Stereoselective "Electrophilic" Cyclometalation of Planar-Prochiral (η^6-Arene)tricarbonylchromium Complexes with Asymmetric Metal Centers: pseudo-*T*-4 $[Cp^*RhCl_2]_2$ and $[Cp^*IrCl_2]_2$

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The reactivity of a set of prototypical (η^6-arene)tricarbonylchromium complexes bearing amino, oxazolyl, and pyridyl ancillary ligands versus $[Cp^*RhCl_2]_2$ and $[Cp^*IrCl_2]_2$ has been investigated. Successful cyclometalation reactions were achieved essentially in the presence of hydrated sodium acetate with planar-prochiral 2-phenylpyridine and 3-methyl-2-phenylpyridine complexes with yields ranging from 60% to 92%. The most salient feature of the reported reactions is their stereoselectivity, as the only diastereomers to be produced are those with the Rh- and Ir-bound chloro ligand located *trans* with respect to the $Cr(CO)_3$. According to X-ray diffraction analyses, a relative *rac*-(p*R*,*T*-4-*S*) configuration may be assigned to the complexes: the Cp* ligand sits unexpectedly *syn* with respect to the tricarbonylmetal moiety. Introduction of the $Cr(CO)_3$ moiety by treatment of cycloiridated 2-phenylpyridine with tricarbonyl-(η^6-naphthalene)chromium resulted in a unique diastereomer of the same relative configuration. Quantum calculations using the density functional theory were carried out on models of *syn* and *trans*-chloro isomers. Owing to strong electrostatic repulsion between the chloro ligand and the $Cr(CO)_3$ moiety, the *syn*-chloro isomers were found less stable by 7−8 kcal/mol than the *trans* counterparts, suggesting that cyclorhodation and cycloiridation reactions are thermodynamically controlled.

Introduction

The pioneering reports of V. I. Sokolov on the enantioselective cyclopalladation of planar prochiral *N*,*N*-dimethyl,2-ferrocenylethylamine published in the late 1970s[1] have paved the way for numerous applications of nonracemic planar-chiral metallacycles in metal-mediated organic synthesis. According to existing literature, four 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 excesses. These routes consist of (1) the enantioselective[2] or diastereoselective metalation of planar-prochiral substrates or nonracemic substrates by C−H bond activation,[3] (2) the oxidative addition of an electron-rich metal center to a nonracemic halogenated substrate,[4] (3) the transmetalation of a racemic or nonracemic *ortho*-metalated or cyclometalated substrate,[5] and (4) the optical resolution of planar-chiral cyclometalated substrates from a mixture of diastereomers.[6] In the past decade several authors have emphasized the potential of Lewis-type acidic nonracemic planar-chiral metallacycles (essentially palladacycles) as promoters of Claisen-type rearrangements,[7] thus reviving the search for more efficient catalysts and, consequently, for stereoselective metalation procedures.

Because the majority of nonracemic planar-chiral metallacycles hitherto reported are square-planar (*SP*-4) palladium complexes, we deemed essential addressing the stereochemical aspects of the metalation of planar-prochiral substrates by asymmetric tetrahedral (*T*-4) or octahedral (*OC*-6) metal centers. Cases of nonracemic octahedral (*OC*-6)[8] and pseudo-tetrahedral (*T*-4)[5a] planar-chiral metal complexes are relatively rare in the literature. A reason for that might be the challenging issue of diastereoselectivity since cyclometalation of a planar-prochiral ligand by an asymmetric metal center creates, in the same molecule, two different elements of chirality: planar-chirality

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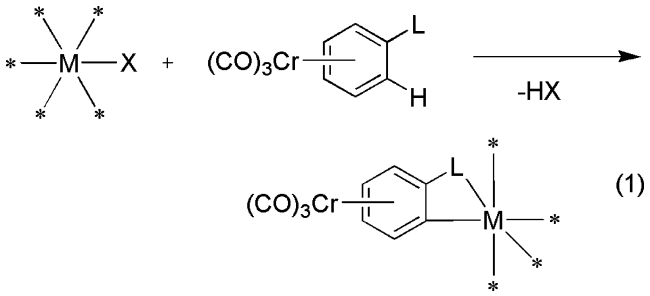
at the chelating ligand and metal-centered chirality at the chelated metal (eq 1). In our previous reports we have demonstrated that enantiopure *SP*-4 palladacyclic and nonracemic pseudo-*T*-4 ruthenacyclic (η^6-arene)tricarbonylchromium complexes could be efficiently prepared by transmetalation of racemic chloromercurated substrates. These results have significantly extended the number of available synthetic routes toward metalated (η^6-arene)tricarbonylchromium complexes.[9−11]



(1)

Recently, by modeling the most likely transition state in the *ortho*-iridation[12] and palladation[13] reactions, Davies and McGregor have established the determining role of the acetate ion, which acts as an ambiphilic ligand capable of assisting the *oxidative addition* of the metal center at the C−H bond via an agostic intermediate. This important result has motivated the present study, which constitutes the first part of a comprehensive investigation of the cyclometalation of (η^6-arene)tricarbonylchromium complexes by "electrophilic" asymmetric pseudo-tetrahedral (*T*-4) and octahedral (*OC*-6) complexes such as $[Ru(CO)_2Cl_2]_n$.[14,15]

In this report, we address the direct cyclometalation of planar-prochiral (η^6-arene)tricarbonylchromium complexes containing a pendant ancillary ligand with Lewis acidic and electrophilic asymmetric metal centers originating from $[Cp^*MCl_2]_2$ (M = Rh,[16] Ir[17]) complexes in the mild conditions first used by Davies et al.[18] We show that despite the electron-withdrawing effect of the $Cr(CO)_3$ moiety, so-called cyclorhodation and -iridation are both efficient and diastereoselective with 2-phenylpyridine chromium derivatives.

Results and Discussion

A first series of experiments was carried out in order to evaluate the reactivity of a set of prototypical substrates bearing ancillary ligands of various nature, viz., **1a**−**d** (eqs 2 and 3) versus $[Cp^*RhCl_2]_2$ and $[Cp^*IrCl_2]_2$. The conditions applied for

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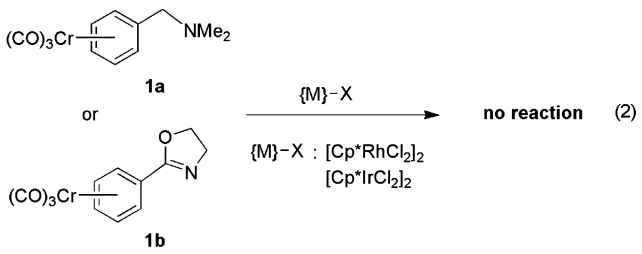
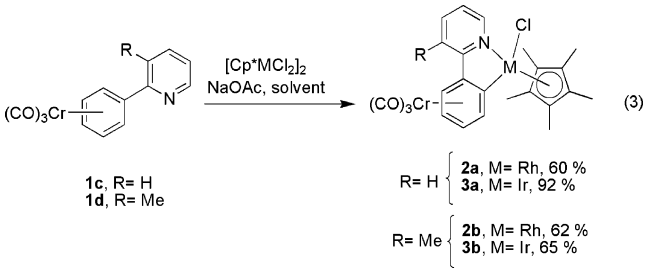
cyclometalation with the Ir(III) and Rh(III) complexes were slightly different from those used by Davies for reactions with amines, imines, and oxazolines:[18] we favored the use of hydrated sodium acetate in all cases, and MeOH as a solvent was preferred to CH_2Cl_2 in cyclorhodation experiments, because rapid decomposition of the (η^6-arene)tricarbonyl substrate would occur in the latter solvent.



In our hands, all experiments conducted with substrates **1a**[19] and **1b**[10] failed to produce any cyclometalated compound (eq 2): starting material was fully recovered in all cases except for rhodation experiments, which showed signs of partial decomposition of the substrates. Contrasting results were obtained for experiments carried out with **1c**,**d**, as described in the following (eq 3).

Cyclorhodation and Cycloiridation of Arylpyridines 1c and 1d. Our attention was particularly attracted by the relative efficiency of the cyclometalation of **1c**,**d**[3n] with both $[Cp^*RhCl_2]_2$ and $[Cp^*IrCl_2]_2$ at room temperature. Reactions generally reached maximum conversion within 24 h depending on the concentration of substrates. As hydrated acetate is only sparingly soluble in CH_2Cl_2, high stirring speed was also found essential in order to ensure optimal yields. In the absence of this base no cyclometalation reaction was observed. Cyclorhodation reactions were characteristic in that the products, e.g., **2a** and **2b**, precipitated out of the methanol solution as dark orange solids. In all cases, reactions afforded a single product, air- and moisture-stable in the solid state or when dissolved in nonhalogenated solvents, with yields spanning from 60% to 92% (eq 3).



The ^{1}H NMR data collected for **2a**,**b** and **3a**,**b** presented signals typical of (η^6-arene)tricarbonylchromium moieties between 5 and 6 ppm, the signals arising from the pyridyl moiety appearing between 7 and 9 ppm. ^{13}C NMR spectra of the rhodium and iridium complexes displayed a sharp signal at δ 235 ppm, which was assigned to the resonance of the carbonyl ligands of the pseudosymmetric $Cr(CO)_3$ moiety. The proton-decoupled ^{13}C NMR spectra of **2a**,**b** displayed characteristic $^{13}C-^{103}Rh$[20] couplings for at least three ^{13}C nuclei resonating at ca. δ 97, 146, and 162 ppm: these signals were putatively assigned to the cyclopentadienyl ring, the metalated arene's carbon, and the quaternary α-pyridyl carbon, respectively. A

Table 1. Crystal Data and Structural Refinement Details for the Structures of 2b and 3b

	2b	**3b**
cryst size (mm)	0.22×0.20×0.18	0.24×0.10×0.02
empirical formula	$C_{25}H_{25}ClCrNO_3Rh$,1/2(C_7H_8)	$C_{25}H_{25}ClCrIrNO_3$, 3/2(CH_2Cl_2)
mol wt	623.89	794.50
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a (Å)	12.834(1)	35.086(5)
b (Å)	14.251(1)	11.191(5)
c (Å)	15.433(1)	15.171(5)
α (deg)	73.610(1)	
β (deg)	77.837(1)	105.962(5)
γ (deg)	85.641(1)	
V (Å ^{3})	2646.8(3)	5727(3)
Z	4	8
calcd density (g cm^{-3})	1.566	1.843
abs coeff (cm^{-1})	1.165	5.424
2θ max (deg)	60.06	60.06
F(000)	1268	3096
index ranges	−15 to +18; −19 to +20; −19 to +21	−49 to +49; −14 to +15; −21 to +21
no. of collected/indep rflns	33 109/15 413	14 811/8360
no. of rflns used	12 389	7208
R_{int}	0.0200	0.0220
abs corr	multiscan; 0.7836 min., 0.8177 max.	multiscan; 0.3560 min., 0.8993 max.
no. of params refined	653	337
no. of rflns/params	18	21
final R_1[a]/wR_2 ($I > 2\sigma(I)$)[b]	0.0381/0.1105	0.0285/0.0745
goodness of fit on F^2	1.075	1.005
diff peak/hole (e Å $^{-3}$)	1.313(0.090)/ −1.014(0.090)	2.209(0.136)/ −1.891(0.136)

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

two-dimensional HMQC $^1H-^{103}Rh$ experiment carried out at room temperature in $CDCl_3$ revealed that the Rh nucleus of **2a** resonating at δ +271 ppm was coupled to the arylene *ortho* proton and to the pyridyl's α-proton, which respectively resonated at δ 5.85 and 8.68 ppm. A similar experiment carried out with chromium-free complex **4a** (*vide infra*) indicated a slight downfield shift of the ^{103}Rh resonance as compared to **2a**, which was detected at δ +281 ppm. The HMQC (cf. Supporting Information) plot displayed two cross-peaks located in the ^{1}H NMR domain at δ 7.13 and 8.75 ppm, which were assigned to the *ortho* phenylene's proton and the α-pyridyl proton. Solution IR spectra of **2a**,**b** and **3a**,**b** in CH_2Cl_2 displayed two strong A_1 and E carbonyl stretching vibration bands at ca. 1950 and 1870 cm^{-1} at reciprocal wavelengths 20 cm^{-1} lower than for **1c** (A_1 1970 cm^{-1}, E 1895 cm^{-1} in CH_2Cl_2), which suggests a significant electron-donating effect of the Cp*MCl fragment (M = Rh, Ir).[21]

The relative stereochemistry of these rhodium and iridium complexes was established by X-ray diffraction analysis of crystals of racemates of **2b** and **3b**. Table 1 (cf. Experimental Section) lists the X-ray diffraction acquisition data and structure refinement parameters for the latter two compounds. Figure 1 displays the CCDC Mercury[22] ellipsoid diagrams for compounds

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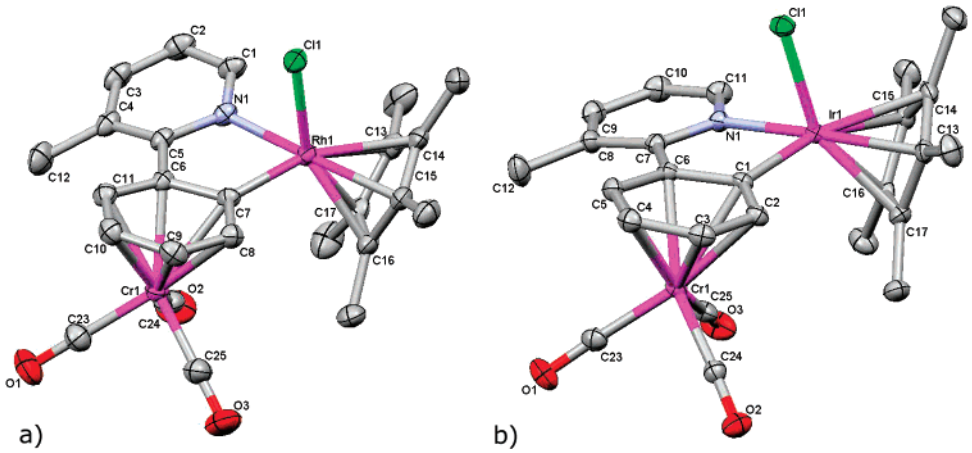

Figure 1. CCDC Mercury "ellipsoid" diagrams of compounds **2b** (a) and **3b** (b) drawn at the 40% probability level. Hydrogen atoms and molecules of solvent have been omitted for clarity. Selected interatomic distances (Å), angles (deg), and dihedral angles (deg) for **2b**: Rh(1)−C(7) 2.023(2), Rh(1)−N(1) 2.088(2), Rh(1)−C(13) 2.251(2), Rh(1)−C(14) 2.245(3), Rh(1)−C(15) 2.157(3), Rh(1)−C(16) 2.178(2), Rh(1)−C(17) 2.156(2), Rh(1)−Cl(1) 2.4072(6), Cr(1)−C(7) 2.325, Cr(1)−C(6) 2.208(2), Cr(1)−C(10) 2.194(2), C(8)−C(7)−C(6) 116.7(2), C(7)−Rh(1)−N(1) 78.2(1), C(7)−Rh(1)−Cl(1) 87.90(6), N(1)−Rh(1)−Cl(1) 86.06(5), C(7)−C(6)−C(5)−N(1) 12.86. Selected interatomic distances (Å) and angles (deg) for **3b**: Ir(1)−C(1) 2.033(3), Ir(1)−N(1) 2.089(2), Ir(1)−C(13) 2.154(3), Ir(1)−C(14) 2.240(3), Ir(1)−C(15) 2.261(3), Ir(1)−C(16) 2.161(3), Ir(1)−C(17) 2.167(3), Ir(1)−Cl(1) 2.4078(7), Cr(1)−C(1) 2.322(2), Cr(1)−C(4) 2.224(3), C(1)−Ir(1)−N(1) 77.4(1), C(1)−Ir(1)−Cl(1) 83.62(7), N(1)−Ir(1)−Cl(1) 87.04(6), C(2)−C(1)−C(2) 117.4(2), C(3)−C(4)−C(5) 119.4(3), C(1)−C(6)−C(7)−N(1) 9.72.

2b (Figure 1a) and **3b** (Figure 1b). The former was found to crystallize in the $P\bar{1}$ space group and the latter in the $C2/c$ space group. According to the *ad hoc* extensions of the CIP rule for planar-chiral metallocenes[23] and pseudo-tetrahedral metal complexes,[24] the relative configuration of these diastereomers is *rac*-(p*R*,*T*-4-*S*). The chloro ligand lies in an *anti*-relationship with respect to the $Cr(CO)_3$ fragment, which is characterized by a typical Cl−M−C_{ipso} angle (M = Rh, Ir) of ca. 83°, the M−Cl vector being almost perpendicular to the chelate's mean plane. The C_{ipso}−metal distances are very similar in the two Ir(III) and Rh(III) complexes. It is interesting to note that the staggered conformation of the $Cr(CO)_3$ tripod differs significantly in **2b** and **3b**. In the former the conformation is almost *anti*-eclipsed with respect to the Rh center, whereas in the latter it is nearly *syn*-eclipsed with respect to the Ir center: the shortest distance measured between a Cp* methyl carbon atom and the closest oxygen atom of a CO ligand is ca. 3.6 Å in **2b** and 3.3 Å in **3b**. These observations indicate that the steric bulk of the Cp* ligand does not influence significantly the conformation of the $Cr(CO)_3$ tripod in the solid state. In addition, it may be noticed that the pentamethylcyclopentadienyl ligand asymmetrically binds the Rh and Ir centers in **2b** and **3b**. Significant disparities among C_{Cp^*}−M interatomic distances can be noticed in both cases: the shortest carbon-to-Rh and -Ir distances are observed with carbon atoms C(15)−(17) (2.16 Å) in **2b** and with atoms C(13) and C(16)−(17) in **3b**, and the longest ones are observed with C(13)−(14) (2.25 Å) in **2b** and C(14)−(15) in **3b**. Such asymmetry of the η^5-bonding mode in pseudo-tetrahedral pentamethylcyclopentadienyl iridium(III) and rhodium(III) metallacycles has also been noticed with other cycloiridated and -rhodated complexes[25] and can be related to different *trans* influences exerted by the C−N chelating ligand and the chloro ligand on the Cp* ligand.

Origin of the Observed Diastereoselectivity. At this stage we assumed that a reasonable starting point in understanding the reasons for the observed high diastereoselectivity of the acetate-mediated cyclometalation was to consider, similarly to Davies,[12,18] that the chloro ligand re-enters the iridium's or rhodium's coordination sphere only upon completion of the cyclometalation process, by a thermodynamically controlled acetato−chloro ligand exchange that favors the production of the *anti*-chloro product versus the *syn*-chloro isomer. An unfavorable steric and/or repulsive electrostatic interaction between the chloro ligand and the $Cr(CO)_3$ moiety is responsible for the marked bias in favor of the *anti*-chloro isomer. The steric bulk of the Cp* ligand seemed unexpectedly far less relevant than the repulsion caused by the chloro ligand on the chelated metal, as far as influencing diastereoselectivity.

This was indeed verified by introducing the $Cr(CO)_3$ moiety by a ligand-exchange reaction between a "chromium-free" cycloiridated substrate and labile tricarbonyl(η^6-naphthalene)-chromium. The treatment of chromium-free **4a** and **5a** with tricarbonyl(η^6-naphthalene)chromium[26] in tetrahydrofuran at 67

(23) Chirality descriptors for so-called planar-chiral molecules are generally defined by *ad hoc* sequence rules that depend upon the nature of the considered molecule. The authors would like to point out that despite the sustained efforts of the IUPAC to unify both the terminology of stereochemistry and the nomenclature of chiral molecules, two definitions of chirality descriptors for metallocenic planar-chirality, which are based on different perceptions of planar-chirality itself, still coexist and can be found in the literature. The first one is based on Schlögl's first nomenclature, which was proposed in 1964 in two consecutive reports; it is based on the determination of the succession of the aromatic ring's substituents (either clockwise (*R*) or anti-clockwise (*S*)), by order of decreasing priority, as the molecule is observed from its principal axis perpendicularly to the aromatic ligand's plane, the π-bonded metal sitting underneath the plane. The second one is an extension of the Cahn−Ingold−Prelog (abbreviated CIP) priority, or sequence, rule proposed in 1967 again by Schlögl, who recommended it in place of his first nomenclature: "We shall therefore *in the future* make use of the nomenclature proposed by Cahn, Ingold and Prelog...". 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. Engl.* **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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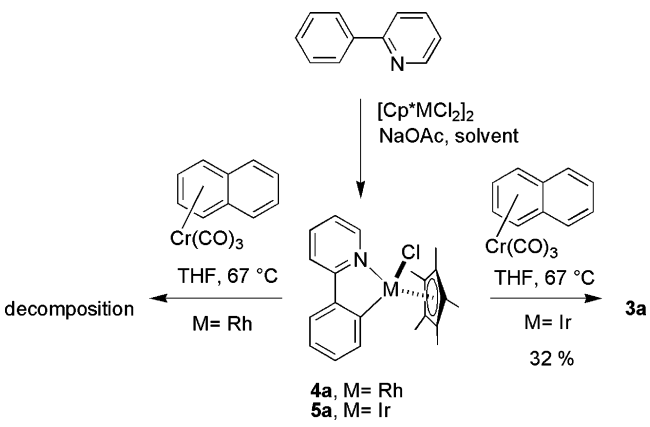
Scheme 1



°C was attemped in order to probe the facial stereoselectivity of the transfer of a "$Cr(CO)_3$" moiety (Scheme 1). Noteworthy, the two Cr-free Rh (**4a**) and Ir (**5a**) complexes were prepared in 57% and 89% yields by treatment of 2-phenylpyridine with the corresponding $[Cp^*MCl_2]_2$ dimer in the presence of hydrated NaOAc. The reaction of tricarbonyl(η^6-naphthalene)chromium with **4a** resulted essentially in the full decomposition of the starting Cr(0) complex most probably as a consequence of an oxidation of the latter by **4a**. The same treatment applied to **5a** proceeded smoothly and yielded a single product, which was isolated in 32% yield upon chromatographic purification and subsequently identified as compound **3a**. The same product was obtained in similar yield when the experiment was carried out at room temperature.

Tricarbonyl(η^6-naphthalene)chromium is well known for its propensity to undergo haptotropic rearrangements[27] and for its lability, two properties that have been frequently applied to the synthesis of new (η^6-arene)tricarbonylchromium complexes;[28] it outperforms other sources of "$Cr(CO)_3$" especially when tetrahydrofuran is used as solvent. This property has been used in the preparation of numerous (η^6-arene)tricarbonylchromium complexes, which are not readily accessible by the conventional thermolysis of $Cr(CO)_6$ in a mixture of THF and di-*n*-butyl ether.[29] Worthy to note, the transfer of $Cr(CO)_3$ to σ-metalated arene complexes has been reported only in a limited number of cases, essentially with aryl-Hg(II),[30] -W(IV),[31] -Fe(II),[32] and -Ti(IV)[33] complexes. The formation of **3a** starting from **5a** is therefore a new case of successful "$Cr(CO)_3$" transfer reaction in which the facial selectivity, again in favor of the *anti*-chloro isomer, is the salient feature. Such ligand-exchange reactions are well known to be relatively sensitive to steric hindrance owing to the nature of the Cr-bound intermediates. The naphthalene complex undergoes a $\eta^6-\eta^4$ haptotropic shift in the early stages.[34] This η^4-form may swiftly evolve either by a direct η^2-coordination of the phenylene fragment of **5a** or, in the presence of tetrahydrofuran, by forming solvates formulated $(thf)_n(\eta^{6-2n}$-naphthalene)$Cr(CO)_3$ (with $1 \le n \le 3$), which then may react with **5a**. At this point it is surprizing that again the $Cr(CO)_3$ entity binds the metalated arene in an *anti* fashion with respect to the iridium-bound chloro ligand. It is well known that the stereochemical course of $Cr(CO)_3$ transfer can be influenced by the presence of an assisting ligating moiety at the arene ligand, thus leading to partial or full facial discrimination. Several authors have outlined the potentials of tricarbonyl(η^6-naphthalene)chromium for the facial-stereoselective coordination of $Cr(CO)_3$ to prochiral and nonracemic free arene ligands.[35] In the case described here, the observed facial selectivity is seemingly the consequence of a major repulsion operated by the Ir-bound chloro ligand.

Stability of *syn*- versus *anti*-Chloro Isomers, a DFT Investigation. Steric and/or electrostatic repulsion were therefore suspected to be the key interactions responsible for the exclusive formation of the *anti*-chloro products **2a**,**b** and **3a**,**b**. This was supported by DFT calculations carried out on Cp-containing models of the *anti*- and *syn*-chloro isomers of these Rh(III) and Ir(III) complexes, e.g. **2c**,**3c** and **2d**,**3d**, respectively (Figure 2). The geometric features of the optimized models, e.g., metal-to-carbon distances and angles, were found to be reasonably consistent with the structural data obtained for **2b** and **3b**. Calculations showed that *anti*-chloro stereoisomers are more stable than *syn*-chloro by 7.43 and 8.05 kcal/mol for Rh and Ir products, respectively. The lowest stability of *syn*-chloro stereoisomers was assigned to significant electrostatic repulsion between the chloro ligand and the $Cr(CO)_3$ moiety. A good illustration of this is the significant difference of the $C_{ipso}-Rh-(Ir)-Cl$ angle found in the *syn*- and *anti*-isomers respectively. For instance, in **2c** this angle is 87.10°, whereas in **2d** it is 94.25°. The geometry and the conformation of the $Cr(CO)_3$ moiety in the *syn*-isomers are significantly altered by the proximity of the chloro ligand. The $Cr(CO)_3$ tripod adopts a nearly *anti*-eclipsed conformation with respect to the σ-bonded metal substituent in **2d** and **3d**, whereas the conformation is *syn*-eclipsed in **2c** and **3d**. Furthermore, the Cr-to-*ipso*-carbon atom distance increases from values of 2.368 and 2.402 Å in **2c** and **3c** to 2.408 and 2.433 Å in **2d** and **3d**, respectively.

The distribution of partial charges in these models conspicuously establishes the electrostatic nature of the effects that destabilize the *syn*-isomers. Figure 3 displays the orientation

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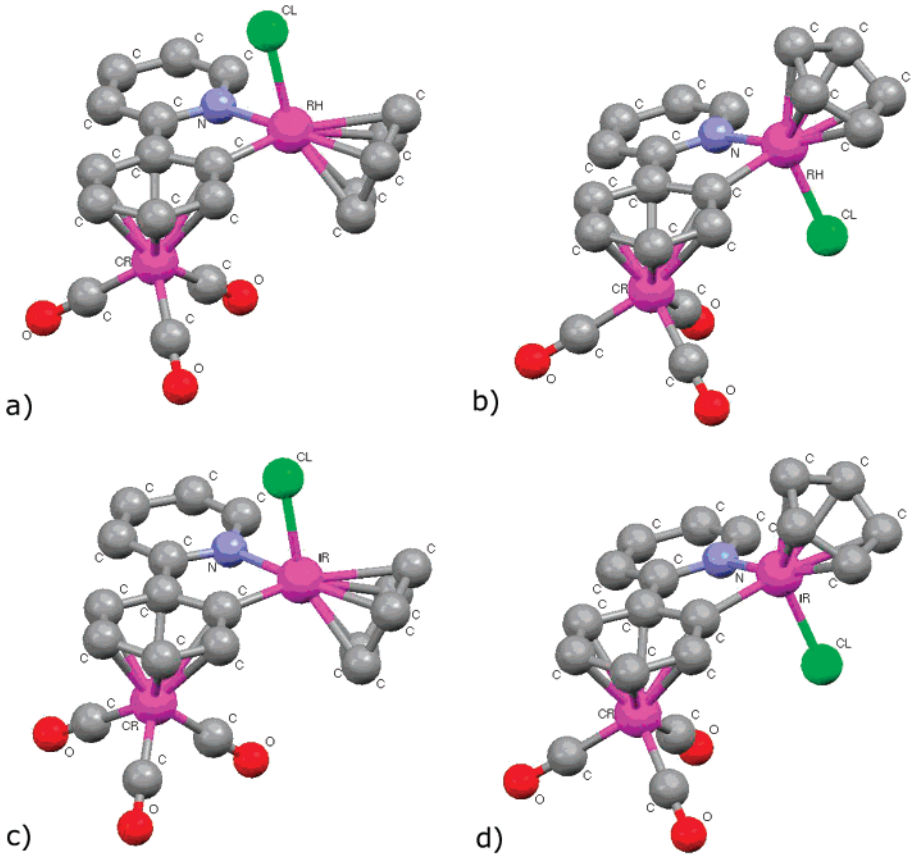


Figure 2. Optimized B3LYP/6-31G**/LANL2DZ geometries for models **2c** (a), **2d** (b), **3c** (c), and **3d** (d). Selected interatomic distances (Å) and angle (deg) for **2c**: Cr−C_{ipso} 2.368, C_{ipso}−Rh 2.011, N−Rh 2.099, Cl−Rh 2.409, C_{ipso}−Rh−Cl 87.10. Selected interatomic distances (Å) and angle (deg) for **2d**: Cr−C_{ipso} 2.408, C_{ipso}−Rh 2.009, N−Rh 2.095, Cl−Rh 2.387, C_{ipso}−Rh−Cl 94.25. Selected interatomic distances (Å) and angle (deg) for **3c**: Cr−C_{ipso} 2.402, C_{ipso}−Ir 2.014, N−Ir 2.089, Cl−Ir 2.432, C_{ipso}−Ir−Cl 86.89. Selected interatomic distances (Å) and angle (deg) for **3d**: Cr−C_{ipso} 2.433, C_{ipso}−Ir 2.012, N−Ir 2.091, Cl−Ir 2.410, C_{ipso}−Ir−Cl 94.05.

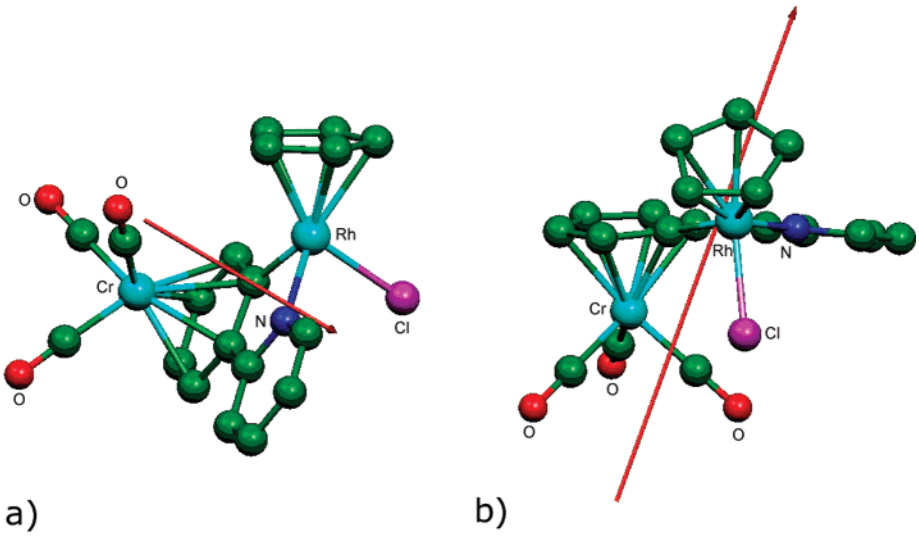
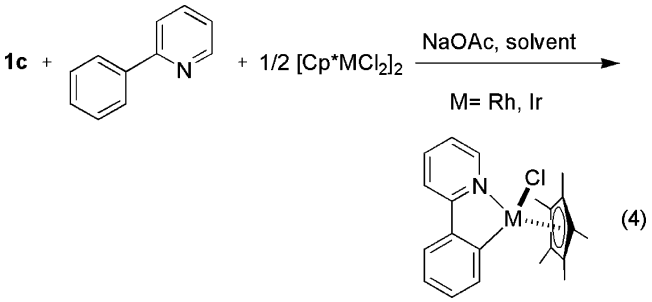


Figure 3. Molekel drawing of the position and relative modulus of the dipolar moment vector in **2c** (a) and **2d** (b) represented as an arrow: (a) the dipolar moment vector ($|\vec{\mu}| = 4.0235$ D) is nearly parallel to the plane of the chelate; (b) the dipolar moment vector ($|\vec{\mu}| = 10.5644$ D) is nearly perpendicular to the plane of the chelate.

and related modulus of the resulting dipolar moment vector for **2c** and **2d**. The orientation and modulus of this vector give an informative illustration of the partial charges' distribution in these molecules. In **2d** the dipolar moment is oriented nearly perpendicular with respect to the 2-phenylenepyridine ligand's mean plane and is almost parallel to the Cl−Rh vector: according to our calculation, an important concentration of negative partial charges is located mostly underneath the chelate's ring at Cr, Cl, and carbonyl ligand oxygen atoms, resulting in a molecular dipolar moment of ca. 10 D (Figure 3b). In turn, the dipolar moment vector calculated for **2c** has a modulus of ca. 4 D and is oriented nearly parallel to the chelate's plane, suggesting that the distribution of negative charges on the two faces of the chelate's ring is more balanced than in **2d** (Figure 3a). The same observations can be made with **3c** and **3d**.

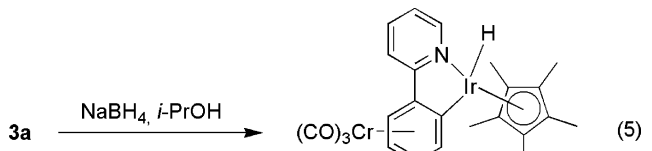
Qualitative Competing Cyclometalation Experiments. From a qualitative point of view, the cyclometalation of **1c** by $[Cp^*MCl_2]_2$ (M = Rh, Ir) is less efficient than that of chromium-free 2-phenylpyridine, all things considered. The competing cyclometalation of 1:1 mixtures of these ligands with substoichiometric amounts of $[Cp^*MCl_2]_2$ (M = Rh, Ir) afforded exclusively complexes **4a** and **5a** as the sole products after 24 h of reaction (eq 4). This result suggests that the presence of the $Cr(CO)_3$ moiety significantly hampers the cyclometalation reaction for steric reasons, most probably in the early stages of the reaction, i.e., those implying the labile coordination of the pyridyl moiety of the metal prior to acetate-assisted rhodium's or iridium's oxidative addition to the C_{ArCr}−H bond.



(4)

4a, M= Rh, 25 %
5a, M= Ir, 33 %

Displacement of Cl^- by H^- in 3a: Formation of a Hydrido Ir(III) Species. In order to probe the influence of the Cl ligand on the configurational stability of the chiral Ir center, we undertook the replacement of this electronegative ligand by a smaller and softer Lewis base, i.e. hydride, expecting that the substitution reaction would result in a mixture of two diastereomers. The reaction of **3a** carried out overnight with a large excess of $NaBH_4$ and 2-propanol in dry refluxing THF afforded an air-sensitive admixture of the starting complex with a single new compound, which was subsequently identified as hydrido complex **6** (eq 5). Careful separation and purification of **6** by low-temperature chromatography over silica gel afforded a dark red-colored material, which was recrystallized from mixtures of dichloromethane and pentane and recovered in 52% yield.



(5)

6

This new compound, although stable for months in the solid state under an atmosphere of argon, proved to be moderately reactive toward deuterated chloroform: a concentrated solution of **6** in this solvent would evolve within 15 h to yield quantitatively $CDHCl_2$ and compound **3a**, which was identified on the basis of its ^1H and ^{13}C NMR signature. It is not clear yet how coordinatively saturated **6** could interact with $CDCl_3$ to yield **3a**. This peculiar property of **6** compelled us to use d_6-benzene as solvent especially for ^{13}C NMR spectroscopic characterizations, *d*-chloroform being suitable only for ^1H NMR experiments lasting less than 40 min. A typical feature of the ^1H NMR spectrum of **6** measured at 283 K was the upfield resonance of the hydrido ligand at δ −14.5 ppm.[36] The methyl groups belonging to the η^5-bonded Cp* ligand were detected at δ 1.70 ppm. The eight protons of the 2-(phenylene)pyridine ligand were located in the typical δ 4.69 to 8.39 ppm region. The IR spectrum of **6** obtained from a KBr pellet displayed two strong A_1 and E carbonyl ligand stretching bands at 1949 and 1870 cm^{-1}, that is, at frequencies not different from those noted for **3a**. This would suggest that the change of anionic ligand does not affect significantly the electronic communication between the Cr(0) and Ir(III) centers. Unfortunately, the exact structure of this new compound could not be confirmed crystallographically, as we repeatedly failed to crystallize it in a suitable form. The $^1H-^1H$ NOESY NMR experiment did not provide any structural information as to the position of the hydrido ligand relative to the $Cr(CO)_3$ moiety: the singlet of the hydrido ligand was found to correlate only with the strong singlet arising from the methyls of the Cp* ligand. Although it is not yet possible to elaborate on the origin and nature of this diastereselective ligand-exchange reaction, we anticipate that other ligand-exchange reactions undertaken with **3a** should be as much stereoselective as the one described here.

Conclusion

In this report we have shown that the cyclometalation of 2-phenylpyridine chromium complexes such as **1c** or **1d** with pseudo-tetrahedral Ir(III) and Rh(III) complexes was relatively efficient. These results further support the findings of Davies and Mcgregor on the mechanism of iridation that involves the oxidative-addition of the Ir(III) center to the C_{Ar}−H bond.[12] The reasonably good efficiency of the cyclorhodation reactions reported here suggests that rhodation proceeds similarly via a C_{Ar}−H oxidation step and not via an arenium intermediate.[18] The lack of reactivity of the *N*,*N*-dimethylbenzylamine and 2-phenyl-2-oxazoline derivatives **1a** and **1b** is somewhat puzzling. In a previous report dealing with *ortho*-mercuration reactions, we already noticed that **1a**,**b** were much less reactive toward $Hg(OAc)_2$ than 2-phenylpyridine complex **1c**, affording the corresponding *ortho*-mercurated products only in 38% and 17% yield.[10] Davies et al. reported that Cr-free *N*,*N*-dimethylbenzylamine and 2-phenyl-[5′,5′-dimethyl(2-oxazoline)] could react fairly well with $[Cp^*IrCl_2]_2$, contrasting results being however noted with $[Cp^*RhCl_2]_2$, which failed to react with the tertiary amine.[18] In the cases reported here, we believe that the $Cr(CO)_3$ moiety sterically inhibits the coordination of the pendant amino and oxazolyl ligands to the Cp*Ir(III) moiety, which is a prerequisite for the cyclometalation to occur.

We have demonstrated that electrostatic repulsion governs the stereochemical course of the reactions that leads to planar-chiral metallacycles with high diastereoselectivity. The nature of the intermediates in cycloiridation and -rhodation reactions is another issue deserves future attention: in no case were acetate precursors of **2a**,**b** and **3a**,**b** observed. The kinetic configurational stability of the complexes reported herein has yet to be evaluated. Fast inversion of configuration at Rh or Ir centers in solution is not excluded, although not supported by preliminary low-temperature ^1H NMR investigation of complex **3a** in $CDCl_3$. We have recently reported that such inversion was possible with rigid and scalemic *T*-4 2-phenylenepyridine chloro ruthenium complexes only if the dissociation of the Ru−

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Cl bond was assisted by a Lewis acid such as $HgCl_2$ in a polar solvent.[37] Further research is currently addressing the reactivity and the stereochemical course of nucleophilic substitution reactions involving the departure of the chloro ligand and its replacement by ligands different from H^- in iridium and rhodium complexes: relevant results will be disclosed in due time. Because the most noteworthy feature of the cyclometalation reactions presented here is their diastereoselectivity, further efforts are therefore dedicated to the search for viable routes toward scalemic planar-chiral metallacycles such as **2a**,**b** and **3a**,**b**, which may bear high potential for applications in metal-mediated organic transformations.

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 Avance 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 constants 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. Elemental analyses (reported in % mass) were performed at the Service d'Analyses of the "Institut de Chimie de Strasbourg". 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.

X-ray Diffraction Analyses of Compounds 2b and 3b. Data collection by ϕ and ω scans for **2b** and **3b** were carried out at 150 K 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 Table 1. The crystal structures were solved using SIR97 and refined with Shelxl97. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 637161 and 637162. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; web: www.ccdc.cam.ac.uk/data_request/cif).

^{1}H−^{103}Rh HMQC NMR Analysis of 2a and 4a. A standard HMQC sequence was used by considering the ^2J−^4J ^{1}H−^{103}Rh coupling constant as having an average value of 5 Hz, consistent with an apparent value for T_2 of 100−150 ms. Dwell times in the proton and in the rhodium domains were 100 and 10 μs, respectively. Data were acquired with a Bruker Avance 500 spectrometer with 512 increments of 16 scans each. Referencing was based on the frequency of tetramethylsilane taking into account the gyromagnetic constants of the considered nuclei. The field was locked against the deuterium signal of *d*-chloroform in both cases.

DFT Calculations on Models 2c,d and 3c,d. DFT calculations were carried out using the Gaussian 98 program.[38] Geometries were optimized and the energies were calculated using the Becke three-parameter exchange functional (B3) and the Lee−Yang−Parr correlation functional (LYP) levels of theory. The LANL2DZ basis set was chosen for iridium and rhodium atoms, and 6-31G** basis set was chosen for all other atoms. CCDC Mercury and Molekel v4.3[39] software were used to visualize the optimized geometries.

***rac*-(p*R*,*T*-4-*S*)-Chloro(η^5-pentamethylcyclopentadienyl){2-[tricarbonyl(η^6-phenylene-$\kappa C^{1'}$)chromium]pyridine-κN}rhodium(III), 2a.** $[Cp^*RhCl_2]_2$ (300 mg, 0.487 mmol), **1c** (283 mg, 0.972 mmol), and $NaOAc\cdot 3H_2O$ (132 mg, 0.97 mmol) were dissolved in methanol (20 mL), and the corresponding mixture was stirred during 6 h at room temperature under argon. The resulting dark red suspension was filtered through Celite, the filtrate was concentrated to ca. 5 mL, and silica gel was added. Solvents were removed under reduced pressure, and the coated SiO_2 was loaded on the top of a silica gel column packed in dry pentane at 0 °C. The fraction containing the product was eluted with a 60:40 mixture of dichloromethane and pentane. The resulting eluate was evaporated to dryness under reduced pressure to afford **2a** as an orange solid, which was recrystallized from pentane (3 × 10 mL) and dichloromethane (10 mL) and dried under reduced pressure overnight (332 mg, 60%). Anal. Calcd for $C_{24}H_{23}NClRhO_3Cr\cdot 1/2CH_2Cl_2$: C, 48.53; H, 3.99; N, 2.31. Found: C, 48.92; H, 3.92; N, 2.26. IR (CH_2Cl_2) ν(CO): 1951, 1875 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.68 (d, 1H, ^3J = 5.3, H_{py}), 7.77 (td, 1H, ^3J = 7.7, ^4J = 1.7 H_{py}), 7.46 (d, 1H, ^3J = 8.1), 7.24 (td, 1H, ^3J = 6.5, ^4J = 1.4, H_{py}), 5.85 (m, 2H, H_{Ar}), 5.43 (m, 2H, H_{Ar}), 1.73 (s,15H, H_{cp}). {^{1}H}^{13}C NMR ($CDCl_3$, 400 MHz): δ 235.3 ($Cr(CO)_3$), 164.2, 150.7, 142.4 ($^1J_{Rh-C}$ = 38.6), 137.6, 123.5, 120.2, 110.5, 101.4, 96.8 (*Cp*Me_5, 5C, $^1J_{Rh-C}$ = 6.6), 94.4, 91.2, 89.5, 9.21 (Cp *Me*$_5$).

***rac*-(p*R*,*T*-4-*S*)-Chloro(η^5-pentamethylcyclopentadienyl){3-methyl-2-[tricarbonyl(η^6-phenylene-$\kappa C^{1'}$)chromium]pyridine-κN}rhodium(III), 2b.** The mixture of $[Cp^*RhCl_2]_2$ (300 mg, 0.487 mmol), **1d** (165.7 mg, 0.97 mmol), and $NaOAc\cdot 3H_2O$ (132 mg, 0.97 mmol) was dissolved in methanol (20 mL), and the corresponding mixture was stirred during 6 h at room temperature under argon. The workup and purification procedures were akin to that described for **2a**. Compound **2b** was recovered as a red powder (350 mg, 62%). Anal. Calcd for $C_{25}H_{25}NClO_3CrRh\cdot 1/4C_7H_8$: C, 53.94; H, 4.7; N, 2.35. Found: C, 54.24; H, 4.57; N, 2.17. IR (CH_2Cl_2) ν(CO): 1950, 1872 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.69 (d, 1H, ^3J = 5.6, H_{py}), 7.57 (d, 1H, ^3J = 7.5, H_{py}), 7.16 (dd, 1H, ^3J = 7.9, ^3J = 5.5, H_{py}), 6.0 (d, 1H, ^3J = 6.3, H_{Ar}), 5.8 (d, 1H, ^3J = 6.1, H_{Ar}), 5.46 (td, 1H, ^3J = 6.1, ^4J = 1.1, H_{Ar}), 5.38 (td, 1H, ^3J = 6.4, ^3J = 1.2, H_{Ar}), 2.58 (s, 3H, *Me*py), 1.69 (s, 15H, Cp*Me*$_5$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.69 (d, 1H, ^3J = 5.6, H_{py}), 7.57 (d, 1H, ^3J = 7.5, H_{py}), 7.16 (dd, 1H, ^3J = 5.5, ^3J = 7.9, H_{py}), 6.03 (d, 1H, ^3J = 6.3, H_{ArCr}), 5.79 (d, 1H, ^3J = 6.1, H_{ArCr}), 5.46 (td, 1H, ^3J = 6.1, ^4J = 1.1, H_{ArCr}), 5.39 (td, 1H, ^3J = 6.4, ^4J = 1.2, H_{ArCr}), 2.58 (s, 3H, H_{Me-py}), 1.69 (s, 15 H, H_{Me5Cp}). {^{1}H}^{13}C NMR ($CDCl_3$, 400 MHz): δ 235.3 ($Cr(CO)_3$), 162.2 ($^2J_{C-Rh}$ = 2.1), 149.3, 146.3 ($^1J_{C-Rh}$= 37.5), 141.4, 133.1, 123.0, 111.2, 101.8, 97.0 (5 C, $^1J_{C-Rh}$ = 6.5, *Cp*Me_5), 94.0, 93.7, 91.3, 22.1 (*Me*-py), 9.2 (Cp *Me*$_5$).

Competing Cyclorhodation of 2-Phenylpyridine versus 1c. $[Cp^*RhCl_2]_2$ (100 mg, 0.162 mmol), 2-phenylpyridine (100 mg, 0.648 mmol), **1c** (188 mg, 0.648 mmol), $NaOAc\cdot 3H_2O$ (102 mg, 0,75 mmol), and 1,3,5-tris-*tert*-butylbenzene (10 mg, 0.04 mmol) as internal ^{1}H NMR standard were dissolved in methanol (20 mL), and the corresponding mixture was stirred during 6 h at room temperature under argon. The resulting suspension was evaporated to dryness under reduced pressure to afford a raw orange solid, which was analyzed by ^{1}H NMR spectroscopy in $CDCl_3$. Compound **4a** was the only product to be formed with a yield of 25%.

***rac*-(p*R*,*T*-4-*S*)-Chloro(η^5-pentamethylcyclopentadienyl){2-[tricarbonyl(η^6-phenylene-$\kappa C^{1'}$)chromium]pyridine-κN}iridium-**

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(III), 3a. $[Cp^*IrCl_2]_2$ (500 mg, 0.628 mmol), **1c** (365 mg, 1.25 mmol), and $NaOAc\cdot 3H_2O$ (170 mg, 1.25 mmol) were dissolved in dichloromethane (20 mL), and the resulting mixture was stirred at room temperature for 24 h under argon. The resulting red solution was filtered through Celite, the filtrate was concentrated to ca. 5 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 silica gel column packed in dry pentane at 0 °C. The fraction containing the product was eluted with a 60:40 mixture of dichloromethane and pentane. The resulting eluate was evaporated to dryness under reduced pressure to afford an orange solid, which was recrystallized from a mixture of pentane (15 mL) and dichloromethane (15 mL) and dried under reduced pressure overnight. Compound **3a** was recovered as an orange powder (760 mg, 92%). Anal. Calcd for $C_{24}H_{23}NClO_3CrIr\cdot 1/2CH_2Cl_2$: C, 43.30; H, 3.51; N, 2.07. Found: C, 43.50; H, 3.71; N, 1.95. IR (CH_2Cl_2) ν(CO): 1950, 1871 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.67 (d, 1H, $^3J = 5.4$, H_{py}), 7.75 (td, 1H, $^3J = 7.9$, $^4J = 1.4$, H_{py}), 7.52 (d, 1H, $^3J = 8.0$, H_{py}), 7.17 (td, 1H, $^3J = 6.6$, $^4J = 1.3$, H_{py}), 5.98 (m, 1H, H_{Ar}), 5.85 (m, 1H, H_{Ar}), 5.42 (m, 2H, H_{Ar}), 1.74 (s, 15H, Cp*Me*$_5$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 235.2 (Cr(*CO*)$_3$), 165.7, 151.0, 137.4, 126.9, 123.7, 120.1, 111.6, 100.4, 95.1, 90.5, 90.4, 89.4 (5 C, *Cp*Me$_5$), 8.5 (Cp*Me*$_5$).

***rac*-(p*R*,*T*-4-*S*)-Chloro(η^5-pentamethylcyclopentadienyl){3-methyl-2-[tricarbonyl(η^6-phenylene-$\kappa C^{1'}$)chromium]pyridine-κN}iridium(III), 3b.** The mixture of $[Cp^*IrCl_2]_2$ (300 mg, 0.376 mmol) and **1d** (230 mg, 0.753 mmol) and $NaOAc\cdot 3H_2O$ (103 mg, 0.75 mmol) were dissolved in dichloromethane (20 mL), and the corresponding mixture was stirred during 24 h at room temperature under argon. The resulting red solution was filtered through Celite, the filtrate was concentrated to ca. 5 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 silica gel column packed in dry pentane at 0 °C. The fraction containing the product was eluted with a 70:30 mixture of dichloromethane and pentane. The resulting eluate was evaporated to dryness under reduced pressure to afford **3b** as an orange solid, which was washed with dichloromethane (15 mL) and pentane (15 mL) and dried under reduced pressure overnight (350 mg, 65%). Anal. Calcd for $C_{25}H_{25}NClO_3CrIr\cdot 1/2CH_2Cl_2$: C, 43.59; H, 3.70; N, 1.99. Found: C, 43.16; H, 3.74; N, 1.88. IR (CH_2Cl_2) ν(CO): 1950, 1871 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.7 (d, 1H, $^3J = 3.7$, H_{py}), 7.55 (t, 1H, $^3J = 7.2$, H_{py}), 7.10 (d, 1H, $^3J = 8.1$, H_{Ar}), 6.22 (d, 1H, $^3J = 4.9$, H_{Ar}), 5.84 (t, $^3J = 4.6$, 1 H, H_{Ar}), 5.49 (m, 1H, H_{Ar}), 5.40 (d, 1H, $^3J = 4.5$, H_{Ar}), 2.65 (s, 3H, CH_3), 1.73 (s, 17H, H_{cp}). $\{^1H\}^{13}C$ NMR ($CDCl_3$, 400 MHz): δ 235.0 (Cr(CO)$_3$), 163.2, 149.8, 141.1, 132.7, 130.2, 123.1, 111.7, 100.7, 94.9, 94.4, 90.3, 89.5 (5C, *Cp*Me$_5$), 22.0 (*Me*py), 8.5 (Cp*Me*$_5$).

***rac*-(*T*-4)-Chloro(η^5-pentamethylcyclopentadienyl)(2-phenylene-$\kappa C^{1'}$,pyridine-κN)rhodium(III), 4a.** $[Cp^*RhCl_2]_2$ (300 mg, 0.487 mmol), 2-phenylpyridine (114 mg, 0.734 mmol), and $NaOAc\cdot 3H_2O$ (132 mg, 0.97 mmol) were dissolved in methanol (20 mL), and the corresponding mixture was stirred during 1 h at room temperature under argon. The resulting red suspension was filtered through Celite, the filtrate was concentrated to ca. 5 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 silica gel column packed in dry pentane at 0 °C. The fraction containing the product was eluted with a 70:30 mixture of dichloromethane and pentane. The resulting eluate was evaporated to dryness under reduced pressure to afford **4a** as an orange solid, which was recrystallized from pentane (15 mL) and dichloromethane (15 mL) and dried under reduced pressure overnight. Compound **4a** was recovered as an orange powder (160 mg, 57.6%). Anal. Calcd for $C_{21}H_{23}NClRh\cdot 1/2CH_2Cl_2$: C, 54.90; H, 5.14; N, 2.97. Found: C, 55.02; H, 5.14; N, 2.47. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.75 (d, 1H, $^3J = 5.6$, H_{py}), 7.81 (dd, 1H, $^3J = 7.6$, $^4J = 1.4$, H_{Ar}), 7.77 (d, AH, $^3J = 7.8$, H_{Ar}), 7.70 (td, 1H, $^3J = 7.6$, $^4J = 1.5$, H_{py}), 7.60 (dd, 1H, $^3J = 7.6$, $^4J = 1.5$, H_{Ar}), 7.23 (td, 1H, $^3J = 7.5$, $^4J = 1.6$, H_{Ar}), 7.13 (td, 1H, $^3J = 6.2$, $^4J = 1.6$, H_{py}), 7.06 (ddd, 1H, $^3J = 8.0$, $^4J = 1.3$, H_{Ar}) 1.68 (s, 15H, Cp*Me*$_5$). $\{^1H\}^{13}C$ NMR ($CDCl_3$, 400 MHz): δ 178.8 ($^1J_{Rh-C} = 32$), 165.5, 151.3, 143.7, 137.0, 136.9, 130.4, 123.5, 122.8, 121.9, 119.0 ($^2J_{Rh-C} = 1.6$), 96.0 (5 C, $^1J_{Rh-C} = 6.5$, *Cp*Me$_5$), 9.1 (Cp*Me*$_5$).

***rac*-(*T*-4)-Chloro(η^5-pentamethylcyclopentadienyl)(2-phenylene-$\kappa C^{1'}$,pyridine-κN)iridium(III), 5a.** A mixture of $[Cp^*IrCl_2]_2$ (300 mg, 0.376 mmol), 2-phenyl,pyridine (116.85 mg, 0.753 mmol), and $NaOAc\cdot 3H_2O$ (132 mg, 0.97 mmol) was suspended in dichloromethane (20 mL) and stirred during 24 h at room temperature 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 under reduced pressure. The coated silica gel was loaded on the top of a column of SiO_2 packed in dry pentane at 0 °C. The fraction containing the product was eluted with a 70:30 mixture of dichloromethane and pentane. The eluate was evaporated to dryness under reduced pressure to afford **5a** as a yellow solid, which was recrystallized from a mixture of pentane and dichloromethane and was dried under reduced pressure overnight (350 mg, 89%). Anal. Calcd for $C_{21}H_{23}NClIr\cdot CH_2Cl_2$: C, 43.89; H, 4.18; N, 2.32. Found: C, 43.59; H, 4.28; N, 2.25. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.67 (d*, 1H, $^3J = 5.7$, H_{py}), 7.80 (m, 2H, $H_{py} + H_{Ar}$), 7.65−7.68 (m, 2H, $H_{py} + H_{Ar}$), 7.20 (t, 1H, $^3J = 7.4$, $^4J = 1.4$, H_{Ar}), 7.07 (td, 1 H, $^3J = 6.6$, $^4J = 1.4$, H_{Ar}), 7.03 (td, 1H, $^3J = 7.4$, $^4J = 1.2$, H_{Ar}), 1.68 (s, 15H, Cp*Me*$_5$). $\{^1H\}^{13}C$ NMR ($CDCl_3$, 400 MHz): δ 167.4, 163.3, 151.3, 144.1, 136.9, 135.8, 131.0, 123.8, 122.3, 122.1, 118.9, 88.5 (*Cp*Me$_5$), 9.9 (Cp*Me*$_5$).

Reaction of 5a with Tricarbonyl(η^6-naphthalene)chromium: Formation of 3a. 5a (250 mg, 0.628 mmol) and tricarbonyl(η^6-naphthalene)chromium (117 mg, 0.473 mmol) were dissolved in dry and degassed tetrahydrofuran (15 mL), and the resulting dark red solution was stirred and warmed to 67 °C for 1 h under argon. The resulting solution was filtered through Celite, the filtrate was concentrated to ca. 5 mL, and silica gel was added. The solvent was 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 product was eluted with a 50:50 mixture of dichloromethane and pentane. Analytical and spectroscopic data of the latter were in all aspects identical to those of **3a** (100 mg, 32%).

Competing Cycloiridation of 2-Phenylpyridine versus 1c. The mixture of $[Cp^*IrCl_2]_2$ (100 mg, 0.125 mmol), 2-phenylpyridine (78 mg, 0.502 mmol), **1c** (146 mg, 0.502 mmol), $NaOAc\cdot 3H_2O$ (132 mg, 0.97 mmol), and 1,3,5-tris-*tert*-butylbenzene (10 mg, 0.04 mmol) as internal standard was dissolved in dichloromethane (20 mL), which was stirred for 24 h at room temperature under argon. Upon removal of the volatiles under reduced pressure, ^1H NMR analysis of the residue in $CDCl_3$ confirmed the formation of a single product, i.e., **5a** (33% yield), and the presence of unreacted **1c**.

(*T*-4)-Hydrido(η^5-pentamethylcyclopentadienyl){2-[tricarbonyl(η^6-phenylene-$\kappa C^{1'}$)chromium]pyridine-κN}iridium(III), 6. To a solution of **3a** (100 mg, 0.15 mmol) in tetrahydrofuran (15 mL) at −20 °C were added 2-propanol (150 μL) and $NaBH_4$ (300 mg, 7.9 mmol) in small portions over 30 min. The resulting suspension was then warmed to room temperature and refluxed overnight. The reaction was monitored by thin-layer chromatography over silica gel by elution with a 1:2 mixture of CH_2Cl_2 and pentane. Heating was stopped before the complete disappearance of **3a**. The resulting dark red solution was stripped of solvents and redissolved in CH_2Cl_2; silica gel was added to the solution, and the solvent was swiftly evaporated to dryness. The resulting coated silica was loaded on the top of a silica gel column packed in dry distilled pentane. Compound **6** was eluted as a red-colored band with a 1:2 mixture of CH_2Cl_2 and pentane. Evaporation of the solvents under reduced

pressure afforded a brick-red powder, which was further purified by recrystallization from CH_2Cl_2 and pentane (48.6 mg, 52%). Anal. Calcd for $C_{24}H_{24}O_3NCrIr\cdot 2CH_2Cl_2$: C, 39.64; H, 3.56; N, 1.78. Found: C, 39.86; H, 3.51; N, 1.79. IR (KBr) ν(CO): 1949, 1870 cm^{-1}. ^1H NMR (C_6D_6, 283 K): δ 8.39 (d, 1H, $^3J = 5.3$, H_{py}), 6.64 (t, 1H, $^3J = 7.3$, H_{py}), 6.59 (d, 1H, $^3J = 7.7$, H_{py}), 6.12 (t, 1H, $^3J = 6.1$, H_{py}), 5.65 (d, 1H, $^3J = 6.0$, H_{ArCr}), 5.49 (d, 1H, $^3J = 5.9$, H_{ArCr}), 5.01 (t, 1H, $^3J = 6.0$, H_{ArCr}), 4.69 (t, 1H, $^3J = 6.0$, H_{ArCr}), 1.70 (s, 15H, Cp*Me*$_5$), −14.52 (s, 1H, Ir-*H*). {^1H}^{13}C NMR (C_6D_6, 283 K): δ 236.2 ($Cr(CO)_3$), 166.4, 151.6, 134.3, 130.8, 121.7, 118.7, 110.8, 99.3, 95.8, 91.7, 90.5 (5 C, *Cp*Me$_5$), 87.3, 9.4 (5 C, Cp*Me*$_5$).

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Supporting Information Available: (1) Analytical and spectral characterization data (^1H, ^{13}C) for compounds **2a**,**b**, **3a**,**b**, **4a**, **5a**, and **6**. (2) Cartesian coordinates and tables of frequencies for the optimized geometries of complexes **2c**,**d** and **3c**,**d**. (3) Crystallographic information file related to compounds **2b** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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