuclear complex. In the same region, compound **3b** displayed only eight signals, viz., four doublets and four triplets, indicating that the two chelate units were geometrically related by symmetry. Structural characterization was attempted by X-ray diffraction analysis with both compounds.

Figure 2 presents the structures of **3a** and **3b**, which were established on the basis of available NMR and X-ray diffraction structural data. Figure 3 displays a CCDC Mercury drawing of the structure of **3a**. Compound **3a** is asymmetric and consists of an association of two ruthenacycles of *endo* and *exo* geometry in which the *cis* Ru-bound CO ligands are oriented differently with respect to the $Cr(CO)_3$ moiety. The compact molecular arrangement in **3a** is characterized by a distance of 3.29 Å between atom O(7) belonging to the *endo* $Cr(CO)_3$ fragment and atom C(23) of the neighboring phenylene ligand. The hydroxo ligand occupies the axial position at ruthenium in the two metallacyclic units, the chloro sitting at the equatorial position *cis* to pyridyl's nitrogen atom. An original feature of this complex is the formal "encapsulation" of the hydroxo ligand between the metallacycles. A close analysis indicates relatively short distances between oxygen atom O(11) and atoms O(6), O(7), and Cr(1), which suggests that the hydroxo hydrogen atom H(11) interacts weakly with the vicinal $Cr(CO)_3$ moiety. The IR spectrum of **3a** taken from a sample dispersed in a KBr pellet displayed a relatively weak and broad band at 3420 cm^{-1}. Although the position of hydrogen atom H(11) was not accurately defined, it is estimated that this atom is separated by ca. 3.0 Å from atoms O(6) and O(7) and 2.9 Å from atom Cr(1), that is, by distances larger than the sum of atomic covalent radii for atoms H and O, and H and Cr. Taking into account the reasonable Brønsted- and Lewis-type basicities[18] of the $Cr(CO)_3$ fragment, a H-bonding interaction with the $Cr(CO)_3$ moiety is possible in the case of **3a**, although difficult to ascertain.

Compound **3b** possesses two metallacyclic units of *endo* geometry that are related by a C_2-symmetry axis defined by the chloro and the oxygen atom of the hydroxo ligand. Acceptable crystallographic data could not be obtained because of a failure to assign a significant amount of residual electron density content (cf. Supporting Information). However, a crystal of trace compound **3c** (Figure 2), which plausibly results from the formal loss of one $Cr(CO)_3$ moiety in **3b**, was serendipitously found among the crop of crystals of the latter. A CCDC Mercury ellipsoid diagram of **3c** displayed in Figure 4 indicates that the bridging hydroxo ligand occupies an axial position in both Ru-centered octahedral units, viz., *trans* to the axial Ru-bound CO ligand, the bridging chloro ligand being placed at an equatorial

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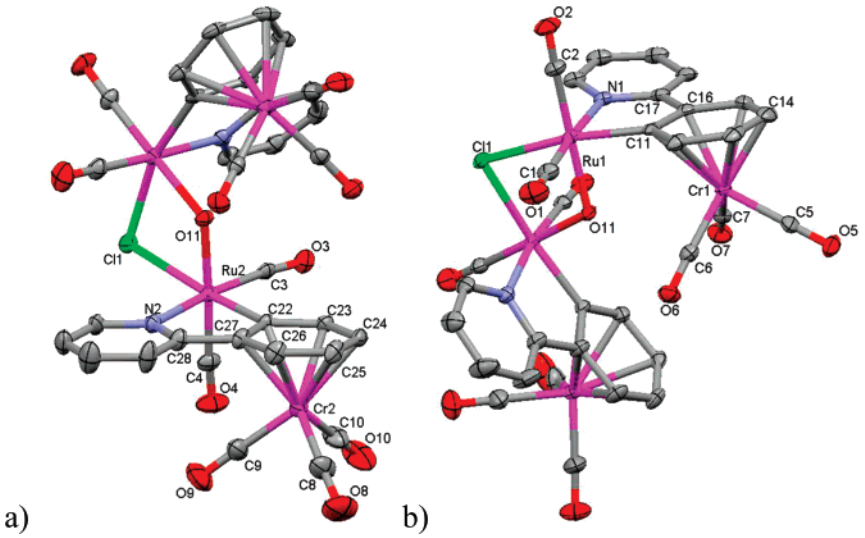


Figure 3. CCDC Mercury "ellipsoid" diagrams of **3a** drawn at the 30% probability level with full atom-numbering scheme for the two ruthenium-bound fragments (views a and b). Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ru(1)−C(11) 2.038(5), Ru(1)−N(1) 2.130(4), Ru(1)−C(1) 1.869(6), Ru(1)−C(2) 1.884(6), Ru(1)−O(11) 2.078(4), Ru(1)−Cl(1) 2.541(1), Cr(1)−C(11) 2.301(5), Cr(1)−C(14) 2.214(6), Ru(2)−O(11) 2.062(4), Ru(2)−Cl(1) 2.534(1), Ru(2)−C(22) 2.043(5), Ru(2)−N(2) 2.142(4), Ru(2)−C(3) 1.859(6), Ru(2)−C(4) 1.858(6), O(6)−C(27) 3.724(5), O(7)−C(23) 3.290(5), O(11)−Cr(1) 3.502(5), O(11)−O(7) 3.642(5), O(11)−O(6) 3.418(5), N(1)−Ru(1)−C(11) 80.1(2), C(11)−Ru(1)−O(11) 90.1(2), Cl(1)−Ru(1)−C(2) 102.9(2), C(27)−C(22)−C(23) 117.1(4), Ru(1)−O(11)−Ru(2) 115.9(2), Ru(1)−Cl(1)−Ru(2) 87.46(4), C(22)−Ru(2)−N(2) 79.6(2), C(4)−Ru(2)−Cl(1) 100.8(2), C(6)−Cr(1)−C(7) 88.2(2).

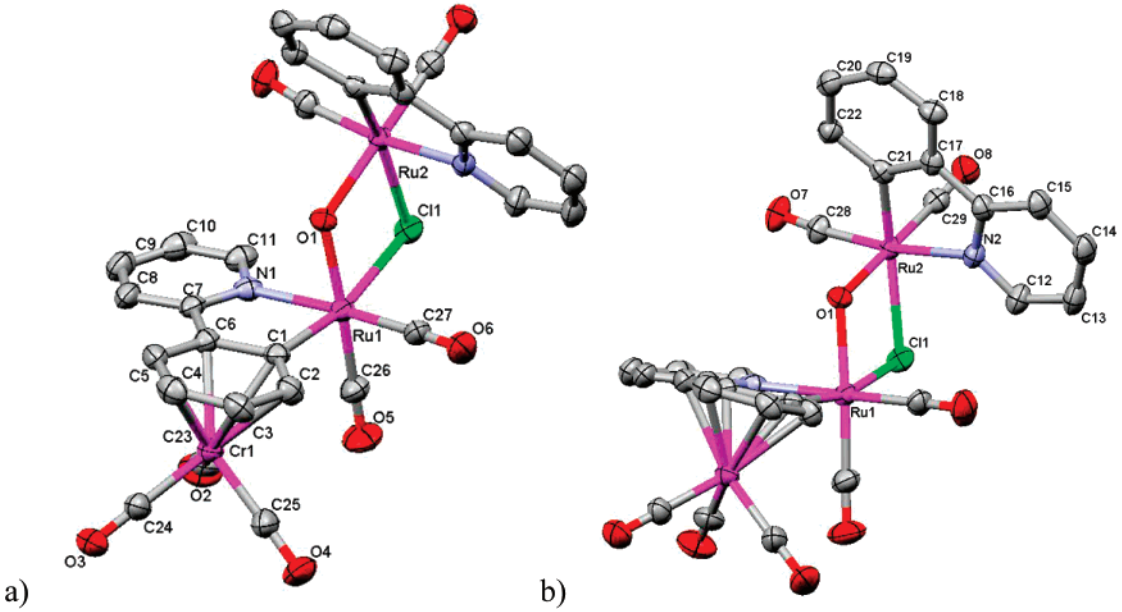


Figure 4. CCDC Mercury "ellipsoid" diagrams of **3c** drawn at the 40% probability level with full atom-numbering scheme for the two ruthenium-bound fragments (views a and b). Molecules of solvent and hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ru(1)−C(1) 2.020(8), Ru(1)−N(1) 2.136(7), Ru(1)−C(27) 1.872(9), Ru(1)−C(26) 1.869(9), Ru(1)−O(1) 2.095(5), Ru(1)−Cl(1) 2.535(2), Cr(1)−C(1) 2.304(8), Cr(1)−C(4) 2.214(9), Ru(2)−O(1) 2.106(5), Ru(2)−Cl(1) 2.563(2), Ru(2)−C(21) 2.023(8), Ru(2)−N(2) 2.135(7), Ru(2)−C(28) 1.873(9), Ru(2)−C(29) 1.858(9), N(1)−Ru(1)−C(1) 79.2(3), C(1)−Ru(1)−O(1) 80.7, Cl(1)−Ru(1)−C(26) 99.1(3), C(2)−C(1)−C(6) 115.2(7), Ru(1)−O(1)−Ru(2) 112.4(3), Ru(1)−Cl(1)−Ru(2) 86.46(6), C(21)−Ru(2)−N(2) 79.4(3), C(29)−Ru(2)−Cl(1) 103.1(2), C(22)−C(21)−C(17) 117.0(7).

position *trans* to the carbon atom of the 2-phenylenylpyridine ligand. The Ru(1)−O(1) and Ru(2)−O(1) distances are nearly identical at 2.10 Å, as are the Ru(1)−Cl and Ru(2)−Cl distances at about 2.55 Å.

The formation of **3a** and **3b** may be due to adventitious water since there is no reaction of **2** with anhydrous $NaHCO_3$, while deliberate addition of small amounts of water in THF at room temperature afforded a complex mixture that certainly contained **3a**. Similarly neither **3a** or **3b** was detected when **2** was prepared by the treatment of **1c** with $[Ru_2(CO)_2Cl_2]_n$ in the *absence* of Na_2CO_3. In this case compound **2** was recovered in 60% yield.

Determination of the Stereochemistry of 2. As compound **2** failed to provide crystals suitable for X-ray diffraction analysis, the relative stereochemistry at the ruthenium atom in this mixture of dimeric stereisomers was investigated by converting this rather insoluble solid into monomeric heterodinuclear soluble adducts. The preparation of monomers $\mathbf{4}^-$ and **5** was achieved by a separate treatment of **2** with bistriphenylphosphoranilide-

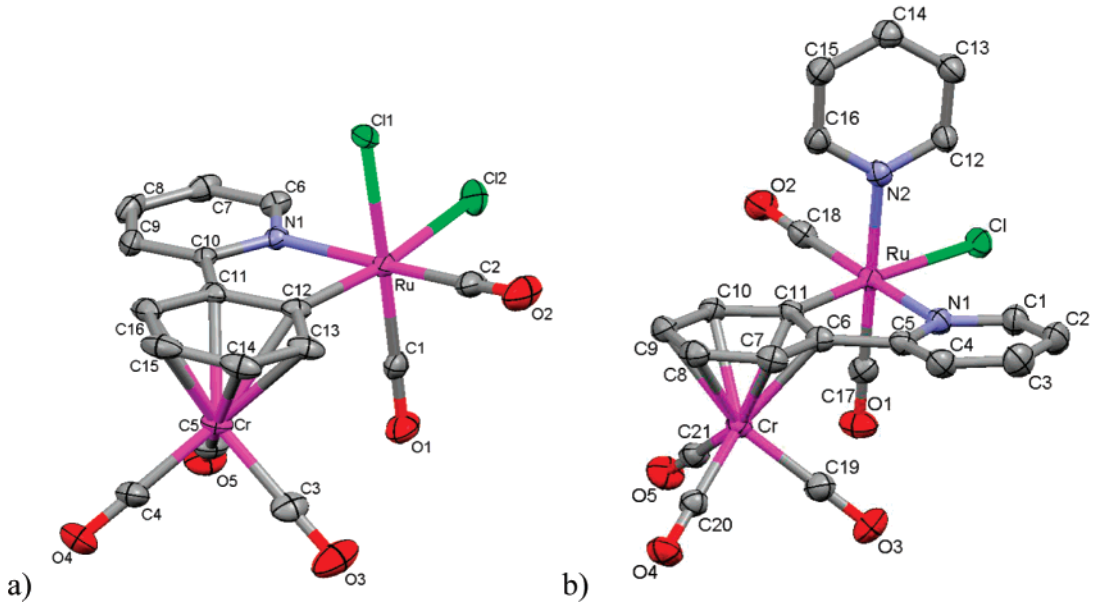
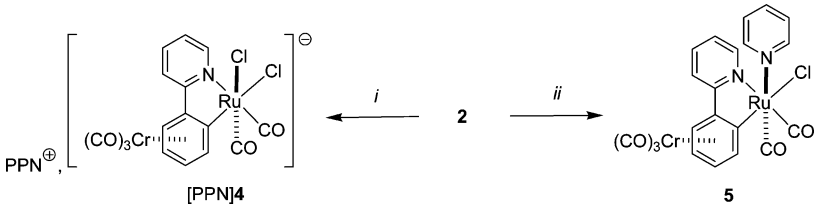


Figure 5. (a) CCDC Mercury "ellipsoid" diagram of anion **4**$^-$ drawn at 30% probability. PPN$^+$ countercation and atoms of hydrogen have omitted for clarity. (b) CCDC Mercury "ellipsoid" diagram of anion **5** drawn at 40% probability. Hydrogen atoms have been removed for clarity. Selected interatomic distances (Å) and angles (deg) for **4**$^-$: Ru−Cl(1) 2.4286(8), Ru−Cl(2) 2.4895(10), Ru−N(1) 2.129(2), Ru−C(1) 1.861(3), Ru−C(2) 1.860(3), Ru−C(12) 2.046(3), Cr−C(12) 2.290(3), Cr−C(15) 2.199(4), Cl(1)−Ru−Cl(2) 90.12(3), Cl(1)−Ru−N(1) 87.54(7), Cl(1)−Ru−C(12) 86.07(8), Cl(2)−Ru−N(1) 92.39(6). Selected interatomic distances (Å), angles (deg), and torsion angle (deg) for **5**: Ru−C(11) 2.050(3), Ru−N(1) 2.141(2), Ru−C(18) 1.866(3), Ru−Cl 2.4782(7), Ru−C(17) 1.883(3), Cr−C(11) 2.289(3), Cr−C(8) 2.210(3), Ru−N(2) 2.161(2), C(11)−Ru−N(1) 78.7(1), C(11)−Ru−N(2) 89.1(1), C(6)−C(11)−C(10) 116.7(3), C(11)−C(6)−C(5)−N(1) 0.90.

Scheme 1 [a]



[a] *i*: [PPN]Cl. *ii*: pyridine.

neammonium chloride ([PPN]Cl) and pyridine, respectively (Scheme 1). The formation of **4**$^-$ was formally quantitative: this lipophilic and soluble salt was readily purified by flash chromatography through a short silica gel column. Complex **5** was also readily purified by chromatography and characterized by NMR spectroscopy. Both compounds were structurally characterized by X-ray diffraction analysis. Figure 5 displays the CCDC Mercury ellipsoid diagrams of **4**$^-$ and **5** with their atom-numbering scheme. In compound **5**, the pyridine ligand occupies the axial position at ruthenium, in a *trans* manner relative to the axial carbonyl ligand. This would suggest that in precursor **2** the more reactive bond toward "borderline" hard bases and nucleophiles such as pyridine is the one that binds the chloro ligand to the ruthenium center at its axial position. In **4**$^-$, chloro ligands are located *cis* to each other. The chloro-to-ruthenium distances are not significantly different; the Ru−Cl(1) distance is shorter than Ru−Cl(2) only by ca. 0.06 Å. In both structures the $Cr(CO)_3$ tripod is nearly *anti*-eclipsed with respect to the ruthenium center and the chromium-to-ruthenated-arene-carbon distance is only slightly longer than the average of Cr−C_{Ar} bonds. Both **4**$^-$ and **5** possess a *rac*-(p*R*, *OC*-6-42-*C*)[19,20] relative configuration and the *endo*-type geometry.

Therefore, the structural similarity between these two complexes suggests that the *monomerization* of **2** preserves the relative stereochemistry at the Ru center. Hence, it may be concluded that compound **2**, which most probably consists of a mixture of μ-chloro-bridged dimeric stereoisomers, is most certainly stereochemically *homogeneous* as far as the Ru-centered and planar chiralities are concerned.

Similar observations were made while submitting ferrocenyl derivative **6**[21] to a treatment with $[Ru(CO)_2Cl_2]_n$. In a typical experiment, the reaction of compound **6** with $[Ru(CO)_2Cl_2]_n$ in the presence of Na_2CO_3 in boiling 1,2-dimethoxyethane (Scheme 2) afforded in 41% yield a mixture of μ-chloro-bridged dimers **7**, which presented a sufficient solubility to allow their separation from unreacted **6** and $[Ru(CO)_2Cl_2]_n$ by conventional low-temperature chromatography on silica gel. A ^{1}H NMR analysis of **7** in noncoordinating $CDCl_3$ revealed the presence of at least three different isomers in a 2:1.5:1 ratio. Similarly to **2**, which

(19) Throughout the present article this *extended* CIP sequence rule is used to assign the p*S* or the p*R* stereochemical descriptors to planar-chiral molecules. Readers are referred to the following references for more details: (a) Schlögl, K.; Fried, M. *Monatsh. Chem.* **1964**, *95*, 558−575. (b) Schlögl, K.; Fried, M.; Falk, H. *Monatsh. Chem.* **1964**, *95*, 576−597. (c) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed.* **1966**, 385−415. (d) Schlögl, K. *Top. Stereochem.* **1967**, *1*, 39−91. For IUPAC's basic terminology of stereochemistry see: Moss, G. P. *Pure Appl. Chem.* **1996**, *68*, 2193−2222.

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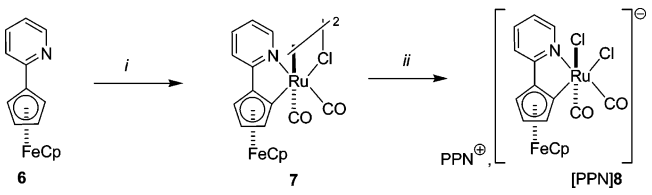
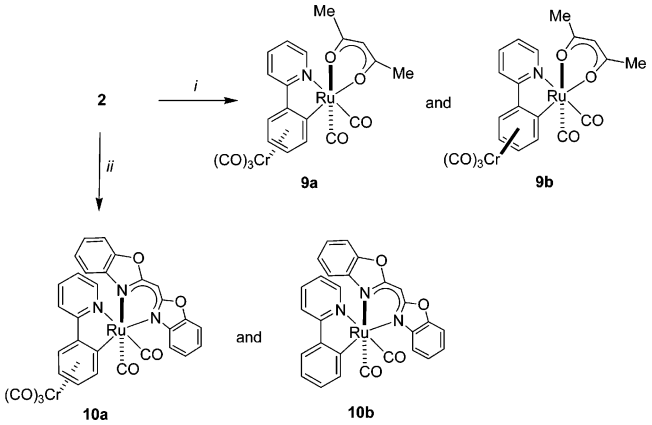
Scheme 2 [a]



[a] *i*: $[Ru(CO)_2Cl_2]_n$, Na_2CO_3, 1,2-dimethoxyethane. *ii*: [PPN]Cl.

Scheme 3 [a]



[a] *i*: H*acac*, Na_2CO_3, 1,2-dimethoxyethane. *ii*: H*bbom*, Na_2CO_3, 1,2-dimethoxyethane.

could readily be cleaved upon addition of chloride, this mixture was readily converted into a single product, i.e., [PPN]**8**, upon treatment with [PPN]Cl (Scheme 2).

Crystallization of **7** afforded several crystals suitable for X-ray diffraction analysis, among which one was arbitrarily selected. The structures of dimer **7a** and **8**$^-$ are displayed in Figure 6. The two compounds possess the same relative *rac*-(p*R, OC*-6-42-*C*) configuration at the planar-chiral ruthenacycle. Worthy of note, the mean planes of the two [C,L] chelating units in **7a** are not parallel but perpendicular, which strikingly contrasts with the few known structures of chloro-bridged non-π-coordinated ruthenacycles: according to the data deposited with the Cambridge structural database,[22] all structures show a parallel arrangement of the [C,L] units.

In view of our previous observations on the composition of **2** and assuming again that the *monomerization process* takes place with retention of relative configuration, we tentatively conclude that all isomers of **7** possess the same local relative configuration.

Reaction of Anionic Bidentate Ligands with Planar-Chiral Chloro-Bridged Dimers: Signs of Configurational Lability. The treatment of **2** with acetylacetone (abbreviated H*acac*) in the presence of excess Na_2CO_3 afforded a 5:1 mixture of two compounds, **9a** and **9b**, with an overall yield of 68% (Scheme 3). A pure sample of **9a** was obtained by fractional recrystallization of this mixture and characterized structurally by X-ray diffraction analysis.

Figure 7 displays a CCDC Mercury drawing of this complex, which possesses the relative *rac*-(p*R-OC*-6-43-*C*) configuration. The chelating 2-phenylenepyridine ligand is only slightly bent, with an interplanar angle between the pyridyl and the phenylene moieties of ca. 1.8°. Similarly to **4**$^-$, **5**, **7**, and **8** the two Ru-bound carbonyl ligands are in a *cis* configuration and the axial one points toward the $Cr(CO)_3$ moiety, conferring an *endo* configuration to the complex.

A *rac*-(p*S, OC*-6-43-*C*) relative configuration was tentavively assigned to **9b**, considering that the acetylacetonato complexes **9a** and **9b** differ only by the position of the $Cr(CO)_3$ moiety relative to *acac* or, in other terms, by an opposite relative planar-chiral configuration. This assumption was based on the similarities noticed in the spectroscopic data of **9a** and **9b**. For example, the IR spectra of **9a** and **9b** proved to be very similar: they contained four well-separated CO stretching bands that clearly indicated that the two Ru-bound CO ligands of the rigid $Ru(CO)_2$(*acac*) moiety are in a *cis* relationship. For reasons of symmetry, a *trans* arrangement of the CO ligands at ruthenium atom would have resulted ideally in a single active CO stretching band or at least in two bands very close in frequency.[23] The two bands assigned to the $Ru(CO)_2$(*acac*) fragment were detected at 2045 and 1958 cm^{-1}. ^{1}H and ^{13}C NMR spectroscopic analyses carried out with **9a** and **9b** in $CDCl_3$ at room temperature confirmed the coordination of the acetylacetonato ligand in both compounds. Only a tiny difference of chemical shifts distinguished the signals of the protons of the methyl group located in close vicinity to the chelating [C,N] ligand in **9a** and **9b**. The signal of this methyl group in **9b** was deshielded by ca. 0.2 ppm with respect to its equivalent in **9a**. Unfortunately, we were not able to establish the actual stereochemistry of **9b**, as it failed to provide crystals of sufficient quality for a pertinent X-ray diffraction structural analysis.

We decided to probe the facial selectivity of the transfer of "$Cr(CO)_3$" to complex **11**[11] expecting that **9a** would be the major product: steric repulsion was expected to prevent π-coordination of the $Cr(CO)_3$ moiety in the vicinity of the *acac* ligand. The treatment of complex **11** with tricarbonyl(η^6-naphthalene)chromium[24] in warm tetrahydrofuran for 90 min provided an unexpected result: a 1:9 mixture of **9a** and **9b** was produced with an overall yield of 37% (Scheme 4). This reversed product ratio, which putatively illustrates the precedence of path a over path b in Scheme 4, can reasonably be explained by a directing effect of the *acac* ligand. In this case, the $Cr(CO)_3$-transfer process is assisted by the binding of the Cr center to the axial oxygen atom of the acetylacetonato ligand of **11**, as depicted in Scheme 4. This facial selectivity of the π-coordination of **11** somewhat parallels other known cases of face-selective transfer of $Cr(CO)_3$ to metal-free arene ligands containing ancillary σ-donating substituents.[25]

It is important to note here that neither **9a** or **9b** isomerized into **9b** and **9a**, respectively, upon heating in dry and distilled d_8-toluene; rather they decomposed slowly over 24 h, as indicated by ^{1}H NMR monitoring.

In order to evaluate the importance of the steric factor over the distribution of isomers, we decided to submit complex

(22) The reader is referred to the structures with the following CCDC reference codes. LUQMOZ: Osintseva, S. V.; Dolgushin, F. M.; Petrovskii, P. V.; Shtel'tser, N. A.; Kreindlin, A. Z.; Rybin, L. V.; Rybinskaya, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **2002**, 1610−1619. VIGWIR: Osintseva, S. V.; Petrovskaya, E. A.; Rybin, L. V.; Kreindlin, A. Z.; Dolgushin, F. M.; Yanovsky, A. I.; Petrovskii, P. V.; Rybinskaya, M. I. *Izv. Akad. Nauk SSSR Ser. Khim.* **2000**, 1616−1623. See also: Zhang, Q. F.; Cheung, K. M.; Williams, I. D.; Leung, W. H. *Eur. J. Inorg. Chem.* **2005**, 4780−4787.

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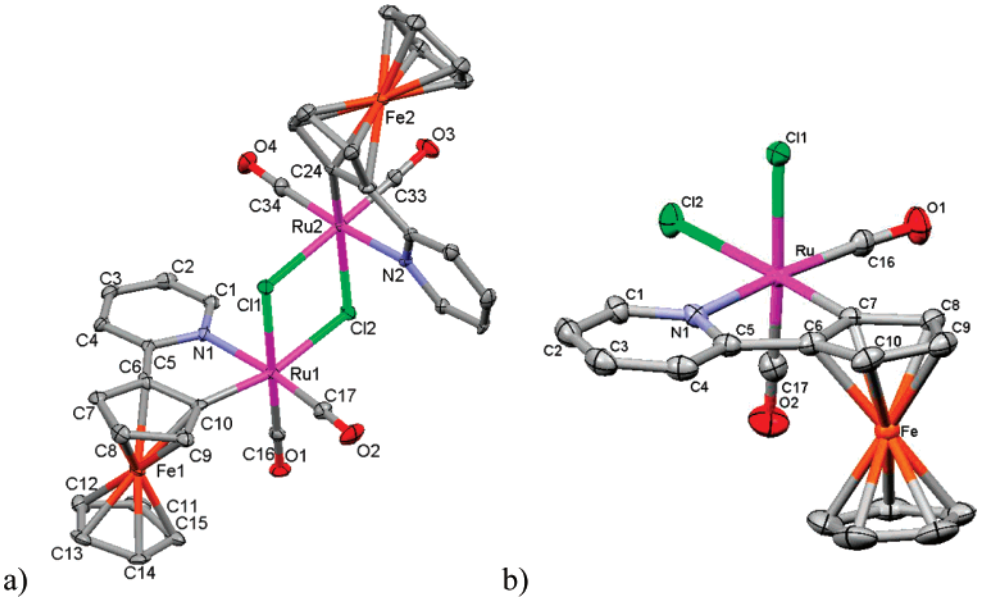
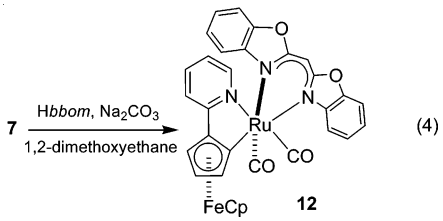


Figure 6. (a) CCDC Mercury "ellipsoid" diagram of **7a** drawn at the 30% probability level. Hydrogen atoms and CH_2Cl_2 molecules have been omitted for clarity. (b) CCDC Mercury "ellipsoid" diagram of $\mathbf{8}^-$ drawn at the 40% probability level. Hydrogen atoms and the PPN^+ countercation have been omitted for clarity. Selected interatomic distances (Å) and angles (deg) for **7a**: Ru(1)−Cl(1) 2.475(2), Ru(1)−Cl(2) 2.521(3), Ru(2)−Cl(1) 2.486(3), Ru(2)−Cl(2) 2.535(3), Ru(1)−N(1) 2.180(9), Ru(1)−C(17) 1.883(12), Ru(1)−C(16) 1.845(10), Ru(1)−C(10) 2.050(10), Ru(2)−C(24) 2.033(10), Fe(1)−C(10) 2.090 (11), C(10)−Ru(1)−N(1) 79.6(4), Ru(1)−Cl(1)−Ru(2) 98.31(8), Ru(1)−Cl(2)−Ru(2) 95.86 (8), C(24)−Ru(2)−N(2) 79.4(4), Cl(1)−Ru(1)−Cl(2) 83.16(8). Selected interatomic distances (Å) and angles (deg) for $\mathbf{8}^-$: Ru−C(7) 2.047(2), Ru−Cl(1) 2.4450(4), Ru−Cl(2) 2.5036(5), Ru−N(1) 2.165(1), Ru−C(16) 1.849(2), Ru−C(17) 1.840(2), Fe−C(7) 2.118(1), Fe−C(10) 2.027(2), C(16)−O(1) 1.143(2), C(17)−O(2) 1.145(2), N(1)−Ru−C(7) 79.07(6), Cl(1)−Ru−Cl(2) 88.06, Cl(2)−Ru−C(16) 98.23(5), N(1)−C(5)−C(6)−C(7) 4.59.

2 and **7** to a treatment with 1,1-bis(2-benzoxazolyl)methane[26] (abbreviated H*bbom* according to Cenini et al.) in the presence of Na_2CO_3: this ligand, a bulky "diaza analogue" of H*acac*, is reportedly capable of forming particularly stable metal-chelates upon deprotonation according to Pagani et al.[26a] The experiment carried out with **2** afforded a mixture of two products, i.e., **10a** and **10b** in a 9:1 ratio (Scheme 3). These two compounds displayed different IR spectra consisting for **10a** of four bands appearing at ca. 2051, 1987, 1957, and 1885 cm^{-1} and for **10b** of two bands at 2041 and 1973 cm^{-1}, indicating that the latter was missing the $Cr(CO)_3$ moiety. Consistently, the ^{13}C NMR spectrum of the latter did not display any singlet at around 236 ppm. Compound **10a** was recovered upon chromatographic purification in 80% yield. Compound **10b** was recovered only in trace amounts. Compound **7** treated similarly with H*bbom* converted into a single product, viz., **12**, which was recovered in 63% yield (eq 4).



(4)

Compounds **10a** and **12** share strong similarities with regard to their structure (Figure 8): in both cases the planar-chiral ruthenacycle has the *endo* geometry with a *rac*-(p*R*, OC-6-42-*C*) relative configuration. Both the *bbom* and the chelating [C,L] ligands are slightly folded. The shortest distance separating H(16), viz., the hydrogen atom connected to atom C(16), from *bbom* amounts to 2.53 and 2.59 Å in **10a** and **12**, respectively (Figure 8). The distortion of the *bbom* ligand is best described

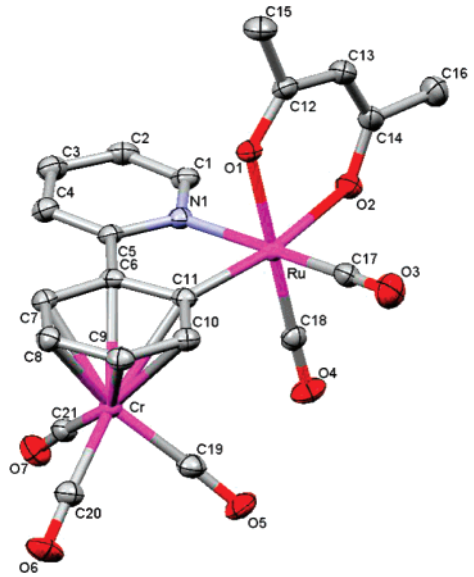


Figure 7. CCDC Mercury ellipsoid diagram of **9a** drawn at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg) for **9a**: Ru−C(11) 2.056(4), Ru−N(1) 2.121(4), Ru−O(1) 2.089(3), Ru−O(2) 2.121(3), Ru−C(17) 1.876(5), Ru−C(18) 1.863(5), Cr−C(11) 2.306(4), Cr−C(8) 2.208(5), O(1)−C(12) 1.280(6), C(12−C(13) 1.391(7), C(13)−C(14) 1.387(8), C(14)−O(2) 1.279(6), N(1)−Ru−C(11) 79.3(2), C(6)−C(11)−C(10) 117.3(4), O(1)−Ru−O(2) 88.8(1), C(17)−Ru−C(18) 90.4(2), N(1)−C(5)−C(6)−C(11) 0.05.

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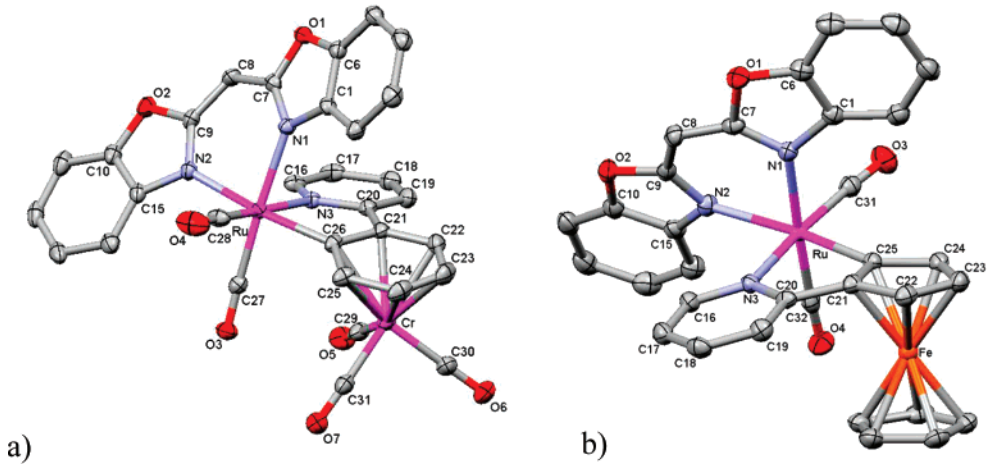
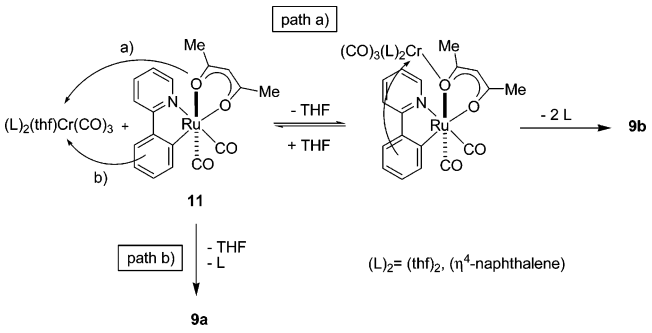


Figure 8. (a) CCDC Mercury "ellipsoid" diagram of **10a** drawn at the 40% probability level. Hydrogen atoms and molecules of acetone have been omitted for clarity. (b) CCDC Mercury "ellipsoid" diagram of **12** drawn at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg) for **10a**: Ru−C(26) 2.057(2), Ru−N(1) 2.158(2), Ru−N(2) 2.152(2), Ru−N(3) 2.136(2), Ru−C(28) 1.874(3), Ru−C(27) 1.873(3), Cr−C(26) 2.314(2), Cr−C(23) 2.227(3), N(1)−C(7) 1.327(3), C(7)−C(8) 1.399(4), C(8)−C(9) 1.380(4), C(9)−N(2) 1.340(3), C(9)−O(2) 1.381(1), C(6)−O(1) 1.383(3), C(26)−Ru−O(3) 78.5(1), N(1)−Ru−N(2) 85.37(8), C(27)−Ru−C(28) 87.7(1), C(21)−C(26)−C(25) 116.9(2), C(26)−C(21)−C(20)−N(3) 1.99. Selected interatomic distances (Å) and angles (deg) for **12**: Ru−C(25) 2.063(2), Ru−N(1) 2.154(2), Ru−N(2) 2.174(2), Ru−N(3) 2.169(2), Ru−C(31) 1.867(3), Ru−C(32) 1.856(2), Fe−C(25) 2.118(2), Fe−C(22) 2.022(2), N(1)−C(7) 1.325(3), C(7)−C(8) 1.382(3), C(8)−C(9) 1.385(3), C(9)−N(2) 1.333(3), C(9)−O(2) 1.382(3), C(7)−O(1) 1.384(3), C(25)−Ru−N(3) 78.64(8), N(1)−Ru−N(2) 85.28(7), C(31)−Ru−C(32) 88.4(1), C(25)−C(21)−C(20)−N(3) 6.98.

Scheme 4. Face-Selective Transfer of the $Cr(CO)_3$ Moiety from Tricarbonyl(η^6-naphthalene)chromium to Compound 11



by the interplanar angle formed between two benzoxazolyl fragments, which amounts to 18.4° in **10a** and 21.8° in **12**. Likewise, the distortion of the [C,L] chelating unit is characterized by a significant bending of the chelate's plane toward either the $Cr(CO)_3$ or the CpFe moiety: the interplanar angle between the mean plane of the pyridyl moiety and that of the cyclopentadienyl and the aryl fragments amounts to 14.1° and 14.9° in **10a** and **12**, respectively.

In the reaction of **2** with H*acac* under basic conditions, three hypotheses could be produced to rationalize the formation of minor compound **9b**:

(i) Starting compound **2** is not configurationally homogeneous; it contains unknown amounts of the ruthenacycle of *exo* geometry, and the chelation of the ruthenium center by homobidentate ligands does not perturb the configuration at ruthenium. This hypothesis, which questions the conclusions drawn previously on the *stereochemical homogeneity* of compound **2**, is not valid in our opinion. Even though compound **9b** represents about 20% of the recovered admixture in which **9a** is the major component, neither direct or indirect evidence was found to support that **2** contained the same amount of ruthenacycle of *exo* geometry.

(ii) **9a** and **9b** interconvert by a heat-promoted transfer of the $Cr(CO)_3$ group from one face of the chelate's phenylene ring to the other in favor of **9a**. Metallotropic rearrangements in scalemic (nonracemic) chiral (η^6-arene)tricarbonylchromium complexes have been investigated and evidenced by Oprunenko in the recent past.[27] Uemura recently reported a striking case of inversion of planar configuration with a scalemic tricarbonylchromium benzylalcohol derivative, which underwent epimerization upon heating in a nonaromatic ligand.[28] However, the thermal stability of both **9a** and **9b** mentioned previously seemingly invalidates the hypothesis of a metallotropic rearrangement.

(iii) The chelation of the Ru center by *acac* or *bbom* is subjected to polytopal isomerization[29] by a multistep reversible Berry pseudorotation[30] of putative five-coordinate electron-deficient intermediates involving *monodentate acac*, such as **A** and **B** (Scheme 5), formed in the course of the reaction of **2** with H*acac*. It is generally admitted that under thermodynamic control electronic effects, such as *trans*-influence[31] and *anti*-symbiosis,[32] impact the stereochemical course of reactions that take place at a metal center. Steric interactions may also play a role by favoring the formation of the less sterically encumbered product. In the present system, if *anti*-symbiotic effects compel the π-acidic carbonyl ligands to adopt (i) a *cis* configuration at the Ru center and (ii) a *trans* position with respect to the relatively hard σ-donating atoms of the two chelating units, there seems to be no major intervention of a steric control upon the orientation of the *acac* ligand in the final products. Geometry optimizations using the density functional theory (B3LYP/LANL2DZ (Cr, Ru), 6-31G**) indicated that the energy difference between **9a** and **9b** was only ca. 0.57 kcal/mol, the

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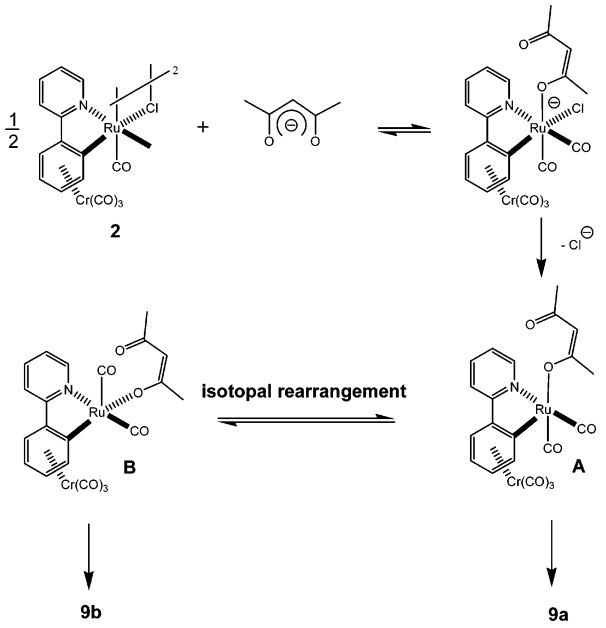
Scheme 5. Proposed Mechanism for the Formation of Minor Isomer 9b from the Reaction of Dimeric Planar-Chiral Metallacycle 2 with Acetylacetonate



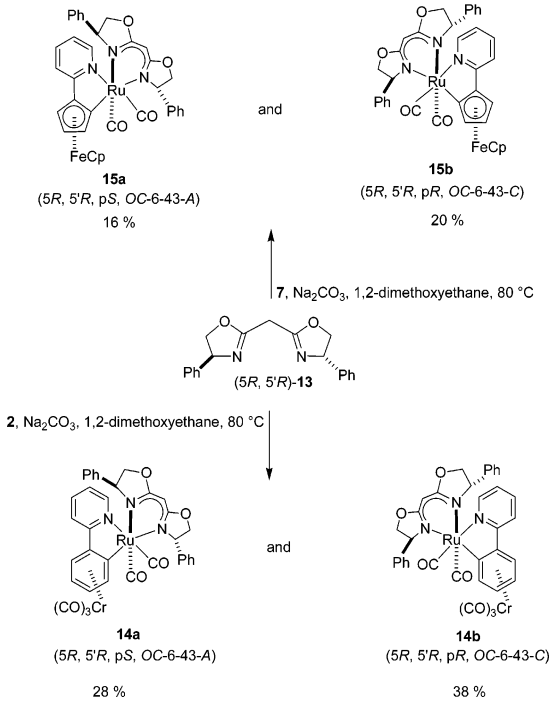
latter being slightly more stable (cf. Supporting Information). Hence, it appears that the formation of **9a** and **9b** should be thermodynamically equally favored.

Therefore, we speculate that the unbalanced ratio in **9a** and **9b** in the reaction of **2** with H*acac* is most probably a consequence of an effective isotopal rearrangement of intermediate five-coordinate species **A** into its isomer **B** (Scheme 5). The lack of interconversion between related compounds, which was evidenced by the absence of isomerization of **9b** upon heating, rules out the polytopal isomerization of the final electron-saturated six-coordinate ruthenium species.[33]

Preparation of Scalemic (Nonracemic) Planar-Chiral Cycloruthenated Complexes. In light of the above-mentioned results we undertook to probe the behavior of **2** and **7** toward scalemic ligand (5*R*,5′*R*)-**13**[34] (ee ≥ 98%) in a base-assisted reaction (Scheme 6). We expected that the two phenyl groups attached at the 5 and 5′ positions of the latter chiral ligand would disfavor the formation of products exhibiting *exo*-type geometry, which in principle would lend access to pairs of nonracemic diastereomeric planar-chiral ruthenacycles displaying exclusively the *endo*-type geometry. The treatment of **2** and **7** with excess **13** in the presence of Na_2CO_3 afforded pairs of diastereomers **14a**/**14b** and **15a**/**15b** in 1:1.35 and 1:1.25 ratios, respectively. All four compounds were readily separated by conventional chromatography at low temperature, isolated, and analytically characterized.

The structures of **14a**, **14b**, and **15a** were assessed by X-ray diffraction analyses; CCDC Mercury diagrams of these compounds, which crystallized in non-centrosymmetric space groups, are displayed in Figure 9 and Figure 10. As expected, the three structures possess the *endo*-type geometry with a Ru-bound CO axial ligand sitting close to the $Cr(CO)_3$ and FeCp moieties. Pertinent values for Flack's *x* parameter[35] validated the following assignment of absolute configurations for the structures of **14a**,**b** and **15a**: (5*R*, 5′*R*, p*S*, *OC*-6-43-*A*) for both **14a** ($[\alpha]_D$ −881 in CH_2Cl_2) and **15a** ($[\alpha]_D$ −1465 in MeOH) and (5*R*, 5′*R*, p*R*, O*C*-6-43-*C*) for **14b** ($[\alpha]_D$ −168 in CH_2Cl_2), planar as well as carbo- and rutheno-centered chiralities being accounted for here. A (5*R*, 5′*R*, p*R*, OC-6-43-*C*) configuration was assumed for **15b** ($[\alpha]_D$ +445 in MeOH) assuming that on steric grounds the chiral diaza ligand was not likely to bind the Ru(II) center in a *cis* fashion relative to the FeCp moiety. In light of these results, the slightly favorable bias for diastereomers **14b** and **15b** in the reaction of the chloro-bridged dimeric substrates with **13** was tentatively ascribed to a weak chiral recognition, the reaction of (5*R*,5′*R*)-**13** with *rac*-**2** and *rac*-**7** being putatively p*R*-selective. We therefore attempted the resolution of *rac*-**2** by applying the "half-equivalent" method,[36] which consisted in a reaction of the former racemate with half an equivalent of (5*R*,5′*R*)-**13** per Ru atom. To our disappointment, not only was the yield of **14a**,**b** poor but the ratio between these two species was found to be roughly equal to that found previously.

Scheme 6. Yields Are Given Relative to *rac*-2 and *rac*-7



A common structural feature of **14a** and **15a** is the almost parallel stacking of one of the phenyl groups of the chiral bis-(2-oxazolyl)methylidene ligand with the [C,L] chelating unit. This overlap is characterized by an interplanar angle of 10.3° in **14a** and 12.4° in **15a**. In both cases, the shortest interplanar distance amounts to ca. 3.3 Å. In the structure of **14b**, the phenyl ring connected to C(1) remains roughly parallel to the 2-phenylenepyridine moiety, although slightly shifted away from the [C,L] ligand; its *ipso* atom C(8) lies at the vertical of atom C(30) with an interatomic distance C(8)−C(30) of 3.3 Å.

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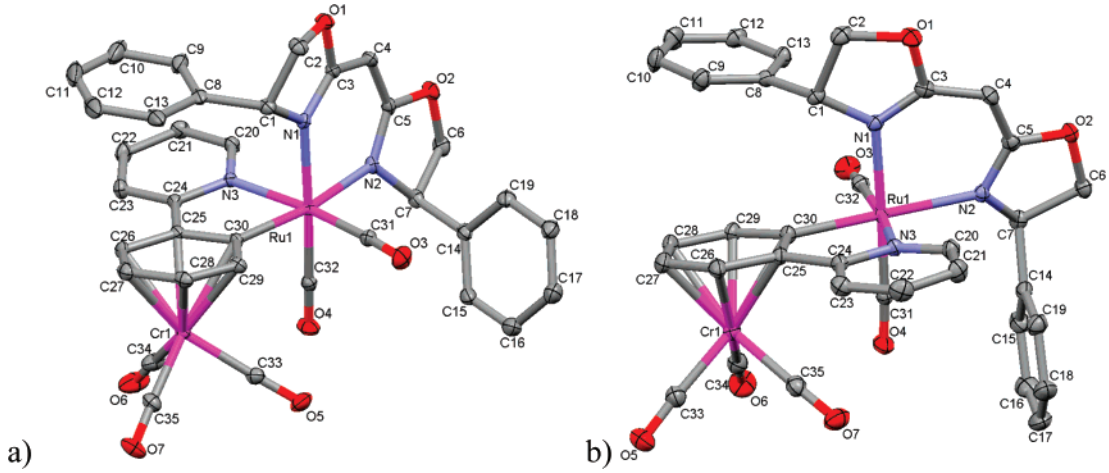

Figure 9. (a) CCDC Mercury "ellipsoid" diagram of **14a** drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity (Flack's *x* parameter: −0.012(14)). (b) CCDC Mercury "ellipsoid" diagram of **14b** drawn at the 30% probability level; hydrogen atoms and molecules of CH_2Cl_2 have been omitted for clarity (Flack's *x* parameter: −0.010(18)). Selected interatomic distances (Å) and angles (deg) for **14a**: Ru−C(31) 1.874(2), Ru−C(32) 1.882(2), Ru−C(32) 1.882(2), Ru−C(30) 2.063(2), Ru−N(1) 2.131(2), Ru−N(3) 2.141(2), Ru−N(2) 2.143(2), Cr−C(30) 2.302(2), Cr−C(27) 2.214(2), C(31)−Ru−C(32) 91.6(1), C(32)−Ru−C(30) 90.6(1), C(30)−Ru−N(3) 78.61(7), N(1)−Ru−N(2) 86.80(7), C(25)−C(30)−C(29) 116.4(2), C(26)−C(27)−C(28) 119.8(2). Selected interatomic distances (Å) and angles (deg) for **14b**: Ru−C(32) 1.862(3), Ru−C(31) 1.879(3), Ru−C(31) 1.879(3), Ru−C(30) 2.075(2), Ru−N(1) 2.134(2), Ru−N(3) 2.149(2), Ru−N(2) 2.171(2), Cr−C(30) 2.319(3), Cr−C(27) 2.214(3).: C(31)−Ru−C(30) 87.2(1), C(30)−Ru−N(3) 78.6(1), C(32)−Ru−C(30) 94.9(1), N(1)−Ru−N(2) 86.71(8).

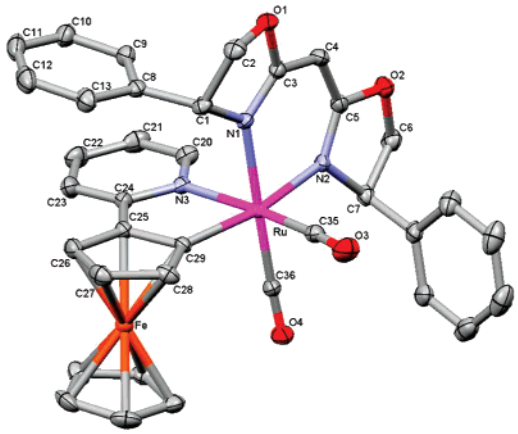

Figure 10. CCDC Mercury "ellipsoid" diagram of **15a** drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. (Flack's *x* parameter: −0.020(11)). Selected interatomic distances (Å) and angles (deg): Ru−C(29) 2.069(2), Ru−N(1) 2.134(2), Ru−N(2) 2.150(2), Ru−N(3) 2.163(2), Ru−C(35) 1.872-(2), Ru−C(36) 1.864(2), Fe−C(29) 2.120(2), Fe−C(26) 2.025(2), N(1)−C(3) 1.315(3), C(3)−C(4) 1.388(3), C(4)−C(5) 1.390(3), C(5)−N(2) 1.314(2), C(3)−O(1) 1.378(2), C(5)−O(2) 1.376(2), C(29)−Ru−N(3) 78.51(7), N(1)−Ru−N(2) 85.93(6), C(35)−Ru−C(36) 88.1(1), C(3)−C(4)−C(5) 121.7(2).

Circular dichroism[37] spectra of **14a**,**b** and **15a**,**b** are displayed in Figure 11. Because the CD responses of **14a** and **15a** are overall similar, it is tempting to consider the strong negative Cotton effect observed in both cases at 318−330 nm as a typical chiroptical signature of their stereochemistry.

Conclusion

In this report we have shown that the cyclometalation of the 2-phenylpyridine chromium complex **1c** with $[Ru(CO)_2Cl_2]_n$ was relatively efficient. At this stage, the lack of reactivity of *N*,*N*-dimethylbenzylamine and 2-phenyl-2-oxazoline complexes **1a** and **1b** is somewhat surprizing. In a previous report dealing with the ortho-mercuration of similar substrates, it was already noticed that the latter two substrates were much less reactive toward $Hg(OAc)_2$ than 2-phenylpyridine **1c**, affording the corresponding ortho-mercurated products in 38% and 17% yield.[38] It is important to note that there has been hitherto no report of ortho-ruthenation of *N*,*N*-dimethylbenzylamine and 2-phenyl-2-oxazoline by $[Ru(CO)_2Cl_2]_n$ in the literature.[39] Notwithstanding the possible relevance of the nature of the ligand appended to the (η^6-aryl)$Cr(CO)_3$ moiety in the substrate, we believe that the $Cr(CO)_3$ moiety sterically inhibits the necessary preliminary coordination of the pendant ligand to the electrophilic metal center. The salient feature of the cyclometalation reactions presented here is their high diastereoselectivity. As mentioned in the Introduction, such an outcome was unexpected, and more efforts must now be dedicated in defining the factors that determine the stereochemistry of the planar-chiral products particularly at the chelated ruthenium center. We anticipate that both steric and electrostatic repulsion govern the stereochemical course of cyclometalation by asymmetric *OC*-6 metal centers. To support this is the predominance of isomers with the *endo*-type geometry among all the products described here.

Further studies will also have to give a ruling on the extent of polytopal isomerization in the chemistry of six-coordinate dicarbonyl ruthenium complexes, such as those reported herein. For instance, the peculiar combination of *exo*- and *endo*-type metallacyclic geometries in compound **3a** might well stem from a polytopal rearrangement in the process implying the replacement of a chloro group by the hydroxo ligand in complex **2**.

Finally, in this report we have shown that scalemic planar-chiral *OC*-6 ruthenacycles were readily accessible. However, the use of an enantiopure bidentate anionic auxiliary is certainly not the most direct way toward scalemic compounds **2** or **7**.

(37) *Circular Dichroism, Principles and Applications, Second Edition*; Berova, N., Nakanishi, K., Woody, R. W., Eds.; Wiley-VCH: New York, 2000.

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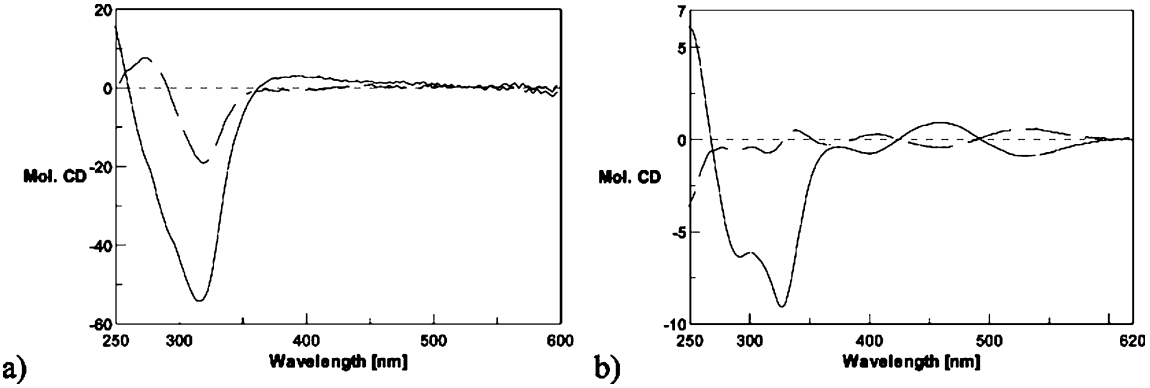

Figure 11. Molar circular dichroism ($L \cdot mol^{-1} \cdot cm^{-1}$) vs wavelength (nm) at 20 °C. (a) Circular dichrograms of 10^{-4} M solutions of **14a** (continuous line) and **14b** (dashed line) in dry dichloromethane measured in a 1 mm optical path length cell. (b) Circular dichrograms of 2.5×10^{-4} M solutions in absolute methanol of **15a** (continuous line) and **15b** (dashed line) measured in a 1 cm optical path length cell.

All our attempts to remove chemically the bis(2-oxazolyl)-methylidene fragment and release scalemic **2** and **7** have hitherto failed. Further efforts are currently under way to search for viable alternative routes toward scalemic complexes such as **2**, **7**, **3a**, and **3b**, as they display high potentials for applications in homogeneous catalysis.

Experimental Section

General Procedures. All experiments were carried out under a dry atmosphere of argon with dry and degassed solvents. NMR spectra were acquired on Bruker DRX 500, AV 400 (^{13}C and ^1H nuclei), and AV 300 (^1H nucleus) spectrometers at room temperature unless otherwise stated. Chemical shifts are reported in parts per million downfield of Me_4Si, and coupling constant are expressed in Hz. IR spectra were measured with a Perkin-Elmer FT spectrometer. Mass spectra were recorded at the Service of Mass Spectrometry of University Louis Pasteur. Electrospray MS experiments were carried out with a MicroTOF Bruker spectrometer. Elemental analyses (reported in % mass) were performed at the Central Analytical Service of the CNRS at Vernaison, France. Chromatographic separations were performed at subambient temperatures with Merck Geduran silica (Si 60, 40−60 μm) in columns packed in *n*-hexane or *n*-pentane with a maximum positive argon pressure of 0.5 bar. CD spectra were recorded with a JASCO 810 spectropolarimeter with 1 cm and 1 mm optical path length quartz cells, and specific rotations were measured with a Perkin-Elmer polarimeter in 10 cm optical length quartz cells at a wavelength of 589 nm.

Crystallography. Data collection by ϕ and ω scans for **3c**, [PPN]-**4**, **5**, **7a**, [PPN]**8**, **9a**, **10a**, **12**, **14a**, **14b**, and **15a** were carried out on a Nonius KappaCCD diffractometer using an Mo Kα (λ = 0.71069 Å) X-ray source and a graphite monochromator. Experimental details are described in Tables 1 and 2. The crystal structures were solved using SIR97 and refined with Shelxl97.

Diffusion-Ordered 2D NMR (DOSY) Experiments. Spectra were recorded on a Bruker Avance 500 spectrometer, at 11.7 T, at the frequency of 500.13 MHz for ^1H, using a 5 mm BBI Bruker gradient probe. Temperature was regulated at 298 K, and no spinning was applied to the NMR tube. Diffusion-ordered NMR experiments were performed with a pulsed field gradient stimulated echo sequence, using bipolar gradients.[40] Bipolar gradient duration and diffusion time were respectively equal to 200 and 1.5 ms. The evolution of pulsed field gradient during the NMR diffusion experiments was established in 20 steps, applied linearly between 4 and 48 G/cm. Each step required 256 scans. 2D DOSY spectra were generated by the DOSY module of the GIFA version 5.2 software developed by NMRTec.[41]

Bis-μ-chloro{dicarbonyl{2-[tricarbonyl(η^6-phenylene-κC^1)-chromium(0)]pyridine-κN}ruthenium(II)}, 2, and μ-Chloro,μ-hydroxo-bis{dicarbonyl{2-[tricarbonyl(η^6-phenylene-κC^1)-chromium(0)]pyridine-κN}ruthenium(II)}, 3a and 3b. A mixture of $[Ru(CO)_2Cl_2]_n$ (980 mg, 4.29 mmol), **1c** (1.2 g, 4.12 mmol), and Na_2CO_3 (1 g, 9.4 mmol) in dry and degassed 1,2-dimethoxyethane (30 mL) was boiled for 15 h under argon. The orange suspension was filtered to separate the yellow solid from the dark red-orange liquor. The yellow-orange solid was washed with water (50 mL), acetone (20 mL), pentane (50 mL), and dichloromethane (50 mL) and dried under reduced pressure overnight. Compound **2** was recovered as a yellow-orange powder displaying low solubility in dimethylsulfoxide, acetone, 1,2-dimethoxyethane, *N*,*N*-dimethylformamide, and chloroform (1.6 g, 83%). The red-orange liquor was diluted with CH_2Cl_2, and silica gel was added. Solvents were removed under reduced pressure, and the coated SiO_2 was loaded at the top of a silica gel column packed in dry pentane at 5 °C. Two overlapping red bands containing **3a** and **3b** were eluted with a gradient of acetone increasing from 6% to 25% in pentane. The mixture of **3a** and **3b** was collected and stripped of solvent to afford a red-orange solid (223 mg, 11.4%). A sample of pure **3a** was subsequently obtained by recrystallization from a concentrated solution in a mixture CH_2Cl_2 and pentane. Compound **2**: Anal. Calcd for $C_{32}H_{16}N_2O_{10}Cl_2Cr_2Ru_2 \cdot 3CHCl_3$: C, 31.76; H, 1.45; N, 2.12. Found: C, 31.94; H, 1.67; N, 1.93. IR (KBr pellet) ν(CO): 2049, 1995, 1957, 1878 cm^{-1}. ^1H NMR (C_2D_6SO): δ 9.42 (br d, 1H), 8.09 (m, 2H), 7.55 (br t, 2H), 6.38 (br d, 1H), 6.02 (br d, 1H), 5.80 (br t, 1H), 5.50 (br t, 1H) ppm. $\{^1H\}^{13}C$ NMR (C_2D_6SO): δ 236.7, 201.2, 193.9, 162.6, 159.9, 139.5, 136.5, 123.8, 120.9,114.6, 107.5, 95.0, 94.1, 90.5. Major component, ^1H NMR (C_3D_7NO): δ 9.69 (d, 1H, ^3J = 5.4, H_{py}), 8.17 (m, 2H, H_{py}), 7.58 (br, m, 1H, H_{py}), 6.43 (d, 1H, ^3J = 6.4, H_{ArCr}), 6.16 (d, 1H, ^3J = 6.2, H_{ArCr}), 5.83 (t, 1H, ^3J = 6.4, H_{ArCr}), 5.59 (t, 1H, ^3J = 5.9, H_{ArCr}) ppm. $\{^1H\}^{13}C$ NMR (C_3D_7NO): δ 236.5, 201.5, 193.9, 163.2, 162.3, 149.8, 138.9, 123.1, 120.4, 114.2, 107.0, 94.2, 93.6, 90.0. Minor component, ^1H NMR (C_3D_7NO): δ 9.50 (d, 1H, ^3J = 5.4, H_{py}), 8.31 (m, 2H, H_{py}), 7.72 (t, 1H, ^3J = 5.9, H_{py}), 6.57 (d, 1H, ^3J = 6.7, H_{ArCr}), 6. 26 (d, 1H, ^3J = 6.2, H_{ArCr}), 5.99 (t, 1H, ^3J = 6.7, H_{ArCr}), 5.69 (t, 1H, ^3J = 6.2, H_{ArCr}). ^{13}C NMR (CP-MAS, 500/125 MHz): δ 237.7 (1C, Cr(CO)), 235.7 (2C, Cr(CO)), 195.5 (Ru(CO)), 191.9 (Ru(CO)), 167.4, 161.4, 150.4, 140.6, 130.7, 125.1, 123.0, 111.6, 103.9, 94.0, 91.7. Compound **3a**: Anal. Calcd for $C_{32}H_{17}N_2O_{11}Cr_2ClRu_2 \cdot 1/2CH_2Cl_2$: C, 39.44; H, 1.83; N, 2.83. Found: C, 39.40; H, 2.20; N, 3.01. IR (CH_2Cl_2) ν(CO): 2044, 1977, 1954, 1886 cm^{-1}. ^1H

(40) (a) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288−292. (b) Tanner, J. E. *J. Chem. Phys.* **1970**, *52*, 2523−2526.

(41) Delsuc, M. A.; Malliavin, T. E. *Anal. Chem.* **1998**, *70*, 2146−2148.

Table 1. Crystal Data and Structural Refinement Details for the Structures of 3a, 3c, [PPN]4, 5, 7a, and [PPN]8

	3a	**3c**[c]	[PPN]**4**
formula	$C_{32}H_{17}ClCr_2N_2O_{11}Ru_2$	$C_{29}H_{17}ClN_2O_8CrRu_2,C_3H_6O$	$C_{52}H_{38}Cl_2N_2O_5P_2CrRu$
mol wt	947.07	869.11	1056.75
cryst habit	red block	red block	orange block
cryst dimens (mm)	0.10 × 0.10 × 0.10	0.20 × 0.20 × 0.20	0.12 × 0.10 × 0.08
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	8.8470(6)	16.297(1)	9.6520(2)
b (Å)	13.1010(9)	28.842(1)	15.4920(3)
c (Å)	16.4400(16)	13.838(1)	17.4660(3)
α (deg)	77.640(2)		68.6210(10)
β (deg)	82.649(2)	91.436(1)	84.5020(9)
γ (deg)	77.564(6)		73.4510(8)
V(Å^3)	1810.9(2)	6502.3(7)	2331.13(8)
Z	2	8	2
D (g cm^{-3})	1.737	1.776	1.506
F(000)	928	3440	1072
μ (cm^{-1})	1.534	1.384	7.91
T (K)	173K	150.0(1)	173(2)
θ_{max}	30.01	30.03	30.07
hkl ranges	−10/12; −18/18; −23/23	−22/22; −40/40; 0/19	−13/13, −21/21, −24/24
no. of reflns measd	16 111	18 619	13 604
no. of unique data	10 511	18 619	9343
no. of reflns used ($I > 2\sigma(I)$)	7097[b]	13 730	7169
no. of params refined	454	858	586
wR_2	0.1642	0.2905	0.1167
R_1	0.0617[a]	0.0816	0.0490
GoF	1.013	1.056	1.047
diff peak/hole (e Å^{-3})	1.789(0.146)/−0.857(0.146)	1.981(0.247)/−1.764(0.247)	0.929(0.088)/−1.240(0.088)
Flack's *x* param			

	5	**7a**	[PPN]**8**
formula	$C_{21}H_{13}ClN_2O_5CrRu$	$C_{34}H_{24}Cl_2N_2O_4Fe_2Ru,2(CH_2Cl_2)$	$C_{36}H_{30}NP_2,C_{17}H_{12}Cl_2NO_2FeRu$
mol wt	561.85	1079.14	1028.65
cryst habit	vermilion plate	vermilion block	vermilion block
cryst dimens (mm)	0.20 × 0.18 × 0.04	0.10 × 0.10 × 0.10	0.22 × 0.18 × 0.12
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1$/c	$P\bar{1}$	$P\bar{1}$
a (Å)	8.533(1)	11.5130(8)	10.137(1)
b (Å)	17.422(1)	13.3500(9)	14.365(1)
c (Å)	14.069(1)	14.5880(12)	16.712(1)
α (deg)		116.896(5)	84.883(1)
β (deg)	95.806(1)	101.656(4)	76.604(1)
γ (deg)		96.700(5)	78.399(1)
V (Å^3)	2080.8(3)	1902.0(3)	2316.7(3)
Z	4	2	2
D (g cm^{-3})	1.794	1.884	1.475
F(000)	1112	1064	1048
μ (cm^{-1})	1.413	1.990	0.867
T (K)	150.0(1)	173(2)	150.0(1)
θ_{max}	27.48	27.86	30.02
hkl ranges	−11/11, −20/22, −18/18	−15/14, −15/17, −19/18	−14/14, −20/20, −23/22
no. of reflns measd	7625	13 323	20 088
no. of unique data	4723	9004	13 503
no. of reflns used ($I > 2\sigma(I)$)	3704	5712	11 334
no. of params refined	280	461	568
wR_2	0.0880	0.2031	0.0875
R_1	0.0333	0.1099	0.0315
GoF	1.008	1.070	1.059
diff peak/hole (e Å^{-3})	0.786(0.086)/−0.694(0.086)	1.241(0.168)/−1.151(0.168)	0.781(0.067)/−0.632(0.067)
Flack's *x* param			

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$. [c] Note: The PLATON TWINROTMAT function indicated that the sample presents a small twin component by 2-fold rotation about the 1 0 0 reciprocal space direction (BASF = 0.18).

NMR (C_3D_6O, 400 MHz): *δ* 9.57 (d, 1H, ^3J = 5.4, H_{py}), *δ* 9.46 (d, 1H, ^3J = 5.4, H_{py}), 8.32 (t*, 1H, ^3J = 7.7, H_{py}), 8.27 (t*, 1H, ^3J = 8.0, H_{py}), 8.17 (d, 1H, ^3J = 7.9, H_{py}), 8. 08 (d, 1H, ^3J = 8.0, H_{py}), 7.89 (t*, 1H, ^3J = 5.6, H_{py}), 7.79 (t*, 1H, ^3J = 5.4, H_{py}), 6.21 (d, 1H, ^3J = 6.7, H_{ArCr}), 6.00 (d, 1H, ^3J = 6.9, H_{ArCr}), 5.93 (t, 1H, ^3J = 6.2, H_{ArCr}), 5.85 (d, 1H, ^3J = 6.5, H_{ArCr}), 5.72 (d, 1H, ^3J = 6.2, H_{ArCr}), 5.66 (t*, 1H, ^3J = 6.5, H_{ArCr}), 5.35 (t*, 1H, ^3J = 6.2, H_{ArCr}), 5.35 (t*, 1H, ^3J = 6.3, H_{ArCr}), −2.92 (s, 1H, RuO*H*). {^{1}H}^{13}C NMR (C_3D_6O, 400 MHz): *δ* 235.7 (Cr(CO)$_3$), 235.4 (Cr(CO)$_3$), 199.0 (RuCO), 198.4 (RuCO), 195.68 (RuCO), 195.6 (RuCO), 163.5, 162.4, 151.8, 151.4, 141.2, 140.7, 136.6, 131.9, 126.2, 125.1, 121.9, 115.7, 112.4, 108.8, 105.4, 96.6, 94.4, 93.7, 91.1, 91.08, 87.7. Compound **3b**: ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 9.54(d, 2H, ^3J = 5.6, H_{py}), 8.08 (t*, 2H, ^3J = 8.0, H_{py}), 7.69 (d, 2H, ^3J = 8.1, H_{py}), 7.69 (t*, 2H, ^3J =7.4, H_{py}), 5.70 (d, 2H, ^3J = 6.5, H_{ArCr}), 5.58 (t, 2H, ^3J = 6.3, H_{ArCr}), 5.39 (t*, 2H, ^3J = 6.4, H_{ArCr}), 5.08 (t*, 2H, ^3J = 6.1, H_{ArCr}), −3.3 (s, 1H, RuO*H*). {^{1}H}^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 233.8 (Cr(CO)$_3$), 198.3 (RuCO), 193.3 (RuCO), 162.6, 151.1, 139.5, 130.3, 123.9, 120.1.109.5, 104.1, 92.5, 90.9, 87.6.

Table 2. Crystal Data and Structural Refinement Details for the Structures of 9a, 10a, 12, 14a, 14b, and 15a

	9a[a]	**10a**[b]	**12**
formula	$C_{21}H_{15}NO_7CrRu$	$C_{31}H_{17}N_3O_7CrRu,1/2(C_3H_6O)$	$C_{32}H_{21}FeN_3O_4Ru$
mol wt	546.41	727.10	668.44
cryst habit	orange plate	orange block	orange block
cryst dimens (mm)	0.22 × 0.13 × 0.02	0.20 × 0.16 × 0.16	0.16 × 0.16 × 0.14
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a (Å)	6.536(1)	14.161(1)	13.137(1)
b (Å)	8.366(1)	13.992(1)	11.616(1)
c (Å)	18.743(1)	15.2740(1)	17.177(1)
α (deg)	81.955(1)		
β (deg)	84.080(1)	105.695(1)	92.078(1)
γ (deg)	85.724(1)		
V (Å^3)	1007.5(2)	2913.6(3)	2619.5(3)
Z	2	4	4
D (g cm^{-3})	1.801	1.658	1.695
F(000)	544	1462	1344
μ (cm^{-1})	1.334	0.949	1.176
T (K)	150.0(1)	150.0(1)	150.0(1)
θ_{max}	27.45	30.03	30.02
hkl ranges	−8/8, −10/10, −8/24	−19/19, −19/16, −21 /21	−18/18, −16/16, −24/ 24
no. of reflns measd	4551	15 018	14 121
no. of unique data	4551	8498	7634
no. of reflns used ($I > 2\sigma(I)$)	3890	7053	5461
no. of param refined	283	389	370
wR_2	0.1246	0.1396	0.0901
R_1	0.0460	0.0407	0.0357
GoF	1.078	1.113	0.995
diff peak/hole (e Å^{-3})	0.773(0.119)/−1.244(0.119)	1.419(0.118)/−0.987(0.118)	1.713(0.091)/−0.772(0.091)
Flack's *x* param			

	14a	**14b**	**15a**
formula	$C_{35}H_{25}CrN_3O_7Ru$	$C_{35}H_{25}CrN_3O_7Ru,CH_2Cl_2$	$C_{36}H_{29}FeN_3O_4Ru$
mol wt	752.65	837.58	724.54
cryst habit	vermillion block	vermilion plate	vermilion plate
cryst dimens (mm)	0.20 × 0.18 × 0.15	0.22 × 0.20 × 0.08	0.22 × 0.22 × 0.14
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.101(1)	10.785(1)	9.600(1)
b (Å)	10.307(1)	11.946(1)	13.460(1)
c (Å)	16.428(1)	26.128(1)	23.374(1)
α (deg)			
β (deg)	95.100(1)		
γ (deg)			
V (Å^3)	1534.9(2)	3366.3(4)	3020.3(4)
Z	2	4	4
D (g cm^{-3})	1.629	1.653	1.593
F(000)	760	1688	1472
μ (cm^{-1})	0.902	0.985	1.027
T (K)	150.0(1)	150.0(1)	150.0(1)
θ_{max}	30.03	30.03	30.03
hkl ranges	−12/12, −14/12, −23/23	−15/15, −12/16, −36/36	−13/13, −18/18, −32/32
no. of reflns measd	7411	17 743	8664
no. of unique data	7411	9653	8664
no. of reflns used ($I > 2\sigma(I)$)	7242	9021	8352
no. of params refined	425	452	407
wR_2	0.0657	0.0938	0.0666
R_1	0.0238	0.0351	0.0248
GoF	1.024	1.050	1.032
diff peak/hole (e Å^{-3})	0.793(0.062)/−0.548(0.062)	0.813(0.090)/−0.965(0.090)	0.626(0.064)/−0.804(0.064)
Flack's *x* param	−0.012(14)	−0.010(18)	−0.020(11)

[a]The sample was found to be twinned by 2-fold rotation about the 0 0 1 reciprocal lattice direction; twin ratio 0.91/0.09, BASF = 0.09. [b]An acetone molecule located near a symmetry center was accounted for using the PLATON SQUEEZE function.

Synthesis of Bis(triphenyl)phosphoranylideneammonium *rac*-(p*R*,*OC*-6-42-*C*)-dicarbonyl,dichloro{2-[tricarbonyl(η^6-phenylene-κC^1)chromium]pyridine-κN}ruthenate, [PPN]4. A mixture of **2** (50 mg, 0.051 mmol) and bis(triphenyl)phosphoranylideneammonium chloride (120 mg, 0.209 mmol) in acetone (15 mL) was stirred for 2 h at room temperature. The resulting solution was filtered through Celite in order to remove the remaining suspension, and the filtrate was passed through a 1 cm long column of SiO_2 packed in a Pasteur pipet. The resulting eluate was evaporated to dryness under reduced pressure and the residue dissolved in dry CH_2Cl_2 (5 mL). Dry, distilled pentane was then added to induce the precipitation of anion [PPN]**4**, which was recovered as an orange solid (105 mg, 96.1%). Anal. Calcd for $C_{52}H_{38}N_2O_5Cl_2CrRuP_2$: C, 59.10; H, 3.62; N, 2.65. Found: C, 58.79; H, 4.02; N, 2.21. IR (CH_2Cl_2) ν(CO): 2039, 1969, 1947, 1871 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.70 (d, 1H, ^3J = 4.9, H_{py}), 7.77 (t*, 1H, ^3J = 7.6, H_{py}), 7.62−7.41(m, 30 H, H_{PPN}), 7.56 (d, 1H, ^3J = 8.7, H_{py}), 7.21 (t*, 1H, ^3J = 6.1, H_{py}), 6.04 (d, 1H, ^3J = 6.3, H_{ArCr}), 5.73 (d, 1H, ^3J = 6.4, H_{ArCr}), 5.40 (t*, 1H, ^3J = 6.4, H_{ArCr}), 5.20 (t*, 1H, ^3J = 6.1, H_{ArCr}).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 235.5 ($Cr(CO)_3$), 199.6 (RuCO), 192.8 (RuCO), 162.4, 150.4, 137.4 (2C), 133.6 (PPN), 131.75 (PPN), 129.3 (PPN), 126.6 ($J_{PCipso} = 107$), 122.3, 119.0, 112.0, 105.7, 92.3, 92.2, 88.5. ^{31}P NMR ($CDCl_3$): δ 21.26. HRMS (ES^-) calcd for $C_{16}H_8NO_5Cl_2CrRu$: 517.8235. Found: 517.8540. HRMS (ES^+) calcd for $C_{36}H_{30}P_2N$: 538.1848. Found: 538.1891.

Preparation of *rac*-(p*R*,*OC*-6-42-*C*)-Dicarbonyl,chloro{2-[tricarbonyl(η^6-phenylene-κC^1)chromium]pyridine-κN}-pyridineruthenium, 5. A mixture of complex **2** (75 mg, 0.07 mmol) and pyridine (12.5 μL, 0.15 mmol) in THF (15 mL) was refluxed for 24 h under argon. The resulting solution was cooled to room temperature and filtered through a thin mixture of Celite and silica. The filtrate was concentrated to ca. 3 mL, and pentane was added to induce the precipitation of **5**. The supernatant was removed by suction, and the solid was filtered and further recrystallized from dry pentane (70 mg, 85%). Anal. Calcd for $C_{21}H_{13}O_5N_2CrRu{\cdot}CH_2Cl_2$: C, 43.20; H, 2.47; N, 4.58. Found: C, 43.60; H, 2.52; N, 4.90. IR (CH_2Cl_2) ν(CO): 2057, 1992, 1958, 1878 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.68 (d, 1 H, $^3J = 5.6$, H_{Phpy}), 8.48 (m, 2H, H_{py}), 7.93 (t, 1H, $^3J = 8.0$, H_{Phpy}), 7.68 (t*, 1H, $^3J = 7.6$, H_{py}), 7.53 (d, 1H, $^3J = 8.0$, H_{Phpy}), 7.46 (t, 1H, $^3J = 5.6$, H_{Phpy}), 7.21 (t*, 2H, $^3J = 5.3$, H_{py}), 6.12 (d, 1H, $^3J = 6.2$, H_{ArCr}), 5.60 (d, 1H, $^3J = 6.5$, H_{ArCr}), 5.50 (t, 1H, $^3J = 6.4$, H_{ArCr}), 5.34 (t, 1H, $^3J = 6.2$, H_{ArCr}). $\{^1H\}^{13}C$ NMR ($CDCl_3$): δ 234.1 ($Cr(CO)_3$), 198.6 (Ru(CO)), 193.8 (Ru(CO)), 163.3, 151.6, 150.3, 139.4, 138.5, 133.5, 125.2, 123.9, 119.8, 109.6, 104.4, 92.9, 91.7, 87.4.

Synthesis of *cis*-Dicarbonyl[acetylacetonato-κO^1,κO^2]{2-[tricarbonyl(η^6-phenylene-κC^1)chromium]pyridine-κN}-ruthenium, *rac*-(p*R*,*OC*-6-43-*C*)-9a and *rac*-(p*R*,*OC*-6-43-*A*)-9b. Compound **2** (350 mg, 0.36 mmol), 2-acetylacetone (0.082 mL, 1.44 mmol,) and Na_2CO_3 (152 mg, 1.44 mmol) were mixed in dry dimethoxyethane (15 mL), and the resulting suspension was boiled for 15 h. The resulting solution was cooled to room temperature and filtered through Celite. The orange filtrate was diluted with dichloromethane, and the resulting solution was washed with water and dried over $MgSO_4$. The solvents were evaporated under reduced pressure. The resulting residue was first recrystallized from dry $CHCl_3$/heptane to afford a 5:1 mixture of **9a** and **9b** (292 mg, 68%), which was subsequently recrystallized from dry CH_2Cl_2/pentane to afford pure **9a**. Compound **9a**: Anal. Calcd for $C_{42}H_{30}N_2O_{14}Cr_2Ru_2{\cdot}CH_2Cl_2$: C, 43.85; H, 2.74; N, 2.38. Found: C, 43.87; H, 3.04; N, 2.13. IR (CH_2Cl_2) ν(CO): 2047, 1979, 1954, 1882 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.16 (d, $^3J = 5.5$, H_{py}), 7.92 (t, 1 H, $^3J = 8.1$, H_{py}), 7.63 (d, 1 H, $^3J = 8.1$, H_{py}), 7.29 (t, 1 H, $^3J = 6.2$, H_{py}), 5.99 (d, 1H, $^3J = 6.5$, H_{ArCr}), 5.75 (d, 1H, $^3J = 6.5$, H_{ArCr}), 5.53 (t, 1H, $^3J = 6.4$, H_{ArCr}), 5.30 (t, 1H, $^3J = 6.2$, H_{ArCr}), 5.25 (s, 1H), 2.11 (s, 3H, CH_3), 1.68 (s, 3H, CH_3). $\{^1H\}^{13}C$ NMR ($CDCl_3$): δ 234.7 ($Cr(CO)_3$), 198.7 (RuCO), 195.4 (RuCO), 189.2, 188.2, 163.4, 147.8, 139.0, 132.6, 122.9, 119.9, 110.2, 105.7, 99.8, 92.8, 91.7, 87.8, 28.2, 27.7. Compound **9b**: Anal. Calcd for $C_{21}H_{15}NO_7CrRu$: C, 46.16; H, 2.77; N, 2.56. Found: C, 46.54; H, 3.13; N, 2.80. IR ($CHCl_3$) ν(CO): 2045, 1977, 1958, 1889 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, 294 K): δ 8.01(d, 1 H, $^3J = 5.5$, H_{py}), 7.90 (t, 1 H, $^3J = 7.6$, H_{py}), 7.63 (d, 1 H, $^3J = 8.1$, H_{py}), 7.27 (t, 1 H, $^3J = 6.7$, H_{py}), 5.92 (d, 1 H, $^3J = 6.3$, H_{ArPh}), 5.56 (m, 2 H, H_{ArPh}), 5.33 (s, 1 H, H_{acac}), 5.15 (t, 1 H, $^3J = 5.9$, H_{ArPh}), 2.12 (s, 3 H, CH_3), 1.88 (s, 3 H, CH_3). $\{^1H\}^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 235.1 ($Cr(CO)_3$), 189.5 (Ru(CO)), 188.7 (Ru(CO)), 163.2, 147.8, 140.7, 139.1, 134.9, 123.2, 119.7, 119.2, 111.4, 105.8, 100.0, 92.4, 89, 85.7, 28.1, 27.0.

Reaction of (*OC*-6-43)-*cis*-Dicarbonyl(acetylacetonato-κO^1,κO^2)-[2-(phenylene-κC^1)pyridine-κN]ruthenium 11 with Tricarbonyl-(η^6-naphthalene)chromium. Compound **11** (200 mg, 0.48 mmol) and tricarbonyl(η^6-naphthalene)chromium (129 mg, 0.48 mmol) were dissolved in dry THF (15 mL), and the corresponding mixture was stirred at reflux for 90 min. The resulting solution was filtered through Celite, the filtrate was concentrated to ca. 10 mL, and silica gel was added. Solvents were evaporated under reduced pressure, and the coated silica gel was loaded on the top of a silica gel column packed in dry pentane at 0 °C. A band containing a 9:1 mixture of **9b** and **9a** as an orange powder (98 mg, 37%) was eluted with a 1:8 mixture of acetone and pentane. The eluate was concentrated to ca. 10 mL, silica gel was added, and the solvents were evaporated to dryness under reduced pressure. This coated silica was then loaded on the top of a second column prepared like the previous one. A fraction containing **9b** (80 mg) was eluted with a 1:10 mixture of acetone and pentane. A second fraction containing **9a** (less than 10 mg) was eluted with a 1:8 mixture of acetone and pentane. The resulting eluates were evaporated to dryness under reduced pressure. An analytically pure sample of **9b** was obtained by fractional recrystallization from a mixture of CH_2Cl_2 and pentane followed by thorough drying under reduced pressure.

Synthesis of *rac*-(p*R*,*OC*-6-42-*C*)-*cis*-Dicarbonyl[(bisbenzoxazolyl)methylidene-$\kappa N^{1'}$,$\kappa N^{1''}$]{2-[tricarbonyl(η^6-phenylene-κC^1)-chromium]pyridine-κN}ruthenium, 10a, and *rac*-(p*R*,*OC*-6-42-*C*)-*cis*-Dicarbonyl[(bisbenzoxazolyl)methylidene-$\kappa N^{1'}$,$\kappa N^{1''}$(2-phenylene-$\kappa C^{1'}$,pyridine-κN)ruthenium, 10b. Complex **2** (249 mg, 0.258 mmol), bisbenzoxazolylmethane (200 mg, 0.6 mmol), and Na_2CO_3 (65 mg, 0.6 mmol) in 1,2-dimethoxyethane (15 mL) were refluxed for 15 h under argon. The resulting solution was extracted with CH_2Cl_2, and the organic phase was washed with water, dried over $MgSO_4$, and filtred through Celite. The filtrate was concentrated to ca. 10 mL, and silical gel was added. This suspension was stripped of solvent, and the resulting coated silica gel was loaded on the top of SiO_2 packed in dry and distilled pentane. A band containing compounds **10a** and **10b** was eluted with a 9:1 mixture of CH_2Cl_2 and pentane, and they were recovered as a deep orange powder upon removal of the solvents under reduced pressure. The resulting solid was recystallized from $CHCl_3$ and heptane and afforded solely compound **10a**, which was then submitted to full characterization (290 mg, 80.7% yield). Compound **10a**: Anal. Calcd for $C_{31}H_{17}O_7N_3CrRu$: C, 53.45; H, 2.68; N, 5.96. Found: C, 53.15; H, 2.46; N, 6.03. IR (CH_2Cl_2) ν(CO): 2050, 1986, 1956, 1884 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.91 (d*, 1H, $^3J = 5.6$), 7.78 (t, 1H, $^3J = 7.6$), 7.56 (d*, 1H, $^3J = 7.9$), 7.37 (d, 1H, $^3J = 8.1$), 7.34 (d*, 1H, $^3J = 7.9$), 7.29 (t*, 1H, $^3J = 7.8$), 7.13 (m, 2H), 7.01 (m, 1H), 6.81 (m, 2H), 6.45 (d, 1H, $^3J = 6.1$, H_{ArCr}), 5.62 (t, 1H, $^3J = 6.3$, H_{ArCr}), 5.57 (d, 1H, $^3J = 6.5$, H_{ArCr}), 5.35 (t, 1H, $^3J = 6.2$, H_{ArCr}), 4.89 (s, 1H, H_{CH}). $\{^1H\}^{13}C$ NMR ($CDCl_3$): δ 234.67 ($Cr(CO)_3$), 199.2 (Ru(CO)), 195.9 (Ru(CO)), 167.1, 163.7, 149.7, 149.3, 148.9, 143.1, 141.1, 139.0, 133.3, 124.4, 122.8, 122.7, 121.7, 120.5, 119.9, 115.5, 114.3, 110.9, 109.2, 108.5, 107.5, 94.9, 90.2, 86.5, 77.2, 59.8. Compound **10b**: IR ($CDCl_3$) ν(CO): 2041, 1973 cm^{-1}. ^1H NMR ($CDCl_3$, 294 K): δ 8.11(d, 1H, $^3J = 7.3$), 7.95 (d*, 1H, $^3J = 5.6$), 7.82 (d, 1H, $^3J = 8.1$), 7.73 (m, 2H), 7.50 (d, 1H, $^3J = 7.8$), 7.2−7.4 (m, 4H), 7.09 (t, 1H, $^3J = 7.6$), 6.99 (m, 2H), 6.73 (t, 1H, $^3J = 7.6$), 6.58 (t, 1H, $^3J = 7.6$), 6.01 (d, 1H, $^3J = 8.2$), 5.02 (s, 1H). $\{^1H\}^{13}C$ NMR ($CDCl_3$): δ 200.1 (RuCO), 197.3 (RuCO), 167.6, 167.3, 167.0, 156.0, 164.6, 149.5, 148.9, 148.7, 144.8, 143.9, 142.5, 141.9, 138.5, 130.2, 125.2, 124.1, 123.0, 121.9, 121.1, 120.2, 119.4, 115.2, 113.8, 109.0, 108.1, 59.2.

Synthesis of *cis*-Dicarbonyl{5′,5″-diphenyl{1,1-[bis(2-oxazolyl)-methylidene-$\kappa N^{1'}$,$\kappa N^{1''}$]}{2-[tricarbonyl(η^6-phenylene-κC^1)-chromium]pyridine-κN}ruthenium, (5′*R*,5″*R*,p*S*,*OC*-6-42-*A*)-14a and (5′*R*,5″*R*,p*R*,*OC*-6-42-*C*)-14b. A mixture of **2** (500 mg, 0.51 mmol), (5*R*,5′*R*)-**13** (580 mg, 2.07 mmol), and Na_2CO_3 (219.6 mg, 2.07 mmol) in 1,2-dimethoxyethane was boiled for 15 h (25 mL). The resulting orange solution was then extracted with CH_2Cl_2. The organic phase was washed twice with water (50 mL) and with brine, dried over $MgSO_4$, and filtered through Celite. The filtrate was concentrated to ca. 10 mL, and silica gel was added. The solvents were evaporated under reduced pressure, and the coated silica gel was loaded on the top of a 30 cm long (2.5 cm diameter) silica gel

column packed in dry pentane at −2 °C. A fraction containing **14a** was eluted with a 1:1 and a 9:1 mixture of CH_2Cl_2 and pentane. A second fraction containing **14b** was eluted with a 7:3 mixture of dichloromethane and acetone. The resulting eluates were evaporated to dryness under reduced pressure to afford **14a** (220 mg, 28.2%) and **14b** (298 mg, 38.2%) as yellow-orange powders. Both compounds were recrystallized from CH_2Cl_2/pentane mixtures. Compound **14a**: $[\alpha]_D$ −881 (CH_2Cl_2, 26 °C, 1.8×10^{-2} g/100 mL). Anal. Calcd for $C_{35}H_{25}N_3O_7CrRu$: C, 55.85; H, 3.35; N, 5.58. Found: C, 55.57; H, 3.59; N, 5.14. IR (CH_2Cl_2) ν(CO): 2042, 1974, 1952, 1878 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.41 (dd, 1H, $^3J = 5.5$, H_{py}),7.66 (t*, 1H, $^3J = 7.9$, H_{py}), 7.35 (m, 6H, $H_{Phoxa} + H_{py}$), 6.90 (m, 2H, $H_{py} + H_{Phoxa}$), 6.73(t*, 2H, $^3J = 7.0$, H_{Phoxa}), 6.15 (d, 2H, $^3J = 7.3$, H_{Phoxa}), 6.04 (dd, 1H, $^3J = 6.2$, H_{oxa}), 5.42 (d, 2H, $^3J = 6.4$, H_{ArCr}), 5.16 (m, 2H, $H_{ArCr} + H_{oxa}$), 4.84 (d, 1H, $^3J = 5.9$, H_{ArCr}), 4.68 (t*, 1H, $^3J = 8.4$, H_{oxa}), 4.35 (m, 2H, H_{oxa}), 4.25 (t, 1H, $^3J = 7.2$, H_{oxa}), 4.22 (s, 1H, H_{oxa}), 3.69 (d, 1H, $^3J = 7.8$, H_{oxa}). $\{^1H\}^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 235.2, 199.6, 194.4, 170.8, 170.5, 163.6, 148.1, 143.5, 143.2, 138.2, 132.1, 128.9, 128.3, 127.8, 127.1, 126.4, 125.3, 123.6, 120.2, 113.1, 106.9, 94.3, 90.4, 86.5, 77.2, 74.5, 74.4, 72.8, 68.3, 54.3. Compound **14b**: $[\alpha]_D$ −168 (CH_2Cl_2, 26 °C, 1.8×10^{-2} g/100 mL). Anal. Calcd for $C_{35}H_{25}N_3O_7CrRu{\cdot}CH_2Cl_2$: C, 53.63; H, 3.30 ; N, 5.28. Found: C, 53.47; H, 3.35; N, 4.97. IR (CH_2Cl_2) ν(CO): 2044, 1976, 1954, 1881 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.40 (d, 1H, $^3J = 5.5$, H_{py}), 7.88 (t*, 1H, $^3J = 7.9$, H_{py}), 7.56 (d, 1H, $^3J = 8.0$, H_{py}), 7.45 (m, 2H, H_{Phoxa}), 7.33 (m, 7H, $H_{Phoxa} + H_{py}$), 6.90 (d, 2H, $^3J = 5.7$, H_{Phoxa}), 5.64 (m, 2H, H_{ArCr}), 5.45 (d, 1H, $^3J = 5.9$, H_{ArCr}), 4.95 (m, 2H, $H_{ArCr} + H_{oxa}$), 4.72 (t, 1H, $^3J = 8.7$, H_{oxa}), 4.28 (t, 1H, $^3J = 9.1$, H_{oxa}), 4.05 (s, 1H, H_{oxa}), 3.93 (dd, 1H, $^3J = 6.2$, H_{oxa}), 3.84 (t, 1H, $^3J = 8.0$), 3.78 (dd, 1H, $^3J = 8.04$, H_{oxa}), 3.72 (d, 1H). $\{^1H\}^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 235.2 ($Cr(CO)_3$), 199.4, 190.3, 189.4, 170.7, 169.4, 162.9, 149.7, 143.0, 141.4, 138.5, 135.3, 129.3, 129.1, 128.5, 128.4, 127.8, 126.8, 123.0, 119.8, 111.6, 107.6, 94.3, 89.8, 85.9, 77.2, 74.4, 73.7, 73.4, 66.9, 54.7.

Synthesis of Bis{*cis*-dicarbonyl,μ-chloro[2-(ferrocenyl-κC^1)-pyridine-κN]ruthenium}, 7. A mixture of $[Ru(CO)_2Cl_2]_n$ (50 mg, 0.219 mmol), 2-ferrocenylpyridine **6** (55 mg, 0.219 mmol), and Na_2CO_3 (30 mg) in 1,2-dimethoxyethane (30 mL) was brought to reflux for 8 h under argon. The resulting solution was evaporated to dryness and the residue dissolved in CH_2Cl_2. Silica gel was added to the resulting solution, and the solvent was removed *in vacuo* to afford a coated silica gel, which was loaded on the top of a column of SiO_2 packed in dry pentane. A mixture of at least three isomers of **7** present in a 2:1.5:1 ratio was eluted with a 1:6 acetone/pentane mixture, and the corresponding fraction was evaporated to yield a red-colored solid (40 mg, 41% overall yield). The major isomer was isolated (20 mg) by a second chromatographic separation, and an analytically pure sample was crystallized by the solvent-layer diffusion technique from a concentrated solution in CH_2Cl_2 using *n*-heptane as the nonpolar solvent. It is important to note that the latter proved to be unstable in solution and displayed some propensity to isomerize partly over time into the two minor isomers obtained previously. Therefore, the characterization by ^{13}C NMR spectroscopy provided the spectrum of a mixture, from which we extracted the component that putatively belongs to the major isomer. A crystal of one of these diastereomers, e.g., **7a**, which was suitable for X-ray diffraction analyses, was obtained by the slow diffusion of a CH_2Cl_2 solution of the above-mentioned major isomer into *n*-heptane. The reported structure is not necessarily that of the major product of the ortho-ruthenation. Major component of **7**: Anal. Calcd for $C_{34}H_{24}N_2O_4Cl_2Fe_2Ru_2{\cdot}CH_2Cl_2$: C, 40.07; H, 2.61; N, 2.60. Found: C, 40.01; H, 2.97; N, 2.85. IR (CH_2Cl_2) ν(CO): 2030, 1957 cm^{-1}. ^1H NMR ($CDCl_3$, 294 K): δ 9.31 (d*, 1H, $^3J = 5.7$, H_{py}), 7.79 (t*, 1H, $^3J = 7.6$, H_{py}), 7.47 (d*, 1H, $^3J = 7.8$, Hpy), 7.32 (m, 1H, H_{py}), 4.67 (dd, 1H, $^3J = 2.5$, $^4J = 0.9$, H_{Cp}), 4.28 (t, 1H, $^3J = 2.3$, H_{Cp}), 4.22 (dd, 1H, $^3J = 2.3$, $^4J = 0.9$, H_{Cp}), 3.93 (s, 5H, H_{Cp}). $\{^1H\}^{13}C$ NMR ($CDCl_3$): δ 198.0 (CO), 194.4 (CO), 166.9, 150.5, 138.2, 119.9, 119.8, 101.5, 86.9, 75.3, 70.1, 69.8 (5C, Cp), 63.9.

Synthesis of Bis(triphenyl)phosphoranylideneammonium *rac*-(p*R*,*OC*-6-42-*C*)-*cis*-Dicarbonyl,dichloro[2-(ferrocenyl-κC^1)-pyridine-κN]ruthenate, [PPN]8. A mixture of **7** (50 mg, 0.056 mmol) and [PPN]Cl (64 mg, 0.112 mmol) in acetone (15 mL) was stirred for 2 h at room temperature. The resulting red-colored solution was concentrated to ca. 5 mL, and dry pentane was added to induce the precipitation of compound [PPN]**8**. The resulting solid was washed with pentane and dried under reduced pressure (107 mg, 93%). Several attempts to obtain a consistent titration of carbon element failed. We therefore complemented the analytical characterization of [PPN]**8** by submitting it to high-resolution electrospray mass spectrometry, which afforded pertinent results for composition and purity. Anal. Calcd for $C_{53}H_{42}N_2O_2Cl_2P_2FeRu$: C, 61.88; H, 4.11; N, 2.72. Found: C, 64.55; H, 4.45; N, 2.50. IR (CH_2Cl_2) ν(CO): 2024, 1947 cm^{-1}. ^1H NMR ($CDCl_3$, 294 K): δ 9.40 (d, 1H, $^3J = 5.2$ Hz, H_{Py}), 7.2−7.8 (m, 32 H, H_{py} and H_{PPN^+}), 6.88 (t, 1H, $^3J = 6.3$ Hz, H_{Py}), 4.63 (m, 1H, H_{Cp}), 4.48 (m, 1H, H_{Cp}), 4.32 (m, 1H, H_{Cp}), 3.99 (s, 5H, H_{Cp}). $\{^1H\}^{13}C$ NMR ($CDCl_3$): δ 200.8 (Ru(CO)), 196.1 (Ru(CO)), 167.1, 150.6, 136.5, 133.9 (PPN), 131.9 (PPN), 129.5 (PPN), 126.7 ($J_{PC} = 110$, PPN), 118.5, 118.4, 109.2, 87.5, 75.3, 69.5, 69.3 (Cp), 63.4. HRMS (ES^-) calcd for $C_{17}H_{12}NO_2Cl_2FeRu$: 489.8634. Found: 489.8610. HRMS (ES^+) calcd for $C_{36}H_{30}P_2N$: 538.1848. Found: 538.1835.

Synthesis of *rac*-(p*R*,*OC*-6-42-*C*)-*cis*-Dicarbonyl[(bisbenzoxazolyl)methylidene-$\kappa N^{1'}$,$\kappa N^{1''}$][2-(ferrocenylene-κC^1)pyridine-κN}ruthenium, 12. A mixture of **7** (80 mg, 0.09 mmol), 1,1-bisbenzoxazolylmethane (64 mg, 0.256 mmol), and Na_2CO_3 (70 mg, 0.66 mmol) in 1,2-dimethoxyethane (15 mL) was refluxed for 6 h under argon. The solution was concentrated to ca. 10 mL, and silica gel was added. This suspension was stripped of solvent, and the resulting coated silica gel was loaded on the top of a SiO_2 column packed in dry and distilled pentane. Compound **12** was eluted with a 1:15 mixture of acetone and pentane and recovered as an orange powder, which was recrystallized from a mixture of CH_2Cl_2 and pentane (71 mg, 63.3% yield). Anal. Calcd for $C_{32}H_{21}N_3O_4FeRu{\cdot}1/2CH_2Cl_2$: C, 54.90; H, 3.11; N, 5.91. Found: C, 54.74; H, 3.42; N, 5.68. IR ($CDCl_3$) ν(CO): 2037, 1868 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.67 (m, 2H, $H_{Arbbom+py}$), 7.55 (t, 1H, $^3J = 8.1$, H_{py}), 7.23−7.34 (m, 2H, $H_{Arbbom+py}$), 7.11 (t, 1H, $^3J = 7.9$, H_{py}), 6.92 (m, 1H, H_{bbom}), 6.85 (t*, 1H, $^3J = 5.8$, H_{bbom}), 6.67 (m, 2H, H_{bbom}), 4.94 (d, 1H, $^3J = 2.2$, H_{Cp}), 4.76 (d, 1H, $^3J = 2.4$, H_{Cp}), 4.81(s, 1H, Ar_2CH_{hbbom}), 4.62 (d, 1H, $^3J = 2.3$, H_{Cp}), 4.00 (s, 5H, H_{Cp}). $\{^1H\}^{13}C$ NMR ($CDCl_3$, 300 MHz): δ 167.6, 167.2, 167.1, 149.4, 149.3, 148.6, 143.8, 141.3, 137.8, 142.0, 122.4, 121.1, 120.2, 119.3, 118.7, 116.1, 114.3, 108.9, 107.8, 102.2, 88.1, 79.3, 77.2, 71.8, 70.6, 70.2, 64.7, 59.3, 59.1, 34.2, 30.9, 22.4, 14.1.

Synthesis of *cis*-Dicarbonyl{5′,5″-diphenyl{1,1-[bis(2-oxazolyl)-methylidene-$\kappa N^{1'}$,$\kappa N^{1''}$]}}[2-(ferrocenylene-κC^1)pyridine-κN]ruthenium, (5′*R*,5″*R*,p*S*,*OC*-6-42-*A*)-15a and (5′*R*,5″*R*,p*R*,*OC*-6-42-*C*)-15b. A mixture of **11** (100 mg, 0.17 mmol), (*R*,*R*)-**17** (189 mg, 0.68 mmol), and Na_2CO_3 (72 mg, 0.34 mmol) in 1,2-dimethoxyethane was boiled for 6 h (25 mL). The filtrate was concentrated to ca. 10 mL, and silica gel was added. Solvents were evaporated under reduced pressure, and the coated silica gel was loaded on the top of a silica gel column packed in dry pentane at 0 °C. The first fraction containing **15a** was eluted with a 1:9 mixture of acetone and pentane. The second fraction containing **15b** was eluted with a 1:4 mixture of acetone and pentane. The resulting eluates were evaporated to dryness under reduced pressure to afford **15a** (37 mg, 16%) and **15b** (45 mg, 19.5%) as orange powders. The overall yield was 35.5% (82 mg). Both compounds were recrystallized from $CHCl_3$/pentane and CH_3OH/pentane. **15a**: $[\alpha]_D$ −1465 (MeOH, 20 °C, *c* 1.7×10^{-2} g/100 mL). Anal. Calcd for $C_{36}H_{29}N_3O_4FeRu{\cdot}CHCl_3$: C, 52.67; H, 3.56; N, 4.98. Found: C,

52.51; H, 3.99; N, 4.78. IR (CH_2Cl_2) ν(CO): 2027, 1955 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.18 (d*, 1H, ^3J = 5.3, H_{py}), 7.20−7.40 (m, 6H, H_{Phoxa} + H_{py}), 7.01 (t, 1H, ^3J = 6.7, H_{py}), 6.81 (t, 1H, ^3J = 7.13, H_{Phoxa}), 6.68 (m, 2H, H_{Phoxa}), 6.59 (d, 1H, ^3J = 7.8, H_{py}), 6.13 (m, 2H, H_{Phoxa}), 5.26 (dd, 1H, ^2J = 8.3, H_{oxa}), 4.66 (t, 1H, ^3J = 8.3, H_{oxa}), 4.47 (m, 2H, H_{oxa}), 4.32 (dd, 1H, ^2J = 8.1, H_{oxa}), 4.21 (d, 1H, ^3J = 7.5, H_{oxa}), 4.13 (s, 1H, $(Phoxa)_2CH$), 4.05 (t, 1H, ^3J = 7.5, H_{Cp}), 3.9 (m, 6H, H_{Cp} + H_{oxa}), 3.56 (d, 1H, ^3J = 7.4, H_{Cp}). $\{^1H\}^{13}C$ NMR ($CDCl_3$, 75 MHz): δ 200.9 (Ru(CO)), 197.2 (Ru(CO)), 170.8, 170.5, 167.5, 147.9, 143.9, 143.7, 137.0, 128.7, 127.8, 127.3, 127.0 125.7, 125.0, 119.4, 102.3, 88.7, 76.2, 74.3, 74.2, 72.7, 70.0, 69.1, 66.6, 65.2, 53.6. **15b**: $[\alpha]_D$ +445 (MeOH, 20 °C, *c* 1.7 × 10^{-2} g/100 mL). Anal. Calcd for $C_{36}H_{29}N_3O_4FeRu{\cdot}CH_3OH$: C, 58.74; H, 4.41; N, 5.50. Found: C, 58.75; H, 4.16; N, 5.68. IR (CH_2Cl_2) ν(CO): 2029, 1957. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.28 (d*, 1H, ^3J = 5.5, H_{py}), 7.74 (d, 1H, ^3J = 7.1, H_{Phoxa}), 7.62 (t, 1H, ^3J = 7.4, H_{py}), 7.4 to 7.2 (m, 6H, H_{Phoxa} + H_{py}), 7.00 (t, 1H, ^3J = 5.7, H_{py}), 6.92 (m, 1H, H_{Phoxa}), 5.27 (t, 1H, ^3J = 8.8, H_{Phoxa}), 5.00 (t, 1H, ^3J = 9.1, H_{oxa}), 4.81 (dd, 1H, ^2J = 2.3, H_{oxa}), 4.66 (m, 2H, H_{oxa}), 4.55 (t, 1H, ^4J = 2.2, H_{oxa}), 4.22−4.16 (m, 3H, H_{oxa} + H_{Cp}), 4.02 (m, 1H, H_{Cp}), 3.89 (s, 5H, H_{Cp}), 3.66 (dd, 1H, ^2J = 7.8, H_{oxa}), 3.56 (d, 1H, ^3J = 8.1, H_{oxa}), 3.66 (dd, 1H, ^2J = 8.3, H_{oxa}). $\{^1H\}^{13}C$ NMR ($CDCl_3$, 75 MHz): δ 200.5 (Ru(CO)), 196.2 (Ru(CO)) 170.5, 168.8, 166.8, 149.5, 144.1, 141.8, 137.4, 134.2, 129.0, 128.7, 128.0 126.8, 125.6, 119.1, 104.2, 88.1, 78.2, 75.4, 74.3, 73.7, 73.2, 70.4, 69.4, 66.2, 63.9, 54.0.

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Supporting Information Available: (1) Analytical and spectral characterization data (^1H, ^{13}C, and ESMS), (2) crystallographic information file (CIF), (3) structural X-ray data for compound **3b** in CIF format, (4) Cartesian coordinates for optimized geometries of **9a** and **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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